

The Fischer-Tropsch Process

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Abstract

The Fischer-Tropsch (F-T) process is a gas to liquid process that involves reacting CO with H₂ on a metal catalyst to form various hydrocarbon chains. Franz Fischer and Hans Tropsch produced the Fischer-Tropsch process to create hydrocarbons from coal derived gas in the 1930s during World War II. The thermodynamic expectation of hydrogenation of carbon monoxide is methane and water with negligible amounts of heavier carbon chains. However, the observed concentrations of hydrocarbons formed from the F-T process, with an iron catalyst at 600K, is less than half methane and having propene, an unsaturated hydrocarbon, as the highest concentration. The polymerization is described by the Anderson-Schulz-Flory distribution which shows selectivity of different chain hydrocarbons based on a growth probability constant, that changes with temperature, H₂/CO composition, pressure, type of catalyst and presence of catalyst promoters. Iron and Cobalt are common catalysts for the F-T process. Iron is more susceptible to carbon deposition. The iron catalyst is Iron (II,III) Oxide. There are three main types of reactors wherein the F-T process is carried out. There are two main mechanisms for which the reactions may undergo; a carbide mechanism, and a CO insertion mechanism.

Background



Franz Joseph Emil Fischer Hans Tropsch

The Fischer-Tropsch process was created by Franz Fischer and Hans Tropsch in the 1920s. Along with the Bergius hydrogenation process, the Third Reich used the Fischer-Tropsch process, which employs heat, pressure, and metal catalysts to transform carbon monoxide and hydrogen into fuels, which provided more than one-third of the total fuel capacity with which Nazi Germany went to war. South Africa's apartheid regime employed it to ease the effects of the embargo in the 1980s. Sasol has spent decades refining the process.



General Process

There are three steps involved with the application F-T technology

Synthesis gas (Syngas) preparation

Syngas is developed from a carbonaceous feedstock. The only requirement is that the feedstock contains carbon. If there are deficient amounts of hydrogen in the feedstock then hydrogen is provided by water. The gasification of coal is done by heating coal along with steam and oxygen. Natural gas has been found that isn't commercially viable to be transported along pipelines to where it can be sold. These sources have been called 'stranded'. These reserves can be converted to shippable liquids using FT. The main component of natural gas is methane. The conversion of natural gas to syngas is called methane reformation.

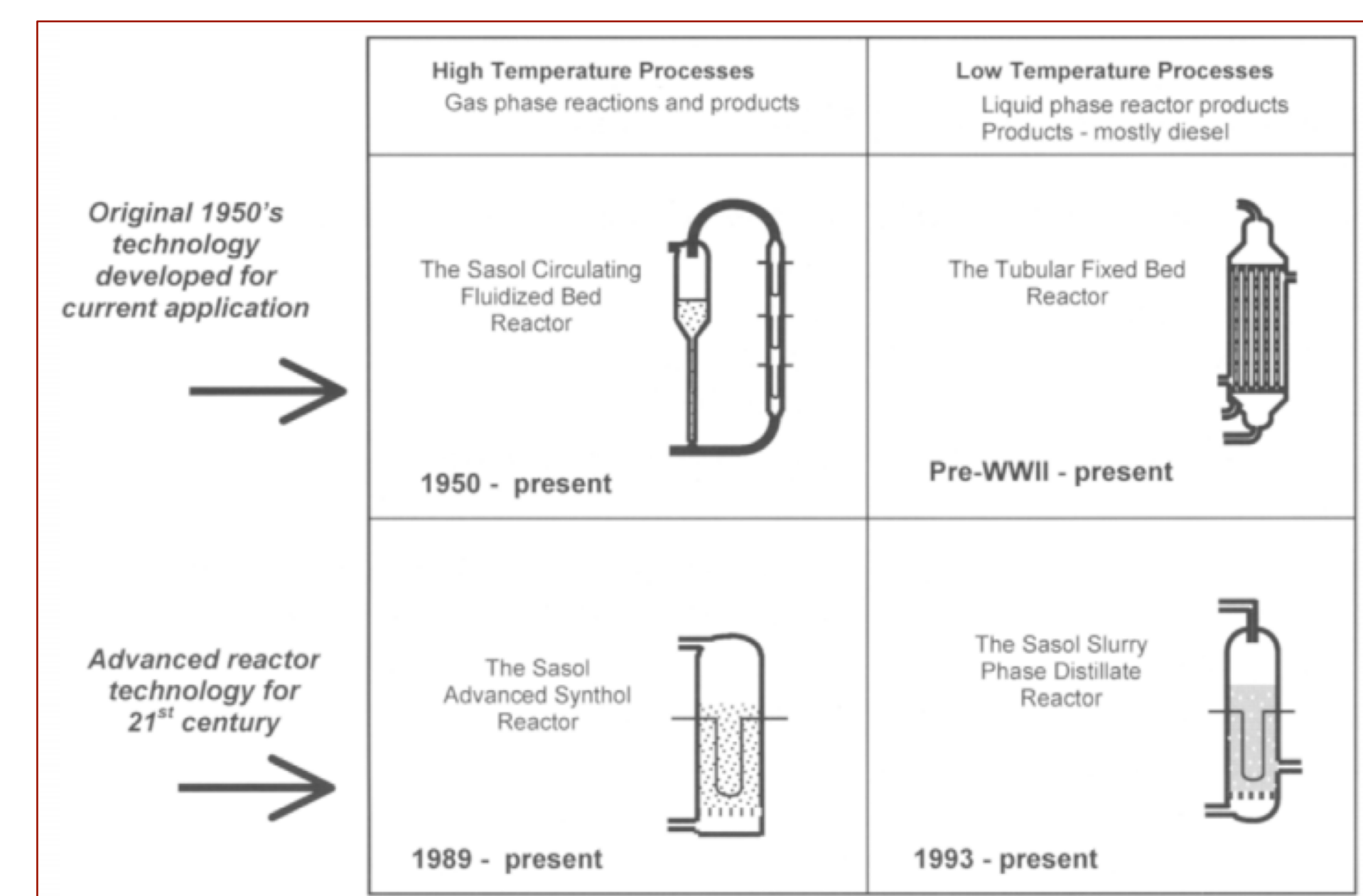
F-T Process

The wax producing low temperature Fischer-Tropsch (LTFT) process with use of iron catalysts eliminates the need for an upstream shift reactor to increase hydrogen content in the syngas. Produces lubricant based oils and lubricant feedstocks. High temperature Fischer-Tropsch (HTFT) process uses upstream shift reactor may still be commercially competitive because of valuable light olefin products that are produced. It is generally easy to remove potential FT catalyst poisons from natural gas prior to the reforming step. Its more expensive to use LTFT iron catalyst because it's not possible to achieve high per pass conversions resulting in the need for expensive recycles or multiple reactor stages. The choice for natural gas feed is between HTFT and LTFT but with cobalt catalyst instead of iron catalyst. The four types of FT reactor systems that may find commercial use:

- HTFT fluidized bed reactors using iron catalysts
- LTFT slurry reactors using precipitated iron catalysts
- LTFT slurry reactors using supported cobalt catalysts
- LTFT tubular fixed bed reactors for special circumstances

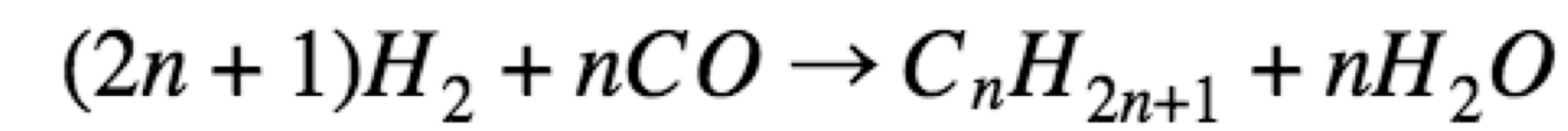
Upgrading of Products

The last step in the application of F-T technology is the upgrading of products to shippable final products. The primary liquid upgrading will typically start with removal of light hydrocarbons and dissolved gases to make the hydrocarbons suitable for atmospheric pressure storage. Olefins may be removed from the straight run liquid products for use as chemical feedstocks. This is achieved by fractionation and extractive distillation. Olefins may be oligomerised, alkylated or hydroformylated to produce special final products. The remaining material is generally converted to paraffins in a hydrogenation step and fractionated into naphtha, and diesel and optionally a kerosene/jet fuel cut. The naphtha can be further refined to gasoline. The hydrogenation step may be combined with other processing steps to make use of hydrogen such as hydro-isomerisation. The production of ethylene and propylene is possible and the market for use of these monomers to produce plastics is large. In summary the dominant future product is expected to be a high quality diesel motor fuel. Important secondary products are high quality lubricant base oils and olefinic hydrocarbons used in the petrochemical industry.

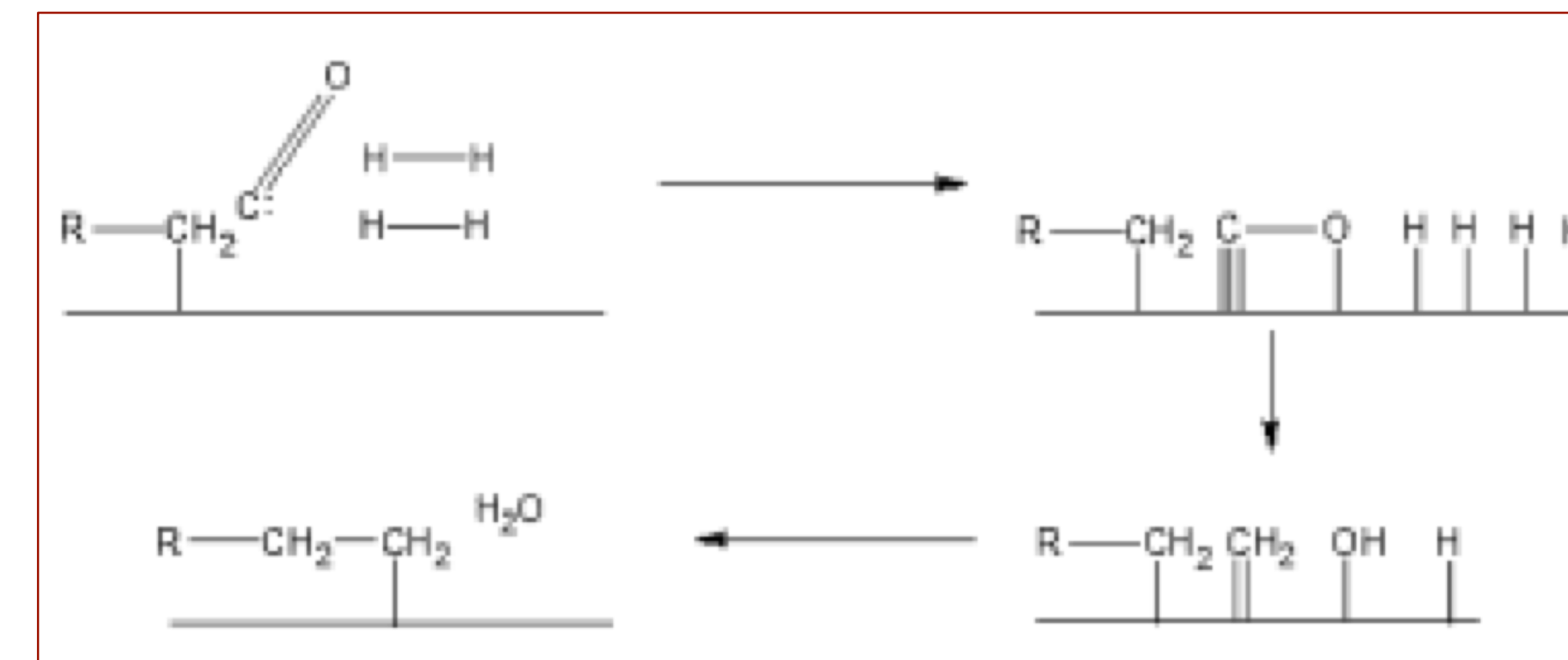


Mechanisms

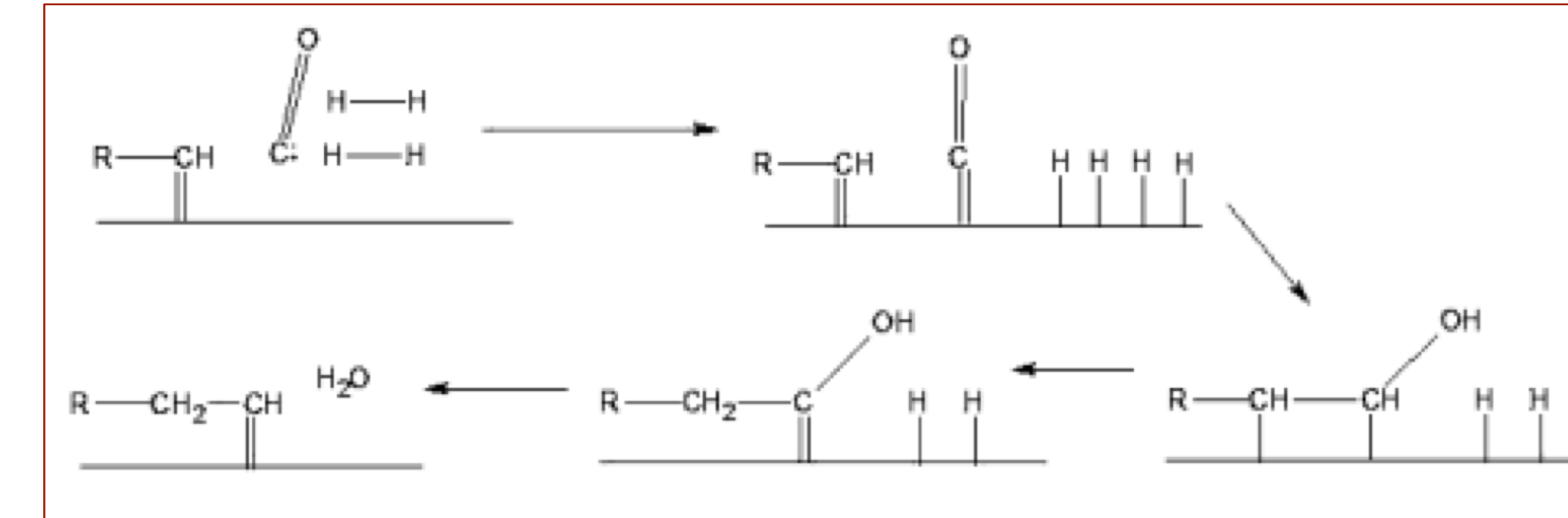
Alkane reaction



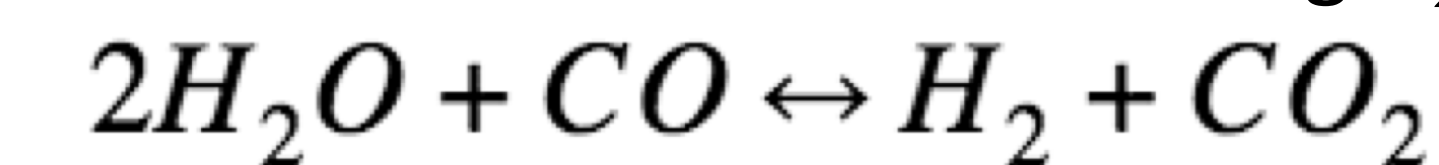
Carbide Mechanism



CO Insertion Mechanism



Water Gas Shift reaction for controlling H₂/CO ratio



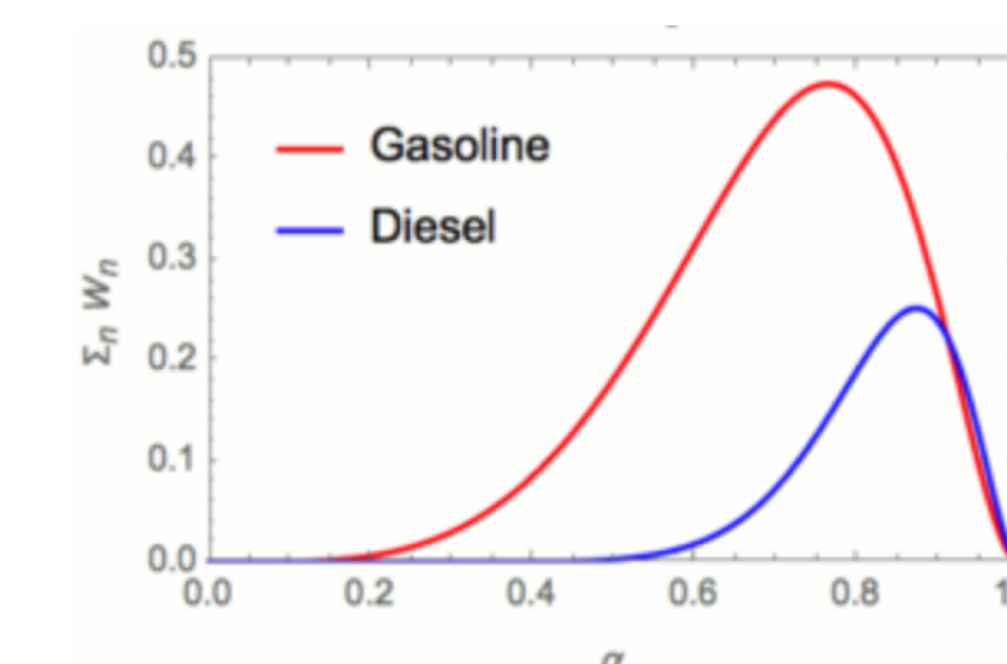
Selectivity and Anderson-Schulz-Flory model

The probability of chain growth follows the Anderson-Schulz-Flory distribution

$$P_n = \alpha^{n-1}(1 - \alpha)$$

Where P_n is the probability of producing a hydrocarbon of length n (mole fraction). The expected chain length $\langle n \rangle = nP_n = 1/(1 - \alpha)$ the weight fraction is

$W_n = n\alpha^{n-1}(1 - \alpha)^2$ the maximum probability for a given set can be found by taking the derivative with respect to and setting it equal to zero $\frac{dP_n}{d\alpha} = 0, \alpha = \frac{n-1}{n+1}$. By summing the weight fractions for a given set of n like n=5-11 for gasoline or n=12-18 for diesel, we can find the distribution of weight fractions of the given set across values of α .



Performance and the growth change probability constant depends on gas composition (feed/product component partial pressures), catalyst formulation and operating temperature.

Higher temperature favors methane formation, carbon deposition and other deactivation mechanisms (particularly with iron based catalysts), reduces the average chain length of product molecules. Rate of reaction increases and quality of steam produced by the reactor heat removal system.

Chain-growth probabilities (α) to maximize various product cuts and the minimum reactor temperature required to avoid a liquid phase [4]	α	Minimum temperature to avoid liquid condensation (°C)
Cut maximized (by mass fraction)		
C ₂ - C ₅	0.5081	109
C ₅ - C ₁₁	0.7637	329
C ₅ - C ₁₈	0.8164	392
C ₁₂ - C ₁₈	0.8728	468

Iron as a catalyst

There are two types of iron catalysts. Fused catalysts and precipitated catalysts.

Precipitated iron catalyst

The precipitated iron catalysts that are used for sasol's LTFT process is geared towards high molecular mass waxes. The process for creating the catalysts was first developed by Ruhrchemie for the first sasol plant. The method used today is essentially the same, with some differences within the process depending on whether the catalyst will be used in a fixed bed, slurry, or tubular reactor. The main difference is the calcining of the catalyst used in the slurry reactor due to requiring higher mechanical strength to prevent break-up of the catalyst. The catalyst is magnetite structured promoted with copper, potassium, and supported with silica. The catalyst is pre reduced under mild conditions before undergoing the F-T process.

Fused iron catalyst

Fused iron catalysts are used by sasol for HTFT process and is prepared by fusion of iron oxide with the chemical promoter, K₂O and structural promoters, MgO or Al₂O₃. In the presence of air, molten iron oxide at 1500°C should consist only of molten magnetite Fe₃O₄ but because of the carbon electrodes within arc furnace makes the situation somewhat reducing, some wustite, FeO, is formed in the furnace. The molten mixture of oxides is poured into ingots and cooled. The ingots are then crushed in a ball mill to the particle size required for the effective fluidization in the FT reactors. Magnetite is the preferred phase for effective structural properties. The catalyst is pre-reduced before undergoing the F-T process.

Iron versus other catalysts for FT

Only the four group VIII metals, Fe, Co, Ni and Ru have sufficiently high activities for the hydrogenation of carbon monoxide to warrant possible application in the FT synthesis. Ruthenium is the most active but its high cost and low availability rules it out for large scale application. Nickel is also very active but is a powerful hydrogenating catalyst and produces much more methane than Co or Fe catalysts. Nickel also forms volatile carbonyls resulting in continuous loss of the metal at the temperatures and pressures at which practical FT plants operate.

Both catalysts form iron carbide on the surface initially which is a very exothermic process. The process begins just with hydrogen and slowly replacing the hydrogen with syngas over a predetermined time to prevent high localised surface temperatures.

Modern and Future Use

Since the major requirement for the feedstock is to contain carbon, the FT can use a wide variety of feedstock to create long hydrocarbon chains even after fossil fuels have depleted. FT process can be used for converting "stranded" natural gas, that wasn't as feasible to transport, into liquid products for transport.

Sasol Ltd. in Secunda produces 160,000 barrels of gasoline, diesel fuel, and jet fuel a day which is enough to account for 28% of South Africa's needs without the use of crude oil.

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