

Fischer-Tropsch Synthesis: Current Mechanism and Futuristic Needs

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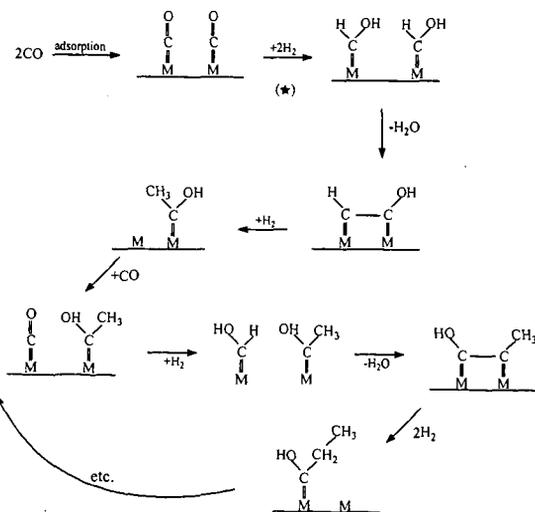
INTRODUCTION

The original **carbide mechanism** for the formation of hydrocarbon and oxygenate products with the Fischer-Tropsch synthesis (FTS) included the formation of the metal carbide followed by hydrogenation of the metal carbide to produce the products [1]. It was eventually recognized that this mechanism was inconsistent with thermodynamic data for the formation of hydrocarbons by hydrogenation of the carbide at the temperatures used for the synthesis reaction [2,3]. The direct hydrogenation of the metal carbide was investigated by Kummer et al. [4]. These workers performed iron carbide by the reaction of a reduced iron catalyst and ^{14}C O. The fraction of methane that is $^{14}\text{CH}_4$ when synthesis is effected with unlabeled CO is a measure of the contribution of direct hydrogenation of the preformed iron carbide to the synthesis. The data showed that carbide hydrogenation could be responsible for no more than 8 to 30% of the methane that is formed. These authors made a special effort to obtain data at low conversion levels that would represent the hydrogenation of only a percent of the total surface carbon; even under these conditions direct hydrogenation was responsible for only a small fraction of the methane produced. In addition, the same conclusion applied for the higher carbon number compounds. This study led most investigators to abandon the formation of a bulk metal carbide as an intermediate in the FTS mechanism.

About 1950, the **oxygenate (enol) mechanism** gained widespread acceptance [5,6]. This mechanism involves the chemisorption of CO which reacts with adsorbed hydrogen to form a species such as:



This structure grows by a combination of condensation and water elimination steps using adjacent groups. This enol group can condense as depicted in Scheme I below [7].

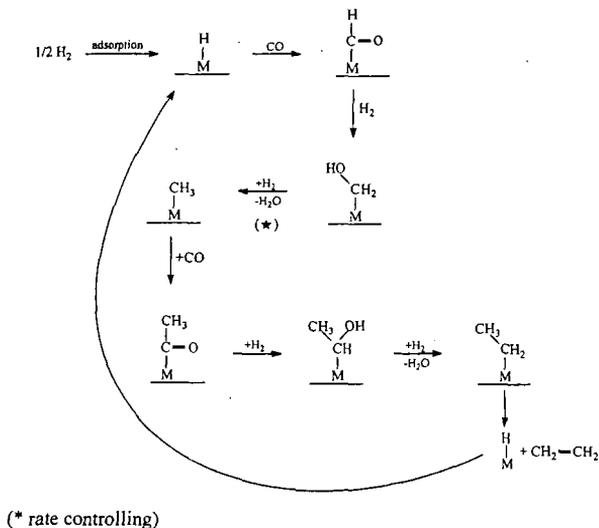


(* rate controlling)

Scheme I

The results obtained by Emmett and coworkers [2,8-12] for their ^{14}C -tracer studies provided strong support for this mechanism. In these studies, ^{14}C -labeled alcohol or alkene was added together with the synthesis gas and the distribution of the isotopically labeled products was determined. It was found that the added alkene or the alcohol was able to serve to initiate chain growth. Much of the work by Emmett and coworkers was conducted at atmospheric pressure. However, our later work [13] using medium pressure synthesis and slurry phase reaction conditions produced results that were in agreement with the conclusions of Emmett and coworkers. In addition, our work showed that ethanol was incorporated 50 to 100 times as rapidly as ethene when the two reactants were converted under the same reaction conditions [14].

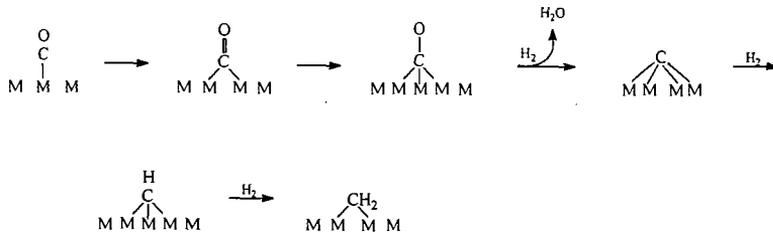
An **insertion mechanism** involves the insertion of CO into a metal-methyl or metal-methylene carbon bond which is then hydrogenated to produce an alcohol or alkene; the alcohol or alcohol precursor can also eliminate oxygen to produce an alkene product. One form of this mechanism is shown in Scheme II below [7,15]:



Scheme II

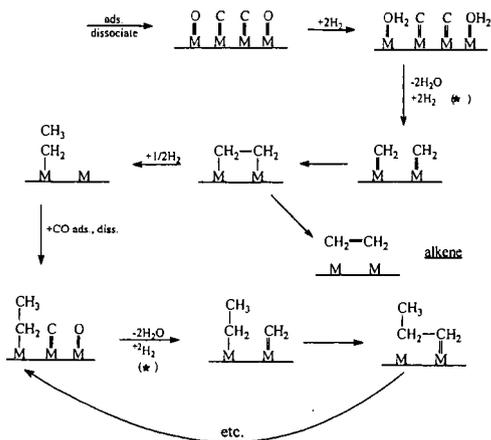
Hydrogenation and water elimination of the COH_2^* surface species are assumed to be the rate controlling step.

With the general availability of surface science instruments, it was found that CO adsorbs on single crystal metal surfaces to produce a surface covered with carbon, and little oxygen. This led to the conclusion that the CO chemisorbs and dissociates to adsorbed C and O. This step is followed by the rapid hydrogenation of adsorbed O to produce water. The hydrogenation of adsorbed carbon to form CH_2 is much slower. This mechanism may be viewed as a revival of the carbide theory but with the requirement that carbide formation is limited to the surface, or near surface, layer. Maitlis [16] has advanced this mechanism as the Fischer-Tropsch-Brady-Pettit-Biloen-Sachtler Mechanism and is illustrated in Scheme III below:



Scheme III

A more elaborate version of this mechanism has been provided by Dry and is shown in Scheme IV:

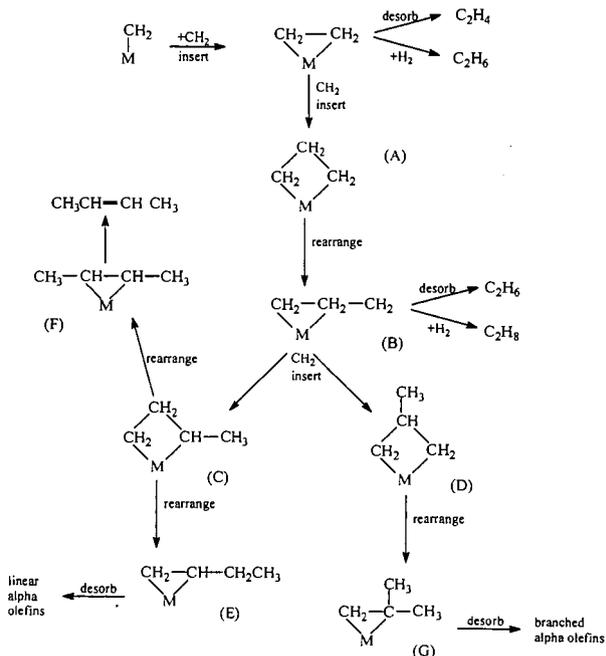


(* rate controlling)

Scheme IV

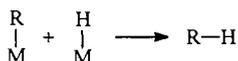
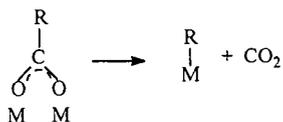
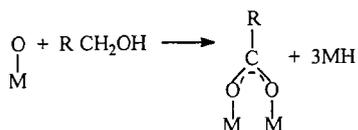
Dry considers the step(s) involving the hydrogenation of surface C to be rate-limiting; the other reactions are assumed to be at equilibrium.

A current view of the **carbide (carbene) theory** is illustrated in Scheme V [7]:

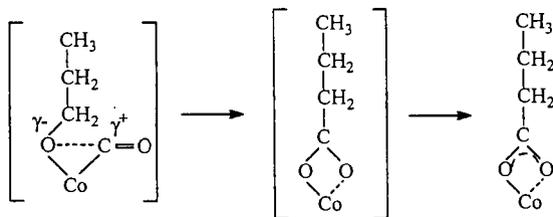
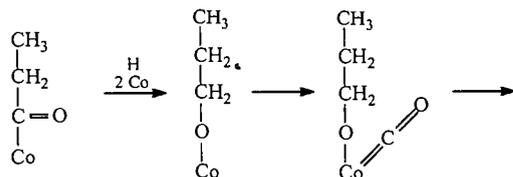
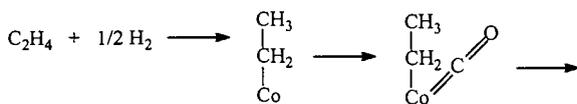


Scheme V

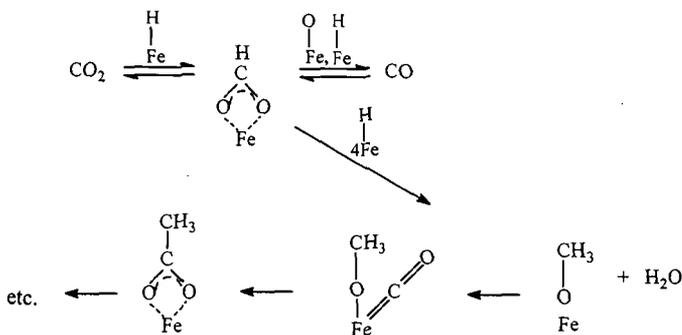
In the following we consider characterization data and try to combine this with results from isotopic tracer studies in an attempt to provide a mechanism that more nearly applies under conditions amenable to industrial practice. The consideration will be limited to the lower severity conditions likely to be encountered in slurry phase synthesis with an iron catalyst.



The conversion of ^{14}C labeled alcohols is consistent with the following reaction pathway: This reaction pathway allows for the direct formation of CO_2 and an alkane with one less carbon than the added alcohol, and is in agreement with the experimental results. Furthermore, there is valid infrared data to support the type of structure as being formed on metal (Fe and Co) surfaces. Thus, Blyholder et al. [17] offers the following mechanism for the reaction of CO , H_2 and C_2H_4 :



A similar adsorption model has been proposed by Kölbl and Tillmetz [18]. A pathway similar to the above would account for the chain initiation by CO_2 ;



The oxygenate mechanism is able to account for the initiation by CO_2 as well as requiring chain propagation to occur only by CO since it appears unreasonable to expect CO_2 to be adsorbed with the structure shown in the Blyholder model.

In summary, there is clearly evidence for the participation of an oxygenate intermediate in the Fischer-Tropsch synthesis using an iron catalyst. It is also clear that a carbide is the more active form of the iron catalyst. The intermediate leading to the 1-alkenes remains to be identified.

On the other hand, the tracer studies with a cobalt catalyst are in agreement with a mechanism involving the carbene intermediate. Both CO_2 and alcohols behave as inert gases for the cobalt catalyst.

The next step is to provide more conclusive data to show that the mechanism for the iron and cobalt catalysts are indeed different. If, as the data suggest, they are different then the objective is to define the catalyst properties responsible for the difference.

ACKNOWLEDGMENT

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recovery technology continues to improve, one should expect that this price range will continue into the foreseeable future. However, this same history shows that the margin gap between gasoline prices and crude oil costs has been collapsing for the oil refining industry. Therefore, if crude oil prices continue to stay near \$20 per barrel, and the refining margins and gasoline prices continue to decline, it will be economically difficult to justify developing alternative fuel substitutes for gasoline and diesel.

Chart 5 shows the whole sale prices of a number of possible alternative fuels (on a energy equivalent basis) compared to conventional gasoline [4]. Only CNG (compressed natural gas) and LPG (liquid petroleum gas) appear to have some economic advantage relative to gasoline while ethanol, methanol and electricity are at a severe economic disadvantage. However, even these simple economics do not capture the added cost necessary to build the supporting fuel distribution infrastructure as well as the added cost of the vehicle to use that alternative fuel. These added costs will usually eliminate most if not all of CNG's and LPG's economic advantage over gasoline and further disadvantages the other alternative fuels. These unfavorable economics help explain the very small market share of AFVs that has developed since the crude oil price spike of the early 1980's. As shown in Chart 6, all the AFV fleets combined represent less than a quarter percent of the total U.S. vehicle fleet, and even these AFVs are usually found in niche markets that are supported by central fueling locations and favorable tax supports[5].

The economics do not appear to support the switch to alternative fuels and may not in the foreseeable future if crude prices stay near \$20 dollars a barrel. Therefore, AFV supporters have been using non-economic arguments such as using AFVs to reduce mobile source emissions from the vehicle fleet. Air quality agencies have been reducing tailpipe emission standards which provides an incentive to switch to AFVs with their lower emissions. In response, the oil and auto industries combined have found ways to further clean up gasoline and diesel fuels which not only reduces the emissions from the current vehicle fleet, but also allows the automakers to develop even cleaner burning vehicles that approach the lower emissions of the AFVs. Chart 7 shows the estimated emission reductions using the typical California Reformulated Gasoline in the current fleet relative to using 1990 industry average gasoline. As a result of the cleaner burning gasoline, the auto industry is now introducing cars that not only meet California's ULEV (ultra low emission vehicle) standard but also the SULEV (super ultra low emission vehicle) standard without using AFVs [7-11]. As new model gasoline vehicles becomes cleaner, the shrinking emission advantage of the AFVs diminishes to a point where the cost of reducing this small remaining emission becomes very costly compared to other options for reducing emissions elsewhere.

The most recent social quest has been to reduce the production of greenhouse emissions (mainly CO₂). To decrease mobile sources of these gases, the drive has been to reduce vehicle fuel consumption by moving to a higher efficiency vehicle with a fuel economy of 80 miles per gallon or 3 liters per 100 kilometers. To achieve this goal, many have thought it would require using a higher efficiency power train such as a fuel cell running on an alternative fuel such as hydrogen or methanol. However, the old workhorse combustion engine again appears to be rising to the challenge with the development of the high efficiency diesel engines coupled with hybrid drive trains [8,9,12-17]. Although the responsiveness and performance of the diesel engine has been improved to be comparable to that of the gasoline engine, a major hurdle still exists for reducing the diesel's NO_x (nitrogen oxides) and PM (particular) emissions to be comparable to gasoline engines. To help reduce these emissions, the reformulation of diesel continues to be studied. An example of recent work is shown in Chart 8 which shows that increasing the hydrogen content of the fuel will help reduce PM emissions by as much as 30 %. In addition, adding as much as 5 % oxygen can reduce emissions by another 25%[6]. With some success, the exhaust after-treatment technology for reducing emissions further may be able to decrease diesel tailpipe emissions enough to be comparable to that of gasoline [9,12-14,16].

CONCLUSIONS

When one looks at the recent history and current events, it suggests that the fuels of the foreseeable future will still be gasoline and diesel, but be improved, cleaner burning versions. These cleaner fuels will allow automakers to further develop even cleaner vehicles that will produce minimal emissions and consume much less fuel. Major improvements in the diesel engine performance and cleanliness will likely create a shift in the light duty vehicle market toward the higher efficiency and more economical diesel engine vehicle that seems to be occurring already in Europe. Future crude oil supplies always seem to be more plentiful than estimated in the past, and the technology and economic hurdles to convert other alternative energy sources into diesel and gasoline-like fuels also continues to improve. As a result of all these improvements combined, the economic incentives to switch to AFVs will not likely exist in the foreseeable future except for niche markets.

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Chart 1

Non-OPEC Oil Production Forecasts for 1987-89

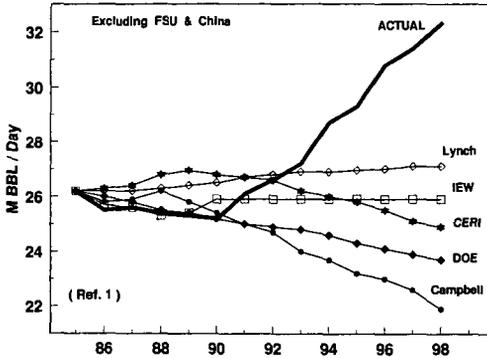


Chart 2

1987-89 Crude Oil Price Forecast

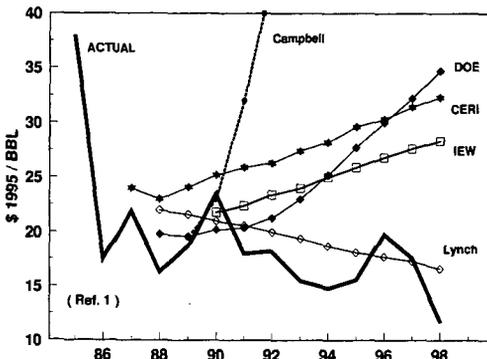


Chart 3

World Oil Consumption vs Oil & Gas Resources

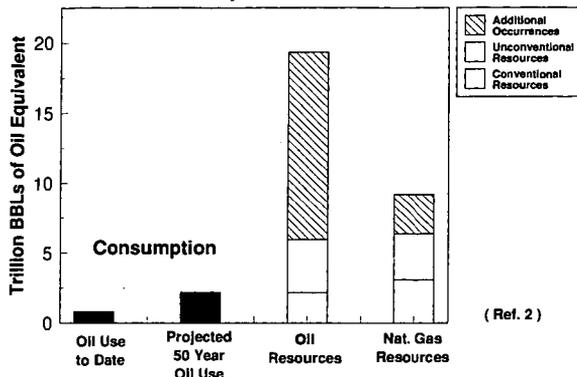


Chart 4

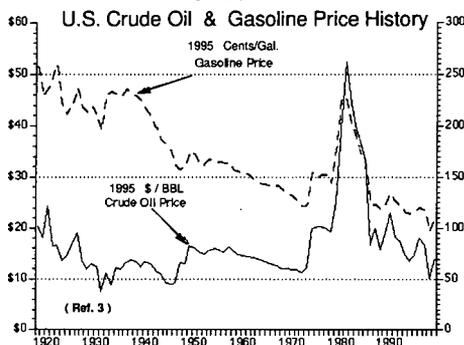
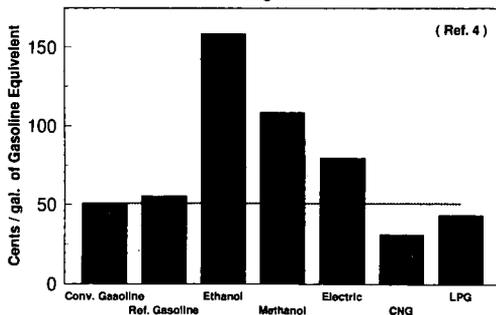


Chart 5

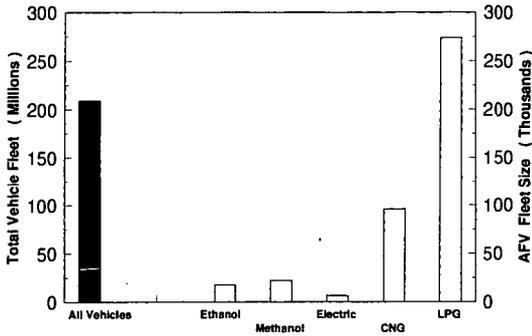
Economics Of Gasoline Alternative Fuels
1995 Wholesale Cost Before Adding Market Infrastructure & Vehicle Costs



Source: Alternative Transportation Fuels: A Comparative Analysis, AICHE Government Relations Committee, Sept 1997

Chart 6

1999 U.S. Vehicle Fleet: Alt. Fuel Vehicles vs Total Fleet



(Ref. 5)

Chart 7

Emission Reductions with Calif. Reformulated Gasoline

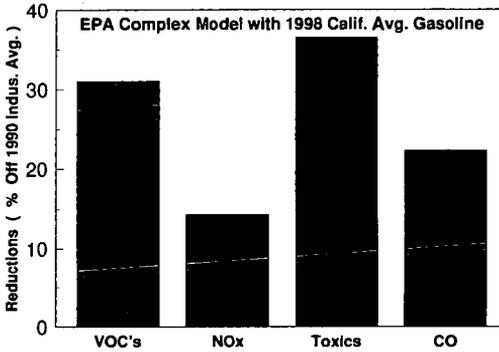
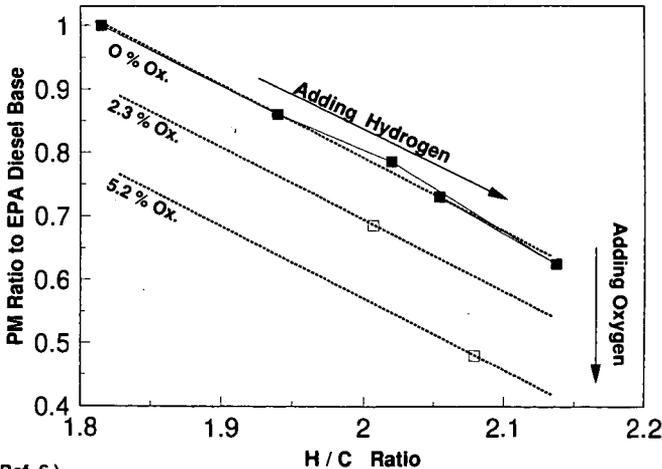


Chart 8

Adding Hydrogen & Oxygen Reduces Diesel PM



(Ref. 6)