Review

A Review of Current and Emerging Production Technologies for Biomass-Derived Sustainable Aviation Fuels

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Abstract: The aviation industry is a significant contributor to global carbon dioxide emissions, with over 920 million tonnes per year, and there is a growing need to reduce its environmental impact. The production of biojet fuel from renewable biomass feedstocks presents a promising solution to address this challenge, with the potential to reduce greenhouse gas emissions and dependence on fossil fuels in the aviation sector. This review provides an in-depth discussion of current and emerging biojet fuel conversion technologies, their feasibility, and their sustainability, focusing on the promising conversion pathways: lipids-to-jet, sugar-to-jet, gas-to-jet, alcohol-to-jet, and whole biomass-to-jet. Each technology is discussed in terms of its associated feedstocks, important chemistries, and processing steps, with focus on recent innovations to improve yields of biojet product at the required specifications. In addition, the emerging power-to-liquid technology is briefly introduced. With the integrated biorefinery approach, consideration is given to biomass pretreatment to obtain specific feedstocks for the specific technology to obtain the final product, with the embedded environmental sustainability requirements. In addition, the review highlights the challenges associated with the biojet production technologies, with embedded suggestions of future research directions to advance the development of this important and fast-growing sustainable fuel industry.

Keywords: biojet fuel; lipid feedstock; lignocellulosic biomass; conversion technologies; sustainable aviation fuel

1. Introduction

The aviation industry has been a major contributor to greenhouse gas emissions, and there is an increased drive to develop and deploy aviation biofuels (biojet) as a sustainable alternative. In particular, there is a growing trend to adopt the use of cheap low-quality biomass feedstocks and wastes, which could reduce the overall cost of production and environmental impact. Sustainable Aviation Fuels (SAFs) are a promising solution to reduce greenhouse gas emissions in the aviation industry. To ensure their successful integration, SAFs must meet specific fuel property specifications. These properties include energy content for efficient aircraft performance, density for optimal fuel load and payload capacity, viscosity to ensure smooth engine operation, flash point for safe handling, freeze point for cold climate operations, low sulphur content to minimise emissions, and specific distillation characteristics for compatibility with aircraft engines [1,2]. Striking a balance between these properties is essential to produce SAFs that not only adhere to safety and operational standards but also contribute to a greener and more sustainable future for aviation. The last few years have witnessed significant developments in this field, in terms of SAF production feedstocks, pathways, capacity, and quality.

Biojet fuels have been gaining traction in the aviation industry as a more sustainable alternative to traditional jet fuel for over a decade now. According to a report by the

International Air Transport Association (IATA), in 2022, the production capacity of SAFs including biojet fuels, surpassed 300 million litres (79.2 million gallons) globally [1]. This represents an increase of 300% compared to the previous year, despite the challenges posed by the COVID-19 pandemic. Several countries, including the United States, Canada, Brazil, and France, have established targets for the use of biojet fuels in aviation in the coming years. For example, in the United States, the Federal Aviation Administration (FAA) has set a goal of achieving three billion gallons of SAF production by 2030 [2]. Additionally, the European Union has proposed a plan to increase the use of SAFs in aviation to 6% by 2030 [3].

Furthermore, several airlines have also started using biojet fuels on selected flights. For instance, in 2018, United Airlines began using a blend of biojet fuel and traditional jet fuel on flights between Los Angeles and San Francisco and has taken it further with a national flight filled with passengers entirely on SAFs [4]. In 2021, Delta Air Lines announced a partnership with Airbus and Air BP to develop and test sustainable aviation fuel on flights from North America to Europe [4–6]. Indeed, since the take-off of the first aircraft using sustainable fuel in 2008, over 490,000 flights have been powered by biojet to date [1]. This drive is promoted by the potential of sustainable aviation fuels to reduce emissions by 80% over the life cycle of aircrafts when compared with conventional jet fuel [1]. In addition to these, Virgin Atlantic has announced the take-off of the first net zero, 100% SAF transatlantic flight, to happen in November 2023 [7].

However, the main challenge lies in selecting an efficient process for the production of aviation biofuels that uses low-quality feedstocks while meeting the target capacity in billions of litres per year. This is because, despite these advances, biojet fuel production still represents a small fraction of the aviation fuel market. According to the IATA, in 2022, biojet fuels accounted for only 0.1% of total aviation fuel consumption [8]. However, the increasing demand for SAFs, driven by environmental concerns and regulatory pressures, is expected to drive further growth in this market in the coming years [3]. In fact, production capacity and usage are steadily increasing due to the global push towards sustainability and the need to reduce greenhouse gas emissions. These pressures mean that the aviation biofuels industry has significant potential for growth in the near future and several emerging technologies are likely to have a significant impact on biojet fuel production in the coming years. These technologies are based on new feedstocks, such as algae and cellulosic materials, which could increase the availability of sustainable biofuels. Additionally, advances in biotechnology, such as synthetic biology and genetic engineering, could enable the creation of more efficient and cost-effective production of biojet fuels using biochemical, thermochemical, and hybrid processes. Each process has its advantages and disadvantages and selecting the most efficient process for a given feedstock and product specification requires careful considerations.

According to a report published by the International Air Transport Association (IATA), the aviation industry is responsible for around 2% of global carbon emissions. This has prompted airlines to look for alternative fuels that can reduce their carbon footprint. Considering the rising interests in the biojet production, it is important to keep track of the growing trends in the successful research around the transformations of different biomass and biomass-derived feedstocks. In this context, this present review covers some of the latest research papers in this area and provides data on the progress being made in this field [1]. Therefore, this review paper aims to provide an overview of the current state of aviation biofuel production. It explores the various pathways and technologies, with a focus on the existing commercial routes, both certified and uncertified by regulatory organisations and the aviation industry. In addition, the review also highlights the emerging processes that could contribute to expanding the potential range of available feedstocks as well as enhancing the yields and quality of biojet fuel. The challenges of large-scale biojet production are also covered.

2. Biojet Fuel Technologies

Jet A1 is the conventional jet fuel, which has become the benchmark for SAF in terms of molecular compositions and overall fuel properties [9]. Typically, Jet AI consists of C_8–C_{16} hydrocarbons, with approximate compositions of 26.8% n-paraffins, 39.7% iso-paraffins, 20.1% cycloparaffins, and 13.4% aromatics [9,10]. Of these, iso-alkanes (for specific energy, good thermal stability, and low freezing points) and cycloalkanes (for density and seal-swelling capacity requirements) are most desirable to provide the specific energy and energy density for thermal stability, low particular emissions, increased range, higher payload capacity, or fuel savings [10]. While aromatics are relatively less energy dense than the various alkane components of jet fuel, they are currently required to ensure proper swelling of airplanes' nitrile seals, which is essential to minimise fuel leakage [11]. Crucial to fuel properties of standard are the H/C ratio of 2, lower heating value (LHV) of 43.2 MJ/kg, and its oxygen content of zero [9–11]. These molecular functionalities of aviation fuels such as Jet A are of paramount importance as they directly influence the fuels' performance, safety, and environmental impact. The compatibility of the fuels' molecular structure with aircraft engines and infrastructure is crucial to ensure smooth combustion, efficient energy release, and safe aircraft operations. Additionally, adherence to aviation fuel specifications, guided by molecular functionalities, is essential to meet stringent industry standards, ensuring uniformity and reliability across the aviation sector. The energy content, combustion characteristics, volatility, flash point, freezing point, and emissions profile of aviation fuels are all intricately linked to the molecular compositions of the fuel [9,11]. Therefore, an important research area is the production and optimisation of the molecular compositions of SAF to be similar to those of conventional fuels, allowing for enhanced fuel efficiency, reduced emissions, and a lower carbon footprint compared to conventional fossil-based aviation fuels. Hence, a deep understanding and consideration of molecular functionalities in synthetic candidates of SAF play vital role in their eventual approval for use in aircrafts to advance sustainable aviation practices, improve aircraft performance, and reduce environmental impacts [10].

The ASTM D7566 [9], which contains the stringent specifications required for SAF, had its first pathway approved in 2009. This is the standard specification for biojet fuel containing hydrocarbons derived from biomass, wastes, and hydroprocessed plant oils and animal fats. The sustainable aviation fuel used today contains a maximum of 50% blend from biofuel mixed with fossil jet fuel for use in conventional engines [12]. A number of collaborations are ongoing between airline companies that are keen on the deployment of biojet fuels in their fleets and fuel production companies as shown in Table 1 [12–27].

Biojet fuel production technologies have gained significant attention in recent years with the main goal of reducing carbon emissions and increasing the sustainability of aviation operations. Biojet fuels, made from renewable sources such as plant oils, agricultural waste, and algae, are one promising option [28]. A study published in the journal Environmental Science and Technology in 2020 found that the use of biojet fuel produced from forestry residues and waste cooking oil could reduce life cycle greenhouse gas emissions by up to 165% [29]. There have been several successful biojet fuel flights in recent years [1,30]. The advancement of biojet fuel as a sustainable alternative to petroleum jet fuel has been bolstered by incorporating life cycle analysis (LCA) studies. LCA provides a comprehensive assessment of the environmental impact of alternative fuels production, encompassing all stages from feedstock cultivation to fuel distribution. By quantifying greenhouse gas emissions, energy consumption, land, and water use, LCA offers a data-driven comparison of Biojet's lower carbon footprint compared to petroleum jet fuel. These analyses reveal the potential environmental benefits of biojet and SAFs, highlighting their role in mitigating greenhouse gas emissions and reducing overall environmental impact. Moreover, LCA can shed light on the social and economic implications of biojet fuel and SAF production, such as job creation and economic development [22]. Indeed, the definition of SAF stemmed from its three life cycle benefits, including the requirements to: "(i) achieve net reduction in greenhouse gases (GHG) emissions; (ii) respect the areas of high importance for biodiversity,

conservation and benefits for people from ecosystems, in accordance with international and national regulations; and (iii) contribute to local social and economic development, and competition with food and water should be avoided" [31]. Many companies and research institutions are actively working on developing biojet fuel technologies. For example, Boeing and the Air Force Research Laboratory have partnered to develop a plant-based biojet fuel made from Camelina, a type of oilseed. Researchers at the University of Bristol in the UK are working on a process to produce biojet fuel from seawater-tolerant plants [32]. Despite the promising progress in biojet fuel technologies, there are still some challenges that need to be addressed. One of the biggest challenges is the cost of production, which is currently higher than that of traditional jet fuel. However, with continued research and development, it is hoped that the cost of production will decrease over time. There is a growing consensus that biojet fuels are a promising option for reducing carbon emissions in the aviation industry. The progress made in this field has been encouraging, with successful biojet fuel flights and ongoing research and development. However, there is still work to be done to address the challenges facing this technology, such as cost of production.

Several biojet fuel production pathways have been developed and approved by the ASTM, each with its own advantages and disadvantages. The nine ASTM-approved biojet fuel production pathways are presented in Table 1, and they offer different methods for converting biomass and biomass-derived feedstocks into aviation fuel. The Fischer–Tropsch process (FT), also known as Gas-to-Jet, can convert various biomass feedstocks to synthetic gas (syngas) that can be catalytically reformed to hydrocarbons including biojet fuel. The Fischer–Tropsch Synthetic Paraffinic Kerosene with Aromatics (FT-SPK/A) is similar to the FT process but the pathway produces sustainable aviation fuel containing aromatics. Hydroprocessed Esters and Fatty Acids (HEFA) and Catalytic Hydrothermolysis (CH) are similar to traditional petroleum refining and can use various oils and fats (lipids) as feedstocks. Hydroprocessed Hydrocarbons Hydroprocessed Esters and Fatty Acids (HH-SPK or HC-HEFA) is similar to HEFA but uses algae as feedstock. Synthesised Iso-Paraffins (SIP) (formerly known as Direct Sugar to Hydrocarbon (DSHC)) is a pathway that directly converts sugars into hydrocarbon molecules, while Alcohol to Jet (ATJ), HC-HEFA, CH, and Gas-to-Jet have the potential to use non-food biomass feedstocks such as algae and aquatic plants. The choice of pathway will depend on factors such as feedstock type and availability, number of processing steps, conversion efficiencies, and sustainability credentials including economic viability, environmental impact, and life cycle analysis. FT, HEFA, and CH pathways exclusively rely on thermochemical processes, whereas SIP and ATJ employ a combination of biological or enzymatic conversion of feedstocks into platform molecules (alcohols or farnesene) before undergoing subsequent thermochemical conversion steps. Another sustainable aviation fuel production pathway that has also been broadly recognised but is yet to be ASTM approved is Power-to-Liquids (PtL). This pathway is part of the power-to-X (PtX) group of technologies that use green hydrogen from the electrolysis of water to produce SAFs from carbon dioxide [33]. However, the pathway only becomes truly bio-based if it involves biogenic CO_2. In general, this pathway is forecast to contribute 1.4 billion litres of sustainable aviation fuel by 2040 [33]. Table 2 shows the main commercially relevant biojet fuel technologies, their owners/operators, their capacities, and current statuses.

Table 1. Biojet fuel technologies and production companies.

Biojet Fuel Technology	Year of Approval	Feedstock Type	Production Company	Airline Company	Blends (%)	Ref.
Gasification and Fischer–Tropsch (FT) D 7566 Annex 1	2009	Woody and lignocellulosic biomass	Syntroleum (Tulsa, OK, USA), SynFuels International (Dallas, TX, USA), Rentech (Los Angeles, CA, USA), Shell (London, UK), Solena (Gilroy, CA, USA), Coskata (Warrenville, IL, USA), INEOS (London, UK), Bio/Lanza Tech (Skokie, IL, USA), Swedish Biofuels (Lidingö, Sweden), Fulcrum BioEnergy (Pleasanton, CA, USA), Red Rock Biofuels (Fort Collins, CO, USA), Velocys (Harwell, UK)	Qatar Airways, United Airlines, Air bus, British Airways, Virgin Atlantic, Southwest Airlines	50	[12,13,20–23]
Hydroprocessed Esters and Fatty Acids (HEFA) D 7566 Annex 2	2011	Plant oils, food industry waste oils, algal oil, animal fats	HoneyWell UOP (Des Plaines, IL, USA), SG Biofuels (San Diego, CA, USA), AltAir Fuels (Paramount, CA, USA), Agrisoma Biosciences (Gatineau, QC, Canada), Neste Oil (Espoo, Finland), Petrochina (Beijing, China), Sapphire Energy (San Diego, CA, USA), Syntroleum (Tulsa, OK, USA)/Tyson Food (Springdale, AR, USA), PEMEX (Mexico City, Mexico), ASA, Renewable Energy Group (Ames, IA, USA), ENI (Rome, Italy), UPM (Helsinki, Finland) Valero Energy Corp. and Darling Ingredients Inc (Norco, CA, USA), World Energy (Boston, MA, USA)	Boeing, Lufthansa, Virgin Atlantic, Virgin Blue, GE Aviation, Air New Zealand, Rolls-Royce, Continental, CFM, JAL, Airbus, KLM, Pratt & Whitney, Air China, TAM Airlines, Jet Blue Airways, IAE, United Airlines, Air France, Finnair, Air Mexico, Thomson Airways, Porter Airlines, Alaska Airlines, Horizon Air, Etihad Airways, Romanian Air, Bombardier, DHL Express, Amazon (Cargo), SG Preston	50	[12,13,24,25]
Synthesised Iso-Paraffin (SIP) D 7566 Annex 3	2014	Sugars, cellulosic materials	Amyris (Emeryville, CA, USA)/Total (Courbevoie, France), Solazyme (South San Francisco, CA, USA), LS9 (South San Francisco, CA, USA)	Boeing, Embraer, Azul Airlines, GE, Trip Airlines	10	[12,13,27]
* Fischer–Tropsch Synthethic Paraffinic Kerosene with Aromatics (FT-SPK/A) D 7566 Annex 4	2015	Wastes (MSW, etc.), coal, gas, sawdust	Shell (London, UK), Sasol (Johannesburg, South Africa)	Boeing, Embraer, Azul Airlines, GE, Trip Airlines	50	[12,13,20–23]

Table 1. *Cont.*

Biojet Fuel Technology	Year of Approval	Feedstock Type	Production Company	Airline Company	Blends (%)	Ref.
Alcohol-To-Jet (ATJ) D 7566 Annex 5	2016	Sugars, starches, alcohol	Terrabon (Houston, TX, USA)/Advanced BioFuels (Frederick, MD, USA) LanzaJet (Skokie, IL, USA), LanzaJet/LanzaTech (Skokie, IL, USA), Coskata (Warrenville, IL, USA), Gevo (Englewood, CO, USA), Byogy (San Jose, CA, USA), Albemarle (Charlotte, NC, USA)/Cobalt (Mountain View, CA, USA), Solazyme (South San Francisco, CA, USA), HoneyWell UOP (Des Plaines, IL, USA), Nova Pangea (Redcar and Cleveland, UK), Swedish Biofuels (Stockholm, Sweden)	Airbus, Boeing, Virgin Atlantic, Continental Airlines, United Airlines, British Airways, Air New Zealand, Delta Airlines	50	[12–19]
Co-hydroprocessing of esters and fatty acids D1655 Annex 1 Co-hydroprocessing of Fischer–Tropsch hydrocarbons D1655 Annex A1	2018	Fischer–Tropsch hydrocarbons co-processed with petroleum	-	-	5	[12,13]
Catalytic Hydrothermolysis (CH) D 7566 Annex 6	2020	Plant oils, food industry waste oils, algal oil, animal fats	Applied Research Association (Albuquerque, NM, USA), Aemetis (Cupertino, CA, USA)/Chevron Lummus Global (Rio De Janeiro, Brazil)	Rolls-Royce, Pratt & Whitney	50	[12,13,26]
Hydroprocessed Hydrocarbons Hydroprocessed Esters and Fatty Acids (HH-SPK or HC-HEFA) D 7566 Annex 7	2020	Algae (*Botryococcus braunii*)	Applied Research Association (Albuquerque, NM, USA)	-	10	[12,13]

* FT-SPK/A is an annex of FT-SPK, which includes the use of MSW and was approved in 2015.

Table 2. Technology readiness level of some biojet fuel technologies [25,33–42].

Biojet Technology	Company	Feedstocks	Capacity L/year	Status
HEFA/HRJ	Neste (Espoo, Finland)	Veg. oil, WCO, animal fat	2 B	Operational
	ENI (Rome, Italy)	Veg. oil	155 M	Operational
	Valero Energy Corp. and Darling Ingredients Inc. (Norco, CA, USA)	Veg. oil, WCO, animal fat	2.13 B	Operational
	World Energy (Boston, MA, USA), AltAir Fuels (Paramount, CA, USA)	Non-edible oil, waste oil	150 B	Operational
	Total (Courbevoie, France)	WCO, Veg. oil	453 M	Operational
	UPM (Helsinki, Finland)	Crude tall oil	120 M	Operational
	Renewable Energy Group (Ames, IA, USA)	High and low free fatty acid feedstocks	284 M	Operational
FT	Fulcrum Bioenergy (Pleasanton, CA, USA)	MSW	1.8 B	Planned
	Red Rock Biofuels (Fort Collins, CO, USA)	Wood	909.2 M	Planned
ATJ	Swedish Biofuel Technology (Stockholm, Sweden)	Ethanol	10 M	Operational
	Biochemtex (Ortona, Italy)	Lignocellulosic biomass	<10 M	Operational
	LanzaJet (Skokie, IL, USA)	Ethanol	180 B	Operational

WCO = waste cooking oil.

2.1. Biojet Fuel Technology Based on Lipid Feedstocks

Lipids are typically used for biodiesel fuel production. However, conventional biodiesel, which is typically composed of fatty acid methyl esters (FAME) does not meet the key requirements for aviation fuels, in terms of specific energy and energy density to ensure appropriate engine performance [9], mainly due to the presence of oxygen atoms in its molecular structure. To be used in aviation fuel, lipids need to undergo additional processing steps, such as hydrotreatment or hydroprocessing, to remove the oxygen atoms. Such processing steps convert lipids into a suitable hydrocarbon-based blendstock for aviation use [9].

Both Hydroprocessed Esters and Fatty Acids (HEFA) and Catalytic Hydrothermolysis (CH) pathways utilise lipid-based feedstocks, specifically triglycerides, for biojet fuel production. However, there are significant differences in the processes employed by each pathway. HEFA converts triglycerides into hydrocarbons through a propane cleavage process. This involves breaking the carbon–carbon bonds in the triglycerides with hydrogen gas, which leads to the production of propane, water, and longer-chain hydrocarbons within the jet fuel range. On the other hand, CH produces free fatty acids (FFA) and glycerol through thermal hydrolysis of the triglycerides, followed by the hydrogenation of the FFA to produce jet fuel-range hydrocarbons. While both pathways can use lipid-based feedstocks, their specific processes for converting these feedstocks into biojet fuel offer unique advantages and disadvantages in terms of conversion efficiency and environmental impact.

The HEFA and CH pathways for biojet fuel production employ different reaction conditions, which influence the processing conditions and types of catalyst functionalities that are used in case. In HEFA, the catalysts used are primarily focused on 'dry' conventional hydrotreating processes, promoting hydrogenation reactions to remove oxygen and other heteroatoms from triglycerides derived from vegetable oils or animal fats [12,13]. In contrast, the CH pathway utilises catalysts tailored for wet lipid feedstocks and sources, particular algae, without the need for dewatering or drying, thus providing energy savings. CH operates in a high-temperature and high-pressure environment, using suitable catalysts, after the hydrolysis stage [26]. These catalysts facilitate deoxygenation reactions of fatty acids obtained from the hydrolysis stage, converting them into hydrocarbons. The catalyst functionalities in CH are designed to remove oxygen, carbon dioxide, and other functional groups from the biomass-derived compounds, resulting in hydrocarbons suitable for aviation use in the desired carbon range. The distinct catalyst functionalities in HEFA and CH are critical in determining the specific reaction conditions and transformations that occur during each process, leading to the formation of biojet fuel from different starting materials.

The processing conditions in HEFA and CH pathways are tailored to the nature of their respective feedstocks and the specific reactions required to produce biojet fuel. While both pathways focus on deoxygenation, the reaction conditions are different, leading to different compositions of the final hydrocarbon product. For instance, the processing conditions during CH enable the initial hydrolysis of lipids, giving rise to the formation of a variety of intermediate liquid organic compounds with minimal gas formation. The intermediate liquid products can undergo different reactions, such as dehydration, decarboxylation, isomerisation, cyclisation, and dehydrogenation, to produce a variety of hydrocarbons including aromatics. In contrast, the reactions involved in HEFA include mainly hydrogenation and hydrogenolysis (hydrocracking), which mostly give liquid n-alkanes and iso-alkanes and propane gas. CH employs nickel, copper, and zinc-based catalysts for the decarboxylation step but both pathways use similar hydrotreating catalysts typically consisting of metals such as nickel, cobalt, or molybdenum supported on materials such as alumina or zeolites [12,13,26]. However, the development of CH has helped to significantly expand the range of feedstocks that could be processed for biojet fuel. With CH, feedstock availability has expanded to algae and other wet feedstock with much lower lipid contents than vegetable oils, animal fats, and waste cooking oil, on which HEFA is based. Essentially, both lipid-based pathways will continue to contribute to the advancement of sustainable

alternatives to traditional jet fuel, reducing the carbon footprint of aviation and mitigating environmental impacts.

2.1.1. Hydroprocessed Esters and Fatty Acids (HEFAs)

Hydroprocessed Esters and Fatty Acids (HEFAs) are a complex series of catalytic reactions designed to convert lipids (vegetable oils and animal fats) into hydroprocessed renewable jet fuel. It involves several key steps, including deoxygenation, hydrogenation, hydro-isomerisation, and hydrocracking (Figure 1). Deoxygenation is a crucial step in the HRJ process. It takes place in the presence of hydrogen and appropriate catalysts. The primary objective of deoxygenation is to remove oxygen from the lipids and transform the feedstock into a hydrocarbon-rich product suitable for jet fuel production [43].

Biodiesel (fatty acid methyl esters (FAMEs)) is the conventional commercial fuel produced from triglycerides via transesterification. Compared to biodiesel, which still contains molecules with oxygen atoms, HEFA makes liquid hydrocarbons within the range of aviation fuels [44]:

- Higher Heating Value: HEFA fuel exhibits a higher heating value than biodiesel. This means it contains more energy per unit volume, resulting in increased fuel efficiency and improved overall performance in aviation engines. The higher energy content allows aircraft to achieve better fuel economy and potentially extend their flight range.
- Superior Energy Density: HEFA fuel boasts a higher energy density, which means it can store a greater amount of energy per unit mass. This characteristic is highly desirable for aviation fuel, as it allows for longer flights without the need for frequent refuelling. The higher energy density of HRJ fuel contributes to increased aircraft endurance and reduces the need for additional fuel stops.
- Improved Cold Point Qualities: HEFA fuel possesses superior cold point qualities when compared to biodiesel. It exhibits enhanced low-temperature flow properties, ensuring that the fuel remains in a liquid state and flows smoothly even in cold climates or high altitudes. This characteristic is of particular importance during aircraft take-off and landing in colder regions, as it helps maintain optimal fuel flow and prevents fuel line blockages caused by cold temperatures. The two important parameters in this context are viscosity at low temperatures ($-20\,°C$ and $-40\,°C$) and the freeze point. These properties play a crucial role in determining the fuel's ability to perform under cold conditions, especially during aircraft take-off and landing in colder regions [9,43].

These advantages collectively position HEFA fuel as a highly promising alternative to biodiesel for aviation applications, contributing to enhanced aircraft performance, extended flight range, and improved operability in cold weather conditions. It is worth noting that the specific details and performance characteristics of HEFA fuel may vary depending on the lipid feedstock used, the specific catalytic processes employed, and the refining techniques applied [43]. Researchers and industry experts continue to explore and optimise the HEFA process to further improve its efficiency, environmental sustainability, and economic viability as a renewable jet fuel option [43–45].
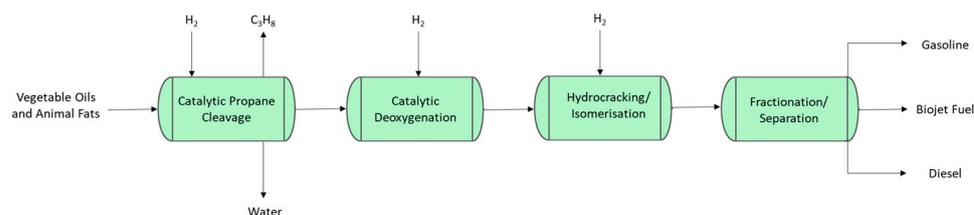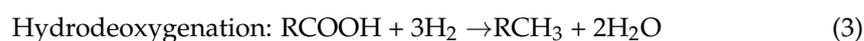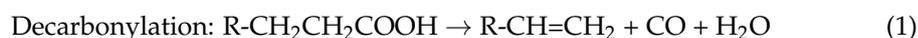

Figure 1. HEFA flow chart [45].

The conversion of fatty acids through deoxygenation offers a promising pathway for developing renewable alternatives to traditional fossil fuel-based resources. By utilizing these hydrocarbons as feedstocks for various applications, a transition towards more

sustainable and eco-friendly practices becomes attainable. Additionally, HEFA fuel has a lower carbon footprint compared to traditional jet fuel derived from fossil fuels [43]. This makes it an attractive option for airlines and other industries looking to reduce their carbon emissions and meet sustainability targets. Overall, the HEFA process represents a significant advancement in renewable energy technology and has the potential to continue to play a key role in the sustainability of the aviation industry.

Common feedstocks used in the HEFA process include Soybean oil, sunflower oil, and palm oil [46], which are hydrogenated and cleaved to produce liquid hydrocarbons. Hydrogenation is achieved by introducing hydrogen into the feedstock under specific conditions, such as high temperature and pressure. This process first converts the feedstock's unsaturated carbon–carbon double bonds (C=C) into saturated carbon chains [47]. After the hydrogenation process, the next step is hydrogenolysis. Hydrogenolysis involves breaking the carbon–oxygen bonds in the triglyceride molecule present in the feedstock. This results in the release of molecules of long-chain fatty acids, alcohols, and alkanes as well as propane gas (from the glycerol fraction), which is sold as an alternative to liquefied petroleum gases (LPG) [47]. A further step is taken to completely deoxygenate the HEFA by removing any remaining oxygen from the liquid product mixture. This step is crucial to ensuring that the final product of HEFA fuel is free from impurities and has the desired properties for jet fuel [47].

The limiting step in this HEFA process involves catalytic deoxygenation of fatty acids into hydrocarbons, which includes combinations of several specific reactions, namely, decarbonylation (Equation (1)), decarboxylation (Equation (2)), and hydrodeoxygenation (HDO) (Equation (3)) [48,49]. Under the process of decarboxylation, a carboxyl group is eliminated by releasing of carbon dioxide and paraffinic hydrocarbon. Moreover, decarbonylation deals with the elimination of carbonyl group and produces paraffins, carbon monoxide, and water. Finally, hydrodeoxygenation deals with the cleavage of carbon to oxygen bond especially in fatty acids and is achieved by using excessive hydrogen gas pressures resulting in the formation of hydrocarbons and water.

$$\text{Decarbonylation: } R\text{-}CH_2CH_2COOH \rightarrow R\text{-}CH=CH_2 + CO + H_2O \tag{1}$$

$$\text{Decarboxylation: } R\text{-}COOH \rightarrow R\text{-}H + CO_2 \tag{2}$$

$$\text{Hydrodeoxygenation: } RCOOH + 3H_2 \rightarrow RCH_3 + 2H_2O \tag{3}$$

The fatty acids present in structure of triglycerides exhibit a wide range of carbon chain lengths, spanning from approximately C_8 to C_{24}. Among these various lengths, the fatty acids that are frequently found in abundance are C_{12}, C_{16}, and C_{18} [50]. The deoxygenation process of fatty acids leads to the production of paraffinic hydrocarbons, which possess the remarkable ability to serve as substitutes for, or undergo transformation into, paraffinic petrochemical feedstocks and conventional liquid transportation fuels derived from petroleum.

The study conducted by Doll et al. [50] sheds light on the significance of fatty acids in the development of paraffinic hydrocarbons as alternatives to petroleum-based fuels, providing a foundation for further exploration and advancements in this field. Extensive research has been conducted on the liquid-phase deoxygenation of free fatty acids and fatty acid esters in the presence of hydrogen [51]. This process has been studied at a temperature of 330 °C using catalysts such as Pd/SiO_2 and Ni/Al_2O_3 under various gas phase conditions, including the presence of hydrogen or nitrogen [52]. The use of hydrogen as a gas during the deoxygenation process has been found to be more favourable, as it ensures a stable catalytic activity and facilitates the decarboxylation reaction. In one study, researchers employed a Pd/C catalyst to carry out the liquid-phase deoxygenation of oleic acid in a continuous-flow reactor. The experiment was conducted at a temperature of 330 °C for a duration of 3 h, utilizing both nitrogen and hydrogen as the reaction environments

without the addition of any solvents [33]. However, the results showed that the production of hydrocarbons, primarily olefins including aromatics, was less than 10 mol%.

These findings highlight the importance of hydrogen in the liquid-phase deoxygenation process of carboxylic acids and emphasise its role in achieving higher yields of desirable hydrocarbon products. The presence of hydrogen promotes a stable catalytic activity during the decarboxylation reaction, leading to the formation of valuable hydrocarbon compounds [51–53]. Further studies in this area are necessary to optimise the reaction conditions and catalysts, with the aim of improving the overall efficiency and selectivity of the deoxygenation process.

There are also several investigations on the "decarboxylation of the unsaturated oleic acid" described in literature [54–56]. Due to the high proportion of oleic acid in many lipids, it has been used as model compound for the catalytic conversion of triglycerides to hydrocarbons. In the majority of these experiments, the catalyst support is either a comparatively non-acidic substance, including silica or non-acidic alumina, or a catalytically inert substance (such as carbon) [57]. However, substantial research has been done mostly on hydrocracking as well as isomerisation of hydrocarbons using Pt maintained on highly acidic supports (such as Pt-zeolites). Cheah et al. also pointed out that the distribution of hydrocarbons produced was influenced by the strength, surface density, and pore size of such acidic sites [58].

According to Hossain et al. [59], hydrogenated derived renewable diesel (HDRD) is a liquid fuel that is synthesised from vegetable oils and animal fat. The production of HDRD involves a catalytic process known as hydrodeoxygenation (HDO), which utilises a Mo/Al_2O_3 catalyst. In this study, a 1:5 volume ratio of oleic acid to water was employed and the reaction carried out for 4 h at a temperature of 375 °C under a N_2 pressure environment. The resulting product obtained from this process exhibited a promising yield of 71%. Further analysis revealed that the HDRD product primarily consisted of linear paraffinic hydrocarbons, which bear both physical and chemical similarities to the hydrocarbons found in conventional petroleum distillates [59]. This research evaluated the potential of HDRD as a renewable alternative to traditional petroleum-based fuels. The utilisation of a Mo/Al_2O_3 catalyst in the HDO process highlighted the significance of catalyst selection in achieving desirable product yields. The presence of linear paraffinic hydrocarbons in the HDRD product further emphasised its compatibility with existing infrastructure and engines designed for petroleum distillate fuels.

Commercialisation Challenges of HEFA

Hydroprocessed Esters and Fatty Acids (HEFAs) or Hydroprocessed Renewable Jet (HRJ) is the only technology that currently produces biojet fuel at a commercial scale for utilisation in aircrafts [14]. The current global capacity of HEFA biojet production facilities is 5.5 billion litres per year, which includes both biojet and green diesel (Table 2). However, the majority of this capacity is directed towards the production of green diesel, which currently has a larger market than biojet fuel, with potentially up to 15–20% biojet fuel that can be produced. Furthermore, the current global capacity of HEFA biojet fuel production is only 1% of the global jet fuel demand of 360 billion litres, which highlights the need for further investment and development to meet the aviation industry's growing demand for sustainable fuels [25,34]. Overall, while HEFA fuels have shown promising results in terms of its properties and potential as a sustainable alternative to traditional jet fuel, more research and development is needed to scale up its production and increase its commercial viability. Future research can be dedicated to increasing the yield of biojet fraction during HEFA, e.g., by catalytic cracking of the major diesel fraction.

Indeed, the high cost of HEFA production is one of the primary limitations associated with the technology. One of the major costs associated with HEFA production is the use of excess hydrogen to minimise carbon loss and increase biojet yield. In the HEFA process, the excess hydrogen is utilised to saturate the unsaturated fatty acid chains in the feedstock,

eliminating oxygen, and converting them into hydrocarbons and to render them suitable for aviation fuel applications.

Furthermore, the cost of feedstock also represents a significant portion of the production cost, considering that HEFA technologies have relied on clean and mainly food-based lipid feedstocks. According to the International Renewable Energy Agency (IRENA), feedstock accounts for around 70% of the production cost of biofuels, including HEFA. This can be a major challenge for airline companies as fuel represents approximately 30% of their total expenses [60].

In addition to these cost-related challenges, other technical challenges exist with HEFA processes. For example, pre-treatment of feedstock is required to ensure high yields of HEFA. Without feedstock pre-treatment, the presence of impurities such as water, non-triglyceride molecules, and solid particles can negatively impact the hydrotreating process, leading to lower yields and lower quality of the final product. Additionally, the high exothermic heat generated during the hydrogenation reaction requires thorough process control to prevent issues such as coking and fouling of the reactors [61]. In addition, compared to fossil-based jet fuel, which contains up to 25% aromatic hydrocarbons, the lack of or low percentage of aromatic hydrocarbon in HEFA fuels is a major drawback, such that blending with aromatic hydrocarbon-rich fuels is inevitable [62].

Overall, HEFA fuel offers several advantages over biodiesel, including higher heating value, superior energy density, and improved cold point qualities. These characteristics make HEFA fuel more efficient, suitable for longer flights, and better adapted to cold weather conditions applicable at high operational altitudes of aircrafts. HEFA fuel also has a lower carbon footprint compared to traditional jet fuel, making it an attractive option for reducing the environmental impact of the aviation industry. In conclusion, while HEFA shows promise as a sustainable alternative to traditional jet fuel, further research, development, and investment are needed to scale up production, reduce costs, and address technical challenges. Diversifying the supply of sustainable jet fuels and exploring other alternative technologies will also be crucial in meeting the aviation industry's demand for fuel while reducing its environmental impact. Despite these challenges, the potential benefits of HEFA fuel as a sustainable alternative to traditional jet fuel have spurred ongoing research and development efforts aimed at improving the efficiency and commercial viability of the technology. For example, researchers are exploring new feedstocks and refining techniques to reduce the production costs associated with HEFA [63]. Additionally, researchers are investigating alternative processes such as hydrogen-free catalytic cracking, which may offer a more cost-effective and efficient method for producing biojet fuels [64]. In any case, all lipid-based pathways, including Catalytic Hydrothermolysis (discussed below), have challenges of feedstock limitation.

2.1.2. Catalytic Hydrothermolysis (CH)

Catalytic Hydrothermolysis (CH) is an advanced process in the realm of renewable fuel production, with the potential to make a significant impact on addressing the increasing demand for sustainable drop-in and aromatic fuels. Developed by Applied Research Associates (ARA), this cutting-edge technology provides a promising pathway towards achieving a complete substitute for conventional biofuels. The key feature of CH lies in its ability to use algal or plant oils as feedstocks to produce sustainable and renewable fuels. This aligns perfectly with global efforts to move towards a low-carbon economy and combat the detrimental environmental consequences associated with traditional fuel production and consumption [47,65,66].

The process of CH involves subjecting the feedstocks, such as algal or plant oils, to high-temperature and high-pressure conditions in the presence of a catalyst. The catalyst plays a crucial role in the conversion of the feedstocks into renewable fuels, making the process efficient and effective. The CH pathway involves high-temperature and high-pressure treatment of lignocellulosic biomass in the presence of water, and while catalysts can be used, they are not a mandatory component of the process. For aviation fuel, the

focus of CH is on the hydrothermal treatment of lipids to obtain valuable intermediates for further conversion into suitable hydrocarbons.

The efficiency and versatility of this process can be attributed to the unique combination of catalytic reactions and hydrothermal conditions involved. Under high temperature (400–475 °C) and pressure (up to 210 bar), lipids undergo a series of chemical transformations, facilitated by the presence of catalysts and water as reaction medium and reactant [65]. High pressure and temperature are required for water to solubilise the oil in water, enhancing mass transfer and reaction rates with both reactants in the same solution phase [66]. During the process, triglycerides are firstly converted to fatty acid (Equations (4)–(6)), which are subsequently hydrotreated to aliphatic and aromatic hydrocarbons [67]. Hence, the process involves a chain of reactions including thermal hydrolysis, decarboxylation, cracking, cyclisation, and isomerisation [68].

$$\text{Triglyceride} + H_2O \leftrightarrow \text{Diglyceride} + \text{FFA} \tag{4}$$

$$\text{Diglyceride} + H_2O \leftrightarrow \text{Monoglyceride} + \text{FFA} \tag{5}$$

$$\text{Monoglyceride} + H_2O \leftrightarrow \text{Glycerol} + \text{FFA} \tag{6}$$

The products obtained after hydrotreatment range typically from C_6 to C_{28} hydrocarbons comprising of iso-alkanes, n-alkanes, aromatics, and cyclo-alkanes, which can be fractionated by distillation into naphtha, diesel fuel, and jet fuel as shown in Figure 2 [69]. Research has shown that the yields of the different fractions depend on the reaction conditions of pressure, temperature, oil to water ratio, catalyst, and residence time [70].
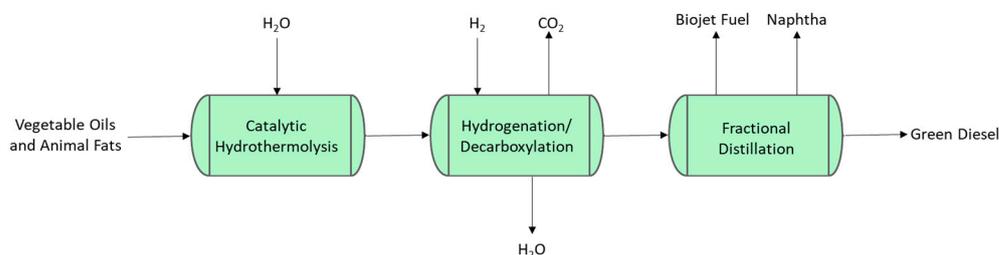
Figure 2. Catalytic Hydrothermolysis (CH) process [69].

The CH process has been extensively investigated in the literature, both with and without the use of a catalyst (Figure 2). Wang et al. [47] explored the CH process and its applicability in the absence or presence of a catalyst. They found that under the specified conditions, CH could proceed effectively, regardless of the presence of a catalyst. However, the presence of catalysts was found to enhance the selectivity of the specific reactions that lead to the production of the liquid hydrocarbon component within the target fuel range. For example, certain catalysts promote the decarboxylation of fatty acids with less random C–C bond cleavage, compared to non-catalysed CH [70]. To highlight the potential of CH as a versatile conversion method, several developments have been reported including its double ASTM approval for commercial production [12,13,26,70].

Li et al. [71] investigated reported one of the earliest details of CH of different vegetable oils, such as Soybean oil, tung oil, and Jatropha oil, using commercially available reduced and stabilised nickel catalyst (BASF Nysofact 120, Ludwigshafen, Germany). The researchers carried out the experiments at temperatures ranging from 450 °C to 475 °C and a pressure of 210 bar. The yields of liquid hydrocarbons were 52.4 wt% for Soybean oil, 42.6 wt% for tung oil, and 41.1 wt% for Jatropha oil. Their findings revealed that both tung oil and Soybean produced around 10–12 wt% JP-8 fuel, with tung oil producing the highest yield of naval distillates of 24.3 wt%. These results emphasised the feasibility of

using various feedstocks in the CH process and the importance of selecting the appropriate catalyst for the process.

Research has also indicated that isomers of long straight-chain alkanes exist as the process starts and sequential reaction cracks them to branched structure [72]. Cracking results in the production of gases and shorter chain hydrocarbons, and the saturation of paraffin. After cracking light hydrocarbon species containing carbon numbers from C_5 to C_8 (within the naphtha range) were produced. Jet fuel consists of a paraffins, naphthenes, and aromatics. Table 3 shows a summary of the many studies done in attempt to convert different lipid feedstock sources into hydrocarbons that have the potential to substitute commercial jet fuel. Most of the research done (Table 3) only made mention of the hydrocarbons produced falling in the jet fuel range of C_9–C_{16}.

Table 3. Some current results from literature on conversion of different feedstock to hydrocarbons.

Feedstock	Process Route	Operating Conditions	Catalysts	Yields	Reference
Algal oil	Decarboxylation	T = 360 °C Solvent = water Residence time = 45 min	Pt/C	53.63% heptadecane	[73]
Castor oil	Hydrodeoxygenation	T = 300 °C– 360 °C P = 3 MPa (H$_2$) WHSV = 2 h^{-1}	NiAg/SAPO-11	87.12% C$_8$–C$_{15}$ hydrocarbons	[74]
FAME	Deoxygenation	T = 300 °C P = 0.8 MPa (H$_2$) LHSV = 4 h^{-1} H$_2$/oil molar ratio = 15	Ni/HZSM-5	26.90% C$_8$–C$_{16}$ alkane yield	[75]
Jatropha oil	Deoxygenation without H$_2$	T = 200 °C P = 4 MPa (N$_2$) LHSV = 1.33 h^{-1}	WO$_x$/Pt/TiO$_2$	75% C$_8$–C$_{16}$ hydrocarbons	[76]
Macauba oil	Decarboxylation	T = 300 °C P = 1 MPa (H$_2$) Residence time = 5 h	Pd/C	33% C$_9$–C$_{16}$ hydrocarbons	[77]
Microalgae biodiesel	Deoxygenation	T = 275 °C Injection rate= 0.02 mL/min	Ni/meso-Y zeolite	48.6% alkanes 2.7% aromatics 0.18% alkenes	[78]
Oleic acid	Deoxygenation without H$_2$	T = 300 °C P = 1 atm. (N$_2$) Residence time = 3 h	CoMo	20.1% C$_9$–C$_{16}$ hydrocarbons	[79]
Palm oil	Hydrodeoxygenation	T = 300 °C P = 1 MPa (H$_2$) Residence time = 5 h	Pd/C	90% C$_9$–C$_{15}$ hydrocarbons	[80]
	Hydrodeoxygenation	T = 330 °C P = 5 MPa (H$_2$) LHSV = 1 h^{-1} H$_2$/oil = 1000 Ncm^3/cm^3	Ni-MoS$_2$/ɣ-Al$_2$O$_3$	60% C$_{10}$–C$_{12}$ hydrocarbons	[81]

Table 3. *Cont.*

Feedstock	Process Route	Operating Conditions	Catalysts	Yields	Reference
Soybean oil	Decarbonylation	T = 390 °C	Ni-Mo/HY	30% aromatics	[82]
		P = 1 MPa (H$_2$) Residence time = 8 h		30% alkanes	
	Hydrodeoxygenation	T = 370–385 °C P = 3 MPa (H$_2$) LHSV = 1 h^{-1}	Pt/Al$_2$O$_3$/SAPO-11	15% aromatics	[83]
		H2/oil = 800 NL/L			
	Decarboxylation	T = 350 °C	NbOPO$_4$	62% C$_9$–C$_{16}$ hydrocarbons	[46]
		P = 1 MPa (H$_2$) Residence time = 5 h			
	Deoxygenation	T = 350 °C	Ni-Al$_2$O$_3$	80% C$_8$–C$_{17}$ hydrocarbons	[84]
		P = 0.7 MPa (N$_2$) Residence time = 4 h			
	Deoxygenation	T = 400 °C	CoMo-Al$_2$O$_3$	13.5% biojet fuel range hydrocarbons	[85]
		P = 9.2 MPa (H$_2$) Residence time = 1 h			
Waste cooking oil	Decarbonylation	T = 400 °C	Ni/Meso-Y	37.5% alkanes	[74]
		P = 3 MPa (H$_2$) Residence time = 8 h		10% aromatics	
	Hydrodeoxygenation	T = 300 °C	Ni-Mo/ɣ-Al$_2$O$_3$	80% alkanes	[86]
		P = 4 MPa (H$_2$) Residence time = 7.5 h		3% alkenes	
				6% aromatics	
Waste cooking oil + waste lubricating oil + vacuum gas oil	Deoxygenation	T = 380 °C	Ni-Mo/Al$_2$O$_3$	65% kerosene range hydrocarbons	[87]
		P = 7 MPa (H$_2$) LHSV = 1.5 h^{-1}			
		H$_2$/oil = 400/400 Nm^3/m^3	Ni-W/SiO$_2$/Al$_2$O$_3$		

However, some authors went further to specify the yield and group of compounds. For instance, Chen et al. [75] obtained 26.9% C_9–C_{16} alkane yield from the deoxygenation of FAME with Ni/HZM-5 at 300 °C and 0.8 MPa H_2 pressure. Both Cheng et al. [78] and Li et al. [74] carried out decarbonylation reactions for 8 h to produce hydrocarbons. The former used Soybean oil with Ni-Mo/HY as catalyst at 390 °C and 1 MPa H_2 and obtained 30% alkanes and 30% aromatics, while the latter used waste cooking oil and Ni/Meso-Y catalyst at 400 °C under 3 MPa H_2 pressure to obtain 37.5% alkanes and 10% aromatics. Wang et al. reported that very high yields of products consisting of 80% alkanes, 3% alkenes, and 6% aromatics were obtained from the hydrodeoxygenation of Soybean oil for 7.5 h at 300 °C under 4 MPa H_2 with Ni-Mo/γ-Al_2O_3 as catalyst [86].

2.2. Biojet Production from Lignocellulosic Biomass

Current biojet production routes rely on lipid feedstocks with a global production capacity projection of 330 million tonnes by 2030 [88]. The typical HEFA biojet fuel yield from lipids is about 15–20%. Using all the global lipid supply for HEFA would give a maximum biojet fuel production capacity of 82 billion litres per year, which will correspond to only 9.4% of current aviation fuel demand. These best-case statistics show the limitation of relying of lipid feedstocks for biojet fuel production if global decarbonisation targets are to be met. In contrast, based on US Department of Energy figures [89], about 340 million tonnes per year of biomass is available in the US and can deliver 79.5 billion litres of biojet fuel, which is not far off from the US annual jet fuel demand of 98.4 billion litres. Using the same statistics, the global biomass availability from agriculture and forestry of about 11.9 billion dry tonnes per year [90] would deliver about 2.78 trillion litres of SAF, which far exceeds the 871 billion litres of projected global jet fuel demand by 2050 [10,89].

Due to the limitations of the availability of lipids as feedstock for biojet production, there has been a growing trend to use more readily and vastly abundant lignocellulosic biomass feedstocks. However, the use of this type of heterogeneous and highly varied feedstock is challenging, with significant impact of low yields of target product (biojet), application of multiple processing steps, and unavoidable generation of waste. The challenge of multiple processing steps is an inherent problem but there are two main strategies for tackling the challenge of low yields and waste generation as shown in Figure 3.
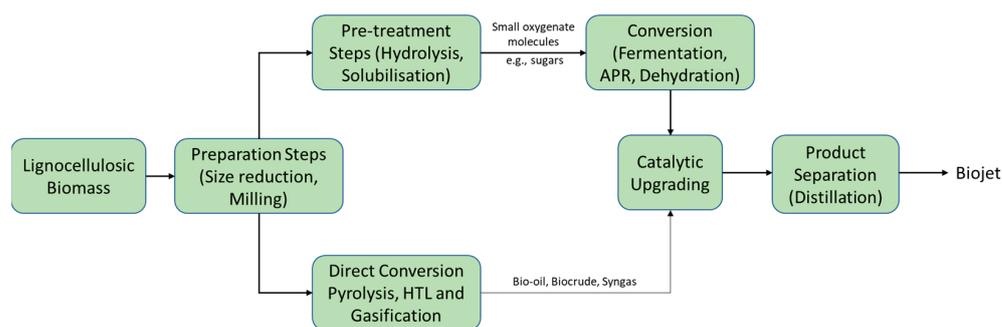

Figure 3. Schematic of lignocellulosic conversion pathways to biojet fuel.

Biojet Production Routes Based on Alcohol Feedstocks (Alcohol to Jet)

Several alcohol feedstocks have garnered attention as suitable candidates for biojet fuel production due to their wide availability, sustainable sources, and compatibility with existing fuel distribution systems. These feedstocks can be derived from various sources, including biomass, agricultural residues, and dedicated energy crops. One prominent biojet production route based on alcohol feedstocks is the Alcohol-to-Jet (ATJ) process, which refers to aviation fuel-range hydrocarbons produced from the various alcohols including methanol, butanol, and ethanol alongside long-chain fatty alcohols [66] through a series of catalytic reactions depicted in Figure 4. The ATJ process includes three main stages: dehydration, oligomerisation, which converts alcohol into linear olefins, and hydrogenation,

to saturate the olefinic bonds [91]. The hydrocarbons produced through ATJ can include various isomers of alkanes, cycloalkanes, and aromatic compounds, which are within the specified carbon range for conventional jet fuel. This makes ATJ hydrocarbons a suitable blendstock for aviation fuel [9].
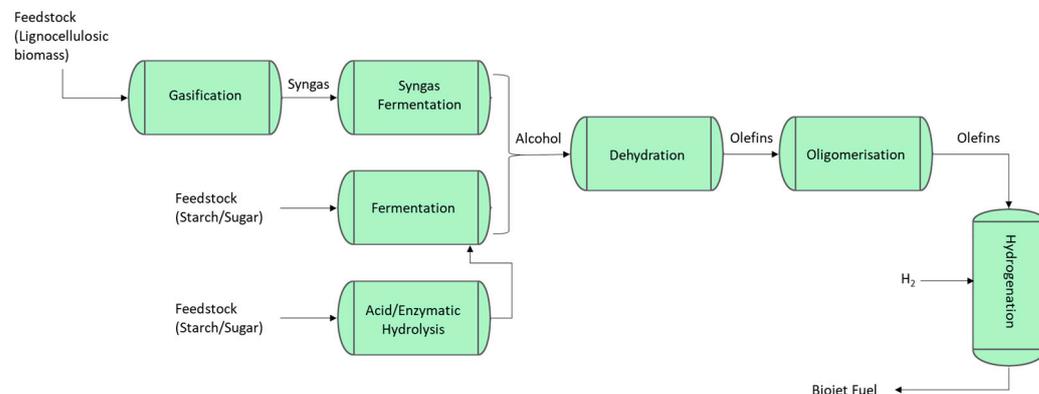
Figure 4. Alcohol-to-Jet flow chart [66].

Furthermore, ongoing research and development efforts aim to enhance the efficiency and sustainability of alcohol-based biojet fuel production. These efforts involve the optimisation of catalytic processes, the exploration of novel alcohol feedstocks, and the integration of advanced technologies such as microbial fermentation [92] and thermochemical conversion [93].

Essentially, the carbon number of alcohols used in the conversion process has been found to influence the distribution of hydrocarbons produced. Lower carbon alcohols (ethanol) tend to result in a more even distribution of hydrocarbons [94], consistent with dehydration, oligomerisation, and hydrogenation to jet fuel-range hydrocarbons as shown in Figure 5a. However, higher carbon alcohols (butanol) necessitate a lesser degree of oligomerisation, cutting down the processing steps to achieve the required carbon range for biojet fuel. Figure 5b shows that this alternative approach eliminates the need for extensive oligomerisation and dehydration chemistries. By bypassing these steps, the overall process complexity and associated costs can be reduced, potentially making the production of alternative jet fuels more economically viable. Geleynse et al. [94] emphasised the importance of selecting appropriate alcohol feedstocks based on carbon number, with lower carbon alcohols favouring a more even hydrocarbon distribution. In addition, Atsonios et al. [95] propose the use of upgraded alcohols with higher carbon content to potentially reduce costs by circumventing certain process steps.
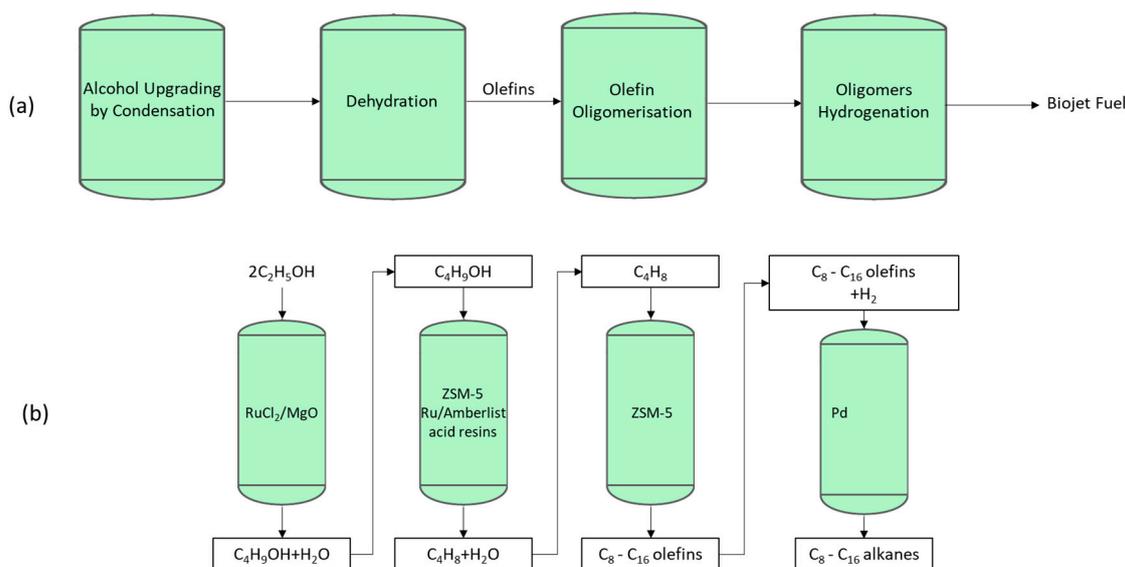
Figure 5. Main approved ATJ pathways (**a**) dehydration of alcohol before oligomerisation of alkenes, and (**b**) oligomerisation of alcohols before dehydration and further oligomerisation [95].

Dehydration catalysts play a crucial role in the conversion of alcohols to hydrocarbons, and extensive research has been conducted to explore various catalysts for this purpose. Among the catalysts investigated, alumina and transition metals, silicoaluminophosphates, H-ZSM-5 zeolite catalyst, and heteropolyacid have been widely studied [96,97]. Tao et al. [96] demonstrated that H-ZSM-5 zeolite catalyst was highly reliable, achieving nearly 100% conversion of ethanol and yielding 99% ethylene at a temperature of 350 °C. To further utilise the dehydrated ethylene, a catalytic oligomerisation process is employed to convert it into α-olefins, during which 95% yield of longer-chain α-olefins (>C10) was achieved using a Ziegler catalyst at temperatures ranging from 90 to 120 °C. In addition, Aldrett and Worstell achieved a higher yield of 97% using a Ziegler–Natta type catalyst at 100 °C and 89 bar pressure [97]. The longer-chain α-olefins were processed to produce diesel range fuels, jet range fuels, and light olefins [96,97]. The production of jet fuel-range alkanes requires the hydrogenation of the light olefins. Gevo Inc. (Englewood, CO, USA) [98] reported that Pd/C or Pt/C catalysts can be used to convert for this purpose at a temperature of 370 °C and a weight-hourly space velocity (WHSV) of 3 h^{-1}.

In the case of n-butanol dehydration, the γ-alumina catalyst has been found to be effective. At a temperature of 380 °C and a pressure of 2.1 bar, γ-alumina can facilitate the conversion of n-butanol to 1-butene. The yield of biobutenes, particularly 1-butene, can reach as high as 98%, with a selectivity of 95%. The remaining product, 2-butene, could be isomerised from 1-butene. Furthermore, the 1-butene can undergo oligomerisation to produce olefins in the C_8 to C_{32} range at a conversion rate of up to 97%. The use of $ZnAl_2O_4$ as a catalyst resulted in a product distribution for mixed olefins in the jet fuel range, including 26.46% C_8, 25.4% C_{12}, and 17.64% C_{16} [99,100], which can produce the corresponding alkanes upon hydrogenation.

Several studies have investigated the technical feasibility and environmental sustainability of biojet fuels produced from alcohol feedstocks. For instance, a study by Kolosz et al. [101] evaluated the life cycle greenhouse gas emissions of ethanol-derived biojet fuel and found that it could achieve a 60–70% reduction in CO_2 emissions compared to conventional jet fuels. Another study by Phillips et al. [102] explored the techno-economic viability of butanol-based biojet fuel production and demonstrated its potential to be cost-competitive with conventional jet fuels. These studies have paved the way for the commercialisation of the ATJ process. For instance, Lanzatech has pioneered the first global Alcohol-to-Jet (ATJ) facility, which operates at a commercial scale and converts waste ethanol into biojet fuel [103]. In addition, Oak Ridge National (ORN) in the United States

has also developed a catalytic upgrading process that enables the conversion of ethanol and other alcohols to hydrocarbons in a single step. This process operates in the absence of hydrogen and at temperatures ranging from 275 °C to 350 °C. Although high yields have been achieved, this pathway is not yet approved by the ASTM-D7566 and will require further qualification [104].

The production of biojet fuel from alcohols has continued to gain significant attention as a promising alternative to traditional aviation fuels. Overall, ATJ fuel production is contributing to the ongoing exploration of sustainable alternatives to traditional aviation fuels. These advancements hold great promise in reducing dependence on fossil fuels and mitigating the environmental impact of aviation industry in general.

Researchers have explored various pathways for converting biomass-derived feed-stocks into hydrocarbons suitable for aviation applications. Additionally, studies have successfully demonstrated the conversion of biomass-derived syngas into valuable hydrocarbons through a multi-step process.

2.3. Biojet Fuel Production Routes Based on Sugar Feedstocks

Biomass-derived sugar feedstocks are also gaining attention for biojet production. The key starting point for obtaining sugar feedstocks from lignocellulosic biomass is the hydrolysis step. In this process, the biomass undergoes various types of pre-treatment and eventual hydrolysis to sugars. Initial work in this area involved the use of homogeneous mineral acids, especially sulfuric acid as catalyst [105–109], with the challenge of post-processing catalyst recovery [110,111]. Recently, successful biomass hydrolysis using heterogeneous catalysts has been reported. Wang et al. [70], synthesised and characterised perfluoroalkylsulfonic (PFS) and alkylsulfonic (AS) acid-functionalised magnetic nanoparticles for hydrolysing hemicelluloses in wheat straw, achieving significantly higher hemicellulose conversion compared to the control experiment at both 80 °C and 160 °C. PFS nanoparticles demonstrated superior hemicellulose solubilisation compared to AS nanoparticles, making them promising candidates for efficient biomass conversion [70].

These sugar feedstocks can be obtained from first generation food-based sugar and starch crops such sugarcane, sugar beet, maize (corn), and wheat [105–108]. In addition, the sugars may be obtained from non-food sustainable lignocellulosic biomass such forestry residues, agricultural wastes and biogenic fractions of municipal solid wastes and industrial waste [109]. The cellulose and hemicellulose fraction of lignocellulosic biomass can be hydrolysed to hexoses (C_6 sugars) and pentoses (C_5 sugars) through well-developed processes [110,111]. The resulting sugars can be used directly for biojet production (synthesised iso-paraffins pathway) or transformed into intermediates such as oxygenates (aqueous phase reforming) and furanics (e.g., furfural and 5-hydroxymethyl furfural) before final conversion to hydrocarbons.

2.3.1. Synthesised Iso-Paraffins (SIP) (Formerly Direct Sugar to Hydrocarbon (DSHC))

SIP is a biological platform, which uses micro-organisms to primarily convert C_6 sugars into farnesene, which is hydrogenated to farnasane for use as SAF (Figure 6). While there are multiple biologically catalysed routes from sugars to farnesene, the ASTM approve pathway was developed by Amyris Inc. [112], using the mevalonate pathway in yeast cells [113–115].
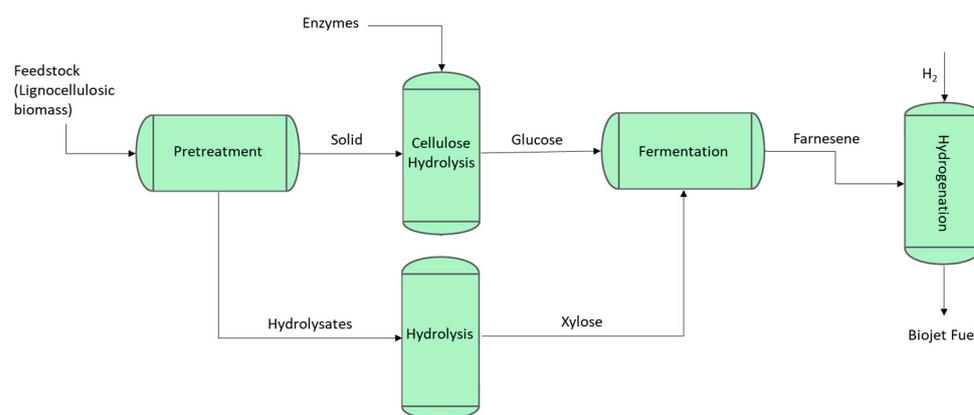
Figure 6. Amyris SIP pathways to biojet fuel.

The aerobic fermentation process could generate a farnesene peak yield of 16.8 g farnesene/100 g sugar at a productivity of 16.9 g/L/d and a carbon efficiency of 60% [116]. One of the innovations of the Amyris process it that the yeast cells are able to convert both C_5 and C_6 sugars [115]. The process flow chart is shown in Figure 6. From the fermenter, the broth is transferred to a centrifuge for solid–liquid separation [117], with the supernatant containing the farnesene. Up to 95% of the farnesene is recovered by de-emulsification and further centrifugation to give a purity of up to 97% [113,118]. The recovered and purified farnesene is then hydrogenated to farnesane, which is used as 10% blendstock for biojet [119] due to its being a single molecule. Potentially, further processing of the farnesane involving hydrocracking and hydroisomerisation may give 100% renewable jet from this SIP process [114].

Other biological routes to biojet fuel have been reported and are yet to be approved for aviation use. An important one to mention is the LS9 work on biological conversion of sugar to fatty acids using *E. coli*. [120]. The fatty acids are then catalytically hydrotreated to biojet fuel hydrocarbons [121]. Other pathways based on biologically generated molecules such as isoprene [122–125] and 2,3-butanediol (2,3-BDO) [126–128] have been recognised as having good potential for biojet fuel production in large-scale.

2.3.2. Thermocatalytic Routes for Sugar-to-Biojet

Various sugar feedstocks can be utilised in the SIP process, including sucrose from sugarcane or sugar beet, glucose from corn or cellulosic biomass, and xylose from hemicellulosic biomass. The choice of feedstock depends on availability, cost, and sustainability considerations. Lignocellulosic biomass, with its abundant availability and potential for reducing competition with food crops, is of particular interest for sustainable biojet fuel production via the Sugar-to-Biojet pathway [129,130]. Sugars, with their carbon backbone and oxygen-based functional groups, can be transformed into hydrocarbon molecules suitable for jet fuel through deoxygenation and C–C coupling reactions as shown in the schematic in Figure 7. These carbohydrates can be converted through hydrogenation or hydrogenolysis into polyhydric alcohols or short-chain length oxygenates, respectively [131]. Deoxygenation converts sugars into hydrocarbons and C–C coupling reactions such as aldol condensation and oligomerisation are utilised to link sugar molecules together, creating larger hydrocarbon chains. These combined reactions produce hydrocarbons with carbon chains ranging from C_8 to C_{16} [129,130]. One advantage of these reactions is that they can be carried out in the aqueous phase. This is beneficial for two reasons: (1) sugars are obtained from biomass in aqueous solutions, so no need for extensive dewatering before use, and (2) hydrocarbon products generated during the conversion process are insoluble in water, facilitating easier separation and improving overall energy efficiency [132].
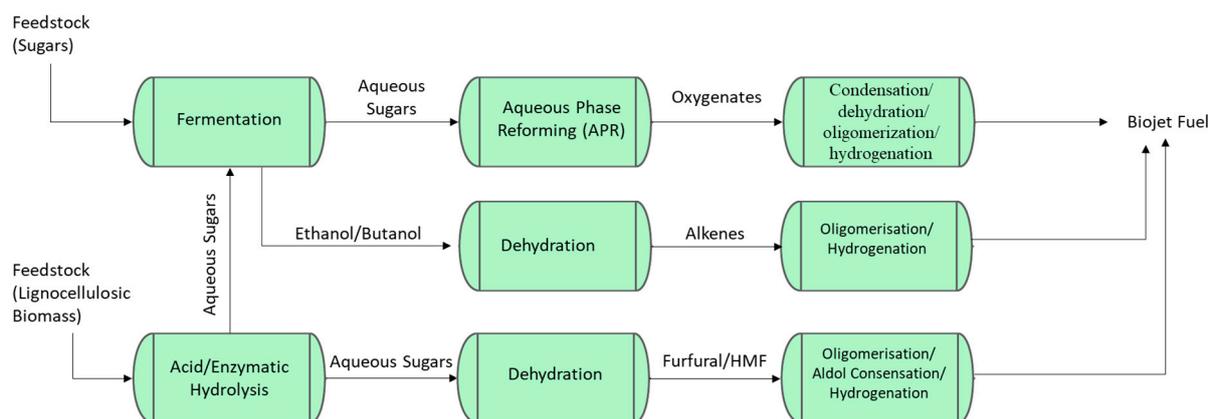
Figure 7. Biojet fuel production from sugar-platform.

Sugar conversion along with hydrocarbon yields and selectivity during SIP are influenced by catalysts and the reaction conditions of temperature, pressure, and residence time. Research efforts have focused on developing efficient catalysts that enhance sugar conversion and hydrocarbon yield while minimizing unwanted byproducts to achieve process optimisation. However, several challenges exist, including catalyst deactivation, control of reaction selectivity, scalability of the process, and techno-economic feasibility [59]. Recent research has focused on improving catalyst design, exploring new catalytic materials, and understanding the reaction mechanisms involved in the SIP process [133]. Integrated approaches, such as combining Sugar-to-Biojet with other biomass conversion technologies such as pyrolysis or gasification, have also been investigated to enhance overall process efficiency and product yields. The most advanced thermochemical Sugar-to-Biojet processes are aqueous phase reforming and Furanics-to-Biojet as presented below.

Aqueous Phase Reforming (APR) for Biojet Fuel

Aqueous Phase Reforming (APR) is a promising technology that has gained significant attention in the field of biofuel production, particularly for the synthesis of biojet fuel. In Figure 7, one route highlights the SIP pathway involving APR of sugars and biomass-derived oxygenates (e.g., glycerol) to produce syngas, which is then upgraded into liquid hydrocarbon fuels through Fischer–Tropsch (FT) synthesis. This APR route which requires relatively mild temperatures (225–300 °C) has been adopted by Virent Energy Systems, renamed as the Bioforming Process and being commercialised [134].

APR involves the catalytic conversion of biomass-derived aqueous solutions into a mixture of hydrogen (H_2) and oxygenates which can be further processed to produce biojet fuel. This process offers several advantages over traditional biofuel production methods, such as higher energy efficiency, reduced carbon emissions, and the utilisation of a wide range of biomass feedstocks [132,134–136].

The APR process typically consists of several steps, including biomass pretreatment, hydrolysis, reforming, and upgrading. In the pretreatment stage, biomass feedstocks, such as lignocellulosic materials or waste streams, are processed to remove impurities and enhance their accessibility for subsequent conversion. Hydrolysis is then performed to break down complex carbohydrates into simple sugars, which can be further converted into biofuel precursors [137].

The reforming step is the heart of the APR process, where some of the aqueous solution hydrolysis products obtained from hydrolysis are catalytically converted into H_2 via reforming reactions. Various catalysts, such as supported metal catalysts (e.g., nickel, ruthenium), are employed to promote the reforming reactions and improve the efficiency of H_2 production.

In a different reaction step, various C–C coupling reactions of the compounds from the carbohydrate hydrolysis product are used to make new compounds with higher carbon

chain-length molecules. The reaction conditions, including temperature, pressure, and residence time, are carefully controlled to optimise the yield and selectivity of biojet fuel precursors [134–136,138]. Thereafter, the H_2 obtained from the other reaction step is used to hydrogenate these larger molecules to produce liquid hydrocarbons, including those within the jet fuel range [138,139].

These upgrading steps involve the use of additional catalysts and operating conditions tailored to achieve the desired fuel properties, such as high energy density, low freezing point, and excellent combustion performance. The APR process has shown great potential in the production of biojet fuel due to its ability to utilise various biomass feedstocks, including non-food crops and waste materials, thus avoiding competition with food resources. Additionally, the process offers improved energy efficiency compared to conventional thermochemical conversion routes, as it operates under milder conditions and allows for the direct use of water as a solvent, reducing energy requirements for feedstock drying [140,141].

Several studies have demonstrated the feasibility and effectiveness of APR for biojet fuel production. For example, a study by Wang et al. [140] investigated the APR of biomass-derived sugar/polyol (60 wt% sorbitol and 40 wt% xylitol) over Ni@HZSM-5/MCM-41 catalysts and obtained liquid fuel yield of 32 wt% with aromatics content of 84.3%. The authors used conditions of 300 °C, WHSV of 1.25 h^{-1}, GHSV of 2500 h^{-1}, and 4.0 MPa of hydrogen pressure. In another study, the same research group [96] focused on the sorbitol alone as a feedstock for APR using a fixed-bed reactor under the conditions of 593 K, WHSV of 0.75 h^{-1}, GHSV of 2500 h^{-1}, and 4.0 MPa of hydrogen pressure to also obtain and oil yield of 40.4 wt% with 80% of the oil composed of aromatics and cyclic-hydrocarbons. This is an attractive route because sorbitol can be sourced from biomass in large quantities (1.8 million tonnes per year) from cellulosic glucose [134].

Typical catalyst using in APR include Pt-Re/C and high-acidity zeolites such as HZSM-5 and MCM-41. For instance, Kunkes et al. [136] used a combined process of glycerol conversion over Pt–Re/C catalyst to obtain C_{5+} liquid alkanes. The catalyst was able to catalyse deoxygenation, C–C coupling, and hydrogenation reactions to give increased yield of alkane products [136]. Chheda et al. [132] introduced the chemical catalytic transformations of biomass-derived sugars and sugar–alcohols under APR conditions to value-added chemicals and fuel. The authors provided details of the APR reaction pathways and process conditions that led to the production of furan compounds by selective dehydration of carbohydrates, and to produce liquid alkanes by the combination of aldol condensation and dehydration/hydrogenation processes [132].

Furanics-to-Biojet Fuel

Figure 7 also shows a second route that explores the use of precursors such as furfural or 5-hydroxymethyl furfural (5-HMF), also known as furanics, for conversion into biofuels and other sustainable chemicals [132,134–136]. First, lignocellulosic biomass is fractionated to remove lignin and obtain the cellulose and hemi-cellulose fractions for conversion to hydrocarbons. The lignin generated in this process is often dewatered and combusted to generate process heat. The fractionated hemicellulose and cellulose are hydrolysed into sugars that have five (pentoses) or even six (hexoses) carbons with the use of acid or enzyme catalysts. Further processing of pentoses yield furfural while hexoses produce 5-HMF. Obtaining furfural from C_5 sugars such as xylose is a mature industrial process, whereas the production of 5-HMF from hexoses is still challenging due to the following complications:

i.   limited selectivity due to poor control over side reactions;
ii.   the limited control associated with glucose the feedstock;
iii.   the extra steps required to isomerise glucose into fructose as fructose gives higher yields of HMF with better selectivity and rates as seen in Table 4.

Both furfural and 5-HMF are viable intermediates for biojet fuel production through the cascade process of dehydration, hydrogenation and aldol condensations reactions [131]. Furanics serve as aromatics contributors to the jet fuel hydrocarbon pool as reported

by Li et al. [142]. For example, 5-HMF can be easily transformed into dimethylfuran (DMF), whose reaction with ethylene via Diels–Alder Cycloaddition reaction followed by hydrogenation has been reported to give 90% p-xylene yield [142]. Besides being a source for aromatics, 5-HMF and furfural can produce liquid hydrocarbon fuels. Sutton et al. [138] examined the production of alkanes from mono-HMF and di-HMF. In their work, Pd/C catalyst was used for hydrogenation while La(OTf)$_3$ catalyst was applied for HDO, with 20.7 bar H$_2$. After 16 h of reaction, mono-HMF gave 87% C$_9$ alkane yield (1:1 HMF and acetone) and di-HMF gave 76% C$_{12}$ alkane yield (2:1 HMF and acetone) [138].

Condensation and degradation of 5-HMF production is known to promote catalyst deactivation via coke formation [143]. However, several strategies have been investigated to minimise or eliminate this problem. For example, to prevent coking during HDO, initial hydrogenation can be used to convert 5-HMF and acetone to water soluble linear alcohols prior to biojet fuel production [144]. Using this strategy, Huber [144] obtained >70% C$_{16}$ using Pt/SiO$_2$–Al$_2$O$_3$, at temperatures from 250–265 °C, pressures of 50–52 bar, and GSHV from 1000–3000 h^{-1} H$_2$ gas hourly space velocities.

Table 4. Conversion of sugars and cellulose to 5-HMF.

Feedstock	Solvent	Catalyst	Temp. (°C)	Time (min)	Yield (%)	Reference
Fructose	CHClO	Malonic acid	80	60	41	[51]
	CHClO	Oxalic acid	80	60	62	[51]
	Water	HCl (aq)	95	90	68	[145]
	Water-acetone	Dowex-50wx8-100	150	15	73	[145]
	CHClO	Citric acid	80	60	76.3	[53]
	1:1 water-DMSO/7:3 MIBK/2-BuOH	HCl	170	4	85	[145]
	DMSO	CNT-PSSA	120	30	89	[53]
	[HexylMIM]Cl	SO_4^{2-}/ZrO_2	100	30	89	[145]
	[BMIM]Cl	LS	100	10	94.3	[146]
	[BMIM]Cl	$NHC/CrCl_2$	100	360	96	[145]
	1:7 DMSO/MIBK	Acidic ion exchange resin	76	-	97	[145]
	DMSO	NH_4Cl	100	45	100	[145]
	DMSO	Amberlyst-15 powder	120	120	100	[145]
Glucose	Water	TiO_2/ZrO_2	250	5	29	[145]
	[EMIM]Cl	Boric acid	120	180	41	[147]
	Water	H_3PO_4/Nb_2O_5	120	180	52	[145]
	DMSO	CNT-PSSA	140	60	57	[145]
	1:2.25 Water-MIBK	$AgPW_{12}O_{40}$	130	240	76	[145]
Cellulose	Water	HCL	300	30	21	[145]
	1:5 Water/MIBK	TiO_2	270	2	30	[145]
	[EMIM]Cl	Boric acid	120	480	32	[147]
	Water	$Cr[(DS)H_2PW_{12}O_{40}]_3$	150	120	53	[145]
	[EMIM]Cl	$CrCl_2$	120	360	89	[145]

Key: DMSO (dimethyl sulfoxide), MIBK (methylisobutylketone), BMIM (1-butyl-3-methylimidazolium chloride), HexylMIM (1-hexyl-3-methylimidazolium chloride), EMIM (1-ethyl-3-methylimidazolium chloride), CHClO (choline chloride) [98].

2.4. Biojet Fuel Production Routes Based on Whole Biomass

2.4.1. Biomass Pyrolysis and Hydrothermal Liquefaction (HTL) to Jet Fuel

Pyrolysis and Hydrothermal Liquefaction (HTL) have emerged as promising conversion routes for the production of sustainable jet fuels (Figure 8). While these methods are yet to be approved by the ASTM (American Society for Testing and Materials) as standard jet fuel conversion processes, they offer significant potential for the aviation industry's transition to renewable energy sources. Pyrolysis, a thermal decomposition process of biomass, involves the conversion of organic materials into bio-oils in the absence of oxygen or air, typically at temperatures ranging from 400 to 600 °C [148]. The feedstock composition, heat transfer rate, residence times, and experimental objectives influence the various types of pyrolysis processes are available in Table 5.

Table 5. Types of pyrolysis [80,111,142].

| Pyrolysis Type	Residence Time	Heating Rate	Temperature (°C)	Major Product
Carbonisation	h–days	very low	400	char
Conventional	10 s–10 min	low–moderate	<600	gas, char, liquid
Flash (liquid)	<1 s	high	<600	liquid
Flash (gas)	<1 s	high	>700	gas, char, liquid
Ultra	<0.5 s	very high	1000	gas, chemicals
Vacuum	2–30 s	moderate	400	liquid
HTL	≤60 min	moderate	300–350	liquid

Bio-oils obtained from pyrolysis can be further processed through deoxygenation, a common step in the production of Catalytic Hydroprocessed Esters and Fatty Acids (HEFA) fuels. Deoxygenation removes oxygen content from the bio-oils, enhancing their suitability as jet fuel feedstocks. On the other hand, HTL is a similar biomass conversion method to pyrolysis but involves the use of pressurised hot water as the medium to degrade biomass into three main products: bio-crude, biochar, and gases. The bio-crude obtained through HTL shares similarities with pyrolysis bio-oil, but it typically has reduced acid contents [149–151]. Research and development efforts are actively exploring the technical feasibility and commercial viability of both pyrolysis and HTL for jet fuel production. ASTM plays a crucial role in evaluating and approving these conversion routes to ensure their compatibility with existing aviation fuel specifications. Once these methods receive ASTM approval, they have the potential to contribute significantly to the decarbonisation of the aviation sector by providing renewable and sustainable alternatives to conventional jet fuels.

Pyrolysis is a thermal decomposition process that breaks down biomass into various products, one of which is bio-oil. Fast pyrolysis, conducted at temperatures ranging from 500 °C to 600 °C, yields bio-oil as the primary product. Bio-oil is a complex mixture primarily composed of alcohols, aldehydes, carboxylic acids, alkenes, aromatics, sugars, ketones, furans, phenols, and heavy molecular weight oligomers. These oxygenated compounds can be converted into hydrocarbons through hydrodeoxygenation (HDO) using hydrogen and appropriate catalysts. Several studies have been conducted to explore the pyrolysis of pinewood for bio-oil production. Yildiz et al. [152], Kumar et al. [153], and Westerhof et al. [154] were among the researchers who investigated this process. Westerhof et al. discovered that a one-step pyrolysis process at 530 °C produced a higher bio-oil yield (59%) than to a two-step reaction, which resulted in less moisture and char [154]. Kumar et al. achieved the highest bio-oil yield at 500 °C (62.7%) compared to other temperatures, namely 600 °C (47.1%) and 700 °C (17.9%) [153]. While bio-oil can theoretically be used as fuel for boilers, turbines, gasifiers, and engines, it requires upgrading to remove oxygen and crack the heavy molecular weight oligomers to a certain extent before it can be used as a liquid transportation fuel [152]. Catalytic upgrading of bio-oil aims to increase its heating value, enhance compatibility with petroleum hydrocarbons by reducing the oxygen content, improve chemical stability, and decrease its viscosity. Table 6 provides a comparison between bio-oil and crude oil, highlighting the incompatibility of the latter as

a direct substitute. Figure 9 shows the pathway route for conversion of bio-oil into biojet fuel [155–157].

Table 6. Comparison of properties; bio-oil and crude oil [158,159].

Properties	Bio-Oil	Crude Oil
Density (kg/m^3 @ 15 °C)	818.4–923.6	772.1–936.0
Total acid number (mgKOH/g)	116.2–207.5	0.0–2.0
Aromatics (%)	20.4–60.5	32.6–53.0
C (%)	55–65	83–86
H (%)	5–7	11–14
O (%)	28–50	<1
Water (%)	15–30	0.1
Heating value (MJ/Kg)	16–19	44
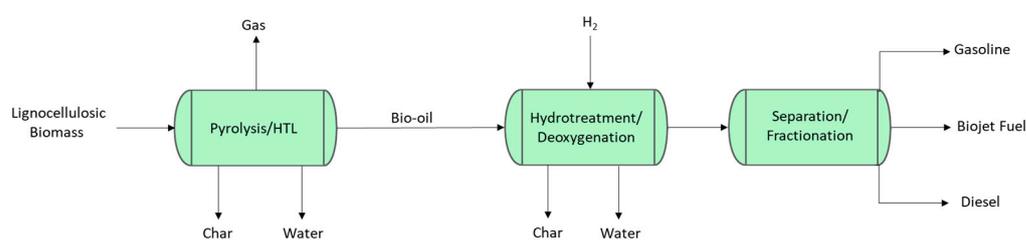
Figure 8. Pyrolysis/HTL bio-oil jet fuel pathway [155–157].
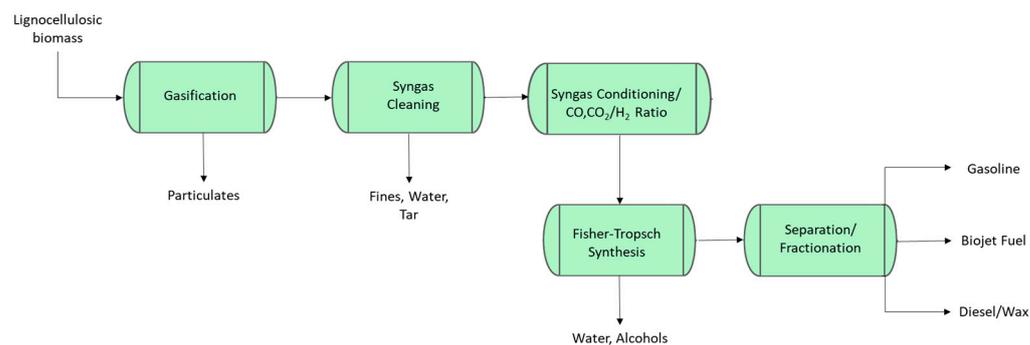
Figure 9. Biojet fuel from biomass gasification and FT synthesis pathway.

Mortensen et al. reviewed the catalytic upgrading of bio-oil (Table 7). This review summarised the process variables and the yield produced under two main categories: HDO and zeolite cracking. The main differences that stand out are the relatively less pressure required, and low yields obtained over the zeolite cracking reactions [158]. Aside from the challenge of storage as the acidic nature of bio-oils lead to corrosion, another major problem with catalytic pyrolysis to obtain hydrocarbons is the efficiency of deoxygenation reactions, especially at an industrial scale [160]. An improvement in the type of catalysts used and the process chemistries will be essential to improve the quality of the process [152]. Research has shown that hydrothermal liquefaction of cornstalk can produce bio-oil to be converted to jet fuel range hydrocarbons. The catalyst for the process was Ni/ZrO$_2$ in supercritical cyclohexane. The conditions include a moderate temperature of 300 °C and 50 bar pressure of hydrogen. The catalyst converted all the components of the bio-oil, obtaining 73.44% yield of biojet and biodiesel range hydrocarbons [161].

Table 7. Some literature on catalytic upgrading of bio-oil [158].

Catalyst	Reactor Type	Time (h)	P (bar)	T (°C)	Degree of Deoxygenation (%)	Upgraded Oil Yield (%)
			Hydrodeoxygenation (HDO)			
$CoMoS_2/Al_2O_3$	Batch	4	200	350	81	26
$CoMoS_2/Al_2O_3$	Continuous	4	300	370	100	33
$NiMoS_2/Al_2O_3$	Batch	4	200	350	74	28
$NiMoS_2/Al_2O_3$	Continuous	0.5	85	400	28	84
Pd/C	Batch	4	200	350	85	65
Pd/C	Continuous	4	140	85	64	48
$Pt/Al_2O_3/SiO_2$	Continuous	0.5	85	400	45	81
Ru/Al_2O_3	Batch	4	200	350	78	36
Ru/C	Continuous	0.2	230	350–400	73	38
Ru/C	Batch	4	200	350	86	53
Ru/TiO_2	Batch	4	200	350	77	67
			Zeolite cracking			
HZSM-5	Continuous	0.32	1	380	50	24
HZSM-5	Continuous	0.91	1	500	53	12

Following the fast pyrolysis of straw stalk at temperature 550 °C, the bio-oil produced was catalytically cracked and deoxygenated over HZSM-5 catalyst to obtain C_2–C_4 olefins and C_6–C_8 aromatics, which are further upgraded to jet fuel range hydrocarbons with a selectivity of 88.4% [162]. Duan et al. explored the catalytic processing of combined feeding of lignocellulosic biomass and low-density polyethylene (LDPE) to mitigate catalyst deactivation by reducing coke generating and to increase aromatic yield. This process produced bio-oil yield of 50% with selectivity of jet fuel range hydrocarbons at 88% [163].

2.4.2. Biomass Gasification—Fischer–Tropsch to Biojet (Gas-to-Jet)

The Gas-to-Jet (GTJ) pathway is seen as a highly efficient method that enables the production of liquid hydrocarbon fuel from syngas, which is a mixture of carbon monoxide, carbon dioxide, and hydrogen, obtained through the process of biomass gasification (Figure 9). The hydrocarbons are produced from the syngas via Fisher–Tropsch synthesis. By employing this pathway, the GTJ technology offers several advantages over traditional jet fuel, including being hydrocarbons, which are free from sulphur. This eliminates the release of sulphur dioxide during combustion, which is a major contributor to air pollution and acid rain [10].

Gasification is a thermochemical process that converts the pretreated biomass into syngas by exposure to high temperatures and controlled amounts of oxygen or steam or CO_2. This process breaks down the biomass components into their constituent gases, primarily carbon monoxide and hydrogen. These gases are then collected and further processed to remove impurities and adjust the syngas composition to the desired ratio of carbon monoxide to hydrogen. The syngas produced through gasification is then directed into the Fischer–Tropsch (FT) synthesis stage, where it undergoes a catalytic reaction to produce liquid hydrocarbon fuels. The FT synthesis converts the carbon monoxide and hydrogen present in the syngas into a range of hydrocarbon molecules, including long-chain paraffins and olefins. These hydrocarbons can be further refined and processed to obtain different grades of liquid fuels, including jet fuel [10,11].

Before gasification, the biomass feedstock is often pretreated by drying (to reduced moisture contents to about 10 wt%) and size reduction to enhance both smooth feeding of the biomass into the gasifier and to enhance the gasification rate. These pretreatment stages consume energy and must be considered in the overall efficiency of the gasification process. Recently, slagging gasification, which involves high pressure operations, has been applied in converting biomass to raw synthesis gas at about 1300 °C in presence of limited oxygen and steam. A combustor is integrated into the system to supply heat for drying biomass while direct quench syngas cooling arrangement eliminates ash and tars. The process also takes place in the reformer. Generated syngas is refined and processed via Fisher–Tropsch synthesis to yield liquid fuel [164].

Typically, the FT process can be operated at high temperatures between 300 and 350 °C with iron as a catalyst, yielding gasoline and linear low-molecular weight olefins. Alternatively, the low-temperature FT process runs at 200–240 °C using iron or cobalt as catalysts generating linear waxes of high molecular weight. In addition to high and low temperature FT processes, micro and monolithic FT reactors are under investigation to improve rates of reaction, with enhanced heat as well as mass transfer features [165]. Microlithic structures proposed and developed to include minute parallel channels, one using FT reaction while the other is for circulating cooling water, therefore increasing the efficiency of transferring heat between channels leading to isothermal operation. Monolithic catalysts are basically ceramic structures composed of supports such as alumina or silica [165].

In general, FT process yields alkanes, alkenes, and oxygen-based compounds such as alcohols, aldehydes, and carboxylic acids [95,166,167]. In addition, ketones and aromatics are generated in a high-temperature process [168,169]. The use of cobalt-based catalysts yields more output compared to iron catalysts at a high level of conversion [164]. In existing plants, a portion of the unconverted syngas is taken back to the FT reactor after acid gas removal system while the remainder is used to power the air separation unit [170]. Further processing of FT products is often required to produce fuel-grade hydrocarbons [171,172]. For instance, hydrogenolysis, isomerisation, hydrogenation, and fractionation are used to upgrade FT synthesis products to high-quality, low-aromatic, and sulphur free fuels. Hydrogenolysis converts wax into low weight products with shorter chain length and lower boiling points. These are then heated and distilled to generate jet fuel, diesel fuel, and lubricants [173].

The GTJ pathway has garnered increased attention due to its promising results in terms of hydrocarbon production and different chemical synthesis routes are being explored once the syngas is obtained [95]. Dagle et al. [174] presented an intriguing study where they successfully converted biomass-derived syngas into valuable hydrocarbons. In their experimental setup, they initially obtained ethanol from the syngas and subsequently transformed it into isobutene utilising a mixed oxide catalyst known as $ZnxZryO_2$. Isobutene, a key intermediate, was then subjected to oligomerisation over a solid acid catalyst, Amberlyst-36. This process yielded a range of olefins, which were further hydrogenated to generate approximately 75% hydrocarbons falling within the jet fuel range.

Overall, the GTJ pathway provides a sustainable and environmentally friendly solution for producing liquid hydrocarbon fuels from biomass. LCA studies have shown that the GTJ or FT-SPK pathways delivers the highest GHG savings among all other biojet pathways (please see Section 2.7). Furthermore, the FT hydrocarbons produced through the GTJ pathway are sulphur-free, so that the FT-SPK easily meets the sulphur limit of 0.0015 wt% according to ASTM D7566 Table A.1.2 [9]. However, the GTJ also has low contents of aromatic hydrocarbons and the compatibility of existing aircraft engines with such a fuel needs further investigation. At present, external sources of aromatic hydrocarbons via blending appear to be an appropriate solution [10].

2.5. Biojet Fuel Production from Biogenic CO_2 as Part of Power-to-Liquid Pathway
Power-to-Liquids Fuel

Although not strictly a biojet fuel route, Power-to-Liquids (PtL) technology is currently being developed as a promising route to synthetic hydrocarbon fuels including SAF. PtL involves the use of renewable electricity (mainly from solar, wind, and geothermal) for electrolysis water to produce green hydrogen. Then, the green hydrogen is reacted with CO_2 captured from the atmosphere, which serves as the carbon feedstock to produce liquid hydrocarbons, from which synthetic aviation fuel can be obtained [33]. This pathway falls within the E-Fuels domain, which is receiving significant attention from governments, policy makers, and industrial and environmental stakeholders. CO_2 represents almost 70% of greenhouse gas emissions which are generated from the combustion of fossil fuels, but an increasing amount is now coming from bioenergy. With the expected growth in bioenergy applications, including biomass power plants, AD plants, bioethanol plants, and

combustion of biomass-derived fuels (solid, liquid, and gas), biogenic contribution to the atmospheric concentrations of CO_2 will increase [175].

The synthesis of sustainable aviation fuel through the PtL process has been reported to be achieved through (1) the methanol pathway and (2) the Fischer–Tropsch pathway as shown in Figure 10 [176]. The provision of carbon in this process can be obtained from the separation of biogenic gases generated from biomass fired power plants [177] or through direct capture of CO_2 from air (DACCS) [178,179]. The use of extracted CO_2 helps to balance out the CO_2 produced from the combustion of the PtL produced biojet fuel, which can create a closed carbon cycle. Even though this process is still in development, a number of companies are investing and forming consortiums to minimise the risks. For example, Inifinium and Engie are in partnership to capture 300,000 tonnes of CO_2 to produce PtL [180]. Another consortium consisting of Porsche, Siemens Energy, Enel, ENAP, Empresas Gasco, and ExxonMobil is aiming to produce PtL at industrial scale by 2026, using DACCS [181]. This year, 2023, the German aerospace research centre DLR received a 12.7 million EUR grant to ramp up the development of the production of PtL as a source of sustainable aviation fuel [182]. The motivation for the formation of these alliances is also backed by the "Fit 55 Package" proposal deployed by the European Commission in July 2021, which enforces that E-fuels account for a certain fraction of the total sustainable aviation fuels used [183].
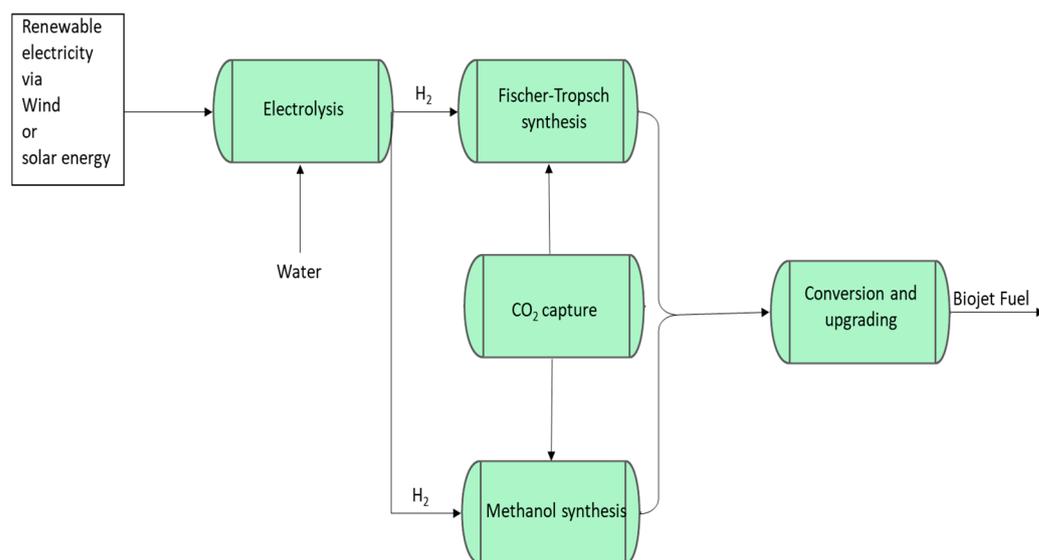
Figure 10. Biojet fuel from Power-to-Liquids using FT and methanol synthesis pathway.

This PtL pathway is attractive because it has the benefit of minimal impact of land availability when compared with the other biojet fuel production technologies. However, it still faces similar challenges such as high cost of production [10]. Perhaps, PtL is relatively even costlier than other biojet fuel pathways due it being very energy intensive and will also require investments in electrolysers and CO_2 capture, in addition to the components for the FT synthesis. Furthermore, this pathway creates competition with the use of renewable energy sources for direct electricity consumption [33].

2.6. Comparison of Yields and Properties of Biojet Fuels from Different Routes/Pathways

Due to the various process routes available for producing biojet fuel, it becomes crucial to thoroughly compare the physical and fuel properties of the final liquid products with those of commercial jet fuel [14,16,100,184]. A recent overview of the performance of approved biojet fuels was carried out by Yang et al. [185]. This is an area that is not evaluated in as much detail as the combustion performance of biojet fuel but can be important in highlighting the overall feasibility of biojet fuels production, and particularly for identi-

fying bio-jet fuels' properties relevant to safe handling and stability concerns [185]. This comparative analysis is essential to ensure that biojet fuel meets the necessary standards and requirements for its effective utilisation as a sustainable alternative in aviation. Physical properties such as density, viscosity, flash point, and freezing point play a vital role in the safe and efficient operation of aircraft. By examining these properties, researchers and industry experts can ascertain whether biojet fuel can be seamlessly integrated into existing aviation infrastructure and aircraft systems without compromising performance or safety (Table 8).

Table 8. Comparison of properties of biojet fuel technologies [14,61,100,184].

Properties	JET-A	HEFA	ATJ	FT	SIP
Acid n°. (mgKOH/g)	0.10 max.	0.02 max.	0.02 max.	0.02 max.	0.02 max.
Flash point (°C)	38 min.	38 min.	48 min.	38 min.	100 min.
Freezing point (°C)	−47 max.	−40 max.	−80 max.	−40 max.	−60 max.
Density @ 15 °C (kg/m³)	775–840	730–770	763	730–770	765–780
Net heat of combustion (MJ/Kg)	42.8 min.	42.8 min.	43.2 min.	42.8 min.	43.5 min.
Additive antioxidants (mg/L)	24.0 max.	17 min. 24 max.	17.2 min. 24 max.	17 min. 24 max.	17 min. 24 max.
Aromatics (%)	25 max.	0.5 max.	-	0.5 max.	0.5 max.
Sulphur content (ppm)	0.30 max.	15 max.	10 max.	15 max.	2 max.

Table 8 shows that there are mostly subtle variations in the properties of the biojet fuels from the different process routes considered except for properties such as the aromatics content. Table 8 shows that the maximum aromatics content of these potential biojet products is still 98% less than the amount required to be a potential Jet-A substitute. The aromatic content is an important parameter for the performance of conventional aviation fuels and must have a critical influence on the performance of bio-jet fuels [185]. A minimum of 8% aromatics is required for the blend fuel to ensure the desirable fuel fit-for-purpose properties, especially for volume swell of seal materials (elastomers) [185]. The low level of aromatics is the main reason all the current biojet fuels are still blended with fossil aviation fuel. Therefore, one method to resolve this deficiency would be to blend biojet fuels with biomass-derived fuel range aromatics, in order to make 100% bio-based. Several researchers have reported the production of light aromatics from biomass sources including catalytic microwave pyrolysis of biomass [186,187], Diels–Alder cycloaddition of furans [142,188], and catalytic processing and co-processing of lipids [189–191].

2.7. Comparative Life Cycle GHG Emissions of Approved Bio-Based SAF

As mentioned earlier in Section 2, LCA is being used as a powerful tool for determining the life cycle greenhouse gases (GHG) emissions savings of synthetic aviation fuels to qualify as SAFs. Specifically, the ICAO has established the Carbon Offsetting and Reduction Scheme for International Aviation (CORSIA) as an international scheme of LCA methodology for reducing CO_2 emissions by the aviation industry [192,193]. There are two main elements of the methodology; (1) Core Life Cycle Assessment (LCA) emissions, and (2) Induced Land-Use Change (ILUC) emissions [193]. The specific components of each element of the ICAO methodology can be found in the relevant literature [193]. To be a CORSIA-eligible fuel (CEF), a SAF pathway must meet the sustainability criteria under the ICAO Sustainability Criteria Scheme (SCS). This scheme defines that CEF must have life cycle GHG emissions of at least 10% below those of the petroleum jet fuel baseline. In addition, the SAF must not be made from biomass from land with high carbon stock [192,194]. Table 9 presents the life cycle GHG emissions data of the various ASTM-approved biojet pathways discussed in this present review.

Table 9. Life cycle GHG emissions values for biojet technologies.

Biojet Technology	Core LCA Values (gCO$_2$e/MJ)			ILUC LCA Values (gCO$_2$e/MJ)	
	Lowest	Highest	GHG Emissions Savings Based on Core LCA Values)	Lowest	Highest
FT-SPK	7.7	12.2	86.3–91.3%	−12.6	8.6
HEFA	13.9	60	32.5–84.4%	13.4	26
SIP	32.4	32.8	63.1–63.6%	11.1	11.2
FT-SPK/A *	5.2	86.2	3.04–94.2%	N/A	N/A
ATJ	23.8	65.7	26.1–73.2%	−23.6	34.9
Co-processing bio-oils with petroleum	N/A	N/A	N/A	N/A	N/A
CHJ	N/A	N/A	N/A	N/A	N/A
HC-HEFA	16.7	40.7	54.2–81.2%	N/A	N/A

* including MSW with 0–45% non-biogenic carbon.

As a basis for comparison, the life cycle GHG emissions/carbon intensity (CI) of petroleum-based jet fuels have been estimated at between 84.5 and 95 gCO$_2$e/MJ as the baseline, with a global volume-weighted (average of 88.7 gCO$_2$e/MJ [195–197]. Table 9 shows that bio-based SAFs have low CIs compared to petroleum jet fuels. The primary reason for this is the acquired biogenic carbon neutrality of bio-based SAFs, which means that carbon emissions from combustion of biomass and SAFs released during fuel production and combustion are offset by carbon uptake during biomass growth [194]. In general, the biojet SAFs can deliver a wide range of GHG savings from 26.1% to 94.2%.

The low value recorded against FT-SPK/A* is due to accounting for the presence non-biogenic carbon (NBC) when municipal solid waste (MSW) is used as feedstock. Indeed, the highest proportion of NBC considered in such for LCA studies is 45%, as above this value the technology pathway becomes worse than the baseline petroleum-based jet fuel [193]. The wide range of Core LCA values seen in Table 9 for a given technology pathway is as a result of differences in biomass feedstock classification as main products, co-products, residues, wastes and by-products [194]. The classification defines the system boundaries used during LCA studies and therefore leads to large variability in values obtained. In addition, the ILUC LCA values apply to technologies that use feedstocks that are classified as crops, and not for those classified as residues, wastes and by-products. As shown in Table 9, some of the recently approved pathways such as CHJ do not yet have reliable LCA data; therefore, further work is needed in this area [192,198].

3. Conclusions

In this review paper, the main technologies for the conversion of biomass and biomass-derive feedstocks into sustainable aviation fuels were presented. In the last three years, the production capacity of biojet fuels has exceeded 300 million litres per year; however, this quantity is still only about 1% of fuel currently used by the aviation sector. Hence, for biojet fuel to make any significant contribution to reducing GHG emissions from the aviation industry, there is a need to increase the production capacities from existing technologies and to develop new sustainable high-volume pathways for commercial deployment. Plants that will produce additional 2.3 billion litres per year are being planned in the next three years, based on the seven ASTM-approved SAF production technologies. These technologies can produce biojet fuels with GHG emissions savings of up to 94% compared to petroleum-based jet fuels. Presently, these biojet fuels are being blended with conventional fossil kerosene for commercial aircraft operations. Among these, the most advanced technologies HEFA and CH, rely on lipid feedstocks (vegetable oils, animal fat, and fatty acids) and interestingly, CH can produce biojet with no requirement for fossil fuel blending. However, the larger-scale applications of the lipid-based technologies are hampered by feedstock availability and competition for food as well as changes in land use. Therefore, there is a growing trend to diversify the feedstock sources and there is a recognition that

non-food lignocellulosic biomass resources can play a significant role in biojet fuel production. The range of technologies available for biomass conversion to biojet fuel include fermentation, aqueous-phase reforming (APR), gasification, pyrolysis, and hydrothermal liquefaction (HTL). Apart from pyrolysis, gasification, and HTL, the other alternative technologies rely on specific biomass-derived feedstock following certain pre-treatment procedures. In general, using lignocellulosic biomass for biojet production has the major challenge of low yields and multiple processing steps, for which two main strategies include (1) multiple front-end pre-treatment steps to obtain specific biomass-derived feedstocks for simpler conversion steps to obtain biojet fuel, and (2) simpler front-end conversion of whole biomass, followed by multiple product post-treatment steps to biojet fuel. The new and rapidly developing, yet-to-be approved Power-to-Liquid (PtL) is a variant of the Power-to-X (PtX) group of technologies, using green hydrogen from electrolysis to product E-fuels, including liquid hydrocarbons within the SAF range. With a forecast of 1.4 billion litres production capacity, PtL would make significant contributions to SAF production. Using biogenic CO_2 would enrich the sustainability criteria of the pathway, if electrical energy costs can be lowered.

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