REACTIONS OF SELECTED 1-OLEFINS AND ETHANOL ADDED DURING THE FISCHER-TROPSCH SYNTHESIS: TOPICAL REPORT

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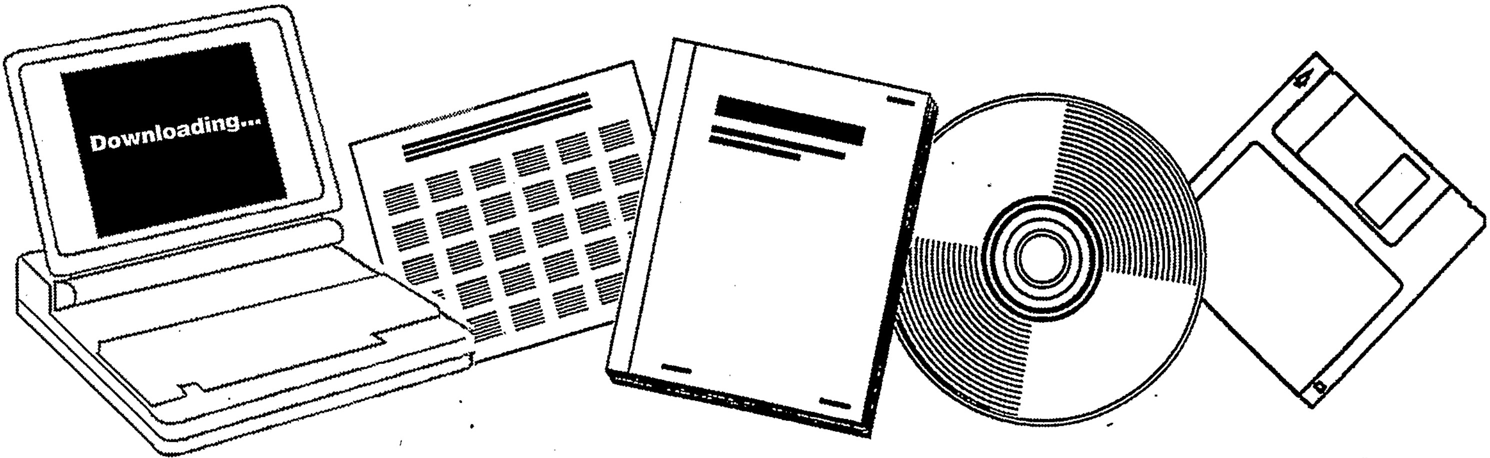

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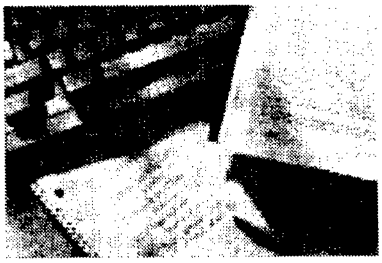

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Process Variations . . ."

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Reactions of Selected 1-Olefins and Ethanol Added During the Fischer-Tropsch Synthesis

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Abstract

The effects of addition during synthesis of C_2, C_4, C_6, C_{10} or C_{20}, normal 1-olefins, was studied in a continuous well-stirred liquid phase reactor. Studies were at 248°C and 0.78 to 1.48 MPa, using a reduced fused magnetite catalyst containing potassium. Incorporation of these olefins into growing chains could be detected, but was relatively minor. Instead the olefin was hydrogenated to the corresponding paraffin or isomerized to the 2-olefin. Excluding ethylene, which is unusually reactive, the reactivity of the olefins increased with molecular weight.

Disappearance of all added species was much less at low synthesis conversions than at high, attributed to competitive adsorption with CO. The reactions of added ethanol were also studied. Ethanol or ethylene decreased the hydrogenation capabilities of the catalyst as reflected in decreased formation of CH_4 and increased olefin/paraffin ratio of the products. Neither addition affected the chain growth probability, α.

Introduction

In the Fischer-Tropsch synthesis on an iron catalyst, in addition to paraffins, 1-olefins and 1-alcohols are significant primary products. Once formed, these latter species can undergo secondary reactions such as hydrogenation and isomerization. There is also evidence that they may become incorporated into growing chains, but the extent to which this occurs seems to vary greatly with reaction conditions, reactant concentrations and catalyst composition, especially the presence or absence of potassium.

It is now well documented that the products from a variety of iron catalysts generally exhibit two chain growth probabilities, the dominating probability distribution changing at about C_{10}[1]. A plausible explanation is that two kinds of sites are present on the catalyst, but it has also been suggested that the effect instead may be caused by secondary incorporation of olefins into growing chains. Such incorporation is hypothesized to be much greater for higher molecular weight olefins, because of their reduced volatility and longer reactor residence time. The fact that the change in the dominating distribution occurs at about C_{10} lends some plausibility to the suggestion. We will show however that we could not adduce any substantial evidence for this hypothesis.

As a test, ethanol, ethylene, 1-butene, 1-hexene, 1-decene or 1-eicosene ($C_{20}H_{40}$) were added to the synthesis gas feedstream or directly to the reactor under representative Fischer-Tropsch synthesis conditions. In the primary synthesis ethanol is the dominant alcohol and C_2 species appear to be unusually reactive. Studies with other olefins were made it to see if significant differences might be encountered along the homologous series. Comparison of additive conversions at high and low syngas conversions showed that major competitive adsorption effects between CO and olefins occurred.

Experimental Apparatus and Materials

The experiments were conducted using a 1-liter, well-mixed, continuous flow, slurry phase reactor. In such a system exit concentrations are truly representative of the uniform conditions within the reactor. The experimental apparatus and materials were as described previously[2,3], except that liquid additives were introduced with a liquid pump. The catalyst was a fused magnetite (United Catalysts, C-73-1) sold for use in ammonia synthesis. Its analysis was 64.4 wt% Fe, 0.76 wt% Al, and 0.31 wt% K (Galbraith Labs). For each run, about 70 grams of crushed catalyst (270-325 mesh) were reduced in a separate vessel and then slurried in the reactor with about 420 grams of purified n-octacosane. The behaviour of the same fused magnetite catalyst under a variety of conditions has also been described[1,4]. The additives used in this study are listed in Table 1.

Experimental Procedure

In general, experiments without and with each compound listed in Table 1 were conducted at 248 °C, pressures of 0.78 to 1.5 MPa, high and low CO conversions, and with high and low concentrations of the additive in the feed. CO conversion was varied by changing the flow rate of synthesis gas to the reactor.

Three lengthy sets of runs were made. For each run, at least 40 hours were first allowed to elapse after the freshly reduced catalyst was brought on-stream to insure that steady state activity had been achieved. A material balance was then run without additive addition for about 6 hours to establish a base case. The additive was then introduced continuously for some 4 to 10 hours after which steady state was essentially achieved and a material balance was then obtained over a 6 to 7 hour period. The same additive at a different concentration or another additive was then introduced and the same procedure repeated. Each run extended over several hundred hours and from time to time the base case was re-run to insure that no significant change in catalyst activity or selectivity had occurred. To avoid any systematic bias the order of experiments was randomized both with respect to reactor conditions and the nature of the additive.

Ethylene and 1-butene were introduced by using tanks of premixed gases. Ethanol, 1-hexene and 1-decene were fed as liquids by a liquid pump. For 1-eicosene the reactor was taken off stream after 50 hours of synthesis and a quantity of melted 1-eicosene was directly injected into the reactor under inert gas pressure. The reactor was then put back on stream and a sample of the reactor wax was taken shortly thereafter and again after 8 hours of resumed synthesis.

The base case experiments previous to addition of ethylene or 1-butene were conducted at each of two pressures, 0.78 and

1.48 MPa. The subsequent experiments were done at slightly higher total pressure in the reactor to maintain constant partial pressure of CO in the presence of the increased partial pressure of the feed additive. This increase in pressure amounted to a maximum of about 100 kPa for the highest concentration of ethylene or about 40 kPa for the highest concentration of 1-butene. Because of physical limitations of the pump, the highest operating pressure when a liquid was fed was 0.92 MPa. The operating pressure for the 1-eicosene addition was also 0.92 MPa. For direct comparison each additive was studied at least in part at the same set of synthesis conditions (248°C, 0.92 MPa, high CO conversion).

RESULTS AND DISCUSSION

The experimental conditions for all studies are summarized in Table 2, including CO and H_2 conversions and the partial pressures of the feed additive in the exit gas of the reactor. In all cases the addition of the selected olefin or ethanol significantly increased the partial pressure of the additive in the reactor above that which existed during normal Fischer-Tropsch synthesis.

Results - Ethanol

The addition of ethanol to the feed did not significantly affect the CO or H_2 conversions at low CO conversions (40-42%) (Table 2). At high CO conversions (88-93%), the ethanol addition resulted in a slight decrease in H_2 conversion but had no significant effect on CO conversion.

Shown in Table 3 are the pertinent selectivity results. At both high and low CO conversions, the increased partial pressure of ethanol in the reactor caused a decrease in methane selectivity, and an increase in the olefin/paraffin and α-olefin/β-olefin ratios. The latter two ratios were more affected by ethanol at high CO conversions. The ethylene concentration in the exit gas significantly increased upon ethanol addition, especially at high CO conversions. However, that of ethane decreased by approximately an equal amount, as reflected by the essentially constant overall selectivity to form ethylene plus ethane.

The selectivity to form C_3 hydrocarbons (propane and propylene) remained essentially constant, but there was an increased selectivity to form ethanal (acetaldehyde), C_3 oxygenates, (propanal and propanone) and ethyl acetate. The last compound was positively identified (Cambridge Analytical Associates, Inc.) using g.c. mass spectrometer analysis and further confirmed in our laboratories using ethyl acetate as a spike in the g.c. samples. The C_3 oxygenates could not be accurately separated quantitatively into propanal and propanone, but careful analysis of the samples containing the C_3 oxygenates revealed that an increase in the overall C_3 oxygenate selectivity was caused by an increase in propanone.

The conversion of the ethanol in the feed was calculated by first subtracting the flowrate of ethanol leaving the reactor for the experiments with no feed addition (base case) from the flowrate of ethanol leaving the reactor for the feed addition experiments conducted at the same conditions. From the ethanol flowrate fed to the reactor, the conversion was calculated. At high CO conversion, the averaged conversion of ethanol in the feed was about 30%, while for the single experiment conducted at low CO conversion, the conversion of the ethanol in the feed was less than 1%.

About one-half of the calculated conversion of ethanol at high CO conversion could not be accounted for by the increased selectivities of the aforementioned oxygenated species. In our experimental system the liquid ethanol was pumped into a vaporizer, then into the reactor, and was finally condensed in a trap from the reactor effluent. The lack of closure on the ethanol material balance was caused by the difficulty of determining the difference between the volume of ethanol pumped and vaporized into the reactor and the volume trapped out, especially when the volumes were small, as they were at high CO conversion (low reactant flowrate). This difficulty affected only the ethanol conversion results for the high CO conversion experiments; it did not affect the selectivity results since these were based on relative effluent gas flowrates. This same difficulty occurred with the 1-olefins fed as liquids, 1-hexene and 1-decene; however, the material balance closures for these cases were considerably better.

The effect of ethanol addition at a high CO conversion on the C_1-C_7 product distribution is shown in Figure 1. This is normalized excluding the C_2 fraction. Notably, the methane selectivity dropped but the chain growth probability as characterized by α was not significantly affected. Because of the normalization procedure, the amounts of C_1 and C_3-C_7 must add up to unity. The results presented in Fig. 1 do not mean that more C_3-C_7 is produced with higher ethanol addition. Ethanol addition had no significant effect on the amount of CO_2 formed per mol of CO consumed, i.e., it did not affect the water gas shift. Similar normalization procedures were used in all the other Flory plots, except for Fig. 11, discussed later.

Discussion - Ethanol

Added ethanol did not significantly affect the conversion of CO, suggesting either weak adsorption of the ethanol relative to CO or, less likely, adsorption of the ethanol on sites other than those active for CO adsorption. A similar lack of synthesis inhibition by ethanol was also observed by Kokes et al.[5] In that study, synthesis gas ($H_2/CO = 1$) containing ^{14}C labelled ethanol (1.5 vol%) was passed over a reduced, singly-promoted iron catalyst (0.64% Al_2O_3 and 2.00% ZrO_2) at 239°C and 0.1 MPa, and over a reduced, doubly-promoted iron catalyst containing potassium (4.6% MgO, 0.6% K_2O, 0.6% SiO_2, and 0.6% Cr_2O_3) at 241-275 C and 0.1-2.18 MPa. For both catalysts the ethanol addition did not retard the synthesis.

In an earlier and similar study by Kummer et al.[6], when synthesis gas ($H_2/CO = 1$) was passed over a reduced, singly promoted iron catalyst (1.55% Al_2O_3 and 0.58% ZrO_2) at about 230 C and 0.1 MPa, the addition of ^{14}C labelled ethanol (1.6 vol%) reportedly retarded the synthesis. However, catalytic activity was characterized indirectly by gas contraction, rather than CO conversion. The constant CO conversion and decreased H_2

conversion upon ethanol addition observed here, of course corresponds to decreased overall contraction.

The added ethanol decreased the hydrogenating characteristics of the catalyst, as reflected in the decrease in methane selectivity and the increase in C_2-C_4 olefin/paraffin ratios. Both of these trends could be caused by the inhibition of H_2 adsorption by ethanol, although no supportive evidence was found for this. The increase in olefin-paraffin ratios also suggests that the ethanol was competitively adsorbing with the α-olefins for active sites, thus inhibiting the secondary reactions of the α-olefins. This is supported by the observation that the α-olefin/β-olefin ratios also increased with increasing ethanol partial pressure. Kummer et al.[6] also noted this decrease in the hydrogenating activity of the catalyst with added ethanol as evidenced by the increase in the C_2, C_3, and C_4 olefin/paraffin ratios.

The decrease in methane selectivity cannot be attributed to the reaction of adsorbed ethanol with adsorbed methane precursors such as CH_3^*. Such a reaction should result in a significantly increased selectivity to form C_3 species, but this was not found. The increased selectivity to form propanone was not nearly enough to account for the missing CH_4. The increase in the C_2 olefin/paraffin ratio is not the result of an increased formation of ethylene caused by ethanol dehydration, since then the total C_2 hydrocarbon selectivity, ethylene plus ethane, would increase with added ethanol. Once again, this was not observed.

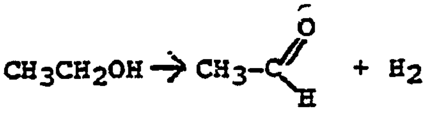
It is noteworthy that while added ethanol decreased the hydrogenating capability of the catalyst, it did so without affecting α, the chain growth probability. Such a phenomenon was also observed in other studies in this laboratory[7] in which water was added to the system. These results suggest that the mechanism governing CH_4 formation is not the same as that governing the Fischer-Tropsch synthesis.

All of the above effects were more dominant at the higher CO conversions. At the correspondingly lower CO partial pressures, more sites are presumably available for the ethanol to adsorb and interact with the ongoing synthesis.

Ethanol did not significantly incorporate into growing hydrocarbon chains to form higher hydrocarbons, as evidenced by the lack of increase in the C_3 hydrocarbon (i.e., propane plus propylene) selectivity with added ethanol. In contrast, in the study of Kummer et al.[6] about 35% of the labelled ethanol added was incorporated and the resulting hydrocarbon products (up to C_{10}) had approximately a constant radioactivity per mole, suggesting that ethanol could act as a chain initiator. However these studies were at atmospheric pressure. Kokes et al.[5] extended the work of Kummer et al. by conducting ^{14}C tracer experiments with a doubly-promoted catalyst at varying pressure and temperatures (239-275° C). The percent incorporation of the ethanol was not a function of temperature or contraction, but fell from 18% to 7% to 2.2% as the pressure was increased from 0.1 to 0.75 to 2.1 MPa. They also concluded by comparison to Kummer et al.'s results that less incorporation occurred over a doubly-promoted catalyst containing potassium (MgO, K_2O) than over a singly-promoted catalyst without potassium (ThO_2).

The lack of evidence for significant ethanol incorporation in the present study is consistent with the conclusions of Kokes et al. since the experiments here were at relatively high pressures (0.92 MPa) over a triply-promoted catalyst containing potassium (Al_2O_3, K_2O, CaO). A small degree of incorporation could not have been detected with the analytical techniques employed here.

The observed increase in selectivity to form both acetaldehyde and ethyl acetate with an increase in ethanol partial pressure are probably interrelated. The acetaldehyde is probably produced by dehydrogenation of the ethanol and the ethyl acetate by the subsequent reaction of the acetaldehyde with ethanol, as shown below:



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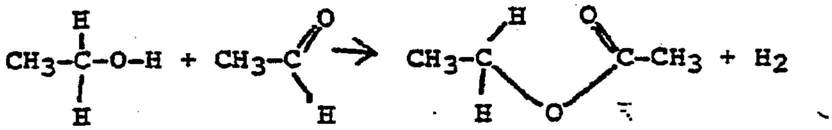

(2)

The observed increase in selectivity to form propanone (acetone) with an increase in ethanol partial pressure suggests that the ethanol is possibly reacting with some surface methylene species. The fact that propanone was formed instead of 1-propanol further suggests that the ethanol is bonded to the catalyst surface at the oxygenated carbon.

In a very recent paper, published after the present studies were completed, Tau et al.[8] report on the oxygenates formed from ethanol added during the Fischer-Tropsch synthesis on a Fe/silica catalyst. As here, acetaldehyde and ethyl acetate were principal oxygenated products. Propanal and propanone were not reported. They also reported an increase in the quantities of methanol, 1-propanol and 1-butanol formed, but we did not look for this. Several factors might cause considerable differences between their results and ours. The presence or absence of potassium in the catalyst can have major effects, as shown in the series of early papers by Emmett and co-workers. Degree of conversion or reactor gas compositions were not reported by Tau et al, but we find this is an important variable. Further they noted that their silica support itself was catalytically active and was probably responsible for the formation of acetals that they found, but we did not.

Results - Olefins

Ethylene

The addition of ethylene did not significantly affect the CO conversion but H_2 conversion increased, especially at high CO conversions (Table 2).

The effect of the ethylene partial pressure in the reactor on the methane selectivity is shown in Figure 2 for all of the experiments. Methane selectivity decreased with increasing ethylene partial pressure at both high and low CO partial pressures. Increased ethylene partial pressure increased the C_3 and C_4 olefin/paraffin ratios (Figure 3). Although not shown, the α-olefin/β-olefin ratios also increased with ethylene partial pressure, but only slightly.

The effect of ethylene on the Fischer-Tropsch product distribution at 91-93% CO conversion is shown in Figure 4. The C_1-C_7 product distribution is normalized without the C_2 fraction. The decreased methane selectivity at high ethylene partial pressure is clearly evident, but notably there was no effect of ethylene concentration on α.

The conversion of the ethylene in the feed was calculated from an overall material balance. The rate of formation of a compound resulting from the reaction of ethylene was estimated by subtracting the base case rate of formation of that compound from the rate of formation of that compound during the feed addition experiments.

At high CO conversions (86 to 94%) the conversion of the ethylene in the feed was between 56 and 86%, while at low CO conversions (27 to 29%) it was between 8 and 11%. At low CO conversions, essentially all of the ethylene in the feed that was consumed, formed ethane. At high CO conversions, between 70 and 80% of the ethylene consumed formed ethane. Presumably then, for these latter conditions, between 20 and 30% of the consumed ethylene, or about 15% of the ethylene fed to the reactor, was incorporated into the growing hydrocarbon chains on the catalyst surface to form heavier hydrocarbon products. This is supported by Figure 5, which plots the selectivity to form C_3 hydrocarbons (i.e., propane and propylene) as a function of ethylene partial pressure in the reactor. Under otherwise similar conditions, with increasing ethylene partial pressure in the reactor there is an increase in the formation of heavier hydrocarbons. This effect is most pronounced at high CO conversions.

Some previous studies, although fragmentary, showed effects in the same direction found here. Snel and Espinoza[9] working at 270°C and 2.0 MPa with an iron-calcium catalyst containing about 3 atomic % C reported addition of 10 mole % ethylene to syngas ($H_2/CO = 0.5$) to depress methane formation, to increase formation of higher hydrocarbons, and to increase the olefin content of products formed. Molina et al.[10] working with a 10% Fe/Al_2O_3 catalyst at atmospheric pressure and 250°C were primarily concerned with studying the effect of introduction of CO into a $H_2-C_2H_4$ mixture. However, they likewise reported that the presence of C_2H_4 in a H_2/CO reaction mixture enhanced C_3 products and reduced methane formation.

With increasing ethylene partial pressure in the reactor the selectivity to form 1-propanol increased, as shown in Figure 6, although the concentrations were small relative to the total C_3 hydrocarbons. This does not appear to be dependent on the CO partial pressure. There was also an increasing selectivity to form 2-butanone. For example, for $P_{C_2H_4} = 5.1$ kPa, the ratio of 2-butanone production to CO consumption was 9.3×10^{-6}, while for $P_{C_2H_4} = 68$ kPa, the ratio was 6.3×10^{-4}.

1-Butene

The addition of 1-butene to the syngas feedstream did not significantly affect the CO or the H_2 conversions, methane selectivity, olefin/paraffin ratio or the α-olefin/β-olefin ratios. No significant changes in the C_3 hydrocarbon selectivity or in C_4 skeletal isomerization selectivity were observed. At the low CO conversions, the 1-butene conversions were very small (<1%). At the high CO conversions, the conversion of the 1-butene was between 26 and 57%, and of the 1-butene reacted about 60% formed 2-butene, and 30% n-butane. The remaining 10% may have been converted to some extent to higher hydrocarbons, as indicated by Figures 7 and 8. In Figure 7 a slight increase in C_5 selectivity is seen with increased 1-butene partial pressure at each set of conditions. Figure 8 is a Flory plot excluding C_4 products, at high CO conversion and for low and high 1-butene partial pressures. There appears to be a slight increase in the selectivity to form C_5-C_7 products relative to the C_1-C_3 products with an increased 1-butene partial pressure. However, there is no change in α.

1-Hexene

The addition of 1-hexene with varying CO conversions did not significantly affect the CO or the H_2 conversions, methane selectivity, olefin/paraffin or α-olefin/β-olefin ratios. Only a slight increase was observed in selectivity to the C_6 skeletal isomer. n-Hexane and 2-hexene were formed in essentially equal amounts at both high and low CO conversions. At a CO conversion of 26% only about 15% of the 1-hexene reacted and there was no change in the selectivity to form C_7-C_{10} products relative to C_1-C_5 products.

At a CO conversion of 90% (0.92 MPa), about 70% of the 1-hexene in the feed reacted, and there seemed to be an increase in the C_7-C_{10} products. This is shown in Figure 9, a Flory plot of C_1-C_{10} products excluding C_6 for three experiments, two with 1-

hexene feed addition and one without. 75% of the 1-hexene that disappeared formed hexane or the β-olefin. 25% was unaccounted for. Although the results in Figure 9 would seem to indicate considerable incorporation of hexene into growing chains, we are dubious about the reliability of these results. In our analytical system the C_6-C_{10} products are distributed between a liquid phase in a trap and a gas phase, the analytical results of which are combined. During 1-hexene addition the C_7-C_{10} products are present in relatively small concentrations in the liquid compared to C_6, which also reduces the accuracy with which they could be determined. We are inclined to believe that some enhanced formation of C_7-C_{10} was a real effect, but that the change in slope with increased hexene content may well have been an artifact.

1-Decene

As with 1-butene and 1-hexene, the addition of 1-decene to the feed stream at high CO conversion did not significantly affect the H_2 or CO conversions, methane selectivity, the olefin/paraffin ratio, the α-olefin/β-olefin ratio, or the C_9 hydrocarbon selectivity. The selectivity to form C_{10} skeletal isomers, (paraffin plus olefin) defined as the ratio of the rate of C_{10}-isomer production to the rate of CO consumption was very low, but did increase from 3.7×10^{-4} to 20.4×10^{-4}.

The conversion of the 1-decene in the feed was about 80%. Of this, 24% formed n-decane, 43% formed 2-decene, 10% formed C_{10}-isomer, and the remaining 23% was unaccounted for, the reason for which was most likely the same as that for the ETOH and

1-hexene additions. Shown in Figure 10 are Flory plots for the results with and without 1-decene in the feed. The selectivity to form C_{10}^{+} products increased slightly upon the addition of 1-decene to the feed. The partial pressure of the added decene was much less than that of the lower olefins added; more evidence of chain incorporation might have appeared at higher concentrations.

1-Eicosene

A sample of 1-eicosene was melted and injected into the reactor after 50 hours of synthesis, and the synthesis was then continued for an additional 8 hours. The amount of C_{20} compounds vaporized from the reactor was negligible. The reactor contents were sampled and analyzed shortly after the 1-eicosene addition and again 8 hours later.

The 1-eicosene concentration was increased markedly by the addition, from 0.15×10^{-3} to 13.89×10^{-3} moles. The predominating reaction was hydrogenation; olefin isomerization was negligible. Table 4 lists the C_{20} compositions in the reactor before, shortly after, and 8 hours after the addition of 1-eicosene.

After 8 hours of synthesis, the number of moles of 1-eicosene had decreased significantly (~76% conversion) while the moles of n-eicosane increased by an almost proportional amount; the total number of moles of the 3 compounds decreased from 16.9×10^{-3} to 16.3×10^{-3} after 8 hours of synthesis.

A slight degree of incorporation did occur, as shown in Figure 11, where the absolute numbers of C_{17}-C_{25} moles in the reactor wax, excluding 1-eicosene, are shown on a Flory plot for the samples taken initially and after 8 hours of synthesis. The

[redacted]

C_{17}-C_{19} quantities remained essentially constant, while the C_{21}-C_{25} molar quantities increased slightly. These individual high molecular species are present in low amounts and their concentrations cannot be determined with high accuracy. Also, some incorporation might have occurred before the first post-addition sample was taken.

Discussion - Olefins

An overview of the fate of added normal 1-olefins is presented in Table 5, which summarizes the results of seven representative experiments. The first four listed were conducted at high CO conversion (low p_{CO}), while the final three were conducted at low CO conversion (high p_{CO}).

Table 5 gives the estimated percent conversion of the olefin in the feed and the percent of the olefin added that was converted to paraffin, to β-olefin, to skeletal isomers, to incorporation products, and to that which was unaccounted for. The incorporation products are taken to be the increase in hydrocarbons that contain 1 carbon atom more than the olefin additive. The amount of feed unaccounted for is the difference between the total amount converted and the amount converted that can be attributed to the four categories of products listed above.

The conversions to paraffins and β-olefins are consistently higher at the lower values of p_{CO} for each olefin studied. This finding supports the finding of Sudheimer and Gaube[11] that the hydrogenation and isomerization reaction rates of 1-hexene and 1-decene during Fischer-Tropsch synthesis over a precipitated iron catalyst containing potassium were inversely proportional to p_{CO}. In other Fischer-Tropsch studies in our laboratories we also find significant changes in product distribution at high CO conversions[12]. The effect of CO conversion on the general reaction network of Fischer-Tropsch synthesis can be an important variable, to which little attention has been paid. It is difficult to isolate this effect in plug-flow reactors, the type usually used for Fischer-Tropsch studies, but the well-mixed continuous flow reactor, as used in our studies, is particularly suitable for these kinds of studies.

Ethylene is clearly more reactive than 1-butene. Schulz et al.[13] added ethylene and propylene to the Fischer-Tropsch synthesis feedstream utilizing a precipitated alkalized iron catalyst at 220 °C and 2.0 MPa. 76% of the ethylene was consumed as compared to 44% of the propylene. In an earlier, brief study[14] on this same catalyst at 248°C and 1.5 MPa we observed that while from 18% to 32% of the ethylene added to the Fischer-Tropsch synthesis feedstream was hydrogenated to ethane, less than 0.5% of the added 1-butene was hydrogenated to n-butane under similar synthesis conditions.

The drop in reactivity from ethylene to 1-butene is, however, reversed as higher olefins are considered. n-Olefin reactivities estimated as a first order process, decrease in the following order: 1-decene > 1-hexene ≈ ethylene > 1-butene. For olefin hydrogenation the order of decreasing activity is ethylene > 1-decene > 1-hexene > 1-butene. For $\alpha \rightarrow \beta$-olefin isomerization activity the order is 1-decene > 1-hexene > 1-butene. In general the reactivity of the primary olefins increases with increasing molecular weight, the exception being ethylene. This probably reflects that fact that, other factors being equal, the degree of adsorptivity increases with molecular weight.

For present reaction conditions, at low values of p_{CO} the quantity of olefins hydrogenated is somewhat less than the quantity isomerized. At the higher values of p_{CO}, the quantities are about equal.

Skeletal isomerization of all added olefins was small relative to $\alpha \rightarrow \beta$ isomerization and hydrogenation. No detectable amount of any of the olefins was cracked, as measured by the rate of formation of hydrocarbons containing one carbon atom less than the added olefin. Absence of cracking reactions was also observed in other studies. As discussed by Dry[15], Kolbel et al.[16] found that hydrocracking over an Fe catalyst accounted for less than 3 percent of the CH_4 produced at temperatures up to 573 °K, and Forney et al.[17] reported that with iron catalysts the oil they studied was not cracked until temperatures were in excess of 573 °K. We[14] found no evidence for the skeletal isomerization of 1-butene nor for the cracking of ethylene or 1-butene. Likewise, Dwyer and Somorjai[18] did not find cracking of ethylene or propylene to occur. Hall et al.[19] concluded that hydrocracking of ethylene is unimportant, and Schulz et al.[13] reported that less than 1% of the added ethylene or propylene cracked under the conditions of their study.

Although olefin incorporation under our conditions was minor relative to hydrogenation and $\alpha \rightarrow \beta$ isomerization, it clearly could be detected. With added ethylene, the selectivity to form C_3 hydrocarbons increased with increasing $p_{C_2H_4}$, (Figure 5) and with added butene the selectivity to form C_5 hydrocarbons increased with increasing $P_{C_4H_8}$ (Figure 6). Likewise, with 1-hexene, the selectivity to form hydrocarbons containing more than 1 additional carbon atom above the number of carbon atoms in the olefin also increased (Figure 8). Similar results from 1-decene and eicosene are shown in Figures 10 and 11. All these results suggest then that the primary olefin can act as a chain initiator or that it could directly react as a chain terminator with surface species larger than methylene.

As far as ethylene is concerned, Fig. 4 suggests that ethylene initiates chains, since added ethylene did not significantly affect the C_3-C_7 chain growth probability. However Schulz et al.[12] reported that ethylene terminated chains since upon addition of ethylene-^{14}C to synthesis gas, the molar radioactivity of the C_3 and higher reaction products decreased rapidly with the C number. Dwyer and Somorjai[18] reported that the chain growth probability increased with the addition of ethylene to the feed stream and concluded that ethylene participates in chain propagation. However, the results may have been magnified by a combination of low conversion ($x_{CO} < 1\%$), lack of alkali promoter in the catalyst, unsteady-state activity and catalyst phase composition in their experiments[13].

An increase in the partial pressure of ethylene is seen to decrease methane selectivity (Figure 2) and increase the C_3 and C_4 olefin/paraffin ratios (Figure 3). With increasing ethylene concentration there is an associated decrease in the hydrogenating character of the catalyst. Dwyer and Somorjai[18] also observed a slight inhibition of methanation at high ethylene partial pressures. No significant effects of 1-butene, 1-hexene, and 1-decene on the above product distribution characteristics were observed in our work.

It is noteworthy that with all the olefins the CO conversion remains essentially constant with increased olefin partial pressure. This suggests that CO is much more strongly adsorbed than the olefins. Presumably they compete for the same sites, since the secondary reactions of olefins increase markedly at low CO concentrations, corresponding to high conversions.

Increased ethylene partial pressure causes an increase in the formation of 1-propanol and 2-butanone. The first could be formed by reaction of ethylene with an adsorbed oxygenate or possibly by CO insertion. The fact that 2-butanone is formed instead of 1-butanol suggests that the iron-carbon bond is formed with the oxygenated carbon.

A similar phenomenon was observed by Pijolat and Perrichon[20]. In their studies using a 10 wt% Fe on τ-alumina in a microreactor at 225°C and 1.8 MPa, they observed a five-fold increase in the formation of n-pentanol-1 upon the addition of n-butene-1 to a H_2/CO (2/1) feed. They also observed a lesser enhancement of n-hexanol-1 and possibly n-pentanol-2 and n-hexanol-2. They proposed that the increased n-pentanol-1 formation was caused by the insertion of CO into the adsorbed n-butene-1, followed by hydrogenation. To support their hypothesis, they noted an earlier study of theirs[21] wherein they used I.R. spectroscopy to reveal the presence of non-dissociated CO on the metallic iron sites of their Fe/Al_2O_3 catalyst after reaction at 14 bars and 300°C.

Summary and Conclusions

The existence of two Flory-Schulz product distributions from Fischer-Tropsch synthesis on a variety of iron catalysts is now well documented. It has been suggested that the effect is associated with reduced volatility and longer reactor residence time of higher molecular weight intermediates, especially 1-olefins, that become incorporated into growing chains. However, we could find no evidence to support this hypothesis. Under a set of conditions in which the double distribution has been clearly shown to occur, we observed only a very slight degree of chain incorporation upon additions of various 1-olefins or ethanol in major amounts.

Instead, the principal reactions of the added 1-olefin were hydrogenation to the corresponding paraffin and isomerization to the correpsonding 2-olefin. The reactivity of the additive was markedly enhanced at high CO conversions (low CO partial pressure), attributed to a decrease in competitive adsorption by CO. By extension and from other studies in our laboratories, we conclude that the reaction network in the Fischer-Tropsch synthesis may be markedly affected by CO conversion. This variable has received little attention in the past, probably because it is difficult to isolate its effect by studies in a plug-flow (fixed bed) reactor. A continuous flow stirred tank reactor (CSTR), as used here, is particularly well suited to study effects of this sort.

Acknowledgment

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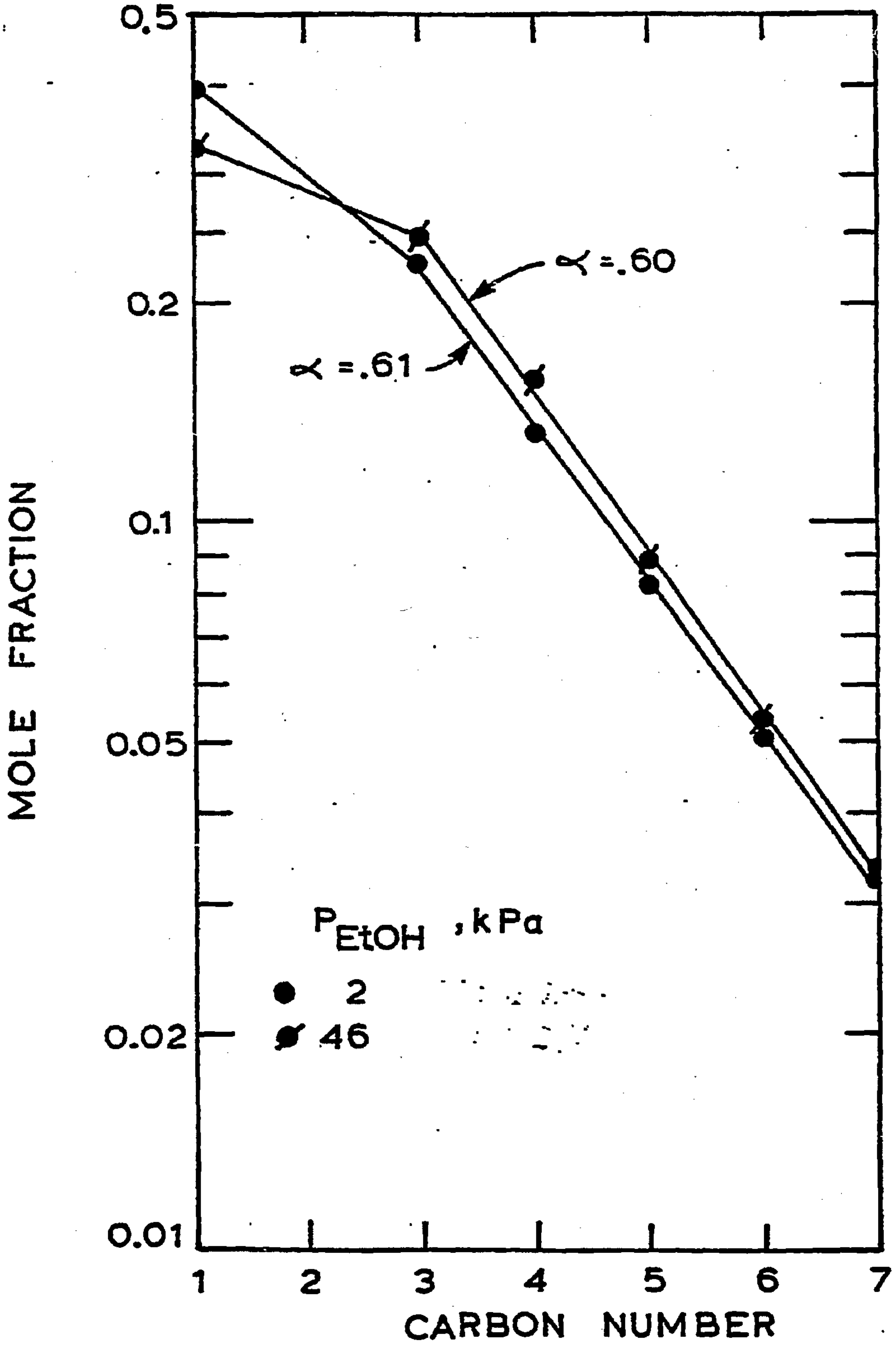
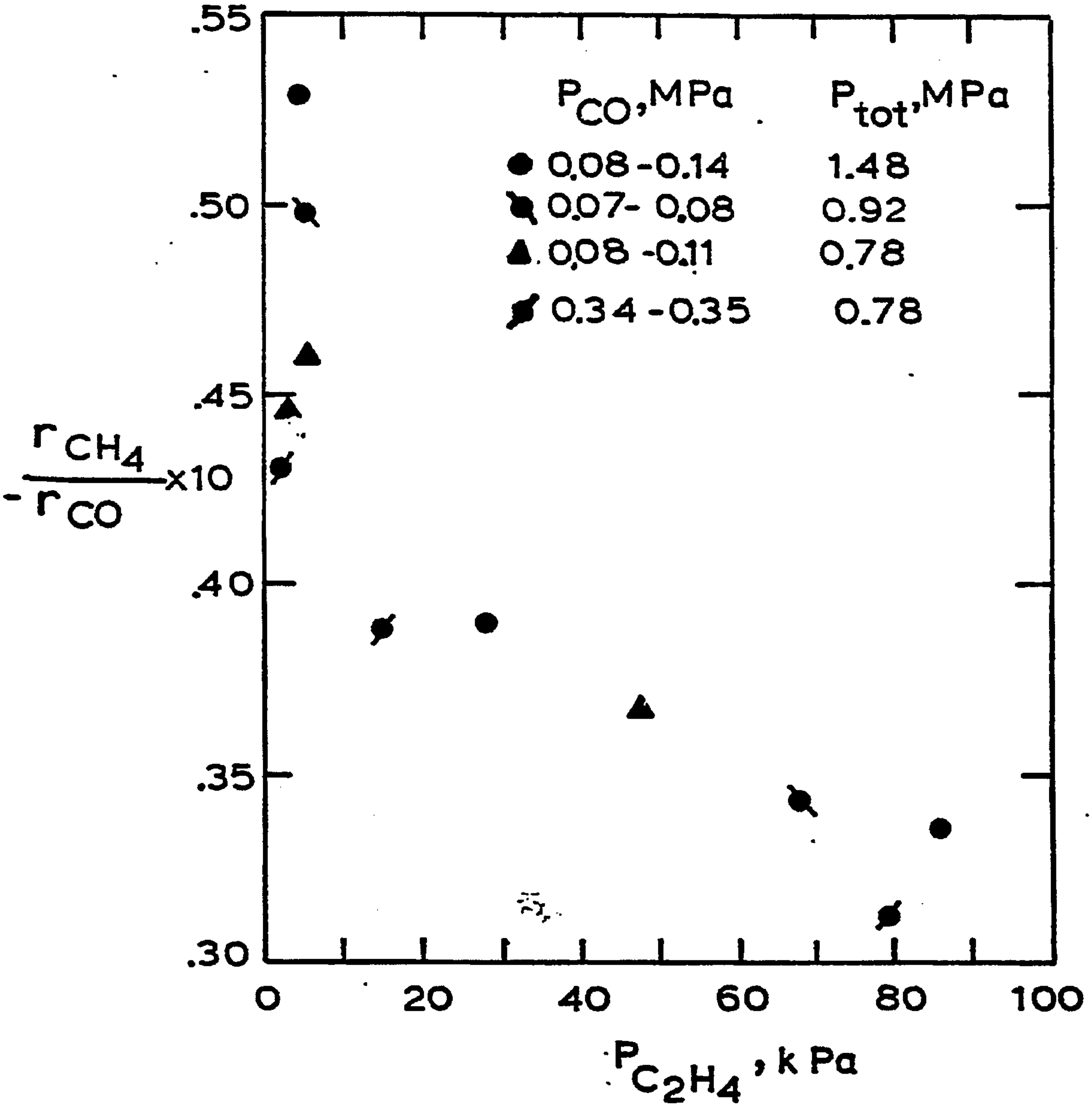
Figure Captions

Figure 1	Ethanol addition has no effect on Flory distribution except for methane. Data normalized excluding C_2 fraction. Total pressure = 0.92 MPa, 248 °C.
Figure 2	Ethylene addition decreases methane selectivity.
Figure 3	Ethylene addition increases olefin/paraffin ratio. Legend shown on Figure 2.
Figure 4	Ethylene addition has no significant effect on Flory distribution except for methane. Data normalized excluding C_2 fraction. Total pressure = 0.92 - 0.98 MPa, 248° C, high CO conversions.
Figure 5	The effect of ethylene on formation of propane plus propene. Total pressure = 0.78 - 1.58 MPa. Legend shown on Figure 2.
Figure 6	Ethylene increases 1-propanol selectivity. Total pressure = 0.78 - 1.58 MPa. Legend shown on Figure 2.
Figure 7	The effect of 1-butene on formation of C_5 hydrocarbons. Oxygenates excluded. Total pressure = 0.78 - 1.58 MPa. Legend shown on Figure 2. ■ points correspond to p_{CO} = 0.46 - 0.49 MPa and total pressure = 1.48 MPa.
Figure 8	1-Butene addition slightly increases C_5+ fraction. Overlapping points at C_2 and C_3. Data normalized excluding C_4 fraction. Total pressure = 0.92 - 0.95 MPa.

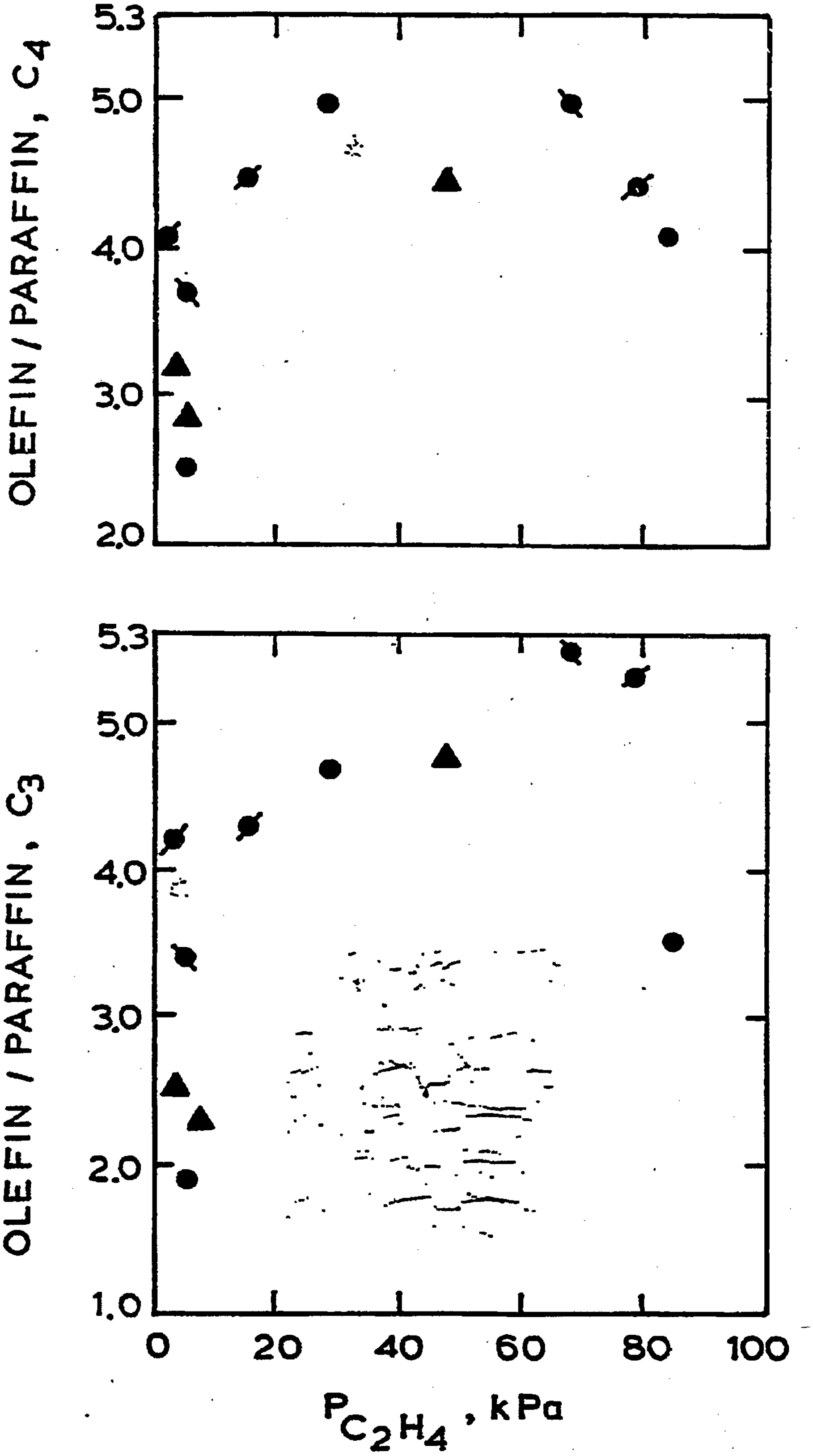
Figure 9	1-Hexene addition increases C_7+ fraction. Overlapping points at each of C_1-C_5. High CO conversions. Data normalized excluding C_6 fraction. Total pressure = 0.92 MPa. See text for discussion.
Figure 10	1-Decene addition slightly increases C_{11}+ fraction. Overlapping points at C_2 and C_{13}. Data normalized excluding C_{10} fraction. Total pressure = 0.92 MPa.
Figure 11	1-Eicosene addition moderately increases C_{21}+ fraction. Data normalized excluding C_{20} fraction. Total pressure = 0.92 MPa.


0.5
0.2
0.1
0.05
0.02
0.01
MOLE FRACTION
1
2
3
4
5
6
7
CARBON NUMBER
∝ =.60
∝ =.61
P_{EtOH} , kPa
● 2
● 46

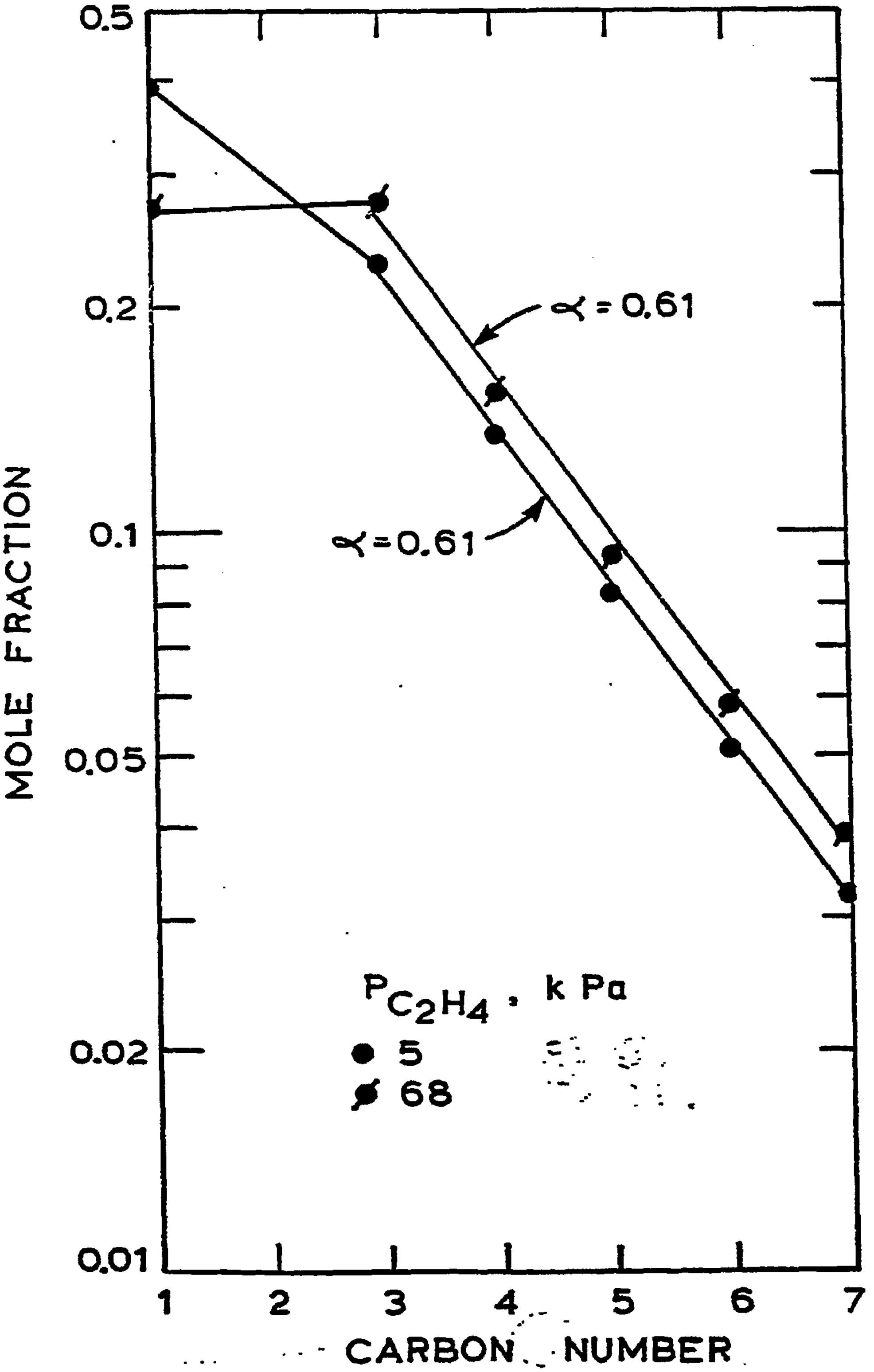
①


.55
.50
.45
.40
.35
.30
0
20
40
60
80
100
$\frac{r_{CH_4}}{-r_{CO}} \times 10$
$P_{C_2H_4}$, k Pa
P_{CO}, MPa
P_{tot}, MPa
● 0.08-0.14 1.48
0.07- 0.08 0.92
▲ 0.08 -0.11 0.78
0.34-0.35 0.78

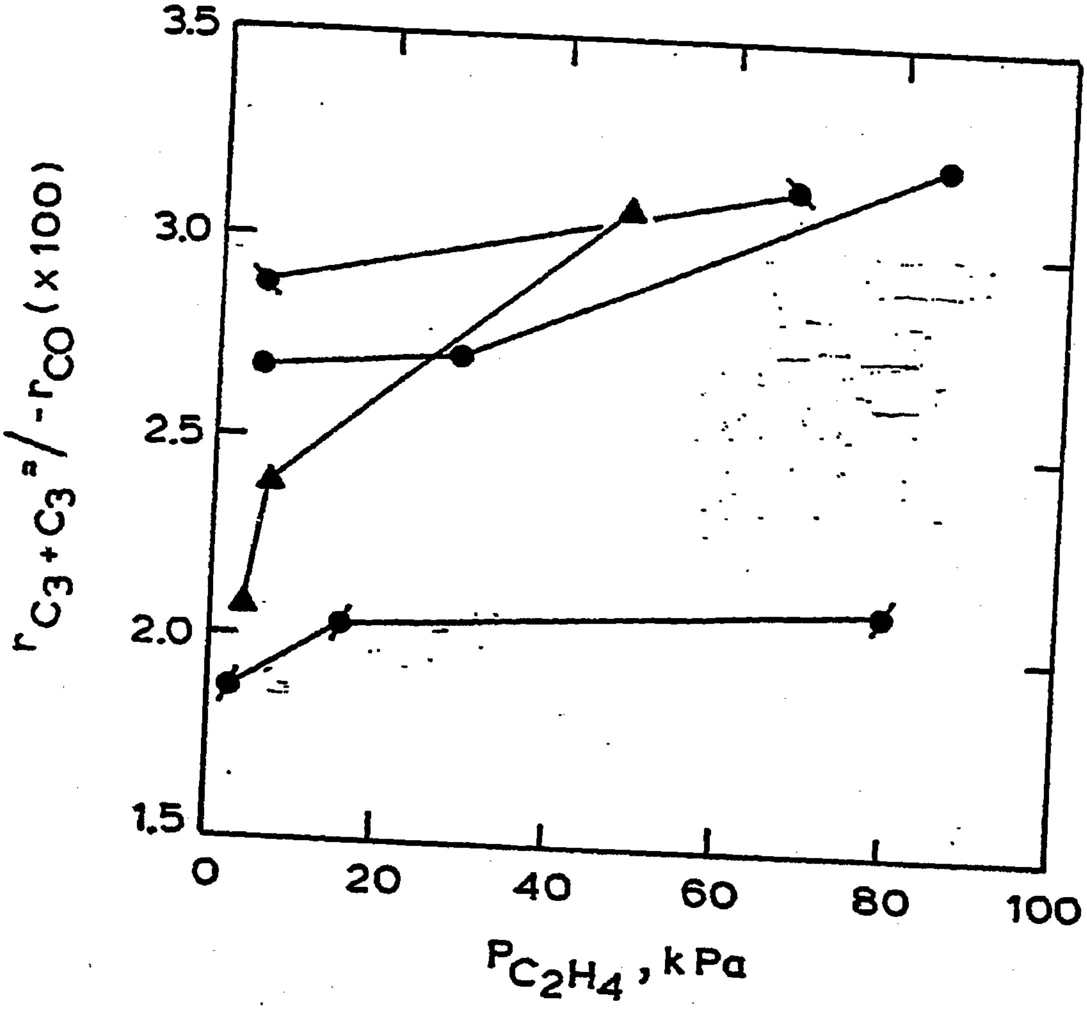
②


5.3
5.0
4.0
3.0
2.0
OLEFIN / PARAFFIN, C_4
5.3
5.0
4.0
3.0
2.0
1.0
OLEFIN / PARAFFIN, C_3
0
20
40
60
80
100
$P_{C_2H_4}$, kPa

③


0.5
0.2
0.1
0.05
0.02
0.01
MOLE FRACTION
1
2
3
4
5
6
7
CARBON NUMBER
$\alpha = 0.61$
$\alpha = 0.61$
$P_{C_2H_4}$, k Pa
● 5
ø 68

(4)



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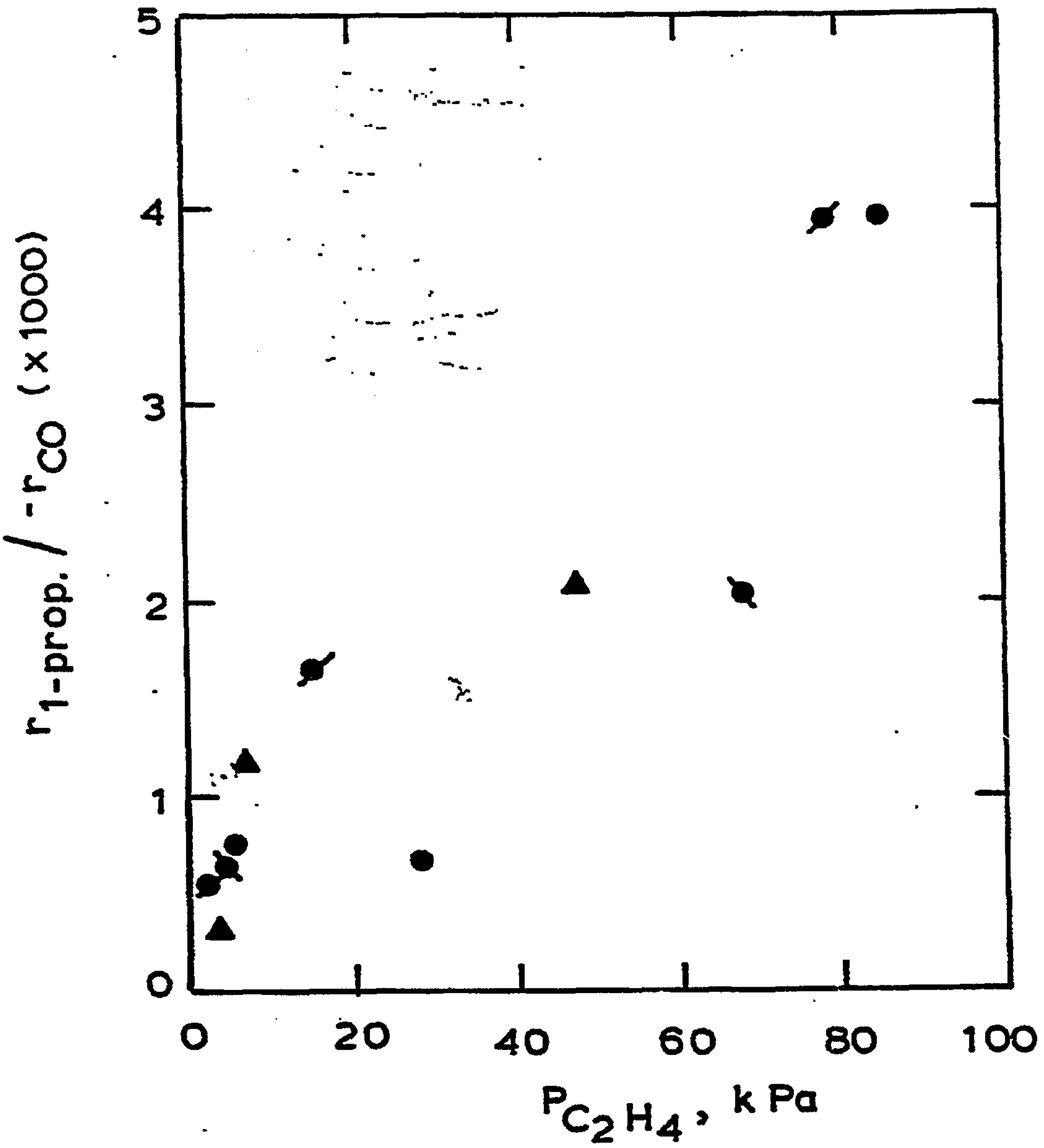

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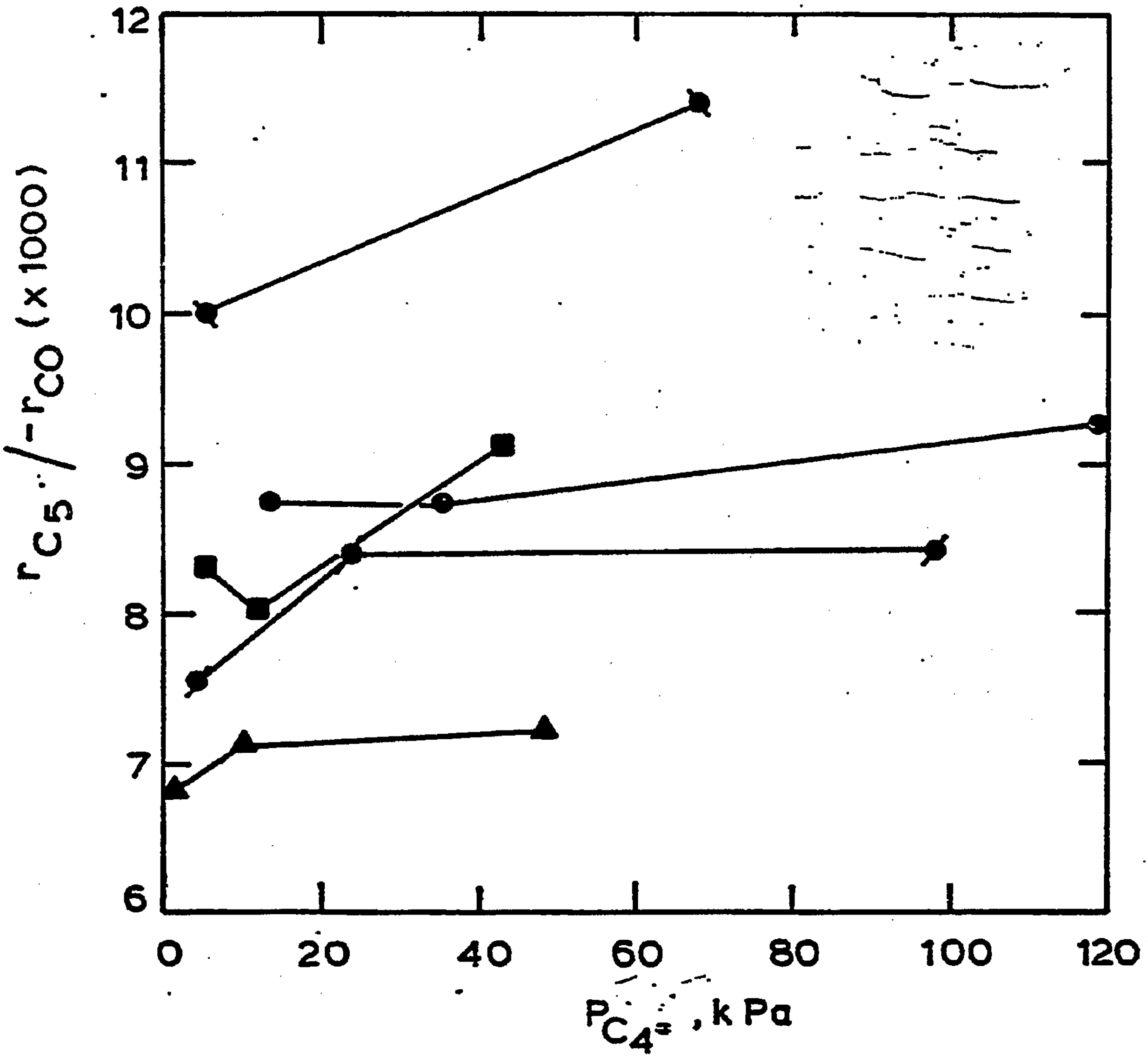

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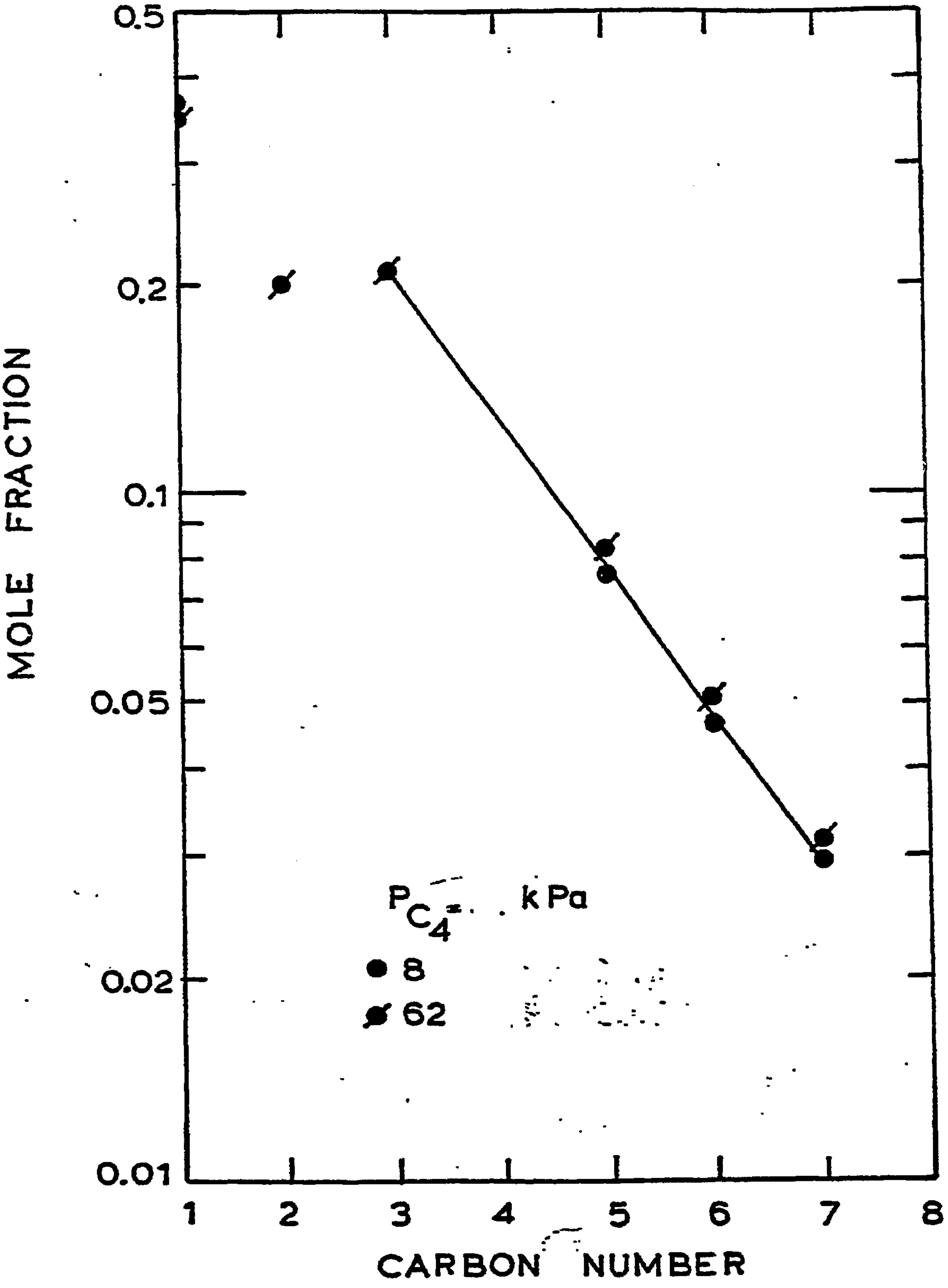
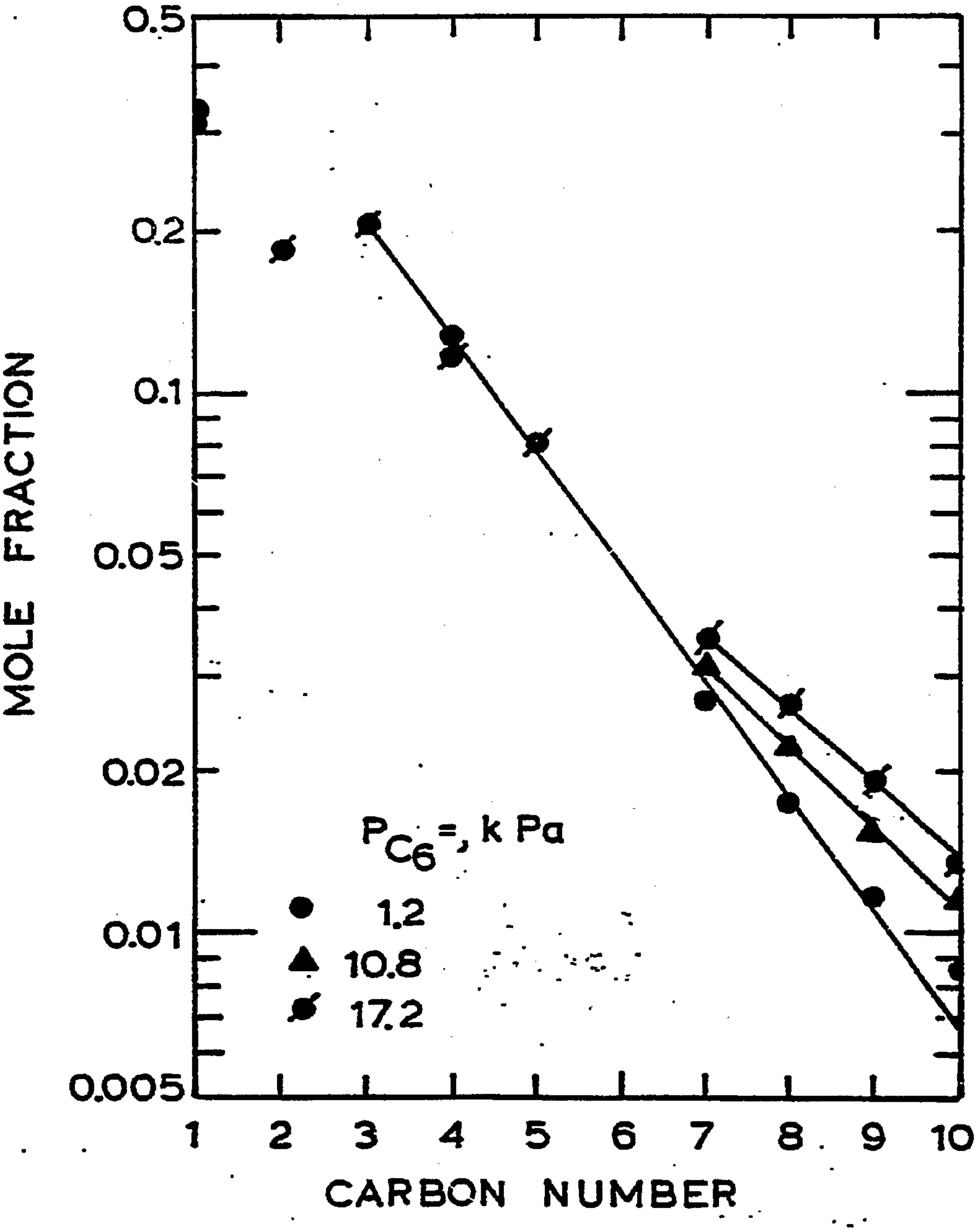
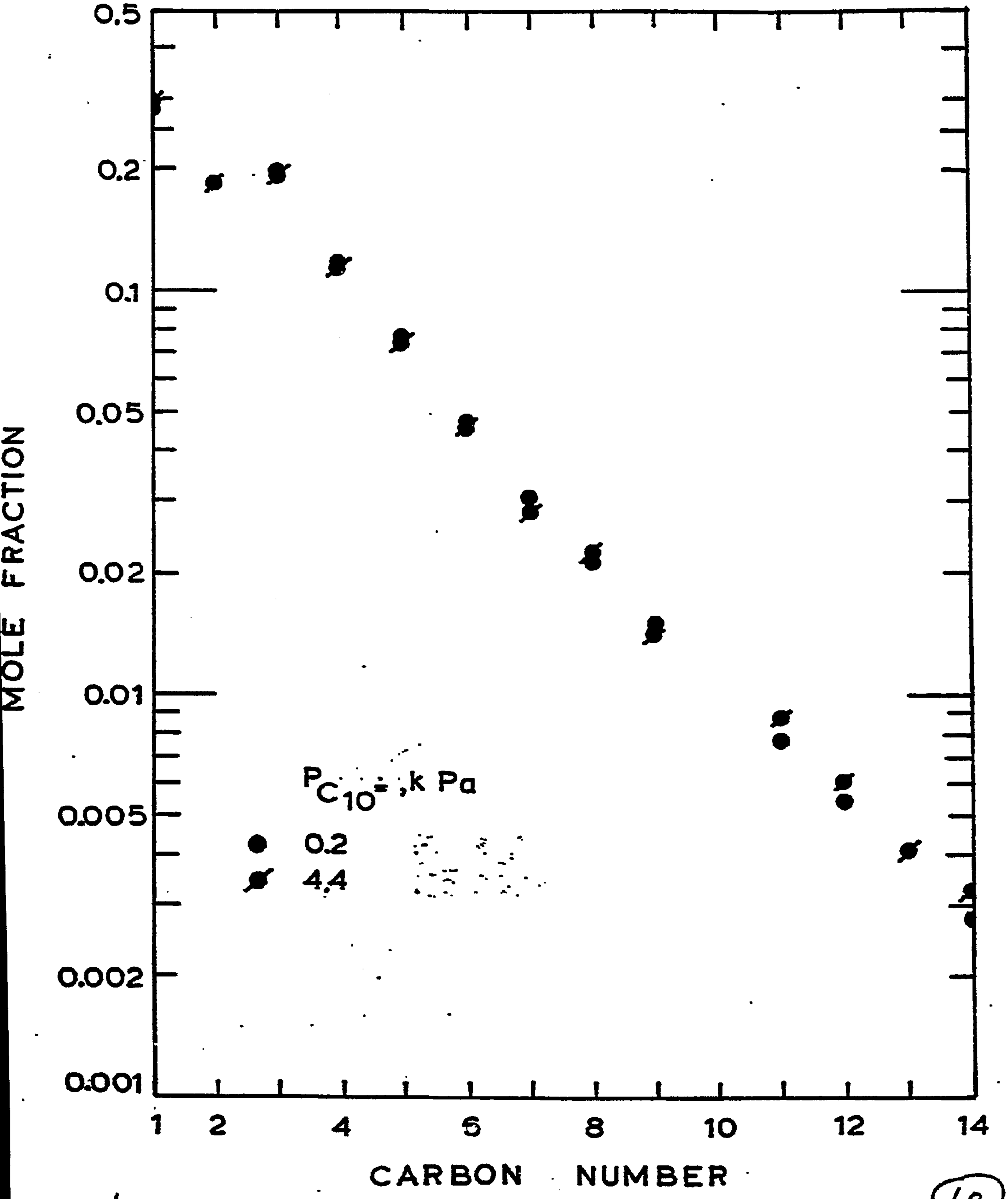

0.5
0.2
0.1
0.05
0.02
0.01
MOLE FRACTION
1
2
3
4
5
6
7
8
CARBON NUMBER
$P_{C_4^=}$, kPa
● 8
62

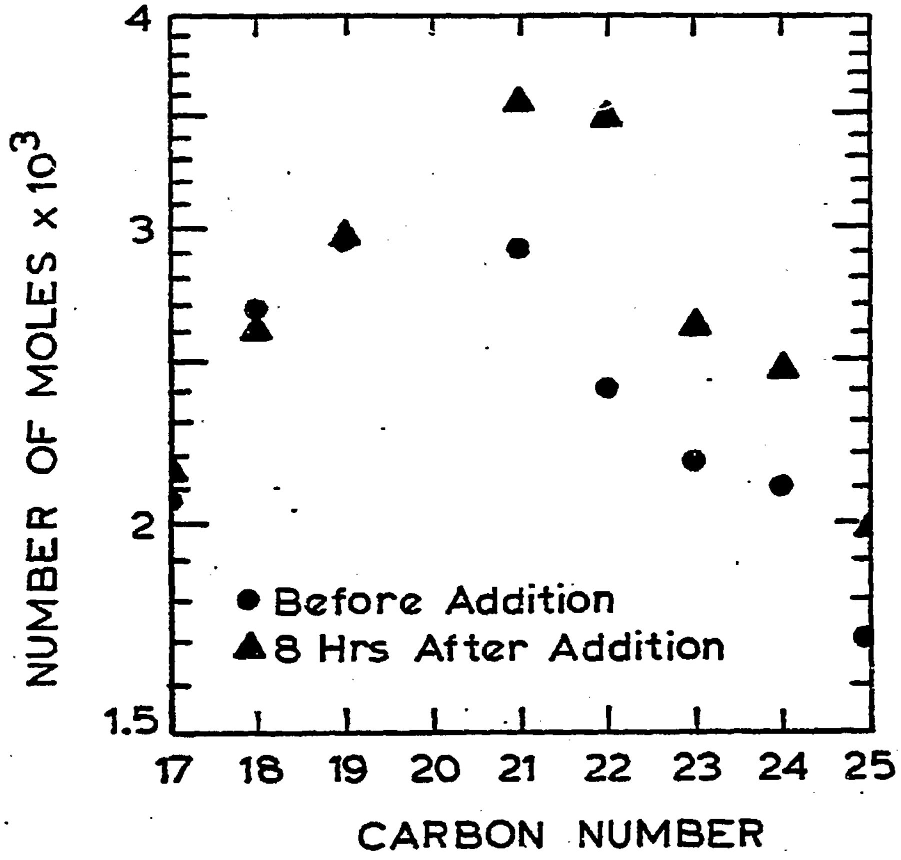


0.5
0.2
0.1
0.05
0.02
0.01
0.005
MOLE FRACTION
1
2
3
4
5
6
7
8
9
10
CARBON NUMBER
$P_{C_6^=}$, k Pa
● 1.2
▲ 10.8
17.2

9


0.5
0.2
0.1
0.05
0.02
0.01
0.005
0.002
0.001
MOLE FRACTION
$P_{C_{10}^{=}}$, k Pa
● 0.2
4.4
1
2
4
6
8
10
12
14
CARBON NUMBER

⑩


4
3
2
1.5
NUMBER OF MOLES × 10^3
17
18
19
20
21
22
23
24
25
CARBON NUMBER
● Before Addition
▲ 8 Hrs After Addition

(11)

Table I - Compounds Studied

Compound	Description
Ethanol	200 proof (U.S. Industrial Chemicals)
Ethylene	2 sets of premixed tanks (Matheson), 0.92 H_2/CO, 1.6 or 8.6 mol% ethylene
1-Butene	2 sets of premixed tanks (Matheson), 0.92 H_2/CO, 0.99 or 4.9 mol% 1-butene
1-Hexene	99.9% (Aldrich)
1-Decene	99% (Alfa Products)
1-Eicosene	98.5% (Wiley Organics)

Table 2. Experimental Conditions for all Studies.[a]

Species	% Conversion without additive		% Conversion with additive		Partial Pressure of Species in Exit, kPa		Total Pressure, MPa
	CO	H_2	CO	H_2	without additive	with additive	
Ethanol	40	26	42	27	1.0	33	0.92
	89	65	89	59	2.0	35	0.92
			88	56		58	
	93	68	89	59	2.0	46	0.92
Ethylene	27	21	29	23	2.0	15	0.78 - 0.79
			29	25		78	0.84
	86	63	90	67	3.0	6.0	0.78 - 0.79
			85	70		47	0.84
	92	69	94	73	5.0	28	1.48 - 1.49
			94	79		84	1.58
	93	68	91	73	5.0	68	0.92 - 0.98
1-Butene	27	21	31	24	1.0	10	0.78
			31	24		48	0.81
	86	63	90	66	5.0	11	0.78
			88	66		42	0.81
	38	31	42	34	3.0	24	1.48
			40	33		98	1.52
	91	69	91	71	13.0	34	1.48
			89	69		118	1.52
	93	68	92	67	8.0	62	0.92 - 0.95
1-Hexene	26	19	27	20	0.4	28	0.92
	91	67	89	65	1.2	11	0.92
			90	66		17	
1-Decene	95	70	94	68	0.2	4.4	0.92
1-Eicosene[b]	92	65					

---

[a] 248°C, $(H_2/CO)_{feed}$ = 0.90 - 0.97

[b] See text.

Table 3 - Selectivity results from ethanol feed addition experiments (248°C, 0.92 MPA, 0.90-0.94 H_2/CO).

	CO Conversion = 88 - 93%					CO Conversion = 40-42%	
P_{H_2}, kPa	298	310	307	280	299	407	395
P_{CO}, kPa	97	93	90	67	86	367	346
P_{CO_2}, kPa	385	353	313	402	342	110	113
P_{H_2O}, kPa	26	36	59	35	34	12	9
P_{EtOH}, kPa	2	35	58	2	46	1	33
Vol. % EtOH in Feed	—	3.1	6.4	—	4.0	—	2.9
	Moles Product per Mole CO Consumed (x 100)						
Methane	5.5	3.7	3.5	5.0	4.2	3.1	2.6
Ethylene	0.37	0.78	1.00	0.6	1.5	0.97	1.08
Ethane	2.0	1.5	1.3	1.9	1.3	0.54	0.43
Ethylene + Ethane	2.4	2.2	2.3	2.5	2.8	1.5	1.5
Propylene + Propane	2.6	2.3	2.3	2.7	2.8	1.4	1.3
Ethanal (Acetaldehyde)	0.01	0.18	0.35	0.01	0.10	0.04	0.36
Ethylacetate	0.00	0.17	0.30	0.00	0.29	0.00	0.02
Propanal + Propanone	0.03	0.17	0.25	0.08	0.28	0.03	0.11
CO_2	46.9	46.8	46.4	47.1	49.3	45.1	44.4
Olefin/ Paraffin C_2	0.19	0.52	0.77	0.33	1.15	1.8	2.5
C_3	1.9	4.0	4.7	3.4	6.7	4.6	4.8
C_4	2.6	4.0	4.6	3.7	6.0	4.0	4.2
α-Olefin/ β-Olefin C_4	1.7	5.3	8.0	2.8	13.4	17.0	28.0
C_5	1.7	5.7	9.0	2.7	12.9	20.0	35.0

TABLE 4

Molar Quantities of C_{20} Compounds Before and After 1-Eicosene Addition to the Reactor[a]

Moles x 10^3	Initial	Shortly After Addition	After 8 Hours of Synthesis
1-Eicosene	0.15	13.9	3.4
n-Eicosene	2.48	3.0	12.9
TOTAL	2.63	16.9	16.3

---

[a] 248°C, 0.92 MPa, x_{CO} = 0.92

Table 5 - Fate of Added Olefins (248°C)

Olefin Feed Additive	P_{CO}, MPa	P_{H_2}, MPa	Vol % Olefin in Feed	% Conversion of Olefin	% Olefin in Feed Converted to: Paraffin	β-Olefin	Isomer[a]	Incorporation[b]	Unaccounted for[c]
Low CO Partial Pressure:									
Ethylene	0.080	0.23	8.6	59	47	--	--	4	8
1-Butene	0.071	0.27	4.9	38	13	28	0.0	0.9	-4
1-Hexene	0.090	0.28	3.7	(70)	20	24	0.5	1.2	(24)
1-Decene	0.054	0.28	1.3	(80)	19	35	8	0.0	(20)
High CO Partial Pressure:									
Ethylene	0.34	0.33	8.6	9.2	10	--	--	0.6	-1.4
1-Butene	0.57	0.59	4.9	<1	(d)	(d)	0.0	0.0	0.0
1-Hexene	0.39	0.41	3.2	(15)	2	2	0.0	0.1	(11)

---

[a] Isomer formation at same carbon number as olefin additive

[b] Formation of hydrocarbons containing 1 carbon atom more than the olefin additive

[c] % Unaccounted = (% Olefin Conversion) - % Olefin converted to paraffin, β-olefin, isomer and incorporation.

[d] The ratio of paraffin to β-olefin was about unity.

Figures in parentheses are estimates.

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