# Advanced Sustainable BIOfuels for Aviation

## **Deliverable 4.1**:
## Process Technological performance: report of the performance on the value chain and comparison with alternative pathways

### Consortium:

| **Acronym** | **Legal entity** | **Role** |
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| RE-CORD | CONSORZIO PER LA RICERCA E LA DIMOSTRAZIONE SULLE ENERGIE RINNOVABILI | CO |
| ENI | ENI SPA | BEN |
| SKYNRG | SKYENERGY BV | BEN |
| CENER | FUNDACION CENER-CIEMAT | BEN |
| ETA | ETA - Energia, Trasporti, Agricoltura Srl | BEN |
| CCE | CAMELINA COMPANY ESPANA S.L. | BEN |
| JRC | JOINT RESEARCH CENTRE - EUROPEAN COMMISSION | BEN |

*CO…Coordinator, BEN…Beneficiary*

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| **PP** | Restricted to other programme participants (including the Commission Services) | |
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## Acronyms

| | |
|---|---|
| APR | Aqueous Phase Reforming |
| ASTM | American Society for Testing and Materials |
| ATJ-SPK | Alcohol To Jet - Synthetic Paraffinic Kerosene |
| BTX | Benzene, toluene and xylene |
| CAAFI | Commercial Aviation Alternative Fuels Initiative |
| CAPEX | Capital Expenses |
| CE-O | CanmetENERGY In Ottawa |
| CH-SK | Catalytic Hydrothermolysis Synthesized Kerosene |
| CORSIA | Carbon Offset and Reduction Scheme for International Aviation International |
| CPK | Cycloparaffinic Kerosene |
| DMF | Dimethylfuran |
| DSHC | Direct Sugar to Hydrocarbons |
| db | dry basis |
| FCC | Fluid Catalytic Cracking |
| FPP | Farnesenyl Pyrophosphate |
| FRL | Fuel Readiness Level |
| FT-SPK | Fischer-Tropsch - Synthetic Paraffinic Kerosene |
| GHG | Greenhouse Gases |
| H | Hydrogen |
| HDCJ | Hydro-Treated Depolymerized Cellulosic Jet |
| HDO | Hydrodeoxygenation |
| HDO-SK | Hydrodeoxygenated Synthetic Kerosene (without aromatics) |
| HDO-SAK | Hydrodeoxygenated Synthetic Kerosene with Aromatics |
| HEFA | Hydroprocessed Esters And Fatty Acid |
| HFS-SIP | Hydroprocessed Fermented Sugars to Synthetic Isoparaffins |
| HHC-SPK | Hydroprocessed Hydrocarbons, Esters and Fatty Acids Synthetic Paraffinic Kerosene |
| HHV | High Heating Value |
| HMF | Hydroxymethylfurfural |
| HTFT | High-Temperature Fischer-Tropsch |
| HTL | Hydrothermal Liquefaction |
| ICAO | International Civil Aviation Organization |
| ILUC | Indirect Land Use Change |
| IPP | Isopentenyl Pyrophosphate |
| KPI | Key Performance Indicator |
| LCA | Life-Cycle Assessment |
| LHV | Low Heating Value |
| LTFT | Low-Temperature Fischer-Tropsch |
| MFSP | Minimum Fuel Selling Prize |
| MSW | Municipal Solid Waste |
| MVA | Mevalonic Acid |
| NABC | National Advanced Biofuels Consortium |
| OPEX | Operating Expenses |
| PFAD | Palm Fatty Acid Distillate |
| PNNL | Pacific Northwest National Laboratory |

| | |
|---|---|
| RED II | Recast of the Renewable Energy Directive |
| RJF | Renewable Jet Fuel |
| TEA | Techno Economic Analysis |
| TRL | Technology Readiness Level |
| toe | Ton of Oil Equivalent |
| UCO | Used Cooking Oil |
| USA | United States of America |
| VGO | Vacuum Gas Oil |
| WGS | Water-Gas Shift |
| WtW | Well-to-Wake |

# 1 Summary

This document is part of Task 4.2 “*Process comparison with other technological pathways*” and reports the main findings of an extensive literature review on a selection of alternative Renewable Jet Fuel (RJF) production pathways.

Three ASTM-certified pathways were analyzed, together with other two promising but not yet certified pathways:

- Alcohol-to-Jet Synthetic Paraffinic Kerosene (ATJ-SPK) – ASTM-certified pathway.
- Fischer-Tropsch Synthetic Paraffinic Kerosene (FT-SPK) – ASTM-certified pathway.
- Hydroprocessing of Fermented Sugars - Synthetic Iso-Paraffinic kerosene (HFS-SIP), formerly known as Direct Sugars to Hydrocarbons (DSHC) – ASTM-certified pathway.
- Hydro-treated depolymerized cellulosic jet (HDCJ) via pyrolysis process and via HTL process.
- Aqueous Phase Reforming (APR).

The review covered the main aspects of all the considered production pathways, such as:

- Existing production processes, considering all the main production routes.
- Blending level with fossil jet fuel (for the ASTM-certified pathways).
- Suitable feedstocks, taking into account their effect on fuel price, GHG emissions and process yield.
- Existing, operating plants (if any): all the publicly available information have been gathered and summarized, together with information on the production capacity.
- Technology status, describing the current TRL and FRL of the pathway.
- Technology development potential.
- Cost estimates in terms of Minimum Fuel Selling Price (MFSP).
- Sustainability, covering, among others, life cycle GHG emissions, as well as ILUC-related issues.

The information collected within this report has then been used to produce a synthetic table of Key Performance Indicators (KPIs) to briefly describe each pathway, as required by Task 4.2.

# 2 Introduction

Current production of Renewable Jet Fuel (RJF) is mainly obtained from vegetable oil by means of the Hydroprocessed Esters and Fatty Acid (HEFA) process since it is the only commercially available technology [1]. Oil crops for both food, such as palm oil, soybean or rapeseed, and non-food crops, such as jatropha, camelina or castor, have been the main feedstocks for RJF, together with some wastes, such as used cooking oil (UCO) and animalfat (tallow) [2]. As function of the biomass selected, the estimated production cost by ton of RJF is slightly higher with respect to the fossil-based jet fuel. However, current real production cost is far from the cost of producing the conventional jet fuel, since values between 4 and 10 times higher have been reported [3]. This has been caused by the high price of these feedstocks with respect to the comparatively low price of kerosene, and, in turn, this has not allowed the industrial boom of this technology for RJF production. Moreover, both the competitiveness on the use of the food crops for producing RJF in front of their use in the food industry, and the use of oil-based waste that are limited through RED II Directive, have not encouraged a largest development that could have ensured a large-scale HEFA-RJF production capacity [4]. Therefore, the interest for researching other RJF alternative conversion pathways, using cheaper lignocellulose-based biomass, such as forestry residues, agricultural wastes or municipal solid waste (MSW), has recently been increased. Figure 1 shows an overview of the main conversion pathways for producing RJF [3,5] and highlights both the Fuel Readiness Level (FRL) and the Technology Readiness Level (TRL) of the different involved processes (i.e., biological, chemical, thermal or hybrid).

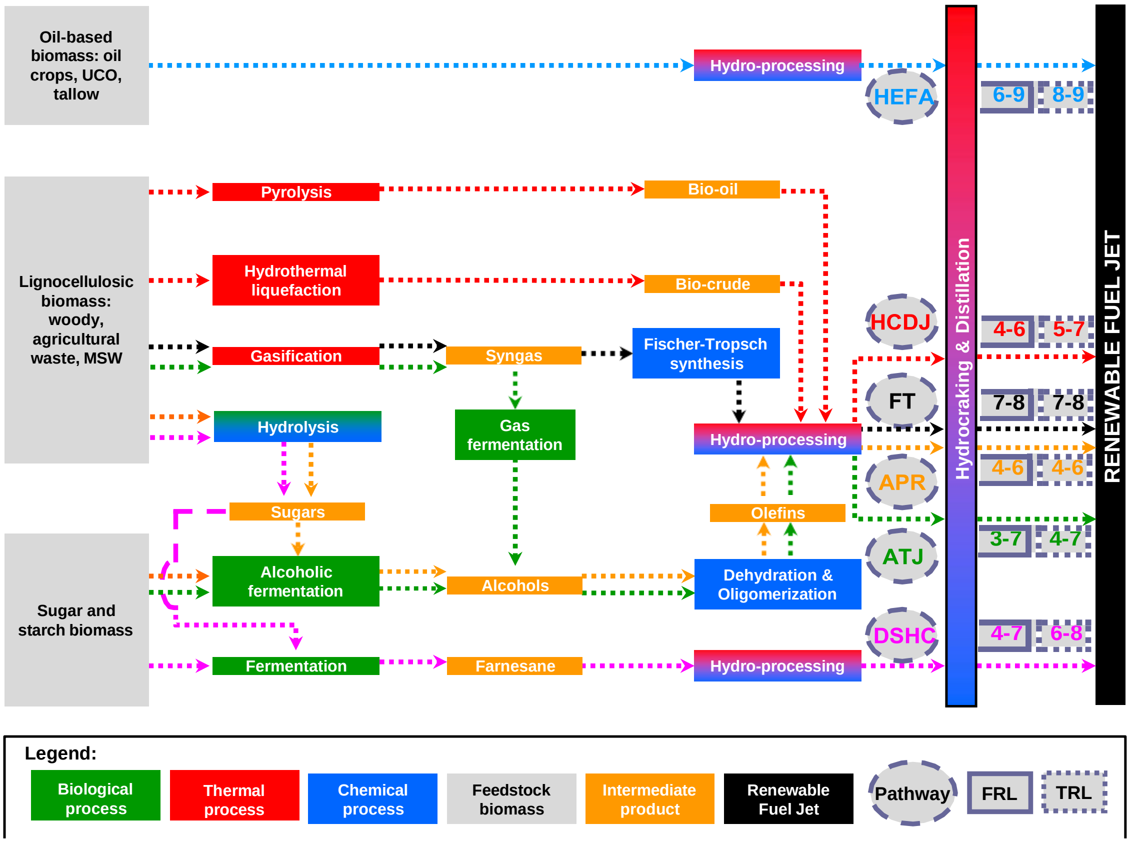

**Figure 1: Current conversion pathways to produce Renewable Fuel Jet; adapted from [3,5,6]**

The TRL index assesses the development level of the technology (i.e., from initial scale of research and development in lab until its arrival to commercial market), while the FRL assesses the certification status for use in civil aviation and is emitted by CAAFI. Thus, the two indexes could slightly differ; the ranging values in Figure 1 are due to the different feedstock used to produce RJF. Whatever the considered index, the range from 6 to 7 is the demonstration scale threshold, defining the stage before commercial development [5,6].

Since 2009, seven processes have been approved for use as 'drop-in' jet fuels containing synthesized hydrocarbons to be blended at a certain percentage with conventional Jet-A1 under the specifications of the ASTM D7566 standard through [7]:

- Annex 1: Fischer-Tropsch Synthetic Paraffinic Kerosene (FT-SPK), which was certified in 2009 to be blended with petroleum-based jet fuel, up to a 50% maximum level.
- Annex 2: Hydroprocessed Esters and Fatty Acids Synthetic Paraffinic Kerosene (HEFA-SPK), which was certified in 2011 to be blended with petroleum-based jet fuel, up to a 50% maximum level.
- Annex 3: Hydroprocessed Fermented Sugars to Synthetic Isoparaffins (HFS-SIP), which was certified in 2014 to be blended with petroleum-based jet fuel, up to a 10% maximum level. It is also known as Direct Sugars to Hydrocarbons (DSHC).
- Annex 4: Fischer-Tropsch Synthetic Paraffinic Kerosene with Aromatics (FT-SPK/A), which was certified in 2015 to be blended with petroleum-based jet fuel, up to a 50% maximum level.
- Annex 5: Alcohol to Jet Synthetic Paraffinic Kerosene (ATJ-SPK), which was certified in 2016 to be blended with petroleum-based jet fuel, up to a 50% maximum level.

- Annex 6: Catalytic Hydrothermolysis Synthesized Kerosene (CH-SK, or CHJ), which was certified in 2020, to be blended with petroleum-based jet fuel, up to a 50% maximum level.
- Annex 7: Hydroprocessed Hydrocarbons, Esters and Fatty Acids Synthetic Paraffinic Kerosene (HHC-SPK or HC-HEFA-SPK): Certified in 2020, to be blended with petroleum-based jet fuel, up to a 10% maximum level.

Furthermore, there are other six processes currently under ASTM D4054 Qualification Process and seventeen under Pre-Qualification Process. The assessment of all of them is considered out of deliverable scope, since the aim of the Task 4.2 to assess the different RJF pathwaysvs. HEFA as a function of their TRL, using KPIs indicators such as FRL or certification level, feedstock used or estimated costs. Therefore, this deliverable reports a comprehensive evaluation of some of the most promising conversion pathways aside from the HEFA route, distinguishing between those technologies above and below TRL value of 6-7. More specifically, the following pathways are examined: alcohol-to-jet (ATJ), direct sugar to hydrocarbons (DSHC), Fischer-Tropsch (FT), hydro-treated depolymerized cellulosic jet (HCDJ) and aqueous phase reforming (APR). For each of them a brief description of the technical process is provided, together with information on feedstock types, existing plants, current technology status and expected development potentials. Moreover, fuel cost estimates are provided, and specific sustainability issues are examined.

## 2.1 Sustainability of RJF

Sustainability-derived of an alternative jet fuel is a priority for the most of worldwide governments and other politic institutions, such as the European Union (EU), just as for other nonprofit organization and thus for airline companies. The greenhouse gases (GHG) emission savings of a Renewable Jet Fuel, compared to a fossil jet fuel on a well-to-wake basis, is usually the main sustainability indicator, and is commonly calculated using life-cycle assessment (LCA) methods. Thus, a well-to-wake GHG emission average value for kerosene of 87.5 $gCO_2eq/MJ$ can be considered as a baseline [6,8]. This figure has widely been applied into LCA studies, and it denotes emission intensity for conventional fossil-based jet fuel consumed in USA. A very similar value of 89 $gCO_2eq/MJ$, has been defined from ICAO as reference level of GHG emissions [9]. RJF obtained from biomass could be always considered as carbon-neutral because biomass acts as a carbon sink by gathering $CO_2$ from air along its growth. This concept is known as biogenic emissions and it assumes biomass releases during its combustion the same amount of $CO_2$ which has previously been collected by the crop. Therefore, each type of biomass would have inherently an amount given of $CO_2$ emissions, which would be related to its carbon intensity. However, same feedstock can have associated different GHG emissions as a function of pathway used to produce jet fuel, in this case [6]. This fact is related to the called non-biogenic emissions, which are released during cultivation practices and harvesting in the case of crops, handling and transport for all biomasses,managing (more specifically with wastes), and finally conversion to fuel. Therefore, it is very important to always take into account all $CO_2$ emissions derived from each “biomass-pathway” in order to reach a suitable comparison with both petroleum-based jet fuel and RJF produced from other conversion routes.

Furthermore, sustainability is related to other impacts such as land use change which is promoted by crops that compete with food for its land. Thus, those biofuels, which are defined as low ILUC-risk [4], are the ones based in feedstock such as UCO, food waste or any type of wood waste and biofuel crop cultivated on disused or abandoned lands. Moreover, these waste-based biofuels might have zero emissions associated to cultivation phase unlike any food crop-based fuels. Therefore, total GHG emissions from low ILUC risk would be lower thancrop-based bio-jet.

## 2.2 Feedstock used for RJF production

Lignocellulosic biomass, sugar and starch-based biomass and algae are used as feedstock to produce RJF through all conversion pathways assessed in this report; see Figure 1. Lignocellulosic biomass can be in turn divided into four types [2]: (1) wood, such as softwood, hardwood and wastes from wood industries, forestry managing or paper production; (2) agricultural wastes, such as cereal straw and tree pruning; (3) energy crops, such as oil-seeds many varieties of grasses; and (4) urban wastes, such as MSW, garden pruning and sewage sludge. These types of feedstock are considered as precursor for producing second generation or advanced biofuels. Sugar-based biomass comes usually from agricultural sugar- rich crops, such as corn, wheat, sugarcane or sugar beets. Likewise, nuts, grain and legumes are usually used as starch-based biomass. Both types of feedstock are used for producing first generation biofuels. Different types of algae have been used, which are considered as feedstock for producing third generation biofuels. A comprehensive explanation on all characteristics of these feedstocks, just as on their advantages and disadvantages can be found elsewhere [10].

Regarding feedstock selection (and consequently RJF conversion pathway), it should be taken into account some factors regardless of their performance. Thus, first key factor is the competitiveness of each one with other already mature industrial sectors. It must be noted that using most of sugar and starch-based feedstock could compete with their use for food, which would minimize their use to produce biofuels. One solution could be to increase the cultivation area, but it could be in conflict with factors as sustainability, irrigable land exploiting, or water consumption. Likewise, the use of some lignocellulosic biomass, mainly those grouped into wood category, could be limited by the competing uses from others sectors such as panel, sawmill and pulp industries, and power and energy sectors [11]. Therefore, the second key factor is the availability of feedstocks. In the shorter-term, it is estimated an increase of up to95 million of tons in dry basis (Mt, db), regarding their current used, for forest and wood processing industry residues in EU by 2030 [12]. Likewise, an increase of up to 355 Mt, db of available volume of agricultural waste is expected within EU by 2030 regarding its current use. Similarly, it is estimated an increase in EU of up to 45 Mt, db in the availability of wastes, such as paper waste, wood waste from MSW or garden waste, regarding their current use by 2030. In the same line, the figures of availability of feedstocks in the longer-term are expected. Thus, agricultural residues and energy crop, together with MSW, are the feedstock with larger availability per year by 2050 for use in aviation biofuels production [13].

## 2.3 Effects of COVID-19 pandemic and war in Ukraine on RJF development

It is worth noticing that the COVID-19 pandemic has had large impacts on all the aviation-related industry, including RJF production. As a matter of fact, air transport decreased around 10-15% of corresponding 2019 levels in April and May 2020, and still down to 75% in August [14,15]. International travel restrictions, together with the contraction of economic activity and changes in transport behavior, have prevented a return to pre-crisis demand levels. This has turned into a slow recovery, in which the global number of commercial flights remained 40% below pre-crisis level on September 2020 [16], while an overall reduction of air passengers (both international and domestic) of around 60% was reported in 2020, compared to 2019. By April 2021, the International Capacity Index kept around 20% (as compared to 2019), which meant almost no variation over the previous 10 months. The domestic capacity index grew up to 80%, representing a significant recovery from the 30% registered a year ago. By April 2022, the International Capacity Index increased up to 60%, while the Domestic Index remained circa 80%. This represents a narrowing in the gap between international and domestic capacity indexes, considering the pandemic had a larger impact on international aviation. Regarding the Load Factor Index, a similar trend has been observed, in which the international index has almost reached the same value as the domestic index (94%). Overall, an increased demand for international air travel is observed, but it is soon expected that the addition of new capacity will come at a higher cost [17]. In any case, Total recovery with respect to passenger volumes of

2019 is not expected up until 2024 at the earliest, with domestic services recovering faster than international flights [18]. Anyway, by August 2020, governments had already provided about 160 billion USD of support to airlines in response to the COVID-19 crisis. Such post-crisis recovery programs could represent a clear opportunity to align public policies with climate objectives in a much closer way, thus representing a support to the low-carbon transition. This is of great relevance, especially in the framework of energy investments that require long-term planning horizons [16].

Another significant factor which has largely affected global aviation since February 2022 is the war in Ukraine. Jet fuel prices have sharply increased since the conflict started and are expected to prevail as long as more stringent sanctions are applied on Russia's energy sector. As an example, the jet fuel barrel price on 2022, March 21st was at USD 150 (up 38% on the month and 121% year-on-year). This has put additional pressure on aviation companies, which have faced challenges regarding the management of their margin of benefits, in an already troubled market state [18b]. Indeed, fossil-based kerosene evolution costs still will play an important role in near-term. Currently, kerosene price has already recovered the half of the fall that it had during worst moths of pandemic (i.e., February-April) respect to 2019 prices [19]. Even if this trend continued and kerosene price would reach the 0.5 €/L (price of 2019), it should be taken into account that further increase, which allows reducing the gap between this and RJF production, could be delayed. This might be connected to $CO_2$ emission market, which current situation allows conventional jet fuel production at low cost. However, it is expected that price of emitted $CO_2$ ton is multiplied up to 3 by 2030 [20], which would allow matching the production prices of conventional and renewable jet fuels.

# 3 RJF alternative production pathways with TRL above 6-7

## 3.1 Alcohol to Jet Synthetic Paraffinic Kerosene (ATJ-SPK) pathway

ATJ is a certified conversion pathway to produce synthesized paraffinic kerosene (not containing aromatics) as RJF, which can be blended up to 50% with fossil-based jet fuel. Currently, both iso-butanol (from 2016) and ethanol (from 2018) are the only certified feedstocks to produce ATJ-SPK. The alcohols can come from any source, but are usually derived from fermentation of starches/sugars1 or biochemical conversion of other forms of hydrogen and carbon (e.g., via organisms that convert CO, H2 and CO2 to alcohol). The production process could evolve into various chemical pathways, each producing different intermediates. They all converge into two typical refinery processes: (1) hydrotreatment, wherehigh pressure hydrogen is used to remove oxygen from fuel; and (2) fractionation, where a range of final product is distilled. ATJ processes are reported to be at TRL 7 and are being developed by several companies, such as BYOGY, Cobalt, Gevo, Swedish Biofuels, Terrabon, UOP, LanzaTech/Lanzajet, Zeachem, and Vertimass.

ATJ is considered among the most capital-intensive conversion technologies and this reflects in a quite high minimum fuel selling prize (MFSP), ranging from 1.6 €/L to 4.2 €/L, depending on feedstocks and studies. Likewise, GHG savings by fossil kerosene substitution also have high variability because of the strong relationship of feedstock and process chain with GHG emissions from ATJ pathway. Thus, GHG reduction ranging from the 11% in the case of corn grain-based ATJ up to the 83% when ATJ is produced from agricultural-based residues can be reached. Regarding development potential, CAAFI has reported global forecasts for ATJ production capacity of at least 300 kt/y by 2025.

### 3.1.1 ATJ process description

Alcohols typically used in the ATJ route include small C2 and C4 compounds such as ethanol (the most widely produced bioalcohol worldwide) and butanol (n-butanol and iso-butanol) [21]. The production of fuel via ATJ route consists of two separate steps: (1) production of alcohol; and (2) conversion of alcohol to fuel. These steps are in principle independent of each other and can take place at different locations. Although the source of the alcohol can be of decisive importance from a sustainability point of view, it is only the conversion process of the alcohol to a fuel that is of relevance for technical certification.

Alcohol to fuel conversion process is formed of four steps: (1) alcoholic dehydration to form the respective alkene product containing the same number of carbon atoms. This is then separated from liquid water and impurities by fractionation, and enters the next process step as a gas; (2) oligomerization of the gaseous material into unsaturated compounds with a higher molecular weight roughly similar to that of a jet fuel; (3) hydrogenation of separated unsaturated oligomers over a solid-phase catalyst with hydrogen gas; and (4) distillation of hydrogenated product in order to yield a range of final products, of which kerosene is one [22].

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[1] either from starch/sugar producing feedstocks (e.g. field corn, sweet sorghum, cane, sugar beets, tubers) or derived from cellulosic biomass (e.g. via hydrolysis from lignocellulosic materials)

These four individual steps are well-known and have been widely employed in the petrochemical industry [21].

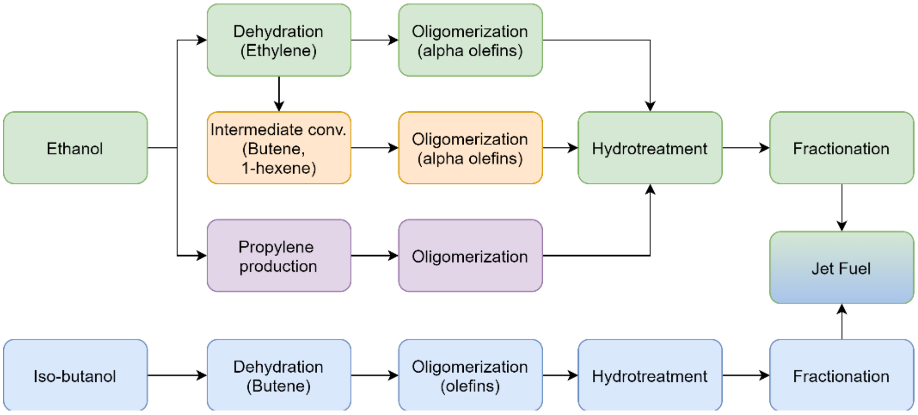

**Figure 2: Main ATJ conversion pathways**

The conversion pathways of ethanol to SPK jet fuel can be categorized according to the chemistry involved; in this document, SPK production through ethylene as an intermediate, as well as through propylene as an intermediate are evaluated. The conversion pathway of iso-butanol to SPK jet fuel is evaluated as well [23]. Figure 2 schematically shows the four steps involve in the SPK jet fuel route from both ethanol and iso-butanol.

#### 3.1.1.1 Ethanol pathway

Ethanol dehydration, to produce ethylene, is a well-developed and commercially practiced process, with high yields achievable. This allows no technology development to be required for this initial step. As an example, a reported process achieves 99.7% ethylene selectivity at 240°C using an HZSM-5 catalyst [24].

Anyway, oligomerization of this intermediate product to jet-range paraffins can be challenging and several alternative approaches are discussed in the followings. In all cases, the productsof the oligomerization process undergo hydrotreating, a well-developed technology in the petrochemical industry, performed with relatively modest levels of hydrogen, pressure, and temperature conditions to achieve near 100% conversions to paraffins [25].

Direct oligomerization of ethylene is the most straightforward route, as shown in Figure 3. Despite being the simplest process available, its selectivity is not high and the economics of these reactions have not been favourable, which has not allowed its development beyond the laboratory.

Heterogeneous catalysts are generally preferred over homogeneous-type ones to produce long-chain alpha-olefins for chemical use, since, when using last one, separation of product could become difficult because of reactants, products, and catalyst being all in the same phase [26]. Recent studies have been focused on investigating the use of ZSM-5 zeolite in the formation of higher hydrocarbons [27]. The reported performance for ethylene conversion is quite low, around 14%, with selectivity toward short olefins rather than jet fuel. Thus, these processes would require significant recycle to obtain C10-C16 range olefins. The use of amorphous or mesoporous silica-alumina catalysts lead to conversion rate of ethylene reaching 97-99%, but with C10+ oligomers yields have been reported to reach only 30-35% by mass [28,29].

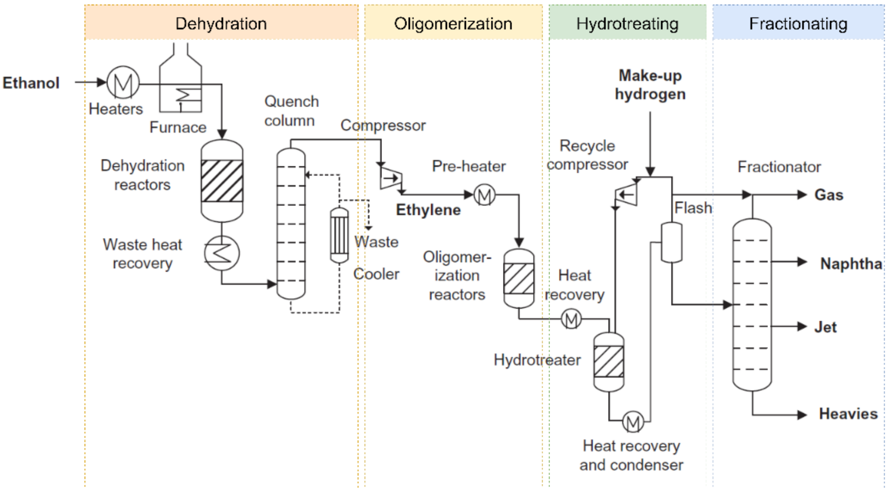

**Figure 3: Ethylene-intermediate, Ethanol to Jet process (Authors elaboration on [23])**

Alternative pathways have been developed to first convert ethylene to an intermediate higher olefin mixture (C4-C10), which are more easily oligomerized to jet fuel than ethylene itself. Butene and hexene are only considered here (see Figure 4). Single pass yields for butene conversion can be as high as 70% and higher yields can be achieved with adequate recycle [30-32]. The processes for converting ethylene to butene and subsequently butene to higher hydrocarbons are commercially available at full scale. 1-Hexene can instead be efficiently generated from ethylene with a variety of homogenous catalysts via trimerization [33]. Chevron Phillips Chemical's proprietary catalyst achieved selectivities of 93 wt% [34] and conversion of 1-hexene to jet fuel can be performed with a homogeneous Cp2ZrCl2/methylaluminoxane catalyst at ambient temperature and pressure, with 100% conversion and with a selectivity greater than 80% to a mixture of the dimer and trimer that can be separated to produce jet and diesel fuels.

It is possible to convert the ethanol to propylene as an intermediate rather than to ethylene. Propylene is more easily oligomerized and, because the second intermediate is removed, it results in a simpler process than the one previously described. However, lower yields of around 32% with an HZSM5-type zeolite containing alkaline earth metals are produced [35], which requires higher recycles than butene intermediate pathway. Successive yields to jet fuel have been documented to be less than 35% using a catalyst with moderate acidity and medium pore size [36]. Therefore, less reactive catalyst, such as solid phosphoric acid, is preferred in order to improve the selectivity toward jet fuel.

Overall, Ethanol-to-Jet fuel process yields range between 56% [37] and 67.1% [38] with a theoretical 95% [39].

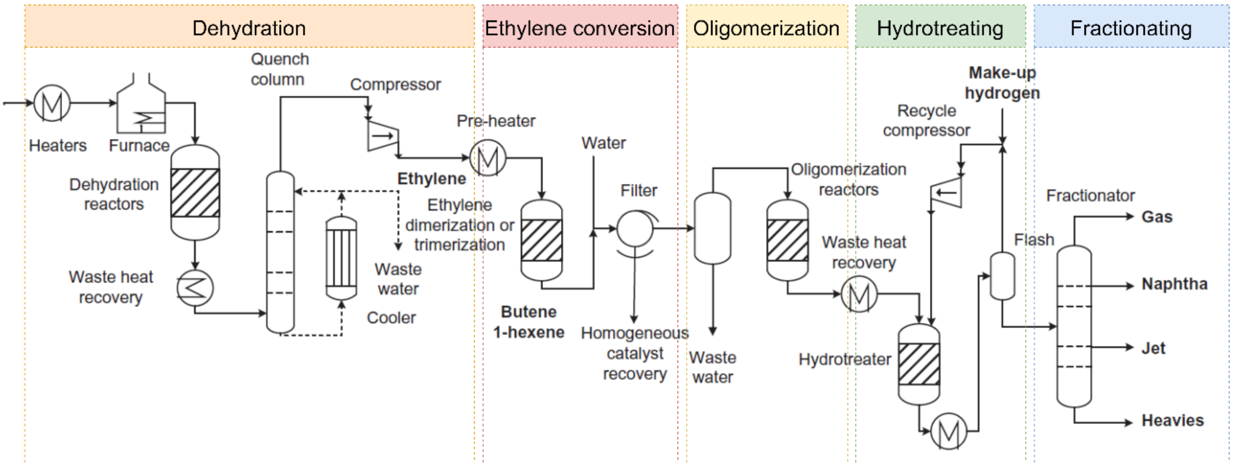

**Figure 4: Ethylene intermediate with butene/1-hexene conversion, Ethanol to Jet process (Authors elaboration on [23])**

#### 3.1.1.2 Iso-butanol pathway

UOP, Gevo, and Cobalt/US Navy based their ATJ technology on butanol, with Gevo and Cobalt/Navy producing a highly branched jet fuel. In all cases, the alcohols follow the already explained basic four-step process (see Figure 2). The Cobalt process is based on the use of n-butanol and Ziegler-Natta chemistry [40], while Gevo produces iso-butanol using alcoholic fermentation with genetically modified yeast cells [41]. Iso-butanol production shows more advantages than ethanol production, since this alcohol has higher energy content and lower water solubility. Moreover, it dehydrates at lower temperatures and pressures than ethanol,and its derivatives can be easily oligomerized reaching higher yields toward jet fuel. Furthermore, an ethanol plant can be refitting to produce butanol with rather minor changes but with a lower volumetric yield of alcohol [42].

The conversion of butanol to butene has a conversion rate of 98-99% using $\gamma$-alumina or ZSM-5 catalysts. The butene can be further converted to higher olefins, while unreacted butene and its dimer C8 from oligomerization can be recycled or sent to a separate dimerization reactor. The final olefin product is hydrotreated to produce SPK jet fuel.

Iso-butanol-to-Jet fuel process yields are reported to be around 61.5-63% [43].

### 3.1.2 Feedstocks used in ATJ route

The feedstock for the ATJ is the respective alcohol used, while the feedstock for the alcohol production, in turn, could be highly variable. Bioethanol is commonly produced from raw materials containing sugar. Depending on if their use is in competition with food industry or not can produce first or second generation biofuels, just as it was explained into section 2.1 of introduction. Thus, first generation biofuels are usually produced by using agricultural crop-based feedstocks, such as sugarcane, sugar beet, corn starch, wheat, rye, barley, cassava and potato starch. On the contrary, second generation biofuels are produced by using biogenic feedstocks without direct rivalry with food industry, which can be such diverse as switch grass, cornstalks, wood, herbaceous crops, waste paper and paper products, agricultural and forestry residues, pulp and paper mill waste, municipal solid waste and food industry waste [44]. Sugar- and starch-based materials have high sugar content, which can be converted to bioethanol using microbial fermentation. The fact that first-generation bioethanol production uses crops that have been diverted from the food chain has led researchers to seek non-food- based alternatives, such as lignocellulosic feedstocks. However, it should be taken into account that lignocellulosic materials are much more structurally complex, which requires an additional pre-treatment step to render the cellulose susceptible to hydrolysis [45].

LanzaTech company has developed a gas fermentation technology, which captures CO-rich gases and converts the carbon into fuels, i.e., ethanol. This CO-rich flue gas stream could be derived from industrial waste gas as the ones from steel-making plants and ferro-alloys industries, but also from syngas produced from MSW gasification.

The iso-butanol production process could use the same input feedstock as bio-ethanol: in fact, its process could mainly share the same plant layout, or at least could integrate in an existing bio-ethanol plant. Anyway, it would be using different yeasts to convert the sugars to iso- butanol. GEVO's process is reported to be using mainly yellow dent corn, which is around the 99% share of all corn grown in the U.S. and is currently used for animal feed and industrialuses [46].

At EU level, the recent S2Biom estimates for the 2030 base potential, addressing the sustainability criteria as stated within the RED, amount to 1,093 Mt/y of dry lignocellulosic biomass. Considering a weight-based yield of 22% there results a theoretical potential for 2nd generation bioethanol of 240 Mt/y, equal to 153 Mtoe/y [12]. The theoretical maximum EU kerosene production based on wheat is reported to be 31.9 Mt/y, so to 20.3 Mtoe/y. At global level, ethanol production potential is reported to be of around 1,8 Bt/y from residual biomass, 90 Mt/y from MSW and 180 Mt/y from off-gases related to refineries, steel mills and ferro-alloy industries [47].

### 3.1.3 ATJ plants and technology status

Despite scientific literature defines Alcohol to Jet as a technology at TRL of about 6-7 [48], it must be highlighted the fact that the supply of aviation biofuels for commercial flights has been already occurred. This fact demonstrates the high maturity level of this technology Other international initiatives (CAAFI [49]) use the Fuel Readiness Level (FRL) scale that includes descriptions that are customized to fuel research and certification events and includes specific items and required fuel quantities. Scale rates ASTM-certified fuels at FRL7 or higher [50]; in fact ATJ pathway is rated at FRL 7 [48].

Technologies for converting alcohols and other oxygenates to SPK jet fuel are being developed by several companies. A partial list includes BYOGY, Cobalt, Gevo, SwedishBiofuels, Terrabon, UOP, LanzaTech, Zeachem, and Vertimass [23].

Table 1 reports existing or planned pilot, demonstration and commercial plants for ATJ production.

**Table 1: Existing or planned ATJ pilot, demonstration and commercial plants**

| Company | Project type | Location | Feedstock | ATJ capacity | Status | Bio-fuel capacity | REF |
|---|---|---|---|---|---|---|---|
| Byogy | Pilot | Bryan, Texas, USA | Agave, sugarcane, corn, sweet sorghum, cassava, sugar beet | YES | Operational | N.A. | [5] |
| GEVO | Commercial | Luverne, Minnesota, USA | Sugary feedstocks (maize, grains, sugar cane) | YES (Isobutanol, ethanol) | Planned, 2022 | 72 Ml/yr | [51] |
| | Demo | Silsbee, Texas | | | Operational | 265kl/yr | [51] |
| LanzaTech | Demo | Shougang Steel Mill, Beijing, China | Steel flue gas | YES (ethanol) | Operational | 300t/yr | [5] |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Swedish Biofuels | Pilot | Stockholm, Sweden | N.S. | YES | Operational | 4.8t/yr | [5] |
| Swedish Biofuels | Demo | N.S. | MSW, biogas, grain crops, | YES | Planned 2019 | 5kt/yr | [5] |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | | | agricultural & forestry residues | | | | |
| Vertimass | Demo | Madison, WI, USA | Woody biomass | YES | Operational | 38kl/yr | [52] |

CAAFI reports expected Lanzatech ATJ production volumes to grow to 30 kt/y at Freedom Pines plant by 2022, and then globally to 300 kt/y by 2024 with a total of 4 facilities. In the same report, GEVO is projected to grow from demonstration quantities to 30 kt/y at its Lucerne facility [53].

### 3.1.4 Costs Estimates for ATJ pathway

The EU-financed project BFSJ “Production of fully synthetic paraffinic jet fuel from wood and other biomass”, ended on December 2019, had as its scope to design and operate a plant with a capacity of 5 kt/y of fully synthetic paraffinic jet fuel, based on Swedish Biofuels and LanzaTech technology. Within the project, cost estimates and financial parameters for differently sized plants were developed. Thus, a smaller plant, with an annual production capacity of 20.5 kt of a mix of gasoline, jet fuel and diesel is calculated to have a CAPEX of €49 million. A bigger plant with an annual production capacity of 200 kt of a similar mix of gasoline, jet fuel and diesel is expected to have a CAPEX of €399 million. The smaller plant is planned to use mostly ethanol as feedstock, while for the bigger one a total of 750 kt/y of wood and 150 kt/y of ethanol is expected to be used [54]. Other sources report CAPEX – for a 230 ML/y plant - of €355 million if based on conventional, crop-based feedstocks (i.e., sugars and starches) and of €548 million if based on corn stover, a cellulosic agricultural residue (2019 figures) [55].

Each conversion pathway could be economically characterized according to its CAPEX, feedstock costs, and OPEX. ATJ is among the most capital-intensive conversion technologies (in terms of total equipment costs per ton of RJF produced). More specifically, the pre-treatment, hydrolysis and fermentation units represent the greater share of the costs.

ATJ is accounted for relatively higher MFSPs, largely due to the lower conversion yields (on a dry matter basis) and the high capital cost of lignocellulosic sugar extraction and fermentation.

ATJ is expected to have a MFSP, for a nth plant, at around 3 €/L if forest residues are used; instead, if wheat straw is used as feedstock a MFSP of 4.2 €/L is expected (2015 figures) [56]. Other sources report quite lower MFSP, ranging from 1.6 €/L if using corn grain as feedstock to 2.5 €/L when using energy crops or agricultural residues (2019 figures) [55]. As usually happens for capital-intensive technologies, ATJ pioneer plants show a significantly higher MFSP when compared to nth plants (a 60% to 85% increase is reported).

The above-mentioned lignocellulosic feedstocks are reported to be approximately 40% more expensive to convert into fuel than corn and sugarcane. The upgrading process represents around 50% of the MFSP for these, whereas for lignocellulosic ATJ conversion, it raises to around 80% of the MFSP. In fact, a large share of the ATJ production cost for food crop- derived fuels is related to ongoing feedstock and energy costs, whereas for lignocellulosic ATJ pathways is attributable to CAPEX costs, accounting for approximately 40% of the levelized cost [55].

A possible strategy to reduce fuel production cost is co-locating. This refers to installing a separate ATJ facility near to an existing facility in order to use part of the feedstock supply, infrastructure and utilities of the existing facility. Such choice shows an average reduction in MFSP of around 4-8% with respect to localized greenfield production [56]. This costs reduction is largely ascribed to a reduction of capital and maintenance costs, which shows the bigger potential on capital-intensive technologies, such as ATJ.

Finally, although the aviation sector provides a huge potential market for biofuel producers, RJF is a rather unattractive product in terms of selling price when compared to chemicals. The trade-off between these markets is especially significant for the ATJ pathway, which produces high-valued intermediate. A parallel production of RJF and biochemicals in the same biorefinery could stimulate RJF development by enabling producers to gain experience with their production while making profit of the higher margins of biochemicals.

### 3.1.5 Sustainability of ATJ process

As already reported in the introductory section, the baseline carbon intensity of petroleum jet fuel is assumed to be 87 $gCO_2eq/MJ$. In terms of GHG emissions, almost all pathwaysperformed better than that along their life cycle, with the exception, among others, of ATJ by isobutanol intermediate from corn grains feedstock. ATJ from sugarcane is instead assessed to be at around 25 $gCO_2eq/MJ$ [57].

This substantial variability of GHG savings within the ATJ pathway depends on feedstock, having crop-derived ATJ fuels higher direct emissions than lignocellulosic feedstock-derived fuels [55]. In fact, corn grain-based ATJ has a GHG emissions associated of 79 $gCO_2eq/MJ$, of which 14 $gCO_2eq/MJ$ related to ILUC emissions, leading to a 11% GHG savings compared to baseline. Sugarcane-based ATJ performs better, totaling 65.1 $gCO_2eq/MJ$, of which 17 $gCO_2eq/MJ$ related to ILUC emissions, leading to a 27% GHG reduction from fossil baseline. ATJ of agricultural residues causes 14.9 $gCO_2eq/MJ$, without ILUC emissions. This allows GHG of 83% to be reduced in comparison to fossil baseline. Finally, ATJ process by using energy crops releases 20.3 $gCO_2eq/MJ$, which allows GHG reduction of 77% compared to fossil jet fuel [55]. Moreover, using other sources also entail estimated values similar GHG savings. Thus, a wood residuals based ATJ pathway is accounted for 66% reduction compared to fossil jet A-1, with wider range extremes, from -69 $gCO_2eq/MJ$ in the low end and 34 $gCO_2eq/MJ$ in the high end. This large discrepancy is related to different substitution effects of co-products; i.e., using C5-molasses as animal feed could help substituting imported soy bean fodder, thus avoiding associated ILUC emissions. Anyway, depending on prices and market request, it is possible that a producer would prefer to eliminate the by-product by converting it into additional biofuel. This in turn would reduce the related climate benefits, making the higher end 34 $gCO_2eq/MJ$ a more likely estimate. Adding some further processing required, the emissions from straw- based ATJ would be in the range of 30-45 $gCO_2eq/MJ$, which implies a 66-45% $CO_2eq$emissions saving compared to conventional fossil jet [58]. A similar scenario could also be found when using sugarcane as feedstock, where the associated use of bagasse to generate electricity in sugarcane mills could displace conventional power generation, thus bringing an additional mitigation effect [57].

### 3.1.6 ATJ technology development potential

The processes used in the ATJ pathway are considered individually mature, since they are widely used in commercial petrochemical applications. However, complete feedstock-to-fuel process chains are still at pilot and demonstration stages. Nevertheless, the technologies that synthesize alcohol intermediates, such as ethanol and butanol, are at higher development stages than those used to convert the intermediates to jet fuel [5].

CAAFI reported on the announced intentions of ATJ producers, in terms of new capacity forecast: GEVO is already accounted for demonstration-level quantities for 2020 in its Silsbee plant, while projects a production capacity of around 30 kt/y at Luverne plant by 2023 [53].

GEVO and Praj Industries Ltd. have announced to have signed Framework Agreement to collaborate on providing RJF, among other fuels, in India and neighboring countries. GEVOwill license its technology to Praj to produce renewable isobutanol from both first generation and second generation feedstocks, and for converting it into RJF and premium gasoline.

Lanzajet, a new company launched by Lanzatech for the production of RJF, totaled USD25 million of investments from Canadian integrated energy company Suncor Energy and Mitsui. This initial investment, coupled with participation from All Nippon Airways (ANA), will complement an existing USD14 million grant from the US Department of Energy. The funding will be used to build in Soperton (Georgia) the Freedom Pines demonstration plant with a throughput capacity of 30 kt/y, whose operating activity is expected to start by 2022. Suncor has also contracted to take a significant portion of the RJF and renewable diesel produced on the site. [59]. Successively, three new plants set in various international locations are expectedto start operation for Lanzajet by 2024, with a total projected capacity of 270 kt/y [53].

One of those plant is a new European ATJ plant funded with a €20 million grant from the EU H2020 program, is expected to be fully operational by 2024, using waste-based ethanol sourced from multiple European producers. The plant will be designed and operated under the FLITE consortium led by SkyNRG, with LanzaTech as the technology provider. Plant expected scale is of over 30 kt/y [60].

## 3.2 HFS-SIP Pathway

HFS-SIP received ASTM certification in 2014, for a maximum 10% blend with fossil-derived jet fuel. The reason for the low blend limit could be found in the fact that HFS-SIP is almost corresponding to a pure chemical compound (98% farnesane) and not to a complex mixture of hydrocarbons with a continuous distillation curve, as it is the case for any fossil and most of the alternative jet fuels.

This pathway conversion process comprises technologies that use genetically engineered yeasts to convert sugars directly to renewable hydrocarbons. The development process is being led by a joint venture between Amyris and Total, that use sugarcane-derived glucose to produce the isoprenoid intermediate farnesene, through the proprietary Biofene® technology. Farnesene is then upgraded to farnesane through hydroprocessing.

The key feedstock of HFS-SIP, like ATJ, is sugarcane, which is highly available but has significant land and water use concerns. Next generation feedstocks are mostly composed by lignocellulosic biomass, and, on a longer term, by wastes, algal and cyanobacterial biomass.

Life-cycle GHG emissions are estimated in the range of 21 g$CO_2$eq/MJ to 45 g$CO_2$eq/MJ.

HFS-SIP, alongside CHJ, is currently reported as the most expensive pathway, with very high operational costs related to processing steps and low yields. Literature reports MFSP ranging between 65 and 95 €/GJ (3,060-4,470 €/t) for the sugarcane pathway, and between 104 and 140 €/GJ (4,895-6,600 €/t) for the forestry residues and straw pathway.

### 3.2.1 HFS-SIP process description

The Synthesized Iso-Paraffins produced from Hydroprocessed Fermented Sugars (HFS-SIP) pathway, formerly known as Direct Sugar to Hydrocarbon (DSHC), comprises technologies that use genetically engineered yeasts to convert sugars directly to renewable hydrocarbons [5,13] (Figure 5).

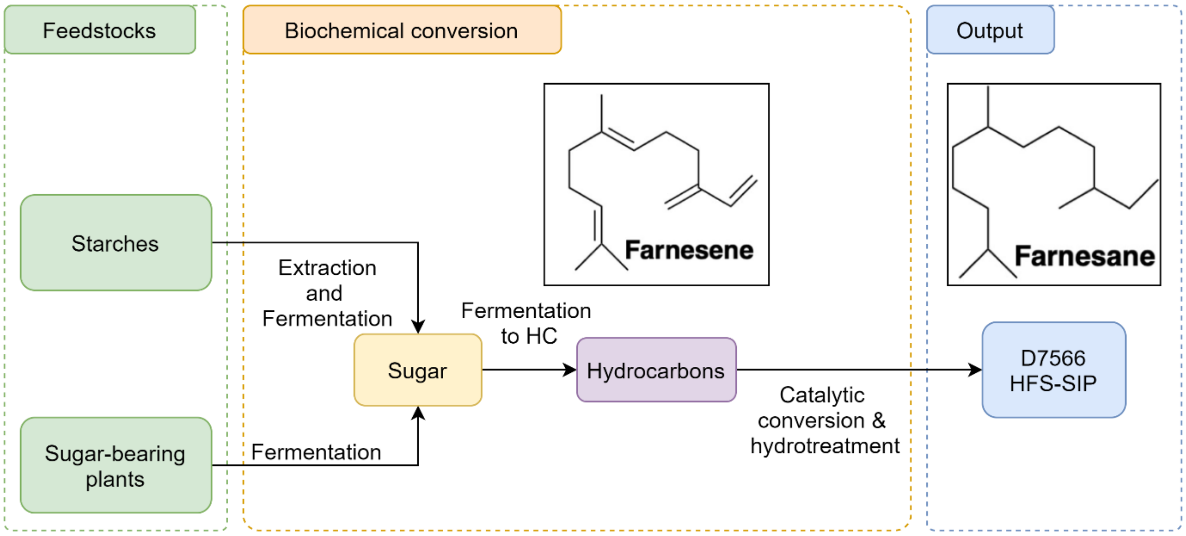

**Figure 5: High-level description of HFS-SIP production pathway**

Several biological pathways could be used to make to make hydrocarbon intermediates: biological conversion can occur in both anaerobic and aerobic conditions, and products can range from pentadecane, farnesene, fatty esters, fatty acids, fatty alcohols, isoprene. Anyway, only HFS-SIP received ASTM certification in 2014, for a maximum 10% blend with fossil- derived jet fuel; pathway development is being led by a joint venture between Amyris andTotal. They use sugarcane-derived glucose to produce the isoprenoid intermediate farnesene, through the proprietary Biofene® technology, using the mevalonate pathway in yeast cells [61]. Farnesene in turn can be used as the basis for a range of petroleum replacement products [5]; it can then be upgraded to farnesane through hydroprocessing, in order to be blended with fossil jet fuel.

In fact, farnesene itself is a fuel precursor. It is highly unsaturated and this in turn results in a low cetane number and low oxidative stability. Farnesane, instead, has a good cetane number of 58 and excellent cold-flow properties. It is worth noticing that the chemical hydrogenation step can add significant cost to farnesane manufacturing and could result in an overall lower yield [62].

Farnesane is a 15-carbon single molecule, with a density of 0.77 t/m$^3$, a kinematic viscosity of 2.325 mm$^2$/s and a flash point of 110°C; thus, its characteristics are globally corresponding to FT-SPK and HEFA-SPK, but it also has pure component properties instead of those of a mixture, as it occurs for the latter [63]. This is the reason for the 10% blend limit in conventional jet fuel: HFS-SIP is almost corresponding to a pure chemical compound (98% farnesane) and not to a complex mixture of hydrocarbons with a continuous distillation curve, as it is the case for any fossil and most of the alternative jet fuels [64].

Other main routes under development, whose products can be further processed into jet fuel, can be found using heterotrophic algae or yeast converting sugars into lipids within their cells [13].

Farnesene itself could be produced through either the mevalonic acid (MVA) pathway, or 1-deoxy-d-xylulose 5 phosphate (DXP) pathway, or anaerobically [37].

Amyris and Total process are based on fermentation of lignocellulosic sugars to isoprenoids, following the mevalonate pathway. Acetyl-CoA is converted into isopentenyl pyrophosphate (IPP), which is further transformed into farnesenyl pyrophosphate (FPP) and into C15 isoprenoids, as described by Figure 6.

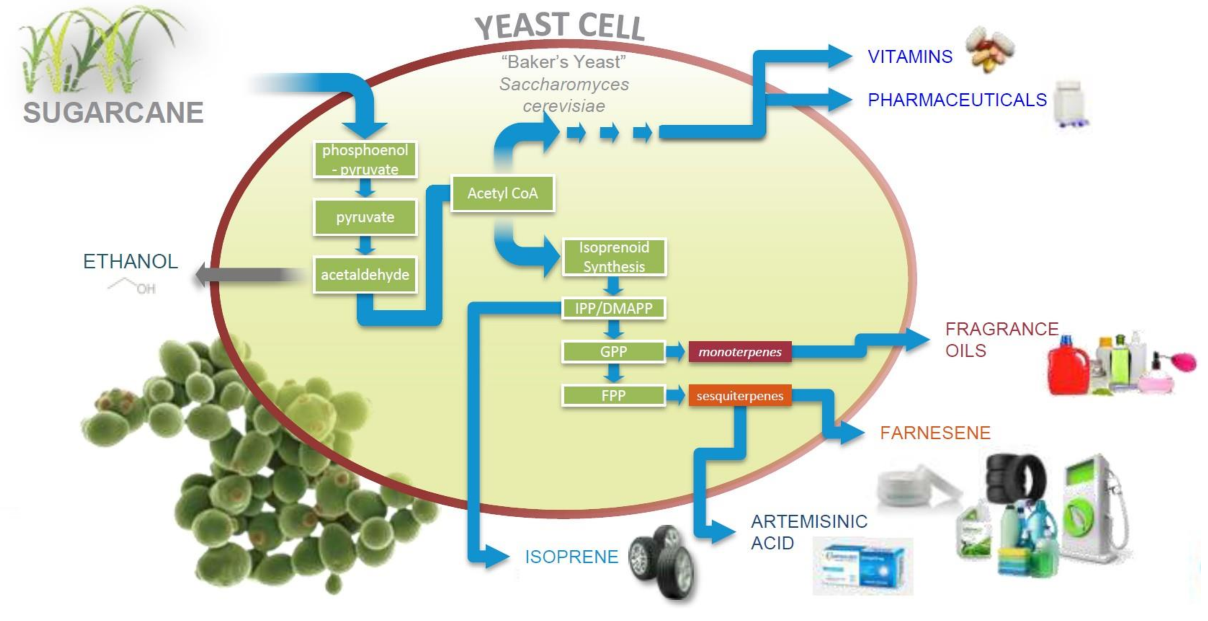

**Figure 6: High-level description of HFS-SIP production pathway based on sugarcane feedstock, describing the different possible outputs [65]**

A pretreatment step is necessary to separate cellulose and hemicellulose from lignin if the feedstock is raw biomass. Then the cellulose is transformed to sugars through hydrolysis process and, in a following step, sugars are converted through fermentation to farnesene. Such bioconversion of sugars to product occurs in a system of stirred-tank aerated vessels, using heavily engineered *S. cerevisiae* strain, developed by Amyris [67], and capable of converting both C5 and C6 sugars, with ammonium hydroxide and diammonium phosphate supplied as nutrients [66]. The very low solubility in water that farnesene has over short-chain alcohols comes as an advantage at this stage: the molecule forms a separate phase on thetop of the fermentation broth, hence facilitating subsequent recovery and purification [68]. Moreover, centrifugation can be used to separate these compounds from fermentation broth, resulting in considerable energy savings, compared with distillation [62]. A two-stage centrifugation process is used together with a de-emulsification process, with a reported 95% recovery of farnesene and 97% purity [37]. In a first stage, the yeast biomass and a large portion of the aqueous phase are removed. Prior to further centrifugation, the pH and salt concentration are adjusted to disrupt the emulsion created by the presence of extracellular material [66]. Finally, the olefin is mildly hydrotreated to the corresponding iso-paraffin called farnesane, by introducing 4% of its mass in $H_2$ [69]. Figure 7 describes Farnesane production process, using sugarcane as feedstock, also highlighting the synergies between the various plant sections.

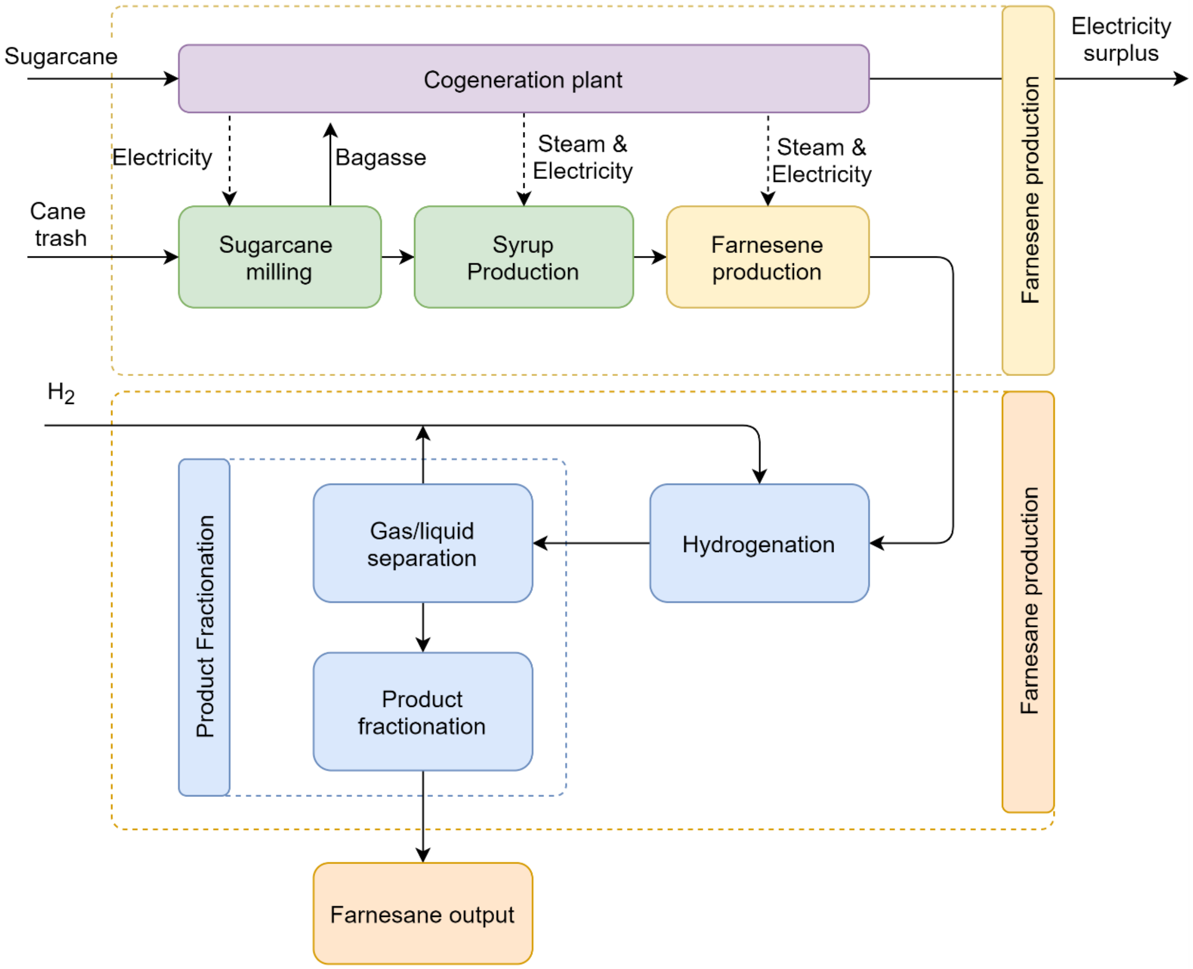

**Figure 7: The HFS-SIP production process, broken down in farnesene and farnesane production steps**

An example based on the fermentation of biomass to farnesane (Amyris) is given for the SIP process. The yield gain from lignocellulosic biomass is only indicative for this type of process, but the tendencies and philosophy are still valid for any biofuel process based on fermentation to alcohols or to hydrocarbons. Within the National Advanced Biofuels Consortium (NABC) a research focusing on tracking the carbon losses in the different steps of the SIP process has been developed. The pretreatment step, with the removal of lignin plus clarification and evaporation, accounts for the largest percentage of carbon losses during the process, with a 50% to 54% share. The next largest carbon loss is related to the fermentation step, including fermentable sugars lost to yeast biomass and $CO_2$ production by the yeast metabolism, with a carbon loss ranging between 20% to 40%. Also the downstream steps, such as separations, account for important carbon losses of about 10%. Summing everything up, the lost carbon across farnesane production, compared with the initial biomass, ranges across 76% to 94%. By optimizing the technology and the process steps, a possible yield doubling is reported, from6% to 12%, which in turn also positively affects the final cost of the product [64].

Corresponding farnesene yields are reported at 16.8 g farnesene/100 g of sugar, with an average productivity of 16.9 g/L/d. The theoretical mass yields of sesquiterpenes compounds, among which is farnesene, are approximately 30-45% lower than ethanol, with metabolic mass yields ranging across 25% and 35%, compared to 51%. Anyway, their energy densities are significantly higher than ethanol and as a result, the enthalpy of combustion yields forthese diesel compounds approach 90%, against ethanol 97%. The farnesene made from the mevalonate pathway is an exception, with a lower yield of 75%, resulting from a 4% to 5% lower mass yield [62]. Several reports point out performance can achieve about 50-65% of the theoretical value; Amyris reported in 2010 a 17 wt% farnesene yields from glucose [70].

This demonstrates the increased burden placed on the present approach to achieve cost targets for hydrocarbon pathways relative to ethanol. These example products are all diesel- range molecules; however, products in the gasoline or jet-range (e.g., isobutanol, C6-C10 alcohols, etc.) generally compare similarly.

### 3.2.2 Feedstocks in HFS-SIP production

The key feedstock of HFS-SIP, like ATJ, is sugarcane, which is highly available but has significant land and water use concerns [71]. Additionally, there is a variety of feedstocks that can be used for biological conversion of sugars to fuels, including beets, corn grain, and pretreated lignocellulosic biomass [37].

The fermentable sugars are readily available on the feedstock in the case of sugar-bearing plants such as sugarcane, sugar beet, and sorghum. They are obtained by mechanical processes such as milling or diffusion. Sugarcane, a semi-perennial crop, has the highest global production of sugar-bearing plants, with 1.887 Mt/y; it has an average agricultural yieldof 70 t/ha and an average sugar content of 12 to 16%. Brazil is the major global producer witha 39% share, followed by India with 18% and China with 7% [57].

Sugarcane has been reported to be facing a short-term gap due to supply shortage and lower yields. This in turn requires larger investments to promote the expansion of the production. Moreover, sugarcane expansion is taking place towards regions with longer water deficitperiods, low fertility and towards non-traditional areas, increasing inherent risks and costs.

One of the main economic barriers related to the use of sugarcane in the jet biofuel market, is the high opportunity cost of both the cane, which is already extensively used as a feedstock for the sugar and ethanol markets, and the bagasse, since the latter is largely used for electricity generation, thus it cannot be considered a freely available residue of the cane crushing. Furthermore, sugar crops use for jet fuel production raises food security concerns [69].

Additional feedstock choice considerations could be made at process level. In fact, if the whole hydrolysate from lignocellulosic feedstocks is used, it can produce the effect of reducing the oxygen mixing levels in the bio-reactor, thus reducing aerobic biological conversion. In order to increase conversion, the hydrolysate should be processed through conditioning andprocessing steps prior to conversion [37].

### 3.2.3 HFS-SIP plants and technology status

HFS-SIP development is being led by a joint venture between Amyris and Total which was restructured in 2015, with Total claiming a 75% stake in the partnership. Their proprietary 'Biofene' technology uses sugarcane-derived glucose to produce farnesene, which is used as the basis for a range of petroleum replacement products through upgrading to farnesane. Their first commercial plant in Brota, Brazil, has been operational since December 2012 and has the capacity to produce up to 50 ML of farnesene per annum (38.6 kt/y), with six reactors with 200 kL capacity each [69]. The facility has been certified by the Roundtable on Sustainable Biomaterials.

Total and Amyris' Biofene jet fuel has reached the following milestones, thus is considered to have a FRL of 7, moving towards 8, since:

- It has achieved ASTM certification.
- A fuel purchase memorandum of understanding has been signed with an airline.
- A first commercial plant capable of producing jet fuel is operational.

A two-year programme between Amyris and Cathay Pacific began in May 2016, in which its 10% blended sugarcane-derived fuel would be used on all Airbus A350 delivery flights from Toulose to Hong Kong. Airbus announced that such programme will continue with A350-1000 delivery flights, which commenced in June 2018 [72].

LS9 is another company that has previously worked on commercializing biojet fuel, with a pilot plant in 2008, but since being purchased by REG Life Sciences the company has changed focus to biodiesel and biochemicals. Other sugar-to-jet pathways have yet to be commercialized, including isoprene. The publicly available literature on HFS-SIP fuels produced by other companies is insufficient to assess their FRLs, but since none are pursuing ASTM certification, FRL 5 is assumed as a maximum [5,13].

### 3.2.4 Costs Estimates to produce HFS-SIP

HFS-SIP, alongside CHJ, is currently reported as the most expensive pathway because of the very high operational costs due to necessary processing steps [71] and the low yields: for the production of 1kg of farnesane, at least 5 kg of sugar is needed [69]. Klein-Marcuschamer et al. [66] reported that most of the facility-dependent cost is related to hydrocracking, accounting for around 85% of total, with fermentation equipment accounting for around 10% and separation equipment for the remaining share. De Jong et al. [56] pointed out the necessity of a Total Capital Investment of €205 million for a plant processing sugarcane feedstock, with a reference input capacity of 262 MW; considering the equivalent input in molasses, the reference input capacity lowers to 153 MW and the TCI to €169-174 million. With molasses feedstock costs set at 190 USD/t, based on industry experience, and nutrients feed costs set at 230 USD/t for ammonium hydroxide and 703 USD/t for diammonium phosphate, the corresponding farnesane MFSP is obtained at 2449 USD/t. Modeling the process as using less expensive hydrogenation processes lower the MFSP at 1969 USD/t. Sensitivity analyses of the major economic drivers suggest that technological and market developments could bring the previous cost figures of 2449 USD/t down to 1367 USD/t (2015 figures). De Jong et al. reported MFSP ranging between 65 and 95 €/GJ for the sugarcane pathway, and between 104 and 140 €/GJ if forestry residues and straw are respectively used as feedstock. Bauen et al. [13] indicated projections for HFS-SIP costs to remain high at above €4000 per ton (around 85€/GJ[2], 2020 figures).

Not only SIP and ATJ bio-jet routes are expensive, thus limiting their usage, but also the produced intermediates, such as butanol and farnesene, are worth more as chemical feedstocks or for applications in the cosmetics and pharmaceutical industries. As an example, farnesene MFSP is reported to be around 5.500 €/t (117 €/GJ) [50,56]; this makes potential HFS-SIP developers target more the chemical, pharmaceutical, food and feed markets, which generally present higher value than bulk transport fuels. On the other hand, this could help in

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[2] Considering a farnesane HHV of 46.9 MJ/kg and a density of 0.773 t/$m^3$

proving the technology and reach the needed scale to lower production costs to the level that may be required for fuels [13].

### 3.2.5 Sustainability of HFS-SIP

The literature mainly reports on GHG emissions and sustainability of biochemical conversion pathways using sugarcane and corn grains [68]; it is worth noticing that the HFS- SIP process is in at earlier stage of technological readiness and therefore there are fewer comparable studies in the literature. Partly due to uncertainty over the farnesene yield from this process, GHG emissions estimated from a LCA can vary considerably across different studies [73].

According to the National Advanced Biofuels Consortium (NABC), the carbon efficiency of the Amyris process is in the order of 60%, with the remaining 40% available for energy production. While on one hand this results in low farnesene yields, on the other hand it can translate into a GHG credit through renewable electricity production, which can also be used as a positive attribute for marketing the technology. Such remaining 40% of carbon is made available in the form of non-farnesene carbohydrates, ending up in the facility internal anaerobic digester. Thus, according to Karatzos et al. [70], for every energy unit of farnesene, one energy unit of methane is produced. If the methane is combusted to generate heat and power, this results ina significant GHG savings credit to the overall process.

CORSIA default GHG direct emissions for sugarcane-based HFS-SIP are estimated by ICAO at 32 $gCO_{2eq}$/MJ, of which more than half are attributable to feedstock cultivation [73]. Moreover default ILUC emissions have been calculated by ICAO as around 13 $gCO_{2eq}$/MJ, fora total Well-to-Wake GHG emissions value of 45 $gCO_{2eq}$/MJ.

Moreira et al. [68] analyzed Amyris' proprietary technology platform for the production of farnesane. Effects from direct and indirect LUC were addressed, resulting in a reference case with life cycle emission of 8.5 g $CO_{2eq}$/MJ. A further Monte Carlo analysis over several different scenarios was carried out by authors, reporting possible life cycle emissions of the process in the range of 21±11 $gCO_{2eq}$/MJ, with substantial influence from the LUC factor and the level of electricity exports. The analysis was based on the consequential approach adopted by the CARB report for the LCFS, from which the Brazil-based sugar cane production emissions values, used for the base case, were also inherited. LUC emissions were instead recalculated to better represent the expansion of the renewable fuel in Brazil. The above-mentioned agricultural emissions were added to the estimated emissions from sugar cane processing, fuel production, and fuel use, in order to define the overall biofuel life cycle emissions [68]. Table 2 summarizes the main contribution to life cycle emissions of farnesane as jet fuel.

**Table 2: Life cycle GHG emission for the HFS-SIP production pathway, as modelled in [68]**

| Life cycle stage | GHG emissions ($gCO_2eq$/MJ) |
|---|---|
| Sugar cane production | 14.6 |
| Land use change (LUC) | 12 |
| Farnesene production | |
| *Chemicals* | *2.8* |
| *Biomass combustion* | *3.5* |
| *Electricity surplus* | *-33.9* |
| *Yeast* | *-0.6* |
| Farnesene transport | 0.3 |
| Hydrogenation | 9 |
| Fuel transport | 0.3 |
| Fuel use | 0.6 |
| Net emissions | 8.5 |

It can be noted that GHG emissions associated with sugar cane production and transport account for more than two-thirds of the total, but are completely offset by the avoided emissions due to the electricity co-production during the farnesene production stage, as reported in Figure 8 [74]. Anyway, Moreira et al. highlighted how such influential parameter is basically affected by the energy self-consumption for farnesene production. Finally, Moreira et al. estimated such life cycle performance as highly uncertain and the base case results as rather optimistic.

The Institute for International Trade Negotiations (ICONE) conducted a life-cycle assessment for GHG emissions of biojet fuel produced from sugarcane sugars, using Amyris process parameters. It reported life-cycle GHG emissions of around 15 $gCO_2eq/MJ$, without taking into account the possible land use change effects related to sugarcane energy use [37]. Finally, Davis, et al. [75] reported an average water usage ratio of 30.2 L water/GJ fuel.

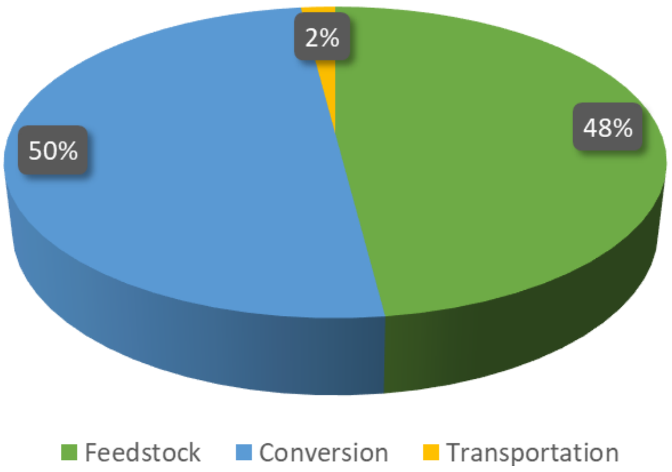

**Figure 8: Attribution of GHG emission to the various life-cycle phases (authors elaboration on [74])**

### 3.2.6 HFS-SIP technology development potential

Commercial scale biosynthesis of isoprenoids using microbial cell factories has been achieved using *S. cerevisiae* by Amyris that first highlighted the potential during the development of semi-synthetic artemisinin. In a successive phase, the strain was adapted for farnesene production, as an advanced biofuel precursor [76]. However, the value of artemisinin, a pharmaceutical product was set at around 150 USD/kg [77]. The market price of jet fuels is considerably lower, thus, in order to reach industrial feasibility, dramatic production cost reductions would be required.

Within the framework of productivity increase research, Meadows et al. presented results where the conversion of sugar to farnesene was improved 25% and oxygen demand was reduced by 75%. Farnesene concentrations of around 130 g/L were achieved using unrefined cane syrup in a fermentation process that accurately predicts performance at 200 kL fermenterscale [78]. Even with substantial progress and dramatic increases in productivity, however, production costs continue to limit farnesene to specialty chemical production. Bauen et al. [13] reported on planned farnesene additional capacity for the near future of around 140-150 kt/y, which is much lower than the 320 kt/y of ATJ planned additional capacity or of the 220 kt/y Gasification/FT planned additional capacity.

Another development pathway of the isoprenoid-based jet fuels is related to the use of non- food crops, such as lignocellulosic biomass, wastes, algal and cyanobacterial biomass, as summarized in Figure 9.

A major challenge reported for the use of lignocellulosic feedstocks in this context is the high content of xylose, a pentose sugar which cannot be naturally metabolized by some of the widely used microbial hosts such as *E. coli* and *S. cerevisiae*. In addition, pre-treatment could lead to inhibitory compounds release, which in turn could hinder cell viability and productivity.

The use of crude glycerol is a promising low-cost, second generation feedstock, since it is a major waste product of biodiesel production. You et al. [79] reported on the production of farnesene from glycerol by an engineered E. coli strain; anyway, the good results achieved with pure glycerol were not completely confirmed in subsequent experiments using crude glycerol. A possible solution to this problem was proposed in the form of an additional pre-treatment to reduce the presence of inhibitory compounds and maximize productivity.

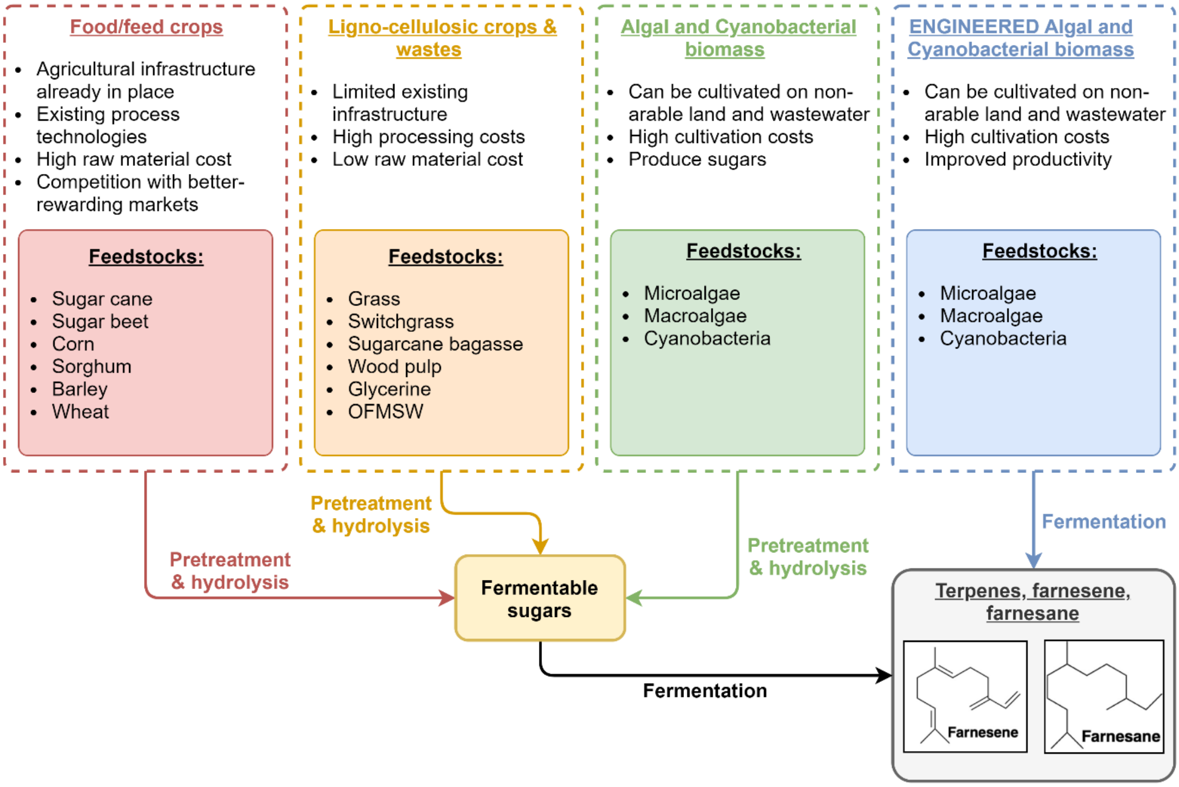

**Figure 9: Possible farnesane production pathway, using conventional and advanced feedstock [76]**

Photosynthetic organisms including algae and cyanobacteria exhibit higher rates of photosynthesis and growth than terrestrial plants, thus are of growing interest for biofuel production. One production pathway would see the algal and cyanobacterial biomass as the carbon source provider for an engineered host. In this case, following biomass pretreatment and hydrolysis steps, needed to degrade the cell wall and release fermentable sugars, the resulting sugar was then fermented by S. cerevisiae yielding bioethanol [80].

Another, more advanced production pathway, would see an engineered algae or cyanobacterium directly capable of synthesizing the terpene of interest. As the primary carbon source of such organisms is $CO_2$, such organisms provide a means of capturing and recycling carbon from waste gases.

Lanzatech recently commercialized an innovative waste gas to bioethanol process using *C. autoethanogenum* [81]. The company has also engineered the species for the production of farnesene from a CO-containing waste gas [82].

Table 3 reports the main results in alternative farnesane production pathway reported in literature.

**Table 3: Main results in alternative farnesane production pathways**

| Microbial host | Feedstock | Farnesane Titer (mg/L) | Scale | Operation | Ref. |
|---|---|---|---|---|---|
| *E. coli* | Pure glycerol | 8,740 | 7 L Bioreactor | Batch | You et al. [76, 79] |

| | | | | | |
|---|---|---|---|---|---|
| | Crude glycerol | 2,830 | 7 L Bioreactor | Batch | You et al. [76, 79] |
| *S. cerevisiae* | Unrefined cane syrup | 130,000 | 200,000 L Bioreactor | Fed-batch | Meadows et al. [76, 78] |
| *Y. lipolytica* | Glucose | 2,555 | 1 L Bioreactor | Batch | Liu Y.et al. [76, 83] |

## 3.3 FT-SPK/SPKA Pathway

The Fischer-Tropsch synthesis (FT) pathway was the first to receive ASTM certification as alternative fuels in aviation in 2009, for up to 50% blending into conventional jet fuel, for a fuel produced from coal, natural gas or biomass. On the FRL scale, the FT pathway can be categorized at FRL 7 (corresponding with ASTM certification) with evidence of progress toward FRL 8. FT processes convert catalytically synthesis gas (named syngas) into hydrocarbon liquids, among which jet fuels. Previously, syngas is first generated through a gasification process using a wide range of low-cost feedstocks, such as agricultural residues, energy crops, and municipal solid waste (MSW), being afterwards subjected to a cleaning and conditioning step.

Switchgrass, corn stover, and more in general lignocellulosic biomass such as agricultural and forestry residues could be used as feedstock for the process, and this makes the gasification-FT pathway as one of the best-performing in terms of ILUC-related emission and overall WtW emissions, estimated in the range of 5 to 22 $gCO_{2eq}$/MJ.

FT pathway is considered as quite capital-intensive, putting pressure on feedstock logistics and increasing investment risk. This entails in a quite high MFSP, ranging from 1.34 €/L to 1.87 €/L, depending on feedstocks and studies.

Despite setbacks in the development of some production plants which occurred in the last decade, a total planned gasification + FT potential capacity of more than 200 kt/y is reported as to become operational in the next years.

### 3.3.1 FT process description

FT processes convert syngas with given hydrogen to carbon monoxide ratio into hydrocarbon liquids and waxy solids with water as a byproduct via a stepwise polymerization process [84].

The Fischer-Tropsch synthesis was pioneered in 1920s by Franz Fischer and Hans Tropsch [85]. A syngas consisting mainly of carbon monoxide (CO) and hydrogen ($H_2$) is prepared through gasification of the solid feedstock, either coal or biomass, or steam reforming of methane in case of natural gas. The syngas is cleaned and conditioned and then catalytically converted to hydrocarbons.

The gasification and Fischer-Tropsch (gasification- FT) route for fuel production can be usedto convert a range of low-cost agricultural residues, energy crops, and municipal solid waste (MSW) into a slate of liquid fuels, including renewable diesel, jet fuel, and gasoline [55], besides paraffinic waxes, lubricants, petrochemical base products [86].

There are two different technologies to produce liquid hydrocarbon from synthesis gas through FT process, currently: a high-temperature (HTFT) and a low-temperature (LTFT) based technology. Temperature generally used in HTFT ranges from 320 to 350°C, while LTFT reactor temperature ranges from 200-240°C. Main difference between them concerns the number of phases present during normal operation: HTFT reactor configuration foresees two phases (gas-solid), whereas LTFT application shows a liquid (i.e., wax) phase in between the gas and solid (catalyst) means [87] (see Figure 10).

The process has extensively been used in Germany during WWII, and later in South Africa, to convert coal and natural gas to liquid fuels. The only commercial coal to oil plants operating in the world today are based on Fischer-Tropsch technology at the Sasol plants in South Africa using bituminous coal [88], while at least 6 plants are currently operating from natural gas with capacities ranging from 430 $m^3/d$ to 22,250 $m^3/d$. Shell operates two in Malaysia and one in Qatar, Sasol operates one in South Africa, and the fifth is a joint venture between Sasol and Chevron in Qatar [89], plus a sixth plant in Nigeria, operated by Chevron (with Sasol technology) and a capacity of 5,280 $m^3/d$ of diesel and naphta.

Generally, larger scale plants are more economical. The Shell GTL (Gas to Liquid) plant in Malaysia produced liquid fuels at 1,990 $m^3/d$ (i.e., ~1000 $MW_{th}$ fuel input-natural gas), while a newer plant in Qatar has a capacity 6 times higher with 11,925 $m^3/d$ of liquid fuels production (~6000 $MW_{th}$ as fuel input-natural gas). A plant size of ~1000 $MW_{th}$ is typical and would require about 5 kt of dry biomass per day [90].

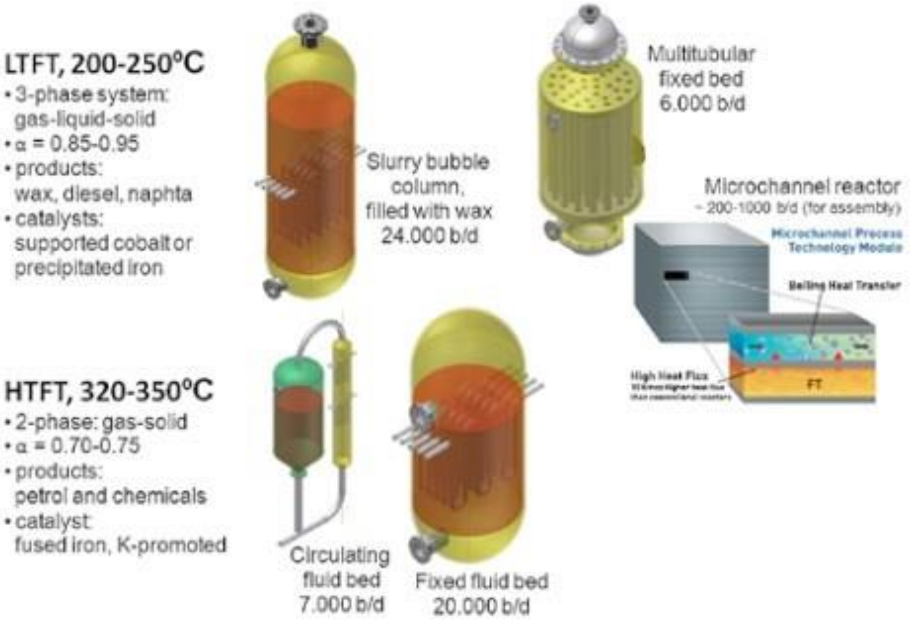

**Figure 10: Reactor types and characteristics for LTFT and HTFT processes [37]**

Fuels produced by FT synthesis were the first of their kind to receive certification as alternative fuels in aviation. A generic FT fuel certification was approved by ASTM as for up to 50% blending into conventional jet fuel in 2009 [58] for a fuel produced from coal, natural gas or biomass [91]. Descriptions of the synthesis of alternative jet fuel from FT-SPK pathway are available elsewhere [5,92].

The gasification-FT process can be broken down into four main process steps: (1) biomass feedstock pretreatment (particle size reduction, drying, leaching/washing); (2) gasification and gas cleanup; (3) FT-synthesis; and (4) upgrading to produce high-quality fuels. A conceptual representation of the process' PFD is reported in Figure 11.

Application of the process to biomass, however, is considered to require considerable further development, particularly regarding the handling of biomass feedstocks and syngas cleaning [5].

**Figure 11. Conceptual PFD of a FT-SPK process (adapted from [58])**

### 3.3.2 Feedstocks used in FT pathway

Carbon content is the essential requirement in terms of feedstock for the production of gas-derived fuels. Woody biomass has a 46%-53% average carbon content, while agricultural residues account for average 38%-58% carbon content.

Additionally, hydrogen presence in the feedstock allows increasing the efficiency of the process. The feedstocks for the FT process can be composed of any carbon materials. Thus, different types of biomass have different carbon contents that can affect jet fuel yield. A wide variety of woody biomass and agriculture waste feedstocks, which contain abundant carbon and hydrogen, can be used. Anyway, such different feedstock and related needed pretreatment steps could easily influence the economic results [37].

At European level, Adelung et al. [93] reported a Fischer-Tropsch kerosene production potential of around 8 EJ/y, using forest residues and municipal waste, with a conversion yieldof 0.363 $P_{LHV,Kerosene}/P_{LHV,Biomass}$. In other terms, it depicts a theoretical European kerosene production capacity based on such feedstocks for FT kerosene of 68.4 Mt/y.

### 3.3.3 FT plants and technology status

The technological maturity of the pathway is commercial when the feedstock is fossil (coal or natural gas), while to date no commercial facility processing biomass as feedstock has been reported in operation [90].

A list of planned installations based on FT-SPK pathway has been compiled from [5,91,94]. Fulcrum Bioenergy, Red Rock Biofuels, SG Preston, Kaidi, Sasol, Shell, Syntroleum have all commercialization proposals for the aforementioned pathway. However, just two industrial scale plants are expected to break ground between 2021 and 2022 worldwide.

The California-based biofuels producer Fulcrum Bioenergy is building a plant in Nevada with a capability to produce 33,000 t/y of RJF. It expects the expansion of the Sierra BioFuels waste-to-fuel plant in Nevada to be completed by 2021. Fulcrum has developed and demonstrated a proprietary thermochemical route that converts MSW into low-carbon renewable transportation fuels including jet fuel and diesel by means of gasification and FT-synthesis.

The Colorado-based company Red Rock Biofuels's first plant is expected to break ground in 2022 in Lakeview, OR (USA). This plant will convert approximately 166,000 dry tons of waste woody biomass into 16.1 million gallons/year of low-carbon, renewable jet and diesel fuels. The FT section of the process will be provided by Velocys. On October 8th, Red Rock and Shell have entered into a Cellulosic Fuel Purchase and Sale Agreement, in which Shell will purchase RJF and cellulosic renewable diesel fuel from Red Rock's new biorefinery [95].

### 3.3.4 Costs Estimates for FT route

Morgan et al. [90] reviewed the estimates of Tijmensen et al. [96], Hamelinck et al. [97], Swanson et al. [98] on biomass-to-liquids production based on gasification and FT-synthesis.

Tijmensen et al. [96] estimated the cost for a 367 $MW_{th}$ fuel input FT synthesis plant in 2002 to be in the range of USD280-450 million. Similar results were reported by Hamelinck et al. [97], who estimated the total capital investment cost of a similar scale plant (400 $MW_{th}$ fuel input) to be €286 million in 2004. Authors included a 25 bar oxygen-blown gasifier, a tar cracker, wet gas cleaning, and a solid bed FT reactor with 70% conversion in once-through conversion mode. In such a configuration, the overall efficiencies (energy in the liquid fuel productsdivided by the energy in the biomass fuel) for the best configuration were 40-45% on a higher heating value (HHV) basis. Production cost of FT liquids were estimated as 16 €/GJ or 0.65 €/L (0.57 USD/L in 2002).

Swanson et al. [98] compared the capital and production costs for two temperature scenarios, low temperature (LT) scenario and high temperature (HT) scenario, based on a gasification platform with a 2 kt/d corn stover feed rate. The gasifier selected in the LT scenario was an oxygen blown, low-temperature (870 °C), non-slagging, fluidized bed gasifier. The HT scenario is based on an oxygen blown, high-temperature (1 300 °C), slagging, entrained flow gasifier. The producer gas from the gasifier is used for FT synthesis, hydroprocessing, and electricity production in both scenarios. Authors reported that the total capital investment required for the

$n^{th}$ plant scenarios has been calculated as USD610 million for the HT scenario and USD500 million for the LT scenarios. The product value for the HT and LT scenarios are estimated to be USD4.30 and USD4.80 per GGE (1.46 USD/L and 1.62 USD/L), respectively, based on a feedstock cost of USD82 per dry ton.

More recently, Pavlenko et al. [55], largely drawing from previous literature and extending the results of the TEA performed by [99], provided and updated estimates of plant cost for 5 ASTM-approved RJF pathways, including FT-SPK. Authors pointed out that estimates for the capital expenditure on gasification vary widely, spanning between €339 million and €1,230 million for a project with a capacity of approximately 220 million liters per year, and reporting prior estimates, on average, gasification-FT capital costs were assessed in the range from €4 to €6 per liter of annual production capacity. As a result of their comparative assessment of 5 ASTM-certified pathways, Pavlenko et al [55] stated that the most cost-effective sources of carbon reductions come from the fuels produced via gasification using low-carbon feedstocks, such as MSW, energy crops, and agricultural residues. The levelized costs of these fuels range from €1.34 to €1.87 per liter (2018 costs), and their cost of carbon reductions ranges from €400 to €500 per ton of carbon. Relative to the carbon costs of fuel switching from other pathways, which either have negligible carbon savings or even higher levelized costs, these pathways provide the most cost-effective carbon reductions among those assessed.

### 3.3.5 Sustainability of FT process

O'Connel et al. [100] analysed and assessed the GHG emissions reduction potential of alternative fuels for aviation and providing insights on the energy efficiency of pathwaysrelevant for European biofuel production. As a result of their work, from a GHG reduction standpoint, the production of aviation fuels from lignocellulosic biomass has a much greater potential to provide reductions per MJ of final fuel than the vegetable oil pathways.

Wang et al. [37] reported that GHG emissions from the FT process as 92%-95% lower than those of conventional jet fuel. Such result is related to both the considered feedstock, woody biomass or forestry residues, which has a very low contribution to GHG emissions and also to the fact that half of the energy consumed for the conversion processes, either gasification or FT synthesis, comes from the biomass own energy content. In the same report, the FT-SPK production pathway is accounted for life-cycle GHG emissions of 9.0, 12.2, and -2.0 g$CO_2$eq/MJ respectively from the use of corn stover, forest residue, and switchgrass. Strategies and technologies such as carbon sequestration, co-production of fuels and power, co-processing of coal and biomass would help reducing GHG emissions from the FT process.

Pavlenko et al. [73] reported that the results of CORSIA's gasification-FT LCA, with direct emissions estimates of 5-12 g $CO_2$eq/MJ for FT diesel produced from biomass. Such results are in line with RED II default direct LCA GHG emission estimates, which range from 3 to 12 g$CO_2$eq/MJ [4]. Figure 12 reports the direct GHG emissions related to several possible feedstocks that could be used within FT-SPK pathway.

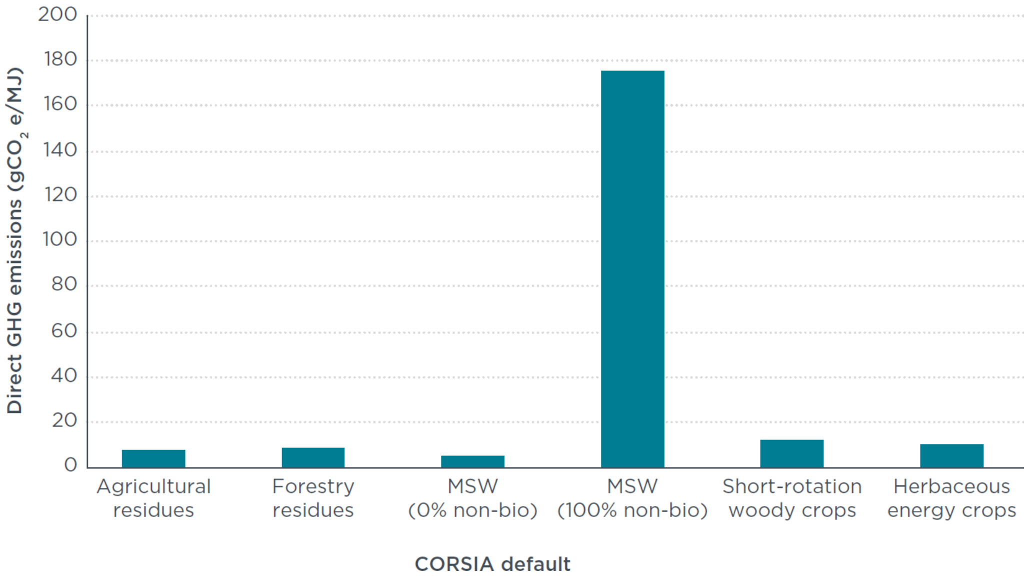

**Figure 12: ICAO CORSIA values for direct GHG emissions for the FT-SPK pathway [73]**

Pavlenko et al. [73] describes the gasification-FT pathway as one of the best-performing in terms of ILUC-related emission and overall WtW emissions. As reported in Figure 12, feedstocks with high carbon savings in this category include agricultural residues, forestry residues, and the biogenic fraction of MSW. By using such feedstocks, emissions are cut by 58%-140% compared to the petroleum baseline. MSW-derived fuels may have high indirect emissions savings due to avoided methane emissions at landfills.

Capaz et al. [74] reported similar life cycle emissions estimates, between 5 and 15 $gCO_2eq/MJ$, for jet fuels from corn stover, forest residue, and switchgrass, within the F-T pathway. Considering the effect of carbon sequestration, F-T fuels from switchgrass are projected to move to GHG emission levels of 22.0 $gCO_2eq/MJ$. F-T fuels from corn stover, are expected to move to 13.6 $gCO_2eq/MJ$, considering soil carbon change. Figure 13 highlightsthe attribution of GHG emission shares to the various life-cycle phases, such as feedstock production and harvesting, transportation and biomass conversion to jet fuel, for switchgrass and forest residues feedstocks.

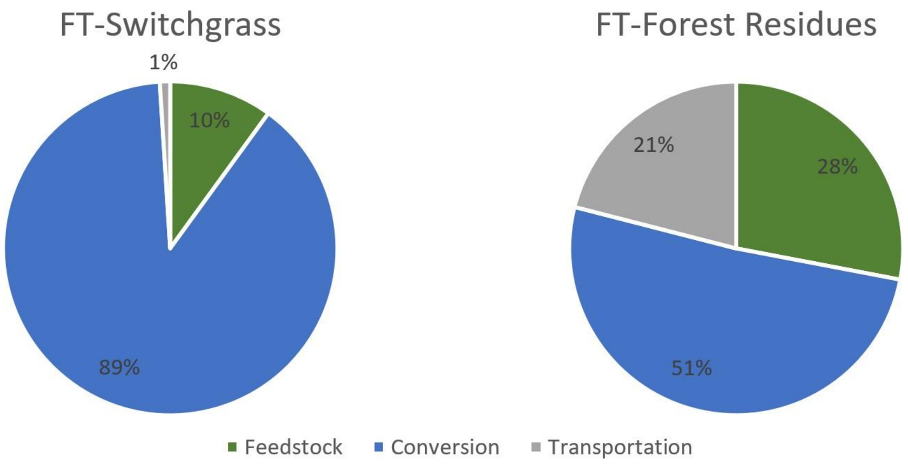

**Figure 13: Attribution of GHG emission to the various life-cycle phases (authors elaboration on [74])**

### 3.3.6 FT technology development potential

A major constraint and source of incertitude in developing large project based on gasification, at least at the scale required to attain favorable economics, lies in the unprecedented size of the gasification section, for which reliable capital cost estimates are simply not available.

Nonetheless, there is a generalized consensus in literature that the FT-SPK pathway offers remarkable advantages compared other ASTM-approved processes, which can be summarized as follows:

- Taking into account the feedstock base, the gasification and Fischer-Tropsch route of fuel production can be used to convert a range of low-cost agricultural residues, energy crops, and MSW.
- In terms of GHG reduction performance, Pavlenko et al. [55] calculated that, when compared to four HEFA value chains (from soy oil, palm oil, PFAD and UCO), all the three FT-SPK value chains analyzed (from municipal solid waste, agricultural residue, energy crop) exhibit lower direct emissions (6.3-14.8 vs 19.4-36.5 $gCO_2eq/MJ$), lower ILUC emissions (150-231 $gCO_2eq/MJ$ for HEFA), lower carbon intensities (6.3-14.8 vs 19.4-267.5) and superior GHG savings.

Landalv et al. [94] provided a list of other project in planning phase, which includes for the FT pathway the Bayou Fuels project (900 tons/day of dry wood input, 250m$^3$ FT fuel output plant developed by Velocys located in Natchez), Adams County, Mississippi (using the TRI gasification technology and Velocys FT system), the Ajos. Kaidi plant (full-scale demonstration plant, 800MW feedstock 670 tons/day FT liquids, in 2020 at the Ajos island, Kemi, Finland).

In terms of product slate composition, current FT technology results in a maximum of about 40% of the final product comprised of bio-jet fuel and middle distillates, requiring the marketingof the other 60% of the output [50].

Bauen et al. [13] reported a total planned gasification + FT potential capacity of more than 200 kt/y to become operational in the next years.

# 4 RFJ alternative production pathways with TRL below 6-7

## 4.1 Hydro-treated depolymerized cellulosic jet (HDCJ) pathway

Hydro-treated depolymerized cellulosic jet (HDCJ) technology encompasses conversion pathways based on pyrolysis, hydrothermal liquefaction (HTL), or hybrid process of both. All of them produce a bio-oil, also named bio-crude, which is usually subjected to an upgrading step via hydro-processing. This process is commonly developed through catalytic cracking (thermochemical processes), although other non-catalytic thermal processes have been suggested in order to prevent possible deactivation of catalyst by coke deposition [101,102]. Following, comprehensive study on each pathway, i.e., pyrolysis and HTL, is described.

### 4.1.1 Production of RFJ via pyrolysis

Fast pyrolysis route allows producing a bio-oil from lignocellulosic biomass, mainly based on woody residues, into inert atmosphere at temperature ranging 400-600 ºC. Bio-oil needs to be subjected to an upgrading step to produce RJF since its physic-chemical characteristics must be improved.

Non-catalytic (using two proprietary technologies: RTP® and BTG-BTL) and catalytic (by using VTT's technology) fast pyrolysis are commercially available (TRL 8). Catalytic pyrolysis bio-oils present higher carbon content and acid character and lower oxygen and water percentages, which implies a light upgrading step.

Bio-oil upgrading step is less developed than pyrolysis step, since its current status is at pilot level (TRL 4-5) because of mainly larger investment (between 3-5 times) compared to pyrolysis plant. Upgraded bio-oils present significant level of compliance with main ASTM7655 specifications, although further upgrading to remove residual oxygen is still necessary. MFSP for a n<sup>th</sup> plant of 0.74-0.78 €$_{2020}$/L is estimated with an emissions saving ranging 70-75%. Nevertheless, fast pyrolysis and upgrading maturity is not expected before 2027.

Co-processing blending in 5-15% bio-oil with VGO into FCC unit of existing refineries is a via alternative to upgrade bio-oil in order to limit equipment investment and operating cost. Trials at TRL 7 blending with VGO, either up to 5% of non-catalytic pyrolysis bio-oil or up to 15% of catalytic pyrolysis bio-oil, have proved to be able generating green biofuels with low or not investment. However, RJF production by co-processing is not suitable because of injection point of bio-oil into refinery. Nevertheless, 75-84% emissions saving are estimated.

Fast hydropyrolysis is the latest alternative to generate bio-oil, which has a demonstration level (TRL 7) with a patented technology available (IH$^2$ of Shell). Its scaling has been planned until commercial scale (1,000 tons per day of dry woody residues) by means of a project in Norway with a total investment of €350 million. IH$^2$ technology has an additional second step built in based on hydrotreatment that allows obtaining RJF based on cycloparaffinic kerosene with 0% of aromatic content (CPK-0) in 35-40% ranging, which is into phase 2 of ASTM D4054 approval process for blending up to 50%. CPK-0 has estimated a MFSP of 1.04 €$_{2020}$/L for a nth plant and an emissions saving range of between the 68% and the 89% as a function of $H_2$ source used.

### 4.1.1.1 Pyrolysis process description

Pyrolysis technology is the thermal decomposition of organic matter contained into biomass in oxygen-free environment at moderate-high temperature, which usually varies between 400 to 600ºC. When talking about the process or steps to be performed (not specifically about technology terms), it is sometimes also known or associated to devolatilization mechanism of biomass, since this is the primary chemical reaction being precursor for gasification and combustion processes. Therefore, it is important to see the difference between both concepts in order to clarify from the beginning that pyrolysis process will be always here referred like a technology that promotes drop-in biofuel development (bio-jet in this case) from biomass. Pyrolysis produces: (1) bio-oil, which is a freely flowing organic liquid made up of the condensable vapors formed; (2) bio-char, which is a carbonaceous residue with different properties; and (3) gas stream containing mainly methane, hydrogen, carbon monoxide and carbon dioxide. One essential aspect to take into account in pyrolysis is related to moisture content of the feedstock, which needs to be 10% as a maximum [104]. This limit is related to maximizing bio-oil yield and minimizes both water and oxygen contents in bio-oil. Therefore, feedstock is usually subject to drying step as pre-treatment measurement.

Three types of pyrolysis processes can be categorized: (1) slow pyrolysis that can run for several hours, which is more focusing to maximize bio-char yield; (2) fast pyrolysis taking seconds with quick both heating and cooling rates, where bio-oil is the main product; and (3) catalytic pyrolysis defining as a fast pyrolysis in presence of a catalyst for minimizing oxygen content in bio-oil. Slow pyrolysis is evidently out of this assessment since it is not applied to produce bio-oil as precursor of bio-jet fuel.

Both fast and catalytic pyrolysis can be jointly explained since both demand the same requirements for the thermal decomposition of feedstock. This starts at 350-450 ºC and its promotion is due to break of the long carbon chains bonded with hydrogen and oxygen of the compounds in biomass. With this in mind and thinking about RJF production, it is desirable a soft chemical breakdown of polymeric chains to maximize condensable vapors in order to increase bio-oil yield, since further cracking brings increasing non-condensable compounds leaving from reactor as gas. This is the purpose or fundament of fast pyrolysis, by which is most widely being used [104,105]. Thus, bio-oil yield as high as 75% (regarding feedstock in dry basis) could be achieved after pyrolysis of wood biomass running a few seconds (usually less than 2 s) at 500-600 ºC [50]. Biomass is usually subjected a milling-based pre-treatmentto obtain fine particles of about 3 mm. This allows high heat transfer to be achieved, which maximizes vaporization (devolatilization) promoting an increase on bio-oil yield. It must be highlighted that besides of kinetic reactions both heat and mass transfers and transition phenomena play an important role because of very short residence time of biomass.

Fast pyrolysis bio-oil needs an upgrading step to remove mainly the moisture and oxygen content, since these compounds are still presented into bio-oil in high ranges (i.e., moisture: 15-30%; and oxygen: 28-40%) [105,106]. In addition, its physical properties, such as high viscosity, high non-homogeneous character or high corrosively factor, do not make this material suitable to be used untreated (without upgrading). The disposal of high water and oxygen quantities in order to guarantee a suitable quality implies higher costs into a second step, which is commonly known as upgrading. There are several upgrading techniques, although those based on catalysts use and concreting hydrodeoxygenation (HDO) (i.e., catalyst + hydrogen) seems the most favorable [104]. Mono- and bi-metallic catalysts based on Ni, Cu, Mo, Pt, Co and W, and supported on $SiO_2$ and $Al_2O_3$, are being most used, sinceare able to achieve HDO degree as high as 99%. Despite their high performance, it must be also evaluated roles such as the expensive price of these metals and their tendency toinactivation by poisoning. Nevertheless and taking into account that using one catalyst improves the final biofuel characteristics, and with target of further soften upgrading post- treatment, catalytic pyrolysis has also been widely developed. This can be divided into *in-situ* and *ex-situ* catalytic pyrolysis depending if pyrolysis is run in one or two steps, obtaining a bio- oil with different final properties [107]. Nevertheless, similar liquid (i.e., organics + produced water), gas and solids residue yields are obtained for both approaches, which are different to those from non-catalytic fast pyrolysis. Thus, lower liquid yield and higher gas and coke generation may be observed when using a catalyst compared to a non-catalytic route [108]. Figure 14 shows a proposal full layout of a plant to obtain drop-in biofuels from both non- catalytic and catalytic fast pyrolysis.

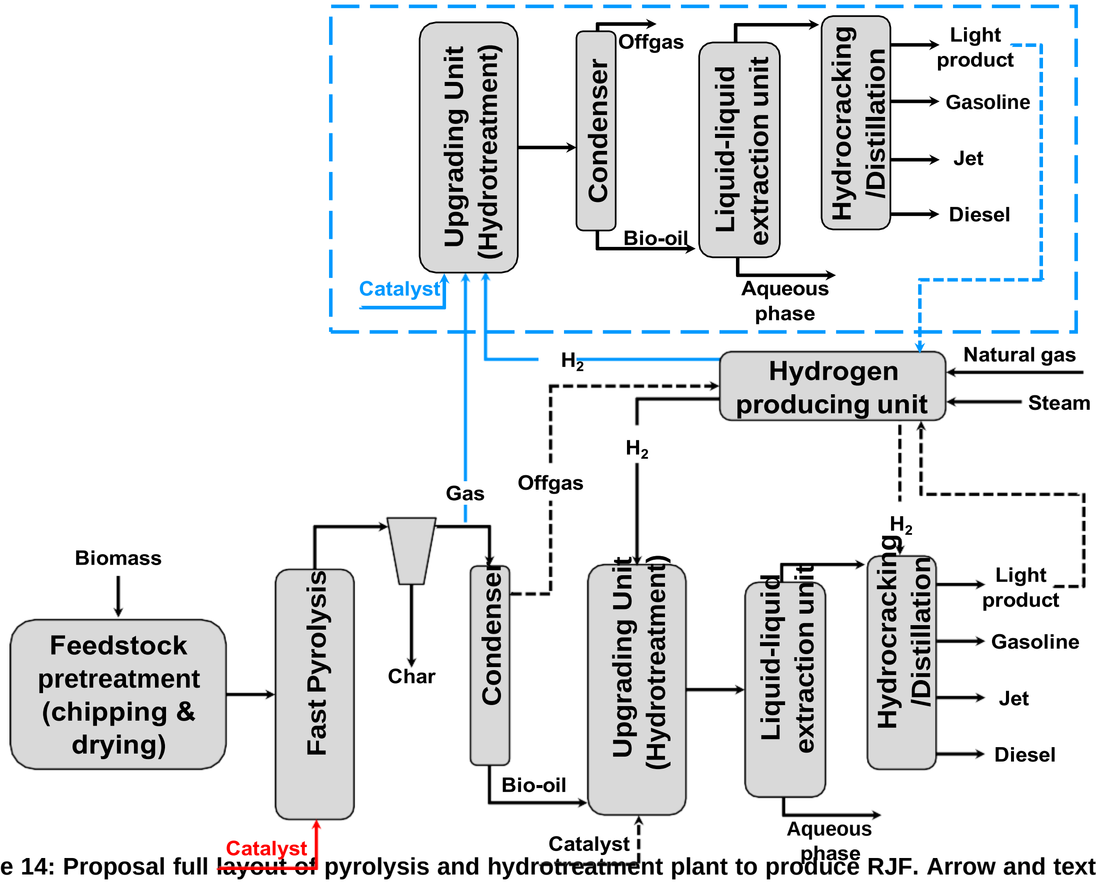

**Figure 14: Proposal full layout of pyrolysis and hydrotreatment plant to produce RJF. Arrow and text in red corresponding to in-situ catalytic fast pyrolysis mode, while all into blue box corresponding ex-situ catalytic fast pyrolysis mode. Dashed lines denote possibility actions**

*Ex-situ* catalytic pyrolysis is carried out into two steps: first a conventional fast pyrolysis (i.e., un-catalyzed), followed by catalytic post-treatment of pyrolysis vapors obtained before condensation forming bio-oil takes place. This allows deoxygenation of vapors to be occurred, producing similar amount of aromatics (such as BTX: benzene, toluene and xylene) and olefins (such as C2-C6: ethylene, propene and butene) as main components into bio-oil [109]. This version allows developing first pyrolysis step at lower temperature and obtaining a bio-oil with lower oxygen content (as less as 4%) at the same time. Cheaper zeolite-based catalysts than HDO catalysts are usually used, and the major advantage is that some polymerization and gum formation into bio-oil obtained are avoided. This allows both high viscosity and instability to be reduced. *In-situ* catalytic pyrolysis lies in catalyst use with feedstock at lower temperature (i.e., $^{<}$ 500 ºC) than conventional fast pyrolysis. A sand bed-based pyrolyzer designed mainly as fluidized bed or rotating cone is usually being used, since allows acting as both heating medium and catalyst integrating [105]. This second approach increases up to five times the amount of aromatic-based compounds in exchange for olefins, as opposed to *ex-situ* catalytic pyrolysis where higher aromatics are slightly obtained [109]. It is believed that differences in gas flow and heat transfer between both approaches are responsible for it. On the one hand, conventional civil jet fuel is formed by C9-C14 chains, being mainly paraffins (around 70 wt.%) but also naphthalene- and aromatic-based compounds (around 15 wt.% of each); and on the other hand, most of bio-jet fuels obtained from already certified pathwaysare mainly based on paraffins [110]. In any case, minimum or residual amount of olefins are present into jet fuel, either petroleum-based or bio-based. Therefore, it seems, a priori, *in-situ* catalytic pyrolysis is better option to produce more suitable biofuels as precursor of bio-jet. However, re-polymerization of furanic compounds during *in-situ* catalytic pyrolysis must be extremely controlled since promotes forming a higher amount of char instead of olefins [109,111]. This could entail both decreasing of bio-oil yield and inactivating of catalyst by coke deposition, which reduces performance and raises costs.

Recently, a last approach on pyrolysis of biomass to biofuels called *fast hydropyrolysis* is being researched and developed [105]. It could be considered as a mixture of fast catalytic pyrolysis and HDO-based upgrading post-treatment, since a hydrogen flow is fed to pyrolyzer. Several configurations, either by usage or not of catalyst into pyrolyzer, either by using or not of ex-situ catalytic hydrotreatment unit, have been studied. Fast hydropyrolysis generates higher bio-oil yield than catalytic fast pyrolysis with lower tendency to inactivation of catalyst due to hydrogen presence. Aromatics compounds are mainly obtained through fasthydropyrolysis, although paraffins, such as alkanes and cycloalkanes, could be also generatedby passing pyrolysis vapors exhaust through catalytic *ex-situ* upgrading unit. Moreover, this approach reports bio-fuel with oxygen content as less as 0.5%, which entails a key advantage [112]. Nevertheless, the use of continuously hydrogen flow opens a debate on viability of hydropyrolysis regarding the obtaining source and final costs in comparison with other biofuels conversion routes.

Regardless of pyrolysis approach selected, feedstock type (i.e., biomass) , the amount of their compounds, and pyrolysis system design, as pyrolyzer configuration as upgrading post-treatment type, have also a high influence on both yield and characteristic of, first the bio-oil, and then the biofuel. Both facts will be addressed below into next sections of the deliverable.

#### 4.1.1.2 Feedstocks used in pyrolysis

Lignocellulosic biomass is ideally the most appropriated feedstock to be used in pyrolysis process for biofuel production. Three main types of feedstock have traditionally been used [105]: (1) wood, such as softwood, hardwood and wastes from wood industries; (2) agricultural wastes; and (3) energy crops, such as sorghum and many varieties of grasses. Among them, wastes from sawmill industry and forestry management have been used as feedstock indemonstration and commercial pyrolysis plants [113]. However, although it is estimated an increase on their availability by 2030 [12], there may not be enough amounts for all uses or operating cost (regarding its current commercial exploitation) is expensive. Moreover, a strong use into pyrolysis process could become a competitive issue for power and energy sectors, since they use mainly wastes from wood and pulp industries as biofuel [11]. Therefore, a wide range of different wastes are currently being checked in pyrolysis route as alternative their management through combustion in incinerator plants. Between them, MSW (either foodwaste or paper and textile wastes), end-of-life tires, and plastic wastes, either isolated polymers or mixture of plastics, can be highlighted [114]. Furthermore, several industrial residues, such as sludge, both from sewage and paper factories, manure and digestate could be also used as feedstock into catalytic pyrolysis process [115].

It is clear that using wastes, such as MSW and sludge, as feedstock is in line with sustainability and circularity concepts, besides being cheaper materials than forest and wood industry wastes [50]. In turn, this would aid investment to be reduced compared to current costs, which would decrease the MFSP of the biofuel. However, less maturity of pyrolysis process using these feedstocks could be an obstacle in order to produce a quality bio-crude. Furthermore, other limiting aspects, such as geographical availability or transport costs from origin sources, could become key factors to define the best feedstock to be used.

A last consideration to take into account is related to technical factors which can influence the effectiveness and performance of process, thus positively or negative. It should be highlighted that this would be particularly important when catalytic fast pyrolysis of non-wood wastes is running, since this is the one that gives the better performance. On the one hand, waste-based biomass from lignin or highly rich in lignin are preferred, since they will provide better bio-oil qualities owing to their lower oxygen content compared to biomasses with high content of cellulose and lignocellulose. Moreover, the presence of aromatic remain in lignin encourages phenolic intermediates production, which can be transformed to aromatic hydrocarbons under suitable catalyst presence. On the other hand, biomass wastes with high ash content, such as agricultural residues, are not desirable because of potential appearance of several associated issues. Among them, the catalytic cracking of the condensable vapors, the deactivation of catalyst and the increase of undesirable acids compounds can be highlighted [107].

#### 4.1.1.3 Pyrolysis plants and technology status

A correct assessment of the status or development level of pyrolysis technology to produce drop-in biofuels requires an analysis from one side of the pyrolysis step and from the subsequent upgrading, since both have different maturity level.

Pyrolysis technology has already achieved commercial status, with different units which produce a variety of biofuels at TRL 8-9 [113]. Table 4 collects both demonstration and commercial pyrolysis plants with a feeding rate higher than 1 tons per day (t/d). Most of them are operating under non-catalytic fast pyrolysis conditions except the VTT's technology plant that run a catalytic fast pyrolysis and IH$^2$ plant of Shell, which is based on hydropyrolysis and hydroconversion processes. This last plant is made up two units: (1) one first, where the biomass is introduced into fluidized bed of catalyst under hydrogen pressure of 2-3.5 MPa at 350-460 ºC, and (2) a second one with a hydroconversion reactor where free vapor phase of char from first step is processed to obtain a deoxygenated drop-in fuel [116,117]. Most of demonstration and commercial pyrolysis plants are designed as fluidized beds although BTG- BTL technology is based on a rotating cone pyrolyzer and the Biogas Energy project is based on ablative fast pyrolysis [118].

At commercial scale, the 3 technological processes developed (i.e., RTP®, BTG-BTL, and VTT) use woody residues, either from forest or sawmill industry as feedstock, and bio-oils produced are allocated for co-processing in conventional refinery. Thus, bio-oil from RTP®- based plants is used for co-processing in conventional refineries and as feedstock for food industry [119]. Only 5% of bio-crude has been co-processed with Vacuum Gas Oil (VGO) in the FCC unit for producing green diesel and gasoline [120]. Bio-oil from BTG technology has been also blended (up to 10%) with VGO for co-processing into FCC unit of a conventional refinery in order to produce somewhat greener fuels [121]. Bio-oil from VTT plant is also allocated for co-processing since has similar characteristics than BTG´s bio-oil [122]. In addition, this VTT concept plant allows producing electricity and heat by integrating fast pyrolysis plant to existing industrial or district heating combined heat and power plants, just asit takes place with the Joensuu power plant [123].

The maturity of bio-oil upgrading process to drop-in biofuels is still inadequate with a low development level since operations are running at small scale with pilot prototypes (TRL 4-5) [124]. This is essentially due to limited knowledge of continuous operating the process for upgrading a bio-oil because of its complex qualities. Thus, there are still several challenges to reach, such as the stabilization of the bio-oil changing properties (by its tendency to polymerize and to raise viscosity and acidity), or the catalyst deactivation because of the presence of water and oxygenated compounds. Although most units are developing upgrading tests at laboratory level with different results [104], two main upgrading pilot plants must be highlighted placing at CanmetENERGY in Ottawa (CE-O) and at Pacific Northwest National Laboratory (PNNL) in Richland Washington. Although both prototypes develop catalytic hydroprocessing, the CE-O facility design is based on one-stage bubble column reactor feeding bio-oil with petroleum distillates as reaction medium, while PNNL plant approach is based on continuous down-flow packed-bed reactor [125]. Therefore, the main difference isthat the CE-O plant feeds 18% of bio-oil bended with fuel oil as strategy to suppress undesirable solids formation into reactor caused by pyrolysis oil polymerization. This implies two different hydroprocessing approaches: dedicated hydrotreatment at PNNL and co- processed hydrotreatment at CE-O [126]. Different trial tests using bio-oils from both non- catalytic pyrolysis (from BTG and RTP plants) and catalytic fast pyrolysis (from VTT plant) were carried out [125,127]. Several conclusions were obtained: (1) biofuels obtained aremainly consistent with petroleum gasoline, being suitable their use as gasoline without blending because of the meeting many of the ASTM gasoline specifications; (2) better performance of the upgraded product starting from bio-oils obtaining by catalytic pyrolysis for use as RJF; (3) it is recommended blending the portion of distillate product into fuel range with fossil-based jet or other RJF from FT and HEFA pathways. In this sense, biofuel from non- catalytic bio-oil pyrolysis fulfill more ASTM D7566 specifications, being still high density and aromatic content.

**Table 4: Demonstration and commercial pyrolysis plants [113]**

| Process/Plant | Technical provider | Developer | Country | Feedstock | Reactor type | Throughput (ML/y) | TRL | Products | State | Capital investment |
|---|---|---|---|---|---|---|---|---|---|---|
| Demonstration plants | | | | | | | | | | |
| na(1) | ABRI-tech Inc. | Pyrobiom Energies Inc. | Canada | Wood residues (50 t/d) | Auger | 6 | 6 | na | Active | CaD7M |
| na | Shanxi Yingjliang-Shanghai Jiao Tong Univ. | Shanxi Yingjliang-Shanghai Jiao Tong Univ. | China | Rice husks (1-3t/d) | CFB | 2-6 | 6-7 | na | Active | na |
| na | Univ. Sci. Tech. China | Univ. Sci. Tech. China | China | Wood and agricultural wastes (15t/d) | CFB | 2 | 6 | na | Active | na |
| IH² | GTI-CRI | Shell | India | Forestry, agricultural and urban waste (5t/d) | FB | 0.5 | 6-7 | Jet & diesel | Commissioned 2019 | na |
| na | MASH Energy (spin-off from Tech. Univ. Denmark) | MASH Energy | India | Sewage sludge (na) | na | na | 7 | na | na | na |
| na | Bioenergy Concept and ELP group | Biogas Energy | USA | Demolition wood, forestry and agricultural wastes (500kg/h) | Ablative | 1.3 | 6-7 | na | Commissioned Q2-2020 | na |
| Commercial plants | | | | | | | | | | |
| RTP® | Evergent | Ensyn & Suzano | Brazil | Eucalyptus forest residue (2.3Mt/y) | CFB | 83 | 8 | na | Under development | USD77M |
| RTP® | Evergent | Ensyn & Albec Forest Product & Groupe Remabec | Canada | Sawmill (65kt³/y) | CFB | 38 | 8-9 | na | Active | USD78M |
| RTP® | Evergent | Kerry Group (Ensyn) | Canada | Mill and forest residues (na) | CFB | 11 | 9 | Fuel-oil (co-processing) | Active | CaD4M (refiting) |
| na | VTT/Valmet | Fortum, Valmet | Finland | Forest residues and sawdust (50kt/y) | VTT-FB riser | 43 | 8 | Co-processing | Active | €38M |
| BTG-BTL | BTG BioLiquids | Green Fuel Nordic OY | Finland | Sawdust and mill residues (na) | Rotating cone | 20 | 8 | na | Q4-2020 | €25M |
| BTG-BTL | BTG BioLiquids | Twence Univ. | The Netherlands | Wood residues (120t/d) | Rotating cone | 20 | 8 | Biofuel for producing steam | Active | €19M |
| BTG-BTL | TechnipFMC and BRG | Pyrocell AB | Sweden | Sawdust (25kt/y) | Rotating cone | 21 | 8 | Co-processing (5-15% HVO) | Q4-2021 | €12M |
| RTP® | Evergent | Ensyn and Renova Capital | USA | Mill forest residues (na) | CFB | 76 | 8 | Co-processing and heating & cooling | na | USD70M |
| RTP® | Evergent | Kerry Group | USA | Wood resid.(30-40t/d) | CFB | 9 (5 facilities) | 9 | Chemicals for food industry | Active | na |

(1)na: not available

Conclusions on suitability of these biofuels for use as RJF, together with the high capital costs of the upgrading process units is promoting the idea to develop upgrading step through co-processing in conventional refinery for targeting lower bio-oil price in the short-term [128]. This option is already being carried out at demonstration scale (TRL 7) under real conditions, feeding up to 10% of bio-oils from pyrolysis with VGO into FCC prototype plant [127,129]. This way for upgrading bio-crudes has a carbon conversion into liquid products of around 30%, but requires further research mainly because bio-oil characteristics promote catalyst deactivation. Nevertheless, synergies by co-processing bio-oil and VGO regarding coke formation have been found. Thus, preventing of coke appearance was seen at laboratory scale by bio-oil blending at 20% [130], just as by mixing bio-oil/VGO by 5/95% at pilot scale [129]. In last pilot plant, an increase of bio-oil percentage blended up to 10% drove to obtain similar coke formation compared to test using only VGO. This fact may be due to oxygen amount into bio- oil. Bio-oil used at laboratory scale had an oxygen content of 39% [130], while bio-oil used at pilot scale was formed by 50% of oxygen. Therefore, it seems that a lower oxygen amount into bio-oil would allow its co-processing at higher blend percentages (i.e., 15-20%). Thus, the co- processed of a bio-oil from catalytic pyrolysis with oxygen content of 22% blending up to in 15% with VGO promoted a slightly reduction in coke formation without observing decrease on gasoline and naphtha yields, which if was seen when blending in 20% bio-oil [131,132]. Therefore, it seems that co-processing in 5-15% range bio-oil with VGO into FCC unit of an existing refinery is highly profitable, being oxygen content of raw bio-oil which defines the percentage of bio-oil to blend.

A last option of upgrading approach can be adopted through hydropyrolysis process, just as Shell is developing at demonstration scale by using $IH^2$ catalytic fast pyrolysis technology. This produces specific fuels, either diesel or jet depending on operation mode, instead of a bio-oil for co-processing [117]. This change compared to bio-oil use from commercial scale is due to the type of pyrolysis configuration, since both the *in-situ* catalytic pyrolysis process and the hydrogen promote a deoxygenated bio-oil with oxygen content lower than 0.7% [133,134]. Ranging 35-40% jet yield according to boiling point distribution could be obtained when operating under jet mode. The RJF is based on cycloparaffinic kerosene (CPK), and is named CPK-0, being 0 the percentage of aromatic content. This RJF is currently in ASTM D4054 approval process, specifically into phase 2: research report reviewed, ready for ASTM ballot. ASTM certification for a 50%blend limit with conventional jet fuel has been proposed [117].

#### 4.1.1.4 Cost estimates for pyrolysis pathway

Direct investment costs to start up one fast pyrolysis plant at commercial scale seem very changeable according to pyrolysis technology; see Table 4. Thus RTP® technology needs between 3-4 times more investment (USD70-78 million) than BTG-BTL technology (~ €20 million), and the twice compared to VTT technology (€38 million). No information was found for isolated fast hydropyrolysis, for example by using $IH^2$ technology. These investment figures given are only for pyrolysis plant, since they would increase when including the needed hydrotreatment step of the bio-oil in order to complete the drop-in biofuel process. Thus, for facilities converting 2,000 ton per day (dry basis) of biomass into biofuels, estimated total capital investment for fast pyrolysis are estimated in a highly vary range of €$_{2020}$[3]160-280 million [135,136]. These figures are depending essentially of import/export of electricity and of the both natural gas and $H_2$ sources for the upgrading process since feedstock costs are almost similar ranging €$_{2020}$65-100 per dry ton [136,116] in the case of use mill and forest residues. For fast catalytic pyrolysis, estimated costs investment are about €$_{2020}$365 million,and around €$_{2020}$210 million is the estimated investment in the case of hydropyrolysis process [135,136]. It should be noted that all these figures are theoretical and for an nth plant, which cannot be agreed with current reality. In this sense, for example for hydropyrolysis ($IH^2$

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[3] €$_{2020}$ calculated as follows: €$_{2020}$ by converting first the USD$_{2011}$ values found by using the factor 1 €$_{2011}$/1.4 USD$_{2011}$, and after by applying the factor 1.12 €$_{2020}$/1 €$_{2011}$.

technology), a project building a plant with capacity of processing 1,000 tons per day of dry woody residues has an investment of €350 million, which is higher than calculated converting the half of feedstock [137].

Fast pyrolysis and hydrotreatment route for drop-in fuels has an estimated minimum fuel selling price (MFSP) for a nth plant, including CAPEX and OPEX in ranging 0.74-0.78 €$_{2020}$/L [137,138], which is estimated to increase up to 1.04 €$_{2020}$/L in the case of catalytic fastpyrolysis [139]. These values are slightly lower than MFSP for HEFA or FT pathways, which can be estimated in ranging 0.88-1.15 €$_{2020}$/L [3,6,50,55,138]. It should be remembered that a range of 0.45-0.50 €$_{2020}$/L is the MFSP for fossil-based kerosene, which means that bio-jet from pyrolysis would cost less of the twice. Despite this difference could be further reduced when increasing CO$_2$ price into emission rights market from 2025 [20], it should be also taken into account that the high capital investment costs could burden to achieve the full maturity of the pyrolysis and upgrading route against others RJF conversion pathways. In this sense, upgrading of bio-oil through co-processing into conventional refinery could decrease the capital investment.

Saving costs by co-processing of bio-oil still brings some uncertainties related to refinery performance, such as catalyst deactivation, removal of nitrogen and content of both fenols and aromatics in the biofuel. In addition, the refinery configuration can vary, which would affect the calculation of co-processing cost of a bio-oil from biomass. Nevertheless, development level of co-processing of bio-oil from pyrolysis in conventional refinery is the highest between all biomass conversion pathways producing bio-oils, being at pilot scale (TRL 6-7) but simulating real conditions. Furthermore, bio-oil from fast pyrolysis co-processed (up to 15%) into FCCunit has lowest production cost compared to other bio-oil co-processing pathways [128]. However, co-processing of bio-oil has overall conversion efficiency from feedstock to hydrocarbon of around 30%, which is lower than standalone upgrading step (56%) [140]. This means biofuel production cost per energy unit (e.g., €/GJ) could match between the co-processing and upgrading step pathways. Furthermore, bio-oil origin (either non-catalytic or catalytic pyrolysis) and blending percentage can also affect to economic feasibility because of this value indicates the volume of the modification into refinery. Thus, for non-catalytic pyrolysis bio-oil, it seems blending in 5% of this is always economically positive while increasing the percentage in blend up to 10% would be only feasible with progress in industry and technology [132]. No economic data were found in the case of catalytic pyrolysis bio-oil, although could be expected that monetary positivity was maintained at blending percentages higher than 5% because better characteristics of raw bio-oil. Therefore, co-processing of low bio-oil percentages (as minimum as 5%) as upgrading option of pyrolysis bio-oil should be highly taken into considered in near-term, since would aid to minimize the investment of bio-oil upgrading step.

#### 4.1.1.5 Sustainability of pyrolysis process

Sustainability of fast pyrolysis process of forest residues depends if bio-oil production is done via catalytic or not, and subsequently it is also influenced of the upgrading system. Thus, bio- oil production via non-catalytic pyrolysis has much lower associated emissions (8.2 gCO$_2$eq/MJ) compared to *in situ* catalytic pyrolysis (18.7 gCO$_2$eq/MJ) [125]. This is due to catalytic pyrolysis implies higher emissions associated to the higher feedstock amount to be use because of lower bio-oil yield is obtained compared to non-catalytic route. These figures evidently increase during subsequent upgrading step rising up to the 22.5 gCO$_2$eq/MJ for a non-catalytic pyrolysis bio-oil and the 37 gCO$_2$eq/MJ when the bio-oil comes from catalytic pyrolysis. This fact implies that using non-catalytic pyrolysis savings by 75% on GHG emissions compared to lower emissions reduction potential of the catalytic pyrolysis route (58%). It should be noted that reduction values are always in comparison with the emissions from fossil kerosene. However, the differences on associated emissions found between a bio- oil from non-catalytic or catalytic pyrolysis must be further discussed since type of catalytic pyrolysis approach (either *in-situ* or *ex-situ*) affects GHG emission value. Thus, *in-situ* catalytic pyrolysis entails lower emissions (23-26 $gCO_2eq/MJ$) than *ex-situ* catalytic route (40-63 $gCO_2eq/MJ$), which implies emissions saving percentages of the 68-72% and the 23-51%, respectively [38]. This difference is essentially due to associated emissions for the use of $H_2$, since the *ex-situ* option entails more consumption of this gas for upgrading step. Therefore, it seems that non-catalytic pyrolysis and in-situ catalytic pyrolysis pathways have lower and similar emissions reduction potential (70-75%), while ex-situ catalytic pyrolysis process is able only to prevent about 50% of GHG emissions in comparison with those emitted by fossil kerosene. Regarding other RJF pathways already mature, it should be noted that the first cases have slightly lower associated emissions compared to HEFA process of UCO (28 $gCO_2eq/MJ$), while ex-situ catalytic pyrolysis pathway associated emissions are placed between previous and HEFA route of Camelina (46 $gCO_2eq/MJ$) or Jatropha (54 $gCO_2eq/MJ$) [38].

Regarding sustainability of co-processing bio-oil as upgrading option, there were found differences when 10% of bio-oil from either non-catalytic pyrolysis or catalytic pyrolysis was blended. Thus, $CO_2$ emissions were reduced by 84% when co-processing non-catalytic pyrolysis bio-oil, while $CO_2$ emissions decreased by 75% by using a catalytic pyrolysis bio-oil [128]. These figures were estimated through an LCA, but are agreed with data from Honeywell Company (Envergent technology), which reported emissions reduction by ranging 79-80% during green gasoline and diesel production when co-processing 5% bio-oil from RTP® plant (non-catalytic pyrolysis) with VGO [120]. Therefore, as a summary, emissions savings from bio-oil co-processing are at least equal or better than those avoided emissions by using upgrading step (i.e., 70 and 75% for in-situ catalytic pyrolysis and non-catalytic pyrolysis, respectively). This shows bio-oil co-processing is a recommended option from sustainable point of view compared to bio-oil upgrading.

Finally, sustainability of fast hydropyrolysis is evaluated through $IH^2$ process data. $IH^2$ pyrolysis technology has associated emissions between 10 and 29 $gCO_2eq/MJ$, which entail emissions reduction percentages ranging 68-89% compared to fossil fuels [116]. The variability of this range is due to $H_2$ source used, since several options were explored within the emissions study developed. Thus, the best values found, i.e., 10 $gCO_2eq/MJ$, corresponding to emission reduction by 89%, was achieved by considering that $H_2$ is produced from C1-C3 stream made in the distillation process; see Figure 14. Therefore, fast hydropyrolysis a priori would allow obtaining largest percentage of emissions reduction within all pyrolysis and upgrading options from forest and wood industry residues.

#### 4.1.1.6 Pyrolysis technology development potential

At near-medium term, pyrolysis technology development potential is related with the upgrading step development potential, since fast pyrolysis process is already available at commercial scale. The way to upgrade bio-oil will be key to achieve a drop-in renewable jet fuel from woody biomass. Two bio-oil upgrading approach is competing: catalytic hydroprocessing into second past and co-processing. First option implies strong investment in a new installation while the second entails the use of existing refineries by applying modification with capital and operating cost reduction. This last approach feeding 5% bio-oil in blending with VGO into a FCC unit seems to be currently winning on upgrading option of 100% bio-oil because due to essentially three reasons [106]: (1) low-expenditure adjustments to reactors, catalysts and associated processes; (2) much smaller production scale (about 30 times) of commercial pyrolysis plants compared to typically processing scale of hydrotreating and hydrocracking units into refineries; (3) FCC unit is much more tolerant to process bio-oils rich in oxygen than higher sensitive hydrotreater. Nevertheless, co-processing bio-oil into FCC unit in existing refineries promotes the production of gasoline and marine fuels. To generate RJF is recommended using the hydroprocessing units inside refinery, which demands highly deoxygenated pyrolysis bio-oils ($O_2$: <20%) and at lower blending percentage (ranging 3-5%). These can only come from either catalytic pyrolysis or hydrodeoxygenated oils (HDO).

However, bio-oils co-processing with lower oxygen content can be more advantage into FCC units since $H_2$ use would be not necessary [106]. Therefore, it seems that co-processing bio- oils is associated to feed them inside FCC unit, which drives to not obtain RJF. This fact implies pyrolysis technology development potential to produce drop-in renewable jet fuel can only come from subjecting bio-oil to upgrading step by catalytic hydrotreatment, or produces HDOs through hydropyrolysis, for example by $IH^2$ technology. This could delay the contributionof pyrolysis technology inside RJF mix in the short-medium term.

The growth of pyrolysis and upgrading route is estimated to start by 2022 reaching full maturity not before 2026-2027, where is expected to achieve a share of 12-18% into biofuels capacity production [20,141]. Regarding the weight of the bio-jet from pyrolysis and upgrading into EU global RJF production by 2030, it is estimated to be needed 0.3 Mt representing almost 5% of share within mix of advanced jet fuels [142].

In the short term, only one pyrolysis facility at commercial scale (TRL 8) is planned to be built in Norway by 2022 [143]. This plant is designed to feed 1,000 tons per day (in dry basis) of forest residues and by-products from sawmill industry to produce 100kt/y of bio-oil, which can be refined, blended and distributed as green fuel. In this sense, it has never been commented the possibility to produce RJF, although as pyrolysis technology selected is Shell's $IH^2$ (i.e., hydropyrolysis and hydroconversion) [144], this can obtain CPK in an estimated 35-40%ranging by operating under jet mode [117]. It should be remembered that this RJF is into phase 2 of ASTM D4054 approval process for blending up to 50% [117]. Total investment of this project is estimated at about €350 million, which will come from shareholders, of which about €3 million has been received from Norwegian Government for the preliminary biorefinery design study. This brings to light the importance of institutional support to start a project to produce biofuels. It should be highlighted that the preliminary project is scheduled to be completed in 2021 [137].

### 4.1.2 Production of RFJ via HTL

HTL is a thermochemical conversion pathway to transform lignocellulosic feedstock into bio-oil formed by large-chain hydrocarbons comparable with crude oil. Organic compounds of feedstock are degraded because of operating conditions: moderate temperatures (250-450 ºC), high pressure (10-30 MPa), and wet environment. Besides, catalysts are commonly used in order to improve both yield and bio-oil characteristics. Nevertheless, it is essential to develop a second upgrading bio-fuel step based on, either hydrotreating, catalytic cracking or combination of both, in order to be it mainly deoxygenated. Finally, a distillation step will end drop-in obtaining renewable jet fuel and other biofuels. Currently, bio-crude production throughHTL is at TRL 5-7 (demonstration scale has already been achieved), but bio-oil upgrading process is placed at lower maturity level (TRL 4-5). There are two patented technologies with plants at demonstration scale: Cat-HTR™ from Licella Holdings, and Hydrofaction® fromSteeper Energy.

Residues based on woody (from forest and wood industry) or on industrial waste, such as sewage sludge and derived from paper industry, are the most used feedstocks into larger throughput due to advantage of its low price. This fact implies low MFSP for a nth plant, ranging 0.75-1.1 €/L to 4.2 €/L. GHG emissions saving by processing these types of feedstock via HTL route are around 80%. Regarding development potential, HTL and upgrading route is estimated to reach its maturity by 2027 with plants of a capacity biofuels production at least 3ML per day, of which about 17% is assumed being able converted to bio-jet fuel.

#### 4.1.2.1 HTL process description

HTL technology lies in biomass degradation in wet conditions, which implies not applying a drying pretreatment on biomass to reduce its raw moisture. This allows energy to be saved in overall process, which is in itself a first great advantage. HTL process needs pressure and temperature values close to (by above or below) critical water conditions. Figure 15 shows at a glance where HTL process is placed as a function of thermodynamic water characteristics. Thus, pressure can vary between 10-35 MPa, while temperatures can change between 250- 450 ºC [145]. The choice of these values entails operating at sub- or super-critical conditions into the reactor. This entails products and yield to be closely depended of thermodynamic water conditions set; see Figure 15. Thus, in the case of HTL process, biomass is converted in four phases: (1) a bio-oil with high heating value (40-45 MJ/kg), which is the main product of process; (2) an aqueous phase containing polar organic compounds; (3) a solid residuenamed char, and (4) a gas stream more or less-rich in $CO_2$ [146]. Catalysts are commonly used owing to reach encouraging higher bio-oil yield to the detriment of mainly char fraction [147]. Between them, there would be homogeneous catalysts based on alkali salts, such as $NaOH$, $Na_2CO_3$, $KOH$, $K_2CO_3$ and $KHCO_3$, and heterogeneous catalysts based on metallic oxides, such as $ZrO_2$, Ni-Cu/$SiO_2$-$Al_2O_3$, and Zn-Cu-$NiCl_2$. Besides, their combination has been widely explored obtaining higher bio-oil performance regarding quantity and sometimes also quality.

Due to use of catalysts this pathway is sometimes called *catalytic hydrothermolysis*, however this must be not confused with catalytic hydrothermolysis (CH) conversion route to produce biofuel from oil-containing biomass or algae [2]. Sometimes there is confusion between both technologies (i.e., HTL and CH) because of both require moderate temperatures (i.e., 300-500 ºC) and high pressure values (i.e., 5-30 MPa). However, CH is a glycerides-to-fuel conversion route based on feedstock richness in both lipids and fatty acid. In addition, CH jet fuel conversion technology has recently been certified to produce CH-SK through Annex 6 of the ASTM D7566 standard [148]. In this sense, the patented process named ISOCONVERSION™ is able to produce jet fuel named ReadiJet®, which can be used in blending of up to 50% with petroleum-derived jet fuel. It is worth noted that Euglema (a Japan company) has licensed the patent from Chevron/ARA, and is already ready to produce almost 800 liters per day (L/d) of RJF [149]. This raises TRL and FRL of CH conversion pathways above 7, being out of this section.

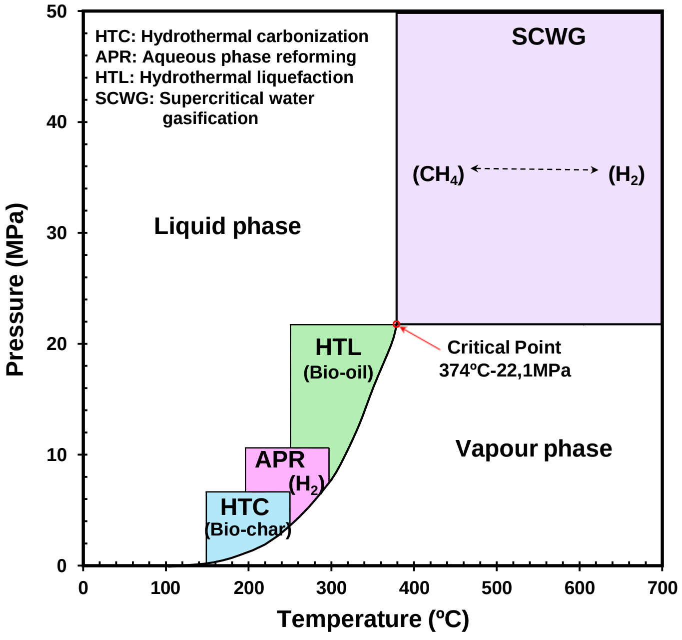

**Figure 15: Hydrothermal processes classification based on thermodynamic water diagram [146]**

HTL process entails three major steps: (1) depolymerization of biomass; (2) decomposition of intermediate products; and (3) recombination of reactive fragments [147], which can be seen in a schematic overview presented in Figure 16.

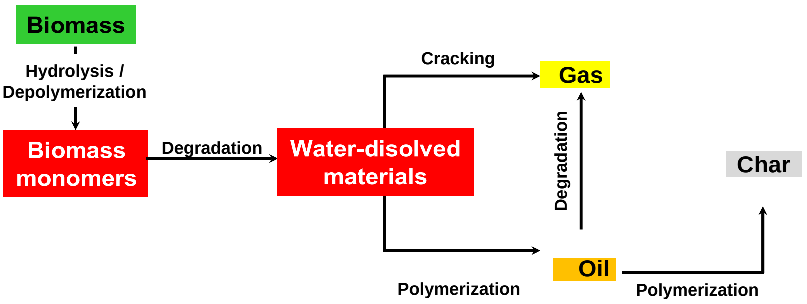

**Figure 16: Reaction pathways of HTL process**

First, organic material undergoes the breakdown of polymer chains of the different biomass compounds through mainly hydrolysis and depolymerization reactions giving place to monomers and unit structure. This is caused by water at high temperature and pressure, which promotes breaking down the hydrogen bonds of the macromolecules of long chain. Afterwards, degradation or decomposition of produced monomers takes place to form water- soluble intermediates through cleavage, dehydration, decarboxylation, deamination and cracking reactions. It should be noted that dehydration and decarboxylation mechanismscause the removal of oxygen in form of $H_2O$ and $CO_2$, respectively. This allows oxygen contentto be decreased in the oil fraction via HTL in comparison with other bio-oils production pathways, e.g., pyrolysis [106]. Finally, repolymerization reactions take places, which aremainly condensation and cyclization mechanisms forming the water insoluble products, i.e., bio-oil and bio-char [150,151]. Bio-oil to char ratio obtained in this last step is mainly depended of the availability of free hydrogen, promoting a higher freely hydrogen concentration, a higher bio-oil formation [145]. Mixing with the bio-oil, aqueous fraction containing polar organic molecules, such as furfurals, glycoaldehydes, phenols and organic acids, is obtained as by- product, which must be separated. This by-product could be recirculated to reactor in order to improve the bio-oil yield or could be subjected to other processes such as anaerobic digestion [145], catalytic hydrothermal gasification [145], or integration of several of them [152]. Likewise, char could be fed to anaerobic digester to obtain solid soil fertilizer. Figure 17 shows a possible full layout of RJF conversion route through HTL technology, which includes differentoptions to manage both aqueous fraction and char.

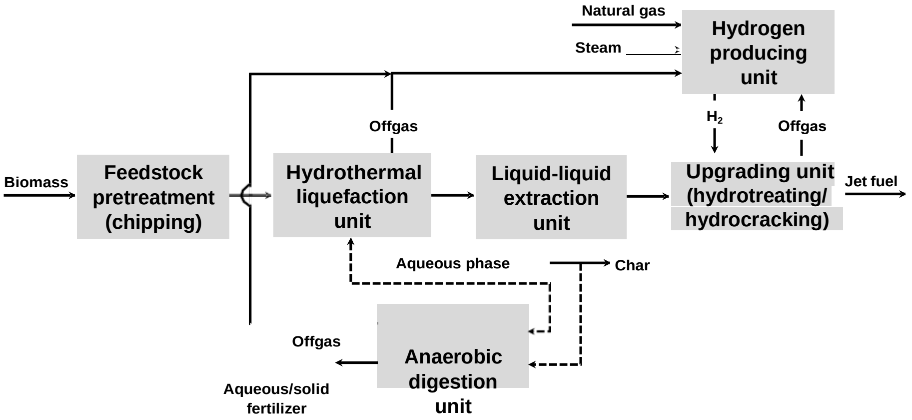

**Figure 17: Proposal full layout of HTL plant to produce RJF. Dashed lines denote possibility actions**

As it was mentioned above, bio-oil is the main product from HTL process and its performance, as well as others by-products, is highly dependent on feedstock (i.e., type, sizing, etc.),operating conditions (i.e., temperature, pressure, residence time, and heating rate), catalyst use, and other factors, such as reactor design and improvement by aqueous fraction recirculation. With this in mind, it could be said that potential bio-oil yield could widely vary in a range between 8 to 70%

[145,151,153,158-161]. It might be said average yield ranges for each fraction obtained from HTL process could vary between 30-50% for bio-oil, 20-30% for aqueous, 30-40% for char, and 20-30% for gas. Once bio-oil is isolated from by-products, its quality is not enough to be considered like feedstock for producing renewable jet fuel yet. Thus, it must be subject to an upgrading stage to remove the oxygen and other heteroatoms [102], of which usually lies in a hydrotreatment via catalytic process because of oxygen is almost removed [154]. It barely exists information regarding hydrocracking and distillation processes for bio-oil from HTL process, although it might be said that both naphtha, diesel and jet fuel would be the fractions obtained [2]. Recently, Hidrofraction™ proprietary thermochemical technology developed from Steeper Energy Company and Aalborg University has been reporting information and results of its HTL process at supercritical conditions using forest and sawmill residues, such as pine, spruce and birch [155,156]. Authors point out that bio-oil obtained can be mainly destined for use as diesel and marine fuels based on boiling point curves, emphasizing that 16.6% of bio-oil could be driven to jet fuel [157].

#### 4.1.2.2 Feedstocks used in HTL

Lignocellulosic biomass, either woody or wastes, have mainly been used as feedstock in HTL process, but algae-based biomasses have also been tested [145,150]. The latest have not been considered here since it should be taken into account that jet fuel processing from algae although is called catalytic hydrothermolysis, it must be not considered like HTL conversion process to RJF [162]. A further explanation of this can be found about in the text. Therefore, lignocellulosic biomass described below is focused on trees, forest residues, agricultural residues, MSW and industrial wastes. Overall, all of them are composed mainly of organic substances, such as cellulose, hemicellulose, lignin and extractives, and a small percentage ofinorganic substances, such as nitrogen, chlorine, sulfur, and all metals forming the ash. The nature of biomass feedstock, i.e., percentage of each component, affects bio-oil yield and quality owing to different biomass compositions. Thus, the higher presence of hemicellulose and cellulose, the higher bio-oil yield, while a large lignin percentage generates higher amount of char because of its high polymerization degree and complex interlinkage.

Analyzing continuous HTL units in literature [154], wood and industrial wastes, such as sewage sludge and kraft lignin, were the most used into larger throughput. This could be related to the availability of woody biomass for use in HDCJ conversion routes since could be limited by the competing uses from other sectors such as panel, sawmill and pulp industries, and power and energy sectors [11]. Moreover, it is estimated a wide increase, regarding its current use, in the availability of both wastes, such as paper waste, wood waste from MSW or garden waste, of forest and wood processing industry residues, and of available volume of agricultural waste, such as cereal straws by 2030 [12], just as it was explained into section 2.1.Regarding the use of straw-based feedstock to produce bio-oil, it should be noted that it is being brought into question because of its low qualities [163]. Finally, in spite of this type of biomass seems being guaranteed, their supply must also be evaluated by geographical areas since these could be a limiting aspect from feedstock cost point of view by raising logisticcosts.

It is worth noted the preferential use of wastes as feedstock which agrees with sustainability and circularity concepts. Cities are increasingly growing, and is in turn generating higher waste amount, such as MSW and sewage sludge. This will force to design new-green valorization routes, just as is pointed out in general from the Circular Economy Action Plan into the European Green Deal [164], and more specifically through Annex IX of RED II Directive where feedstocks to produce advanced biofuels are listed in detail [4].

The cost of suitable feedstock for use HTL process is not well known since public reporting of full RJF production through HTL route, including biomass estimated costs, is almost inexistent because of commercial sensitivity and maturity status of HTL bio-oil. Nevertheless, it is known that municipal and industrial wastes, e.g., from paper and water treatment, will be cheaper than forest residues or sawmill wastes and much cheaper than wood biomass. Furthermore, negative-cost ranging up to – 100 €/t (in dry basis, db) for industrial wastes may be considered (by acting it as waste manager) in comparison with lignocellulosic forestry biomass supply channel estimating in ranging 50-100 €/t (db) [50]. However, the cheaper feedstock, the higher could be technical efforts in order to achieve a suitable RJF [3].

#### 4.1.2.3 HTL plants and technology status

HTL technology is still a relatively novel process for generating bio-oil comparable to crude-oil as feedstock to produce jet and others fuels. In general, its development is found in pilot or demonstration scale with the majority of continuous plants being able to produce between 1 to 360 kg/h of bio-oil [147,154]. Table 5 compiles continuous HTL plants with a bio-oil production capacity of > 20 kg/h. Despite of existing 12 plants/processes, the majority of these have not been able to achieve its scale-up to demonstration plant, or they have even stopped the activity. As an example, DPT process from Changing World Technologies managing turkey wastes feeding rate of 250 tons per day stopped its activity in 2009. Currently, only two companies or platform have running plants at demonstration scale: Cat-HTR™ from Licella Holdings, and Hydrofaction® from Steeper Energy.

**Table 5: Continuously HTL plants with bio-oil performance higher than 20 kg/h [147,154]**

| Process/Plant | Developer | Country | Feedstock | Operating conditions | Throughput (kg/h) | Bio-oil yield (%) |
|---|---|---|---|---|---|---|
| PDU | Pittsburgh Energy Research Centre | USA | Wood chips | Subcritical | 43-360 | 53 |
| STORS | EPA's Water Engineering Research Laboratory | USA | Sewage sludge | Subcritical | 30 | 10-20 |
| STORS | Organo Corp. | Japan | Sewage sludge | Subcritical | 240 | 38 |
| HTU | Shell Research Institute | The Netherlands | All types of wastes and wood | Subcritical | 100 | 45 |
| na(1) | Aalborg University | Denmark | Wood | Subcritical | 20 | na |
| na | Aarhus University | Denmark | Wood, sewage sludge | Subcritical | 60 | na |
| Cat-HTR™ | Licella Holdings | Australia | Pulp paper, plastic waste | Supercritical | 350 t/y | na |
| Hydrofaction® | Steeper Energy-Aalborg University | Denmark | Wood | Supercritical | 30 | 45 |
| Geen2black™ | Muradel Corp. | Australia | Tires, algae | Subcritical | 168 | na |
| Cat-Liq® | SCF Tecnologies A/S | Denmark | Wet digested grain with solubles | Subcritical | 30 | 34 |
| Cat-Liq® | Altaca Enerji | Turkey | Different waste and residues | Subcritical | 15,000 | na |
| DPT | Changing World | USA | Turkey waste | Subcritical | 8,500 | na |

(1)na: not available

Licella is an Australian pioneer company owner of Cat-HTR$^{TM}$ technology, which lies in a catalytic HTL process at supercritical conditions allowing a bio-oil in-situ upgrading step [5]. It had scaled its facilities for three years passing from a small pilot plant (100 tons per year, t/y) up to two large pilot plants (1,000 and 10,000 t/y, respectively), and all news indicate that has already been built the world's first commercial scale hydrothermal upgrading plant jointly with Canfor Pulp in Canada to process kraft pulping wastes [165]. The annual production capacity is estimated in 79.5 million of liters of biocrude, which are equivalent to 350 t/y of bio-oil, which could define it at TRL of 7-8. Its final use has not been specified, but Licella signed memoranda of understanding to develop jet fuels with Virgin Australian and Air New Zealand at the beginning of scaling to commercial plant in 2011 [166]. Currently, there is no record regarding of initiating ASTM 4054 evaluation process (i.e., FRL 5), although a comprehensive study on characterization, engine performance, combustion and exhaust emissions from softwood flour Cat-HTR™ process has been reported [167]. It should be taken into account that authors suggest the use of this biofuel like diesel and in up to 30 % blends.

In fall of 2020, Licella and Carfor annunciated a new joint venture named Arbios™ Biotech, which is currently building the world's first small-commercial HTL plant with the ability to process 5,000 t/y of post-consumer biomass (producing 1.59 million of liters per year of biocrude) [168]. Licella has already completed both a number of successful trial run on their Cat-HTR™ small pilot plants and also commenced commissioning of the new plant. Full commissioning and feedstock testing for Arbios's plant is scheduled for the beginning of spring of 2021. Nothing suggests that this biocrude, or part of this, can be driven to jet fuel, however this project undertakes to generate green fuels at very short-term from biomass waste using HTL pathway, becoming this conversion route imminent and palpable reality for producing RJF.

Steeper Energy is a Canadian company owner of Hidrofaction® technology, which lies in a catalytic HTL process at supercritical conditions using hardwood and softwood forest and mill residues as feedstock [156]. Biocrude quality postulate it to produce jet fuel applying an upgrading process, estimating a performance roughly 17%, such as it was noted about section [157]. The experience of Steeper Energy is based on more of 1200 oil production hours gathered in a small continuous pilot plant with a capacity of 30 kg/h (placed at Aalborg University; see Table 1), being capable to produce roughly 1 barrel (> 150 kg) during an experimental campaign [168]. This would define it at TRL 5. At the beginning of 2018, Steeper was partnered with Green Silva (A Norwegian-Sweden platform) to build an industrial scale demonstration plant in Norway with producing capacity of 0.1 million of metric tons per year (4,000 liters per day) using residual product from forestry industry [169]. It is scheduled its launch for the beginning of summer of 2021, having in target a full plant operational for end of 2022 [170]. This allows TRL 7-8 to be reached, although nothing is known regarding ASTM 4054 evaluation process for Hidrofaction® process, which makes it establishing at FRL 5-6.

#### 4.1.2.4 Cost estimates for HTL pathway

RJF cost via HTL pathway is difficult to determine, since there is not an available commercially product, and biofuel prices from patented processes at higher TRL (i.e., Cat-HTR™ and Hidrofraction®) are not usually disclosed. However, there are techno-economic analyses that can aid to establish costs although it must be treated with caution because of these can vary while technology status is still growing. Therefore, estimated capital costs must be taken even more caution when comparing RJF conversion routes. Thus, HTL & upgrading process at pilot/demo scale producing 500 t of fuel per day could have capital costs for a nth plant ranging €$_{2020}$[4]290-544 million, which is slightly higher than already commercial pathways, such as HEFA, ATJ or DSHC [50]. Besides immaturity status, one key factor keeping high capital costs comes from the investment in the upgrading unit, which can be estimated around 36% of total capital investment [171]. Recently, Steeper Energy has disclosed investment data for its demonstration plant, which come to €50 million. In addition, the company advertised that in a second phase of the project in Norway an investment of €200 million will be done to build a commercial plant capable of producing 100,000 tons of fuel per year [172].

Minimum fuel selling price (MFSP) is commonly used as an assessment parameter for estimating cost of each technology for its comparison with others. For this calculation both

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[4] €$_{2020}$/L calculated as follows: Eur$_{2020}$ by converting first the USD$_{2013}$ values found by using the factor 0.76 €$_{2013}$/1 USD$_{2013}$, and after by applying the factor 1.06 €$_{2020}$/1 €$_{2013}$. L was obtained applying a jet density of 800 kg/m$^3$.

CAPEX and OPEX including feedstock are considered. Thus, estimated MFSP for a nth HTL plant of forest residues would be in ranging 0.75-1.10 $€_{2020}$/L, which is similar than MFSP for HEFA process of UCO and vegetal oil estimated in ranging 0.88-1.15 $€_{2020}$/L [3,6,50,55,173]. Nevertheless, HTL route is not competitive yet, since its development is currently starting to approach commercial status. It is expected its full commercialization and maturity not before of 2025, from where it could be trusted a reduction costs up to 50% (by 2030) mainly at the expensed of FT conversion pathway [20]. In that moment, RJF from HTL route could be competitive with kerosene-type jet fuel price, which comes keeping stable in ranging 0.45-0.50 $€_{2020}$/L from 2019 with the exception of 2020 where price slumped because of COVID-19 pandemic-related crisis [19]. This competiveness of RJF from HTL with conventional jet fuel comes marked because fossil-derived jet fuel price raise is expected by 2030 because of the $CO_2$ price increase, which could go up to three times more [20].

At this point, it has to be highlighted that betting on HTL route can be winning horse in comparison with the current bet on HEFA commercial pathway. Despite of last one has production costs only the twice than conventional kerosene, the much expensive feedstock used, i.e., vegetable oils and UCO, could become a burden in the longer term. It should be noted that HEFA's feedstocks cost is in ranging 400-650 €/t [20], which would be between 6 to 12 times more than forestry biomass supply; see section 4.1.2.2. Furthermore, these figures could be shockingly lower when being used industrial wastes, such as sewage sludge and pulp wastes, since these even may have negative price. Therefore, cheaper feedstock used in HTL route may be the key investment factor to encourage the rise of RJF production through this pathway in the longer term, driving to HEFA commercial pathway to a dead end.

### 4.1.2.5 Sustainability of HTL process

Sustainability is mainly evaluated through a life-cycle assessment (LCA) study calculating well-to-wake $CO_2$ emissions to compare with a base case, which is usually fossil-based kerosene [6,8]. For HTL process there are hardly LCA studies that estimate $CO_2$ emission saving. First reported data estimated emissions saving percentages in the range of 0-50% for HTL of microalgae [3]. This range could seem relativity low in comparison with other RJF conversion pathways [6], which could be related to requirements of algae cultivation regarding high water use and energy resources. In this sense, it should be taken into account that the use of other lignocellulosic feedstocks such as forest and agricultural residues, and industrial wastes, over algae or energy crops biomass, could aid to prevent higher $CO_2$ emissions.

Forest resources (either tree or residues from felling, pruning or milling) and industrial wastes can be an incentive from sustainability point of view over energy crops since these have not land requirement. This would allow in turn energy requirement and water consumption associated with cultivation to be decreased Furthermore, industrial wastes, such as sewage sludge and pulp paper waste, could become positioned ahead of forestry feedstock since they do not have any environmental burden associated to its production. However, this assertion would be not valid for example if marginal lands were used to plant trees since in this case it would become a beneficial. This fact is directly related to politics of each country, since natural resources are exploited of different way. Nevertheless, resources needed for treating and upgrading wastes up to produce jet fuel must be always less than that for cultivated or planting feedstocks.

More current studies on GHG emissions associated to RJF obtained from HTL of wastes are presented in this section. $CO_2$ emissions saving of 75% has been given for a jet fuel obtained from softwood through HTL & upgrading pathway, which is reached by the almost full reduction of emission-related to combustion in jet engine [173]. Similar value of 77% has been reported from HTL conversion route of woody biomass and assuming that a 25% of bio-oil obtained is driven to bio-jet fuel [20]. In both cases, complete assessment and accounting of all $CO_2$ emissions, i.e., from feedstock acquisition until jet fuel combustion, has been taken into account. From technologies closer to commercial status (i.e., Cat-HTR™ and Hydrofaction®), similar values has been given. Bio-oil from Licella's Cat-HTR™ technology points out to achieve a reduction of > 80% carbon intensity, which could be equivalent to $CO_2$ emissions [165]. Similar $CO_2$eq saving value of 77% is reported from bio-oil obtained by Steeper's Hydrofaction® process [156]. This study stated that it could be further reduced to reach almost neutral $CO_2$ emissions by using renewable electricity instead of standard grid electricity and by implanting a $CO_2$ capture technology. It states that even negative $CO_2$ emissions could be achieved if $CO_2$ exhaust from biomass conversion to fuel was sequestered and storage [174].

In view of this, it seems clear saving around 80% $CO_2$ emissions is achieved by selecting different forest residues (they seem the most suitable) as feedstock for producing jet fuel via HTL and upgrading pathway in comparison with conventional jet fuel. This figure could be considered similar or slightly lower than those reported from already certificated conversion pathways following ASTM D7566 standard [55,10]. This allows HTL route to be defined as highly suitable from sustainability point of view.

#### 4.1.2.6 HTL technology development potential

Technological development forecast for HTL conversion route is dependent on two clear facts: political strategies and competitiveness against other jet fuel conversion pathways.

Within political strategies, the bet by using RJF, either alone or blended, instead of conventional jet fuel can be a powerful tool in the large term to encourage its use in order to fight against global warming. This implies rigid environmental policies to be applied, which must come accompanied by institutional support, either by fiscal aids, by subventions associated to research project or by others, in the short term. On this, serve as an example theUSD75 million that Licella received from Australian government founding to develop its Cat- HTR™ technology [175]. However, this fact can be currently unviable due to different socio- economic factors, such as crisis-associated to COVID-19. In absence of economical contraindications, although governments promote the development of green technologies, the worldwide policy must be common (e.g., under Paris Agreement umbrella), and now there is some of uncertainty. This could increase, if the knowledge of that the use of conventional jet fuel will continue being necessary in the short term by being decarbonization of fuels a gradual way is summed. All of them could delay the entering of other un-certificated RJF pathways by ASTM D7566 standard in spite of being potentially suitable and economically solvent to produce bio-jet fuel. Currently, there are seven certified routes to produce different RJFs, which are being blending up to 50% with kerosene. Nevertheless, the large cost mainlyassociated with feedstock, their availability, the land requirements in competition with food- crops and lower $CO_2$ emission saved are inviting other RJF conversion routes to be further developed. The assessment of these pathways and their successful in future must come from the hand of presenting technological advantages and saving costs in comparison with current RJF conversion pathways. In one word: competitiveness, because if a new RJF production technology is further competitive and rentable in the long run, although politics remains aside, the aviation companies will invest because know that changing of fuel is ineludible.

HTL of forest residues theoretically represents the most competitive RJF conversion route because it has the lower minimum fuel selling price between all bio-jet conversion pathways [175]. This is mainly due to relativity high yield respect to feedstock and low delivered equipment cost. However, this potential is still not taking advantage due to immaturity of technology, by which could in turn further increase costs. Nevertheless, it might be said that the technical development of HTL route is almost completed since there is already several cases with commercial success or almost close to it, such as Cat-HTR™ and Hydrofaction® processes. At this point, it is worth noted that operating HTL unit at supercritical conditions seem the most suitable for the process scale-up in view of how demonstration plants are being operated. This fact could become expensive the equipment costs due to higher pressure requirements, although on the other hand would decrease upgrading step severity, which would save $H_2$. At the end a trade-off between initial investment and direct process costs must be considered to decide between sub- and supercritical conditions.

Competitiveness of HTL route comes also marked from availability of enough suitable biomass supply for producing RJF. It seems forest residues and industrial wastes are the most suitable for use HTL process (see section 4.1.2.2), which is in accordance with its availability in the short term. Forest residues and wastes, such as MSW, sludge and manure, is estimated to represent in EU 50% and 20%, respectively, of feedstock to produce biofuels by 2021-2030 period [20]. Nevertheless, HTL and upgrading route is estimated to start taking off 2024-2025 up to reach its maturity by 2027-2028 where it could replace part of HEFA and FT pathways [141]. As an example, it is worth to note the expansion forecast of Hidrofaction®-basedcommercial plants from Steeper Energy. They estimate to have 8 commercial facilities of 318,000 liters per day of bio-oil by 2027, with a growing rate of 4 plants per year up to have 32 facilities by 2032 [156]. At the moment, the company has recently advertised the starting of commercial plant build once demonstration plant starts to run, which could be between 2021 and 2022 [172]. Each facility planned would produce 54,000 liters per day of RJF, since Steeper Energy assumes almost 17% is able converting to bio-jet fuel [157].

There is one concept that could delay technological development potential of HTL route for producing RJF: ASTM D7566 or ASTM 4054 standard qualification process timing. It is worth noted that first certification is indispensable for jet fuels containing synthesized hydrocarbons (i.e., bio-jet in blending), and second qualification is necessary for use of new jet fuels [176]. Both certification processes can go on between 3-5 years, although this time could be extensively reduced to less than a year if RJF use is limited to a 10% blend percentage [177]. Nevertheless, if ASTM qualification process of RJF from both Cat-HTR™ and Hydrofaction® processes was now started, when HTL technology reaches its maturity by 2027, the certification issue would be resolved. Nowadays, ASTM D7566 specifications can be compared to bio-jet characteristics after completing the upgrading step of bio-crude to see weak points of biofuel. Thus, bio-crude produced at Aalborg University continuous plant (Hydrofaction® technology; see Table 5) was upgraded at PNNL's facility and then distillated to obtain jet fraction [126]. RJF had low flash point, which could be easy increased by adjusting the distillation curve to remove some of lower boiling compounds. Low smoke point was also observed in RJF because of high aromatics content, which would need being to remove through further hydrogenation and hydrocracking. This approach would be fully needed since oxygen and especially nitrogen must be further removed. Despite the bio-jet has not all ASTM specifications, other option is developing the HTL process joint to some airline company in order to obtain a bio-jet with marked specifications and this way to exploit it in exclusive, just as Licella (Cat-HTR™ technology) made with Qantas and Virgin Australia [166]. In summary, HTL conversion pathway to produce RJF is a promising option that has all wickers to become an important route by the middle of this decade. It should be highlighted that with this option, in addition, would aid to reduce energy loss when using industrial residues, such as sewage sludge and MSW, because of these wastes are currently managed through incineration or landfill deposition. Therefore, energy contained would be introduced into energetic system encouraging circular economy. Furthermore, by-products, such as bio- diesel, chemicals from bio-oil and fertilizers from aqueous fractions and char, could generate further adding value increasing the technological development potential. This last by-product would aid to marginal lands be recovered for new farming, for example for non-food crops to obtain feedstock for other RJF conversion route such as HEFA or ATJ. From all points of view, HTL process represents an integral solution for fight global warning.

## 4.2 Aqueous Phase Reforming (APR) pathway

Aqueous phase reforming (APR) is a catalytic pathway that converts sugars-rich plants into a mixture formed by water, hydrogen and chemical intermediates, being the last one transformed to biofuels. Food crops, such as maize, sugarcane, beet sugar and corn starch for producing 1st generation biofuels, and residues, such as bagasse and corn stover, grasses and wood to produce 2nd generation biofuels are used as feedstocks. In addition, aqueous fractions containing organic compounds, such as by-product streams from other process, are taking currently interest as feedstock. RJF produced is based on hydrodeoxygenated synthetic kerosene with/without aromatics (HDO-SAK/HDO-SK). APR has 4 step: (1) pretreatment of biomass, usually enzymatic or thermochemical hydrolysis, to extract hemicellulose; (2) hydrotreatment of hemicellulose; (3) APR at moderate temperatures (180-250ºC) and pressures (1-9MPa) on a catalyst to produce oxygenates intermediates; (4) conversion or upgrading of oxygenates intermediates.

One only patented technology called BioForming® of Virent Company has reached the demonstration scale level with a combined annual production capacity of almost 60,000 liters of fuels and chemical. This process is able to produce a bio-jet based on Cyclo-Paraffinic Kerosene (CPK) with similar characteristics than conventional Jet-A, which is currently in Phase 2 of the ASTM D7566 certification procedure.

MFSP of 1.2-1.4 €/L ranging have been estimated for a APR plant with capability to produce 100ML/y with a capital investment of €470 million and annual operating costs of €140 million. GHG emission reduction between 24 to 29% compared to fossil kerosene are reached, which could be further reduced (up to 55-60%) by decreasing bio-jet production at the expense of chemical production.

### 4.2.1 APR process description

Aqueous phase reforming (APR) pathway converts soluble sugars into a mixture formed by water, hydrogen and chemical intermediates, such as alcohols, ketones, acids, furans, paraffins and other oxygenated hydrocarbons [5]. It should be highlighted that APR is acatalytic process, so this route has alternative names such as sugar to hydrocarbons via catalysis, catalysis of lignocellulosic sugars and aqueous phases processing (APP). RJF produced by APR route is commonly called hydrodeoxygenated synthetic kerosene with/without aromatics (HDO-SAK/HDO-SK) [178]. Biomass to drop-in biofuels through APR has several steps, which in a general way are shown in Figure 18. First step of APR route lies in a pretreatment of feedstock, which usually entails an enzymatic or thermochemical hydrolysis to separate biomass compounds (i.e., cellulose, hemicellulose and lignin). Second step usually is based on hydrotreating of both hemicellulose and cellulose through hydrogenolysis and/or hydrogenation, which generates short-chain oxygenated compounds and polyhydric alcohols, respectively [2,179]. Once hydrotreated carbohydrates have been extracted from biomass, these are dissolved in water before begging the third step, which is itself APR of sugars. During APR process, the solution is reacted on catalyst at moderate temperatures (180-250ºC) and pressures (1-9MPa), which promotes several reactions, such as reforming to generate hydrogen, dehydrogenation of alcohols and hydrogenation of carbonyls, deoxygenation, hydrogenolysis and cyclisation [178]. The products from APR consist of two phases: gas and liquid [180]. On the one hand, $H_2$ is the main compound into gaseous stream, observing also $CO_2$ and sometimes CO, as a function of the water-gas shift (WGS) equilibrium influence. On the other hand, liquid phase is constituted by mixture of hydrocarbons and oxygenates compounds, such as alcohols, ketones, aldehydes, alkanes, organic acids, and furans, which are the intermediate products needed to produce RJF via APR route. Regarding hydrogen produced, this can be consumed into APR process, but it can also be used in the previous hydrotreating stage and/or the final distillation. It should be noted that two by-products from APR are obtained: unconverted lignin and lighter alkanes (C1-C4), which could be burnt in a combustor to improve additional process heat. Last step of this route to biofuels production (regardless of final distillation) is the conversion or upgrading of oxygenates intermediates from APR step into fuel-range hydrocarbons. Three routes have been identified: acid condensation, base condensation and dehydration and oligomerization [179]; see Figure 18.

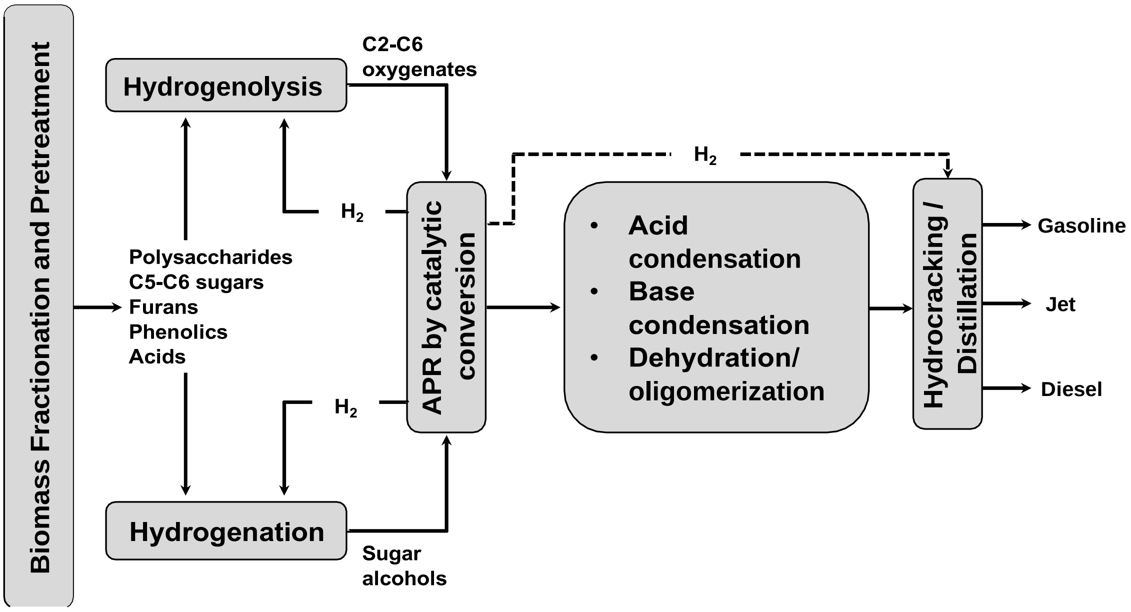

**Figure 18: Proposal layout of APR conversion route. Dashed line denote possibility action [2]**

**Acid condensation** lies in using acid catalyst, such as zeolites, to convert oxygenates intermediates into alkanes, iso-alkanes and aromatics. The reactions involved are dehydration of oxygenates to alkenes, oligomerization of alkenes to heavier alkenes, cracking, cyclization and dehydrogenation of heavier alkenes to aromatics, alkane isomerization, and hydrogen-transfer to form alkanes. This route promotes highly the gasoline production, but the heavier species can be distilled into jet fuel. **Base condensation**, also called direct catalytic condensation, lies in using multifunctional solid-base catalysts to convert the intermediates to hydrocarbons by condensation. Several condensation reactions take place: (1) aldol condensation to produce β-hydroxyketone or β-hydroxyaldehyde; (2) dehydration of β-hydroxyketone or β-hydroxyaldehyde to produce conjugated enones; (3) hydrogenation of the conjugated enones to produce ketones and aldehydes or further to alcohol, and (4) removal of hydroxyls by dehydration/hydrogenation or hydrogenolysis to form alkanes. This second route mainly promotes products in the jet fuel range. **Dehydratation/oligomerization** lies in converting oxygenates intermediates to alkanes and alkenes via dehydration and hydrogenation-dehydration reactions. The alkenes are then oligomerized to produce gasoline, keronese or diesel with solid phosphoric or zeolite catalysts.

Other conversion routes have been proposed based on using the biomass forming compounds, once these have been previously separated, to generate jet fuel and commodity chemicals. A catalytic route developed into a two-stage biphasic reactor is able to produce on the one hand furfural and levulinic acid from hemicellulose oligomers (i.e., xylose and fructose), and on the other hand both levulinic and formic acids from glucose from cellulose [181]. All of them can be subsequently subjected to upgrading through catalytic hydrotreatment producing a mixture of branched, linear, and cyclic alkanes of molecular weight ranges appropriate for use in aviation. It should be noted that carbon yield into jet fuel is 80% from hemicellulose and 50% from cellulose. Other route using acid catalysts to process plant sugar/mixed polyols (sorbitol and xylitol) was defined to produce a suitable RJF formedby 72% of aromatics and napthenes [182]. Other process based on dehydration of hexones using acid catalysts can produce hydroxymethylfurfural (HMF), which can ben then converted to alkanes [183]. Finally, the last process is presented to furan-based fuels (e.g., HMF) production from fructose by using an acid catalyst and an ionic liquid. HMF can be subsequently purified to dimethylfuran (DMF) [184]. Similar approach of producing intermediate DMF to its subsequent hydroxyalkylation/alkylation condensation to C15 intermediate was carried out using $H_2SO_4$ as catalyst [185]. High liquid alkanes (C8-C15) yield of 83% was obtained by catalytic hydrogenation of C15 intermediate with excellent stability of the catalyst owing to the significantly decreased of carbon deposition.

### 4.2.2 Feedstocks used in APR

APR traditionally uses soluble plant sugar, which can be from sugar, starch or lignocellulosic feedstocks [178]. As a function of feedstock source both 1st and 2nd generation biofuels can be produced. Thus, transforming food crops, such as maize, sugarcane, beet sugar and corn starch, 1st generation biofuels are generated. However, by using residues, such as sorghum, bagasse and corn stover, grasses, such as elephant grass, miscanthus and switchgrass, and woody biomass from timber harvesting (e.g., pine), 2nd generation or advanced biofuels are obtained. Feedstock to produce 1st generation biofuels have been mainly used, but corn stover and wood is being currently explored to produce 2nd generation biofuels.

Moreover, aqueous fractions containing organic compounds, such as by-product streams from other process, are taking currently interest as feedstock of APR route [180]. This allows these by-products to be managed and recover part of contained energy into aqueous stream. Thus, on the one hand could be used the glycerol, which is the main by-product from first generation biodiesel production. APR of glycerol would drive not to produce RJF but commodity chemical, such as ethanol, propylene glycol and ethylene glycol, which can be then converted into hydrogen [186]. On the other hand, aqueous fraction leaving from both Fisher-Tropsch [187], pyrolysis [188,189] and HTL [190] processes can be managed via APR route, since this is formed by soluble compounds, such as acetic acid, sugars, hydroxyacetone, methanol, furfural and acetaldehyde. This allows hydrogen to be obtained, which could be supplied into upgrading stage needed of these processes saving costs.

### 4.2.3 APR facilities and technology status

APR conversion route is in general considered to be an immature technology to produce SAF, with different development level as function of feedstock. Thus, APR of lignocellulosic sugars is at pilot prototype scale (TRL 4-5) while APR using conventional sugars is at demonstration scale (TRL 6) [142]. In total, 0.04 kt/y of bio-crude are being currently produced [13]. The milestone at demonstration level has been reached by the Virent`s patented technology called Bioforming®, which is being run through two demonstration plants with a combined annual production capacity of almost 60,000 liters of fuels and chemical [5]. This company counts on Shell as collaborator to develop APR route from lignocellulosic biomass and sugars to obtain a RJF commercially named as BioForm™ jet fuel following two routes [64]: (1) **aromatics processing**, which entails a cracking process on a modified zeolite-based catalyst to produce an aromatic rich reformate stream suitable for producing a bio-jet based on HDO-SAK. This could be blended up to 25% with conventional fossil kerosene; (2) **distillates processing**, which lies in a condensation + hydrotreating process to produce a jet fuel based on HDO-SK. This has been recently renamed as Cyclo-Paraffinic Kerosene (CPK) because of its high cycloparaffin content, which could be blended up to 50% with fossil jet fuel. It should be highlighted that BioForm$^{TH}$ CPK jet fuel is currently in Phase 2 of the ASTM D7566 certificationprocedure [13]. This Virent`s CPK has the same type of hydrocarbons that are forming the typical Jet-A with a broad carbon number range, although it has a lower paraffin content (19%), a much high cyclo-paraffin content (80%), and much lower aromatic content (<1%)[64]. This allows obtaining a bio-jet with equal characteristics compared to Jet-A, highlighting the very high thermal stability regardless the feedstock used (i.e., corn syrup, corn stover and woody biomass) [191].

### 4.2.4 Cost estimates for APR route

When a technology is too immature, it is difficult to get access to data related on costs. Thus, only two works were found analyzing APR process to produce RJF from a techno-economic point of view. In the first [192], the authors considered one APR plant with a capacity of bio-jet fuel production of 1 kt/y (~1.2 ML) by using corncob as feedstock. A total operation cost range between USD1,420-1,820 per ton of bio-jet fuel produced was indicated, which be equal to

1.05-1.35 €$_{2020}$/L. These figures are reached from different assumption such as that bio-jet fuel yield of 0.125 t/t feedstock and whole system thermal efficiency of 32%. In the second study [193], 7 biorefinery configurations and 12 hydrogen generating processes were evaluated with a jet fuel capacity of 100ML/y (~80kt/y) processing red maple wood. Higher MFSP were estimated in the range of 1.2-1.4 €$_{2020}$/L as a function of mainly hydrogen source chosen and the produced volume chemical to fuels. The difference between both studies could be due to both differences on feedstock, configuration of plant, hydrogen source and production capacity. Between refinery configurations, it is explored the possibility of producing either 800 ML/y or 10 ML/y to see the costs variation. When increasing the jet fuel production the MFSP increases up to 1.5-1.6 €$_{2020}$/L while when reducing the jet production in favor of furfural production as chemical the MFSP decreases up to 0.4-0.6 €$_{2020}$/L. In addition, this last work shows data of fixed capital investment and annual operating costs, which are estimated of average for all refinery configurations in €470 million and €140 million, respectively.

Nevertheless, estimated costs could be increased owing to current uncertainty on catalyst performance, since the low lifetimes of this opens the need of further investigation to do it more reliable. In addition, feedstock price can also affect estimation of costs, since it represents the largest percentage into total costs. Thus, there is always uncertainty on the biomass price increase from food crops due to pressure of food producing and transforming sector. For this, and taking into account the future uncertainly on the availability of this type of sugar sources to produce fuels, it would be more advantageous to use lignocellulosic biomass or residues. It should be noted that using residues, such as bagasse and woody waste, would aid to reduce widely final cost of production because of these wastes are much cheaper than energy crops [124]. However, the higher both impurities and complex polymers formed into these feedstocks, the higher challenge to reach find suitable catalyst with high lifetime. Therefore, in order to better estimate the associated costs to APR technology it would be recommendable further investigation developing deep techno-economic studies stressing on issues with catalyst lifetime, which could still take to occur.

### 4.2.5 Sustainability of APR pathway

Just as costs evaluation, there are barely sustainability studies of APR pathway to produce biofuels. However, it is clear that there could be a variation of associated GHG emissions as a function of the feedstock, just like it was observed in other pathways. In order to provide data, two sources were found. From a LCA study consists on several biorefinery configurations and hydrogen sources producing 100ML/y of bio jet, GHG emission of between 62 to 66.5 g$CO_2$eq/MJ were estimated [193]. This entails well-to-wake emissions to be reduced of between the 24 to 29%. If jet fuel production would increase by 8, it is estimated that GHG emissions reduction would decrease being only saving a 20% compared to fossil kerosene. In contrast, if jet fuel production would decrease by 10 (i.e., 10ML/y) at the expense of increase chemicals production, GHG emissions would be widely reduced up to a value of 55% in comparison with fossil fuel. Similar results were found from the other source identify, which is the BioForming® process of Virent [194]. The company shows a carbon emissions reductionof at least 20%, and up to 60%, depending on feedstock chosen, when producing bio-gasoline. Higher emission reductions were observed during chemical production as well as it was view into LCA previously discussed.

### 4.2.6 APR technology development potential

APR is usually designed for producing hydrogen, rather than liquid fuel than as RJF. However, the suitable selection of the operating conditions, the catalyst composition and the reactor design can promote RJF production route. Nevertheless, there are mainly two technical challenges for generating drop-in jet fuel via APR technology at commercial scale [141]. First challenge is increasing the selectivity to liquid long-chain hydrocarbons (i.e., heavier alkanes) instead of current production with higher gas yield and wide range of aromatics mainly with lignocellulosic biomass. This could be reached through operating condition optimization and/orspecific catalyst development. The second challenge is related with the tolerance and poisoning level of the catalyst. Catalyst lifetime is currently short because of deactivation and coking deposition mainly due to formation of phenolic oligomers [195]. This fact has made limited testing number and the hydrocarbons yield mainly using lignocellulosic biomasses since these are less homogeneous and contain impurities. This, in turn, has promoted low production capacity to validate at high scale. Therefore, these two characteristic, i.e., selectivity and catalyst lifetime, make APR expensive from a capital and operational cost standpoint. In addition, resolving issues such as improved reactor design and process integration are also other of identified needs to aid for scaling of APR to RJF production.

APR route is estimated to start taking off not before 2028-2029 with a projected share of 5% within the global capacity of drop-in advanced biofuels by 2030 [141]. Much lower RJF capacity of production is estimated in EU by 2030 with a testimonial percentage of <0.5% into total mix of advanced jet fuel [142].

Despite of high time-to-market of APR technology to produce RJF in comparison with other technologies at short-term, and of low share that this will be when it is reached, its development could be accelerate as part of other RJF conversion route that generates an aqueous stream as by-product, such as FT, pyrolysis and HTL. It should be noted that APR has lowest liquid performance and energy efficiency between all biomass to liquid fuel technologies [179], being the gas stream, which is mainly formed by hydrogen, the majority product obtained. Thus, APR would be used as technology not for producing drop-in bio-jet fuel but to generate the hydrogen that must be used into upgrading steps into pyrolysis or HTL routes. This would allow costs to be decreased into RJF production technologies without ASTM certification, increasing their growth at the same time.

# 5 Conclusions

A technical analysis of several alternative Renewable Jet Fuel production pathways has been carried out, highlighting the advantages and the disadvantages of each of them. The extensive literature research work that has been conducted allows reviewing the actual capability and the expected potential of each pathway. The gathered information has then been successfully used to prepare a detailed comparison KPIs evaluation grid, as required by Task 4.2 objectives.

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