FISCHER-TROPSCH STUDIES WITH ACETYLENIC COMPOUNDS AS PROBES

by

Li Hou

B.S. in Chemical Engineering, Hefei University of Technology, China, 1997

M.S. in Chemical Engineering, Hefei University of Technology, China, 2000

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SCHOOL OF ENGINEERING

This dissertation was presented

by

Li Hou

It was defended on

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and approved by

John W. Tierney, PhD, Professor

James T. Cobb, PhD, Professor

Badie I. Morsi, PhD, Professor

Rachid Oukaci, PhD

Dissertation Director: Irving Wender, PhD, Professor

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Incorporation of probe molecules has been widely used in elucidation of the mechanism of the Fischer-Tropsch (F-T) reaction. In this study, we used acetylenic molecules, including 1-hexyne, 2-hexyne, 4-phenyl-1-butyne, and 1-phenyl-1-propyne as well as acetylene as probes with cobalt and iron catalysts.

Experiments were carried out in a tubular microreactor of 3/8 inch diameter. Long chain alkynes were added via a saturator or a syringe pump. Acetylene was introduced from a cylinder containing carbon monoxide and hydrogen plus 1% of acetylene.

We found that acetylenic compounds can initiate the F-T synthesis at temperatures more than 100°C lower than those at which normal F-T reactions are carried out. Since products obtained from linear alkyne-initiated F-T and those from normal F-T synthesis are indistinguishable, we used phenyl-substituted acetylenes as probes to distinguish the alkyne initiated products from normal F-T products. At low temperatures, only alkyne-initiated F-T reactions take place; at normal F-T temperatures, both alkyne initiated reactions and normal initiated F-T reactions occur. Although the degree of incorporation of internal alkynes is much less than that of the terminal alkynes, they can also initiate F-T chain growth to form mostly

branched products. Under the same reaction conditions, internal olefins have little effect on the F-T reaction.

When an acetylenic probe molecule is added to cobalt catalyzed F-T reactions, aldehydes or alcohols with one carbon more than the added probe molecule are the only oxygenates formed, perhaps by a hydroformylation type of reaction. Incorporation of alkynes (with carbon number n) on iron catalysts increased the rate of formation of C_{n+1}^{+} oxygenates, via Anderson-Schulz-Flory distribution.

The F-T synthesis is a complex process in which a large number of hydrocarbon and oxygenated species are present on the catalyst surface. The nature of these adsorbates and how they react differ as reaction conditions and the nature of the catalyst changes. This work, combined with results of experiments on incorporation of ethylene, lends credence to the postulation that unsaturated two-carbon entity, possibly vinylidenes or ethylidynes, may be involved in initiation of the F-T synthesis.

DESCRIPTORS

Acetylene
Acetylenic compounds
Alkynes
Chain initiation
CO hydrogenation
Cobalt
Fischer-Tropsch synthesis
Fixed-bed reactor
1-Hexyne
2-Hexyne
Iron
1-Phenyl-1-propyne
4-Phenyl-1-butyne
Probe molecules

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1.0 INTRODUCTION

The Fischer-Tropsch (F-T) synthesis involves the conversion of synthesis gas (CO/H_2), which can be produced from coal, natural gas, petroleum coke and any other carbonaceous material, into high quality, environmentally clean transportation fuels, essentially middle distillate liquids used as diesel and jet fuels. Application of the F-T process has been limited since it has not been able to compete with transportation fuels derived from petroleum on an economic basis. But currently processes for the conversion of coal and natural gas into liquid fuels (Gas to Liquid or GTL) via F-T technology are drawing increased attention commercially. The large resources of coal and natural gas are a driving force for this renewed interest. The presently known natural gas and coal reserves worldwide are about 1.5 and 25 times, respectively, that of crude oil(1). The F-T process is being used to convert remote or associated natural gas, currently handled by reinjection and pipelining, into fuel products; it provides an opportunity to expand the use of stranded natural gas. Another driver for F-T technology is increased global demand for environmentally clean fuels. An important part of the future energy policy for the United States will be the availability of ultra-clean fuels. The reduction of sulfur in petroleum-derived diesel and gasoline is difficult and expensive. New U. S. regulations to reduce the amount of allowable sulfur in diesel from 500 ppm to 15 ppm and from 350 to 30 ppm in gasoline are scheduled to go into effect in 2006(2, 3). A reduction of aromatics in gasoline is also required. Fuels from the F-T synthesis are of excellent quality and free of sulfur, nitrogen and aromatics, the presence of the latter in petroleum-based fuels produces emission of solid particles, soot and other deleterious material. F-T products can be blended with crude oil-derived diesel fuel to meet the restrictions for clean fuels. The products from F-T plants can be transported and sold through the present conventional infrastructure, such as tankers, storage facilities and existing retail distribution systems.

Despite a long history of research on the F-T synthesis, there is relatively little understanding of the mechanistic aspects involved in converting synthesis gas to liquids and chemicals. What we know of the F-T process is still controversial, due to its complexity. Research into fundamental F-T chemistry is therefore likely to be extremely valuable with the present stimulus to invest in the F-T process. Many researchers have used probe molecules to obtain information on the nature of the F-T synthesis. The use of probe molecules, such as olefins(4-16), alcohols(17-23) and C1 monomers(24,25,26,27,28), has played an important role in developing an understanding of the pathways involved in the F-T synthesis. Olefins and alcohols have been added to the F-T synthesis as probe molecules to produce hydrocarbon or oxygenated intermediates. Addition of C1 monomers has led to a general consensus that chain growth occurs by addition of methylene (CH_2) groups to a growing chain. Application of probe molecules in the F-T studies will be discussed in Section 2.3.

In this work we used acetylenic compounds as probes to obtain information on pathways followed in F-T reactions. We were intrigued by a resemblance between carbon monoxide and acetylene; both contain triply bonded structures (see Figure 1.1). Three resonance structures of CO have been suggested, with the triply-bonded structure thought to be the one best describing CO. Interestingly, CO and nitrogen molecules are isoelectronic and have a striking similarity in physical properties; the nitrogen molecule has no dipole moment, while CO has a dipole moment which is very small (0.1 Debyes). CO is more reactive compared to nitrogen, though the dissociation energy of CO (256.1 kcals) is higher than that of nitrogen (225.1 kcals). The greater reactivity of CO is attributed to the electron-donor properties of CO, since the carbon atom of CO has a lone pair of electrons in the hybridized sp orbital which is directed away from the C-O bond. The lone pair of electrons in nitrogen is in an s orbital close to the nitrogen nuclei.

Structure of CO

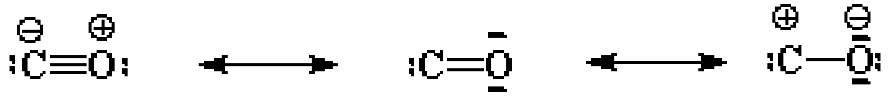


Figure 1.1 Structures of CO

Acetylene is a linear molecule, with a carbon-carbon triple bond consisting of one sigma bond and two pi bonds. Each carbon in acetylene provides three electrons to form shared pairs, while the carbon in carbon monoxide contributes two electrons and oxygen contributes four electrons to bonding in the molecule. Carbon atoms in both CO and acetylene are sp hybridized which have stronger and shorter bonds than sp^2 carbons in ethylene. The electrons in acetylene are held more tightly and closer to the nucleus than they are in ethylene. It has been reported that alkenes can initiate and be incorporated into the F-T synthesis(5). It is interesting that acetylene forms structures similar to those of ethylene when adsorbed on transition metals(29, 30). Surface science studies on the adsorption of acetylene and H_2 on Pd have shown that it forms a vinylidene species ($CH_2=C=$)(30). A flat-lying acetylene species has been identified as a precursor to ethylene on Pd. Since the negative charge is held relatively closer to the positive nucleus in acetylene, acetylene is more acidic and is more strongly adsorbed on the solid surface than ethylene. Strongly adsorbed acetylene impedes adsorption of ethylene when acetylene-ethylene mixtures are passed over Pd catalysts(31). Acetylene is adsorbed on cobalt or iron before CO when both are present (32). New information, possibly on the manner in which chains are initiated in the F-T synthesis, may be found using alkynes as probes.

It has been shown that dicobalt octacarbonyl, $Co_2(CO)_8$, is formed during the cobalt catalyzed F-T synthesis(33). Indeed, the early cobalt catalyzed F-T synthesis carried out in Germany during WWII had to be occasionally terminated due to blockage of lines by solid cobalt carbonyl formed during the reaction. Pichler(34) suggested that optimum conditions of pressure and temperature for hydrocarbon synthesis are close to the conditions at which formation of carbonyls and hydrocarbonyls can be detected. Wender et al.(35, 36) showed that $Co_2(CO)_8$ and related carbonyls of cobalt react readily with acetylene and acetylenic compounds to give a variety of liquid and solid derivatives; the triply-bonded acetylene compound replaced part of the CO in the carbonyl. Most of the known complexes of formula $Co_2(CO)_6RC_2H$ has been summarized by Dickson and Fraser(37). It is evident that almost all acetylenic compounds react with cobalt octacarbonyl according to equation (1).

$$Co_2(CO)_8 + RC{\equiv}CR' \longrightarrow Co_2(CO)_6(RC_2R') + 2CO \tag{1}$$

Acetylenic compounds also react with iron carbonyls to form complexes of a similar nature (38). After this work was started, we discovered that Russian scientists, searching for ways of producing long-chain alcohols, added acetylene to fused iron catalysts at 180-190°C and the very high pressure of 150 atm(39, 40). They found that addition of small amounts of acetylene favored formation of aliphatic oxygenated compounds. They showed that acetylene is inserted only once into each molecule of the alcohols obtained. The addition of acetylene contributed to an increase in rate of the primary C_1 entity but the remainder of the carbon chain involved only addition from synthesis gas.

A review of co-fed ethylene studies suggests that the unsaturated C2 species can play a role in the F-T synthesis as a chain initiator, especially on Co catalysts(4, 5, 10, 41). There is, however, no report on incorporation of acetylenes into the F-T synthesis using precipitated iron and cobalt catalysts. This dissertation focuses on the study of product distribution when acetylenes are added as probes to the F-T synthesis, with consideration of the possible differences in the pathways that occur with cobalt and iron catalysts.

Chapter 2.0 presents an introduction to the background of the F-T synthesis. The focus is on the reaction intermediates including investigations with probe molecules and previously proposed pathways from literature reviews. A comparison of Fe and Co catalysts is presented as well.

In this study, we have used three types of acetylenic molecules as probes: (1) straight-chain alkynes with different chain lengths and different triple bond positions. This work is described in Chapter 3.0. The chain length dependence of alkyne incorporation was studied by using 1-hexyne, 1-heptyne and 1-decyne as probes. Internal alkynes, such as 2-hexyne and 3-hexyne, produced branched hydrocarbons in addition to straight chain products. Information on alkyne-initiated chain growth was explored by addition of thiophene and pyridine; the former is known as a poison for the F-T synthesis while the latter has been claimed to inhibit the hydroformylation reactions. Comparisons of the incorporation of 1-hexyne and the corresponding olefin, 1-hexene are also included. (2) Phenyl-substituted acetylenes in which the phenyl group serves as a marker were used as probes to ascertain the origin of the initiating species. The effects of several phenyl-substituted acetylenes on the Co-catalyzed F-T are presented in Chapter 4.0. Products containing the phenyl group can be separated easily by GC and identified by GC-MS. (3) Acetylene, as the first member of the acetylene series and most active alkyne, is of a great interest. It has been reported that ethylene initiates and is incorporated into the carbon chain 10-40 times more easily than higher olefins but essentially all olefins can initiate the chain and can incorporate(5). Chapter 5.0 deals with the effect of acetylene addition. Different product distributions and selectivity to reactions of acetylene on Co and Fe catalysts are addressed. Influences of operating conditions on acetylene incorporation for these two catalysts are presented as well.

In the last two chapters (Chapter 6.0, 7.0 and 8.0), results of our research are discussed, and conclusions and future work are proposed.

2.0 BACKGROUND

The Fischer-Tropsch synthesis is a process in which carbon monoxide (CO) and hydrogen (H_2) are catalytically converted into hydrocarbons (paraffins and olefins), and small amounts of oxygenated species. A large number of reactions occur during the F-T reaction, the major ones are given below: (42, 43)

Paraffins: $nCO + (2n+1)H_2 \rightarrow C_nH_{2n+2} + nH_2O$

Olefins: $nCO + 2nH_2 \rightarrow C_nH_{2n} + nH_2O$

Alcohols: $nCO + 2nH_2 \rightarrow C_nH_{2n+1}OH + (n-1)H_2O$

Water Gas Shift: $CO + H_2O \rightarrow CO_2 + H_2$

Boudouard Reaction: $2CO \rightarrow C + CO_2$

2.1 F-T CATALYSTS

The F-T synthesis is commonly catalyzed by group VIII metals such as Fe, Co, Ru and Ni. The high price and limited world resources of Ru exclude its industrial application. Nickel is not used as a F-T catalyst principally because it gives too high a yield of methane(44). Only Fe and Co catalysts are currently utilized in industrial practice. Iron catalysts have been used by SASOL (South Africa Synthetic Oil Limited) since 1955 to yield a variety of fuels and chemicals from synthesis gas produced by the gasification of coal (45). Currently, cobalt catalysts are used commercially in the Shell F-T plant in Malaysia and Syntroleum in Oklahoma. Planned commercial plants by Sasol/Qatar, SasolChevron, and ConocoPhillips are all based on natural gas with cobalt catalysts (46).

Iron catalysts, usually used with addition of an alkali, preferably potassium oxide, are good water-gas shift (wgs) catalysts. Coal has a low hydrogen to carbon ratio, and gasification of coal results in high ratios of CO to H_2. Since iron is a wgs catalyst, it would seem to be the catalyst of choice when coal is the source of syngas. Fe is undesirable for the F-T synthesis with hydrogen-rich syngas as produced from natural gas(1). Iron catalysts usually prepared by precipitation or fusion tend to be unstable and gradually lose activity; they cannot be regenerated and must be replaced periodically(47). Fused Fe catalysts are the most suitable catalysts for the high temperature F-T process in circulating fluidized bed or fixed fluidized bed reactors to produce low molecular weight olefinic hydrocarbons. Many additives such as chemical promoters (usually K_2O) and structural promoters such as Al_2O_3 or MgO, have been added to Fe catalysts to improve their mechanical and catalytic properties(1, 48). After reduction with hydrogen, fused magnetite has low catalyst porosity with small pore diameters. Precipitated iron catalysts are used for wax production at low reaction temperatures. Typically, precipitated iron catalysts are obtained through precipitation from nitrate solutions. Alkali is an important promoter to attain high activity and stability; it modifies the adsorption of H_2 and CO, and increases selectivity to desired products(49, 50). Copper promotes the reduction processes and decreases the temperature required for the activation of iron oxide (51). SiO_2 or Al_2O_3 is added for structural promotion and possibly some manganese is applied for selectivity control (e.g. high olefinic products)(47).

Although iron catalysts are about 200 times cheaper than cobalt catalyst and have been studied more extensively, their structural instability restricts the attainable degree of conversion and leads to gas recycle operation. Due to its high wgs activity, it is undesirable for F-T plants based on natural gas feedstocks. Very cheap natural gas is found in various regions of the world outside of the U.S. Cobalt has low wgs activity, an advantage for such syngas. At present, essentially all new F-T plants, which are based on stranded natural gas to produce syngas at close to or higher than the F-T stoichiometric H_2/CO ratio will use cobalt catalysts. Co produces mainly straight-chain hydrocarbons and higher ratios of paraffins to olefins and fewer oxygenated products such as alcohols and aldehydes than Fe catalysts(52). Due to its high activity and high price, Co is dispersed on high area stable supports such as alumina, silica, and titania to maximize the available surface area of the metal(53-57). Incorporation with strong supports enhances the strength of Co catalysts and results in better attrition resistance compared to Fe catalysts. Co catalysts are usually promoted with a small amount of a noble metal, e.g. Pt, Ru, Re which are reported to improve the reduction of cobalt by increasing hydrogen adsorption and improving regeneration of the deactivated catalyst(58, 59). However, it was found that the support has no effect on the turnover frequency of Co sites.

Both Fe and Co catalysts yield products consistent with Anderson-Schulz-Flory (ASF) polymerization kinetics; however, there are some distinctive differences between these two catalysts in the F-T synthesis:

(1) States of the metal are very different. The cobalt catalyst contains mainly the metallic phase(60), while Fe catalysts, whether introduced as iron metal or iron oxides, exist as a mixture of α-Fe, magnetite (Fe_3O_4) and iron carbide under reaction conditions. Although magnetite and

iron carbide are formed rapidly and coexist in the F-T process, Fe_3O_4 is relatively inactive and iron carbide has been claimed to be responsible for F-T activity(61,62,63).

(2) In the presence of alkali, iron is very active in the wgs, which converts CO and water to H_2 and CO_2, so that Fe catalysts are suitable for coal-based syngas with high CO/H_2 ratios. In comparison to Fe catalysts, Co catalysts show little wgs activity, and are used when syngas is produced from methane.

(3) Due to its high price and activity, Co is dispersed on high area stable supports such as alumina, silica, and titania (53-57) and promoted with a noble metal, like Ru, Re, Pt. Fe loading is high (> 85 wt%) in Fe catalyst, with SiO_2 and Al_2O_3 used as structural promoters. K is essential for activity and chain growth for Fe catalysts.

(4) Co catalysts are only used for low temperature F-T processes, since them tend to produce excess methane at high temperature. Fe catalysts prepared by the precipitation method are used in wax production at low temperatures, while fused Fe catalysts are used in high temperature F-T processes.

(5) Cobalt catalysts produce mainly saturated hydrocarbons and a negligible amount of oxygenates, while iron catalysts generally yield more olefins and oxygenated products. Currently Co catalysts are the preferred catalysts for the synthesis of high molecular weight products from natural gas based syngas. Table 2.1 summarizes different properties of Fe and Co catalysts:

Table 2.1 Comparison of properties of Co and Fe catalysts

F-T catalyst	Co	Fe	References
Price (ratio)	200	1	(64)
Activity	Higher conversion rate	Lower	(42)
Active phase	Cobalt metal	Iron carbide	(60-63)
Source of carbon	Natural Gas; higher H_2/CO ratio	Coal; lower H_2/CO ratio	(65, 66)
Catalyst life	Longer	Shorter	(66, 67)
Promoters	Ru, Rh, Pt	K	(49, 50, 58, 59, 68)
Supports	Cobalt content: < 20 wt%; alumina, silica and titania as supports	Iron content: >85 wt%; alumina, silica as structural promoters	(55, 57, 69-72)
Products	Tends to produce more CH_4 at high temperature; more olefins and branched hydrocarbons; lower oxygenates	Less sensitive to reaction temperature; more linear paraffins; higher oxygenates	(73)
Oxygen sink	H_2O	Active water gas shift catalyst; part of H_2O is converted to CO_2	(74)

2.2 F-T REACTION MECHANISMS

The mechanism of the F-T synthesis has been the subject of much speculation and experiment since the reaction was first discovered by Fischer and Tropsch in 1923. There is a general acceptance that a polymerization-like process effectively describes the product distribution of the F-T synthesis. Plots of log(Wn/n) against the carbon number n yield straight lines over a fairly large range of products. This gives the so-called ASF product distribution:

$$\mathbf{W_n=n(1-\alpha)^2\,\alpha^{(n-1)}}$$

Where W_n is the mass fraction of the C-atoms with a chain containing n C-atoms. The chain growth probability, α, is the ratio of the chain propagation rate constant to the chain propagation plus the termination rate constants. The ASF equation predicts selectivities towards methane, gasoline, diesel and waxes that will be produced in the F-T reactions. Methane can be synthesized in 100% selectivity; all other products have well-defined maxima in allowed selectivities as shown in Figure 2.1(43). The highest selectivities attainable by the F-T synthesis are, in wt%, methane 100; ethylene 30; gasoline (C_5-C_{11}) 48; diesel fuel (C_{12}-C_{18}) 25.

Based on the nature of intermediates, several schemes of the F-T reactions have received dominant attention since the discovery of the process. The first one, proposed by Fischer and Tropsch in 1926, suggested that chain growth of hydrocarbon proceeds through a carbide intermediate(75). It was later modified by Brady and Pettit to methylene addition to a growing chain(24, 25). Elvins and Nash(76) and Anderson et al.(77) suggested oxygenate intermediates for the

F-T products as another picture of chain growth, while Pichler(78, 79) believed chain growth was achieved via insertion of undissociatively adsorbed CO.

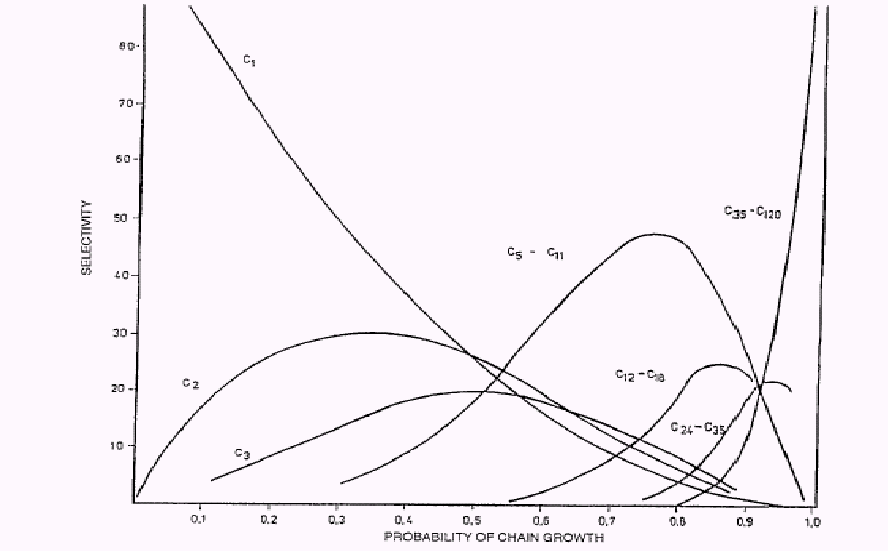


Figure 2.1 Plots of calculated selectivities (percent carbon atom basis) of carbon number product cuts as a function of the probability of chain growth(43)

2.2.1 Schemes with hydrocarbon intermediates

The earliest pathway proposed by Fischer and later refined by Rideal(80) is based on surface carbides. In 1926, Fischer and Tropsch(75) proposed that the F-T synthesis proceeds through formation of metallic carbides; methylene (CH_2) may be formed primarily from H_2 and carbide carbon, which is in turn polymerized to higher hydrocarbons. Craxford and Rideal(80) gave a more detailed description, suggesting that the F-T synthesis involves the following steps: (1) chemisorption of CO; (2) formation of carbide by reaction of chemisorbed CO and H_2; (3)

formation of CH_2 groups by carbide and H_2. Selectivity to CH_4 and higher hydrocarbons is determined by the amount of chemisorbed H_2; association of CH_2 to give higher molecular weight compounds; (4) the higher molecular weight hydrocarbons cracking to smaller molecules; (5) desorption of the molecules to produce olefins and paraffins.

Formation of metal carbides has been reported extensively on Fe to constitute the active sites for F-T reactions(61, 65, 81). Co catalysts usually exist as the metallic phase during the F-T synthesis, small sizes and low concentrations of cobalt carbide particles have also been detected; they are unstable and easily decomposed to metallic cobalt and polymeric carbon.

Different methods have been exploited to test the carbide theory. Biloen et al(83) have presented data indicating that chain growth proceeds via CHx entities. ^{13}C atoms, predeposited on a F-T catalyst, become incorporated in the product hydrocarbons during reaction of ^{12}CO and hydrogen in a manner which is consistent with formation of metal carbides. The possibility that a methylene group can be inserted into a metal-carbon bond has also been demonstrated (84, 85). The carbide theory has been criticized by Zelinskii and Eidus(86) who tested the role of surface carbide by passing CO, N_2, H_2 in rapid succession separately over a Co-ThO_2-kieselguhr catalyst. If the carbide is an intermediate, carbide on the surface, treated by CO, would react with H_2 to produce liquid hydrocarbons, which were not observed. They came to the following conclusions: CO poisons the Co catalyst; the carbide formed when CO reacts with this catalyst is neither an intermediate nor the catalyst for gasoline formation with cobalt. The same conclusions were also drawn by researchers at the Bureau of Mines(87). Kummer et al.(21) used the newly available radioactive carbon isotope, ^{14}C, as a probe to determine whether the formation of hydrocarbons involved carbides as intermediates over Fe catalysts. They concluded that bulk phase carbide doesn't participate in the F-T synthesis, while surface carbide only accounts for about 10% of the hydrocarbons formed. Some other process produced the greater part of the product.

Brady and Pettit (24, 25) reacted diazomethane, CH_2N_2, with H_2 over Fe, Co and Ru at 210°C and atmospheric pressure (details will be discussed in section 2.3.3). Since similarities in the hydrocarbon products of the F-T reactions and CH_2N_2 hydrogenation have been observed, Brady and Pettit suggested a common pathway followed by these two reactions. The adsorbed methylene species could be produced by reduction of metal-carbide formed from dissociative chemisorbed CO, as suggested by the Fischer and Tropsch carbide mechanism. An alkyl scheme was proposed based on the carbide mechanism (Figure 2.2); polymerization is initiated by metal-hydride bonds and chain growth occurs via insertion of a surface CH_2 species into a metal-alkyl bond to generate the next higher hydrocarbons.

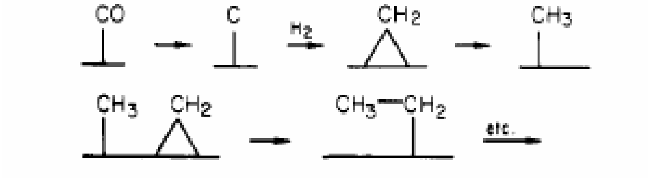


Figure 2.2 The alkyl polymerization: addition of methylene to alkyl chains (25)

The alkyl scheme has some difficulties in explaining a few anomalies, such as the relatively small amount of C_2 hydrocarbons, the presence of small amounts of branched chain hydrocarbons, and the β-elimination of metal hydrides under a positive pressure of hydrogen.

2.2.2 Schemes with oxygenated intermediates

The carbide theory did not explain the formation of oxygenated compounds. Elvins and Nash(76) reported the presence of oxygen-containing compounds in addition to hydrocarbon products; they suggested an oxygenated intermediate in the formation of hydrocarbons. In 1951, Storch et al.(77) proposed that oxygenated complexes containing OH groups are the intermediates and chain growth proceeds via a condensation reaction of two hydroxycarbene species with the elimination of water. Their theory was supported by extensive studies with various alcohols as probes conducted by Emmett et al(88); they added radioactive alcohols, such as methanol, ethanol, n-propanol or isobutyl, to syngas and passed them over an iron catalyst. The results showed that primary alcohols adsorbed on iron catalysts can act as initiators in building up higher hydrocarbons; isopropyl alcohol was incorporated to a much smaller extent than primary alcohols. The results were interpreted as indicating that complexes resembling adsorbed alcohols were formed from carbon monoxide and hydrogen during synthesis and acted as intermediates in chain propagation over iron catalysts. In Figure 2.3 the attachment of the complex to the surface is assumed to be through a carbon-metal bond(20).

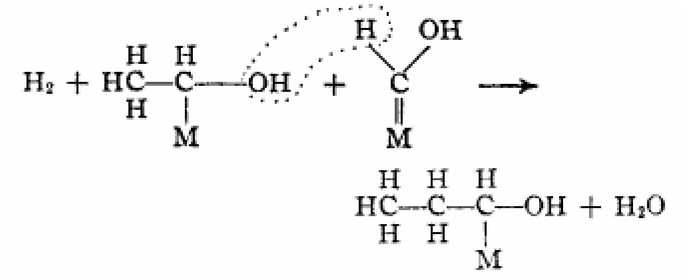


Figure 2.3 Hydroxycarbene scheme (25)

Attachment to the surface through both carbon-metal and oxygen-metal bond has been suggested(89). Later on, the idea of alcohols as intermediates received indirect evidence via oxygenated species adsorbed on metal surfaces. Blyholder and Neff(90) examined the infrared spectroscopy of a variety of CxHyO compounds, such as alcohols, aldehydes, and acetone, adsorbed on Fe. Their study indicated that the stable structure produced by the adsorption of a number of CxHyO compounds on Fe occurs as an alkoxide structure (R-CH_2-O-Fe).

Pichler modified Fischer and Tropsch's interpretation of the mechanism of hydrocarbon formation on iron catalysts. He proposed that higher iron carbides do not themselves act as synthesis intermediates, but that they are important for the structure of the catalyst and that in their presence other products, such as surface compounds, may be formed. Pichler and Schulz(79) proposed that chain propagation proceeds via carbon monoxide insertion into metal-H (initiation) and metal-alkyl (chain growth) bonds as shown in Figure 2.4 (91), analogous to the well known CO insertion into such bonds in homogeneous catalysis, with subsequent reduction of the acy1 groups. This mechanism received both support (92-95) and criticism(23).

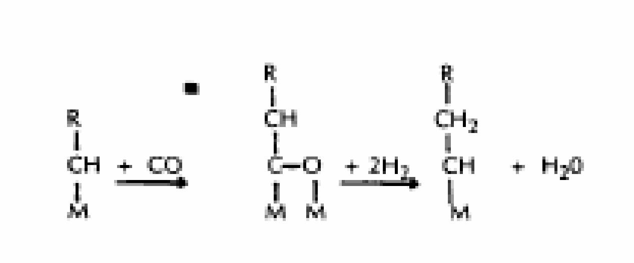


Figure 2.4 CO insertion scheme (91)

2.3 USE OF PROBE MOLECULES IN THE STUDY OF F-T MECHANISM

In section 2.2, we discussed proposed major pathways suggested during the past 80 years of F-T studies. The complexity of coexisting different F-T schemes is partially due to the difficulty in identification of reaction intermediates. Various methods have been exploited to detect surface intermediates, such as using surface analytical techniques to detect surface species during CO hydrogenation(96), mimicking C-C bond formation in F-T reactions by homologation of C1 species or olefins(97), modeling steps in the F-T process derived from organometallic chemistry(98), and adding probe molecules or labeled CO into the syngas(4). Utilization of a small amount of probe molecule which would react with one or more of the intermediates to produce distinctive products has played an important role in developing an understanding of the mechanism of the F-T synthesis. Maitlis(4) pointed out that "The elucidation of mechanistic information for a heterogeneously catalyzed reaction by adding a labeled probe molecule to the reactants and then analyzing for the labels in the products is a well-established and widely used technique. It is based on the principle that if the probe resembles an active species in the reaction under investigation, incorporation of the probe will occur. It has the advantage in that it does not depend on identifying very small amounts of labile and highly reactive species on surfaces that are themselves changing and difficult to characterize.” Different probe molecules, ranging from olefins, to alcohols, and to C1 compounds have been added to F-T reactions. Since we used acetylenic compounds as probe molecules in F-T studies, a review of the studies using probe molecules will be presented here to serve as background for discussion of our research.

2.3.1 F-T studies using alcohols as probes

The earliest investigation of the F-T mechanism using ^{14}C labeled alcohols as probes was carried out by Emmett and coworkers(20, 21, 99). Small amounts of ethanol, 1-propanol, and 1-butanol were added to syngas at about 235°C and one atmosphere pressure over Fe catalysts. It was found that F-T hydrocarbon products had an approximately constant radioactivity per mole, indicating that alcohols act as chain initiators. Experiments with labeled ethanol were also carried out on cobalt catalysts (88). Three important differences were observed between these two catalysts: (1) the activity of methane was high over Co catalysts, suggesting appreciable cracking of added ethanol, while it was negligibly small over Fe catalysts. (2) About 35% of the products from Fe catalysts originated from the ethanol and chain initiation occurred preferentially (90% of the time) at the carbon atom to which the OH group was attached. In contrast to Fe catalysts, incorporation of ethanol was as low as 2% for Co catalysts. (3) C2 products had the highest radioactivity for Co catalysts and much lower radioactivity for Fe catalysts, indicating intermediates are not the same over Co and Fe catalysts. The ethanol dehydrated to ethylene which built-in hydrocarbons over Co catalysts, while ethanol may be an intermediate product in building higher hydrocarbons from CO and H_2 over Fe catalysts.

Davis and his co-workers(100), with analysis by gas chromatography now available, carried out reactions similar to those Emmett had carried out earlier. Tau et al.(18) added [1-^{14}C] ethanol to F-T synthesis with a United Catalyst Inc. C-73 doubly promoted fused Fe catalyst at 260°C and 7 atm pressure. They found that the activity per mole of the products was constant with increasing carbon number, in agreement with the results of Emmett et al. Both groups came to the same conclusion that ethanol initiated chain growth but did not serve as a propagator. Later on they compared labeled 1-propanol (C-C-^{14}C-OH) and 2-propanol (C-^{14}C-OH-C) in the F-T synthesis under the same reaction conditions. About 10-20% of added 1-propanol was incorporated into straight chain products, while only 1-3% of 2-propanol was incorporated into mainly branched products. As with ethanol addition, both normal and iso-C3 alcohols initiated the F-T reactions without participation in chain propagation. Since alkenes have been proposed as chain initiators, it is possibly that alkenes were intermediates formed via alcohol dehydration. However, Davis et al.(100) rejected this assumption, as dehydration of alcohols to alkenes with the same carbon number was surprisingly low. They concluded that an alcohol is not the primary source of alkene products in the F-T synthesis with iron catalysts. To provide further evidence, they studied conversion of alcohols over iron oxide (Fe_2O_3) and iron carbide catalysts(17). Both catalysts dehydrogenated normal alcohols to aldehydes, while dehydration of alcohols to produce olefins made a minor contribution to the F-T synthesis with an iron catalyst. Since alkenes are primary products for Fe catalyzed F-T reactions, and dehydration of alcohol is not appreciable in the F-T synthesis, it is possible that olefins, formed through two steps with incorporation of alcohols, serve as chain initiators. Aldehydes are formed by dehydrogenation of alcohols as shown in reaction (2). Then they could convert to terminal alkenes with one fewer carbon atoms (reaction (3)). However, this pathway is not possible with ethanol since aldehyde will convert to methane and CO.

$$RCH_2{-}CH_2{-}CH_2{-}OH \longrightarrow RCH_2{-}CH_2{-}CH{=}O + H_2 \qquad (2)$$

$$RCH_2{-}CH_2{-}CH{=}O \longrightarrow RCH{=}CH_2 + CO + H_2 \qquad (3)$$

Comparison of published data indicate that alcohols are indeed intermediates leading to hydrocarbons to some extent for Fe catalysts, but it is still not clear if the F-T reaction produces hydrocarbons in the same pathway followed by alcohol reactions under F-T conditions. However, we can surmise that Fe and Co catalyzed F-T reactions follow different pathways, and oxygenate intermediates are not important with Co catalysts.

2.3.2 F-T studies using alkenes as probes

Addition of olefins in the F-T reaction as probe molecules has been extensively reported. The first use of ethylene as a probe was carried out by Smith et al. in 1930 (101). At first, they passed pure ethylene over a cobalt-copper-manganese oxide catalyst at 206°C; no reaction was observed. Then a mixture of ethylene and H_2 and a mixture of ethylene and CO were passed over the catalyst; the former produced only ethane while the latter gave no reaction. However, when ethylene reacted with CO and H_2, higher hydrocarbons and oxygenates were produced. Results obtained with iron-copper catalyst were different as ethylene did not enter into the F-T products. An oxygenated intermediate was proposed to explain the F-T mechanism for Co catalysts on the basis of the finding that, upon ethylene addition, a considerable amount of oxygenates and of methane, considered a decomposition product of oxygenated compounds, were produced with

Co catalysts. For Fe catalysts, since extremely small amount of oxygenates and methane were produced with ethylene, a different mechanism of the reaction was considered. However, a large amount of oxygenated products are not necessarily an indication of oxygenated intermediates; they may be produced by a hydroformylation reaction, as indicated later by Roelen(33). The increase in methane might be due to cleavage of the ethylene molecule into single carbon units, in agreement with their finding that methane increases with increase in temperature.

Hydrogenation is the most important reaction when olefins react under F-T conditions. Hydrogenolysis of ethylene on Co catalysts has been observed. Gibson(102) passed a mixture of ethylene, H_2 and 5% of radioactive CO over a Co catalyst and found that C1 fragments from ethylene served as monomers for chain growth. A small amount of methane was found with Fe catalysts under normal reaction conditions, but an increase in formation of methane was observed at temperatures as high as 472 °C due to breakage of ethylene to form one carbon units(103).

The literature strongly suggests that ethylene added to the F-T reaction acts as a chain initiator. A study of the effect of adding 1 to 2% of ethylene to the F-T synthesis over a Co catalyst on kieselguhr was conducted by Adesina et al. at 200°C and 1 atm (10). The C3~C5 products increased from 40% to 160%, while there was a 50% increase of C6~C8 when ethylene was added. For $H_2/CO=1$, about 12% of the co-fed ethylene was incorporated into C_{3+} products. An important observation was that the alpha value was not changed upon ethylene addition, which suggests that large-scale propagation by ethylene is unlikely; ethylene serves mainly as a chain initiator. Snel(12) conducted co-feeding ethylene experiments with Fe catalysts and showed that ethylene initiates the F-T without altering the chain-growth probability even when it is present in high concentrations. Propagation by ethylene was found to be unlikely. When present in concentrations of 5 mol% or higher, ethylene substantially suppresses methane formation by scavenging surface hydrogen and surface intermediates.

Schulz et al.(5) investigated the effects of olefins of different chain lengths on Co catalyzed F-T synthesis at 1atm, 190°C and H_2:2CO by addition of 0.1~0.3 vol.% of ^{14}C labeled olefins to the syngas. A marked incorporation of ethylene (29%) and propene (31%) and a considerably lower one of 1-hexadecene (6%) were observed. Hydrogenolysis of ethylene as a side reaction was detected for Co catalysts. Less incorporation of ethylene were observed with Fe catalysts. When 0.2% of ^{14}C labeled ethylene and 0.3% of 1-^{14}C labeled 1-propene were added separately to a Fe/K catalyzed F-T reaction at 190°C and 1 atm, 9% incorporation of ethylene and 1% incorporation of 1-propene were obtained(104). In experiments with a fused Fe catalyst at 248°C with addition of C2, C4, C6, C10 and C20 terminal olefins, only a slight degree of incorporation of these olefins into F-T products was observed (4). The major reactions of the added 1-olefins were hydrogenation and isomerization. It was concluded that addition of olefins to the reactant stream is not a viable method of altering the molecular-weight distribution over an iron catalyst.

Incorporation of ethylene into F-T products over Fe catalysts is low, as suggested in most of the literature. A much higher extent of incorporation has been attained by Snel et al.(12) on iron-calcium catalysts prepared by partial combustion of an iron citrate complex. The synthesis was carried out in a fixed-bed reactor at 20atm, 270°C, with reactant gas H_2:2CO. Up to 66% of ethylene was incorporated to higher hydrocarbons. The differences between this study and others may be due to the method of catalyst preparation and the low H_2 to CO ratio. Boelee et al.(105) provided an explanation of different results reported in the literature about ethylene incorporation. They carried out a large number of co-feeding ethylene experiments(105) under various reaction conditions over a fused Fe catalyst. The results showed that the effects of ethylene are determined mainly by two factors: one is the C_2H_4/CO ratio representing competitive adsorption between C_2H_4 and CO, and the other is CO conversion which reflects the activity of the catalyst under reaction conditions.

In addition to Co and Fe catalysts, alkenes were also added to F-T reactions over Ru catalysts. Jordan and Bell examined the reactions of ethylene with ^{13}CO and H_2 on a 4.3% Ru/SiO_2 catalyst. The results showed that ethylene has a strong influence on CO hydrogenation. Conversion of CO hydrogenation was suppressed at high C_2H_4/CO ratio, while the hydroformylation of C_2H_4 to form propanal and 1-propanol was increased. C3+ hydrocarbons were increased with increasing C_2H_4/CO ratios, indicating that C_2H_4 is more efficient for chain initiation than is CO.

Under F-T conditions, hydrogenation is a predominant reaction of co-fed olefins. It has been shown that olefins are readily incorporated into higher products when co-fed with Co catalysts; the incorporation of ethylene varies from 10~30% depending on the operating conditions. Hydrogenolysis and isomerization have been observed. Different effects of ethylene on F-T over Fe and over Co catalysts are noted by many researchers. Olefins mainly serve as chain initiators. Less incorporation of olefins into F-T products over Fe is generally observed.

2.3.3 F-T studies with C1 and C2 probes

The carbide mechanism assumes that hydrocarbons are formed via the dissociation of CO followed by stepwise insertion of monomeric units. To determine which monomers lead to polymerization, several C_1 probes such as diazomethane (CH_2N_2), chlorinated methane (CH_xCl_{4-x}), methyl iodide (CH_3I), and nitromethane (CH_3NO_3) have been used. To probe the possible role of C_2 species in chain initiation, C_2 compounds such as nitroethane ($CH_3CH_2NO_3$) and vinyl bromide ($H_2C=CHBr$) have been added as probes.

Evidence for insertion of methylene groups into hydrocarbon chains was provided by Brady and Petit(24, 25). Brady and Pettit examined the products of reaction of diazomethane (CH_2N_2) with and without H_2 over various transition metals, such as Fe, Co, and Ru. When CH_2N_2 was passed alone over these catalysts, only ethylene and nitrogen was produced. When CH_2N_2 was mixed with H_2, a mixture of hydrocarbons ranging form 1 to 18 carbons and higher, depending on conditions was produced. When CH_2N_2 was added to the CO and H_2 feed stream, hydrocarbons with the same type of molecular weight distribution (ASF distribution) were formed, but with a higher alpha value than that of $CO+H_2$ alone, under the same conditions. Based on similarities between the products from CO and H_2 and those from $CH_2N_{2,}$ CO and $H_{2,}$ they proposed an alkyl mechanism.

Van Barneveld and Ponec(106) studied the reactions of CH_xCl_{4-x} with hydrogen or with a CO/H_2 mixture. They showed that CH_xCl_{4-x} could react with H_2 to produce higher hydrocarbons both in the absence and presence of CO over Ni, Co and Fe, indicating that oxygen-free intermediates lead to the formation of hydrocarbon chains. $CHCl_3$ had a greater chance to participate in F-T reactions than did CH_2Cl_2, while CH_3Cl did not polymerize. Some interesting points were made by these researchers: one is that lack of F-T activity of Pd and Cu in the reaction of CH_xCl_{4-x} indicates that the inability of these catalysts in F-T synthesis is not just due to their inability to dissociate CO; another is that CH_xCl_{4-x} reacts with H_2 on CO-pretreated Fe catalysts while CO did not, indicating that Fe carbides may serve mainly as active sites rather than reactive intermediates.

Cavalcanti et al.(107) studied the effects of the addition of small amounts of nitromethane (CH_3NO_2) to syngas during CO hydrogenation. A substantial incorporation of carbon originating from the added nitromethane into hydrocarbons was observed. Addition of CH_3NO_2 caused significant increase in the yields of C3 to C6 hydrocarbon products, while there was only a minor increase in the C2 fraction. This suggests that the rate of C2 formation is different from that of C3+ hydrocarbons. "Perhaps C2 formation is related to the chain initiation rate and C3 to C6 formation to the rate of chain propagation". They also used nitroethane ($C_2H_5NO_2$) as a probe to investigate the special role played by C2 surface species during CO hydrogenation(108). There was no significant change in alpha value, indicating that chain initiation and chain growth were increased by a similar amount. Increases in production of C2+ hydrocarbons and a decrease in methane formation have been observed. The results suggest that $C_2H_5NO_2$ serves as a chain initiator for formation of higher hydrocarbons. CHx generated by hydrogenolysis of $C_2H_5NO_2$ enter the hydrocarbon formation pathway as C1 monomers.

Vinyl bromide (C_2H_3Br) and ethyl bromide (C_2H_5Br) were added to F-T reactions over Ru/SiO_2 to study the role of C2 species in hydrocarbon formation(41). C2 units generated from vinyl bromide are readily incorporated into the F-T products while addition of ethyl bromide resulted only in an increase in the yield of the C2 fraction. This provides evidence for importance of unsaturated C2 units in chain initiation.

Results with these small molecules suggest that the species derived from decomposition of these C1 and C2 molecules can be incorporated into the F-T synthesis. C1 monomers serve as building units to lengthen the carbon chains; C2 unsaturated species play an important role in chain initiation.

2.4 F-T vs. ETHYLENE POLYMERIZATION

With the availability of surface science instruments, it was found that dissociative adsorption of CO occurs on the surface of many transition metals. The tendency for dissociation of CO decreases from left to right of the periodic table. The division between transition metals which dissociate CO and those which do not is shown in

Figure 2.5. Those metals to the left of the line dissociate CO and metals to the right of the line do not. The activation energy for dissociation increases from left to right across a row. For instance, at room temperature, CO adsorption is dissociative on Fe, while a higher temperature is necessary for CO dissociation on Co. It is interesting to notice that transition metals from groups IVB to VIB of the period table are important components in Ziegler-Natta catalysts (letters in bold in

Figure 2.5) (109).

Both the F-T synthesis catalyzed by Fe and Co and ethylene polymerization catalyzed by Ziegler-Natta catalysts follow stepwise chain growth mechanism (Schultz-Flory Distribution) to form high molecular weight hydrocarbons with the same structure. In the F-T reaction, the chain grows by $-CH_2-$ addition; for ethylene polymerization, the chain grows by addition of ethylene (two carbon addition). Infrared spectra of polymethylene and high density polyethylene are essentially the same(110) (Figure 2.6). The band at 7.25 corresponds to methyl side groups. High density polyethylene has eight side methyl groups per 1000 carbon atoms; polymethylene from

F-T gives a lower ratio. Both polymethylene from CO and H_2 and high density polyethylene have a markedly linear structure.

IVB	VB	VIB	VIIB	-------- VIII--------			IB
Ti	**V**	**Cr**	Mn	Fe	Co	Ni	Cu
Zr	**Nb**	**Mo**	Tc	Ru	Rh	Pd	Ag
Hf	Ta	W	Re	Os	Ir	Pt	Au

Figure 2.5 Transition metals in periodic table (109)

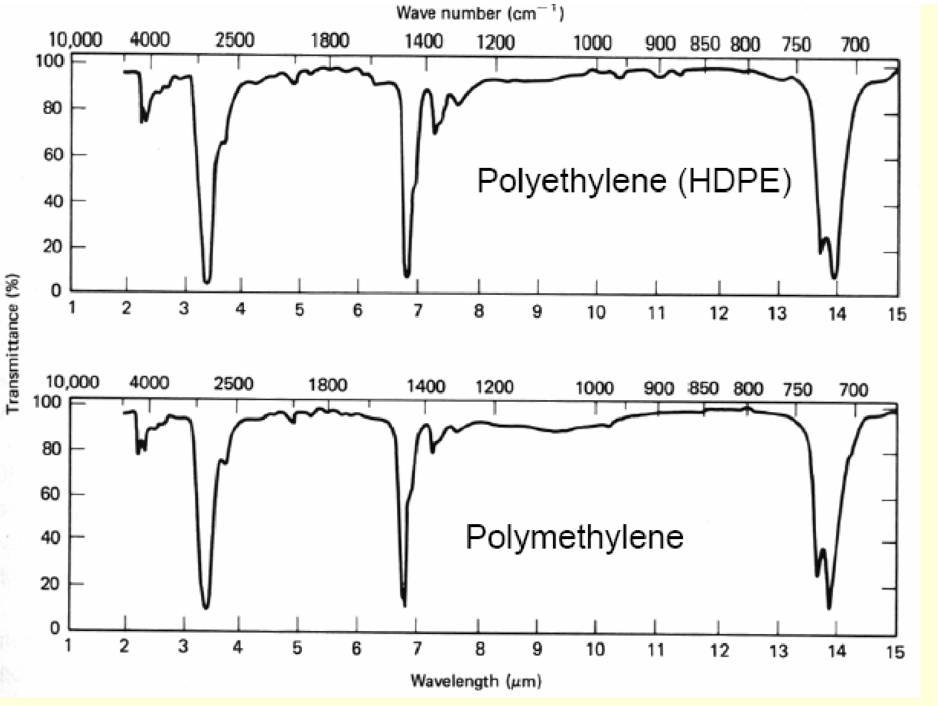


Figure 2.6 Infrared spectra of polymethylene (bottom) and high density polyethylene (top) (110)

Metals in group VB to VIB metals are active in CO dissociation. Titanium carbide is highly stable; a striking parallel between the stability of metal carbides and the ability of the metal to dissociate CO has been reported (109). However, these metals are not used for F-T reactions since they have a too high metal-carbon bond strength and hydrogenation of surface carbon is difficult (111). Hydrogenation of surface carbon to methylene (CH_2) or methylidyne (CH) species is necessary as building units of F-T products. The optimum metal-carbon bond strength for the F-T reactions lies at Ru and Co.

2.5 THE HYDROFORMYLATION REACTION

In the hydroformylation process, an olefin reacts with syngas to form aldehydes or alcohols with one carbon more that the starting olefin.

$$RCH{=}CH_2 + CO + H_2 \xrightarrow{\text{Co or Rh}} RCH_2{-}CH_2{-}CH{=}O + RCH_2{-}CH_2{-}CH_2{-}OH$$

The reaction was discovered by Roelen in 1938 when he was investigating the mechanism of the F-T reaction by adding ethylene to the synthesis gas over a cobalt catalyst(33). The hydroformylation of olefins with syngas is a rapid reaction catalyzed chiefly by soluble complexes of cobalt or rhodium. Pichler (34) compared catalysts which were active for F-T synthesis in order to identify common properties of various catalysts.

- They are active for hydrogenation reactions.

- They are capable of metal carbonyl formation.
- The FT reaction conditions (temperature, pressure) are not far from those where thermodynamics would allow the metals to be converted into metal carbonyls.

From the latter observation it was suggested that surface carbonyls play an essential mechanistic role in the formation of hydrocarbons. He pointed out that the optimum conditions of pressure and temperature for hydrocarbon synthesis on nickel, cobalt, iron and ruthenium are close to the conditions at which formation of carbonyls and hydrocarbonyls can be detected. Pressure “requirements” for the F-T catalytic synthesis and for metal carbonyl formation appear to be closely parallel.

3.0 EFFECT OF STRAIGHT-CHAIN ALKYNES ON F-T SYNTHESIS

3.1 INTRODUCTION

The first alkyne we chose as a probe molecule was 1-hexyne (C_4H_9-C≡CH). We obtained concentrations of about 1 mole% in the gas stream when the synthesis gas was passed through a saturator filled with 1-hexyne at room temperature. Extensive studies have been carried out with 1-hexyne addition, such as effect of reaction temperature, comparison with the corresponding olefin (1-hexene), deactivation of Co catalyst in the presence of 1-hexyne, and effects of selective poisons on hydrocarbon and oxygenated products.

To study the effects of the chain length of added alkynes, we employed a syringe pump to introduce two long-chain linear acetylenic molecules as probes, 1-heptyne and 1-decyne. We will be comparing incorporation of acetylenic molecules with different chain lengths.

1-Hexyne has terminal carbon-carbon triple bonds ($CH_3CH_2CH_2CH_2C{\equiv}CH$). In addition to alkynes with a triple bond at the terminal position, we also added 2-hexyne ($CH_3CH_2CH_2C{\equiv}CCH_3$) which has an acetylenic triple bond at an internal position.

3.2 EXPERIMENTAL

3.2.1 Catalyst preparation

Supported cobalt catalysts were prepared by the incipient-wetness impregnation of cobalt nitrate ($Co(NO_3)_2 \cdot 6H_2O$) on vista B alumina (Catapal B from Sasol) which had been calcined at 500°C for 10 hours before the impregnation. The Co catalysts were dried for 10 hours in an oven with flowing air, followed by calcination at 300°C in air for 5 hours.

The iron catalyst was obtained from Dr. Burt Davis of the University of Kentucky; it had been prepared by a precipitation method.

The properties of cobalt and iron catalysts are listed in Table 3.1.

Table 3.1 Catalyst Properties

Catalyst	Composition (wt%)	Particle size (microns)	Surface area (m^2/g)	Pore volume (cm^2/g)	Pore diameter (Å)
Co	$10Co-90Al_2O_3$	37-88	196	0.37	75
Fe	$100Fe-10.9SiO_2-2.5CuO-6.0K_2O$	powder	121	0.17	53

3.2.2 Experimental Setup

The experiments were carried out with the automatic reaction system. Briefly, the apparatus consists of the gas supply, the fixed-bed reactor, condensers and the on-line GC and off-line GC-MS analysis.

F-T reactions were carried out in a stainless-steel tubular microreactor of 3/8 in (0.95cm) diameter. A thermocouple was inserted into the middle of the catalyst bed. F-T catalysts was loaded using the following procedures:

- Loaded 10.5 grams of quartz sand into the bottom of the reactor.
- Loaded 0.5 grams of a cobalt catalyst or 1gram of an iron catalyst mixed with 1 gram of quartz sand into the reactor.
- 3 Grams of quartz sand was loaded and 1.5 grams of glass wool was inserted tightly on the top of the catalyst acting as a distributor to support the catalyst.

The catalyst was then activated by H_2 at a flow rate of 50 ml/min, with a temperature program ramping from room temperature to 350°C at 1°C/min, holding at 350°C for 10 hours. After reduction, the temperature of the reactor was lowered to the 1 reaction temperature in H_2. The gas stream was then switched to argon. The F-T reaction was started by gradually increasing the CO and H_2 flow rates and, at the same time, decreasing the Ar flow rate in 2 h to avoid a temperature surge due to highly active sites present in the fresh catalyst. Probe molecules in the liquid phase were added into the F-T reaction continuously by a syringe pump.

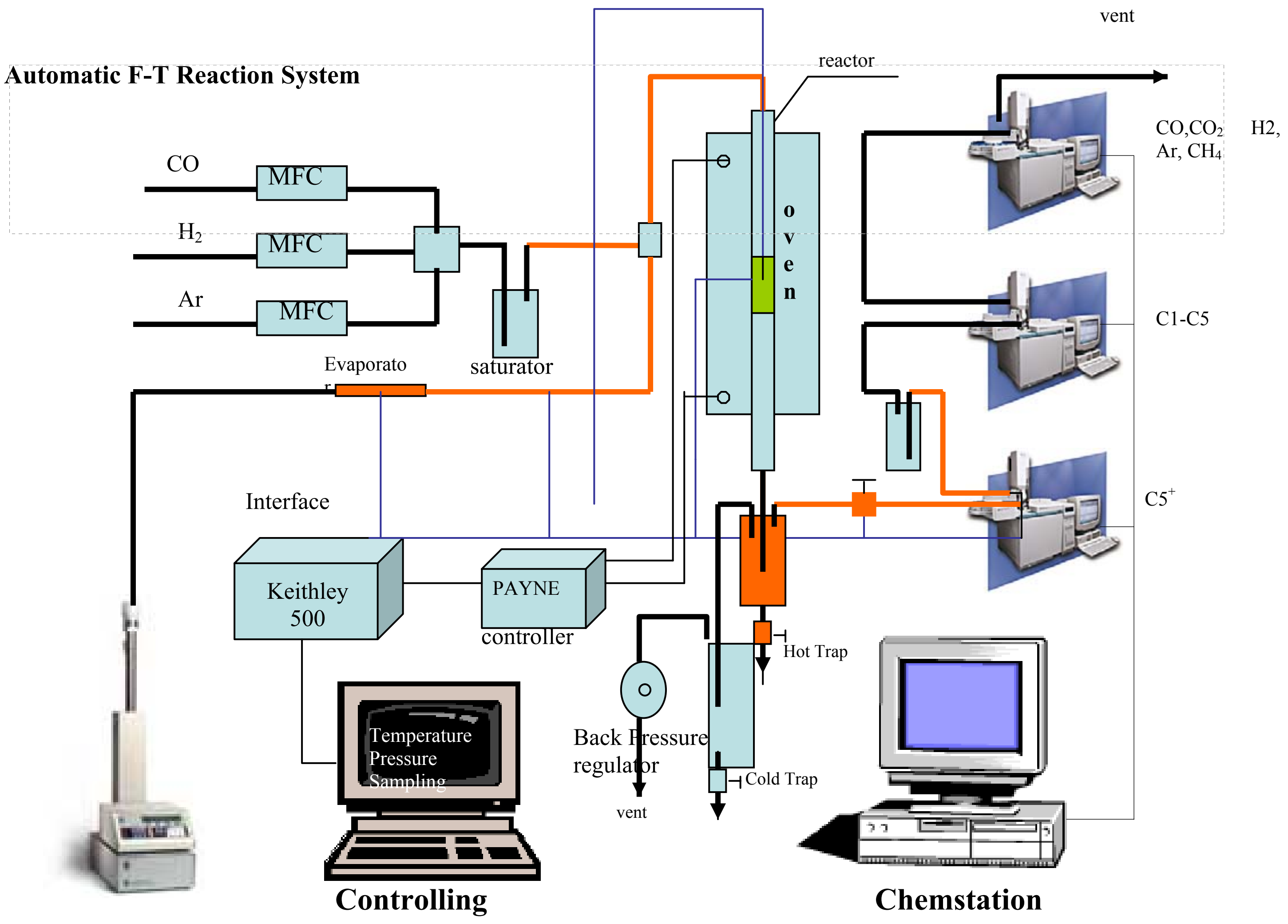


Figure 3.1 Sketch of Fischer-Tropsch reactor system

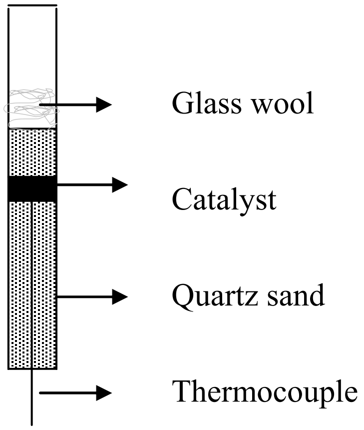


Figure 3.2 Catalyst loading diagram

3.2.3 Addition of alkynes

Probe incorporations were carried out at 100 psi (0.7MPa), a flow rate of 4.2 l/h with $H_2/CO=2$, and temperature ramping from 80°C to 220°C. In most runs with 1-hexyne addition, the synthesis gas was passed through a saturator filled with 1-hexyne at room temperature. In some runs with 1-hexyne addition and all runs with other alkynes addition, probes were added via a syringe pump. The probe molecules were dissolved in pentane (10% by volume) and added to the reactant stream with a total flow rate of 2ml/h.

1-Hexyne (98^{+}%), 2-hexyne (99%) were purchased from GFS Chemicals; 1-Hexene (99%), 2-hexene (99%) (cis- and trans- mixture), 1-heptyne (98%) and 1-decyne (98%) were all purchased from Aldrich Chemicals.

3.2.4 Product sampling and analysis

Liquid product was collected by a cold trap in an ice-water bath. A hot trap was maintained at about 200°C in order to collect higher boiling hydrocarbons. Liquid products collected in the cold trap were analyzed by a HP GC-MS (HP5890 Gas Chromatography and HP5970 Mass Selective Detector).

A stream of effluent gas was split between hot and cold traps, sent through three sampling valves and analyzed by two GCs (HP6890 and HP5890) controlled by an HP Chemstation equipped with three GC columns (HP-5 capillary column, Porapak Q packed column, and Carbonsphere packed column) for online analysis of all products except for heavy waxes.

Prior to addition of probes, several GC analyses were made to obtain base case reaction results. After addition of probes, products were analyzed every three to six hours. Liquid samples were collected at 10h and 21h of TOS (Time on Stream). Liquid products collected in the cold trap were analyzed by HP GC-MS with an HP-5 capillary column to identify components of the F-T products.

The syringe pump and the transfer lines of the reaction system were washed with pentane after each experiment to reduce possible interference by remaining probes and condensations of previous runs. CO conversions were kept at low levels (< 5%) to ease condensation of the heavier hydrocarbons in the transfer lines. As CO conversions didn't change much (in the range of 1 to 5%) in different experiments, we don't report CO conversion for individual runs.

3.3 RESULTS AND DISCUSSION

3.3.1 Incorporation of 1-hexyne addition with cobalt catalysts

3.3.1.1 Product distribution without/with 1-hexyne addition The F-T reactions were carried out with a cobalt catalyst at 220°C, 100psi with a H_2 to CO ratio of 2. A GC chromatogram of F-T liquid products collected 20 hours after addition of 1-hexyne is shown in **Figure 3.3**.

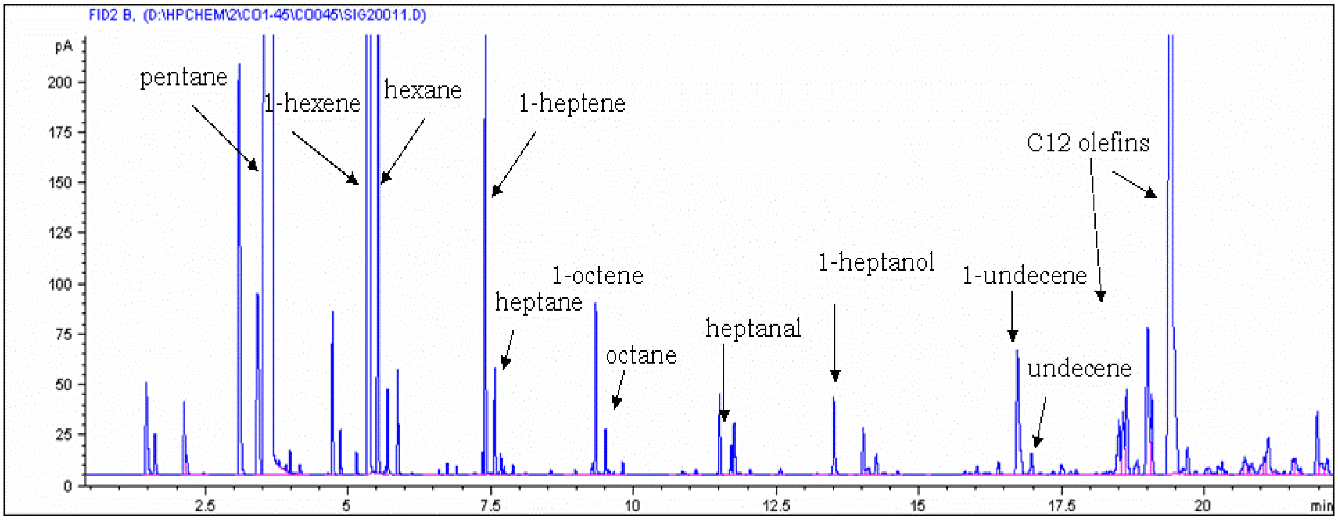


Figure 3.3 GC chromatogram of F-T products over a cobalt catalyst with 1-hexyne at 220°C

(10Co/90Al_2O_3, T=220°C, P=100psi, H_2/CO=2, 1-hexyne (10%) in pentane was added with a flow rate of 2ml/hour)

Mass spectroscopic analysis identified the major peaks as linear products: terminal olefins and normal paraffins, as well as C7 oxygenates. 1-Hexene is the hydrogenation product of 1-hexyne. A significant amount of C7 oxygenates (1.56 mg/h), specifically heptanal and 1-heptanol were also produced with 1-hexyne addition. The absence of oxygenates from the products observed during CO hydrogenation without addition of 1-hexyne indicates that the oxygenates arise as a direct consequence of 1-hexyne addition. Oxygenates are possibly the products of a reaction similar to hydroformylation, since they have only one more carbon added to the acetylenic compound.

Yields of F-T hydrocarbon products obtained by adding a 1-hexyne probe at 220°C are shown in Figure 3.4. Since pentane was used as a solvent, C5 products are not shown. Incorporation of 1-hexyne into F-T products increased C7+ products at 220°C, while formation of C1-C4 hydrocarbons decreased. There were two possible reasons for the decrease of C1-C4 hydrocarbons: possibly more C1 monomers are consumed in building carbon chains of higher hydrocarbons with 1-hexyne addition, or because of deactivation of the cobalt catalyst, which will be discussed in section 3.3.1.4. C7 hydrocarbon products increased by a factor of five when 1-hexyne was added. C9 and C10 products are only slightly higher than the base case. Two thirds of the added 1-hexyne was hydrogenated to hexenes and hexane while 20% was dimerized to C12 products. C11 and C13 hydrocarbons increased greatly with incorporation of 1-hexyne as a result of production of large amounts of C12 hydrocarbons. The increase in yields of C11 hydrocarbons may be caused by breakage of the double bond of 1-dodecene. Unsaturated C12 hydrocarbons initiated chain growth and enhanced yields of C13 products.

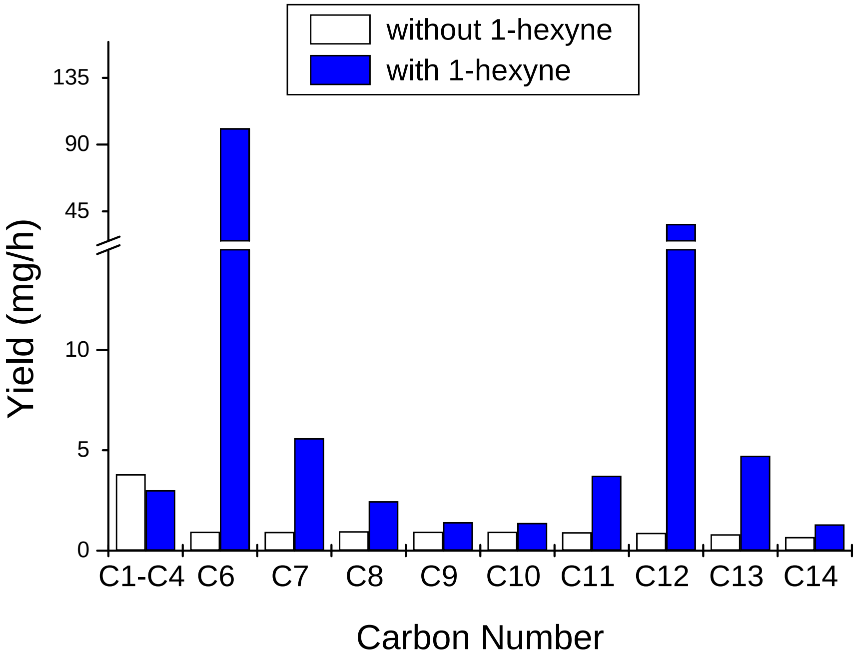


Figure 3.4 Product distributions of the F-T reactions in the absence and presence of 1-hexyne at 220°C

(10Co/90Al$_2$O$_3$, T=220°C, P=100psi, H$_2$/CO=2, 1-hexyne (10%) in pentane was added with a flow rate of 2ml/hour)

3.3.1.2 Effect of temperatures on incorporation of 1-hexyne The F-T synthesis is generally conducted at 220^{o}C with cobalt catalysts. Addition of 1-hexyne greatly enhances the reaction rate of CO hydrogenation so that the synthesis proceeds at lower temperatures in the presence of the probe molecule. We carried out the F-T reactions on a cobalt catalyst at 150^{o}C, 100psi with a H$_2$ to CO ratio of 2. A GC chromatogram of F-T liquid products collected 20 hours after addition of the acetylenic compound is shown in Figure 3.5. Compared to 220°C, a larger amount of heptanal and smaller amount of 1-heptanol were produced upon addition of 1-

hexyne at 150 °C. At the lower temperature, heptanal predominates; at higher temperature, heptanal is hydrogenated to 1-heptanol.

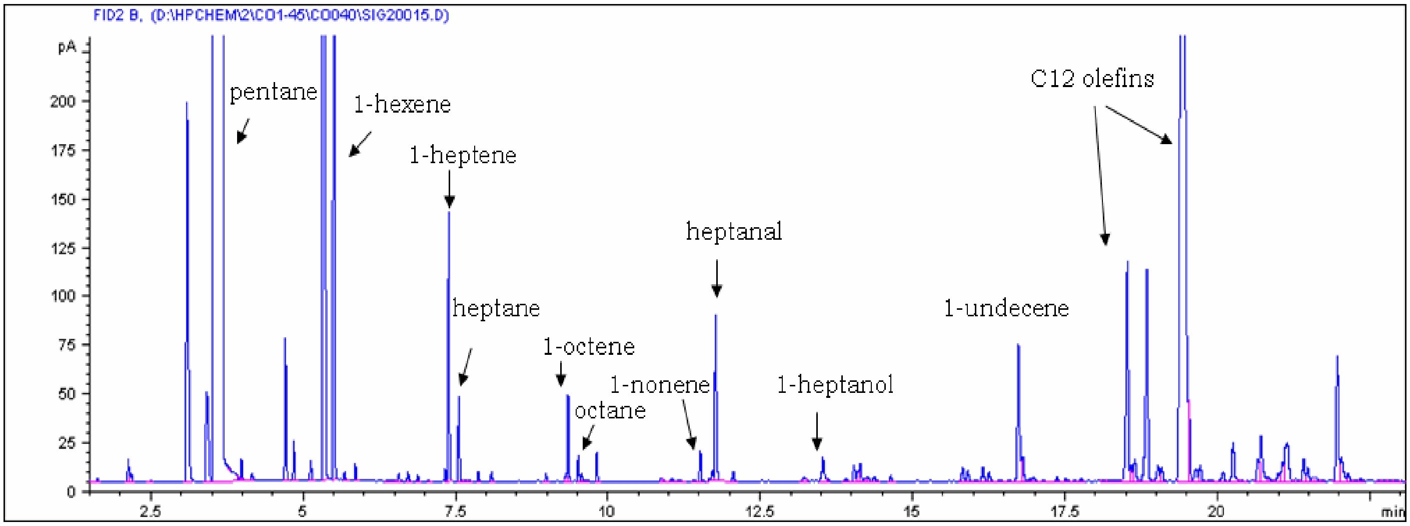


Figure 3.5 GC chromatogram of F-T products over a cobalt catalyst with 1-hexyne at 150°C

($10Co/90Al_2O_3$, T=150°C, P=100psi, $H_2/CO=2$, 1-hexyne (10%) in pentane was added with a flow rate of 2ml/hour)

The product distribution in the presence of 1-hexyne at 150°C is shown in Figure 3.6. Without addition of 1-hexyne, the cobalt catalyst was inactive at 150°C. 1-Hexyne, however, was readily incorporated at 150°C and C7+ products were formed. Conversion of 1-hexyne to hexenes decreased but alkyne polymerization increased when the reaction temperature was changed from 220 to 150°C; 10-12% of the added 1-hexyne was hydrogenated to hexane at 150°C. Yield of C12 hydrocarbons from dimerization of 1-hexyne was high at 150°C. Initiation of chain growth resulted in production of large amounts of C13 hydrocarbons. The significant increase in yields of C11 hydrocarbons was due to breakage of the double bond.

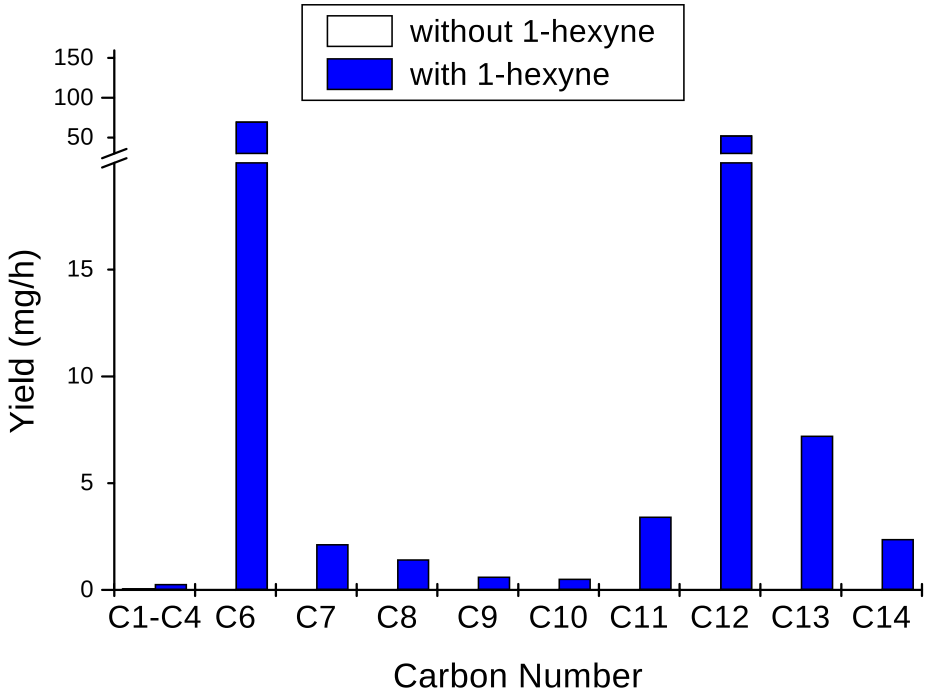


Figure 3.6 Product distributions of the F-T reactions without/with 1-hexyne at 150°C

($10Co/90Al_2O_3$, P=100psi, $H_2/CO=2$, 1-hexyne (10%) in pentane was added with a flow rate of 2ml/hour)

We have observed that the incorporation of 1-hexyne occurred at temperatures as low as 80°C. Yield of C7+ hydrocarbons increased with incorporation of 1-hexyne. To make it simple, only yields of C7 hydrocarbon products in the absence and presence of 1-hexyne at temperature ranges from 80°C to 220°C are shown in Figure 3.7. Since there is no F-T activity without 1-hexyne at 150°C, but a small amount of C7+ hydrocarbons at 80^{o}C, we conclude that all products obtained at this low temperature are initiated by 1-hexyne. C1 species, serving as building units of growing hydrocarbon chains, could be derived from two sources: breakage of the carbon-carbon triple bond of 1-hexyne to produce C5 hydrocarbons and C1 species; CO dissociation to form surface carbide followed by hydrogenation. Results from Russian scientists(39, 40) are more consistent with the latter source. They added double labeled acetylene to fused iron catalysts at 180-190^{o}C and 150 atm and showed that acetylene is inserted only once into each molecule of the alcohols obtained and the remainder of the carbon chain involved only addition of C1 species from synthesis gas. Temperature programmed hydrogenation analysis of F-T reactions with a Co/SiO_2 catalyst suggested that CO dissociation took place at 162-167°C, lower than that corresponding to hydrocarbon formation at 178-188°C (112). We found that the formation rate of methane remained unchanged in the absence or presence of 1-hexyne. It seems that C1 building units are originated from CO dissociation; however, formation of C1 monomer from hydrogenolysis of 1-hexyne can not be ruled out.

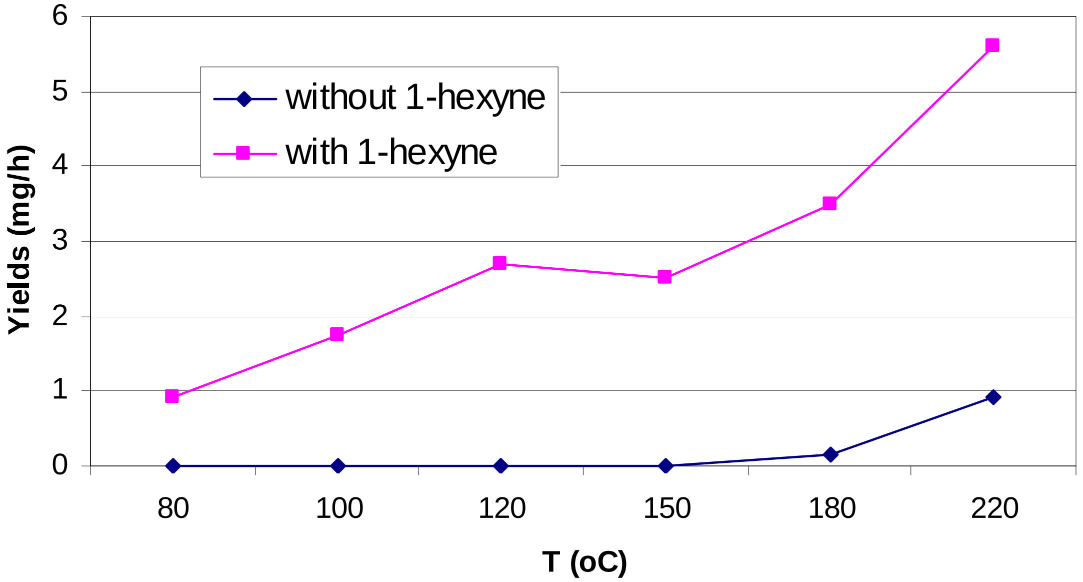


Figure 3.7 Effect of temperature on C7 hydrocarbons without/with 1-hexyne over a cobalt catalyst

(10Co/90Al_2O_3, P=100psi, H_2/CO=2, 1-hexyne (10%) in pentane was added with a flow rate of 2ml/hour)

While temperature has a positive effect on the production of hydrocarbon products, heptanal and 1-heptanol, were more readily formed at lower temperatures (Figure 3.8). Formation of heptanal was reduced, while that of 1-heptanol was enhanced with increase in reaction temperature. 1-Heptanol is the hydrogenation product of heptanal, and temperature has a significant effect on hydrogenation reactivity. Yields of total C7 oxygenates keep decreasing with reaction temperatures, consistent with the fact that hydroformylation is active at low temperature and high pressure(92).

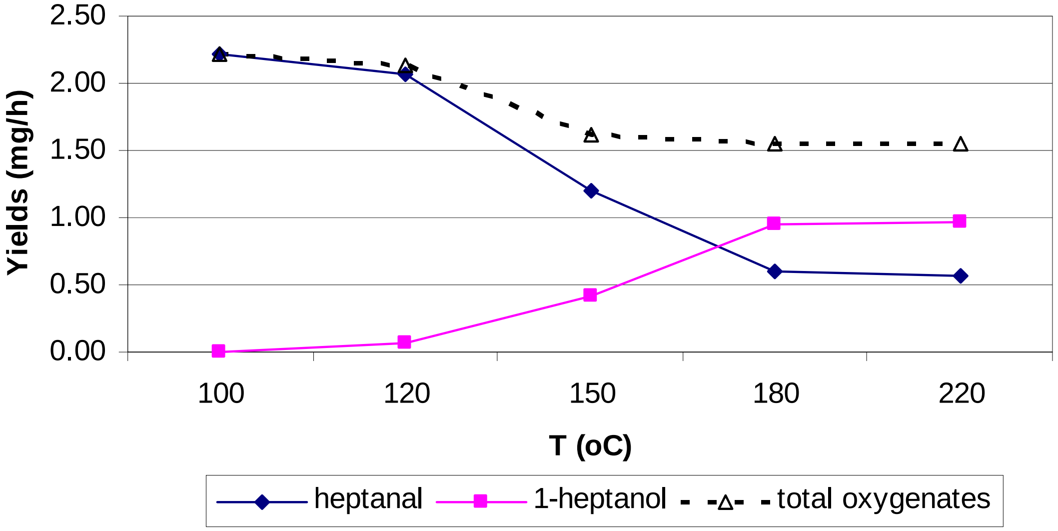


Figure 3.8 Effect of temperature on heptanal and 1-heptanol production over a cobalt catalyst with 1-hexyne addition

($10Co/90Al_2O_3$, P=100psi, $H_2/CO=2$, 1-hexyne (10%) in pentane was added with a flow rate of 2ml/hour)

3.3.1.3 Comparison of 1-hexyne and 1-hexene incorporation Olefins have been used as probe molecules extensively in F-T studies. However, results from investigations vary due to different reaction systems, composition of catalysts, and reaction conditions. To make results somewhat comparable, we carried out F-T reactions with 1-hexyne and with 1-hexene addition at the same base conditions: 220°C, 100 psi and H_2/CO of 2. The results of F-T reactions with 1-hexene addition are shown in Figure 3.9.

There is a large difference in the yield of C7 products upon addition of 1-hexyne and 1-hexene probes. C7 products increased by a factor of two when 1-hexene was added; they increased by a factor of five when 1-hexyne was added. About 12% of the added 1-hexene was hydrogenated to hexane. Unlike incorporation of 1-hexyne which produced large amounts of

C12 hydrocarbons, no appreciable dimerization occurred with incorporation of the olefin. C9 and C10 products are essentially the same for incorporation of 1-hexyne and 1-hexene, only slightly higher than the base case.

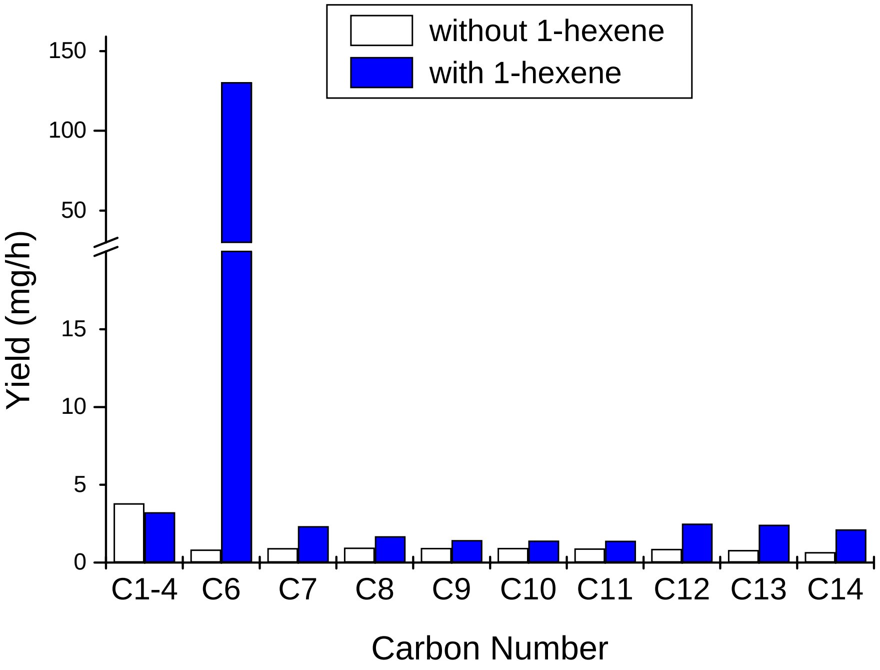


Figure 3.9 Product distribution of the F-T reactions without/with 1-hexene with a cobalt catalyst at 220°C

(10Co/90Al_2O_3, P=100psi, H_2/CO=2, 1-hexene (10%) in pentane was added with a flow rate of 2ml/hour)

When the reaction temperature was changed from 220 to 150°C, 1-hexene was inactive as shown in Figure 3.10. Essentially no hexane was formed upon addition of 1-hexene. 1-Hexyne was still active at 150°C. The strong CO adsorption on cobalt may prevent hydrogenation of 1-hexene at 150°C. Hydrogenation of 1-hexyne to 1-hexene is not hindered by CO adsorption;

alkynes are more strongly adsorbed than CO on the catalyst. Only traces of heptanal were detected on addition of 1-hexene. Addition of 1-hexene did not promote the F-T synthesis at 150°C as did 1-hexyne; about 80% of the added olefin remained unreactive. Adsorption of CO likely decreases the adsorption of the olefin on the catalyst.

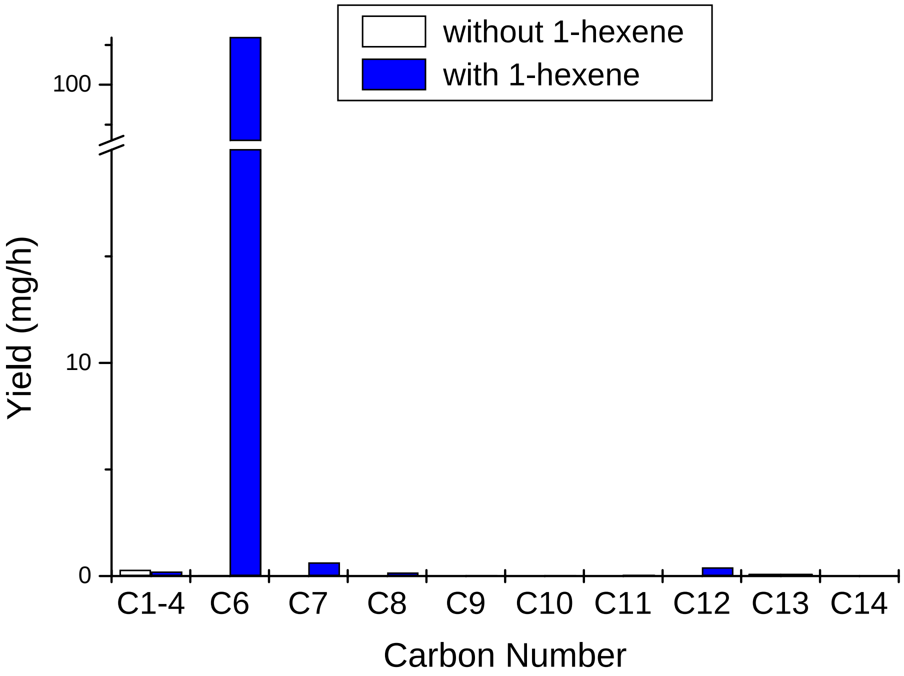


Figure 3.10 Product distribution of the F-T reactions without/with 1-hexene with a cobalt catalyst at 150°C

(10Co/90Al_2O_3, P=100psi, H_2/CO=2, 1-hexene (10%) in pentane was added with a flow rate of 2ml/hour)

3.3.1.4 Time dependence of C7 oxygenates formation With 1-hexyne incorporation, heptanal and 1-heptanol are the only oxygenated products from cobalt catalyzed F-T reactions. To explore the time dependence of formation of C7 oxygenates in the presence of 1-hexyne, we carried out two runs at the same conditions, but at which 1-hexyne was introduced at different time. When 1-hexyne addition began at 5h of TOS in the first run, we observed an enhancement of C7 oxygenates with reaction time (Figure 3.11). Since a large amount of C7 oxygenates was produced at 20h of TOS, we began addition of 1-hexyne at 20h of TOS in the second run and expected to obtain a similar amount of C7 oxygenation. Surprisingly, very little C7 oxygenates were produced at 21h of TOS after addition of 1-hexyne, and production of C7 oxygenates in the second run followed a similar trend as that in the first run.

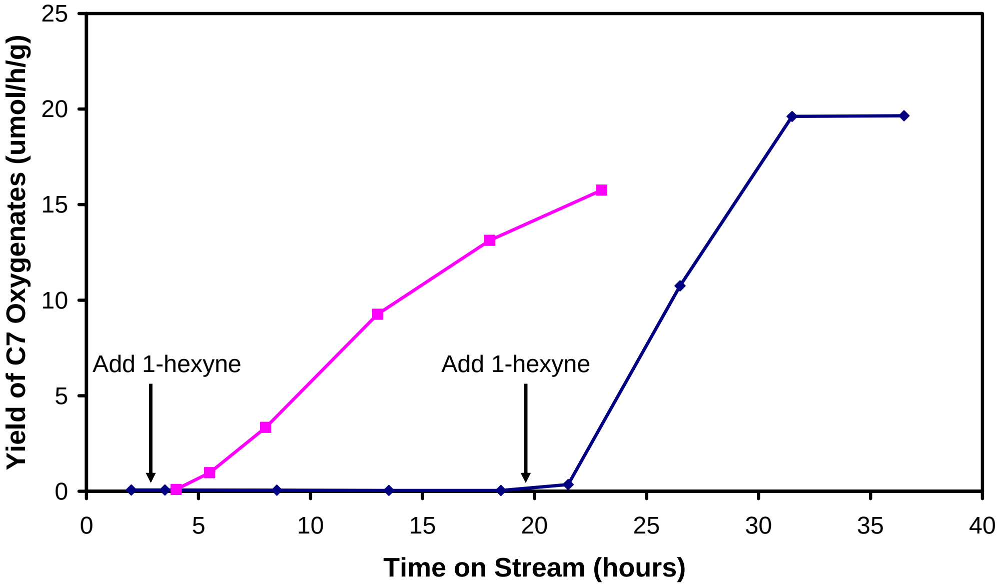


Figure 3.11 Yields of C7 oxygenates (heptanal and 1-heptanol) vs. time-on-stream

(10Co/90Al$_2$O$_3$, T=220^{o}C, P=100psi, H$_2$/CO=2, 1-hexyne (10%) in pentane was added with a flow rate of 2ml/hour)

Increases in yields of heptanal and 1-heptanol with reaction time with incorporation of 1-hexyne suggests that a time period after addition of 1-hexyne is necessary for formation of the C7 oxygenates. The possibility exists that the triple bond in the acetylenic molecule plays a special role in the initiation of the synthesis by inducing a surface restructuring of the cobalt surface, which will be discussed in section 6.0.

3.3.1.5 Deactivation of F-T synthesis in the presence of 1-hexyne The effects of probes on catalyst deactivation was studied by comparing changes in C7 hydrocarbon yields with time-on-stream in the base case and in the presence of 1-hexyne, as shown in Figure 3.12. Two runs (base case and with 1-hexyne) were carried out under the same reaction conditions: T=220°C, P=100psi, $H_2/CO=2$, flow rate= 4.2l/h; all of them lasted over 20 hours. C6 probes were added at 4 hours of TOS. The data in Figure 3.12 shows that formation of C7 hydrocarbons is stable in base case reactions, while it decreases with TOS with incorporation of 1-hexyne. Incorporation of 1-hexyne increased catalyst deactivation, possibly by oligomerization to high molecular weight molecules or carbon lay down on the catalyst surface.

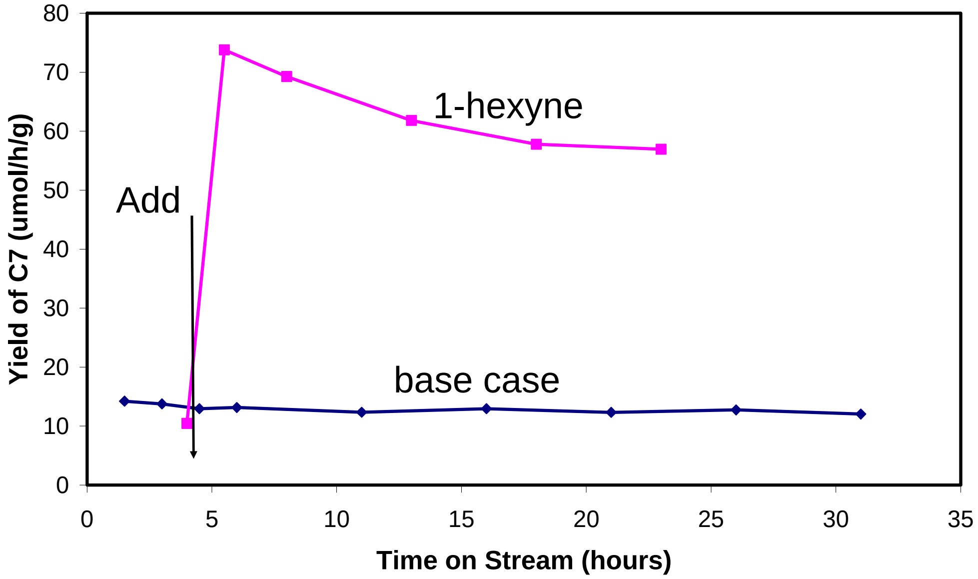


Figure 3.12 C7 hydrocarbon yields versus time-on-stream

($10Co/90Al_2O_3$, T=220°C, P=100psi, $H_2/CO=2$, 1-hexyne (10%) in pentane was added with a flow rate of 2ml/hour)

3.3.2 Incorporation of 1-heptyne and 1-decyne with cobalt catalysts

1-Heptyne and 1-decyne were added to the F-T reaction at 220°C to evaluate the chain length dependence of alkyne incorporation; results are shown in Table 3.2. As with 1-hexyne, where incorporation to C7+ products increased, incorporation of higher molecular weight alkyne probe molecules (with carbon number n) increased to $C_{(n+1)}^{+}$ products. The degree of incorporation of these two acetylenes of different chain lengths is given in Table 3.2, for simplicity, only C_{n+1} products are shown.

The yield of C7+ hydrocarbons increases with addition of 1-hexyne, and the yield of C8+ hydrocarbons increases with 1-heptyne. In a similar way, the yield of C11+ hydrocarbons also increases with 1-decyne addition. With increase in the size of the acetylenic probe, both the percentage increases of n+1 hydrocarbon products and oxygenates decrease. These results suggest that the acetylenic compounds can act as chain initiators, while the degree of incorporation decreases with increasing chain length. The reactivity of added acetylenic molecules in chain initiation reactions decreases in the order: 1-hexyne>1-heptyne>1-decyne. The formation of oxygenates is low for high molecular weight alkynes. Similar reactivity sequences of the olefins in F-T synthesis with Co and Ru catalysts have been reported by Iglesia et al. (113).

Table 3.2 Incorporation of normal alkynes of different carbon chain lengths

Probes	1-hexyne	1-heptyne	1-decyne
Products	C7	C8	C11
Ratio of hydrocarbons (with probe/without probe)	5.4	2.2	1.5
Oxygenate content (%)	28	18	2

$10Co/90Al_2O_3$, T=220^{o}C, P=100psi, $H_2/CO=2$, 1-hexyne (10%) in pentane was added with a flow rate of 2ml/hour

3.3.3 Incorporation of 2-hexyne and 2-hexene with cobalt catalysts

We have shown that incorporation of terminal alkynes produces straight-chain hydrocarbons. Incorporation of 2-hexyne ($CH_3CH_2CH_2C{\equiv}CCH_3$) is of interest because it has an internal carbon-carbon triple bond, sterically less accessible for incorporation into F-T products. A GC-MS chromatogram of the F-T product distribution before and after addition of 2-hexyne at 220^{o}C, 100 psi on a cobalt catalyst is shown in Figure 3.13.

Addition of 2-hexyne yielded 2-hexene, 2-methyl-1-hexene, 2-methylhexanal, and 2-methyl-1-hexanol in addition to normal F-T products. As expected, 2-hexyne incorporates into the F-T synthesis more slowly than does 1-hexyne; the products consist of both straight- and branched-chain hydrocarbons at 220^{o}C. 2-Hexene is the hydrogenation product of 2-hexyne. 2-Methyl-l-hexene is produced by chain growth starting at the second carbon atom of 2-hexyne. Differing sharply from addition of 1-hexyne, no dimerization of the alkynes was observed with 2-hexyne addition. Branched oxygenates, including 2-methylhexanal and 2-methyl-1-hexanol, were formed. The carbon structure of the hydrocarbon chain in the oxygenates produced is the same as in the corresponding C7 branched hydrocarbons (2-methyl-1-hexene). F-T products from 2-hexyne incorporation consist of both straight- and branched-chain hydrocarbons; branched products are evidently produced by 2-hexyne initiated F-T reactions.

Unlike 2-hexyne, addition of the corresponding 2-hexene to the F-T shows little incorporation. A small amount of 2-hexene was hydrogenated to hexane and isomerized to 1-hexene, while most of 2-hexene added remained unreacted (Figure 3.14). The strong CO adsorption on cobalt inhibited the adsorption of 2-hexene for further reactions.

We also carried out F-T reactions with 3-hexyne ($CH_3CH_2C{\equiv}CCH_2CH_3$) as a probe molecule with Co at 220°C, 100psi and $H_2/CO=2$. Interestingly, even for the triple bond in the middle of the acetylenic compound, it may also initiate F-T reactions and produce branched products. To simplify the analysis, the product was hydrogenated with a 1% Pt/Al_2O_3 catalyst at 200°C and 100 psi in H_2 in a batch reactor for 20 minutes. The GC-MS chromatogram of the hydrogenated products is shown in Appendix C; both branched straight-chain products are shown. However, due to our analysis limit, we have difficulties in identifying some peaks, such as the one with retention time of 16 and 20 minutes.

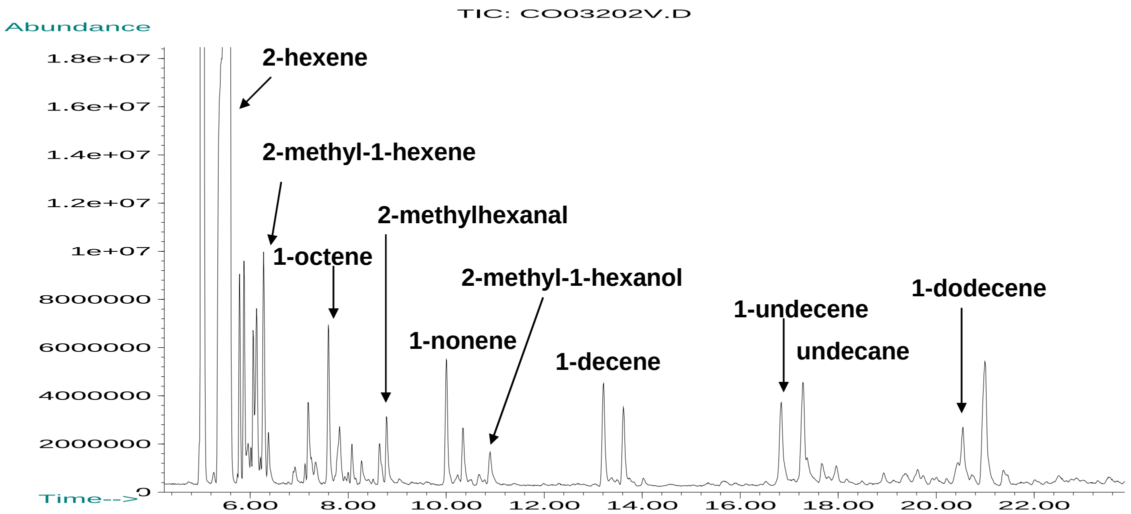


Figure 3.13 GC-MS of F-T with 2-hexyne addition on a cobalt catalyst

(10Co/90Al$_2$O$_3$, T=220°C, P=100psi, H$_2$/CO=2, 2-hexyne (10%) in pentane was added with a flow rate of 2ml/hour)

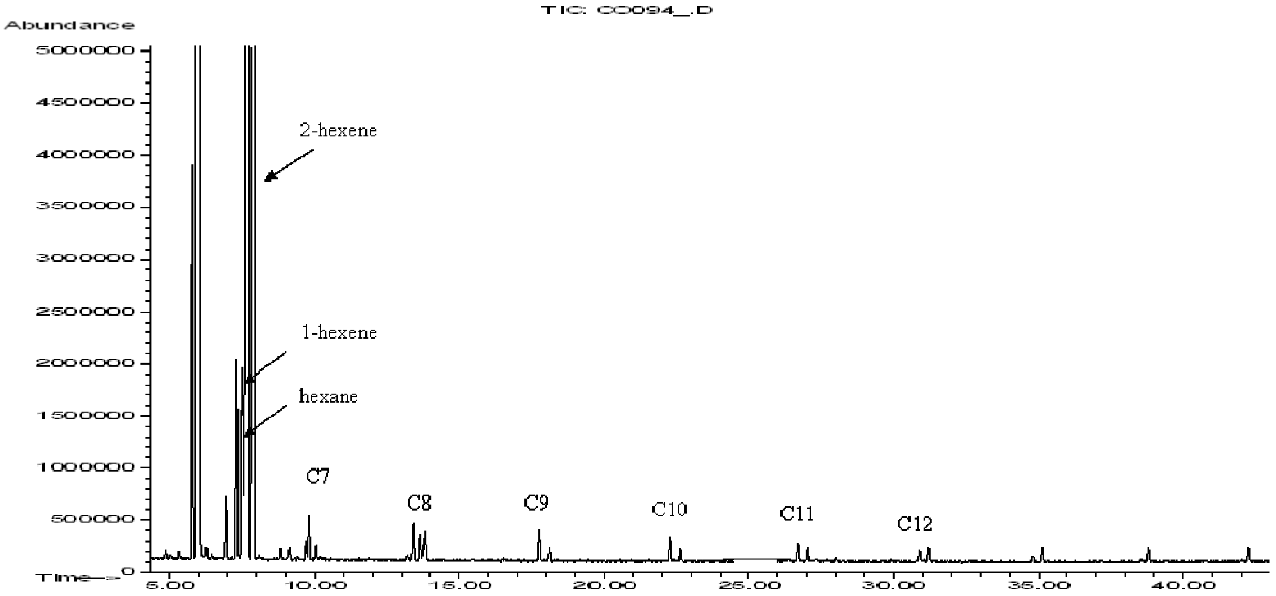


Figure 3.14 GC-MS of F-T with 2-hexene addition on a cobalt catalyst

(10Co/90Al$_2$O$_3$, T=220°C, P=100psi, H$_2$/CO=2, 2-hexene (10%) in pentane was added with a flow rate of 2ml/hour)

3.3.4 Effect of selective poisoning agents on cobalt catalysts

Addition of 1-hexyne to the F-T reaction resulted in a sharp increase in formation of linear C7+ hydrocarbons and C7 oxygenates. Addition of 2-hexyne produced branched hydrocarbons and C7 oxygenates. Higher molecular weight hydrocarbons are produced by base case reactions and 1-hexyne initiated F-T reactions. Oxygenates were probably produced via hydroformylation-type reactions since heptanal and 1-heptanol have one more carbon than 1-hexyne, typical of such reactions.

To provide evidence that some such occurrence takes place, we added thiophene to the F-T in the presence of 1-hexyne with a cobalt catalyst. It is known that F-T reactions are poisoned by the presence of sulfur, especially with cobalt catalysts(114, 115), but the hydroformylation reaction is not significantly affected by the presence of sulfur(116). On the other hand, pyridine reacts with cobalt carbonyls that function as hydroformylation catalysts to forms salts, which inhibit the hydroformylation reaction(117). The addition of pyridine to the F-T reaction has little effect, perhaps reducing the rate of reaction to some extent. If we add thiophene along with 1-hexyne to syngas, hydrocarbons produced via the F-T reactions should decrease while oxygenates formed via hydroformylation should hardly be affected. Similarly, addition of pyridine together with 1-hexyne to the F-T is expected to decrease the yield of oxygenates while formation of hydrocarbons should be affected to only a small extent.

3.3.4.1 Effect of thiophene addition on cobalt catalysts A microsyringe was used to inject thiophene into the reaction stream at 220°C. Results show that while hydrocarbon products from both the normal F-T and the probe-initiated F-T were essentially absent on thiophene injection, oxygenate formation was much less affected (Figure 3.15).

Evidence is provided that heptanal and 1-heptanol formed during addition of 1-hexyne to the F-T reaction are not produced by the F-T chain growth scheme. The alkynes may be adsorbed on the catalyst to form olefinic intermediates that then undergo hydroformylation, perhaps catalyzed by a cobalt carbonyl formed during the synthesis. Pichler pointed out that the F-T reaction occurs at conditions just below those at which metal carbonyls are formed (34). The hydroformylation reaction was also observed by Schulz et al.(5) in the incorporation of olefins into the F-T on cobalt catalysts. A glance at Figure 3.14 reveals that the formation of C12 is due to dimerization of 1-hexyne and is not formed via an F-T synthesis.

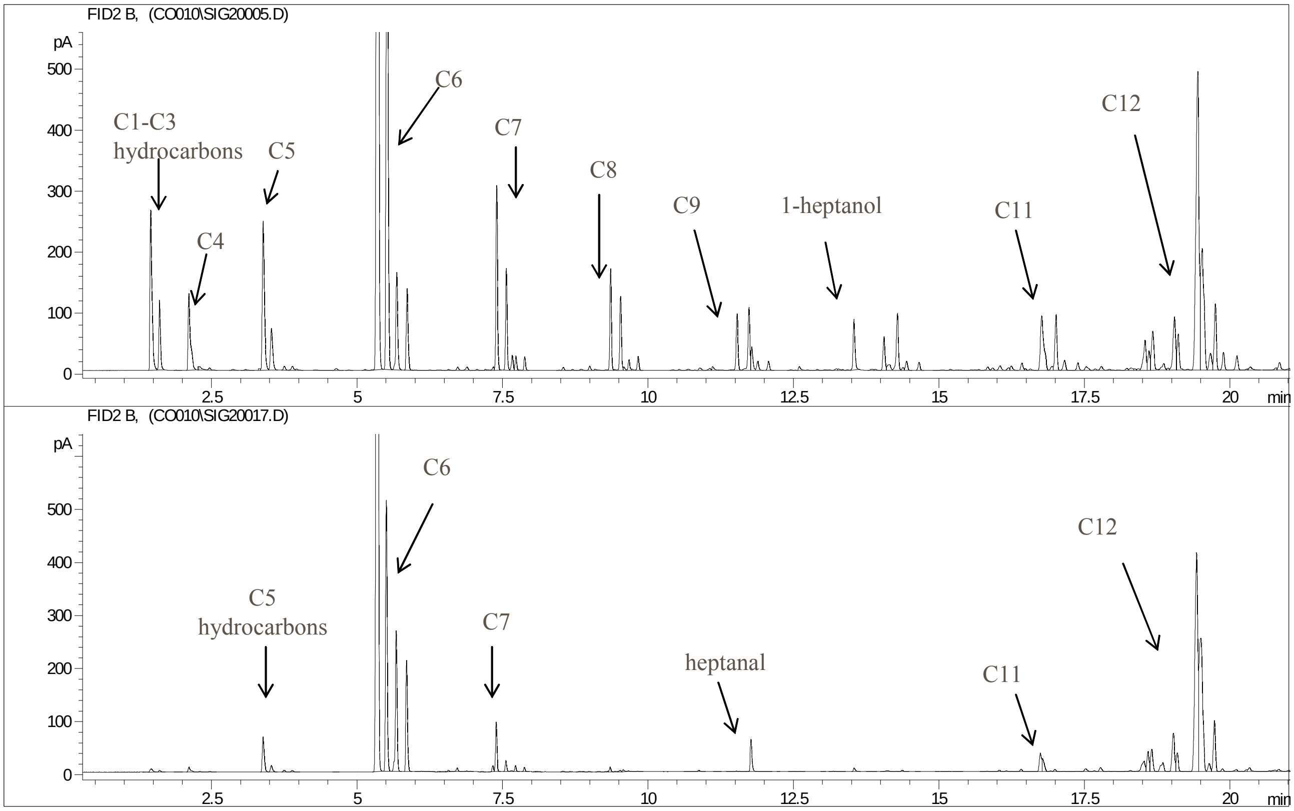
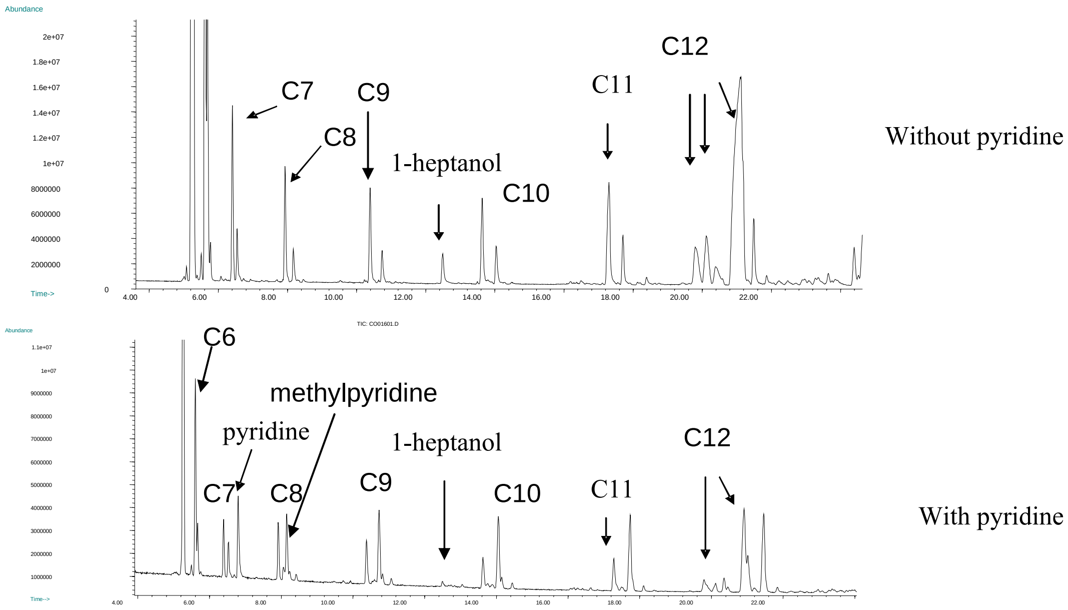


Figure 3.15 Online GC chromatograms of F-T products with incorporation of 1-hexyne before and after injection of thiophene

($10Co/90Al_2O_3$, T=220°C, P=100 psi, $H_2/CO=2$)

3.3.4.2 Effect of pyridine addition on cobalt catalysts

The effect of the addition of pyridine to the F-T in the presence of 1-hexyne over cobalt is shown in Figure 3.16. The peak for 1-heptanol disappears almost entirely, while the F-T reaction continues. This result supports our postulation that C7 oxygenates are produced via hydroformylation because pyridine poisons the hydroformylation reaction. Pyridine blocked F-T chain growth to some extent. Another change that occurred upon pyridine addition was the appearance of methylpyridine. Pyridines can pick up the methylene intermediates on the surface of cobalt catalysts and form methylpyridine.



$Co_{10}Al_{90}$, T=220C, P=100psi, H2/CO=2, 1-hexyne: pyridine=1:1

Figure 3.16 Effect of pyridine addition on a cobalt catalyst

3.3.5 Incorporation of 1-hexyne with an iron catalyst

F-T reactions were carried out with iron catalysts at 260^{o}C, 100 psi of pressure with CO/H_2=1.5 and flow rate of 4.2 l/h. F-T product distributions without and with 1-hexyne additions are shown in Figure 3.17.

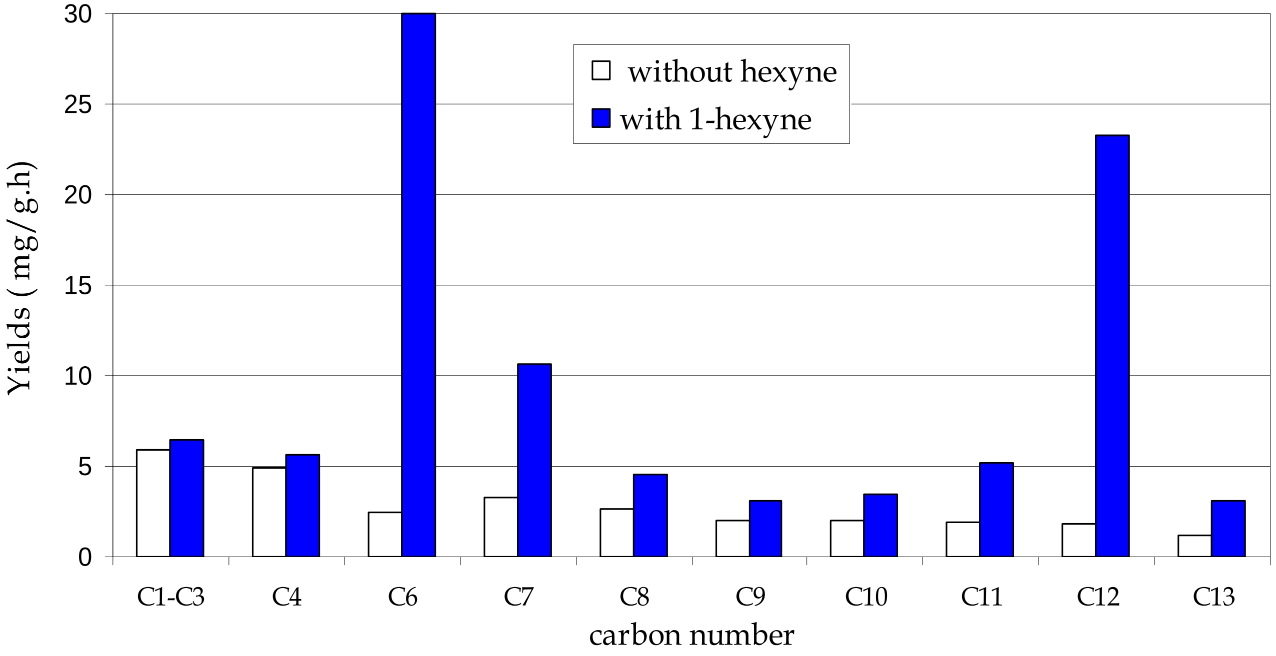


Figure 3.17 F-T product distribution without/with 1-hexyne addition

(100Fe-5.1Si-2.0Cu-5.0K_2O, T=260°C, P=100psi, $H_2/CO=2/3$; 1-hexyne (10%) in pentane was added with a flow rate of 2ml/hour)

Incorporation of 1-hexyne into iron catalyzed F-T reactions, as found with cobalt catalysts, increases F-T reaction activity. C7+ products increase sharply with 1-hexyne addition. The amount of C12 hydrocarbons formed on the iron catalyst was less than that on the cobalt catalyst, indicating that dimerization of 1-hexyne proceeds more easily on cobalt catalysts.

While the incorporation of 1-hexyne was similar to that on cobalt catalysts, a striking difference with iron is in the formation of oxygenates. With 1-hexyne, iron catalysts produced greater yields of oxygenated compounds than found with cobalt catalysts. We found that the only oxygenates formed over cobalt catalysts had one carbon more than the acetylenic probe molecule; oxygenate formation on iron catalysts was not so limited. A series of oxygenates with one and more carbons than the probe were produced as shown in Figure 3.18, a GC-MS chromatogram of F-T liquid products. C8+ oxygenates were not detectable from online GC during reaction, however, they could be detected by off-line GC-MS following specific procedures to collect the liquid sample. These procedures are: after F-T reaction for at least 20 hours, change syngas to argon with a flow rate of 50 ml/hour to flush out the remains in the reactor. Increase reactor temperature to 350^{o}C. In order to collect sufficient amounts of liquid products from the cold trap in an ice-water bath for GC-MS analysis, pentane was added by a syringe pump with a flow rate of 2 ml/hour. After one hour, the liquid was collected and analyzed by GC-MS. A large amount of C6+ oxygenates were produced. Due to the high boiling point of some higher alcohols (for example, 195^{o}C for 1-octanol which is higher than our reaction temperature: 170^{o}C), they may remain in the pores of catalysts during the F-T reactions. Difficulties in comparing oxygenated and hydrocarbon products quantitatively could perhaps be overcome by using acetylene (HC≡CH), the smallest alkyne compounds, as shown in chapter 5.0.

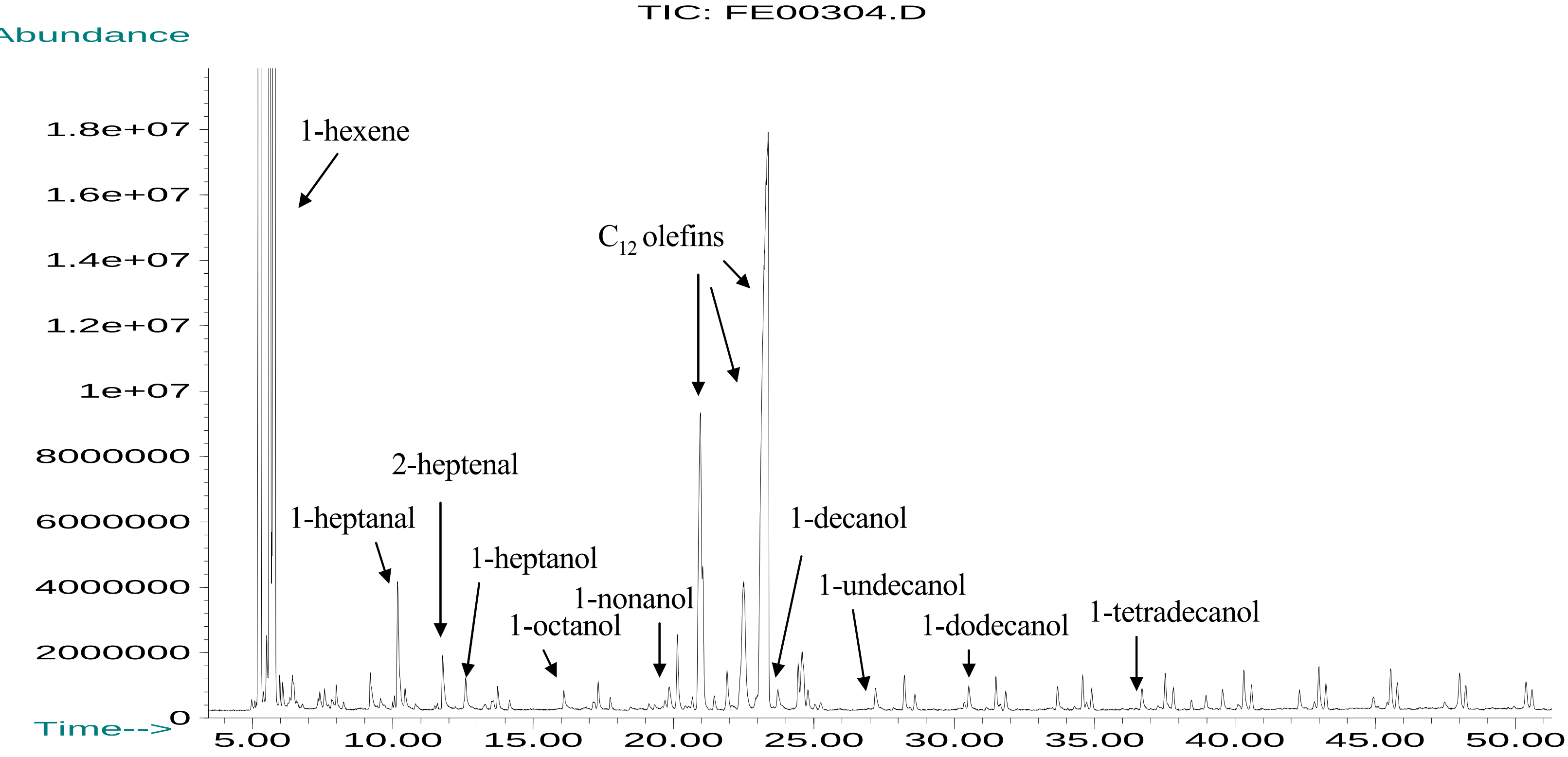


Figure 3.18 GC-MS of F-T products with 1-hexyne addition on an iron catalyst

(100Fe-5.1Si-2.0Cu-5.0K_2O, T=170°C, P=100psi, H_2/CO=2/3, 1-hexyne in pentane (2% in volume) was added by a syringe pump with a flow rate of 2ml/h.)

3.4 CONCLUSIONS

Acetylenic compounds can initiate the FT synthesis at temperatures more than 100°C lower than those at which base case F-T reactions are carried out. When acetylenic probe molecules are added to a base case F-T synthesis, both the probe-initiated and the conventional F-T synthesis proceed simultaneously. The observed increase in the yields of higher hydrocarbons when acetylenic compounds are added can be accounted for by the increase in the chain initiation rate. The acetylenic probe molecule and CO compete for the catalyst surface; the carbon-carbon triple bond is evidently adsorbed preferentially on both iron and cobalt catalysts and initiates the F-T reactions.

When 1-hexyne and 1-hexene are added under similar conditions, a smaller amount of 1-hexene is incorporated into F-T hydrocarbons. Incorporation of terminal alkynes produces straight chain hydrocarbons while incorporation of internal alkynes produces both branched- and straight-chain hydrocarbons. Part of the internal alkyne can isomerize to the terminal position and then start chain growth to produce straight chain products; we will provide evidence for these statements in the next chapter in discussions of F-T reactions with 1-phenyl-1-propyne added as a probe molecule.

Addition of 1-hexyne produces a significant amount of C7 oxygenates over cobalt catalysts. To investigate the nature of oxygenate formation when 1-hexyne is incorporated on a cobalt catalyst, we used selective poisoning agents, thiophene and pyridine, along with 1-hexyne addition. A small amount of added thiophene selectively deactivates the F-T reaction, while the formation of C7 oxygenates is affected to a much smaller degree. With pyridine addition, the amount of C7 oxygenates decreases, but the F-T continues. These experimental results on addition of selective poisoning agents supports the conclusion that C7 oxygenates are produced via a reaction similar to hydroformylation.

Oxygenates are also formed with incorporation of alkynes in the F-T products over iron catalysts. Oxygenates formed on cobalt catalysts are limited to the aldehyde and alcohol with one carbon more than the probe. Incorporation of alkynes on iron catalysts produces a series of oxygenates; further investigation will be carried out with the addition of acetylene itself in section 5.0.

4.0 PHENYL-SUBSTITUTED ALKYNE PROBE MOLECULES AS MARKERS IN THE F-T SYNTHESIS

4.1 INTRODUCTION

We have added long-chain linear alkynes as probes into the F-T synthesis. Products of the incorporation of 1-hexyne can be divided into a fraction produced by CO hydrogenation in conventional F-T, and another fraction which contains at least one probe molecule derived from 1-hexyne in each chain. Since products of incorporation of 1-hexyne overlap normal F-T products, it is difficult to distinguish the alkyne-initiated products from normal F-T products. To ascertain the origin of the initiating species, several phenyl-substituted acetylenes were used as probe molecules. With the phenyl group as a marker, these two types of products were easily distinguished. Products containing the phenyl group can be separated easily by GC and identified by GC-MS.

We used 4-phenyl-1-butyne ($C_6H_5CH_2CH_2C{\equiv}CH$), and phenylacetylene ($C_6H_5C{\equiv}CH$), in which triple bond is at the terminal position, as probe molecules. For comparison, incorporation of the olefinic counterpart, 4-phenyl-1-butene ($C_6H_5CH_2CH_2CH{=}CH_2$) was also investigated. To study the incorporation of internal alkynes: 1-phenyl-1-propyne ($C_6H_5C{\equiv}CCH_3$) was used as a probe.

4.2 EXPERIMENTAL

4.2.1 Catalyst preparation

Co (10 wt %) and Al_2O_3 (90wt %) was prepared by the same method as described in 4.1. The iron catalyst was obtained from Dr. Burt Davis, University of Kentucky; it had been prepared by a precipitation method and had a composition of 100Fe-5.1Si-2.0Cu-5.0K_2O.

4.2.2 Reactions Conditions

For cobalt catalysts, F-T reactions were carried out at 180 and 220^{o}C, 100psi, $H_2/CO=2$, with a flow rate of 4.2 l/h. For iron catalysts, F-T reactions were carried out at 170 and 260^{o}C, 100psi, $H_2/CO=2/3$, with a flow rate of 4.2 l/h.

4.2.3 Addition of alkynes

4-phenyl-1-butyne (98+%), 4-phenyl-1-butene(98+%), phenylacetylene(98+%), and 1-phenyl-1-propyne(98+%) were all obtained from GSF Chemicals. Alkynes were added via a syringe pump. The probe molecules were dissolved in pentane (10% by volume) and added in the reactant stream with a total flow rate of 2ml/h.

4.3 RESULTS AND DISCUSSION

4.3.1 Incorporation of 4-phenyl-1-butyne with cobalt catalysts

The F-T reactions were carried out with a cobalt catalyst at 220°C, 100psi with a H_2 to CO ratio of 2. A GC-MS chromatogram of F-T liquid products with addition of 4-phenyl-1-butyne ($C_6H_5CH_2CH_2C\equiv CH$) is shown in Figure 4.1. Mass spectroscopic analysis shows that two types of products are produced: normal F-T products (labeled underneath) and hydrocarbons labeled with a phenyl group. As with the incorporation of other terminal alkynes, the chain grows from the end of the carbon-carbon triple bond and produces a series of products with α-olefins and normal paraffins as the main products. Only straight-chain alkylbenzene were obtained. Propylbenzene is obtained from 4-phenyl-1-butyne by splitting of the carbon-carbon triple bond in the molecule. 5-Phenyl-1-pentanol is obtained from a hydroformylation reaction. Not unexpectedly, a substantial amount of the probe is dimerized with the incorporation of 4-phenyl-1-butyne, similar to other terminal alkynes.

Incorporation of 4-phenyl-1-butyne results in significant catalyst deactivation, possibly by oligomerization to high molecular weight molecules or carbon laydown which covers the catalyst surface. Figure 4.2 shows that at 7.5 h of TOS with 4-phenyl-1-butyne, half of the normal F-T activity remained; at 21 h TOS, only one fourth of the normal FT activity was retained.

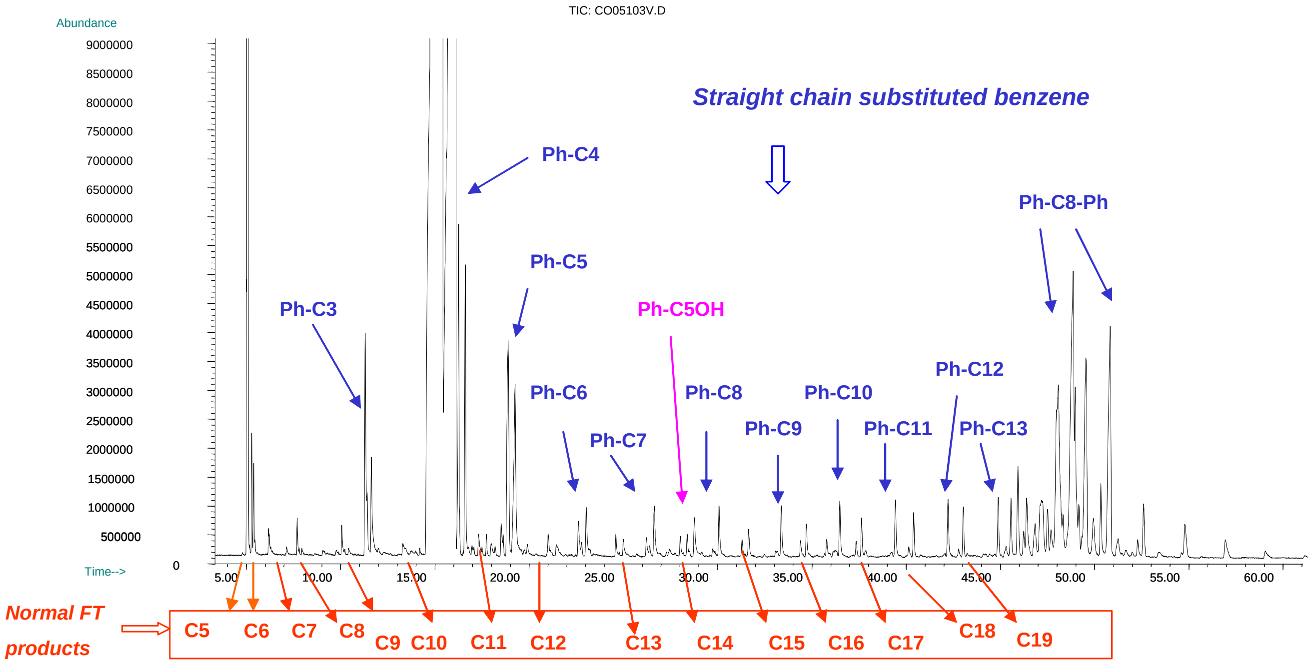


Figure 4.1GC-MS chromatogram of F-T products over a cobalt catalyst with 4-phenyl-1-butyne addition

(10Co/90Al$_2$O$_3$, T=220^{o}C, P=100psi, H$_2$/CO =2, 4-phenyl-1-butyne (10%) in pentane was added with a flow rate of 2ml/hour)

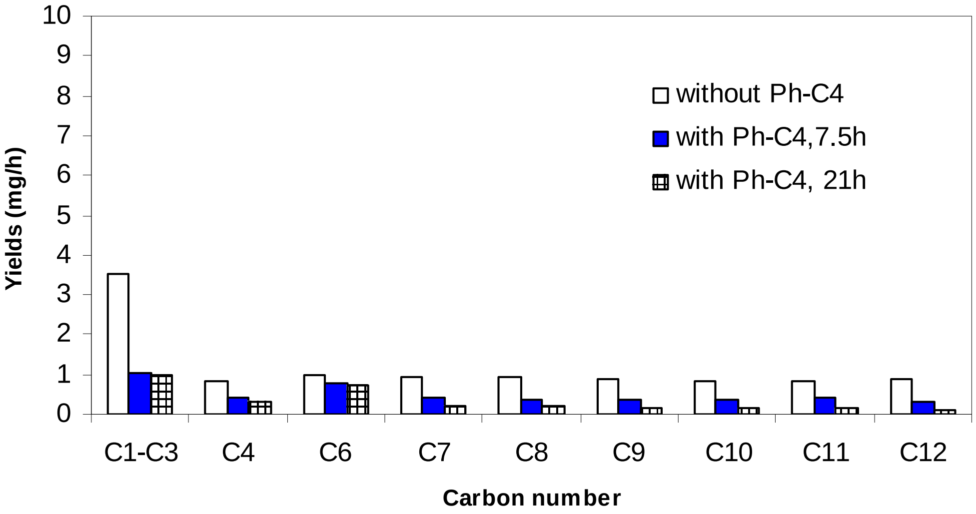


Figure 4.2 Effects of 4-phenyl-1-butyne (Ph-C4) on F-T linear hydrocarbon products over a Co catalyst

(10Co/90Al$_2$O$_3$, T=220^{o}C, P=100psi, H$_2$/CO=2, 4-phenyl-1-butyne (10%) in pentane was added with a flow rate of 2ml/hour)

Clearly, two types of chain growth are involved, aliphatic linear hydrocarbons and hydrocarbons containing a phenyl group. The phenyl-containing hydrocarbon product distributions obtained by adding 4-phenyl-1-butyne to the F-T reaction are shown in Figure 4.3. Obviously, the chain growth factor (the alpha value) for linear hydrocarbons differs from that of phenyl-substituted hydrocarbons. The alpha value for linear hydrocarbons decreased from 0.86 in the base case to 0.84 at TOS of 7.5h and 0.78 at TOS of 21h with addition of 4-phenyl-1-butyne. The alpha value of phenyl-substituted F-T products at TOS of 7.5h is 0.34, less than half that of linear hydrocarbons and the base case. The yields of 3-phenyl-1-propene and 1-phenyl-1-propane are much higher than that of ethylbenzene, toluene and benzene, indicating hydrogenolysis occurs mainly at the carbon-carbon triple bond. In contrast to the decreasing trend of formation of hydrocarbon products with TOS in the presence of 4-phenyl-1-butyne, the formation of oxygenates increased with TOS as shown in Appendix B.

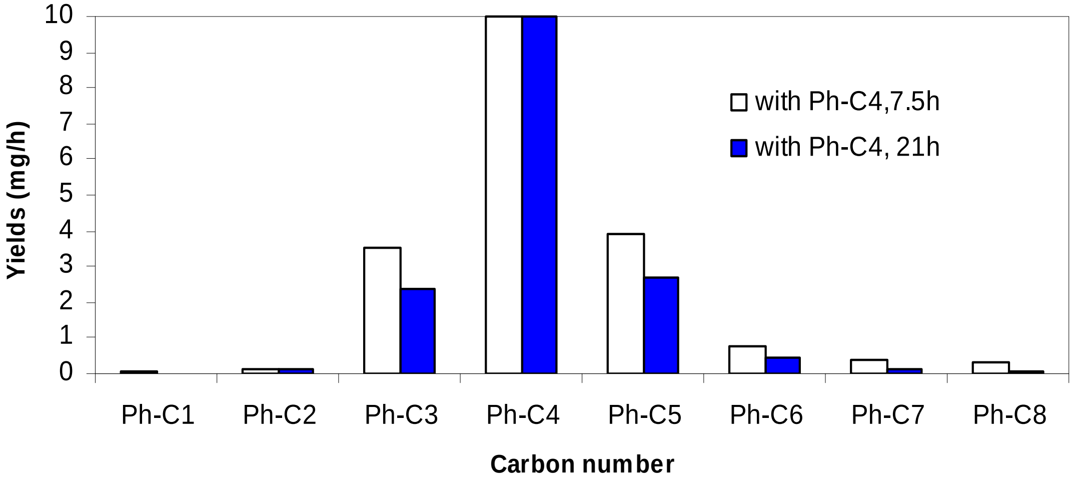
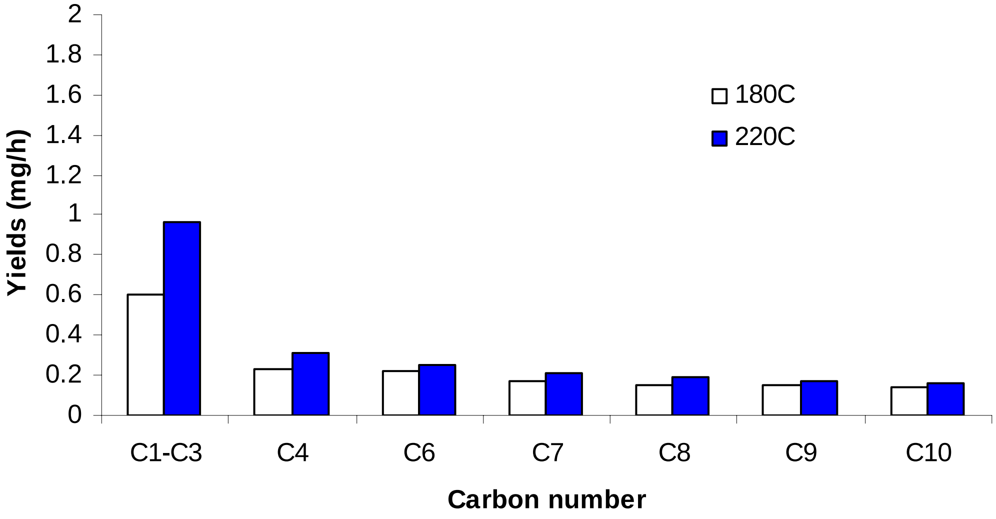


Figure 4.3 F-T phenyl-substituted products initiated by 4-phenyl-1-butyne (Ph-C4)

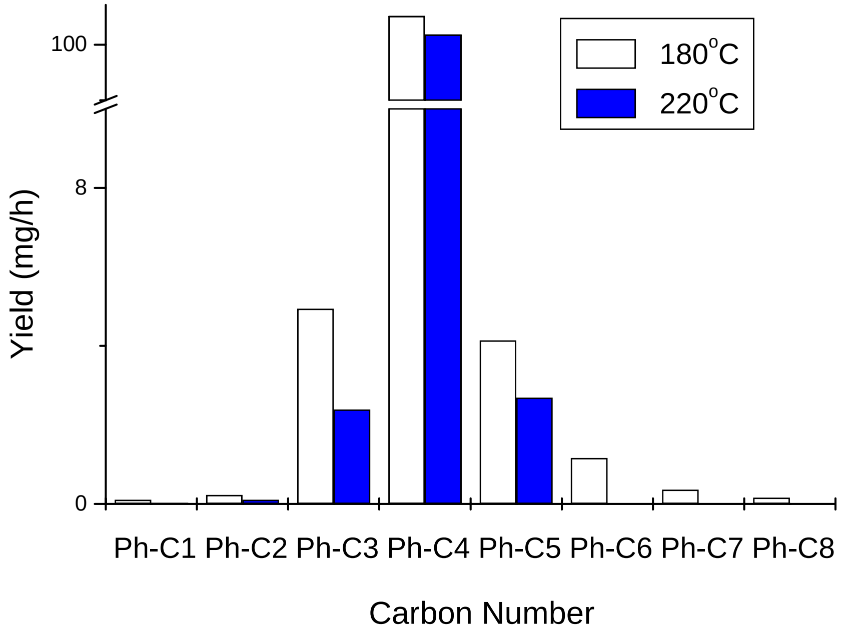
($10Co/90Al_2O_3$, T=220°C, P=100psi, $H_2/CO=2$, 4-phenyl-1-butyne (10%) in pentane was added with a flow rate of 2ml/hour)

Interestingly, we found that temperature has different effects on hydrocarbons produced from base case F-T synthesis and from 4-phenyl-1-butyne initiated F-T reactions. As expected, yields of linear hydrocarbon products from base case F-T reactions were higher at 220°C than at 180°C (Figure 4.4 (a)). However, production of phenyl-substituted hydrocarbons initiated by 4-phenyl-1-butyne increased with decrease in temperature from 220 to 180°C (Figure 4.4(b)). 4-Phenyl-1-butyne and CO were adsorbed and initiated chain growth competitively on Co catalysts. Higher yields of phenyl-substituted hydrocarbons at lower temperature of 180°C indicate that 4-phenyl-1-butyne initiated F-T reactions more easily than CO and H_2.

In summary, with incorporation of 4-phenyl-1-butyne, the F-T reaction is initiated by the terminal alkyne with growth from the carbon attached to the hydrogen atom in the carbon-carbon triple bond. The behavior, after initiation, is similar to typical F-T reactions, suggesting that the intermediates formed from adsorption of terminal alkynes are similar to intermediates which occur in the usual F-T reaction.



(a)



(b)

Figure 4.4 F-T Products in the presence of 4-phenyl-1-butyne at 180 and at 220°C (a) linear hydrocarbons (b) phenyl-substituted hydrocarbons

($10Co/90Al_2O_3$, P=100psi, $H_2/CO=2$, 4-phenyl-1-butyne (10%) in pentane was added with a flow rate of 2ml/hour)

To compare incorporation of an alkyne and alkene, 4-phenyl-1-butene was added to the F-T reaction under the same reaction conditions as with 4-phenyl-1-butyne. Very little incorporation is observed with the addition of 4-phenyl-1-butene; 4-phenyl-1-butyne is more easily incorporated than 4-phenyl-1-butene (Figure 4.5).

There are interesting differences in the products from F-T reactions in the presence of the 4-phenyl-1-butene and 4-phenyl-1-butyne: (1) 4-phenyl-1-butyne produces a large amount of Ph-C3, while 4-phenyl-1-butene does not. Although the breakage of the carbon-carbon triple bond requires more energy than the breakage of carbon-carbon double bond in the absence of catalysts, alkynes are adsorbed on the surface of the catalyst more easily than alkenes. When 4-phenyl-1-butyne is adsorbed onto the surface of catalysts, the breakage of the carbon-carbon bond is facilitated by formation of carbon-metal bond, so less energy is required to break the bond. (2) 4-phenyl-1-butyne forms large amounts of dimers; dimerization does not occur for 4-phenyl-1-butene. (3) With 4-phenyl-1-butyne addition, a large amount of Ph-C5OH is formed via a hydroformylation reaction, not observed with 4-phenyl-1-butene addition.

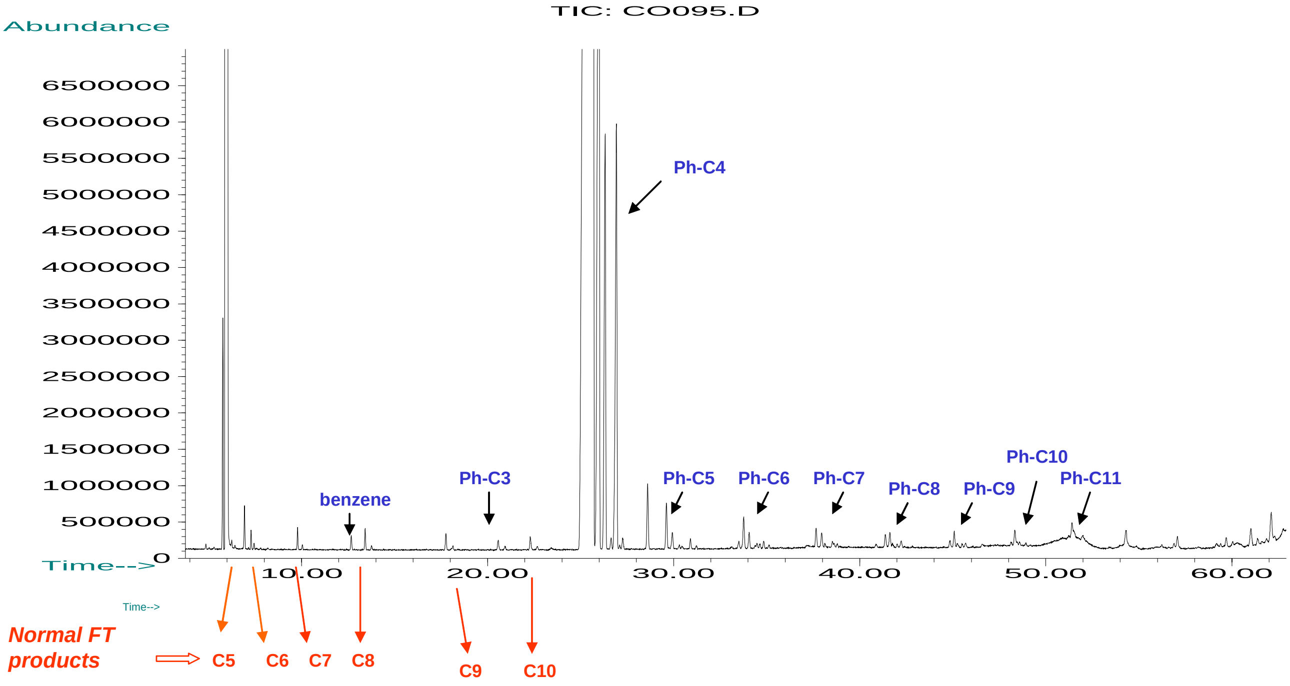


Figure 4.5 GC-MS chromatogram of F-T products over a cobalt catalyst with 4-phenyl-1-butene addition

(T=220°C, P=100psi, $H_2/CO=2$, flow rate of 4-phenyl-1-butene(10%) in pentane is 2ml/hour)

4.3.2 Incorporation of 1-phenyl-1-propyne with cobalt catalysts

Incorporation of internal alkynes behaves differently from incorporation of terminal alkynes as shown by addition of 2-hexyne and 1-hexyne. Branched hydrocarbon chains are formed with incorporation of 2-hexyne. Incorporation of a phenyl-substituted internal alkyne, 1-phenyl-1-propyne ($C_6H_5C{\equiv}CCH$), was investigated to further evaluate the reaction of internal alkynes by using the phenyl group as a marker. F-T reactions were conducted with 1-phenyl-1-propyne at 220°C, 100psi, $H_2/CO=2$. The GC-MS chromatogram of the products of incorporation of 1-phenyl-1-propyne in the F-T is complex. It shows products from the normal FT together with branched- and straight-chain substituted benzenes with some unsaturated side chains. To simplify the analysis, the product was hydrogenated with a 1% Pt/Al_2O_3 catalyst at 200°C and 100 psi in H_2 in a batch reactor for 20 minutes. The GC-MS chromatogram of the hydrogenated products is shown in Figure 4.6; products with both straight and branched chains attached to a phenyl group are shown.

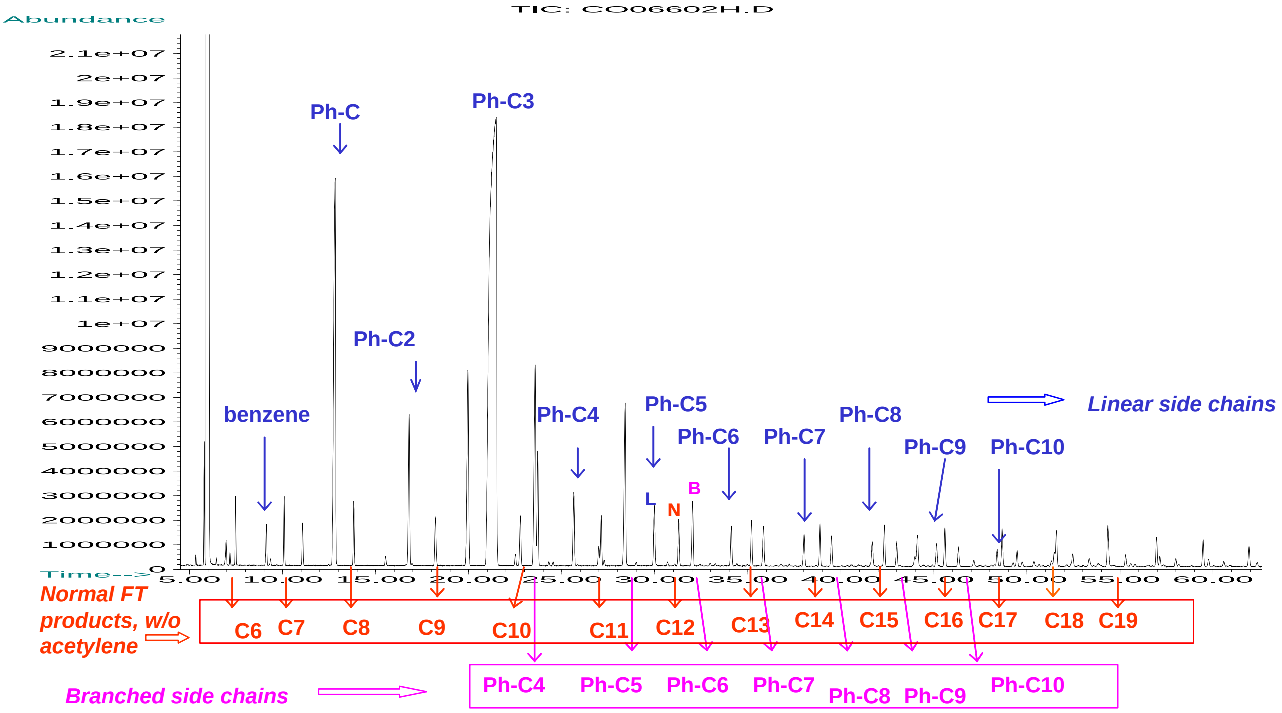


Figure 4.6 GC-MS chromatogram of F-T products over a cobalt catalyst with 1-phenyl-1-propyne addition

($10Co/90Al_2O_3$, T=220°C, P=100psi, H_2/CO =2, 1-phenyl-1-propyne (10%) in pentane was added with a flow rate of 2ml/hour)

Figure 4.6 shows three types of hydrocarbon products from F-T reactions with participation of 1-phenyl-1-propyne: linear hydrocarbons from CO hydrogenation, branched alkylbenzenes from 1-phenyl-1-propyne-initiated F-T reactions and straight-chain alkylbenzenes from 3-phenyl-1-propyne ($C_6H_5CH_2C{\equiv}CH$), an isomer of 1-phenyl-1-propyne. Isomerization of the internal triple bond to the terminal position evidently occurs and no polymerization is observed. Substantial amounts of toluene are formed by splitting of the carbon-carbon triple bond. Some diphenylethylene was formed, probably by coupling of two precursors to the formation of toluene. Ethylbenzene was formed either by addition of a methyl group to a toluene precursor or by splitting of the isomerized carbon-carbon triple bond located in the terminal position. Benzene is also formed, probably by further loss of a methyl group from toluene. Carbon-carbon bond splitting is observed with added alkenes(15, 118). It has been reported that when double ^{13}C-labeled ethylene was added to the F-T, a substantial amount of the added ethylene splits to form C1 units(41). Schulz(154119) has suggested the possible reversibility of chain growth in the F-T synthesis in which carbon-carbon bond formation and breakage both exist. The activity of 1-phenyl-1-propyne initiated F-T reaction at 220°C is relatively low compared with 4-phenyl-1-butyne and phenylacetylene at the same reaction temperature. Internal acetylenes are harder to incorporate than are terminal acetylenes, probably because of steric reasons.

4.3.3 Incorporation of phenylacetylene with cobalt and iron catalysts

Phenylacetylene ($C_6H_5C{\equiv}CH$) was added to both cobalt and iron catalyzed F-T reactions; two samples were taken at 5 hours and 20 hours after addition of phenylacetylene. For the cobalt catalyst, participation of phenylacetylene into the F-T reactions resulted in a significant decrease in yields of linear hydrocarbon products from the base case as shown in Figure 4.7. Similar deactivation of cobalt catalyzed F-T synthesis was observed in the presence of 1-hexyne addition. As we stated before, the deactivation may be due to occupation of active sites for F-T reactions by the long chain hydrocarbons or by carbon laydown on the surface.

Incorporation of phenylacetylene results in the decrease of the chain growth value. Figure 4.8 compares alpha values of three types of products: linear F-T products in the absence of phenylacetylene (α_1), alkylbenzenes formed by phenylacetylene initiated F-T reactions (α_2), linear F-T products in the presence of phenylacetylene (α_3). The alpha value was reduced from 0.83 to 0.43 after phenylacetylene was added. The decrease in chain growth probability of linear hydrocarbons was possibly due to consumption of C1 monomer by extra initiators formed by phenylacetylene.

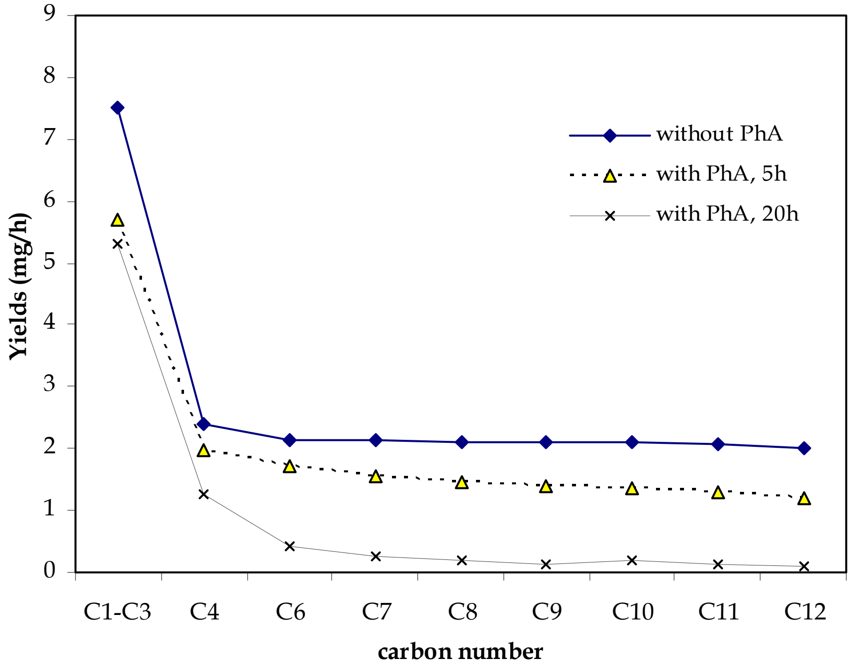


Figure 4.7 Yields of F-T products over a cobalt catalyst with phenylacetylene (PhA) addition

(10Co/90Al, T=220°C, P=100psi, H_2/CO =2, phenylacetylene (10%) in pentane was added with a flow rate of 2ml/hour)

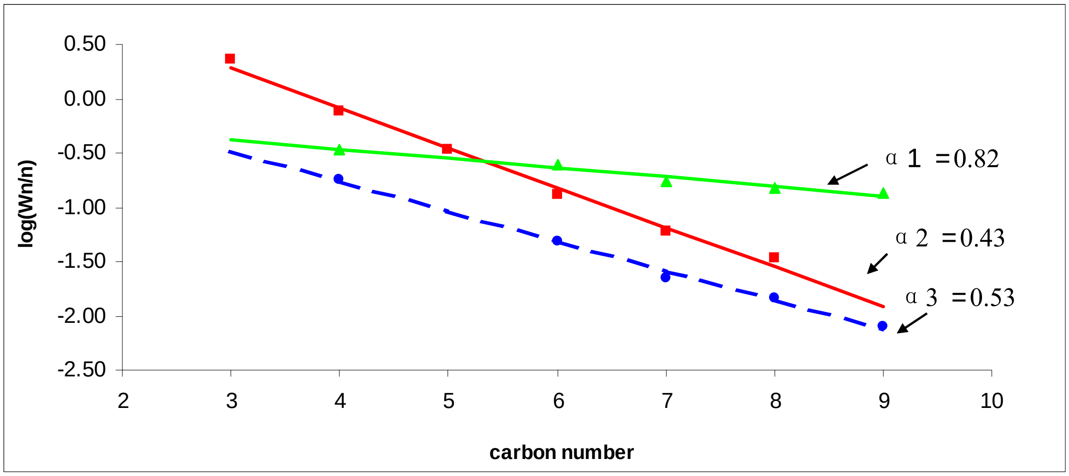


Figure 4.8 Alpha values of F-T products over a cobalt catalyst with phenylacetylene

(10Co/90Al_2O_3, T=220°C, P=100psi, H_2/CO =2, phenylacetylene (10%) in pentane was added with a flow rate of 2ml/hour)

α_1- chain growth probability of normal FT
α_2- chain growth probability of phenyl-substituted hydrocarbons with phenylacetylene addition
α_3- chain growth probability of linear hydrocarbons with phenylacetylene addition

Incorporation of the probes on an iron catalyst was carried out at 170°C and 260°C. At 260°C, both normal initiation and the initiation of F-T by the probe molecule are observed. Unlike cobalt catalysts, which were deactivated rapidly by phenylacetylene; phenylacetylene had little effects on normal F-T reactions with iron catalysts, as shown in Figure 4.9. F-T reactions remain active after TOS of 20 hours.

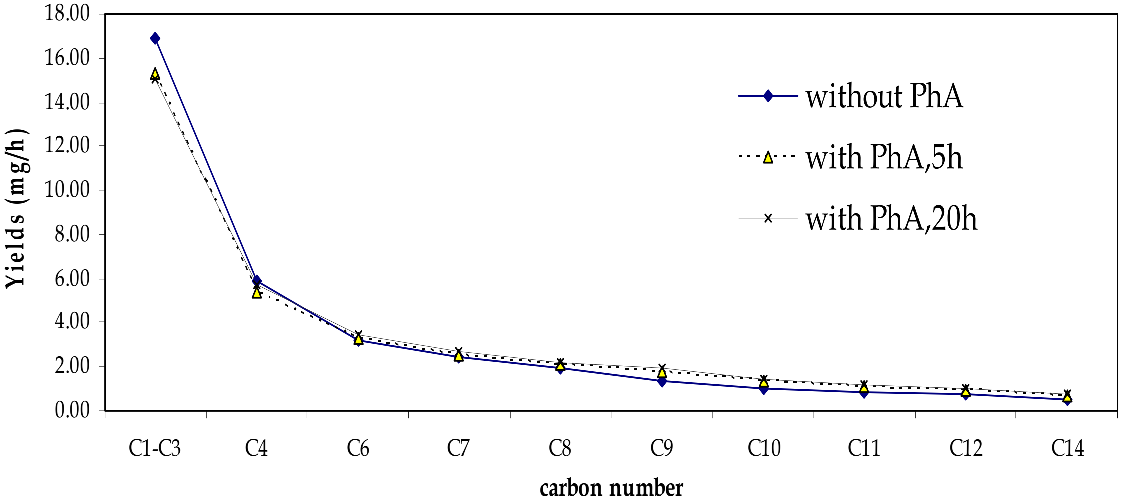


Figure 4.9 Yields of F-T products over an iron catalyst with phenylacetylene (PhA)

(100Fe-5.1Si-2.0Cu-5.0K_2O, T=260^{o}C, P=100psi, H_2/CO=2/3; phenylacetylene (10%) in pentane was added with a flow rate of 2ml/hour)

At 170°C, normal FT activity with an iron catalyst is negligible and the observed products originate only from incorporation of acetylenic probe molecules. Figure 4.10 shows the GC-MS analysis of liquid products of F-T with phenylacetylene addition at 170^{o}C.

Oxygenates originating from phenylalkyne addition were observed. With iron catalysts, oxygenates produced in the presence of alkynes were not limited to those with one more carbon than the added alkynes, as was with cobalt catalysts. Ph-C3+ products were formed with incorporation of phenylacetylene. With addition of phenylacetylene at 170°C, about half of the Ph-C3+ products were oxygenates, mainly phenyl-substituted aldehydes and alcohols. Oxygenates decreased and aldehydes were hydrogenated to alcohols when the reaction temperature increased from170 to 260°C.

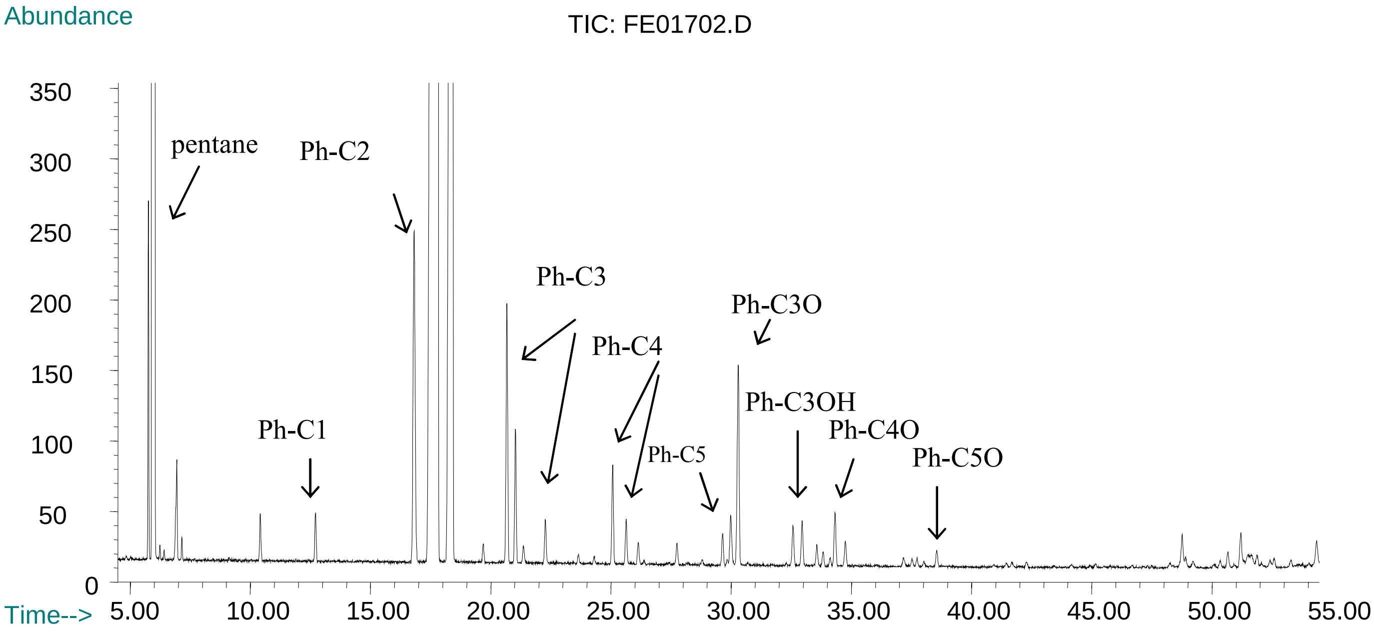


Figure 4.10 GC-MS analysis of F-T liquid products with phenylacetylene addition

(100Fe-5.1Si-2.0Cu-5.0K_2O, T=170°C, P=100psi, H_2/CO=2/3; phenylacetylene (10%) in pentane was added with a flow rate of 2ml/hour)

4.4 CONCLUSIONS

The use of phenylalkyne probes allows the probe-initiated products to be easily distinguished from the conventional FT products by GC-MS analysis. When phenylalkynes were added to the F-T synthesis, both the alkylbenzenes from alkyne-initiated F-T reactions and linear hydrocarbons from the conventional F-T synthesis were produced. 4-Phenyl-1-butyne produced straight-chain alkylbenzenes, while 1-phenyl-1-propyne produced both branched and straight-chain alkylbenzenes.

When the temperature was decreased from 220 to 180°C, linear products from CO hydrogenation were reduced, while phenyl-substituted products initiated from 4-phenyl-1-butyne increased. CO and 4-phenyl-1-butyne initiate F-T reactions competitively; 4-phenyl-1-butyne initiation proceeds more easily at the lower temperature.

4-Phenyl-1-butyne and 4-phenyl-1-butene have been added into F-T reactions on cobalt catalysts. We found that the alkynes initiate chain growth much more effectively than do olefins. The stronger adsorption bond and more adsorption sites available for 4-phenyl-1-butyne on the catalyst surface may be the reason for higher degree of incorporation.

Phenylacetylene had different effects on the deactivation of the F-T reactions with cobalt and with iron catalysts. On cobalt catalysts, the activity of CO hydrogenation decreased significantly with time on stream with incorporation of phenylacetylene, while it was much less affected by addition of phenylacetylene with iron catalysts. As we noted before, deactivation of the F-T reactions with incorporation of alkynes is likely caused by occupation of active sites on the surface of F-T catalysts by dimerization products or deposited carbon. Since less dimerization and triple bond breakage were observed with iron catalysts than with cobalt catalysts, addition of long-chain alkynes caused less deactivation of the F-T synthesis with iron catalysts.

5.0 EFFECTS OF ACETYLENE ON F-T SYNTHESIS

5.1 INTRODUCTION

We have used long-chain alkynes, such as 1-hexyne and 4-phenyl-1-butyne as probes and obtained interesting results. However, our initial interest was in incorporation of acetylene, the first member of carbon-carbon triple bonded series. Acetylene, as a two carbon compound without an attached alkyl group, is a special case. Long chain terminal alkynes and alkenes are different than acetylene and ethylene since they have electric dipole moments, while acetylene and ethylene have a center of symmetry and therefore have a zero net dipole moment. It has been reported that ethylene initiates the F-T synthesis 10 to 40 times more easily than higher olefins (5). The only work with acetylene has been carried out by Russian scientists who introduced 1% of acetylene, labeled with ^{14}C into the F-T synthesis on fused iron catalyst at 150-190°C and high pressure (1500-3000 psi) in an effort to obtain higher alcohols (39). Acetylene as a probe, unlike that with long-chain alkynes, doesn't form higher molecular weight hydrocarbons by dimerization which leads to rapid catalyst deactivation. We used long-chain alkynes as probes to obtain preliminary results since carrying out experiments with acetylene presents safety problems. After careful consideration and reading of the literature on reactions of acetylene, we used a reaction system with 1% of acetylene addition which is below the explosive limits as described in Appendix C. In this chapter we show the effect of addition of acetylene to the F-T synthesis on cobalt and iron catalysts and compare the results to that of addition of ethylene. Rhodium has the catalytic capability of carrying out syngas reaction in which CO is added both associatively and dissociatively in various reactions. It was of interest to use acetylene as a probe in rhodium catalyzed reactions of syngas in one case.

5.2 EXPERIMENTAL

5.2.1 Catalyst preparation

Co (10 wt %) and Al_2O_3 (90wt %) was prepared by the same method as described in 3.1. The precipitated iron catalyst ($100Fe/4.71SiO_2/1.51K_2O$) and the fused iron catalyst (C-73) were obtained from Dr. Burt Davis, University of Kentucky. Copper, which can replace the hydrogen atoms in acetylene to form explosive acetylides, was not used as a promoter in these catalysts.

A supported rhodium catalyst was prepared by incipient-wetness impregnation of rhodium (III) chloride hydrate ($RhCl_3.nH_2O$) on vista B alumina which had been calcined at 500°C for 10 hours before the impregnation. Multiple impregnation steps for Rh were used due to the high metal content of the Rh catalyst. The composition of the Rh catalyst is Rh (5 wt %) and Al_2O_3 (95wt %). The Rh catalyst was dried for 10 hours in an oven with flowing air, followed by calcination at 573 K in air for 5 hours.

5.2.2 Reactions conditions

For cobalt catalysts, F-T reactions were carried out at temperatures of 180 and 220°C, pressures of 100, 300 and 700 psi, and a flow rate of 4.2 l/h. We used a mixture of gases which contains 1% of acetylene and has a prefixed H_2/CO ratio of 1. With long chain alkyne addition, we used reactant gases with a H_2 to CO ratio of 2 for cobalt catalysts. We examined effects of acetylene on F-T reactions with a H_2 to CO ratio of 2. Although the activities toward paraffins and olefins differed somewhat, similar effects of acetylene on F-T product distributions were obtained with a H_2 to CO ratio of 1 and 2.

For precipitated iron catalysts, the F-T reactions were carried out at temperatures ranging from 120 to 260°C, pressures of 100, 300 and 700 psi, a H_2 to CO ratio of 1, and a space velocity in the range of 4.2 l/h.

For fused iron catalysts, the F-T reactions were carried out at temperature of 180°C, pressure of 300 psi, a H_2 to CO ratio of 1, and a flow rate of 4.2 l/h.

For Rh catalysts, F-T reactions were carried out at temperature of 220°C, pressure of 100 psi, a H_2 to CO ratio of 2, and a flow rate of 4.2 l/h.

5.2.3 Addition of acetylene

We obtained a mixture of gases containing acetylene from Praxair; it had the following composition (mol): 1% acetylene, 10% Ar, 44.01% CO, and 44.99% H_2. This gas mixture was specially made for us. We chose 1% of acetylene based on safety considerations (Appendix C). Argon was used as an internal standard gas to calculate CO conversion.

After 20h TOS of base case F-T reactions, the reactant gases were switched to the mixture of gases with 1% of acetylene. Products were analyzed every three to five hours prior to and after the addition of acetylene to compare results of base case reactions and reactions with acetylene addition.

5.3 RESULTS AND DISCUSSION

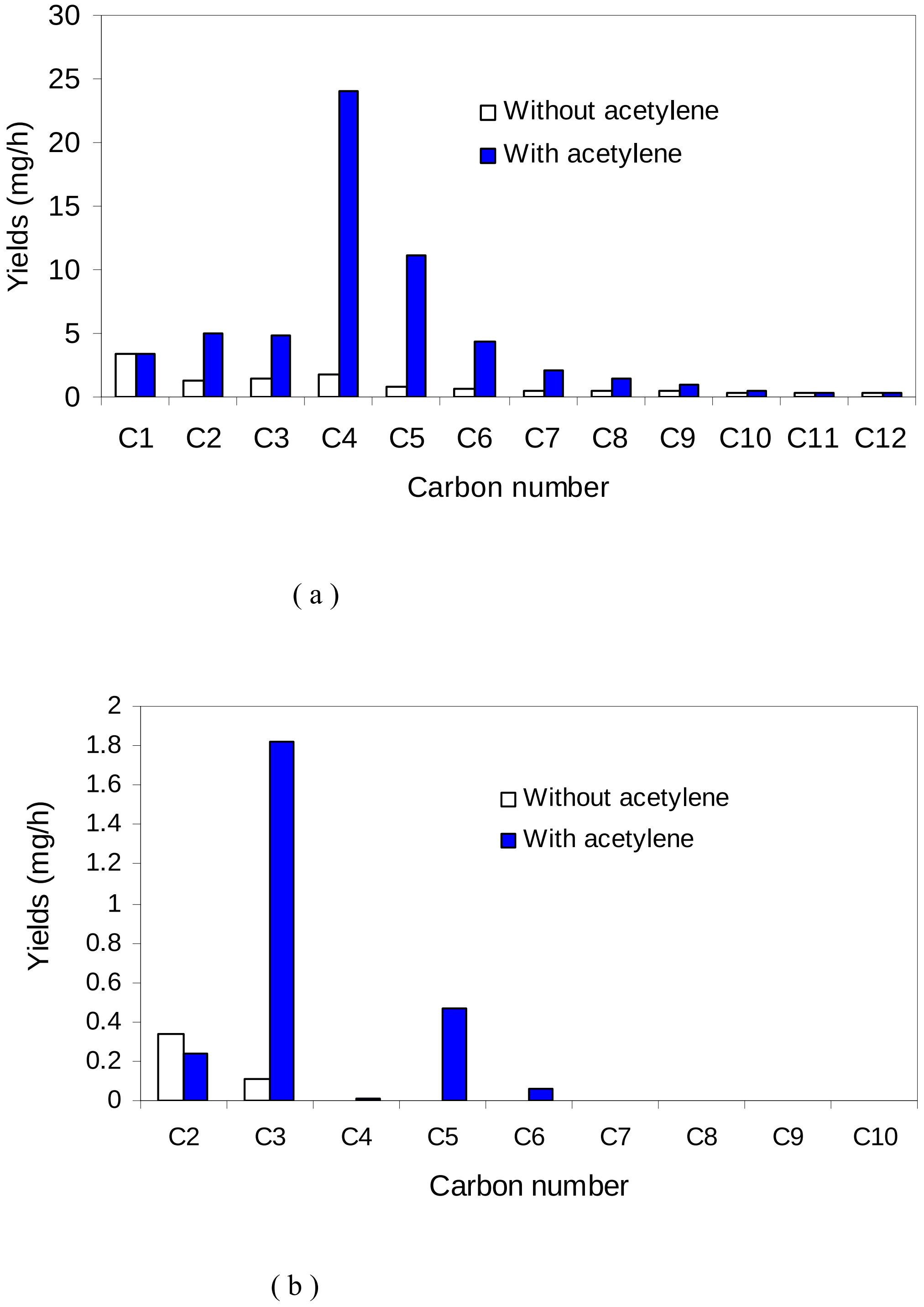
5.3.1 Incorporation of acetylene with cobalt catalysts

5.3.1.1 Product distribution without/with acetylene addition The F-T reactions were carried out with a cobalt catalyst at 180°C and 300psi with a CO to H_2 ratio of 1. Yields of hydrocarbon products from the base reaction and F-T synthesis with acetylene are shown in Figure 5.1 (a). Addition of acetylene caused an increase in the yields of C2+ hydrocarbons up to C10 hydrocarbons. The most significant products in the presence of acetylene were C4 hydrocarbons. We observed a peak of 2-butene in the GC-MS spectrum of F-T liquid products upon acetylene addition. This peak was absent in the products from base case reactions. 2-Butene arises from dimerization of acetylene.

Both products from base case reactions and from F-T reactions with acetylene follow ASF distribution and the presence of acetylene causes a decrease in alpha value from 0.74 to 0.65. Similar results with olefin incorporation have been reported by Patzlaff et al.(6, 120) They found that, when 1-hexene was added to a cobalt catalyst in the F-T synthesis, a relative increase of fractions past C7 declined strongly as the carbon number decreased “so that the distribution approaches that obtained without addition of 1-hexene within a few carbon numbers". If acetylene serves as a chain propagator, an increase in alpha value would be observed. The decrease in alpha value is consistent with acetylene acting only as a chain initiator. C1 monomers add stepwise onto C2 species formed by acetylene adsorption, in addition to the initiation of F-T reactions that normally take place at high temperatures in base case reactions.

We have reported that incorporation of long chain alkynes into the F-T synthesis on cobalt catalysts produced only oxygenates with one added carbon. Heptanal and 1-heptanol were formed with addition of 1-hexyne; 5-phenylpentanal and 5-phenyl-1-pentanol were produced with incorporation of 4-phenyl-1-butyne. Aldehydes are undoubtedly the primary products formed by a hydroformylation type of reaction; they are later hydrogenated to the corresponding alcohols. With acetylene, 1-propranol was increased greatly upon addition of acetylene as shown in Figure 5.1(b). 1-Pentanol was also increased due to a large amount of C4 unsaturated hydrocarbons from acetylene dimerization.

It's important to note that addition of acetylene resulted in formation of branched hydrocarbons; mostly 2-methylbutane, and 3-methylpentane, which were negligible when acetylene was absent (Figure 5.2). These branched products undoubtly originated from 2-butene. 2-Butene formed by acetylene dimerization was adsorbed on the catalyst surface with an internal carbon atom and the CH_2 groups inserted into the metal-carbon bond to form a branched product. It served as an additional initiator which allowed the detection of branched products. Unsaturated C4 hydrocarbons formed during F-T reactions with acetylene addition are more efficient initiators than butenes co-fed with syngas. Bell added 1-butene(15) and 2-butene (16) into syngas over a Ru/SiO_2 catalyst and observed that about 4% of 1-butene and less than 0.1% of 2-butene were converted to C1-C3 and C5+ hydrocarbons. Adsorption of co-fed olefins was necessary for



(a)

(b)

Figure 5.1 Product distributions of incorporation of 1% of acetylene on a cobalt catalyst

((a) hydrocarbons (b) oxygenates; $10Co/90Al_2O_3$, 300psi, 180°C, $H_2/CO=1$)

further catalytic reactions, but CO inhibits the adsorption of olefins, leading to inactivity of added olefins. Since in-situ formed C4 hydrocarbons from acetylene dimerization have already been adsorbed on surface of F-T catalysts, competition only exists between chain propagation and termination.

In summary, the following reactions of co-fed alkynes may occur under F-T conditions: hydrogenation of alkynes to olefins and to paraffins, dimerization, and incorporation into F-T products. Schulz found that hydrogenation was the fastest of all reactions of added olefins with cobalt catalysts (5). Under our reaction conditions, incorporation is the most important reaction of conversions of the added acetylene; as much as 58% of added acetylene was incorporated into F-T products. Selectivity to different reactions of acetylene and 1-hexyne with a Co catalyst at 220°C are listed in Table 5.1. Iglesia et al.(113) studied olefin readsorption by adding C_2-C_{10} olefins to CO hydrogenation reactions with Co and Ru catalysts; ethylene was found to be incorporated more easily than long chain olefins. Table 5.1 shows that acetylene is much more readily incorporated into F-T products than are long chain alkynes. Schulz et al.(5) noted that incorporation of ethylene is more than an order of magnitude higher than propylene, which shows the special role of the two-carbon entity. The ready incorporation of ethylene has been used to explain the extremely low yields of C2 hydrocarbons among F-T products.

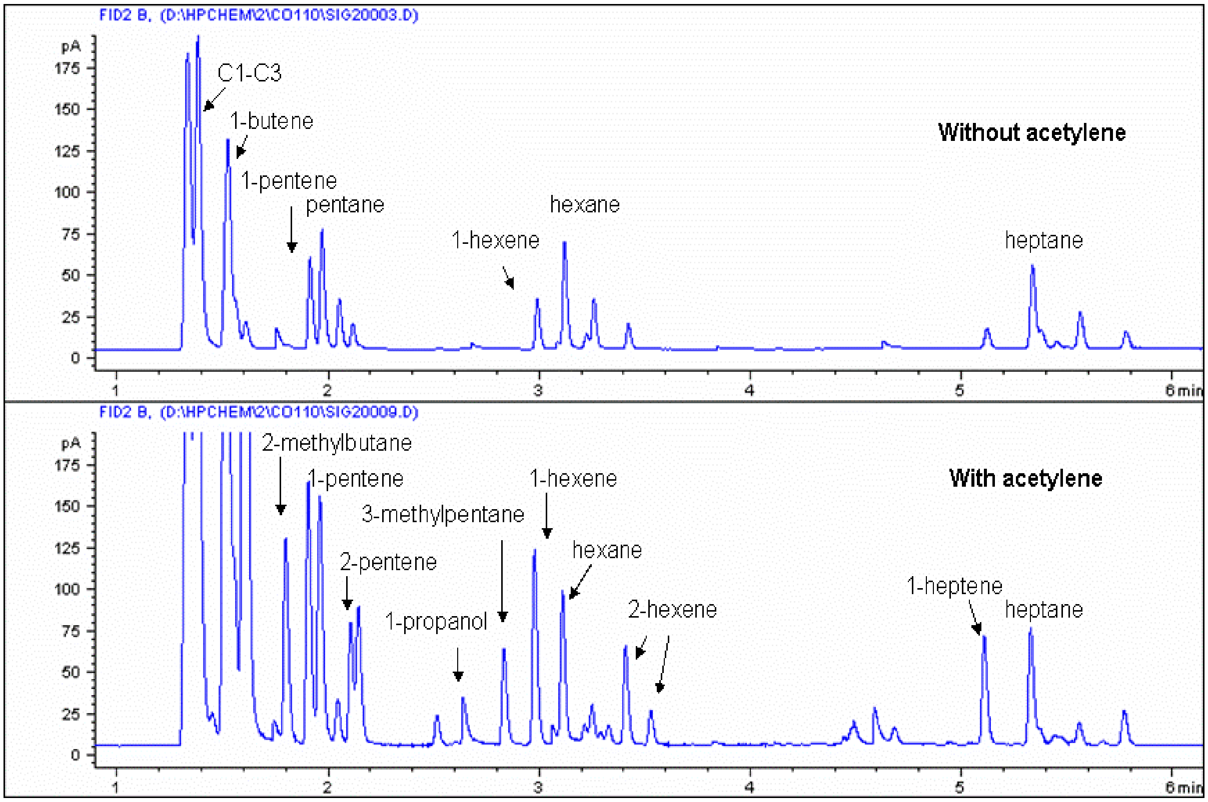


Figure 5.2 GC analysis of F-T Products with incorporation of acetylene on a cobalt catalyst

($10Co/90Al_2O_3$, 300psi, 180C, $H_2/CO=1$, 1% acetylene)

Table 5.1 Reactions of acetylene compared with a long-chain alkyne during F-T synthesis on a cobalt catalyst at 220°C

Selectivity (%)	Acetylene	1-Hexyne
Hydrogenation	14	53
Dimerization	28	29
Incorporation	58	18

5.3.1.2 Effects of temperature on acetylene incorporation Effects of temperature on acetylene incorporation were investigated at 120, 180 and 220^{o}C, with 1% of acetylene addition. Reaction pressure and gas feed composition were kept constant at 300psi and H_2/CO of 1, respectively. Yields of products from base case reactions were enhanced significantly when the temperature was increased from 120 to 220^{o}C (Appendix B). Yields of hydrocarbon products with addition of acetylene are shown in Figure 5.3. Increase of temperature from 120 to 220^{o}C led to increases in the yields of hydrocarbon products. A large increase in methane production was consistent with the catalytic property of Co catalysts which tend to yield a large amount of methane at higher temperatures. However, F-T reactions with acetylene incorporation at 120^{o}C yielded the highest amount of C2 hydrocarbons. About 92% of C2 hydrocarbons was ethylene at 120^{o}C, indicating that reduction of acetylene to ethylene was easier, compared to hydrogenation of ethylene to ethane and incorporation of acetylene to C3+ hydrocarbons by F-T reactions at this temperature.

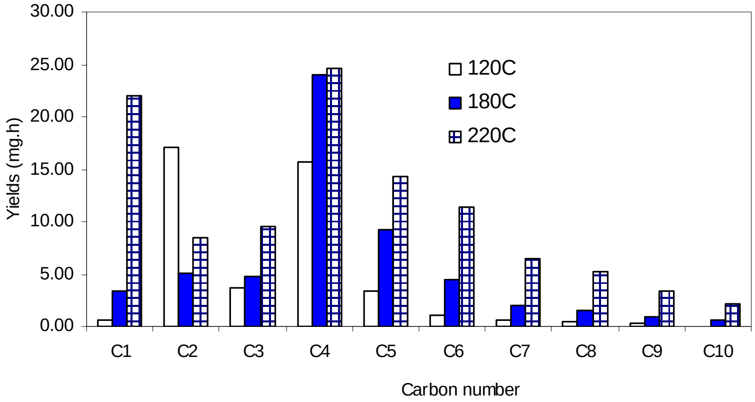


Figure 5.3 F-T hydrocarbon product distribution with 1% acetylene on a cobalt catalyst

(10Co/90Al_2O_3, P=300 psi, H_2/CO=1)

At 120°C, only 32% of added acetylene was incorporated into C3+ hydrocarbons, due to low reaction rate of F-T synthesis with cobalt catalysts at this temperature. Incorporation of acetylene was increased to 56% when temperature was increased from 120 to 180°C. A similar extent of incorporation of acetylene into F-T reactions was observed at 180 and 220°C (Table 5.2).

Table 5.2 Selectivity to reactions of 1% of acetylene with CO/H_2 at different temperatures

T (°C)	Hydrogenation (%)	Dimerization (%)	Incorporation (%)
120	40	28	32
180	8	36	56
220	14	27	59

$10Co/90Al_2O_3$, P=300 psi, $H_2/CO=1$

5.3.1.3 Effects of pressure on acetylene incorporation The F-T reactions without and with 1% acetylene addition were conducted at 100, 300, 700psi to investigate the effect of pressure on product distribution. The reaction temperature and gas feed composition were kept constant at 180°C and $H_2/CO=1$, respectively. The rate of base case F-T reaction was increased significantly with pressure through an increase in the concentration of reactant gases (Appendix B). Yields of hydrocarbon products with addition of acetylene are shown in Figure 5.4.

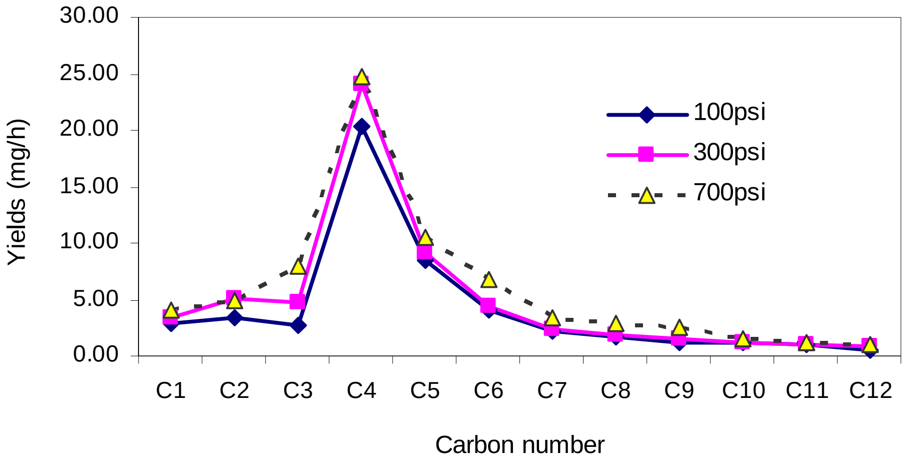


Figure 5.4 F-T hydrocarbon product distribution with addition of 1% acetylene on a cobalt catalyst

($10Co/90Al_2O_3$, 180°C, $H_2/CO=1$)

Pressure has only a small effect on yields of hydrocarbon products in the presence of added acetylene. The major part of the products is initiated by acetylene. Initiation of acetylene is fast and not affected significantly by pressure. Pressure has very little effect on selectivity to different reactions of acetylene (hydrogenation, dimerization and incorporation) under F-T reaction conditions (Figure 5.5).

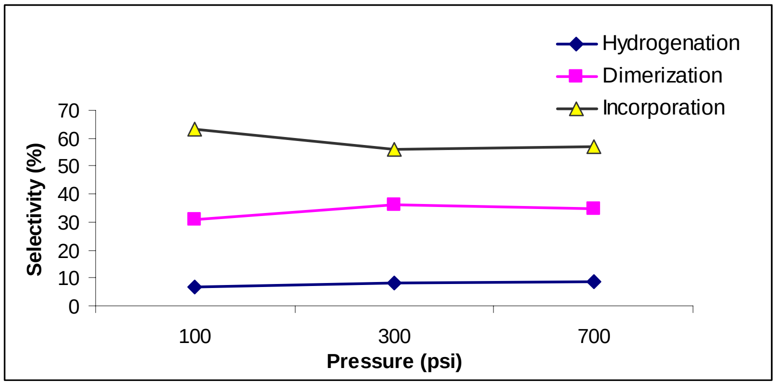


Figure 5.5 Reactions of 1% of acetylene with CO/H_2 on a cobalt catalyst

($0Co/90Al_2O_3$, 180°C, $H_2/CO=1$)

5.3.1.4 Effects of acetylene incorporation on F-T deactivation In section 3.3.1.4, we found that yields of C7 hydrocarbons decreased with time-on-stream in the presence of 1-hexyne. The formation of a large amount of C12 hydrocarbons by dimerization of 1-hexyne is a possible reason for this deactivation of F-T reactions. Low weight hydrocarbons (C4) are produced by dimerization of acetylene, so that acetylene should have a smaller effect on activity of F-T reactions than does 1-hexyne. This agrees with our results of F-T synthesis with addition of acetylene as shown in Figure 5.6. Acetylene was added after 20 hours of base case reactions. For simplicity, only yields of C3 hydrocarbons are shown. C3 hydrocarbons increased about three times after addition of acetylene, and yield of C3 hydrocarbons was stable up to 50 hours of TOS.

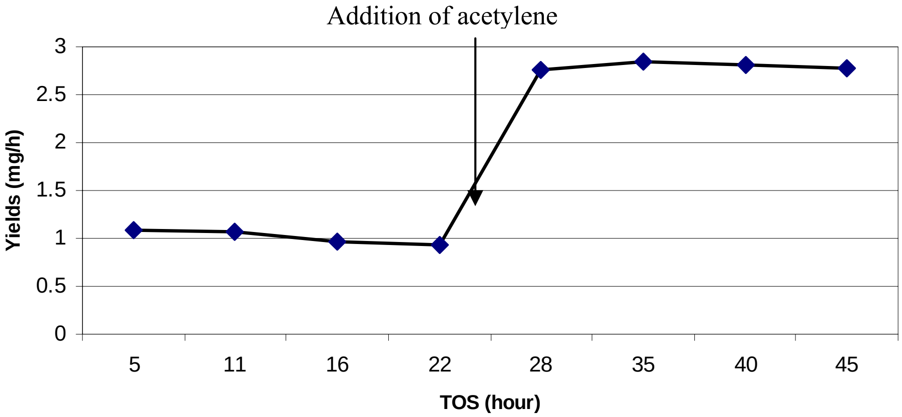


Figure 5.6 Yield of C3 hydrocarbons with TOS on a cobalt catalyst

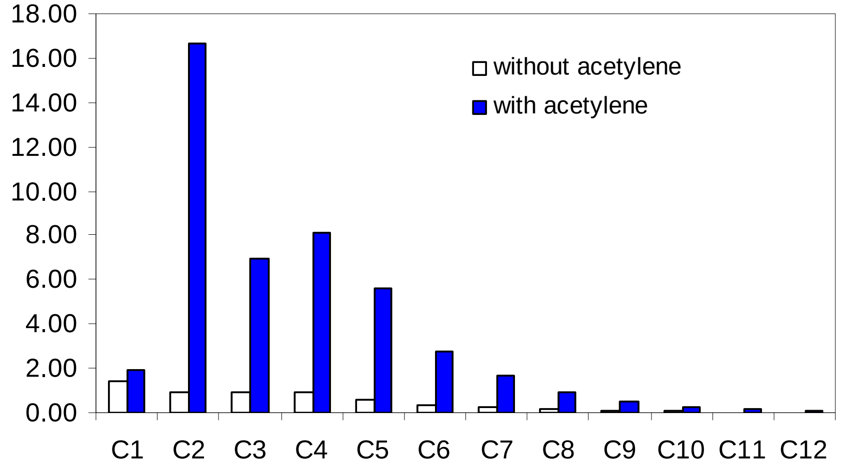
(10Co/90Al_2O_3, 100psi, 180°C, H_2/CO=1, 1% acetylene)

5.3.2 Incorporation of acetylene with a precipitated iron catalyst

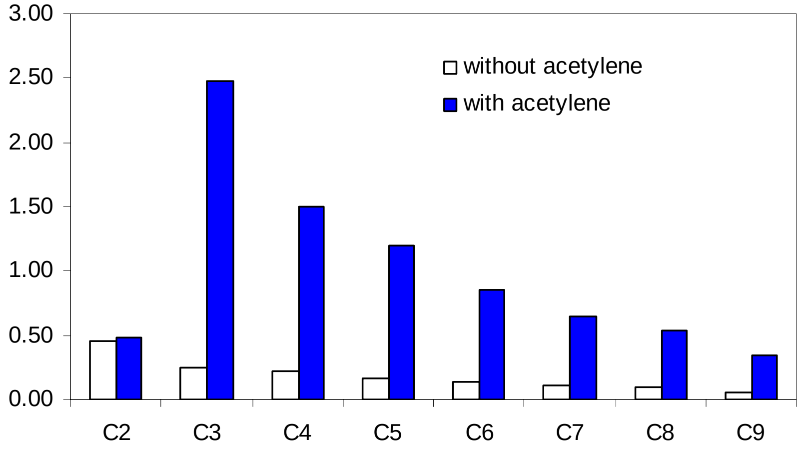
5.3.2.1 Product distribution without/with acetylene addition Effects of acetylene on the F-T reactions were investigated with a precipitated iron catalyst at the same temperature (180^{o}C) and pressure (300psi) as used with cobalt catalysts.

Yields of hydrocarbon products from F-T reactions in the absence and presence of 1% of acetylene on an iron catalyst are shown in Figure 5.7. As with the F-T reactions with cobalt catalysts, addition of acetylene with iron catalysts enhanced formation rates of C2+ products while the yield of methane was not changed upon acetylene addition. As previously noted, 2-butene formed from dimerization of acetylene initiates the carbon chain, producing branched products. Unlike cobalt catalysts, which show great activity for dimerization of acetylene, hydrogenation is a preferred reaction with iron catalysts. About 30% of added acetylene was hydrogenated to ethylene and to ethane. Not surprisingly, smaller amounts of branched hydrocarbons initiated by 2-butene are produced from iron compared to those from cobalt catalysts.

One striking difference between iron and cobalt catalysts is in the distribution of oxygenates. On a cobalt catalyst only C3 and C5 oxygenates increase to a significant degree with addition of acetylene due to high concentration of C2 and C4 unsaturated hydrocarbons in the reactor; oxygenate formation on iron catalysts is not so limited. With acetylene large amounts of C2+ oxygenates were detected by online GC. The oxygenated product distributions without and with acetylene are plotted as log(Wn/n) against n in Figure 5.8. (Wn: weight fraction, n: carbon number). Figure 5.8 indicates that with iron catalysts, oxygenates under either base F-T synthesis



(a)



(b)

Figure 5.7 Product distributions of incorporation of acetylene on an iron catalyst

((a) hydrocarbons (b) oxygenates; 100Fe/4.4Si/1.25K, T=180°C, P=300psi, H_2/CO=1, 1% acetylene) or the F-T synthesis with acetylene follow the ASF distribution, just as with hydrocarbons. With iron catalysts, addition of acetylene results in an increase in oxygenates as well as hydrocarbons, an indication that oxygenate formation involves growing hydrocarbon chains. Oxygenated products with iron catalysts have been suggested to be formed through oxygenated intermediates(121). However, the increase of yields of oxygenated products with addition of acetylene and their ASF distribution indicate that formation of oxygenates follow the same chain initiation and propagation steps as formation of hydrocarbons. The only difference is the chain termination. Oxygenates are formed via CO insertion. Once CO is inserted, chain growth is terminated, leading to desorption of oxygenated products.

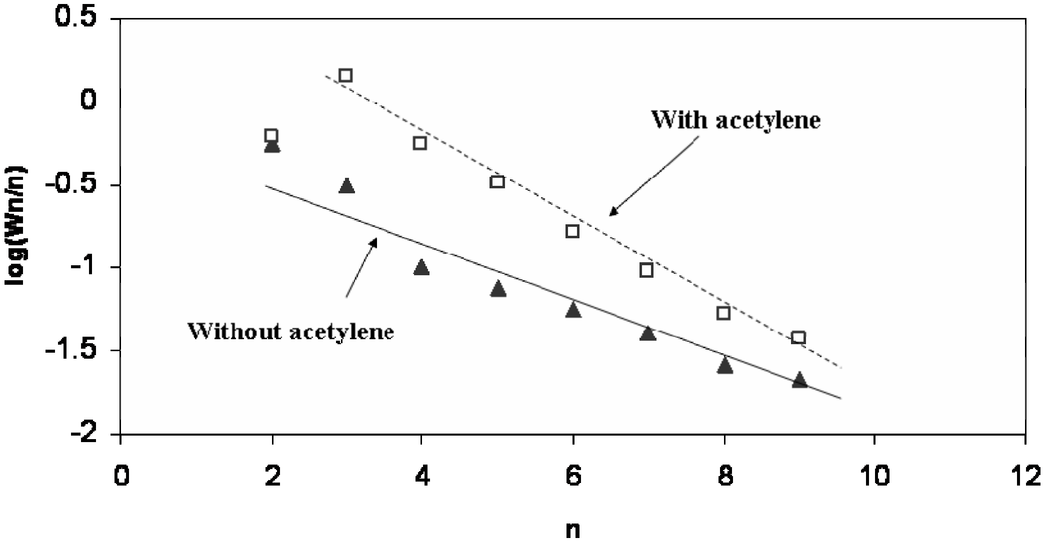


Figure 5.8 Chain length distributions of oxygenated products without/with 1% of acetylene addition

(100Fe/4.4Si/1.25K, T=180°C, P=300psi, H_2/CO=1)

5.3.2.2 Effects of temperature on acetylene incorporation Effects of temperature on acetylene incorporation with an iron catalyst were investigated at 120~260°C with 1% of acetylene addition. Reaction pressures and gas feed compositions were kept constant at 300psi and $H_2/CO=1$, respectively. Incorporation of acetylene into F-T reactions was 15% at 120°C, about 80% of acetylene was hydrogenated to ethylene and 6% of acetylene dimerized to C4 hydrocarbons (Appendix B). When reaction temperature was increased from 180 to 260°C, we found that yields of hydrocarbon products increased with an increase in reaction temperature (Figure 5.9), while incorporation of acetylene did not vary much over this temperature range (Table 5.3). Enhancement of hydrocarbon production was caused by greater activity of CO hydrogenation at higher temperature. Increase of temperature enhanced CO conversion from 3.6% at 180°C, to 11.7% at 220°C and 18.9 at 260°C in the presence of acetylene.

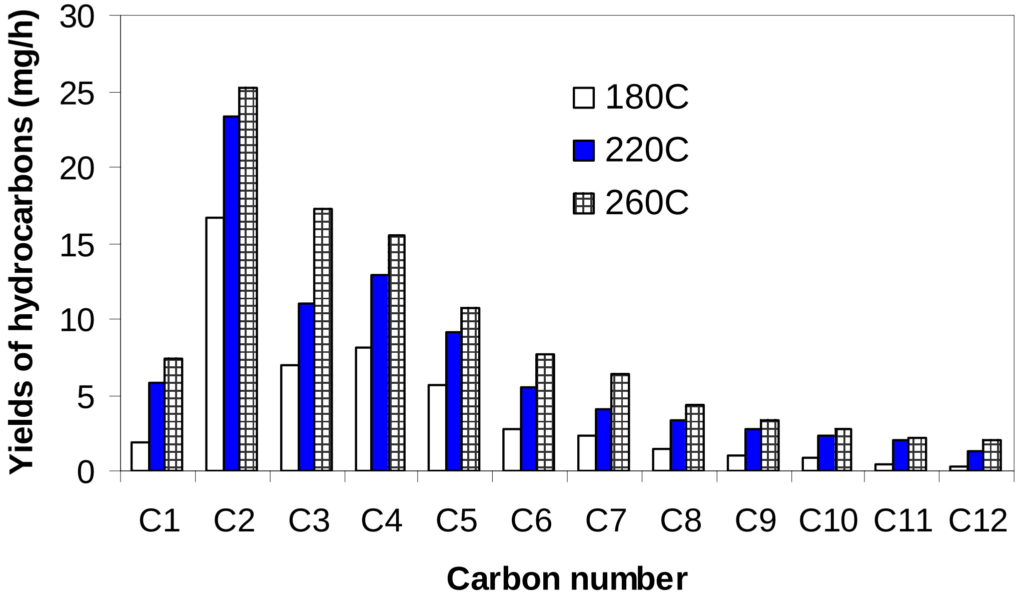


Figure 5.9 Hydrocarbon product distributions at different temperatures with addition of 1% acetylene

(100Fe/4.4Si/1.25K, P=300psi, $H_2/CO=1$, 1% acetylene)

Table 5.3 Reactions of acetylene during F-T synthesis on an iron catalyst at different temperatures

T (^oC)	Hydrogenation (%)	Dimerization (%)	Incorporation (%)
180	30	7	63
220	33	7	60
260	34	5	61

100Fe/4.4Si/1.25K, 300psi, $H_2/CO=1$, 1% acetylene

At 120°C, only a small amount of C3 and C4 oxygenates were produced. When the temperature was increased from 180 to 220°C, yields of oxygenated products were increased as shown in Figure 5.10. However, the ratio of oxygenated products to hydrocarbons was about 17% at both 180 to 220°C. It was reduced to 11% at 260°C.

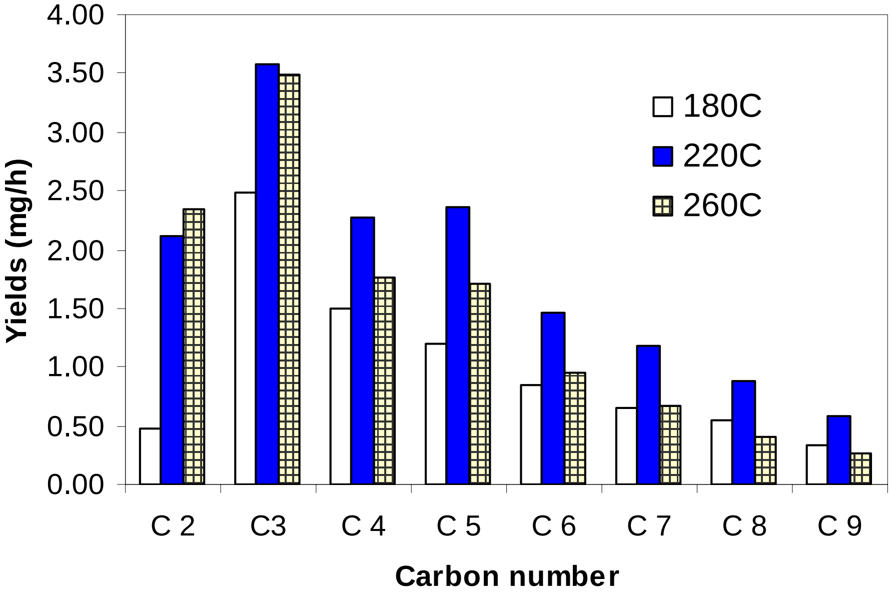


Figure 5.10 Oxygenated product distributions at different temperatures with addition of 1% acetylene

(100Fe/4.4Si/1.25K,P=300psi, H_2/CO=1, 1% acetylene)

The temperature dependence of the reaction rate on the Fe catalyst was obtained from an Arrhenius plot of CO conversion data at temperature ranging from 120 to 260°C, a H_2/CO ratio of 1 and a flow rate of 4.2 l/h. From Figure 5.11, a linear correlation was found and from the Arrhenius equation

K = A * exp (-Ea / R * T)

where K is the rate coefficient, A is a constant, Ea is the activation energy, R is the universal gas constant with a value of 8.314 x 10^{-3} kJ $mol^{-1}K^{-1}$, and T is the temperature in degrees Kelvin.

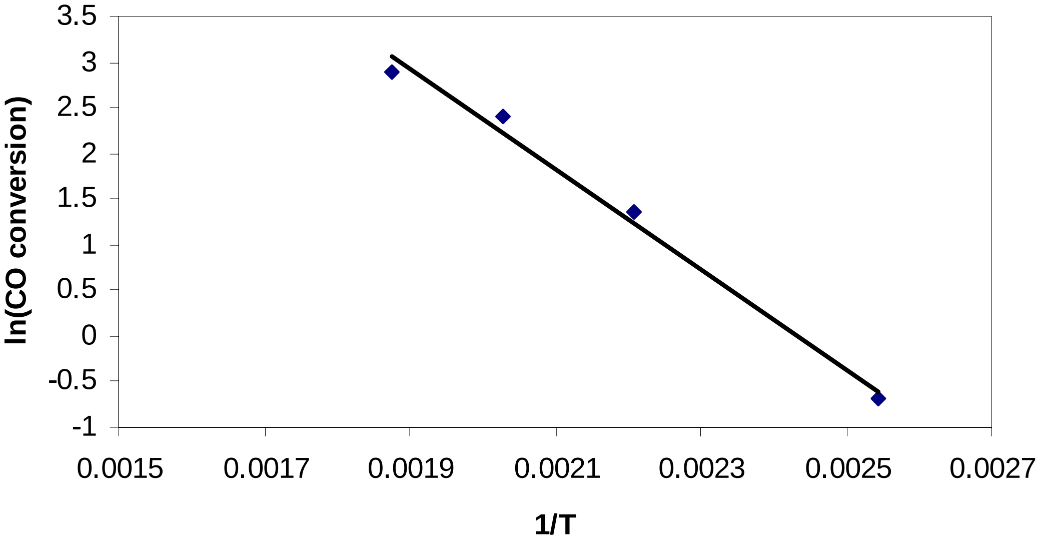


Figure 5.11 Arrhenius plot of CO conversion over an iron

(100Fe/4.4Si/1.25K, P=300psi, H_2/CO=1)

The calculated apparent activation energy is 11 kcal/mol. Dry reported the value of the activation energy is 6 kcal/mol for the high temperature fluidized bed and 15 kcal/mol for the low temperature fixed-bed processes. We used a fixed-bed reactor at 120 to 260°C temperature range and our activation energy is lower than reported value of Ea. However, the difference might be due to catalyst formulation and structure.

5.3.2.3 Effects of pressure on acetylene incorporation To explore the effect of pressure on acetylene initiated F-T reactions over an iron catalyst, we conducted experiments at 100, 300 and 700psi with addition of 1% of acetylene. Reaction temperature and gas feed composition were kept constant at 180°C and H_2/CO=1, respectively. Yields of hydrocarbon products are presented in Figure 5.12. The olefinic content of the products decreased with increasing pressure. Hydrogenation of acetylene to total C_2 hydrocarbons, ethylene and ethane, is not affected by increase of pressure, but the ratio of ethylene to ethane was reduced from 5.3 to 2.6 when the pressure is increased from 100psi to 300psi. The rate of formation of hydrocarbon products increased with pressure through an increase in the concentration of reactant gases. Incorporation of acetylene was in the range of 60% to 65% at the different pressures used.

To find out optimum reaction conditions at which acetylene is most easily incorporated into the products using an iron catalyst, we explored F-T synthesis with acetylene addition at different temperatures and pressures. In a previous section 5.3.2.2, we showed that temperature has little effect on the extent of incorporation of acetylene with Fe and Co catalysts. Conversions of acetylene during F-T reactions at different pressures are shown in Table 5.4. The differences between selectivity of acetylene conversions over iron at various pressures are also not significant. It seems that hydrogenation and dimerization are competitive reactions of acetylene. Selectivity to these two reactions is essentially dependent on whether the catalyst is iron or cobalt. Hydrogenation is the main reaction with iron; dimerization is the main reaction with cobalt catalysts. Incorporation is the main reaction on both iron and cobalt catalysts, in contrast to ethylene addition.

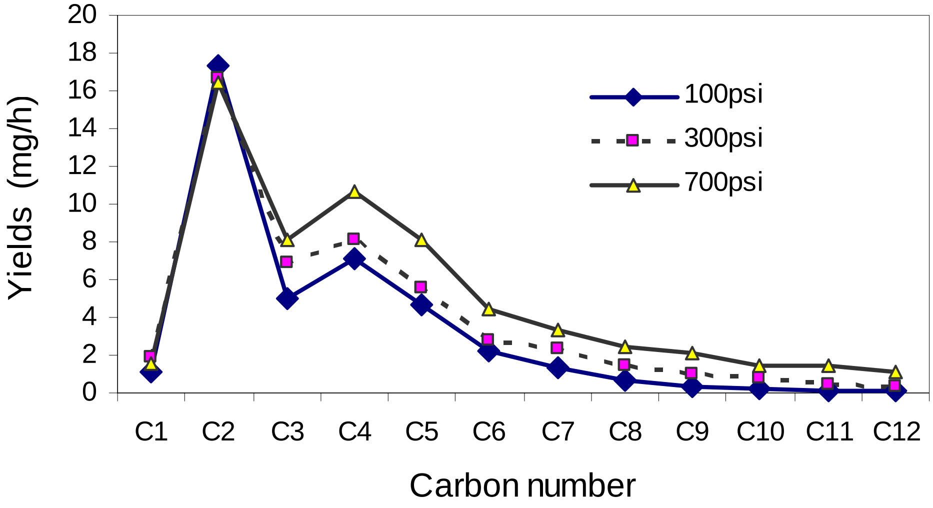


Figure 5.12 Hydrocarbon product distributions at different pressures with addition of 1% acetylene

(100Fe/4.4Si/1.25K, T=180^{o}C, H_2/CO=1, 1% acetylene)

Table 5.4 Reactions of acetylene during F-T synthesis on an iron catalyst at different pressures

P (psi)	Hydrogenation (%)	Dimerization (%)	Incorporation (%)
100	33	6	61
300	33	4	63
700	31	5	64

100Fe/4.4Si/1.25K, 180^{o}C, H_2/CO=1, 1% acetylene

Pressure has a more significant effect on formation of oxygenated products than hydrocarbons. An increase of pressure leads to an enhancement of oxygenated products (Figure 5.13). Only 11% of oxygenated products with carbon number less than 8 were produced on iron catalysts at 100psi; about 17% oxygenates were formed at 300psi. When the pressure was increased to 700psi, oxygenates could be as high as 23% of total products. This trend of increase in oxygenates with pressure is consistent with results obtained by Russian scientists. They carried out F-T synthesis with 1% of acetylene over a fused iron catalyst at high pressure (1500-3000 psi), and over 80% of their products were alcohols(40). The major components of our oxygenated products with iron catalysts were alcohols and aldehydes; a small amount of ketones was produced as well.

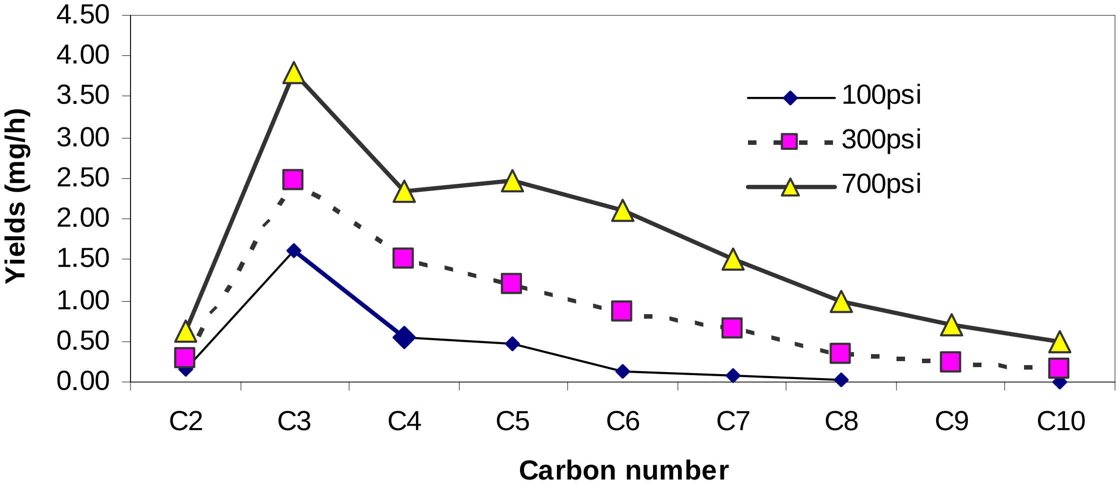


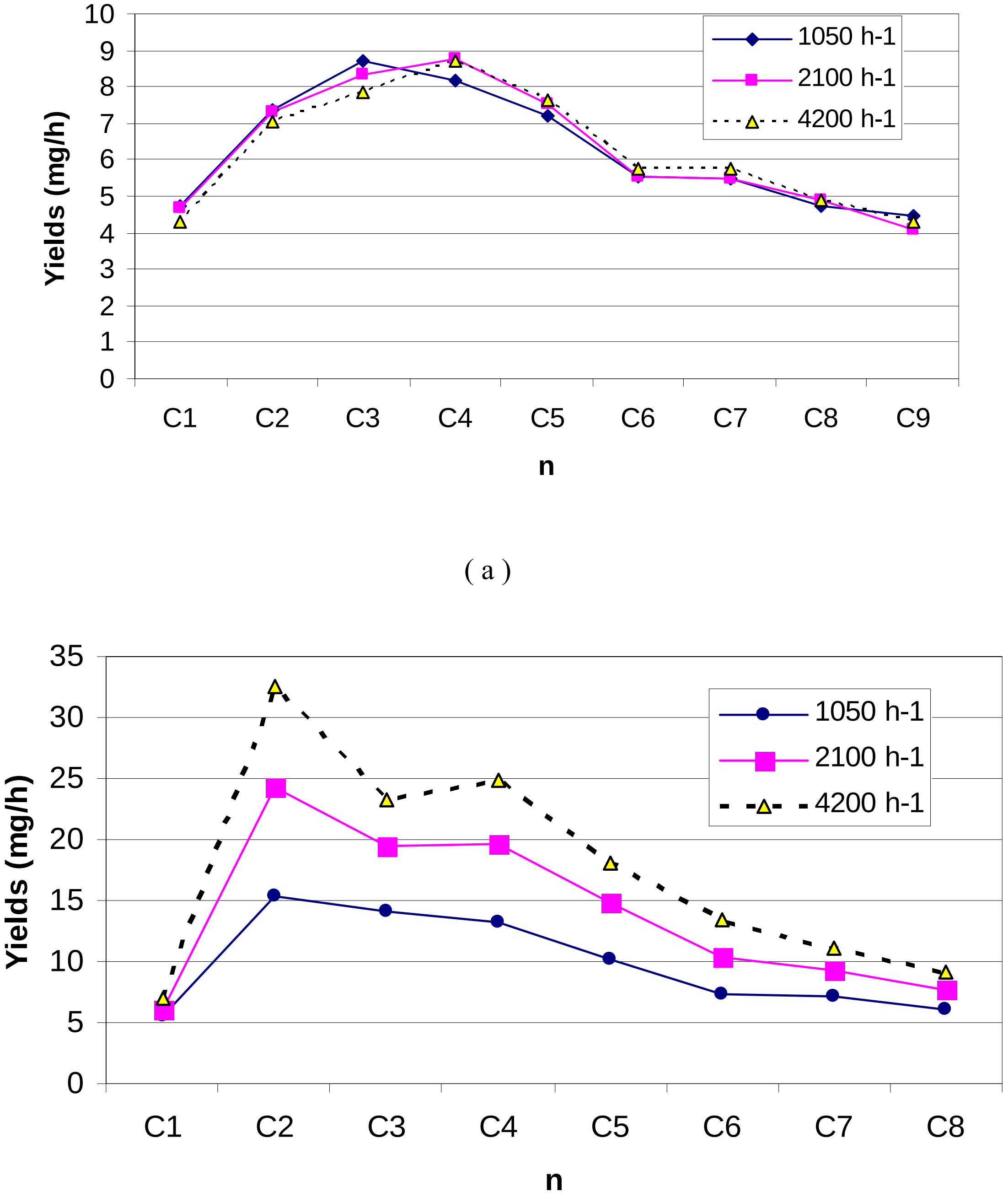
Figure 5.13 Oxygenated product distributions at different pressures with addition of 1% acetylene

(100Fe/4.4Si/1.25K,T=180°C, H_2/CO=1, 1% acetylene)

5.3.2.4 Effect of space velocity on acetylene incorporation The flow rate of reactant gases was varied to investigate effects of space velocity on the rate of base case reactions (Figure 5.14 (a)) and on the rate of F-T reactions with acetylene addition (Figure 5.14 (b)). The H_2/CO ratio was kept constant at one. At low flow rates, the residence times of the gases on the catalyst increased so that CO conversion increased. However, increase in space velocity had little effect on the yield of hydrocarbon products for base case reactions (Figure 5.14 (a)). Hydrocarbon formation rate was not changed with increase in the flow rate of synthesis gas, since the higher conversion is offset by the lower amount of synthesis gas passed over the catalyst per hour.

In Figure 5.14 (b), under the same reaction conditions, the rate of methane formation in the presence of acetylene is not changed with variation of space velocity of reactant gases, while the rates of formation of C2+ hydrocarbons are proportional to the flow rate of the reactant gases. Interestingly, we observed a similar product distribution at various flow rates of synthesis gas in the absence of acetylene, and an enhanced product formation rate with increase in flow rate with participation of acetylene. This indicates that acetylene initiates F-T reactions more rapidly than CO hydrogenation.

Similar to effects of temperature and pressure, variation of space velocities of reactant gases did not affect the level of incorporation of acetylene (Table 5.5).



(a)

(b)

Figure 5.14 F-T product distributions at different space velocity

((a) without acetylene (b) with acetylene; 100Fe/4.4Si/1.25K, T=220°C, P=300psi, H_2/CO=1, 1% acetylene)

Table 5.5 Reactions of acetylene during F-T synthesis on an iron catalyst at different flow rates

Flow rate (h^{-1})	Hydrogenation (%)	Dimerization (%)	Incorporation (%)
1050	33	7	60
2010	34	8	58
4020	33	7	60

(100Fe/4.4Si/1.25K, 220°C, H_2/CO=1, 1% acetylene)

The main oxygenated products are normal alcohols from the F-T synthesis in the absence and in the presence of acetylene. Interestingly, at low contact time, alcohols are reduced, and aldehydes are increased. This can be clearly shown by 1-butanol/butanal ratio as a function of contact time in Table 5.6. 1-Butanol/butanal ratio was reduced when residence time of reactant gases was increased in the absence and presence of acetylene.

Table 5.6 1-Butanol/butanal ratio as a function of contact time in the F-T synthesis without/with acetylene

Space velocity (h^{-1})	Time of Contact (seconds)	1-butanol/butanal ratio (without acetylene)	1-butanol/butanal ratio (with acetylene)
1050	3.4	15.1	18.0
2100	1.7	7.5	6.0
4200	0.9	5.9	4

Increase of 1-butanol/butanal ratio with contact time suggests that the primary oxygenated products of F-T synthesis are aldehydes, while alcohols are formed by successive hydrogenation of aldehydes which is active at high residence time of synthesis gas.

5.3.3 Incorporation of acetylene with a fused iron catalyst

Russian researchers used 1% acetylene as the third reactant in CO hydrogenation over a fused iron catalyst at 150-190°C and high pressure (1500-3000 psi)(40). Over 80% of their products were reported to be alcohols; both the reaction rate and selectivity to alcohols were increased in the presence of acetylene. We carried out a few experiments on the incorporation of acetylene at 180°C and 700psi on a fused iron (C-73) catalyst. Our results were similar to those obtained by the Russian researchers; an increase in the yield of products from 8 mg/h to 58 mg/h was obtained upon acetylene addition, but our primary products were hydrocarbons, rather than alcohols. Addition of acetylene in our experiment did not lead to an increase in selectivity to oxygenate. Production distributions of hydrocarbons and oxygenates were similar to what we reported in section 5.3.2 with a precipitated iron catalyst. The different results between Russian workers' and our results may be caused by higher pressure they used and different composition of the catalysts. Hydrocarbons were main products of acetylene initiated F-T reactions on a fused iron catalyst, although more oxygenates are produced with fused iron than with precipitated iron catalysts. About 30 wt % of the total products are oxygenates with higher alpha value of 0.75.

5.3.4 Incorporation of acetylene with a rhodium catalyst

Rhodium catalysts are useful in converting syngas to alcohols. It’s interesting to investigate the effect of acetylene incorporation on CO hydrogenation on a rhodium catalyst. Product distribution of CO hydrogenation with acetylene over a Rh catalyst at 220^{o}C and 100psi is shown in Figure 5.15. In contrast to Fe and Co catalysts, only 15% of acetylene is incorporated into higher molecular weight hydrocarbons. The extent of incorporation of acetylene was decreased by fewer C1 monomers produced by CO dissociation on the surface of Rh catalyst. Dimerization of acetylene to C4 hydrocarbons (65%) is extremely active with Rh catalyst. Interestingly, selectivity to dimerization of acetylene and CO dissociation ability follow opposite trend for the three catalysts we have tested: Co, Fe and Rh. Yield of C4 hydrocarbons is the lowest with iron catalyst, on which CO dissociates most easily. Rh has the catalytic capability of carrying out syngas reaction in which CO is adsorbed both associatively and dissociatively, while Rh produced the greatest amount of C4 products. CO and acetylene compete for active sites of catalytic surface. Since CO adsorption is weaker on Rh, more active sites are occupied by acetylene, leading to more chances to form dimers.

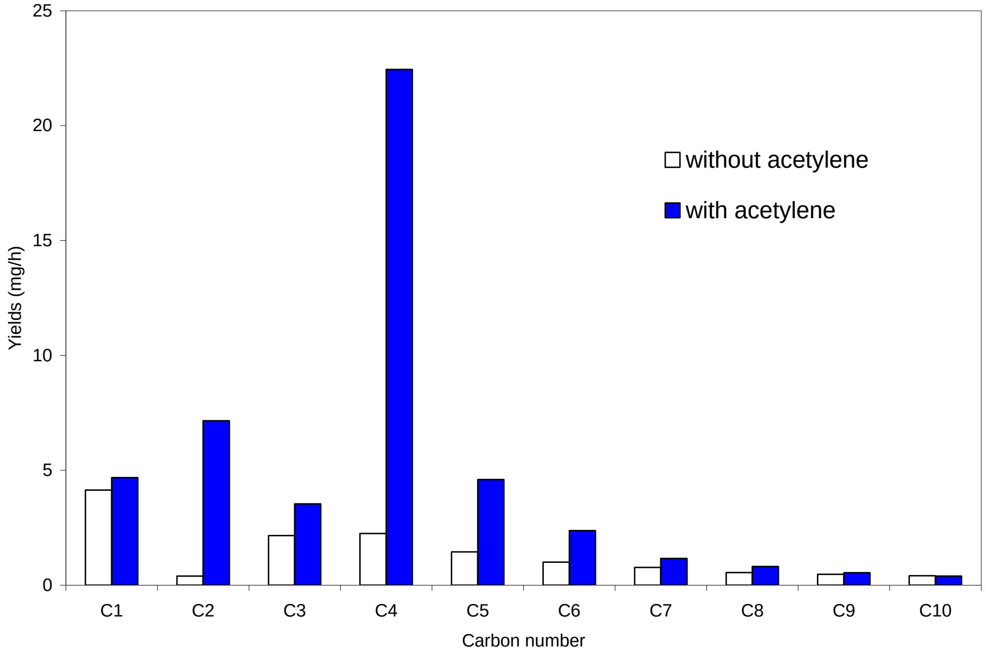


Figure 5.15 Yields of F-T hydrocarbon products without/with 1% of acetylene

(5Rh/95Al_2O_3, T=220°C, P=100psi, H_2/CO=2)

In the absence of acetylene, a large amount of ethanol was produced from the CO hydrogenation reaction. With incorporation of acetylene, the amount of 1-propanol was increased greatly, while ethanol was not affected (Figure 5.16). This indicates that 1-propanol was produced from different reactions than F-T reactions. Similar to reactions of acetylene with Co catalyst, 1-propanol was formed by a hydroformylation type reaction. Yield of ethanol with Rh was much greater than with Co.

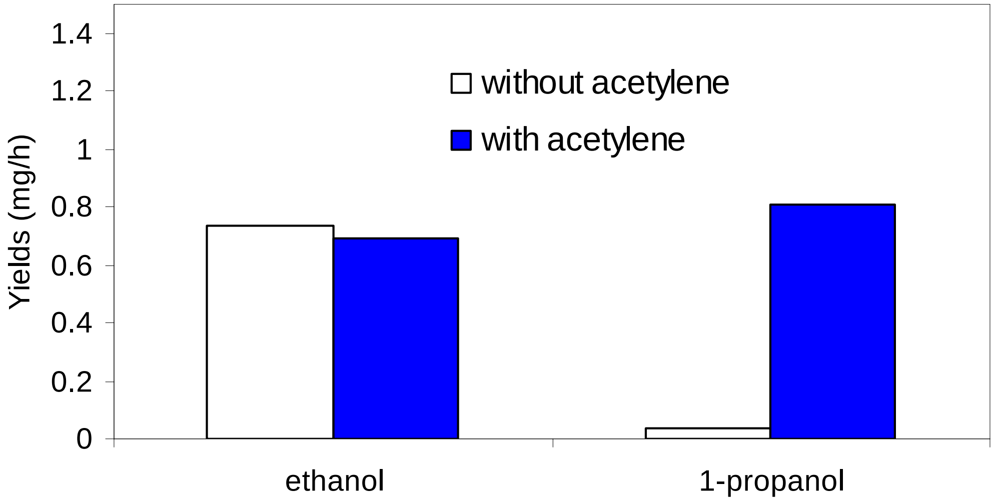


Figure 5.16 Yields of F-T oxygenated products without/with 1% of acetylene

($5Rh/95Al_2O_3$, T=220°C, P=100psi, $H_2/CO=2$)

5.4 CONCLUSIONS

F-T synthesis with acetylene as a probe was conducted over both cobalt and iron catalysts. There are several interesting aspects of the results of incorporation of acetylene into F-T reactions. For iron and cobalt catalysts, incorporation is the predominant reaction of acetylene, while hydrogenation is a favored reaction for co-fed ethylene under F-T conditions. Acetylene is incorporated into F-T reactions much more effectively than are higher acetylenes, similar to results reported with olefin additions. Selectivity to hydrogenation or dimerization of acetylene is more strongly dependent on the catalyst than on reaction conditions. For iron catalysts, hydrogenation is a favored reaction, while for cobalt catalyst dimerization is favored.

Like long-chain alkynes, acetylene serves mainly as a chain initiator which can be supported by the decrease of alpha value upon addition of acetylene. Chain initiation may be the slowest step in base case reactions; addition of acetylene increases the reaction rate by increasing the rate of initiation. Addition of acetylene increases the degree of branching of F-T products, caused chiefly by 2-butene formed by acetylene dimerization reinitiated secondary reactions.

In the presence of acetylene, oxygenates are formed by different mechanisms on cobalt and iron catalysts. Addition of acetylene using cobalt yields only oxygenates with the next higher carbon number via hydroformylation. Addition of acetylene using iron increases yields of a series of oxygenates, which follows ASF distribution, by F-T reactions. Major components of oxygenated products from F-T synthesis are alcohols; the aldehyde/ alcohol ratio is increased with decrease in contact time. It is possibly that the primary oxygenated products of F-T synthesis are aldehydes, and alcohols are secondary products formed by successive hydrogenation of aldehydes.

Incorporation of acetylene with cobalt and iron catalysts is higher than that with rhodium catalysts, indicating that CO dissociation is necessary to provide C1 monomers for chain growth.

6.0 DISCUSSION

The Fischer-Tropsch (F-T) process produces liquid hydrocarbons from synthesis gas; it is a developing option for the environmentally clean production of fuels and chemicals from coal or from natural gas. In the U.S. coal will probably play an expanding role in the coming years. Coal reserves are large while natural gas is expensive and in short supply.

There is a vast literature on the F-T synthesis including hundreds of patents on the process. Interest is now at an all-time high, due to developments to convert stranded natural gas in the Near East to diesel fuel as well as to gasoline. The mechanism of the F-T is very complex and, although various publications often differ in their findings and postulations as to the principal issues involved, there are some areas of general agreement: cobalt and iron are the catalysts of commercial interest and chain growth occurs by addition of C1 species to a growing chain.

Research on the F-T synthesis involves many aspects: catalyst development (compositions, methods of preparation, pretreatments, promoters)(70, 122, 123, 124), process and catalytic reactor development(125, 126, 127), mechanistic studies including in situ characterization of surface species via spectroscopy(96, 128, 129, 130), interception of intermediates by adding probe molecules and using radioactive reactants and probes(4, 27, 108, 131), and kinetics(50, 132, 133) . This thesis investigated the use of acetylenic compounds as probes in an attempt to unravel some aspects of the pathways by which the F-T proceeds. As such, this research is somewhat geared to a comparison of acetylenic probes with olefinic counterparts.

The F-T synthesis is a stepwise polymerization process which includes several main steps: initiation, chain propagation and chain termination. Our choice of acetylenic molecules as probe materials stems from the rather large literature on the use of olefins as probes to gain information on these steps in the F-T synthesis. Olefins added to the F-T are incorporated into the reaction and serve to initiate the reaction; ethylene, a two-carbon entity, is of special interest. It is incorporated much more easily than longer chain olefins, 10 to 40 times faster than its higher homologues. It is also a source of carbon for C1 monomer units by carbon-carbon bond splitting.

It was of great interest to us to use acetylenic molecules as probes. Acetylenes have triple bonded carbon-carbon bonds in contrast to the olefinic double bond. We know that when a mixture of acetylene and ethylene are hydrogenated over a nickel catalyst, for instance, the ethylene does not react until all the acetylene is reduced to ethylene. The thesis contains referenced experiments in which ethylene and CO, as well as acetylene and CO (in the absence of H_2) are reacted over a metal catalyst. A CO infrared adsorption band exists on the catalyst in the presence of ethylene but it can not be observed if an acetylenic compound is present; however, adsorption of acetylene is modified by the presence of CO. The higher laydown of acetylene on the catalyst and its greater incorporation into the F-T compared to ethylene is consistent with the higher heat of adsorption of acetylene compared to ethylene.

Several schemes by various researchers by which the F-T proceeds is summarized in this thesis. Carbon monoxide splits and various descriptions of initiating species containing both carbon and hydrogen are proposed, but there is little evidence that clarifies the initiation of the synthesis. This work, combined with the aforementioned experiments with olefins, lends credence to the postulation that a two-carbon entity may be involved in initiation of the F-T synthesis; chain growth then proceeds. With addition of the two-carbon acetylenic moiety, a two-carbon species is formed immediately on F-T catalysts.

Acetylenic compounds added to the F-T initiate the reaction through the acetylenic two-carbon entity. We used phenyl-substituted acetylenes to secure this point since chain growth starts from the end of the carbon-carbon triple bond. The phenyl group appears just once in the final F-T product except for dimers of the added acetylenic probe; these dimers are not formed via the F-T reaction. Once formed, these dimers may then participate in the F-T reaction. As with ethylene incorporation, the dimers serve as initiators and also contribute to the pool of C1 monomer units as a result of splitting of carbon-carbon unsaturated bonds.

We postulate that an ethylidyne species initiates the F-T synthesis. Acetylenes form ethylidynes which occupy the catalyst surface in the presence of CO and H_2 and which initiate the synthesis on adsorption. Ethylene and the other two-carbon species initiate the synthesis at normal F-T temperature by converting to ethylidynes.

An important finding is that the triply-bonded probe molecules are adsorbed at temperatures more than 100°C lower than those at which normal (base case) F-T reactions over both cobalt and iron are carried out. The low temperature adsorption of these alkynes initiates the F-T; CO and H_2 react at these low temperatures in the same way as they do in base-case F-T reactions, only they start with a two-carbon entity and chain growth is “normal” at the low temperatures.

It is revealing to add an acetylenic probe to an F-T reaction carried out at a normal F-T temperature (~220°C for Co, 260°C for Fe). The addition of phenyl-substituted compounds to a cobalt catalyst at 220°C reveals that reaction, even at this temperature, is initiated by phenyl-substituted acetylenic compounds, but the normal initiated F-T reaction also occurs. As the temperature of reaction rises, we find two series of products: one has a phenyl-group from the added probe and another without the phenyl marker from an initiating species formed from only CO and H_2. The lower the temperature, the more products have the phenyl initiator. The higher the temperature, the more of a base-case F-T takes place. In any case, the acetylenic compound is found to be a major contributor at all temperatures tested; the two-carbon entity predominates until the temperature rises to the point where the acetylenic probe allows CO and H_2 to form, possibly, a two-carbon initiation species. In the absence of an acetylenic compound, (or even of an olefinic compound to some extent), the usual high temperature employed in F-T reactions may involve a two-carbon initiating species.

Internal alkynes can also initiate F-T chain growth although the degree of incorporation is much less than that of the corresponding normal alkynes. Chain growth proceeds preferentially from the carbon with smaller R group in the carbon-carbon triple bond to form branched products. Under the same reaction conditions, internal olefins have little effect on the F-T reaction.

Our work with acetylenic probes show that molecules containing a carbon-carbon triple bond readily initiate the F-T reaction at temperature lower than those normally used. Ethylene also can initiate the synthesis but only at normal F-T condition. It is possible that similar surface species, formed by hydrogenation of CO or by adsorption of ethylene or acetylene, serve as chain initiators. The alkynes are adsorbed on F-T catalysts more strongly than are alkenes.

There are many studies on the nature of the species formed from two-carbon entities added to an F-T reaction(4, 41, 134). These include ethylene itself ($CH_2=CH_2$), vinyl ($CH_2=CH-$), ethylidene ($CH_2=C=$), ethylidyne($CH_3-C\equiv$) and, undoubtedly, a variety of other similar adsorbates.

Zaera(135) has provided surface science evidence that two-carbon entities interconvert on the surface of a metal catalyst, as shown in Figure 6.1.

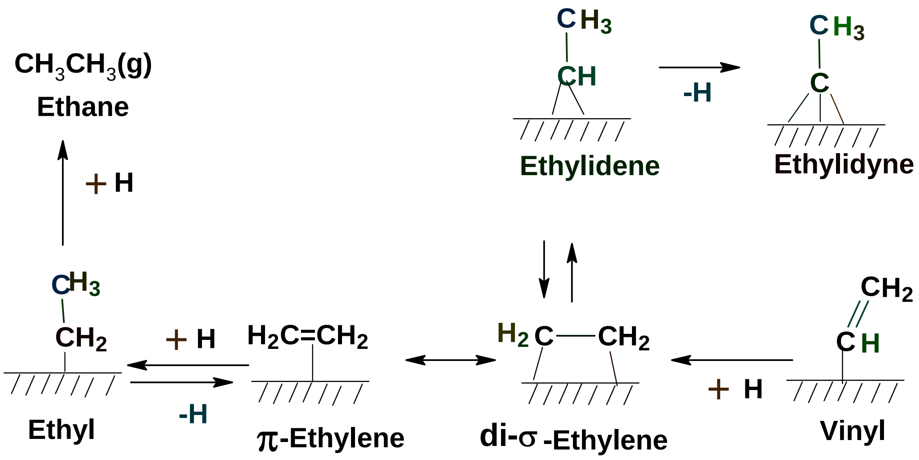


Figure 6.1 Reaction mechanisms for the conversion of ethylene on Pt (111) (135)

When acetylene is added to the F-T reaction, a vinyl species may be formed by addition of a hydrogen:

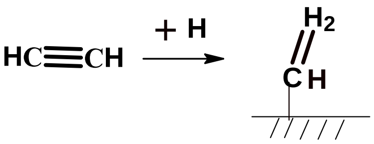


Figure 6.2 Formation of a surface vinyl species

Under F-T conditions, ethylidene species also may be formed:

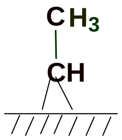


Figure 6.3 A surface ethylidene species

Acetylene is likely adsorbed readily as an ethylidyne:

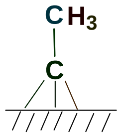


Figure 6.4 A surface ethylidyne species

Alkylidyne species are well-known in adsorption studies on metal atoms. It is possible that terminal acetylenic compounds are adsorbed at low temperature on F-T catalysts to form alkylidynes which initiate the reaction. Stable alkylidyne compounds have been reported in organometallic complexes having one and two metal centers; however, the most stable alkylidyne species is that in which nests in the center of three metal atoms. This has been substantiated by the synthesis of an organometallic compounds, ethylidyne tricobalt nonacarbonyl ($CH_3CCo_3(CO)_9$); its structure is shown in Figure 6.5. There is undoubtedly a close relation between unsaturated hydrocarbon ligands in organometallic compounds and those on metal surfaces.

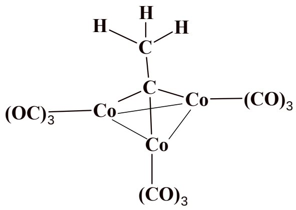


Figure 6.5 Structure of ethylidyne tricobalt nonacarbonyl$^{(136)}$

Interestingly, acetylenic compounds such as 2-hexyne or 1-phenyl-1-propyne, which yield both branched and straight chain products, can not form alkylidynes. There is evidence that they may be adsorbed by forming two-carbon metal bonds as shown below with 2-hexyne:

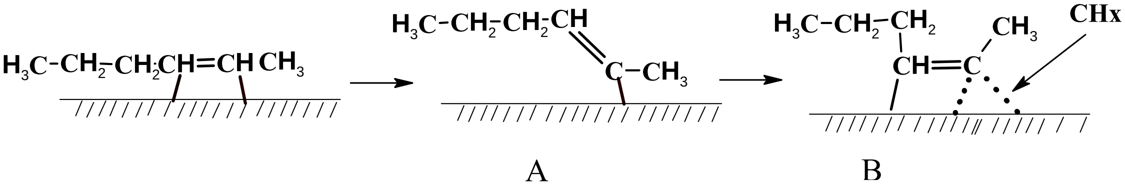


Figure 6.6 Conversion of 2-hexyne and formation of branched products $^{(137)}$

The vinyl intermediate (A in Figure 6.6) can convert into the adsorbed intermediate shown by interacting with the surface through the π-system. The two species A and B, may even be identical, “ there is no obvious reason for an energy barrier for such a π interaction with the surface” (137). The chain grows on a carbon π-bonded to the surface, yielding branched F-T hydrocarbons. The internal triple bond also isomerizes to some extent to form a terminal acetylenic bond; these then react to yield straight chain products.

Oxygenates are formed upon addition of alkynes. With cobalt catalysts, only oxygenates formed by addition of one carbon to the probe are found. The primary oxygenated products are aldehydes and which are hydrogenated to the corresponding alcohol at normal F-T conditions. Oxygenates on cobalt catalysts are formed by a hydroformylation type of reaction, which is supported by further experiments with selective poisoning of F-T reactions by thiophene, a sulfur containing compound. On iron catalysts, a series of oxygenates higher than the added alkyne are produced, following ASF kinetics. With iron catalysts, the formation of these oxygenates, as well as hydrocarbons, is poisoned by thiophene addition, as found in F-T synthesis. Formation of dimers is not poisoned by thiophene on both iron and cobalt, indicating dimerization of the added acetylenic probes is not a product of an F-T reaction.

It is interesting to note that whether 1-hexyne was added at the beginning of F-T reactions or 20 hours later, C7 oxygenates were only produced after 10 hours in the presence of 1-hexyne. This may be evidence that catalyst restructuring take place when alkynes are added to our reaction system. To explain the change of selectivity and activity of the F-T synthesis during the initial stages of a F-T run, Schulz(138) proposed the concept of surface restructuring; CO chemisorbs strongly on F-T catalysts and reacts with the metal surface to construct the "true F-T catalyst" under reaction conditions. Arakawa et al.(56) pointed out that strongly adsorbed reaction intermediates restructure the metal surface and produce new active sites. Exposure of F-T catalysts to 1-hexyne restructures the catalytic surface and produces active sites, some of which favor a hydroformylation type reaction. Formation of C7 oxygenates only occurred 10 hours after addition of 1-hexyne, indicating restructuring of catalyst surface by 1-hexyne for a period of time is necessary for formation of these oxygenates.

Somorjai(139) attributed the surface restructuring to mobility of active metals. When reactant molecules are adsorbed on metal atoms, heat is produced and provides energy to loosen the bonds between the active metal and its neighbors. Consequently, metals can move around and restructuring occurs. As with the adsorption of acetylene on a metal surface, an important derivative species, ethylidyne is formed in ethylene hydrogenation. Although ethylidyne is strongly bound, it still retains the ability to move over the surface.

The concept of F-T catalyst restructuring has been supported by many papers. Both H_2 and CO have been demonstrated to have the effect of altering the catalyst morphology during the catalytic process(140). Planes of cobalt crystals have been observed to be roughened during the base case F-T synthesis. Ethylidyne formed by acetylene adsorption may move over the surface and initiate chain growth. According to Somorjai, ethylidyne is formed readily when ethylene is adsorbed on metals(139). It is also possible that energy gain by strong adsorption of ethylidyne may remodel active sites and increase mobility of catalyst metals.

7.0 CONCLUSIONS

Following are some conclusions from this research:

- The F-T synthesis with incorporation of alkynes takes place at temperatures some 100°C lower than normal F-T temperatures. It is easier to form a chain initiator by adsorption of acetylenic probes than by CO dissociation followed by carbon-carbon coupling in the absence of acetylenic compounds. Without addition of alkynes, the usual temperatures employed in F-T reactions may be necessary to form the initiating species.
- Alkynes only serve as chain initiators; they are not incorporated into chain growth.
- Olefins can initiate F-T reactions, but alkynes initiate chain growth more effectively than olefins. Alkynes are adsorbed on catalyst surface more strongly than olefins, seemingly the reason for their higher degree of incorporation.
- Oxygenates are formed on incorporation of alkynes in the F-T with cobalt and iron catalysts. Oxygenates formed on cobalt catalysts are limited to the aldehyde and alcohol with one carbon more than the probe, probably the products of a hydroformylation type of reaction. Incorporation of alkynes (with carbon number n) on iron catalysts increased the rate of formation of C_{n+1}^{+} alcohols, which follow ASF distribution.
- All added terminal alkynes form dimers which are not a product of the F-T synthesis. The dimers are unsaturated molecules ($HC{\equiv}C\text{-}CH{=}CH_2$ from acetylene,

for instance), which can then be incorporated into the F-T reaction. The triple bond also can break to furnish additional C1 units.

- Added internal olefins are not incorporated easily into the F-T synthesis. Under the same reaction conditions, internal alkynes readily initiate F-T chain growth. Chain growth proceeds preferentially from the carbon with the smaller R group in the carbon-carbon triple bond to form branched products. Part of the internal alkyne can isomerize to the terminal position and then initiate chain growth to produce straight-chain products.
- The alpha value of normal F-T reactions decreases upon addition of alkynes, probably due to consumption of C1 monomer by alkyne initiated F-T reactions.
- At low temperatures, only alkyne initiated F-T reactions take place; at normal F-T temperatures, both alkyne initiated reactions and "normal" initiated F-T reactions occur.
- Incorporation of the simplest alkyne, acetylene, is about 60% with both cobalt and iron catalysts, much higher than that of 1-hexyne (18%) with cobalt catalysts.
- Added long chain alkynes deactivate F-T reactions quickly, possibly by deposit of heavy hydrocarbons formed by dimerization of alkynes on the surface or in the pores of the catalysts. Deactivation does not occur in the presence of acetylene.

The F-T synthesis is a complex process in which a large number of hydrocarbon and oxygenated species are present on the catalyst surface. The nature of these adsorbates and how they react differ as reaction conditions and the nature of the catalyst changes. Catalysts undoubtedly undergo a process of reconstruction during the F-T synthesis. We have endeavored to show types of adsorbates which may be principal players in the initiation of the F-T synthesis.

8.0 FUTURE WORK

Alkenes have been used extensively as probe molecules in F-T studies. Our results with alkyne incorporation suggest that alkynes are more efficient probes in initiating chain growth to provide information about scheme of the F-T synthesis.

The F-T products are predominantly linear, hence the diesel fuel has high cetane numbers. However, branched products are desirable since they result in a low pour point for diesel fuel. Addition of 2-butyne into the F-T synthesis should lead to increase of branched products. 2-Butyne may be added as additive in F-T reactions to find out optimum conditions for high selectivities toward branched products.

From our results, we believe that strong adsorption of acetylene is one reason for its easy incorporation into F-T products. When propyne and CO (1:1 molar ratio) were adsorbed on Pt catalyst, no CO adsorption was observed. CO modified propyne adsorption and increased the extent of carbon deposition. However, these surface studies of alkyne adsorption were not conducted with F-T catalysts at F-T reaction conditions. In-Situ Fourier Transform Infrared Spectroscopy (FTIR) may be used to examine coadsorption of acetylene and CO, under F-T reaction conditions over cobalt and iron catalysts. Coadsorption of ethylene and CO may be examined to probe reasons for different incorporation of acetylene and ethylene in the F-T reactions.

Among all the alkynes we tested, acetylene is incorporated most readily. We deduced the role of acetylene by its effect on product distribution. Double-labeled acetylene ($^{13}C_2H_2$) maybe employed to provide more detailed information, such as: whether acetylene initiates or propagates the carbon chain and to what degree; whether ^{13}C-^{13}C cleavage of the probe is significant and where does C1 species from acetylene go; and what other organic reactions involving the probe were occurring on the surface.

APPENDIX A

MASS BALANCE CALCULATIONS

The mass balance calculations are based on carbon. The amount of carbon entering the reactor is equal to the amount of carbon reacted to form products plus unreacted carbon leaving the reactor.

Percentage of mass balance= [(A+B)/C]*100

Where A is the mol carbon unreacted, B the mol carbon reacted and C the mol carbon entering the reactor. A was measured by a TCD with argon as internal standard; B was obtained by sum of area of FID peaks for hydrocarbon products.

The following is an example of one experiment conducted at 220^{o}C, 100psi with a cobalt catalyst in the absence of acetylene:

C: 20 (ml/min) * 60(min/hour) / 22400 (ml/mol)=0.05357 (mol/h)

A: 0.05357 (mol/h)* 93.2%=0.04993 (mol/h)

B: 33.85 (mg/h) /1000 (g/mg) /14 (g/mol)= 0.00241 (mol/h)

Percentage of mass balance

= [(A+B)/C]*100= [(0.04993+0.00241)/0.05357]*100= 97.7%

When acetylene was added, the amount of carbon entering the reactor is equal to the sum of carbon from CO and carbon from acetylene; the amount of carbon leaving the reactor is equal to the amount of carbon reacted to form products plus unreacted carbon in the form of CO (there is always no acetylene left).

Percentage of mass balance= [(A+B)/ (C+D)]*100,

Where A is the mol carbon unreacted, B the mol carbon reacted; C the mol CO and D the mol acetylene entering the reactor.

C: 20 (ml/min) * 60(min/hour) / 22400 (ml/mol)=0.05357 (mol/h)

D: 45(ml/min) * 60(min/hour) / 22400 (ml/mol)* 1% =0.001205 (mol/h)

A: 0.05357 (mol/h)* 93.0%=0.04982 (mol/h)

B: 53.6 (mg/h) /1000 (g/mg) /14 (g/mol)= 0.003829 (mol/h)

Percentage of mass balance

= [(A+B)/(C+D)]*100= [(0.04982+0.003829)/(0.05357+0.001205]*100= 97.5%

APPENDIX B

REACTION RESULTS

Table 1 F-T product distributions without/with 1-hexyne at 80~120°C

T (°C)	**80**		**100**		**120**	
Yields (mg/h)	**none**	**1-hexyne**	**none**	**1-hexyne**	**none**	**1-hexyne**
C1-C3	0	0.07	0	0.00	0	0.00
C4	0	0.25	0	0.23	0	0.31
C5	0	-	0	-	0	-
hexenes	0	100.57	0	71.64	0	60.09
hexane	0	10.43	0	19.77	0	14.31

Table 1 (Continued)

T (^oC)	80		100		120	
Yields (mg/h)	**none**	**1-hexyne**	**none**	**1-hexyne**	**none**	**1-hexyne**
C7	0	0.92	0	1.75	0	2.69
C8	0	0.13	0	0.38	0	1.47
C9	0	0.00	0	0.50	0	0.53
C10	0	0.00	0	0.07	0	0.28
C11	0	0.35	0	1.02	0	2.03
C12	0	14.00	0	33.59	0	50.61
C13	0	0.93	0	1.87	0	7.17
C14	0	0.00	0	0.12	0	3.51
C15+	0	0.00	0	0.00	0	8.16
heptanal	0	0.70	0	2.23	0	2.06
1-heptanol	0	0.00	0	0.00	0	0.08

10Co/90Al_2O_3, P=100psi, H_2/CO=2, 1-hexyne (10%) in pentane was added with a flow rate of 2ml/hour

Table 2 F-T product distributions without/with 1-hexyne at 150~220^{o}C

T (℃)	**150**			**180**		**220**		
Probes	**none**	**1-hexene**	**1-hexyne**	**none**	**1-hexyne**	**none**	**1-hexene**	**1-hexyne**
$c_{CO\ (\%)}$	0.02	-	-	0.3	-	2	-	-
C1-C3	0.09	0.09	0.09	0.53	0.43	2.88	2.36	1.89
C4	0.02	0.47	0.48	0.16	0.59	0.93	0.88	1.12
C5	0.02	-	-	0.17	-	0.85	-	-
hexenes	0.01	139.54	58.43	0.12	57.3	0.75	113.17	88.87
hexane	0.00	0.05	12.00	0.04	13.14	0.19	17.37	12.1
C7	0	0.32	2.15	016	3.36	0.93	2.34	5.6
C8	0	0.09	1.44	0.14	1.54	0.96	1.69	2.46
C9	0	0.02	0.63	0.17	0.59	0.94	1.44	1.42
C10	0	0.02	0.53	0.13	1.05	0.94	1.41	1.38
C11	0	0.02	3.44	0.15	3.18	0.91	1.40	3.73

Table 2 (Continued)

T (℃)	150			180		220		
Probes	**none**	**1-hexene**	**1-hexyne**	**none**	**1-hexyne**	**none**	**1-hexene**	**1-hexyne**
C12	0	0.21	53.07	0.17	49.62	0.88	2.51	36.44
C13	0	0.07	7.23	0.13	4.48	0.81	2.43	4.72
C14	0	0	2.39	0.14	1.31	0.68	2.13	1.31
C15+	0	0	2.4	0.9	3.2	5.14	15.8	7.8
heptanal	0	0	1.2	0	0.59	0	011	0.58
1-heptanol	0	0	0.42	0	0.95	0	0.01	0.98

10Co/90Al_2O_3, P=100psi, H_2/CO=2, 1-hexyne (10%) in pentane was added with a flow rate of 2ml/hour

Table 3 F-T products without/with 4-phenyl-1-butyne

Yield (mg/h) of linear hydrocarbons			
	Base case	**with 4-phenyl-1-butyne**	**with 4-phenyl-1-butyne**
TOS (h)	4.5	7.5	21
C1-C3	3.50	1.06	0.97
C4	0.84	0.44	0.31
C6	0.98	0.78	0.70
C7	0.94	0.41	0.22
C8	0.91	0.38	0.19
C9	0.90	0.37	0.17
C10	0.83	0.38	0.16
C11	0.83	0.39	0.15
C12	0.87	0.30	0.12

Table 3 (Continued)

Yield (mg/h) of aromatics			
	Base case	**with 4-phenyl-1-butyne**	**with 4-phenyl-1-butyne**
TOS (h)	4.5	7.5	21
phenyl-C1	---	0.06	0.02
phenyl-C2	---	0.16	0.10
phenyl-C3	---	3.52	2.39
phenyl-C4	---	125.17	109.24
phenyl-C5	---	3.93	2.69
phenyl-C6	---	0.74	0.42
phenyl-C7	---	0.41	0.10
phenyl-C8	---	0.35	0.05
phenyl-C5OH	---	0.00	0.93
α(linear hydrocarbons)	0.86	0.84	0.78
α(aromatic hydrocarbons)	---	0.34	0.19

$10Co/90Al_2O_3$, T=220°C, P=100psi, $H_2/CO=2$, 4-phenyl-1-butyne (10%) in pentane was added with a flow rate of 2ml/hour

Table 4 F-T product distribution with incorporation of phenylacetylene (PhA)

Catalyst	**Co**^{1}			**Fe**^{2}		
	Base Case	**With PhA**	**With PhA**	**Base Case**	**with PhA**	**with PhA**
TOS (h)	**5**	**5**	**20**	**5**	**5**	**20**
Yield (mg/h) of linear hydrocarbons						
C1-C3	3.76	2.84	2.66	16.92	15.27	15.08
C4	1.20	0.99	0.64	5.93	5.38	5.74
C6	1.07	0.86	0.21	3.22	3.25	3.41
C7	1.05	0.78	0.13	2.47	2.56	2.73
C8	1.05	0.73	0.10	1.97	2.08	2.22
C9	1.06	0.78	0.06	1.34	1.81	1.90
C10	1.07	0.67	0.10	1.03	1.35	1.43
C11	1.06	0.85	0.07	0.88	1.10	1.22

Table 4 (Continued)

Catalyst	**Co[1]**			**Fe[2]**		
	Base Case	**With PhA**	**With PhA**	**Base Case**	**with PhA**	**with PhA**
TOS (h)	**5**	**5**	**20**	**5**	**5**	**20**
C12	1.11	0.85	0.09	0.73	0.93	1.04
Alpha value	0.82	0.79	0.53	0.71	0.73	0.74
Yield (mg/h) of aromatic hydrocarbons						
phenyl-C1	--	14.66	8.83	--	5.82	6.22
phenyl-C2	--	144.24	172.12	--	132.79	132.81
phenyl-C3	--	5.09	6.09	--	13.74	13.41
phenyl-C4	--	2.37	2.65	--	4.12	3.97
phenyl-C5	--	1.63	1.47	--	1.86	1.85

Table 4 (Continued)

Catalyst	**Co**[1]			**Fe**[2]		
	Base Case	**With PhA**	**With PhA**	**Base Case**	**with PhA**	**with PhA**
TOS (h)	**5**	**5**	**20**	**5**	**5**	**20**
phenyl-C6	--	1.18	0.68	--	0.91	0.93
phenyl-C7	--	0.87	0.37	--	0.52	0.56
phenyl-C8	--	0.67	0.24	--	0.38	0.34
Alpha value	--	0.56	0.43	--	0.35	0.34

[1] **$10Co/90Al_2O_3$, T=220°C, P=100psi, H_2/CO =2, phenylacetylene (10%) in pentane was added with a flow rate of 2ml/hour)**

[2] **100Fe-5.1Si-2.0Cu-5.0K_2O, T=260°C, P=100psi, H_2/CO=2/3; phenylacetylene (10%) in pentane was added with a flow rate of 2ml/hour**

Table 5 F-T products without/with acetylene on cobalt catalyst at different temperatures

T (^oC)	**120**		**180**		**220**	
Yields (mg/h)	**Base case**	**With acetylene**	**Base case**	**With acetylene**	**Base case**	**With acetylene**
C1	0.06	0.59	3.36	3.36	18.33	22.01
C2	0.02	17.00	1.21	5.07	2.02	8.49
C3	0.04	3.63	1.52	4.77	5.80	9.54
C4	0.02	15.63	1.82	24.06	7.19	24.62
C5	0.00	3.39	0.88	9.19	7.03	14.34
C6	0.00	1.10	0.64	4.39	6.13	11.43
C7	0.00	0.68	0.54	2.44	4.32	6.41
C8	0.00	0.45	0.46	1.85	3.42	5.26
C9	0.00	0.26	0.43	1.56	2.21	3.43
C10	0.00	0.05	0.37	1.23	1.35	2.15

Table 5 (Continued)

T (^oC)	120		180		220	
Yields (mg/h)	**Base case**	**With acetylene**	**Base case**	**With acetylene**	**Base case**	**With acetylene**
C11	0.00	0.00	0.33	1.02	1.00	1.13
C2OH	0.00	0.00	0.34	0.24	0.65	0.69
C3OH	0.00	1.39	0.11	1.82	0.11	1.97
C4OH	0.00	0.00	0.00	0.01	0.00	0.21
C5OH	0.00	0.00	0.00	0.47	0.00	0.00
C6OH	0.00	0.00	0.00	0.06	0.00	0.00

$10Co/90Al_2O_3$, P=300 psi, $H_2/CO=1$, 1% of acetylene

Table 6 F-T products without/with acetylene on a cobalt catalyst at different pressures

P (psi)	**100**		**300**		**700**	
Yields (mg/h)	**Without acetylene**	**With acetylene**	**Without acetylene**	**With acetylene**	**Without acetylene**	**With acetylene**
C1	1.69	2.84	3.36	3.36	3.31	4.06
C2	0.52	3.44	1.21	5.07	0.76	4.83
C3	0.63	2.76	1.52	4.77	3.46	8.04
C4	0.61	20.27	1.82	24.06	3.51	24.74
C5	0.43	8.51	0.88	9.19	2.98	10.53
C6	0.36	4.09	0.64	4.39	2.77	6.84
C7	0.33	2.28	0.54	2.44	2.31	3.34
C8	0.33	1.74	0.46	1.85	2.00	2.81
C9	0.31	1.24	0.43	1.56	1.71	2.47
C10	0.29	1.16	0.37	1.23	1.36	1.53

Table 6 (Continued)

P (psi)	**100**		**300**		**700**	
Yields (mg/h)	**Without acetylene**	**With acetylene**	**Without acetylene**	**With acetylene**	**Without acetylene**	**With acetylene**
C11	0.20	0.94	0.33	1.02	1.14	1.17
C12	0.13	0.57	0.20	0.78	0.80	1.04
C 2OH	0.21	0.10	0.34	0.24	0.29	0.17
C 3OH	0	1.80	0.11	1.82	0.06	1.91
C 4OH	0	0	0.00	0.01	0.08	0.09
C 5OH	0	0.42	0.00	0.47	0.08	0.87
C 6OH	0	0	0.00	0.06	0.00	0.07

10Co/90Al_2O_3, 180^{o}C, H_2/CO=1, 1% of acetylene

Table 7 F-T products without/with acetylene on an iron catalyst at different temperatures

T (^{o}C)	120		180		220		260	
Yields (mg/h)	**Without acetylene**	**With acetylene**	**Without acetylene**	**With acetylene**	**Without acetylene**	**With acetylene**	**Without acetylene**	**With acetylene**
C1	0.03	0.32	1.40	1.93	4.79	5.81	3.99	7.41
C2	0.04	32.83	0.93	16.68	4.29	23.28	5.49	25.21
C3	0.02	1.84	0.94	6.92	5.63	10.94	12.58	17.20
C4	0.00	4.20	0.89	8.13	6.16	12.97	10.00	15.53
C5	0.00	1.60	0.56	5.61	4.11	9.11	8.07	10.71
C6	0.00	0.56	0.33	2.74	3.13	5.52	6.15	7.65
C7	0.00	0.17	0.25	2.3	2.88	4.00	5.11	6.36
C8	0.00	0.00	0.14	1.5	2.40	3.33	3.88	4.40
C9	0.00	0.00	0.09	1	2.03	2.80	3.15	3.33
C10	0.00	0.00	0.05	0.8	1.84	2.33	2.91	2.70

T (°C)	**120**		**180**		**220**		**260**	
Yields (mg/h)	**Without acetylene**	**With acetylene**	**Without acetylene**	**With acetylene**	**Without acetylene**	**With acetylene**	**Without acetylene**	**With acetylene**
C11	0.00	0.00	0.03	0.5	1.80	2.00	2.89	2.20
C12	0.00	0.00	0.02	0.3	1.76	1.33	2.84	1.98
C 2OH	0.00	0.00	0.46	0.48	1.64	2.11	1.70	2.35
C 3OH	0.00	0.32	0.25	2.48	0.89	3.58	1.48	3.49
C 4OH	0.00	0.19	0.22	1.50	0.85	2.27	1.04	1.76
C 5OH	0.00	0.00	0.16	1.20	0.80	2.35	1.03	1.71
C 6OH	0.00	0.00	0.14	0.85	0.77	1.47	0.70	0.95
C 7OH	0.00	0.00	0.11	0.65	0.74	1.18	0.59	0.67
C 8OH	0.00	0.00	0.09	0.54	0.70	0.88	0.53	0.40
C 9OH	0.00	0.00	0.05	0.34	0.50	0.59	0.47	0.27

100Fe/4.4Si/1.25K, P=300psi, H_2/CO=1, 1% acetylene

Table 8 F-T products without/with acetylene on an iron catalyst

P (psi)	**100**		**300**		**700**	
Yields (mg/h)	**Without acetylene**	**With acetylene**	**Without acetylene**	**With acetylene**	**Without acetylene**	**With acetylene**
C1	0.77	1.08	1.40	1.93	1.68	1.54
C2	0.49	16.56	0.93	16.68	1.68	16.48
C3	0.46	4.96	0.94	6.92	2.95	8.07
C4	0.36	7.84	0.89	8.13	4.38	10.67
C5	0.30	5.20	0.56	5.61	3.42	8.09
C6	0.15	2.51	0.33	2.74	2.53	4.44
C7	0.10	1.48	0.25	1.69	1.91	2.74
C8	0.06	0.78	0.14	0.92	1.35	1.65
C9	0.04	0.41	0.09	0.50	0.96	0.97
C10	0.02	0.21	0.05	0.27	0.67	0.56

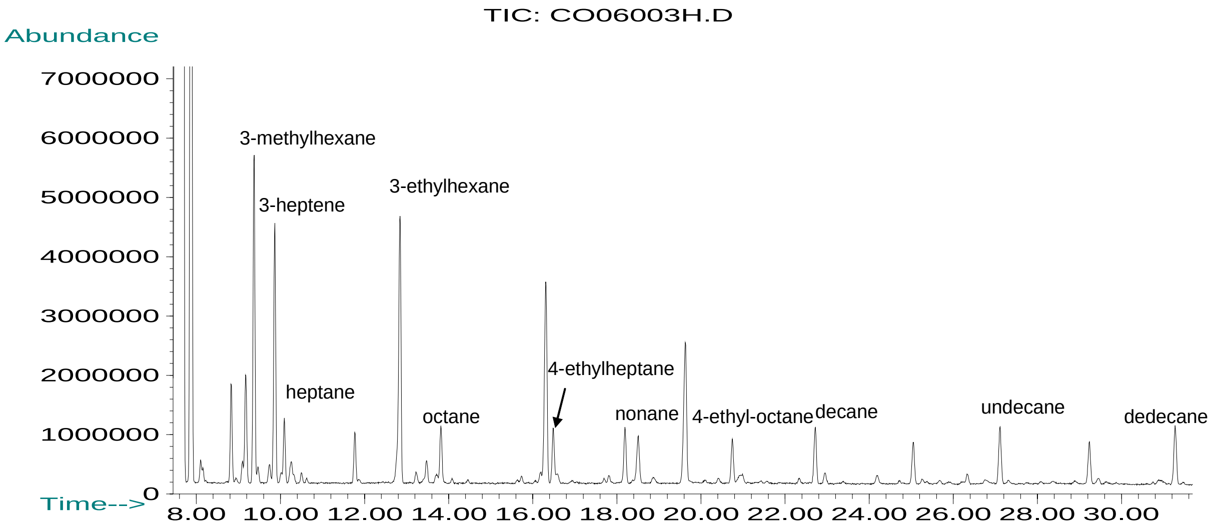
Table 8 (Continued)

P (psi)	100		300		700	
Yields (mg/h)	**Without acetylene**	**With acetylene**	**Without acetylene**	**With acetylene**	**Without acetylene**	**With acetylene**
C11	0.01	0.11	0.03	0.14	0.46	0.32
C12	0.01	0.06	0.02	0.07	0.32	0.18
C 2OH	0.04	0.16	0.46	0.48	1.39	0.63
C 3OH	0.10	1.88	0.25	2.48	1.45	3.81
C 4OH	0.08	0.71	0.22	1.50	1.27	2.15
C 5OH	0.06	0.62	0.16	1.20	1.10	2.48
C 6OH	0.04	0.53	0.14	0.85	0.77	1.9
C 7OH	0.03	0.38	0.11	0.65	0.65	1
C 8OH	0.02	0.29	0.09	0.54	0.52	0.72
C 9OH	0.01	0.18	0.05	0.34	0.44	0.52
Oxygenate (%)	14	11	26	17	34	23

100Fe/4.4Si/1.25K, T=180^{o}C, H_2/CO=1, 1% acetylene

APPENDIX C

GC-MS ANALYSIS RESULT WITH 3-HEXYNE ADDITION



10Co/90Al_2O_3, T=220°C, P=100psi, H_2/CO=2, 3-hexyne (10%) in pentane was added with a flow rate of 2ml/hour

APPENDIX D

SAFETY WORKING WITH ACETYLENE

Acetylene is a highly flammable and explosive gas. The explosive limits in air range from 2% to 80%. Pure acetylene in cylinder is usually dissolved in acetone for transport and storage (141). We used a mixture gas containing 1% of acetylene, and two safety critical parts of reaction system are addressed in the following discussions:

(1) Acetylene gas cylinder

We used a mixture of 44% carbon monoxide, 45% hydrogen, 10% argon and 1% acetylene gases, prepared by Praxair Incorporation. Risk of acetylene decomposition is dependent on working pressure and diameter of pipe as shown in Figure 1. Lines A and B in Figure show three areas corresponding to the following levels of risk associated with acetylene decomposition.

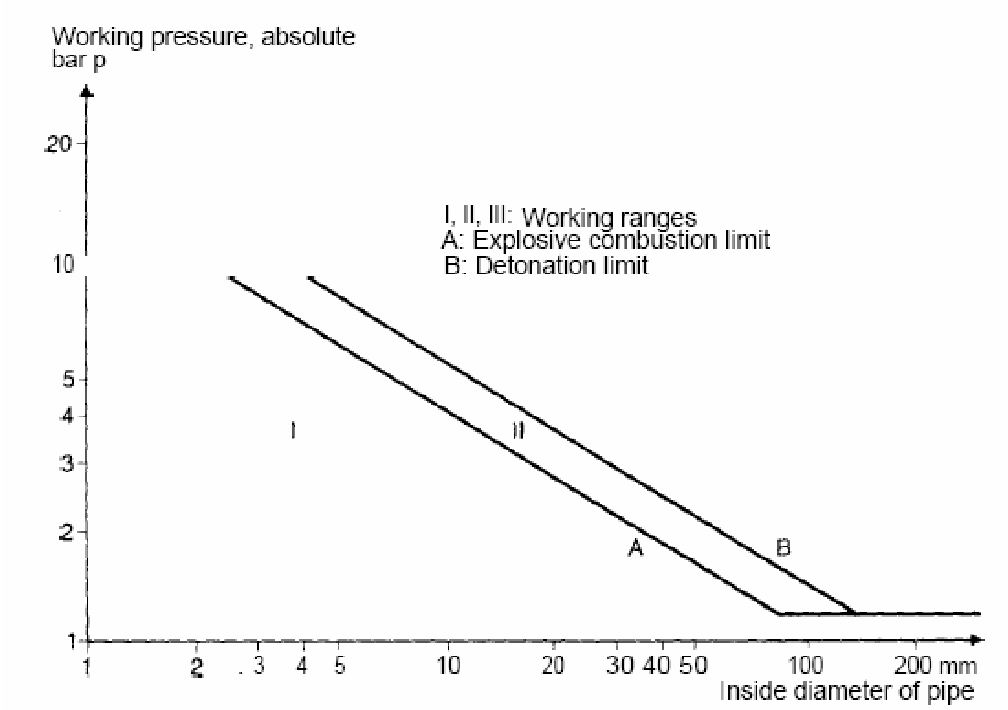


Figure 1. Working ranges for acetylene(142)

Working range I: Below line A. The risk of acetylene decomposition is insignificant

Working range II: On or above line A, but below line B. Upon initiation, acetylene decomposition can occur in the form of explosive combustion.

Working range II: On or above line B. Upon initiation, acetylene decomposition starts as an explosive combustion. In a sufficiently long pipeline, detonation can occur.

Inside diameter of our mixture gas cylinder is about 100 mm which corresponds to a maximum working pressure of 1.2 bar. Since original total pressure of mixture gas cylinder was 100 bar and only 1% of acetylene was contained, initial partial pressure of acetylene in the cylinder was 1 bar. Our operation of acetylene was in working range I which had low risk.

Cylinder was firmly secured upright to keep it from falling or being knocked over. When work was finished, we closed the cylinder at the valve.

(2) Transferring lines and reactor

Inside diameter of our fixed-bed reactor is only 10 mm, which corresponds to maximum working pressure of 4.5 bar. This is much higher than our partial pressure of acetylene which is in the range of 0.1 to 0.5 bar.

The reactor was surrounded on one side by a wall and on three sides by a safety shield made of impact resistant 0.5 inch-thick polycarbonate. Copper, which can replace the hydrogen atoms in acetylene to form explosive acetylides, was not present in the reaction system. Only steel materials were used for piping, fitting, regulators and shut-off valves.

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