

Review

Application of Fischer–Tropsch Synthesis in Biomass to Liquid Conversion

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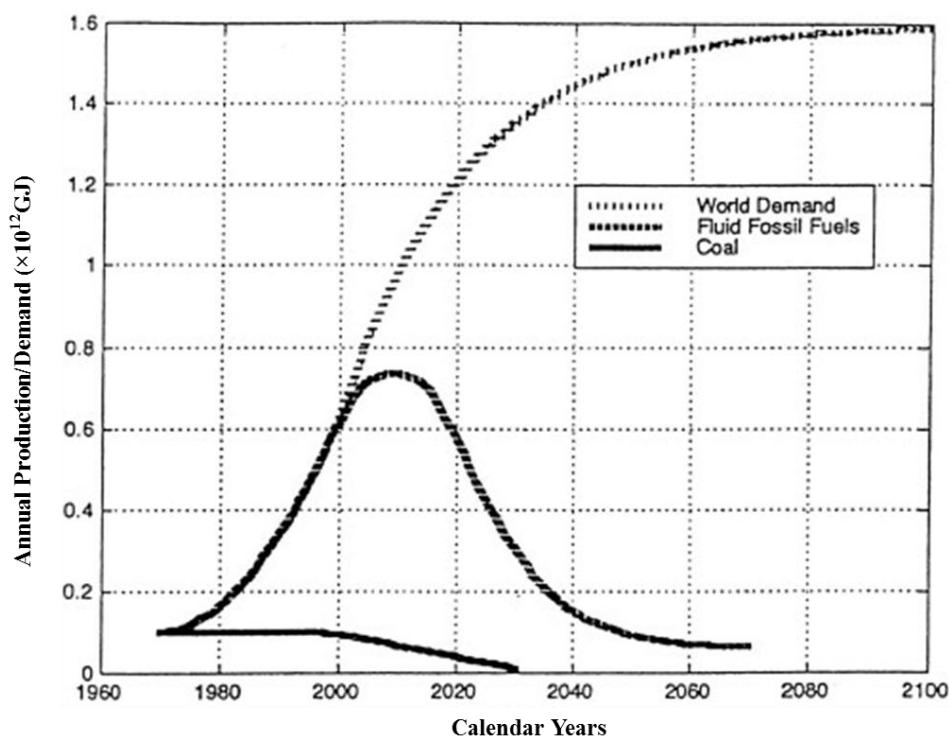
Abstract: Fischer–Tropsch synthesis is a set of catalytic processes that can be used to produce fuels and chemicals from synthesis gas (mixture of CO and H₂), which can be derived from natural gas, coal, or biomass. Biomass to Liquid via Fischer–Tropsch (BTL-FT) synthesis is gaining increasing interests from academia and industry because of its ability to produce carbon neutral and environmentally friendly clean fuels; such kinds of fuels can help to meet the globally increasing energy demand and to meet the stricter environmental regulations in the future. In the BTL-FT process, biomass, such as woodchips and straw stalk, is firstly converted into biomass-derived syngas (bio-syngas) by gasification. Then, a cleaning process is applied to remove impurities from the bio-syngas to produce clean bio-syngas which meets the Fischer–Tropsch synthesis requirements. Cleaned bio-syngas is then conducted into a Fischer–Tropsch catalytic reactor to produce green gasoline, diesel and other clean biofuels. This review will analyze the three main steps of BTL-FT process, and discuss the issues related to biomass gasification, bio-syngas cleaning methods and conversion of bio-syngas into liquid hydrocarbons via Fischer–Tropsch synthesis. Some features in regard to increasing carbon utilization, enhancing catalyst activity, maximizing selectivity and avoiding catalyst deactivation in bio-syngas conversion process are also discussed.

Keywords: biomass to liquid; Fischer–Tropsch; biomass; bioenergy; biofuel; bio-syngas; gasification; gas cleaning; bi-functional catalyst; carbon utilization

1. Introduction

Currently, a large portion of the world's energy needs is being met by traditional fossil fuels, such as petroleum and natural gas. It has been estimated that the global energy demand will continue to rise because of world's increasing population [1]. However, due to the limited reserves, the traditional fossil fuel supplies will be depleted in the near future, as shown in Figure 1, which make searching for alternative energy sources necessary and critical [2]. Moreover, the burning of traditional fossil fuels can also emit extensive greenhouse gas, such as carbon dioxide, into the atmosphere and cause some other severe environmental issues [3–5].

Figure 1. Estimated global energy demand and fossil fuel production [2].



In order to meet increasing global energy needs, ensure energy security and help with environmental protection, many efforts have been made to develop renewable biofuels. In the United States, the Energy Independence and Security Act (EISA) of 2007 has increased the volume of renewable fuel required to be blended into transportation fuel from 9 billion gallons in 2008 to 36 billion gallons by 2022 [6].

Production of renewable fuels, such as gasoline, diesel and jet fuel, using the Biomass to Liquid via Fischer–Tropsch Synthesis (BTL-FT) process has been gaining increasing attention during recent years. Renewable fuels from BTL-FT are usually much cleaner and environmentally friendly, and they contain little or even no sulfur and other contaminant compounds. In this regard, they can easily satisfy the upcoming stricter environmental regulations in both Europe and the USA [7]. In the BTL-FT process, biomass, such as woodchips, is firstly gasified with air, oxygen, and/or steam to produce raw bio-syngas. Then, a cleaning process is applied to the raw bio-syngas to remove contaminants like small char particles, ash, and tar. The cleaned bio-syngas is conducted into a catalytic reactor to perform FT synthesis to produce renewable liquid fuels [8,9].

Bio-syngas resulting from biomass gasification contains CO, H₂, CO₂, CH₄, and N₂ in various proportions [10,11]. The average bio-syngas from a downdraft gasifier with air as the oxidant contains 22.16% CO, 17.55% H₂, 11.89% CO₂, 3.07% CH₄, with N₂ and other gases as the balance [12].

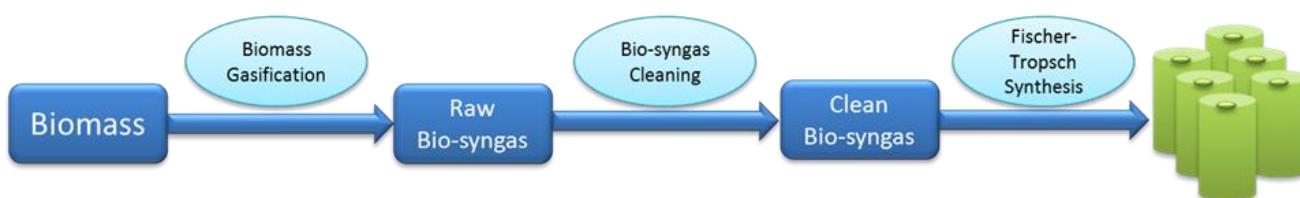
Fischer–Tropsch synthesis (FTS) is the process of producing liquid hydrocarbons from synthesis gas (CO and H₂). Its feedstock can be coal, natural gas, biomass or other solid carbon sources. Traditional FTS catalysts, such as Fe-, Co-, and Ni-based catalysts, have been extensively studied in the literature [13–20].

This review will analyze the three main steps of the BTL-FT process and discuss the issues related to biomass gasification, bio-syngas cleaning methods and conversion of bio-syngas into liquid hydrocarbons via Fischer–Tropsch synthesis. Some features regarding increasing carbon utilization, enhancing catalyst activity, maximizing selectivity and avoiding catalyst deactivation in the bio-syngas conversion process are also discussed.

2. Process Analysis

Generally, there are three main steps in the Biomass to Liquid via Fischer–Tropsch (BTL-FT) synthesis [8,9,21]. Biomass is firstly converted into biomass-derived syngas (bio-syngas) by gasification. In a second step, a cleaning process is applied to the bio-syngas in order to remove impurities, resulting in clean bio-syngas which meets the Fischer–Tropsch synthesis requirements. Finally, the cleaned bio-syngas is then conducted into Fischer–Tropsch catalytic reactor to produce green gasoline, diesel and other clean biofuels. The flow sheet of the BTL-FT process is depicted in Figure 2.

Figure 2. Flow sheet of the Biomass to Liquid via Fischer–Tropsch Synthesis (BTL-FT) process.



2.1. Biomass Gasification

Gasification is a process that can be used to convert carbonaceous feedstock into gas mixtures which mostly contain carbon monoxide, hydrogen, carbon dioxide, nitrogen, and methane. Various biomass feedstocks can be utilized to produce bio-syngas, such as wood and agricultural wastes. Each type of biomass possesses specific properties. A basic understanding of the types and sources of appropriate biomass and their basic properties will be a foundation for the utilization of biomass in gasification technology. Raveendran *et al.* [22] have reported the composition and other properties of different kinds of biomasses, and Kirubakaran *et al.* [23] reproduced them in an ultimate analysis of biomass (chemical formula C_xH_yO_z) as shown in Table 1. It was observed that clean wood can produce a relatively clean syngas which has low levels of contaminants, and wood produced from dedicated plantations can be a major source for renewable fuel production from biomass [24].

Table 1. Ultimate analysis of biomass [23].

Biomass	Ultimate analysis (wt%)				HHV ^a (MJ/kg)	Density (kg/m ³)	x	y	z	Percentage conversion of carbon
	C	H	N	O						
Bagasse	43.8	5.8	0.4	47.1	16.29	111	3.65	5.8	2.94	81
Coconut coir	47.6	5.7	0.2	45.6	14.67	151	3.97	5.7	2.85	72
Coconut Shell	50.2	5.7	0	43.4	20.5	661	4.18	5.7	2.71	65
Coir pith	44	4.7	0.7	43.4	18.07	94	3.67	4.7	2.71	74
Corn Cob	47.6	5	0	44.6	15.65	188	3.97	5	2.79	70
Corn stalks	41.9	5.3	0	46	16.54	129	3.49	5.3	2.88	82.3
Cotton gin waste	42.7	6	0.1	49.5	17.48	109	3.56	6	3.1	87
Ground nut shell	48.3	5.7	0.8	39.4	18.65	299	4.03	5.7	2.46	61.2
Millet husk	42.7	6	0.1	33	17.48	201	3.56	6	2.06	58
Rice husk	38.9	5.1	0.6	32	15.29	617	3.24	5.1	2	62
Rice straw	36.9	5	0.4	37.9	16.78	259	3.08	5	2.37	82.4
Subabul wood	48.2	5.9	0	45.1	19.78	259	4.02	5.9	2.82	70.2
Wheat straw	47.5	5.4	0.1	35.8	17.99	222	3.96	5.4	2.24	56.5
AVERAGE	44.6	5.5	0.3	41.8	17.32	253.84	3.72	5.49	2.61	70.89

^a Higher Heating Value.

Pre-treatment before gasification is necessary and generally includes screening, size reduction, and drying [25]. Smaller biomass particle size will provide more surface area and porous structures per unit biomass, which will facilitate heat transfer and biomass conversion during the gasification process. However, in most gasifiers, the biomass feed has to withstand the flow of gasifying agent with an appropriate size and weight; feed particle sizes are most often in the range of 20 to 80 mm [26]. Drying is the most important process in the pre-treatment. Drier biomass can improve the efficiency of gasification, but also reduces the hydrogen content in the gas product, which is unfavorable in the following Fischer–Tropsch synthesis. Drying can reduce the moisture content of the biomass feedstock to 10%–15% [27].

Some other pretreatment technologies, such as torrefaction, pyrolysis, and pelletization, also need to be mentioned.

Torrefaction is a thermal pretreatment technology which is performed at atmospheric pressure without the appearance of oxygen at around 200 to 300 °C. Torrefaction can convert fresh biomass into a solid uniform product, which has a low moisture content and high calorific value. The torrefaction process involves initial heating, pre-drying, post-drying and intermediate heating stages [28].

Pyrolysis is a process involving the direct thermal decomposition of biomass in the absence of oxygen at a moderate temperature of around 400 to 800 °C. The pyrolysis products are generally gas, liquid, and solid char. Their proportions depend on the pyrolysis method employed and the properties of the feed biomass [29,30].

Pelletization can be described as drying and compressing biomass to produce cylindrical biomass pellets. Those pellets have smaller volume and higher volumetric energy density compared to raw biomass and thus are easy and efficient to store, transport and use in energy conversion [31].

Torrefaction can provide the highest process efficiency (94%) compared to pyrolysis (64%) and pelletization (84%) [32].

Several types of gasifiers are designed with different hydrodynamics, using different gasification agents (air, oxygen, oxygen-rich air and/or steam) and operation conditions. The most widely used types are updraft fixed bed gasifiers, downdraft fixed bed gasifiers, fluidized-bed gasifiers, and entrained flow gasifiers [33].

In the updraft fixed bed gasifier, as shown in Figure 3, the biomass feed is introduced into the top of the gasifier and falls downwards when the gasifying agent comes into the bottom of the grate and then goes upwards. The combustion happens at the bottom of the bed, and the gas product is released out of the gasifier at around a temperature of 500 °C. In the downdraft fixed bed gasifier, as shown in Figure 4, both the biomass feed and gasifying agent move downward, and the gas exits at a higher temperature of 800 °C [34].

Figure 3. Schematic of an updraft gasifier [26].

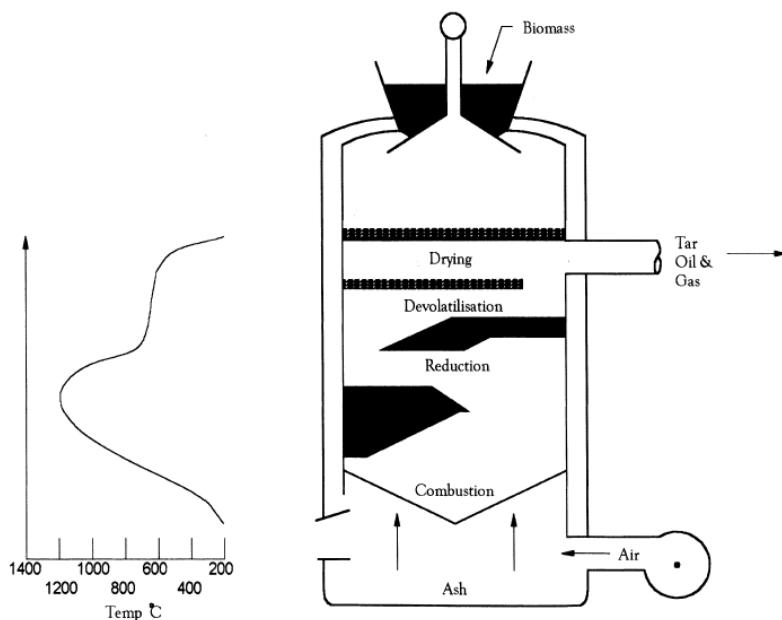
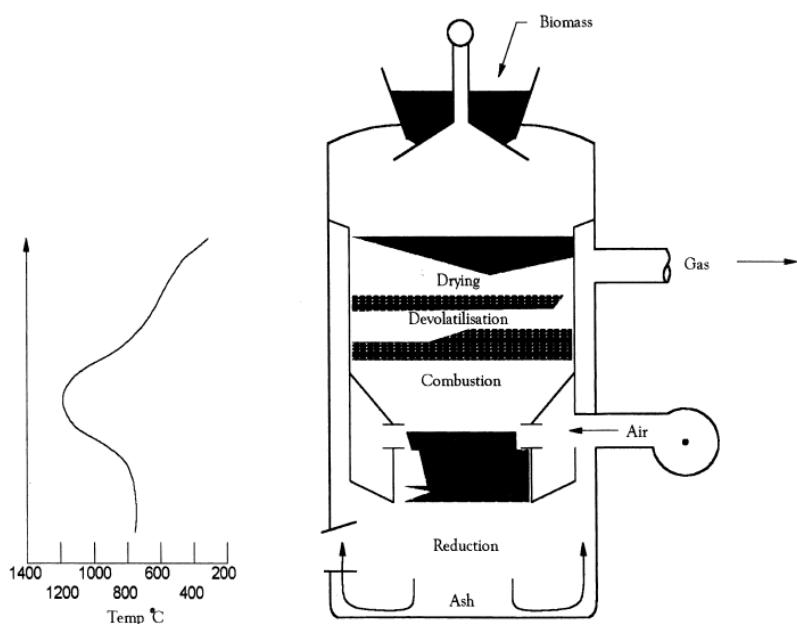


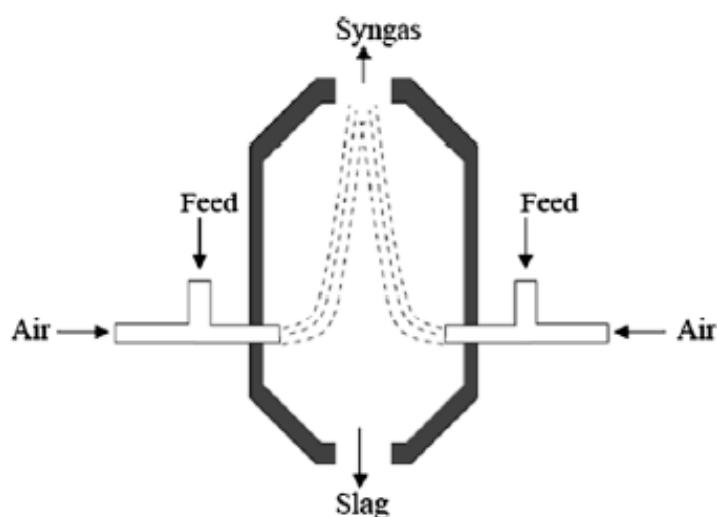
Figure 4. Schematic of a downdraft gasifier [26].



In the fluidized bed gasifier, the biomass feed is introduced into the gasifier bottom and then fluidized using air, oxygen or another gasifying agent. Such kinds of gasifiers can increase the reaction rates and conversion efficiencies by enhancing the heat transfer during the gasification. Fluidized beds can be further divided into bubbling fluidized beds and circulating fluidized beds [34].

In the entrained flow gasifier, as shown in Figure 5, the feed and air are introduced into the reactor co-currently and the reactions happen at high pressures (between 19.7 and 69.1 atm) and high temperature (more than 1000 °C) [35,36]. The entrained flow gasifier has been developed for coal gasification, but it requires a fine feed (<0.1–0.4 mm) which requires a stricter pretreatment process for biomass fibrous materials, such as wood [26].

Figure 5. Configuration of an entrained flow gasifier [35,36].



The advantages and disadvantages of various gasifiers have been summarized and compared by Rampling [37] and are shown in Table 2.

Table 2. Properties of selected gasification technologies [37].

Advantages	Disadvantages
<i>Fixed/moving bed, updraft</i>	
Simple, inexpensive process	Large tar production
Exit gas temperature about 250 °C	Potential channeling
Operates satisfactorily under pressure	Potential bridging
High carbon conversion efficiency	Small feed size
Low dust levels in gas	Potential clinkering
High thermal efficiency	
<i>Fixed/moving bed, downdraft</i>	
Simple process	Minimum feed size
Only traces of tar in gas product	Limited ash content allowable in feed
	Limits to scale up capacity
	Potential for bridging and clinkering

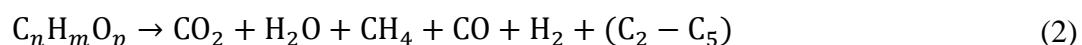
Table 2. *Cont.*

<i>Fluidized bed</i>	
Flexible feed rate and composition	
High ash fuels acceptable	Operating temperature limited by ash clinkering
Able to pressurize	High gas product temperature
High CH ₄ in gas product	High tar and fines content in gas
High volumetric capacity	Possibility of high C content in fly ash
Easy temperature control	
<i>Circulating fluidized bed</i>	
Flexible process	Corrosion and attrition problems
Up to 850 °C operating temperature	Poor operational control using biomass
<i>Double fluidized bed</i>	
Oxygen not required	
High CH ₄ due to low bed temperature	More tar due to lower bed temperature
Temperature	Difficult to operate under pressure
Temperature limit in the oxidizer	
<i>Entrained bed</i>	
Very low in tar and CO ₂	Low in CH ₄
Flexible to feedstock	Extreme feedstock size reduction required
Exit gas temperature	Complex operational control
	Carbon loss with ash
	Ash slagging

The reaction in biomass gasification is generally like this [38]:



In the first step of the gasification process, the cellulose, hemicelluloses and lignin compounds in the biomass are thermo-chemically decomposed. Then the gasification of char generated from the first step and some other equilibrium reactions occur. A detailed description of the reactions that happen in the gasification process can be the following [39,40]:





The composition of the product gas from a gasifier will be influenced by several parameters [41,42], such as feedstock composition, moisture content of the feedstock, gasifying agents, operation pressure, operation temperature, *etc.* It is difficult to predict the composition of the gas product from a gasifier due to the complex reactions occurred during the gasification. Table 3 shows the typical composition of gas produced from gasification of wood and charcoal with low to medium moisture content with ambient air as the gasifying agent in a downdraft gasifier [43] and composition of bio-syngas from biomass gasification [44–46].

Table 3. Composition of gas produced from gasification of wood and charcoal in ambient air [43] and also the composition of typical nitrogen free bio-syngas [44–46].

Component	Wood gas (air)	Charcoal gas (air)	Bio-syngas (nitrogen free)
N ₂	50–60	55–65	0
CO	14–25	28–32	28–36
CO ₂	9–15	1–3	22–32
H ₂	10–20	4–10	21–30
CH ₄	2–6	0–2	8–11
C ₂ H ₄	n/a	n/a	2–4
BTX	n/a	n/a	0.84–0.96
C ₂ H ₅	n/a	n/a	0.16–0.22
Tar	n/a	n/a	0.15–0.24
Others	n/a	n/a	<0.021

Some other critical issues in biomass gasification, such as the effects of gasification temperature, biomass flow rate, type and properties and gasifying agent types on the product properties, can be found in previous research work [47–51].

2.2. Bio-Syngas Cleaning

The biomass feedstock is pretreated and the gasification technologies are optimized to efficiently produce bio-syngas with the desired content of carbon monoxide and hydrogen. However, some amounts of impurities will show in the raw bio-syngas. Those impurities can lower the FT activity in the bio-syngas catalytic conversion, so it is necessary to remove them to meet the Fischer–Tropsch synthesis specifications [52], which are shown in Table 4.

Generally, the impurities in bio-syngas produced from the gasifier can be grouped into three types: (1) organic impurities, such as tars, Benzene, Toluene, and Xylenes (BTX); (2) inorganic impurities, such as O₂, NH₃, HCN, H₂S, COS, and HCl; (3) other impurities, such as dust and soot.

Table 4. The requirements of syngas cleaning for Fischer–Tropsch synthesis [52].

Impurity	Specification
H ₂ S + COS + CS ₂	<1 ppmv ^a
NH ₃ + HCN	<1 ppmv
HCl + HBr + HF	<10 ppbv ^b
Alkali metals (Na + K)	<10 ppbv
Particles (soot, ash)	“almost removed”
Organic components (tar)	below dew point
Hetero-organic components (S, N, O)	<1 ppmv

^a Parts Per Million by Volume; ^b Parts Per Billion by Volume.

2.2.1. Organic Impurities Removal

Tars are condensable mixtures which include single ring to 5-ring aromatic compounds, other oxygen containing hydrocarbons and the polycyclic aromatic hydrocarbons (PAHs) [53]. They will foul the equipment in the following steps or even cover the surface of catalysts to slow or stop the reaction of the FT conversion, so the concentration of tars should be reduced to below dew point during the FT conversion. However, tars can be cracked into CO and H₂ to increase their contents in the bio-syngas, and eventually to increase the overall carbon utilization efficiency of the feedstock. There are two types of tar cracking methods: thermal cracking (primary method) and catalytic cracking (secondary method) [54]. Catalytic cracking has been proved effective. A tar conversion rate of over 99% has been achieved by using dolomite and Ni based catalysts [55]. Tars can also be removed by using the oil based scrubbing [56].

2.2.2. Inorganic and Other Impurities Removal

Raw bio-syngas contains 0.5–1 vol% oxygen, which may cause severe explosions during the hydrogen compression before FT reaction, oxidization of the catalysts and lower the activity of FT synthesis; it is necessary to reduce the O₂ content to below 0.5 vol%. For Cu/Zn/Al/HZSM-5 catalyst, O₂ content should be reduced to less than 0.1 vol% [57]. Li *et al.* designed two deoxidizers packed with Pd/Al₂O₃-based de-oxidant before the compressor and the fixed-bed reactor to reduce the O₂ content to the desired value [57]. In another research, tubular zirconia- yttria membranes have been developed to remove oxygen from low oxygen containing gas to produce oxygen-free gas streams [58].

In the gasification process, nitrogen in the biomass will form NH₃, HCN, and NO_x. Nitrogen containing species are unfavorable in the bio-syngas, they will poison the catalyst or act as the precursor of NO_x. Ammonia can be removed by aqueous scrubber, or can be decomposed and selectively oxidized [59]:



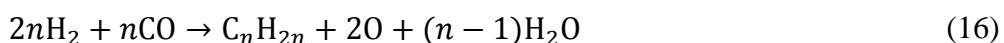
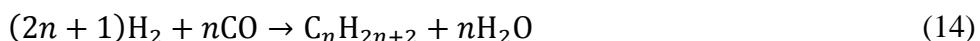
These two methods are desirable because they will not introduce any contaminants to the following steps. NO_x is one of the significant pollutants in the atmosphere; it can be removed over the platinum and metals (Cu, Cr and Fe) based on zeolite (H-ZSM-5) catalysts [60]. Dust, soot and other impurities can be removed by using cyclones, metal filters, moving beds, candle filters, bag filters, and special soot scrubber [25].

Sulfur contaminants from the biomass gasification can take up the active sites of catalysts and reduce the catalytic activity during the reaction. A current approach in the coal industry is the use of a sulfur sorbent, like ZnO, to absorb H₂S and form ZnS to protect catalysts from sulfur poisoning [61].

2.3. Fischer–Tropsch Synthesis

The Fischer–Tropsch process or Fischer–Tropsch synthesis is a set of catalytic processes for converting synthesis gas (syngas, carbon monoxide hydrogen and/or other gases mixture) into liquid hydrocarbons. It was first introduced by Han Fischer and Franz Tropsch in 1923 [62]. The Fischer–Tropsch process has now become a key component in Gas to Liquid (GTL) technology.

The reactions in the Fischer–Tropsch process are generally described as the following:



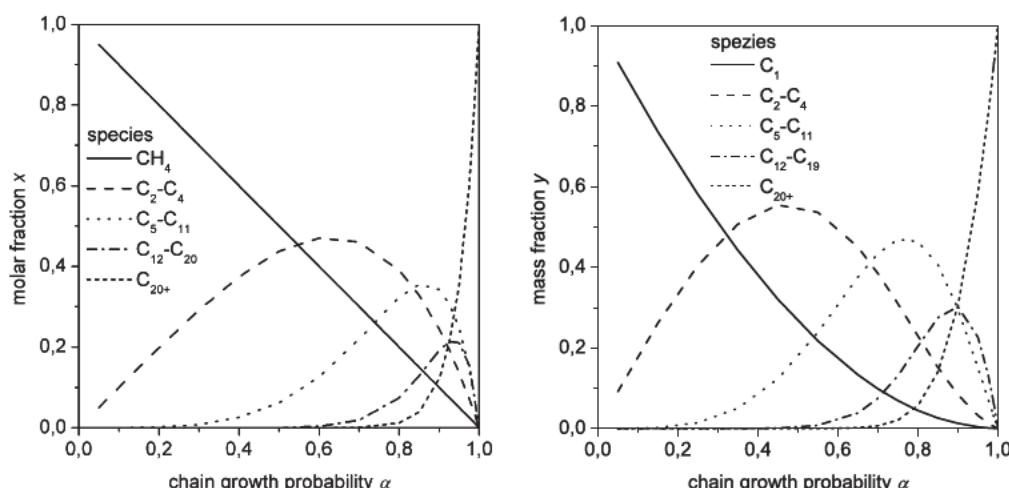
Except alkanes (Equation 14) and alkenes (Equation 15), some oxygenates (Equation 16) may be also formed during the Fischer–Tropsch process. A water gas shift (WGS) reaction (Equation 17) occurring during the process can be used to adjust the ratio of carbon monoxide and hydrogen.

The products from Fischer–Tropsch process generally follow the statistical hydrocarbon distribution—Anderson–Schulz–Flory (ASF) distribution [63]. The molar fraction M of a certain carbon number of n can be described as:

$$M_n = (1 - \alpha)\alpha^{n-1} \quad (18)$$

So product distribution can be determined by the chain growth probability α value. The product distribution from the Fischer–Tropsch synthesis as a function of chain growth probability in molar fraction and mass fraction are depicted in Figure 6 [64]. It can be predicted from the ASF distribution that the maximum selectivity to gasoline range (C5–C11) and diesel range (C12–C20) hydrocarbons are around 45% and 30%, respectively [65].

Figure 6. FT product distribution as a function of chain growth probability [64].



Commercially available FT reactors nowadays have two different temperature ranges. The high temperature FT (HTFT) reactor runs with iron catalysts at around 340 °C, and is used to produce olefins and gasoline. The low temperature FT (LTFT) reactor uses iron or cobalt based catalysts at around 230 °C, and is used to produce diesel and linear waxes [66]. Generally, commercially established FT reactors can be divided into three main categories: fixed bed, fluid bed and slurry FT reactors [67]. The critical features of FT reactors, such as heat transfer and mass transfer, are summarized and compared in Table 5 [68]. Other theoretical and practical aspects of selecting and designing FT reactors can be found in previous works [69–73].

Table 5. Comparison of selected FT reactors [68].

Feature	Fixed bed	Fluid bed (circulating)	Slurry
Temperature control	Poor	Good	Good
Heat exchanger surface	240 m ² per 1000 m ³ feed	15–30 m ² per 2000 m ³ feed	50 m ² per 1000 m ³ feed
Max. reactor diameter	<0.08 m	Large	Large
CH ₄ formation	Low	High	As fixed bed or lower
Flexibility	Intermediate	Little	High
Product	Full range	Low mol. Weight	Full range
Space-time yield (C ₂₊)	>1000 kg/m ³ day	4000–12000 kg/m ³ day	1000 kg/m ³ day
Catalyst affectivity	Lowest	Highest	Intermediate
Back-mixing	Little	Intermediate	Large
Minimum H ₂ /CO feed	As slurry or higher	Highest	Lowest
Construction			Simplest

Fe-, Co-, Ru- and Ni-based catalysts are mostly used in the Fischer–Tropsch process [66]. Ru is very active in the FT reaction, however, its availability is very limited and its price is very high. Ni is also very active, but produces too much methane due to its strong hydrogenating properties. Moreover, Ni will form volatile carbonyls under high pressure and will be lost from the reactors slowly. This leaves Fe and Co as the only practical catalysts in industrial application [74].

3. Increasing Carbon Utilization

The bio-syngas from the biomass gasification usually contains 9–15 vol% (air as the gasifying agent) and 21–30 vol% (nitrogen free gasifying agent) CO₂. Such a relatively high amount of CO₂ will be separated before the syngas is fed into FT reactors in conventional methods, which will cause a large portion of carbon loss from the biomass and make the overall carbon utilization rather low. In order to increase carbon utilization in the whole process, hydrogenation of CO₂ in the bio-syngas into liquid hydrocarbons may be a possible route to be investigated [75–79]. The utilization of CO₂ will reduce CO₂ emission into the environment and also help with bringing down the capital investment and operation cost of the FT process.

Water gas shift (WGS) reaction and reverse-water gas shift (r-WGS) reaction (Equation 17) play an important role in CO₂ hydrogenation. In traditional FT reactions, iron catalysts are used to perform WGS to increase hydrogen content in the CO₂-rich syngas. For CO₂-rich syngas, sufficient H₂ is needed to perform the r-WGS reaction to convert CO₂ into CO and then continue with the FT reactions [80,81–83]. The mechanism of FT reaction using CO₂-rich syngas is proposed as [81]:



The reaction stoichiometry of CO₂ hydrogenation suggests the ratio of hydrogen to CO and CO₂ to be between 2 and 3 in the bio-syngas. However, the ratio of hydrogen to CO and CO₂ in bio-syngas from the biomass gasification is lower than 2, thus more investigations into increasing the hydrogen content in bio-syngas or finding additional cheap hydrogen source are needed in the future.

Thomas Riedel [84] made a comparative study of CO₂ by using iron and cobalt based catalysts in the environments of both H₂/CO and H₂/CO₂. They found that iron and cobalt catalysts behaved differently in CO₂ hydrogenation. By using cobalt catalysts, CO₂ acts only as a diluent. With more CO₂ in the feed gas, more methane was formed. However with iron catalysts, the composition of the hydrocarbon products of H₂/CO₂ feed gas is the same as obtained from H₂/CO feed gas, with no excessive methane formed. So it is possible to use an iron catalyst to perform Fischer–Tropsch CO₂ hydrogenation rather than cobalt catalyst. Zhang [85] found similar results regarding cobalt catalyst in CO₂ hydrogenation. With cobalt catalysts, the products of CO₂ hydrogenation are 70% or more methane. Dorner *et al.* [86] added Pt to Cobalt catalyst to investigate conversion of CO₂ into valuable hydrocarbons. Different feed gas ratios of H₂ and CO₂ (3:1, 2:1, and 1:1) were used in the research. With the shift of gas ratios of H₂ and CO₂ from 3:1 to 1:1, it was found that the product distribution moved from methane to higher hydrocarbons.

4. Enhancing Catalyst Activity

Promoters are used to enhance activity and modify the selectivity to target products [87–93]. In Fischer–Tropsch synthesis, there is no need to use any promoter for Ru-based catalysts due to its high catalytic activity. However, Fe- and Co-based catalysts generally require alkali metals, transition metals and noble metals to promote their activities to achieve desired performance [94].

For Fe-based catalysts, alkali metals are used to change the electronic properties of Fe-based catalysts, and to enhance the CO chemisorption during the reaction, and then to promote the activity of the Fe-based catalysts. The effect of potassium promoter on the performance of the iron-manganese catalyst was investigated by Yang *et al.* [95]. The relatively large crystallite sizes of α-Fe₂O₃, inhibition of the reduction of catalyst and enhancement carbonization of the catalyst were observed due to the addition of potassium in the experiment. A maximum FTS activity was achieved in 0.7% K content. With increasing potassium level, selectivity to olefins was promoted and the formation of methane and light hydrocarbons was restrained. The addition of potassium was found to enhance the activity of the catalyst and also the water gas shift reaction. However, a high content of potassium may lead to deactivation of the catalyst [96,97].

The addition of copper into Fe-based catalyst was found to help with the reduction of catalyst precursor and then to increase its activity. Catalytic behavior of Cu-promoted Fe–Mn–K/SiO₂ catalysts was studied by Zhang *et al.* [98]; copper improved the catalyst activation rate and shortened the induction period, but the addition of Cu showed no apparent influence on the steady-state activity of the catalyst.

The effects of various transition metals (Cr, Mn, Mo, Ta, V, W, and Zr) on the catalytic performance of Fe-based catalysts were investigated by Lohitharn *et al.* [99]. They found that those transition metals (except W) increased CO hydrogenation activity in Fe-based catalysts. Cr-, Mn- and

Zr-promoted catalysts showed higher catalytic activities than the other transition metals did. However, the presence of transition metal did not affect the hydrocarbons distribution in the products.

Some transitional metals, noble metals and rare earth metals are used as promoters in the Co-based catalyst. The addition of Pt, Ru and Pd to the Co-based catalysts enhanced the reduction of the cobalt oxides, and increased the overall activity of the promoted catalysts [100]. Rhenium is also widely used to promote the cobalt catalyst [101,102]. ZrO₂ proved to be a very good promoter for cobalt catalyst, it can improve the CO conversion rate and C5+ selectivity [103–105].

5. Selectivity Maximization

Conventional FT synthesis usually generates products which follow the ASF distribution and is typically unselective to generate from light to heavy hydrocarbons. Thus, controlling and maximizing selectivity is one of biggest challenges in FT synthesis research. A lot of research progress has been made in the past [106–113]. Here we will primarily discuss selectivity control and maximization through bi-functional FT catalysts.

The bi-functional catalysts were first successfully proposed by Chang *et al.* [114] in 1978. Traditional Fischer–Tropsch synthesis needs post-cracking or refinery to achieve the desired products. However, by using bi-functional catalysts, the transformation of syngas into liquid hydrocarbons directly with the certain desired carbon number range was made possible. Bi-functional catalysts contain metallic (syngas to alcohol) and acidic (alcohol to hydrocarbon) components, they can be used in a single reactor to synthesize methanol with metallic component and transform methanol into hydrocarbons with zeolite simultaneously [115].

The bi-functional catalyst Cr₂O₃-ZnO/ZSM-5 was extensively investigated [114,116–118] in the past decades due to its satisfactory performance in high octane gasoline synthesis. Liu *et al.* [119,120] recently developed a Mo/HZSM-5 bi-functional catalyst and found it active in Fischer–Tropsch synthesis to produce high octane gasoline range hydrocarbons. The catalysts were evaluated under various reaction conditions with H₂/CO = 1 syngas which is the typical composition of the bio-syngas from biomass gasification. Liquid hydrocarbons from Mo/HZSM-5 catalyst were composed mainly of alkyl-substituted aromatics and lower branched and cyclized alkanes. Small amount of alcohols were detected in the water phase. They proposed the mechanism of formation of hydrocarbons on Mo/zeolite is through molybdenum metal catalysis via mixed alcohols as the intermediates.

Other than alcohol intermediate route bi-functional catalysts, many studies have added zeolites to the conventional Fischer–Tropsch system. In the traditional Fischer–Tropsch process, the product distribution follows ASF function, so the syngas to gasoline range hydrocarbon (C5–C12) selectivity can only achieve around 48% [121]. Besides, traditional Fischer–Tropsch synthesis products contain primarily linear paraffins and olefins [122], which lead to a low octane number of the gasoline. Zeolites have a shape-selective property, which can restrain the formation of products that are larger than the size of the channels of zeolite and result in lighter hydrocarbons. Moreover, the acid site of zeolites can help with cracking, isomerization and aromatization reactions for the Fischer–Tropsch products. The cracking of longer chain hydrocarbons and light olefins oligomerization will increase the yield of certain carbon range hydrocarbons, such as gasoline range hydrocarbons (C5–C12), the branched and oligomerized hydrocarbons from zeolite catalysts containing catalysts possessing high

octane number. This property can help with overcoming the limitation of ASF distribution and adjustment of the Fischer–Tropsch product distributions.

Various combinations of Fischer–Tropsch catalysts and zeolites have been investigated. Guczi *et al.* [123] found that Ru/NaY was very active in Fischer–Tropsch conversion with 86% of CO conversion rate, while Co/NaY showed a very low CO conversion rate in the test. Wang *et al.* [124] concluded that Fe/NaX and Fe/NaY provided higher conversion rates and higher C5+ selectivity than other combinations of Fe and zeolites. The other zeolites mixed with FT catalyst system which have been investigated were faujasites, MCM-22 [125], ITQ-2, ITQ-6, ZSM-5, ZSM-11, ZSM-12, ZSM-34 [126], etc.

6. Catalyst Deactivation

The activity and catalyst life time have been primary concerns in the large-scale catalytic process, since they can greatly affect the productivity and the economic aspect of the whole process. Thus, it is essential to study how to avoid catalyst deactivation during the bio-syngas liquefaction process. Catalyst decay can be found in many pathways: mechanically, thermally and chemically. Here we will primarily discuss three categories of catalyst deactivation.

6.1. Carbon Deposition Related Deactivation

Fouling is the mechanical deposition of impurities from the feed gas, which will block the active sites or catalyst channels and then decrease the catalytic activities. The organic impurities, such as tar, when condensed could be a source of catalyst fouling. Therefore, it is beneficial to remove the tar from raw bio-syngas cleaning in the upstream process [127].

The origin of coke and carbon deposition is different from fouling, which is the product of CO disproportionation and decomposition or condensation of hydrocarbons on the catalyst surfaces during the catalytic reactions. Typically, coke and carbon deposition will form polymerized long chain hydrocarbons or primarily carbons, like graphite, according to specific reaction conditions [128,129].

By studying coke and carbon formation mechanisms during the reaction, researchers have made much progress in developing carbon deactivation resistant catalysts. Rostrup-Nielsen *et al.* investigated carbon nucleation rate and tried to slow the coking during the reaction [130]. They used theoretical density functional theory (DFT) to show that nickel particle size affected the carbon nucleation rate. Bengaard [131] and Besenbacher [132] also controlled the coking rate by promoting the nickel catalyst with potassium and gold. Other metal catalysts, such as Ru and Rh, have also been investigated in controlling catalyst deactivation caused by coking [133].

6.2. Sintering (Aging)

Sintering, or aging, is the loss of catalytic activity, which is the result of reducing the catalytic surface area caused by crystallite growth and loss of support area caused by support collapse or pore collapse. Sintering mostly occurs at high reaction temperature and its rate will be increased with the presence of water vapor during the reaction. Various factors can affect the sintering rate of catalysts, which has been summarized by Bartholomew [134] and is shown in Table 6.

Table 6. Effect factors in catalyst sintering [134].

Variable	Effect
Temperature	Sintering rates are exponentially dependent on T ; E_{act} varies from 30 to 150 KJ/mol; E_{act} decreases with increasing metal loading; it increases in the following order with atmosphere: NO, O ₂ , H ₂ , N ₂
Atmosphere	Sintering rates are much higher for noble metals in O ₂ than in H ₂ and higher for noble and base metals in H ₂ relative to N ₂ ; sintering rate decreases for supported Pt in atmospheres in the following order: NO, O ₂ , H ₂ , N ₂
Metal	Observed order of decreasing thermal stability in H ₂ is Ru > Ir ≈ Rh > Pt; thermal stability in O ₂ is a function of (1) volatility of metal oxide and (2) strength of metal oxide-support interaction
Support	Metal-support interactions are weak (bond strengths of 5–15 KJ/mol); with a few exceptions, thermal stability for a given metal decreases with support in the following order Al ₂ O ₃ > SiO ₂ > carbon
Promoters	Some additives decrease atom mobility, e.g., C, O, CaO, BaO, CeO ₂ , GeO ₂ ; others increase atom mobility, e.g., Pb, Bi, Cl, F, or S; oxides of Ba, Ca, or Sr are “trapping agents” that decrease sintering rate
Pore size	Sintering rates are lower for porous <i>vs.</i> non-porous supports; they decrease as crystallite diameters approach those of the pores

6.3. Poisoning

Poisoning is the strong chemisorption of impurities on sites which should be catalytically active, and will then retard the catalyst activity [135,136]. Sulfur will selectively adsorb on many metal catalysts to form sulfides which is either reversible or irreversible. There are several approaches to reduce the potential negative effects of H₂S in bio-syngas, either to remove the H₂S in the raw bio-syngas cleaning process mentioned above or to develop the sulfur tolerant catalysts [137]. Srinakruang *et al.* investigated the property of sulfur tolerance of Ni/dolomite catalysts and they found them to be more sulfur resistant than Ni/Al₂O₃ and Ni/SiO₂ catalysts in the presence of 100 ppm H₂S [138].

Other contaminants from the bio-syngas may also cause poisoning during the catalytic conversion; these contaminants can be Cl, Mg, Na, K, P, Si, Al, Ti, and Si [139]. Elliott *et al.* have studied the effects of those contaminants on Ru/TiO₂ catalysts and found they negatively affected the catalyst and proposed the result of a combination of competitive adsorption and poisoning.

7. Conclusion and Outlook

One of the promising thermal-chemical routes to convert biomass into liquid transportation fuels via Fischer–Tropsch synthesis has been discussed. Biomass gasification, as the upstream step in the BTL-FT process, needs special attention. Pretreatment of the biomass should be properly performed to create suitable gasification feed with low cost and efficient logic chain. In the gasification process, several parameters, such as feed speed, gasification temperature, gasifying agent, and so on, should be optimized to convert biomass into hydrogen sufficient raw bio-syngas with a satisfactory carbon conversion rate. With the cleaning process, the organic and inorganic impurities, such as tar, sulfur, chloride, and oxygen, will need to be removed to meet requirements in the following catalytic conversion.

Heat and mass transfer are the critical issues in FT reactor design and selection. The catalyst is the heart of Fischer–Tropsch synthesis. Higher activity with desired product selection and longer life time with less catalyst decay should be the priority of the FT catalyst design in future research. More attention should be paid to increase the carbon utilization in the bio-syngas conversion, to reduce the greenhouse emissions and to promote the overall rate of carbon conversion into liquid fuels.

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