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FROM GASIFICATION TO SYNTHETIC FUELS VIA FISCHER-TROPSCH SYNTHESIS

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Abstract: *This article presents aspects regarding the Fischer-Tropsch (FT) synthesis method. Several reactor types are taken into account and operation modes are presented with their advantages. Production of syngas from methane or coal and conversion of the syngas to a range of fuels and chemicals could become increasingly of interest as the reserves of crude oil are depleted and the price of crude oil rises, as seen in Figure 1 [7]. Experiments undertaken in Güssing, Austria, proved that biomass represented by woodchips can be a valuable feedstock for FT biodiesel production.*

Key words: *Fisher-Tropsch synthesis, synthetic fuel, biomass, gasification.*

1. Introduction

The industrial application of the FT-process started in Germany during the Second World War.

Given its availability, methane is preferred to coal for syngas production. The capital costs of the methane conversion plant are lower and also the process is more efficient. In methane reforming, about 20% of the carbon is converted to CO_2, whereas with coal gasification the percent is about 50% due to coal's much lower hydrogen content. Since the cost of syngas is a main concern, it is important that the maximum amount is converted in the downstream FT reactors. This requires that the composition of the syngas matches the overall usage ratio of the reactions. For cobalt-based FT catalysts, the main reaction is the FT reaction itself, as follows [5]:

$$CO + 2.15H_2 \rightarrow \text{hydrocarbons} + H_2O. \quad (1)$$

This means that the H_2/CO usage ratio is about 2.15. In the case of iron-based catalysts the water-gas shift (WGS) reaction also takes place:

$$CO + H_2O \rightarrow CO_2 + H_2. \quad (2)$$

This reaction changes the overall usage ratio. For the low-temperature FT (LTFT) process, the H_2/CO usage ratio is typically about 1.7. In higher temperatures conditions, the WGS is rapid and goes to equilibrium allowing CO_2 to be converted to FT products,

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via the reverse WGS followed by the FT reaction. Thus, if the syngas has a ratio of $H_2/(2CO + 3\ CO_2)$ to about 1.05, all of the H_2, CO and CO_2 can, in principle, be converted to FT products.

Producing a syngas having H_2 and CO in the ratio 2:1 the overall reaction stoichiometry should follow the steps [5]:

$$1.11\ CH_4 + 0.72\ O_2 \rightarrow 2\ H_2 + 1\ CO + 0.11\ CO_2 + 0.22\ H_2O, \qquad (3)$$

$$1.78\ CH_{0.5}(\text{coal}) + 0.5\ O_2 + 1.56\ H_2O \rightarrow 2\ H_2 + 1\ CO + 0.78\ CO_2. \qquad (4)$$

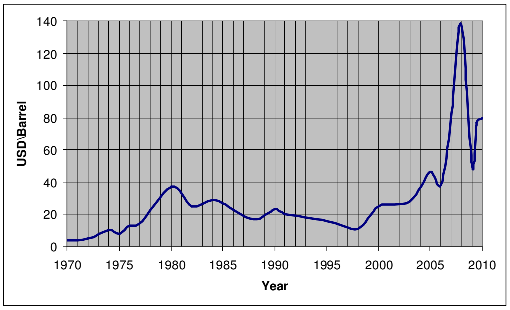


Fig. 1. *The variation of oil barrel price*

In eq. (3), the CH_4 and O_2 are the totals of that fed inside the catalytic reformers and outside to the furnace.

Equations (1) to (4), illustrate why core coal is required than CH_4 to produce the same amount of (H_2 + CO). In practice instead, the crude syngas is a mixture of mainly H_2, CO, CO_2 and CH_4, the actual compositions are depending on the process conditions and the types of reformers or gasifiers used. For both methanol and FT process, the purified syngas composition should in such a manner that the ratio $H_2/(2CO + 3CO_2)$ is slightly greater than 1.0. Both the Cu based methanol and Fe based FT catalysts are active water gas shift (WGS) catalysts and so all the CO and CO_2 can be consumed in the synthesis [5]. For a CO_2 rich gas the following reactions occur:

$$CO_2 + H_2 \rightarrow CO + H_2O\ (\text{WGS}), \qquad (5)$$

$$CO + 2H_2 \rightarrow CH_2 + H_2O\ (\text{FT}), \qquad (6)$$

$$CO_2 + 3H_2 \rightarrow CH_2 + 2H_2O\ (\text{Overall}). \qquad (7)$$

This does not apply for cobalt based catalysts as Co is a poor WGS catalyst [4].

Generalizing eq. (3) and (4) it can be seen that all hydrocarbons can be gasified, following eq. 8. According to this, biomass can also be used to produce a syngas rich in H_2 and CO:

$$C_nH_m + O_2 \rightarrow H_2 + CO + CO_2. \qquad (8)$$

Section 4 gives a short description of the biomass gasification process with some particularities of the gasifier used.

2. FT Reactor Types

According to the thermal process used, FT reactors are divided into two types. To produce gasoline and linear, low molecular mass olefins, iron-based catalysts with the high-temperature process (300-350 °C) is used. For producing diesel fuels and high molecular mass linear waxes iron or cobalt catalysts with low-temperature process (200-240 °C) is used.

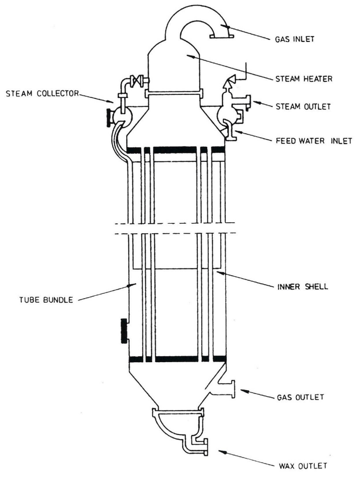
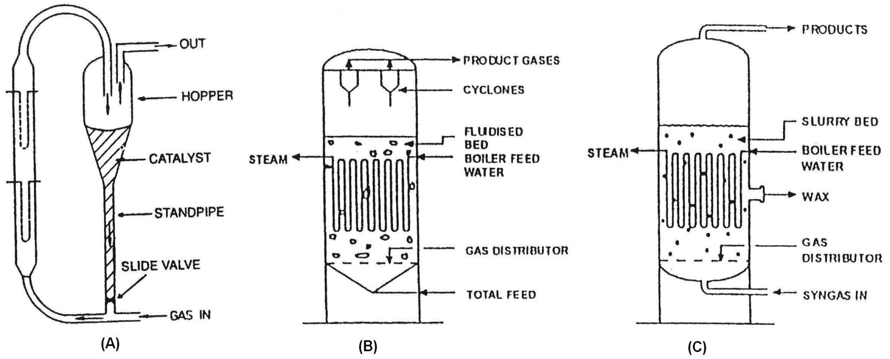


Fig. 2. *Multitubular fixed bed FT reactor* [5]

Since the FT reactions are highly exothermic, it is important to rapidly remove the heat of reaction from the catalyst particles in order to avoid overheating of the catalyst which would result in an increased rate of deactivation due to sintering and fouling and also in the undesirable high production of methane. High rates of heat exchange are achieved by forcing the syngas at high linear velocities through long narrow tubes packed with catalyst particles to achieve turbulent flow, or better, by operating in fluidized catalyst bed reactor. Figure 2 presents a multitubular fixed bed reactor and Figure 3 shows three types of fluidized bed reactors [5].



Fluidised bed FT reactors: (A) CFB reactors; (B) ebulating or FFB reactor; (C) slurry phase bubbling bed reactor

Fig. 3. *Types of fluidized bed FT reactors* [5]

2.1. High-Temperature Operation

The commercial FT reactors in Brownsville, TX plant, which only operated for a brief period in the mid 1950s, were of the fixed fluidized bed (FFB) type (Figure 3B). The reactors operated at about 2 MPa and 300 °C, i.e. they were HTFT reactors. For the first Sasol plant at Sasolburg the Kellogg-designed circulating fluidized beds (CFBs) (Figure 3A) were chosen. These reactors operated at about 2 MPa and 340 °C. After making some process and catalyst improvements, these reactors operated very well for many years. The improved reactors were named Synthol reactors. For the two new Sasol plants constructed about 25 years later at Secunda, the same type of reactors were installed but with improved heat exchangers and the capacity per reactor was increased three-fold (wider diameter and higher operating pressure). The same larger types of CFB reactors, with further improved heat exchangers, were installed in the Mossgas FT complex. In

CFB reactors there are two phases of fluidized catalyst. Catalyst moves down the standpipe in dense phase while it is transported up the "reaction" zone (left-hand side of Figure 3A) in lean phase. To avoid the feedgas going up the standpipe, the differential pressure over the standpipe must always exceed that over the reaction zone. At the high operating temperature carbon is deposited on the iron-based catalysts and this lowers the bulk density of the catalyst and thus the differential pressure over the standpipe. It is therefore not possible to raise the catalyst loading in the reaction section in order to compensate for the normal decline of catalyst activity with time-on-stream [1].

The main advantages of FFB over CFB reactors are as follows:

- The building costs are lower. For the same capacity, the FFB reactor is much smaller in size.
- Because of the wider reaction section, more cooling coils can be installed, increasing its capacity (More fresh gas can be fed by either increasing the volumetric flow or by increasing operating pressure. Pressures up to 4 MPa are feasible).
- All of the catalyst charge participates in the reaction, in any given moment whereas in the CFB only a portion of it does.
- For the reasons previously discussed, the lowering of the bulk density by carbon deposition is of less significance in the FFB and thus a lower rate of in-line catalyst removal and replacement with fresh catalyst is required to maintain high conversions. This lowers the overall catalyst consumption.

Because the iron carbide catalyst is very abrasive and the gas/catalyst linear velocities in the narrower sections of the CFB reactors is very high, these sections are ceramic lined and regular maintenance is essential. This problem is absent in the lower linear velocities FFB reactors and this allows longer on-stream times between maintenance inspections [3], [5], [7].

2.2. Low-Temperature Operation

Under the operating conditions used, the large amount of wax produced is in the liquid phase in the FT reactors and so, three phases are present, liquid, solid (catalyst) and gas. In top-fed multitubular reactors (Figure 2) the wax produced trickles down and out of the catalyst bed. In slurry reactors (Figure 3C), the wax produced accumulates inside the reactors and so the net wax produced needs to be continuously removed from the reactor.

For the Sasolburg FT plant which came on stream in 1955, five multitubular ARGE reactors (designed by Lurgi and Ruhrchemie) were installed for wax productions. These reactors are currently still in operation. Each reactor contained 2050 tubes, 5 cm i.d. a 12 m long. They operated at 2.7 MPa and 230 °C. The production capacity of each is about 21×10^3 t per year. Based on Sasol R&D pilot plant studies, an additional high capacity reactor operating at 4.5 MPa was installed in 1987.

In the Shell Bintuli plant, which came on stream in 1993, there are four large multitubular reactors each with a capacity of about 125×10^3 t per year. There are probably about 10000 tubes per reactor. As cobalt-based catalysts are used, which are much more reactive than the iron-based catalysts used in the Sasolburg reactors, the tube diameters of the Shell reactors are narrower in order to cope with the higher rate of reaction heat released.

The use of slurry bed reactors for FT synthesis was studied by several investigators in the 195s, e.g. Kolbel developed and operated a 1.5 m i.d. unit. In the late 1970s, Sasol R&D compared the performance of fixed and slurry bed systems in their 5 cm i.d. pilot plants and found the conversions and selectivities to be similar. In 1990, an efficient filtration device was tested in a 1 m i.d. demonstration slurry bed reactor. In 1993 a 5 m i.d. commercial unit was commissioned and has been in operation ever since. Its capacity is about 100×10^3 t per year which equals that of the combined production of the original five ARGE reactors. Note again that only about 40 years after Kobel's pioneering work did the first commercial slurry reactor come on-line. Using a cobalt-based catalyst, Exxon successfully operated a 1.2 m i.d. slurry reactor for wax production. The unit's capacity was 8.5×10^3 t per year.

The advantages of slurry over multitubular reactors are as follows:

- The cost of a reactor train is only 25% of that of a multitubular system.
- The differential pressure over the reactor is about four times lower which results in lower gas compression costs.
- The lower catalyst loading translates to four-fold lower catalyst consumption per tone of product.
- The slurry bed is more isothermal and so can operate at a higher average temperature resulting in higher conversions.
- On-line removal/addition of catalyst allows longer reactor runs.

The disadvantage of a fluidized system is that should any catalyst poison such has H_2S enter the reactor, all of the catalyst is deactivated, whereas in a fixed bed reactor, all the H_2S is adsorbed by the top layers of catalyst, leaving the balance of the bed essentially unscathed [2].

3. Tuning of the FT Process

Inside an FT reactor inevitably are taking place a multitude of reactions, producing a wide range of products. Modifying certain parameters and applying various downstream work-up processes, the yields of the desired products can be optimized.

3.1. Gasoline

For maximum gasoline production, the best option is using the high capacity FFB reactors at about 340 °C with iron catalyst. This produces about 40% straight run gasoline. Twenty percent of the FT product is propene and butane. These can be oligomerised to gasoline and because the oligomers are highly branched, it has a high octane value. The straight run gasoline, however, has a low octane value because of its high linearity and low aromatic content. The C_5/C_6 cut needs to be hydrogenated and isomerised and the C_7-C_{10} cut needs severe platinum reforming to increase the octane value of these two cuts. Di-isopropyl ether can be produced from propene and water and this will further boost the octane number of the gasoline pool. The overall complexity of gasoline production, however, makes it less attractive than the diesel fuel option [5].

3.2. Diesel Fuel

The very factors that count against the production of high quality gasoline, namely high linearity and low aromatic content are very positive factors for producing high cetane diesel fuel. The recommended process option is the use of the high capacity slurry bed reactors with cobalt catalysts and operated to maximize wax production. The straight run diesel selectivity is about 20% and after hydrotreatment its cetane number is about 75. The heavier than diesel products accounts for about 45-50% of the total and mild hydrocracking produces a large proportion of high quality diesel, virtually free of aromatics. The final diesel pool has a cetane number of about 70. As the market normally requires a cetane number of about 45, the FT diesel can either be used in areas where there are very tight constrains on diesel quality or it can be used as blending stock to upgrade lower quality diesel fuel. The naptha produced would need severe reforming to convert it to high octane gasoline. Preferably it could be steam cracked as it would produce a high yield of ethylene.

The mild hydrocracking of wax was investigated at the Sasol R&D division during the 1970s. The product heavier than diesel was recycled to extinction. The overall yields were about 80% diesel, 15% naphta and 5% C_1-C_4 gas. When the decision to construct the third Sasol plant was made, the wax hydrocracking proposal was rejected because at that time, making gasoline was the more economic option and the straight duplication of the second plant resulted in huge savings in time and capital. Also at that stage, the FT slurry reactors had not yet been developed. About 20 years later, the same concept of wax hydrocracking was implemented at the Shell Bintuli plant where multitubular FT reactors are used and currently Sasol/ Chevron are designing a slurry FT plant with wax hydrocracking in Nigeria. A similar plant at Quatar is in the pipeline [5].

3.3. Chemicals

The high-temperature fluidized bed FT reactors with iron catalyst are ideal for the production of large amounts of linear α-olefins. As petrochemicals, they sell at much higher prices than fuels. The olefin content of the C_3, C_5-C_{12} and C_{13}-C_{18} cuts are typically 85, 70 and 60%, respectively. Ethylene goes to the production of polyethylene, polyvinylchloride etc. and propylene to polypropylene, acrylonitrile etc. The extracted and purified C_5-C_8 linear α-olefins are used as comonomers in polyethylene production. The longer chain olefins can be converted to linear alcohols by hydroformylation. The only required purification of the narrow feed cuts is the removal of the acids. The hydroformylation was investigated at the Sasol R&D laboratories in the early 1990s. The alcohols are used in the production of biodegradable detergents. Their selling prices are about six times higher than that of fuel.

The LTFT processes produce predominantly longer chain linear paraffins. After mild hydrotreatment to convert olefins and oxygenates to paraffins, the linear oils and various grades of linear waxes can be sold at high prices [5].

4. FT Fuels from Biomass

In the town Güssing in Austria, an 8 MW (fuel power) demonstration plant shows the feasibility of the dual fluidized bed gasification process. Biomass chips are transported from a daily hopper to a metering bin and fed into the fluidised bed reactor via a rotary valve system and a screw feeder. The idea behind the gasifier concept consists of two divided reaction zones: 1) a gasification zone fluidized with steam and 2), a combustion zone fluidized with air, which provides the energy for the gasification zone. There is a circulation loop of bed material between the two zones. Heat from the combustion zone is transferred with the bed material into the gasification zone. Product gas is kept separately from flue gas. The resulting product gas is nearly nitrogen-free and rich in hydrogen.

The producer gas is cooled and cleaned by a two stage cleaning system. A water cooled heat exchanger reduces the temperature from 850 °C - 900 °C to about 160 °C - 180 °C. The first stage of the cleaning system is a fabric filter to separate the particles and some of the tar from the producer gas. These particles are returned back into combustion zone of the gasifier. In a second stage the gas is liberated from tar by a scrubber as seen in Figure 4. The product gas for the FT-synthesis is taken from the gasification plant after a blower [8].

The flow chart from Figure 5 shows the test rig for the Fischer Tropsch synthesis. The experimental FT synthesis installation from Güssing is divided in the following main parts:

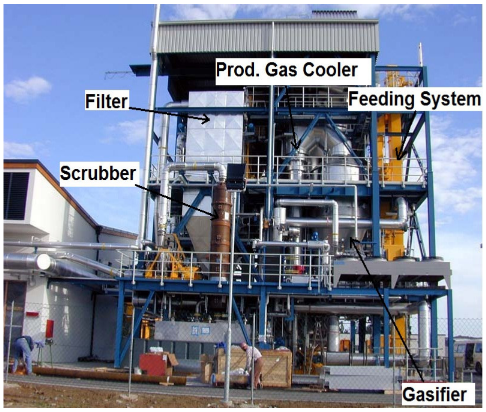


Fig. 4. *View over the CHP Güssing* [6]

1. Steam reformer.
2. Gas drying by biodiesel scrubber.
3. Additional atmospheric gas cleaning by activated charcoal.
4. Compression of the gas to 20-30 bars.
5. Various fixed bed reactors (HDS, ZnO, CuO, $NaAlO_2$) for further gas cleaning.
6. Slurry FT reactor.
7. Offgas scrubber for removing waxes from the offgas.
8. Offgas cooler to remove liquid FT products from the offgas [8].

The test series started with adjusted operation conditions of 230 °C, 20 bars and a product gas flow of 5 Nm³ per hour. The first two experiments tried to stabilize the process by keeping conditions on a constant value. The aim of the stabilization process is to achieve equilibrium in the slurry reactor (as seen in Figure 3C) between the starter waxes and the new product. At interruptions during the experiments the temperature of the slurry reactor was kept on constant value and the FT-plant was operated with nitrogen to avoid any settling of the catalyst.

In the primary experiments, the product gas flow was adjusted to approximately 6 Nm³ per hour and the pressure level was by about 20 bars. The installation was functioning for a week. The product can be separated into diesel fuel with properties described in section 3.2 and high linear waxes.

The total product distribution was used for the calculation of the chain growth probability α. The average product distribution over the experiments tends to a chain growth probability of 0.85 to 0.9, which is in the suitable range for a low-temperature operation of FT synthesis, as described in section 2.2.

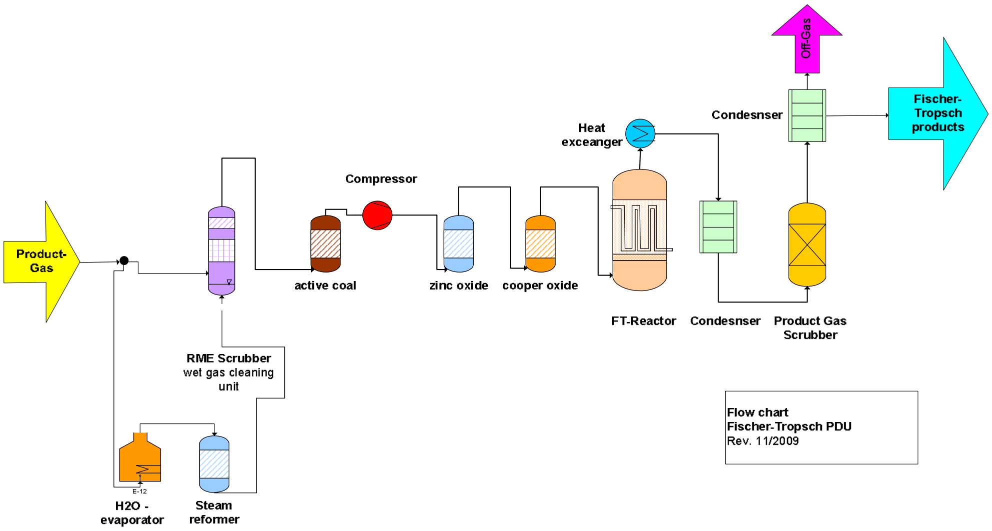


Fig. 5. *The Fischer-Tropsch pilot plant flow chart* [8]

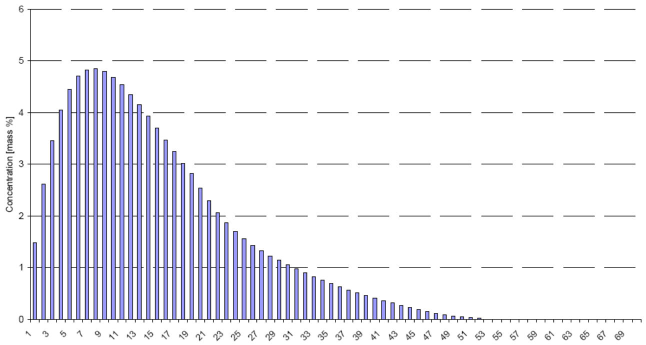


Fig. 6. *Corrected total product distribution* [8]

Figure 6 shows a corrected total product distribution. This figure includes also the FT-product, which was produced, but could not be condensed.

5. Conclusions

An important parameter in the production of synthetic fuels is the type of catalyst used. The FT reactors can be optimized to produce gasoline, diesel fuel or chemicals. It is very important to produce synthetic fuels, as the oil prices are high and world supplies will run out. The FT process has a high potential as the production of syngas from biomass is starting to emerge. The FT fuels from biomass can offer a clean and carbon neutral automotive fuel. Furthermore, the syngas from the gasification unit can be suitable as hydrogen source. The FT-synthesis enables the possibility to produce a Biofuel of the second generation with high quality, which is not in competition to food industry. The FT-product is free of aromatic components and incinerates without the formation of soot.

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