Project Status Report

Mechanism of Promotion of Iron Fischer-Tropsch Catalysts (Quarterly Report for the Period Ending September 30, 1986)

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Applications of ^{14}C Tracer Techniques to the Study of Reactions Occurring Over Iron-Based Fischer-Tropsch Catalysts

ABSTRACT

Alcohol, added to the syngas feed to an unpromoted iron catalyst, causes a decrease in CO conversion and an increase in the olefinic content of the products; this change is reversible since both the activity and selectivity recover to their original value when alcohol addition is terminated. The olefin selectivity obtained with alcohol addition is similar to that obtained for a doubly promoted C-73 iron catalyst. The data for the conversion of carbinol labeled alcohols support the view that gas phase CO_2 is formed directly from the alcohol rather than through CO. Higher boiling hydrocarbon products accumulate in the reactor over a several week period operation. This accumulation in the slurry reactor introduces problems in interpreting the ^{14}C incorporation data. The ^{14}C data generated in our studies to date suggest that this product accumulation may be a major factor in the introduction of the need for two, or more, alpha values in the Anderson-Schulz-Flory plots.

INTRODUCTION

The Fischer-Tropsch reaction is a complex combination of many reactions. Among those that have been demonstrated to occur on the catalyst surface are CO dissociation, build-up of carbon chains by a polymerization process, desorption of products such as olefins and oxygen-containing compounds, water formation and its subsequent shift reaction to form CO_2, olefin hydrogenation, isomerization and reincorporation in the synthesis and, probably, other reactions yet to be identified and studied. The tracer technique, involving the feeding of ^{14}C-labeled compounds to the synthesis, is being used here in an effort to learn how catalyst additives and supports influence these reactions and determine the final product distribution.

During this past quarter, attention has been focused largely on determining the fate of the ^{14}C in labeled alcohols added to the synthesis reaction over 10% Fe/SiO_2 and United Catalyst's C-73 (Fe-K-Al-Ca-Si) catalysts.

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A new fixed-bed catalyst test unit, which operates at atmospheric rather than elevated pressure, has been placed in operation and shown to be useful both in catalyst characterization and in ^{14}C tracer studies. An umpromoted Fe_2O_3 catalyst prepared from precipitated hydroxide has been shown to provide a reasonably active, stable catalyst. Related catalysts containing 0.3% Al_2O_3, ThO_2 and ZrO_2 have been prepared but have not yet been tested.

EXPERIMENTAL

A detailed schematic drawing of the new fixed bed, atmospheric pressure catalyst study unit is shown in Figure 1. Gas flows are regulated by Brooks flow controllers. The reactor is a glass tube 1.25 inches in diameter and 24 inches long, with a central thermocouple well containing two thermocouples. Liquid products are condensed in a series of traps chilled with dry ice and liquid nitrogen. The liquid nitrogen traps are made of stainless steel and rated for operation at 200 psi to withstand the gas pressure developed when they are warmed to room temperature without venting. The non-condensable gases are analyzed by an on-line gas chromatograph as described in the March 1986 Quarterly Report. Ethanol or pentanol have been added to the feed using a liquid metering pump. Ethylene addition has been accomplished by dehydration of a metered stream of ethanol over locally produced basic Al_2O_3 catalyst operating at 300°C. Catalysts were reduced with H_2 *in situ* for 48 hours at 450°C at a space velocity of about 180 $(hr)^{-1}$. The gas feed was then changed to synthesis gas and the test started. The test conditions chosen are 260°C, one atmosphere total pressure, $CO/H_2 = 1$, space velocity = 120 $(hr)^{-1}$ for supported catalysts and 60 $(hr)^{-1}$ for unsupported catalysts.

The 10% Fe/SiO_2 catalyst was prepared as described in the March 1986 Quarterly Report. Unsupported Fe_2O_3 was prepared by precipitation of iron hydroxide from $Fe(NO_3)_3$ with NH_4OH. An 0.6% K-promoted catalyst was prepared from the Fe_2O_3 by an incipient wetness technique, using KNO_3 as the source of the potassium. Catalysts promoted with 0.3% Al_2O_3, ThO_2 or ZrO_2 were prepared by coprecipitation from a mixture of their nitrates and $Fe(NO_3)_3$ with NH_4OH. The precipitates obtained were washed several times with cold water, then dried overnight at 120°C and calcined four hours at 400°C. Analysis of the calcined oxides showed them to contain the expected quantities of promoters, i.e., 0.3 ± 0.1% Al_2O_3, ThO_2 or ZrO_2 and 0.6 ± 0.1% K.

The ^{14}C contents of alkane hydrocarbon fractions isolated by liquid phase chromatography from the liquid products obtained from a 10% Fe/SiO_2 catalyst were determined using Beckman and Packard liquid scintillation counters.

RESULTS

Effects of Alcohol Feed on Synthesis Gas Conversion:

Both carbinol- and methyl-labeled ethanol, $CH_3{}^*CH_2OH$ and $^*CH_3CH_2OH$, and carbinol-labeled n-pentanol, $C_4H_3{}^*CH_2OH$, were added to the feeds to Fe/SiO_2 and United Catalyst's C-73 catalysts. Conversion, based on dispersion of CO, decreased when the alcohol was added to the

Fe/SiO_2, but not when it was added to the C-73 catalyst, as shown in Figure 2. Furthermore, the alkane fraction in the hydrocarbons produced decreased when ethanol was added to the Fe/SiO_2 catalyst, but not when it was added to the C-73 catalyst, as shown in Figures 3 and 4.

Distribution of ^{14}C Tracer in Synthesis Products:

The ^{14}C contents of the gaseous products were determined by the use of a proportional counter in series with the on-line gas chromatograph. Results of feeding $*CH_3CH_2OH$, CH_3*CH_2OH and $*CH_2 = CH_2$ are shown in Figures 5, 6 and 7; these data are for the atmospheric reactor operating with Fe/SiO_2 catalyst. It is evident from inspection of Figures 5 and 6 that some of the labeled carbon from CH_3*CH_2OH appeared in the outlet CO and CO_2, but no detectable amounts of $*CO$ or $*CO_2$ was formed when $*CH_3CH_2OH$ was fed. Carbinol-labeled pentanol also gave $*CO$ and $*CO_2$ just as the carbinol-labeled ethanol.

Whether the alcohol fed was labeled in the carbinol or the alkyl group, and whether the catalyst was Fe/SiO_2 or C-73, the hydrocarbons produced were labeled. When the carbinol-labeled C_2 alcohol was fed to the C-73 catalyst operating in the slurry reactor at 7 atm., the specific activity of the hydrocarbons was virtually constant from C_2 to C_5, as shown in Figure 8. The scatter in the results shown for the C_5 hydrocarbons is probably due to poor counting statistics (small sample size).

When the C_5 alcohol was fed, the results shown in Figure 9 were obtained. The activities of the C_2-C_4 hydrocarbons are finite but low relative to those of the C_5, C_6 and C_7 hydrocarbons, indicating that an important path for incorporation of the alcohol in the synthesis leaves the alkyl moiety intact. Some decomposition of the hydrocarbon chain must occur over the C-73 catalyst, though, in view of the activity found in the C_2-C_4 hydrocarbons.

Another possible mechanism of incorporation of alcohols in the growing Fischer-Tropsch hydrocarbon chains involved their dehydration to olefins and subsequent re-adsorption as surface alkyl groups. To investigate the importance of this reaction, labeled ethylene was fed to the atmospheric reaction system operating with Fe/SiO_2 catalyst, at approximately the same level that had been used for the ethanol feeds. The ethylene was indeed incorporated, and the gas phase product spectrum shown in figure 7 resembles quite closely those obtained when labeled ethanols were fed, as shown in Figures 5 and 6.

Atmospheric pressure experiments with Fe/SiO_2 and precipitated Fe_2O_3 showed that most of the dehydration of ethanol to ethylene was caused by the SiO_2. Conversion of ethanol to ethylene was 90% over Fe/SiO_2 but less than 5% over an unsupported Fe_2O_3 divided catalyst.

As was pointed out in the June 1986 Quarterly Report, the residence times of added alcohols were unexpectedly long in the slurry reactor when the catalyst was with Fe/SiO_2. A comparison of the results of feeding ethanol to the Fe/SiO_2 and C-73 catalysts is shown in Figure 10. It will be seen that the labeled ethanol disappeared from the outlet gas much more rapidly after cutting off the ethanol feed when using the C-73 catalyst than when using the Fe/SiO_2 catalyst. Similar results were obtained when feeding labeled pentanol. In that case, though, the product monitored was the C_5 hydrocarbons, since pentanol did not appear in the gas phase sample. In order to obtain a better understanding of this phenomenon a fixed bed reactor was packed with the support used in preparing the Fe/SiO_2 catalyst and operated under the conditions used in operation of the slurry reactor. Over SiO_2, CO/H_2 did not react at all, as expected. Both $CO/H_2/C_2H_5OH$ and He/C_2H_5OH did react, however. Products are shown in Table I. The outlet ethanol concentration in the two latter cases dropped very slowly with time after cutting off its feed, and attained background level only after two days.

^{14}C Distribution in C_9 - C_{15} Alkanes:

When ethanol labeled with ^{14}C at the carbinol carbon was added to the CO/H_2 feed to an Fe/SiO_2 catalyst operating in the slurry reactor at 260°C and 7 atmospheres, only 15% or less of the ^{14}C was incorporated in the hydrocarbon products. The activity level of the C_9-C_{15} products recovered was too low to measure by the proportional counter when it was used in conjunction with the gas chromatographic analyzer to separate the products by carbon number. To determine the activity in these materials a sample of liquid was collected and the paraffins separated by dry columns silica gel chromatography. Liquid chromatography was then used to separate the paraffin fraction by carbon number and the C_9-C_{15} fractions obtained were analyzed for ^{14}C by liquid scintillation counting. Similar scintillation results were obtained on two different liquid scintillation instruments. The results are shown in Figure 11. The observed decrease in (counts/minute/ ole of hydrocarbon) with increasing carbon number is not consistent with the usual interpretations of the fate of additives to the Fischer-Tropsch reaction nor with the results of analyses of the gas phase hydrocarbons reported above. This problem is considered further in the following Discussion section.

DISCUSSION

This discussion will follow the order used in presenting the results above, i.e., the effects of alcohols on synthesis gas conversion and olefin hydrogenation will be considered first, then the information gathered on the fate of the ^{14}C in the reaction, and finally the observations on distribution of ^{14}C in the C_9-C_{15} paraffins first reported in the June 1986 Quarterly Report which have been extended in the past quarter.

Effects of Alcohol Feed on Synthesis Gas Conversion:

The effects of adding alcohol to the feed on the extent of synthesis gas conversion and on alkane formation (olefin hydrogenation, presumably) depend on the catalyst under study. When 10% Fe/SiO_2 is used, both synthesis gas formation and the percent alkane in the hydrocarbons produced decrease in the presence of added alcohol. When the C-73 catalyst is used, neither conversion nor fraction alkane change when alcohol is introduced. It is tempting to attribute this difference in the behavior of the two catalysts to the now-proven activity of the SiO_2 as a dehydration catalyst. The ethylene and/or the water produced could easily serve as reaction inhibitors. Ethylene, for example, could compete with hydrogen for the available catalyst surface sites and, if adsorbed, it would be expected to consume some of the available surface hydrogen. The rate of the synthesis reaction over iron catalysts increases with increasing hydrogen pressure, as shown by Vannice (1), for example. Surface hydrogen concentration should be directly related to the hydrogen pressure.

The same surface hydrogen that controls the rate of synthesis can reasonably be expected to control the rate of hydrogenation of olefins over these catalysts. Thus the effects of ethanol on synthesis gas conversion and on alkane concentration in the hydrocarbons produced can be viewed as having a common cause.

CO and CO_2 from Added Alcohols:

The appearance of labeled CO and CO_2 when carbinol-labeled alcohols are feed but not when methyl-labeled ethanol is fed (see Figures 5 and 6) demonstrates that some cleavage of the alkyl-carbinol bond occurs. Dehydrogenation of ethanol to acetaldehyde was shown here to be a facile process (March 1986 Quarterly Report), and Blyholder showed several years ago (2) that aldehydes adsorb on some first row Group VIII metals with decomposition to CO and an alkyl group. If this is the process by which the alkyl-carbinol bond in alcohols is cleaved over these Fischer-Tropsch catalysts, though, it is necessary to explain why the specific activity of the outlet CO is lower than that of the accompanying CO_2, by a factor of three in the case of ethanol feed and by a factor of nearly ten in the case of pentanol feed. The explanation almost certainly lies in the difference between the heats of chemisorption of the two compounds. CO, by virtue of its pi-bonding ability, has a high heat of chemisorption, around 40 Kcal/mole, on Group VIII metals (3), while the heat of non-dissociative CO_2 adsorption is low. This will be reflected in the relative rates of CO and CO_2 desorption. CO should desorb relatively slowly while CO_2 should desorb almost instantaneously at synthesis temperatures. In that situation the adsorbed CO formed from the aldehyde should remain on the catalyst surface long enough to react with a surface O. Candidate sources of surface O would be either H_2O or the O formed by the CO dissociation required by the synthesis reaction. The former is the more likely since H_2O rather than CO_2 is the principal primary product.

Reaction of H_2O with adsorbed CO would produce CO_2 and H_2, i.e., the shift reaction. The thermodynamics of the shift reaction are such that it cannot proceed to completion, but the equilibrium constant is readily calculated from tabulated thermodynamic data (4). If the shift reaction proceeded to equilibrium, equilibrium should also exist in the reaction:

$$CO + {}^{*}CO_2 \rightleftharpoons CO_2 + {}^{*}CO$$

The fact that this equilibrium is not established implies that the shift reaction proceeds relatively slowly and does not reach equilibrium under the experimental conditions. This conclusion can be confirmed. In Table II the value of the equilibrium constant,

$$Kp = [CO_2]\ [H_2]\ /\ [CO]\ [H_2O] \text{ at equilibrium,}$$

is compared with the partial pressure ratios determined while feeding ethanol and pentanol. It is evident from the data given there that the shift reaction has not gone to equilibrium. Since the partial pressures of CO and

H_2 are essentially fixed by the feed composition, the deviation of the experimental pressure ratio from its equilibrium value can be attributed to the CO_2/H_2O ratio. Evidently the ($CO + H_2O$) reaction proceeds about a third of the way to equilibrium at the experimental conditions employed.

If alcohols decompose over the iron catalysts in the manner suggested above, through aldehydes which adsorb as CO and an alkyl group of carbon number one less than that of the starting alcohol, some evidence of this should appear in the hydrocarbon product distribution. In Figure 9, though, which shows the specific activities of the C_3-C_7 hydrocarbons produced when labeled pentanol as fed to the C-73 catalyst in the slurry reactor, the specific activity of the C_4 hydrocarbons is very close to that of the CO_2 and the C_3 hydrocarbons rather than to that of the higher hydrocarbons. This argues against the idea that C-C bond cleavage is involved in the incorporation process. It is still possible, though, that the bond cleavage reaction does take place but is responsible for only a small fraction of the incorporation. The specific activity of the CO_2 produced in the experiment giving the data shown in Figure 9 was less than a tenth of that of the C_5-C_7 hydrocarbons. Similarly, the specific activity of the CO_2 produced while feeding carbinol-labeled ethanol to the Fe/SiO_2 catalyst in the fixed bed reactor was only 1/10 to 1/20 that of the C_2-C_4 hydrocarbons collected from the experiment.

One other feature of Figure 9 is deserving of special mention. Just as in the case of the C_4 hydrocarbons shown in Figure 8, there are apparently real differences in the specific activities of the separate C_5, C_6 and C_7 hydrocarbons produced by the C-73 catalyst when labeled n-pentanol is fed. Another study will be required to arrive at a rationalization of the differences between the isomers. Pending that, the averages of the activities for all hydrocarbons of a given carbon number have been used to draw up in Figure 9. It will be noted that the average specific activity of the C_5 hydrocarbons collected is no higher than that of the C_6 and C_7 hydrocarbons being produced in the same experiment. Since n-pentanol was the feed, any direct dehydration would form pentanes. Pentanes formed by that reaction should have the specific activity of the starting pentanol, of necessity higher than that of the higher hydrocarbons since the latter are produced in part via the synthesis reaction from unlabeled CO. There actually is no detectable perturbation of the product distribution as a result of feeding pentanol. It can be concluded that, over C-73 catalyst operating at 7 atmospheres, the amount of dehydration that takes place is negligible. That is not the case when feeding ethanol to the Fe/SiO_2 catalyst at atmospheric pressure.

^{14}C Distribution in C_9 Alkanes:

Several scenarios with respect to ^{14}C distribution in the hydrocarbon products are possible when ^{14}C-labeled ethanol is added to the synthesis gas feed. Some of them are outlined below and shown schematically in Figure 12.

I. The carbon in ethanol may become equivalent to that of the CO. If this is the case we would expect the activity to increase with carbon number;

if f is the fraction of ^{14}C in the equilibrated ethanol and CO carbon we expect the following.

	C_1	C_2	C_3	C_4	etc
activity/mole	f	2f	3f	4f	etc

The above sequence applies since the number of doubly labeled compounds is very small ($1/f^2$) with f_1, in the case of ^{14}C, being 10^{-5} or less ^{14}C/mole. A plot of the activity versus carbon number is shown schematically in Figure 12; our results are clearly inconsistent with this scenario.

II. The ethanol initiates chain growth and CO propagates the chain. In this case the ^{14}C cpm remains constant with increasing carbon.

III. The ^{14}C ethanol undergoes chain growth independently of CO chain growth; this is equivalent to polymerization of ethylene so only even carbon number compounds will be labeled.

IV. The ^{14}C ethanol incorporates randomly along the growing Fischer-Tropsch chain; i.e., the chains are initiated and propagated by C from CO with a C_2 from the ethanol inserting in a statistical manner in a growing chain.

None of the above scenarios leads to results consistent with those reported in Figure 11. A possibility that would be more consistent with the experimental data would involve termination of the chain growth process by the combination of two growing chains, as is sometimes found in free radical polymerizations (5). If that mechanism obtains, though, it must represent only a small fraction of the terminations which occur. Otherwise the overall distribution of products with respect to carbon number would deviate from the Anderson-Schulz-Flory universally reported for the Fischer-Tropsch reaction. Actually the hypothesis would not be inconsistent with a distribution having two superimposed linear ASF distributions. Combination might be expected to result in paraffin rather than olefin formation, and there is the possibility that paraffins produced as primary products might be formed by this mechanism at least one group of authors has reported (6) a product distribution in which the C_1 - C_{10} paraffin production was high relative to the production of olefins of the same carbon number. Blyholder and Emmett (7) several years ago reported tracer experiments using ^{14}C-labeled $^{*}CH_3CHO$ in which the ethane formed had nearly twice the specific activity per mole of the ethylene produced. Primary paraffin formation is almost certainly low, though, and most of the paraffins found in the present products must be produced by the secondary hydrogenation of the olefins which are primary products. Thus paraffin formation by coupling seems an unlikely explanation of the observations reported here.

Perhaps the most likely explanation for the decrease in specific activity with chain length in the heavy products recovered from these experiments is varying dilution of the hydrocarbons produced during the period when labeled ethanol was being fed by hydrocarbons of the same carbon number held in the suspending medium in the slurry reactor. Because the volatilities of hydrocarbons decrease with increasing carbon number the equilibrium inventory must increase with carbon number. This in fact, more rapidly than the amount produced decreases, is the case as a gc analysis of the contents of the reactor is shown. Because the inventory increases while the molar rate of production decreases with carbon number, the time required to establish equilibrium conditions increases with increasing carbon number. A recent publication by Bell et al. (8) discusses this behavior quantitatively. If the system has not come to equilibrium for a given carbon number the ^{14}C content of the product recovered will be less than its equilibrium value, and the deviation from equilibrium will increase with increasing carbon number. This explanation would account for the fact that the specific activity of the C_2-C_5 hydrocarbons is independent of carbon number, as shown in Figure 8, although the activities of the C_9-C_{15} hydrocarbons decrease with carbon number. Referring to Figure 12, the data in Figure 8 can be seen to be consistent with Case II, in which the alcohol serves as an initiator (or terminator) of the growth reaction.

CONCLUSIONS

1. Alcohols are incorporated in the growth reaction occurring on iron-based Fischer-Tropsch catalysts by more than one reaction mechanism. The principal route involves dehydration to an olefin which then apparently serves as a chain growth initiator. Another route involves dissociation of the alcohol at the carbinol carbon which then decomposes to CO which can enter into the synthesis reaction or react with water to form CO_2.

2. Silica, when used as a support for iron-based Fischer-Tropsch catalysts, itself catalyzes a variety of reactions of alcohols. This complicates the product distribution obtained from these catalysts and increases the difficulty of interpreting the results. It will not be included in catalysts used in this project in the future. There is reason to expect that alumina, too, will catalyze many extraneous reactions.

3. The inventory of products in the slurry reactor introduces complications in product collection which require additional investigation. The stability and temperature control provided by this reaction largely outweigh its disadvantages; however, so it will continue to be operated on this project, supplemented by the new atmospheric pressure reactor.

FUTURE WORK

1. Testing of precipitated Fe_2O_3 catalysts will continue and a series of promoter-containing catalysts prepared from the pure precipitated material by the incipient wetness technique.

2. The variations of residence time in the slurry reactor with carbon number of the product, and the effects of these variations on the observed product distribution, will be investigated in some detail.

3. Synthesize labeled pentenes.

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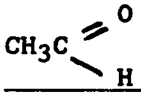
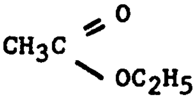
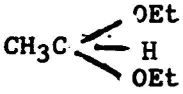
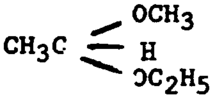
Table I

The Effect of SiO_2 During $CO/H_2/C_2H_5OH$

Catalyst/Product	C-73	Fe/SiO_2	SiO_2
C_2H_4	✓	✓	✓
C_2H_6	✓	✓	X
 CH_3CHO	✓	✓	✓
 $CH_3COOC_2H_5$	Tiny	✓	✓
 $CH_3CH(OEt)_2$	X	✓	✓
 $CH_3CH(OCH_3)(OC_2H_5)$	X	✓	X

Compound was formed in significant quantities.

Compound was not detected by g.c. analysis.

Table II

Shift Reaction - Approach to Equilibrium[a]

Condition	$P_{CO2}P_{H2}/P_{CO}P_{H2O}$
Equilibrium (Kp, calc.)	65 ± 2
2% $CH_3{*}CH_2OH$ in feed	28 ± 3
2% $C_4H_9CH_2OH$ in feed	24 ± 3

a. 10% Fe/SiO_2 catalyst, slurry reactor, 261°C, 7 atm. absolute, $H_2/CO=1$, gas flow = 130cc/hr/gm. catalyst.

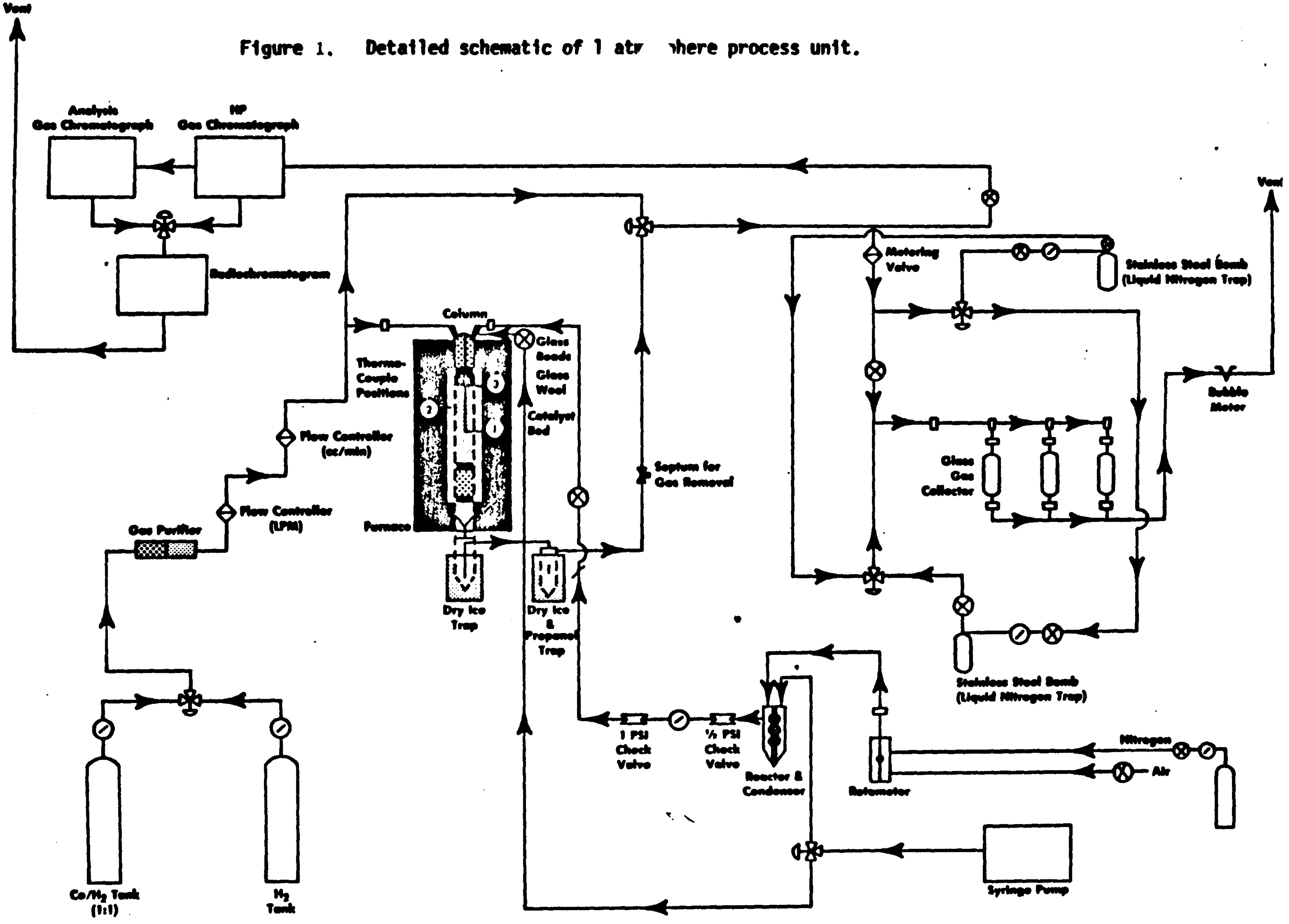


Figure 1. Detailed schematic of 1 atmosphere process unit.

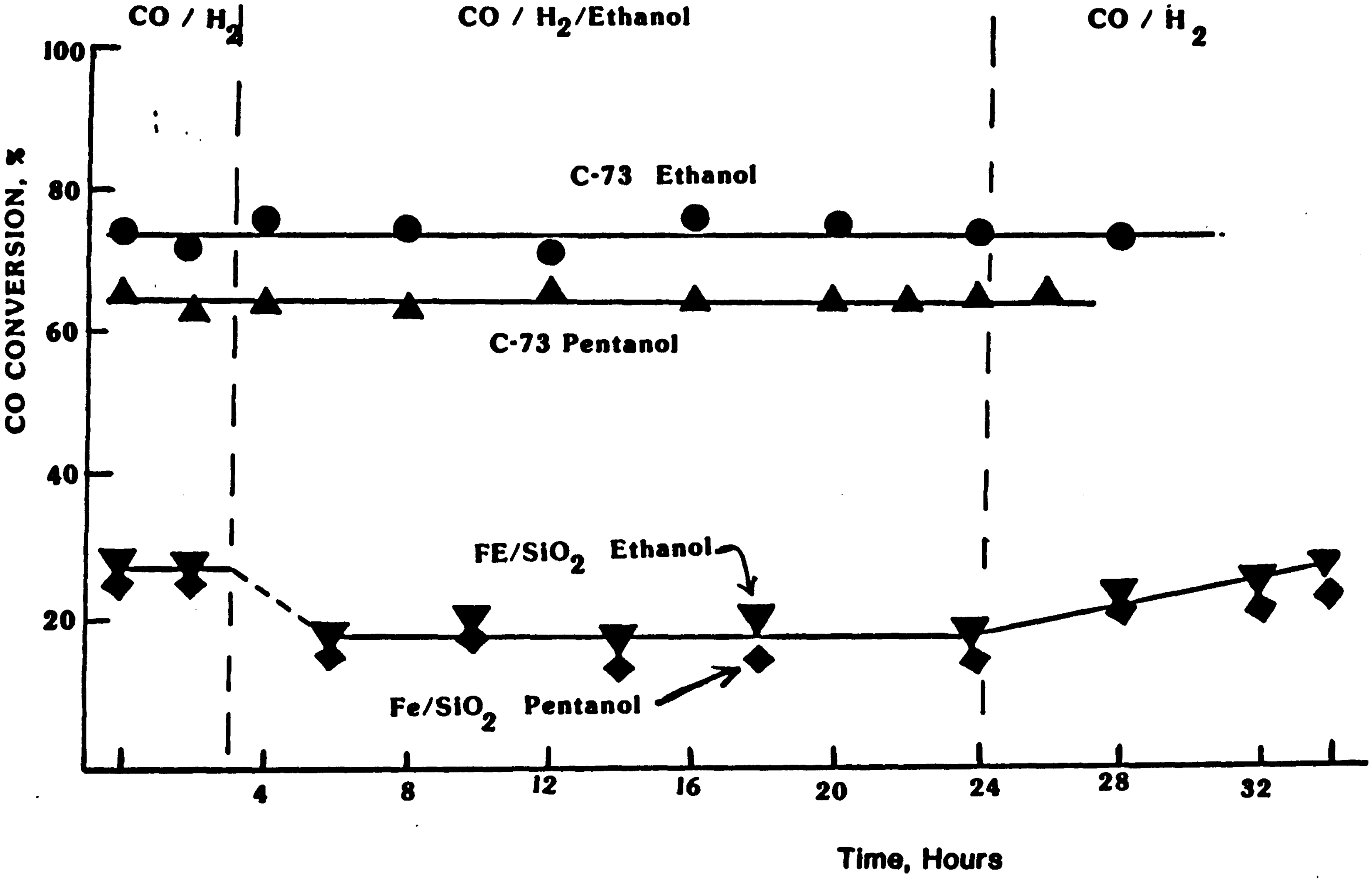


Figure 2. Conversion of CO with a C-73 or Fe-SiO$_2$ catalyst for a syngas only feed or a syngas with added ethanol or pentanol (conversion at 260°C and 7 atmospheres).

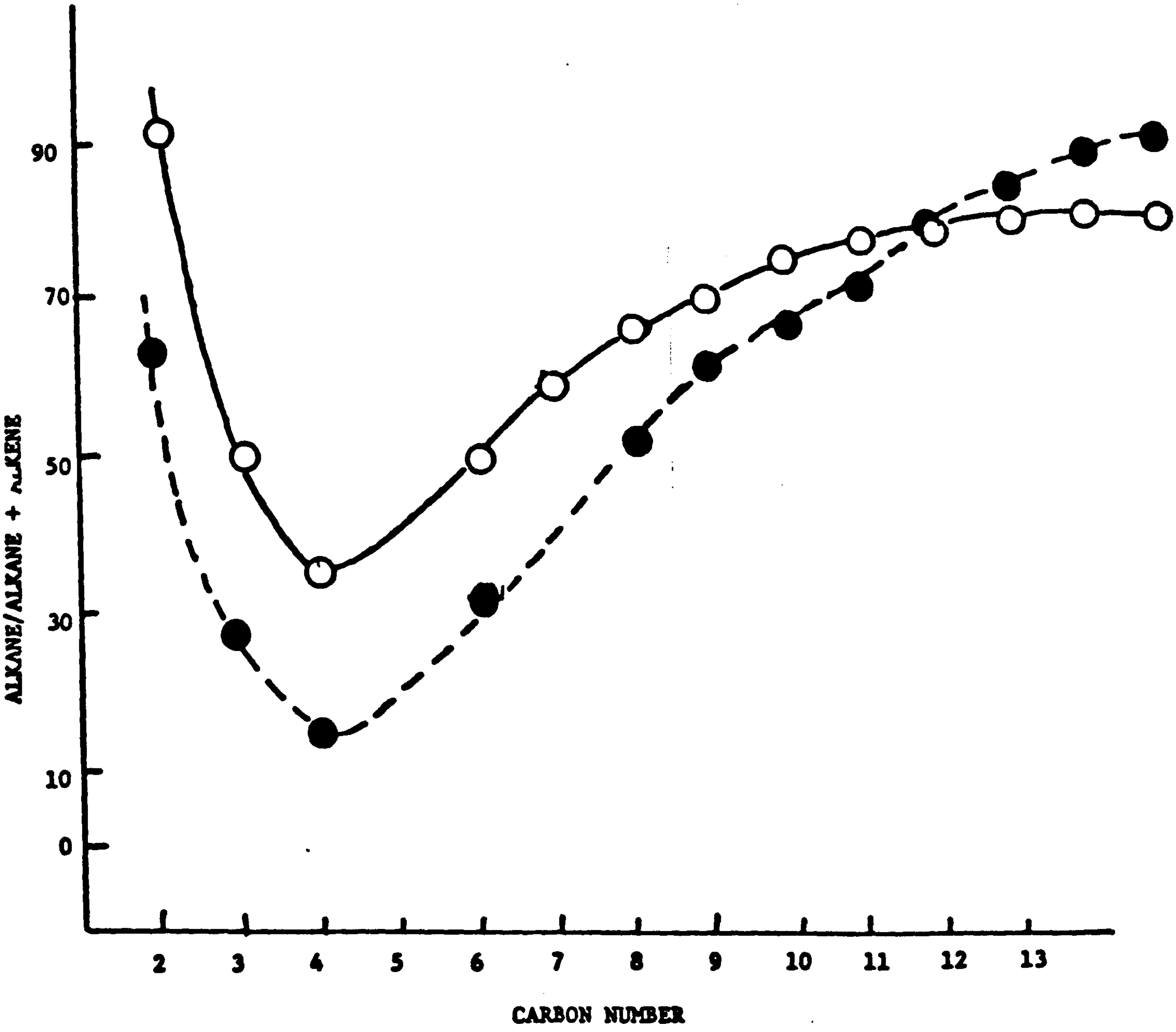


Figure 3. Alkane percentage for the conversion at 7 atmospheres, CO/H_2 = 1, GHSV = 130 (○); 7 atmospheres, CO/H_2 = 1 with 2 mole ethanol (based on CO), GHSV = 130 (●);

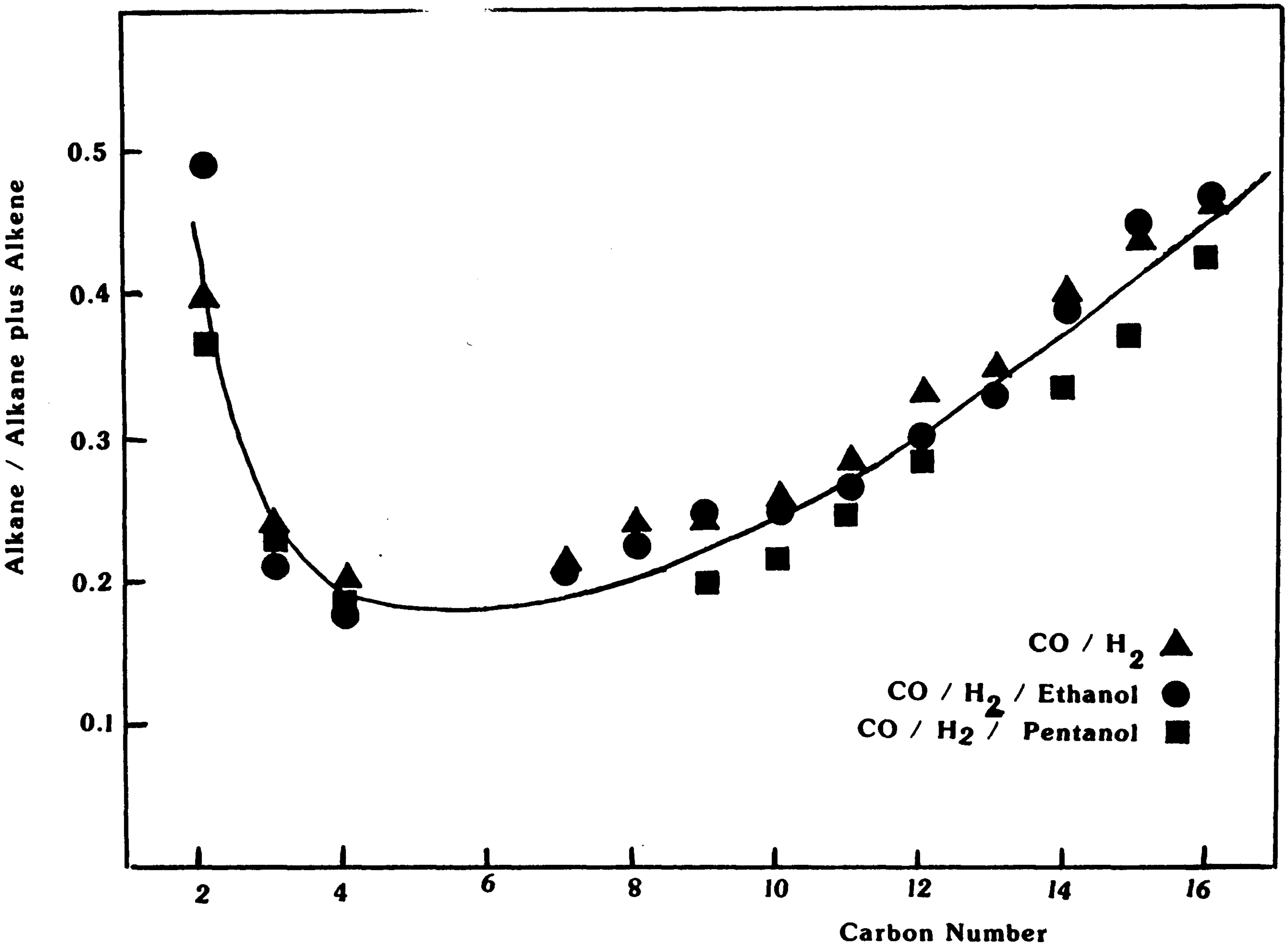


Figure 4. Percentage of alkane, by carbon number, formed during syngas conversion (▲), with ethanol addition (●) or with pentanol addition (■) (C-73 catalyst at 7 atm. and 260°C).

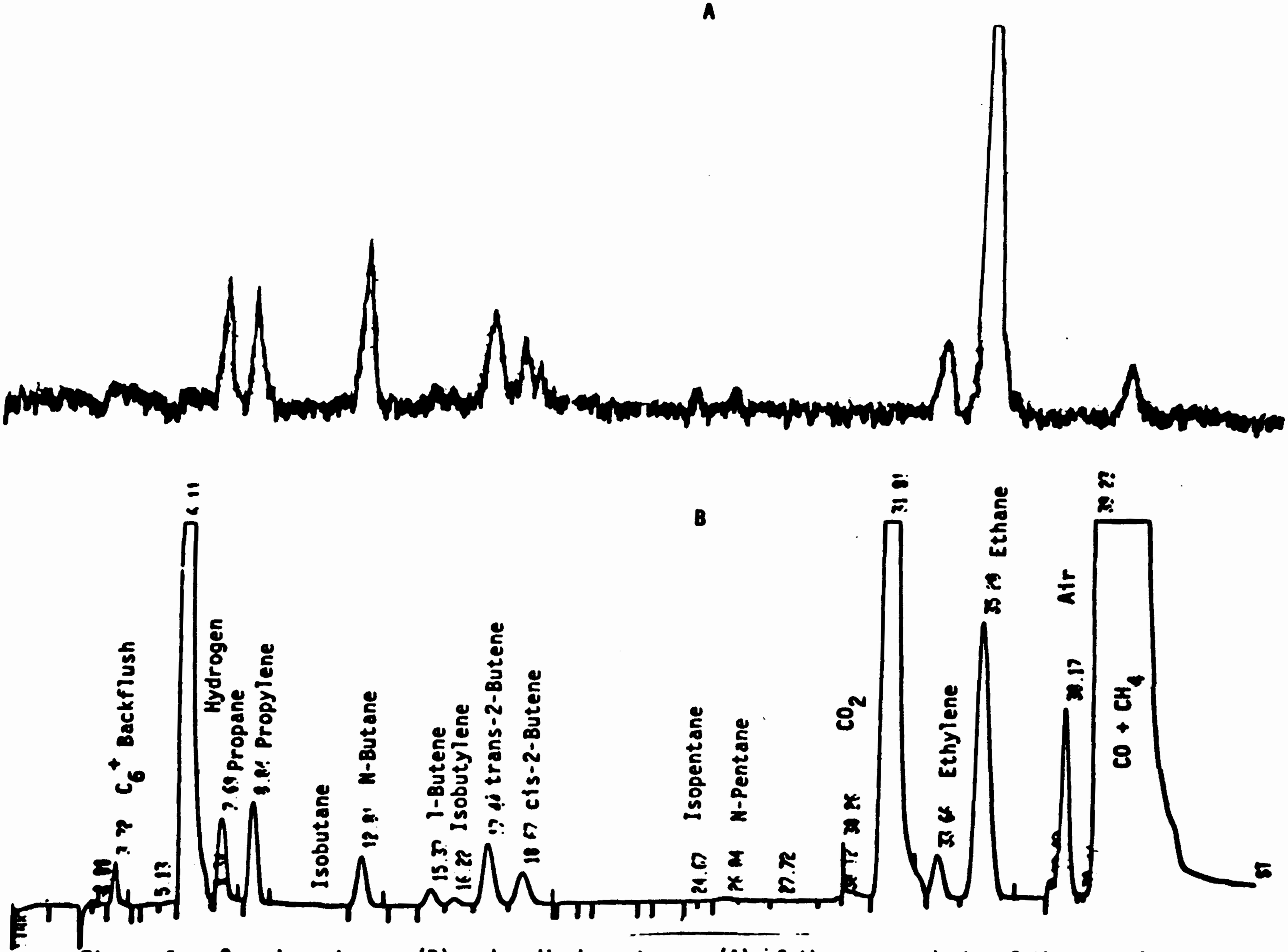


Figure 5. Gas chromatogram (B) and radiochromatogram (A) of the gas products of the reaction of CO/H_2 (50:50) and $^{14}CH_3$-CH_2OH at 260 +2°C, LHSV 231/hr.

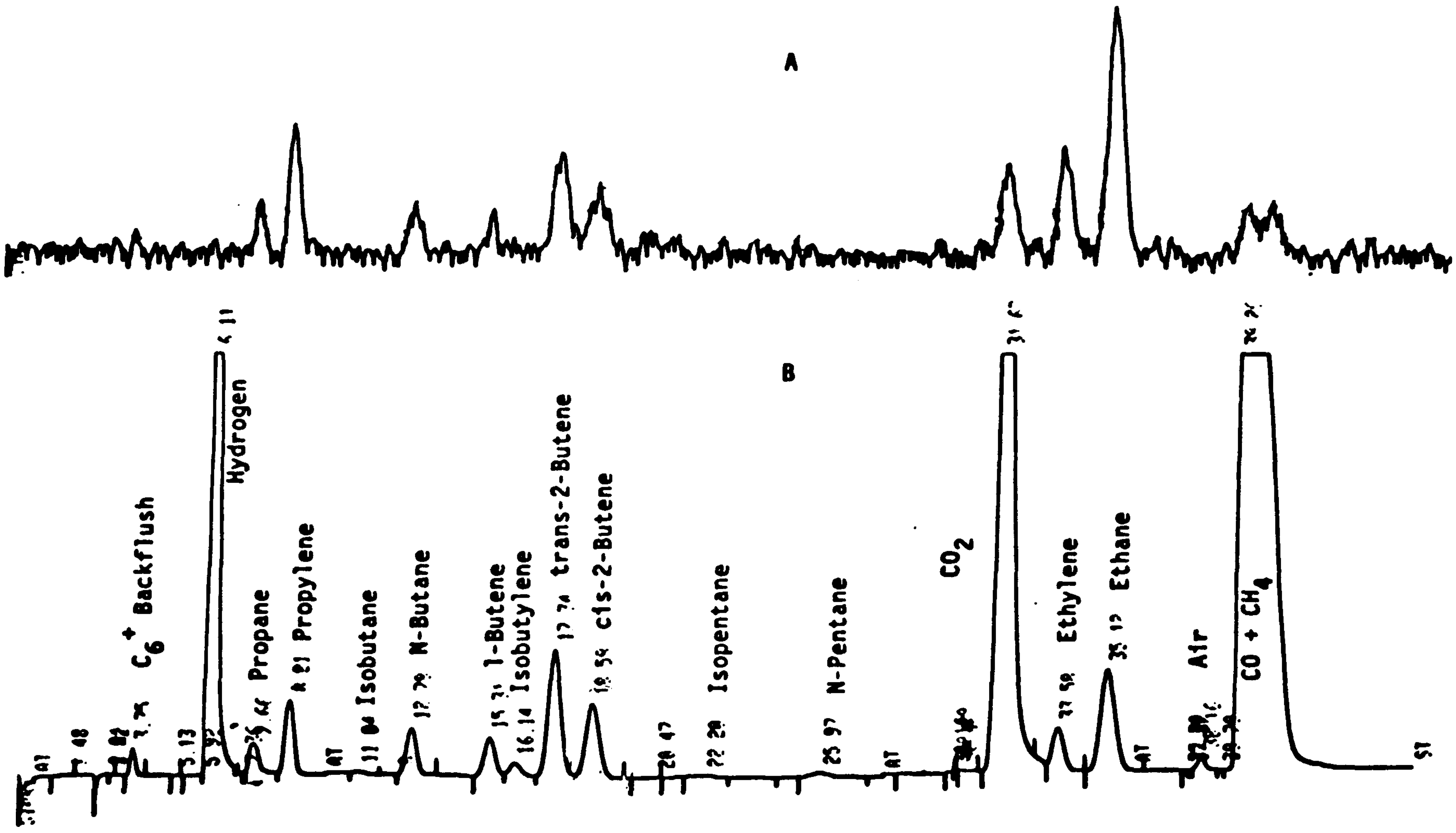


Figure 6 . Gas chromatogram (B) and radiochromatogram (A) of the gas products of the reaction of CO/H_2 (50:50) and CH_3-$^{14}CH_2OH$ at 260 +2°C, LHSV 231/hr.

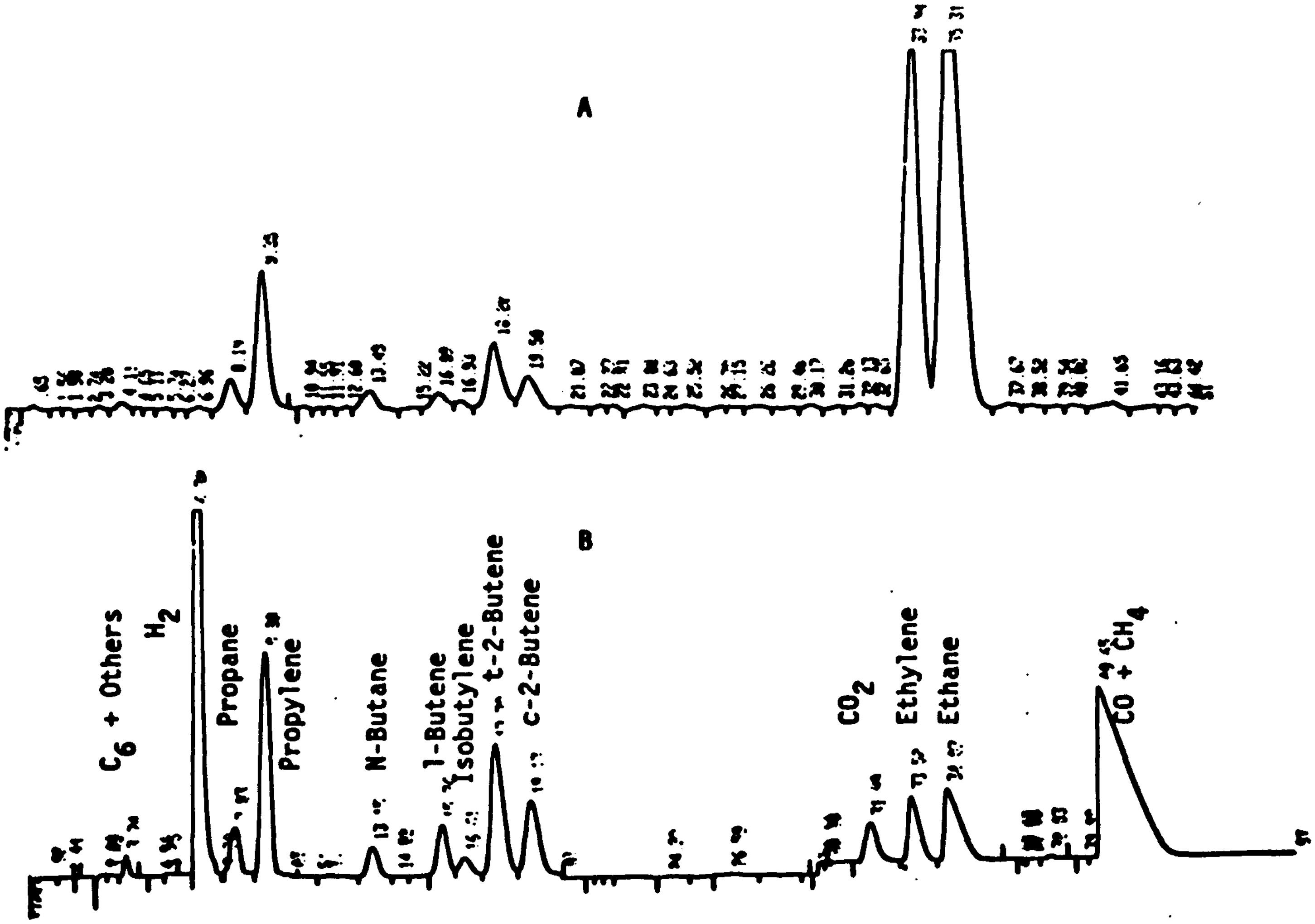


Figure 7. Gas chromatogram (B) and radiochromatogram (A) of the gas products of the reaction of CO/H_2 (1:1) and $^{14}CH_2 = CH_2$ at 260°C ± 2°C GHSV 231/hr.

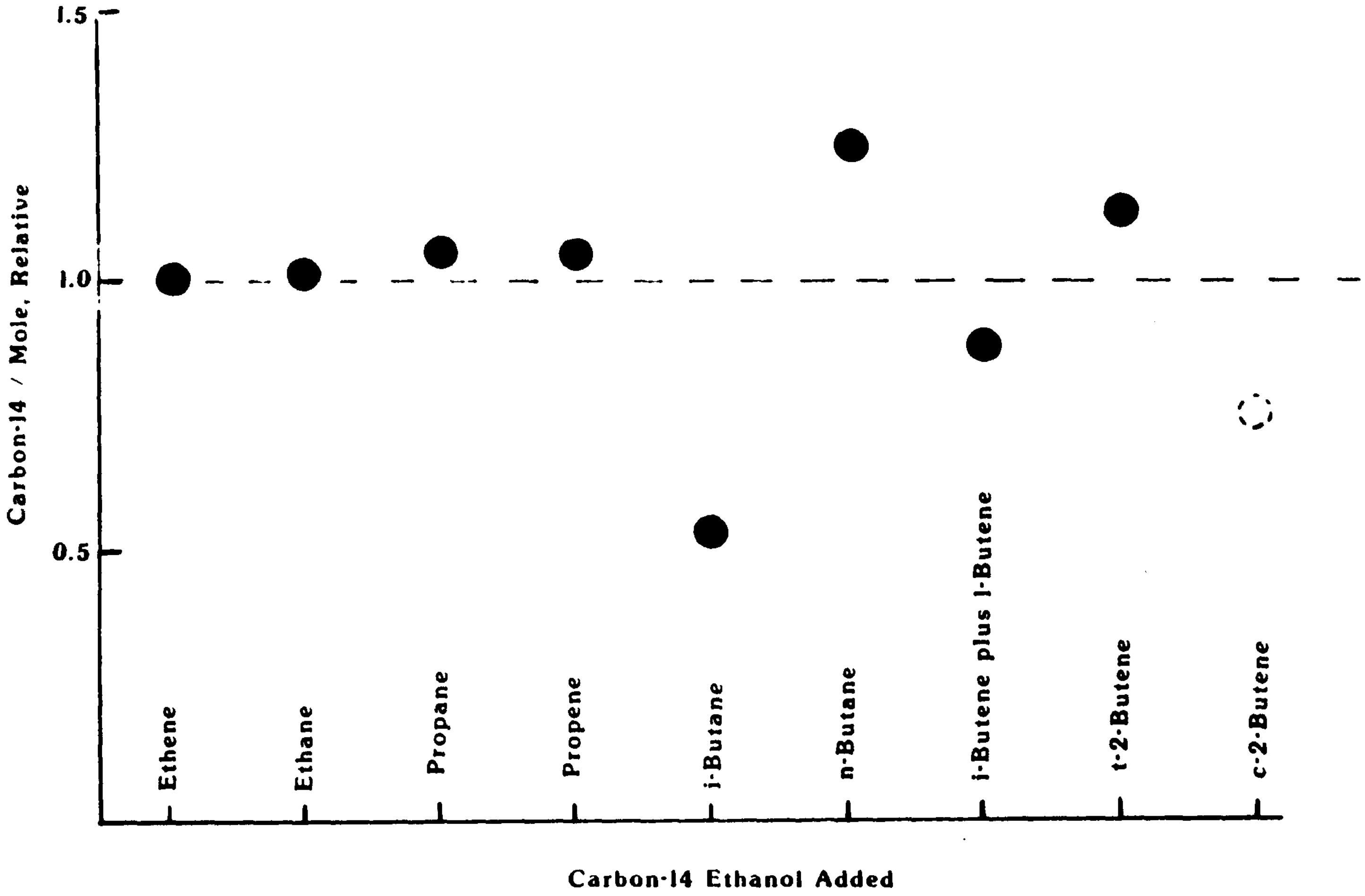


Figure 8. Relative ^{14}C/mole of products formed when labeled ethanol is added to the syngas and converted with a C-73 catalyst at 260°C and 7 atm.

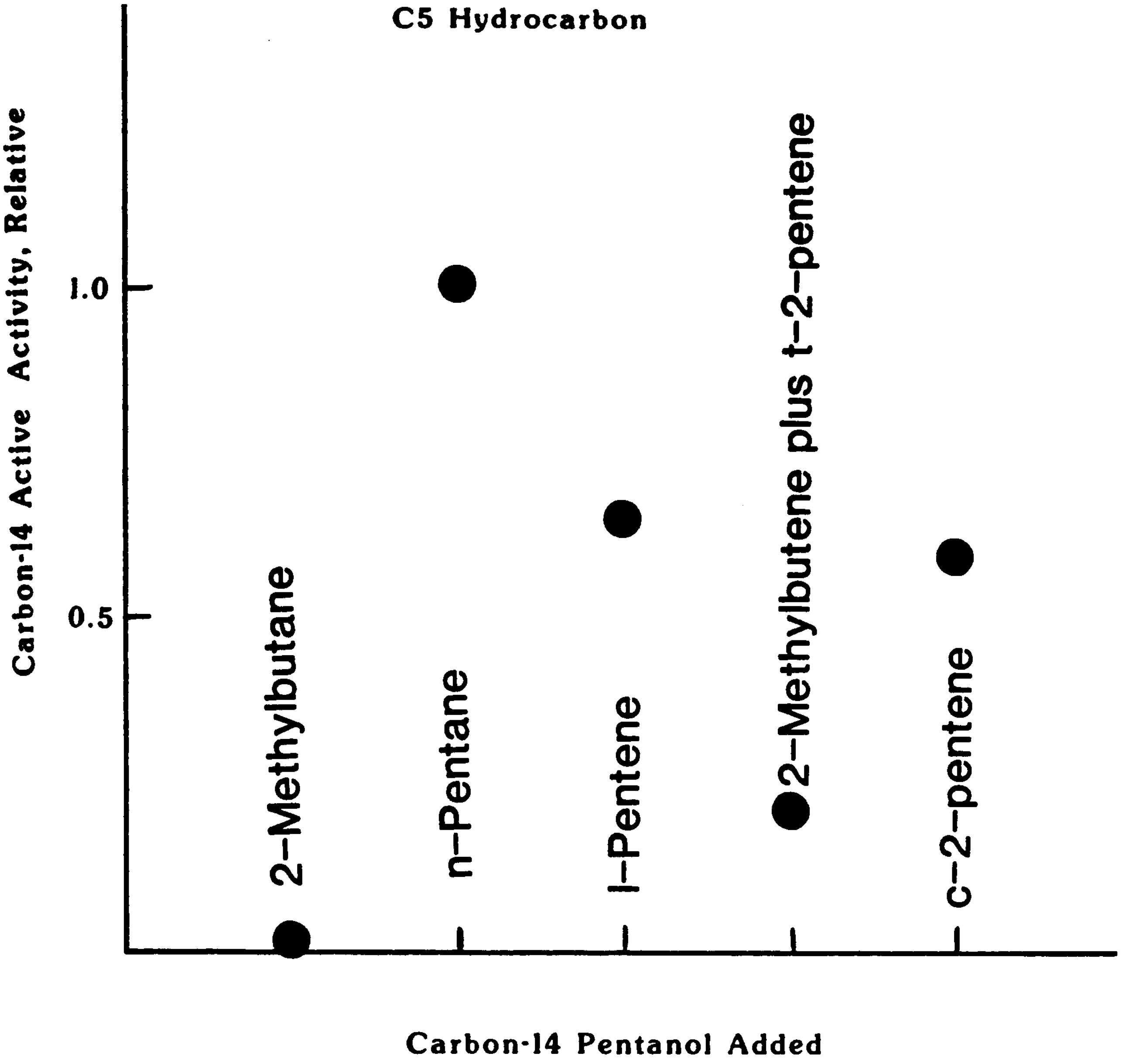


Figure 9. C-5 products from the conversion of syngas containing ^{14}C labeled pentanol with a C-73 catalyst at 260°C and 7 atm.

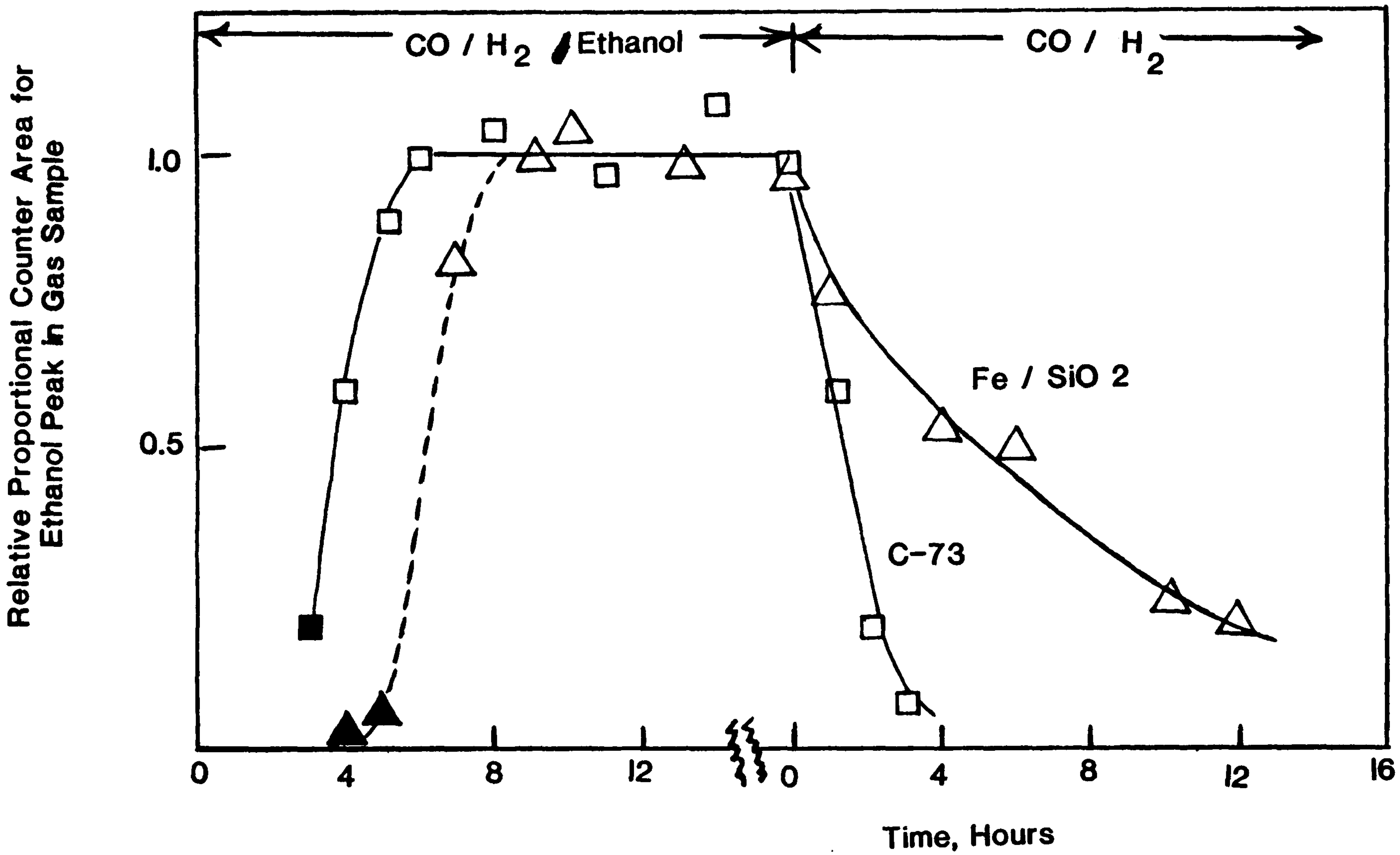


Figure 10. Relative radioactive ethanol in gaseous effluent when C-14 labeled ethanol is added to a syngas feed to a 10% Fe-SiO_2 (△) or a C-73 catalyst (□).

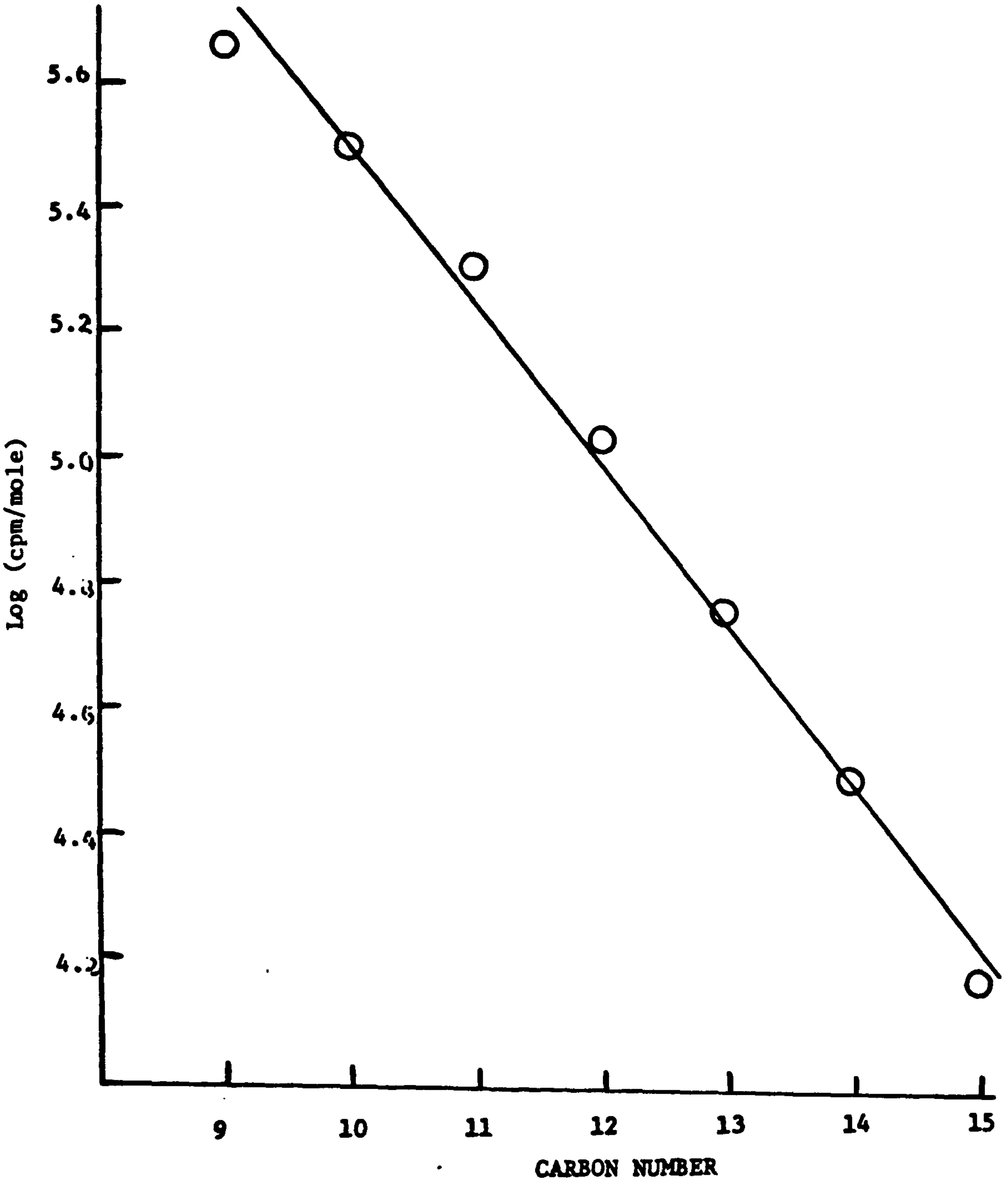


Figure 11. Log (counts per minute/mole hydrocarbon) of the n-alkane fraction separated from the products produced from CO/H_2 with added C-14 labeled ethanol conversion over an $Fe-SiO_2$ catalyst at 260°C and 7 atmospheres pressure.

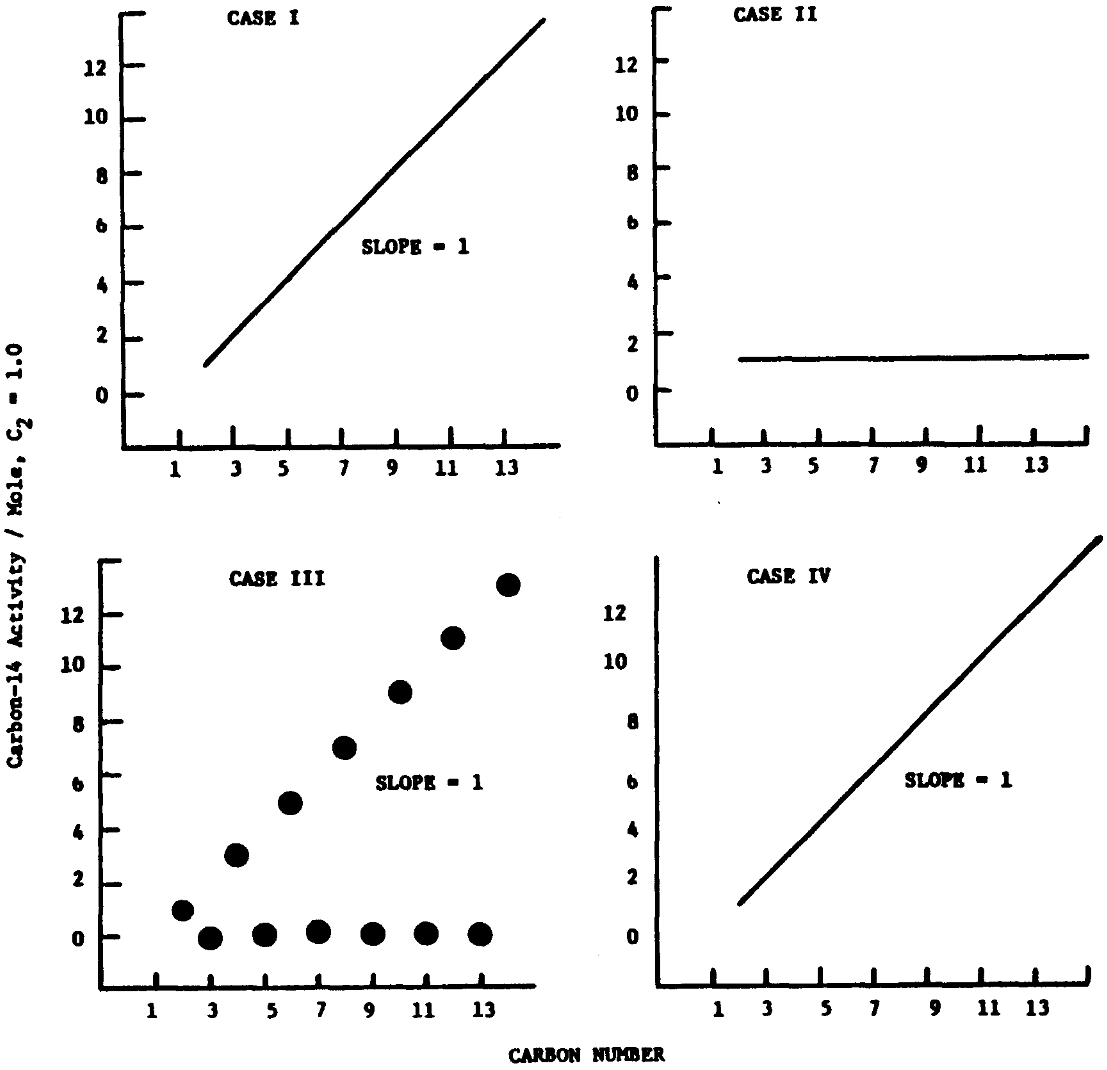


Figure 12. Schematics for the carbon-14 distribution in the products from Fischer-Tropsch synthesis with added C-14 ethanol.