Fuels and Chemicals Via Fischer-Tropsch

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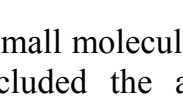
Diesel engines are more efficient than gasoline engines, but they emit 10-20 times more particulate matter than do gasoline engines. It is known that addition of oxygenates to diesel from petroleum lowers particulate matter emissions (PMEs). Just adding oxygenated compounds to diesel fuel has problems involving availability, toxicity, cost, solubility and biodegradability. Our aim is to increase the amount of oxygenates in diesel fuel from Fischer-Tropsch (F-T) products, thus decreasing PMEs in the fuel.

We are pursuing three methods of increasing oxygenates in F-T products: (a) incorporate certain small molecules into the F-T reaction to increase the oxygen content of the product, (b) modify F-T catalysts and reaction parameters to obtain more oxygenates and (c) hydroformylate olefinic F-T products to aldehydes and alcohols.

Preliminary tests were made out by adding small molecules to the F-T reactor. The compounds selected included the addition of epoxides  vinyl ethers ($ROCH{=}CH_2$),and acetylenic compounds ($RC{\equiv}CH$). The addition of the latter produced intriguing results and the remainder of our F-T work has since been focused on the effect of adding hexynes, compounds containing a triple bond (CO also has a triple bond) in a chain of six carbon atoms ($CH_3(CH_2)_3C{\equiv}CH$ and $CH_3(CH_2)_3C{\equiv}CCH_3$).

An outline of the continuous F-T unit, with excellent analytical facilities, is shown in Figure 1. An iron catalyst (Fe 100, Si 5.1, Cu 2.0, K 5.0) was used at temperatures from 170 to 260ºC, 300 psi and a CO/H_2 of 3/2. Analysis was by GC online and GCMS offline. Olefins were the main product on this iron catalyst. Surprisingly, 1-hexyne addition to the reactor showed that the hexyne had reacted to produce significant amounts of heptanal and 1-heptanol with a trace of 1-octanol (Figure 2). The distribution of F-T products with and without addition of 1-hexyne is shown in Figure 3. It is obvious from this Figure that acetylenic compounds initiate carbon chain in the F-T reaction.

Addition of 2-hexyne to the F-T reaction gave a more complex mixture of products, including a 2-methyl-branched C_7 aldehyde and a similarly branched alcohol (Figure 4).

Further work will be carried out with iron catalysts that do not contain copper, to avoid formation of acetylides. Possible mechanisms of oxygenate formation with

addition of acetylenic compounds to the F-T reaction catalyzed by iron and by cobalt will be explored. The addition of acetylene itself, a cheap, readily available compound, will be investigated.

It is interesting to postulate a mechanism for the reaction of a triple-bonded molecule such as occurs with 1- and 2-hexyne with an F-T catalyst. If 1-hexene is added to an iron-catalyzed F-T catalyst, it is converted to n-hexane. It is known that olefins combine exothermically with metal surfaces. A possible structure follows in which the dashed lines (Figure 5) infer partial bonding while half of the double bond is weakened but probably not fully broken.

If we apply this to an acetylenic bond, one pair of electrons would bond with the F-T catalyst in a similar way. This, however, leaves a pair of electrons still available for further reaction and may undergo the equivalent of a hydroformylation (oxo) reaction with synthesis gas as shown in Figure 5. This could account for the formation of C_7 alcohols from the hexynes.

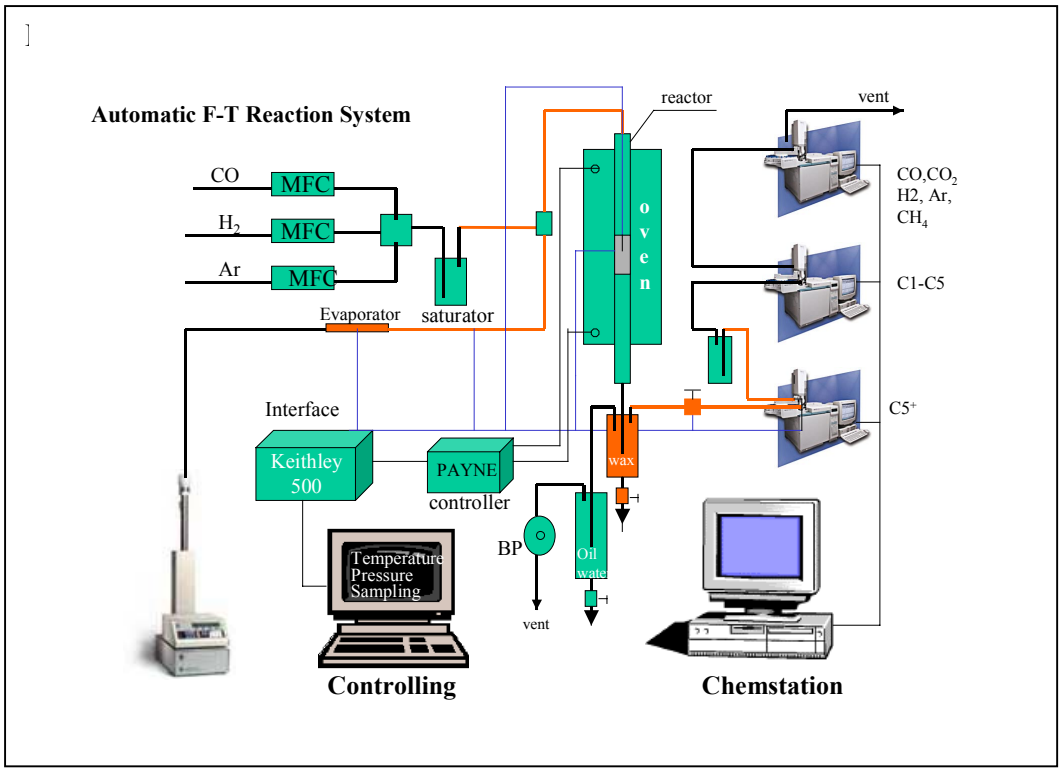


Figure 1. Sketch of Fischer-Tropsch Reactor System.

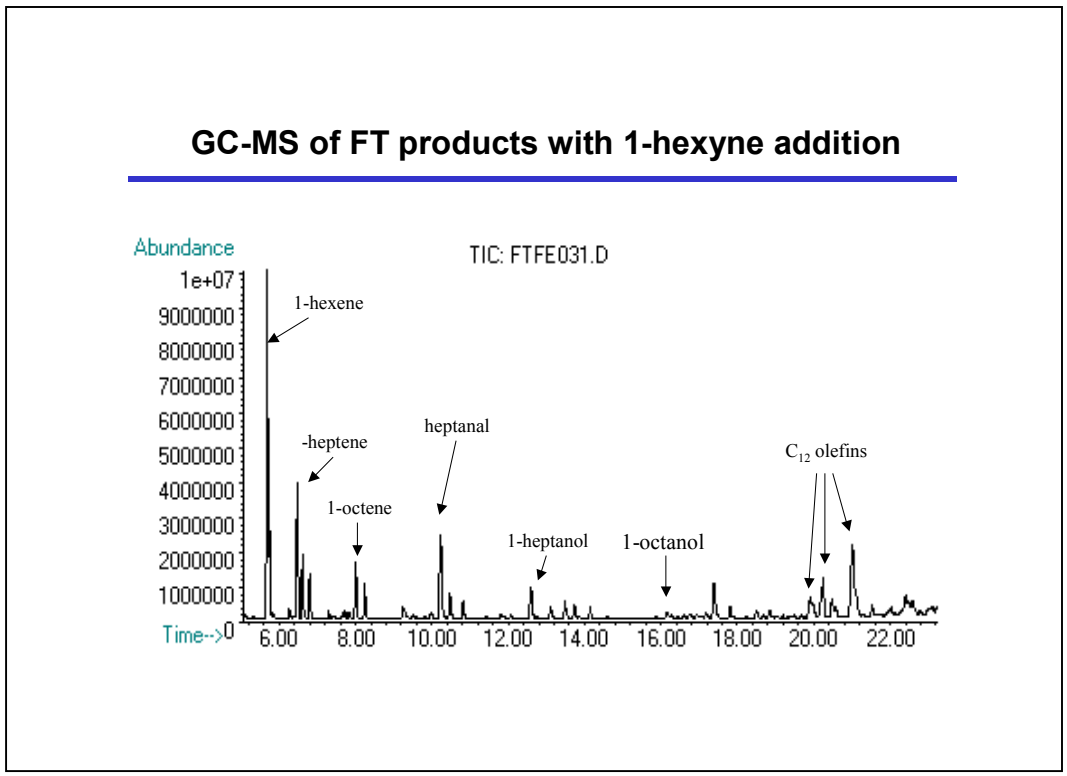


Figure 2. Addition of 1-hexyne produces significant amounts of heptanal and 1-heptanol.

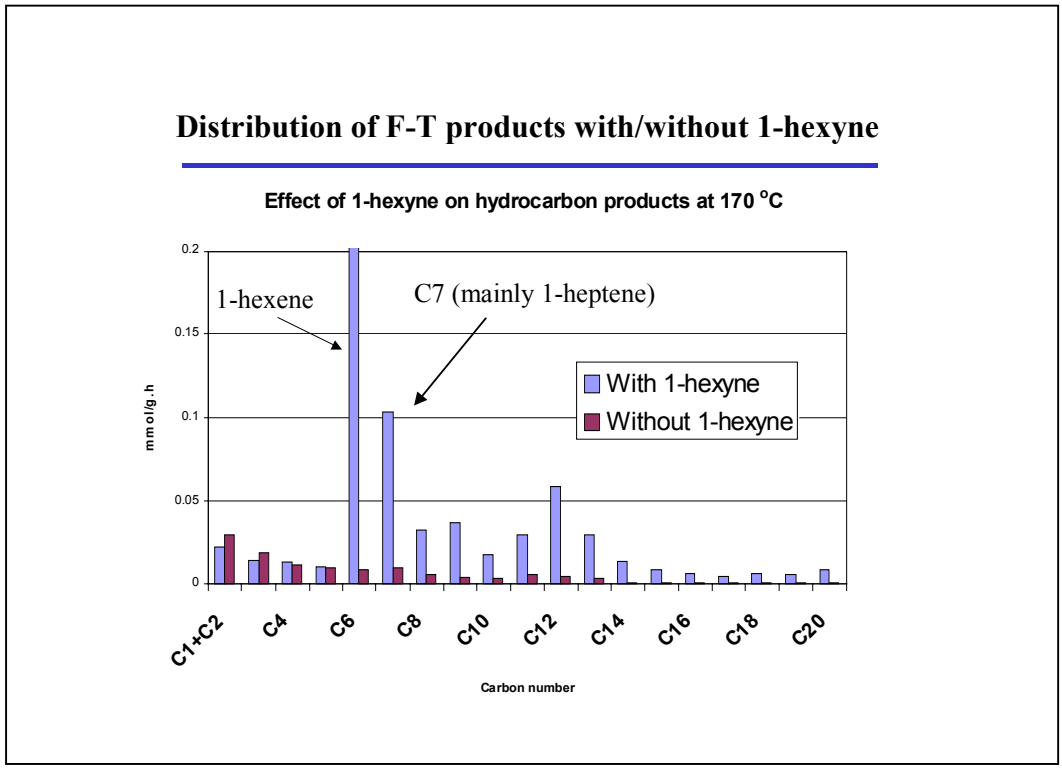


Figure 3. Participation of hexyne in Fischer-Tropsch reaction is indicated by change in product distribution when adding 1-hexyne.

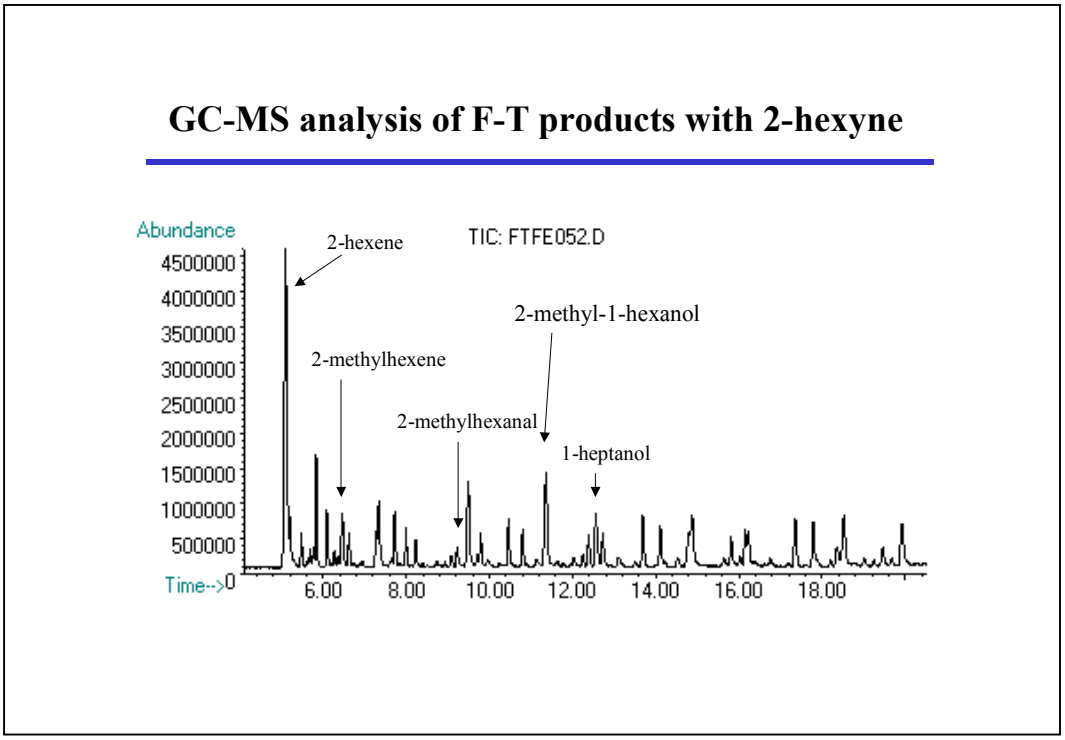


Figure 4. Addition of 2-hexyne gives a more complex mixture of products.

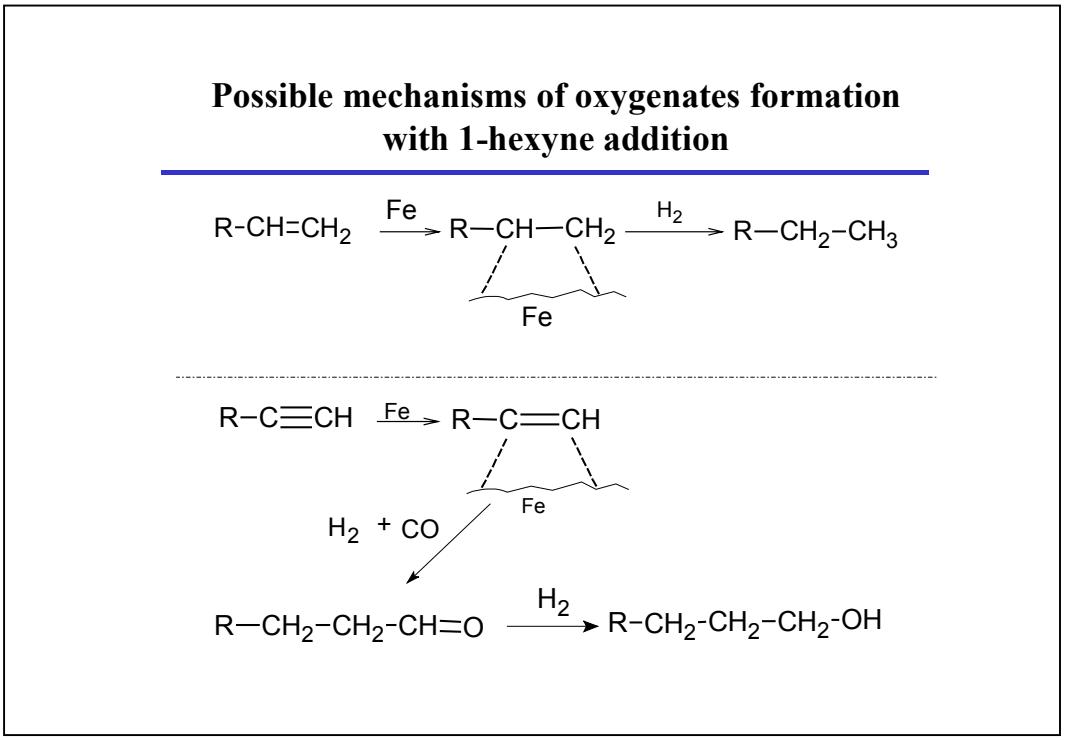


Figure 5. Possible mechanisms for reaction of 1-hexene and 1-hexyne in the Fischer-Tropsch reaction.