Fischer Tropsch Process

The **Fischer–Tropsch process** is a collection of chemical reactions that converts a mixture of carbon monoxide and hydrogen into liquid hydrocarbons. These reactions occur in the presence of metal catalysts, typically at temperatures of 150–300 °C (302–572 °F) and pressures of 1 to 10 atmosphere. The process was first developed by Franz Fischer and Hans Tropsch in the year 1925.

As a premier example of C1 chemistry, the Fischer–Tropsch process is an important reaction in both coal liquefaction and gas to liquids technology for producing liquid hydrocarbons. In the usual implementation, carbon monoxide and hydrogen, the feedstocks for FT, are produced from coal, natural gas, or biomass in a process known as gasification. The Fischer–Tropsch process then converts these gases into a synthetic lubrication oil and synthetic fuel. The Fischer–Tropsch process has received intermittent attention as a source of low-sulphur diesel fuel and to address the supply or cost of petroleum-derived hydrocarbons.

Reaction:

The Fischer–Tropsch process involves a series of chemical reactions that produce a variety of hydrocarbons, ideally having the formula (C_nH_{2n+2}). The more useful reactions produce alkanes as follows:

$$(2n + 1)\,H_2 + n\,CO \rightarrow C_nH_{2n+2} + n\,H_2O$$

where, n is typically 10–20. The formation of methane ($n = 1$) is unwanted. Most of the alkanes produced tend to be straight-chain, suitable as diesel fuel. In addition to alkane formation, competing reactions give small amounts of alkenes, as well as alcohols and other oxygenated hydrocarbons

Fischer–Tropsch intermediates and elemental reactions

Converting a mixture of H_2 and CO into aliphatic products is a multi-step reaction with several intermediate compounds. The growth of the hydrocarbon chain may be visualized as involving a repeated sequence in which hydrogen atoms are added to carbon and oxygen, the C–O bond is split and a new C–C bond is formed. For one $–CH_2–$ group produced by $CO + 2\,H_2 \rightarrow (CH_2) + H_2O$, several reactions are necessary:

- Associative adsorption of CO
- Splitting of the C–O bond
- Dissociative adsorption of 2 H_2
- Transfer of 2 H to the oxygen to yield H_2O
- Desorption of H_2O
- Transfer of 2 H to the carbon to yield CH_2

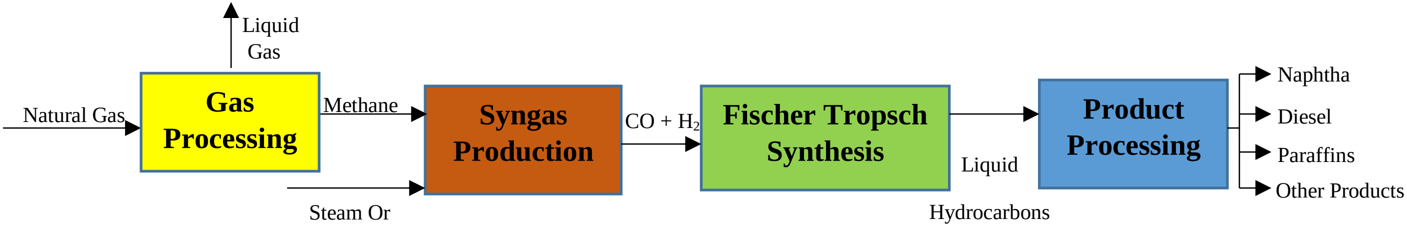

Figure 1. Flow chart of Fischer Tropsch process.

The conversion of CO to alkanes involves hydrogenation of CO, the hydrogenolysis (cleavage with H_2) of C–O bonds, and the formation of C–C bonds. Such reactions are assumed to proceed via initial formation of surface-bound metal carbonyls. The CO ligand is speculated to undergo dissociation, possibly into oxide and carbide ligands. Other potential intermediates are various C_1 fragments including formyl (CHO), hydroxycarbene (HCOH), hydroxymethyl (CH_2OH), methyl (CH_3), methylene (CH_2), methylidyne (CH), and hydroxymethylidyne (COH). Furthermore, and critical to the production of liquid fuels, are reactions that form C–C bonds, such as migratory insertion. Many related stoichiometric reactions have been simulated on discrete metal clusters, but homogeneous Fischer–Tropsch catalysts are poorly developed and of no commercial importance.

Addition of isotopically labelled alcohol to the feed stream results in incorporation of alcohols into product. This observation establishes the facility of C–O bond scission. Using ^{14}C-labelled ethylene and propene over cobalt catalysts results in incorporation of these olefins into the growing chain. Chain growth reaction thus appears to involve both ‘olefin insertion’ as well as ‘CO-insertion’

Feedstocks: gasification

Fischer–Tropsch plants associated with coal or related solid feedstocks (sources of carbon) must first convert the solid fuel into gaseous reactants, *i.e.*, CO, H_2, and alkanes. This conversion is called gasification and the product is called synthesis gas ("syngas"). Synthesis gas obtained from coal gasification tends to have a H_2:CO ratio of ~0.7 compared to the ideal ratio of ~2. This ratio is adjusted via the water-gas shift reaction. Coal-based Fischer–Tropsch plants produce varying amounts of CO_2, depending upon the energy source of the gasification process. However, most coal-based plants rely on the feed coal to supply all the energy requirements of the Fischer–Tropsch process.

Feedstocks: GTL

Carbon monoxide for FT catalysis is derived from hydrocarbons. In gas to liquids (GTL) technology, the hydrocarbons are low molecular weight materials that often would be discarded or flared. Stranded gas provides relatively cheap gas. GTL is viable provided gas remains relatively cheaper than oil.

Several reactions are required to obtain the gaseous reactants required for Fischer–Tropsch catalysis. First, reactant gases entering a Fischer–Tropsch reactor must be desulfurized. Otherwise, sulphur-containing impurities deactivate ("poison") the catalysts required for Fischer–Tropsch reactions.

Several reactions are employed to adjust the H_2: CO ratio. Most important is the water-gas shift reaction, which provides a source of hydrogen at the expense of carbon monoxide:

$$H_2O + CO \rightarrow H_2 + CO_2$$

For Fischer–Tropsch plants that use methane as the feedstock, another important reaction is steam reforming, which converts the methane into CO and H_2:

$$H_2O + CH_4 \rightarrow CO + 3\ H_2$$

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Process conditions

Generally, the Fischer–Tropsch process is operated in the temperature range of 150–300 °C (302–572 °F). Higher temperatures lead to faster reactions and higher conversion rates but also tend to favor methane production. For this reason, the temperature is usually maintained at the low to middle part of the range. Increasing the pressure leads to higher conversion rates and also favors formation of long-chained alkanes, both of which are desirable. Typical pressures range from one to several tens of atmospheres. Even higher pressures would be favorable, but the benefits may not justify the additional costs of high-pressure equipment, and higher pressures can lead to catalyst deactivation via coke formation.

A variety of synthesis-gas compositions can be used. For cobalt-based catalysts the optimal H_2:CO ratio is around 1.8–2.1. Iron-based catalysts can tolerate lower ratios, due to intrinsic water-gas shift reaction activity of the iron catalyst. This reactivity can be important for synthesis gas derived from coal or biomass, which tend to have relatively low H_2: CO ratios (< 1).

Design of the Fischer–Tropsch process reactor

Efficient removal of heat from the reactor is the basic need of Fischer–Tropsch reactors since these reactions are characterized by high exothermicity. Four types of reactors are discussed:

Fischer-Tropsch Reactors

The reactions involved in the FT process are highly exothermic therefore, the elimination of heat is important when designing a commercial reactor. Three types of reactors are generally used for FT synthesis:

- ✓ Slurry bed reactor
- ✓ Fluidized bed reactor
- ✓ Fixed bed reactor

Commercially, all three types of reactors are in use. Heavy FT liquid hydrocarbons are produced in Arge reactors, the multitubular fixed-bed reactors developed by Ruhrchemie and Lurgi and used by Sasol.

Most of these Arge reactors are now replaced by slurry-bed reactors, which are regarded as the state- of-the-art technology for low temperature FT synthesis. Slurry-bed FT reactors have higher conversion rate and better temperature control.

Fluidized-bed FT reactors were developed for producing low molecular gaseous hydrocarbons and gasoline through high temperature FT synthesis.

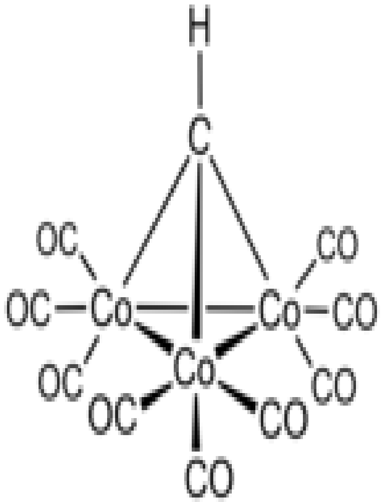
They were originally developed in a circulating mode and have been replaced by Advanced Synthol reactors of fixed fluidized bed type design. These reactors have high throughputs.

Catalysts

A variety of catalysts can be used for the Fischer–Tropsch process, the most common are the transition metals cobalt, iron, and ruthenium. Nickel can also be used, but tends to favour methane formation (“methanation”).

Cobalt

Cobalt-based catalysts are highly active, although iron may be more suitable for certain applications. Cobalt catalysts are more active for Fischer–Tropsch synthesis when the feedstock is natural gas. Natural gas has a high hydrogen to carbon ratio, so the water-gas shift is not needed for cobalt catalysts. Iron catalysts are preferred for lower quality feedstocks such as coal or biomass. Synthesis gases derived from these hydrogen-poor feedstocks has a low-hydrogen-content and require the water-gas shift reaction. Unlike the other metals used for this process (Co, Ni, Ru), which remain in the metallic state during synthesis, iron catalysts tend to form a number of phases, including various oxides and carbides during the reaction. Control of these phase transformations can be important in maintaining catalytic activity and preventing breakdown of the catalyst particles.



Methylidynetricobaltnonacarbonyl is a molecule that illustrates the kind of reduced carbon species speculated to occur in the Fischer–Tropsch process.

In addition to the active metal the catalysts typically contain a number of "promoters," including potassium and copper. Group 1 alkali metals, including potassium, are a poison for cobalt catalysts but are promoters for iron catalysts. Catalysts are supported on high-surface-area binders/supports such as silica, alumina, or zeolites. Promoters also have an important influence on activity. Alkali metal oxides and copper are common promoters, but the formulation depends on the primary metal, iron vs cobalt. Alkali oxides on cobalt catalysts generally cause activity to drop severely even with very low alkali loadings. $C_{\geq 5}$ and CO_2 selectivity increase while methane and C_2–C_4 selectivity decrease. In addition, the alkene to alkane ratio increases.

Fischer–Tropsch catalysts are sensitive to poisoning by sulfur-containing compounds. Cobalt-based catalysts are more sensitive than their iron counterparts.

Iron

Fischer–Tropsch iron catalysts need alkali promotion to attain high activity and stability (e.g. 0.5 wt% K_2O). Addition of Cu for reduction promotion, addition of SiO_2, Al_2O_3 for structural promotion and maybe some manganese can be applied for selectivity control (e.g. high olefinicity). The working catalyst is only obtained when—after reduction with hydrogen—in the initial period of synthesis several iron carbide phases and elemental carbon are formed whereas iron oxides are still present in addition to some metallic iron. With iron catalysts two directions of selectivity have been pursued. One direction has aimed at a low-molecular-weight olefinic hydrocarbon mixture to be produced in an entrained phase or fluid bed process (Sasol–Synthol process). Due to the relatively high reaction temperature (approx. 340 °C), the average molecular weight of the product is so low that no liquid product phase occurs under reaction conditions. The catalyst particles moving around in the reactor are small (particle diameter 100 µm) and carbon deposition on the catalyst does not disturb reactor operation. Thus a low catalyst porosity with small pore diameters as obtained from fused magnetite (plus promoters) after reduction with hydrogen is appropriate. For maximising the overall gasoline yield, C_3 and C_4 alkenes have been oligomerized at Sasol. However, recovering the olefins for use as chemicals in, e.g., polymerization processes is advantageous today. The second direction of iron catalyst development has aimed at highest catalyst activity to be used at low reaction temperature where most of the hydrocarbon product is in the liquid phase under reaction conditions. Typically, such catalysts are obtained through precipitation from nitrate solutions. A high content of a carrier provides mechanical strength and wide pores for easy mass transfer of the reactants in the liquid product filling the pores. The main product fraction then is a paraffin wax, which is refined to marketable wax materials at Sasol; however, it also can be very selectively hydrocracked to a high quality diesel fuel. Thus, iron catalysts are very flexible.

Ruthenium

Ruthenium is the most active of the FT catalysts. It works at the lowest reaction temperatures, and it produces the highest molecular weight hydrocarbons. It acts as a Fischer–Tropsch catalyst as the pure metal, without any promoters, thus providing the simplest catalytic system of Fischer–Tropsch synthesis, where mechanistic conclusions should be the easiest—e.g., much easier than with iron as the catalyst. Like with nickel, the selectivity changes to mainly methane at elevated temperature. Its high price and limited world resources exclude industrial application. Systematic Fischer–Tropsch studies with ruthenium catalysts should contribute substantially to the further exploration of the fundamentals of Fischer–Tropsch synthesis. There is an interesting question to consider: what features have the metals nickel, iron, cobalt, and ruthenium in common to let them—and only them—be Fischer–Tropsch catalysts, converting the CO/H_2 mixture to aliphatic (long chain) hydrocarbons in a ‘one step reaction’. The term ‘one step reaction’ means that reaction intermediates are not desorbed from the catalyst surface. In particular, it is amazing that the much carbided alkalized iron catalyst gives a similar reaction as the just metallic ruthenium catalyst.

HTFT and LTFT

High-Temperature Fischer–Tropsch (or HTFT) is operated at temperatures of 330–350 °C and uses an iron-based catalyst. This process was used extensively by Sasol in their coal-to-liquid plants (CTL). Low-Temperature Fischer–Tropsch (LTFT) is operated at lower temperatures and uses an iron or cobalt-based catalyst. This process is best known for being used in the first integrated GTL-plant operated and built by Shell in Bintulu, Malaysia.

Fischer-Tropsch Process - Commercial Aspects

The FT process has been used for large-scale applications in certain industrial sectors, even though its popularity is hampered by high maintenance and operation costs, high capital costs and uncertain price of crude oil.

Several companies are developing the process to enable practical exploitation of stranded gas reserves. Some of them include the following:

- Sasol - Series of plants operated by Sasol in South Africa were implemented with FT technology. The company now uses coal and natural gas as feedstocks and produces a wide range of synthetic petroleum products.

- PetroSA - It is another South African company having the world's largest Gas to Liquids complexes. It uses this technology to convert coal, biomass and natural gas into synthetic fuels.
- Linc Energy - The Australian company constructed the world's first gas-to-liquid plant operating on synthesis gas in 1999, using underground coal gasification. The plant first produced liquids using FT technology in 2008.

Fischer-Tropsch in nature

A Fischer–Tropsch-type process has also been suggested to have produced a few of the building blocks of DNA and RNA within asteroids. Similarly, the hypothetical abiogenic petroleum formation requires some naturally occurring FT-like processes.

Fischer-Tropsch Catalysts

Although several catalysts can be used for Fischer-Tropsch synthesis, the transition metals of ruthenium, nickel, cobalt and iron are some of the most common catalysts. Selection of FT process catalysts is based on the diesel fuels production and high molecular weight linear alkanes.

Nickel can be also be used as the catalyst, but it tends to promote methane formation. Cobalt is more active and usually preferred over ruthenium owing to the high cost of ruthenium.

On the other hand, iron is relatively inexpensive and has high water-gas-shift activity, so it is more suitable for obtaining synthetic gas with low hydrogen/carbon monoxide ratio like those derived through coal gasification.

In addition to the active metal, the catalysts include various promoters such as copper, potassium and high surface area binders such as alumina or silica. The presence of sulphur compounds in the synthetic gas can poison the FT catalysts.

The cobalt-based catalysts have higher sensitivity to sulphur than its iron counterparts, which in turn contributes to higher catalyst replacement costs for Co.

Therefore, cobalt catalysts are preferred for FT synthesis of synthetic gas derived from natural gas, where the synthetic gas has relatively low sulphur content and high hydrogen to carbon monoxide ratio. Iron catalysts are preferred deriving synthetic gas from low quality feedstocks such as coal.