# IEA Bioenergy

*Technology Collaboration Programme*

# Progress in Commercialization of Biojet /Sustainable Aviation Fuels (SAF):

## Technologies, potential and challenges

IEA Bioenergy Task 39

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May 2021

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# Executive Summary

Biojet/ Sustainable Aviation Fuels (SAF) must play a major role if the aviation sector is to significantly reduce its carbon footprint. To meet its carbon reduction targets, large volumes of biojet fuel will be required (likely more than 100 billion litres per year). However, to date, commercialization has been slow and current policies preferentially incentivize the production of other fuels, such as renewable diesel, from the limited available volumes of oleochemical feedstocks.

Although alternative lower-carbon intensive propulsion systems based on electric, hybrid-electric and hydrogen will likely be used in the future, in the short-to-mid-term, biojet fuels will predominate. Ongoing challenges with these other alternatives include issues such as "green" electric aircraft being limited in their range and the number of passengers carried while longer term options, such as "green" hydrogen, will require novel supply chains and new aircraft. Thus, it will be some time before low-carbon-intensity options other than biojet fuels will be commercially available, particularly for long-haul flights.

Although annual volumes of biojet fuel have increased from <10 million litres in 2018, to possibly more than 1 billion litres by 2023 (and potentially ~8 billion litres by 2030), the vast majority of this volume will be derived from oleochemicals/lipids. The upgrading of fats, oils and greases (FOGs) to HEFA-SPK (hydrotreated esters and fatty acids synthesized paraffinic kerosene) is fully commercialized and biojet production is relatively simple. It is anticipated that increased volumes of biojet will be derived via this "conventional" pathway based on expansion of current facilities and the building of new facilities. However, as demonstrated by Neste, these facilities will be primarily used for renewable diesel production with the potential to add biojet production after additional infrastructure investment, and modification of final processing, e.g. adding a distillation step, likely driven by incentivizing policies.

Other technologies which could be producing commercial volumes of biojet fuel by 2025 are Fischer-Tropsch synthesized paraffinic kerosene (FT-SPK) (based on gasification), alcohol-to-jet synthesized paraffinic kerosene (ATJ-SPK) and catalytic hydrothermolysis jet (CHJ). However, all of these processes produce multiple fuel products which typically include a biojet fuel fraction. Therefore, even though "stand-alone" biorefineries could produce more of the biojet fraction, this will be influenced by market demand, economics and policy drivers as currently, in many cases, the biojet-range molecules are diverted to the renewable diesel fraction due to policy drivers. For each of the technologies, although the percentage of the jet fraction within the total liquid fuels varies, processing conditions can be modified to increase the amount of the biojet fraction. Thus, if HEFA refiners were encouraged to produce biojet, in addition to renewable diesel, at least 15% of the current low-carbon, drop-in fuels produced could be biojet. This would immediately increase the amount of biojet that could be available, at a moderate investment cost.

As will be mentioned several times, although there are several ways to make biojet fuels, the vast majority of the biojet fuel used today are produced via the HEFA pathway. It is anticipated that this pathway will predominate for at least the next ten-to-fifteen years

## Hydrotreated esters and fatty acids (HEFA) technology

The Hydrotreated esters and fatty acids (HEFA) pathway is fully commercial. Although there are limited opportunities for technical improvements there is considerable scope to reduce

the cost and carbon intensity of the oleochemical feedstocks (as demonstrated by the increasing use of used cooking oil (UCO)). However, although several waste, lipid/oleochemical feedstocks have not been used to date (although supply chains, as pioneered by companies such as Neste, are developing rapidly), these "waste lipids" are a finite feedstock. Consequently, existing and evolving oilseed crops will be needed to increase oleochemical feedstock availability. However, there will be ongoing concerns about the sustainability and cost of oleochemical feedstocks.

## Gasification and Fischer-Tropsch synthesis

The major challenge of gasification-based biojet production is the high investment cost that will be encountered when constructing these facilities. Although operational costs are projected to be relatively low, certain gasifiers, such as those using plasma technology, will be higher. While reducing the cost of the gasification reactor is desirable, work to date has shown that this can compromise the quality of the syngas. Another costly component is the need for "cleanup" of the raw syngas prior to Fischer-Tropsch synthesis. Cleanup typically involves the multiple process steps needed to remove different contaminants, with feedstock variability and different levels of contaminants increasing complexity and cost. It should be noted that Fischer-Tropsch synthesis has been commercialized by the oil and gas sector for many decades with this knowledge more recently applied to biomass feedstocks. Technical improvements using biomass feedstocks, such as faster reaction rates, are currently being pursued by companies such as Velocys. Other areas of improvement include the development of bifunctional catalysts that can produce a larger jet fraction (up to 70%) and the ability to use low-cost feedstocks such as municipal solid waste (MSW). The gasification/FT pathway is certified under ASTM D7566 for biojet production based on any type of feedstock and the Fischer-Tropsch liquids are certified for co-processing in existing refineries.

## Pyrolysis and hydrothermal liquefaction (HTL)-based technologies

Although direct thermochemical liquefaction technologies such as pyrolysis and hydrothermal liquefaction are in the process of being scaled-up, ongoing technical challenges (e.g. the removal of high oxygen levels from the biomass feedstock, high hydrogen requirements and catalyst stability/lifespan, etc.) have yet to be fully resolved. These pathways do not have ASTM certification and, even if an application is launched soon, it is likely to take several years to complete due to the complexity and variability in feedstock and technologies. It is worth noting that, currently, there is not enough volume of biocrude available to do the upgrading and testing of a biojet component through all stages of the ASTM certification process. Thus, it is probable that any biojet fuel based on these technologies will only become available after 2030. Recent techno-economic analyses have suggested that, once commercial, these technologies have the potential to produce biojet fuels at a competitive price. It has also been shown that hydrothermal liquefaction technologies can process a variety of low cost, wet feedstocks such as sewage, manure and food processing waste.

## Alcohol-to-jet technologies

Current alcohol-to-jet technologies are ASTM certified for isobutanol- and ethanol-to-jet, with other companies pursuing certification for n-butanol-to-jet. Gevo has delivered "demonstration quantities" of biojet fuel to various customers and is expected to complete construction of their commercial scale facility by 2023. The Lanzajet ethanol-to-jet process is expected to deliver commercial volumes by 2022, with a full-scale commercial facility planned for 2024. While the conversion of ethanol-to-jet is more complex than the

isobutanol-to-jet process, the production of the alcohol feedstock is the most expensive part of the process. Although conversion of existing ethanol facilities could significantly reduce capital costs, the greatest potential for improvement lies in optimizing the biochemical production of the alcohol by maximizing yield, productivity and titer. As demonstrated by the "conventional" ethanol sector, this can be done through genetic modification of the microbial strain used to make the alcohol while improvements and cost reduction can also be achieved by enhancing alcohol removal from the fermentation broth. One challenge for the Lanzajet process, which ferments syngas/waste gases, is to achieve high yields in spite of limitations such as the gas transfer rate in the broth. Also, from an economic perspective, the value of the alcohol intermediate will impact the decision to divert the alcohol into jet production rather than just sell the ethanol into the fuel/biochemicals market. Thus, policy drivers will play a key role in this decision.

## Power-to-Liquids (PtL) technologies

Power-to-liquids (PtL) technologies have significant potential to produce fuels with very low carbon intensities. However, a crucial component of this technology is having ready access to cheap, renewable electricity, which will dictate suitable locations. It is also likely that demand for renewable energy/electricity will increase as electric vehicle deployment expands while excess energy can also be diverted to other types of energy carriers such as hydrogen. This will be influenced by the economics and policy environment as it is very likely that PtL technologies for synthetic jet fuel production will be more expensive than many other technologies. It should also be noted that direct air capture of $CO_2$ is expensive and at early stages of development, with concentrated sources of waste gases (e.g. brewery emissions) a more likely source of feedstock gas.

## Coprocessing technologies

Coprocessing of liquid intermediates, such as lipids, biocrudes and FT liquids, in existing petroleum refineries is of increasing interest. The most likely insertion points are the fluid catalytic cracker (FCC) and the diesel hydrotreater. As the FCC is mostly used to produce gasoline, the hydrotreater is the more likely insertion point if the objective is to produce low carbon intensive jet fuel. However, the majority of the jet fuel produced in a refinery is derived from the straight-run kerosene fraction obtained after atmospheric distillation, rather than from the hydrotreater. As only 5% blends of lipids and FT liquids are currently allowed under ASTM D1655 (coprocessing), the amount of renewable molecules in any final jet product is likely to be low. Another challenge will be that quantifying the renewable content will also be influenced by the allocation method used to determine the "green molecule" content in fuel fractions (e.g. $C_{14}$ measurements or a mass balance approach) as green molecules are not equally distributed between fuel products. However, although coprocessing is not likely to result in large volumes of low carbon intensive jet fuel, at the large scale that petroleum refineries operate, even low coprocessing volumes could be significant.

## Key take-home messages

Meeting the climate targets of the aviation sector will require significant volumes of biojet fuels. However, current production volumes are less than 150 million litres per year which is considerably less than 0.5% of total jet fuel demand, even during these times of restricted air travel. Although recent investments will see production grow to more than 1 billion litres over the next few years, the vast majority of these biojet fuels will come from HEFA

feedstocks and technology. Other, alternative, technologies are only at the "pioneering" scale of development. Currently seven direct pathways and two coprocessing pathways have received ASTM certification with the introduction of a fast-track certification process hopefully reducing the time required for certification. The time taken to obtain certification has been a significant barrier to more rapid biojet expansion.

As well as the various biojet processes encountering high capital and high feedstock costs, for many of the "advanced" pathways, significant technology challenges still need to be resolved, for example, upgrading challenges (HTL and pyrolysis), achieving higher biojet yields and dealing with variable bio-feedstocks with different chemistry and contaminants. It should be noted that, for all of the biojet processes, the minimum selling price of the biojet fuel is significantly higher than that of fossil derived jet fuel. Thus, policy will play a very important role in trying to bridge this price gap. In parallel, there will be an increasing focus on cost reductions such as accessing low-cost feedstocks, optimizing supply chains, increasing product yield and diversifying the product slate to include higher value commodities. It is also anticipated that, as the various technologies mature, learning rates should result in significant cost reductions. Despite these process improvements, the cost of biojet fuels will be closely linked to policies that incentivize their production and use. These policies will likely provide an opportunity for companies to improve their overall sustainability, lower the carbon intensity of fuels and become more economically competitive. As the driving force behind biojet fuel production and use is emission reduction and climate mitigation, the overall sustainability and the reduced carbon intensity of the finished fuel will be a priority.

Finally, all of the technologies described in this report will need to be pursued, if we are to deliver the significant biojet volumes that will be required. Although it is likely that ongoing improvements and optimization of processes will continue to reduce costs and facilitate biojet fuel production and use, meeting the sector's decarbonisation targets will be challenging.

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# Introduction

Human-induced emissions which have and continue to contribute to climate change are problematic. The aviation sector accounts for approximately 2-3% of human-induced carbon dioxide emissions and 12% of emissions from transportation. In response, the aviation sector has aggressively targeted measures to reduce emissions such as improving fuel efficiency by 1.5% per year (from 2009 to 2020), achieving carbon neutrality by 2020 and targeting a 50% reduction in emissions by 2050.

However, the aviation sector is unique in its dependency on liquid fuels for today and for the foreseeable future, despite ongoing research on alternative technologies such as electric motors and the use of green hydrogen. Unfortunately, these latter low-carbon-intensity alternative options are unlikely to be ready for commercial, large-scale and sector-wide deployment in the near term plus an additional hurdle is the long lifespan of aircraft and the high renewal. Thus, biojet fuels represent the single greatest opportunity for airlines to achieve significant, long-term carbon reductions and they will be essential if the sector is to achieve a 50% emission reduction by 2050.

In 2017, the International Civil Aviation Organisation (ICAO) adopted a $CO_2$ emissions standard for new airplanes which seeks to limit new aircraft emissions (ICAO, 2017). More recently, the industry recognized that global market-based measures (GMBM) were needed to fill the remaining emissions gap. As a result, ICAO developed CORSIA which is a global carbon offsetting[1] scheme that will be used to address CO2 emissions from international aviation. This will come into effect in 2021 with CORSIA recommending that airlines try and achieve carbon-neutral growth from this date. Although emissions will also be reduced by the use of more efficient aircraft operations and infrastructure improvements (including modernized air traffic management systems) biojet use is still expected to be the major contributor to achieving COSIA's goals. It should be noted that International Air Transport Association's (IATA's) longer-term goal of cutting net $CO_2$ emissions in half by 2050 relative to 2005, has yet to be adopted by ICAO (IATA, 2019).

Although biojet fuels can reduce greenhouse gas (GHG) emissions (compared to fossil jet fuels, based on a well-to-wheel life cycle analysis) the emissions-reduction potential of different feedstocks and technology pathways will be influenced by factors such as the specific geographical location of the facility and nature of the local utilities and infrastructure. ICAO has determined default life cycle assessments for current SAF technologies, showing up to 90% carbon reductions (ICAO, 2019).

As mentioned earlier, achieving the GHG emissions-reduction targets proposed by the aviation industry and by organizations such as the International Civil Aviation Organization (ICAO), will require a significant increase in biojet fuel production and use. The exact volume required to achieve specific goals is not clear as multiple factors have to be considered. These include the sector's future fuel consumption, the extent of emissions reductions achieved through offsets and the specific emissions-reduction potential of the various routes to make biojet fuels. Prior to the effects of CoVid, it was projected that fuel consumption for international

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[1] A carbon offset is a reduction in emissions of carbon dioxide or greenhouse gases made in order to compensate for or to offset an emission made elsewhere.

aviation could be as high as 852 million tonnes by 2050 (ICAO, 2016). Thus, volumes of 426 million tonnes or more of biojet fuels could be needed to meet this GHG reduction goal. Although organizations such as the International Renewable Energy Agency (IRENA) project that 100 billion litres of sustainable aviation fuels will be needed by 2050, current production is still very limited and is considerably less than 0.1% of the current global jet fuel consumption.

Currently, jet fuel can represent about 30% of an airline's operating cost and, as jet fuel prices are volatile, this can result in extreme and rapid price swings, dramatically affecting the profitability and long-term financial stability of airlines.  As well as initially using oleochemical/lipid feedstocks, it is anticipated that biojet fuel will eventually be produced by other technologies, including "biocrudes" derived from sustainably sourced forest and agriculture biomass.  As well as providing more local/regional control of production and supply and reducing price volatility, it is hoped that these "advanced" biojet fuels will have a significantly lower carbon footprint.

As mentioned earlier, although there are several technologies that can produce biojet fuels, and seven pathways have been certified under ASTM D7566, only the HEFA pathway is currently contributing significant volumes of biojet fuel. In order to achieve the significant volumes needed to meet the sector's targets, aggressive commercialization and scale-up of all biojet fuel technologies will be required. For example, some workers have suggested that hundreds-to-thousands of new facilities will be required, needing billions-to-trillions of Euros/Dollars of investment (Staples et al., 2018).

# 2. Definition and characteristics of jet fuel

The aviation sector uses high specification fuels to power jet turbine aircraft and these are typically classified as Jet A/A1 fuels. Strict specifications are defined by the engine and airframe Original Equipment Manufacturers (OEMs) and approved by regulatory bodies such as ASTM. Examples of fuel specifications that have been shown to meet these requirements are ASTM 1655[2] and Def Stan 91-091.

Jet fuel is defined by its functional characteristics and physicochemical properties such as viscosity, carbon number, boiling point range, freezing point, flash point, aromatic content, etc., as strict specifications are essential to ensure safety in airline operations.

However, there is no standard formula for jet fuel as it is comprised of a mixture of hydrocarbons from the middle distillate refinery stream with carbon numbers in the range of C7-C17. The carbon numbers range from C4-C12 for gasoline to C12-C20 for diesel fuel[3]. However, the fractionation of different fuels is based on boiling point (secondary y-axis on the diagram in Figure 1), with different cutoff points selected to achieve individual product streams. As the gasoline and diesel fractions overlap with the jet carbon range the selection of appropriate cutoff points can exclude jet fuel from the product slate (Figure 1).

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[2] ASTM D1655 - Standard Specification for Aviation Turbine Fuels
[3] https://www.iea–amf.org/content/fuel_information/
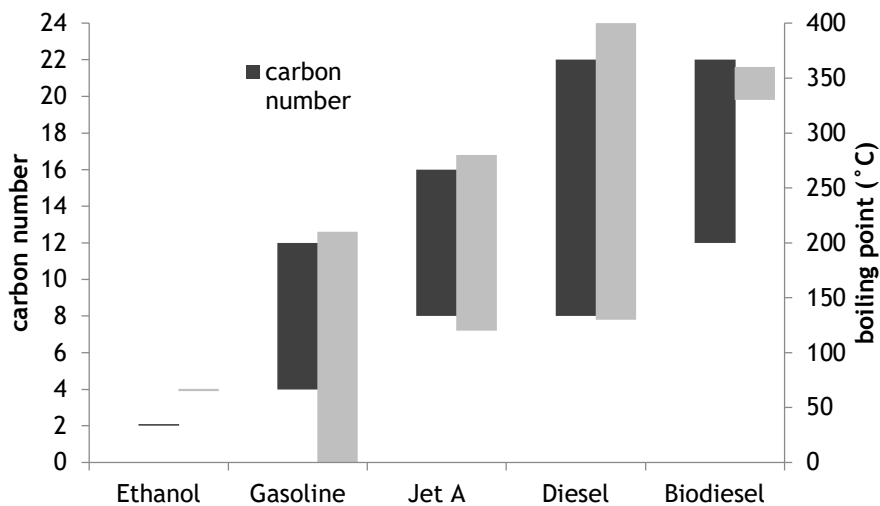
*Figure 1: Carbon number and boiling point range of commercial transportation fuels. Source: (Hileman, Ortiz, Bartis, & Wong, 2009)*

A recent report from the USDOE illustrates the chemical composition of jet fuel derived from crude oil (Figure 2), with the different types of hydrocarbons in jet fuel identified as n-alkanes (straight-chain paraffins), iso-alkanes (branched paraffins), cycloalkanes and aromatics within a carbon range of C8-C16 (Holladay et al., 2020).
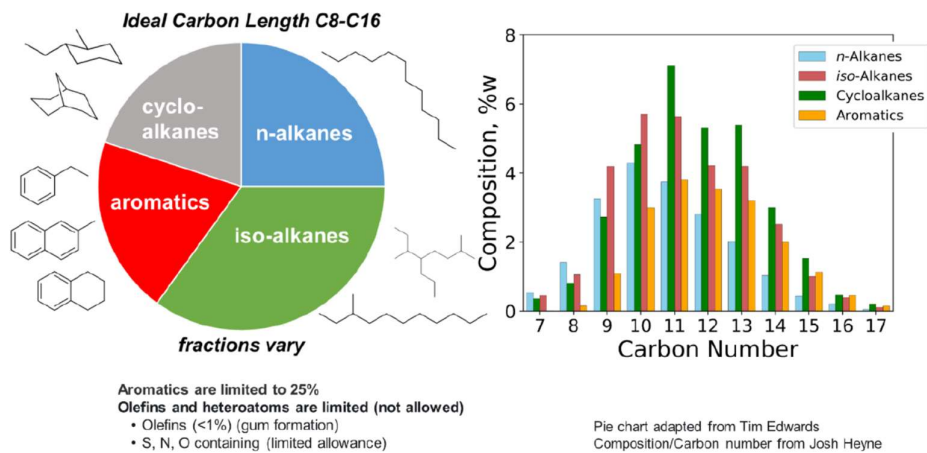


*Figure 2. Composition of an average Jet A (POSF 10325) (Edwards 2017). n-Alkanes, iso-alkanes, cycloalkanes, and aromatics are approximately normally distributed across the carbon number range. A molecule with 11 to 12 carbons is approximately average (Holladay et al., 2020).*

However, as mentioned earlier, it is the functional characteristics of jet fuel that are important, regardless of the specific chemical composition such as some of the key specifications identified by ASTM D7566 (Table 1).

*Table 1. Key specifications for blended fuels as specified in ASTM D7655*

| COMPOSITION | |
|---|---|
| - | *Acidity, total mg KOH/g Max 0.10* |
| - | *Aromatics, volume percent Max 25* |
| - | *Sulfur, mercaptan,C mass percent Max 0.003* |
| - | *Sulfur, total mass percent Max 0.30* |
| *VOLATILITY* | |
| - | *Flash point, °C Min 38* |
| - | *Density at 15 °C, kg/m3 775 to 840* |
| *FLUIDITY* | |
| - | *Freezing point, °C Max −47 Jet A-1I* |
| - | *Viscosity −20 °C, mm2/sJ Max 8.0* |
| *COMBUSTION* | |
| - | *Net heat of combustion, MJ/kg Min 42.8* |
| *- One of the following requirements shall be met:* | |
| *(1) Smoke point, mm, or Min 25.0* | |
| *(2) Smoke point, mm, and Min 18.0* | |
| - | *Naphthalenes, volume, percent Max 3.0* |
| *CORROSION* | |
| - | *Copper strip, 2 h at 100 °C Max No. 1* |
| *CONTAMINANTS* | |
| - | *Existent gum, mg/100 mL Max 7* |
| - | *Microseparometer, O Rating* |
| *Without electrical conductivity additive Min 85* | |
| *With electrical conductivity additive Min 70* | |

It should be noted that the specifications for the different ASTM-approved biojet fuels in ASTM D7566 differ from the overall specifications in ASTM D1655 for the neat biojet fuel before blending. However, once blending has taken place, the blended fuel has to meet the full specifications and functional characteristics of Jet A-1 identified in ASTM D1655. As indicated below, some limits apply for aromatics, olefins and cycloparaffins for different types of biojet fuel pathways. In some cases, the specification for a biojet fuel varies from the standard specification of ASTM D7566.

Initial certification of neat biojet fuel batches has to follow the standards listed in the Annexes, which considers the specific process and characteristics of the biojet fuel prior to blending. Some of the differences with ASTM D7566 (for the blended fuel) are listed below:

1) **Density** – Standard specification 775-840 kg/m$^3$
   - Variations
     o Fischer-Tropsch biojet and HEFA-SPK – 730-770 kg/m$^3$
     o SIP (farnesane) – 765-780 kg/m$^3$
     o SPK/A – 755-800 kg/m$^3$
     o ATJ – 730-770 kg/m$^3$
2) **Maximum freeze point** – Standard specification Maximum -47°C
   - Variations
     o FT and HEFA-SPK – Maximum -40°C
     o SIP - -60°C
     o SPK/A - -40°C
     o ATJ - -40°C
3) **Aromatics** – Standard specification 8.4-26.5% by volume
   - Variations
     o FT and HEFA-SPK – Maximum aromatic mass content 0.5%
     o SIP – Maximum 0.5% mass content

- o SPK/A and CHJ – Maximum aromatic mass content 20%
- o ATJ – 0.5%
4) **Cycloparaffins, paraffins and olefins** are not specified for the blended fuel but included in the Annexes
   - o FT, HEFA-SPK – maximum cycloparaffin mass content 15%
   - o SIP – Maximum olefin mass content 300 mg (Br)/100g
   - o SPK/A – maximum cycloparaffin content – 15%
   - o ATJ – 15%
5) **Nitrogen** is not included in the standard specification for conventional or blended fuels, but included in the Annexes for the neat biojet fuels – Maximum 2 mg/kg
6) **Water** – maximum 75 mg/kg
7) **Metals** (Al, Ca, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Pd, Pt, Sn, Sr, Ti, V, Zn)- Maximum 0.1 mg/kg per metal
8) **Halogens** – Maximum 1 mg/kg
9) **Flash point** – Minimum 38°C for most Annexes except SIP – 100°C
10) **FAME** (fatty acid methyl esters) in HEFA-SPK <5 ppm
11) **Thermal stability** measurements – specified to be carried out at 260°C in the specification for the blended fuel
    - – Variations
        - o FT, HEFA-SPK – at 325°C
        - o SIP at 355°C
        - o SPK/A at 325°C
        - o ATJ at 325°C

# 3. ASTM certified biojet fuels and specifications

## 3.1 ASTM CERTIFICATION PROCESS

All jet fuels have to meet strict specifications defined by engine and airframe OEMs documentation and approved by the regulatory authorities. Examples of fuel specifications that have met requirements are ASTM 1655, Def Stan 91-091 (Europe), EI/JIG AFQRJOS, GOST 10227 (Russia), GB 6537 (China) (CBSCI, 2019).

A separate standard, ASTM D7566 was created for alternative jet fuels, including biojet fuel, to ensure that the same high standards are maintained.  The ASTM D4054 standard was created as a guide for testing and to cover the properties the OEMs evaluate in approving a new fuel from non-conventional sources. Further guidance documents are published by organizations such as CAAFI and IATA to assist in navigating this complex area.

The key documents that provide guidance on requirements and certification of alternative jet fuel include:

- o ASTM D1655 – specification for Jet A/A1
- o ASTM D7566 - Standard Specification for Aviation Turbine Fuel Containing Synthesized Hydrocarbons
- o ASTM D4054 - Standard Practice for Qualification and Approval of New Aviation Turbine Fuels and Fuel Additives

Although the guidelines for certification of new alternative jet fuels are detailed in ASTM D4054, the full procedure can take several years, with four tiers of testing and review of a research report by OEMs. However, depending on how novel a fuel type is, not all four tiers of testing may be required. To try to expedite certification, a fast track certification procedure

was recently implemented, to try to reduce delays in biojet fuel approval[4]. The procedure is summarised below (Figure 3).
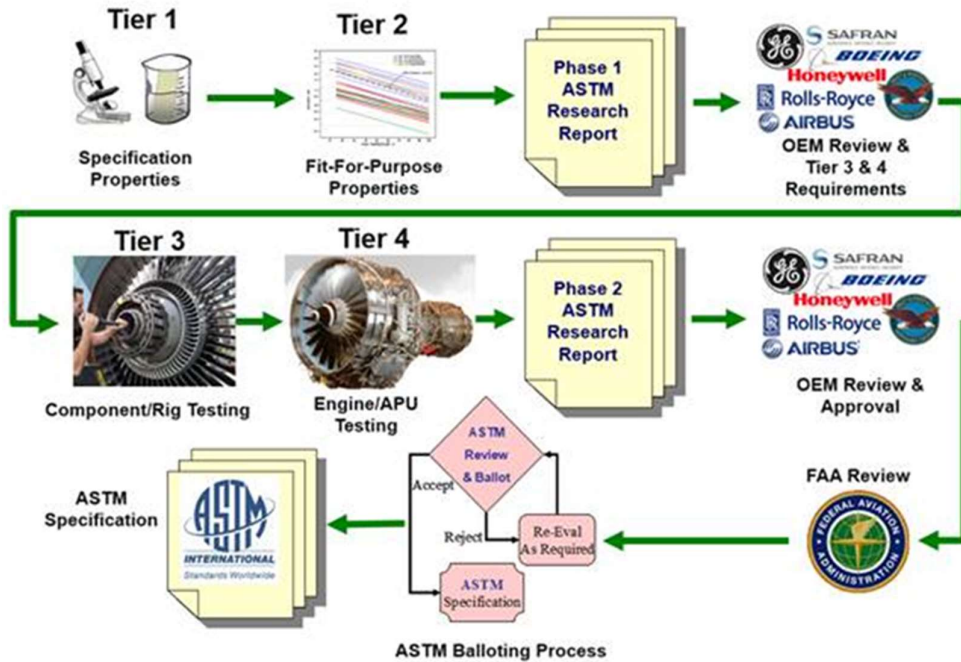


*Figure 3. Graphic illustration of the fuels approval process as set out in ASTM D4054 (CAAFI - http://www.caafi.org/resources/pdf/D4054_Users_Guide_V6_2.pdf)*

Once an alternative fuel has been approved, a new ASTM specification is created as an Annex, under ASTM D7566. Currently, all alternative fuels can only be used in a blend with fossil jet fuel while ASTM D7566 specifies the blend limit, e.g. maximum 50% blends for hydrotreated esters and fatty acids (HEFA). Before an alternative fuel can be used in an aircraft, the neat biojet has to meet the requirements listed for the Annex. This is followed by blending the alternative fuel within allowable blending limits with the fossil jet fuel. The blended fuel must meet all of the requirements listed in Table 1 and the extended table in D7566. Once the blended fuel meets the requirements in D7566, it's reclassified as a D1655 fuel.

As any biojet fuel used in commercial flights has to be certified to gain market access, the lengthy, arduous and expensive certification process represents a significant obstacle.

The list of different ASTM applications summarised in Table 2 indicates the time from the first review date to final approval plus the volumes of fuel used for testing. It is apparent that certification can take a long time, depending on the complexity of the jet product and the similarity to other processes. In order to streamline the certification process and overcome delays, a D4054 Clearinghouse was established at the University of Dayton Research Institute where every tier of testing can take place under one roof (Csonka, 2020). In addition, a Fast

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[4] http://www.caafi.org/focus_areas/fuel_qualification.html#process

Track Annex to ASTM D4054 was implemented to allow alternative jet fuels with conventional hydrocarbon composition to obtain speedy certification. However, this is limited to a 10% blend percentage (Csonka, 2020).

*Table 2. Estimated duration and fuel requirements for ASTM certification of biojet fuels (CAAFI)*

| Fuel pathway | Estimated time from first review to approval | Volume of fuel used in testing (gallons) |
|---|---|---|
| FT-SPK | 3 years | 710,000 |
| HEFA-SPK | 3 years | 626,000 |
| SIP-SPK | 3 years | 16,000 |
| ATJ-SPK (isobutanol-Gevo) | 5.5 years | 93,100 |
| ATJ-SPK (ethanol-Lanzatech) | 16 months | 50 |
| ARA-CHJ | 7 years | 79,900 |

*CAAFI - http://www.caafi.org/focus_areas/fuel_qualification.html#approved*

It should be noted that ASTM D7566 is not only concerned with biojet fuels but any alternative fuel from non-petroleum sources. For example, Annex A1 and Annex A4 fuels were derived from coal, although biomass-based fuels produced using the same process would also qualify under this standard. It should also be noted that the Annexes contain a brief description of the production process and the feedstock to be used. The implication is that similar fuels produced by a significantly different process or feedstock would not qualify under the same Annex. For example, the initial alcohol-to-jet certification was based on the conversion of isobutanol to jet fuel (application by Gevo). The production of biojet from ethanol was approved separately (application by Lanzatech). However, efforts are underway by organizations such as CAAFI to simplify the description to be more inclusive. However as safety concerns are paramount, the approach is quite conservative. Once the blended fuel meets the requirements of ASTM D7566, it can be comingled with conventional jet and is treated as conventional jet fuel.

## 3.2 CURRENT ASTM CERTIFIED PATHWAYS

As mentioned earlier, to date, seven alternative jet fuel production pathways have been approved under ASTM D7566 with each process described in specific Annexes. A brief description of each Annex is summarised below.

- Annex A1: The Fischer-Tropsch Hydroprocessed Synthesized Paraffinic Kerosene (FT SPK) pathway was certified in 2009 for blend levels up to a 50%. Feedstocks can include both renewable biomass such as municipal solid waste (MSW), agricultural and forest wastes, wood and energy crops; as well as non-renewable feedstocks such as coal and natural gas. This is a thermochemical pathway based on gasification of feedstock prior to FT synthesis of hydrocarbons from CO and H2.
- Annex A2: The Synthesized Paraffinic Kerosene from Hydroprocessed Esters and Fatty Acids (HEFA SPK) pathway was certified in 2011 for blend levels up to 50% blend. Feedstocks include plant oil, animal fats, oils and greases (FOGs). It should be noted that only hydrotreatment processing is included under this Annex and therefore, processes using other methods are currently not included even where lipids are used as feedstock.
- Annex A3: The Synthesized Iso-Paraffins from Hydroprocessed Fermented Sugars (SIP SPK) pathway was certified in 2014 at blend levels up to 10%. Feedstocks include sugars from any source. This is a biochemical pathway using modified yeasts to

ferment sugars into a C15 hydrocarbon molecule, farnesene, which has to be further hydrotreated to produce farnesane.

- Annex A4. The Synthesized kerosene with aromatics derived by alkylation of light aromatics from nonpetroleum (SPK/A) pathway was certified in 2015 for blend levels up to 50%. Potential feedstocks are the same as Annex A1. This is a thermochemical process based on gasification and FT synthesis with the addition of alkylation of light aromatics (primarily benzene) to create a hydrocarbon blend that includes aromatic compounds. This biojet fuel includes aromatics in the biocomponent, unlike most of the other pathways where paraffinic hydrocarbons are predominant.
- Annex A5. The Alcohol-to-jet synthetic paraffinic kerosene (ATJ-SPK) pathway was certified in 2016 (using an isobutanol intermediate) and 2018 (using an ethanol intermediate) for blend levels up to 50%. Feedstocks can include sugars from starches, e.g. corn, or from cellulosic biomass. The pathway using an ethanol intermediate was based on the Lanzatech process involving the fermentation of carbon dioxide off-gases into ethanol. The production of the alcohol intermediate using a biochemical fermentation process is followed by production of hydrocarbons using dehydration, oligomerization and hydrogenation to yield hydrocarbons.
- Annex A6: The Catalytic Hydrothermolysis jet (CHJ-SPK) pathway received certification in February 2020. It is based on lipids (free fatty acids) as a feedstock and a hydrothermal liquefaction technology. The blending of up to 50% is permitted. The product contains paraffins, isoparaffins, cycloparaffins, and aromatic compounds over the jet and diesel boiling point range and fractionation are required to produce jet and diesel.
- Annex A7: Production of paraffins derived from hydrogenation and deoxygenation of bio-derived hydrocarbons, fatty acid esters, and free fatty acids (HC-HEFA). The current approved source of the bio-derived lipids is from *Botryococcus braunii*, a microalgal species, and up to 10% blends with conventional petroleum jet fuel are permitted. This was the first biojet certified through the express process.

Co-processing of lipids within existing petroleum refineries was granted certification on April, 2018, based on an amendment to the *ASTM1655 standard*[5]. Co-processing of up to 5% fats and oils (plant oils and animal fats) is permitted in petroleum refinery processes, provided that hydrotreatment is one of the processing steps. In addition, the co-processing of Fischer-Tropsch liquids at 5% blends in existing refineries was approved in 2020.

Multiple additional pathways are at various stages in the ASTM certification pipeline, e.g. Global BioEnergies, Shell IH[2]. Although the application for ASTM certification of High Freezepoint HEFA as suitable for use in aviation has been launched by Neste with support from Boeing, this is still "in-process". This would allow diesel-range paraffins, produced from hydrotreatment of lipids, to be used in low blends with conventional jet fuel. Other fuels in the pipeline include Hydro-deoxygenation Synthetic Kerosene (HDO-SK), Hydro-deoxygenation Synthetic Aromatic Kerosene (HDO-SAK), High Freeze Point Hydroprocessed Esters and Fatty Acids Synthetic Kerosene (HFP HEFA-SK), Integrated Hydropyrolysis and Hydroconversion (IH[2]), Alcohol-to-Jet Synthetic Kerosene with Aromatics (ATJ-SKA) [6].

[5] All the other biojet pathways are certified under ASTM D7566
[6] http://www.caafi.org/focus_areas/fuel_qualification.html#clearinghouse

In total, although about fifteen additional biojet producers are exploring potential ASTM application, they are not formally in the ASTM queue. These companies include Vertimass, GSR/GTI, SBI BioEnergies, Joule, and POET. Although initiated, several of these applications have since been abandoned or are inactive, including the KiOR application based on catalytic pyrolysis (hydrotreated depolymerized cellulosic jet).

## 3.3 BLENDING LIMITS FOR BIOJET FUELS AND IMPLICATIONS

Currently, all alternative fuels can only be used in a blend with fossil jet fuel. ASTM D7566 specifies the blend limit, e.g. a maximum 50% blends for most pathways and 10% for the SIP-SPK pathway and the HC-HEFA pathway. In addition, coprocessing is limited to a 5% insertion of feedstock (lipids or FT liquids) within a refinery.

Blending is required to overcome the limitations of the neat biojet fuel to meet overall specifications for jet fuel under ASTM D1655. For example, HEFA technologies produce predominantly paraffins or isoparaffins, while jet fuel specifications require at least 8% aromatic content. Thus, blending can overcome such limitations to meet overall fuel specifications. Regardless of the blending limit, the final blended fuel must meet ASTM D1655 specifications. Consequently, it may not be possible to blend to the allowed maximum.

There is no specific regulation for blending two types of biojet fuels within the same fuel mix. For example, where different airlines purchase different types of biojet fuels for insertion into an airport hydrant system. Blend restrictions limit the extent that emission reductions are possible. However, due to the low availability of commercial volumes of biojet fuel this is unlikely to be critical for some time.

Currently, some biojet fuel technology providers are trying to produce fully synthetic biojet fuels that could potentially be used without any blending with conventional jet fuel with ASTM D7566 Annex A4 approving a fully synthetic fuel based on the addition of aromatics (FT-SPK/A). The catalytic hydrothermolysis process also produces aromatics and cyclo-alkanes, similar to conventional jet fuel. Although the alcohol-to-jet process with aromatics are in the ASTM certification pipeline, to be used as a potential "direct drop-in" fuel, the ASTM certification only permits a 50% blend with conventional jet fuel for the FT-SPK/A and the catalytic hydrothermolysis jet (CHJ). The Swedish Biofuels and Byogy companies have applied for a fully synthetic alcohol-to-jet certification (ATJ-SKA) and the certification process is in Phase 1 testing.

## 3.4 DOWNSTREAM LOGISTICS AND USE OF BIOJET FUELS AT AIRPORTS

After production of the biojet fuel, downstream blending and transportation to the airport take place. There is a specific process for the biojet fuel producer and user to certify that the blended biojet fuel, at various stages in the downstream supply, meets the ASTM standards (CBSCI, 2019). Most European airports operate according to JIG (Joint Inspections Group) guidelines (CBSCI, 2019). The different steps are summarised below:

1) Every batch of neat biojet fuel must be certified at the producer's site, to meet the relevant standard based on the specific Annex for that pathway in ASTM D7566.
2) If blending with conventional jet fuel takes place at the biofuel producer's site, the blend has to be certified against the standards as set out in
3) Table 1 of the ASTM D7566 standard.

4) Once the blend has been certified under ASTM D7566, it is considered to have met all ASTM D1655 specifications. The blend is considered functionally equivalent to conventional jet fuel.
5) The blended fuel can then be transported to the specific airport where it can be inserted into the airport hydrant system.
6) If the neat biojet fuel is transported to the airport, the biojet fuel has to be blended with conventional jet fuel prior to entering the airport in a separate blending facility and cannot take place at the airport tank farm.
7) The blended fuel must then be certified according to Table 1 in ASTM D7566
8) The blended fuel can then be transported to the airport and inserted into the airport fuel hydrant system.

A recent study looked at various scenarios for SAF integration at US airports, including logistics and blending locations (Moriarty & Kvien, 2018). Currently, there are no guidelines for using multi-blends of biojet fuel, e.g. having a mixture of various types such as HEFA, ATJ, PtL, etc. within the same hydrant system. A recent project completed at Leipzig airport looked at the potential impact of using multi-blends on safety and identifying legal and regulatory obstacles (Müller-Langer et al., 2020).

## 3.5 COMPARING BATCH FUELING AND AIRPORT HYDRANT SYSTEMS

Conventional jet fuel can be supplied into the wing of aircraft in two ways. Either through bowser trucks delivering fuel directly from the tank farm to the airplane, or via a hydrant system which involves a network of underground pipes that transport the fuel from the tank farm to refueling pits on the apron (CBSCI, 2019). The hydrant system is a facility shared by all of the airlines and strict quality assurance guidelines are used to govern the operation of the system. If the blended biojet fuel is supplied to the airport fuel tank farm, it becomes co-mingled with the other fuel in the system. As all airlines are supplied *via* this tank farm, some biojet may end up in all aircraft. Alternatively, if the biojet fuel blend is delivered by a dedicated bowser truck, all of the renewable molecules end up in that particular aircraft.

Early biojet fuel supply chains trials used in-wing fueling and bowser trucks. However, this system proved more costly and less efficient compared to an airport hydrant system (CBSCI, 2019). As a result, several biojet fuel systems have been assessed to demonstrate their effective delivery through the airport hydrant system (CBSCI, 2019; IATA, 2018). For example, the Canada Biojet Fuel Supply Chain Initiative (CBSCI) demonstrated the effective supply of biojet fuel into the commingled hydrant system at Toronto Pearson International Airport (CBSCI, 2019).

Batch delivery of a biojet blend through a bowser truck into the aircraft allows the biojet to be traced to the specific aircraft, whereas biojet fuel supplied into a hydrant system cannot be physically traced. However, inserting biojet blends into the commingled hydrant system does not impact the ability of an airline to claim the environmental benefits, such as $CO_2$ reduction, as this is an administrative process based on a "book-and-claim" system (Pechstein et al., 2020). The airline that purchased the biojet fuel can claim the $CO_2$ benefits based on requirements such as proof of procurement, proof of sustainability, proof of transport and delivery to the airport. Thus, based on a mass balance procedure, an airline can administratively allocate the benefits of using biojet fuels to a specific flight. It has also been suggested that an airline should also be able to allocate biojet fuel use to flights that did not

originate from that airport (Pechstein et al., 2020). This system circumvents the need to transport biojet fuel to smaller and remote airports as the biojet fuel does not have to be physically present in the airplane.

The "book and claim" system is strongly supported by airlines as it will facilitate use of biojet fuels near the refinery which will also be more cost effective. This will also be more cost-effective as transport costs are reduced, while also providing better emission reductions as transport emissions are reduced.

# 4. Status of biojet fuel commercialization

In spite of the early ASTM certification of several technology pathways, commercialization of biojet fuel technologies has been slow, with limited availability of commercial volumes of biojet fuels Figure 4. The first regular, substantial volumes of biojet fuel became available when the World Energy facility in Paramount, California came online. As summarised in Figure 5, the vast majority of biojet fuel used in 2007-2018 came from HEFA-SPK, with minor contributions from ATJ-SPK. based on the Gevo isobutanol-to-jet pathway. Production volumes increasing dramatically in 2019 when Neste contributed 100,000 tonnes (~125 million litres) of biojet fuel (Fernandes, 2020).
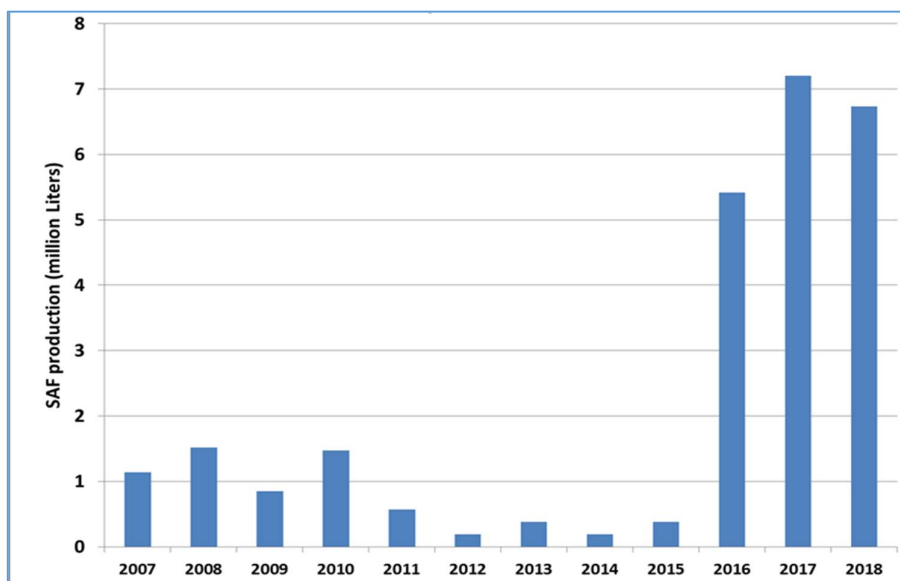


*Figure 4. Biojet fuel production volumes from 2007-2018 (Dickson, 2019)*

In the future, biojet production volumes should increase significantly, based on the expansion of existing facilities and investment in the specific infrastructure required to make HEFA-SPK derived biojet fuel (e.g. Neste) (Table 3). Further into the future, new facilities built by companies such as Fulcrum Bioenergy and Red Rock Biofuels will, hopefully, also contribute such that by 2025, between 3-4.5 billion litres should be readily available (if the planned facilities become fully operational at full capacity).

*Table 3 Current and announced biojet fuel facilities and capacities (Csonka, 2020) (Volumes have been estimated by CAAFI). Note that biojet is a fraction of total capacity (in brackets) and estimates are made based on technology pathway.*

| Company | Technology pathway | Biojet vol MGPY (MLY) | Start-up date |
|---|---|---|---|
| World Energy (Paramount) | HEFA | 25 (95) | 2020 |
| Neste (Porvoo) | HEFA | 34 (128) | 2020 |
| Gevo (Silsbee) | Isobutanol-to-jet | Demo | 2020 |
| Total (La Mede) | HEFA | Not available | 2020 |
| Fulcrum Bioenergy (Sierra) | Gasification/FT | 7 (26) | 2021 |
| Red Rock Biofuels (Lakeview) | Gasification/FT | 6 (23) | 2021 |
| Neste (Singapore & Rotterdam) | HEFA | 480 (1,816) | 2022 |
| SkYNRG (Delfzijl) | HEFA | 33 (125) | 2022 |
| Lanzajet (Freedom Pines) | Ethanol-to-jet | 10 (38) | 2022 |
| World Energy (Paramount) | HEFA | 150 (568) | 2022 |
| Gevo (Luverne) | Isobutanol-to-jet | 19 (72) | 2023 |
| Go Sunshine (New Orleans) | HEFA | 29 (110) | 2023 |
| Fulcrum #2 (Indiana) | Gasification/FT | 21 (80) | 2023 |
| Readifuels | Catalytic hydrothermolysis | 24 (91) | 2023 |
| Phillips 66 (San Francisco) | HEFA | 290 (1,098) | 2024 |
| Total (Grandpuits) | HEFA | 56 (212) | 2024 |
| Preem (Gothenburg) | HEFA | ~70 (265) | 2024 |
| Lanzajet | Ethanol-to-jet | 90 (340) | 2024 |
| Velocys (Altalto, UK) | Gasification/FT | 16 (60) | 2025 |

As noted earlier, all of the technology pathways produce multiple fuel products with the biojet fraction being just one product. Thus, expected production volumes should not be based on the total capacity of a facility with the fraction of biojet as a theoretical maximum percentage of the total fuel production varying depending on the technology. Although this fraction can be adjusted to some extent (based on modified processing conditions, e.g. cracking of longer chain hydrocarbon molecules (>16) into shorter molecules within the jet range, as cracking cannot be precisely controlled), it may also result in the formation of short-chain molecules such as gases that have a lower value and result in an overall lower yield of liquid fuel products.

As discussed earlier, jet range molecules overlap with the naphtha and diesel range. Consequently, a biorefinery can choose to produce a jet fraction by varying the boiling point cutoffs during distillation. However, as production of the jet fraction will depend upon market demand and economics, any policies that incentivize production of biojet fuels will play a crucial role in the decision on what fraction of the liquid product will be diverted to biojet fuel.

Those companies listed in Table 3 have stated their intent to produce biojet fuel, primarily based on having long-term offtake agreements for biojet fuel. However, many other companies that currently produce only renewable diesel can potentially divert more product to the biojet stream. Thus, with limited investment in additional infrastructure more biojet could become readily available under favourable economic conditions (likely created by policy).

Increased commercialization of biojet fuels is reflected in the expanded use of this lower-carbon-intensive fuel at multiple airports by multiple airlines. At this point in time, seven airports are regularly distributing biojet fuel blends and about 300,000 commercial flights

have used such biojet blends (Table 4) [7]. Thus, it is likely that the increased availability of commercial volumes will see an increase in the establishment of regular downstream supply at multiple locations.

*Table 4. Airport locations where biojet blends are provided, either on an ongoing or a batch basis (information from the ICAO website)*

| Batch deliveries | Ongoing deliveries (off take agreements) |
|---|---|
| Karlstad Airport | Los Angeles Airport |
| Chicago O'Hare Airport | Oslo Airport |
| Brisbane Airport | San Francisco Airport |
| Toronto-Pearson Airport | Stockholm Arlanda Airport |
| Montreal Trudeau Airport | Bergen Airport |
| Åre Östersund Airport | Vaxjo Smaland Airport |
| Göteborg Landvetter Airport | Halmstad City Airport |
| Visby Airport | Stockholm Broma Airport |
| Luleå Airport | Kalmar Öland Airport |
| Van Nuys Airport | |
| Jackson Hole Airport | |
| Umeå Airport | |
| Malmö Airport | |

# 5. Technology pathways used to produce biojet fuels

Currently, there are several companies producing or trying to commercialize biojet fuel production and they are at various stages of technology readiness. Apart from the hydrotreated vegetable oil (HVO)/ hydrotreated esters and fatty acids (HEFA) pathway, which is fully commercial, the commercialization of the other pathways is ongoing. However, it should be noted that technical challenges constitute only one component of a viable technology with sustainability and economics two other important components. Even if all of the technical challenges can be solved, the extent to which a fuel can provide emission reductions will be integral to the value of the fuel. It is the cost of carbon abatement that is the true indication of the real value of a biojet fuel. Thus, the challenges associated with commercialization of a low-carbon-intensive fuel may differ between different technologies with some processes requiring high capital investment (gasification-FT) and others high feedstock costs (HVO).

The technologies used to produce drop-in biofuels, including biojet fuel, can be divided into four broad categories. This has been described in detail in previous IEA Bioenergy Task 39 reports (Karatzos et al. 2014; Van Dyk et al. 2018):

- oleochemical,
- thermochemical,
- biochemical, and
- hybrid processes.

In this update, these pathways are only briefly described with an emphasis on the different opportunities and challenges associated with each pathway, specifically as it relates to biojet

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[7] https://www.icao.int/environmental-protection/GFAAF/Pages/default.aspx

fuel production.

As noted earlier, the volume of the biojet fraction varies substantially between different technologies (Table 5) and is similar to the production of conventional jet fuel from crude oil, where the jet fraction is about 10% of the total liquid fuel production of an oil refinery.

Although, to some extent, variations in technology or processing can increase the percentage of the jet fraction, this is usually at a cost, such as a reduced yield in the overall product stream.

*Table 5.Approximate percentage of the biojet fraction produced by different technologies*

| Technology | Approximate percentage of the jet fraction |
|---|---|
| HEFA upgrading | 15-50% |
| Alcohol-to-jet | 70% |
| Fischer-Tropsch synthesis | 25-40% |
| Upgrading of biocrudes from pyrolysis, hydrothermal liquefaction, etc. | 10-30% * |

**\* From (Van Dyk et al., 2019a)**

Figure 5 illustrates the product slates for different technologies using the HEFA and FT pathways. Also showing the potential maximum jet fractions that can be achieved with modified processing.
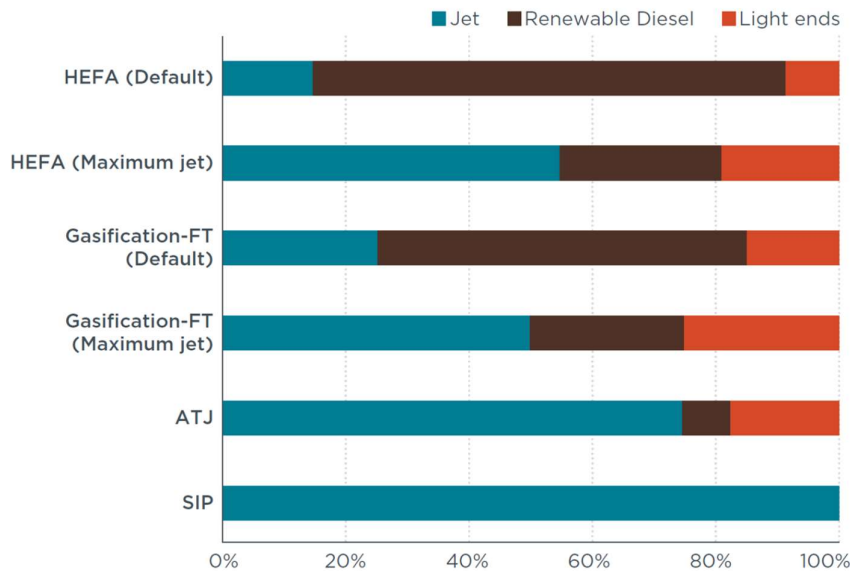


*Figure 5. Comparison of product slates for different fuel conversion pathways (A. N. Pavlenko et al., 2019)*

As mentioned in the executive summary, there is currently no "winning" technology. Thus, continued development of all of the processes will be needed if we are to expand production volumes, with different technologies more successful in various regions based on factors such as, feedstock availability, infrastructure, etc.

## 5.1 THE OLEOCHEMICAL CONVERSION PATHWAY

This technology is mature and currently operates at a commercial scale. These biofuels are often referred to as hydrotreated esters and fatty acids (HEFA) but are also termed hydrotreated vegetable oil (HVO) biofuels. Biojet fuel produced *via* this process is called HEFA-SPK (synthetic paraffinic kerosene) and this term is used within the ASTM D7566 standard. More than 5 billion litres of HEFA, as renewable diesel, is produced worldwide and significant expansion of multiple facilities is currently underway (Table 6).

*Table 6: Current world annual production capacity of HEFA drop-in biofuels*

| Company | Location | Feedstock | Capacity |
|---|---|---|---|
| Neste | Rotterdam | Vegetable oil, UCO and animal fat | 1.26 bn L/y |
| Neste | Singapore | Vegetable oil, UCO and animal fat | 1.26 bn L/y |
| Neste | Porvoo, Finland | Vegetable oil, UCO and animal fat | 240 m L/y |
| Neste | Porvoo 2, Finland | Vegetable oil, UCO and animal fat | 240 m L/y |
| ENI | Venice, Italy | Vegetable oils | 450 m L/y |
| Diamond Green Diesel | Norco, Louisiana | Vegetable oils, animal fats and UCO | 500 m L/y |
| UPM | Lappeenranta, Finland | Crude tall oil | 120 m L/y |
| World Energy | Paramount, California | Non-edible oils and waste | 150 m L/y |
| Renewable Energy Group | Geismar, Louisiana | High and low free fatty acid feedstocks | 315 m L/y |
| Emerald Biofuels | Port Arthur, Texas | Vegetable oils | 330 m L/y |
| TOTAL | | | |

### 5.1.1 The basic process for HEFA production

The basic process for HEFA production involves the removal of oxygen from the feedstock in the presence of hydrogen followed by an isomerization step to improve the cold-flow properties of the diesel stream (Figure 6). Several products are produced with the first reactor removing propane from the triglyceride molecules and producing deoxygenated fatty acids (with $CO_2$ and $H_2O$ waste products). In the second isomerization reactor, light fuels and renewable diesel are produced. Isomerization is essential to improve the cold flow properties (cold filter plugging point - CFPP) of the fuel as fatty acids produce long-chain paraffinic molecules. These are rearranged into branched molecules in the isomerization reactor. As isomerization catalysts have a limited cracking function (acid catalyst) to allow rearrangement reactions to take place, this results in the formation of some light naphtha products. The severity of the reactor conditions determines the extent of cracking taking place.

While a component of the liquid product falls in the jet range (depending on the chain-length of the fatty acids), production of biojet is optional and can be separated from the renewable diesel fraction[8]. This would occur with a distillation step and may require additional infrastructure.

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[8] All jet range molecules can be burnt in a diesel engine so separation does not have to occur to produce renewable diesel.
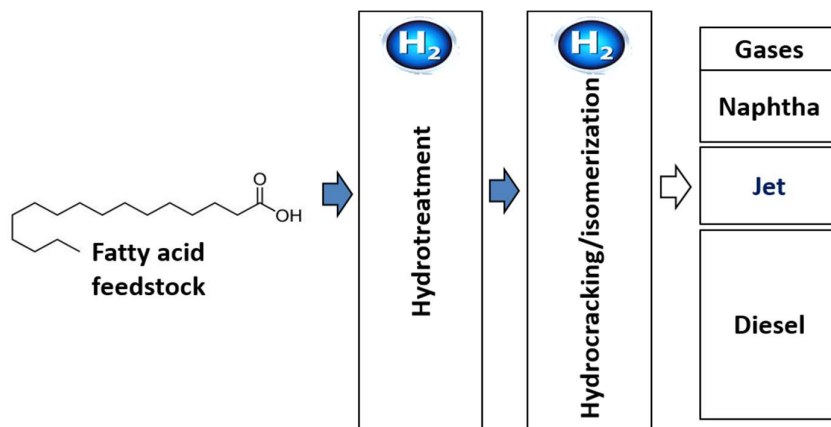
*Figure 6 Simplified Hydroprocessed Esters and Fatty Acids (HEFA) process depicting the 2 stages of hydroprocessing*

Several chemical reactions take place during HEFA production, with the carbon-carbon double bonds present in the triacyl glyceride (TAG) saturated first. This is followed by the removal of the propane backbone within the TAG, leaving three free fatty acids per TAG molecule. Finally, the fatty acids are deoxygenated through three reactions, hydrodeoxygenation (HDO - where oxygen leaves as $H_2O$), decarboxylation (where oxygen leaves as $CO_2$) and decarbonylation (where oxygen leaves as CO and $H_2O$) resulting in the formation of alkyl chains (see Figure 7). During hydrodeoxygenation (HDO) the alkyl chain length is typically preserved whereas during decarboxylation/decarbonylation (DCO) the alkyl chains are shortened due to the loss of a carbon atom as $CO_2$.

A combination of these three deoxygenation reactions usually takes place in commercial hydrotreating facilities, even with the addition of hydrogen. The ratio of these deoxygenation pathway reactions (typically HDO/DCO = 35/65) is important in hydrotreating operations as it determines hydrogen consumption, product yields, catalyst inhibition, gas consumption and heat balance (Egeberg et al., 2010). The "tuning" of the deoxygenation pathway ratio can be achieved via catalyst adjustment, depending on the strategic manufacturing priorities as well as the feedstock and hydrogen costs and the value of the fuel product or blendstock being produced. For example, the UOP-Honeywell facility opts for more decarboxylation in order to reduce capital costs while Syntroleum prioritizes the preservation of longer carbon chains (higher product quality) and thus uses more hydrodeoxygenation (Matthew Noah Pearlson, 2011).
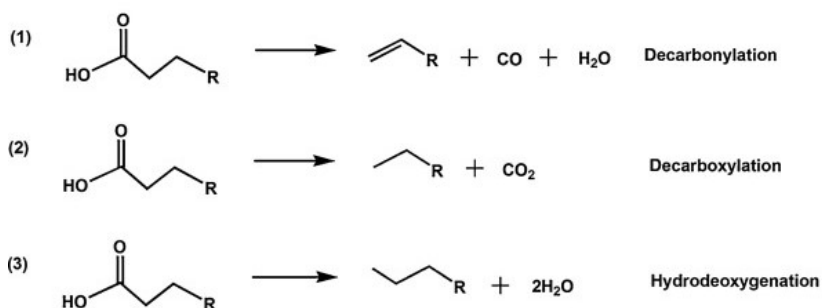
*Figure 7 Deoxygenation reactions*

When decarbonylation (DCO) takes place, the carbon in the feedstock is lost by oxidation and, as a result, the yield of hydrocarbons is reduced. For example, for lipids, the decarboxylation reactions of C18 fatty acids will yield C17 paraffins, etc., and when hydrogen inputs are used to remove oxygen through HDO, the yields of hydrocarbons are higher. This has an impact within the context of biojet fuel production as reducing the length of fatty acids may increase the fraction of molecules in the jet range.

While all three reactions take place during deoxygenation, the reaction conditions can be adjusted to favour either hydrodeoxygenation (HDO) or decarboxylation/decarbonylation (DCO). This has considerable significance for a refinery from an economic and operational point of view as it influences hydrogen consumption, product yield, catalyst inhibition, off-gas composition and the heat balance (Egeberg et al., 2010).

Achieving hydrodeoxygenation through the addition of hydrogen may not be desired when a refinery does not have excess hydrogen available. In addition, the cost of hydrogen and the impact of HDO versus DCO on the carbon intensity of the final fuels through life cycle assessment and the source of imported hydrogen will also have to be considered. Although the addition of hydrogen in the hydrotreater automatically appears to favour hydrodeoxygenation, this is not the case under all circumstances. For example, the choice of catalyst could impact the selectivity of HDO versus DCO, as well as the temperature, pressure and space velocity within the hydrotreater (Al-Sabawi & Chen, 2012; De Paz Carmona et al., 2019; Donnis et al., 2009).

Previous work has shown that triglyceride deoxygenation can be manipulated to mainly proceed through either the HDO; HDO and DCO, or the DCO pathways by varying the type of catalysts while maintaining identical reaction conditions (Zeuthen & Rasmussen, 2016). Other work has shown that NiMo catalysts favour the DCO pathway, while a bimetallic NiCu catalyst favoured the HDO pathway (Vonortas & Papayannakos, 2014). When the temperature is decreased, exothermic reactions, e.g. HDO, are favored while endothermic reactions, e.g. DCO, are inhibited. Related work has shown that increasing the pressure inhibits the DCO pathway while favoring the HDO pathway (Jęczmionek & Porzycka-Semczuk, 2014).

While most current commercial HEFA production removes oxygen through the addition of hydrogen, other technology variations are being commercialized that achieve deoxygenation without the addition of hydrogen, e.g. SBI Bioenergy. However, it should be noted that these pathways require separate ASTM D7566 certification as the current HEFA-SPK pathway only covers biojet production using hydrogenation.

## 5.1.2 Feedstocks and Pretreatment

Any type of lipid can be used to produce HEFA, generally referred to as fats, oils and greases (FOGs). Although pure vegetable oils from any source can be used, typically there are differences in the price of these oils. Table 7 shows prices for a number of different lipid feedstocks. However, an equally crucial element is the "sustainability" and the overall carbon intensity of making the feedstock. Not only does vegetable oil utilization come into competition with food, but the source of oil will impact a fuel life cycle assessment which has a direct impact on the carbon intensity of the final fuel.

*Table 7 Average annual prices ($US/tonne) of oleochemicals/lipid feedstocks, 2016-2019*

| Oleochemicals/lipid feedstocks (location) | 2016 | 2017 | 2018 | 2019 (Jan-Oct) |
|---|---|---|---|---|
| Canola oil (Port of Vancouver)[1] | 738 | 791 | 781 | 745 |
| Soybean oil (any origin in the US)[2] | 814 | 850 | 789 | 758 |
| Palm oil (Malaysia, c.i.f. N.W. Europe)[2] | 735 | 750 | 638 | 576 |
| Rapeseed oil (Rotterdam)[2] | 827 | 879 | 820 | 849 |
| Sunflower oil (Gulf of Mexico)[2] | 867 | 817 | 765 | 734 |
| Beef tallow, packer (Chicago) | 638 | 682 | 556 | - |
| Yellow grease (used cooking oil) (Missouri River) | 505 | 524 | 408 | - |

[1] *Canola Council of Canada, 2019. Statistics, current canola oil, meal and seed prices. https://www.canolacouncil.org/markets-stats/statistics/current-canola-oil,-meal,-and-seed-prices/*
[2] *Indexmundi, 2019. Commodity prices. https://www.indexmundi.com/commodities/*
[3] *The international Magazine of Rendering, 2019. US Market Report. https://rendermagazine.com/wp-content/uploads/2019/07/Render_Apr19.pdf*

In addition, vegetable oils contain different amounts and types of fatty acids which differ in chain length and number of double bonds. This will have an impact as fatty acids with double bonds will require increased hydrogen and this will have an impact on costs associated with hydrogen use. Also, fatty acids have chain lengths between C8 and C24 with the majority of fatty acids in canola oil C18 while the fatty acids in coconut oil are mostly C12 (Giakoumis, 2018). This is important as vegetable oils containing fatty acid chains in the jet range will theoretically produce a larger jet fraction.

In addition to containing water and oxygen, bio-based feedstocks typically contain alkali metals such as Mg, Na, K, Ca and contaminants such as chlorides and phosphorous (Marker, 2005). As contaminants such as metals can potentially cause deactivation of catalysts, they have to be removed prior to co-processing (Marker, 2005).

A number of different pretreatment steps can be used to remove potential contaminants from feedstocks before insertion into a refiner. These include hydrocyclonic removal of particles, desalting, acid washing and ion exchange or fixed guard beds for contaminant removal prior to feeds entering a reactor (Marker, 2005).

## 5.1.3 Production of biojet fuel *via* the HEFA process

The main product derived through the HEFA process is renewable diesel and, under normal processing conditions, only about 15% of the total liquid yield consists of biojet unless further cracking takes place to generate smaller hydrocarbons in the jet range (M N Pearlson, 2011). However, as significant policy incentives are available for the production of renewable diesel, the majority of HEFA producers sell all of their product as renewable diesel, without separating out the jet fraction.

After the initial deoxygenation step in the first reactor, long-chain, paraffinic hydrocarbons

are formed. In order to improve the cold-flow properties of the fuel, isomerization is performed in the second reactor. As rearrangement reactions are required, some hydrocracking takes place in this reactor to produce lighter hydrocarbon fuel molecules. The severity of the isomerization step can be varied depending on the fuel requirements with companies such as Neste varying the cloud point between -5°C and -40°C (Neste Corporation, 2015).

These light hydrocarbons have a lower value, particularly in areas such as the EU where there is limited demand for gasoline blending components. Some workers have argued that relaxing the severity of the isomerization can produce high jet yields without producing a large fraction of lights, if the freezepoint specification of the HEFA is relaxed. They showed that, at lower than 50% blends with conventional jet fuel, the overall freezepoint specification can still be met (Starck et al., 2016).

The need for additional infrastructure and processing means that biojet fuel production is more expensive than the production of renewable diesel. Many policies provide incentives for renewable diesel production, and in the US, stackable incentives from the US RFS and the California LCFS means that renewable diesel is a more lucrative product. Thus any future policies that are used to promote biojet fuels have to take this competition into consideration through the use of mechanisms such as a fuel multiplier.

As noted in the executive summary, additional infrastructure and processing, at relatively low cost, can be introduced at current HEFA facilities to immediately produce a billion litres of HEFA-SPK. However, the key driver to achieve this will be policies that target biojet fuel production.

Previous work has shown the product distribution of a HEFA facility based on maximum distillate (diesel and jet) versus maximum jet production, (Table 8) (based on Pearlson et al. 2013).

*Table 8 Mass-based product yields in the production of HEFA comparing maximum distillate versus maximum jet (M. Pearlson et al., 2013)*

| Product profiles (wt%) | Maximum distillate | Maximum jet |
|---|---|---|
| Soybean oil (pounds) | 100.0 | 100.0 |
| Hydrogen | 2.7 | 4.0 |
| Total In | 102.7 | 104.0 |
| Water | 8.7 | 8.7 |
| Carbon dioxide | 5.5 | 5.4 |
| Propane | 4.2 | 4.2 |
| LPG | 1.6 | 6.0 |
| Naphtha | 1.8 | 7.0 |
| Jet | 12.8 | 49.4 |
| Diesel | 68.1 | 23.3 |
| Total Out | 102.7 | 104.0 |

The maximum distillate scenario has about 13% jet fuel, 1.6% LNG, and 1.8% naphtha co-products. However, to achieve maximum jet fuel production (50%) increases the LNG and naphtha to 6.0% and 7.0% and uses more hydrogen (M. Pearlson et al., 2013). It should be noted that maximizing jet production increases the potential price of the jet fuel due to higher volumes of lower value products that result in lower overall revenue. Although, based on techno-economic analysis a gate price of $1-$1.16 per gallon was determined, the additional cost for jet fuel would be $0.07-0.08 per gallon based on increased hydrogen required and reduced yield of diesel (M. Pearlson et al., 2013). These authors also showed that feedstock cost is the most significant portion of fuel cost, although facility size,

financing and capacity utilization also influence production costs.

As it is easier and cheaper to produce renewable diesel, the production of these two streams based on the HEFA process are in competition. Consequently, minimum amounts of biojet fuel are produced. However, policies could be introduced, such as a fuel multiplier, to make biojet fuel production more competitive with renewable diesel production (N. Pavlenko et al., 2019).

Although World Energy has been producing biojet fuels routinely as a fraction of their product slate, their major fuel product is renewable diesel. The biojet fraction is separated and processed to comply with ASTM D7566 specifications and sold to airlines. Current total production of biofuel of this facility (renewable diesel and biojet) is reported to be 38 million gallons per year[9], but expansion is underway to increase the total production to 306 million gallons per year with expected completion by 2022.[10] Although the actual biojet fuel production at World Energy is not clear, it is likely to be about 15% of capacity.

In 2019, Neste carried out additional fractionation and processing to produce 100 tonnes (125 million litres) of HEFA-SPK. Current upgrades and construction at the Neste Singapore facility to establish permanent infrastructure for biojet production will mean that Neste could produce 1 million ton/a (1.25 billion litres) of biojet fuel routinely by 2023 at the Singapore facility, with another 450 kton/a produced at the Rotterdam facility (Fernandes, 2020). Texmark Chemicals (US) also imports renewable diesel from Neste into the US where it is then fractionated to produce a biojet fraction[11].

### 5.1.4 High freezepoint HEFA as a biojet fuel

To expand the availability of biojet fuels, in 2017 Boeing and Neste launched an ASTM for high freezepoint HEFA (HEFA+) to become certified as an approved biojet fuel that can be used in blends with conventional jet fuel (N. Pavlenko & Kharina, 2018). This would immediately expand the potential volumes of biojet fuel available as it would allow renewable diesel to be used in blends with conventional jet fuel without a fractionation step. However, this application has stalled in the ASTM process and it is not clear when it is expected to be completed.

### 5.1.5 Other technologies based on lipid feedstocks

There are a number of other oleochemical based technologies, (e.g. using lipids as a feedstock) to make biojet fuels. While current HEFA technologies involve hydrotreating to remove oxygen from the feedstock, companies such as SBI Bioenergy and Forge Hydrocarbons use decarboxylation to remove oxygen in the absence of hydrogen.

It should be noted that the ASTM D7566 standard is limited to the described process in that particular Annex. For the case of HEFA-SPK, hydrotreatment has to take place as part of the process. Therefore, technologies that do not fall within the scope of the description in the

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[9] https://labusinessjournal.com/news/2020/jan/22/world-energy-gets-11-million-state-tax-credit/
[10] https://www.icao.int/environmental-protection/Pages/SAF_Stocktaking.aspx
[11] http://biomassmagazine.com/articles/16539/epa-approves-rfs-fuel-pathway-filed-by-texmark-neste

ASTM D7566 Annex must apply separately for ASTM certification (ASTM, 2017).

SBI Bioenergy is currently in the pipeline for ASTM certification (Csonka, 2020) with the company using a unique approach to drop-in biofuel production (Figure 8). Fatty acid methyl esters (FAME, biodiesel) are produced from lipid feedstocks in the same way that biodiesel is produced, with glycerin as a byproduct, and this is followed by catalytic deoxygenation that does not require any hydrogen.

SBI's continuous flow process is called "Process Intensification and Continuous Flow-Through Reaction" (PICFTR) and uses proprietary catalysts, called "Continuous Green Catalysts" (CGCTM). They are reported to be inexpensive, have a long active life and are reported to be easy to regenerate. It has been claimed that CGCTM catalysts function in a way that does not require the addition of hydrogen, consumable chemicals, or water to the reaction, and therefore does not generate any waste stream.[12] However, the SBI process involves production of fatty acid methyl esters using methanol and this will impact the life cycles emissions.
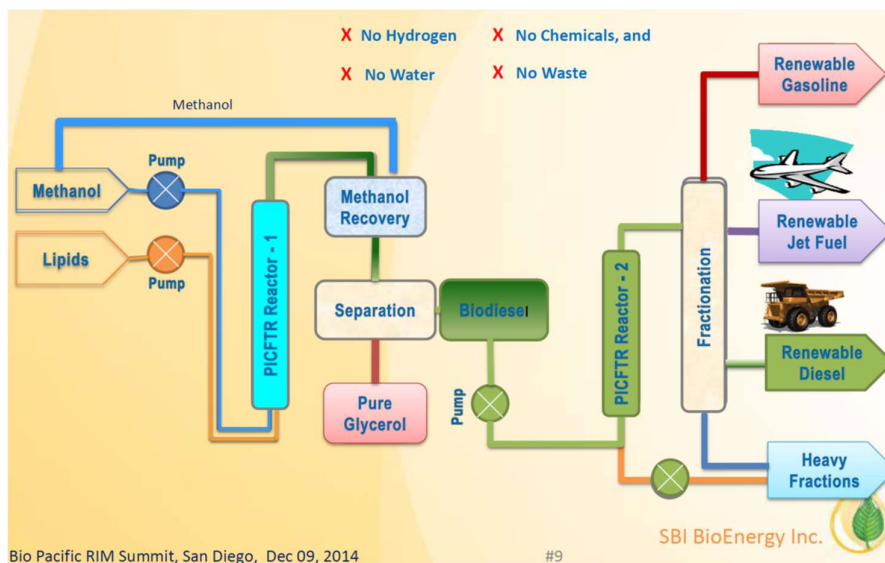


*Figure 8. Illustration of the SBI Bioenergy Technology (https://www.sbibioenergy.com/about)*

In 2020, IHI received ASTM D7566 approval (Annex 7) for their biojet fuel based on hydrotreatment of algal lipids produced by *Botryococcus braunii*, an algae with an exceptionally high growth rate and high hydrocarbon oil content. IHI's fuel is based on the hydroprocessing of oil from *Botryococcus braunii* (Bb oil)[13].

## 5.1.6 Economics and sustainability of HEFA-SPK production

The price of HEFA-SPK in the market as at 18 September 2020, according to Argusmedia, was $2124 per tonne, as compared with conventional jet fuel which cost $329 per tonne

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[12] https://www.sbibioenergy.com/about
[13] https://www.greencarcongress.com/2020/05/20200514-ihi.html

(Argusmedia, 2020). Information on contracts and prices are not generally available publicly although several technoeconomic analyses are available in the literature that indicates minimum fuel selling prices (MFSP) for HEFA technologies based on different feedstocks. It should be noted that the MFSP is a break-even price based on a net present value (NPV) of zero. Previous work has suggested a price range of $825-1550 for HEFA based on yellow grease, $988-1775 based on tallow, and $1086-2000 based on soybean oil, reflecting the difference in feedstock price (Bann et al., 2017). As indicated by this work, feedstock can amount to up to 80% of the cost of HEFA. Thus, lower costs should be achieved by using cheaper, waste feedstocks. Although Jatropha oil has received a lot of attention as a sustainable feedstock, Neuling and Kaltschmitt calculate a high MFSP of $2360 for this feedstock and a MFSP, based on palm oil, of $1050 (Neuling & Kaltschmitt, 2018). However, the ongoing perception that most palm oil is "non-sustainable" makes it unlikely that airlines will approve of palm oil-based biojet fuel, in spite of the sustainability certification of some companies by the Roundtable on Sustainable Palm Oil (RSPO).

In addition to the MFSP of biojet fuels, the overall sustainability and specifically the carbon intensity of the fuel is an important metric that contributes to the value of the biojet. Work has been done on the impact of using renewable hydrogen through electrolysis on sustainability, but analysis has shown that this increases the cost of the fuel compared with hydrogen sourced through steam methane reforming (Müller-Langer et al., 2019)

Thus, policies that place a price on carbon will be important. In addition, under ICAO's Carbon Offsetting and Reduction Scheme (CORSIA), airlines can use sustainable aviation fuel to reduce offset obligations and this is linked to potential emission reductions. It is worth noting that ICAO has published default carbon intensity values or Life cycle Emission factors (LSf (gCO$_2$e/MJ) for different technology and feedstock pathways consisting of the core LCA plus induced land-use change (ILUC) (ICAO, 2019). As expected, HEFA derived fuels based on waste feedstocks have the lowest carbon intensities, including tallow (22.5 gCO$_2$e/MJ), UCO (13.9 gCO$_2$e/MJ), palm fatty acid distillate (PFAC) (20.7 gCO$_2$e/MJ), and corn oil (17.2 gCO$_2$e/MJ) (using 89 gCO$_2$e/MJ as a baseline for conventional jet fuel). Vegetable oil derived HEFA LSf values are much higher, including soybean oil (USA) (64.9 gCO$_2$e/MJ), soybean oil (Brazil) (67.4 gCO$_2$e/MJ) and rapeseed oil (EU) (71.5 gCO$_2$e/MJ). Where palm oil is used as a feedstock, production using an open pond system has a carbon intensity higher than conventional jet fuel at 99.1 gCO$_2$e/MJ. However, closed pond palm oil production does achieve a reduction in carbon intensity (76.5 gCO$_2$e/MJ) against the baseline of 89 gCO$_2$e/MJ.

It should be noted that refineries can achieve carbon intensities that differ from default values by carrying out their own life cycle analysis based on procedures determined by ICAO.

### 5.1.7 Opportunities and challenges for the oleochemical pathway

As the HEFA technology is fully commercial, there is only limited scope for significant improvement and cost reduction from a technology perspective. Consequently, feedstock is the largest operational expense for a facility based on lipid feedstocks and the biggest area for potential cost reduction. As vegetable oils (Table 7) have a higher price than jet fuel (~$650/metric ton – Jan 2020) this is a key opportunity area for lowering the price of the final product. Unfortunately, cheaper vegetable oil feedstocks such as palm oil have significant sustainability issues and most airlines refuse to use any biojet fuel from palm oil due to the stigma associated with this crop. The relatively low cost of palm oil is primarily due to the high productivity of the crop. Currently, many palm oil producers are trying to improve the sustainability of their product under the umbrella of the Roundtable on Sustainable Palm Oil

(RSPO)[14].

More recently, HEFA derived jet fuel producers have increasingly targeted waste feedstocks to reduce feedstock cost and simultaneously improve the carbon intensity of their fuels (which should add additional value). Feedstocks such as used cooking oil (UCO), tallow, fish waste, brown grease, etc., have been used. However, in many cases, new supply chains had to be established, e.g. collection of UCO. In addition, these feedstocks can contain contaminants as well as a high free fatty acid content. Thus, more extensive pretreatments are likely to be required to prevent downstream catalyst inhibition and other impacts such as corrosion due to the low pH of some of these feedstocks. However, as existing companies are expanding significantly, the availability of waste feedstocks will become challenging.

Another feedstock with good sustainability is tall oil which is currently used by Preem (Sweden) to produce co-processed drop-in biofuels (Ecofys, 2017). Other, alternative feedstocks are also under development as more sustainable options that don't compete with food. These include Brassica carinata, Camelina sativa, Pennycress, Salicornia, tobacco, pongamia, jatropha, etc. In some cases, these feedstocks also have shorter hydrocarbon chains that fall in the jet range, e.g. babassu and coconut. However, these alternative feedstocks are only available in small quantities.

In summary, the HEFA technology offers the opportunity to produce significant volumes of biojet through additional processing at relatively low investment cost at existing facilities (without sacrificing yields in order to maximise biojet fuel production). However, the existing policy framework poses a critical obstacle as HEFA derived renewable diesel is worth more than HEFA biojet, placing these products in direct competition. Unless policies are developed to encourage more biojet production, such as a fuel multiplier, the competition between renewable diesel and biojet will continue to restrict the expansion of biojet fuel based on this technology.

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[14] https://rspo.org/

## 5.2 THERMOCHEMICAL ROUTES FOR BIOMASS-TO-BIOJET

Thermochemical technologies include technologies such as gasification with Fischer Tropsch synthesis and direct thermochemical liquefaction (e.g. fast pyrolysis, catalytic pyrolysis, hydrothermal liquefaction and similar technologies). All thermochemical technologies produce a solid, gas and liquid intermediate, with the ratio of these three fractions varied depending on the conditions used. For the case of gasification, the gas intermediate is of interest for fuel production while the liquid intermediate or biocrude is of interest in the direct thermochemical liquefaction technology. The solid or gas co-products can be utilized in a number of ways, for example burning the char and gas to produce heat and power or using the char as a soil amendment. Figure 9 is a simplified diagram to illustrate the two pathways.
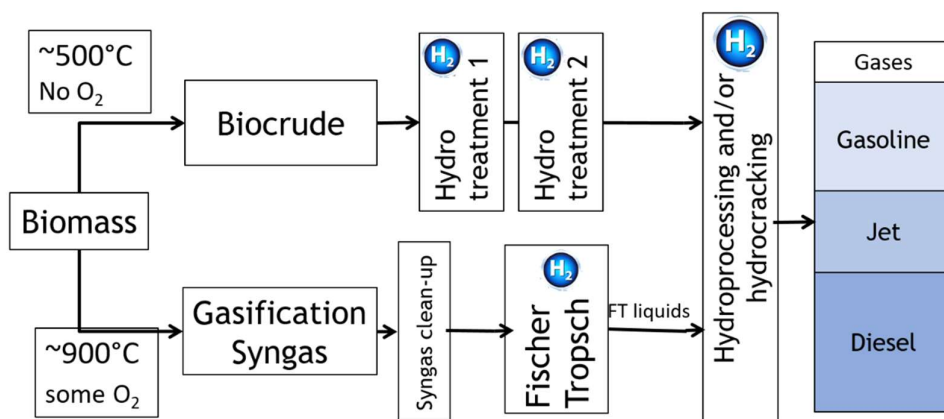


*Figure 9 Schematic of thermochemical conversion routes*

### 5.2.1 Gasification and Fischer-Tropsch synthesis for the production of biojet fuel

Gasification technologies have been used for decades in applications such as heating and power generation. However, its application in drop-in biofuel production using Fischer-Tropsch synthesis has been less common and has been based on feedstocks such as coal and natural gas. Using biobased feedstocks a different set of challenges are introduced which has an impact on the selection of the gasification technology and the type of syngas cleanup and conditioning carried out. While the Fischer-Tropsch synthesis process remains the same at a theoretical level, different technologies are currently being pursued to allow small-scale FT and to try to improve yields.

The characteristics of the biobased feedstock, including oxygen content and types and concentration of contaminants all contribute to a complex process to produce drop-in biofuels such as biojet. As discussed in further detail below, the quality of the syngas is critical for FT synthesis and stricter than for other applications. Consequently, syngas cleanup is a key step to ensure efficient production of liquid fuels. While the choice of gasification technology can reduce the extent of cleanup required, this has to be balanced with the cost of the technology. Plasma gasification produces the cleanest syngas and has flexible feedstock specifications. However, it has the highest operational cost. In contrast, simpler and cheaper gasification technologies produce a lower quality syngas that requires more extensive cleanup. It should be noted that syngas production from natural gas, which requires limited syngas cleanup, can contribute more than 50% of the investment cost and this increases when feedstocks such as biomass are used (Leviness et al., 2014). While individual syngas cleanup technologies do not have significant technical challenges, it can be a very

costly component as multiple cleanup technologies must be used. Finding a balance in terms of quality and cost for each step is essential if a successful pathway to drop-in biofuels is to be established.

The gasification of biomass can generally be viewed as proceeding in four main sequential steps (Karatzos, McMillan and Saddler, 2014a):
1. Drying - moisture is removed from the biomass particles
2. Devolatilization - as the dry particle is heated, it devolatilizes and the resulting volatiles exit the particle and come into contact with oxygen and other gases in the reactor.
3. Combustion - After contacting oxygen ($O_2$ or steam), the volatilized carbon is converted to carbon oxide gases (CO and $CO_2$). An exothermic reaction occurs which, if sufficient oxygen is present, provides enough heat for the last reduction step.
4. Reduction - This step converts the carbon and carbon oxides to the main components of syngas, i.e. $H_2$ and CO. Four main reactions take place during this step:
   o Water Gas         $C + H_2O \rightarrow CO + H_2$
   o Boudouard       $C + CO_2 \rightarrow 2CO$
   o Water-Gas-Shift   $CO + H_2O \rightarrow CO_2 + H_2$
   o Methanation      $CO + 3H_2 \rightarrow CH_4 + H_2O$

The chemical composition of the produced syngas depends on the relative prevalence of the reactions taking place at the reduction step of gasification. For example, when adding steam to the reactor, the water-gas-shift (WGS) reaction is favoured and more hydrogen is generated and which boosts the $H_2$/CO ratio of the resulting syngas. Alternatively, when feeding hydrogen into the reactor favours the methanation reaction and the generated syngas is rich in $CH_4$.

The gasification and Fischer-Tropsch synthesis process produce a blend of Fischer-Trospch liquids which contain a mixture of hydrocarbon molecules that can be fractionated into multiple fuel products including a jet fraction. Gasification combined with FT synthesis was certified under ASTMD7566 in 2009 as an approved biojet fuel pathway. The application at the time was launched by Sasol and was based on coal as the feedstock. However, as the syngas intermediate (prior to FT synthesis) is the same, the certification covers any type of feedstock.

Currently, commercial volumes of biojet based on biomass gasification are not available, although several companies are in the process of constructing commercial-scale facilities. Fulcrum Bioenergy is currently building a facility that will use municipal solid waste as the feedstock. Red Rock Biofuels plans to use woody residues as the feedstock. These facilities use different gasification and Fischer-Tropsch technologies. As other gasification facilities, such as Enerkem, produce methanol and ethanol rather than FT fuels, they have not been covered here.

### 5.2.1.1 Comparison of Gasification reactors

Gasification technologies can be carried out through different reactor configurations that maximize heat transfer through the biomass particles. Although the reactors used for gasification are similar to the ones used for pyrolysis, they typically operate at higher temperatures (>800°C) and pressures from 1 to 50 bar. Four types of reactors can be used for biomass gasification including fixed bed, fluidized bed, entrained flow and plasma gasifiers.

The **fixed bed reactor** is the simplest and most established design and it tends to be found in

older, smaller-scale systems. There are two types of fixed bed reactors and, depending on whether the gases are blowing countercurrent or concurrent to the biomass feed, they are called updraft or downdraft fixed bed reactors. Fixed bed reactors are typically quite simple to build and operate. However, their use is limited by poor heat and mass transfers. They are not suitable for large scale applications.

In **fluidized bed gasifiers,** the bed particles are composed of very hot and small inert particles which greatly improve the heat transfer throughout the gasifying biomass particles. There are two types of fluidized bed reactors, the Bubbling Fluidized Bed (BFB) and the Circulating Fluidized Bed (CFB) reactor. Compared to fixed beds, fluidized beds generally have higher carbon conversion efficiencies and they tend to be more easily scaled-up (Swanson et al., 2010). However, fluidized bed reactors produce relatively high levels of tar and require more extensive cleanup of the syngas.

In an **entrained flow reactor,** the feed is in the form of very fine particles which are entrained into a high-velocity stream of air or oxygen. The advantage of entrained flow gasifiers is a clean and tar-free syngas due to thermal cracking taking place at the higher temperatures. Conversions close to 100% can be achieved.

Although **plasma gasifiers** have a similar structure to entrained flow reactors, they operate using plasma torches at extremely high temperatures of 1500°C – 5000°C (atmospheric pressure). Although they are costly to operate, they produce a very high-quality syngas which needs little further cleanup. The biomass is converted to syngas and the inorganic ash is vitrified to inert slag. Projects that have proposed using a plasma gasifier (e.g. Solena) have been based on municipal solid waste as a feedstock[15]. However, the high cost has proven prohibitive and the planned project was cancelled. Supplying energy for the plasma torches can require 40-50% of the total electrical power generated, while the technology also has high maintenance and operational cost (Shahabuddin et al., 2020).

The selection of a gasifier technology is based on obtaining a balance between a number of factors, such as investment and operating cost, suitability for the targeted feedstock, and importantly, the quality of the syngas produced. Table 9 lists key advantages and disadvantages of the gasifier types.

*Table 9 Some advantages and disadvantages of gasifier technology types(Molino et al., 2016)*

| Gasifier type | Advantages | Disadvantages |
|---|---|---|
| Fixed bed | **Simple to build and operate** **Good for small scale applications** | **Poor heat transfer** **High tar formation.** **Not suitable for large scale** |
| Fluidized bed | **Flexible feedstock requirements** | **Extensive syngas cleanup required** |
| Entrained flow | **Low tar formation & clean syngas** | **High plant cost** **High maintenance cost** **Strict feedstock size requirement** |
| Plasma | **High quality syngas** **Flexible feedstock requirements** | **High operating cost** |

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[15] The Solena project in England was proposing to use a plasma gasifier, but the project was cancelled. The original gasifier chosen by Fulcrum Bioenergy was a plasma gasifier, but the commercialisation is taking place with a bubbling fluidized bed reactor.

### 5.2.1.2 Feedstock specifications for different gasifiers

Different types of gasification technologies each have their own feedstock specifications. These are summarised in Table 10 with strict feedstock specifications such as small particle size and low moisture content increasing the cost of feedstock preparation.

*Table 10 Feedstock specifications for different types of gasification technologies*

| Gasifier type | Feedstock specifications |
|---|---|
| Fixed bed | Particle size: 1-50 mm<br>Moisture content: < 40%<br>High tolerance for low-quality feedstocks |
| Bubbling Fluidized Bed | size: <50 mm,<br>moisture: < 45%<br>ash content: < 5%<br>Medium tolerance for low-quality feedstocks |
| Circulating Fluidized Bed | size: <10 mm,<br>moisture: <45%<br>ash content: < 5%<br>Medium tolerance for low-quality feedstocks |
| Entrained Flow | size: <1mm,<br>moisture: < 15%<br>Low tolerance for low-quality feedstocks |
| Plasma | size: very flexible<br>moisture: flexible<br>High tolerance for low-quality feedstocks |

Entrained flow gasifiers feedstock specifications are very strict as a very small particle size (<1mm) is required as well as low moisture content (<15%). This gasification technology has been successfully used for coal feedstocks where pulverization can achieve these small particle sizes. For biomass feedstocks, achieving this size of feedstock will require extensive pretreatment and will probably be very costly.

The company KIT in Germany ("bioliq" technology)[16] use entrained flow gasifiers with pyrolysis slurries, bio-oil and char combined, as an alternative to mechanically processes the biomass to feedstock specifications. This approach offers the opportunity for large-scale gasification facilities based on densified biomass pyrolysis liquids that can be produced at distant locations. The opportunity for large facilities and economies of scale is generally limited by the low energy density of feedstocks such as wood residues. Although these feedstocks are not economical to transport over great distances the conversion of biomass into high-energy-dense pyrolysis liquids can facilitate large-scale facilities based on a decentralized configuration (Eberhard et al., 2020).

### 5.2.1.3 Municipal solid waste (MSW) as a feedstock for gasification

An under-utilized feedstock source for gasification-based biofuel production is municipal solid waste which offers low cost and high sustainability. However, this feedstock can contain high levels of contaminants, including corrosive and toxic components such as carbonyl sulfide (COS), HCl, $SO_2$, and $H_2S$, and often requires extensive syngas cleanup (Pieta et al., 2018). Before gasification, MSW must be separated based on combustible and non-combustible

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[16] https://www.bioliq.de/english/55.php

components. The organic composition can vary from 5-60%, and this will have an impact on the final carbon intensity of fuels and syngas cleanup.

The New Energy and Industrial Technology Development Organization (NEDO) in Japan have developed biojet production using algae as a feedstock, integrated with gasification[17].

### 5.2.1.4 Syngas cleanup and conditioning

Syngas cleanup has been identified as one of the significant challenges for production of liquid fuels from biomass. As mentioned earlier, the Fischer-Tropsch catalyst can only deal with very low levels of contaminants. For example, syngas from biomass can contain hydrogen sulfide ($H_2S$), carbonyl sulfide (COS), ammonia ($NH_3$), hydrogen cyanide (HCN), hydrogen chloride (HCl), alkali metals, particulate matter, and tar (T. R. Brown, 2015). Biomass from different sources, such as agricultural residues, forest residues, municipal solid waste, and even from different tree species, could contain different types of contaminants at different levels. This will likely require multiple stages of cleanup and additional infrastructure.

The characteristics of biobased feedstocks make them particularly prone to high levels of tar formation due to polymerisation reactions of the oxygen-containing molecules. In addition, biomass has high levels of alkali metals, nitrogen, sulfur, and other compounds. In applications such as drop-in biofuel production and fuel cells, contaminants can inhibit downstream catalysts, while tar can block piping.

As coal can contain similar impurities, cleanup technologies for many of these contaminants are commercially available. However, iron and cobalt catalysts, used in the FT reactor, have different sensitivity towards common contaminants. Most coal-based facilities have operated with iron catalysts, while biomass-based facilities have operated on cobalt catalysts (Lillebø et al., 2013). Alkali metals have a detrimental effect on cobalt catalysts while having a negligible or even beneficial effect on iron catalysts. Cobalt catalysts are also very sensitive toward $NH_3$ and HCN while iron catalysts are largely unaffected by these contaminants (Lillebø et al., 2013)

Every syngas cleanup strategy has to be designed based on the nature of the feedstock and the likely formation of contaminants based on the type of gasification technology. The requirements of the syngas for its downstream application in FT synthesis and purity of syngas must be considered as well as the type of FT catalyst used. Lastly, the integration and sequence of different cleanup technologies must be considered and optimised (Sikarwar et al., 2017). As some cleanup technologies contain catalysts, the impact of contaminants on such catalysts must be considered. Ideally, a refinery based on gasification should be designed with a specific feedstock in mind (De Klerk, 2016) as different feedstock characteristics require different gasification conditions or gas cleanup processes. For example, feedstocks such as agricultural residues will contain much higher particulate/ash content and will require more extensive cleanup of these contaminants (Lillebø et al., 2013).

The "clean up" of syngas based on gasification of biomass is one of the key aspects of biofuel production using this technology. It is the most expensive investment cost after the gasification itself. Failure to carry out the cleanup to a sufficiently high standard can also be

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[17] https://www.youtube.com/watch?v=MdcK7tRNf-8

costly as downstream catalysts may be deactivated.

Raw biomass syngas is recovered along with numerous impurities such as small char particles, tar vapors as well as volatile nitrogen and sulfur compounds. Char is entrained in the syngas and it is comprised of non-volatilized biomass as well as ash. The tar component is formed during the polymerization of biomass vapors and it can stick to reactor walls and catalysts causing clogging and deactivation. The types of tar compounds formed during biomass gasification vary depending on the temperature in the reactor with higher temperatures favoring heavier (larger) compounds (Ghosh, 2018).

Sulfur and nitrogen gases are derived directly from the biomass feed and these components are deleterious to downstream processes as they cause NOx and SOx emissions upon combustion. They can also "poison" the Fischer-Tropsch catalysts (Dayton et al., 2011).

When the syngas is simply burned in heat and electricity applications, these impurities are of lesser concern. However, when the syngas is used for Fischer-Tropsch (FT) synthesis, exhaustive cleanup is required. For FT synthesis the particulate matter must be less than 0.03 mg/Nm3, compared with internal combustion (IC) engine applications which permit particulates, tars and acids at concentrations below 50 mg/Nm3. In most cases, the raw syngas leaving the gasifier has contaminant concentrations that typically exceed these limits by some orders of magnitude. This is especially true for fluidized bed gasifiers which, when compared to entrained flow gasifiers, operate at lower temperatures and circulate the gas through beds that are rich in fine char solids. As summarised in Table 11, a Circulating Fluid Bed (CFB)-derived syngas typically contains about 10,000 mg/Nm$^3$ of either char or tar particles, Bubbling Fluidised Bed (BFB) up to 43,000 mg/Nm$^3$ and downdraft fixed beds as much as 30,000 mg/Nm$^3$.

*Table 11 Char and Tar content of biomass syngas from different reactor types (Karatzos, Mcmillan et al., 2014a)*

| Reactor type | Tar content (mg/Nm3) | Particulate/Char content (mg/Nm3) |
|---|---|---|
| Updraft | 50,000 | nd |
| Downdraft | 1,000 | 9,300 – 30,000 |
| BFB | 10,000 | 1,040 – 43,610 |
| CFB | 10,000 | 1,700-13,100 |
| Specification for IC engines | <50 | <50 |
| Specification for FT synthesis | <0.02 | < 0.02 |

Although there are various ways to reduce the accumulation of these contaminants during gasification, this typically involves much higher temperatures and come at a cost. Therefore, thorough cleanup of the raw syngas must be carried out. Table 12 lists types of impurities and potential cleanup methods. This typically involves various sequential steps that follow the gasification reactor including gas cyclone removal of most of the particulate matter above 10 μm and removal of the smaller particles by methods such as wet scrubbers or electrostatic precipitators.

*Table 12. Impurities in syngas and possible removal techniques (Ghosh, 2018)*

| Impurities | Issues | Treatment method |
|---|---|---|
| Particulates (ash, unconverted tar) | Erosion | Cyclones, Electrostatic precipitators, barrier filters |
| Tars (vapours and liquids) | Clogging and deposition, corrosion | Wet scrubbers, Electrostatic precipitators, barrier filters, catalytic beds |
| Alkali metals (Na/K salts) | Hot gas corrosion | Cooler, scrubber, filter |
| N (ammonia/HCN) | Combustion NOx | Wet scrubber |
| Halides (Cl, F) | Catalyst poisoning, corrosion | Scrubber, activated carbon |
| Sulphur (H2S, COS, SO2) | corrosion | Scrubber, activated carbon, Fe |

Gasification can be carried out in an environment of air, oxygen, or steam. The introduction of steam during gasification reduces the buildup of tar by reforming it to $H_2$ and CO. However, steam can act as a heat sink and significantly compromise the heat balance and overall efficiency of the gasification plant. Higher air to fuel ratios result in oxidative conditions and they can be beneficial in reducing the char and tar content of syngas. However, these conditions favour full oxidation of gases to $CO_2$, thus recovering lower CO concentrations. Pure oxygen can be used instead of air in order to improve the specificity of the gasification reaction while also reducing the nitrogen contaminants coming from atmospheric air. It should be noted that the isolation and purification of oxygen weigh significantly on the economics of the facility (Bain & Broer, 2011; Mueller-Langer et al., 2007; Swanson et al., 2010). A balance between these trade-offs must be found to achieve the optimal quality syngas for each given application. Even if the gasification process is optimised to minimize syngas impurities by adjusting gasification conditions, some cleanup is always needed. As mentioned earlier, syngas cleanup is one of the most expensive steps of a gasification biofuel platform.

### 5.2.1.5 Adjustment of the $H_2$/CO ratio in biomass-derived syngas

For the synthesis of liquid hydrocarbon fuels, a ratio of H2/CO of 2:1 is usually ideal. Generally, biomass-derived syngas has a low H2/CO ratio (0.6-0.8) and therefore additional hydrogen must be added to the syngas prior to synthesis. Unless an iron catalyst is used which has water-gas-shift capability to allow adjustment of the H2 level during the FT process (Lillebø et al., 2013). As cobalt catalysts do not display WGS activity, adjustment of the ratio must be carried out separately.

Adjustments of the H2/CO ratio can take place through addition of steam within the gasifier, with a dedicated WGS reactor and/or production of hydrogen from steam reforming of natural gas or the C1-C4 product from the FT process. It should be noted that the addition of hydrogen will also increase the amount of CO2 in the syngas (Lillebø et al., 2013).

### 5.2.1.6 Fischer-Tropsch synthesis

The company Sasol in South Africa has been using FTS for decades to produce fuels from coal. The process has undergone continued investigation and optimisation and has been adapted for a diversity of feedstocks. The production of liquid hydrocarbon fuels from biomass through this process has received significant attention in the development of drop-in biofuels. However, the complexity of biomass and various challenges has somewhat stymied the commercialization of biofuels through this pathway.

The Fischer-Tropsch process uses synthesis gas (syngas - $H_2$ & CO) derived from any source including biomass, coal or natural gas to produce a range of hydrocarbon molecules for drop-

in biofuels, including a biojet fraction. The gas product formed after gasification contains multiple compounds that have to be removed, treated and conditioned so that only $H_2$ & CO remain. The FTS reaction takes place over specialized catalysts and is essentially a dehydration reaction (Swanson et al., 2010).

Fischer-Tropsch reactors have different designs and configuration and three different reactor types have been used commercially, fixed bed, fluid bed, or slurry bubble-column reactors. As FT synthesis reactions are highly exothermic, the reactor performance with respect to heat removal, control of the catalyst surface temperature, and intraparticle mixing of reactants and products are important parameters (Lillebø et al., 2013).

### 5.2.1.7 Catalysts used in FT synthesis

Current industrial FT technology is generally limited to two types of catalysts, Fe and Co. The process description for biojet fuel through FTS in ASTM D7566 (Annex 1) refers to Fe and Co catalysts and FTS biojet production using other types of catalysts might not be covered under the ASTM specification as it is currently written.

The choice of catalyst is important for effective Fischer-Tropsch Synthesis (FTS). The group VIII transition metal oxides are regarded as good CO hydrogenation catalysts, based on the three main performance characteristics of lifetime, activity and selectivity. The lifetime of the catalyst largely depends on the quality of the syngas. Prime quality natural gas-derived syngas catalysts have been reported to last up to 3-5 years and the most active metal catalysts for FTS, ranked in order of activity, are Ru>Fe>Ni>Co. Ruthenium catalysts are the most active, but they are considerably more expensive than the iron catalysts and about 100 times more expensive than Nickel and Cobalt. Nickel is a methanation catalyst and does not have the broad applicability in FTS that other FT catalysts have. Iron has Water-Gas-Shift (WGS) activity but is an acidic catalyst and promotes carbon deposition and coking, resulting in lower yields and reduced catalyst lifetimes. Cobalt is more alkaline than Fe, and although about 200 times more expensive, it produces higher yields and provides for longer catalyst lifetimes. However, it has low WGS activity and needs a separate WGS step to boost the H2/CO ratio of the feed to >2. Finally, as well as being highly active, a catalyst must also be selective in promoting the reactions that are most desirable. For example, Iron/manganese/potassium catalysts have shown high selectivity for C2-C4 olefins(Bain & Broer, 2011).

Table 13 shows a more detailed comparison of Co and Fe catalysts.

*Table 13 Comparison of cobalt and iron catalysts for FT synthesis (Snehesh & Dasappa, 2016)*

| Parameter | Co- catalyst | Fe catalyst |
|---|---|---|
| Operating temperature | 190-240oC<br>Used only in LTFT reactors<br>High temperature increases CH4 selectivity and causes catalyst deactivation | 200-350ºC<br>Operates in HTFT and LTFT reactors |
| Feed gas | Syngas with H2/CO ratio in the range of 2.0-2.3 due to very low WGS activity | Flexible H2:CO ratio in the range 0.5-2.5 due to high WGS activity |
| Activity | More active at higher CO conversions, i.e. lower space velocities | More active than Co at higher space velocities |
| Product spectrum | Primary products are n-paraffins with marginal production of olefins | Primary products n-paraffins with considerable production of olefins |
| Promoters | Noble metals (Ru, Rh, Pt, Pd); Oxide promoters (ZrO2, La2O3, CeO2) | Alkali metals (Li, Na, K, Rb, Ca) |
| Life & cost | Longer life time, more expensive | Lower life time, less expensive |

Two categories of FTS conditions are used, high temperature FTS (HTFT) (>320ºC) and low temperature FTS (LTFT) (170-270ºC) (De Klerk, 2016). Although Fe catalysts are able to

operate successfully at both high and low-temperature conditions, Cobalt catalysts are only used at low-temperature conditions.

### 5.2.1.8 The basic FT reaction

The basic reaction is represented in the equation below:

$$CO + 2.1\ H_2 \rightarrow -\ (CH_2) - +\ H_2O\ (\Delta Hr = 227°C)$$
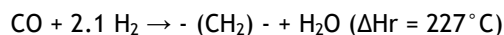
As an exothermic reaction, about 165 kJ/mol of CO is released during synthesis. The catalyst surface acts as an "anchor" upon which the carbon monoxide and hydrogen adsorb, followed by chain growth. The chain growth begins once the carbon monoxide has been broken down, enabling the coupling of carbon and hydrogen and the separation of oxygen (which leaves as a water molecule, i.e. dehydration). Chain growth continues by adding further CO and $H_2$ until the newly formed hydrocarbon molecule is desorbed from the catalyst surface. From this simplified explanation it might be assumed that only straight-chain paraffins are formed in FT synthesis. However, in reality, the synthesis process produces a more complex mixture of molecules.

### 5.2.1.9 FT products and distribution

The FT polymerization reaction is described by the Anderson-Shulz-Flory (AFS) distribution model where the distribution depends on parameter α, the chain growth probability factor[18]. This parameter can be "tuned" by the temperature, syngas composition, pressure, catalyst choice and the presence of promoters. An α value close to 1 will result in a high production of long-chain hydrocarbons (>C20), while a lower α value (e.g. 0.80) will result in a majority of products <C10 (See Table 14 below). The optimal α value for jet-range products is 0.90.

*Table 14 Comparison of product distribution after the FT synthesis as a function of the chain growth probability factor α (Hannula & Kurkela, 2013)*

| α value | Products <C10 (wt%) | Products C10-C20 (wt%) | Products >C20 (wt%) |
|---------|---------------------|------------------------|---------------------|
| 0.80 | 62.4 | 31.8 | 5.8 |
| 0.90 | 26.4 | 37.1 | 36.5 |
| 0.95 | 8.6 | 19.8 | 71.7 |
| 0.99 | 0.4 | 1.4 | 98.2 |

The Fe-based process can further be divided into two types, high temperature (HTFT) and low temperature (LTFT) conditions. The product types and distribution vary depending on the different catalyst or processing conditions (Table 15). As shown, the HTFT conditions produced both oxygenates and aromatics, although the HTFT produce more oxygenates and aromatics. In addition, the major product at high temperatures is alkenes (>50%), while straight chain paraffins (alkanes) represent >70% of product distribution at low temperature.

*Table 15 Main product types produced industrially in FT synthesis (De Klerk, 2016)*

| Product property | HTFT | LTFT |
|------------------|------|------|
| Carbon number range | C1-C30 | C1-C120 |
| COMPOUND CLASSES | | |
| Alkanes (paraffins) | 20-30% | Major product (>70%) |
| Cycloalkanes (naphthenes) | <1% | <1% |
| Alkenes (olefins) | Major product (>50%) | 15-20% |
| Aromatics | 1-5% | <1% |
| Oxygenates | 10-15% | ~5% |

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[18] John Dodaro 2015 http://large.stanford.edu/courses/2015/ph240/dodaro1/

When looking at the product distribution with respect to chain length, the high and low-temperature conditions show significant differences (see Table 16). Higher temperature FT proceed at 300 – 350°C using iron catalysts to produce mainly gasoline, while lower temperatures (200 -240 °C) and iron or cobalt catalysts produce diesel and waxes.

*Table 16 Mass percentage of straight run Fischer-Tropsch products available for the production of jet fuel blending components. (De Klerk, 2016)*

| Straight run product | HTFT Fe-catalyst | LTFT Fe-catalyst | Co-catalyst |
|---|---|---|---|
| Light alkenes (C3-C5) | 20-30% | 5-10% | 3-5% |
| Heavy naphtha and kerosene (C9-C14) | 10-15% | 10-15% | 10-15% |
| Heavy distillate and wax (>C23) | None | 45-50% | 40-50% |

Naturally occurring straight run products can be further processed to increase the production of a jet fraction. For example, light alkenes can be oligomerized and hydrogenated and long-chain distillates and waxes can be hydrocracked and isomerized into jet-range fractions (De Klerk, 2016). In addition, even the straight run jet-range fractions require hydroprocessing. For the case of HTFT, alkenes and oxygenates form the bulk of the product (Table 16) and hydrogenation is used to saturate double bonds and remove oxygen. In the LTFT (for both cobalt and iron catalysts) hydroprocessing is mainly used to saturate double bonds in alkenes.

The distribution of heavier and lighter hydrocarbons can be estimated by employing the Anderson-Schulz-Flory probability model in which the distribution shifts to longer chain hydrocarbons as the temperature decreases. However, while the Anderson-Schulz-Flory model applies to existing industrial processes with Fe and Co catalysts, new research is underway to develop FT reactions that do not necessarily obey this model, in order to achieve a larger jet fraction (further discussed below).

The ratio of $H_2$ to CO also influences the product distribution with high ratios favouring the formation of lighter hydrocarbons.

It is also recognised that temperature control is crucial for effective Fischer-Tropsch synthesis. The FTS reaction is so exothermic that the heat generated can irreversibly deactivate the catalyst if it is not dissipated. Another reason why FTS temperatures must be kept under tight control is that, as the temperature approaches 400°C, the methanation reaction is favoured. However, this is only desirable when the target of the conversion is synthetic natural gas (SNG). Therefore, FT synthesis reactor design must be such that the heat from the reactors can be readily dissipated. Various reactor designs, such as tubular and slurry-based have been developed for this purpose (Swanson et al., 2010). The microchannel reactors, as commercialised by Velocys and the German company INERATEC, are designed to be very effective in heat dissipation while maintaining optimal conditions for FT synthesis.

Overall, the FTS-from-biomass process involves four major steps that include, a) syngas production, b) syngas cleanup, c) FT synthesis and, d) product upgrading. Each one of these steps is performed at different temperature and pressure conditions. From an energy balance and economic viability perspective, the high pressure and temperature fluctuations throughout the process are of concern. The high pressure consumes energy and it also results in greater capital expenditures on gas compressors needed to feed the pressurized reactor vessels. These are among the most costly pieces of equipment in a gasification plant. Similarly, heating and cooling cycles result undesirable energy "losses". If the syngas is cleaned of tars through thermal cracking at >1300 °C, it then has to be cooled down to about

300 °C and pressurized to >30 bar before it enters the FT synthesis reactors. If, on the other hand, the tars are removed by way of quenching, they have to be cooled down before they enter the wet scrubbers and again heated and pressurized before they enter the FT synthesis reactors. All of these heat-cool and compression operations are costly and they add significantly to the capital cost of biomass to liquids facilities. Ongoing research and development is underway to improve gasification platforms so as to minimize these costly fluctuations in temperature and pressure.

### 5.2.1.10 Selectivity for jet-range hydrocarbons and potential for increasing the jet fraction

The Anderson-Shulz-Flory (ASF) model predicts that the maximum selectivity for jet fuel is 41% (Li et al., 2018). However, the behaviour of modified bifunctional catalysts cannot be accurately described using this model and the product distribution might deviate from the distribution predicted by the ASF model.

The fractionation of fuel products based on the straight run FT liquid product separation gives a jet-range fraction of about 10-15% for both HTFT and LTFT (De Klerk, 2016). If biojet fuel production is a key objective, increasing this fraction would be desired. One approach that can increase the maximum jet fraction to 50-60% is the application of post-synthesis processing, oligomerization of short hydrocarbons (from HTFT) or hydrocracking of long-chain hydrocarbons (from LTFT) (De Klerk, 2016). However, these post-synthesis approaches require significant investment in infrastructure and affect the economics of a refinery.

Ongoing research has explored the impact of catalyst modifications, bifunctional catalysts and different catalyst supports (e.g. nano-structured carbon supports), with different pore sizes, to control selectivity during FT synthesis (Jahangiri et al., 2014; Yang, 2020). Li et al. (2018) reported an integrated selective Fischer-Tropsch synthesis process that doesn't require subsequent post-synthesis hydrorefining of waxes. By using mesoporous Y-type zeolites in combination with cobalt nanoparticles, the types of fuel products can be "tuned" by controlling the porosity and acid properties of the zeolites. As these bifunctional catalysts do not obey the traditional Anderson-Shulz-Flory distribution (Li et al., 2018), these researchers were able to achieve as high as 72% selectivity for jet fuel with a high isoparaffin content (Li et al., 2018).

### 5.2.1.11 Yields from gasification and Fischer-Tropsch synthesis

The yield of liquid products (synfuel) from gasification/FT tends to be quite low compared to other technologies. Based on cellulosic biomass, a theoretical yield of 0.35 kg synfuel per 1 kg of biomass has been suggested (Noureldin et al., 2014). Depending on the type of biomass, the yield can vary ± 25%, with the oxygen content in the biomass having a large impact. During gasification, multiple products are formed, including $CO$, $CO_2$, $H_2$, $CH_4$, $H_2O$, etc. Based on the low hydrogen content in biomass syngas, the hydrogen levels can be increased through the water-gas-shift reaction. However, this leads to increased formation of $CO_2$ and loss of carbon yield. In the reverse reaction, the addition of hydrogen can lead to increased CO production from $CO_2$. However, this reduces the hydrogen in the FT synthesis with an impact on the products. As discussed earlier, production of hydrocarbon paraffins requires an H2/CO ratio of 2:1. If the H2/CO ratio can be increased to 3:1, a synfuel yield increase can be achieved from 0.35 kg to 0.42 kg/kg of feedstock (Noureldin et al., 2014). However, it should be noted that increasing the ratio to 4:1 will shift the products to increased production of $CH_4$, which is not desirable for biojet fuel production.

Increasing the hydrogen input to achieve an improved ratio will require an external hydrogen

source and this is one of the challenges of FT fuels from biomass. The source of hydrogen and the cost will have an impact on the economics and the life cycle assessment.

The addition of methane to the gasification reaction could substantially enhance gasification yields. As methane has a high H/C ratio of 4, the hydrogen from the methane reacts with the $CO_2$ to form $H_2O$ and CO (Hayes, 2013).

### 5.2.1.12 Micro-channel Fischer-Tropsch technology

The company Velocys has modified the Fischer-Tropsch process to operate at small scale. The reactor has a modified design with microchannel architecture (Lerou et al., 2010) and can produce from 175 bpd to 1000 bpd (Green Car Congress, 2016). Catalysis takes place in microchannels with dimensions in the range of 0.1-10 mm which is dramatically smaller than conventional FT technology (Robota & Richard, 2014). The benefits of this architecture include an increased surface area, which improves heat and mass transfer performance. Catalysis is therefore accelerated to occur at rates up to 1000 times faster than conventional systems (Lerou et al., 2010) with other benefits including higher product yield and better energy efficiency.

The Velocys microchannel reactors are also reported to have much higher per pass conversion rates than conventional FT reactors. Single-pass conversion rates of greater than 75% are possible due to the very high heat removal capability (Leviness et al., 2014). With limited recycling, productivities of up to 94.5% have been achieved (Leviness et al., 2014). In conventional FT technology, single-pass conversion rates of 43-57% (H. Gruber et al., 2019), 40% (Swanson et al., 2010), 60-70% (Luque et al., 2012) have been reported.

As Fischer-Tropsch systems are usually operated at very large scale this is not ideal for biomass-based facilities where limited biomass volumes can be aggregated and transported economically. Based on biomass logistics and cost, feedstock volumes of 500-2000 tons/day are feasible, producing about 500-2000 bpd of liquid product. By scaling down the reactor through microchannel technology, a compact reactor could still produce sufficient and cost-effective volumes of product (Lerou et al., 2010). Due to the nature of the architecture, each unit behaves identically, and therefore scale-up could take place through larger assemblies of the basic unit. Due to the standardised, modular nature of the reactors, multiple trains could be rapidly assembled and further modules added at a later stage (Robota & Richard, 2014).

### 5.2.1.13 Fischer-Tropshc post-synthesis processing

Depending on the Fischer-Tropsch catalysts and processing conditions, a variety of post-synthesis processing must be carried out to produce a fully synthetic biojet fuel that meets specifications (De Klerk, 2016).

After the production of FT liquids, further upgrading is required to produce finished fuels, most likely through hydrotreating, hydrocracking, isomerisation and fractionation. This can readily be carried out at existing petroleum refineries and refinery integration through coprocessing, co-location or other means can have an impact on biofuel expansion.

For example, the Karlsruhe Institute of Technology (KIT) has proposed the co-location of its bioliq® process (a "hub and spoke" pyrolysis-then-gasification approach) with an oil refinery (Dahmen et al., 2012). The core gasification-FT facility would be located next to a petroleum refinery where the final hydroprocessing steps would be performed without the need to build separate hydroprocessing reactors. As FT liquids consist of a range of hydrocarbons, fractionation through distillation might also be carried out. The quality of FT liquids,

including low oxygen content, poses a very low risk for the refinery. However, very limited information is available publicly on how effective this integration might be.

It should be noted that, in 2020, jet fuel produced through coprocessing of FT liquids received certification under ASTM D1655. Insertion of up to 5% FT liquids into a refinery is permitted.

### 5.2.1.14 Investment cost, economies of scale and supply chain configurations

The infrastructure cost for gasification is the most significant contributor to investment cost, with the syngas cleanup the second highest cost. Comparison between a facility based on natural gas with a facility based on biomass can result in a 60% higher investment cost (Boerrigter, 2006). A related study indicated that feedstock pretreatment, gasification and syngas cleanup could amount to 75% of the total investment cost of a facility (Tijmensen et al., 2002). More recent work also showed that the gasification and syngas cleanup and conditioning account for 60-70% of the running cost of a facility (Daniell et al., 2012).

Achieving economies of scale is considered one of the major challenges when producing biofuel from biomass as the low energy density of the feedstock makes transport over long distances economically challenging (T. R. Brown, 2015). Typical gasification/FT facilities (based on coal and natural gas as feedstocks) are operated at very large scale, with the largest facilities producing 140,000 (Qatar) and 160,000 (Sasol) bpd (8-9 BLY) (Karatzos, McMillan et al., 2014). One option for overcoming this challenge is combining the gasification and pyrolysis pathways, using the production of biocrudes as a feedstock densification method to facilitate transport over greater distances to a centralized gasification/FT facility (T. R. Brown, 2015). An advantage of this approach is that simple, small-scale, and low-cost pyrolysis technology can be utilised and biocrude transported over long distances. This is the approach taken by Bioliq process, although the primary focus of this work was gasoline production (Eberhard et al., 2020). As both bio-oil and char are processed in the gasifier, char removal is therefore not required.

However, one techno-economic analysis found that, while such an integrated pyrolysis/FTS pathway was technically feasible, it involved very high capital cost with an MFSP more than 70% higher than of a standalone FTS plant based on coal or biomass (T. R. Brown, 2015). Related work has also indicated that centralised facilities are preferable to decentralised facilities, to achieve economies of scale, specifically for technologies such as gasification (Lundmark et al., 2018). Consequently, it has been shown that improvements in supply chains, to achieve high biomass efficiencies, can overcome the cost of longer transportation and taking advantage of economies of scale (Lundmark et al., 2018).

In related work, larger gasification facilities show a clear cost-benefit, offsetting the added transportation cost of feedstock (Lillebø et al., 2013). De Jong also concluded that decentralised facilities did not show a significant cost advantage and that limiting the potential economies of scale had a much larger impact (de Jong et al., 2017a).

The extent of post-synthesis processing will also contribute to the CAPEX due to additional reactors and potential internal hydrogen production facilities required for hydroprocessing/hydrocracking, as well as fractionation. Although these processes may not be cost-effective at a small scale, it opens up the opportunity for final downstream processing to take place in existing petroleum refineries, e.g. through a coprocessing approach.

**5.2.1.15 Economics and sustainability of the gasification and FT pathway**

The cost of biojet fuel via the gasification and Fischer-Tropsch pathway has been reported to vary considerably. According to Bann, the gasification/FT pathway based on municipal solid waste (MSW) can achieve an MFSP of $1188-1738 per tonne (Bann et al., 2017) while De Jong suggested an MFSP of $2124-3127 per tonne for a forest residue or wheat straw feedstock (de Jong et al., 2017b). Other studies have reported significantly lower costs with Neuling and Kaltschmitt suggesting an MFSP of $1982 based on wheat straw and $1244 based on willow pretreated via torrefaction (Neuling & Kaltschmitt, 2018). The lowest cost for this pathway is $898-1724, when using a biomass feedstock, and $635-1245 when using a waste feedstock, although this is for a generic drop-in biofuel, not just biojet, and based on an optimised process (A. Brown et al., 2020)

The gasification/FT pathway has some of the lowest carbon intensity values of all the technologies. In some cases, even negative values. According to the default carbon intensity values or Life Cycle Emission factors (LSf (gCO$_2$e/MJ) (core LCA plus induced land use change (ILUC)) under CORSIA, LSf values range from -22 gCO$_2$e/MJ (miscanthus – USA) to 8.3 gCO$_2$e/MJ for forestry residues feedstock (ICAO, 2019). The LSf for MSW feedstock will depend on the biogenic content of the waste, with MSW of 100% biogenic carbon achieving a value of 5.2 gCO$_2$e/MJ. Miscanthus feedstock achieves the lowest and negative LSf values.

**5.2.1 16 Opportunities and challenges of the gasification-FT pathway**

As the gasification/FT pathway can utilise multiple feedstocks its ability to use MSW presents an opportunity to access very low, or negative cost feedstocks for fuel production. As a result, the fuels produced through the gasification/FT pathway have been shown to have some of the lowest carbon intensities compared to other technologies (Ringsred, 2018).

For the specific production of biojet fuels, the development of new catalysts that can achieve a jet fraction of up to 70% show great promise. This has the potential to reduce the additional infrastructure normally required to either crack longer waxes or oligomerisation of shorter naphtha molecules into jet-range molecules.

## 5.2.2 Direct thermochemical liquefaction

Direct thermochemical liquefaction includes technologies such as pyrolysis, where a liquid energy carrier is produced after heating biomass, as well as solvent liquefaction technologies such as hydrothermal liquefaction. The liquid products are termed bio-oils, pyrolysis oils, or biocrudes and can be further upgraded into transportation fuels. Throughout this report, for convenience, a general term of "biocrudes" is used to denote all types of liquid intermediates produced through this technology

Three types of direct thermochemical liquefaction technologies are discussed including conventional fast pyrolysis, catalytic pyrolysis and hydrothermal liquefaction. Other variations of these technologies include the IH[2] as commercialised by Shell.

It should be emphasised that no direct thermochemical liquefaction technology has yet achieved ASTM certification for the commercial production of jet fuel. Although the company KiOR, using a catalytic pyrolysis technology, applied for ASTM certification (hydrotreated depolymerised cellulosic jet - HDCJ), the closure of the company stalled this process indefinitely. It is unlikely that this application would be continued as certification is directly linked to the specific technology and large volumes of the jet fraction are required for

testing. Any company in this space would have to apply for certification separately.

Typically, a technology readiness assessment must consider the production of biojet fuel via this pathway as two stages, namely production of the liquid intermediate, followed by upgrading to the final fuel. In many cases these stages are not at the same technology readiness level. For example, while bio-oil production through fast pyrolysis is commercial, the upgrading of the liquid intermediate to transportation fuels is still at the pilot stage. In some cases, such as hydrothermal liquefaction, both biocrude production and upgrading are at the pilot stage of development.

Companies such as Ensyn in Canada have been producing fast pyrolysis bio-oils for many years and their product has been used in "niche" applications such as food flavouring (barbeque flavour). Energy applications have been primarily restricted to heavy fuel oil used in stationary heating and power-generating facilities. Although Ensyn has obtained regulatory approval for RFDiesel and RFGasoline, which are fuel products generated via co-processing in petrochemical refineries, biojet fuel produced in this manner has not received certification. In the Netherlands, BTG has commercialised the flash pyrolysis technology via its EMPYRO[19] project. Although the biocrude is primarily used to replace natural gas in a heating application in a milk factory, BTG has also been testing possible co-processing of bio-oil in a petroleum refinery.

From a technical perspective, upgrading biocrudes into zero oxygen liquid transportation fuels has been challenging, with the high levels of oxygen, up to 40/50% oxygen in fast pyrolysis biocrudes, requiring extensive upgrading and hydrogen inputs for oxygen removal. Processing costs, as well as the need for external hydrogen, represent a large proportion of equipment and production costs (Sb Jones et al., 2009). A further challenge in upgrading biocrudes is the cost and stability of the catalysts that are required. Catalytic pyrolysis or processes such as hydrothermal liquefaction (HTL) can produce a biocrude intermediate with significantly lower oxygen content, 5-20%, which should be easier to upgrade into fuels. However, there are many other considerations, including differences in biocrude yields, engineering challenges for high-pressure HTL biocrude production as well as others constraints that impact the overall performance of a pathway.

Although the production of high specification *biojet* fuels through direct thermochemical technologies (as opposed to road transportation fuels) has received limited attention, some information is available. A recent project compared biojet fuel production based on hydroprocessing of three biocrudes, from fast pyrolysis, catalytic pyrolysis, and hydrothermal liquefaction technologies. The comparison encompassed technology, feedstock supply chains, techno-economic analysis and life cycle assessment and demonstrated the feasibility of upgrading biocrudes from all three technologies into biojet (Van Dyk et al., 2019a). It was demonstrated that production of biojet fuel through these pathways was feasible and the quality of the biojet fraction was very good, even though the upgrading was not optimised.

Although biocrude production can be combined with standalone upgrading processing, the direct thermochemical liquefaction technologies are uniquely suited for upgrading through a co-processing approach where liquid biocrude intermediates are inserted at low blends into existing refinery infrastructure. This has the potential to leverage existing oil refinery

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[19] http://www.empyroproject.eu/

infrastructure and thus reduce the capital and operating costs of making biojet. However, technical challenges include selecting the point of insertion, the extent to which upgrading is required prior to insertion and the disparate types of catalysts needed for bio-oils compared with those used in oil refining (Van Dyk et al. 2018). Refinery insertion strategies should be synergistically beneficial but are likely to be technically challenging for biocrudes. While co-processing of lipids is already done at a commercial scale at present, the co-processing of biocrudes has not been pursued at this scale, primarily because of a lack of biocrude availability.

### 5.2.2.1 Fast pyrolysis technology

Fast pyrolysis is a thermal decomposition process which requires rapid heating of biomass to about 500°C and subsequent rapid cooling of the resulting vapours to room temperature. Upon cooling, these vapours condense to form the liquid bio-oil/biocrude product. It has been demonstrated that rapid heating and cooling is crucial to maximizing bio-oil liquid yields at the expense of char and gas production (Bridgwater, 2012). To maximize bio-oil yields (to about 75% of starting biomass by mass) rapid heating to the target temperature must be achieved throughout each biomass particle (i.e., within about one second). These high heat transfer rates (up to 1000°C/s) ensure maximum devolatilization (vaporization) of the biomass solids. Different types of reactors can be used, including a bubbling fluidized bed reactor, circulating fluidized bed reactor, and ablative or rotating cone reactor (Bridgwater, 2012). A detailed description of these technologies can be found in Karatzos et al. (2014).

The Bubbling Fluidized Bed (BFB) reactor type is well suited for fast pyrolysis (and effective heat transfer). This reactor uses a hot sand fluidized bed to achieve high rates of heat transfer to biomass particles. The reactor beds are fluidized using a compressed carrier gas which is fed through the bottom of the reactor at sufficiently high rates to "fluidize" the solids (sand and biomass) while transferring the gas-entrained char upwards. They are robust systems that achieve high heat transfer rates and uniform bed temperatures (Ringer et al., 2006), which are both highly desirable attributes for fast pyrolysis reactions.

A more complex version of the bubbling fluidized bed (BFB) reactor is the circulating fluidized bed (CFB) reactor. This reactor configuration has been used by the petroleum industry for many decades, and it has a long history of industrial operations especially in the fluidized catalytic cracking (FCC) units. This type of system is similar to the BFB process except the compressed recycle gas is fed at much higher velocities, such that the entire loose contents of the reactor (vapors, gases, char as well as the fluidized bed's sand particles) are carried into the downstream cyclone. The char and sand are then recovered from the cyclone and fed together to a combustor, where the char is burned off to heat up the sand. The cleaned hot sand (at about 800°C) is then fed back to the main reactor entrained in the compressed carrier gas and the process cycle is repeated. This system is more expensive to install and operate than the BFB process. However, it comes with the advantages of constantly regenerating clean sand bed particles and achieving higher throughputs. Circulating fluidized bed (CFB) processes require careful sizing of the biomass particles since the rapid gas flow only permits a very short residence time in the hot zone of the pyrolysis reactor. The CFB pyrolysis is the configuration of choice for the company "Ensyn" who markets their technology under the name RTP (Rapid Thermal Processing).

The main drawbacks of fluidized bed reactors are their reliance on a compressed carrier gas which often carries char contaminants to the bio-oil product. Gas compression also requires

high capital and operating costs. The carrier gas, used to mix and circulate the sand bed, typically carries char particles of such a small submicron size that even the solids separation cyclone cannot capture them. Thus, these tiny particles remain entrained in the vapour that enters the quench cooler, ending up in the bio-oil product (Bridgwater, 2012). This can be a problem as char particles can catalyze tar and coke formation, plugging reactor pipes and filters upon subsequent bio-oil upgrading. It should also be noted that the compressors used to deliver high-speed carrier gases are capital-intensive plus they are not well suited for small scale applications (Wright et al., 2010).

Alternative reactors that do not use a carrier gas have recently been developed and use centrifugal forces and mechanical motion to achieve the high rates of heat transfer needed to rapidly volatilize the biomass particles. These types of pyrolysis reactors include ablative and rotating cone designs based on the principle of sliding biomass particles against a hot surface. Ablative pyrolysis reactors do not use a fluidized bed or sand particles while rotating cone reactors use sand particles contacting biomass particles, but without fluidization by a carrier gas (Bridgwater, 2012; Venderbosch & Prins, 2011).

Table 17 is a current list of direct thermochemical liquefaction facilities around the world.

Table 17: Commercial and demonstration direct thermochemical liquefaction facilities in 2020 (Wijeyekoon et al., 2020)
Commercial facilities (blue), Demonstration facilities (yellow)

| Owner Company | Location | Technology provider (type of reactor) | Status | Capacity | Primary product | Feedstock |
|---|---|---|---|---|---|---|
| Ensyn | Brazil, Aracruz | Envergent (CFB) | Under development | 83 ML/y | Pyrolysis oil | Forest residues |
| Canfor/Licella | Canada, BC, Prince George | Licella (HTL) | Under development | 80 ML/y | Biocrude | Wood and pulp residues |
| Ensyn | Canada, Quebec, Cote du Nord | Envergent (CFB) | Active (2018) | 38 ML/y | Pyrolysis oil | Sawmill residues |
| Kerry Group/Ensyn | Canada, Ontario, REnfrew | Ensyn (CFB) | Active (2006) | 11 ML/y | Pyrolysis oil | Mill and forest residues |
| Fortum, Valmet | Finland, Joensuu | Valmet (VTT fluid bed riser) | Active (2013) | 43 ML/y | Pyrolysis oil | Forest residues and sawdust |
| Green Fuel Nordic Oy | Finland, Lieksa | BTG Bioliquids (Rotating Cone Reactor) | Active (Q4 2020) | 20 ML/y | Pyrolysis oil | Sawdust and wood residue |
| Twence | The Netherlands, Hengelo | BTG Bioliquids (rotating cone reactor) | Active (2015) | 20 ML/y | Pyrolysis oil | Clean woody biomass |
| Pyrocell AB | Sweden, Kastet, Gavle | TechnipFMC and BTG | Under construction (2021) | 21 ML/y | Pyrolysis oil | Sawdust |
| Ensyn & Renova Capital | USA, Georgia | Envergent (CFB) | Late stage development | 76 ML/y | Pyrolysis oil | Mill and forest residues |
| Kerry Group | USA, Wisconsin | Ensyn (CFB) | 5 active licensed facilities (1995) | 9 ML/y | Specialty chemicals | Wood residues |
| Licella | Australia, NSW, Somerby | Licella (HTL) | Active (2012) | 9 ML/y | HTL biocrude | Wood, ag residues, pulp, paper |
| | | Licella (HTL) | Under planning | 114 ML/y | Recycled oil | End-of-life plastics |
| Muradel | Australia, NSW, Whyalla | Muradel (HTL) | Inactive | unknown | HTL biocrude | Sewage sludge, microalgae, recycled tyres |
| Pyrobiom Energies | Canada | ABRI-Tech | Active | 6 ML/y | Pyrolysis oil | Woody residues |

| Shanxi Yingjiliang Biomass Company and Shanghai Jiao Tong University | China, Shanxi Province | Shanxi Yingjiliang Biomass (Rotating cone reactor) | Active | 2-6 ML/y | Pyrolysis oil | Rice husks |
|---|---|---|---|---|---|---|
| University of Science and Technology of China | China, Hefei | University of Science and Technology of China | unknown | 2 ML/y | Pyrolysis oil | Wood and agricultural waste |
| Shell Catalysts & Technologies | India, Bangalore | (IH²) Gas Technology Institute and CRI Catalyst Company | Active (2018-2019) | 0.5 ML/y | Gasoline, jet and diesel fuel | Forest, agricultural, and urban waste |
| MASH Energy | India, Gujarat | MASH Energy (Denmark( | Unknown | unknown | Pyrolysis oil | Waste materials, nuts, sewage sludge |
| Silva Green Fuel | Norway, Tofte, Buskerud | Steeper Energy | Active | 1 ML/y | HTL biocrude | Forest residues |
| Altaca Energy | Turkey, Gonen | Altaca Energy (Catalytic HTL) | Active | 20 ML/y | HTL biocrude | Various biomass sources |
| Biogas Energy | USA, California, Sacramento | Bioenergy Concept (Germany) and EnergoLesProm (Russia) (Ablative reactor | Under development | 1.3 ML/y | Pyrolysis oil | Demolition wood, beetle infested trees, forest and ag residues |

## 5.2.2.2 Catalytic pyrolysis technology

The catalytic pyrolysis process produces a biocrude with a lower oxygen content than fast pyrolysis, with the rationale that a low-oxygen biocrude will be easier to upgrade and will require less hydrogen.

The technology is divided into *in situ* and *ex situ* pyrolysis processes. *Ex-situ* catalytic fast pyrolysis is an uncatalyzed fast pyrolysis integrated with a catalytic post-treatment of pyrolysis vapors before condensation (e.g. a zeolite catalyst such as HZSM-5) to deoxygenate pyrolysis vapors. *Ex-situ* catalytic pyrolysis produces bio-oil with a lower oxygen content (ranging between 4 – 35%) and allows a lower temperature processing regime than conventional uncatalyzed fast pyrolysis. The advantage of *ex-situ* catalytic fast pyrolysis is that some of the polymerization and gum formation reactions are prevented that greatly reduce viscosity and instability of bio-oil (Pham et al., 2014).

During *in-situ* catalytic pyrolysis, the biomass is pyrolyzed at a lower temperature (i.e. less than 500°C) in the presence of a catalyst (i.e. solid acid, alkali, non-acidic mixed metals, transition metal or precious metal catalysts) in the heating medium or impregnated with the biomass prior to the pyrolysis. KiOR is an example of a company that employed *in-situ* catalytic pyrolysis with KiOR's technology using a zeolite catalyst during the pyrolysis process.

Yields of bio-oil from catalytic pyrolysis is quite low and the aqueous fraction contains a high amount of water-soluble compounds that reduce the yield of the hydrocarbon fraction.

Hydropyrolysis technology, as used by IH[2], is a type of *in-situ* catalytic pyrolysis process. The process involves fast pyrolysis of the lignocellulosic biomass in a catalytic fluidized bed at around 400–430°C under 14–35 bar of hydrogen (i.e. hydropyrolysis) with a hydropyrolysis catalyst 500–850 μm in size.  The second stage of the process incorporates a second catalytic step to convert the intermediate products into hydrocarbons which can be subsequently fractionated to fuels.

### 5.2.2.3 Hydrothermal liquefaction technology

Hydrothermal liquefaction (HTL) is a solvent liquefaction process that produces a biocrude intermediate that can be further upgraded into fuels. However, it is quite distinct from pyrolysis as it can utilize wet biomass. The process converts feedstocks (biomass, manure, algae) to low oxygen biocrude (5-20% oxygen), depending on the specific processing conditions. The HTL process uses high pressures (e.g. 50 - 250 bar or more) and moderate temperatures (around 250-450°C) to liquefy and deoxygenate the feedstock (Elliott, 2007). Conditions can be altered to be at subcritical or supercritical state and catalysts can be used.

Potential feedstocks for HTL include lignocellulosic biomass (non-food), organic waste, sludge, manures, peat, algae, as well as low-grade coals like lignite. While organic substances are insoluble in water under normal conditions, water can be a good solvent for non-polar substances under supercritical conditions (Tekin et al., 2014). An increase in the ionic character of water can facilitate acid-base catalyzed reactions (Elliott, 2011). The hydrothermal liquefaction of biomass usually occurs in the presence of an alkali metal and alkaline earth metal carbonate, bicarbonate or formate catalyst (e.g., $Na_2CO_3$). However, HTL biocrudes are very viscous and melting points of about 80°C have been reported (Elliott, 2007).

The HTL reaction involves both hydrolysis and/or degradation of macromolecules of biomass into small molecules. In this process, a substantial part of the oxygen in the biomass is removed by dehydration or decarboxylation. Compared to fast pyrolysis, HTL has a lower oil yield of around 30% but produces a relatively stable oil and the process does not require energy to dry the biomass feedstock.

Several prominent companies are commercialising technology in this field, including Licella and Steeper Energy, who are both using supercritical reaction conditions. The Pacific Northwest National Laboratory (PNNL), with funding from the Bioenergy Technologies Office of the US Department of Energy, has carried out extensive research and investigation into hydrothermal liquefaction of lignocellulosics, food processing wastes, and algae in subcritical water. The PNNL HTL technology has been licensed by Genifuel who is planning to scale up of this technology.

Although some studies have suggested that this process could potentially produce the lowest cost biojet fuel (de Jong et al. 2016), issues such as the high-pressure requirements of HTL and the challenges encountered when using woody feedstocks during biocrude production have impacted scale-up.

### 5.2.2.4 Composition and characteristics of biocrudes

Unlike any of the other biojet technologies, the liquid bio-oil or biocrude intermediates are extremely complex, containing over 300 different compounds. In comparison, lipid feedstocks (fatty acids) are relatively homogenous from a chemical perspective. Biochemical methods for biojet production use intermediates such as ethanol, butanol, farnesene and other molecules with simple and homogenous chemistry.

Major chemical components of biocrudes include hydroxyaldehydes, hydroxyketones, sugars, carboxylic acids and phenolics (Bridgwater, 2012). The amount of these compounds in the bio-oil depends on the composition of the original biomass or feedstock as well as the liquefaction conditions used. Some of these components, such as the sugars, are hydrophilic while others, such as the phenolics, are more hydrophobic. When water is formed during the liquefaction process some of these water-soluble components may be lost in the water

fraction, reducing the yield of carbon in the biocrude. During the production of the biocrude, chemical interactions may also take place between various components to form larger molecules.

The oxygen content of biocrudes is a key parameter and has an important impact on upgrading these intermediates into oxygen-free biojet fuels. Fast pyrolysis generally produces a biocrude with very high oxygen levels (>40%) while much lower levels of oxygen are achievable with catalytic pyrolysis and/or hydrothermal liquefaction (5-25%), depending on process conditions. Supercritical HTL can obtain oxygen levels below 10%, while subcritical HTL conditions result in biocrudes with higher oxygen content (~10-20%).

From a technical upgrading perspective, the oxygen content is very important as it will impact the stability of the bio-oil during storage and transport. More importantly, it impacts the upgrading of biocrudes and the external hydrogen required during upgrading to produce oxygen-free fuels. However, it is not merely the oxygen content, but also the chemistry of the oxygen-containing compounds that is important. Removal of oxygen may be relatively simple in some molecules, but in other molecules it might require high severity processing conditions (temperature and pressure) in order to remove the oxygen.

As summarised in Table 18 a comparison between biocrudes from fast pyrolysis, catalytic pyrolysis and hydrothermal liquefaction biocrudes indicates their major differences. Processing conditions can vary substantially, even within the same technology category, and this can result in substantial variation in biocrude characteristics. For example, the HTL biocrude (Table 18) was based on a subcritical process which resulted in 14.5% oxygen compared with the literature which indicated that subcritical processing conditions can result in lower oxygen content (9.8%) (Jensen et al., 2017). The use of alkali catalysts in HTL can also result in a biocrude with alkaline pH (Jensen et al., 2017). Other notable features when comparing the biocrudes are the higher water content and lower pH in the fast pyrolysis biocrude and the higher aromaticity of the catalytic pyrolysis and HTL biocrudes.

*Table 18 Comparison of the characteristics of the Fast, Catalytic and HTL biocrudes (Van Dyk et al., 2019b)*

| | Units | Testing method | Fast pyrolysis biocrude | Catalytic pyrolysis biocrude | Hydrothermal liquefaction biocrude |
|---|---|---|---|---|---|
| Density @ 15°C | kg/m³ | ASTM D4052 | 1198 | 1163 | 1169.2[a] |
| Specific gravity 60/60F | | ASTM D4052 | 1.197 | 1.164 | - |
| Elemental analysis: | | | | | |
| C | wt% | ASTM D5291 | 44.1 | 64.6 | 70.4 |
| H | wt% | ASTM D5291 | 7.5 | 7.3 | 7.44 |
| N | wt% | ASTM D5291[b] | 0.132 | 0.16 | 0.12 |
| S | ppm | ASTM D5453 | 84 | 360 | 1050[c] |
| O (dry basis) | wt% | In-house | 35.6 | 16.5 | 14.5 |
| Water content by Karl-Fisher | wt% | ASTM E203 | 23.5 | 9.1 | 8.91 |
| Heat of combustion (net) | MJ/kg | ASTM D240 | 16.39 | 26.09 | 27.40 |
| Total acid number (TAN) | mg KOH/g | ASTM D664 | 125 | 82.6 | 28.6 |
| Kinematic viscosity at 40°C | cSt | ASTM D445 | 20.67 | 236.4 | 503.4[d] |
| Ash content | wt% | ASTM D482 | 0.013 | 0.93 | 0.61 |
| Pyrolysis solids content | wt% | ASTM D7579 | 0.03 | 1.32 | 1.48 |
| pH | pH | In-house | 2.66 | 3.00 | 4.53[e] |
| Flash point | °C | ASTM D93 | 50.5 | <40.0 | Not detected[f] |
| Pour point | °C | ASTM D5460 | -36 | -6 | 33 |
| Aromaticity by ¹³C NMR | % | ASTM D5461 | 42.9 | 63.9 | 60.9 |
| Total Carbonyl | mol/kg | ASTM E3146 | 4.5 | 3.2 | Not determined |

[a] density @ 28°C, In-house (Helpyc); [b]:ASTM D5762; [c]:ASTM D4294; [d]: Kinematic viscosity at 80°C; [e]: pH at 21°C, ASTM D1293C; [f]: No flash was detected before the sample began to boil.

As indicated in Table 18, water is a major component of fast pyrolysis biocrudes and its concentration varies depending on the initial moisture content of the biomass and the pyrolysis conditions used. Although severe pyrolysis conditions (high temperature and residence time) remove more water they also promote vapor polymerizations, thus increasing the viscosity and solids content of the resulting bio-oil. The higher viscosity in the catalytic pyrolysis and HTL biocrudes are as a result of the lower water content.

Water is derived from both the original water in the feedstock and from the water formed during the dehydration reactions occurring during pyrolysis. An excessive amount of water in bio-oils is undesirable because it acts as a heat sink during combustion and it can also promote destabilization and phase separation of the fuel during storage. In order to minimize the water content of the bio-oil the moisture content of the biomass feedstock is best kept below about 10 wt% when using fast and catalytic pyrolysis. This is not applicable to hydrothermal liquefaction where much higher moisture levels in the feedstock can be tolerated.

Most bio-oils can be considered micro-emulsions with the continuous phase of the emulsion an aqueous solution primarily containing polysaccharide decomposition products. The discontinuous phase primarily contains the hydrophobic molecules. The breakdown of this emulsion results in the formation of two phases, a lighter, more aqueous phase and a heavier, less aqueous phase (Bridgewater, 2012). If the aqueous phase is separated from the heavier phase, a significant amount of feedstock carbon can be "lost" when water-soluble molecules are dissolved in the aqueous phase. For the case of catalytic pyrolysis, this leads to low yields of biocrude and impacts the economics of the process (Van Dyk et al., 2019a). Waste water treatment will therefore be required for catalytic pyrolysis and hydrothermal liquefaction technologies which will add to the capital cost. Waste water from HTL has been reported to have a very high biological oxygen demand (BOD) (Van Dyk et al., 2019a).

Pyrolysis oils are prone to degradation over time ("ageing") resulting in increased viscosity through polymerization reactions between the oxygenated carbon molecules in the bio-oil emulsion. Polymerization reactions produce high molecular weight, water-insoluble components such as gums. These reactions lead to increased viscosity and, ultimately, to phase separation of the bio-oil into an upper aqueous phase (containing a higher proportion of acids and sugars) and a lower tar phase (containing less water and a higher proportion of water-insoluble solids and lignins) (Lehto et al., 2013).

Ageing reactions are affected by time, temperature and the presence of char particles in the biocrude. After storage for about 6 months or more, degradation is likely to occur, while increases in storage temperature can accelerate degradation significantly. The presence of char particles (mainly alkali metals) also catalyzes polymerization reactions to increase bio-oil viscosity. Although ageing is undesirable, pilot co-processing studies at Petrobras in the FCC was carried out with one-year old pyrolysis oil without any significant impact.

Processes such as hot filtration to remove char particles can improve the stability of bio-oils or by adding solvents such as methanol. These techniques can be costly and/or lead to bio-oil yield loss. Although the impact of added solvents on the life cycle analysis has not been thoroughly investigated the limited work that has been carried out has shown that solvent addition can have a significant negative impact on the potential carbon intensity of the final fuels (Van Dyk et al., 2019a).

For bio-oils/biocrudes to be used as transportation fuel, subsequent upgrading is needed. Although both hydroprocessing and catalytic cracking processes can be used to upgrade

biocrudes, it is most likely that a hydroprocessing approach will be used to produce biojet fuels.

### 5.2.2.5 Upgrading bio-oils/biocrudes to transportation fuels

Upgrading of biocrudes proceeds through both physical and catalytic processes. While some uses of biocrudes, such as stationary heat and power processes, do not require extensive upgrading, biojet fuels have very high specifications. Thus, significant processing and upgrading must be done.

Initial physical upgrading of biocrudes can be carried out using hot-vapour filtration, liquid filtration and centrifugation to remove char and particulates (Bridgewater, 2013). Hot vapour filtration can reduce the ash content of the oil to less than 0.01% and the alkali content to less than 10 ppm (Diebold et al., 1994). Removal of char particulates is important as it is catalytically active and can potentially crack the vapours and reduce the bio-oil yields. As discussed earlier, removal of char also reduces ageing of the biocrude.

Biocrudes have compounds ranging in molecular weights from small to very large. For the case of crude oils, a distillation step is usually carried out before any upgrading to separate compounds into different size fractions based on boiling point. However, biocrudes contain substantial amounts of non-volatile materials, such as sugars and oligomeric phenolics, etc., which make it less suitable for distillation as the heating of biocrudes during distillation accelerates the polymerization reactions resulting in the formation of heavy and non-volatile compounds. Heavy Fuel Oil typically leaves 1% residue after vacuum distillation whereas a bio-oil leaves up to 50% of the starting material as distillation residue. This poor distillation performance has implications for further processing of biocrudes into drop-in fuels. Whereas crude oils are first subjected to distillation, after which fractions are upgraded into finished products, bio-oils have to first be at least partially upgraded before any fractionation through distillation can take place.

Some authors have indicated that a partially upgraded pyrolysis oil with ~8% oxygen content could potentially be integrated into a distillation column based on previous work (Arbogast et al., 2017). However, when Hoffman and colleagues investigated the potential for insertion of HTL biocrudes (with 5.3% oxygen) at the distillation phase they concluded that further hydrotreatment is still required to produce a suitable co-processing feed (Hoffmann et al., 2016). When further upgrading of the HTL biocrude was carried out the oxygen content was reduced to 0.3%, which was considered suitable as a co-processing feed (Jensen et al., 2015a).

While insertion of biofeeds at the distillation phase of a refinery is likely to be challenging, prior fractionation of biocrudes may be a useful step prior to refinery insertion as it may facilitate more appropriate upgrading steps of heavy and light fractions. Although some researchers have successfully used vacuum distillation, molecular distillation offers many advantages including "low temperature, short heating time and high separation efficiency" (S. Wang, 2013). In this work the carboxylic acids and water fractionated preferentially into the light fraction, improving the quality and stability of the heavy fraction for further upgrading, while the carboxylic acid light fraction could be esterified to produce a stable intermediate (S. Wang, 2013). Unlike crude oils, where contaminants such as N and S preferentially fractionate to the heavier fractions, biocrude displays an even distribution of contaminants, such as oxygen, into all the fractions (Jensen et al., 2015b). Thus, it is likely that all the fractions of a biocrude will need upgrading to remove heteroatoms such as N and O.

One of the main objectives during the upgrading of biocrudes is the removal of oxygen and achieving high hydrogen-to-carbon ratios in the finished fuel. The two main upgrading techniques that have been used are hydroprocessing and zeolite cracking (Solantausta, 2011). Both processes are catalytic and selectively promote hydrogenation reactions. Hydrotreating uses large amounts of hydrogen to remove oxygen from bio-oils in the form of $H_2O$ molecules. In contrast, zeolite cracking uses no hydrogen but instead rejects oxygen in the form of $CO_2$, consequently lowering the biofuel yield. Both technologies try to elevate the effective H/C ratio of bio-oils from about 0.2 to about 2 in order to fit the functional properties of hydrocarbon transportation fuels. The H/C ratio will also be reflected in the paraffinic or aromatic nature of the finished fuel and the maximum limits set under fuel specifications. While aromatics may be more desirable in gasoline to boost octane levels, it is less desirable in jet fuels. The majority of approved biojet fuels under ASTM D7566 are paraffinic with aromatic content limited to 0.5%. This is further discussed in the context of biocrude upgrading as all biocrudes contain high levels of aromatics.

It should be noted that deoxygenation of biomass intermediates is essential if we are to produce drop-in biofuels and it is typically achieved through three main chemical reduction processes: (1) decarbonylation (producing CO & $H_2O$); (2) decarboxylation (DCO) (producing $CO_2$) and (3) hydrodeoxygenation (HDO) (producing $H_2O$). These reactions are illustrated in Figure 7 for the deoxygenation of fatty acids but are generally applicable to the deoxygenation of any oxygen-containing biomass.

During hydrodeoxygenation, the hydrogen present in the biomass intermediates (or supplied externally) is oxidized and the oxygen can be removed as water ($H_2O$). During decarboxylation, the carboxyl group carbon is oxidized and the oxygen is removed as carbon dioxide. During decarbonylation, oxygen is removed as carbon monoxide with a water molecule also formed. While the reaction conditions can be adjusted to favour one reaction (e.g. the type of catalyst used), in practice these processes take place simultaneously. The HDO process is typically favoured when hydrogen is externally added (e.g. hydrogen gas derived from natural gas) while, in the absence of hydrogen, the DCO route is favoured (NSF, 2011; Matthew Noah Pearlson, 2011). However, it should be noted that some co-processing trials using the fluid catalytic cracker (where no additional hydrogen is added) resulted in hydrogen transfer between molecules and all three reactions still took place (from fossil molecules to biomolecules) (Pinho et al. 2015, 2017).

When decarboxylation or decarbonylation takes place, feedstock carbon is lost by oxidation and, as a result, the yield of hydrocarbons is reduced. Although, when hydrogen inputs are used to remove oxygen the yields of hydrocarbons are generally higher, the cost and sustainability of the imported hydrogen have to be considered.

### 5.2.2.6 Hydrotreating

Hydrotreatment is a catalytic process in the presence of external hydrogen used to deoxygenate and upgrade bio-oils to drop-in transportation fuels. The amount of hydrogen required depends on the oxygen content of the starting biocrude intermediate. Higher levels of hydrogen are needed to hydrotreat fast pyrolysis bio-oils because they contain about 40-50 wt% oxygen compared to catalytic pyrolysis and HTL biocrudes. Vegetable oils have an $H/C_{eff}$ ratio of about 1.8 while the bio-oil/biocrude is around 0.2 (the same as wood). Thus bio-oils require more hydrogen and processing effort to become functionally equivalent to petroleum diesel. Similar to hydrotreating vegetable oils, the targeted chemical reaction during bio-oil hydrotreating is the rejection of oxygen in the form of $H_2O$.

This hydrodeoxygenation (HDO) reaction of bio-oil is conceptually represented as:

$$C_1H_{1.33}O_{0.43} + 0.77H_2 \rightarrow CH_2 + 0.43H_2O \text{ (Bridgwater, 2012)}$$
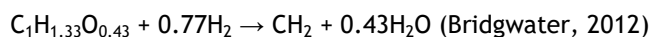
As described in the equation, the process uses about 1.5 (0.77 x 2) hydrogen atoms for every carbon atom produced in the final fuel. As the carbon conversion is 100% (as every carbon in the bio-oil is converted to a hydrocarbon) the resulting hydrocarbons should be of high quality since the H/C ratio is equal to 2. However, in practice, hydrotreatment is not very selective and the HDO reaction described above does not take place in isolation but rather in association with other reactions which divert carbon and/or hydrogen from the targeted liquid fuel product. These reactions include polymerization and condensation to form tars and coke, gasification reactions that form methane or $CO_x$ and reactions that form low H/C hydrocarbons such as aromatics and olefins (Bridgwater, 2012). Thus, the low selectivity of the hydrodeoxygenation and hydrogenation reactions often leads to low fuel yields and high hydrogen requirements.

In most of the hydrotreating processes modelled so far the biomass to fuel yield is around 25% mass (55% energy) when hydrogen is provided externally and 15% (33%) when hydrogen is produced by gasifying the biomass (Brown, 2011; Bridgwater, 2012). However, these relatively poor carbon yields and hydrogen use efficiencies can be improved by the use of more selective catalysts and optimized processes.

Due to the highly heterogeneous, oxygenated and reactive nature of bio-oils, their hydrotreatment is a lot more complex than that of petroleum. In oil refineries, hydrotreatment is mainly used to remove sulfur and nitrogen contaminants from petroleum feeds in processes known as hydrodesulfurization (HDS) and hydrodenitrogenation (HDN). The process conditions include temperatures that range from 300-to-600 °C, hydrogen pressures of 35-to-170 bar and liquid hourly space velocities (LHSV) of 0.2-to-10 per hour. The catalysts used in petroleum HDS are typically sulfided Co-Mo and Ni-Mo supported on porous alumina or aluminosilicate matrices. Unfortunately, for a number of reasons and as described below, these conditions are not suitable for processing bio-oils:

Sulfided Co-Mo and Ni-Mo catalysts, when in contact with bio-oils, are rapidly stripped of their sulfur and require constant resulfurization (addition of $H_2S$) to prevent catalyst deactivation (Huber, 2007). This deprives bio-oils of their low sulfur content advantage (Wang et al., 2013). Alumina supports create an acidic environment and they are not stable in the presence of water (irreversible dealumination) (Mortensen et al., 2011).

Bio-oils are unstable at high temperatures as they can rapidly become viscous and eventually phase separate. Bio-oils tend to form coke residues, particularly in acidic environments and at high temperature and pressure. Coke is undesirable as it deactivates the catalysts by depositing on their active sites and it can severely plug reactor components (Wang et al., 2013). The water in bio-oil inhibits hydrotreating by modifying and deactivating the catalysts and by adsorbing onto active sites (Furimsky & Massoth, 1999). Aside from the water content of bio-oils (up to 30%) typically, more water is produced after hydrotreatment.

These and other limitations have motivated the search for hydrotreating processes and catalysts that are better suited to the highly oxygenated and heterogeneous nature of bio-oils/biocrudes. Early research focused on adjusting process conditions and working with model bio-oil mixtures while using the same sulfided catalysts that oil refineries use for desulfurization (Corma et al., 2007). Although alumina supported Co-Mo and Ni-Mo catalysts have encountered various problems when processing bio-oils, they improve hydrotreating selectivity and they are widely

available at a relatively low cost.

Bio-oils are thermally unstable and it is generally thought that they would likely first have to be pretreated at lower temperatures in order to form a stable oil intermediate that can then be further hydrotreated at high temperatures. Single-stage hydrotreating of bio-oil at high temperatures results in a heavy, tar-like product (de Miguel Mercader et al., 2010; Jones et al., 2009) due to the polymerization, charring and eventually coking reactions. At high temperatures these take place faster than the desired hydrotreating reactions. However, effective hydrotreatment often requires high temperatures, high hydrogen pressures and extended reaction times (up to 4 hours) (Elliott, 2007).

In order to overcome these challenges, a two-stage bio-oil upgrading approach has been successfully used (Elliott, 2007; Jones et al. 2009). The first, mild, catalysed hydrotreatment stabilizes the bio-oil and a second, higher severity hydrotreatment stage deoxygenates the fuel to transport-grade liquids. The first hydrotreatment typically forms at least two phases, one hydrophobic and one hydrophilic and effectively separates out a large proportion of the water within the bio-oil. The resulting hydrophobic liquid is more stable and amenable to further catalytic upgrading. While two-stage hydrotreating is required to make fast pyrolysis bio-oils, a two-stage hydrotreating approach may not be required for catalytic pyrolysis. HTL biocrude upgrading and one-stage upgrading of catalytic pyrolysis oil has been successful trialed (Van Dyk et al., 2019a).

A deeper and ongoing better understanding of the chemistry of biocrude components and their reactivity should clarify the reasons for bio-oil instability and the need for two-stage hydrotreating at different temperatures. As summarised in Figure 10, under various hydrotreatment conditions, different model compounds are hydrogenated and stabilised at various temperatures (Centeno et al., 1995; Ferrari et al., 2001).

The olefins and other double bond species are the most reactive and can be hydrogenated to more stable components such as alcohols and alkanes at temperatures around 250°C and below. Alcohols are dehydrated to olefins at temperatures closer to 300°C, while carboxylic groups are more recalcitrant than alcohols. Aromatics are the most recalcitrant and will only react at temperatures in the vicinity of 400°C. This reactivity scale is a very useful rule of thumb in the absence of precise reaction kinetics.
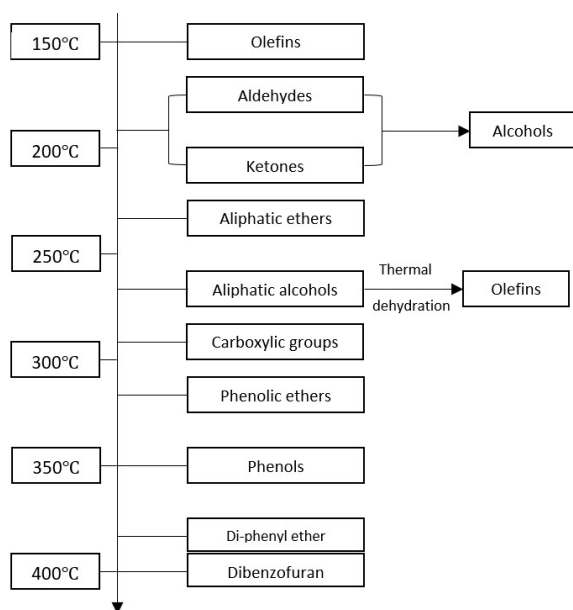
*Figure 10: Reactivity of oxygenated compounds under hydrotreatment conditions. (Elliott, 2007)*

As noted earlier, coking is a major problem during hydrotreatment as it can lead to catalyst deactivation and reactor plugging. In general, the parameters that promote coking are high temperatures, low hydrogen pressures, high acidity and the presence of low H/C components such as phenolics, alkenes and highly oxygenated carbon molecules (Huber, 2007; Mortensen, 2011). Double bond molecules such as olefins, ketones and aldehydes are particularly prone to polymerization and coking. Fortuitously, these species can be hydrogenated relatively easily during the first, low severity, hydrotreatment stage. This improves the thermal stability of the resulting bio-oil before the second hydrotreatment step. Refinery HDS catalysts promote the formation of coke by creating an acidic environment and promoting the formation of aromatics. Aromatics are desirable up to certain concentrations since they form part of transport fuel blends, particularly gasoline (40% aromatics) (Bauen, 2009). However, aromatics are a low H/C ratio species and can act as precursors for coking reactions upon upgrading. The hydrogenation of aromatic rings is the most challenging as it requires high temperatures and hydrogen pressures (around 4.0 to 8.0 MPa of $H_2$) as well as highly active catalysts such as precious metals (H. Wang et al., 2013). Another way in which hydrogen can reduce coke formation is by converting catalyst-absorbed reactive species, such as alkenes, to stable molecules such as alkanes. In general, the presence of hydrogen appears to play a pivotal role in minimizing the formation of coke.

Alternative catalysts may circumvent the challenges encountered with traditional HDS catalysts such as CoMo and NiMo supported on alumina materials. Precious metals such as Ruthenium, Palladium and Platinum have been assessed as bio-oil hydrotreatment catalysts (Bridgwater, 2012). These metals performed better than CoMo and NiMo catalysts in terms of both hydrocarbon yields and H/C ratio of the final product (Lin et al., 2011; H. Wang et al., 2013; J. Wildschut et al., 2009). They were also more stable, less acidic and did not promote coking when supported on non-acidic carbon. The company UOP has been a leader in using precious metal catalysts for hydrotreatment of petroleum and together with PNNL they have assessed the potential of non-sulfided metal catalysts such as Ruthenium on bio-oils.

Ruthenium seems to be the lowest cost and most promising of the precious metal catalysts assessed so far (J. Wildschut, Iqbal et al., 2010; J. Wildschut et al., 2009; J. Wildschut, Melian-Cabrera et al., 2010). When Lin et al. (2011) assessed various precious metal catalysts using the model compound guaiacol, they reported that the Ru-based catalyst showed the best HDO activity and a preference to saturate benzene rings. Although Ruthenium is less expensive than Palladium and Platinum, in 2013 the spot price for Ru was about USD $3 million/t, which was more than a 100 times the same day price of Cobalt (ca. USD $30,000 USD/t), Nickel (ca. USD $10,000/t) or Molybdenum (ca. USD $20,000/t) (IndexMundi, 2013; InvestmentMine, 2013). Although precious metal catalysts are more favoured for bio-oil hydroprocessing, as they are more active in comparison to NiMo and CoMo based catalysts, their cost is so prohibitive that their use in industrial applications is very limited.

The ability to recycle and the stability of Ru/C catalysts has been challenged by Wildschut (2009). When he conducted three successive hydrotreatment reactions (200 bar, 350°C and 4.3 h each) where the catalyst was reused after repeated acetone washes, he found that the activity of the catalyst deteriorated even after the first repeat. After 2 repeats the oil yields dropped significantly (55 to 30%-wt.), whereas the amount of gas phase (5 to 11%-wt.) and solids (3 to 20%-wt.) increased. This indicated significant catalyst deactivation. This deactivation mostly affected the ability of the process to hydrogenate while it did not significantly affect its ability to deoxygenate. The deactivation was attributed to sintering and coke formation on the surface of the catalyst. It would therefore be desirable if the catalysts could have been regenerated with a more effective technique than acetone washing.

The prohibitive price of precious metals means that novel catalysts have to be designed if we are to achieve high hydrotreating activity at lower cost. Although phosphide catalysts have been suggested as alternatives to sulfide catalysts, they face similar issues as, once in contact with water, they form phosphates which can deactivate the active sites on the catalyst (Wang et al. 2013).

As well as deoxygenation, the hydrotreatment of bio-oils has several other favourable effects such as decreasing the bio-oils water content, increasing its energy density (from 18 MJ/kg in crude bio-oil to 40 MJ/kg in hydrotreated bio-oil), decreasing its bulk density (from >1 in bio-oils to <0.8 in deoxygenated bio-oils), decreasing the coking propensity and decreasing its viscosity (from > 100cps in raw bio-oil to <5 cps in bio-oil that contains <5% oxygen) (Elliott, 2007). All of these advantages result in higher yields and the higher $H/C_{eff}$ ratio of the final transport fuel product. These benefits are generally absent in any bio-oil upgrading technologies that do not entail any hydrogen inputs.

### 5.2.2.7 Catalytic cracking

Catalytic cracking is a process used in the Fluid Catalytic Crackers (FCCs) of oil refineries and it can be used in bio-oil upgrading as a non-hydrogen consuming, non-pressurized, alternative to hydrotreatment. The main deoxygenation mechanism of catalytic cracking is the rejection of oxygen in the form of coke and $CO_2$. The conceptual reaction of this mechanism is summarised below:

$$C_1H_{1.33}O_{0.43} + 0.26O_2 \rightarrow 0.65CH_{1.2} + 0.34CO_2 + 0.27 H_2O$$
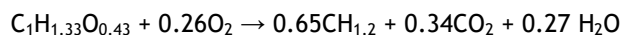
When this formula is compared with the earlier equivalent formula for hydrotreating it is apparent that, in the absence of hydrogen, as occurs in zeolite cracking, the extent of bio-oil upgrading is poor. The theoretical carbon yields for catalytic cracking are low (65% compared

to 100% in hydrotreatment) and the hydrocarbons produced have a low H/C ratio (1.2 compared to 2 for hydrotreatment). This low H/C ratio indicates that the upgraded bio-oil is rich in aromatics and olefins and that the resulting fuel will have a low heating value. Typically about 20-25% lower than crude oil (Balat et al., 2009; Mortensen et al., 2011). Similar to what occurs in hydrotreatment, the cracking reaction takes place alongside other undesirable reactions such as polymerization and coking. This results in the diversion of some of the carbon from the targeted liquid biofuel. Thus, even in the presence of catalysts, cracking typically results in bio-oil-to-fuel yields in the range of 14-23 wt% of bio-oil (Balat et al., 2009). This is much lower than the theoretical 45 wt% yield which can be calculated from the equation above and is largely because 26-39 wt% of the starting bio-oil goes towards the formation of solid tar and cokes (Balat et al., 2009).

Zeolites such as ZSM-5 and HZSM-5 are made of a highly porous aluminosilicate matrix and, as a result, they are typically not stable in the presence of bio-oils at high temperatures and pressures. Zeolite catalysts such as ZSM-5 have a strong acidity, high activities and shape selectivity's which work well for upgrading petroleum feeds. However, for bio-oils, zeolite cracking poses severe catalyst coking and deactivation issues.

On the more positive side, zeolite cracking requires no hydrogen gas and can operate at atmospheric pressure. This means that FCC-type systems can be used for bio-oil processing where the heavily coked catalyst can be rapidly regenerated in the FCC combustor. These systems have great potential to utilise the coke formed on catalysts as a fuel for heat and power generation. However, these systems often convert more biomass carbon to thermal energy than to liquid fuel products. Operating costs of FCCs are higher than regular fixed bed reactors because the faster recycling of carrier gas needed to regenerate the rapidly coked catalyst is highly energy-intensive.

Other workers (Vispute et al., 2010) have proposed an approach that involves a mild hydrotreating step prior to zeolite cracking. The advantage of this approach is that it converts the most reactive oxygenated compounds, the carbonyls, to more thermally stable alcohols. In zeolite cracking carbonyl functionalities go directly to coke formation whereas alcohols contribute to the formation of valuable molecules such as olefins and aromatics. The introduction of a mild hydrotreatment step prior to zeolite cracking appears to result in bio-oil conversion yields (aromatics) which are as much as three times higher than those obtained in direct zeolite cracking. This is particularly desirable for BTX (benzene, toluene, xylene) production which is the target of the company AnelloTech. However, the alkane yields are low and, while this technology may be relevant to making aromatic fractions for gasoline, it is not directly applicable to the production of the longer chain hydrocarbons that are needed for the production of diesel and jet fuels.

### 5.2.2.8 Impact of high aromatic content in biocrudes on potential biojet production

Biocrudes have a high aromatic content when derived from lignocellulosic biomass due to the polyaromatic structure of lignin. It has been demonstrated that fast pyrolysis biocrudes can have about 40% aromatic content, potentially rising to over 60% in catalytic pyrolysis and HTL biocrudes. However, these values may vary depending on operating conditions (Van Dyk et al., 2019b).

As the aromatic content is regulated as part of fuel standards worldwide the European standards for gasoline allow a maximum of 35% aromatic content, with aromatics improving the octane rating of gasoline. Alternatively, for diesel, the European standards limit the polyaromatic content to a maximum of 8%. Although the total aromatic content, according to

manufacturers' specifications, indicate a maximum of 15%, some standards allow up to 35% aromatic content (IEA-AMF, n.d.).

With respect to conventional jet fuel specifications, an aromatic content is desirable to maintain the integrity of elastomer seals. Thus, a minimum of 8% aromatics is specified up to a maximum of 25% (ASTM D1655). Within ASTM D7566, Annex A4 (synthesized paraffinic kerosene plus aromatics (SPK/A) allows a maximum of 20% aromatics. While Annex A6 (catalytic hydrothermolysis jet) allows an aromatic content between 8 and 20% all other Annexes only permit a maximum of 0.5% aromatic content with the minimum aromatic content supplied by blending with conventional jet fuel. It should be noted that a low aromatic content is desirable to reduce soot formation and associated environmental impacts. Where the biojet fraction has a high aromatic content, it will have to blended with a low aromatic conventional jet fuel in order to meet ASTM D1655 specifications for the blended fuel. Producing a biojet fuel through direct thermochemical liquefaction technologies may require significantly lower the aromatic content of any biojet fuel, although it is not known what an allowable maximum would be.

Reduction of aromatics can be achieved through hydroprocessing, but high severity conditions, such as high hydrogen pressure, is required, as well as some cracking function in the catalyst. Additional processing will increase the cost of production and reduce the potential emission reductions. As it is not possible to only target the aromatic compounds, higher severity conditions would likely lead to additional cracking of other molecules consequently leading to smaller and even gaseous molecules which would change the product distribution. For example, a dedicated hydrotreating approach of neat biocrude from fast pyrolysis, catalytic pyrolysis and HTL biocrudes achieved final aromatic concentrations in the biojet fraction of 18%, 30%, and 20%, respectively (Van Dyk et al., 2019b).

### 5.2.2.9 Economics and sustainability of the direct thermochemical pathway with upgrading

The potential cost of drop-in biofuel derived via fast pyrolysis and upgrading indicate that this process could supply fuel at a price of $1120 (S. B. Jones et al., 2013) or $982-1520 (A. Brown et al., 2020). Other workers have suggested that the MFSP from fast pyrolysis and upgrading ($1275-2625) is significantly lower than for HTL and upgrading ($2613-4475) when woody feedstocks are used (Bann et al., 2017). In contrast, other work indicated that HTL can produce a cheaper biojet product ($1062-1530) compared with fast pyrolysis and upgrading ($1534-2183) (de Jong et al., 2017b). When related work compared standalone biofuel production from bio-oil ($982-1520) with a coprocessing pathway ($946-1664) similar MFSP values were obtained (A. Brown et al., 2020).

Although potential emission reductions of 77-80% for hydrothermal liquefaction-based biojet fuel have been reported (De Jong et al., 2017) other work has suggested that fast pyrolysis and upgrading (into gasoline) might achieve emission reductions of between 51-96%, depending on feedstock, process design, fuel yields, H2 sources and co-product applications (J. Han et al., 2011).

### 5.2.2.10 Opportunities and challenges for producing biojet fuel *via* direct thermochemical liquefaction pathways

As direct thermochemical liquefaction technologies use nearly any biomass feedstocks (e.g. sewage sludge, manure, algae, waste plastics, food waste, etc.) the technology has the potential to supply significant volumes of drop-in biofuels. As a liquid intermediate is produced, these biocrudes could be relatively easily co-processed to low-carbon intensive fuels. However, significant challenges remain to be resolved with the high investment cost required for construction of facilities posing a particular barrier. Technical challenges for HTL scale-up include engineering challenges, as high pressures are required during processing, while production of pumpable slurries is still an issue.

The high viscosity of catalytic pyrolysis and specifically HTL biocrudes can cause problems with pumping. As a result, higher temperatures or solvents have been used, although the use of solvents can have an impact on the LCA of the final fuel. Making biojet fuel by this route results in a high aromatic content with any reduction in aromatics requiring high severity conditions and catalysts with cracking capability. Similarly, removing the last oxygen from biocrudes requires high hydrogen pressures and is considered uneconomical by some authors (Jenkins et al., 2016).

## 5.3 CATALYTIC HYDROTHERMOLYSIS (CH)

Catalytic hydrothermolysis is one of seven technology pathways that have been certified under ASTM D7566. The process was developed by Applied Research Associates (ARA) in partnership with Chevron Lummus Global (CLG), called the Biofuels IsoCoversion (BIC) process. The process uses lipids as feedstock, including fats, oils and greases (FOGs). The feedstock is mixed with up to one-third water and converted at pressures between 200 and 250 bar and a temperature between 500 and 600°C (supercritical conditions) (Kaltschmitt & Neuling, 2017). This step is followed by hydrotreatment and fractionation to produce LPG, naphtha, kerosene and diesel. A jet fraction of about 33% can be produced.

One of the advantages of catalytic hydrothermolysis compared to HEFA is a 25% lower hydrogen consumption (Kaltschmitt & Neuling, 2017). Unlike HEFA, where the majority of molecules are paraffinic in nature, catalytic hydrothermolysis also produces cyclo-alkanes and aromatics, similar to conventional jet fuel. According to ASTM D7566, CH biojet can contain between 8 and 20% aromatic content. However, a maximum blend rate of 50% can be used. The company ARA also uses a patented pretreatment process, Hydrothermal Cleanup (HCU), as an integrated part of their technology to remove heavy metals and other contaminants from feedstock prior to production of liquid fuel products.[20] A recent techno-economic study has suggested a price of $829 per tonne for CHJ based on brown grease, $1162 based on yellow grease and $1767 based on carinata oil (Mcgarvey et al., 2018).

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[20] https://www.ara.com/products/hydrothermal-cleanup-fat-splitting-technology/

## 5.4 BIOCHEMICAL METHODS USED TO PRODUCE LIQUID HYDROCARBON DROP-IN BIOFUELS

Biochemical approaches, such as the fermentation of glucose to ethanol (conventional or first generation biofuel production), also include "advanced" biocatalytic processes that convert sugars to less oxygenated, more energy-dense molecules such as longer chain alcohols (butanol, butanediol) and higher molecular weight compounds such as isoprenoids and fatty acids. Earlier work (Karatzos et al. 2014) has provided a detailed overview of the various pathways used by the biochemical platform.

There are numerous biological pathways, feedstocks, and microorganisms that can be utilised for the production of drop-in biofuels and intermediates. Microorganisms such as cyanobacteria and algae can directly capture $CO_2$ from the atmosphere and convert it to ethanol or lipids. Alternatively, bacteria, yeasts and heterotrophic algae can utilise sugars derived from sugar cane, sugar beet, starch and other energy storage polysaccharides, or from the hydrolysis of the cellulose and hemicellulose carbohydrates in cellulosic biomass. Other bacteria can utilise hydrogen and carbon monoxide in syngas to produce alcohols, etc. The three main categories of intermediates that are produced include alcohols (ethanol and butanol), fatty acids (similar to lipids in vegetable oils) and longer hydrocarbons (such as isoprenoids, e.g. farnesene). These intermediates can all be used to make drop-in biofuel products through different routes. Isoprenoids can be upgraded into hydrocarbon fuels through a simple hydrotreating step and this is done by Amyris to produce farnesane, although only at low blends (10%). Fatty acids can be upgraded through the oleochemical pathway into drop-in biofuels as a jet or diesel replacement. Shorter molecules containing oxygen, such as ethanol and butanol, can be used to produce drop-in biofuels through the alcohol-to-jet pathway.

Cyanobacteria, yeasts and bacteria can be selected or engineered to produce either higher alcohols or isoprenoids and lipids. Although the metabolic pathways from one organism can be heterologously expressed in another, after biological production, regardless of which biosynthesis route is used, some form of hydroprocessing of the produced intermediate is typically required to saturate double bonds, etc. before blending with conventional petroleum fuels. As described earlier, the more oxygenated and unsaturated the intermediate, the more hydrogen is required for it to be upgraded to a fungible drop-in functional equivalent to diesel, jet or gasoline blendstock.

From a commercialization point of view, an attractive aspects of biochemical technologies is the potential to "piggy-back" onto existing ethanol facilities by switching the microorganism used in the microbe-to-ethanol process to obtain a "microbe-to-drop-in fuel or fuel intermediate" process. This is the strategy used by the company Gevo that converted an ethanol facility to produce isobutanol. This can substantially reduce the investment cost required.

In earlier work (Karatzos, Mcmillan et al., 2014c), it was concluded that the production of higher value chemicals based on the biochemical platform was a more attractive value proposition than biofuels. While biochemical products can have multiple uses as chemical feedstocks, solvents, or fuels, fuels are generally the lowest value proposition. Consequently, companies such as Amyris moved away from biofuel production as their product is worth far more in the biochemical and cosmetic industry. With fewer processing steps and less hydrogen consumption and higher feedstock conversion yields, biochemical platform technologies can be used to produce oxygenated and low $H_{eff}/C$ products that will likely

generate higher revenues as higher-value chemicals than as biofuels. However, policies that incentivise fuel production may shift production towards fuels.

However, one exception in this trend has been in the production of biojet fuels. Gevo obtained ASTM certification for their isobutanol to jet technology in 2017 while Lanzatech obtained ASTM certification for their ethanol to jet technology in 2018. It is likely that the high demand for biojet fuels and their limited commercial availability has driven development of these pathways, even when these biojet fuels come at a premium cost. Gevo is regularly supplying its biojet product to airlines worldwide. Similarly, Lanzatech recently launched Lanzajet, dedicated to the production of biojet fuels[21], receiving large investments from Suncor and Mitsui for construction of a facility that should be completed in 2022.

The efficiency of biological conversion processes can be measured using the key parameters below and this can be used to differentiate the various biochemical pathways (Karatzos, McMillan et al., 2014).

- **Yield** is calculated as the mass of product per unit mass of feedstock (g/g) and measures the proportion of carbon source feedstock (e.g., sugars or biomass) converted into the desired product as opposed to less desirable products such as cell mass, $CO_2$, or non-target compounds. The minimum product yield required to achieve cost-competitive production is a strong function of feedstock cost.
- **Titer** is the concentration (g/L) of product in the production medium at the completion of the biological production process. The final product titer influences process capital and operating costs since lower titers typically mean more production vessels (or larger volumes) are required to produce a given quantity of product and greater amounts of process energy are usually required to recover a given amount of product.
- **Productivity** is the volumetric production rate (g/L/h) at which the product is formed. Productivity strongly influences capital expenditure since slower production rates mean a longer residence time is required to achieve a given production target and the facility would likely require more fermenter vessels than a facility with a higher productivity. Doubling volumetric productivity, for example, results in a 50% reduction in capital costs per unit of product.
- **Recovery** of the desired product at high yields and in usable form is critical. The percentage product recovery indicates how much of the generated product is economically recoverable from the fermentation broth or from intracellular production. This is often well below 100%. For example, most fatty acids are generated intracellularly and their recovery requires cells to be permeabilised or lysed, making high levels of product recovery more techno-economically challenging.

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[21] https://www.lanzatech.com/2020/06/02/lanzajet-takes-off/

Similarly, the key parameters used for conventional ethanol production from *Saccharomyces cerevisiae* can be used as a benchmark to compare other processes:

- Theoretical yield (g/g of glucose) – 0.51
- Volumetric productivity (g/L/h) – 2.00-3.00
- Titer (g/L) – 47-55 (6-11% v/v)
- Fermentation time – 6-12 h

The product yield in conventional ethanol production processes is very high and yeasts routinely achieve 90–95% of theoretical yield in converting 45 – 48% of feed sugar on a mass basis to ethanol. Thus, lower theoretical and mass yields can be expected for biological conversion processes that produce more reduced molecules with higher $H_{eff}$/C ratios, as proportionally more oxygen, which represents approximately 46% of carbohydrate mass, must be removed.

### 5.4.1 Biochemical production of farnesane from sugars

This pathway has been certified under ASTM D7566 (Annex 3A) and is termed the Synthesized Iso-paraffins (SIP) from hydroprocessed fermented sugars. It was previously known as the Direct Sugar to Hydrocarbons (DSHC) pathway. The scope of certification is limited to the farnesane ($C_{15}H_{32}$) produced by hydroprocessing and fractionation of farnesene ($C_{15}H_{24}$) derived from the fermentation of sugars. Farnesane can only be used in a 10% blend with conventional jet fuel. Farnesene is an example of an isoprenoid, with more than 50,000 molecules in this class. It is a naturally occurring compound and has application in medicine, cosmetics, agriculture, etc. The isoprenoids are most commonly found in plants and are classified based on the number of carbons, with farnesene termed a sesquiterpenoid. Researchers have engineered biosynthetic pathways in various microorganisms, such as yeasts, *E. coli*, etc. to produce isoprenoids at high yields. The chemistry of isoprenoids make them very suitable for use as a liquid hydrocarbon fuel as it has a low freezepoint and high cetane levels (George et al., 2015)

In 2015, Amyris reported that they were able to lower the manufacturing cost of farnesene to $1.79/L[22] (excluding the cost of upgrading to farnesane). Amyris has continued research into strain improvement through metabolic engineering while also investigating the production of farnesene from lignocellulosic sugars (from pine). However, the estimated production cost at a commercial scale was calculated to be $4-5/L[23]. As a chemical reagent, farnesene is sold for research purposes at $459/kg[24]. Thus, it is unlikely that farnesene will ever be cost-competitive with other biojet fuels. Further challenges include the low yields through biological production and challenges of large-scale commercial production. Ongoing research to achieve improvements that include synthetic pathways (Chatzivasileiou et al., 2019) may result in improved yields that could impact the economics. However, it is likely that applications in cosmetics and pharmaceuticals will be a far more lucrative proposition for

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[22] https://cen.acs.org/articles/93/i41/Amyris-Puts-Price-Farnesene.html#:~:text=The%20biobased%20chemical%20maker%20Amyris,chemical%20farnesene%3A%20%241.75%20per%20L.

[23] https://www.biofuelsdigest.com/bdigest/2019/11/24/oh-so-sweet-amyriss-look-at-farnesene-production-from-sugars-the-digests-2019-multi-slide-guide-to-megabio-and-farnesene/22/

[24] https://www.biofuelsdigest.com/bdigest/2019/11/24/oh-so-sweet-amyriss-look-at-farnesene-production-from-sugars-the-digests-2019-multi-slide-guide-to-megabio-and-farnesene/22/

companies as the isoprenoid market continues to grow.

The MFSPs for farnesane production based on techno-economic analyses suggested a cost of $1375-2450 per tonne (sugarcane feedstock), $1625-9673 per tonne (corn grain feedstock), and $5664-7552 per tonne (forest residue feedstock (Bann et al., 2017; de Jong et al., 2017a) which is much higher than any of the other biojet fuels. Life cycle factors based on default ICAO values indicate 32.8 gCO2/MJ (sugarcane feedstock in Brazil), and 52.6 gCO2/MJ (sugarbeet in the EU) (ICAO, 2019).

### 5.4.2 Alcohol-to-jet technology for biojet fuel production

The alcohol-to-jet (ATJ) technology is divided into two components, the alcohol production and the jet production from the alcohol intermediate. The most common method for producing alcohol is through biological fermentation of sugars. This has been used for thousands of years and is the method used to produce bioethanol from corn and sugarcane (so-called first-generation biofuels).

The second step in biojet production uses any alcohol as a base feedstock for conversion into long-chain hydrocarbons. This is achieved through the three basic steps of dehydration of the alcohol into olefins, oligomerization of the olefins followed by hydrogenation. This is a well-established process in the refining industry, e.g. the methanol-to-gasoline process.

Commercial applications of the ATJ technology have focused on using ethanol and butanol (iso- and n-butanol) as the starting material and several companies are working in this area. Although Gevo and Lanzatech/Lanzajet have received a lot of attention, other companies in this space include BYOGY, Cobalt, Swedish Biofuels, Terrabon, UOP, Zeachem, and Vertimass.

### 5.4.2.1 Ethanol production

Bio-ethanol, as a conventional or first-generation biofuel, is biochemically produced *via* fermentation of sugars or starch by varieties of the yeast *Saccharomyces cerevisiae*. It is fully commercial, optimised and serves as a benchmark against which alternative biological conversion pathways can be compared. A typical bioethanol process involves direct utilization of sugars from sucrose, starch or cellulosic feedstocks (enzymatically hydrolysed) for fermentation into ethanol. The ethanol is finally recovered from the broth.

The "ethanologenic" microbe itself typically contains the invertase enzyme needed to break disaccharide sucrose (derived from cane or sugar beet) down to its hexose monomers (fructose and glucose). For starch hydrolysis, externally sourced "amylase" enzymes are usually used and this is the dominant route practiced in the US corn ethanol industry. A more complex process is required to hydrolyse lignocellulosic carbohydrates to fermentable hexose and pentose monosaccharides. A typical cellulosic ethanol production process involves multiple steps, including pretreatment of feedstock, enzymatic hydrolysis of the cellulose and hemicellulose into fermentable sugars, fermentation into alcohol and recovery of the alcohol from the fermentation broth. Cellulosic ethanol uses potential waste feedstocks, such as agricultural residues, that are available in large quantities and are considered more sustainable than feedstocks such as corn or sugarcane. In addition, cellulosic ethanol is able to achieve far greater emission reductions than ethanol from corn. However, despite decades of research and development, commercialisation has been challenging from a technical and

economic perspective. Several commercial facilities around the world have closed down in spite of favourable policies, e.g. in the USA. While cellulosic ethanol, or even butanol, can similarly be used to produce a biojet fuel, the challenges to do this economically are significant.

### 5.4.2.2 Using alternative organisms for ethanol production

Several other microbes are also able to produce alcohols. The so-called ABE process (Acetone, Butanol, and Ethanol) using Clostridia was developed in the earlier part of the 20th century as a commercial process for production of acetone and butanol. However, the low price of fossil fuels made this process uneconomical (Chen & Liao, 2016). Several clostridial species can be utilised for ethanol production, including *Clostridium acetobutylicum*, *C. saccharobutylicum*, *C. beijerincki* and *C. saccharoperbutylacetonicum*. Alternative microorganisms are also being evaluated and developed for ethanol production such as *Zymomonas mobilis,* which is a rapidly fermenting ethanologenic bacterium, and thermophilic bacteria that can operate at the higher temperatures typically used for enzymatic hydrolysis of cellulose.

Thermophilic bacteria such as *Thermoanaerobacterium saccharolyticum* are able to tolerate higher temperatures than 30-35°C which is the optimum temperature range for most mesophilic yeast. An ablity to operate at higher temperatures can have numerous process advantages, especially for enzyme based cellulosic ethanol production. In particular, enzymatic hydrolysis of cellulose is typically performed by cellulolytic enzymes that exhibit temperature optima of 45-50 °C or even higher. The discrepancy in temperature optima between the sequential steps of enzymatic hydrolysis and fermentation creates a need to cool the process medium prior to fermentation. In contrast, thermophilic ethanologens are able to operate at the same temperature as the hydrolytic enzymes, circumventing the need for cooling. Lower feedback inhibition on the enzymes is an additional advantage of this simultaneous saccharification and fermentation approach (SSF) as glucose is simultaneously produced and converted in the same process step. However, to date, the performance of thermophilic bacteria that have been investigated for this application is below that of *S. cerevisiae* and *Z. mobilis,* and their ethanol tolerance is also significantly lower (*cf* 2%-5% vol for thermophilic bacteria vs up to 20% vol or higher for industrial strains of *S.cerevisiae*) (Weber et al., 2010).

### 5.4.2.3 Ethanol recovery from fermentation

Ethanol has a high vapour pressure and can readily be recovered and concentrated by distillation of the aqueous fermentation broth. However, ethanol forms an azeotrope with water such that distilled ethanol still contains 3 wt% or more water. This remaining water can be removed (if required) through molecular sieves or other dehydration technologies (e.g., pervaporation or ternary distillation), which are widely practiced at industrial scale. Ethanol recovery and purification processes are relatively well understood compared to recovery of other potential biofuels such as butanol and higher molecular weight compounds which have lower vapour pressures and are produced at lower maximum titers. Distillation is very energy intensive and improvements in ethanol recovery with lower energy consumption can improve the economics of production.

### 5..4.2.4 Butanol production

Butanol is a four carbon primary alcohol with a volumetric energy content of 28 MJ/L, which is higher than ethanol's 19 MJ/L and closer to gasoline's 36 MJ/L (Pfromm et al., 2010). When compared to ethanol, butanol also has a lower volatility and is less hygroscopic and corrosive.

The octane number of normal butanol (n-butanol) is about 87, while branched chain butanols (isobutanol) have an even higher octane number (Nexant, 2012). The butanol molecule can be directly blended with gasoline at high volumetric ratios (Jin et al., 2011). From 1914 up until WWII, butanol was primarily produced via fermentation using the bacterium *Clostridum acetobutylicum* (Qureshi & Blaschek, 1999).

The fermentation of sugars to n-butanol has been advocated as a potential platform to produce drop-in biofuel intermediates. The equation below describes the theoretical stoichiometric conversion of glucose to butanol via the ABE pathway.

$$C_6H_{12}O_6 + 2ADP + 2\ P_i \rightarrow C_4H_9OH + 2\ CO_2 + H_2O + 2\ ATP + CoA$$
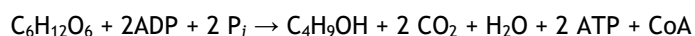
The lipophilic nature of butanol makes it much more toxic to microbial systems than ethanol. As it accumulates intracellularly, it disrupts phospholipid components of the cell membrane causing an imbalance in cellular metabolism by disturbing the selective flow of metabolites, nutrients and toxics in and out of the cell (Jin et al., 2011). Other challenges to using *Clostridium* sp. in industrial settings are their relatively slow growing nature and susceptibility to bacteriophage attack and cell degeneration, as well as a requirement to maintain strictly anaerobic conditions (Weber et al., 2010).

While n-butanol is the isomer that is naturally made by the ABE pathway, some companies such as Gevo and Butamax have engineered pathways in yeast cells to produce isobutanol. This isomer has proven to be easier to produce in yeast and it is also more valuable as a biofuel feedstock as a result of having a branched carbon chain.

Extensive research has been carried out using metabolic engineering of numerous microbes for biobutanol production. Investigations have looked at metabolic pathway design, utilisation of novel strains and strain optimization (Chen & Liao, 2016). However, key obstacles are still present, such as yield, titer and productivity to make the process economically attractive (Chen & Liao, 2016). In the case of butanol, product toxicity also plays a major role and has been a key challenge to high yields (Chen & Liao, 2016).

Another strategy to overcome solvent toxicity of butanol (or ABE pathway products) is to design production systems that enable continuous product removal. Gevo has developed patented processes for the separation of their isobutanol product from the fermentation broth to overcome toxicity problems. At the same time, simultaneous separation allows higher recovery of product from the fermentation broth. This is a critical component of the company's approach.

### 5.4.2.5 Syngas fermentation
Some autotrophic microorganisms can use single carbon compounds such as CO and $CO_2$ as sources of carbon and energy-rich compounds such as CO and $H_2$ as sources of energy to produce a variety of compounds, including ethanol, butanol, butanediol, acetic acid and other molecules.

Some of these microorganisms include acetogenic bacteria such as *Clostridium ljungdahlii* and *Clostridium carboxidivorans* (Munasinghe & Khanal, 2010). This technology is used by Lanzatech and Lanzajet for production of biojet fuel. The CO, $CO_2$ and $H_2$ can be derived from a variety of sources, including the syngas from gasification of feedstocks such as biomass or MSW. Lanzatech is especially known for its use of waste gases from steel production for

fermentation and production of ethanol.

The primary limiting step for syngas fermentation is the low solubility of CO and $H_2$ gases in aqueous solutions as these gases must first be absorbed into the aqueous fermentation broth to be microbially assimilated (Munasinghe & Khanal, 2010). As the gas-liquid mass transfer and solubility of both molecular hydrogen and carbon monoxide in water are quite low compared to more conventional sugar substrates (where gas-liquid mass transfer isn't needed), syngas fermentation rates are typically constrained by physical mass transfer limitations rather than being limited by metabolic capacities. From an energy balance perspective, syngas also has to be cooled down from a production temperature of about 700°C or higher to about 50°C or less before it can be fermented. This significant cooling requirement result in significant engineering challenges and generally have an adverse effect on process energy efficiency.

The gas-liquid mass transfer challenge of syngas fermentation platforms has been a long-standing focus of engineering research, and various reactor designs have been assessed to try to improve the contact surface area between gases and liquids and achieve increased dissolution and diffusion rates. Designs include continuous stirred tank, microbubble dispersion stirred tank, bubble or gas lift columns, hollow fiber and other membrane-based systems, trickle bed and monolithic biofilm reactors. A detailed description of possible reactor designs and their operation and relative efficiencies is provided by several reviews (Acharya et al., 2014; Munasinghe & Khanal, 2010). Reactor design plays an important role to improve mass transfer rates (Acharya et al., 2014). Earlier reviews have described volumetric productivities of 0.37 g/L/h (bubbling column reactor), and 1.6 g/L/h and 15 g/L/h (continuously stirred tank reactor) by varying the pressure in the reactor (Acharya et al., 2014). However, a balance must be found between energy efficiency and productivity and ongoing improvements in reactor design. Productivity is also significantly affected by nutrient composition and a balance must also be found between cost of nutrients, especially at large commercial scale (Acharya et al., 2014). Another factor that has a major impact on yield is the composition of the syngas and the specific ratio of CO, H2, and CO2.

Similar to the gasification/FT process, syngas cleanup is very important. Some authors have indicated that syngas fermentation does not require the same stringent syngas cleanup compared to syngas used for FT synthesis, and should therefore be cheaper (Daniell et al., 2012). However, the company INEOS Bio had extensive difficulty with HCN in their syngas which impacted the microbial catalyst and ethanol production [25].

### 5.4.2.6 Using cellulosic biomass feedstocks for Alcohol production

Using cellulosic feedstocks for production of alcohols can produce fuels with a much lower carbon intensity compared to using corn. For example, a fairly recent well to wake life cycle analysis of ethanol-to-jet from corn or corn stover illustrated the attraction of using a cellulosic rather than a starch/sugar feedstock. Using corn as a feedstock, a 16% reduction in CO2e emission per MJ of ATJ was achieved, compared to 89 CO2/MJ of conventional petroleum jet fuel. In contrast, using corn stover as a feedstock resulted in GHG emissions reductions of 73% (Jeongwoo Han et al., 2017). Despite this clear advantage cellulosic ethanol

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[25] https://www.biofuelsdigest.com/bdigest/2014/09/05/on-the-mend-why-ineos-bio-isnt-reporting-much-ethanol-production/

production commercialisation has not been successful, with many of the commercial facilities closing down or repurposing. Technical challenges and high cost of production were key obstacles to economic production, in spite of the very favourable policy environment under the US Renewable Fuel Standard. Consequently, it seems unlikely that production of jet fuel from cellulosic ethanol or butanol will take place in the short-to-medium term. Although it is expected to be more expensive than using easier feedstocks such as corn or sugarcane the increased cost of producing alcohol from cellulosic feedstock may potentially be offset where policies and incentives consider the overall carbon intensity of the final fuel. Companies such as Gevo have also demonstrated that very low carbon intensities (up to 70% reduction in emissions over the life cycle) can be achieved in spite of using corn as a feedstock for alcohol production (P. Gruber, 2019). This is achieved through improvements in farming practices, use of renewable energy in the facility, (e.g. wind turbines and anaerobic digestion of manure for renewable natural gas production) and production of valuable co-products used for animal feed [26].

### 5.4.2.7 Isobutanol production – the Gevo approach

Gevo developed their process for isobutanol production based on a proprietary yeast and a patented Gevo Integrated Fermentation Technology (GIFT) for the continuous separation of the product from the fermentation broth. As mentioned earlier, butanol at low concentrations (<2 wt%) is highly toxic and inhibitory to the biocatalyst. Under normal circumstances this would result in low productivity, low yields and high energy consumption. Removal of the alcohol product through distillation and molecular sieves is very energy-intensive. In order to overcome the toxicity problem and obtain higher yields, different forms of integrated reactors have been proposed, using gas stripping, pervaporation, liquid extraction or adsorption (Kujawska et al., 2015).

The GIFT process is one such integrated process patented by Gevo in 2012, improving the volumetric productivity and reducing energy use through the simultaneous fermentation and recovery while resulting in higher final butanol concentration. The fermentation broth is continuously circulated through the GIFT process. Low pressure evaporation allows removal of butanol to concentrations greater than 20 times the concentration in the fermenter. Condensation of the vapor leaves a relatively pure isobutanol product which is purified in a stripping distillation step. The water component is returned to the fermenter and biomass remains in the fermenter (Ryan, 2019). It should be noted that the alcohol-to-jet process is tolerant of low levels of water and 100% purification is not required for jet fuel production.

This approach has been shown to be able to reduce both the capital and operating costs (Evanko et al., 2012). By increasing the product yield of glucose to butanol from 50% to 90% of theoretical results in a 44% decrease in direct operating costs (Evanko et al., 2012). This also reduces the capital investment required as equipment can be reduced by 32%. Product yield is therefore very important for the overall economic viability of a facility. Figure 11 illustrates the basic process of the GIFT system.

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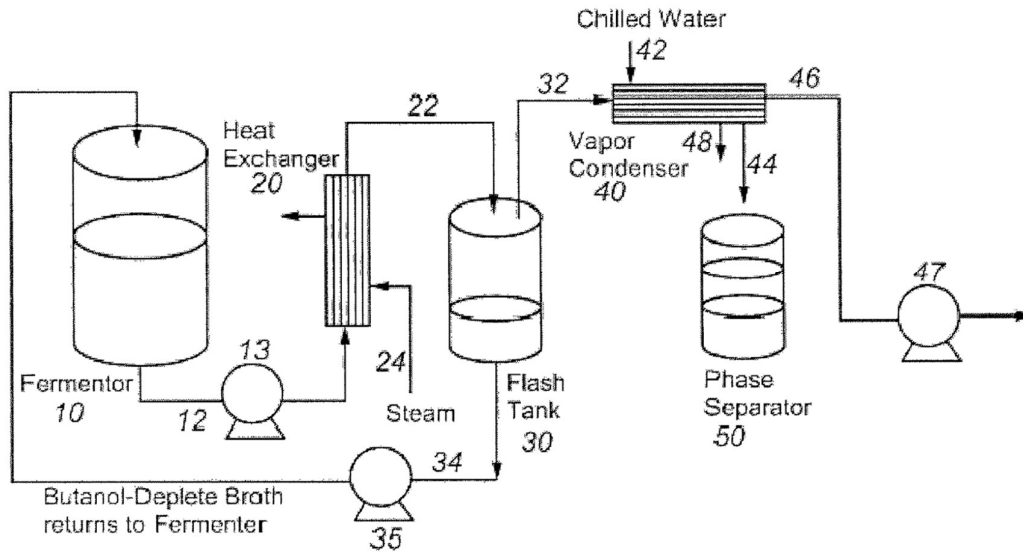[26] https://gevo.com/carbon-neutral-fuel/

Figure 11. Schematic diagram of the continuous vacuum flashing process for isobutanol recovery as shown in the Gevo patent application (Evanko et al., 2012)

Using the GIFT process, an effective titer of ~90 g/L after 65 h has been reported, or a volumetric productivity of about 1.4 g/L/h (Hawkins et al., 2016). This far exceeds yields of butanol reported by other studies, including 0.08-0.46 g/L/h (Jang et al., 2012) and 0.34 g/L/h (Qureshi & Blaschek, 1999), using Clostridium spp.

### 5.4.2.8 Ethanol production through syngas fermentation – the Lanzajet approach

LanzaTech uses a naturally-occurring acetogenic organism to produce ethanol and other products *via* fermentation of syngas. The source of syngas for the Lanzatech fermentation process can be derived from the gasification of biomass, or from industrial waste gases from steel mills (Figure 12).
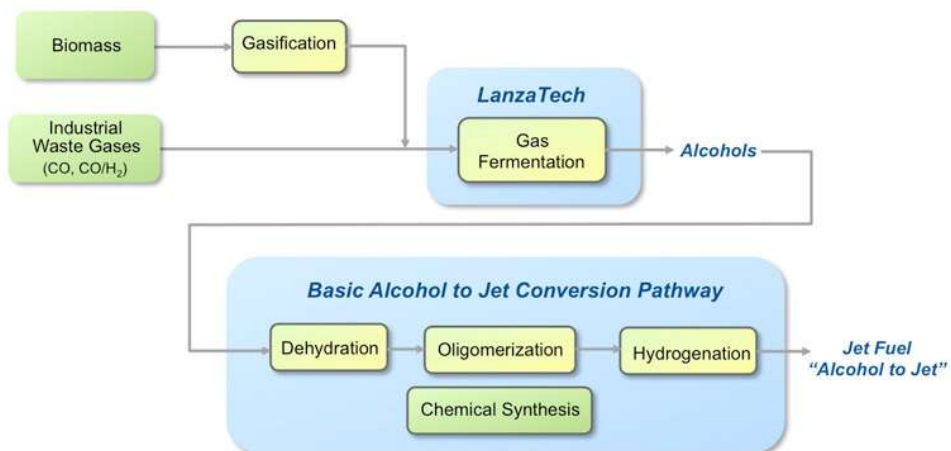


*Figure 12. Graphic illustration of the Lanzatech process*

Multiple gases are produced in steel manufacture and include carbon monoxide (CO), hydrogen (H2), carbon dioxide (CO2), hydrogen sulphide (H2S) and methane (CH4). Gases are cooled, cleaned and injected into the fermentation vessel. As a byproduct of microbial growth, ethanol and other chemicals are produced. The Lanzatech process can utilize gas streams with a range of CO and H2 compositions to produce ethanol and chemicals such as 2,3-butanediol at high selectivities and yields. LanzaTech's proprietary microbes are also able to consume hydrogen-free CO-only gas streams, due to the ability of the microbe to perform a biological water gas shift reaction. This reaction allows the bacteria to compensate for any deficiency in H2 in the input gas stream by catalyzing the release of hydrogen from water using the energy in CO. The Lanzatech microbe is also tolerant to impurities and pollutants and extensive gas clean-up is not required.

The utilisation of gases from steel manufacturing allows for the use of "waste-gases" that would otherwise have been released into the atmosphere. Therefore, although not biogenic in origin, the process is a type of carbon sequestration. The carbon intensity of the final fuel must be considered based on a life cycle assessment and has been calculated to achieve ~67% emission reductions using steel mill off-gases, while gasification of biomass can achieve 88-98% reduction (Handler & Griffing, 2015). A titer of 48g/L ethanol is the highest reported in the literature for Clostridium Ljundalii (Bengelsdorf et al., 2013; Molitor et al., 2016). The Lanzatech microbe also produces 2,3-butanediol (BDO) and methyl ethyl ketone (MEK) as co-products (Lanzatech, 2017). It is likely that the coproduction of biochemicals will play an important role in improving the economics of the ATJ biojet as MEK can be used as an additive to produce synthetic rubber [27] while 2,3-BDO can be used to produce rubber, food additives and cosmetics, or it can be converted to 1,3-butadiene to be used as a chemical intermediate. This has a reported market price of $1378/MT [28]. However, the cost-effective separation of BDO can be expensive due to high energy consumption during distillation, as a result of its high boiling point (177°C) (Lanzatech, 2017).

Although techno-economic and life cycle analyses of the biomass to jet process with and without 2,3-BDO production showed that production, separation of 2,3-BDO and its conversion to butadiene increased the overall capital cost, this was offset by the higher revenue from the sale of this valuable co-product.

### 5.4.3 Alcohol to jet conversion

The basic process for conversion of alcohols to jet is shown in Figure 13. The oligomerization step may have multiple stages depending on the type of alcohol. Although the three main alcohols that are used for commercial development are ethanol, n-butanol and iso-butanol, only ethanol and isobutanol are currently certified for biojet production under ASTM D7566.

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[27] https://www.transparencymarketresearch.com/2-3-butanediol-market.html
[28] https://www.echemi.com/productsInformation/pid_Seven2409-13-butadiene.html#:~:text=Reference%20price%20of%201%2C3,on%202020%2D10%2D23.
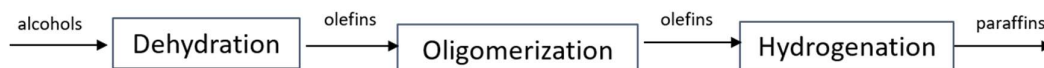
*Figure 13 Basic steps in the alcohol to jet conversion process*

### 5.4.3.1 Dehydration step

Dehydration of ethanol into ethylene is a very well-established commercial process where the ethylene is a precursor for poly-ethylene production. High yields are achieved with current catalytic processes, and no further technology development is really required for this initial step (Brooks et al., 2016). A variety of catalysts can be used, including zeolites, and specialized catalysts such as Syndol are commercially available (Geleynse et al., 2018). However, as described below, an ethylene intermediate is not an ideal intermediate for the oligomerisation step in the production of jet fuel.

Although butanol dehydration is not as established as ethanol dehydration it can be achieved using a variety of heterogenous catalysts, including zeolites, alumina and acid catalysts. While a mixture of butene isomers can be produced, selectivity towards isobutylene, rather than linear butylene, is preferred (Geleynse et al., 2018). High levels of conversion and selectivity to isobutylene can be achieved depending on the catalyst and operating conditions such as pressure (Taylor et al., 2010). Butanol has an advantage over ethanol in this initial step as it dehydrates at lower temperatures and pressures and subsequent oligomerisation of butanol is also much easier (Brooks et al., 2016). For example, a 98-99% conversion rate of butanol to butene can be achieved using ZSM-5, gamma alumina, or Mg-gamma alumina catalysts (Brooks et al., 2016).

Regardless of the type of starting alcohol used, the dehydration step always produces water. Thus, the catalysts used in the dehydration step have to be water-tolerant although the water has to be removed prior to the oligomerisation step. This can be achieved through a number of different processes or combinations such as distillation, liquid-liquid separation or molecular sieves (Geleynse et al., 2018). This means that the starting alcohol does not have to be anhydrous as removing all water from an alcohol can be energy-intensive and expensive.

### 5.4.3.2 Oligomerisation to long-chain hydrocarbons

Direct production of jet-range molecules from an ethylene intermediate is challenging. Although it is the most straightforward method, poor conversion efficiency (requiring significant recycling) and low selectivity for jet-range molecules make the economics unfavourable (Brooks et al., 2016). However, a number of alternative approaches can be used, each with different advantages and disadvantages. These include, (a) converting the ethylene to intermediate olefins, e.g. butene or hexene, prior to oligomerisation into jet-range molecules; (b) converting the ethanol to a propylene intermediate prior to oligomerisation; (c) using a higher alcohol intermediate (carbon-carbon coupling or two or more alcohols); or (d) using a carbonyl intermediate to convert the alcohol via hydroformylation or "oxo synthesis", although this also requires syngas (CO and H2) (Brooks et al., 2016).

Using conventional acid catalysts, such as zeolites, for ethylene oligomerization can be difficult to control and often leads to coke formation and high levels of aromatics. While controlled ethylene oligomerization can be carried out using homogenous catalysts, they are difficult to separate and reuse and generally considered too expensive for fuel production

(Lanzatech, 2017). Alternatively, catalysts resulting in high conversion have shown low selectivity for the jet range. Thus, finding both a high conversion efficiency and a high selectivity for jet-range molecules, without high aromatic content, has been challenging (Lanzatech, 2017).

The PNNL process for alcohol to jet conversion which is used by Lanzatech entails direct oligomerization of the ethylene intermediate to a mixture of C4-C6 olefins followed by further oligomerization into longer-chain hydrocarbons (Lanzatech, 2017). Consequently, a mixture of mainly paraffins and isoparaffins with low aromatic content is obtained. It should be noted that there is ongoing research and "room for improvement" in the catalysts used that should result in higher conversion yields and higher selectivity towards jet range molecules (Guo, Guo, Suzuki et al., 2020; Guo, Guo, Zeng et al., 2020; Saavedra Lopez et al., 2019).

The oligomerisation process differs substantially when using butanol, with butanol oligomerisation requiring fewer steps. This makes it cheaper than ethanol oligomerisation (Geleynse et al., 2018). However, iso- or n-butene oligomerization is not as commercially developed. Although formation of C8, C12 and C16 hydrocarbons take place, some cracking and isomerization may occur, resulting in the formation of other carbon lengths, cyclic olefins or aromatics (Geleynse et al., 2018). Although the use of a branched alcohol, such as isobutanol, results in greater branching in the final jet molecules, which has a positive impact on cold flow properties and freeze point, it also reduces the cetane number.

The products from the ATJ conversion differ depending on the type of alcohol used. Butanol, as a 4-carbon molecule will produce molecules with 8, 12, and 16 carbons, etc. after oligomerisation. In contrast, ethanol/ethylene oligomerisation will form a wider carbon number range of molecules similar to petroleum (Geleynse et al., 2018). However, this will also depend on the chosen oligomerisation method for the ethanol/ethylene. Using a butene intermediate will achieve a similar product range than starting with butanol/butene, although requiring an additional processing step.

When the jet product carbon number distribution from different biojet technology pathways, including Gevo ATJ (isobutanol), Cobalt ATJ (n-butanol), UOP ATJ (isobutanol), and Lanzatech/PNNL ATJ (ethanol) (Lanzatech, 2017) are compared (Figure 14 (B)), the PNNL/Lanzatech ATJ technology shows a wider carbon number distribution between C8-C16, and similar to normal Jet A fuel and to HEFA biojet fuel (Figure 14 (A)). It should be noted that isobutylene conversion can be carried out in converted MTBE facilities that are already used for iso-octene production (Kolodziej & Scheib, 2012).
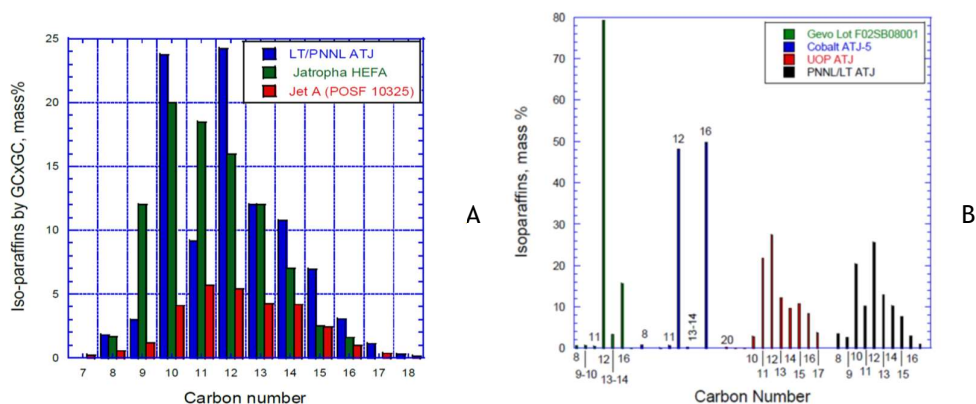
*Figure 14. Distribution of ATJ products by carbon number. (A) comparison of the Lanzatech/PNNL process products with HEFA and Jet A; and (B) comparision of various ATJ products and their carbon number distribution, including Gevo ATJ (isobutanol), Cobalt ATJ (n-butanol), UOP ATJ (isobutanol), and Lanzatech/PNNL ATJ (ethanol) (taken from (Lanzatech, 2017)*

### 5.4.3.3 Hydrogenation

The oligomerised product still contains double bonds that are very reactive and hydrogenation saturates these to form paraffinic hydrocarbons. This will impact the economics and requires a source of hydrogen which can either be produced at the same facility or purchased. Hydroprocessing is a fully commercial process in current petroleum refineries.

When Geleynse et al. (2018) compared the ethanol-to-jet with the isobutanol-to-jet pathway, from a techno-economic perspective, the isobutanol-to-jet conversion was about 34% cheaper than the ethanol-to-jet conversion. However, it was apparent that the alcohol production step will determine the final price of the ATJ fuel as this forms about 80% of the cost of biojet fuel via this pathway (Geleynse et al., 2018).

### 5.4.4 Economics and sustainability of the alcohol-to-jet pathways

Techno-economic analyses of the alcohol-to-jet process indicate a wide range of MFSPs for biojet or other drop-in fuels. A clear difference can be observed between the use of a grain or sugar feedstock compared with a lignocellulosic feedstock, with the lignocellulosic-based processes having higher MFSP values. There is not a significant difference observed where an ethanol intermediate or isobutanol intermediate is used. Geleynse calculated an MFSP of $938 for an ethanol intermediate and $736-1113 for an isobutanol intermediate (both based on a sugar feedstock (Geleynse et al., 2018). A similar low MFSP ($976) is reported by Neuling and Kaltschmitt for ATJ based on an isobutanol intermediate produced using wheat grain (Neuling & Kaltschmitt, 2018). When using a wheat straw substrate, the MFSP in this study increased to $1564 (Neuling & Kaltschmitt, 2018). Related work reported an MFSP of $1387 for ethanol-to-jet based on corn grain and an MFSP of $1773 for ethanol-to-jet using corn stover (nth plants) (Tao et al., 2017). Another study reported MFSPs of $1200 (sugarcane to ethanol), $1263 (corn grain to ethanol) and $1725 (switchgrass to ethanol) (Yao et al., 2017). Much higher MFSPs have been reported with lignocellulose to ethanol processes showing an MFSP of $2832-4130 (de Jong et al., 2017b) and $3430 (Diederichs et al., 2016).

According to the default values from ICAO, lignocellulosic feedstocks achieve lower values of gCO2/MJ, including 29.3 (agricultural residues), 23.8 (forestry residues), -10.7 (Miscanthus -

USA), and 12.4 (miscanthus – EU) (ICAO, 2019). Although much lower emission reductions are achieved when using sugarcane or corn grain, isobutanol shows lower values (gCO2/MJ) and performs better than ethanol. When using corn grain (USA), the default value for ethanol-to-jet is higher than the baseline for conventional jet fuel (ICAO, 2019). However, it should be noted that a company can significantly improve the life cycle analysis of its product by using renewable energy, carbon capture and storage, and many lower-carbon-intensity strategies.

### 5.4.5 Opportunities and challenges of the ATJ technology

It has been argued that most biochemical technology pathways for drop-in fuel and biojet production will be challenged economically as the intermediates (e.g. alcohols) have a higher market value than the fuel itself (Karatzos, Mcmillan et al., 2014b). This conundrum was clearly described by an article in the Biofuels Digest entitled "The Solyndra Effect, why alcohol-to-jet fuel is a tough sell". As summarised, "the value of any intermediate products produced in any process must be significantly exceeded by the value of the end product, or the end product will not be produced."[29]

Biochemical platform technologies are ideal for producing oxygenated and low $H_{eff}/C$ products that can access the higher value chemicals market for the production of bioplastics, and biochemicals. Thus, the proposition for price-competitive alcohol-to-jet fuels is likely to remain challenging. The price of butanol in the chemical market during March 2020 was about $781 per metric tonne (Echemi, 2020), while conventional jet fuel was priced at $328 per metric tonne in October 2020. However, these prices have been affected by COVID19 and the price for jet fuels was 46% lower than it was in October 2019[30].

In spite of these challenges, companies such as Gevo and Lanzajet are progressing the commercialisation of their technologies and the companies have been selling their ATJ fuels to customers. Both the isobutanol-to-jet and the ethanol-to-jet pathways have received ASTM certification and this provided immediate market access that many other biojet technologies do not currently have. It is likely that a combination of low feedstock cost, high alcohol yields, high conversion yields and high sustainability will all play a role in making the ATJ technologies more successful.

It should be noted that biochemical routes to biojet are projected to have significantly lower capital costs than those predicted for thermochemical routes (Karatzos et al. 2014). From a commercialization point of view, one of the most attractive aspects of biochemical technologies is the potential to "piggy-back" onto existing ethanol facilities by switching the microorganism used in the microbe-to-ethanol process to obtain a "microbe-to-drop-in fuel or fuel intermediate" process. This can significantly lower capital investment for alcohol production.

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[29] https://www.biofuelsdigest.com/bdigest/2012/11/16/the-solyndra-effect-or-why-alcohol-to-jet-fuel-is-a-tough-sell/
[30] https://www.iata.org/en/publications/economics/fuel-monitor/

## 5.5 ELECTROFUELS (POWER TO LIQUIDS – PTL)

The PtL pathway has been receiving significant attention as a route to synthetic jet fuel production. Although a complete power-to-jet pathway has not yet been demonstrated, development is progressing in Iceland, Finland, Germany and Norway. In parallel, there are more than 50 pilot and demonstration PtX projects in operation or under construction worldwide (Schmidt et al., 2018). For example, the company Sunfire in Germany is commercialising the integrated production of their e-crude fuel based on PtX[31].

The basic process for the power-to-jet process (Figure 15) involves hydrogen produced through electrolysis of water and $CO_2$ based on direct air capture or using $CO_2$ from a concentrated source such as waste gases. Synthesis of hydrocarbons, including jet, can proceed through Fischer-Tropsch and can also take place via a methanol intermediate. As CO is required, the CO2 is converted through a reverse water-gas-shift reaction (RWGS) into CO. Individual processes, except the reactor for the RWGS process, are all mature and at an industrial scale (Schmidt et al., 2018).
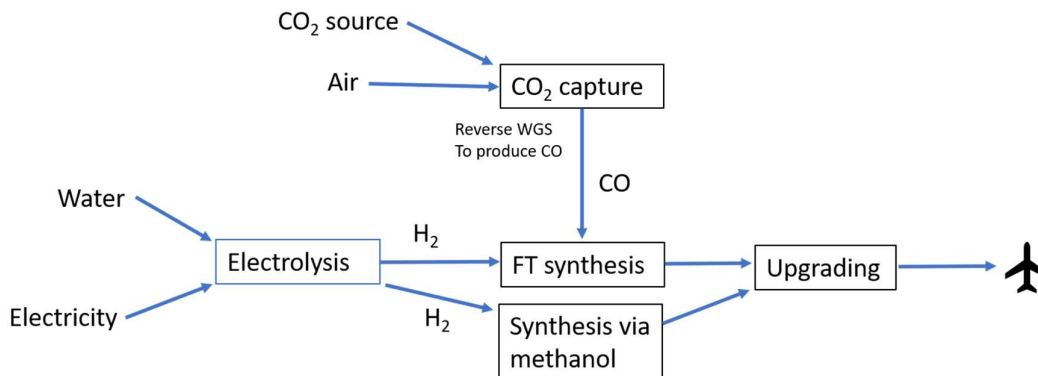


*Figure 15 Simplified illustration of the Power to Liquid process for the production of aviation fuels*

There are several types of electrolysis technologies for hydrogen production, including alkaline electrolysis, proton exchange membrane electrolysis, and solid oxide electrolyser cell electrolysis (Dieterich et al., 2020). The technologies vary with respect to efficiency, investment and maintenance costs, durability and lifespan, capacity, and flexibility.

CO2 can be obtained from point sources, such as industrial flue gases with a high partial pressure, or through direct air capture by physical or chemical methods. Adsorption technologies use liquid or solid adsorbents. Chemical adsorption typically uses alkanolamine, such as monoethanolamine, or potassium carbonate as adsorbents. Direct air capture technologies are categorised into wet air capture with a liquid solution in packed columns, convection towers or spray-tower contractor systems, e.g. using a sodium hydroxide solution. Dry air capture typically uses solid adsorbents such as organoamines (Dieterich et al., 2020).

Direct air capture is more expensive as it requires higher energy inputs and larger volumes of

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[31] https://www.sunfire.de/en/applications/syngas

air has to be processed (Dieterich et al., 2020). Dieterich indicates that direct air capture could be ten times more expensive at present but could attain cost parity with point source capture by 2040 (Dieterich et al., 2020).

Synthesis technologies such as Fischer-Tropsch requires CO which necessitates conversion of $CO_2$ into CO and this may be done in a separate reactor. However, research into direct one-step conversion of $CO_2$ and $H_2$ is under investigation with companies such as Carbon Recycling International in Iceland using this process to produce methanol. Conversion of methanol into longer chain hydrocarbons through the methanol-to-gasoline process is currently used at commercial scale. It has also been used for the production of middle distillates (Schmidt et al., 2018).

It should be noted that, although the production of synthetic jet fuels through Fischer-Tropsch synthesis is certified under ASTM D7566 for production of jet, the methanol pathway is not yet certified.

The source of $CO_2$ is an important aspect of the PtL process that impacts the technology, the final carbon intensity of the fuel and the economics of the pathway. Concentrated sources of $CO_2$ that can be used are gases from industrial processes (from fossil origin), geothermal sources and renewable sources such as biogas or $CO_2$ obtained as a byproduct of ethanol production. Alternatively, $CO_2$ can be produced through direct air capture (Schmidt et al., 2018). However, the use of fossil origin $CO_2$ industrial sources is not always considered sustainable as it is merely a recycling of carbon rather than part of a circular economy (Bracker, 2017).

It has been argued that, based on energy efficiency of different electricity-based transport options, power-to-liquids is not the best option (Bracker, 2017). According to Bracker, battery electric vehicles have 73% efficiency, hydrogen fuel cell vehicles at 22% and PtL with a conventional vehicle is only 13% efficient (Bracker, 2017).

The key sustainability challenge for PtJ fuels is the availability of excess renewable energy. As renewable energy is used in many competing applications, sufficient renewable sources may be challenging.

The other major challenge for this technology pathway is the high cost of fuel production. Schmidt et al. (2018) calculated that a minimum fuel selling price for aviation fuel from PtL based on direct air capture would be USD4974/MT, based on a concentrated $CO_2$ source at USD3829/MT. A comprehensive review on production cost by Brynolf et al. (2018) indicates a cost range of EUR200-280$_{2015}$/Mwh$_{fuel}$ (Brynolf et al., 2018). According to Schmidt, PtL fuels can achieve a 70% reduction in emissions (Schmidt et al., 2018). However, this will depend on the source of electricity as benefits are only achieved where renewable sources of electricity are used (Alhyari et al., 2019).

### 5.5.1 Potential and challenges of the Power to Liquid technology pathway

The PtL process has the potential to produce aviation fuels with near zero carbon intensity. This can be achieved without the need biomass and any associated environmental issues such as water consumption.

As Fischer-Tropsch synthesis of aviation fuels received ASTM certification in 2009, any fuels made *via* this synthesis process will have immediate access to markets. As the syngas in PtL is expected to be relatively pure, limited syngas cleanup will be required.

As mentioned earlier, the main challenges for this technology are the availability of sufficient renewable energy and the high cost of PtL technology. Targeting renewable energy towards liquid fuels production will bring it in direct competition with other "decarbonisation of electricity and transportation" initiatives, including the aggressive drive to increase the number of electric vehicles on the road.

## 5.6 CO-PROCESSING OF BIOBASED INTERMEDIATES IN EXISTING REFINERIES FOR THE PRODUCTION OF LOW CI JET FUEL

During the production of drop-in biofuels, including biojet, many upgrading processes are almost identical to those processes used in conventional oil refineries. Infrastructure such as catalytic cracking, hydrocracking and hydrotreatment require high capital cost and operate at a scale that is difficult to reproduce in a biorefinery (van Dyk et al., 2019). In addition, upgrading requires hydrogen, most frequently produced through a large-scale steam reformer located at the petroleum refinery. Thus, potential biojet fuel focused biorefineries could reduce costs through integration with petroleum refineries in a number of ways. These could include co-processing by insertion of biobased liquid intermediates into an existing refinery. The main liquid intermediates considered for insertion into a refinery are lipids, bio-oils/biocrudes and Fischer-Tropsch liquids.

Co-processing of 5% lipids is certified under ASTM D1655 and is already carried out commercially at refineries such as BP's Cherry Point in Washington State[32] and the Parkland Refinery in Burnaby, British Columbia. Co-processing of tall oil fatty acids have been carried out successfully for some time at 30% blends by companies such as Preem. However, these high co-processing blends for low CI jet fuel production are not approved under ASTM D1655 (Egeberg et al., 2010).

As discussed earlier, post-synthesis processing of FT liquids can become quite significant. At the very least, hydrotreatment must be carried out and, depending on the specific FT process, further hydrocracking and other processing steps may be needed. In addition, a hydrogen source is required and the additional infrastructure that will be required is unlikely to be economical for smaller scale facilities. Thus, utilizing existing refinery infrastructure can overcome many of these obstacles.

Coprocessing of thermochemical liquid intermediates such as pyrolysis or HTL biocrudes are undergoing trials and are currently the focus of substantial research. However, only limited biocrude volumes are currently available. Biocrudes are also significantly more complex than lipids and will likely result in considerable upgrading challenges. However, as biocrudes are mainly produced from biomass, which should be cheaper and available in greater quantities than lipids, it is hoped that biocrude-based processes should be able to supply significant volumes of lower carbon intensive jet fuels in the future. However, any co-processing of biocrudes will have to undergo a rigorous process to become certified under ASTM D1655. Currently, there is no such application in the pipeline and the complexity and variability of biocrudes based on different feedstocks and technologies will likely make certification very

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[32] https://www.bp.com/content/dam/bp/country-sites/en_us/united-states/home/documents/eir-2018/washington-factsheet.pdf

challenging.

Although co-processing can be carried out at the fluid catalytic cracker (FCC) and the hydrotreater/hydrocracker, it is most likely that biojet fuels will be produced by co-processing in the hydrotreater/hydrocracker (van Dyk et al., 2019) as the FCC is mainly used to produce gasoline. To date, using a 5% insertion of lipids for co-processing, no significant technical challenges have been encountered (van Dyk et al., 2019).

By coprocessing lipids, FT liquids, or biocrudes at existing refineries companies can produce lower carbon intensity fuels, substantially increasing the volumes of fuel available at a much lower capital cost compared to freestanding biorefineries. Policies such as California and British Columbia's low carbon fuel standards (LCFS) can motivate refineries to apply coprocessing as one way of meeting their carbon reduction targets.

However, it is not clear whether any of the companies actively coprocessing are also producing a co-processed jet fraction. An ongoing issue under discussion regarding coprocessing is the method of allocation of the renewable molecules to different fractions. This has an impact on the carbon intensity of the fuel products.

### 5.6.1 Potential and challenges of coprocessing strategies for biojet fuel production

The greatest potential for coprocessing is that it can lead to production of low carbon intensity fuels without significant investment for construction of new biorefineries. This is certainly the case of coprocessing of lipids (FOGs) as limited pretreatment is required before direct insertion of this feedstock into existing refinery processes. With respect to biocrude coprocessing, the production of the biocrude intermediate will likely require substantial investment into biocrude production facilities. In addition, biocrudes have to be pretreated prior to coprocessing, and may have to undergo intermediate upgrading to reduce oxygen levels and stabilise the biocrudes. This would add to the infrastructure cost for pretreatment and an additional hydroprocessing reactor.

# 6. Conclusions

Multiple technology pathways using a wide range of feedstocks are able to produce biojet fuels. However, delays in commercialisation have limited the production and use of substantial volumes of biojet fuel for the sector. Although seven pathways and two coprocessing pathways have been ASTM certified, only one, the HEFA pathway, is routinely producing millions of litres of biojet fuel. A large number of facilities using this pathway have been making >6 billion litres of renewable diesel. Ongoing expansions are underway based on construction of new facilities and conversion of existing petroleum refinery infrastructure. Although all these facilities could produce an approximate 15% biojet fuel fraction (of total capacity), favourable policies for renewable diesel has not made it worthwhile for these refineries as additional infrastructure will be required and the production of biojet fuels is not encouraged by current policies. However, the introduction of favourable policies could incentivise renewable diesel facilities to add the infrastructure required to divert a fraction of their product into biojet fuel. In the short to medium term, this is the fastest way to provide substantial volumes of biojet fuel for the aviation market. It should be noted that the HEFA technology is also expected to supply the bulk of biojet over the next 5-10 years until other technologies become fully commercialized. It is hoped that multiple facilities using various technologies/processes will routinely produce biojet as, in the longer-term, significant expansion of HEFA volumes will likely be constrained by the availability of low cost, waste lipid/oleochemical feedstocks.

Large-scale, pioneer facilities for a number of other technologies are under construction or planned and include gasification with Fischer-Tropsch, ethanol-to-jet, isobutanol-to-jet and catalytic hydrothermolysis. In addition, multiple alternative technology pathways, currently in the ASTM approval pipeline, are expected to attain ASTM certification. By 2030, multiple facilities are expected to produce substantial volumes of biojet. Estimates by ICAO are that about 8 billion litres should be available by 2030.

Different technology pathways offer many opportunities for producing sustainable biojet with low carbon intensity at a competitive price through utilisation of low-cost, waste feedstocks such as municipal solid waste, sewage sludge, food processing waste, waste gases and forest and agricultural residues. Feedstock is generally a significant component of the cost of production. Thus, accessing low-cost feedstocks or improvement of cost through supply chain optimisation will play a role in reducing costs of biojet fuels.

Both lipids and biocrudes from direct thermochemical liquefaction can be used as intermediates for coprocessing in existing petroleum refineries, potentially producing low-carbon intensity fuels with much lower investment in infrastructure. Reduced capital investment cost is also possible with technologies based on biochemical methods, as existing ethanol refineries can be readily converted into butanol or isobutanol facilities. It should be noted that, typically, drop-in biofuel production requires much higher capital investment than conventional biofuels such as ethanol and biodiesel, with thermochemical gasification-based technologies having the highest CAPEX. Technical challenges still remain for technologies such as pyrolysis and hydrothermal liquefaction, specifically the upgrading of biocrudes into finished fuels.

**Creating an enabling policy environment for biojet fuels production will play the most important role to accelerate commercialization of technologies. Once pioneer facilities are successfully operating, learning by doing will reduce the cost of biojet fuel production for subsequent facilities.**

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