Fischer-Tropsch process

HIGHLIGHTS

Processes and technology status – Fischer-Tropsch synthesis (FT) converts the syngas to renewable hydrocarbons [1]. FT is a heterogeneous catalytic and polymerization reaction for producing liquid hydrocarbon fuels and chemicals from syngas [2]. The FT process was initially invented to obtain hydrocarbon from coal resources [3]. The green FT production unit is supplied with hydrogen produced by electrolysis and CO_2 from biogas upgrading [4]. FT synthesis can be optimized to produce different range of hydrocarbons, such as synthetic naphtha, diesel fuel, kerosene, lubricating oils, synthetic waxes, and olefins [2].

Cost - Costs for biofuel production from vegetable oil and sugar/starch crops are dominated by feedstock costs. A reference oil price of 59.52 $€_{2006}$[1]/bbl can lead to a competitive biofuel production against fossil-based fuels [5].

Potential and barriers – FT process is a major driver for the production of various hydrocarbons by utilizing biogenic feedstocks [6]. FT synthesis can tune the product distribution depending on regional market needs [7]. 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 – Franz Fischer and Hans Tropsch first demonstrated the main gas-to-liquid conversion process in 1923, in which mixtures of linear hydrocarbons were produced by passing syngas over Fe, Ni, or Co catalysts at 180°C–250°C at 1 bar [6].

The Fischer–Tropsch process (FT) is a very well established, and a mastered technique for the conversion of syngas to higher hydrocarbons, especially liquid transportation fuels [8]. The FT technology produces a wide range of synthetic hydrocarbons (carbon number C_1 to C_{100+}),

---

[1] 1 $€_{2006}$ = 1.26 $\$_{2006}$ [46]; 75 U$/bbl

Provided by Talieh Rajabloo
talieh.rajabloo@uhasselt.be

starting from a syngas stream mainly composed of CO and H_2 [9].

FT synthesis is a catalyzed polymerization process operating on the surface of a heterogeneous catalyst that uses hydrocarbon monomers formed by the hydrogenation of adsorbed CO to produce both short- and long-chain hydrocarbons, and it has a wide range of applications. It is thus a process in which carbon monoxide and hydrogen are converted by a catalytic reaction to a mixture of substances consisting mainly of n-alkanes (linear hydrocarbons), olefins, and alcohols [10].
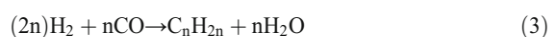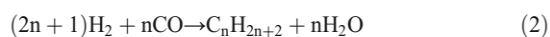
Although the feedstocks for the traditional FT plants are coal and natural gas, the integrated biomass gasification FT system is a novel and renewable technique for the production of green fuels. Gasification is a thermochemical route for the conversion of biomass into so-called producer gas, mainly composed of H_2, CO, CO_2, CH_4, and N_2. The producer gas is subjected to a series of cleaning and refining steps. The state-of-the-art technology for these procedures is defined as cold-gas-cleaning, in which the producer gas is first cooled and then refined to remove contaminants [11]. Generally, gas cleaning technologies can be categorized as 'cold' when performed at temperatures below 200 °C and 'hot' when performed at temperatures above 200 °C [11].

Provided by Talieh Rajabloo
talieh.rajabloo@uhasselt.be

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. Where coal or natural gas coexist in the region where biomass is available, economics may favor producing or blending syngas from multiple resources, making biomass-to-liquids a highly complex scenario. Land use management is essential for sustainable biomass production if used as the carbon source for FT [12]. Economically, FT is favored at larger scales; however, new compact reactor designs are coming into play aimed at monetizing highly localized (e.g. biomass) and stranded resources (e.g. natural gas). These types of reactors, involving microchannel and heat exchanger designs, must be highly efficient at managing heat, cost-effective, and mobile to exploit non-traditional sources of syngas [12].

Process overview - The FT synthesis involves two main chemical reactions: the breaking of the main molecular structure, generating monomers, and next to the polymerization of the monomers, producing larger chemical structures [13]. FT produces a mixture of hydrocarbons (syncrude) with different chain lengths ranging from CH_4 to hydrocarbons with more than 60 carbon atoms [1], [9]. Selectivity

of CH_4, an unwanted product, can vary from as low as 1–100%. At the other end of this product spectrum, the selectivity of long-chain linear waxes can vary from zero to 70%, with the intermediate carbon products produced only in limited amounts. The spread in C number can be varied 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 [8]. Possible products from FT are gasoline, diesel, jet fuel, paraffinic waxes, lubricants, petrochemical base products, and so on [1]. With some properties, synthetic fuels are significantly better (cetane number, very low content of aromatics, do not contain sulfur, nitrogen, heavy metals, asphaltenes, or salts). Compared to conventional petroleum processing, products of FT synthesis do not contain salts, heavy metals, sulfur, nitrogen, or aromatic compounds [10].

The catalytic conversion of H_2 and CO to hydrocarbons is described as a stepwise reaction. CH_2 intermediates (Eq. 1) are formed from H_2 and CO. The chain growth and the production of paraffin (Eq. 2), olefins (Eq. 3), and oxygen-containing components [1].

$$2H_2 + CO \rightarrow (CH_2) + H_2O \qquad (1)$$
$$(2n + 1)H_2 + nCO \rightarrow C_nH_{2n+2} + nH_2O \qquad (2)$$
$$(2n)H_2 + nCO \rightarrow C_nH_{2n} + nH_2O \qquad (3)$$

The chemical reaction between hydrogen and carbon monoxide requires a high quantity of energy to be over. Therefore, catalysts are crucial to guarantee chemical conversion to appreciable quantities of products [13].

The FT synthesis occurs through heterogeneous catalytic reactions, usually conducted on supported metals and, consequently, particularly sensitive to contaminate presence. The catalysts are used essentially to enable CO dissociation. Metal catalysts are preferred in FT commercial processes because of their greater conversion and selectivity. Group VIII elements, especially ruthenium (Ru), iron (Fe), cobalt (Co), and nickel (Ni), are surely eligible catalysts in FT synthesis since they have activity enough for commercial applications, although that only Fe and Co interest indeed for industrial-scale FT processes.

Nickel catalysts usually display high surface activity, but they have a limited chain growth. Despite the high selectivity, Ruthenium usage is almost impeditive for industrial-scale applications because of its high cost and low availability [13]. In general, FT catalysts contain porous support and hydrogenating metals and can be grouped into two major platforms: iron (Fe)-based and cobalt (Co)-based catalysts [6]. Low-cost

Provided by Talieh Rajabloo
talieh.rajabloo@uhasselt.be

Fe-based catalysts present high activity toward WGS reaction, and it is favorable for the conversion of CO-rich syngas. Nevertheless, the presence of water deactivates the iron active species by oxidation inhibiting the rate of FT reaction [14].

The application of Co-based catalysts yields higher productivity than that of Fe-based catalysts at high conversion levels, whereas the productivity is approximately equal at intermediate levels of conversion, making Co as the catalyst of choice [8]. Although cobalt costs more than iron, Co-based catalysts have gained more attention due to their high specific activity, higher C_{5+} selectivity, and more resistance against deactivation compared to iron catalysts. In contrast, Co-based catalysts have a negligible or low activity for the WGS reaction and require modifications to overcome these problems. The incorporation of additives (e.g. Re, Mn, or Ru) promotes the catalytic activity and selectivity of cobalt catalysts modifying the structural or electronic properties of the active phase in the low H_2/CO environment [14].

When the H_2/CO ratio has to be adjusted to the desired level, a Water-Gas-Shift (WGS) reactor is normally used [11]. When this reaction is carried out before the sulfur compounds (H_2S, COS) removal, it is called the sour WGS process, and it employs the use of a cobalt-molybdenum-based catalyst that is resistant to sulfur poisoning as opposed to an iron-based sweet WGS catalyst [11]. Recent studies focus on the development of bimetallic catalytic systems that promotes both FT and WGS reactions showing a synergistic effect. Nanostructured clusters of platinum or gold supported on reducible oxides such as CeO_2 have shown excellent activity in the WGS reaction [14].

The FT process requires clean syngas at pressures typically greater than 25 bar with a preferred H_2/CO ratio of around 2. Removing contaminants in syngas including sulfur (<10ppb), HCN and NH_3 (<20ppb), heavy metals (<10ppb), chlorine (<10ppb), tars and particulates are necessary to support the deactivation of catalysts. Refining syngas is necessary. It is also preferable that the syngas has a low concentration of components that are inert in the FT process, such as CO_2, N_2, and CH_4 [6].

FT reactions can generate undesirable products and the formation of carbon deposits at excessive temperatures. In extreme cases, very high temperatures must lead to catalyst deactivation or disintegration [13]. FT synthesis can be

Provided by Talieh Rajabloo
talieh.rajabloo@uhasselt.be

categorized as low-temperature FT (LTFT) and high-temperature FT (HTFT). LTFT is normally used for fuel synthesis, while HTFT is generally used for light olefin and oxygenate synthesis. The major products of LTFT are Alkanes (paraffin), while the major products of HTFT are Alkenes (olefins) [6].

Low temperature FT reactor (LTFT) -

Modern FT processes employ low-temperature processes for the production of liquid fuels. In these reactors synthesis gas, liquid products, and solid catalysts co-exist. The primary aim of any FT reactor is to remove the large heat of reaction produced during the FT process and maintain a uniform temperature profile within the catalyst bed. Various possibilities for LTFT reactors are as follows: 1) Cooling with internal tubes, where coolant fluid circulates in the tubes, within suspended or fixed bed reactors, 2) External cooling – this is enabled by recycling of gas or liquid into the catalyst bed, 3) Direct cooling by dispersing the feed of inlet synthesis gas in stacked fixed bed reactors [8].

The most common type of fixed bed reactor is a multi-tubular reactor, with the catalyst placed within the tubes and a cooling medium on the shell side. The short span between the catalyst particles and the tube walls and high gas linear velocities significantly augments heat transfer from the catalyst particles to the cooling medium, maintaining a steady FT temperature range.

Syngas recycling aids in improved heat transfer and also in increased overall conversion. Similarly, recycling liquid hydrocarbon products also enhances the temperature profile in the fixed bed reactors. Due to the similarity in behavior of the parallel tubes in multi-tubular reactors, they are easy to handle and design.

Some of the other advantages of the multi-tubular fixed bed reactors include the absence of a catalyst–wax separator since the heavy wax products trickle down the bed and get collected in the receiver pot [8].

Limitations of the fixed bed FT reactor include the pressure drop constraint[2], and hence catalysts in fixed bed reactors have diameters greater than about 1 mm. Intraparticle diffusion plays a limiting factor in the overall reaction rate for catalysts with sizes greater than 1 mm. Consequently, intraparticle diffusion is an important factor that needs to be accounted

---

[2] As the particle diameter decreases, the pressure drop increases [47]

Provided by Talieh Rajabloo
talieh.rajabloo@uhasselt.be

for while choosing catalyst particle size and shape for a fixed-bed FT process [8].

High temperature FT reactor (HTFT) –

High-temperature FT processes operate in the temperature range of 300–350 °C utilizing Fe catalysts and producing gasoline or linear olefins. The high temperatures vaporize all the products under reaction conditions, maintaining just two phases throughout the process. These are called 2-phase fluidized bed systems[3]. Two types of high-temperature fluidized bed systems are in commercial use – fixed fluidized bed reactors and circulating fluidized bed (CFB) reactors. Fixed fluidized bed reactors are also called Sasol Advanced Synthol (SAS) reactors.

Major advantages of SAS over CFB are higher conversion per pass, lower catalyst consumption, uniform product selectivity with products in the range of slightly heavier hydrocarbons, less maintenance, and easier construction. Cyclone separators of SAS very effectively retain the catalyst within the reactor. However, in the case of CFB reactors, scrubber towers need to be

used downstream of the cyclones to remove the last traces of catalyst before the product stream can be condensed [8].

Reactor types for FT process -

Fixed bed, fluidized bed, and slurry bed are the main types of reactors used in the FT synthesis [13] (Figure 1).

Fixed bed reactors - The fixed bed reactor has the advantage to be more flexible for different scale applications, and it does not require a separation step to recover the catalyst from the product mixture. These characteristics make the fixed bed the most used reactor for both small-scaled studies and industrial purposes. For fixed bed reactor, cooling fluid (frequently water) flow is generally required to remove the reaction-released heat to maintain the reactor isothermal conditions [13].

The FT synthesis is a highly exothermic process, requiring a heat exchange system. These characteristics make feasible the coupling of an FT plant with a heat recovery system to the temperature control.

---

[3] Fluidized bed reactors are widely used in material processing industries for processes that require very good heat and mass transfer between particles and a gas. The energy provided to the fluidized bed typically comes from the warm gas that fluidizes
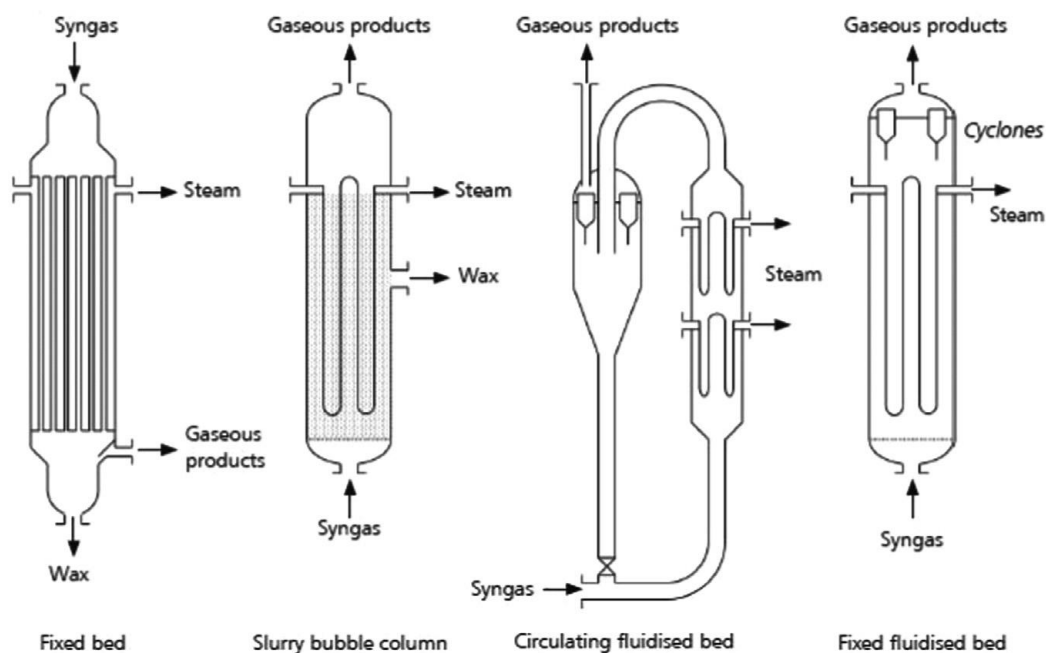
the bed as well. Ref: https://www.sciencedirect.com/science/article/abs/pii/S0167299106816575

Provided by Talieh Rajabloo
talieh.rajabloo@uhasselt.be

Figure 1. Commercial FT reactors [8]

The reaction temperature is a crucial process parameter influencing the FT synthesis. The temperature increasing can lead to the production of a greater methane amount because of the higher propagation and termination reaction rates at high temperatures [13].

Fluidized bed reactors - Fluidized bed reactors operate at a higher temperature and higher pressure conditions on a design that leads to improved efficiency. The fluidized bed allows reaching superior heat transfer, easier catalyst handling, and improved temperature control on the highly exothermic FT reactions. Commercial fluidized bed reactors can be set mainly as bubbling beds (BFB) or circulating beds (CFB) [13].

Slurry bed reactors - The slurry bubble column is another reactor configuration for FT employed in Sasol and Exxon GTL plants. In this type of reactor, the catalyst particles are suspended in a liquid phase, through which syngas is bubbled [15]. Fluidized bed slurry reactors enable the catalyst inventory to be continuously replaced and regenerated offline in a separate system [16]. Slurry bubble column reactors provide higher heat removal efficiencies than fixed bed reactors. Due to their flexibility and lower capital cost, SBCRs have been used in GTL plants [15].

Micro and monolithic FT reactors - Micro-structured reactors have been proposed and are being developed for FT processes. These reactors include two sets

Provided by Talieh Rajabloo
talieh.rajabloo@uhasselt.be

of small parallel channels with one used for FT reaction and the other for circulating cooling water, thus increasing the efficiency of heat transfer between channels and resulting in isothermal operation [8].

Bio-based FT - Amongst the alternative energy sources, biomass plays a major role in the energy sector. The only natural, renewable carbon resource and large fraction of substitute for fossil fuels is biomass [8]. Raw biomass usually needs to be reduced in size before further processing. It can be cut and ground for this purpose. For some processes, the biomass even needs to be pumpable, which means that it needs to be considerably reduced in size and dispersed in a liquid. Pressing is another mechanical process that separates juice or oil from solid substances [17]. Mechanical processes are often used when producing materials incorporating biomass. An example is an extrusion in which biomass components, mainly fibers, are mixed with (bio)plastic to produce composites. Melting, casting, frothing, emulsifying, dispersing, pelleting, mixing, and formulating are also used to create usable products [17].

Biomass is a term used to describe any material of recent biological origin, including organic materials produced by photosynthesis and living microorganisms of animal origin. Food, algae, and animal waste are also encompassed in the biomass designation. Biofuels are defined as fuels obtained from biomass. Microbial materials and microalgae were recently proposed as renewable sources with potential application in the production of biofuels, including bio-hydrogen [13]. Biofuels are renewable energy sources since they can be supplanted by cultivation or breeding. In this way, the production of biofuels has substantially less harmful effects on the environment when compared to the fossil non-renewable processes [13].

Integrating renewable H_2 into a biomass-to-liquid FT concept could increase productivity while product distribution remains almost the same [1]. Integrating renewable H_2 into a biomass-to-liquid FT concept could increase productivity while product distribution remains almost the same [1].

Though all the large-scale plants are either based on CH_4 reforming or coal gasification systems, biomass-based FT plants should not face any major technical challenges [8]. Sasol Oryx (slurry bubble column) and Synfuels (fixed fluidized bed), Shell Bintulu and Pearl (fixed bed), and SynFuels China (slurry bed), utilize a wide range of feedstocks such as coal, heavy oils, or

Provided by Talieh Rajabloo
talieh.rajabloo@uhasselt.be

natural gas [18], [19]. Although the FT process has been applied industrially using natural gas and coal as feedstocks, the conversion of biogenic feedstocks, such as biomass and wastes, is becoming the major focus of recent studies and project proposals. The major driver is to produce renewable fuels and chemicals that can decarbonize the transport sector—one of the largest single generators of greenhouse gases [6].

Vegetable biomass is synthesized from the photosynthesis process, which uses the sunlight to convert CO_2 and H_2O into sugars and polymers as primary products and oxygen and water as a sub-product. During the photosynthesis process, biomass absorbs carbon dioxide from the atmosphere and returns it to the environment as non-polluting gases, O_2 and H_2O [13].

Biofuels have been conveniently labeled in relation to the feedstock nature and origin. According to the biomass usage form, biofuels can be categorized into primary and secondary [13].

Primary biofuels are constituted by unaltered biomass - wood, animal fat, and forest residue are common examples of primary biofuels. The first generation consists of biofuels derived from the harvest (sugar cane, sunflower, corn, and various edible seeds) usually employing oil extraction and microbiological fermentation. Competition with food applications is a major constraint to the widespread use of these fuels. Bioethanol is the highest world's product of first-generation liquid fuels, most notably in Brazil and in the United States [13].

Secondary biofuels are produced from biomass processing to obtain substances with a concentrated energy content and they are often potential substitutes for fossil fuels. Biodiesel, bio-ethanol, and bio-hydrogen are in the category of secondary biofuel [13]. Secondary liquid biofuels are generally the key concern because of the vast infrastructure available for their use and distribution, especially for transport applications [13].

Third-generation biofuels also exist which are synthesized from algae. Third-generation biofuels may contain substantial amounts of lipids, the main function is specifically the storage of energy [13]. The ease of algae cultivation, even in adverse and unsuitable conditions for plant production, makes them a promising source to produce biofuels [13].

The second-generation biofuels use non-edible and lignocellulose wastes. Its feedstock includes large availability of high-yield vegetation that can be sown in poor and marginal lands. The feedstock of

Provided by Talieh Rajabloo
talieh.rajabloo@uhasselt.be

the third-generation biofuels is essentially nonfood marine biomass, macro-algae (seaweed), and microalgae. Nevertheless, algal species display often high cultivation costs, the technical difficulty for process scale-up, and inaccurate conversion models. Finally, second-generation fuels have been preferred among the secondary biofuels [13].

Gasification process - The gasification process is usually divided into four stages (drying, pyrolysis, oxidation, and reduction) on the different types of gasifiers. Biomass moisture can be useful to the gasification process. Hydrothermal liquefication (HTL) is a thermochemical process that utilizes biomass moisture to produce bio-crude oil [13]. The HTL process operates under moderate temperatures and high pressures in two main stages. Initially, the biomass is processed with water at conditions of approximately 200-250 °C and 20-30 bar. The second stage operates at high pressures (typically 100-200 bar) and high temperatures (300-350 °C). Hydrothermal liquefication technologies can mimic the natural fossil formation of oil resulting in a bio-crude oil that can be utilized as a fuel source. Besides, HTL processes did not require the drying stage, since it uses the water present in the feedstock [13].

Figure 2 shows a general scheme with the main process steps for producing FT fuels and power from biomass [20].

Liquid fuels using biomass-derived syngas - Biomass gasification coupled with the FT process plays an assuring and encouraging option for the production of "green" liquid fuel. Here, biomass is gasified, and the generated bio-syngas are used for FT synthesis to produce long-chain hydrocarbons that are converted to fractions like green diesel [8].
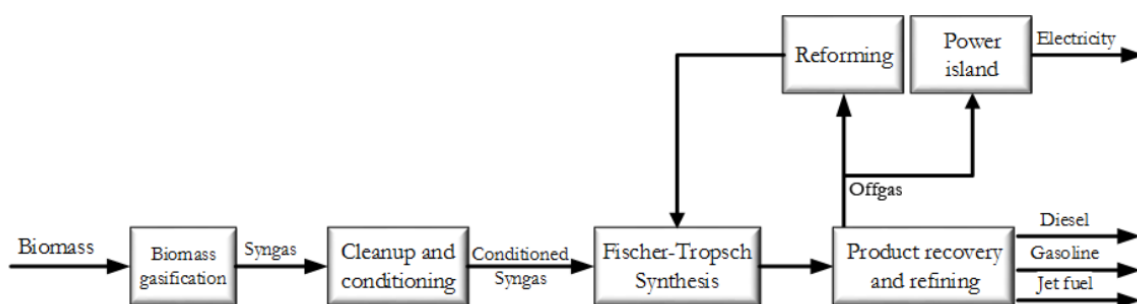

Figure 2. Schematic view of a plant for the production of FT fuels and electricity through biomass gasification [20].

Provided by Talieh Rajabloo
**talieh.rajabloo@uhasselt.be**

A wide range of biomass-based materials has been proposed for use, which includes crop residue, agro-crops, and several tree species. These products can be burnt directly for energy and can also be processed further for conversion to liquid fuels like ethanol and diesel. Thermal processes offer an effective means for the conversion of the energy content of the wood and other lignocellulosic biomass. Wood constitutes 80% or more of volatile matter and nearly 20% of char can be converted to gaseous fuels [8].

In the case of biomass gasification, its integration with the FT reaction is acknowledged as the biomass-to-liquid process (BtL) [9]. BtL is suggested to be a positive route to reducing the inclination towards fossil transportation fuels and is also a key to keeping the environment clean. For 20% of the total liquid fuels produced from carbon-neutral sources, like biomass, 15% CO_2 emissions reduction could be achieved – just by fuel replacement [8].

Processes that have been positively experimented with for conversion of biomass to liquid transportation fuels include fast pyrolysis of biomass, direct liquefaction of biomass, transesterification of vegetable oils to produce diesel fuel, production of bio-ethanol from agricultural crops to blend with gasoline, production of bio-oil from algae, and most recently the FT process for conversion of biomass-derived syngas to higher hydrocarbons [8].

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. According to Eq.1, the transformation of syngas into higher molar-weight hydrocarbons requires an H_2/CO feed ratio close to 2. This ratio can be adjusted through water–gas shift (WGS) reaction (Eq.4), in which CO reacts with water vapor to boost the H_2 concentration rejecting also CO_2 in the process [14]. Depending on the catalyst composition and process conditions, about half of the CO can be transformed through the WGS reaction [14].

$$CO + \left(\frac{m}{2n}+1\right)H_2 \rightarrow \frac{1}{n}(C_nH_m) + H_2O \qquad (3)$$

$$CO + H_2O \rightleftharpoons H_2 + CO_2 \qquad (4)$$
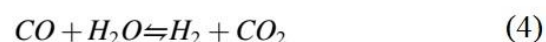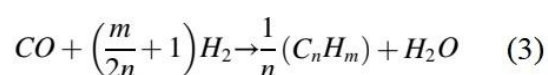
Biofuel production refers to using syngas derived from a biogenic origin, made from biogas, biomass, or wastes. Natural gas and biogas may be converted to syngas using tubular reformers, combined reforming reactors, auto thermal reforming reactors, or partial oxidation reactors. Solid feedstocks are gasified by reacting them

Provided by Talieh Rajabloo
talieh.rajabloo@uhasselt.be

with a deficiency of oxygen at temperatures in the range of 800°C–1400°C [6].

Biomass gasifiers are usually configured to be either fluidized-bed or fixed-bed reactors as entrained-flow reactors are less attractive due to the small particle sizes required. Fixed-bed updraft or downdraft gasifiers can be suitable for small-scale projects while circulating and bubbling fluidized-bed gasifiers can be better suited for larger projects [6]. Gasifiers may be classified by type as either fixed-bed, fluidized bed, or entrained-flow, as shown in Figure 3 [6].

The overall block flow diagram for producing FT biofuels is shown in figure 3. The biomass is pretreated and gasified, and then the raw syngas is cleaned to meet the requirements of the FT catalyst. FT liquids are cooled and recovered and then hydrocracked/hydrotreated to meet final product specifications for diesel, kerosene, and aviation fuel [6].

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. An example is provided by the SOLETAIR project in Finland, where a containerized unit containing a reverse water-gas shift (RWGS) and an FT reactor converted CO_2 from the air into synthetic hydrocarbons. CO_2 captured from biogas of anaerobic digestion is converted into oils and chemicals inside an RWGS + FT containerized unit [9].
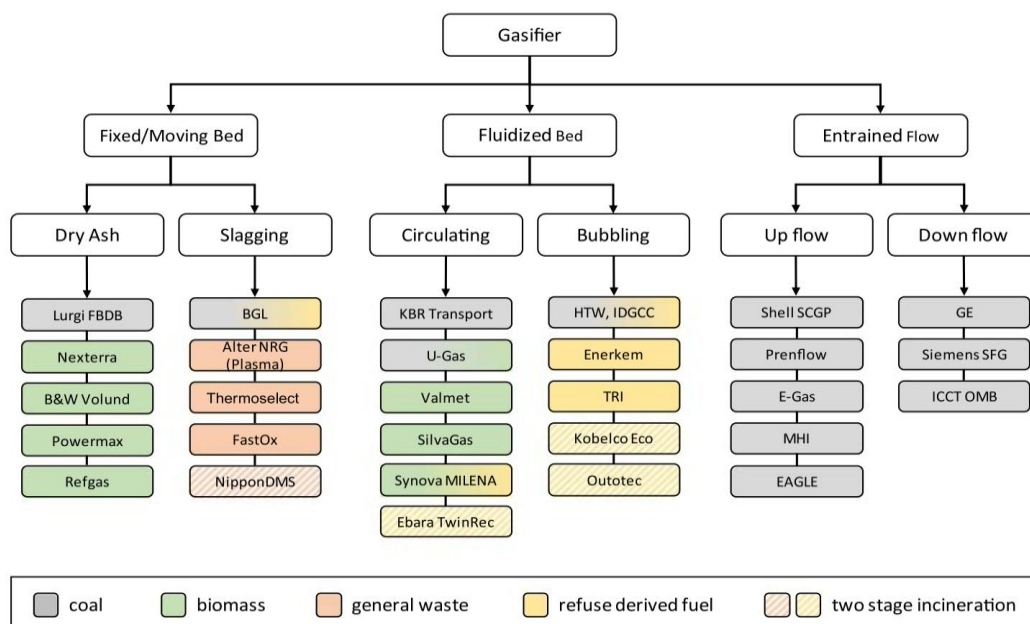

Figure 3. Types of gasifiers and commercially available processes by feedstock type, 2020 [6]

Provided by Talieh Rajabloo
talieh.rajabloo@uhasselt.be

Power-to-X and FT process - FT can convert biomass-based syngas and renewable H_2 from excess electricity to hydrocarbons with different chain lengths [1]. Syngas obtained from biomass can be H_2 deficient, thus demanding a water-gas shift reactor for Co-based FT synthesis [8]. Synthetic fuel can be considered as an energy storage medium in a form that can be readily transported and stored for use weeks, months, or years later [21]. Power-to-X (PtX) technologies can produce fuels that directly replace fossil ones by using the same infrastructure or with little modifications. Moreover, it can add more flexibility and reliability to the electricity sector, which enables more dependence on solar and wind energies [2]. Product flexibility might be one of the biggest benefits of FT [1].

Renewable energy sources regularly produce excess electricity at times and are insufficient at other times, while batteries have proven to be expensive and inefficient in capacity to accommodate the intermittency. When paired with a solid oxide co-electrolysis process FT technology provide an efficient means of storing renewable energy in the form of a liquid fuel [21]. Integrated water electrolysis is a core principle of new process configurations for decarbonized heavy industries. Nordic Blue Crude and Sunfire are planning to build commercial plants to produce FT liquid fuels from CO_2 and green H_2. A substantial portion of production costs for CO_2-based synthetic FT fuels derives from CO_2 capture costs [22], [23].

Hybrid biomass/natural gas to FT liquids process - It is known that the proper ratio of H_2 to CO in the syngas has a profound effect on the yield of FT hydrocarbons. Gasification of biomass typically yields syngas which requires additional processing through the water-gas shift reaction to achieve a proper H_2 to CO ratio for FT synthesis, which will inevitably lose some of the carbon sources in the form of CO_2. An alternative approach is to provide H_2 to the syngas from an external source such as natural gas reforming or water electrolysis and convert CO_2 to CO through reverse WGS and utilize CO in an FT process [20].

Reforming natural gas typically yields syngas rich in H_2 and CO, which might be ready for FT synthesis without a need for the additional shift reaction to adjust an H_2/CO ratio. Reforming of natural gas with steam reforming, auto-thermal reforming, and partial oxidation technologies could yield syngas with H_2/CO ratios of 3, 2.3, and 1.7, respectively. Combining the

Provided by Talieh Rajabloo
talieh.rajabloo@uhasselt.be

syngas of high H_2/CO ratio from natural gas reforming with the syngas of low H_2/CO ratio from biomass gasification could have some synergetic effects on carbon conversion and the yield of FT liquids. The extra amount of hydrogen produced can make up for the hydrogen deficiency in the syngas from biomass gasification to some extent and improves the overall carbon conversion [20]. Utilizing the hybrid feedstock produces more FT liquids for the total energy content of the feedstock [20].

A hybrid NG/biomass process also produces about 23% less CO_2 per unit of FT products produced compared with similar processes using only biomass with the same amount of thermal input [20].

Production and consumption in Belgium – Biomass can be used for either energy purposes (production of heat, electricity, and fuel) or non-energy demand (e.g., chemicals). The non-energy demand is defined as the demand for biomass for raw materials. Belgium presents a non-energy demand corresponding to ~15% of its primary energy mix. However, high-temperature heat is a significant application

for biomass and moving toward carbon neutrality [24].

Simulation results show that biomass imports are key to the energy balance of Belgium. When considering 90% GHG savings, local resources represent the share of 12% to 20% [24]. EU could supply 39 to 76% of the biomass requirements for Belgium depending on the use of biomass and defined reference and high scenarios in the ENSPRESO database[4], released in 2022. Lignocellulosic biomass will be required for intensive decarbonization of the Belgium energy system and the Non-Energy Demand (NED) applications, even if it is available at a very high price [24].

The main biofuel options for Belgium in the short term are biodiesel (methyl ester) from vegetable oil, to be blended with diesel fuel (up to B7[5]), potentially supplemented with hydro-treated vegetable oil (HVO) in the future, and bio-ethanol from sugar or starch crops, to be blended with gasoline fuel (up to E10[6]). Next to general blending, also options of high blends or pure biofuels

---

[5] Diesel B7 is a fuel with added bio components of up to 7%, which meets the requirements of the European diesel standard EN590 [49].
[6] E10 is a biofuel made up of 90% regular unleaded and 10% ethanol

Provided by Talieh Rajabloo
talieh.rajabloo@uhasselt.be

could be envisaged (such as E85[7], ED95[8], B30[9], B100[10], PPO[11], bio-methane) [25]. In the longer term, more advanced technologies could be introduced, and feedstock can be broadened to include waste and lignocellulose-based resources. Typical "2nd generation" fuels could be FT diesel (so-called BTL), cellulose ethanol, Bio-Synthetic Natural Gas (bio-SNG), bio-Di methyl ether (bio-DME), etc [25]. The use of the most harmful biofuel, palm oil, has increased tenfold on the Belgian market between 2019 and 2020 to 231 million liters [26]. However, following the examples of Denmark, France, and the Netherlands, biofuels made from palm oil will no longer be allowed both on the Belgian market as well as in the transport sector, whilst soy will be banned as a raw material for transport biofuels from 2023 [26].

Investment and production costs –

The real (net) impact of building a large bio-based industry in the Netherlands over the coming 3-4 decades will depend strongly on the cost developments of key biomass conversion technologies (such as biorefinery concepts, 2nd-generation biofuel production technology, and advanced power generation) and the prices at which biomass resources can be made available. Other economic factors, such as growth rate, sectoral change in the (national) economy, prices for CO_2, and agricultural policies (subsidies and prices) are also unknown variables [5].

Captured CO_2 (from industrial processes or air) and green hydrogen will make FT process a renewable and clean method of hydrocarbon production [2], [27]. Based on existing technologies, the production cost of green hydrogen via solar or windmill-powered electrolysis was approximately 2 to 3 times that from steam methane reforming (SMR) in 2004, while the cost of the green hydrogen from landfill gas dry fermentation is close to that from SMR. The hydrogen cost drops with 50% for the wide utilizations cases. Moreover, Hydrogen need to be efficiently stored, especially when the energy is derived from the solar system which is only available during the day [28]. Hydrogen storage could ensure a

---

[7] E85 is an abbreviation typically referring to an ethanol fuel blend of 85% ethanol fuel and 15% gasoline or other hydrocarbons by volume. (Wikipedia)

[8] ED95 designates a blend of 95% ethanol and 5% ignition improver; it is used in modified diesel engines where high compression is used to ignite the fuel. (Wikipedia)

[9] carbon offset bio-blend bunker fuel (B30) [50]

[10] B100 (pure biodiesel) is typically used as a blendstock to produce lower blends and is rarely used as a transportation fuel [51].

[11] Pure Plant Oil (PPO) is extracted from the seeds of oil producing plants. It is often further processed to make bio-diesel in order to reduce the fuel's viscosity, thus making it suitable for direct use in diesel engines [52].

Provided by Talieh Rajabloo
talieh.rajabloo@uhasselt.be

steady supply, working as a buffer for the electrolyzers, but also increasing the overall green hydrogen costs. Assuming 30 years of useful life, pressurized tanks add costs of 0.18-0.76 $€_{2022}$[12]/kg [29]. Green hydrogen is currently more expensive than grey hydrogen. IRENA estimates that current green hydrogen costs are in the range of 3.51-5.26 $€_{2020}$[13]/kg, compared with 0.88-1.75 $€_{2020}$[14]/kg for grey hydrogen [29].

Norwegian electrolyzer-maker Nel ASA in January 2021 announced a goal of producing green hydrogen at 1.27 $€_{2021}$[15]/kg by 2025. Malaysian oil and gas giant Petroliam Nasional Bhd., or Petronas, is targeting hydrogen production costs from the nation's hydropower and solar resources in a range of 0.85 to 1.69 $€_{2021}$[16]/kg. Green hydrogen produced with renewable resources costs between about 2.63 $€_{2020}$/kg and 5.75 $€_{2020}$/kg, according to the European Commission's July 2020 hydrogen strategy. Fossil-based hydrogen costs about 1.58 $€_{2020}$/kg, and the commission estimated the cost of blue hydrogen, which pairs carbon capture with steam methane reformation of natural gas, at about 2.10 $€_{2020}$/kg[30]. However, green H_2 is cheaper than grey H_2 across Europe due

to high fossil gas prices by 2022. Moreover, calculations by analyst ICIS challenge the assumption that low-carbon blue hydrogen derived from methane with CCS will be cheaper than renewable H_2 [31].

Costs for biofuel production from vegetable oil and sugar/starch crops are dominated by feedstock costs as, especially for biodiesel from vegetable oil, few conversion processes are required to produce biodiesel. The additional costs for substitution of fossil fuels with biomass depend on the difference between the fossil reference technologies and the biomass substitutes and is ranging from 300 M€ to 2,731 M€ [5].

The liquid fuel cost varies widely depending on the feedstock, but it could be competitive with fossil fuels depending on the considered region. This is especially true for low-cost feedstocks like switchgrass and woody biomasses [7].

Lower feedstock prices and better GHG mitigation performances of biodiesel from palm oil and jatropha oil and ethanol from sugar cane result in a mitigation cost of 15.11 $€_{2009}$[17]/t$_{CO2eq.}$ [5]. A reference oil price of 59.52 $€_{2006}$[18]/bbl can lead to a competitive biofuel production against

---

[12] 1 $€_{2022}$ = 1.12 $\$_{2022}$ [53]
[13] 4-6 USD_{2020}, 1 $€_{2020}$ = 1.14 $\$_{2020}$
[14] 1-2 USD_{2020}
[15] 1 $€_{2021}$ = 1.18 $\$_{2021}$

[16] 1 to 2 $\$_{2021}$/kg
[17] 21 $€_{2009}$, 1 $€_{2009}$ = 1.39 $\$_{2009}$
[18] 1 $€_{2006}$ = 1.26 $\$_{2006}$ [46]

Provided by Talieh Rajabloo
talieh.rajabloo@uhasselt.be

fossil-based fuels [5]. The production of ethanol from corn or wheat is marginally viable. The production costs approximate the selling price of ethanol (550 $€_{2019}$/ton) [17].

The gasifier is suitable for all kinds of wood residues, agricultural residues, and waste-derived feedstocks which are available at a feedstock cost of 0-20 $€_{2022}$/MWh [32].

Energy requirements – FT is a highly exothermic reaction due to a standard reaction enthalpy of -165 kJ/mol$_{CO}$ combined with CO feed

concentrations of more than 25% and high CO conversions [35]. The standard FT reaction enthalpy of -165 kJ/mol$_{CO}$ used in the calculation of Q is underrated, being the reaction enthalpy of methanation equal to -206 kJ/mol$_{CO}$ [35]. Excessive reaction temperatures lead to the higher methane yield, carbon deposition, and catalyst deactivation [12]. Tijmensen et al. reported that the overall thermal efficiency of a BTL process on a lower heating value (LHV) was 33–40% for gasification systems operated at atmospheric pressure and 42–50% for pressurized gasification systems [20].

Table 1. Production capacity (as barrel per day) and liquid fuel production cost for gasification and FT synthesis of some relevant second generation[19] feedstocks. (Switchgrass (2009), Residual Woodstraw (2013), Corn stover (2020), Woody Biomass (2010, 2020)) [7].

Feedstock	Production capacity (BPD)	Liquid fuel cost (USD/L)	Liquid fuel cost (€/L)
Switchgrass (2009)	4630	0.52	0.37
Residual Woodstraw (2013)	5500	1.57	1.18[20]
Corn stover (2020)	2362	1.39	1.22
Woody Biomass (2010) [33]	1700	0.81	0.61[21]
Woody Biomass (2020) [34]	2180	0.4	0.35

[19] Traditionally, biomasses for biofuel production were identified exclusively with direct products from crops cultivation, mainly sugar and starchy crops or oil seeds. Biofuel obtained from these feedstocks are generally referred to as "first generation" (1G) biofuel. Other feedstocks, such as agri-food residues and municipal/industrial wastes is gaining importance. Biofuels obtained from these non food-based sources are usually defined as "second generation" (2G) biofuels. Furthermore,

algae feedstocks are attracting great attention due to their peculiar characteristics, mainly low land occupation, fast growth rate and availability of biomass. Given algae peculiar features and the relative novelty of their exploitation, biofuels obtained from such feedstock are qualified as "third generation" (3G).

[20] 1 $€_{2013}$ = 1.33 $\$_{2010}$ [53]

[21] 1 $€_{2010}$ = 1.33 $\$_{2010}$ [53]

Provided by Talieh Rajabloo
talieh.rajabloo@uhasselt.be

Table 2. CO conversion and selectivity to the main FT products (CH_4, CO_2, C_2-C_4, C_{5+}, C_2-C_{17} olefins) calculated at different temperatures. The propylene/propane ($C_3^{//}/C_3$) and the volumetric heat duty (Q) are also shown. P = 25 bar, H_2/CO_{in} = 2 mol/mol, GHSV = 6410 cm^3(STP)[22]/h/g_{cat}, inerts = 24 vol% [35].

T.o.S. [h]	T [°C]	X_{CO} [%]	S_{CH4} [%]	S_{CO2} [%]	S_{C2-C4} [%]	S_{C5+} [%]	$S^{olefins}$ (C_2-C_{17}) [%]	$C_3^{//}/C_3$ [-]	Q [kW/m^3]
41	180	3.7	3.6	–	–	–	–	–	80.6
65	190	7.8	6.7	–	–	–	–	–	161.2
162	195	12.1	8.4	0.5	11.5	76.6	19.2	1.2	243.9
216	200	16.5	10.9	0.6	13.8	71.6	15.1	0.8	332.5
258	205	21.2	14.6	0.8	14.2	67.4	12.0	0.6	427.3
378	210	28.1	17.3	1.0	14.5	65.2	8.4	0.4	566.3
546	215	33.5	19.6	1.4	–	–	–	–	675.1
597	220	44.7	21.0	2.0	15.4	59.3	6.0	0.3	900.9
688	225	50.3	23.5	2.8	16.0	56.3	4.6	0.2	1013.7
713	230	54.5	27.5	3.8	–	–	–	–	1098.4
736	240	67.5	33.3	7.1	–	–	–	–	1360.4

The products from the biomass conversion are related to the molecular arrangement and the chemical composition of the feedstock. There is a significant distinction among the chemical structure of the different biomass groups, related to their source and origin. Table 3 presents the mean elemental composition of different biomass types [13].

The energy properties of the biomass vary according to plant genetics, local characteristics, harvesting method, and crop treatment. Heat values of biomass depend directly on the carbon content and inversely on the ash content. The heat values of biomass have been usually found in the range of 13-21 MJ/kg [13].

Table 3 - Ultimate analysis of some biomass-derived materials at a dry and ash-free basis [13].

Biomass type	Elemental analysis (Wt.%)					
	C	H	O	N	S	H/C
Wood	52.1	6.2	41.2	0.4	0.1	0.12
Herbaceous	49.2	6.1	43.7	0.9	0.1	0.12
Shell and husks	49.4	6.1	43.2	1.2	0.1	0.12
Animal residues	58.9	7.4	23.1	9.2	1.4	0.13
Algae	43.2	6.2	45.8	2.2	2.6	0.14

Carbon capture and storage (CCS) and FT process –

A sustainability assessment of CCS coupled with FT biofuels from residual biomass shows positive environmental and socio-economic impacts [36]. Implementing carbon capture and storage (CCS) in an FT process producing fuel from residual forest biomass would significantly improve its CO_2 balance while providing carbon-negative replacements for fossil fuels [36].

---

[22] Gas Hourly Space Velocity (GHSV), Spanning Tree Protocol (STP)

Provided by Talieh Rajabloo
talieh.rajabloo@uhasselt.be

A research project (Negem) has explored the feasibility of an FTL-CCS[23] plant producing biofuels from residual woody biomass by evaluating it against six key performance indicators (KPIs), including removal efficiency, the quantity of avoided CO_2 emissions, Levelized cost of stored CO_2 and monetized environmental impacts [36].

Even though CCS would represent an additional cost to produce FT crude (an additional 14-29 EUR/MWh), if the negative emission from the FTL-CCS plant were assigned the EU policy value of 50 EUR per avoided ton of CO_2, the monetary gains from CCS would outweigh the costs in most considered scenarios, thus making the business case more feasible [36].

The Levelized cost of stored CO_2 would be 178 EUR_{2022} per ton with optimal conditions, i.e. having a large capacity plant as close as possible to the port from where the captured CO_2 will be shipped to the storage location via shared infrastructure [36].

Even though at the moment (March 2022) no commercial plants are producing FT fuels from biomass, building such plants is favorable to equip them with CCS provided that negative CO_2 emissions can be credited and that sufficient CO_2 transport and storage infrastructure exists. The recognition of negative emissions would improve the economics of FT liquid production and could speed up the commercial adoption of this technology [36].

CO_2 emissions reduction via biofuels - First-generation biofuels have the potential to reduce CO_2 emissions by about 50% compared to fossil fuels. Second-generation biofuels have the potential to reduce CO_2 emissions by up to 90% compared to fossil fuels [10].

For the internal combustion engines utilization, the FT fuels exhibit lower emission levels compared to gasoline and diesel. This is because FT fuels are free of sulfur, consist of very few aromatics and nitrogen concentrations [8]. If 20% of the total liquid fuels were produced from biomass, then a reduction in CO_2 emissions of 15% could potentially be achieved [12].

According to Schmidt et al. GHG emissions of near carbon-neutral FT synthesis is about 1 g_{co2eq}/MJ_{fuel} when emissions related to the construction of power plants and production facility today is not considered, and from 11 to 28 g_{co2eq}/MJ_{fuel}, when construction emissions today is considered, while GHG emissions of crude oil are 87.5

---

[23] FTL = Fischer-Tropsch Liquids

Provided by Talieh Rajabloo
talieh.rajabloo@uhasselt.be

g_{co2eq}/MJ$_{fuel}$. On the other hand, Biomass-to-liquid (BtL) GHG emissions can be as low as -2 g_{co2eq}/MJ$_{fuel}$ when land-use change is considered [2].

Although BtL can have lower GHG emissions than near carbon-neutral FT synthesis, it has higher land use and water demand. Moreover, the water demand of PtL via FT synthesis is 0.04 m^3/GJ, while it is 112 m^3/GJ from BtL and 14 to 574 m^3/GJ from biofuel [2].

Biomass is a renewable feedstock that offers good advantages over CO_2 emissions, environmental pollution, and low cost. Particularly, microalgal biomass has shown greater carbon efficiency than conventional biomass for the production of higher-grade FT transportation fuels in an environ-economic evaluation [37].

Pre-COVID-19 aviation was responsible for about 2.4% of the CO_2 emissions stemming from the combustion of fossil jet fuel. If no further measures are taken to temper development, the contribution from the sector is expected to be more than triple until 2050 [38].

Regarding some fuel characteristics, FT diesel is even more favorable, i.e. a higher cetane number (better auto-ignition qualities) and lower aromatic content, which results in lower NO_x and particle emissions [39].

Near carbon-neutral FT synthesis can be achieved when having captured carbon dioxide and green hydrogen as feedstock. Producing near carbon-neutral FT products can be done through two approaches. The first one is separately producing syngas from green hydrogen and carbon dioxide using Reverse Water-Gas Shift (RWGS) reaction then FT synthesis takes place. The second approach is direct hydrogenation of carbon dioxide to produce C_{5+} liquid fuels, where RWGS reaction and FT synthesis are activated by the same catalyst in the same reactor simultaneously [2].

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 [6]. The catalyst development has been aimed to produce long-chain hydrocarbons and C_{14}–C_{20} range diesel hydrocarbons [6].

Many research attempts are currently developing catalysts that can improve the selectivity of C_{5+} liquid fuels in the case of direct hydrogenation of carbon dioxide [2]. In addition, zeolites (for example, ZSM-5 and β) have been used to construct bi-functional FT catalysts for the direct production of middle-distillate liquid fuels [3].

Provided by Talieh Rajabloo
talieh.rajabloo@uhasselt.be

F. Song et. al., have prepared and studied a capsule catalyst (FeMn@HZSM-5) with FeMn as core and HZSM-5 for FT to olefins (FTO) reaction. They compared the performance of FeMn@HZSM-5 with bare FeMn catalyst and several hybrid catalysts in which the FeMn@HZSM-5 capsule catalyst showed the best catalytic performance with the highest light olefins selectivity and the lowest CO_2 selectivity [40].

A. Wang et. al. synthesized a bimetallic metal−organic framework (MOF) and prepared a novel bimetallic catalyst for FT synthesis. They showed that the bimetallic catalysts supported on MOF-derived porous carbon display stable and excellent catalytic performance during 100 h compared with a single-metal Fe catalyst [41].

H. Janani et. al. prepared a novel active FT Co–Ni catalyst by glycine–MOF combustion method. This active catalyst showed selectivity for long-chain hydrocarbons (C_{5+}) of ~52% and for short-chain hydrocarbons $(C_2–C_4)$ 30%. The relatively high activity (TOF of 2.08 s^{-1} at 340°C) was ascribed to its high porous structure and large pore size of the catalyst, which facilitated the diffusion of hydrocarbons. The unique features of this catalyst, including structural tailor ability

such as high surface area, porosity, homogeneity and stability enable it to be an active FT catalyst [42].

G. Westphalen et. al. utilized magnesiothermic reduction reaction (MRR) to produce silicon carbide (SiC*), with suitable textural properties to be used as a support for catalysts in the FT synthesis. SiC* exhibited superior performance as support for cobalt-based catalyst than that prepared with a commercial one. Under the reaction conditions used (2.0 MPa, 210 °C, H_2/CO = 2, $GHSV^{24}$ = 2340 h^{-1}), the Co/SiC* synthesized catalyst showed no deactivation $(X_{CO}$~11%) and 96% C_{5+} selectivity without methane formation during 48 h of reaction. High selectivity towards heavy hydrocarbons has been achieved in catalytic tests. This could be associated with a greater mesoporous volume and residual Mg in the support, increasing mass transfer rates inside pores and basicity effects, respectively [43].

H_2O/CO_2 co-electrolysis using solid oxide electrolysis cells (SOEC) can produce syngas with adjustable H_2/CO ratio, revealing good compatibility with the conventional F-T synthesis. A hybrid system integrating H_2O/CO_2 co-electrolysis

---

[24] Gas Hourly Space Velocity

Provided by Talieh Rajabloo
talieh.rajabloo@uhasselt.be

is also a renewable integration of H_2O/CO_2 co-electrolysis and F-T synthesis [44].

OxEon's FT reactor technology produces a mixture of liquid hydrocarbons and a synthetic crude containing components similar to jet and diesel fuel. OxEon utilizes a two-part product collection step in which the longer hydrocarbon chains are condensed at a higher temperature and separated from the shorter chains and produced water [21].

OxEon is also working on the production of synthesis gas via plasma reformer or solid oxide co-electrolysis technologies. Through the integration of these technologies, abundant low-cost natural resources such as natural gas or biogas or renewable electric power can be used to produce a liquid fuel of high value and energy density. OxEon's FT reactor and associated technologies will generate a clean, high-value liquid fuel from low-cost abundant resources [21].

Challenges and opportunities for biofuels (Potential and barriers) –

The use of biogenic feedstocks, such as biomass and wastes, poses new opportunities and challenges that must be seized and addressed to enable FT to be a competitive technology. A major driver for considering biogenic feedstocks is that the

hydrocarbon products will be classed as renewable [6]. The great advantage of FT synthesis compared to other processes is certainly the possibility to tune the product distribution depending on regional market needs [7]. The production of liquid fuels using biomass-derived syngas has received particular interest as a potential alternative for achieving a carbon-neutral and sustainable energy process [14]. FT advanced biofuels are free of aromatics and sulfur and have a significant reduction potential for emissions. FT synthesis not only provides advanced biofuels but also raw materials for the chemical industry [45].

FT biofuels exhibit attractive advantages over available biofuels such as bioethanol and biodiesel from food grains, which include [20]:

1. Being compatible with non-food crops such as woody biomass, wood residue, and grasses;
2. Having similar characteristics to conventional petroleum-derived transportation fuels such as diesel and gasoline but having a near-zero sulfur content and no need for blending with petroleum-based fuels;
3. Compatibility with available infrastructure for fuel transportation

Provided by Talieh Rajabloo
talieh.rajabloo@uhasselt.be

and storage as well as vehicle engine designs.

For the production of FT diesel, the main technological challenges are in the production of the synthesis gas (entrained flow gasifier). These barriers also apply to other gasification-derived biofuels, i.e. bio-methanol, bio-DME, and bio-hydrogen [39].

Biomass has different properties than coal and, therefore, several process changes are necessary. First, the biomass pre-treatment and feeding need a different process, because milling biomass into small particles is too energy-intensive [39]. Moreover, small biomass particles can also aggregate and plug feeding lines. Pre-treatment processes like torrefaction or pyrolysis (which produces a liquid oil) could be developed to overcome these problems. Second, due to the higher reactivity of biomass (compared to coal) the gasification temperature might be decreased, resulting in higher efficiencies, but this will require different gasification and burner design. Third, the ash composition in biomass is different from that in coal, which results in different ash and slag behavior, which is an important factor in the gasifier and still needs to be studied thoroughly. This ash and slag behavior is also important for the cooling of

the syngas, for which innovative development is desired. Other research topics are the cleaning and conditioning of synthesis gas, development of several types of catalysts, and the utilization of by-products such as electricity, heat and steam. In Germany, a pilot production facility for FT liquids from biomass is currently in operation [39]. Most importantly, the behavior of large-scale reactors can be predicted accurately based on the performance of pilot-scale plants [8].

Carbon-neutral FT synthesis is not yet ready for large scale production, mainly because of the reverse water gas shift reaction which has TRL 6 (in 2021), and it was found that the overall efficiency of carbon-neutral FT synthesis is about 39%, so more work needs to be done to increase the efficiency of the process and its readiness for large scale production [2].

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 [20]. FT fuels are 2.5 to 5 times more expensive than their equivalent fossil fuels. Hydrogen price was found to be the main contributor to this high cost, as it accounted for about 80% of the Levelized cost of FT fuels (LCOF). If green hydrogen prices reached 0.5 €$_{2021}$/kg, FT

Provided by Talieh Rajabloo
talieh.rajabloo@uhasselt.be

hydrocarbons will start to be economically competitive with their fossil equivalent hydrocarbons. Therefore, more efforts have to be given to reduce the cost of green hydrogen production to make FT fuels as economically competitive[25] as possible with their fossil counterparts [2].

Moreover, the FT process is a challenging reaction due to its exothermicity, its wide range of products including heavy waxes; the susceptibility of catalysts to deactivation; and the extensive number of parameters influencing kinetics [37].

---

[25] However, the higher costs of fossil resources in 2022, can make FT hydrocarbons competitive with the fossil-based hydrocarbons.

Provided by Talieh Rajabloo
talieh.rajabloo@uhasselt.be

Table 4. Summary Table: Key EO Data and Figures

Technical Performance		
Fischer-Tropsch (FT) processes	Low-temperature (LTFT)	For fuel synthesis
	High-temperature (HTFT)	For light olefin and oxygenate synthesis
Feedstocks	Syngas ($Co + H_2$)	
Syngas resources	Coal, Natural gas (CH_4), Biomass (Food, algae and animal waste)[*], Green H_2 and captured CO_2	
Energy input	The chemical reaction between hydrogen and carbon monoxide requires a high quantity of energy to be over.	
Catalysts	Group VIII elements, especially ruthenium (Ru), iron (Fe), cobalt (Co) and nickel (Ni). Fe and 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 vegetable oil; and bio-ethanol from sugar or starch crops. Biomass imports are key in the energy balance of Belgium.	
Energy requirements		
Methanation reaction	Exothermic reaction; standard reaction enthalpy of $-165\,kJ/mol_{CO}$ **	
Costs		
Feedstock	Production capacity (BPD)	Liquid fuel cost (€/L)
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 €$_{2020}$/kg	
Blue hydrogen (with carbon capture pair)	2.10 €$_{2020}$/kg	
Grey hydrogen	0.88-1.75 €$_{2020}$/kg	
CO$_2$ mitigation potential (compared to fossil fuels)		
First-generation biofuels	50%	
Second-generation biofuels	90%	
For 20% of total liquid biofuels	15%	

[*] Biomass-to-liquid Fischer-Tropsch

** 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 [35].

Provided by Talieh Rajabloo
talieh.rajabloo@uhasselt.be

References

1. Gruber H, Groß P, Rauch R, et al. Fischer-Tropsch products from biomass-derived syngas and renewable hydrogen. *Biomass Convers Biorefinery*. 2021;11(6):2281-2292. doi:10.1007/s13399-019-00459-5

2. Ahmed HS. Power-to-X: Modelling of Fischer-Tropsch synthesis in Aspen Plus. Published online 2021.

3. Li J, He Y, Tan L, et al. Integrated tuneable synthesis of liquid fuels via Fischer–Tropsch technology. *Nat Catal*. 2018;1(10):787-793. doi:10.1038/s41929-018-0144-z

4. Marchese M, Marocco P, Lanzini A, Santarelli M. Economic appraisal of Power-to-Liquid Fischer-Tropsch plants exploiting renewable electricity, green hydrogen, and CO 2 from biogas in Europe . *E3S Web Conf*. 2022;334:02002. doi:10.1051/e3sconf/202233402002

5. Hoefnagels R, Dornburg V, Faaij A, Banse M. *Analysis of the Economic Impact of Large-Scale Deployment of Biomass Resources for Energy and Materials in the Netherlands*.; 2009. http://scholar.google.com/scholar?hl=en&btnG=Search&q=intitle:Analysis+of+the+Economic+Impact+of+Large-Scale+Deployment+of+Biomass+Resources+for+Energy+and+Materials+in+the+Netherlands#0

6. Konarova M, Aslam W, Perkins G. *Fischer-Tropsch Synthesis to Hydrocarbon Biofuels: Present Status and Challenges Involved*. Elsevier Inc.; 2022. doi:10.1016/B978-0-12-823306-1.00006-6

7. Emanuele Oddo MM. Roadmap to 2050: The Land-Water-Energy Nexus of Biofuels 2. Biofuels Technologies. Published 2021. Accessed March 18, 2022. https://roadmap2050.report/biofuels/biofuels-technologies/

8. Ail SS, 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

9. Marchese M, Chesta S, Santarelli M, Lanzini A. Techno-economic feasibility of a biomass-to-X plant: Fischer-Tropsch wax synthesis from digestate gasification. *Energy*. 2021;228:120581. doi:10.1016/j.energy.2021.120581

10. Jenčík J, Hönig V, Obergruber M, et al. Advanced biofuels based on fischer–tropsch synthesis for applications in diesel engines. *Materials (Basel)*. 2021;14(11). doi:10.3390/ma14113077

11. Piazzi S, Patuzzi F, Baratieri M. Energy and exergy analysis of different biomass gasification coupled to Fischer-Tropsch synthesis configurations. *Energy*. 2022;249:123642. doi:10.1016/j.energy.2022.123642

12. Martinelli M, Gnanamani MK, LeViness S, Jacobs G, Shafer WD. An overview of Fischer-Tropsch Synthesis: XtL processes, catalysts and reactors. *Appl Catal A Gen*. 2020;608(July):117740. doi:10.1016/j.apcata.2020.117740

13. Santos RG dos, Alencar AC. Biomass-derived syngas production via gasification process and its catalytic conversion into fuels by Fischer Tropsch synthesis: A review. *Int J Hydrogen Energy*. 2020;45(36):18114-18132. doi:10.1016/j.ijhydene.2019.07.133

14. Bobadilla LF, Egaña A, Castillo R, et al. Understanding the promotional effect of Pt/CeO2 in cobalt-catalyzed Fischer-Tropsch synthesis using operando infrared spectroscopy at moderated pressures. *Fuel*. 2022;312(October 2021). doi:10.1016/j.fuel.2021.122964

15. Teimouri Z, Borugadda VB, Dalai AK,

Provided by Talieh Rajabloo
talieh.rajabloo@uhasselt.be

Abatzoglou N. Application of computational fluid dynamics for modeling of Fischer-Tropsch synthesis as a sustainable energy resource in different reactor configurations: A review. *Renew Sustain Energy Rev.* 2022;160(September 2021):112287. doi:10.1016/j.rser.2022.112287

16. Shahabuddin M, Alam MT, Krishna BB, Bhaskar T, Perkins G. A review on the production of renewable aviation fuels from the gasification of biomass and residual wastes. *Bioresour Technol.* 2020;312(May):123596. doi:10.1016/j.biortech.2020.123596

17. Van Groenestijn J, Harmsen P, Bos H. *Biomass for the Circular Economy.*; 2019.

18. Stigsson C, Furusjö E, Börjesson P. Modelling of an integrated hydrothermal liquefaction, gasification and Fischer-Tropsch synthesis process for conversion of forest residues into hydrocarbons. *Bioresour Technol.* Published online 2021:126070. doi:10.1016/j.biortech.2021.126070

19. Zarandi M, Panahi M, Rafiee A. Simulation of a Natural Gas-to-Liquid Process with a Multitubular Fischer-Tropsch Reactor and Variable Chain Growth Factor for Product Distribution. *Ind Eng Chem Res.* 2020;59(43):19322-19333. doi:10.1021/acs.iecr.0c01951

20. Rafati M, Wang L, Dayton DC, Schimmel K, Kabadi V, Shahbazi A. Techno-economic analysis of production of Fischer-Tropsch liquids via biomass gasification: The effects of Fischer-Tropsch catalysts and natural gas co-feeding. *Energy Convers Manag.* 2017;133:153-166. doi:10.1016/j.enconman.2016.11.051

21. Fischer Tropsch (FT) Reactor | OxEon Energy | Beyond Current Potential. Accessed March 18, 2022. https://oxeonenergy.com/solutions/fischer-tropsch-reactor

22. Ostadi M, Paso KG, Rodriguez-Fabia S, Øi LE, Manenti F, Hillestad M. Process integration of green hydrogen: Decarbonization of chemical industries. *Energies.* 2020;13(18). doi:10.3390/en13184859

23. Marchese M, Buffo G, Santarelli M, Lanzini A. CO$_2$ from direct air capture as carbon feedstock for Fischer-Tropsch chemicals and fuels: Energy and economic analysis. *J CO$_2$ Util.* 2021;46:101487. doi:10.1016/j.jcou.2021.101487

24. Colla M, Blondeau J, Jeanmart H. Optimal Use of Lignocellulosic Biomass for the Energy Transition , Including the Non-Energy Demand : The Case of the Belgian Energy System. 2022;10(March):1-11. doi:10.3389/fenrg.2022.802327

25. Of D, Project THE. *BIOSES - Results Biofuels Sustainable End USe.* Vol 2011.; 2011.

26. Belgium to ban soy and palm oil in biofuels from 2022. Accessed April 14, 2022. https://www.brusselstimes.com/164687/belgium-to-ban-soy-and-palm-oil-in-biofuels-from-2022-environment-climate-zakia-khattabi-sustainability-amsterdam-declatation-partnership

27. Thor Wismann S, Larsen K, Mølgaard Mortensen P. Electrical Reverse Shift: Sustainable CO 2 Valorization for Industrial Scale . *Angew Chemie.* 2022;134(8):2-5. doi:10.1002/ange.202109696

28. Mansoori GA, Agyarko LB, Estevez LA, et al. Fuels of the Future for Renewable Energy Sources (Ammonia, Biofuels, Hydrogen). Published online 2021. http://arxiv.org/abs/2102.00439

29. Renewable I, Agency E. *Green Hydrogen for Industry.*; 2022.

30. Experts explain why green hydrogen costs have fallen and will keep falling | S&P Global Market Intelligence. Published 2021. Accessed April 20, 2022. https://www.spglobal.com/marketintelli

Provided by Talieh Rajabloo
talieh.rajabloo@uhasselt.be

gence/en/news-insights/latest-news-headlines/experts-explain-why-green-hydrogen-costs-have-fallen-and-will-keep-falling-63037203

31. "Green hydrogen now cheaper to produce than grey H2 across Europe due to high fossil gas prices" | Recharge. Accessed April 20, 2022. https://www.rechargenews.com/energy-transition/green-hydrogen-now-cheaper-to-produce-than-grey-h2-across-europe-due-to-high-fossil-gas-prices/2-1-1098104

32. Technology | Comsyn. Accessed March 18, 2022. https://www.comsynproject.eu/technology/

33. Tock L, Gassner M, Maréchal F. Thermochemical production of liquid fuels from biomass: Thermo-economic modeling, process design and process integration analysis. *Biomass and Bioenergy*. 2010;34(12):1838-1854. doi:10.1016/j.biombioe.2010.07.018

34. Zhang C, Jun KW, Ha KS, Lee YJ, Kang SC. Efficient utilization of greenhouse gases in a gas-to-liquids process combined with CO_2/steam-mixed reforming and Fe-based Fischer-Tropsch synthesis. *Environ Sci Technol*. 2014;48(14):8251-8257. doi:10.1021/es501021u

35. Fratalocchi L, Visconti CG, Groppi G, Lietti L, Tronconi E. Intensifying heat transfer in Fischer-Tropsch tubular reactors through the adoption of conductive packed foams. *Chem Eng J*. 2018;349(March):829-837. doi:10.1016/j.cej.2018.05.108

36. A sustainability assessment of CCS coupled with Fischer-Tropsch biofuels from residual biomass shows positive environmental and socio-economic impacts | Negem Project. Accessed March 18, 2022. https://www.negemproject.eu/news/a-sustainability-assessment-of-ccs-coupled-with-fischer-tropsch-biofuels-from-residual-biomass-shows-positive-environmental-and-socio-economic-impacts/

37. Garona HA, Cavalcanti FM, de Abreu TF, Schmal M, Alves RMB. Evaluation of Fischer-Tropsch synthesis to light olefins over Co- and Fe-based catalysts using artificial neural network. *J Clean Prod*. 2021;321(September):129003. doi:10.1016/j.jclepro.2021.129003

38. Fagerström A, Abdelaziz O, Poulikidou S, et al. Economic and Environmental Potential of Large-Scale Renewable Synthetic Jet Fuel Production through Integration into a Biomass CHP Plant in Sweden. *Energies*. 2022;15(3). doi:10.3390/en15031114

39. Elobio: Fischer-Tropsch diesel. Accessed March 18, 2022. https://www.elobio.eu/biofuels/fischer-tropsch-diesel/index.html

40. Song F, Yong X, Wu X, et al. FeMn@HZSM-5 capsule catalyst for light olefins direct synthesis via Fischer-Tropsch synthesis: Studies on depressing the CO_2 formation. *Appl Catal B Environ*. 2022;300(June 2021):120713. doi:10.1016/j.apcatb.2021.120713

41. Wang A, Luo M, Lü B, et al. MOF-Derived Porous Carbon-Supported Bimetallic Fischer-Tropsch Synthesis Catalysts. *Ind Eng Chem Res*. Published online 2021. doi:10.1021/acs.iecr.1c03810

42. Janani H, Rezvani A, Mirzaei AA. Preparation of a Novel Active Fischer–Tropsch Co–Ni Catalyst Derived from Metal-Organic Framework. *Pet Chem*. 2020;60(9):1059-1065. doi:10.1134/S0965544120090121

43. Westphalen G, Baldanza MAS, de Almeida AJ, Salim VMM, da Silva MAP, da Silva VT. Improvement of C–C Coupling Using SiC as a Support of Cobalt Catalysts in Fischer Tropsch Synthesis. *Catal Letters*. 2021;(0123456789). doi:10.1007/s10562-021-03775-6

Provided by Talieh Rajabloo
talieh.rajabloo@uhasselt.be

44. Luo Y, Shi Y, Cai N. *Stabilization of Intermittent Renewable Energy Using Power-to-X*. Elsevier Inc.; 2021. doi:10.1016/b978-0-12-819184-2.00005-5

45. BEST. Accessed March 18, 2022. https://www.best-research.eu/en/competence_areas/all_projects/view/394

46. Euro Dollar Exchange Rate (EUR USD) - Historical Chart | MacroTrends. Accessed April 28, 2021. https://www.macrotrends.net/2548/euro-dollar-exchange-rate-historical-chart

47. Fratalocchi L, Groppi G, Visconti CG, Lietti L, Tronconi E. Packed-POCS with skin: A novel concept for the intensification of non-adiabatic catalytic processes demonstrated in the case of the Fischer-Tropsch synthesis. *Catal Today*. 2022;383:15-20. doi:10.1016/j.cattod.2020.12.031

48. Ruiz P, Nijs W, Tarvydas D, et al. ENSPRESO - an open, EU-28 wide, transparent and coherent database of wind, solar and biomass energy potentials. *Energy Strateg Rev*. 2019;26(September 2019):100379. doi:10.1016/j.esr.2019.100379

49. Diesel B7 - The first step on the way to a greener transport. Accessed April 14, 2022. https://www.biofuel-express.com/en/diesel/

50. Western Bulk Takes Delivery of First Carbon Offset Combined with Bio Fuel from TFG Marine – Advanced BioFuels USA. Accessed April 14, 2022. https://advancedbiofuelsusa.info/western-bulk-takes-delivery-of-first-carbon-offset-combined-with-bio-fuel-from-tfg-marine/

51. Alternative Fuels Data Center: Biodiesel Blends. Accessed April 14, 2022. https://afdc.energy.gov/fuels/biodiesel_blends.html

52. Lawlor V, Olabi AG. Review of scientific research regarding PPO, tallow and RVO as diesel engine fuel. *Fuel*. 2015;145:25-38. doi:10.1016/j.fuel.2014.12.034

53. Euro to US Dollar Spot Exchange Rates for 2017. Accessed January 7, 2022. https://www.exchangerates.org.uk/EUR-USD-spot-exchange-rates-history-2017.html

Provided by Talieh Rajabloo
talieh.rajabloo@uhasselt.be