A Review on Plasma Gasification of Biomass and Conversion to Jet Fuel

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Abstract

Aviation sector is growing rapidly. Several organisations have determined targets to decrease GHG emissions in aviation by replacing fossil fuels with renewable bio-jet fuels. To meet these targets, the most suitable pathway is waste/biomass to jet fuel conversion. In this review, plasma gasification of waste/biomass is investigated. Then, three alternative conversion methods from syngas to jet biofuel which are state of the art or beyond, are briefly examined. When comparing the overall energy efficiencies of the three conversion methods, the values are determined to be 45% for Fischer-Tropsch (FT), 57% for gas fermentation (GF) and up to 67% for syngas to gasoline plus (STG+). FT and GF methods have a technology readiness level near to pre-commercialization. But, among the three methods, STG+ is evaluated to be the most appropriate and simple process in all scales except the technology readiness level. Further studies are needed to mature the STG+ technology to commercialization.

Keywords: waste, biomass, plasma gasification, bio-jet fuel, advanced biofuel, next generation biofuel technologies

1. Introduction

This study is an overview of processes for obtaining liquid jet fuel from biomass which will promote the mitigation of greenhouse gas (GHG) emissions compared to jet fuel produced from fossil fuels. For the time being, aviation sector is responsible from 2-3% of total GHG emissions [1]. Furthermore, this sector is rapidly growing, and its share on the GHG emissions is expected to increase more than 10% by 2050 [2]. European Commission (EC) targets 50% renewable biofuel replacement of fossil fuels by 2050 for aviation sector [3] as Figure 1 depicts. The expected mitigation in the GHG emissions with this replacement is around 80%. Therefore, development of efficient conversion methods yielding advanced bio-jet fuels that involve next generation technologies from a sustainable non-fossil feedstock is necessary.
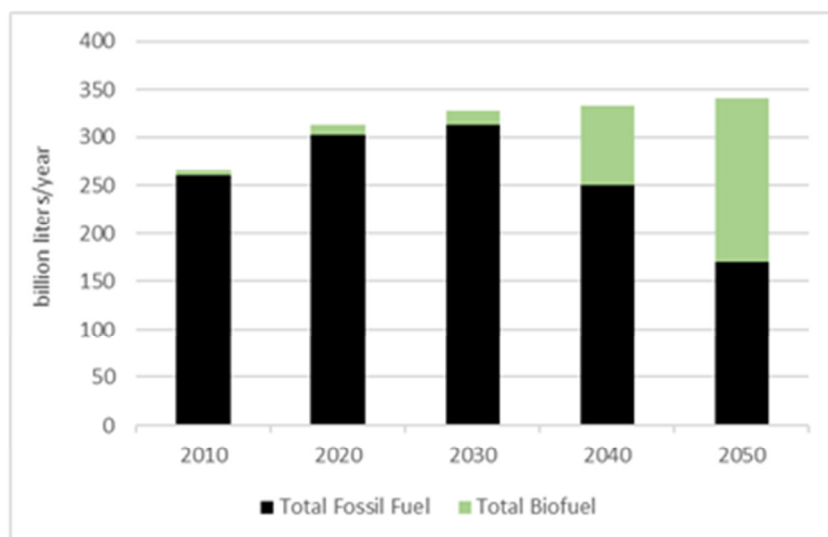

Figure 1. Worldwide yearly jet fuel consumption and expected shares of biofuel vs. fossil fuel productions in aviation sector [4].

Bio-jet fuels were firstly approved for commercial use in 2011 [5]. Various conversion methods are being developed to find an appropriate pathway. Advanced biofuels having the following 3 key properties are the most promising solutions to the demand in aviation sector:

- Produced from renewable sources such as non-food/feed biomass, lignocellulosic feedstocks or wastes
- High reduction in GHG emissions (low CO2 emission) in whole lifecycle
- Decreased ILUC (indirect land use change) impact

Currently, there are four conversion pathways certified by ASTM International to produce advanced bio-jet fuel [5], which are summarised below:

i. Alcohol to Jet Synthetic Paraffinic Kerosene (ATJ-SPK), is the process of obtaining jet fuel from alcohols such as methanol, ethanol or long-chain fatty alcohols. This conversion method is at R&D stage.

ii. Hydrogenated Esters and Fatty Acids (HEFA), is the process of converting vegetable oils into jet fuel. It is at commercial stage and the most used conversion pathway in production. This process is relatively simple, but significant part of the overall cost (around 80%) comes from feedstock.

iii. Renewable Synthesized Iso-Paraffinic (SIP) fuel (renewable farnesane hydrocarbon), is the sugar fermentation process for jet fuel production. It is at R&D stage.

iv. Fischer-Tropsch (FT) Based on Biomass (FT-SPK, with and without aromatics), is a complicated process that can produce jet fuel from biogas and syngas. Due to costless feedstock and high conversion efficiency, this process is the most promising one among other methods. FT conversion is a long-known method for fossil fuels since it can process natural gas and gasified coal, which makes it at commercial stage. However, initial cost of a FT plant for bio-jet fuel production is high.

Since one of the most promising technologies uses syngas as an intermediate, gasification process, including plasma-based gasification will be discussed in Section 2. Afterwards, this article will focus on syngas to bio-jet fuel production methods in Section 3. Lastly, biofuel compatibility with the conventional jet fuel will be examined in Section 4.

2. Gasification

2.1 General Information

Gasification is a high temperature process that converts any hydrocarbon containing material in oxygen poor environment to syngas. The produced syngas mainly consists of CO and H_2. Syngas can be used for heat generation or can be further processed to obtain liquid fuels. Conventional gasification reactions take place at 800 – 1400 ˚C. The gasification reaction for a hydrocarbon can be expressed as below:

$$2C_nH_m + nO_2 \rightarrow 2nCO + mH_2 \qquad (1)$$
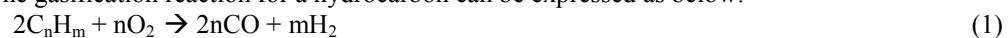
There are several different gasification methods such as [6]:

- Fixed bed gasification (conventional)
- Fluidized bed gasification (conventional)
- Entrained flow reactor (conventional)
- Plasma gasification

2.2 Plasma Gasification

Plasma reduces either the need for heating of the reagents to necessary temperatures or organize nonequilibrium conditions in chemical processes [7]. In plasma gasification, gas temperatures as high as 12400 K can be achieved [8], boosting reaction kinetics. Also, many reactive species are formed by plasma such as atomic oxygen, atomic hydrogen and hydroxyl radicals increasing the gasification reaction efficiency [9]. Thus, plasma gasifiers are superior compared to conventional systems in terms of higher energy balance, improved process control, decreased harmful emissions and simplified system with less components. According to a patented General Electric Co. technology (Patent US9074152B2), electricity production facilities using syngas that consists conventional gasification systems have overall process efficiency around 15%, while overall process efficiency of the same type of facilities with plasma gasification system may reach to more than 25%. Besides, it is possible to achieve overall gasification efficiency with plasma gasifiers on the order of 50% [9].
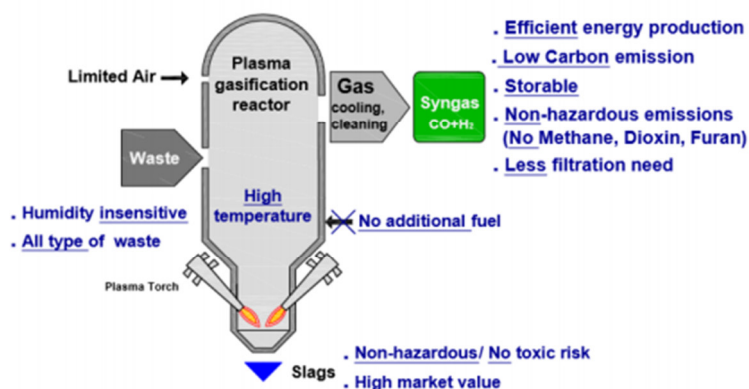
Figure 2. The schematic illustration of a plasma waste to energy concept [10].

Unlike other systems, plasma gasifiers can process almost any kind of feedstock under favour of their superior reaction kinetics. For this reason, they can be used to convert even difficult to process hazardous materials such as sewage sludge, medical waste, tires, petroleum sludge, etc. into syngas along with other common feedstocks for gasification [7].

Thermal plasmas for the plasma gasifiers can be done by alternative current (AC), direct current (DC), radio frequency (RF) or microwave (MW) usage. Although RF and MW generated plasmas do not have electrode erosion, they have relatively low energy efficiency (50 to 60%) as a drawback. Therefore, it is apparent that main plasma torches used in plasma gasification are AC and DC torches. These two commonly used technologies have advantages and disadvantages from different angles.

In terms of less noise, superior stability, better control and lower power consumption, DC plasma torches are more appropriate for gasification process. Yet, they have significant technical and economic limitations since electrodes used in DC plasma torches have short lifetime (between 300 and 500 h) and because of rectifier part of DC torches, cost of power supply boosts approximately 30% [11].

AC plasma torches can be more preferable compared to DC plasma torches since they have higher efficiency in terms of thermal energy conversion (app. 70-90%) [12]. Moreover, since they do not need rectifier part and have longer electrode lifetime which is caused by polarity of electrons synchronized with frequency of electrical system, AC plasma torches employ more durable, more reliable, less complex and cheaper power supply [11].

3. Syngas to Bio-Jet Fuel
This section covers several methods for converting syngas into bio-jet fuel. Fischer-Tropsch synthesis, gas fermentation and syngas to gasoline plus processes will be reviewed.

3.1 Fischer-Tropsch Synthesis
Fischer-Tropsch synthesis is a complicated process and involves a series of chemical reactions that produce mainly alkanes and small amount of cycloalkanes, alkenes, etc. End products are sulphur-free and contain less aromatic hydrocarbons compared to conventional fuels. The overall energy efficiency of the process is about 45% [13]. In general, reaction of FT synthesis can be described as below:

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

This reaction is highly exothermic. Excessive heat must be rapidly removed from the reactor. Process flow diagram for the biomass to FT-SPK is represented as below:
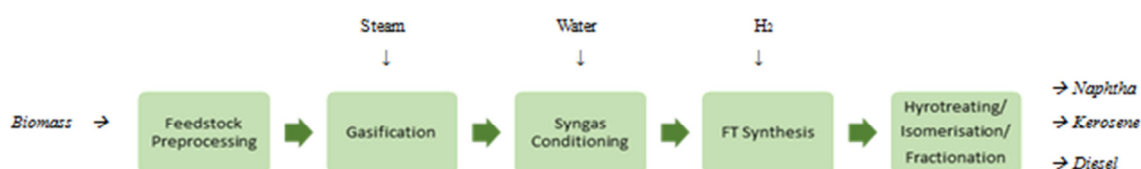

Figure 3. Biomass to FT-SPK flow diagram.

First, biomass feedstock is grinded to obtain smaller particle size for better carbon conversion efficiency. In order to produce syngas, this grinded feedstock is subjected to gasification. The produced syngas is cleaned from soot and cooled via a scrubbing process. Optimal H_2/CO ratio to produce SPK with FT process is about 2.1:1. To acquire this ratio, water-gas shift reaction given below can be used.

$$CO + H_2 \leftrightarrow CO_2 + H_2O \qquad (3)$$
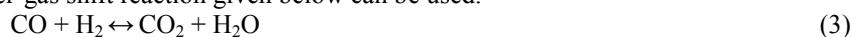
Before proceeding to the FT reactor, the syngas is purified with polishing operations to eliminate hazardous

gases such as SO_x and NO_x. The syngas is then compressed to 25 bars, which is the operation pressure of the FT reaction. FT synthesis yields FT liquid, wax and tail gas. After further hydrotreating, hydrocracking, isomerisation and fractionation processes; naphtha, kerosene and diesel liquids are obtained.

FT process can be operated in two different modes [13]:

High temperature FT process runs at 340 ˚C using iron-based catalysts. This mode is more preferred to obtain shorter chain hydrocarbons such as naphtha.

Low temperature FT process runs at 230 ˚C using ruthenium, iron-based or cobalt-based catalysts. This mode is more preferred to obtain middle and longer chain hydrocarbons such as kerosene and diesel.

Based on processing 2000 metric tons per day of corn stover, the total capital investment for the high-temperature slagging, entrained flow gasification process, including feedstock handling, solids feeding, gasification, amine scrubbing, sour water- gas-shift, pressure swing adsorption, F–T synthesis, hydrocracking, and air separation/power generation, is $500 to $610 million depending on reactor temperature (2007 basis) [14]. As another example, the distillate process at Oryx in Qatar, which is a joint Qatar Petroleum-Sasol GTL plant with a nominal capacity of 34000 barrels (around 4100 metric tons) per day, the capital investment cost is about $1 billion (SASOL 2011) [15].

There are on-going research and development projects to commercialize the FT based biofuel production such as Total's "BioTfueL" project. It is expected to be demonstrated by 2020 in Dunkirk, France [16].

3.2 Syngas Fermentation

Syngas fermentation (SF) is a microbial process done with the help of microorganisms known as acetogens. The overall energy efficiency of this process is around 57% [13]. Process flow diagram is shown in Figure 4..
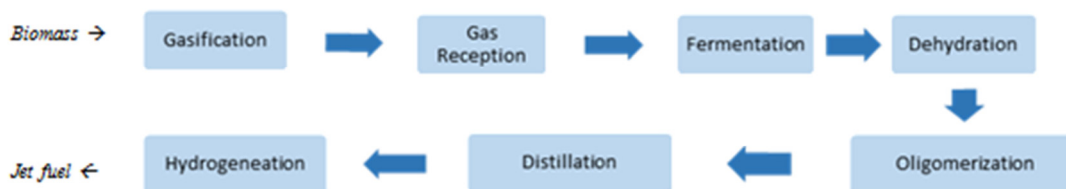

Figure 4. Process flow diagram of gas fermentation process.

The microorganisms convert syngas into ethanol, butanol, acetate, acetic acid, acetone, isopropanol, etc. The produced alcohols are converted to jet fuel with further processing.

The syngas fermentation method is a simpler process; it does not require a specific ratio of H_2/CO. Besides, SF works at lower temperature and pressure. Hence, SF requires lower capital cost compared to FT synthesis. Also, since syngas fermentation involves living organisms; it is superior than FT synthesis in terms of enzymatic costs and final product accuracy.

On the other hand, long process time of syngas fermentation results in lower fuel production rates. Additionally, a costly distillation process is required since the concentration of alcohol in the dilution is very low [13].

Research and development projects by several companies such as LanzaTech from UK, are continuing [15, 17].

3.3 Syngas to Gasoline Plus

Syngas to gasoline plus (STG+) is a thermochemical process which is mainly designed to produce gasoline from syngas. Gasoline synthesis is commercially available with this method. Also, it is technically possible to obtain jet fuel from syngas with this method [18]. STG+ is a simpler method compared to FT synthesis. According to a research conducted by Princeton University, STG+ is more cost effective in terms of both capital and operational costs than FT synthesis [18] at all scales. It is possible to reach an overall energy efficiency up to 67% with STG+ method. Among other methanol to gasoline conversion methods, STG+ is the most energetically efficient method [19].
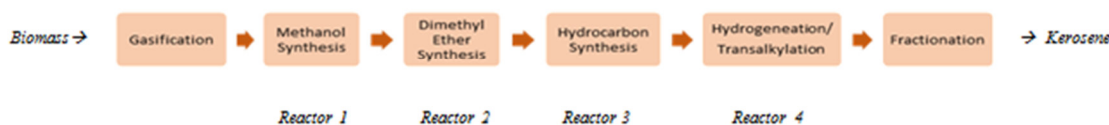

Figure 5. Process flow diagram of syngas to gasoline plus process.

In the first reactor, methanol synthesis is done by the following reaction via catalysts mostly being copper and zinc oxides, supported on alumina at 50-100 bars and 250°C.

$$CO + 2H_2 \rightarrow CH_3OH \tag{4}$$

In the second reactor, the produced methanol is used to generate dimethyl ether via shape-selective solid catalyst such as ZSM-5 zeolite [20, 21].

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O \tag{5}$$

In the third reactor, dimethyl ether is converted to hydrocarbons. These hydrocarbons are further treated to acquire kerosene and small amounts of other components in the fourth reactor. In the last part, the produced kerosene is separated with condensation operation. The uncondensed gas is fed back to the first reactor of STG+ process.

Also, it is possible to acquire dimethyl ether (DME) from syngas in a single reactor which would be more efficient [22]. The reaction catalysts are mostly HZSM-5 zeolite and Cu/ZnO based catalysts. Various organisations such as Karlsruhe Institute of Technology [23], Gazi University [21] and Middle East Technical University [24], are working on research and development projects in this area. Ideal temperature and pressure values are 275°C and over 50 bars, respectively [23, 24]. The catalyst structure for single step DME synthesis from syngas is core and shell as shown in Figure 6.
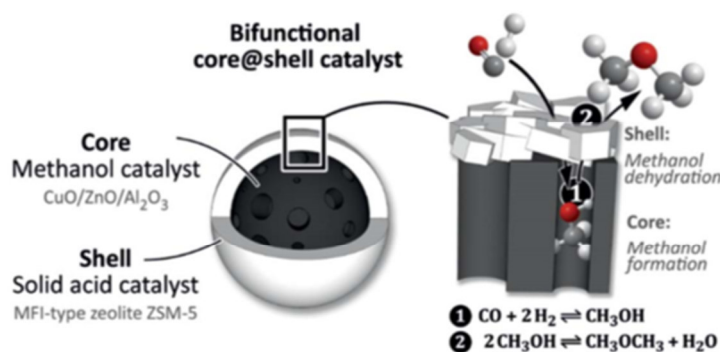

Figure 6. Bifunctional Core and Shell Catalyst [23].

The proposed direct DME synthesis reactions might be one of the below:

$$3CO + 3H_2 \leftrightarrow CH_3OCH_3 + CO_2 \tag{6}$$
$$2CO + 4H_2 \leftrightarrow CH_3OCH_3 + H_2O \tag{7}$$

The type of the DME synthesis reaction will mostly depend on the H_2/CO ratio in the syngas. Several research results show that, increasing CO_2 concentration in syngas would increase the carbon conversion while decreasing DME selectivity. The optimum ratios of $H_2/CO/CO_2$ for maximum DME yield is determined as 5/1/4 [24]. The produced DME is used for hydrocarbon synthesis, which will mostly yield olefins, with lower amount of paraffins and aromatics. The main reaction is given below [22]:

$$nCH_3OCH_3 \rightarrow 2C_nH_{2n} + nH_2O \tag{8}$$
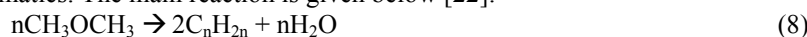
The olefin rich product is then hydrogenated to produce kerosene range paraffins, which can be further processed to acquire jet fuel [18].

$$2C_nH_{2n} + 2H_2 \rightarrow 2C_nH_{2n+2} \tag{9}$$

4. Jet Fuel

4.1 Jet Fuel Specifications

Jet fuel specifications are defined by required performance properties listed below [13]:

- Acceptable minimum energy density,
- Maximum allowable freeze point temperature,
- Maximum allowable deposits in standard heating tests,
- Maximum allowable viscosity,
- Maximum allowable sulphur and aromatics content,
- Maximum allowable amount of wear in standardized test,
- Maximum acidity and mercaptan concentration,
- Minimum aromatics content,
- Minimum fuel electrical conductivity,
- Minimum allowable flash point.

The detailed jet fuel specifications from various organisations are given in Table 1.

Table 1. Jet fuel specifications [25 – 28].

	Jet A-1				JP-8
	ASTM D1655-04a	IATA	Def Stan 91-91	ASTM D7566	MIL-DTL-83,133E
Composition					
Acidity, total (mg KOH/g)	0.1, max	0.015, max	0.012, max	0.1, max	0.015, max
Aromatics (vol %)	25, max	25, max	25, max	25, max (8, min)	25, max
Sulfur, total (wt %)	0.3, max	0.3, max	0.3, max	0.3, max	0.3, max
Volatility					
Distillation temperature:					
10% Recovery (°C)	205, max	205, max	205, max	205, max	205, max
20% Recovery (°C)	-	-	-	-	-
50% Recovery (°C)	-	-	-	(15, min)	-
90% Recovery (°C)	-	-	-	(40, min)	-
Final BP (°C)	300, max	300, max	300, max	300, max	300, max
Flash point (°C)	38, min	38, min	38, min	38, min	38, min
Density @ 15 °C (kg/m3)	775 - 840	775 - 840	775 - 840	775 - 840	775 - 840
Fluidity					
Freezing point (°C), max	-47	-47	-47	-47; -40 for Jet A	-47
Viscosity @ 20 °C (cSt)	8, max	8, max	8, max	8, max	8, max
Combustion					
Net heat of combustion (MJ/kg)	42.8, min	42.8, min	42.8, min	42.8, min	42.8, min
Smoke point (mm)	25, min	25, min	25, min	25, min	25, min
Smoke point (mm) and naphthalenes (vol%)	19 (min), 3 (max)	19 (min), 3 (max)	19 (min), 3 (max)	18 (min), 3 (max)	19 (min), 3 (max)
Thermal stability					
JFTOT Delta P @ 260 °C (mm Hg)	25, max	25, max	25, max	25, max	25, max
Tube deposit Rating (Visual)	< 3	< 3	< 3	< 3	< 3
Conductivity					
Conductivity (pS/m)	50 - 450	50 - 450	50 - 600	-	-
Lubricity					
BOCLE wear scar diameter (mm)	-	0.85, max	0.85, max	0.85, max	-

4.2 Conventional Jet Fuels

Jet fuel range products are kerosene-based, medium chain length (C_9 to C_{15}) saturated hydrocarbons. Combustion reaction of jet fuel can be described as below:

$$2C_nH_{2n+2} + (3n+1)O_2 \rightarrow 2nCO_2 + 2(n+1)H_2O \qquad\qquad (10)$$
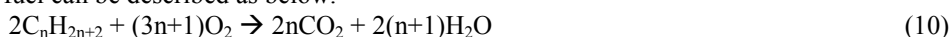
Most common jet fuels are Jet A and Jet A-1, freeze point being the main difference. Jet A is more used in USA while Jet A-1 is used world-wide. Jet A-1 is more suitable for intercontinental flights since its freeze point is lower. A key difference lies in the additives contained within the fuel. For example, Jet A does not usually contain any static dissipater additives, whereas Jet A-1 mostly does [29].

Other jet fuel types are specified below.

TS-1 is the primary Jet fuel grade available in Russia and the CIS states. This kerosene-type fuel is more volatile but has a lower freeze point (-50°C) compared to Jet A-1, which is essential for operations in these colder climates.

Jet B is used in extremely cold areas such as the north of Canada, and has a very low freezing point of -60°C. This fuel contains approximately 30% kerosene and 70% gasoline and is classified as a "wide-cut" fuel. Its composition makes it more flammable than Jet A, and therefore it is more dangerous to handle. However, its lower flash point is an advantage for the cold starting of aircraft.

JP-8 is the military equivalent of Jet A-1. The fuel features some additional ingredients, including anti-icing additives and corrosion inhibitor. JP-8 is the military Jet fuel grade most commonly used by NATO air forces.

JP-5 is a high flash point kerosene-based fuel which is used mainly for military jets based on aircraft carriers.

Additives are chemicals which are added to aviation fuels to improve their overall performance, or to meet the

specific requirements of certain aircraft models or operators. The content of different varieties of Jet fuel varies considerably, particularly between those intended for civil and military use.

The additives used in aviation fuel go through stringent testing before approved to use in order to ensure maximum safety and efficiency. The quantities used are often minuscule, and only measurable in parts per million.

Corrosion inhibitors are added to help reduce corrosion within the aircraft's fuel system and boost the lubricating properties of jet fuel.

Static dissipater additives help to reduce the danger of static charges which build up during the movement of jet fuels.

Fuel system icing inhibitors work by reducing the freezing point of any water present in the fuel system. This helps prevent the formation of ice crystals, which can cause restrictions in the flow of fuel to the engine. These are mandatory for military jets, but are not necessary for civilian aircraft, which have built-in fuel heaters.

5. Conclusion

In this article, processes and conversion methods to produce jet biofuel from waste/biomass are briefly described. Gas to jet pathway is chosen, since waste/biomass is desired as a feedstock being free of charge. Emphasis is given to plasma gasification because of its superior performance in both conversion efficiency and feedstock supply. The plasma gasification overall energy efficiency is determined to be about 50%. It can also process a wide range of feedstock from hazardous medical waste to lignocellulosic biomass with simpler pre-processing. Then, three alternative conversion methods from syngas to jet biofuel which are state of the art or beyond, are briefly examined. When comparing the overall energy efficiencies of the three conversion methods, the values are determined to be 45% for FT, 57% for GF and up to 67% for STG+. Among the three methods, STG+ is evaluated to be the most appropriate and simple process in all scales. In order to increase the competitiveness of bio-jet fuel production technologies versus fossil fuels, a simple and more efficient process must be developed with increased efficiency. Plasma gasification followed by an adaptation of STG+ method to produce jet fuel is found to be the most appropriate one. Further research is needed to reach to the desired technology level before commercialization.

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