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DROP-IN BIOFUELS PRODUCTION FROM MICROALGAE TO HYDROCARBONS: MICROALGAL CULTIVATION AND HARVESTING, CONVERSION PATHWAYS, ECONOMICS AND PROSPECTS FOR AVIATION

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ABSTRACT

In the last few years, governments all around the world have agreed upon migrating towards carbon-neutral economies as a strategy for restraining the effects of climate change. A major obstacle limiting this achievement is greenhouse gases emissions, for which the aviation sector is a key contributor because of its dependence on fossil fuels. As an alternative, biofuels with similar characteristics to current fossil-fuels and fully compatible with the existing petroleum infrastructure (i.e., drop-in biofuels) are being developed. In this regard, microalgae are a promising feedstock thanks to, among other aspects, their potential for lipid accumulation. This review outlines the development status, opportunities, and challenges of different technologies that are capable of or applicable to transform microalgae into aviation fuels. To this effect, a baseline of the existing jet fuels and the requirements for potential aviation biofuels is initially presented. Then, microalgae production and valorization techniques are discussed with an emphasis on the thermochemical pathways. Finally, an assessment of the present techno-economic feasibility of microalgae-derived aviation fuels is discussed, along with the authors' point of view on the suitability of these techniques. Further developments are needed to reduce the costs of cultivation and harvesting of microalgae, and a biorefinery approach might improve the economics of the overall process. In addition, while each of the conversion routes described has its advantages and drawbacks, they

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converge upon the need of optimizing the deoxygenation techniques and the proportion of the suitable type of hydrocarbons that match fuel requirements.

KEYWORDS: DROP-IN BIOFUELS -- JET FUELS -- MICROALGAE -- LIPIDS -- THERMOCHEMICAL PATHWAYS -- DEOXYGENATION

1. Introduction

For decades now, fossil fuels have been ubiquitous in our daily lives, release of greenhouse gases (GHG), such as carbon dioxide, methane, from lighting and heating our homes to propelling our cars and planes, NOx and SOx gases, which has encouraged politicians to adopt multiple allowing people to travel the world [1]. However, the overexploitation of these non-renewable resources has contributed to the problem of climate change. The conversion of petroleum into fuels promotes the initiatives and milestones to reduce GHG emissions [2,3]. This juncture is illustrated by the European Union (EU) policies, the Paris Agreement, the goals of the United Nations (UN) Intergovernmental Panel On Climate Change (IPCC), and the targets adopted by the International Civil Aviation Organization (ICAO) [4–10]. Some of these policies aim to minimize the use of fossil fuels for transportation [11,12]. According to the data published by the International Energy Agency (IEA), about 66% of the world oil was consumed in transportation in 2019 [13], a trend that is expected to increase in the years to come [14]. In parallel, the projections of the UN show that global population is expected to increase by 2 billion in the next 30 years and is projected to reach nearly 11 billion in 2100 [15,16]. Assuming that this increase in population will lead to an increase in their mobility, the energy demand for transportation will also continue to expand [17]. In fact, oil demand for transportation is expanding continuously with expectations to increase by 1.3% annually until 2030 [18,19]. According to a new prediction from Airbus for 2038, it is expected that the aircraft fleet for both civil aviation and freighters will double in the next twenty years [20].

Increasing population, mobility, and the associated environmental and economic issues motivates the development of alternative and sustainable transportation fuels, such as biofuels. Biofuels are made by converting biomass (vegetable oils, agricultural wastes, domestic wastes) into suitable products [21]. Solid biofuels like wood residues, wood pellets, biochar, or animal/vegetal wastes are typically burned to provide heat and light [22]. Liquid (bio-gasoline, biodiesel, bioethanol, biojet fuel) and gaseous (biogas) biofuels are commonly used for transportation means to reduce fossil fuel reliance. Their development for land transportation is less critical due to the emergence of other alternatives to current petroleum-based gasoline and diesel (e.g., hydrogen, electrical vehicles) [12]. Nevertheless, air transport requires compliance with specific fuel properties, aircraft design (wings and turbines), and higher safety standards than land transportation, which tightens the fossil fuel dependence of the aviation sector [17]. This challenge motivates in this review the development of drop-in biofuels, i.e., biofuels with similar characteristics to current fossil-fuels and fully compatible with the existing petroleum infrastructure [23].

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The exploitation of renewable feedstocks for the production of biofuels is typically limited by: (i) biomass feedstock availability, (ii) alternative exploitation of biomass (e.g., food production), and (iii) their intrinsic chemical and physical properties [23,24]. First generation biofuels come from edible crops such as corn, sugarcane, soybean, and rapeseed. Although the production processes of bioethanol and biodiesel are known, controlled, and scaled up, first generation biofuels have an impact on food prices and food security, leading to concerns about the ethical exploitation of crops for biofuels but not for food [12,25,26]. Additional drawbacks are the utilization of non-sustainable fertilizers or reliance of deforestation, implying indirect land-use change [27].

Overcoming these limitations has been a challenge over the years, which prompted the emergence of second- and third-generation biofuels [28]. Second generation biofuels are produced from lignocellulose, often present in agricultural residues, forestry waste, and biomass industrial wastes or municipal wastes [29,30]. This review will not cover the biofuel production pathways exploiting lignocellulosic biomass; the reader can refer to other recent review papers published on the subject [31–36]. Microalgae, the feedstock for third-generation biofuels, seem to be a promising biomass source to produce biofuels. They are mainly composed of lipids and sugars, two potential precursors of hydrocarbons [37]. Some of the benefits of using microalgae as a feedstock for biofuel production are presented in Section 3.

Currently, only 3% of the primary energy consumed for transportation is represented by biofuels, but IEA projected that 21% will be necessary by 2050 to reduce GHG emissions [38]. This review discusses the development of drop-in biofuels applicable in the aviation industry (i.e., biojet fuels). Initially, the baseline for drop-in biojet fuels is described in Section 2. Then, cultivation strategies and production techniques of microalgae as the third-generation feedstock is presented in Section 3. In addition, an overview of thermochemical conversion pathways including lipid and biomass valorization and economic feasibility of these existing processes is provided in Sections 4 and 5. Finally, potential strategies that could be investigated in the future are discussed in Section 6.

2. Fossil-based jet fuels & drop-in biofuels

Kerosene is a middle distillate of the crude oil refining process upgraded for its use as aviation fuel [39], also called jet fuel. It is a transparent liquid mix of hydrocarbons (paraffins, naphthenes, aromatics, and limited amount of olefins) with a chain length between 6 and 16 carbons [39,40]. In general, jet fuel varies in composition, where a typical distribution shows around 20% v/v of normal paraffins, 40% v/v of iso-paraffins, and the rest being aromatics, naphthenes, and trace elements such as sulfur and additives.

There are mainly two types of fossil fuels used in civil aviation: Jet A- 1 and Jet-A [41]. Jet A-1 is the worldwide used jet fuel for commercial flights, which is completely compatible with all existing turbines. Jet A, which has a higher freezing point, is mostly available in the U.S [17,42]. In addition to these two major jet fuels, Jet-B is a blend of gasoline and kerosene which is used in very cold climates (e.g., Alaska and some parts of Canada) [41,43]. Having a typical boiling range of 150–300

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°C, jet fuels can be used for civil or military aviation, implying lots of specifications and requirements [40,44]. In the 1960s, the American Society of Testing and Materials (ASTM) established the specifications for Jet A-1 [45], which limit the concentration of aromatics at a maximum of 25% v/v, together with 3% for naphthalene and 3000 parts per million (ppm) for sulfur among other aspects [46–48]. Correspondingly, for drop-in biojet fuels to meet the ASTM standards and be compatible with existing fuel infrastructures, they have to fill in a range of characteristics including [46,49]:

- High energy density, facilitating long distance flight.
- Low viscosity, a parameter determining fuel pump-requirements.
- Low freezing point, facilitating high altitude flight.
- High flashpoint, the temperature needed for the fuel to produce vapor and form an ignitable mixture in air. Flashpoint is an essential safety consideration.
- Good chemical and thermal stability. Fuel can be used to cool engine components and increase aircraft performance.
- Wide availability. To have a significant positive impact on fuel price and environment, the fuel must be available in significant quantities.

The chemical and physical properties of jet fuels depend on the number of carbon atoms present in the hydrocarbons (carbon number) and the way these atoms are arranged. Generally, an increase in carbon number implies an increase in the boiling point, freezing point, density, and energy density (energy per unit volume) of the fuel but a decrease in its volatility and specific energy (energy per unit mass). Concerning the configuration, an aromatic ring (benzene) will result in a higher freezing point, boiling point, density, and a lower specific energy compared to a paraffin [50]. Table 1 compares some properties of potential biojet fuels, such as hydrotreated vegetable oils and Fischer-Tropsch fuels with those of jet A1 [50,51].

Table 1 *Properties of some potential biojet fuels compared to conventional jet-fuel.*

Property	Fischer Tropsch fuels	Hydrotreated vegetable oils	Jet A1
Specific energy (MJ/kg)	43	43	43
Viscosity (at 40°C) (mm^2/s)	3	3	1.3[a]
Flashpoint (°C)	70	100	38
Freezing point (°C)	− 30	− 29	− 47

[a] As reference, the viscosity of Jet-A1 at − 20 °C, the testing temperature required in the jet fuel specifications, is reported to be 8 mm^2/s [45,50].

Another factor that alters fuel properties is oxygen content. Two common ways to express the oxygen content in biofuels are the oxygen- to-carbon ratio (O/C) and the effective hydrogen-to-carbon ratio (H/C), as is shown in Fig. 1. Fig. 1a displays the inverse linear correlation between the energy density of a biofuel (MJ/L) and the O/C ratio [23]. A high O/C ratio or oxygen content decreases the energy density of the biofuel [52]. It can also attract water molecules, limiting the fuel's compatibility with the existing infrastructure. For the aviation sector, first-generation biofuels are difficult to meet the energy density requirement [41].

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On the other hand, H/C (calculated using Eq. (1) [53]) describes how rich in hydrogen and how energy dense the biofuel is [23].

$$H/C = \frac{n(H)-2n(O)}{n(C)} \quad \text{(Eq.1)}$$

In conventional fossil fuels (gasoline, diesel, kerosene), H/C is close to 2, the "ideal" value due to the very low or even no oxygen in petroleum (Fig. 1b). Hence, the effective H/C ratio for drop-in biofuel feedstocks must be as close to 2 as possible, highlighting the potential of lipids to be employed as raw materials [23,53]. However, due to the presence of oxygen in such compounds, there is a necessity to understand, control, and optimize deoxygenation strategies to effectively convert oxygen containing biomass into hydrocarbons (explained in Section 4) with a low O/C and high H/C ratio that are comparable to petroleum-based fuels.

3. Microalgae as renewable feedstocks

3.1. BENEFITS OF USING MICROALGAE AS FEEDSTOCK

Microalgal biomass exhibits clear benefits over biomass from other plants [39,54–56]. Primarily, in contrast to crop plants used for second generation biofuels production, microalgae do not need arable land to grow, preserving agricultural areas and avoiding environmental problems related to deforestation. Microalgae can be easily cultivated in seawater or wastewater, which is critical for countries where drinking water is a scarce resource [57–59]. Secondly, it has been shown that microalgal photosynthetic efficiency, when supplemented with carbon dioxide, is in general superior to that of plants [60,61]. Moreover, microalgae do not have lignin within their cell wall, which avoids expensive pre-treatments to convert its fractions into valuable products [62]. Microalgae are able to grow continuously for a very long time, with many species capable of doubling their biomass in less than a day [63]. Besides, some microalgal strains are able to accumulate more than 80% of the total weight of their dry biomass in lipids after induction of various stresses [57–59] or particular growing conditions, such as nitrogen starvation or lower temperatures compared with the optimum growth [64–66].

Because of their rich lipid content and fast growth, microalgae show a production yield much higher than plants, ranging approximately from 3 to 7.5 tons of lipids per hectare and per year, depending on the culture condition and the selected strain, against, for instance, 0.4 tons.ha^{-1}.y^{-1} for soybeans or 0.7 tons.ha^{-1}.y^{-1} for rapeseed [67–70]. Table 2 shows different strains studied for biofuel production and their lipid content.

Similar to plants, the storage lipid biosynthesis pathway in microalgae starts with glucose, which is mostly produced during the photosynthesis reaction [71]. Glucose is then used for the synthesis of Triacylglycerol (TAG) or storage polysaccharides biosynthesis [71]. Microalgae are also rich in polyunsaturated fatty acids (PUFA) which are also suitable for aviation fuels [72]. For a given

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quantity, microalgae crude oil contains about 80% of the energy delivered by the same amount of crude oil petroleum, with an average of 35.8 kJ/kg [73].

Carbohydrates are distributed in many locations within the cell, with variable proportions according to the species and culture conditions [79]. For example, some green algae contain cellulose, hemicellulose in the cell wall and starch used as storage polysaccharide [80]. Reserve carbohydrate production can be stimulated by the same stresses or condition as those applied to promote lipids accumulation, although depending on the species one metabolite will be preferentially synthesized over the other [81,82]. As shown in Table 3, carbohydrate content is variable depending on the algal species.

3.2. PRODUCTION TECHNIQUES

Many promising cultivation systems for large-scale microalgae production exist [86]. Depending on the cultivated species, they are exploited for photosynthetic pigments such as secondary carotenoids (e. g. astaxanthin), PUFAs as food supplement [87], in wastewater treatment [59], or for third generation biofuel production [88]. Regardless of the reason for algal biomass production, apart from the water-based culture media (or seawater-based for marine species), it is essential to provide nutrients such as nitrogen, phosphorous, iron and metal trace elements by supplying inexpensive inorganic salts. In addition, it is important to provide a light source and carbon dioxide for the photosynthetic reaction, and to guarantee a temperature generally between 25 °C and 35 °C [89]. Optimum conditions for microalgal growth depend primarily on the microalgal strain, the desired application and the technology selected, but its control is essential to optimize the productivity. The main variables are temperature and pH, but the nutrient supply, light and CO_2 assimilation are also significant [89].

Table 2 *Some microalgal species studied for biofuel production and their corresponding lipid content (% DW).*

Microalgal species	Phylum	Lipid content (% dry weight)	Reference
Neochloris oleoabundans	*Chlorophyta*	29–65	[57,74]
Chlorella protothecoides	*Chlorophyta*	14–57.8	[57,75]
Botryococcus braunii	*Chlorophyta*	25–80	[76,77]
Chlorella vulgaris	*Chlorophyta*	5–58	[57,78]
Nannochloropsis salina	*Ochrophyta*	22	[77]

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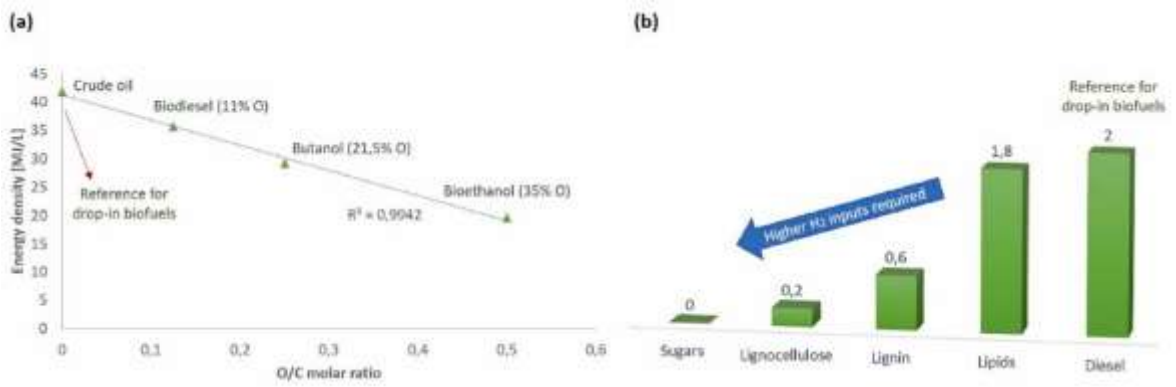
Fig. 1.



a) Effect of O/C ratio on the energy density of a biofuel. b) Effective H/C ratio for fractions contained in biomass. Adapted from Karatzos et al., 2014 [23]

Table 3 *Carbohydrate content (% DW) in different microalgal and cyanobacteria species.*

Microalgal species	Phylum	Carbohydrate content (% dry weight)	Reference
Chlorella vulgaris	*Chlorophyta*	9	[83]
Tetraselmis sp.	*Chlorophyta*	24	[84]
Scenedesmus obliquus	*Chlorophyta*	46.6	[65]
Spirulina sp.	*Cyanobacteria*	20	[83]
Nannochloropsis sp.	*Ochrophyta*	15–50	[85]
Porphyridium cruentum	*Rhodophyta*	40	[83]

In large-scale cultures, continuous process mode is commonly applied. Besides, natural light is preferred to artificial illumination in order to improve economics. However, the geographical location, sunshine duration, and the desired metabolite production also influence the choice of the light source. Two main strategies are preferred: open- ponds, which are open to the outside environment, and photobioreactors, which are closed systems isolating the algal cells from the outside environment [89,90].

Different types of open-ponds systems have been studied, including shallow ponds, tanks, circular ponds and raceway ponds [86]. Raceway pond is the most commonly used system for third generation biofuel production since it features relatively high biomass productivity and low cost (Fig. 2) [91,92].

Raceway ponds are artificial pools with an oval shape in which the microalgae are continuously circulating in a closed loop like an automotive raceway circuit. Current flow is permanently maintained by a paddlewheel to avoid cell sedimentation and driven by baffles around bends [63]. Fresh medium and nutrients are supplied exclusively during the day, below the paddle wheel to ensure their entry into the loop. During the night, about 25% of the biomass produced can be lost due to respiration metabolism. This percentage depends on light intensity and temperature during the day, as well as temperature at night [63]. Harvesting is performed upstream of the paddlewheel before the algae return to the circulation loop. In order to improve photosynthetic yield, CO_2 may be sparged from the bottom of the raceway pond, to increase the dissolved carbon dioxide

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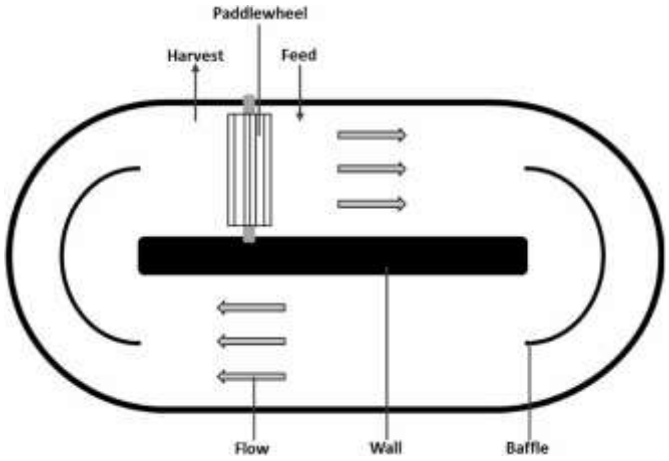
concentration in the water [63,93,94]. Furthermore, to obtain a high biomass productivity in a dense culture broth, raceway pond depth is generally ranged between 10 and 40 cm to ensure maximum sunlight uptake by the microalgae [95].

Fig. 2. *Schematic aerial view of a raceway pond. Adapted from Chisti (2007) [63].*



Nevertheless, biomass productivity may be affected by water losses through evaporation, CO_2 losses to the atmosphere during cell respiration (mostly during the night) [73], damage to the photosynthetic apparatus due to photoinhibition and low control on contamination by other microalgae or microorganisms [96]. Because of contamination issues, extremophile microalgae are widely preferred in open-pond cultures. For instance, *Arthrospira platensis* is well adapted to high pH [97]. *Dunaliella salina* cultures are capable of growing in highly saline environments [98,99].

On the other hand, photobioreactors involve higher capital and operation costs, but offer higher biomass productivity than open-ponds. This is the result of strict control on culture conditions such as temperature, pH, dissolved CO_2 and nutrients availability, which can be optimized depending on the cultivated strain [57,99–101].

A typical configuration for a photobioreactor is presented in Fig. 3. They have a set of horizontal transparent tubes, called solar collector, which main goal is to ensure the best sunlight exposure. Helicoidal tubes fixed vertically on a supporting frame also exist but are less interesting for biofuel production as they have a lower biomass productivity [63]. To maximize land surface, tubes may be oriented in parallel to each other and to the ground, in a fence-wise position [63]. Tube diameters should be limited to 20 cm to ensure photosynthetic efficiency and thus biomass productivity [102,103].

Since photobioreactors are isolated from the outside environment, gas transfer is not possible through the solar collector tubes, leading to a dissolved oxygen accumulation during the light phase of photosynthesis. High oxygen concentrations may inhibit photosynthesis and reduce productivity through oxidative damage in excess of solar radiation [103, 105]. Therefore, the degassing column provides gas exchange with the atmosphere to evacuate the dissolved oxygen accumulated in the medium [63]. The degassing column can also be equipped with a carbon dioxide supply in order to improve photosynthetic efficiency, with caution of detrimental raises in pH [106]. Optimizing

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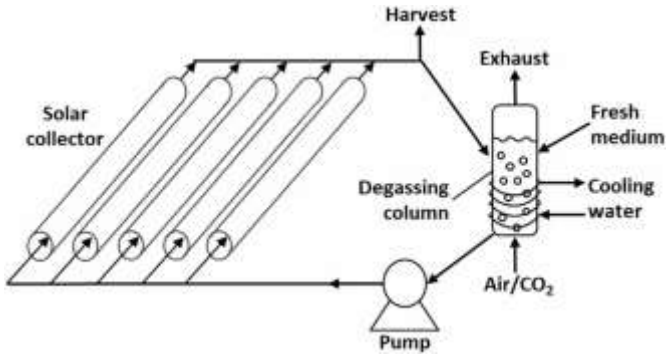
simultaneously the light and CO_2 assimilation would increase the productivity, the biomass concentration and the lipid content [107].

The temperature can be controlled by a heat exchanger located next to the degassing column, which could be expensive but reduces biomass loss, especially due to respiration at night [108]. Photobioreactors are also equipped with a pump in order to maintain a constant flow to prevent sedimentation and to allow microalgae circulation through the different parts of the system. Mechanical pumps are easier to operate but they can damage biomass and reduce productivity [109–111]. To avoid excessive mechanical stress on the cells, it is also possible to maintain flow with air-lift pumps, which are more expensive and complicated to design, but have been promising [112,113]. As in open ponds, nutrients are supplied during the day before the entry of the medium in the solar collector tubes, while biomass is harvested just after passing through these tubes (Fig. 3) [63].

Fig. 3. *Schematic view of a tubular photobioreactor. Adapted from Chisti 2008 [104].*



In raceway ponds, dry weight biomass productivity are between 0.03 $gDW.L^{-1}.day^{-1}$ and 0.2 $gDW.L^{-1}.day^{-1}$ [114]. Conversely, in enclosed photobioreactors biomass productivity range between 0.05 and 1.5 $gDW.L^{-1}.day^{-1}$ [99,114]. Nevertheless, high energy consumption and expensive installation and maintenance costs make photobioreactors less interesting than raceway ponds for biofuel production [88].

In addition to the conventional suspended cultivation, attached cultivation systems are being proposed as an option to facilitate the large-scale implementation of microalgae-based biofuels. In this approach, biofilms of microalgae adhere to the surface of a supporting material, where they grow provided they remain in contact with the culture media, a light source and carbon dioxide. However, the attachment mechanisms will vary depending on the microalgal strains and the distinct solid matrices, which cluster most of the current research [115]. Among the proposed bioreactors for this type of cultivation, fixed beds are the most promising. If designed appropriately, they would increase efficiency and productivity, by optimizing the CO_2 mass transfer, and the nutrients and light uptakes [115,116]. Crucial parameters such as the film and medium thickness, and the support design and disposition would avoid photo-limitation, photo-inhibition and pressure built-ups. A culture medium depth between 0.5 and 3 cm is advised, while the solid supports must be reusable, not expensive and efficient. Pressure built ups can be handled by hydraulically flowing the packing out of the column at the end of the growing phase, simplifying the scrapping of the biofilm [115,116].

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3.3. HARVESTING TECHNIQUES

Another challenge to microalgae-based biofuel production lies in the downstream process [88]. Harvesting is a real challenge for biofuels to be cost-efficient and represents 20%–30% of the total production costs [117]. Most commonly used harvesting techniques include flocculation, flotation, sedimentation, filtration and centrifugation. A qualitative comparison is proposed in Fig. 4, based on data analyzed from the literature [99,118–120]. Both filtration and centrifugation render high recovery efficiencies and can process large volumes of culture, crucial for an industrial application. Notably, filtration offers the flexibility of employing adaptable membranes in terms of pores diameter and size, which represents an advantage when processing different microalgal strains. However, operational costs could increase because of filter clogging and vacuum pressures (when needed). Centrifugation, on the other hand, seems to be the best harvesting operation for dewatering, but it is energy intensive which contributes to its significant cost [119, 120].

Flocculation requires the use of flocculant agents to create aggregates of cells which are then removed from the culture. Chemical agents (often metallic salts) or bio-flocculants are frequently employed; the formers carry the drawbacks of being toxic and must be considered for wastewater treatment, albeit very efficient, while bio-flocculants are not necessarily expensive and they do not impose a purification step afterwards [119]. Flotation is based on the capture of algal cells into gas bubbles, which are then collected in the surface of a tank for an easy harvesting. This allows a high throughput of the slurry for the biomass conversion processes. Nevertheless, the gas bubbles are often generated by energy consuming systems, such as dissolved or dispersed air equipment, or electrolytic cells, which decreases the appeal of an industrial scalability [119,120]. Sedimentation by gravity is reported to be the cheapest and easiest harvesting technique, but it is also the underperformer between common operations, and its long-associated times end-up by undermining this alternative for mass production. Furthermore, cells can suffer from deterioration during these long sedimentation times [120].

Harvest in photobioreactors is more efficient in terms of recovered biomass per volume and biomass concentration, as reported from Molina Grima et al. [117]. In addition, because water does not suffer evaporation inside enclosed photobioreactors, large quantities of water can be recycled to recreate the fresh medium [63,99].

All of the above-mentioned techniques have their advantages and drawbacks, and they are not suitable for every microalgal strain. In consequence, the selection and optimization of the selected method (or methods, if combined) must be based primarily on the application for the microalgal biomass, process economy and industrial scalability [120].

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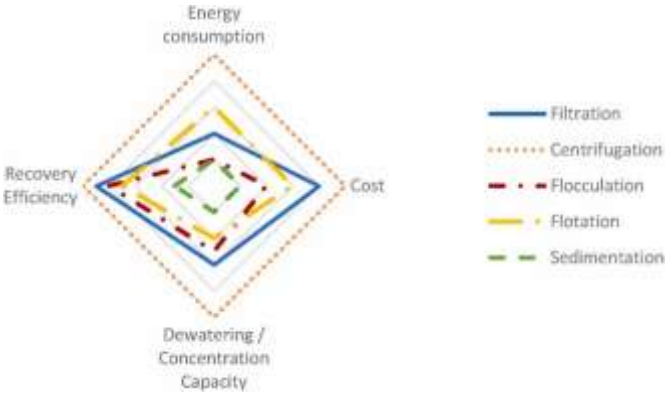
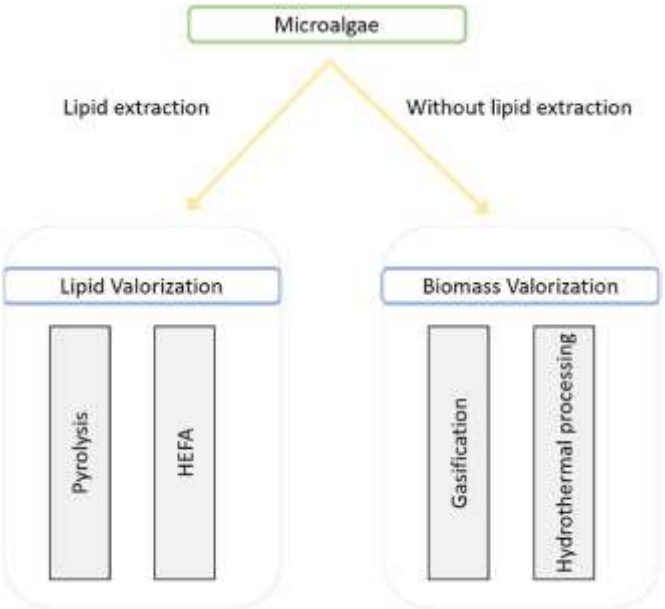
Fig. 4. *Comparison of some harvesting techniques. Generated referring to Chen et al., 2011 [118], Esteves et al., 2020 [120] and Tan et al., 2020 [119].*



4. Thermochemical conversion pathways

Thermochemical pathways have been the focus of the research and development of drop-in biofuels using microalgae as feedstock, given the advantages of exploiting either the entire microalgal biomass or an extracted lipid fraction. In fact, valorization of lipids is very attractive thanks to their high effective hydrogen to carbon ratio (Fig. 1b) and low oxygen content (1–2%) [23,121] In consequence, this review covers pyrolysis, hydro-processed esters and fatty acids (HEFA), gasification, and hydrothermal processing as promising technologies for drop-in biojet fuel production. Fig. 5 shows a suggested distribution of these processes based on their optimization (refer to each section for more information).

Fig. 5. *Microalgae thermochemical conversion pathways to bio-jet fuels.*



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4.1. PYROLYSIS

Microalgae oil is abundant in aliphatic structures [122]. The native distribution of fatty acid chain lengths in microalgae oil yields diesel-range alkanes [123], which have boiling points near or higher than the high temperature limit required for both commercial and military jet fuels [124,125]. When considering the lower temperature limit, the product will have a freezing point higher than − 40 °C and − 47 °C specified on Jet-A and JP-8 requirements, respectively. These limitations lead to the necessity of upgrading microalgae oil to meet the desired physical properties of jet fuel (e.g., freezing point and flash point). Pyrolysis, as a rising technology adopted in converting vegetable oils and waste cooking oils, has the potential of thermochemically upgrading microalgae oil to jet fuel.

4.1.1. General reaction mechanism

Pyrolysis removes oxygen in triglycerides or fatty acids and cracks primary products to hydrocarbons of different types and carbon lengths [122]. Deoxygenation can occur via multiple exothermic reaction pathways [126–128]. Decarboxylation (Eq. 2) or decarbonylation (Eq. 3), where oxygen is lost in the form of CO_2 and CO respectively, can both proceed in either the absence or presence of hydrogen. The resulting hydrocarbons, alkanes and alkenes, respectively, contain one carbon atom less than that present in the original fatty acid [129]. If H_2 is not present, alkenes can also be formed from unsaturated fatty acid chains due to the lack of hydrogenation reactions [123]. In comparison, hydrodeoxygenation (Eq. 4), where oxygen is removed as H_2O, produces alkanes with the same number of carbon atoms as in the original fatty acid. Therefore, carbon chain length of the resulting alkanes/alkenes can be used to judge the deoxygenation mechanism. Heavy hydrocarbons produced from the deoxygenation process undergo a set of reactions to generate hydrocarbon fuels of different properties (Fig. 6), in which process linear hydrocarbons can oligomerize and then undergo cyclization and aromatization [130]. The latter process leads to naphthalene and alkylbenzenes which are precursors to coke formation [131]. Selectivity towards reaction type and the extent of each reaction depend on the catalyst properties and reaction conditions [132,133]. It is noted that hydrodeoxygenation requires excess hydrogen [134]. The high cost associated with it hinders the application of this process [135]. As a result, deoxygenation process with absence or less consumption of hydrogen has been investigated [132,133,136–139].

Eq. 2

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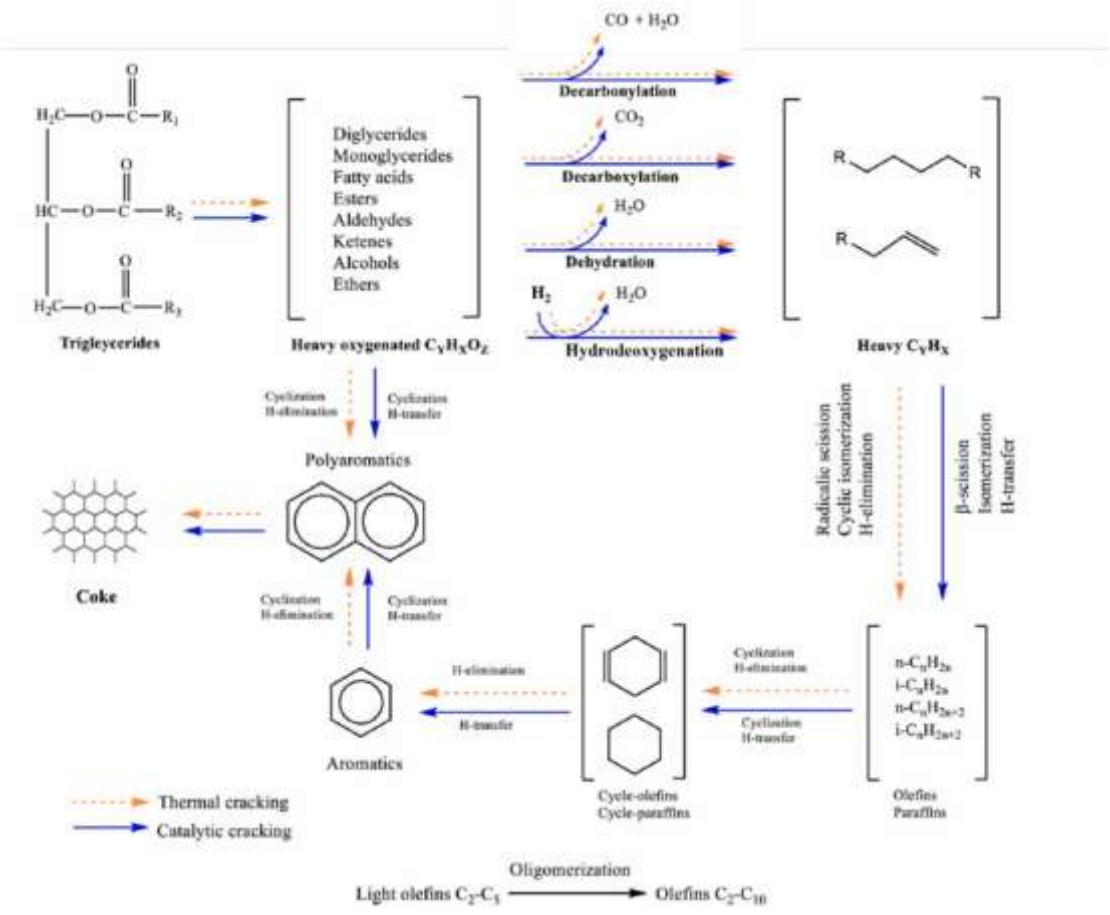
Fig. 6. *General proposed reaction pathway of converting vegetable oils into biofuels (modified from Naji et al., 2021) [131]*



Eq. 3

Eq. 4

4.1.2. Catalytic pyrolysis of model fatty acids

Palmitic acid and stearic acid are often selected as model saturated fatty acids because of their natural presence in vegetable oils and microalgae oil, while oleic and linoleic acid are selected as model monounsaturated and polyunsaturated fatty acids (PUFA), respectively [140–144]. In general, saturated fatty acid pyrolysis can proceed via two routes: i) removal of oxygen through hydrodeoxygenation, decarboxylation, or decarbonylation, followed by cracking and isomerization to shorter alkanes and alkenes, ii) direct cracking of the acids to shorter-chain fatty acids and

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hydrocarbons; the resulting acids are further deoxygenated to hydrocarbons. Details of these two routes are plotted in Fig. 7 [145,146].

The catalytic pyrolysis pathways of oleic acid are summarized in Fig. 8 [147,148]. When hydrogen supply is sufficient, i.e., catalytic pyrolysis with an external source of hydrogen, oleic acid can be hydrogenated to stearic acid where oxygen is sequentially eliminated to form either heptadecane or octadecane. If deoxygenation occurs without an external hydrogen source, alkenes, comprised of 8-heptadecene and 1,8-heptadecadiene, will be dominantly produced through a combination of decarboxylation and decarbonylation reactions as oleic acid remains unsaturated [148–151]. Pyrolysis of PUFA partially overlaps with that of monounsaturated fatty acids. Linoleic acid can be analogously hydrogenated from di-to mono-unsaturated acid and saturated acid, i.e., stearic acid [147]. The hydrogenated products further crack into hydrocarbons following the pathways summarized in the current section. Even without hydrogen addition, hydrogenation of PUFA might still take place. Some authors have reported *in situ* generation of hydrogen during catalytic pyrolysis [148,152]. Cyclization and aromatization processes that respectively form cyclic and aromatic products from linear hydrocarbons during catalytic pyrolysis are significant contributors to *in situ* hydrogen generation, along with hydrogen generated from the water gas shift reaction [153,154].

A summary of some studies where catalytic pyrolysis was performed without an external hydrogen source is shown in Table 4. It is reported that temperature has the greatest impact on product fractions [132,136, 137]. At a higher temperature, pyrolytic products contains a higher content of non-condensable gases (C_1–C_5, H_2, CO, and CO_2) and a shift from predominantly C_{18} to C_{43} hydrocarbons to C_7 to C_{12} in the liquid phase due to a more intensive cracking of large molecules [132]. In addition, the conversion of feedstock appears to get higher as temperature increases [136]. Despite the advantages of higher conversion and hydrocarbon content in the jet fuel range, one risk of conducting catalytic pyrolysis at higher temperatures is the conversion of linear hydrocarbons to aromatic compounds, the level of which is required to be lower than 25% in jet fuel [45,131,136]. Polymerization of aromatics can cover the surface of a catalyst and block the pores, consequently, producing coke as a by-product [155].

Different catalysts have been reported to improve the quality of pyrolysis products. Heterogeneous catalysts, generally supported by metal catalysts, are easier to separate compared to homogenous catalysts, complementary to the fact that they show higher thermal stability. Amongst metallic catalysts, palladium and platinum seem to be promising due to not only their high conversion and selectivity towards deoxygenation products, but also their ability to hydrogenate PUFA in the presence of hydrogen [156,157]. Carbon supports have been reported as the best for these metals when decarboxylation is preferred [156–158], although zeolites are an interesting alternative because they are inexpensive and environmentally friendly [159,160]. They offer high catalyst activity owing to their chemical composition, ion-exchange capacity, generous surface area and porosity [161].

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4.1.3. NON-CATALYTIC PYROLYSIS (THERMAL PYROLYSIS)

Non-catalytic pyrolysis thermally degrades lipid feedstock by heat generally between 300 and 500 °C [163] into alkanes, alkenes, alkadienes, carboxylic acids, aromatics, and small amounts of gaseous products [164,165]. The feasibility of applying this technology in producing renewable fuels from lipid-based feedstock has been widely studied [164,166–173]. The detailed reaction mechanisms are difficult to characterize because of the complexity and multiplicity of reaction pathways and products, but they are influenced by reaction conditions, such as temperature, residence time, and the presence of other gases in the system [174,175]. A primary cracking has been proposed where fatty acids are formed during the thermal cracking of triglycerides by breakdown of C–O bonds between the portion that corresponds to the glycerol and the rest of the molecule, followed by a secondary cracking where fatty acids break down into smaller hydrocarbons [176,177]. The glycerol backbone of triglycerides decomposes to low molecular weight gaseous products, such as propane [176]. The presence of unsaturation in fatty acid chains enhances cracking in the proximity of C⁻C bonds [176,178]. This explains the simultaneous C–C bond cracking in oleic acid with deoxygenation, which was not reported in stearic acid pyrolysis [169,172]. Linoleic acid has two double bonds at ω-9 and ω-6 positions (rather than one in oleic acid), and a portion of ω-6 bonds is reported to crack producing light alkanes that end up in the generation of non-condensable gas phase products [179].

Reaction temperature, typically leads to an increase in gas yield due to over-cracking and an increase in solid formation due to polymerization and/or aromatization as temperature rises; as a consequence, liquid yield drops [136,168,175]. In contrast, an increase in the residence time at an optimal temperature does not necessarily lead to over-cracking, but to a polymerization of low molecular weight species into liquid [168]. This implies that competition exists between cracking into non-condensable gases and condensation of low molecular weight species into liquid, which is sensitive to reaction conditions. To optimize cracking without over-cracking the feedstock, a single-pass reactor operation have been suggested, which offers the opportunity of reducing capital and operating costs [168].

Fig. 7. *General reaction pathway of catalytic pyrolysis of palmitic acid and stearic acid. Generated referring to Liu et al., 2015 [145] and Amber and Kamal, 2019 [146].*

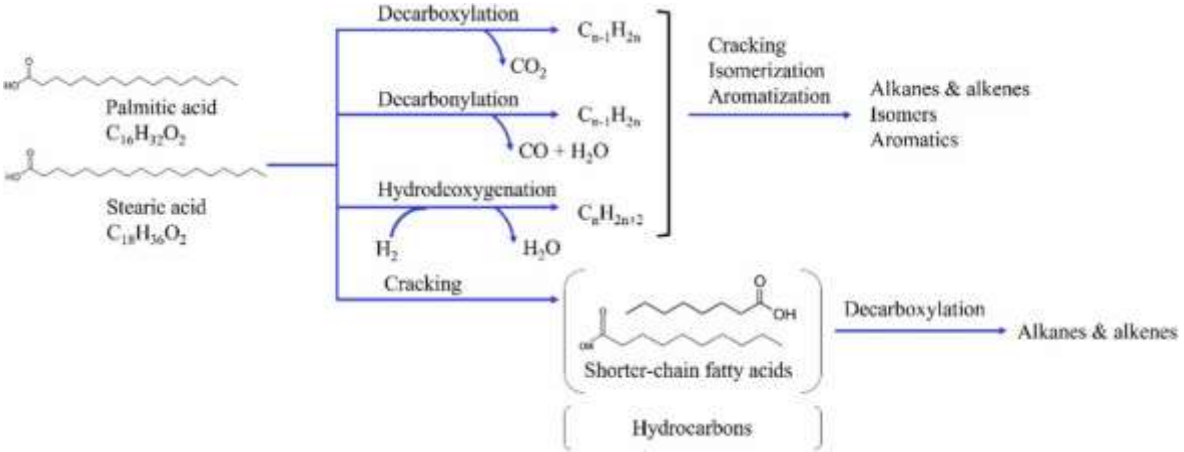

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Fig. 8. *General reaction pathway of catalytic pyrolysis of oleic acid. Generated referring to Snåre et al., 2008 [147]; Krobkrong et al., 2018 [148].*

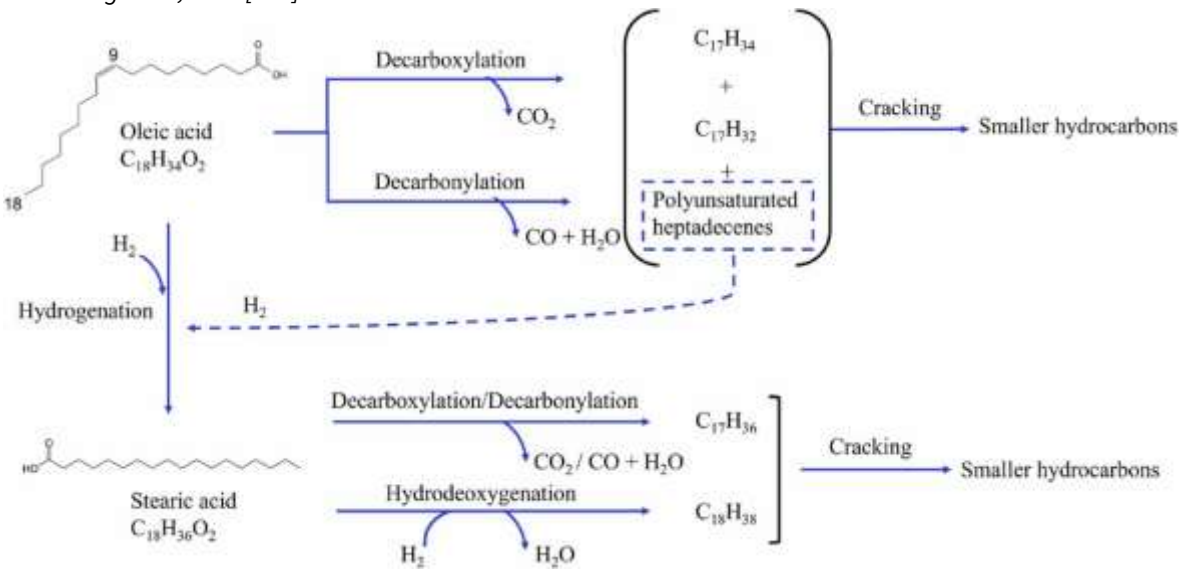

Table 4 *Summary of some catalytic pyrolysis reactions to produce jet fuel without the use of hydrogen.*

Feedstock	Reactor	T (°C)	Catalyst	Yield (wt%)	Reference
Non-edible sunflower oil	Fixed bed reactor	550 °C	ZSM-5	30.1% (hydrocarbon fuel)	[132]
Soybean oil	Benchtop reactor	350–450 °C	Na2CO3	40% (jet fuel range)	[136]
		350 °C	HZSM-5		
		200 °C, 6 MPa	Pd/AC		
Soybean oil	Flow reactor	360–450 °C	ZSM-5	21% (jet fuel range)	[162]
Non-edible waste oil	Single step reactor	270 °C	Pb/beta-zeolite	31% (jet fuel range)	[137]
Waste oil	Batch reactor	300–450 °C	CaO–Na_2CO_3-ZSM-5	42.59% (jet fuel range)	[138]
Non-edible camelina oil	Fixed bed reactor	500 °C	Zn/ZSM-5	19.56% (hydrocarbon fuel)	[132]
Stearic acid	Semi-batch reactor	300 °C, 0.6 MPa	Ni/Cr_2O_3	12% Conversion, 60% Selectivity (hydrocarbon fuel)	[156]
Stearic acid	Semi-batch reactor	300 °C, 0.6 MPa	Pd/C	Complete conversion and 95% Selectivity (alkanes)	[156]
Stearic acid	Semi-batch reactor	300 °C, 0.6 MPa	Pt/C	86% Conversion and 87% Selectivity (alkanes)	[156]

Table 5 *Advantages and disadvantages of catalytic and non-catalytic pyrolysis.*

	Advantages	Disadvantages
Catalytic Pyrolysis	Higher selectivity towards desired product	Expensive and complicated process
	Higher liquid product yield	High requirements for catalyst and feedstock
Non-catalytic Pyrolysis	Simple and fast	Lower selectivity towards desired product
	No requirement for hydrogen and/or catalyst	Lower liquid product yield
	Various feedstock options	

4.1.4. Opportunities and challenges of catalytic and non-catalytic pyrolysis in jet fuel production

The advantages and disadvantages of catalytic and non-catalytic pyrolysis are tabulated in Table 5. Compared to catalytic pyrolysis, non-catalytic pyrolysis has received attention because of its simplicity and speed [180], requiring no hydrogen and being able to perform under atmospheric

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pressure [132]. It also allows flexible usage of various renewable sources of low water content, as opposed to refined oil for catalytic pyrolysis [181,182]. In fact, catalytic pyrolysis uses expensive catalysts applying strict acceptance limits and quality standards to feedstock in order to avoid catalyst deactivation [174]. Because of this limitation, catalytic pyrolysis generally does not process low quality lipids, such as microalgae oil or waste cooking oil [183,184].

However, the selectivity of non-catalytic pyrolysis towards the desired products is lower unless reaction conditions are optimized [168, 185]. Its liquid yield is relatively low due to incomplete cracking or over cracking [145,164]. When cracking is insufficient, the organic liquid phase still contains fatty acids increasing the acid value and consequently lowering the quality of the fuel [163,167]. Regardless of the advantages and disadvantages, both technologies provide value to process economy in a way by which heavy distillation residue from the crude liquid product can be reused [132].

In addition to the advantages mentioned above, non-catalytic pyrolysis of lipid feedstock allows multivariable method modifications, that is, large ranges of temperatures, residence times, flow rates, and pressures can be examined for optimization. The promising result of improving cracking without over-cracking the feedstock to produce more gas points toward increased single-pass reactor conversion efficiency, which offers the opportunity of reducing size and operating costs [168]. Evidence from the study conducted by Kubatov´ a and co-workers ´ indicates that the ratio of n-alkanes to branched alkanes is different from that of linear alkenes to branched alkenes, which is attributed to the different stabilization pathways alkyl radicals proceed. They further discussed the necessity of optimizing temperature with the purpose of balancing between kinetic and thermodynamical control – for reasons that they affect radical reaction mechanisms. Based on the results from previous studies, there is a potential for applying non-catalytic pyrolysis in jet fuel production. However, thorough optimization is needed before the process can be commercialized [176].

4.2. HYDRO-PROCESSED ESTERS AND FATTY ACIDS (HEFA) PRODUCTION

The HEFA fuel production process is the most commercial drop-in biofuel to date, with a production of more than 4 billion liters/year [52]. This process fulfills the challenges of microalgal lipids described in previous sections and the resultant jet fuels show high cold flow properties, making them suitable for high altitude flights [186,187]. The classical HEFA approach is based on hydrotreating. In excess of hydrogen, hydrodeoxygenation and hydrogenation reactions occur releasing water and saturating double bonds of unsaturated fatty acids (Fig. 9) [23]. This reaction pathway is preferable because both decarboxylation and decarbonylation consumes one carbon to remove oxygen. Hydrodeoxygenation reaction takes place between 280 and 340 ˚C and 50–100 bar depending on the composition of fatty acids in oil [188]. The linear chain alkanes can then undergo hydrocracking and isomerization steps (Fig. 9). The chemical composition of the molecule is preserved but physical properties are modified, making them more suitable for aviation applications [17].

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A lot of research and development of catalysts have been carried out on vegetable oils or model fatty acids since the emergence of this technology. A series of metal-based catalysts can be exploited to improve the reactions happening during the HEFA process. Molybdenum nitride supported on alumina was found to be superior to vanadium and tungsten nitrites at 380–410 °C and 70 bar H_2, according to Monnier and coworkers, given its high selectivity for hydrodeoxygenation instead of decarboxylation or decarbonylation [189]. Yang et al. studied the hydrotreating of oleic acid in a fixed bed reactor with a Ni–W/SiO_2–Al_2O_3 catalyst, finding that the yield of hydrocarbon production inside the jet fuel range decreased as temperature rose above 300 °C. Lower temperatures promoted the formation of iso-paraffins [190]. Similarly, Ayandiran et al. studied the potential of copper and iron-based catalysts supported on aluminosilicate. When operating at 300 °C and 20 bar of H_2 pressure, they demonstrated that yield and selectivity could be improved from 59.5% to 73.6% [191] to 71.7% and 76.8%, respectively, when promoting the catalyst with 1%wt of tin [192]. Finally, Xing et al. evaluated the hydro-processing of a mixture of fatty acids over Ni/HZSM-5, which included hydrogenation, hydrocracking and aromatization via the Diels-Alder reactions [193]. They observed that Ni nanoparticles served as active sites for aromatization reactions, with approximately 64% aromatic produced at 360 °C and 40 bar H_2 with a 10% wt loading of Ni. Overall, the choice of the active metal catalyst (and its loading) will affect the yield and the selectivity of the hydrocarbons generated, which have to be taken in consideration in the process development of drop-in biojet fuels and biofuels in general.

The ASTM group approved in 2011 the HEFA process, allowing hydro-processed esters and vegetable oils to be blended with conventional jet fuel [186]. A summary of the known industrial HEFA production facilities and their capacities is shown in Table 6, with Neste oil being the highest producer, to the best of our knowledge [194].

The main drawback of this promising technology is the high dependence on hydrogen. Hydrogen is already industrially consumed in petroleum refining process for the hydrodesulfurization of crude oil and cracking and is often produced from fossil fuels [23]. However, researchers have been working on the development of alternative hydrogen production from renewable feedstocks, which have been already reviewed by our group [195].

Table 6. *World production capacity of HEFA from the IEA Bioenergy Task 39 Demonstration plant database (Values were converted using a density of 0.837 kg/L).*

Company	Feedstock	Billion L/y
Neste	mixed	2.37
Diamond Green Diesel	tallow	0.49
REG Geismar	Tallow	0.27
Preem Petroleum	Tall oil	0.02
UPM biofuels	Tall oil	0.12
ENI	Soy & other oils	0.59
Cepsa	Unknown	0.12
AltAir Fuels	Mixed	0.14
World total		4.12

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Table 7. *Chemical reactions happening during gasification.*

Gasification	
CH_xO_y(***biomass***)+ O_2 + H_2O (***steam***)⇌CH_4 + ***CO***+ CO_2 + H_2 +H_2O (***residual steam***)+ ***C***(***Char***) + ***tar***	
Gas-solid phase	
$C+\frac{1}{2}O_2 \rightleftharpoons CO$	Carbon-oxygen reaction $\Delta H = -110.5$ *MJ/kmol*
$C+CO_2 \rightleftharpoons 2CO$	Boudouard reaction $\Delta H = 172.4$ *MJ/kmol*
$C+H_2O \rightleftharpoons H_2+CO$	Carbon-water reaction $\Delta H = 131.3$ *MJ/kmol*
$C+2H_2 \rightleftharpoons CH_4$	Hydrogenation reaction $\Delta H = -74.8$ *MJ/kmol*
Gas phase	
$CO+H_2O \rightleftharpoons H_2+CO_2$	Water gas shift reaction $\Delta H = -41.1$ *MJ/kmol*
$CO+3H_2 \rightleftharpoons CH_4+H_2O$	Methanation $\Delta H = -206$ *MJ/kmol*
$CH_4+H_2O \rightleftharpoons CO+3H_2$	Steam reforming $\Delta H = 206$ *MJ/kmol*

Fig. 9. *Simplified hydro-processed esters and fatty acids (HEFA) into biofuels production process; 1) Hydrodeoxygenation and hydrogenation; 2) Hydrocracking and isomerization of long chain hydrocarbon into suitable biofuels (based on Karatzos et al., 2014) [23].*

4.3. GASIFICATION

Gasification is another type of thermochemical process using high temperatures (600–1000 °C) in the presence of a gasifying agent to convert biomass to syngas, a mixture of CO, H_2, CH_4, light hydrocarbons, and CO_2. Gasifying agents are oxidizing substances such as air, oxygen, steam or carbon dioxide [196,197]. Syngas can be used in specific engines or turbines to generate heat and electricity, but can also be converted to liquid transportation fuels via the Fischer-Tropsch process or hydrogen consumption [198]. An oxygen-deficient medium is generated in the gasifiers, allowing gas phase and solid phase reactions to happen (Table 7) [199]. Fixed bed (updraft and downdraft) and fluidized bed reactors are the two main types of gasifiers having both advantages and disadvantages well summarized by Warnecke [200]. Biomass composition and gasifying agents can also generate organic and inorganic impurities such as tar, alkali metals, H_2S, HCl, or NH_3 in different proportions [195,201].

Classical biomass gasification can be divided in four main steps [52, 199]:

- *Drying* (<125 °C) refers to the loss of water. Moisture (10–60%) is
- converted to steam that can itself serve as gasifying agent.
- *Pyrolysis* (125–500 °C), following some of the mechanisms discussed in Section 4.1. After this step, 80% of the biomass feed is converted to vapors or gas leaving behind fractions from incomplete conversion of biomass like tar and biochar (a solid carbonaceous powder material) [197,199]. Drying and pyrolysis are essential pre-steps of biomass gasification [202].

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- *Gas-solid reactions* (>500 °C). Biochar reacts with oxygen, steam or gases released during pyrolysis producing hydrogen [195]. Gas-solid reactions include the carbon-oxygen, Boudouard and carbon-water reactions, and the hydrogenation of the solid carbon matter, enriching syngas (Table 7). Exothermic reactions will play an important role of heat supply to drive the endothermic reactions in the system. However, the degree of contribution of the exothermic reactions will depend on the concentration of the gaseous compounds. Heat transfer limitations between gas and solid compounds makes equilibrium state not reachable [199].
- *Gas-phase reactions* contribute to the enrichment of the syngas, specially the steam reforming and the water gas shift reactions. The latter is favored at low temperature due to its exothermicity. Each gas-phase reaction can be favored via the Le Chatelier principle by adding steam in the system and increasing partial pressure of hydrogen [199].

Although syngas can be used for similar applications as natural gas, the difference in energy density (4–18 MJ/Nm^3 and 36 MJ/Nm^3, respectively) is quite high, because syngas still features a high oxygen content. The potential of syngas for liquid biofuels applications is measured by its H_2/CO ratio: higher ratios indicate higher energy density [52]. However, H_2/CO ratio can be modified by feeding steam or hydrogen to the system. Steam initiates water gas shift reactions while hydrogen will generate a syngas rich in CH_4, a suitable composition for synthetic natural gas [199].

A series of parameters affect the set of reactions happening during gasification. Gas yield can be increased by decreasing the particle size [195,203], increasing temperature [197] and residence time [204], or avoiding overfeeding or starve-feeding. Char and tar content can be decreased with smaller granulometry [205] or by using very high temperature (>1000 °C) [199]. Steam to biomass ratio (S/B) measures the supply of steam as a gasifying agent in the system, impacting both solid-gas phase and gas phase reactions alike [197]. High S/B also reduce tar during gasification. Utilization of catalysts enrich syngas composition with hydrogen and carbon monoxide for their further processing into hydrocarbons by the Fischer-Tropsch process and some of them can decrease the tar content. Ni-based catalysts, alkaline metal oxides, olivine and dolomites are catalysts generally used for gasification [196,206,207].

4.4. HYDROTHERMAL PROCESSING

Hydrothermal technology is defined as a thermochemical process performed at high temperature (180–750 °C) and high pressure (5–40 MPa) where water can be in a sub- or a super-critical state [208,209]. It consumes biomass in a heated, pressurized and oxygen-free reactor in a water media where biopolymers undergo chemical transformations including hydrolysis, depolymerization, pyrolysis, condensation, reforming and gasification to produce biofuels [210,211]. Based on the primary products, three different regions delimited by a range of temperature and pressure characterize hydrothermal processing [212,213]:

- *Hydrothermal carbonization* (HTC) from 180 to 250 °C and 2–10 MPa, where biomass is converted into solid fuels.

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- *Hydrothermal liquefaction* (HTL) between 250 °C and 375 °C and 5–35 MPa, generating a bio-oil.
- *Hydrothermal Gasification (HTG)* above the critical point of water (374 °C and 22 MPa) producing syngas.

The advantage of hydrothermal processing is that wet biomass (>10%wt) can be exploited, contrary to other methods such as pyrolysis and classical gasification. The moisture content in microalgal biomass is approximately 80–90%, making this biomass suitable for hydrothermal processing [214]. Beyond the advantage of using wet biomass, sub-critical or supercritical water treatment allows the use of water as a reactant, solvent, and catalyst [215].

Increasing temperature and pressure of water radically changes its physical and chemical properties, as shown in Table 8. In the sub-critical state, below the critical point (Fig. 10), the ionization constant of water ($Kw=(H^+).(OH^-)$) increases. Higher concentrations of H^+ and OH^- ions are present in the media for hydrolysis or basic reactions to happen [209]. Liquid water in its subcritical state also decreases both its density and dielectric constant, two critical parameters affecting the miscibility of a solvent having the ability to dissolve both non-polar and polar compounds [216]. Above its critical point, both density and dielectric constant significantly decrease [209]. Ionization of water in those specific conditions is inhibited, supported by the very low ionization constant ($Kw = 10^{-20}$), promoting the occurrence of free radical reactions, appropriate for hydrothermal gasification (>375 °C) [208]. Affected classical properties of water change the chemical reactions happening during sub- or supercritical water treatment compared to pyrolysis.

4.4.1. Hydrothermal liquefaction (HTL)

Performing HTL on microalgae generates a main product called bio- oil, which is water-insoluble and features an energy density close to that of fossil-based oils. Along with this product, it also generates: (i) an aqueous phase, containing some residual nutrients from the microalgae culture; (ii) a solid fraction constituted mainly by ashes and traces of hydrogen, nitrogen and sulfur and (iii) a gas phase with light gases such as CO_2, CO, H_2, CH_4 and few amounts of ethylene and/or ethane [212, 213].

The properties of the bio-oil depend heavily on the feedstock quality and the production conditions. In fact, the different components present in microalgae, i.e., lipids, proteins, carbohydrates, and algaenans, undergo degradation during HTL. Under near-to-critical conditions, water promotes the decomposition of these macromolecules into smaller compounds, which then react to form the main products. Nevertheless, with temperatures above the supercritical state and/or times longer than 2 h, the products from the different phases could interact altogether leading to further decomposition, condensation or repolymerization. As a result, the bio-oil production yield might decrease, increasing the gas and/or the solid yield [213].

The complete breakdown of proteins eventually results in the formation of compounds such as phenols or nitrogenated heterocyclic hydrocarbons, which are the main source of nitrogen in the bio-oil. Carbohydrates become the principal source of oxygen as they split into organic acids,

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aldehydes, benzene and alcohols. Nonetheless, aldehydes and benzene-like compounds might repolymerize to produce larger hydrocarbons. Algaenans, on the other hand, are believed to degrade into alkanes, alkenes, and alkyl-aromatics with variable length [213].

Operating conditions are very important as they can offset even a low lipid content [213,217]. Overall, it seems that temperatures close to the critical point (300–370 °C) and short to moderate reaction times (5–30 min) enhance the bio-oil yield. By contrast, authors agree that temperatures beyond 370 °C and reaction times of 60 min or more lead to further degradation, thus dropping the product yield [213,217].

At 300 °C, the hydrolysis of lipids into free fatty acids and glycerol is promoted [212]. Several studies validate the degradation of vegetable oils, such as soybean, linseed and coconut oils, and sunflower seeds, obtaining more than 95% conversion of lipids under water at subcritical conditions [216,218–222]. Nevertheless, these fatty acids are very stable in subcritical water. This behavior has been evaluated by Shin and co-workers, observing no appreciable degradation under 370 °C. Over this point, cracking of PUFA was more frequent, possibly because of unsaturations, producing small chain carboxylic acids [223].

For drop-in biofuels production, HTL needs to be evaluated for its ability to promote deoxygenation and cracking of lipids to produce hydrocarbons, which justifies the use of catalysts. HTL of formic acid, palmitic acid, and oleic acid, without any addition of hydrogen, have proven to yield alkanes and alkenes related to decarboxylation pathways in the presence of Pd and/or Pt based-metal catalysts supported on activated carbon [224–227]. They have been shown to be the most effective catalysts for decarboxylation reactions but find economical limitations for commercialization [152,228–233]. Alternatively, the addition of base (KOH or NaOH) and metal oxide (CeO_2 and ZrO_2) catalysts investigated by Watanabe et al., both enhanced decarboxylation reactions with water at subcritical state [234]. Although decarboxylation reactions are also enhanced in sub- or super-critical water [235], development of catalysts for decarbonylation have also been developed.

Table 8 *Physical and chemical properties of water in normal, subcritical and supercritical conditions (taken from Alper, 2020) [209].*

	Normal water	Subcritical water	Supercritical water
Temperature (K)	0–373.15	373.15–647	>647
Phase	Liquid	Liquid	No phase differentiation
Density (g cm^{-3})	0.997 (298 K)	0.692 (603 K; 30 MPa)	0.252 (683 K; 30 MPa)
Dielectric constant	78.5 (298K, 0,1 MPa)	18.2 (603 K; 30 MPa)	5.9 (673 K; 25 MPa)
Ionization constant (mol^2 L^{-2})	10^{-14} (298 K)	10^{-11} (573 K)	10^{-20} (673 K)

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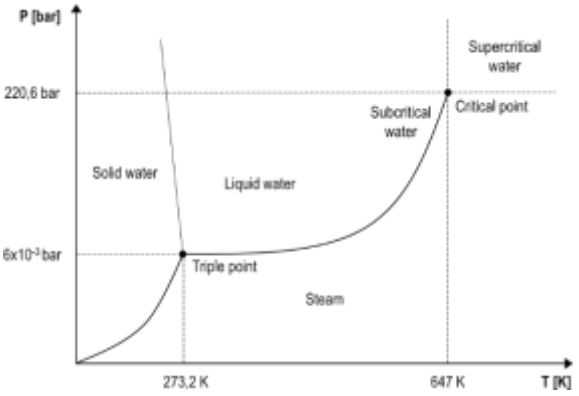
Fig. 10. *Phase diagram of water with region of interest (P° and T°) for hydrothermal liquefaction. Adapted from Hrncic et al., 2016 [215].*



4.4.2. HYDROTHERMAL GASIFICATION (HTG)

HTG is an alternative to classical biomass gasification exploiting wet biomass. It produces a fuel gas rich in CH_4 and H_2, depending on the reaction conditions. A temperature range of 350 °C–500 °C will mainly produce methane, while a temperature range of 500–800 °C will produce more hydrogen [209,236]. Water in its supercritical state acts as a solvent, gasifying agent and catalyst for gas-phase reactions like steam reforming and water gas shift reactions, enriching syngas with hydrogen [212].

Youssef et al. performed HTG of oleic acid at 400–500 °C and 250 bar for 30 min with different commercial catalysts (Ru-, Pt-, Pd-, Ni-based catalysts) [237]. In the absence of catalysts, an increase in temperature produces more hydrogen. Among the studied catalysts, Ru/Al_2O_3 activity resulted in the highest production of hydrogen. Moreover, glycerol have been widely investigated for its ability to produce hydrogen with and without the use of catalysts [236,238–247] but it will not be covered in this review.

5. Economic feasibility of thermochemically produced microalgal aviation biofuels

In this section, diverse aspects are reviewed related to the economic feasibility of microalgal aviation biofuels from thermochemical processes. Firstly, the costs related to microalgal cultivation and harvesting are the most influential parameters that limit the economic feasibility of biojet fuels, regardless of the thermochemical processing method that is considered [248–254]. Three different modes of cultivation exist: autotrophic, heterotrophic and mixotrophic [255]. Autotrophic cultivation mode is the most frequently used. However, it can result in a lower cell density and a higher harvest cost. The heterotrophic mode, on the contrary, would return higher growth rate and yield and reduce harvest costs, offsetting the additional expense on nutrients [256,257]. This seems to be the most convenient approach for large-scale applications in regions with an unreliable sunlight provision, as is the case for some European latitudes. The mixotrophic mode is currently not widely used due to the relatively lower cell density and lipid content.

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Independently of the cultivation system, an alternative to enhance the productivity and the lipids content could be a two-step cultivation, where the microalgae are first cultured towards the highest productivity and then optimized to improve the lipids content and to influence the fatty acid profile. Depending on the algal strains, lipid accumulation can be induced by creating stressing conditions compared to the optimum, such as high salinity, nitrogen or phosphorous depletion in the medium, temperature and/or pH variations and different light intensities [258]. This should not represent a considerable increase in the capital and operational costs at industrial scale, given that progressive successions of bioreactors are typically used for this sector. Nevertheless, a cost-benefit evaluation must still be conducted before considering such methodology.

Numerous techno-economic analyses (TEA) indicate that photobioreactor are more costly than open pond systems, the latter being the focus at the NREL (National Renewable Energy Laboratory) since 2008 [259–262]. Thomassen et al. (2016) concluded from their TEA that an open pond cultivation with recycling of the medium with a specialized membrane is still preferred over a photobioreactor system [263], which is also confirmed by other studies [254]. Integration of microalgae production/cultivation with wastewater treatment could help in reducing the costs of wastewater processing [260,264–266]. However, this requires additional capital costs and energy, which is currently limiting its economic feasibility [267,268]. Thin-layer cascades can be seen as an alternative to conventional open raceway ponds, having lower greenhouse gas emissions and lower costs [253,269,270].

Centrifugation is considered to be the costliest harvest method while flocculation and sedimentation are the least [118–120,255,271–273]. To extract the lipids from the microalgal cells, drying or dehydration are typically needed due to the high water content. Lin and Lu (2021) state that the dehydration process has higher capital and operational costs than the lipid extraction itself [255].

Marx et al., studied the potential of the macroalgae *Sargassum fluitans* and *natans* that bloom in the Atlantic Ocean as feedstock for HTL [274]. Due to the availability of macroalgae, there is an enormous reduction in the typically large capital (78%) and operational (66%) costs related to the cultivation/algae production. For their base case scenario, the capital (CAPEX) and operational expenditures (OPEX) of harvesting and processing were 0.84 USD/L capacity and 0.15 USD/L production respectively, which is significantly lower than the CAPEX and OPEX of land-based algae production, being 5.03 USD/L and 0.41 USD/L, respectively.

Secondly, the emphasis of published research was mainly on cultivation, HTL and HEFA. Based on the recent study of Beal et al., the price of conventional jet fuel is considered to equal 0.78 USD/L [275]. Assuming an available microalgal biomass of 51 GT/year to be treated by either HEFA or HTL process, the corresponding minimum fuel selling prices (MFSP) were 4.43 USD/L for HTL and 8.96 USD/L for HEFA [275]. These MFSP values correspond with the selling price of the fuels that yields a net present value for the facility equal to zero after 30 years. These results are also consistent with earlier assessments: Beal et al., who calculated MFSPs in the range of 2.45–3.02 USD/L for recovered biocrude [179], Jiang et al., who calculated MFSPs in the range of 1.32–4.23 USD/L for HTL [276] and Quinn and Davis who calculated MFSPs in the range of 0.53–9.25 USD/L for various scenarios [184].

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In addition, Bessette et al., studied six biofuel pathways and concluded that the combination of flash hydrolysis with HTL and mineralization for renewable jet fuel was economically the most attractive, with a break-even jet fuel selling price of 0.91 USD/L [277]. Furthermore, Klein-Marcuschamer et al., developed a simulation model in Aspen Plus based on HEFA production from *Nannochloropsis* sp., cultivated in open raceway ponds. From their analysis, a MFSP of 8.45 USD/L was calculated, with CAPEX as the biggest driver with a contribution of approximately 90% from harvesting and cultivation [278]. HTL is a promising technology, which is at low technology readiness level compared with other thermochemical methods such as pyrolysis. Further research to improve the techno-economic feasibility of this method is required [279, 280].

Thirdly, economic feasibility for pyrolysis and gasification, upgrading of bio-oil and biomass-to-liquids pathway are currently lacking and should be part of future work. The combination of gasification with Fischer-Tropsch synthesis requires substantial improvements as it is costly and energy intensive, only costs effective when operated at large scale [121]. Conversely, pyrolysis is a highly interesting technology, as its application has been proven successful on a commercial scale for petroleum-based fuels. However, drying increases the costs and limits its economic feasibility. In addition, the upgrading of the bio-oil towards aviation biofuels needs to be improved, involving the design/selection of catalysts, reduction of H_2-intake and the optimization of the deoxygenation. Moreover, the processing of bio-oil in existing, conventional refineries would also offer opportunities to improve the economic feasibility [121]. Techno-economic studies related to the upgrading of microalgal bio-oil should also be part of future work.

Finally, we want to highlight that at present there is no economically feasible microalgal aviation biofuel production on a commercial scale, despite trial and pilot microalgae plants and demonstration flights with microalgal aviation biofuels [281–285]. Moreover, to make microalgal biorefineries and advanced drop-in aviation biofuels economically feasible, the whole algal biomass needs to be valorized in an integrated biorefinery [254,286–290]. This entails the valorization of the lipid fraction to biofuels and the valorization of the so-called residual biomass into high added value coproducts (such as e.g., polyunsaturated fatty acids, carotenoids, proteins, pigments, biosorbents, nutrients and biosurfactants) [250,289]. Note that it is a high business risk for investors to invest in plants that solely focus on biofuel production due to the relatively low price of conventional aviation biofuels [288]. Moreover, particularly for aviation biofuels, properties and restrictions with respect to compliance to fuel standards are quite severe and nontrivial to meet. In summary, research on more cost-effective microalgal cultivation and harvesting, catalyst development, minimization of hydrogen consumption, process optimization, microalgal biorefinery product portfolio optimization and a cost-effective upscaling are required [251]. Geopolitical conflicts can also severely impact fossil fuel prices and consequently the competitiveness and economic viability of drop-in aviation biofuels.

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6. Upgrading strategies & perspectives

6.1. OLEFIN METATHESIS

Olefin metathesis, an important organic reaction in industry, could be a potential alternative to cracking, allowing the conversion of oil into biojet fuel [291]. Typically, olefin metathesis can be described as a reaction by which the chemical substituents located around the double bond of alkenes are exchanged [292]. The mechanism implying metal transition based-catalysts was described by Herisson and Chauvin in ´ 1970 and was confirmed by Grubbs in 2004 [293,294]. Transition metal based catalysts are exploited for olefins metathesis in the petrochemical [295,296] and polymer [297] industry, but can also be used for renewable feedstocks like unsaturated fatty acids [298].

There are different types of metathesis [294,299] but for the production of straight chain hydrocarbons included in the composition of biojet fuels, two types of olefin metathesis will be discussed: self-metathesis (SM) and cross-metathesis (CM) (Fig. 11). While during self-metathesis two identical olefins react with each other, cross-metathesis involves two different olefins [299]. Researchers have notably studied the distribution of products generated with the metathesis and of triglycerides, fatty acids or fatty esters, emphasizing important applications as plastics, waxes, lubricants, cosmetics or biofuels [300,301]. In this section, we discuss the potential of metathesis and in particular cross-metathesis as a sustainable pathway for the production of drop-in biojet fuels from microalgal oils.

6.1.1. CROSS-METATHESIS AS A NEW UPGRADING STRATEGY

This technology could be very promising to extend all the unsaturated hydrocarbons below C_6 to longer chains in order to enrich the amount of hydrocarbons in the appropriate range for bio-jet fuels [302]. Although a lot of work was achieved concerning catalyst development with the emergence of first- and second-generation Grubbs catalysts, limitations still remain concerning the prediction of the selectivity of cross-metathesis reactions [302]. From a thermodynamic point of view, the difference in stability and reactivity of the generated alkenes does not constitute a significant driving force to increase the selectivity towards the formation of one molecule in particular.

Chatterjee et al. published a categorization of olefin reactivity to predict product selectivity based on four distinct types of olefins [302]. For terminal olefins, categorized as type-1 olefins, cross-metathesis produce a mixture of non-selective products; the cross-metathesis of two type-1 olefins will lead to an equilibrium reaction between the desired cross-products (in this case, kerosene range alkenes) and homodimerized products undergoing secondary metathesis reactions. The proportion of cross-products are affected by the equivalence ratio between both original olefins (Fig. 12). However, for biofuels applications the lack of selectivity is not a major problem provided that the carbon number of the cross-products hydrocarbon chains is in the range of bio-jet fuels.

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Rouen et al. have worked on the conversion of linear α-olefins (C_5–C_8) from bio-sourced Fischer-Tropsch feeds into longer ones (C_9–C_{13}) as precursors for plasticizers and detergents [303]. Ruthenium-based catalysts with unsymmetrical N-heterocyclic carbenes (NHC) ligands achieve high activity and high metathesis selectivity [304,305]. Minimization of cross-metathesis side-products like homodimers is a key point to achieve high selectivity up to 99% [302,303]. The loss of selectivity is initiated by the formation of hydride complexes (decomposition of the metal alkylidene complex) promoting isomerization of the alkenes and secondary metathesis products [306,307]. 1, 4-benzoquinone compounds have shown effectiveness as additives during cross-metathesis to prevent olefin isomerization [308].

Note that this process would maintain an appreciable proportion of olefins in the biofuel which could compromise the properties of the resultant jet fuel, hence the need of transforming those alkenes into alkanes. For this purpose, catalytic hydrogenation could be implemented fueled by a renewable source of hydrogen.

Fig. 11. *Self-metathesis and cross-metathesis of olefins. Adapted from Zimmerer, 2020 [299].*

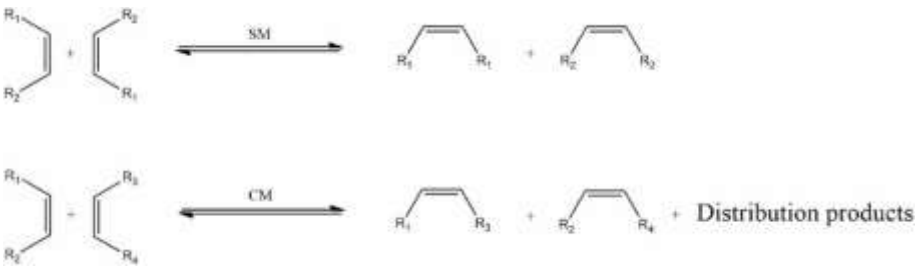
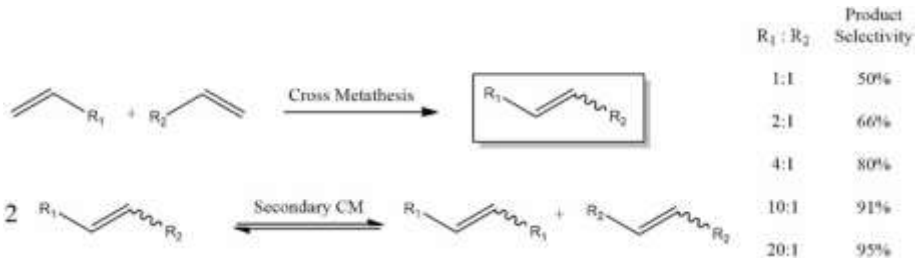


Fig. 12. *Cross-metathesis between two types I olefins leading to a mix of hydrocarbons (Adapted from Chatterjee et al., 2003) [302].*



$R_1 : R_2$	Product Selectivity
1:1	50%
2:1	66%
4:1	80%
10:1	91%
20:1	95%

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6.1.2. ETHENOLYSIS AS A GREEN EFFICIENT TOOL TO CLEAVE C–C BOND

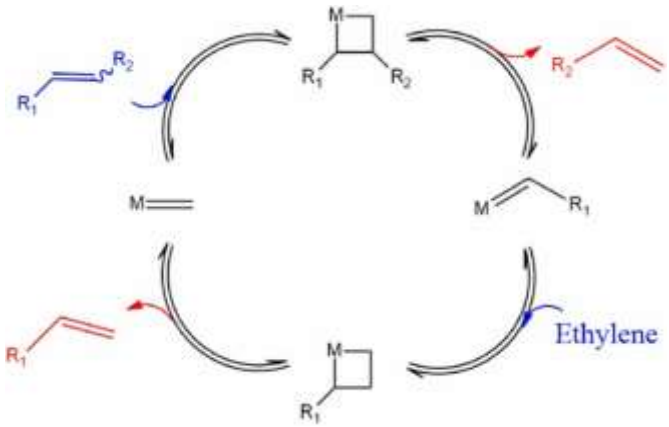

Fig. 13. *Hérisson and Chauvin metathesis mechanism adjusted for ethenolysis (Adapted from Bidange et al., 2016) [309].*

Ethenolysis is a particular cross-metathesis reaction which involve ethylene and an internal olefin as reactants, generating products with a terminal double bond [309,310]. This specific cross-metathesis reaction could be an interesting alternative to break C–C bonds of long chain unsaturated hydrocarbons (sourced from the lipids of microalgae) due to the low cost and abundance of ethylene, but also thanks to the gentle conditions needed (20–80 °C and 4–10 bar) [294,309]. Intramolecular self-metathesis is also possible if the two unsaturations are present in the hydrocarbon chain [310]. The mechanism of ethenolysis follows the steps described by H´erisson and Chauvi (Fig. 13) [293], involving the consecutive coordination of two olefins to the metal to generate metallacyclobutane intermediates, releasing new alkylidene and olefin species [294,299,311]. Other more advanced mechanisms were proposed, justifying phenomena such as isomerization or fragmentation of olefins [293,312].

The turnover number (TON) of a catalyst is a crucial parameter reflecting the economical aspect of the ethenolysis process (a TON >50000 is an economical interesting value) [313]. Commercially, the Grubbs and Hoveyda-Grubbs catalysts are the most commonly used Ru based catalysts in cross-metathesis reactions. However, very low TON (600–8000) [314] have motivated researchers to improve the development of catalysts, with new complexes, more pure ethylene gas or decreasing catalyst loading, significantly increasing the TON to 340000 [310,315].

An important challenge for ethenolysis is to find the balance between productivity and selectivity [310]. An excess of ethylene shifts the equilibrium towards the ethenolysis products, increasing the selectivity by inhibiting self-metathesis at the expense of productivity. However, the production of unstable methylidene complexes compromise the integrity of the catalyst [310]. This and other limitations, like homometathesis, have been reported and are well explained in the review published by Bidange et al. [309]. Pressure of ethylene, its solubility in the solvent and temperature are important parameters for the improvement of this equilibrium [309]. Moreover, the use of small-chain internal olefin avoids the formation of such unstable complexes, generating internal olefins at the end of the process. As such, butenolysis, a cross-metathesis using 2-butene instead of ethylene,

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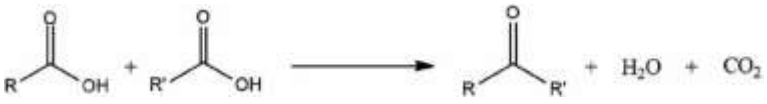
has reported high conversion (90%) and high TON (23000–93000) using a second generation Hoveyda-Grubbs catalyst [299,316].

6.2. KETONIZATION OF CARBOXYLIC ACIDS

A notable amount of carboxylic acids (~10%) could be produced via the thermal decomposition of biomass [317,318]. Their acidity and viscosity imply corrosion and operational difficulties. Ketonic decarboxylation or ketonization of carboxylic acids is highly relevant for the upgrading of bio-based streams to jet fuel grades. Ketonization (Eq. 5) was initially discovered by Friedel in 1858 [319]. Through this reaction, oxygen content and acidity are reduced, while forming C–C bonds in order to produce ketones [320]. Furthermore, the carbon chain can be almost doubled due to the formation of symmetric ketones. Depending on the carbon chain length of the starting carboxylic acid, this also modulates the volatility of the products. These ketones can be processed additionally via the catalytic hydrogenation or dehydration to produce liquid fuels with high energy content, such as kerosene and jet fuel [321]. However, the need for hydrogen is reduced since 3 oxygen atoms (out of the 4 that are present in the starting molecules) are already eliminated. Therefore, ketonization could become an interesting technique to valorize the residual small chain fatty acids resulting from over-cracking of the feedstock, as well as an alternative decarboxylation pathway, provided the upgrading of the produced ketones. For instance, valeric acid has the potential of a proper chemical building block to produce valuable compounds, including fuel and fuel additives for the transportation sector [322,323].



Eq. 5

Developing high performance heterogeneous catalysts for the ketonization reaction is important. In this regard, Glinski, et al. performed ´ the ketonization of propanoic acid over numerous oxide catalysts [324]. Results have been summarized in Fig. 14, which indicates that excluding zinc and chromium, the other metal oxides from the lanthanide and transition metal groups exhibited superior catalytic performance.

In another work, Parida and Mishra studied the ketonization of acetic acid over ZrO_2 based catalysts promoted by alkali metal cations, with sodium being the most effective one [325]. Similarly, Nagashima et al. have claimed that an increase in the carboxylic acid chain length could lead to a decline in the reactivity [326]. Table 9 list several metal oxides catalysts (solely or promoted) used in ketonization reaction along with the desired product, reaction conditions, and yield [327].

Reaction mechanisms depend on the type of catalyst employed. Generally, conventional catalysts can be categorized into highly basic (e. g. magnesium, barium, and calcium oxides) and amphoteric groups (like zirconium, titanium, and cerium oxides). Amphoteric groups, with higher lattice energy, usually show higher catalytic activity and durability [327,328]. They seemingly promote a surface ketonization, although the detailed mechanism is still on debate. In contrast, for highly basic groups, the C–C bond formation occurs through bulk ketonization. During this pathway, metal carboxylate salts and lattice hydroxyls are primarily formed after the deprotonation of the

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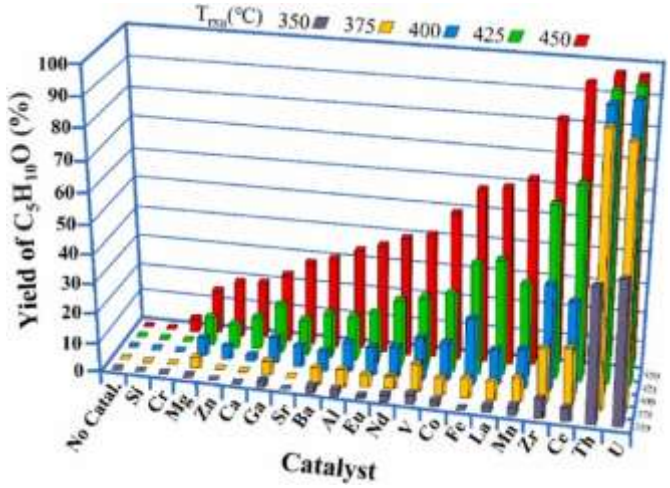
carboxylic acids. Then, metal carbonates and ketones are produced via the thermal decomposition of the salt. Eventually, lattice hydroxyls and carbonates react, recovering the metal catalyst and releasing carbon dioxide and water [327].

It is believed that the carrier gas could influence the chemical composition on the catalyst surface. Zaytseva et al. studied the ketonization of valeric acid over Ce/ZrO_2 catalysts under hydrogen and nitrogen atmosphere. They reported that H_2 could improve the valeric acid conversion significantly compared to when nitrogen was used. This could possibly be explained by the formation of solid solution with uniform cerium distribution, greater Lewis site content, the presence of O-vacancies [344] and the reductive capability of H_2 [345].

Fig. 14. *Ketonization of propanoic acid over various catalysts at GHSV = 11,100 h- 1, and T = 350–450°C [324] (redrawn with copyright permission).*



7. Suitability of thermochemical pathways for biojet fuel production

Among the thermochemical pathways discussed in this review, the suitability of each technology to produce different grades of biojet fuels depends on feedstock type, product specifications, and technology efficiency and performance. Considering the high moisture content in microalgal feedstock, HTL can be a suitable technology because of its advantage in processing wet biomass, whereas drying of the feedstock is needed prior to pyrolysis, HEFA, and Gasification-FT. Lipid accumulation in microalgae makes the lipid conversion pathway—HEFA another technology of choice. While the physical compositions of microalgae make HTL and HEFA preferable, the characteristics of the liquid product are also factors for assessing the suitability for biojet production. Jet fuel properties depend on the ratio between major hydrocarbon classes: linear alkanes, branched alkanes, cycloalkanes, and aromatics. Although HEFA, FT, and HTL have been ASTM certified to produce drop-in biojet fuels, they can be blended with petroleum-based jet fuel to

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a maximum of 50% by volume due to the low contents of aromatics and cycloalkanes. However, these compounds can be formed through cyclization and aromatization in catalytic and non-catalytic pyrolysis. As a result, pyrolytic biojet fuel may not need an addition of aromatics to meet jet fuel specifications; a contrary example would be Fischer-Tropsch Synthesized Paraffinic Kerosene with Aromatics derived from non- petroleum sources (FT-SPK/A) [281]. The chemical compositions also determine other important properties such as flash point, freezing point, viscosity, etc. as illustrated in Section 2. FT and HEFA processes, despite the limited aromatic content, require suitable catalysts that provide high selectivity towards jet-range hydrocarbons; they are therefore suitable for targeting specific product compositions that fulfill the standards of different jet fuels. In addition to high selectivity, HEFA has been reported to have the highest lipid-to-fuel energy conversion efficiency of 76% compared with other biojet fuel production pathways [346]. Given the advantages and limitations of individual pathways, their suitability to produce biojet fuel relies on multiple factors, including feedstock selection, upstream and downstream processes.

Table 9 *Studied catalysts for the ketonization of different resources; reaction conditions and obtained yield.*

Feed	Catalyst	Product	P (bar)	T (°C)	Feed Flow rate	Yield (%)	Ref.
Propanoic acid	CeO2–Mn2O3	3-pentanone	1	375	5 h− 1	65	[326]
Propanoic acid	Co–Mo/Al_2O_3	3-pentanone	1	400	–	44	[329]
Propanoic + Butyric acid	Ce-MnOx/MCM-41	3-Hexanone	–	410	6 cm3 h^{-1}	14	[330]
Octadecanoic acid	TiO2	C_{35} ketone	1	380	0.5 g.$gcat^{-1}$.h^{-1}	89	[331]
Capric acid	TiO2	10-nonadecanone	1	350	3.17 h^{-1}	70	[332]
Acetic acid	TiO2	Acetone	1	360	With 125 ml/min He at 25 °C in bubbler	69	[333]
Acetic acid	Pt/TiO_2	Acetaldehyde	–	400	With 90 ml/min H_2 at 25 °C in bubbler	30	[334]
Ethyl acetate 12.5% v/v	H-USY	Ethylene	1	450	2.16 h^{-1}	48	[335]
Acetic acid	ZrO_2–C	Acetone	–	340	Batch reactor	38	[336]
Dodecanoic acid	Pt/MgO	Triocsane	30	400	1.2 g min^{-1}	58	[337]
Dodecanoic acid	La/ZrO_2	Ketones	–	400	Batch reactor	40	[338]
Hexanoic acid	MnO_x	6-Undecanone	–	360	4 h^{-1}	68	[339]
Valeric acid	10%CeO_2–ZrO_2	5-nonanone	1	450	–	73	[340]
γ-valerolactone	Pd(1%)/Nb_2O_5	5-nonanone	35	325	1.2 h^{-1}	84	[341]
Hexanedioic acid	$Ba(OH)_4$	Cyclopentanone	–	285–295	–	75–80	[342]
hexanedioic acid	NaOH	Cyclopentanone	–	350	Batch	90	[343]

8. Future implications

It should be noted that technical challenges still exist in some thermochemical technologies. Future studies on biojet fuel production could aim for reducing the limitations of current technologies while maintaining the drop-in properties of current biojet. Investigations could focus on improving feedstock pretreatment, for instance, improving the efficiency of cell disruption. Multiple different pretreatments could be applied to increase lipid extraction yield. Development of new catalysts to improve jet fuel selectivity and increase production efficiency could be another approach. Along

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with catalysts, alternative sources of hydrogen, as a needed agent for catalyst functioning in general, could be examined, e.g., recycling the pyrolytic gas to the reactor, hydrogen from electrolysis. To improve fossil jet and biojet blending ratio, research could also include pathways to co-produce cycloalkanes and aromatics in HEFA and FT processes. During biojet production, many upgrading processes are almost identical to those used in traditional refineries. Co- processing biocrude intermediates at a traditional refinery thus could be a future direction for biojet production. This would prevent the high capital and operational costs of reproducing a biorefinery. However, co- processing conditions and production allocation would require further studies.

9. Conclusions

Production of drop-in biojet fuels using microalgae as feedstock is a promising alternative to remove the dependence on fossil fuels of the aviation sector. Microalgae consume less water, occupy less space for cultivation and typically have a high lipid content, which is optimal for jet fuel production. In addition, it is reported that heterotrophic cultivation could eventually reduce harvest costs at industrial scale, which is interesting for some European countries where climate conditions do not secure a constant sunlight provision.

Amongst the different existing technologies to valorize lipids, HEFA production has the greatest commercial development to date. Nonetheless, its dependence on hydrogen is a major drawback. In this case, catalytic pyrolysis and hydrothermal liquefaction are interesting technologies as they can be carried out without the addition of hydrogen and they allow to obtain the right mixture of hydrocarbons providing good fuel properties. Both technologies are more promising when employing Pd or Pt-based catalysts supported on activated carbon, as they promote the decarboxylation of fatty acid, improving its productivity and selectivity towards alkanes. Nevertheless, the cost of these catalysts is not negligible and drying is necessary for catalytic pyrolysis, which increases significantly the capital and operational costs. Conversely, HTL is amenable to wet biomass as feedstock.

Even though these processes also produce small-chain hydrocarbons, alternatives such as cross-metathesis are prominent to increase the jet- fuel range molecules, provided that a renewable source of hydrogen is available to upgrade the produced olefins. Similarly, an interesting alternative pathway to transform bio-oil could be the ketonization of fatty acids, but this technology still requires more development.

Finally, beyond optimization of the reaction mechanisms, there are other options to improve their economic feasibility. For instance, integrating wastewater from the HTL stage into the microalgal cultivation could reduce operational costs associated with nutrients, and valorizing all potential high-value co-products adopting a biorefinery approach would increase incomes at industrial scale. However, more data is still needed to evaluate these opportunities.

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DATA AVAILABILITY

No data was used for the research described in the article.

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