

# **Fischer-Tropsch process**

### HIGHLIGHTS

**Processes and technology status** – Fischer-Tropsch synthesis (FT) converts the syngas to different range of hydrocarbons. Feedstocks for FT process are coal, natural gas, and recently biomass resources. Moreover, the green FT production unit is supplied with hydrogen produced by electrolysis and  $CO_2$  from biogas upgrading.

**Cost** – The dominant costs of biofuel production from vegetable oil and sugar/starch crops are feedstock costs. A reference oil price of  $59.52 \in_{2006}^{1}$ /bbl can lead to a competitive biofuel production against fossil-based fuels <sup>1</sup>.

**Potential and barriers** – FT produces hydrocarbons by utilizing biogenic feedstocks and can tune the product distribution depending on regional market needs. However, the production of the synthesis gas and the lack of economic competitiveness in today's energy market are the main barriers ahead of bio-based FT synthesis.

**Fischer-Tropsch process** – The FT process produces hydrocarbons ranging from  $C_1$  to  $C_{100+}$ . Although the feedstocks for the traditional FT plants are coal and natural gas, the integrated biomass gasification FT system is a novel and renewable technique for the production of green fuels. Moreover, FT can convert biomass-based syngas, captured CO<sub>2</sub>, and renewable H<sub>2</sub> from excess electricity to hydrocarbons. FT is a highly localized industry and depends on the sources of syngas available, the desired products, and the demand for co-production of electricity. The only natural, renewable carbon resource and large fraction of substitute for fossil fuels is biomass.

**Process overview** - The Fischer– Tropsch process (FT) is a heterogeneous catalytic and polymerization reaction for the conversion of syngas to higher

 $<sup>^1</sup>$ 1 €2006 = 1.26 \$2006  $^{11}$ ; 75 U\$/bbl



hydrocarbons, especially liquid transportation fuels starting from a syngas stream mainly composed of CO and H<sub>2</sub>. The spread in C number can vary by changing the operating temperature, the type of catalyst, the amount or type of promoter present, the feed gas composition, the operating pressure, or the type of reactor used. Possible products from FT are gasoline, diesel, jet fuel, paraffinic waxes, lubricants, synthetic naphtha and waxes, olefins, and petrochemical based products.

The catalytic conversion of  $H_2$  and CO to hydrocarbons is described as a stepwise reaction. CH<sub>2</sub> intermediates (Eq. 1) are formed from H<sub>2</sub> and CO. The chain growth and the production of paraffin (Eq. 2), olefins (Eq. 3), and oxygen-containing components <sup>2</sup>.

| $2\mathrm{H}_2 + \mathrm{CO} {\rightarrow} (\mathrm{CH}_2) + \mathrm{H}_2\mathrm{O}$ | (1) |
|--|-----|
| $(2n+1)H_2 + nCO {\rightarrow} C_nH_{2n+2} + nH_2O$                                  | (2) |
| $(2n)H_2 + nCO \rightarrow C_nH_{2n} + nH_2O$  | (3) |

Group VIII elements, especially ruthenium (Ru), iron (Fe), cobalt (Co), and nickel (Ni), are eligible as catalysts in FT synthesis. In FT catalysts contain general, porous support and hydrogenating metals. Two major industrial catalyst groups are iron (Fe)-based and cobalt (Co)-based catalysts. Low-cost Fe-based catalysts present high activity toward WGS reaction, and it is favorable for the conversion of CO-rich syngas. Fixed bed, fluidized bed, and slurry bed are the main types of reactors used in the FT synthesis (Figure 1).

**Bio-based FT** - Biofuel production refers to using syngas derived from a biogenic origin, made from biogas, biomass, or wastes. Depending on the biomass feedstock and the gasification process conditions, the high oxygen content of most biomass sources leads to syngas with a low  $H_2/CO$  ratio that varies in the range of 0.5-1.0.

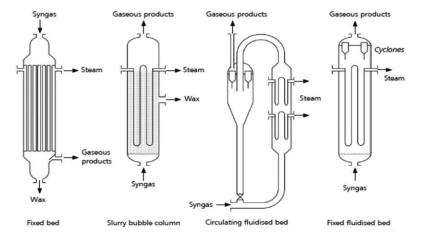


Figure 1. Commercial FT reactors <sup>3</sup>

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**E P O C** – Chemical sector decarbonization

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According to Eq.1, the transformation of syngas into higher molar-weight hydrocarbons requires an H<sub>2</sub>/CO feed ratio close to 2. Adjustment of this ratio is possible through water–gas shift (WGS) reaction, in which CO reacts with water vapor to boost the H<sub>2</sub> concentration rejecting CO<sub>2</sub> in the process.

Recently, research interest has grown in the direction of installing small-scale systems for the FT synthesis to be easily transported and deployed at the carbon feedstock location. Synthetic fuel is one of the energy storage mediums in a form that can be readily transported and stored for use weeks, months, or years later. So. renewable energy can pair with solid oxide co-electrolysis process FT technology to provide an efficient means of storing renewable energy in the form of a liquid fuel.

#### Production and consumption in

**Belgium** – Lignocellulosic biomass will be required for intensive decarbonization of the Belgium energy system and the nonenergy demand applications, even if it is available at a very high price. Belgium presents a non-energy demand

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corresponding to ~15% of its primary energy mix. However, high-temperature heat is a significant application for biomass and moving toward carbon neutrality. Biomass imports are key in the energy balance of Belgium. When considering 90% GHG savings, local resources represent the share of 12% to 20%. EU could supply 39 to 76% of the biomass requirements for Belgium as described in the ENSPRESO database<sup>2</sup>, released in 2022 <sup>4</sup>. The main biofuel options for Belgium in the short term are biodiesel (methyl ester) from vegetable oil which has the properties for blending with diesel fuel.

#### Investment and production costs –

The liquid fuel cost varies widely depending on the feedstock, but it could be competitive with fossil fuels depending on the considered region. The production of ethanol from corn or wheat is marginally viable. The production costs approximate the selling price of ethanol (550  $\in_{2019}$ /ton)<sup>5</sup>. More details of costs are available in table 1.

**Energy requirements** – FT is a highly exothermic reaction due to a standard reaction enthalpy of –165 kJ/mol<sub>CO</sub> combined with CO feed

<sup>&</sup>lt;sup>2</sup> ENSPRESO - an open data, EU-28 wide, transparent and coherent database of wind, solar and biomass energy potentials <sup>12</sup>



concentrations of more than 25% and high CO conversions <sup>6</sup>. Excessive reaction temperatures lead to the higher methane yield, carbon deposition, and catalyst deactivation. Tijmensen et al. reported that the overall thermal efficiency of a BTL process on a lower heating value was 33– 40% for gasification systems operated at atmospheric pressure and 42–50% for pressurized gasification systems <sup>7</sup>.

# Carbon mitigation by FT process -

First-generation and second-generation biofuels have the potential to reduce  $CO_2$ emissions by 50% and 90%, respectively, in comparison to fossil fuels<sup>8</sup>. In addition, for the internal combustion engines utilization, the FT fuels exhibit lower emission levels to gasoline and diesel. compared Furthermore, implementing carbon capture and storage (CCS) in an FT process producing fuel from residual forest biomass would significantly improve its CO<sub>2</sub> balance while providing carbon-negative replacements for fossil fuels. Even though at the moment (March 2022), there are no commercial plants producing FT fuels from biomass, the recognition of its negative emission would improve the economics of FT liquid production and could speed up the commercial adoption of this technology.

FT Innovations - The main areas of innovation in FT over the past decade have involved the improvement of catalysts and the development of novel reactor designs. The other disruptive technology in FT is  $H_2O/CO_2$  co-electrolysis technology using solid oxide electrolysis cells (SOEC) <sup>9</sup>. Plasma reformers or solid oxide coelectrolysis technologies are also novel technologies for the synthesis gas. Integration of these technologies makes possible the conversion of low-cost natural resources such as natural gas or biogas to produce a liquid fuel of high value and energy density.

# Challenges and opportunities for biofuels (Potential and barriers) –

A major driver for considering biogenic feedstocks is that the produced hydrocarbon are in renewable class. Moreover, the great advantage of FT synthesis compared to other processes is certainly the possibility to tune the product distribution depending on regional market needs. FT can also utilize captured  $CO_2$  and green hydrogen to produce high added-value chemicals. The production of liquid fuels using biomassderived syngas has received particular as a potential alternative for interest achieving a carbon-neutral and sustainable energy process.



Biomass has different properties than coal and, therefore, several process changes are necessary. The biggest obstacle to the commercialization of FT biofuels is their lack of economic competitiveness in today's energy market, especially owing to their high capital costs. FT fuels are 2.5 to 5 times more expensive than their equivalent fossil fuels <sup>10</sup>.

| Table | 1. Summar | y Table: | Key EO | Data and Figures |
|-------|-----------|----------|--------|------------------|
|-------|-----------|----------|--------|------------------|

| Technical Performance                        |   |   |  |
|--|---|---|--|
| Fischer-Tropsch (FT) processes               | For light olefin and fuel synthesis   |   |  |
| Feedstocks                                   | Syngas $(Co + H_2)$   |   |  |
| Syngas resources                             | Coal, Natural gas, Biomass*   | , Green H <sub>2</sub> and captured CO <sub>2</sub> |  |
| Catalysts                                    | Group VIII elements, especially iron (Fe) and cobalt (Co) for   |   |  |
|  | industrial-scale FT processes   |   |  |
| Output                                       | Synthetic hydrocarbons (carbon number $C_1$ to $C_{100+}$ )   |   |  |
| FT in Belgium                                |   |   |  |
| Main biofuel options for Belgium             | The on the short term are biodiesel (methyl ester) from<br>vegetable oil; and bio-ethanol from sugar or starch crops.<br>Biomass imports are key in the energy balance of Belgium.              |   |  |
| Energy requirements                          |   |   |  |
| Methanation reaction                         | Exothermic reaction; standard reaction enthalpy of $-165 \text{ kJ/mol}_{CO}$ <sup>**</sup> . While, chemical reaction between hydrogen and carbon monoxide requires a high quantity of energy. |   |  |
| Costs  |   |   |  |
| Feedstock                                    | Production capacity (BPD)   |   |  |
| Switchgrass (2009)                           | 4630  | 0.37  |  |
| Residual Woodstraw (2013)                    | 5500  | 1.18  |  |
| Corn stover (2020)                           | 2362  | 1.22  |  |
| Woody Biomass (2010)                         | 1700  | 0.61  |  |
| Woody Biomass (2020)                         | 2180  | 0.35  |  |
| Green hydrogen                               | 2.63 - 5.75 € <sub>2020</sub> /kg   |   |  |
| Blue hydrogen ***                            | 2.10 € <sub>2020</sub> /kg  |   |  |
| Grey hydrogen                                | 0.88-1.75 € <sub>2020</sub> /kg   |   |  |
|  | ad to food finale)  |   |  |
| CO <sub>2</sub> mitigation potential (compar |   |   |  |
| First-generation biofuels                    | 50%   |   |  |
|  |   |   |  |

\* Biomass-to-liquid Fischer-Tropsch

\*\*\* With carbon capture pair

<sup>&</sup>lt;sup>\*\*</sup> This value is for reaction temperature of 190 °C and CO fraction of 7.8%. It increases at higher reaction temperatures and higher fractions of CO  $^{6}$ .





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