III. Results and Discussion

III-A. Reactant Holdup

The addition of ^{14}C labeled alcohol to the syngas feed to a 10 wt.% Fe on high surface area silica (700 m^2/g) produced two surprising results: (1) there was significant holdup of ethanol in the CSTR and (2) unexpected oxygenate products were formed in significant quantities. The results with this unpromoted iron catalyst, or singly promoted with silica if the support is considered to be a "promoter", are in marked contrast to those obtained with an unsupported, doubly-promoted United Catalysts, Inc. C-73 catalyst.

The holdup when ^{14}C labeled ethanol is added to a syngas feed (H_2/CO ca. 1.25) that is charged to either of the two catalysts in a CSTR operated at 7 atm total pressure at 260°C are shown in figure III-1. The initial delay in the appearance of ^{14}C in the gaseous products is due to filling the tubing connecting the pump to the reactor; it is estimated that this filling will take approximately 3 hours under our experimental conditions. Consequently, since zero time is taken to be the time at which the pump is started, the appearance of ^{14}C labeled ethanol in the gas phase when the C-73 catalyst is used is just what would be expected even though, considering the volume of the reactor, we would not expect it to take about 3 hours to go from the initial appearance of ^{14}C labeled ethanol in the gaseous products to the final, steady-state amount of ^{14}C labeled ethanol. Consequently, even with the C-73 catalyst, it requires more than the "rule-of-thumb" five volumes of flow to attain a steady-state gaseous composition in the CSTR effluent. Since essentially identical flow conditions and experimental volumes were used in the two runs shown in figure III-1, the additional holdup when using the 10 wt.% Fe on silica catalyst is approximately 3 hours.

The holdup is also apparent from the data showing the amount of ^{14}C labeled ethanol in the exit gas stream following termination of elthanol feed to the reactor. It again takes approximately 3 hours for the ^{14}C in the ethanol in the exit gas stream to attain the background level when using the C-73 catalyst. Thus, a similar holdup time is obtained with ethanol addition for either the initiation or the termination of ethanol-addition to the syngas stream. With the 10 wt.% Fe on silica catalyst the holdup is even more pronounced when ^{14}C labeled ethanol is removed from the syngas stream. About 6 hours were required to attain a 50% reduction in the ^{14}C labeled ethanol in the gaseous effluent and the effluent gas still contained ^{14}C labeled ethanol 24 hours after ethanol addition was terminated.

With pentanol we were unable to make a direct measure of the enhanced retention by the silica supported catalyst since: (1) pentanol was not present in measurable amounts in the gaseous effluent and (2) sufficient cold trap sample, containing pentanol, could only be collected after about 20 hours of continuous running. However, the pentenes formed from pentanol could be observed in the gaseous effluent. While the holdup of these hydrocarbons is less pronounced than for the alcohol, it is evident in figure III-2 that the silica support does cause some retention of these hydrocarbons.

The dehydrogenation of ethanol to produce acetaldehyde was lower with the C-73 catalyst than with the 10% Fe-SiO_2 catalyst. As shown in figure III-3, the ratio of ethanol/acetaldehyde was approximately 6 for the CO/H_2 feed

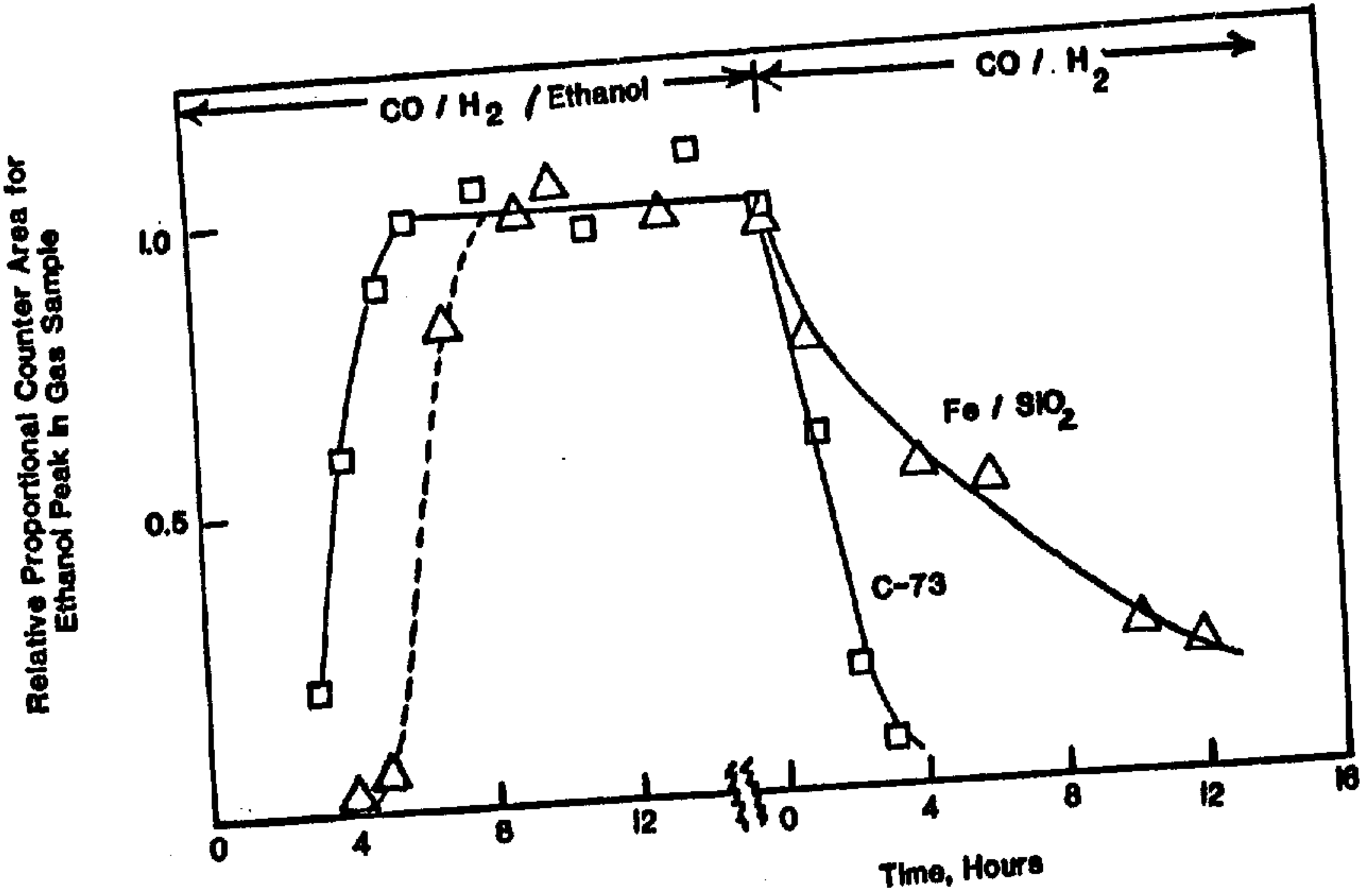

Figure III-1. Relative radioactive ethanol in gaseous effluent when C-14 labeled ethanol is added to a syngas feed to a 10% Fe-SiO_2 (△) or a C-73 catalyst (□).

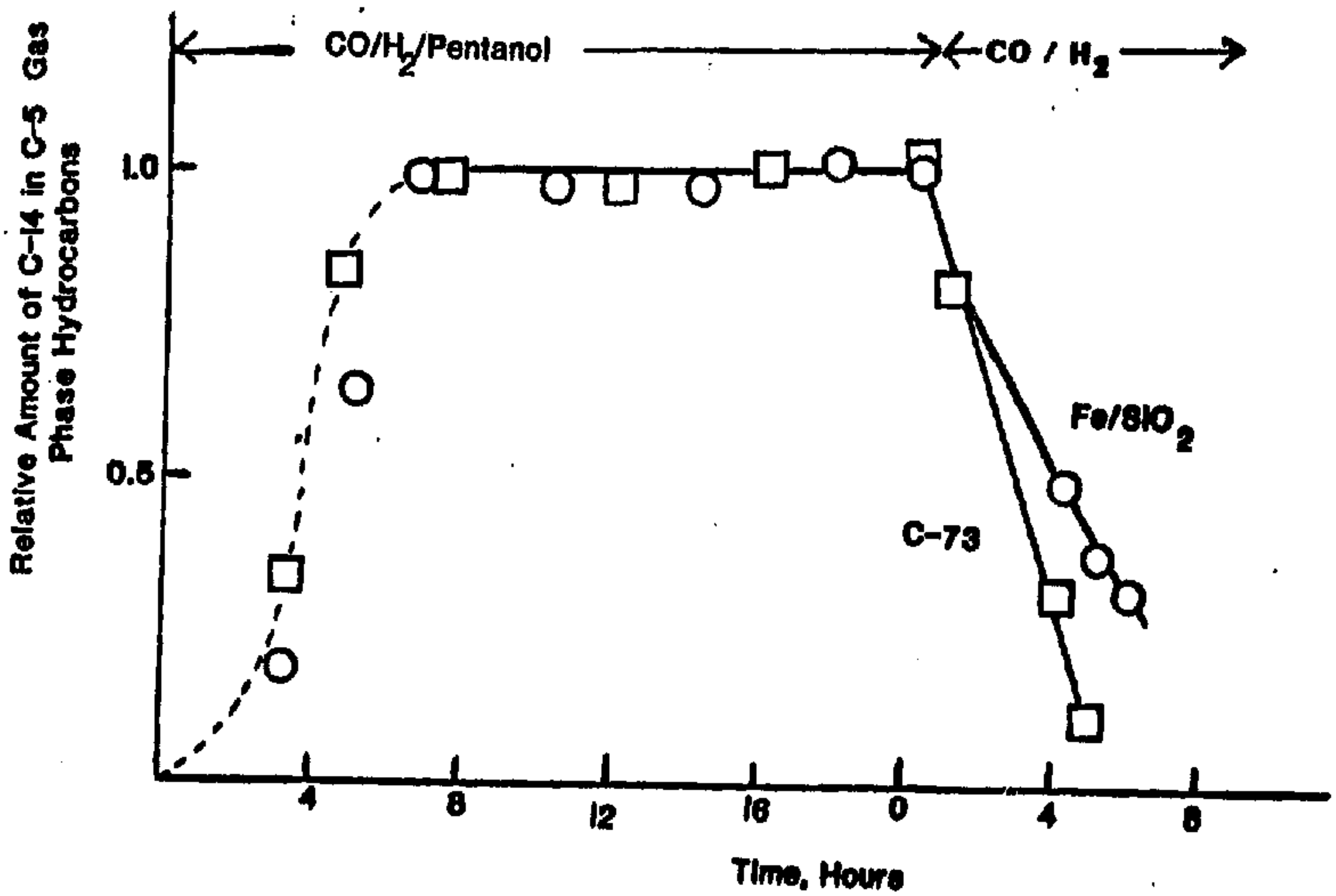

Figure III-2. Relative radioactivity in the C-5 hydrocarbons in the gaseous effluent when C-14 labeled pentanol was added to a syngas feed to 10% Fe-SiO_2 (○) or C-73 (□) catalyst.

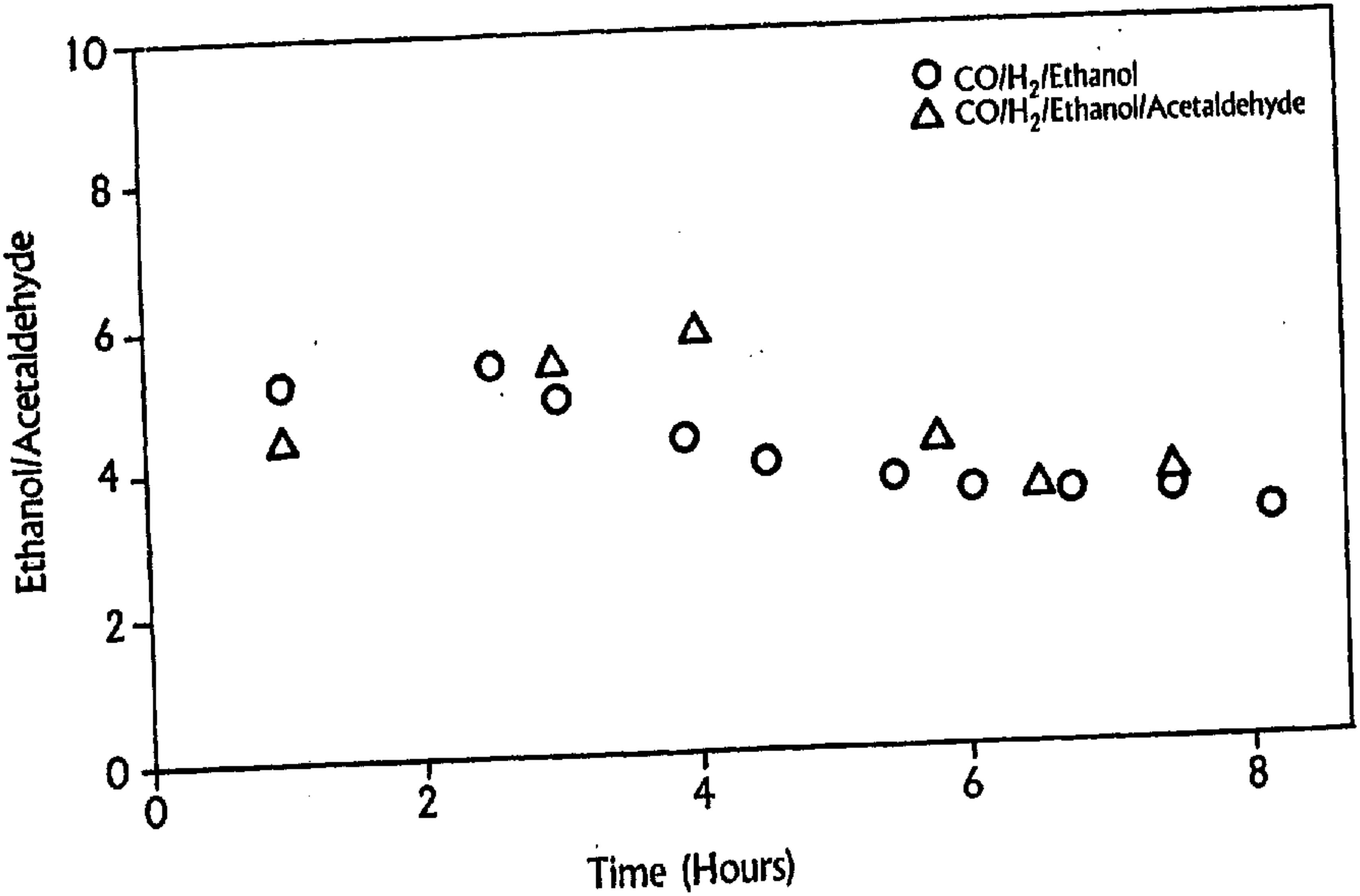

Figure III-3. Plot showing that similar ethanol/acetaldehyde ratios are obtained when the syngas feed contains only ethanol (O) or an equal molar mixture of ethanol and acetaldehyde (Δ).

alone and decreased to about 4 when ethanol was added to the syngas feed. After ethanol addition was terminated, a mixture containing about equal molar amounts of ethanol and acetaldehyde was added to the syngas feed; in this instance acetaldehyde was hydrogenated to give essentially the same ethanol/acetaldehyde ratio as was obtained when ethanol alone was added. With the 10% Fe-SiO_2 catalyst it therefore appears that the dehydrogenation-hydrogenation of the ethanol $\rightleftharpoons$ acetaldehyde reaction is at its equilibrium value. Using the C-73 catalyst under essentially the same conditions, the ratio of ethanol/acetaldehyde was greater than 8 when ethanol was added, and even greater than 10 when ethanol was not added. Note that these ratios are based only upon the gaseous effluent and, since the ethanol/acetaldehyde ratio will be different in the liquid phase due to the different volatility of the two components, they are not true equilibrium values. However, based upon an estimate of the steady-state hydrogen partial pressure in the CSTR and the equilibrium constant, a ratio is about 4 is reasonable.

III-B. Silica Catalyzed Secondary Oxygenate Reactions

Results for the paraffin product distribution, defined as % paraffin = $(C\ paraffin)_i/(C\ total\ products)_i$, are presented in figure III-4 for (a) CO/H_2 syngas feed only (O) and CO/H_2 syngas with added ethanol (◆). The product distributions are similar for the two runs. Thus, adding ethanol at this concentration does not materially alter each carbon number product distribution.

Several oxygenated products were formed from ethanol (Table III-1; next page). Possible pathways for these products are outlined below:

$$C_2H_5OH \rightleftharpoons CH_3CHO \text{ (acetaldehyde)} + H_2 \qquad [III\text{-}1]$$

$$2\ CH_3CHO \rightleftharpoons CH_3C\text{-}O_2C_2H_5 \text{ (ethylacetate)} \qquad [III\text{-}2]$$

$$CH_3CHO + 2\ C_2H_5OH \rightleftharpoons CH_3CH\ (O\ C_2H_5)_2 \text{ (acetal)} \qquad [III\text{-}3]$$

$$CH_3CHO + HCHO \rightleftharpoons CH_3CO_2CH_3 \text{ (methylacetate)} \qquad [III\text{-}4]$$

Mixed acetals are formed in a manner similar to acetal except that another alcohol is substituted for ethanol.

The g.c. trace for a sample of the aqueous layer from the cold trap is shown in figure III-5; no attempt was made to optimize the g.c. analysis since it was used for qualitative purposes only. Of interest for this study was to identify the peaks at retention times 3.13 and 5.75 minutes. The i.r. spectrum for the compound eluting at 3.13 is shown in figure III-6 (bottom) together with the spectrum for a sample of ethyl acetate (top). The agreement between the two spectra is excellent and identifies the compound responsible for the 3.13 peak as ethylacetate (figure III-6). Likewise, the infrared spectrum of diethylacetal and the peak eluting at 5.47 minutes confirm that the peak eluting at 5.47 is acetal as clearly as the spectra in figure III-7 identify ethylacetate.

An ion current g.c.-m.s. spectrum, with peak identification, is shown in figure III-8. The identification of the indicated peaks was accomplished by matching the electron impact (EI) spectrum with published EI spectra.

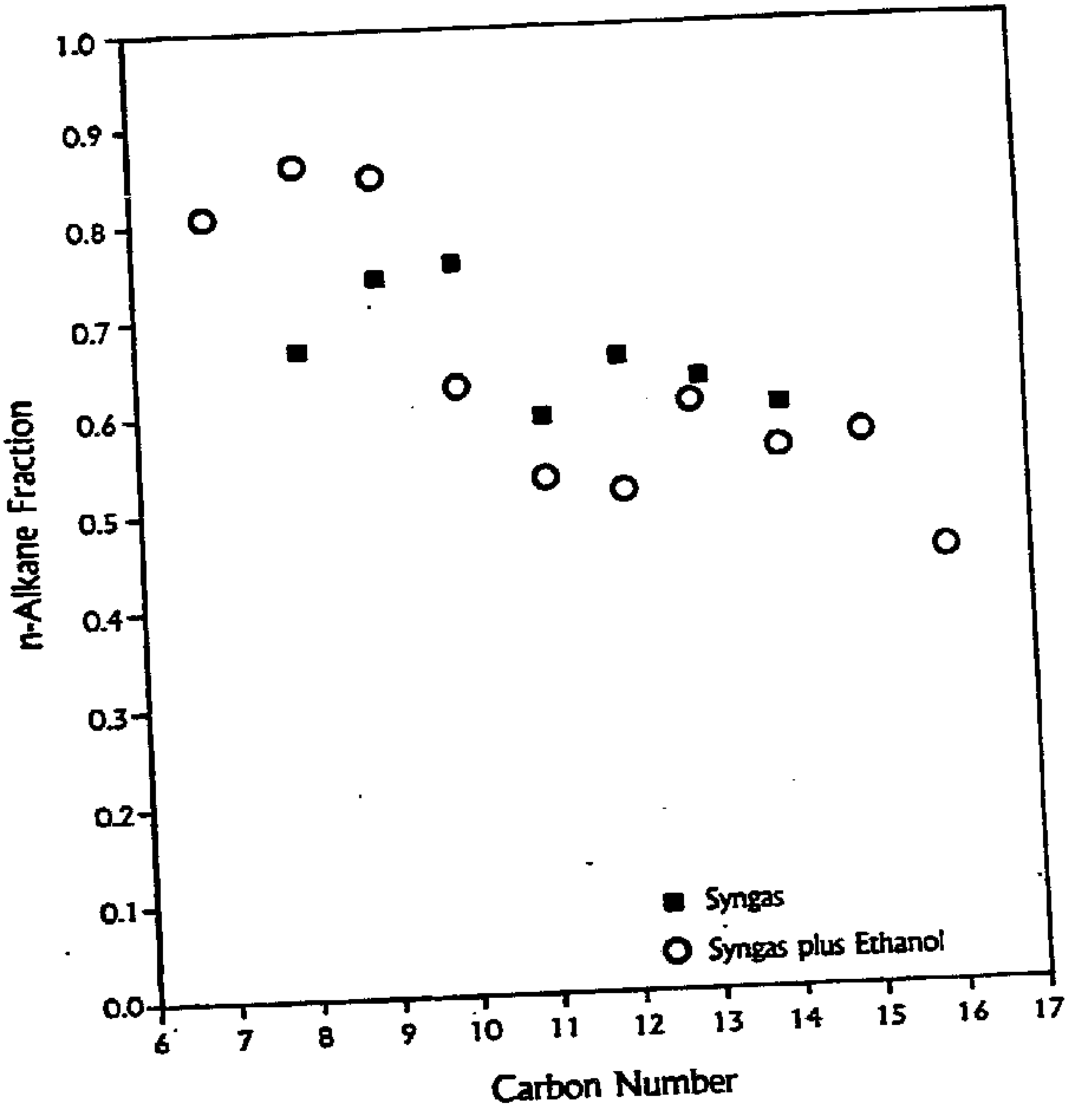

Figure III-4. Fraction of n-alkane, based upon n-alkane plus n-alkenes, formed for each carbon number from C_7 to C_{16} for syngas (■) and for syngas plus ethanol (○) conversions.

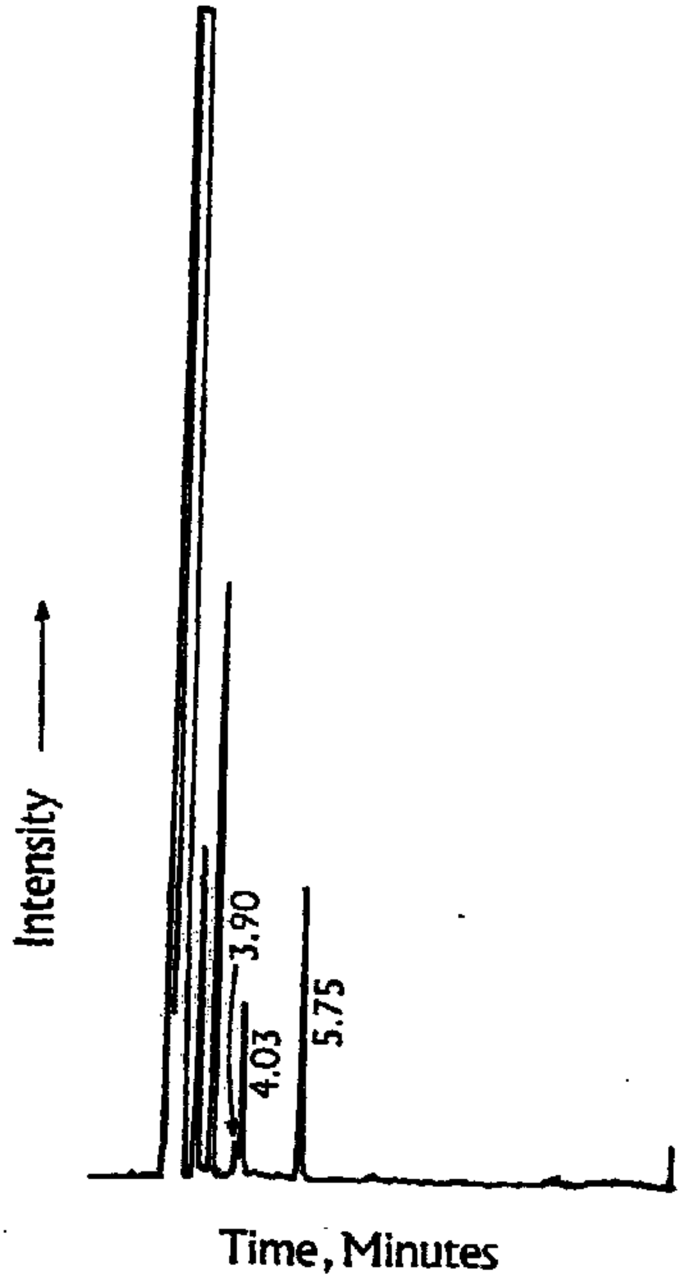

Figure III-5. Capillary g.c. trace for an aqueous phase of a cold trap sample; the peaks correspond to the g.c.-i.r. spectra shown in the following figures.

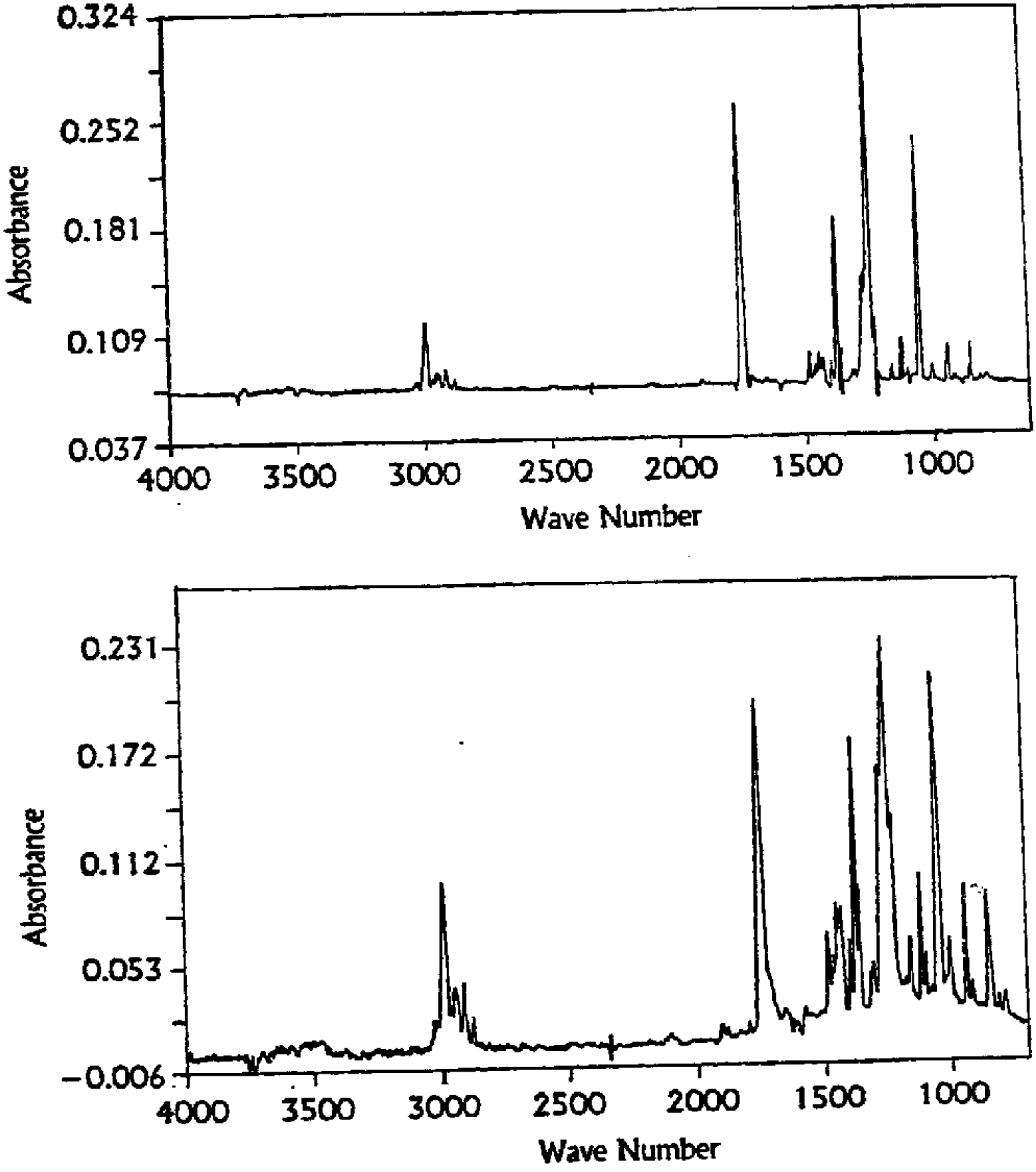

Figure III-6. Ethyl acetate g.c.-i.r. spectrum (top) and the g.c.-i.r. spectrum (bottom) of the peak eluting at 3.13 minutes in figure III-5.

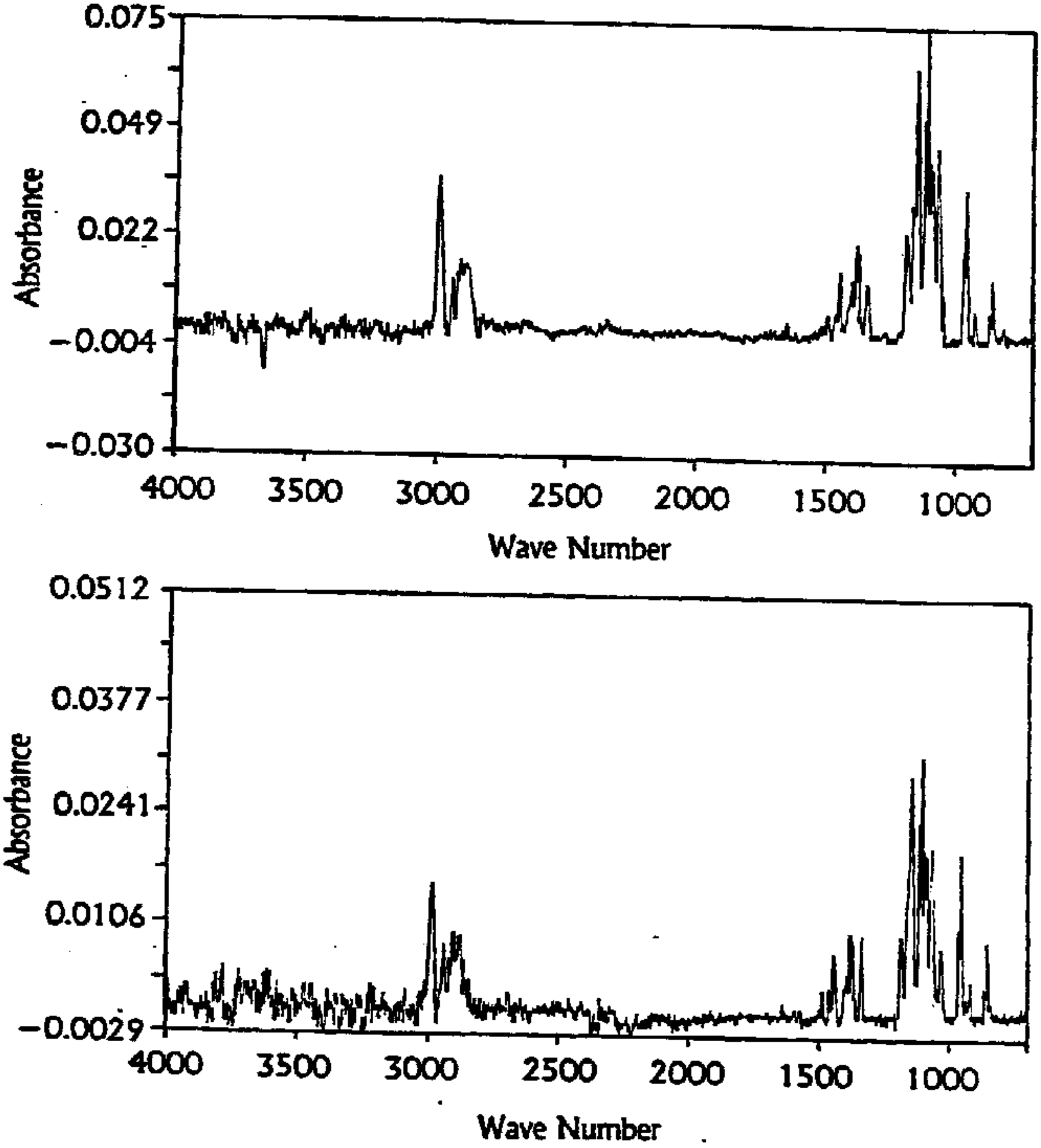

Figure III-7. Diethylacetal g.c.-i.r. spectrum (top) and the g.c.-i.r. spectrum (bottom) of the peak eluting at 5.47 minutes in figure III-5.

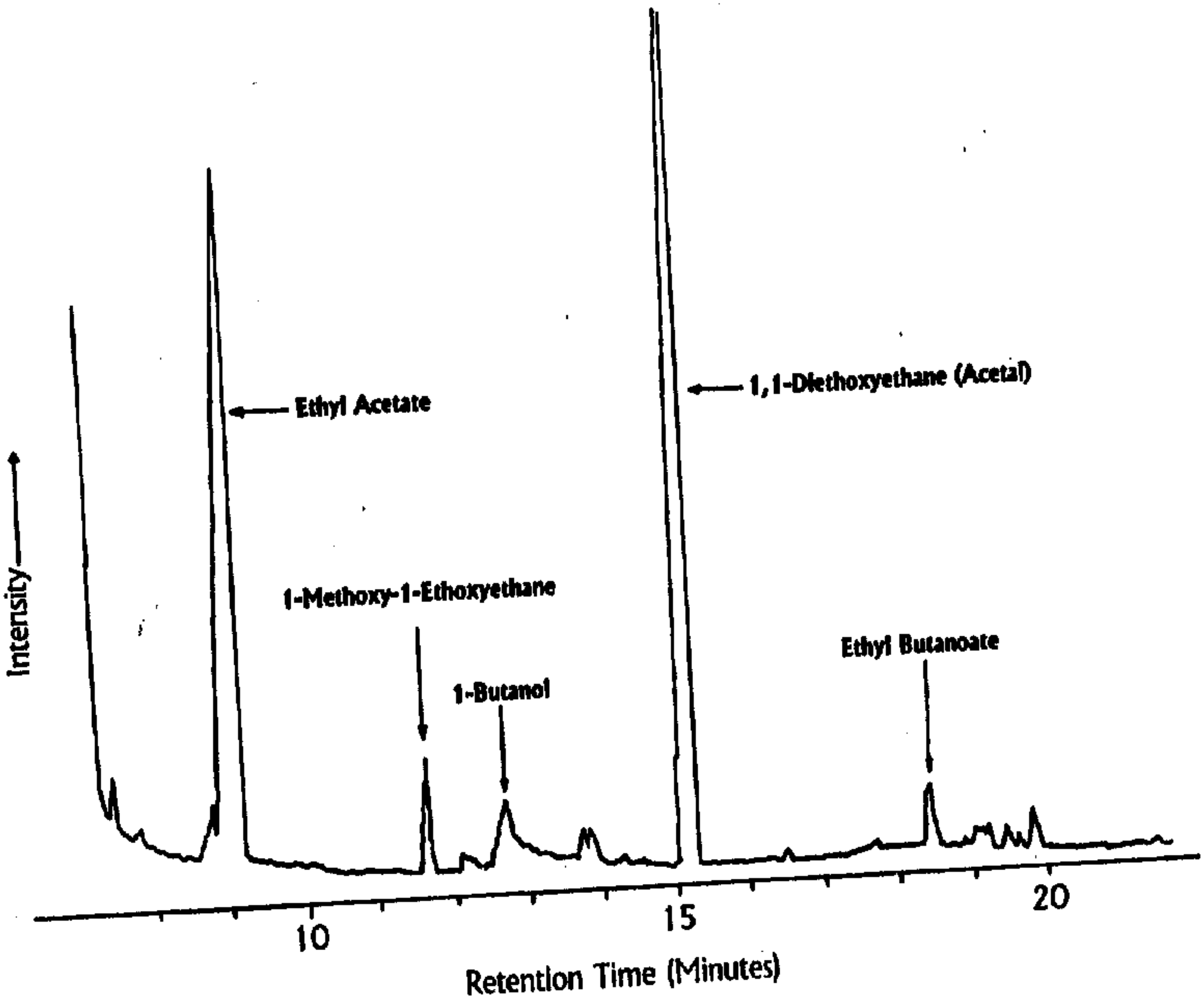

Figure III-8. G.C.-M.S. ion current trace for an aqueous phase from a cold trap sample.

Table III-1

Oxygenated Compounds Formed From Syngas Alone and When ^{14}C Labeled Ethanol was Added

	Reaction Mixture		Relative Radioactivity
Compound	CO/H_2	$CO/H_2/C_2H_5OH$	^{14}C/mole[a]
Alcohols	(g)	(g)	
CH_3OH (methanol)	0.373	0.912	
C_2H_5OH (ethanol)	0.536	12.6	1.0
C_3H_7OH (1-propanol)	0.210	0.293	b
C_4H_9OH (1-butanol)	0.038	0.067	b
$C_5H_{11}OH$ (1-pentanol)	0.01		
Aldehydes			
CH_3CHO (acetaldehyde)	0.07	1.27	1.09
Esters			
$CH_3CO_2CH_3$(methylacetate)	---	0.40	0.94
$CH_3CO_2C_2H_5$ (ethylacetate) 1.93		---	6.11
Acetals			
$CH_3CH(OC_2H_5)_2$ (acetal)	---	0.134	b
$CH_3CH(OCH_3)(OC_2H_5)$		0.084	b
$CH_3CH(OCH_3)$		0.050	b
$CH_3CH(OC_2H_5)(OC_3H_7)$		0.025	b

a. Activity relative to ethanol = 1.0.

b. Small amounts of compound and/or absence of reliable thermal conductivity response factor allows only approximate relative activity determinations.

Acetaldehyde eluted so quickly that it was not amenable to identification by either g.c.-m.s. or g.c.-i.r. without considerable additional effort. Hence, this compound was identified by confirming its retention time by doping a Fischer-Tropsch sample with an authentic sample of acetaldehyde.

A sample of the silica used as a support for the iron catalyst was examined for catalytic activity. A syngas mixture, when passed over the silica (following an overnight pretreatment in hydrogen at *ca*. 350°C) at 260°C and 1 atm, did not undergo measurable conversion. When ethanol was added to the syngas feed at a level equivalent to that utilized in the runs with the Fe-SiO_2 catalyst, both dehydrogenation and dehydration occurred. During the initial five hours the dehydration activity declined to an insignificant level; however, a low level of dehydrogenation to form aldehyde persisted during 24 hours. At this time the ethanol feed was replaced by an equal molar mixture of ethanol and acetaldehyde. This mixture underwent conversion over the silica support to produce significant quantities of ethyl acetate and acetal.

Analytical limitations prevented Emmett and coworkers from making a detailed analysis of the oxygenates in their ^{14}C tracer studies. The introduction of gas chromatographic analysis allowed for more detailed analysis of the products as, for example, was done by one of the pioneers, Pichler, of Fischer-Tropsch synthesis (III-1). Included in reference III-1 was an analysis for C_1 through C_5 alcohols but other oxygenates were not indicated by the g.c. for alcohols that were produced by a promoted Co catalyst; reference III-1 also presents analysis of oxygenates formed using an iron catalyst.

The oxygenates produced in the current study are readily identified by the ^{14}C label if they are derived from the added ^{14}C labeled alcohol. A number of these oxygenates have been identified by g.c.-m.s. and/or g.c.-i.r. The use of g.c.-i.r. is in its infancy and the quality of the i.r. spectra, combined with the high resolution capability of capillary g.c. and the unique quantitative capabilities of g.c. and i.r., point toward rapidly expanding usage of this technique. In Fischer-Tropsch studies, the qualitative and quantitative application for analysis for alkenes, alcohol or carbonyl compounds in peaks comprised of coeluting compounds should make this an important analytical procedure.

The presence of acetaldehyde is not surprising since aldehydes and ketones have been previously reported. The data in figure III-3 show that ethanol and acetaldehyde are at, or near, equilibrium concentrations for the conditions utilized for this run. The ratio of ethanol/acetaldehyde in the gas phase is essentially the same when the reactant feed is CO/H_2/ethanol or when ethanol in the feed is replaced by an approximately equimolar mixture of ethanol and acetaldehyde (figure III-3). Thus, dehydrogenation of the ethanol added as a ^{14}C labeled reactant to acetaldehyde (reaction [III-1]) readily accounts for the presence of acetaldehyde. The ethanol and acetaldehyde have essentially the same specific activity (Table III-1) as is required for a rapidly equilibrating mixture of these two compounds.

For homogeneous catalytic systems, the synthesis of a series of low molecular weight alcohols and esters is readily accomplished (III-2). For example, Knifton et al. (III-3) found that, for a series of ruthenium bimetallic catalysts, alcohol carbonylation of methanol provided a reaction pathways to produce acetic acid and ethanol. In the present study, however, the pathway to ethylacetate formation cannot be through carbonylation to form the acetic acid. First, while more methanol is formed when ethanol was added than when it was absent, the amount of ethylacetate exceeds by a factor of 10 the total methanol plus methylacetate formed when syngas only was used as a feed. Secondly, and more convincing, is that the relative ^{14}C activity of ethylacetate is essentially twice that of ethanol. Methanol and CO present when ^{14}C labeled ethanol was added to the feed does not contain a detectable level of ^{14}C. Thus, any acetic acid formed from methanol and CO is, at our detection level, unlabeled. If this unlabeled acetic acid reacted with ^{14}C labeled ethanol, the relative activity of the ester would be 1 rather than the 1.9 observed experimentally. This means that the predominate quantity of both the acid and alcohol that forms the ester must have come from the added ^{14}C labeled alcohol.

Aldol condensation of acetaldehyde, followed by dehydration and hydrogenation of the C=C unsaturation, produces butyraldehyde; the presence of a larger quantity of ^{14}C labeled ethyl butanoate than of ethyl propanoate is indicative of a minor amount of product being formed by aldol condensation.

The presence of small amounts of ^{14}C containing normal alcohols with three or more carbons suggests that either a small amount of ethanol undergoes carbonylation with subsequent reduction and/or that ethanol initiates a chain that is followed by CO propagation and then a termination step that produces an alcohol. The present data does not permit us to discriminate between these two possibilities. Likewise, 5 to 15% of the added ^{14}C appears to be incorporated into hydrocarbons; a discussion of this aspect of the synthesis is presented later.

The results of the conversion of ethanol and acetaldehyde with the silica support in the absence of iron suggest that the conversion with the 10 wt.% Fe-SiO_2 indicate that some of the oxygenates are formed as a bifunctional reaction. Hence, it appears that the following reaction scheme is applicable:

$C_2H_5OH \rightleftharpoons CH_3CHO$ Fe function [III-5]

$2\ CH_3CHO \rightleftharpoons CH_3CO_2C_2H_5$ silica function [III-6]

$CH_3CHO + 2\ C_2H_5OH \rightleftharpoons CH_3CH(OC_2H_5)_2$ silica support [III-7]

The above scheme is further supported by results from a doubly-promoted, unsupported United Catalysts, Inc. C-73 catalyst. With this catalyst ethanol is dehydrogenated to acetaldehyde but ethyl acetate and acetal are formed in insignificant, or undetectable, amounts under similar reaction conditions. Consequently, the silica should not be viewed as an inert support during Fischer-Tropsch synthesis.

III-C. Anticipated ^{14}C Incorporation Patterns for Alkane Products

A number of scenarios are possible when ^{14}C labeled ethanol is added to the syngas feed; some of these will be outlined below and are shown schematically in figure III-9:

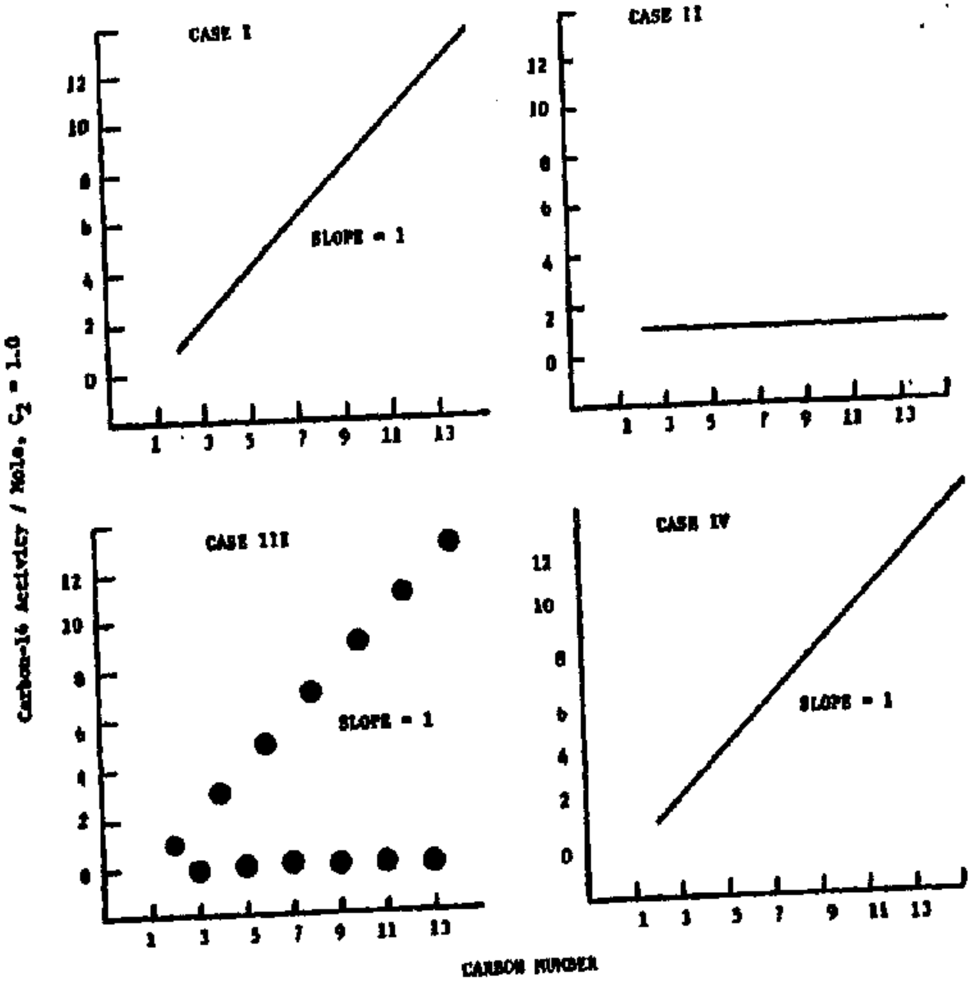

Figure III-9. Schematics for the carbon-14 distribution in the products from Fischer-Tropsch synthesis with added C-14 ethanol.

(a) 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 carbon 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, in the case of ^{14}C, being less than 10^{-5} ^{14}C mole. A plot of the activity versus carbon number is shown schematically in figure III-9a; our results are clearly inconsistent with this scenario.

(b) The ethanol initiates chain growth and CO propogates the chain. In this case the ^{14}C dpm/mole remains constant with increasing carbon.

(c) 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.

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

A linear plot was obtained for the log (CPM/mole) versus carbon number, in the range C_9-C_{15}, for products formed when ^{14}C labeled ethanol was added to the syngas feed to a Fe/SiO_2 catalyst at a temperature of 260°C and 7 atm pressure. Because this does not fit any of the above scenarios, the measurements were repeated to establish the reliability of the data and the slope of the line being less than one. This was effected by obtaining the mole fraction of each of the n-alkanes from flame ionization g.c. analysis as well as from the refractive index detector monitoring the effluent from a liquid chromatographic column. Very similar mole ratios were obtained by these two methods. The samples were analyzed for ^{14}C content on different liquid scintillation instruments and the results provided straight line plots (figure III-10) with essentially the same slope. Thus, the data shown in figure III-10 appears to be reliable.

None of the above chain growth mechanisms produces results that are consistent with the ^{14}C distribution from the labeled ethanol incorporation with the Fe/SiO_2 catalyst. Since we are unable to devise a growth mechanism to account for these results it appears that it is due to product accumulation. The evidence for this is reported later in this report.

III-D. Comparison of Runs at 1 and 7 Atmosphere Pressure

III-D-1. CO Conversion

The CO conversion at 7 atmospheres remains constant for 200 or more days following an initial break-in period of 6 to 8 days. (The conditions used for the two reactors are summarized in Table III-2). On the other hand, the

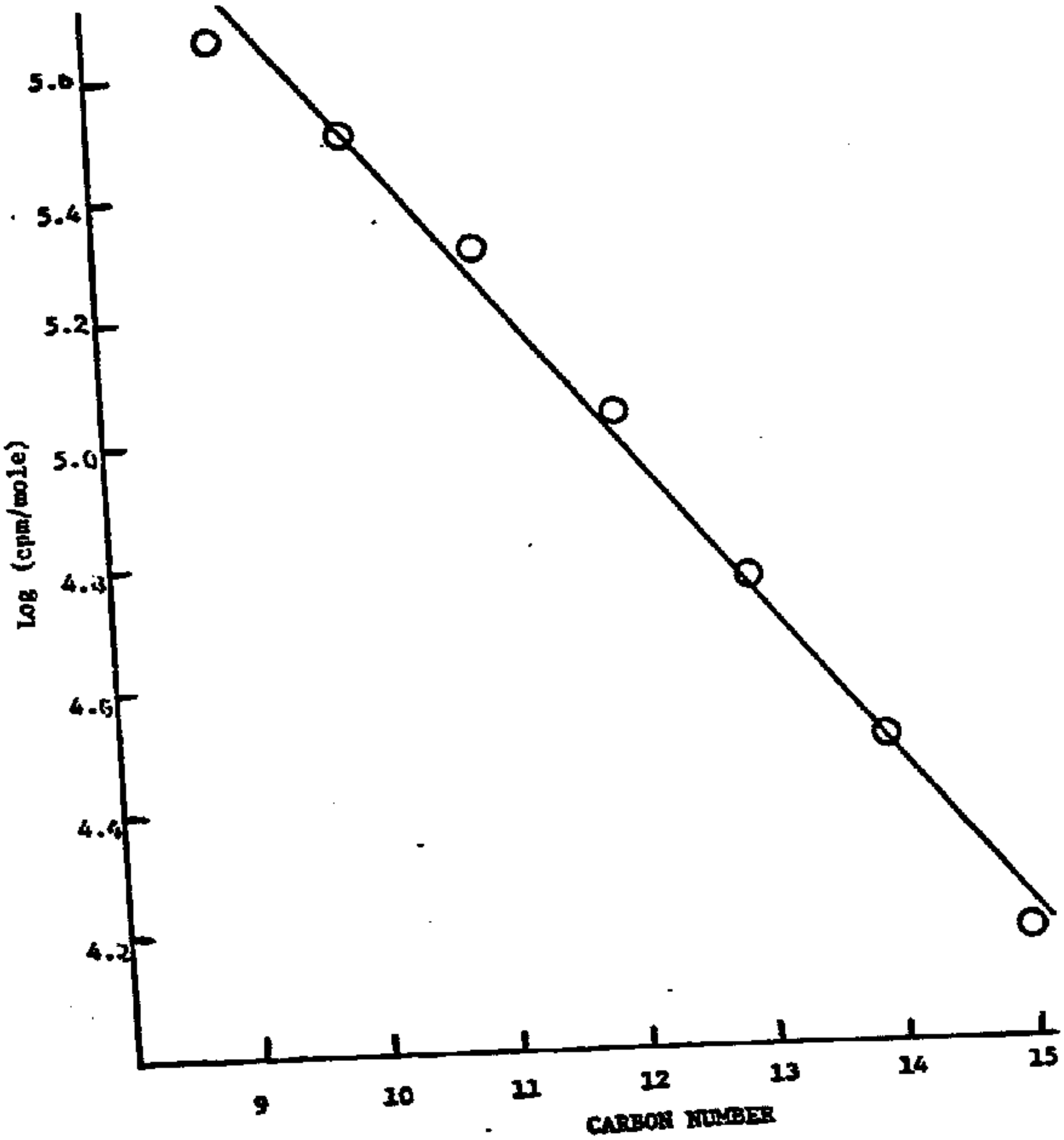

Figure III-10. Log (counts per minute/mole hydrocarbon) of the n-alkane fraction separated from the products produced from CO/H_2 with added C-14 labeled ethanol conversion over an $Fe\text{-}SiO_2$ catalyst at 260°C and 7 atmospheres pressure.

TABLE III-2
Operating Parameters

	APFR	MPSR
Temperature, °C	262	262
Pressure, atm.	1.0	7.0
Amount of catalyst, g	60	150
Flow, cc/min.	60	300
CO/H_2	1.0	0.78
C_2H_5OH, molar %	ca. 5	ca. 2

activity in the plug-flow reactor declined from about 60% to 30% in about 7 days; treatment in hydrogen for 24 hours at 450°C restored the original activity which again declined with time on-stream (figure III-11).

It was argued that retention of activity at intermediate pressures (7-15 atm) in the FTS was due to the formation of a liquid oil film, comprised of relatively low molecular weight hydrogen carbons, on the catalyst surface (III-4). These oils could dissolve wax and high boiling oxygenates to provide a continuous extraction of these from the pores of the catalyst and, consequently, a continuous regeneration of the catalyst activity. In our MPSR (medium pressure synthesis reactor), the octacosane used as the startup solvent should serve to do this and this may be the reason that the activity of the catalyst was retained for more than 200 days. At SASOL, a fixed-bed reactor is maintained at a constant activity under conditions similar to those in Table III-2 by increasing the operating temperature every few months (III-5). Thus, the difference in the two reactors for retention of activity may be due to a solvent effect.

III-D-2. Carbon Number Distribution

Anderson-Schulz-Flory (ASF) plots for products from the two reactors are shown in figure III-12. A very similar distribution is produced in the two reactors. A break in the ASF plot occurs around C_{10} in both cases; this was reported by others (III-6 to III-10). The data in figure III-12 are very similar to those reported by Satterfield and coworkers (III-8). The APFR products above about C-20 have a lower concentration than those from the MPSR; this is most likely due to the fact that a steady state for these higher carbon number hydrocarbons had not been attained when the sample was collected. It has been shown that such an effect should result for sampling periods following startup (III-11).

III-D-3. Selectivity

The FTS is believed to be a kinetically controlled reaction; thus, the product distribution rarely reaches the thermodynamic equilibrium values (III-12, III-13). The FTS is a very complicated reaction with several parallel and series reaction paths. In this section, the kinetic versus thermodynamic control of products will be considered for some of these reactions. The trans-2-alkene to (trans- plus cis-2-alkenes) ratio approaches a constant value at higher carbon numbers; this fraction of ca. 0.7 is the value expected by extrapolation of the equilibrium data in reference III-14,

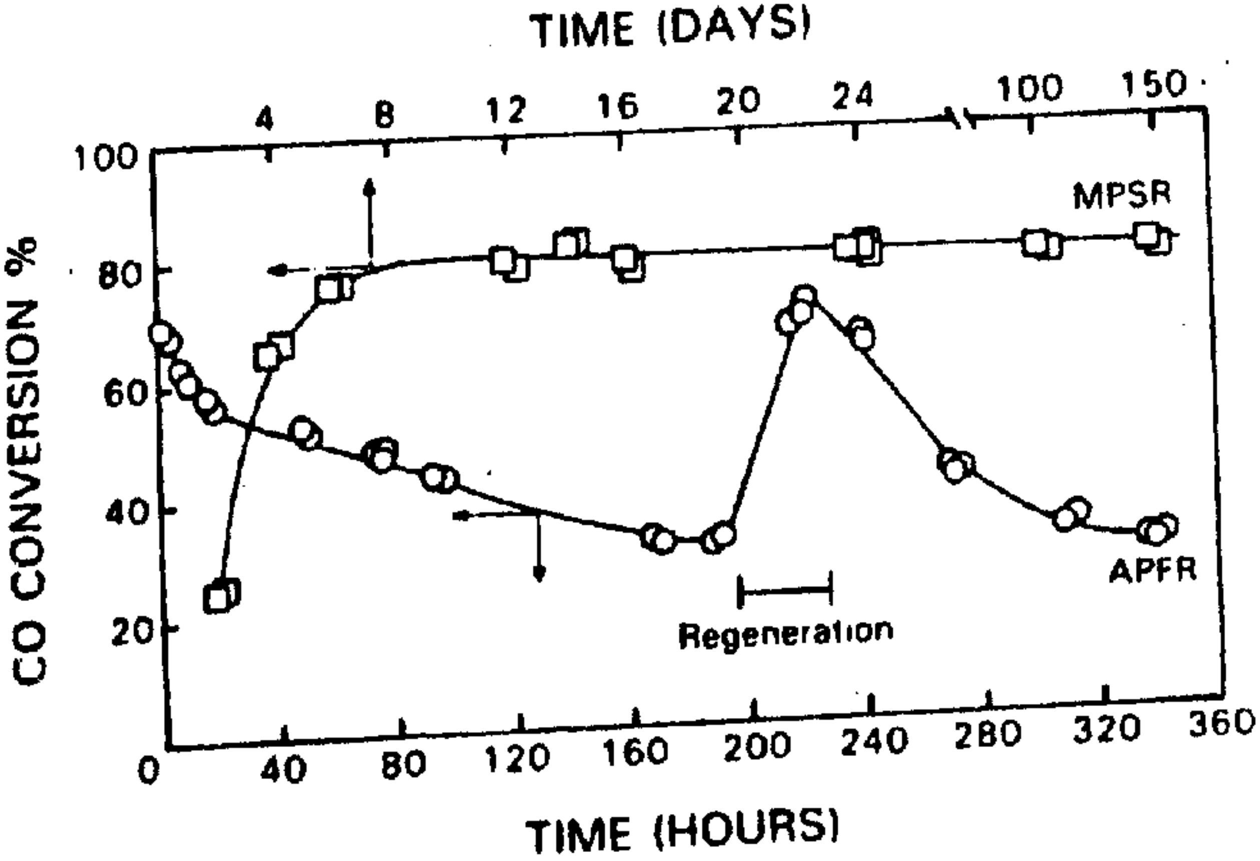

Figure III-11. Carbon monoxide conversion in an atmospheric pressure fixed bed (APFR) and at 7 atmospheres in a stirred autoclave reactor (MPSR).

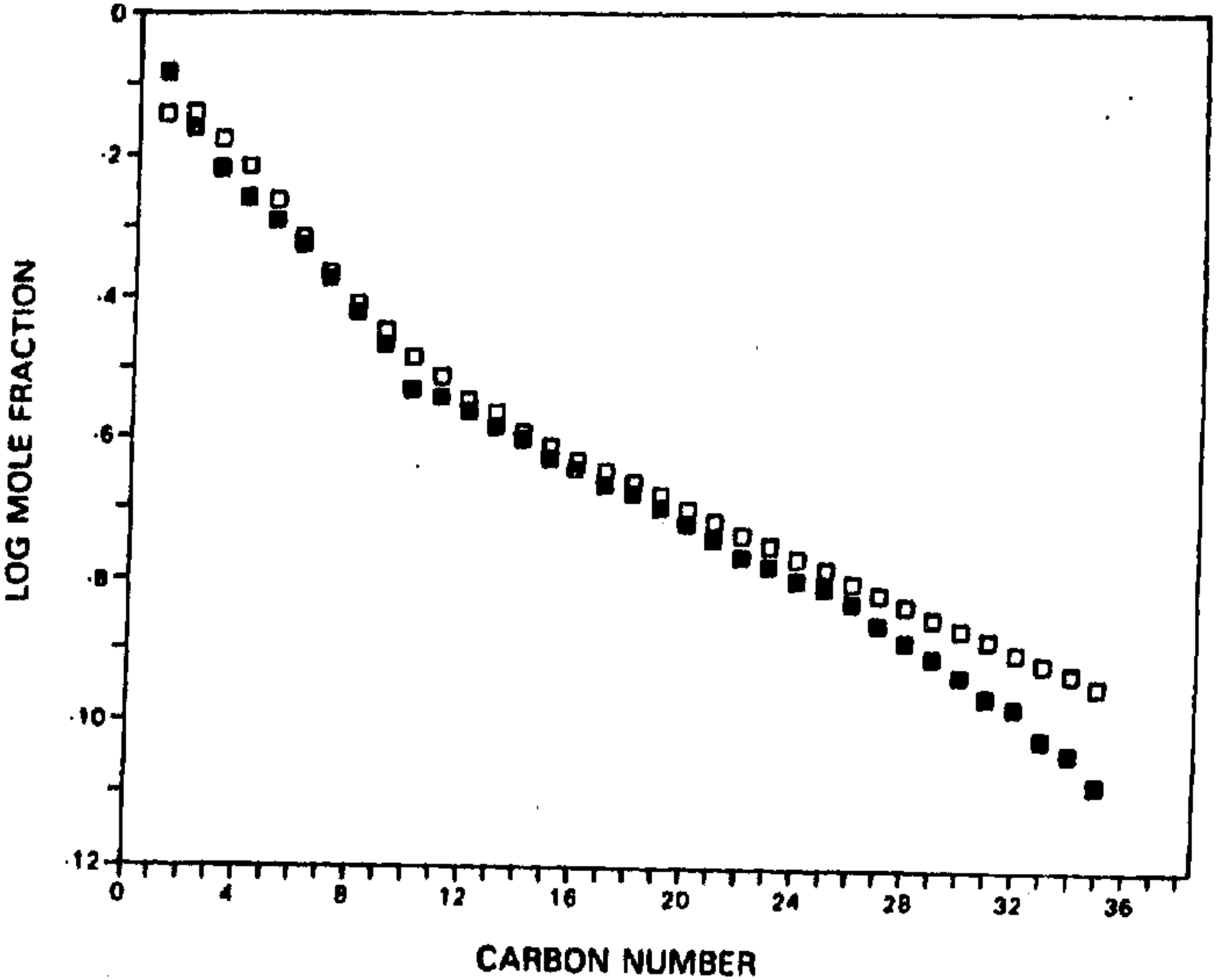

Figure III-12. Anderson-Schulz-Flory plots for the products from Fischer-Tropsch synthesis at 1 (■) and 7 (□) atmosphere conditions.

III-15 (figure III-13). Even for the lowest carbon number alkenes the value is nearly 0.5, a value that is not that far from the equilibrium value. The results imply that the trans-2-alkene and cis-2-alkene reached a near equilibrium value under our operating conditions; this may result from the mechanism of their formation or by a series of secondary reactions.

For the FTS, the primary product has been viewed, by many, to be an alpha-alkene (reference III-16, for example). Thus, the percent of beta alkene, based on alpha plus beta alkene only, is shown in figure III-14. The same general trend is again obtained for the two reactors; however, it is noted that a constant percentage of beta alkene is attained at a lower carbon number for the fixed-bed reactor than for the stirred-tank reactor. It is also noted that the lower carbon number products approach a value expected if alpha alkenes are the primary synthesis product. The percentage of beta alkenes does not attain the value expected if the ca. 90% beta alkenes calculated from thermodynamic data also represents the equilibrium composition for the higher carbon numbers products. If the beta alkenes result from secondary reactions, then these reaction occur more readily in the AFPR than in the MPSR; this implies that higher carbon number hydrocarbons have a longer residence time in the fixed bed reactor.

An obvious question arises from the apparent limiting percentage of beta alkene. Two reasonable possibilities follow. First, the 1-alkene component, identified by g.c. retention time, may, in fact, contain an impurity component; if this were the case the amount of 1-alkene would be overestimated. This impurity, if present, would become more apparent at higher carbon numbers since the alkenes become a progressively smaller fraction for the higher carbon number product. The second possibility is that the thermodynamic data in reference III-14 is not accurate; other sources (III-15) do not exactly agree with the data in reference III-14. In view of these uncertainties, it does not appear appropriate to discuss this point further even though its importance in mechanistic considerations cannot be overemphasized.

The fraction of alkene in the alkane plus 1-alkene products is shown as a function of carbon number in figure III-15. It is apparent that the alkane fraction is at, or near, a minimum at carbon number about 4. Again, hydrogenation appears to be greater for any carbon number above C-4 for the flow reactor. Considering reactor kinetics, the alkane fraction should have been greater in the plug flow reactor than the CSTR slurry reactor if the alkenes are an intermediate in a series of reactions leading to alkanes. Thus, the alkane fraction is also consistent with the higher carbon number products being exposed to a longer reaction time in the catalyst zone in the flow reactor than in the slurry reactor.

III-D-4. CO/H$_2$/^{14}C Labeled Ethanol

Emmett and his coworkers (III-17 through III-22) utilized radioactive compounds to study FTS some 30 years ago, and pioneering results were obtained. However, the limitation of the analytical instrumentation restricted the compounds they could analyze. The data in figure III-16 show the relative radioactivity of gas phase products. Again, the data obtained in these two reactor systems are very similar. There were several aspects of the data in figure III-16 which should be emphasized. First, the amount of

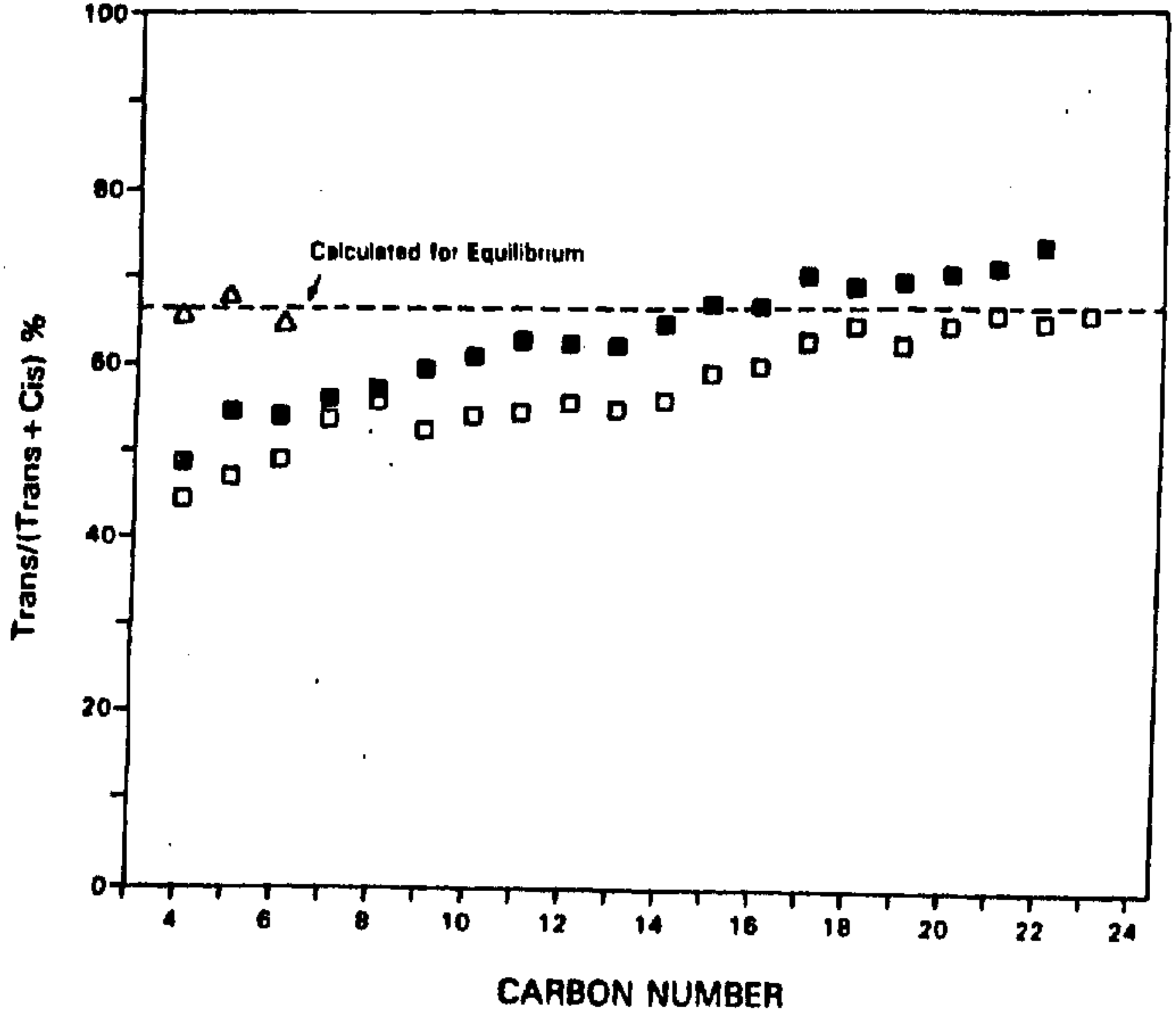

Figure III-13. Percent trans-2-alkene in the 2-alkene fraction of the products of Fischer-Tropsch synthesis at 1 (APFR; (■)) and 7 (MPSR; (□)) atmosphere conditions (equilibrium values calculated using data in reference II-14).

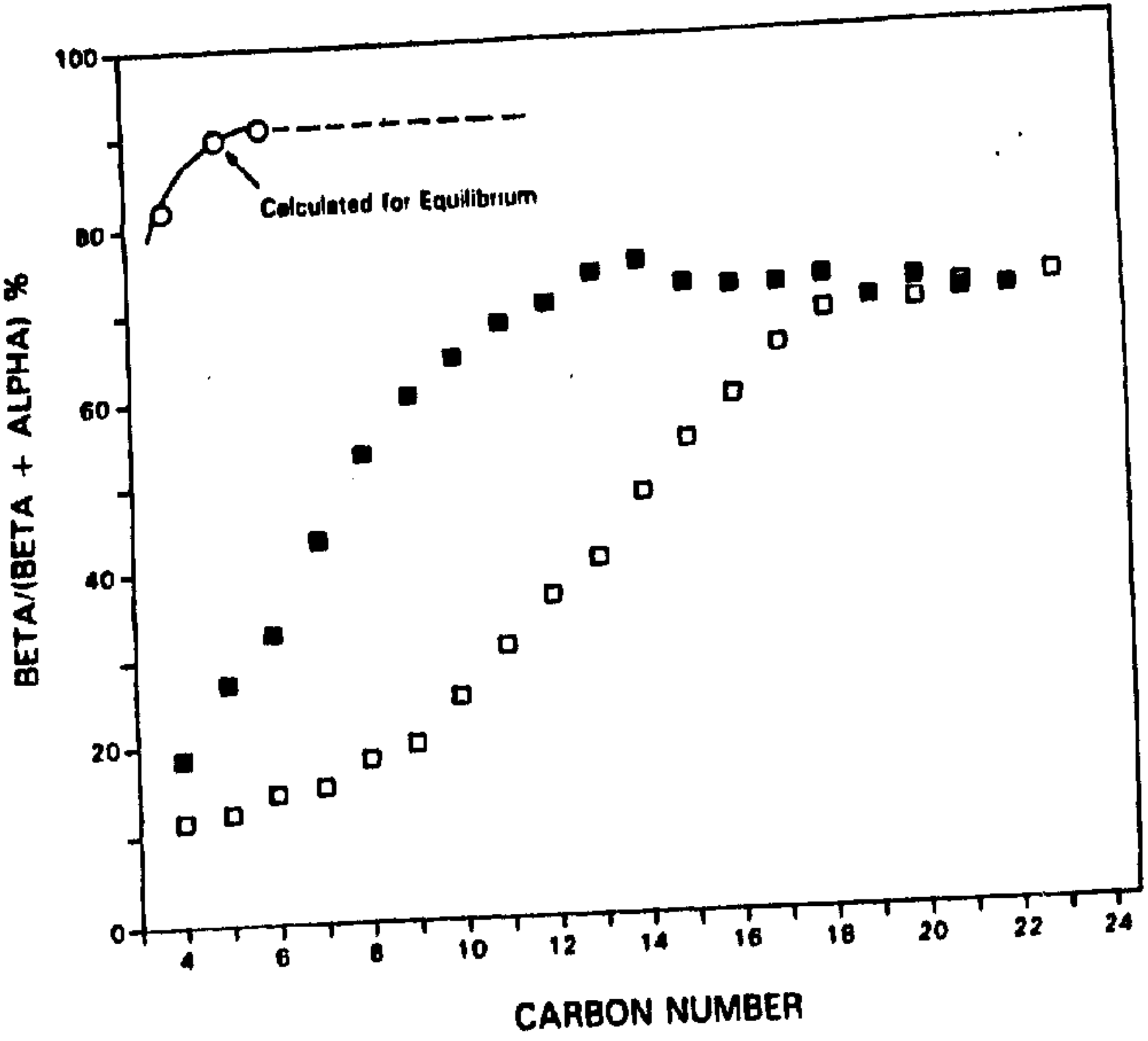

Figure III-14. Percent beta-alkene in the alpha plus beta-alkene products from Fischer-Tropsch synthesis at 1 (APFR; (■)) and 7 (MPSR: (□)) atmosphere conditions (equilibrium values calculated using data in reference III-14).

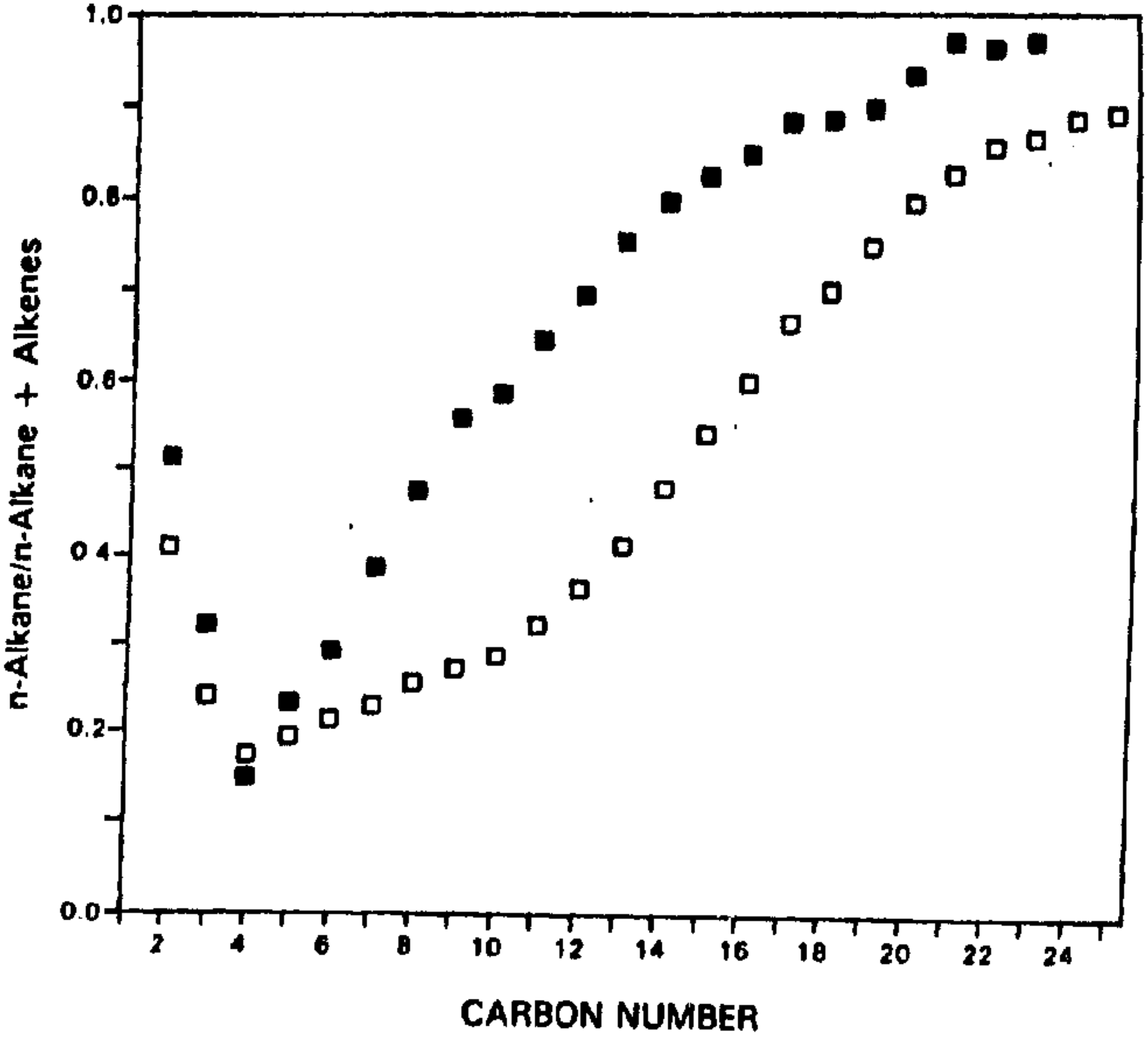

Figure III-15. Fraction of n-alkane in the n-alkane plus 1- + 2-alkene products (from Fischer-Tropsch synthesis at 1 (APFR; (■)) and 7 (MPSR; (□)) atmosphere conditions.

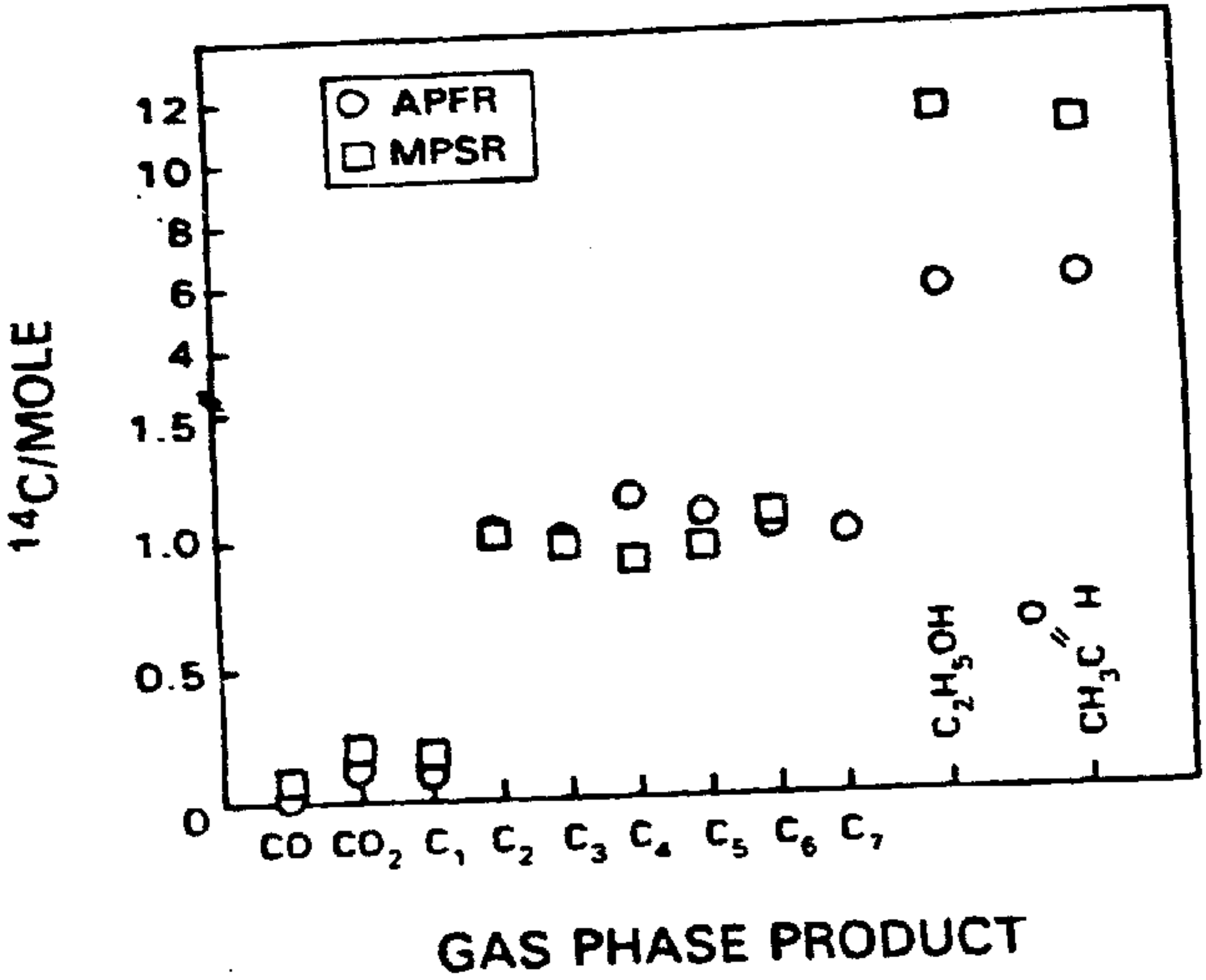

Figure III-16. Relative ^{14}C/mole in the Fischer-Tropsch products in the gas effluent from the fixed bed (○) and stirred tank (□) reactors when ^{14}C labeled ethanol was added to the synthesis gas.

radioactivity/mole in the hydrocarbon products from C_2 to C_6 was essentially the same; this agrees with results of Hall, et al. (III-20). This implies that ethanol acts primarily as a chain initiator for the reaction. The radioactivity of acetaldehyde was essentially the same as ethanol, indicating that it is derived by dehydrogenation of the added ethanol. It appears, considering the relative activity of ethanol and the $C_2 - C_6$ hydrocarbons, that a higher fraction of the ethanol was incorporated at atmospheric pressure than at 7 atmospheres. In both cases, however, our results agree with those of Emmett and coworkers (III-17 through III-22) as well as the later studies by Schulz and coworkers (III-23 through III-27).

In figure III-17, the relative radioactivity of alkanes in the liquid phase products are shown. For the APFR (atmospheric pressure flow reactor), the relative radioactivity/mole decreased slightly from C_{14} through C_{23}. However, for the MPSR (medium pressure slurry reactor) system, the relative radioactivity decreased much more rapidly with increasing carbon number. One of the reasons for the decline in carbon-14/mole is the accumulation of the heavy hydrocarbons in the slurry reactor. Another reason maybe that two independent chains, one that produces ^{14}C labeled alkanes, alkenes and alcohols and another that produces only unlabeled alkanes, contribute to produce these products.

In summary, the general selectivity patterns obtained at atmospheric pressure are very similar to those obtained at 7 atmospheres. Furthermore, the overall pattern of the selectivity data obtained in the plug flow reactor very closely resembles that obtained in a slurry reactor at 7 atmospheres. Thus, apart from catalytic activity and catalyst aging, the atmospheric pressure plug-flow reactor appears to provide a convenient way to screen iron catalysts. Hydrogenation appears to occur more readily in the flow reactor. While some comparisons have been made at the higher pressure, a more detailed comparison of the two reactors at 7 atmosphere and higher operating pressure is clearly merited.

III-E. Isoalkane Formation

About 1950, detailed analyses of Fischer-Tropsch products began to appear (III-28 through III-30); the data included results from pilot plants producing up to 200 liters/day of oil products. At this time, the experimental techniques were limited to lower carbon-number products and it is remarkable that such good agreement could be obtained in different laboratories (figure III-18). With the revised interest in the Fischer-Tropsch synthesis, Pichler et al., (III-31 through III-33) carried out an extensive analysis of the products through carbon-numbers 4 to 17 from the commercial SASOL plant and from fixed bed reactors. SASOL data from reference III-34 are also plotted in figure III-18 together with results we obtained at 262°C in a slurry reactor with a doubly promoted C-73 catalyst. The data for all runs are similar for the C_4 products since the amount of isobutane is small and is far below the amount expected for thermodynamic equilibrium. It appears that the amount of the isoalkane for the higher carbon-number components depends upon the reaction temperature. At the lowest temperature (220°C) the amount of isoalkane approaches a constant fraction of 0.05 to 0.06. The fraction of isoalkane appears to increase with increasing temperature, and this increases with carbon-number. The data for the higher temperature show essentially a

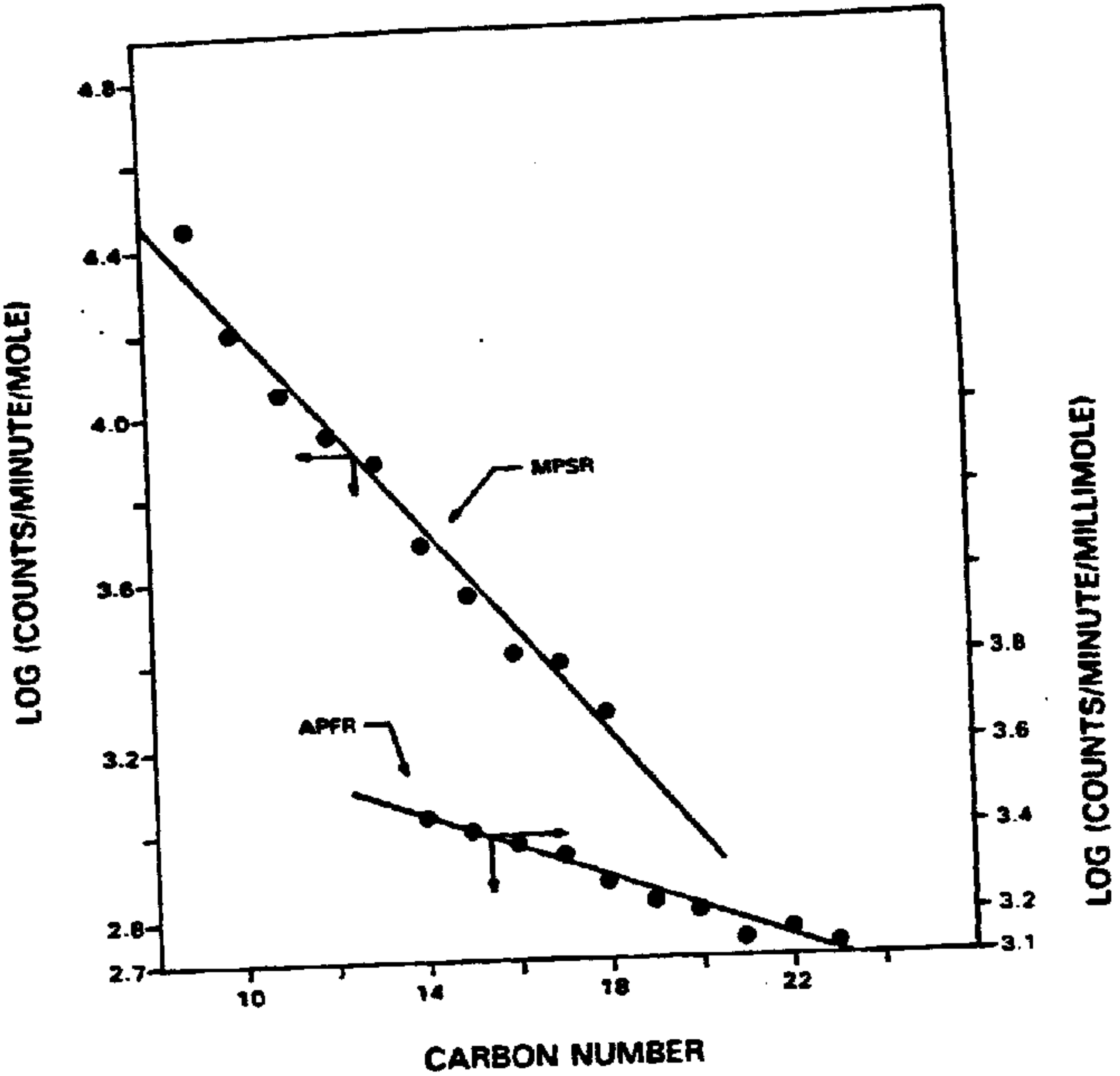

Figure III-17. Relative ^{14}C/mole for higher carbon number alkanes produced during the Fischer-Tropsch synthesis at 1 (APFR) and 7 (MPSR) atmospheres when ^{14}C labeled ethanol was added to the synthesis gas (note the activity of the products from the APFR is on a millimolar basis while those from the MPSR are on a molar basis).

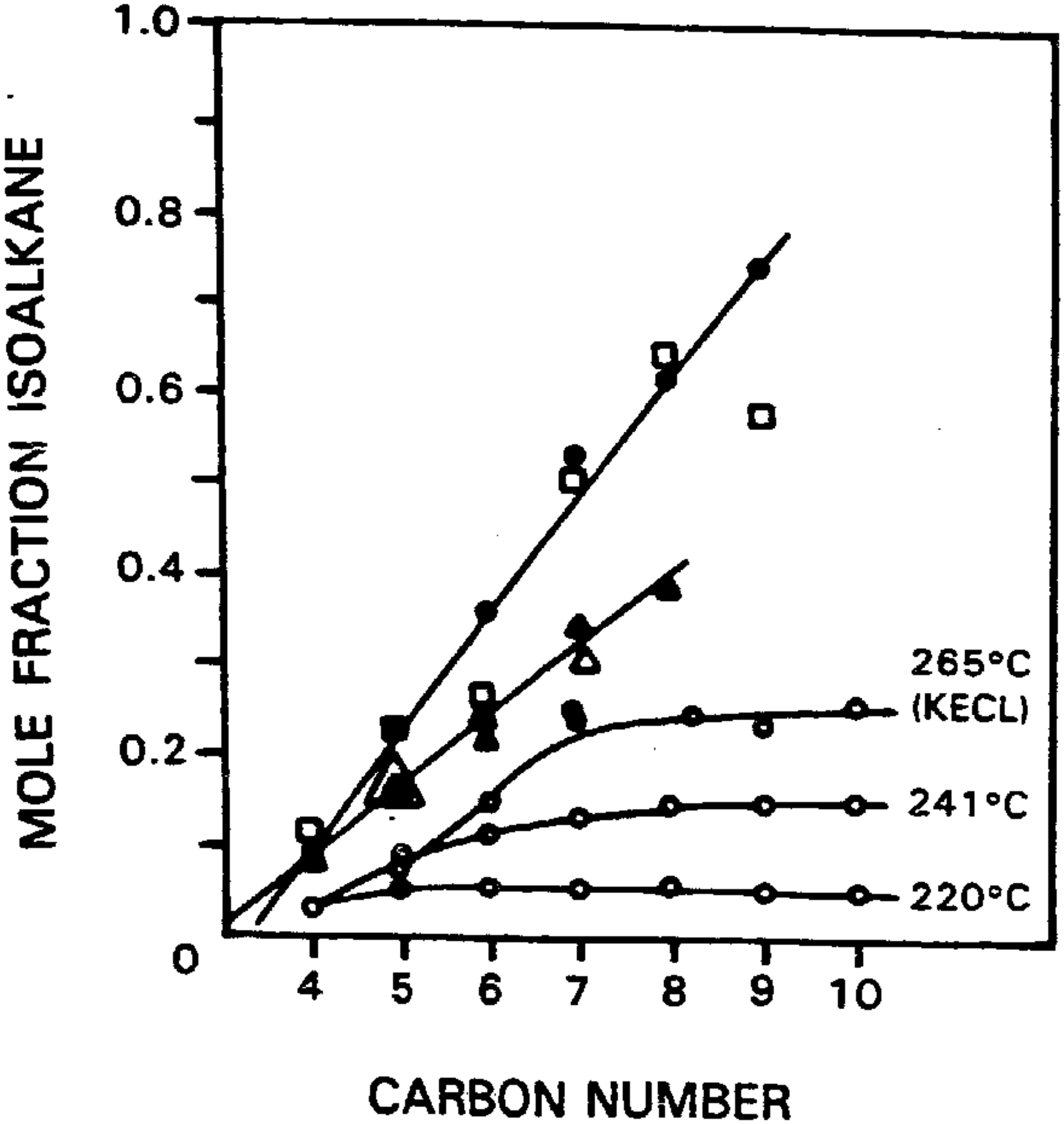

Figure III-18. Mole fraction of iso-alkanes in the products from reference II-31 for runs at 220°C (○), and 241°C (○), data from this study (○) and SASOLfluid-bed products (●); data from reference III-29 (▲) and reference III-30 (△) and old data from reference III-34 (□).