

Fischer-Tropsch synthesis

LAB SCALE BENCH SCALE PILOT PLANT DEMONSTRATION PRODUCTION

DEFINITION & PROPERTIES

Fischer-Tropsch synthesis (FTS) is a catalytic process for converting syngas (CO and H₂) into a petroleum-like product termed as FT crude readily upgradable into a wide range of transportation grade liquid hydrocarbons. It was first developed in the 1920's and was named after its discoverers Franz Fischer and Hans Tropsch. In principle, FT can handle any feedstock that can be supplied in the form of CO and H₂ components. First industrial FT fuels were derived from coal, such as in Germany during World War II and South Africa in the 1950s. Recent FT production facilities shifted to natural gas reforming, such as in Malaysia (1993) and Qatar (2006, 2009) [1]. The polymerization of hydrocarbons in a FT reactor is theoretically governed by the Anderson-Schulz-Flory (ASF) distribution [1,2], which relates the weight fraction (W_n) of hydrocarbons containing n carbon atoms and the chain growth probability factor (α), reproduced in Figure 1. Depending on the reactor configuration, operating conditions and catalyst type, the actual product distribution may deviate from the ASF.

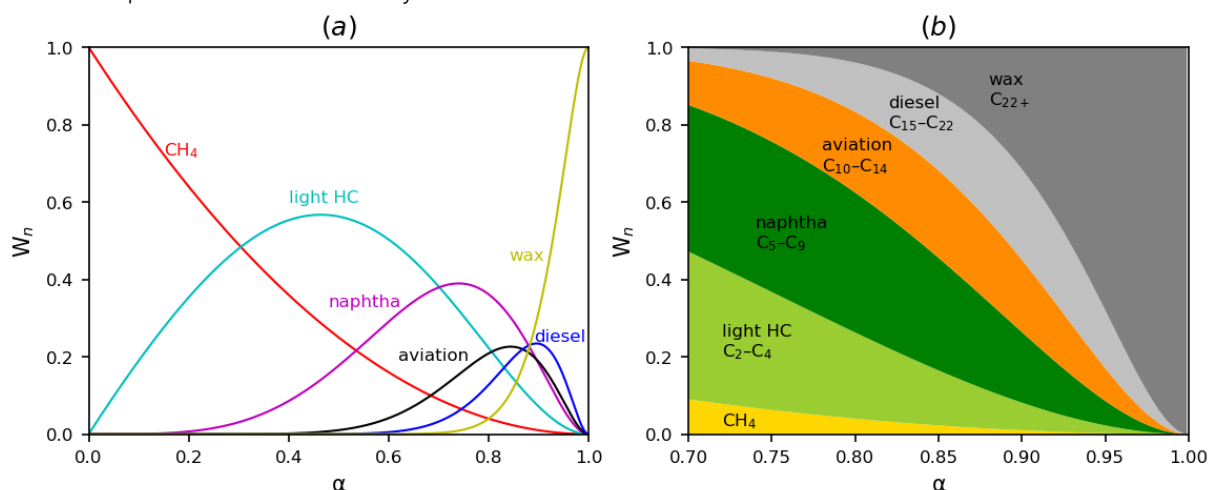


Figure 1: ASF distribution, $W_n/n = (1-\alpha)^2 \alpha^{n-1}$, FT selectivities (a) and high α -values favour long chain products (b)

The Fischer-Tropsch process

Figure 2 shows a process scheme for Biomass-to-Liquid (BtL) via FT. In the process, biomass is thermochemically converted to raw syngas at high temperature using oxygen and/or steam as oxidant. The gasification process can be atmospheric or pressurised. The raw syngas is then conditioned to satisfy FT specifications in terms of H₂ to CO ratio and impurities such as H₂S, COS, NH₃, HCN etc. Syngas conditioning requirements depend on the gasification techniques, operating conditions and feedstock

quality.

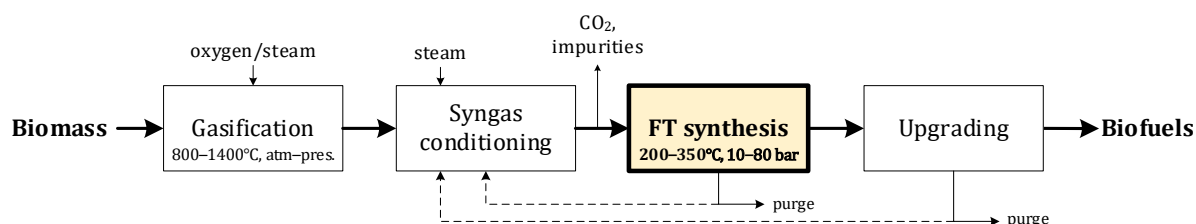


Figure 2: Scheme of biomass-to-liquid via FT synthesis

FT synthesis using iron- or cobalt-based catalysts can be represented by the set of chemical reactions presented in Table 1. Commercial FT reactors have three distinct temperature ranges, high temperature FT (HTFT) 300–350°C, medium temperature FT (MTFT) 250–300°C and low temperature FT (LTFT) 200–250°C. HTFT often runs on iron-based catalysts and favors the production of olefins and naphtha, whereas LTFT runs on iron- or cobalt-based catalysts and favors diesel and wax fractions. The FT process is highly exothermic, hence a rapid heat removal is a major focus during reactor design. Different reactor types are available for use in different applications: a) fixed-bed reactors for LTFT synthesis aiming at high average molecular weight product, b) fluidized-bed reactors for HTFT synthesis aiming at low molecular weight olefinic hydrocarbons, c) modern LTFT slurry phase reactors to produce hydrocarbon wax, offering improved temperature control and high per-pass conversion and d) microchannel reactors, increasingly considered in BtL applications, provide compact reactor configuration suitable for process intensification and improved heat and mass transfer performance, which dissipate heat more quickly than other types making them suitable for more active catalysts.

Table 1: Major reactions during FT synthesis [2]

Major reactions	
Paraffins (alkane)	$(2n+1)H_2 + nCO \rightarrow C_nH_{2n+2} + nH_2O$
Olefins (alkene)	$2nH_2 + nCO \rightarrow C_nH_{2n} + nH_2O$
Water gas shift	$H_2O + CO \rightleftharpoons CO_2 + H_2$
Side reactions	
Alcohols	$2nH_2 + nCO \rightarrow C_nH_{2n+2}O + (n-1)H_2O$
Boudouard reaction	$2CO \rightarrow C + CO_2$
Catalyst (Metals) oxidation/reduction	$M_xO_y + yH_2 \rightleftharpoons yH_2O + xM$ $M_xO_y + yCO \rightleftharpoons yCO_2 + xM$
Bulk carbide formation	$yC + xM \rightleftharpoons M_xC_y$

ADVANTAGES AND APPLICATIONS

Areas of applications for FT fuels include road, air and marine transport sectors. Production of renewable FT fuels have advantages over petroleum derived counterparts because FT fuels are cleaner, containing little or no sulfur and other contaminants. In this regard, they can easily satisfy the increasingly stricter environmental regulations in Europe and the rest of the world. Besides, long distance trucks, aviation and shipping are difficult to decarbonize with the current state of the art renewable alternatives such as batteries or hydrogen; hence substitution fuels derived from renewable sources will be needed in the short- and medium-terms. FT as one of ASTM **D1655** approved pathways can unlock a wide variety of feedstock for aviation fuels. FT, commercially proven technology for coal and natural gas, can facilitate

the commercialization of BtL plants by partially de-risking the difficulties associated with financing first-of-its-kind installations.

EXAMPLES OF DEMOPLANTS IN EUROPE

Operator: BioTfuel
Dunkirk, France
Fischer-Tropsch

Application: Demonstration

Capacity: 60 t/a (SPK jet fuel, diesel)

Technology: BtL

Feedstock: straw, forest waste, dedicated energy crops

Status: active

Source: <https://www.total.com/energy-expertise/projects/bioenergies/biotfuel-converting-plant->

Operator: COMSYN consortia
Espoo, Finland
Fischer-Tropsch

Application: Demonstration

Capacity: 100 kg/h feedstock

Technology: BtL

Feedstock: wood residue, agricultural residue, waste-derivatives

Status: active

Operator: GLAMOUR consortia
Manchester, UK
Fischer-Tropsch

Application: Aviation and marine fuels

Capacity: 2 kg/h glycerol

Technology: BtL

Feedstock: Glycerol

Status: active

Operator: Altolto team/ Velocys
Immingham, UK
Fischer-Tropsch

Application: Commercial (Aviation fuel)

Capacity: 1034 bpd FT liquids (SPK jet fuel, diesel and naphtha)

Technology: BtL

Feedstock: Municipal solid waste

Status: granted planning permit (June 2020)

OUTSIDE EUROPE

Operator: Red Rock Biofuels
Oregon, USA
Fischer-Tropsch

Application: Commercial (transport fuels)

Capacity: 1100 bpd FT liquids

Technology: BtL

Feedstock: forest and sawmill residue

Status: under construction (expected start-up spring 2021)

Operator: Fulcrum bioenergy
Nevada, USA
Fischer-Tropsch

Application: Commercial (road and aviation fuels)

Capacity: 657 bpd FT liquids

Technology: BtL

Feedstock: Municipal solid waste

Status: under construction (expected start-up 2021)

Operator: Bayou Fuels
Mississippi, USA
Fischer-Tropsch

Application: Commercial (road and aviation fuels)

Capacity: 1630 bpd FT liquids

Technology: BtL

Feedstock: woody biomass residues

Status: pre-FFFD and federal granting completed

FURTHER INFORMATION

- <https://www.astm.org/Standards/D1655.htm>
- <https://www.iata.org/contentassets/d13875e9ed784f75bac90f000760e998/saf-technical-certifications.pdf>

REFERENCES

1. Ail, S.S.; Dasappa, S. Biomass to liquid transportation fuel via Fischer Tropsch synthesis – Technology review and current scenario. *Renew. Sustain. Energy Rev.* 2016, 58, 267–286, doi:10.1016/j.rser.2015.12.143.
2. Van Der Laan, G.P.; Beenackers, A.A.C.M. Kinetics and Selectivity of the Fischer-Tropsch Synthesis: A Literature Review. *Catal. Rev. - Sci. Eng.* 1999, 41, 255–318, doi:10.1081/CR-100101170.