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Reducing fossil fuel demand by using biofuels as an alternative hydrothermal liquefaction is a promising process for transforming biomass into drop-in fuels†

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A currently accepted strategy for reducing greenhouse gas (GHG) emissions from fossil fuels is to replace them with biofuels. While total replacement is not considered a feasible option, other technologies such as hybridization, electrification and more efficient engines can help significantly reduce the total amount of fuel needed globally. Several processes are currently available for producing biofuels, of which ethanol and biodiesel are the best known. Other fuel alternatives are emerging, some of which are attracting attention due to their high treatment capacity and the production of aromatic compounds needed to ensure fuel compatibility with conventional fossil fuels. The thermal processing of biomass has proven to be an interesting ally in the rapid transformation of materials to obtain several valuable by-products that can be properly processed to obtain drop-in fuels. Among the different thermal technologies for biomass conversion is hydrothermal liquefaction (HTL). The process has a long history of research experience and is one of the most promising technologies for substituting conventional fuels. However, due to the inherent operational difficulties of the process, many aspects still require further research before it can be considered a feasible solution. The HTL process is carried out in the presence of water under moderate temperature and high pressure, resulting in the breaking of organic molecules and repolymerization to form a gas, oil and solid fraction, the yield of which is highly dependent on the characteristics of the raw material and the process conditions. Some of the challenges and difficulties found during the thermal processing of biomass are discussed, together with the issues that need to be addressed urgently if the rate of substitution of conventional fuels by biofuels is to be accelerated.

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Sustainability spotlight

The present manuscript reviews key aspects of biofuel production and the important parameters related to the hydrothermal liquefaction process. The primary motivation for the authors in undertaking this task is the urgent need to reduce fossil fuel consumption and the significant impact of CO_2 emissions on the global climate. The production of biofuels from biomass is in line with the following sustainable development goals: affordable and clean energy, sustainable cities and communities, and climate action. Producing drop-in biofuels from biomass reduces global CO_2 emissions, provides new renewable energy sources, and promotes job opportunities related to local biomass production and processing, thus promoting economic activity and aligning with circular economy strategies.

1 Introduction

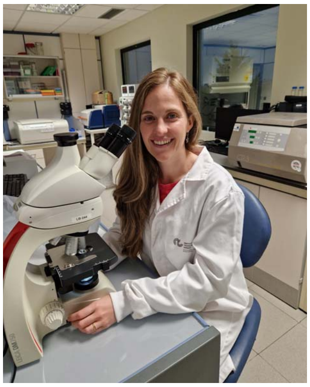
The global energy demand is increasing despite the different efforts carried out to improve process efficiency, with China currently leading the list of countries with the highest energy demand (4030 Mtoe, in 2023), almost doubling that of the United States.[1] The world's primary energy demand is mainly covered by fossil fuels, accounting for 81.5% in 2023 and keeping an increasing trend despite the efforts to install a greater number of renewable energy production centers and the decrease in energy demand by developed countries.[2] There is an urgent need to reduce global CO_2 emissions, but the unavoidable demand for energy means that these emissions will continue to rise in line with population growth and improvements in social welfare. Several alternatives are available for producing biofuels, reducing fossil fuel consumption and developing more efficient engines. However, many of these biofuel alternatives cannot be fully implemented in many regions due to their high costs and adverse impacts on other economic sectors. Competition for land, nutrients, and water resources with food crops, as well as land use changes, along with the impacts on carbon sequestration, are factors that require careful assessment.

The "fit for 55 package" involves a set of regulations intended for reducing greenhouse gas (GHG) emissions by at least 55% by 2030, using 1990 emissions as a baseline.[3] The adoption of this regulation intends for Europe to lead the way in fighting against climate change and move forward towards a green economy. However, the ambitious target may confront several difficulties associated with the limitations of some technological developments and the low energy recovery efficiency of some processes highly recognized as greener options. Reducing fuel consumption in the transport sector is vital to facilitate the widespread adoption of biofuels and other alternatives, such as e-fuels or fuels derived from the "Power-to-X" approach, as well as increasing the profitability of processes associated with direct carbon capture and utilization.[4,5]

Traditionally, ethanol and biodiesel have been widely used in internal combustion engines (ICE) as supplements to conventional fuels. It can be easily assumed that, since these biofuels are derived from biomass, they theoretically help maintain a low carbon balance, as the CO_2 released during combustion has been previously captured by the plant.[6] However, this carbon balance may not always be favorable and may even cause an increase in net CO_2 emissions when considering emissions associated with nutrients, water demand, fossil fuel consumption during crop cultivation and maintenance, and transport and energy requirements of the conversion process.[7]

Bioethanol is commonly produced from the fermentation of carbohydrates, with some specific processes adapted to treat lignocellulosic materials, which require special pretreatments to release sugars. Biodiesel, on the contrary, has traditionally been produced from the transesterification of oils and fats, although recent developments have allowed the production of a biodiesel type fuel from the hydrotreatment of lipid raw materials, with superior performance and 100% compatibility with diesel engines.

Ethanol is typically approved in many European countries up to a mixture of 10%, with most new passenger cars manufactured after 2000 being compatible with this mixture. Other countries, such as the United States, allow mixtures with



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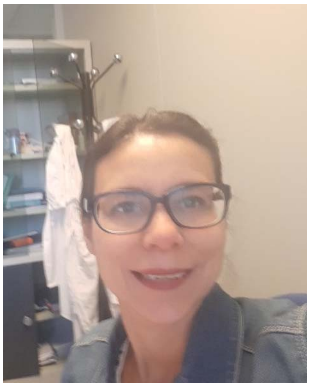

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a higher content but require petrol stations to mitigate errors associated with non-adapted vehicles running on these blends. Vehicles running on E15 up to E85 need modifications to the fuel storage and injection system, ignition, cold start system, and changes in the catalytic converter operation.[8] These vehicles are known as flex-fuel vehicles and can produce more power and show better thermal efficiency when running on high ethanol blends.[9] Although the lower energy density of ethanol causes more frequent refueling, the consumer preference for running with higher or lower ethanol content mixtures is usually based on fuel prices.

Biodiesel is associated with diesel blends of up to 5% or slightly higher, although some countries permit its use in blends of up to 20%. However, the original engine manufacturer has the final say on the compatibility of higher blends. On the contrary, compatibility is 100% in the case of that derived from the hydrotreatment of vegetable oils. The industrial sector has made several efforts to adapt to new regulations aimed at reducing greenhouse gas (GHG) emissions. However, producing sustainable biofuels is full of challenges. Several aspects still need to be addressed, requiring standardized metrics and approaches, along with the development of decision-support tools to identify and quantify environmental trade-offs.[10]

Regarding biofuels suitable for the aviation sector, the different routes for obtaining biofuels that meet the stringent ASTM-D16522 standards share common features with conventional processes. These routes include the transformation of bio-alcohols, direct fermentation to produce long-chain hydrocarbons, hydroprocessing of vegetable oils, and processes involving chemical catalytic conversions of small molecules (such as Fischer–Tropsch technology) derived from renewable substrates.[11] Producing biojet fuels is currently more expensive than obtaining conventional jet fuels, adding to this significant drawback the high amount of land and resources that would be required for cultivating energy crops if biomass is used as the main raw material. Therefore, in addition to the previous list of disadvantages, competition for water, fertilizers, and pollutant related problems such as eutrophication are summed up.[12]

It is also worth noting that many biofuels currently available for the aviation sector must be blended with conventional fuels to comply with all requirements for fuel tank storage, engine compatibility, and burning characteristics, along with the fact that substituting conventional fuels for biofuels is not a warrant for zero net CO_2 emissions.[13]

Several processes are currently capable of producing a variety of fuel-like products suitable for different transport sectors (see Fig. 1). In addition to those already mentioned, biogas and hydrogen can also be produced from different biological processes, with the first one being mainly produced by anaerobic digestion, a widely spread technology that is applied to treat high organic content waste streams and obtaining landfill gas. However, the technology is not free of controversy, and the installation of new biogas plants is facing severe social rejection in some regions due to the so-called NIMBY (Not-in-my-backyard) syndrome. This is the emotional and organized opposition of local residents to projects relevant to the community. Still, the population feels that the impacts created by the project will be detrimental to their current way of living.[14] Bourdin and Delcayre[15] analyzed this phenomenon in France, reporting that the perception the community has regarding the project size and the associated emotional impacts are the main factors to consider when conceiving the installation of a new plant. These aspects are of great relevance because large, centralized plants usually confront greater opposition but have better efficiency in terms of energy production and profitability, against decentralized options which hardly reach profitability and have a much lower energy efficiency.[16]

In the case of biological hydrogen production, several processes are the focus of research, but unfortunately, many of these technologies are in an incipient state with many difficulties encountered when attempting to scale them up. Therefore, the current dominant technology for producing green H_2 is based on electrolyzers. In this case, the energy required is derived from renewable sources (windmills or solar panels). Other types of biofuels currently available and produced through fermentation include biobutanol and fatty acids, which are subsequently upgraded to farnesene. One of the major disadvantages of biological processes is the need for sterilization and the separation stages to recover fuel liquid molecules, with distillation or membrane pervaporation being the main separation processes. Biofuel production routes must overcome economic barriers, regulatory and logistical challenges associated with production and distribution, as well as adapting different propulsion technologies for the transport sector,[17] explaining the difficulties found in attempting to fully substitute fossil fuels without further increasing energy demand.

Regarding thermal processes explicitly designed to transform biomass and waste materials, the main technologies studied include gasification, pyrolysis, and hydrothermal liquefaction. Gasification produces a synthesis gas, or syngas, as the main product. This gas stream contains CO, H_2, and methane as fuel components, along with traces of small noncondensable hydrocarbon molecules. Other components present in syngas include N_2, hydrogen sulfide, ammonia, and high molecular weight aromatics known as tar. The cleaning of syngas is essential if it is to be further valorized, either as a fuel in combined heat and power (CHP) engines, where cooling is needed before serving as an input stream, or as a raw material for other conversion processes. Tar components can stick to valves and clog pipe connections, thus hindering normal operation.[18]

The presence of N_2 is mainly associated with the relatively small amount of air added to attain partial oxidation of the organic material at high temperatures. CO_2 and steam are also commonly used as gasification agents. The latter allows an increase in the hydrogen content of syngas, whereas the presence of CO_2 favors biomass conversion by reducing carbon residual content and tar formation.[19,20] However, in the case of steam, the additional energy demand associated with its production adversely affects the energy balance of the process. Gasification temperatures are usually in the 750–950 °C range, with some processes operating even at higher values, although the high-temperature limit is usually associated with ash melting avoidance.

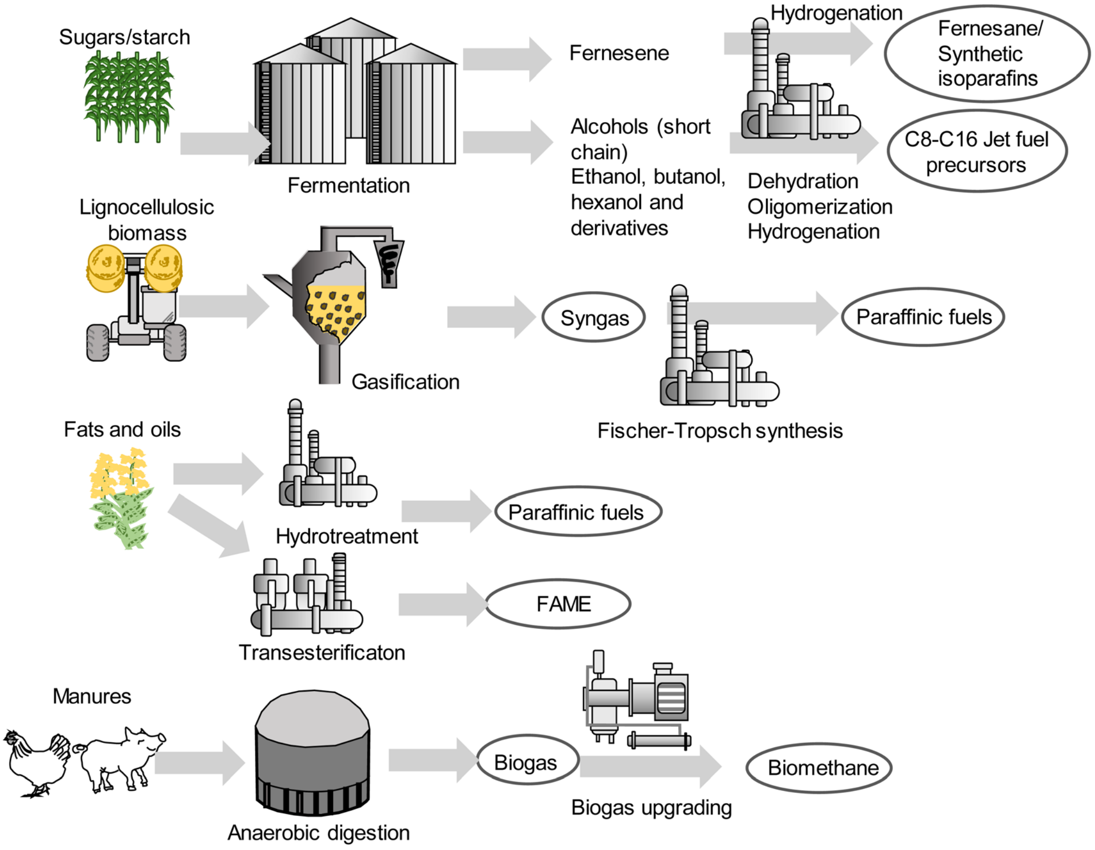

Fig. 1 Processes currently available to produce different types of biofuels.

Pyrolysis is another type of thermal conversion technology, typically classified based on the process temperature range and heating rate. Slow (200–300 °C), fast (700–900 °C), and flash pyrolysis (>1000 °C) are the standard categories, although torrefaction is not usually included in this classification and is generally considered a biomass densification process.[21,22] Other pyrolysis technologies include plasma pyrolysis, which can be carried out using high or low-temperature plasma — in the latter case, the plasma is assumed to be in a quasi-equilibrium state — and non-thermal plasma.[23–25] The response of the process is strongly influenced by the heating rate applied and the residence time of the material in the reactor. The thermal breakdown of molecules takes place in the absence of oxygen, yielding as main products a gas phase, usually denoted as syngas, a liquid phase containing pyrolysis oils but also an aqueous phase containing acids and soluble organics, and finally, a solid product known as biochar, which can be used as a low-grade fuel, a soil amendment for retaining carbon, or as an absorbent in the different processes where these properties are relevant. Despite the extensive research dedicated to this technology, several drawbacks remain associated with the corrosive nature of bio-oils, including their high oxygen content, viscosity, acidity, and immiscibility with petroleum fractions,[26–28] thus requiring upgrading before used as a biofuel. The pyrolysis water obtained as a by-product of the process presents an additional difficulty, needing further treatment to reduce its organic and toxic content, thereby increasing operational complexity.[29]

Conversely, hydrothermal processes can transform organics at lower temperatures than gasification and pyrolysis but require higher pressures. The process is carried out in the presence of water, thus avoiding the high energy demand associated with thermal drying of the raw material, and is therefore, considered a promising technology that yields as main product an oil-rich phase similar to fossil crude oil.[30–32] Oils obtained from this process, as well as from pyrolysis, contain aromatics[33] closer to those found in conventional fuels, thus offering a solution to the critical problem of replacing fuels for heavy-duty transport vehicles and aircraft.

The hydrothermal process is not new, and developments date back as early as 1920, as reported by Usman *et al.*,[34] who described its historical evolution, showing the impact of the economic crisis on the further development of the technology until its renaissance linked to the urgent need to find suitable biofuel replacements. Recently, several documents have been related to this subject, with an exacerbated amount of new work published in the last 10 years (see Fig. 2). It is interesting to find early works dealing with small-scale pilot plants operating under continuous conditions in the 1970s to 1990s and even the construction of a small plant in Illinois (University of Illinois),[35,36] a pilot plant at Aalborg University, Denmark in 2013 (ref. 37) which provided the information for the development of the Hydrofaction™ process (Steeper Energy, Canada).

The review published by Gholizadeh *et al.*[38] lists different pilot plants developed in recent years, where it is worth

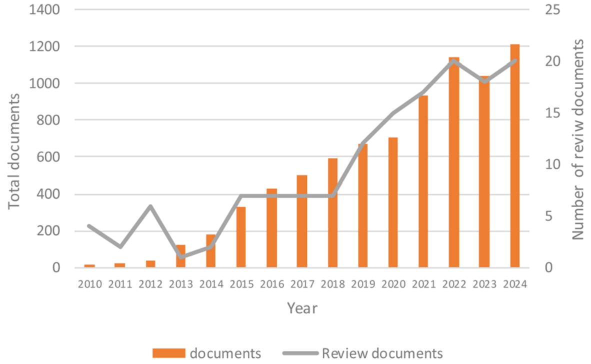

Fig. 2 Number of documents published in the scientific literature on the subject of hydrothermal treatment of biomass.

mentioning the registered processes of Catliq®[39] commercialized by Altaca Energy (Istambul, Turkey),[40] the Cat-HTRTM technology commercialized by Licella™ (North Sidney, Australia),[41] Green2black™ process with a demonstration plant owned by Muradel Pty Ltd,[42,43] and Genifuel (Richland, WA, United States)[44] which commercializes the process developed by Pacific Northwest National Laboratory (PNNL) but seems to have ceased activity at present.

The review by Castello *et al.*[45] describes the technology and its evolution under laboratory and near commercial conditions. Despite all the efforts and research carried out, it is unclear whether this technology is getting closer to commercialization, as several research gaps are still pending a solution. The high capital investment, technological complexity, severe operating conditions, the need to upgrade biocrude, and the proper

Table 1 Shows the challenges and research gaps highlighted in several recent reviews[a]

Process challenge	Reference
Process scale-up: reactor design and engineering	Bassoli *et al.*[48]
Types of materials used for design and associated costs	Watson *et al.*[49]
Continuous product extraction and heat exchanger integration	
Feedstock pumpability	Chaudhary *et al.*[50]
Problems associated with feeding slurry biomass at high pressure due to clogging	El Bast *et al.*[51]
Development of high-pressure pumps capable of dealing with high solid content materials	Watson *et al.*[49]
Feedstock handling and logistics	Fan *et al.*[52]
Productivity of HTL is highly dependent on seasonality	
Insufficient supply of biomass during off-peak season	
Size reduction of biomass to prepare a pumpable slurry becomes too energy intensive	Beims *et al.*[53]
High investment cost and operating costs	Deepika *et al.*[54]
Efficient heat transfer, temperature and pressure control	Ghadge *et al.*[55]
Heat exchangers charring problems and efficient removal of char from reactor under continuous operation	Tran[57]
High pressure in heat exchangers	Lee *et al.*[56]
Biocrude cokization	
Char formation and product separation	Fayshal *et al.*[58]
Higher operating costs for producing and upgrading biocrude compared with fossil fuels	Elhassan *et al.*[59]
Biocrude upgrading costs: H_2 demand and catalyst are the main factors contributing to high costs	Marangon *et al.*[60]
Research regarding co-refining of biocrude and crude oil is needed to reduce production costs	Shahbeik *et al.*[61]
Difficulties in removing nitrogen from biocrude	Sun *et al.*[62]
Corrosion in reactor and salt deposition	Borazjani *et al.*[63] Lee *et al.*[56] Tran[57]
Process safety operational issues	Ghavami *et al.*[64]
Thermal stresses	
Catalyst deactivation	Le *et al.*[65]
Catalyst recovery	
The use of some catalysts may increase the production of carboxylic acids aggravating corrosion problems	
Harmonization of techniques to allow easy comparison of results from different research groups and facilitate predicting yields	Haarlemmer *et al.*[66]
Aqueous phase recovery and treatment	Le *et al.*[65] Watson *et al.*[49]
Co-HTL with biomass and the use of sea water to reduce freshwater demand	Yu *et al.*[67]
The effect of salt on biocrude yield needs further research, as does the risk of corrosion due to the high level of chloride	
Optimizing solvent system to attain valuable product separation	Qiu *et al.*[68]
Environmental sustainability: water demand and land use	Mansuri *et al.*[69]
Performance of engines using HTL derived oil must be evaluated because of its high oxygen and nitrogen content and therefore lower HHV	Obeid *et al.*[70]

[a] HHV: higher heating value.

treatment of by-products remain to be addressed.[46] Despite all these drawbacks, the work of Karimi *et al.*[47] reviewing techno-economic studies for producing biofuel indicated that hydrothermal liquefaction (HTL) was the process capable of attaining the lowest minimum product selling price when compared to other technologies for obtaining biofuels (gasification, pyrolysis, ethanol from lignocellulosic material, among others). However, it is also true that the scale of the HTL process is far from reaching a state close to commercialization. Thus, several aspects regarding industrial application and operational difficulties are unknown, which creates a high degree of uncertainty in the data used to estimate the final selling price of products. Table 1 shows a list of aspects regarding the HTL technology requiring research to circumvent the technological gap for successful implementation on a larger scale.

The present manuscript aims to summarize the information related to the conversion of biomass by hydrothermal liquefaction, focusing on the aspects requiring further research and the common points with other processing technologies for producing biofuels. A search was carried out emphasizing experimental work published between 2000 and 2024, highlighting the difficulties identified by different authors in attempting to scale up the HTL technology. This document is organized by first presenting general aspects of the HTL process, considering main operating parameters and process modifications tested to improve performance. A section was devoted to the use of catalysts for improving biocrude yields and upgrading bio-oils to reduce their oxygen and nitrogen content. The manuscript also contains a final section dedicated to reviewing the information on the technical feasibility of HTL.

2 Hydrothermal liquefaction

The hydrothermal process is dedicated to converting waste and biomass material into a product similar to a petroleum or coal-like product. Temperature, pressure and residence time have a significant influence on the process outcome. In a similar way to other thermochemical processes such as pyrolysis, thus greater production of bio-oil is derived from the fast HTL process, just as in the case of fast pyrolysis,[71,72] with some reports indicating that fast HTL shows a better energy recovery than isothermal HTL.[73]

The family of hydrothermal treatments can be classified into hydrothermal carbonization (HTC), hydrothermal liquefaction (HTL), and hydrothermal gasification (HTG). HTL operates in the temperature range of 200 to 370 °C with pressures between 4 and 20 MPa, keeping water in a liquid state (water critical conditions are 374 °C and 22 MPa). At higher temperatures above 500 °C, the process involves supercritical gasification.[74,75] The distribution of main products derived from the HTL process is highly dependent on the composition of the feedstock, with values ranging from 21 to 53% for biocrude, 4.6 to 31.2% for the aqueous phase, 1.3 to 35% for the char solid phase and the remaining gas accounts for 7.1–35.6% as reported by Li *et al.*.[76] HTL has the advantage of producing an important energetic fraction called biocrude, whereas the HTC process only produces hydrochar as a valuable fraction that seems insufficient to make the process economically feasible.

Fig. 3 shows the evolution of research in HTL technology. Several works found in the scientific literature are related to the processing of algal biomass due to the higher bio-oil production

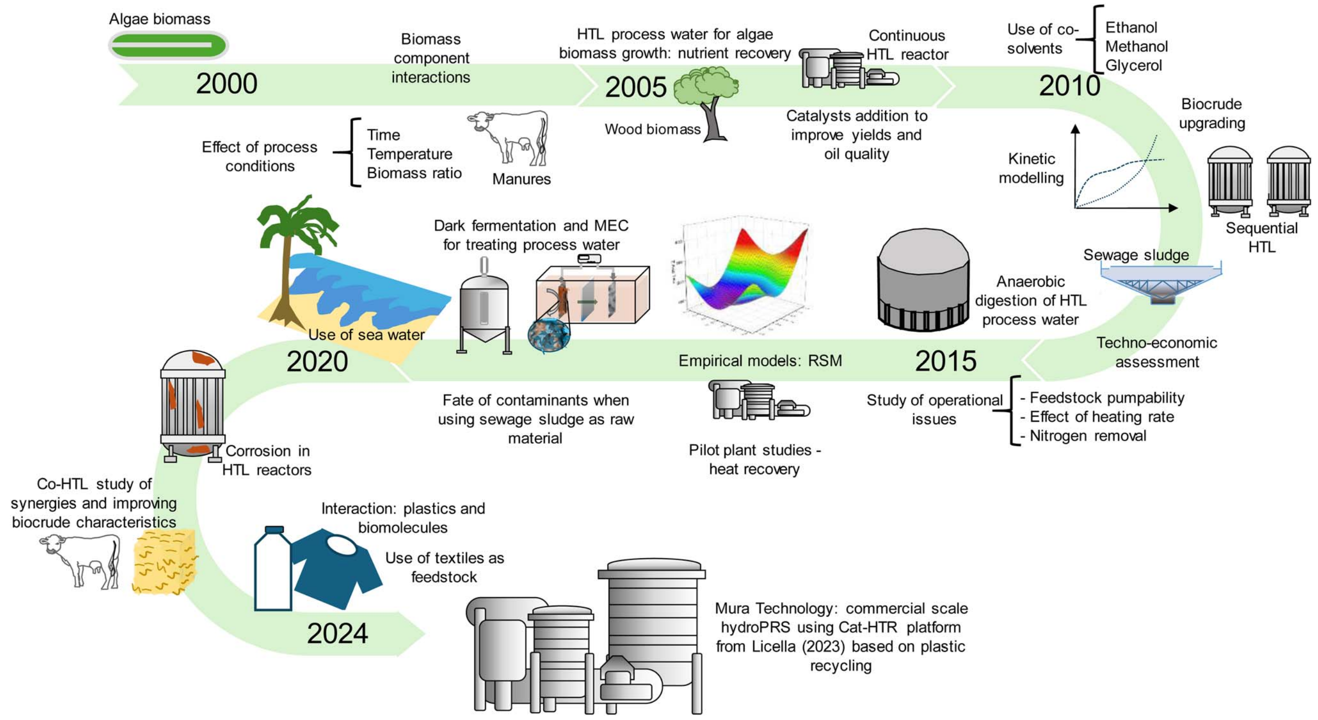

Fig. 3 Evolution of research in the field of HTL technology.

of some species, with yields exceeding 30% and a corresponding higher energy recovery ratio. This is particularly true for lipid-accumulating microalgae. The possibility of integrating CO_2 capture together with using process HTL water for algae cultivation to recycle ammonia and other nutrients such as phosphates are the main features for considering this approach a feasible option for biofuel production.[77–79] However, the latter claimed advantage requires a high dilution of the HTL process water when serving as culture media,[80] which may jeopardize the approach's feasibility under large-scale conditions. López Barreiro *et al.*[81] conducted experiments of growing trials of *Nannochloropsis gaditana*, *Phaeodactylum tricornutum*, *Chlorella vulgaris* and *Scenedesmus almeriensis* using nutrients recovered from the aqueous phase of the HTL process. Only *C. vulgaris* and *N. gaditana* were able to grow at a low dilution rate (75% of nutrients were derived from the HTL water phase), thus highly impacting the economic recycling of the process by-products.

Another relevant advantage of considering algae as a feedstock is that cultivation is performed in water, thus avoiding issues related to land use, land use changes, or competition with feed crops. Additionally, unlike other thermal processes such as combustion, pyrolysis, and gasification, HTL does not require a drying stage, which hurdles the energy balance of the valorization approach. On the contrary, the HTL process requires a certain amount of water; therefore, the processing of algal biomass only includes liquid–solid separation stages, which are less energy intensive. In addition, the high ash content and low energy density of this type of biomass (13–14 MJ kg^{-1}) would not represent a significant problem, as would be the case if combustion is selected as the valorization option.[82] An additional interesting feature is that lipid extraction procedures are avoided when processing high-lipidic biomass. The oil yield obtained is further increased because hydrothermal processing also generates oils from the cellulose and protein contained in the original material.[83] In the case of high protein content microalgae, oil yields are lower, but co-processing with high carbohydrate content biomass may aid in increasing biocrude yields thanks to their interacting effects.[84]

Nevertheless, the advantage of processing wet material disappears when dealing with the treatment of large amounts of process water from the liquefaction and when using seawater-grown algae. Water generally reduces the efficiency of the HTL process because it increases the mass of material to be heated up to the desired working conditions. About 40% of the carbon content of the feedstock can be found in this process water, which can be highly toxic.[85,86] For example, Shanmugam *et al.*[87] reported an organic content of 62.5 g COD/L in HTL process water (where COD represents chemical oxygen demand). It is also important to consider that using fresh water in regions where water scarcity is a concern would reduce the large-scale deployment of the technology.

In the case of growing marine microalgae as raw biomass for the process, the use of seawater also as a solvent may be considered to benefit the water balance. However, using seawater as a solvent has been tested in the HTL process but without showing any promising results when treating high lignocellulosic content biomass. The performance decreased due to the adverse effect of NaCl, which mediated the decomposition of intermediates and increased char production.[88,89] On the contrary, when treating algal biomass, results were more optimistic, showing no adverse effects, or a slight decrease in biocrude yield,[90] which may solve the concerns regarding the use of fresh water in water scarce regions, leaving the expected corrosion problems and higher maintenance costs to await a viable solution.

In addition to algal biomass, different types of raw materials and wastes have been proposed as suitable inputs for obtaining bio-oils, with recent work focusing on exploiting feedstock composition to enhance bio-oil production by promoting interactions between materials. However, there are still many challenges associated with scaling up the technology, which requires research at a pilot plant scale and in continuous operation.

Several experimental works deal with the HTL transformation of sewage sludge, livestock waste, agricultural residues, lignocellulosic biomass, digestate and macro and microalgae indistinctly of its lipid content,[77,82,85,88,91,92] since HTL allows the reaction of biomass components to favor oil type products disregard of its ash content, making it also particularly suitable for valorizing low-lipid microalgae.[93–95] However, in the case of sewage sludge, new concerns have arisen with the fate of some organic contaminants, such as per- and polyfluoroalkyl substances, which may not be fully mineralized in the process.[96] It should also be added that the high nitrogen content of sludge makes the subsequent upgrading process of bio-oil, particularly challenging due to the presence of amines and heterocyclic-N compounds.[97] Therefore, given that bio-oil yields are usually between 10% and 30%,[97–99] the perspective of obtaining valuable oil-type products from this raw material is reduced due to its poor energy recovery and difficulties in removing nitrogen from bio-oil.

2.1 Characteristics of materials frequently used as organic inputs for obtaining bio-oils

Table 2 shows a list of different materials commonly used in HTL experiments. Average values are given in this table based on data published in the scientific literature. The interest in obtaining bio-oils is associated with the expected better economy of the process to produce a liquid fuel that, after upgrading, can replace fossil fuels. This aspect has recently increased its relevance due to the major efforts to decarbonize the economy and explore different technological pathways to supply drop-in biofuels. Given the chemical composition of the raw materials typically considered as suitable feedstock, a biocrude enriched with oxygen and nitrogen is expected, with heating values in the range of 30–36 MJ kg^{-1}, and characterized by high viscosity and instability.[74,100] Table 2 also shows the great diversity in the composition of the different raw materials used as HTL process inputs. It is clear that the high ash content will limit the yield achievable in the global process. Additionally, factors such as localized waste production, seasonal availability, and pretreatment requirements will impose constraints on its feasibility, similar to other biomass fuel

Table 2 Characteristics of raw materials frequently used as substrates in HTL process

					Algae biomass		
Parameter	Sewage sludge	Swine manure	Cow manure	Lignocellulosics	Lipid rich	Protein rich	Carbohydrate rich
References	77, 91, 98, 99 and 101–108	77 and 109–112	104, 111 and 113–117	89, 99, 101, 104, 114–116 and 118–124	83, 105 and 125–127	77, 80, 101, 125, 126 and 128–130	83, 125 and 130–133
Composition (%)							
Carbohydrate	26.8 ± 20.4	36.8 ± 1.6	40.4 ± 4.8	65.9 ± 8.6	18.4 ± 7.2	26.1 ± 5.6	60.6 ± 14.3
Cellulose		12.7 ± 3.6	21.3 ± 8.0	39.2 ± 8.6			
Hemicellulose		24.0 ± 5.8	13.9 ± 1.6	26.5 ± 10.5			
Protein	21.7 ± 11.9	19.7 ± 4.6	11.6 ± 5.2		38.5 ± 12.7	50.3 ± 12.8	14.0 ± 6.0
Lipid	18.4 ± 4.71	4.7 ± 4.0	1.0 ± 0.4		32.0 ± 15.0	8.7 ± 4.5	3.2 ± 2.1
Lignin		2.8 ± 1.8	15.0 ± 12.8	24.6 ± 8.8			
Ash	33.6 ± 14.0	21.4 ± 9.7	14.2 ± 9.9	3.2 ± 4.3	9.5 ± 7.8	13.0 ± 8.0	20.9 ± 9.0
Elemental analysis (%)							
C	34.6 ± 15.6	35.0 ± 6.4	39.8 ± 6.1	46.6 ± 4.4	51.5 ± 7.4	51.2 ± 14.1	33.3 ± 5.0
H	5.3 ± 1.4	4.9 ± 0.6	4.7 ± 1.3	6.0 ± 0.7	7.3 ± 1.4	6.3 ± 1.0	5.0 ± 0.7
N	4.9 ± 2.2	2.6 ± 0.7	1.8 ± 0.6	0.4 ± 0.4	6.2 ± 1.7	8.0 ± 2.3	2.5 ± 1.2
S	1.35 ± 1.0	0.6 ± 0.1	0.7 ± 0.3	0.2 ± 0.2	0.6 ± 0.3	0.6 ± 0.2	1.6 ± 1.0
O	23.0 ± 6.25	40 ± 5.7	44.3 ± 11.3	44.1 ± 3.3	25.7 ± 4.5	22.2 ± 13.7	40.6 ± 11.3
HHV (MJ kg^{-1})	18.5 ± 3.0	12.5 ± 2.1	16.1 ± 2.6	15.7 ± 1.3	25.6 ± 4.1	24.6 ± 8.1	13.2 ± 2.8

production methods like gasification or pyrolysis. However, the specific operating conditions in this case may introduce additional technical restrictions that could hinder the broader application of this approach.

2.2 Reactions taking place during HTL of biomass

Biomass conversion during HTL liquefaction involves initial hydrolysis producing monomer structures, subsequent decomposition, where smaller molecules such as glucose, organic acids and phenolic compounds are produced and finally, recombination where water insoluble products are formed (Biocrude and hydrochar), with main reactions involving condensation, cyclization and polymerization.[61,134] Fig. 4 shows a schematization of reactions involved in liquefaction of organics. Although the scientific literature contains a vast amount of research, reaching a consensus on various experimental results has proven to be quite challenging. This complexity arises from the considerable influence that reactor operating conditions have on the composition and distribution of products, as well as the inherent effects related to the mineral and elemental composition of the biomass.

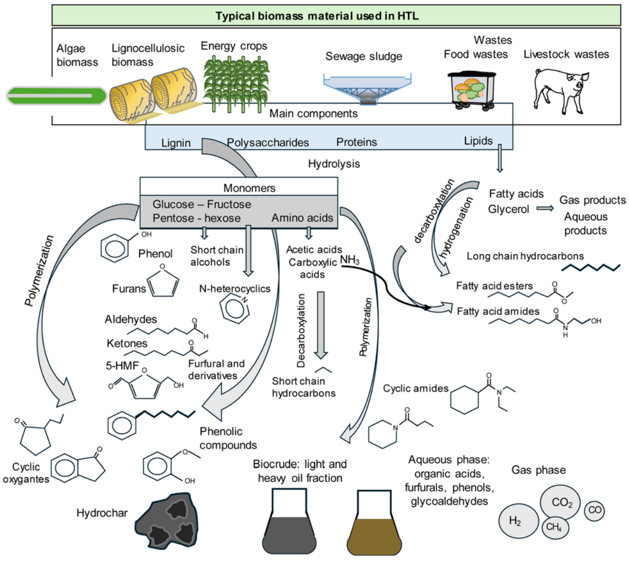

Fig. 4 Schematic representation of organic conversions taking place during the hydrothermal liquefaction process.

Glucose and 5-(hydroxymethyl)furfural (5-HMF) are the main products of cellulose thermal reaction under liquefaction conditions. The crystallinity index affects the conversion, with amorphous cellulose undergoing transformation at lower temperatures.[135] However, glucose usually reacts at the optimum temperatures recommended for favoring biocrude formation, forming condensed species. Thus, its presence is usually not reported in the organic composition of process water,[136] and the HTL treatment of pure saccharides results in high solid residue yields and poor biocrude production.[137] The effect of reaction time is usually smaller than that of temperature, but it has been demonstrated that increasing this parameter affects CO_2 evolution, char formation and oil and process water quality. Nevertheless, quantifying the effect of reaction time is not as simple as it may seem because many researchers do not report on heating or cooling ramps applied, which also affect the final composition of products.

Fig. 5 shows char yields obtained by different authors plotted against the biomass ash content (see in Table ESI†). It is clearly observed that the higher yield obtained from lignocellulosic biomass is in line with its higher lignin and carbohydrate content. Algal biomass data are more dispersed due to the variability in composition.

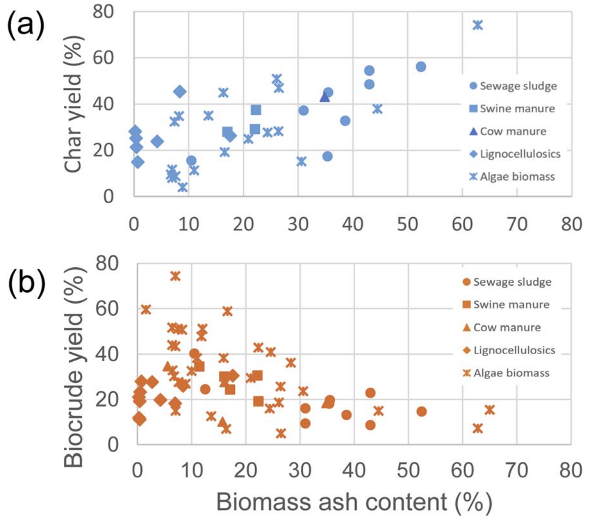

Fig. 5 (a) Char yield reported by different authors, (b) biocrude yield reported by the same authors. Values are represented against the biomass ash content considering data from HTL of sewage sludge, manures, lignocellulosic and algae biomass. Values were obtained from references (see ESI†).[77,91,98–133]

The data plotted in Fig. 5 was grouped without taking into account process conditions. However, some characteristics are easily observable, as it is almost a linear trend of char yield with ash content, and the variability of results when considering bio-oil production, particularly when focusing on data reported from algal biomass, as well as the low productivity of lignocellulosic biomass. The low yield of biocrude from biomass, despite its surprisingly low ash content, can be attributed to its carbohydrate composition. Species with higher carbohydrate content tend to exhibit lower biocrude yields, similar to the trends observed in lignocellulosic materials.

Table 3 lists the main results obtained from experiments carried out with real biomass. As the table shows, many of these experiments were performed under batch conditions using small reactors with volumes of a few milliliters. The effect of retention time, temperature, and solid content of the feed are the parameters usually selected for evaluating process performance. The testing of different waste mixtures has recently been evaluated, focusing on the application of fast heating rates to increase biocrude production.[115,138,139]

2.3 Process parameters affecting biocrude yield

The main process parameters studied are temperature, retention time and biomass solid content. However, the experimental conditions, either batch or continuous process, and the heating rate applied also determine the distribution of the products. Biocrude production is higher at shorter reaction times; thus, it is assumed that biomass compounds are initially converted into oil-type organics and then braek up either forming soluble aqueous fractions or producing gases and solids as the reaction time is increased.[140] However, this is just a simplistic explanation of the whole process, as the interactions between the main components of the sample and the operating conditions dictate the outcome, which can be even contradictory for the same operating conditions when the proportions between carbohydrates, proteins, lipids, and lignin are changed.[137]

Fig. 5b shows biocrude yields reported by several authors from different biomass types, evidencing how low ash content biomass can yield high values of biocrude but also extremely low values (close to 10%). Chopra *et al.*[141] reported a concomitant increase in biocrude and char production with increasing temperature (using as biomass de-oiled yeast), whereas Xu *et al.*[98] reported a decrease in char production with increasing temperature along with an increase in biocrude yield when testing sewage sludge.

The different distribution of components also affects the biocrude yield, reporting synergistic effects when mixing carbohydrate-rich and protein-rich compounds. Thus, greater biocrude yields for the mixture are usually explained by the favoring of Maillard reactions,[142] but this better performance of bio-oil production is accompanied by a disadvantage, which is the increased content of nitrogen-containing compounds. Therefore, when analyzing process outcomes, the combined effect of operating conditions and biomass composition must be clearly highlighted. The explanation of results that at first sight may be cataloged as contradictory is easily understandable from the effect that nitrogen compounds may play during process reactions and the way heating and cooling conditions were applied. No description is typically found in the scientific literature regarding the time required to reach the desired process temperature, and when this information is available, there is often a lack of details associated with the subsequent cooling procedure. It is reasonable to assume that during slow cooling, condensation reactions continue to occur; thus, the results reported are derived from the global experimental conditions, namely, the heating ramp, set reaction temperature, and time, as well as the cooling ramp.

Leng *et al.*[100] analyzed data reported in the scientific literature on the formation of nitrogen compounds, indicating that the composition of the raw material evidently dictates the trend in the formation of N-containing molecules. Therefore, a high protein concentration may lead to higher levels of these compounds as the HTL temperature increases, but a different distribution in the biochemical composition may also lead to opposite results, leading to a lower nitrogen content as the temperature increases. In general, the outcome of the process is better explained using an empirical index proposed by Qian *et al.*,[71] which aggregates temperature and reaction time into a single parameter denoted the severity index (SI). This parameter facilitates a better understanding of the yield expected for different products based on the values adopted by SI for a given type of raw material.

Fig. 6 summarizes the data reported in the literature by plotting char and biocrude yields for the most common types of biomass used as raw material. A clear decrease is observed in char yield with increasing temperature. However, the performance in terms of biocrude yield shows, in many cases, an increase followed by a subsequent decrease as temperature

Table 3 Experimental results on HTL treatment of biomass and waste reported by different authors[a]

Raw material	Conditions	Mains results	Reference
Water hyacinth (WH), rice straw (RS)	Batch reactor: 500 mL temperature: 300 °C Time: 30 min	Main components were acetic acid, *n*-hexadecanoic acids. RS gave a heavy oil yield of −21.6%, WH resulted in a much lower yield of 12.2%, similar to that reported for xylans as model compounds	Ying *et al.*[143]
Corn stalks	Batch reactor: 1 L Temperature range: 180–300 °C Time: 0–40 min water to cornstalk ratio of 6 : 1–14 : 1	Low temperature, high water to cornstalk ratio, and short reaction time favored the formation of bio-oil. Increasing temperature and reaction time increased the yields of gas and volatile organic compounds	Liu *et al.*[144]
Corn stalks	Batch reactor: 500 mL Temperature range: 210–310 °C	Best reaction conditions at 290 °C. Bio-crude yield of 23.3%. Authors evaluated cooling rate once desired temperature was reached	Zhu *et al.*[145]
Eucalyptus	Batch reactor: 150 mL Temperature: 260–320 °C Time: 30 min Solvent: water and ethanol Biomass:solvent ratio: 1 : 10	The authors recommended the use of water rather than ethanol (30.1% biocrude yield). The solid residue was higher when using ethanol as solvent	Wu *et al.*[146]
Corn straw (CS), peanut straw (PS), soybean straw (SS), and rice straw (RS)	Batch reactor: 1 L Temperature: 320 °C Time: 60 min	Poor bio-oil yields (7.9–15.8%), with soybean straw giving the best result. The char residue was high (24.5–35.5%). Bio-oils were characterized mainly by ketones and phenolic compounds	Tian *et al.*[147]
Duckweed (high protein content): derived from wastewater treatment	Batch reactor: 100 mL Temperature: 250–270 °C Time: 15–60 min	The highest bio-oil yield (35.6 wt%) was obtained at 370 °C and 45 min Biocrude with HHV of about 40.3–40.8 MJ kg^{-1} was obtained at the higher temperatures tested (340 and 370 °C) applying different holding times. Nitrogen content of bio-oil was high in all cases (6.4–7.5%)	Chen *et al.*[148]
Penicillin fermentation residue	Batch reactor: Volume no indicated Temperature: 245–315 °C Time: 80–280 min Solid content: 10–20 wt%	The highest bio-oil yield was 25.91 wt% at a temperature of 300 °C, a retention time of 174 min and a solid content of 18 wt%	Hong *et al.*[149]
Biomass of *Spirulina platensis* and lignin derived from Spartina alterniflora	Batch reactor: 50 mL Temperature: 250–360 °C Time: 0–60 min Mixture ratio experiments *Spirulina* : lignin: 0.5–2.0	The highest bio-oil yield was 33.1 wt% at 340 °C, 40 min using a 2.0 : 1.0 *Spirulina* : lignin mixture	He *et al.*[150]
Microalgae *Desmodesmus* sp	Temperature: 175–450 °C reaction time up to 60 min	The maximum oil yield (49 wt%) was obtained at 375 °C and 5 min reaction time	Garcia Alba *et al.*[151]
Macro-alga *Laminaria saccharina*	Batch reactor: 75 mL Temperature: 250–370 °C Time: 5–120 min	Best conditions: 350 °C, 15 min. Bio-crude yield of 19.3% (w/w), HHV 36.5 MJ kg^{-1}. The bio-crude yields increase with increasing temperature, accompanied by a decrease in the solid residue yield	Anastasakis and Ross[82]
Macroalgae *Sargassum patens* C. Agardh	Batch reactor: 1 L Temperature: 320–380 °C Time: 15–90 min Biomass:water ratio: 1 : 6–1 : 30	Maximum oil yield of 32.1% obtained at 340 °C and 15 min. (Nitrogen content of 2.45% and oxygen content of 22%) Optimum biomass to water ratio of 1 : 10 Increasing the biomass to water ratio decreased the bio-oil yield from 38.0 to 26.1%, but gas and solid char yield increased at the same time. Adding 5% Na_2CO_3 as a catalyst decreased oil and solid yields but increased the gas yield	Li *et al.*[152]

Table 3 (*Contd.*)

Raw material	Conditions	Mains results	Reference
Microalgae mixture of *Chlorella* and *Spirulina*	Continuous pilot plant Biomass loadings: 1–0 wt% Temperature: 250–350 °C Time: 3–5 min Pressure: 150–200 bar	The maximum biocrude yield was 41.7 wt% from the processing of *Chlorella* with a solid loading of 10 wt% at 350 °C and 3 min of residence time 30% of the feedstock carbon was found in the aqueous phase at the highest loading, but this value increased to 60% at lower loadings	Jazrawi *et al.*[153]
Microalgae *Chlorella*	Continuous flow hydrothermal processing unit capable of 2.5 L h^{-1} flow rates Temperature of 350 °C and pressure of up to 206 bar Residence times of 1.4 and 5.8 min	40 wt% biocrude yields Bio-crude HHV was approximately 35 MJ kg^{-1}. Nitrogen content of 6% and oxygen content of 11% in bio-oil Upgrading was also tested in this experimental work, reporting a reduction of 65% in nitrogen content	Biller *et al.*[154]
Microalgae *Scenedesmus* and *Chlorella* strains	Continuous operation Temperature: 300–340 °C Flow rates: 3–7 mL min^{-1} Pressure: 160–165 bar Algae loading: 5 wt%	Low bio-crude yields of 21.9 wt% explained by the high ash (29.9 wt%) and low lipid (7.9 wt%) content of the raw algae	Wagner *et al.*[155]
Microalgae *Scenedesmus, Spirulina* biomass	Batch reactor: 500 mL temperature: 300 °C Time: 30 min	Biocrude yield was between 31–45%. Nitrogen content of oils was 6.5–8.1%, and oxygen was 9.2–10.5% (HHV between 35-37 MJ kg^{-1})	Vardon *et al.*[156]
Microalgae *Nannochloropsis gaditana* (N. Gaditana, marine) *Scenedesmus almeriensis* (S. Almeriensis, freshwater)	Continuous CSTR: 190 mL Temperature: 350 °C Time: 15 min Microalgae loadings of 9.1 and 18.2 wt% in the feed	High biomass loading promotes the formation of biocrude oil attaining a maximum yield of 54.8 ± 3.4 wt% for *N. gaditana* Nitrogen content in oil increased with increasing biomass loading	Barreiro *et al.*[157]
Microalgae *Dunaliella tertiolecta*	Batch reactor: 100 mL. Addition of Na_2CO_3 as a catalyst (w/w biomass). Temperature: 280–380 °C time: 10–90 min	Catalyst dosage from 0 to 10%. Maximum bio-oil yield of 25.8% was obtained at a reaction temperature of 360 °C and a holding time of 50 min using 5% Na_2CO_3 as a catalyst	Shuping *et al.*[128]
Galdieria sulphuraria (high-protein microalgae useful for wastewater treatment) and *Nannochloropsis salina* (high-lipid microalgae useful for biofuel production)	Batch reactor: 1.8 L Temperature: 310–350 °C Time: 5–60 min Solid loading: 5–10% TS (slurry concentration tested)	Milder reaction conditions favored bio-crude oil yield and quality for *N. salina*. More severe conditions (350 °C) were needed for *G. sulphuraria* *N*-containing and high molecular weight compounds are a concern when upgrading biocrudes obtained from high-protein algal biomass	Cheng *et al.*[158]
Microalgae *Cyanidioschyzon merolae* (CM) and swine manure (SM)	Batch working volume: 50 mL Temperature: 330 °C Time: 30 min Solid loading: 20%	CM yielded 31.4% of biocrude. In contrast, SM produced just 6.3% of biocrude and a high char value (33.2%). This study focused on biochar production and its characteristics	Dandamudi *et al.*[138]
Textile sludge, tannery fleshing waste	Batch reactor: 30 mL Temperature: 300 °C Time: 60 min	Biocrude production for the different waste mixtures was between 16–38% range. High char production was obtained from all tests. The mixture showed a better performance than the processing of single wastes	Hossain *et al.*[139]
Tetraselmis sp. MUR 233 microalgae, sewage sludge, radiata pine wood saw dust	Batch: 11 mL Temperature: 250–350 °C Time: 5–60 min Biomass loading: 30 wt%	The aim was to propose a kinetic model. Crude yields were generally lower compared to similar experimental work. Microalgae reported a maximum value of 30%, sludge gave a 25% value and 10% was obtained for pine sawdust	Obeid *et al.*[99]

Table 3 (*Contd.*)

Raw material	Conditions	Mains results	Reference
Marine microalgae *Chlorocystis* sp., *Picochlorum* sp	Batch: 500 mL Temperature: 325 °C Time: 30 min	The biocrude yield was between 35–40% range. Nitrogen from the HTL aqueous phase was successfully used for microalgae growth	Das *et al.*[159]
Sewage sludge (primary and secondary) and digested sludge	CSTR: 1 L Feed: 1.5 L h^{-1} Feed concentration: 10–16% TS Temperature: 276–358 °C Residence time: 18–30 min	Treatment of aqueous stream by catalytic hydrothermal gasification. Biocrude yields ranged from 25 to 37%	Marrone *et al.*[160]
Sewage sludge	Batch reactor: 160 mL Temperature: 350 °C subcritical, 400 °C supercritical	Biocrude yields between 32 and 42%	Prestigiacomo *et al.*[106]
Sewage sludge	Batch reactor: 4.4 mL Temperature: 260–350 °C Time: 10 min	Biocrude was reported in two fractions: light and heavy The light biocrude yield was maximum at 340 °C (54.4 wt%) The nitrogen content of the heavy biocrude was 6.6% (almost double that of the light biocrude, 3.44%)	Xu *et al.*[98]
Sewage sludge	Batch reactor: 4.1 mL Temperature: 300–600 °C Time: 0–60 min	Fast HTL produced higher bio-oil yields. Maximum biocrude yields ranged from 20% to 31%. About 32% of N was transferred to the oil and 63% to the aqueous phase products	Qian *et al.*[71]
Sewage sludge	Batch reactor: 1 L Temperature: 290–360 °C Time: 60 min	Both extremes tested in the reaction temperature and time range showed lower biocrude yields, with the optimum point centered around 320–340 °C temperature range and 10–20 min time range	Liu *et al.*[108]
Cow manure, corn stover	Batch reactor: 10 mL Temperature: 375–450 °C	Fast HTL. The highest yield of biocrude (about 24 wt%) was obtained at 400 °C, 16 min, and a mass ratio stover:manure of 1 : 1	Liu *et al.*[115]
	Time: 12–30 min	Hydrochar initially decrease with increasing residence time and then remained at an average value of about 11%. Biocrude increased with increasing time and then kept an average value of about 22%	
Cow manure, corn cob	Batch reactor: 100 mL Temperature: 300–360 °C Time: 30 min	Biocrude yield: corn cob: 28.4%, manure: 36.5%, mixtures: 19.1–20% Best process performance at 340 °C. The char yield was high (40–45%) for manure due to the high ash content of this feed (34.9%)	He *et al.*[114]
Food waste	Pilot scale plug flow continuous: 35 L Temperature 300 °C Flow rate: 0.15 Gal/min (56.7 L min^{-1})	Biocrude yield of 29.5%. Aqueous phase yield of 39.5%. Process energy consumption ratio was 0.53	Aierzhati *et al.*[161]

[a] CSTR: Completely stirred tank reactor.

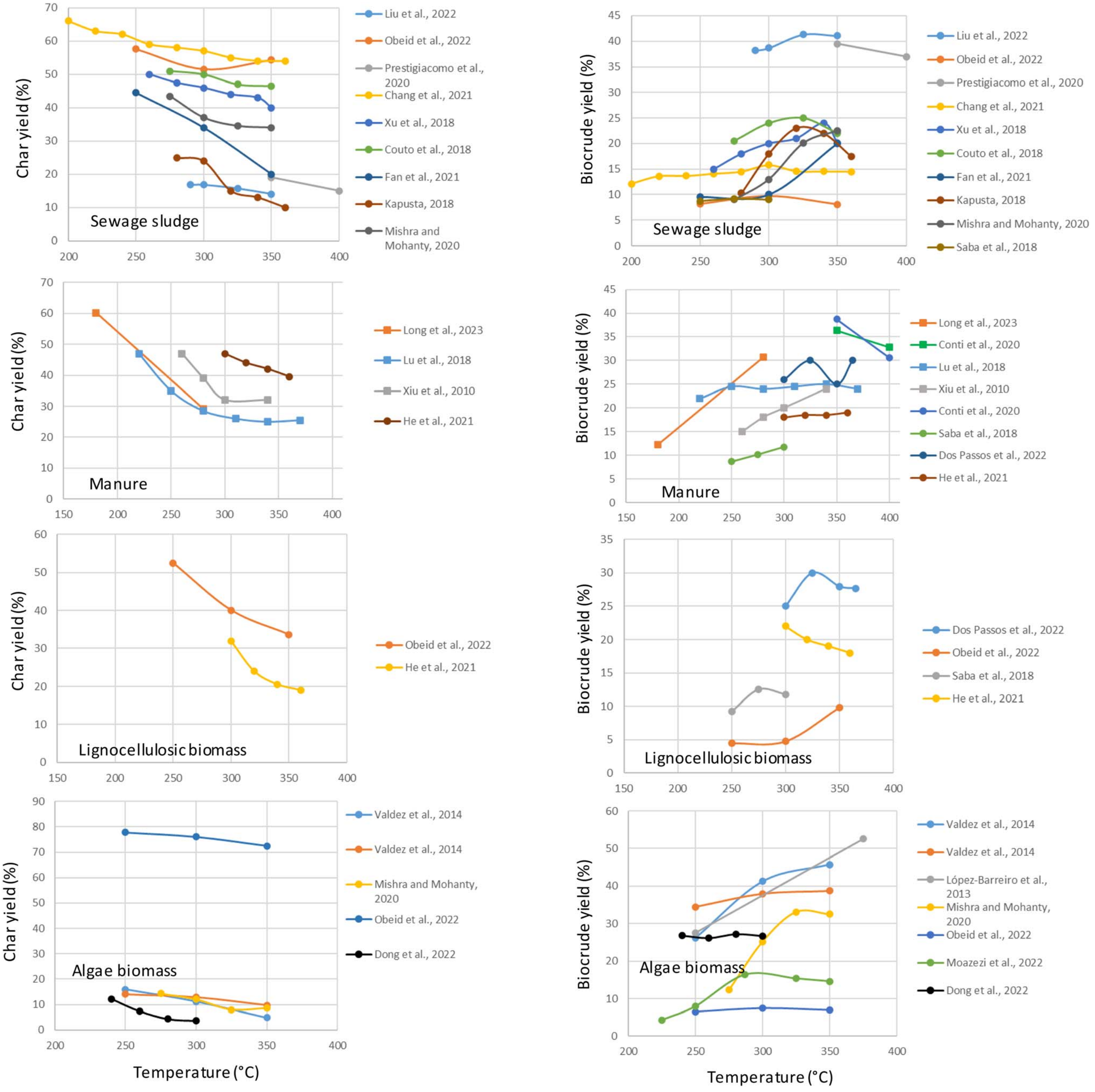

Fig. 6 Representation of char and biocrude yields reported in ref. 77, 91 and 98–133 for different raw materials.

keeps increasing, indicating the presence of an optimum condition, although some results show small changes with temperature variation. The experiment carried out by He *et al.*,[114] using corn cob as biomass and testing temperatures above 300 °C, is notorious because a decrease in biocrude production is observed with temperature increments, probably indicating that optimum conditions may be located in this case at a temperature around 300 °C or even lower. The results reported by Saba *et al.*,[104] may help clarify process performance. The optimal temperature reported in this case was below 300 °C when treating lignocellulosic material.

The distribution of carbohydrates, proteins and lipids in the raw material largely determines the process oil recovery. Therefore, some authors have proposed the treatment of biomass mixtures to enhance performance by taking advantage of the synergies between protein and carbohydrate reactions. Such is the case studied by Wang *et al.*,[162] testing mixtures of microalgae (*Chlorella vulgaris*) and macroalgae (*Enteromorpha clathrata*). The former biomass is high in protein, while the latter is high in polysaccharides. Their HTL experiments showed better yields for the mixtures than for processing any of the two single biomasses.

The abundance of data available in the scientific literature has enabled the assessment of the information to predict process yields, although difficulties associated with identifying process conditions and sometimes the lack of accurate description of experimental results make this task daunting. Guirguis *et al.*[163] assessed these data and reported that biomass component additive models gave good performance when applied to some specific biomass compositions but yielded poor results above certain thresholds, particularly when a single type of compound accounted for most of the biomass content. However, the prediction of the process performance must also consider operating conditions. Empirical models may seem incomplete unless these factors are included in the equation. This is the approach taken by Yang *et al.*[137] and Aierzhati *et al.*,[161] who included temperature, time, and biomass loading as parameters in the empirical model, reporting a high prediction capacity, which is logical given the large influence these parameters have on the outcome.

The maximum oil production is obtained when the water is kept at subcritical conditions, with the gas phase containing mainly CO_2. The oils generated at lower temperatures usually have a high content of fatty acids and alkanes. They can be classified as lipids with some hydrophobic protein fragments. In contrast, increasing the process temperature leads to reactions that resemble pyrolysis, obtaining carbohydrate derivatives such as furans, products derived from the interaction between carbohydrates and proteins (alkyl-pyrrolidinones, pyrazines, pyrroles, and melanoidin-like materials), and polycyclic aromatic hydrocarbons, with the gas phase also containing methane and light hydrocarbon gases. The latter phenomenon is mainly responsible for increasing oil yields and producing nitrogenous compounds in the oil.[164,165]

Fig. 7 shows the composition of biocrudes reported by different authors and the energetic content of these oils. Lignocellulosic biomass reports the highest content of oxygen and, therefore, lower values of energetic density. The reaction temperature is the most influential parameter affecting not only the bio-oil yield but also its quality, with an increase in this parameter leading to higher biocrude production (until a maximum is reached) while reducing its oxygen content and increasing higher heating value (HHV).[166,167] This trend is also evident in Fig. 8, where the dashed lines connecting the data sets of the same authors illustrate the effect of increasing temperature.

The main bio-oil components identified in the literature are presented in Table ESIII in the.† The optimum temperature is usually around 300 °C, and operating above the optimum may lead to an increase in heavy hydrophobic compounds and, in some cases, to higher solid char residue based on the statement of Déniel *et al.*.[168]

The extraction procedure affects the yield and composition of the biocrude, with dichloromethane (DCM) showing the highest recoveries, although the use of different types of solvents gives acceptable performance with yield variation of

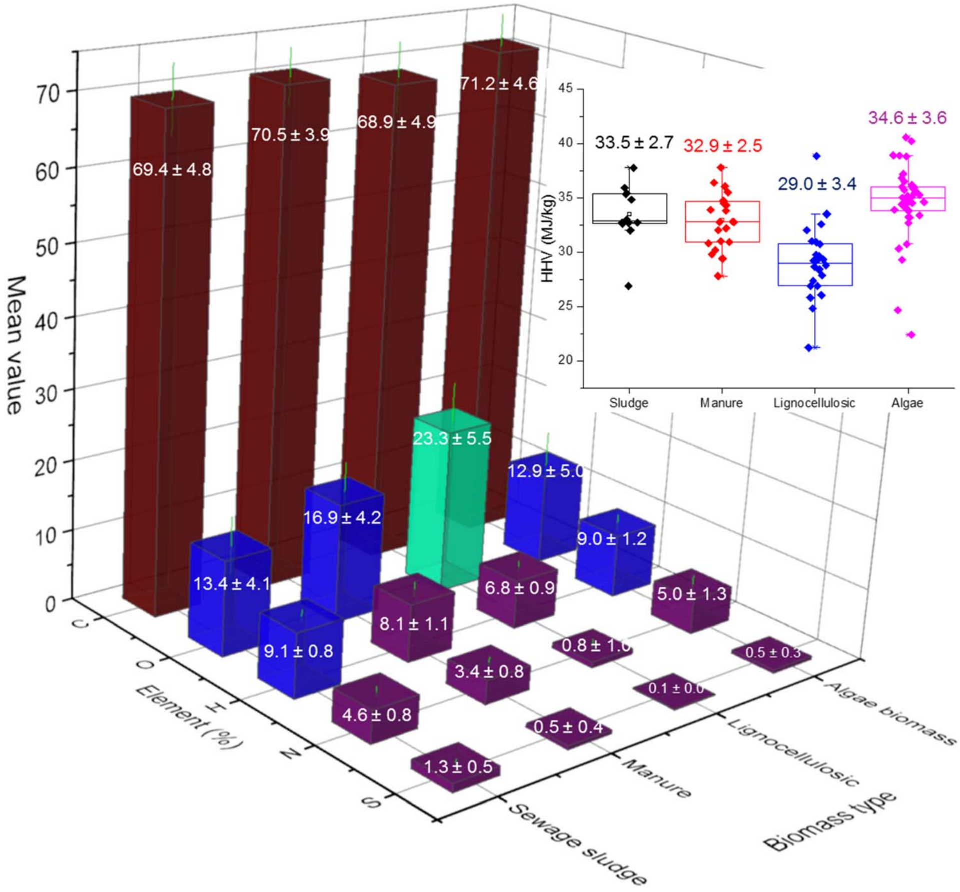

Fig. 7 Biocrude composition reported by different authors and their HHVs. Average values from ref. 77, 91 and 98–133.

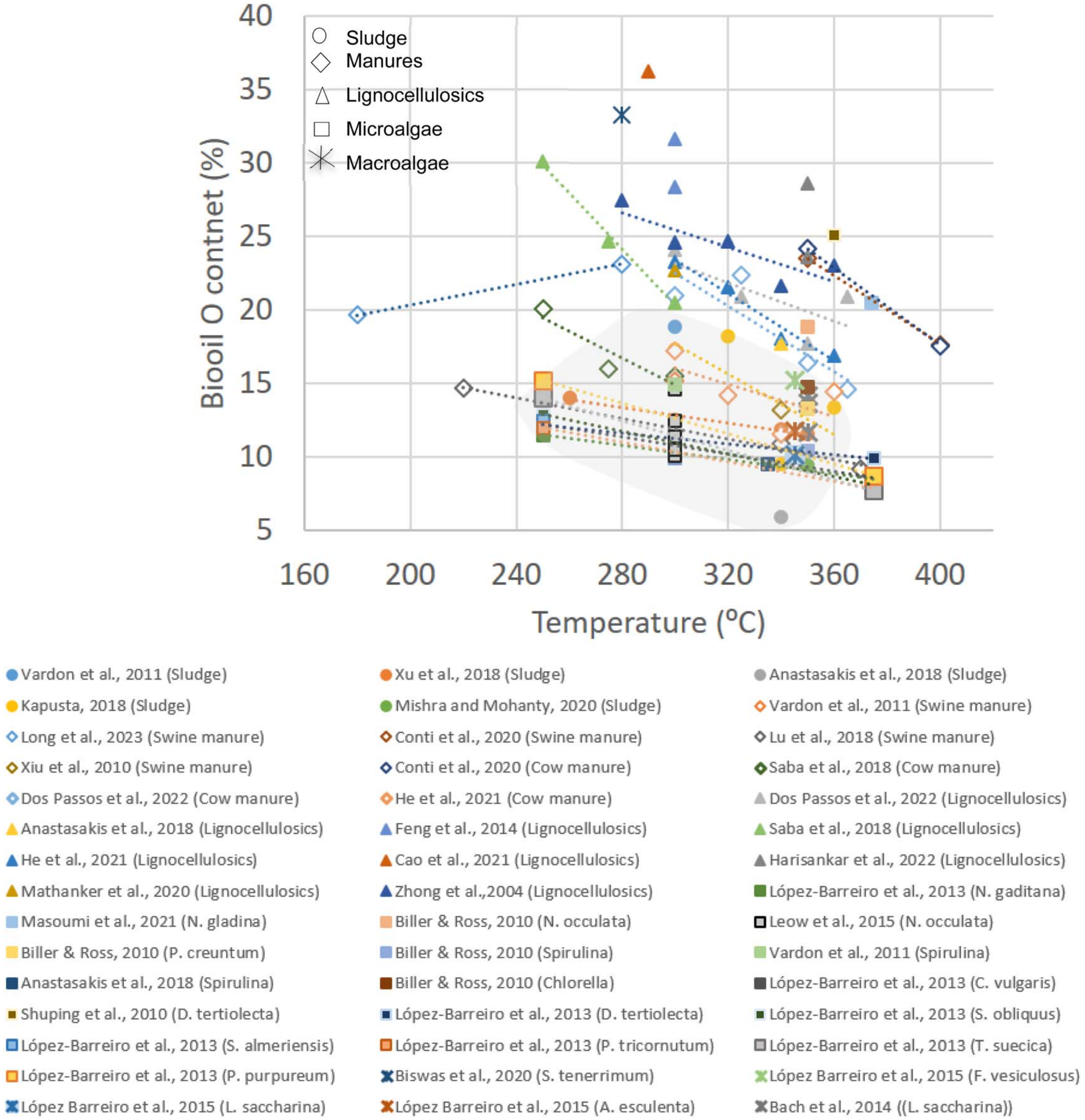

Fig. 8 Oxygen content in bio-oils reported by different authors. Trend lines were used for fitting experimental runs carried out at different temperatures in the same run (see in Table ESII†).

around 20%.[169] Acetone is the most frequent extracting solvent used for obtaining lignocellulosic HTL derived biocrude. The extraction procedure applied for recovering biocrude differs depending on the solvent selected and, therefore, affects the properties of fractions recovered, having different chemical and physical characteristics. However, the selection of the appropriate solvent must take into account the scaling up of the process and the possible challenges associated with the subsequent upgrading of the biocrude. In this line, Jahromi *et al.*[170] tested four different solvents (DCM, acetone, hexane and toluene) for extracting oil components and indicated that although hexane showed poor recovery, it provided the highest quality oil when considering further hydrotreatment. On the contrary, DCM which is commonly used to evaluate process performance, was demonstrated to be challenging in the subsequent upgrading stage, probably due to the high chloride content. Kilgore *et al.*[171] are one of the few works that evaluate the further processing of biocrude through solvent extraction procedures, highlighting the importance of selecting a proper solvent suitable for industrial applications, a fact that is not usually considered in most batch scale experiments.

Several reports exist that deal with batch HTL conditions at the laboratory scale. Still, the number of experimental works carried out on a pilot scale and under continuous operation is scarce in the scientific literature. This is explained by the difficulties of operating with high-pressure equipment, finding suitable pumping devices capable of handling a high solid content feed at a laboratory scale and outstanding elevated pressure, along with the high cost of the installation. The work of Wądrzyk *et al.*[172] is one among the few assessing temperature and residence time. These authors indicated that temperature had a more pronounced impact on the product yields and distribution than reaction time. The substrate treated was microalgae biomass (low lipid *Scenedesmus* sp), which allowed them to infer conclusions on the formation of complex cyclic nitrogen organics. At the highest temperature tested (350 °C), a longer residence time led to a decrease in the content of oxygenated compounds without observing any impact on the molecular weight distribution.

The liquefaction time is typically around a few minutes because retaining the material for longer periods inside the reactor allows time for recondensation reactions and repolymerization.[173] However, based on the type of feedstock used, increasing the holding time may result in greater biocrude yields in some cases, as in the experience carried out by Zhang *et al.*[174] treating lemon peel. Therefore, in some experiments, holding times close to 1 h or longer are applied,[175–177] usually in those performed under batch conditions. In the case of Zhang *et al.*,[174] they tested a series of runs to elucidate the interaction effect of common parameters (temperature, time, and solid content), showing that increasing reaction time, contrary to other studies, led to an increase in biocrude yield which was greater as the solid concentration of the material was decreased. A similar study by Zhuang *et al.*[178] also showed comparable outcomes. These authors treated a waste material with high protein content, but in their experiments, the residence time had a lower impact on oil production. However, the study by Vo *et al.*[179] showed that at high temperatures (400 °C), the liquefaction of algal biomass led to higher biocrude yields with shorter residence times (less than 10 min). The difference in the reported results is primarily attributed to the composition of the raw materials and the heating conditions applied (heating rate and heating homogeneity of the system).

The ratio of biomass to water addition is usually established around 1 : 10 mass units (dry biomass : water) in many experimental works because below supercritical conditions, the density and dielectric constant of water changes, acting as a solvent and hydrogen donor favoring the hydrolysis of organics.[74,180] Lowering the biomass-to-water ratio leads to a higher concentration of organics in the solution, favoring condensation reactions and increasing the amount of char produced and its carbon content. However, reducing the water content also benefits the global energy balance; therefore, some authors have reported working conditions with low values, such as a biomass : water ratio of 1 : 3.[82,181] Higher increases in this ratio do not lead to higher biocrude yields; but merely increases energy consumption.

3 Operating conditions to improve process performance

The diversity of materials suitable for liquefaction imposes some operational constraints related to the composition of the material, the moisture content and the fluid properties attained once the feeding mixture is prepared. In the case of lignocellulosic biomass, large quantities of water need to be added, which would translate into an excessively high water footprint unless the recycling of process water is included as an operational feature of the plant. However, the organic content of the HTL process water has an impact on the biocrude yield and its characteristics. Ramos-Tercero *et al.*[182] tested the recycling of the aqueous phase for up to six cycles, indicating an increase in oil yield until a steady level of oil production is reached. Similar results were reported by Zhu *et al.*[183] who treated barely straw, also indicating an increase in biocrude production with water recycling. Their results are in line with recent experiments carried out by Awadakkam *et al.*[184] who tested softwood and hardwood as suitable raw materials for the liquefaction process, reporting better process performance for the softwood type. These authors obtained a 47% increase in biocrude yield thanks to the recycling of process water and an improvement in bio-oil quality.

A similar approach is adding water containing organic compounds, as it would be the use of wastewater, thus aiding in the transformation and increasing the biocrude yield, as shown by Harisankar *et al.*[89] However, this feature is only possible when the nitrogen content of the feeding material is low; otherwise, it would lead to the accumulation of nitrogen compounds in the bio-oil. The study carried out by Jensen *et al.*[185] demonstrates this fact. Their experiments were carried out under continuous conditions and showed that ammonia initially released during HTL conversion and returned with the recycling water not only increased the nitrogen content of the biocrude, but also inhibited subsequent hydrotreatment. Shah *et al.*[186] tested the biocrude production from sewage sludge applying water recycling as well. Energy recovery was increased up to 50%, but the recycling strategy led to an increase in bio-oil nitrogen content, which almost doubled after 8 cycles.

Mahima *et al.*[187] proposed the use of HTL process water in a pretreatment stage when treating microalgae (*Scenedesmus obliquus*) under mild conditions (60 °C and 120 min), taking advantage of the presence of acids in the aqueous phase and of organics that can be recovered as oil in the HTL treatment. This sequence of operations enabled an increase in the bio-oil to 48.5%, compared to a value of 28.4% obtained without pretreatment, also improving the quality of oil by increasing the HHV to 36.2 MJ kg^{-1}. Although an increase in the solid residue was also reported, this was not as significant as the effect on bio-oil production. The increase in the nitrogen content of the biocrude was small (9.56% N content for the pretreated sample *versus* 8.62% for the one derived after the liquefaction of the raw sample). However, the reduction in oxygen content was more relevant, with a value of 30.5% of elemental oxygen for the raw sample and 11.2% for the biocrude derived from the pretreated system.

Many reports focus on the energy recovery of the process by considering the energetic units associated with the biocrude and that of the raw material. Nonetheless, the energy balance becomes less favorable when considering the energy required to heat the entire slurry mixture and the reactor. Anastasakis *et al.*[101] evaluated the performance of a pilot plant with a feed capacity of up to 100 L h^{-1} and a process volume of approximately 20 L, indicating that a high biomass loading (greater than 15%) is needed to get a positive balance. The best performance was obtained when using *Miscanthus* and *Spirulina* as biomass, with energy recoveries of 2.8 and 3.3 units. However, this value was lowered to 0.5 units in the case of sludge. Anastasakis and Ross[188] reported that the energy output of the process may be similar to that of the anaerobic digestion process when treating different types of macroalgae. If this is the case, opting for the digestion process may be more reasonable, given the lower capital investment associated with this latter technology and the simplicity of upgrading biogas and treating byproducts.

There is a lack of significant work dealing with process characteristics under continuous conditions, energy demand, pumpability issues, and maintenance costs associated with operating under subcritical conditions. The studies by Sintamarean *et al.*[189] and Dărăban *et al.*[190] are among the few that cover pumpability aspects of wood slurry, proposing the use of alkaline conditions to attain flowability at high solid content of biomass. However, alkaline conditions have been shown to increase corrosion in steel alloys, which becomes a relevant issue during prolonged operation.[191] This is a major challenge as lignocellulosic biomass requires the addition of an alkaline substance to improve flow characteristics and liquefaction performance. Therefore, technology deployment is highly dependent on the reactor costs associated with high-endurance steel alloys capable of withstanding highly corrosive conditions, such as acids, chlorides and sulfides which are commonly present during biomass conversion.[192]

The HTL process is claimed as a suitable alternative to other thermal processes such as combustion, gasification, and pyrolysis, with the main advantage being the absence of drying as prerequisite for raw material processing. Nonetheless, the difficulties in handling a wet slurry that must be pumped at high pressures and the subsequent treatment of by-products can negate any initial benefit previously highlighted. Gasification and pyrolysis products also require posterior processing. Fischer–Tropsch synthesis is considered the logical strategy for transforming biomass syngas into valuable hydrocarbons, with several years of scientific experience analyzing the feasibility of the approach.[193–195] Pyrolysis technology also counts with extended experience in this field, with several demonstration plants tested worldwide and a plethora of scientific reports assessing feasibility.[196–198] However, this is not the case for the HTL process, as most scientific documents found in the literature deal with small-batch scale reactors. The limited number of experiences carried out at a pilot scale may be considered a demonstration of the difficulties encountered when following this valorization path.

The application of pretreatments prior to the HTL process has been proposed as a way to increase bio-oil yield and reduce the content of nitrogen and oxygen. Li *et al.*[199] reported an increase in bio-oil yield from 30.85 to 37.95% after pretreating corn stalks with a combination of chemical and biological stages (alkaline-acid stage combined with a fermentation stage using *Saccharomyces cerevisiae* (Angel yeast)). Chen *et al.*[200] also tested the application of an alkaline pretreatment using K_2CO_3 under mild conditions (temperature of 30–100 °C and holding time of 30–120 min), acting this substance also as a catalyst in the subsequent HTL stage. Optimization of the combined approach enabled a bio-oil yield of 34.9%. The review published by Fan *et al.*[52] describes the different effects of pretreatments such as acidic, alkaline, enzymatic, ultrasounds, and microwave assisted HTL, among others. The application of these pretreatments is intended to facilitate and enhance biocrude formation, while also improving oil quality. However, many of these pretreatment options have costs associated with additional equipment units and increased operational expenses due to corrosion issues. Enzymatic hydrolysis requires less energy and is carried out in a less aggressive environment. The high cost of this type of pretreatment is usually the main reason for limiting its application. Therefore, its use appears to be more adequate in biological processing of biomass, where a clear improvement in fermentation performance is achieved rather than as a pre-processing stage to the HTL technology.

Dividing the process into two stages has also been considered a suitable option for attaining better-quality oils. Eboibi *et al.*[201] treated *Tetraselmis* sp. by applying a first thermal hydrolysis stage (150 °C, 20 min) to extract proteins, followed by a second HTL stage at 310 °C and 30 min. This way, they obtained a 50% improvement in biocrude yield, allowing water to be recycled and attaining a reduction in nitrogen content between 32% and 46%. Following this same line of research, Vadlamudi *et al.*[202] proposed a first HTC stage under acidic conditions (using acetic acid as a catalyst) to extract most of the nitrogen and oxygenated compounds in this initial stage and then submit the hydrochar to HTL treatment. However, their approach reduced biocrude production from 35 to 20%, although the quality was improved.

Upgrading bio-oils with high nitrogen and oxygen content poses a challenge, particularly in the formation of hydrochar, which reduces the process energy recovery. Alternatives such as the sequential HTL process were developed by Miao *et al.*,[203] reporting 50% less char production and 5% higher oil yield. The process was initially carried out at lower temperatures (140–200 °C), and extracted polysaccharides were submitted to a second HTL stage at higher temperatures (220–320 °C). Prapaiwatcharapan *et al.*[204] also evaluated a two-stage process using *Coelastrum* sp. microalgae in a semi-continuous operating plant. The sequential process allowed the production of a biocrude with a nitrogen content of 4.1%, whereas the best value obtained was 6.3% for the single-stage process. Similar results were also reported by Huang *et al.*,[178] who reduced the nitrogen content in the biocrude from 6.65% to 4.18% after applying a pretreatment to the low-lipid microalgae (*Spirulina*). In more recent experimental work, a variant of the two-stage process was studied by Usami *et al.*[205] adding sulfated carbon SA powder as a catalyst and HCl. The first stage was carried out at lower temperatures (best conditions at 200 °C for 0 min, followed by a second stage at 320 °C without allowing for further retention time once the desired temperature was reached). The nitrogen content of the biocrude derived from the processing of microalga (*Fistulifera solaris*, JPCC DA0580) was between 1.97–2.21%.

4 Catalyst addition to enhance biocrude production and quality

The use of catalysts can greatly improve the thermochemical process. Common alkaline catalysts tested include the use of sodium hydroxide and sodium salts, whereas acids commonly used to catalyze the reaction include formic acid, acetic acid, and HCl,[83,113,187,206] with early studies already reporting a significant improvement in the amount of bio-oil produced when adding alkaline catalysts such as Na_2CO_3, KOH, NaOH in a similar way to what is observed in thermo-alkaline hydrolysis systems where these compounds enhance the reaction.[82,207,208]

The pH of the liquid phase influences the reaction pathway during biomass conversion, making catalyst selection crucial. Acidic and neutral conditions favor the formation of 5-HMF from cellulose, hurting biocrude formation, whereas under alkaline conditions the main compounds are C2–5 carboxylic acids and the efficiency of conversion is favored along with a significant improvement in feedstock flowability,[181,206] which is essential when scaling up the treatment. Acidic conditions are also known to aid in the formation of char due to the enhancement of monosaccharides dehydration reactions and cellulose conversion, along with increasing the recovery of cyclic furan compounds in the aqueous phase.[209,210]

Using catalysts facilitates the distribution of nitrogen compounds in the liquid phase rather than in the bio-oil. Biller and Ross[83] showed that when *Spirulina* was treated with Na_2CO_3, only 4.5% of the nitrogen ended in the biocrude, whereas a value close to 20% was obtained without a catalyst. However, the use of this sodium salt is not recommended for lipid accumulating algae, despite increasing bio-oil yield in the range of 12 to 30%, because it also causes an increase in the solid residue due to saponification reactions.[211–213] Xu *et al.*[214] reviewed the effect of catalysts in HTL of algal biomass, advising against the use of alkaline homogeneous catalysts because of the difficulties in recycling the catalyst during industrial operation and the adverse effect it may cause in the subsequent treatment of the process water.

Heterogeneous catalysts have also been proposed not only to attain an improvement in reaction conversion but also to aid in removing oxygen from oils.[215] In addition, these types of catalysts can be physically separated, allowing their recovery and continuous use in subsequent cycles.[216] However, as previously stated, the difficulties found in removing nitrogen-containing compounds make it more feasible to consider the idea of treating lignocellulosic biomass rather than keep on studying microalgae as the best option. Long *et al.*[217] tested the HTL treatment of sugarcane bagasse for producing biocrude, reporting a nitrogen content of 0.38% when catalysts were added. Still, the value reported without the aid of catalysts was already low (2.56%), close to that of biocrudes derived from microalgae after catalytic upgrading. However, in the case of sugarcane bagasse, other uses of this material should be considered since the extraction of sugars from this plant requires the use of bagasse as a biomass fuel for heating, thus reducing the actual availability of this material. Table 4 lists various studies found in the scientific literature that report on the use of catalysts for treating a wide range of biomasses. As observed from the table, the amount of work is extensive, with the focus of recent research being placed on heterogeneous catalysts containing metals with higher availability and lower prices.

The application of zero-valent metals as catalysts to enhance biocrude production, along with the use of either Ni or Co catalysts to favor oxygen removal, was proposed by Tai *et al.*[241] in the treatment of oak wood to produce high-quality biocrude. Several authors have proposed the use of Ni as a catalyst to increase the liquefaction performance and, therefore oil yields[233,242,243] or to produce phenolic compounds of commercial interest under low temperature (250 °C) and high pressure (80 bar) conditions as reported by Remón *et al.*[244] using, in this case, a microwave-assisted process. However, the main advantage of thermal recovery is lost, thus making large scale applications unfeasible. De Caprariis *et al.*[245] modified the structure of a Ni catalyst to increase its activity and avoid using metallic supports. These authors reported that the surface modification increased the oil yield at lower temperatures and significantly reduced the reaction time. The combined addition of Ni catalyst under basic conditions was tested by Wang *et al.*[246] using a mixture of isopropanol and water as solvent. The combination of all these conditions resulted in a significant increase in oil yield when treating cellulose and lignin as model compounds, reaching a value of 67% at 240 °C and a low char formation.

De Caprariis *et al.*[226] added zero-valent iron as a catalyst for the HTL treatment of oak wood biomass. The presence of Fe favored the *in situ* production of H_2, which the authors assumed was the main reason for increasing biocrude yield (40% oil yield), despite the low water to biomass ratio used in these experiments (1 : 5). Considering that the final aim is to produce a fuel substitute, adding inexpensive catalysts is of great relevance. The work performed by Cheng *et al.*[247] aligns with the same line of research, using red mud and red clay as catalysts in the HTL of food waste. These authors reported a biocrude carbon yields of 39.5–47.0% (with HHVs of 40.2 for red mud and 37.7 MJ kg^{-1} for red clay). These values were much higher than those obtained without catalyst addition (biocrude yield of 19.7% and HHV of 36.1 MJ kg^{-1}).

The addition of catalysts has been demonstrated to improve energy recovery up to 70% and increase biocrude yields above 40%,[223,230,234,237] but its benefits go beyond improving energetic performance since the addition of alkaline compounds has proven essential for attaining proper biomass flowability and plays a significant role in avoiding char formation and changing the distribution of nitrogen and oxygen species between the oil and the aqueous phase. The impact of catalyst addition is also reflected in the subsequent stages regarding biocrude upgrading and further treatment of HTL process water. Processing lignocellulosic biomass or biomass with high carbohydrate content is ineffective without catalysts. This is because catalytic activity decreases the likelihood of forming condensed species, reducing char formation. However, in some cases, the addition of catalysts has not shown significant improvement in oil HHV.[248] As a notable disadvantage, it is worth mentioning the

Table 4 List of studies reporting on the use of catalysts to improve biocrude production and oil quality[ab]

Biomass	Catalysts	Conditions	Results	References
Dairy manure, poultry litter, pine sawdust, tallow seeds, switchgrass, peanuts, and vegetable oil	Sodium carbonate (Na_2CO_3), potassium carbonate (K_2CO_3), and sodium hydroxide (NaOH)	Batch reactor: 300 mL Temperature: 350 °C Time: 15 min 20% TS biomass slurry. 11% for pine sawdust and switchgrass 1–4 g of catalyst added to 100 mL of feedstock Oil measured as acetone soluble fraction (ASF)	The effect of the catalysts on ASF was not clear. Sodium carbonate catalyst appeared to improve conversion efficiency	Midgett *et al.*[218]
Willow—genus *Salix*—	NaOH used in a pretreatment stage and as catalyst	Tubular batch reactor: 10 mL Pretreatment of feedstock Temperature: 400 °C Time: 0–20 min Mass fraction of NaOH: 0.1 Biomass to water ratio: 1 : 4	The pretreatment improved product yields and quality the of bio-oil by reducing oxyganates, but increased the aromatic character of the oil	Grigoras *et al.*[140]
Sewage sludge	Na_2CO_3, Raney-Ni, $FeSO_4$, MoS_2	Batch reactor: 1 L Temperature range: 200–350 °C Time: 10–100 min initial H_2 pressure: 2–11 MPa Sludge to water ratio: 1 : 0–1 : 15 Catalyist loading: 5 wt% of SS on a dry basis	The highest bio-oil yield was 47.8 wt% at an initial H_2 pressure of 5.0 MPa, at 300 °C, 40 min. Sludge:water ratio: 1 : 5, catalyst loading ($FeSO_4$) of 5 wt% of dry SS	Malins *et al.*[219]
Sludge from food industry and from machinery work from WWTP	K_2CO_3 added with the feed	Continuous up-flow reactor Temperature: 350 °C Mass flow rate: 4.8–10.5 g min^{-1} Recirculation rate: 2 L h^{-1} Dry matter content of the feed: 6.5–12%	65% of the feedstock carbon is recuperated in the bio-oil product	Hammerschmidt *et al.*[220]
	ZrO_2 catalyst used in a fixed-bed reactor	1.5 wt% K_2CO_3	36% of energy in the feedstock is recovered as energy in the bio-oil product after considering thermal demand of the plant	
11 types of biomasses and mixtures (lignocellulosic biomass, micro and macroalgae, household waste and DDGS)	K_2CO_3	Batch reactor: 20 mL Temperature: 350 °C Time: 20 min Biomass concentration: 10% Catalyst loading: 2 wt%	The biocrude and aqueous phase were analyzed to quantify species. The key factors affecting elemental distribution and the course of reactions were the presence of ammonia and amines to form Schiff bases	Madsen *et al.*[221]
Empty fruit bunch (EFB) derived from oil palm residues	CaO, MgO, MnO, ZnO, NiO, SnO, CeO_2, Al_2O_3, La_2O_3	Batch reactor: 8.8 mL	CaO, MnO, La_2O_3 and CeO_2 gave the maximum bio-oil yield. About 1.40 times that without catalyst	Yim *et al.*[222]
		Temperature: 360–450 °C Time: 15–960 min Biomass to water ratio: 1 : 10 Catalyst loading: 1.0 wt%	Optimum conditions: 390 °C, 60 min	

Table 4 (*Contd.*)

Biomass	Catalysts	Conditions	Results	References
Sweet sorghum bagasse	K_2CO_3, KOH, formic acid, Ni/Si–Al, Ni_2P, zeolite	Batch tubular reactor: 25 mL Temperatures: 300 and 350 °C Time: 1 h after target temperature Bagasse was pretreated to release sugars Bagasse content of 20% Heating ramp: 25 °C min^{-1} Catalyst loading: 2.0 wt%	The best catalyst was K_2CO_3 with a crude yield of 61.8% at 300 °C. HHV biocrude: 33.1 MJ kg^{-1}	Bi *et al.*[223]
Sugarcane bagasse	Solid alkali catalyst of MgMOx (M = Mn, Ni, Fe, cr, Zn and Al)	Batch reactor: 500 mL Temperature: 200–330 °C Time: 5–90 min Catalyst loading: 1 g/10 g biomass	Optimum conditions: 250 °C for 15 min using $MgMnO_2$. 93.7% of the bagasse was liquefied Oil yield in the water-soluble fraction was 59.5%	Long *et al.*[217]
Pinewood sawdust	Spent catalyst (V_2O_5-WO_3/TiO_2) from the denitrogenation of flue gas	Batch reactor: 100 mL Temperature: 240–320 °C Time: 0–60 min Bioass to water ratio: 1 : 10 Catalyst loading: 0–20 wt%	The maximum oil yield was 34% at temperature of 320 °C in the presence of a catalyst, whereas this yield was just 24.2% without catalyst addition No significant effect was observed in the oxygen content	Qian *et al.*[224]
Pinewood sawdust	K_2CO_3, Ni/HZSM-5, HZSM-5	Batch reactor: 500 mL Temperature: 300 °C Heating ramp: 5 °C min^{-1} Time: 1 h after reaching reaction temperature Biomass to solvent ratio: 2 : 11 Catalyst loading: 4 g/20 g biomass Addition of ethanol as co-solvent	The oil yield without catalyst was high (approximately 58%) thanks to the presence of ethanol. The best results were obtained with the addition of K_2CO_3 (yield about 65%). However, the oxygen content was still high in all cases tested. A large increase in hydrocarbon fraction was obtained thanks to the presence of a catalyst, with Ni/HZSM-5 reporting the higher content	Cheng *et al.*[225]
Oak wood biomass	Fe, Fe_3O_4, Fe2O3	Tubular microreactor: 10 mL Temperature: 260–320 °C Time: 10–60 min Biomass to water ratio: 1 : 5 Biomass catalyst ratio: 0.5 : 10; 1 : 10; 3 : 10 Heating rate: 60 °C min^{-1}	Highest bio-crude yields (about 40%) were reached using zerovalent Fe H/C ratio in the bio-oil increases by about 15% High oxygen content in bio-oil (23–30%)	De Caprariis *et al.*[226]

Table 4 (*Contd.*)

Biomass	Catalysts	Conditions	Results	References
Wheat stalk	Na_2CO_3, Fe and Na_2CO_3 + Fe	Batch reactor: 300 mL Temperature: 240 °C Time: 30 min Biomass to water ratio: 1 : 10 Catalyst loading: 0.55 g g^{-1} biomass	Na_2CO_3 + Fe can promote the cracking of wheat stalk compared to the performance of the single effect of each catalyst The highest heavy bio-oil yield of 24.25 wt%	Chen *et al.*[227]
Rice straw	CuZnAl	Batch reactor: 250 mL Solvent: water/ethanol mixtures Temperature: 300 °C Time: 30 min Pressure: 1.2 MPa H_2 atmosphere (initial condition) Biomass to water ratio: 1 : 10 Catalyst loading: 0–2 g	Interest in increasing the yield of phenolic monomers High recycling capacity of catalysts Optimum condition: addition of 2 g of CuZnAl catalyst, a ratio of 50% ethanol/50% water (v/v), a temperature of 300 °C and a reaction time of 30 min	Zhou *et al.*[228]
Microalgae *Scenedesmus obliquus* (cultivated from wastewater)	Calcium hydroxide derived from clam shells	Batch reactor: 250 mL Temperature: 240–320 °C Time: 60 min Biomass to water ratio: 1.5 : 20 Catalyst loading: 0.2–1 wt%	The maximum bio-oil yield was 39.6 wt% Solid residue derived from HTL was proposed as catalysts in the gasification of the same algal biomass for H_2 production	Arun *et al.*[229]
Birch sawdust	$FeSO_4$, $ZnSO_4$, $NiSO_4$, Raney-Ni, Ni65%/SiO_2–Al_2O_3, Na_2CO_3, NaOH	Batch reactor: 500 mL Temperature: 200–340 °C Reaction time: 5–90 min biomass to water ratio: 1 : 2–1 : 8 H_2 partial pressure: 0–10 MPa Biomass to water ratio: 1/2–1/8 Catalyst loading: 0.5–7 wt%	Application of H_2 gas phase was not recommendedOptimal conditions: biomass : water ratio of 1 : 4, temperature of 300 °C, residence time of 5 min and NaOH catalyst amount of 5 wt% of dry BS Bio-oil yield was 54.1% and energy recovery was 69.6%	Malins[230]
Chinese herb residue (*Angelica sinensis*)	Fe zero valent, Ni, ZSM-5 and Bifunctional catalysts (Fe/ZSM-5, Ni/ZSM-5, Fe–Ni/ZSM-5)	Batch reactor: 500 mL Temperature: 290–350 °C	The bio-oil yield of the raw material was 24.7% (320 °C, 10 min, 1 : 15 biomass ratio). The addition of catalyst reduced the bio-oil yield for all cases studied. The Fe addition case reported the best results Catalysts increased the proportion of aromatic compounds	Guan *et al.*[177]

Table 4 (*Contd.*)

Biomass	Catalysts	Conditions	Results	References
		Time: 0–60 min Biomass to water ratio: 1 : 7.5–1 : 30 Catalyst loading: 20 wt%	The improvement in HHV was low along with deoxygenation (biocrude oxygen content was reduced from 21.3% to 18.3% after adding Fe catalyst)	
Microalgae *Euglena* sp	HZSM-22, HZSM-5, H beta, MCM-22, SAPO-11	Batch reactor: 50 mL Temperature: 280 °C Time: 30 min Biomass to water ratio: 1 : 10 Catalyst loading: 10 wt%	Catalyst addition did not enhance biocrude formation, showing slightly lower values than the case without catalyst H Beta catalyst allowed the best performance regarding bio-oil quality (37.1 MJ kg^{-1}) reducing N compounds in 31% although the value was still high (4.56% of N content in biocrude)	Zhang *et al.*[231]
Microalgae: *Chlorella vulgaris* and *Nannochloropsis occulta*	$Co/Mo/Al_2O_3$ Pt/Al_2O_3 and Ni/Al_2O_3	Batch reactor 75 mL Temperature: 350 °C Time: 1 h Biomass to water ratio: 1.1 : 10 Catalyst loading: 20 wt%	Biocrude yields from the liquefaction of microalgae were increased slightly with the use of heterogeneous catalysts but the HHV and the level of de-oxygenation increased by up to 10%. Ni, Pt based catalysts reduced the oil N content by 12% compared with the non-catalyst case for *Nannochloropsis occulta*	Biller *et al.*[215]
Microalgae (*Nannochloropsis* sp.)	Pt/C catalyst for biocrude up-grading. Testing also H_2 atmosphere	Batch reactor: 400 mL without catalyst use Temperature: 320 °C Heating time: 4 h (slow heating) Cooling of reactor as soon desired temperature was reached Biomass TS content: 20% Batch reactor for bio-oil upgrading: 4 mL Catalyst loading: 25 wt% relative to biocrude	29% bio-oil yield. Upgrading of bio-oil reduced its oxygen content from 6.52% to 4.3–4.7%, and its nitrogen content from 4.9% to 2.2–2.8%	Duan and Savage[232]
Microalgae *Nannochloropsis* sp	**n**ano-Ni/SiO2, acid catalyst (synthesized zeolite), Na_2CO_3	Batch reactor: 500 mL Temperatures: 210–250 °C Heating rate: 6 °C/min Time: 1 h (after reaching desired temperature) Biomass to water ratio: 1 : 15 Catalyst loading: 5 wt%	The highest bio-oil yield (30.0 wt%) was obtained at 250 °C by using Nano-Ni/SiO_2	Saber *et al.*[233]
Microalgae *Nannochloropsis* sp	Various transition metal M/TiO_2 (M = Fe, co, Ni, Mo, and Mn)	Batch reactor: 1.8 L Temperatures: 240–350 °C Time: 30 min Biomass to water ratio: 2.5 : 10 Catalyst loading: 10 wt%	Ni/TiO2 suggested that 300 °C led to a maximum biocrude yield of 48.23% and the highest liquefaction conversion of 89.28%	Wang *et al.*[234]

Table 4 (*Contd.*)

Biomass	Catalysts	Conditions	Results	References
			Nitrogen content was between 6.75–7.68% in all cases tested, including the no-catalyst case. The oxygen content was lower for the no-catalyst case (11%), whereas catalyzed systems reported a value between 12.2-14.6%. The oil yield with Ni base catalyst reached a maximum value of 48.2% at 300 °C	
Low-lipid microalgae *Dunaliella tertiolecta*	acid catalysts: ZrO_2/SO_4^{2-} and HZSM-5	Batch reactor: 50 mL Temperature: 360 °C Time: 30 min Biomass to water ratio: 1 : 10	Base catalysts are conducive to improving conversion and bio-oil yield	Chen *et al.*[235]
	Base catalysts: MgO/MCM-41 and KtB	Catalyst loading: 10 wt%	KtB obtained a maximum bio-oil yield of 49.1 wt%	
Nannochloropsis salina, housefly larvae (*Musca domestica*)	H_2 atmosphere and Ni–Mo/Al_2O_3	Batch reactor: 2 L Temperature: 340 °C Time: 30 min Biomass to water ratio: 2 : 10	Higher biocrude yields with better properties were obtained under the hydrogenated treatment in the presence of the catalyst	Li *et al.*[236]
		Catalyst loading: Not indicated	Hydrogenation reduced hydrophilic functional groups with more branched cyclic nitrogenous compounds found in the biocrude	
Chlorella pyrenoidosa	HZSM-5, Ce/HZSM-5	Batch reactor: 100 mL Temperature: 300 °C Time: 20 min Biomass to water ratio: 1 : 10 Catalyst loading: 5 wt%	The catalytic cracking effects of Ce/HZSM-5 (50% bio-oil yield) were superior to those of HZSM-5 (34%)	Xu *et al.*[237]
Microalgae *Spirulina*	Reduced graphene oxide (RGO) material loaded with nickel	Batch reactor: 25 mL Temperature: 270 °C Time: 30 min Biomass to water ratio: 1 : 9	The maximum yield of bio-oil was 45.57%	Liu *et al.*[238]
		Catalyst loading: 5 wt%	Results are similar to previous work with no improvement in N or O content	
Microalgae *Spirulina*	Clay catalysts: Montmorillonite KSF, kaolinite, and dolomitic limestone	Batch reactor: 1.8 L Temperature: 270 °C Time: 30 min Biomass to water ratio: 2.5 : 10 Catalyst loading: 10 wt%	Biocrude yield increased from 30.5% (no catalyst case) to 39.7–40.2% (catalyst added). However, the N content of biocrudes was higher in cases where catalyst was added (increasing from 6.8% to 7.0–7.4% along with asphaltene content (from 26.9% to 38.7–58.1%)	Wang *et al.*[239]

Table 4 (*Contd.*)

Biomass	Catalysts	Conditions	Results	References
Macroalgae Ulva lactuca	ZSM-5, MgO	Batch: 100 mL Temperature: 260–300 °C Time: 15–45 min Biomass to water ratio: 1 : 6 Catalyst loading: 10 wt% Formic acid (FA) with solvents (water, ethanol and methanol)	The maximum bio-oil yield under ethanol-formic acid solvent mixture (no catalyst) was 43.8 wt%. (280 °C, 30 min). Adding MgO as catalyst increased oil yield to 55.2% whereas the use of ZSM-5 gave a result of 48.7%, using the same solvent mixture in both cases	Li *et al.*[240]

[a] DDGS: Dried Distillers Grains with Solubles. [b] Catalyst loading expressed in terms of biomass sample.

deactivation of active sites by coking, along with the difficulties found in catalyst recovery.[249] The characteristics of the feedstock influence the likelihood of coke formation, which can lead to catalyst deactivation as coke deposits on active sites. Moreover, other factors related to the catalyst itself are also relevant, such as its acidity, pore size, and structural properties.[250] Other deactivation mechanisms include metal poisoning and erosion by ash components in the feed; thus, deactivation is usually categorized into three main mechanisms: mechanical, chemical, and thermal.[251]

5 The effect of gas phase and liquid phases on biocrude production

Organic conversion in HTL experiments is usually carried out in an inert atmosphere in the presence of water as a solvent. However, modifying the gas phase or the solvent composition has been shown to enhance thermal breakdown and favor chemical reactions. The bio-oil phase can be increased by using a gas phase containing a mixture of gases or a single gas (either air, N_2, H_2, CO, CO_2 along with the addition of catalysts). Yin *et al.*[113] indicated that introducing CO as a gas phase allowed for obtaining a maximum bio-oil yield of 48.8% (310 °C) when treating cattle manure. Air as a gas phase produced much lower bio-oil yields than any of the other gas phases tested (CO, N_2, and H_2). In another study, Theegala and Midgett[252] reported that combining the use of Na_2CO_3 as a catalyst under a CO_2 atmosphere increased the oil yield to 24% when treating dairy manure. Ethylene is another gas phase tested in HTL experiments. Rahman *et al.*[253] used an ethylene atmosphere to convert sewage sludge, adding red mud as a catalyst. The presence of ethylene maximized the biocrude yield, producing 41.6 wt% against a value of 37.1% in the nitrogen atmosphere. The nitrogen content of the bio-oil was reduced by 14% thanks to the addition of the catalyst, but even the lowest value obtained was still high (3.74% of N content in bio-oil).

Some authors have proposed the use of polar and non-polar solvents in HTL experiments to improve the quality of the bio-oil obtained. Such is the work reported by Valdez *et al.*[254] testing hexadecane, decane, hexane, and cyclohexane as non-polar solvents and methoxycyclopentane, dichloromethane, and chloroform as polar solvents. Experiments were performed treating *Nannochloropsis* sp. at 350 °C for 60 min, reporting higher oil yields when hexadecane and decane were added as solvents. Oils recovered when using polar solvents had a higher carbon content and a higher proportion of fatty acids.

Early experiments carried out by Fan *et al.*[255] testing acetone, ethylene glycol, ethanol, water and toluene as solvents in the liquefaction of oil palm empty fruit bunches (EFB) fibers (*Elaeis guianensis*) reported the positive effect of ethanol on the oil quality. The presence of phenolic compounds was increased when either water, ethanol, or toluene were used as solvents. Han *et al.*[256] added isopropyl alcohol and ethylene glycol as co-solvents in the liquefaction experiments of microalgae biomass (*Tetraselmis* sp). They reported that isopropyl alcohol increased the bio-oil yield by 14.5 ± 4.9%, whereas the use of ethylene glycol had no beneficial effect. Cheng *et al.*[257] previously showed that using 50% water mixtures with either methanol or ethanol was highly effective in increasing oil yield. Therefore, in their study, the bio-oil yield reached 65% (treatment conditions of 300 °C and 15 min) when testing pine sawdust as raw material. This approach is beneficial for increasing oil yields from high cellulosic-containing material. Yerrayya *et al.*[88] reported an increase from 12.3% to 36.8% in bio-oil yield during the treatment of rice straw by adding methanol to water (solvent mixture). The presence of methanol improved performance and changed the character of bio-oil, increasing the amount of methyl ester compounds. The addition of an alkaline catalyst further enhanced the biocrude formation, reaching a value of 40%. In addition, when considering the treatment of high lipid-containing biomass, using methanol allows for performing *in situ* transesterification, thus carrying out liquefaction and methyl ester reaction in a single stage, as proved by Patel and Hellgardt.[258]

Nevertheless, adverse effects have also been reported when adding ethanol as a co-solvent. Caporgno *et al.*[259] tested different mixtures of ethanol–water as a solvent during the HTL experiments of the microalgae *Nannochloropsis oceanica*. They reported an increase in the bio-oil yield compared to the HTL water case, but the bio-oil HHV experienced a decrease due to the higher oxygen content. Ji *et al.*[260] also tested ethanol as a co-solvent in a water mixture when treating the low-lipid microalgae *Spirulina*. The addition of ethanol up to 50% increased the biocrude yield, but further addition increased the char yield. It seems that when the material contains large amounts of carbohydrates or carbohydrates-lignin as it is the case of algal biomass and lignocellulosic material, adding an organic co-solvent may promote biocrude formation.[133]

Wang *et al.*[261] tested CO_2, acetone, and ethanol as solvents in the liquefaction of pinewood sawdust, along with the use of K_2CO_3 as a catalyst to increase reaction conversion. The bio-oil yield was between 28 and 31% with the use of solvents, whereas this value was much lower in the presence of water (17.3%). A similar work, but with better results, regarding biocrude quality was that of He *et al.*.[262] These authors used the filamentous freshwater macroalga *Oedogonium* grown under nutrient-depleted conditions to achieve a low nitrogen content (1.1 wt% N). The HTL process was carried out in a continuous flow pilot scale reactor with a treatment capacity of up to 90 L h^{-1} *n*-heptane, toluene, and anisole were used as co-solvents (10% addition). The biocrude presented a nitrogen content between 1.6 and 1.9 wt% N, a value much lower than any previously reported for algal biomass. The use of *n*-heptane allowed the reduction of the nitrogen and oxygen content of bio-oils.

Most of the studies use micro- or macro-algae as input materials for hydrothermal processing due to the higher oil yields derived. Manure has also been tested, although it often results in lower oil yields. However, the experiment by Ye *et al.*[263] reported a 65% oil yield when using a mixture of glycerol, methanol, and water as solvent. The result was higher than any other experiments using these single constituents as solvents. Glycerol was also proposed as a solvent by Chopra *et al.*[141] in the liquefaction of residual yeast biomass after de-oiling. The use of glycerol greatly enhanced biocrude production, although it also increased char formation. Lu *et al.*[264] also tested glycerol and crude glycerol as co-solvent to aid in the formation of biocrude when treating a low-lipid marine macroalgae (*Enteromorpha prolifera*) characterized by a high ash content (about 30%). Crude glycerol showed a better performance because this byproduct from biodiesel production also contains methanol and fatty acids, which enhances the conversion, thus increasing oil production and reducing the nitrogen content of bio-oil.

6 Treatment of the aqueous phase

In recent years, the treatment of the aqueous phase derived from HTL by anaerobic digestion has been considered as a feasible option given the high versatility of the process for transforming a wide variety of organic compounds and its capacity for receiving high-loaded influents. Zhou *et al.*[265] reviewed the main findings on this topic by considering process water derived not only from HTL but also documents regarding HTC process water and that from pyrolysis. Even though early researchers proposed its use as a culture medium for growing algae as a way to close production cycles, the greater tolerance of anaerobic cultures and their capacity for transforming organic strength streams into biogas have turned the focus to this biological process. However, even in this case, several difficulties have been found regarding inhibitory conditions created by the presence of toxic compounds such as cyclic oxygenates, nitrogen heterocyclic compounds, and their derivatives, which categorized this wastewater as having substantial toxicity.[266,267] Kulikova *et al.*[268] studied the composition of this process water derived from the HTL treatment of sewage sludge, reporting as main components fatty carboxylic acids and aromatic carboxylic acids and a low concentration in ketones and aldehydes. Table 5 reports the main characteristics of HTL process water from different authors.

The HTL aqueous phase has been treated by anaerobic digestion with several authors reporting almost total or partial degradability. Zhou *et al.*[86] reported methane yields of 500 mL g^{-1} COD removed, despite the addition of activated carbon to mitigate toxicity and the reduction of the dilution rate. Si *et al.*[273] proposed ozone pretreatment to alleviate acetogenesis inhibition during digestion of this aqueous phase, along with the addition of granular activated carbon to remove recalcitrant organics and enhance carbon conversion by the anaerobic microflora. The possible integration between AD and HTL under different configurations has been reviewed by Tatla *et al.*,[274] highlighting the relevance of reducing toxicity associated with the aqueous phase and that of the hydrochar obtained. Otherwise the global processing of biomass may not be feasible.

Cabrera *et al.*[275] proposed the valorization of grease waste from the trap of a dairy wastewater treatment plant, along with the degradation of the aqueous phase by anaerobic digestion. They reported a significant reduction in the COD content without experiencing inhibitory conditions. Dark fermentation is another biological process capable of treating streams with

Table 5 Characteristics of process water

Parameter	Value
Chemical oxygen demand, COD (g L^{-1})	48.2–89.0 (ref. 87, 136, 160 and 269–271)
Total organic carbon, TOC (g L^{-1})	7.3–32.7 (ref. 87, 167, 175, 231 and 270–272)
Total nitrogen, TN (mg L^{-1})	83.0–22 981.0 (ref. 136, 167, 231, 270 and 271)
Ammonia (mg L^{-1})	614–28 100 (ref. 87, 160,167, 175 and 270–272)
Total phosphorus, TP (mg L^{-1})	4400–33 100 (ref. 160 and 271)
Phosphate (mg L^{-1})	58.9–5300.0 (ref. 87, 167, 175 and 272)
Sulfate (mmol L^{-1})	17.4–73.0 (ref. 175)
pH	3.8–9.49 (ref. 87, 114, 136, 231 and 271)
Formic acid (mg L^{-1})	8509 ± 1542 (ref. 269)
Glycerol	4992 ± 253 (ref. 136)
Lactic acid (mg L^{-1})	9758 ± 1392 (ref. 266)
Acetic acid (mg L^{-1})	4319–29 196 (ref. 136, 175 and 269)
Propionic acid (mg L^{-1})	2730 ± 856 (ref. 269)
Butyric acid (mg L^{-1})	9072 ± 2136 (ref. 269)
Carbohydrates	1200 ± 25 (ref. 167)

high organic content. This process has also been proposed as a suitable option for transforming organics contained in the aqueous phase. Kopperi *et al.*[276] tested the catalytic conversion of *Scenedesmus* sp. biomass at low temperature (200 °C); these conditions allow producing carbohydrate compounds compatible with the dark fermentation process, thus reporting an H_2 yield of 186 mL g^{-1} TOC removed when treating this aqueous phase, along with methane production (131 mL g^{-1} TOC removed).

Some authors have recommended applying lower temperatures to reduce the presence of inhibitory compounds and increase methanogenic production from process water.[277] However, the aim of the HTL process is to produce biocrude, and the optimal temperatures are closer to the higher operating range.[278] The process water is characterized by high organic content, and high ammonia and phosphate concentrations (5000 mg L^{-1} for ammonia and 3900 mg L^{-1} for phosphate[87]). The efficiency of the process is highly linked to the distribution of the raw material carbon content and the formation of high energy density products. Zhu *et al.*[145] reported that about 16.4 to 42.6% of the carbon content present in the input material can be found in the aqueous phase (HTL treatment of corn stalks), with this percentage increasing with the increase in temperature without affecting the carbon recovery in the oil phase, hence the relevance of valorizing this process water. The organic components found in the aqueous phase are characterized by an acidic nature (carboxylic acids), phenolic compounds and simple sugars may be present when the treatment temperature is low, whereas the complexity of these molecules increases with the increase in the HTL temperature.[279]

During the treatment of high lipid-containing microalgae, a lower tendency to accumulate nitrogen in bio-oil was observed, but as the protein content increases, so does the nitrogen content of the bio-oil and that of the aqueous phase, with about 50% of the N input found in aqueous compounds.[127] Lu *et al.*[110] indicated that up to 37% of the nitrogen present in the raw sample can migrate to the aqueous phase, becoming part of ammonia and small molecules of pyrazines, pyrroles, and pyridines. Higher migration to the aqueous phase was reported by Liu *et al.*,[108] with values ranging from 65.8 to 76.3% when treating *Spirulina*, and by Yu *et al.*[93] when treating low-lipid microalgae (*Chlorella pyrenoidosa*), indicating an increase in these compounds with the increase in temperature and time. Wu *et al.*[280] reported that up to 35% of the nitrogen migrated to the biocrude and that the increase in treatment temperatures caused an increase in the aromaticity of the nitrogen-containing compounds constituting the aqueous phase. These results provide an indication of the potential difficulties that may be encountered when attempting to treat this process water biologically. The increase in the treatment temperature causes an increase in the ammonia concentration of the process water,[108,272] but it also results in a higher complexity of nitrogen-containing compounds, creating difficulties when considering a biological stage as a treatment option.

The high complexity of compounds dissolved in the process water has led to the attempt to apply microbial electrolysis cells (MEC) to aid in their conversion. MEC systems have become popular for assisting in various complex biological processes, thanks to the use of bioelectrodes that facilitate the transfer of electrons to cells, resulting in a faster reaction rate for some organics and the biological degradation of recalcitrant compounds.[112,281] Jiang *et al.*[136] reported a nitrogen organic content of 1476 ± 86 mg L^{-1} (mainly pyrazine and pyridine type compounds) for the process water derived from the HTL treatment of food waste. Treating this stream with an MEC allowed for a reduction in carbon content, but the removal of organic nitrogen was only 22%, thereby demonstrating the need to introduce other pre-treatments to facilitate its degradation. Table 6 lists some of the experiments reported in the scientific literature on the treatment of process water.

The integration of anaerobic digestion and HTL has the potential to offer benefits that extend beyond the treatment of process water, encompassing the entire process itself. Specifically, this approach entails the utilization of an existing technology for the digestion of livestock waste, with the subsequent addition of an HTL stage for the treatment of digestate, as proposed by Kassem *et al.*,[284] just as it has been previously

Table 6 Experiments reported in the scientific literature dealing with the treatment of HTL process water

Raw material	HTL conditions	Results	Reference
Corn stalks	Temperature 260 °C	Treatment of process water under continuous conditions using UASB and PBR. COD inlet was set at 8 g L^{-1} Short term operation (8 days) Methane production was reduced by about half compared to synthetic substrate performance	Si *et al.*[269]
Nannochloropsis sp	Temperature: 320 °C Time: 30 min	Precipitation of ammonium and phosphate as struvite crystals improved the methane potential Methane yield was 182 mL CH_4/g COD after struvite removal	Shanmugam *et al.*[87]
Rice straw	Temperature: 170–320 °C Time: 0.5–4 h	The highest methane yield (314 mL CH_4/g COD) was obtained from the treatment at 200 °C and 0.5 h Readily degradable organics (sugars and volatile acids) were present at lower treatment temperatures	Chen *et al.*[277]
Mixed-culture algal biomass grown in a wastewater treatment system	Temperature: 260–320 °C Residence time: 0–1.5 h	Moderate lag phase and the highest cumulative methane production were observed when HTL aqueous phase was obtained at 320 °C (16.3 mmol g^{-1} SSV equivalent to 365 mL g^{-1} SSV). The longest lag phase and the lowest production rate were observed in the process fed with aqueous phase obtained at 300 °C	Tommaso *et al.*[282]
Sewage sludge	Temperature: 290–360 °C Residence time: 0–30 min	Biological tests for treating process water included: aerobic, anaerobic (mesophilic and thermophilic) and dark fermentation. The authors reported that about half of the organic content was readily biodegradable. Increasing HTL process temperature increased inhibitory problems in subsequent biological stages. Phenolic and nitrogenous compounds were the main sources of toxicity. Dark fermentation proved inadequate	Basar *et al.*[283]

proposed with other thermal technologies.[285–287] However, the feasibility of this approach must confront the high capital investment of these units for attaining digestate valorization and the small scale of many farms, which is preferable in many countries due to the intrinsic rejection that the population usually exerts on large farms, despite the better efficiency of centralized units when considering manure treatment.[16,288] Therefore, the integration of HTL and anaerobic digestion initially seems more feasible when considering large scale digesters such as those operating in WWTPs. Cabrera *et al.*[289] analyzed the energy recovery when digestion and HTL are working in a coupled configuration, reporting a recovery of more than 70% when HTL is used either as a first stage (HTL–AD) or as an intermediate stage (AD–HTL–AD). The study carried out by Hussain and Anastasakis[290] is in line with this statement, reporting that only large scale WWTPs may have the capacity to confront the high operating costs of the HTL process.

The most effective treatment to date is to submit the process water to severe thermal conditions, such as the use of supercritical units. Marrone *et al.*[159] successfully tested the complete process under bench-scale conditions. The hydrothermal liquefaction of sludge and subsequent bio crude upgrading, along with the oxidation of the process water in a catalytic hydrothermal gasification unit, effectively reduced nearly all organic materials, resulting in concentrated ammonia water with values ranging from 2080 to 5430 mg L^{-1}. As with the biocrude, the characteristics of the process water depend on the composition of the raw material, with low pH values associated with the liquefaction of high cellulose-containing biomass that releases acidic compounds into the liquid phase, whereas protein-rich materials release ammonia from their thermal decomposition leading to a pH value above neutrality.[114]

Duan *et al.*[175] also reported the treatment of process water derived from eight different types of micro and macroalgae using supercritical conditions. Most of the experimental results indicated a successful removal of the organic content, with values above 84%. However, in two cases, the TOC removal was below 70% (for Macroalgae *Ulva prolifera*, the authors reported a removal of 57.1% and for *Zostera marina* with a removal of 66.8%). Given the severity of the process, the low removal values obtained for some macroalgae are a clear indication of the complexity of organic compounds formed and the difficulties in finding a suitable conversion process capable of achieving high removal rates. Unless all process specific issues can be resolved, the feasibility of translating the technology from a laboratory scale to commercial deployment is far from becoming a reality, given the extreme operating conditions (highly corrosive environments and high pressure) and the high energy demand associated with the conversion itself and subsequent treatment of the bio-oil and byproducts.

7 Upgrading biocrudes

Producing biocrude from the HTL process is only the first step; refining is needed and in particular, adapting further processing to the current technology already available for petroleum crudes is of key importance. Catalysts have become a close partner of all research lines dedicated to the thermal conversion of biomass, whether for gasification, pyrolysis and, of course in the present case, for liquefaction. Catalysts enable the production of higher yields, enhancing product quality and minimizing the presence of undesirable compounds, such as heavy hydrocarbon products.[291,292] Despite several years of research, only a few documents deal with pilot-scale experiments, given the high operating costs at such severe reaction conditions and the requirement for bio-crude upgrading which is also performed at high temperatures. The main exception is the technical work related to the Hydrofaction™ process, which can produce a biocrude with 2.2% oxygen after submitting the material to hydrotreatment using commercial presulfided CoMo and NiMo as catalysts.[293,294]

Upgrading of biocrude under supercritical conditions has been proposed as an option for removing undesirable heteroatoms. Hoffmann *et al.*[295] reported that the bio-crude derived from lignocellulosic biomass would need minor up-grading to make it compatible with current refining up-grading technologies. In subsequent work, Jensen *et al.*[296] reported the feasibility of deoxygenating bio-crude derived from lignocellulosic biomass using a conventional NiMo/Al_2O_3 catalyst. The tested hydrotreatment produced a bio-crude with an oxygen content of 0.3% (w/w) and an HHV of 43.7 MJ kg^{-1}. The experimental result of Yu *et al.*[297] was in the same line, obtaining the best performance with the same type of catalyst, although the oxygen content was higher (2.4%).

However, in the study by Patel *et al.*,[298] where the hydrotreatment of algae-derived biocrude was evaluated, in this case using different types of catalysts, the run with Pt/Al_2O_3 showed the best performance, but the oxygen content was higher (1.6%) than that reported by Jensen *et al.*[296] for lignocellulosic biomass, and the nitrogen content reported in this case was 2.87%. Therefore, as these authors stated, there is a need to develop catalysts capable of reducing the nitrogen content of crudes or include pretreatment stages prior to hydrothermal processing to lower nitrogen content. In the same line, was the previous study by Bai *et al.*,[299] in which a screening of different commercial catalysts was made for upgrading HTL biocrude from *Chlorella pyrenoidosa*. These authors proposed a two-stage upgrading process based on a first hydrotreatment performed without a catalyst and a subsequent stage using a Ru/C–Raney-Ni catalyst mixture. Their process reached a 2% content in nitrogen from a starting point of 8% in the bio-crude. However, the oxygen content in the raw biocrude was already low (2.1%) and did not seem to improve significantly.

Guo *et al.*[300] tested Ni–Mo/Al_2O_3 and NiW/Al_2O_3 catalysts at 250 °C and 400 °C for upgrading biocrude derived from microalgae (*Chlorella vulgaris* and *Nannochloropsis gaditana*). They obtained better results at the highest temperature. The HHV of the biocrude was increased from 33.8 MJ kg^{-1} to almost 43 MJ kg^{-1} for the upgraded oil, and the nitrogen content was decreased from 6.9% to 3.2–3.6% in the best case (using NiMo-based catalyst). A similar work was carried out by Moazezi *et al.*,[301] also using Ni–Mo/Al_2O_3 and *Chlorella vulgaris* as biomass, but in this case, reporting lower nitrogen removal. Thus, the nitrogen content of bio-oil was found to be 6.8% after upgrading.

Shakya *et al.*[302] screened five types of catalysts (Ni/C, ZSM-5, Ni/ZSM-5, Ru/C and Pt/C) for upgrading biocrude derived from HTL of *Nannochloropsis* sp. The best-upgraded quality was obtained at 350 °C (maximum temperature tested), with Ni/C reporting the maximum amount of bio-oil. Ru/C and Pt/C gave the better-upgraded bio-oils in terms of acidity, heating values, and nitrogen values (which were decreased to a value of 1.29%). Xu and Savage[303] tested different catalysts (Pt/C, Ru/C and Mo2C) in an H_2 atmosphere for short retention times (5 min and 400 °C) for upgrading biocrudes derived from the HTL treatment of *Nannochloropsis* microalgae. These authors also proposed reusing processed water from the HTL reactor, thus reducing the water demand. However, the lowest nitrogen content achieved was 2.5% and a value of 4.8% for oxygen content. In a subsequent series of experiments, the use of Ni–Ru/CeO_2 and Ni/CeO_2 was also tested for upgrading biocrudes from Nannochloropsis microalgae,[214] but in this case, the application of more severe conditions (450 °C, 60 min) resulted in a higher nitrogen content than that previously reported by Xu and Savage.[303]

In addition to lignocellulosic and algal biomass, other materials have been considered suitable for obtaining biocrudes and, therefore, studying the upgrading process. Subramaniam *et al.*[304] tested commercial hydrotreating catalysts (CoMo and NiMo) to upgrade biocrudes derived from food wastes and sewage sludge. Their study is one of the few that runs for several hours (1500 h) and reports promising results. The authors described minimal deactivation, producing a diesel-like oil with a high cetane number due to its high alkane fraction.

Given the difficulties in removing nitrogen from bio-oils, it seems a better option to treat woody biomass, such as sawdust, pulp mill waste, or any type of fast growing tree, such as poplar or willow, for bio-crude production rather than keep focusing on algal biomass with high protein content. The main oxygenated components of bio-oils derived from lignocellulosic materials are alcohols, organic acids, aldehydes, ketones, esters, and phenol derivatives,[305] which may be easier to upgrade. In addition, the low presence of nitrogen in this raw biomass facilitates the implementation of a water recycling approach to reduce the water footprint and recover the carbon contained in the aqueous phase. For the same reason, many studies assessing the technical feasibility of the process assume the use of either lignocellulosic biomass or waste with a relatively low content of proteins.

8 Techno-economic feasibility of HTL plants

The Pacific Northwest National Laboratory (PNNL) periodically updates the feasibility of the HTL process. The most recent updated report considers the use of algae liquefaction, indicating that in the case of farm-cultivated algae the cost of biomass production remains too high, thereby adversely affecting the economic balance.[306] Despite the progress in research, the high investment cost of the technology restricts its application only to cases where a large scale is possible, with an input capacity of more than 100 tons per day.[307] The early technical assessment carried out by Funkenbusch *et al.*[308] considered pulp mill waste, a high lignin biomass produced in large quantities (treatment capacity of 400 t dry pulp per day) at a localized point. The technical implementation of the process is greatly facilitated by the avoidance of producing high levels of nitrogen containing compounds. Alkaline conditions (KOH or K_2CO_3 catalysts at 10% loading) and short retention times (3–11 min) were assumed with an HTL temperature of 350 °C and a high rate of water recycling (greater than 95%). The estimated cost of the plant was between $ 114 and $ 124 million. The plant was assumed to produce BTEX and biofuel as valuable products, with a yield in the latter case (after considering upgrading and distillation operations) of 520–600 L biofuel/t biomass. The minimum selling price of the biofuel was estimated as $ 3.52–$ 3.86/gallon ($ 0.93–$ 1.0/L^{-1}).

A different study was published by Pedersen *et al.*[309] also dealing with the treatment of wood biomass, but in this case considering the combined treatment with crude glycerol as a scenario. The common feature is once again the avoidance of using high nitrogen containing biomass. The plant capacity was 500 t per day with a fuel yield (gasoline equivalent) of 27.8%. The minimum selling price, in this case, was in the range of $0.56–$1.87 L^{-1} of gasoline equivalent, with the higher prices obtained being associated with the high cost of crude glycerol. Kilgore *et al.*[171] assessed the impact of introducing a solvent extraction procedure in biocrude processing (derived from sewage sludge) and reported an increment of $0.2/GGE (gallon gasoline equivalent) in the minimum selling price of the biocrude using as model the work of Snowden-Swan *et al.*[310] regarding the updating of the MFSP (minimum fuel selling price) derived from hydrothermal liquefaction of food waste and sewage sludge.

The recent work of Hussain and Anastasakis[290] analyzed the integration of HTL in WWTPs for producing biocrude from sewage sludge. For the case evaluated, corresponding to an equivalent population plant of 100 000 inhabitants, the cost of the HTL plant for treating the sludge produced (primary and waste activated sludge) was € 4.2 million ($ 4.4 million). By increasing the size of the WWTP, the selling price of biocrude can be reduced from € 1.8 to € 0.9 kg^{-1}, in the latter case by considering an equivalent population of one million inhabitants. However, their study does not account for biocrude upgrading which would further increase the fuel price.

The high capital investment in technology forces its application to centralized systems that treat a large amount of locally produced waste, such as municipal solid waste, sewage sludge in wastewater treatment plants (WWTP), or pulp mill wastes. The fixed capital costs range between 40 000–65 000 $ per daily dry ton of raw material[290,311] and up to 240 000 $ when also including the full processing to obtain gasoline-type products.[312,313] When considering complex value chains, pyrolysis, and gasification also present high capital costs, but these technologies have the advantage of a larger experience gained from demonstration plants and can be easily integrated with combined heat and power (CHP) engines[314–317] thus greatly reducing costs associated with upgrading equipment.

Despite the efforts dedicated to implementing modifications in the HTL process for reducing the formation of nitrogen-containing molecules, the approaches associated with pretreatment stages or sequential HTL lead to an increment in the complexity of the plant, thus increasing capital investment and operational costs without reporting significant economic benefits.[309] Therefore, the best option currently available to avoid the presence of nitrogen compounds in bio-oils is the use of raw materials with low nitrogen content, which has the added advantage of allowing water recirculation and enhancing bio crude formation.

The low level of technology development at a large scale introduces substantial uncertainties in techno-economic and life cycle assessment (LCA) studies. The lack of data forces authors to disregard certain stages of the process, such as the treatment of gases and process water, or consider similar characteristics for pyrolysis oil and HTL biocrudes.[318,319] Depending on the assumptions selected, the HTL process may show a worse emission performance compared to pyrolysis,[320] and given the high energy demand, utilizing hydrochar as fuel in the same process may be a better solution than using it for land application,[321] thus negating one of the environmental benefits of the process.

A reduction of 89% in GHG emissions can be achieved by the substitution of fossil fuels with HTL biofuels when considering the transformation of forest residues.[322] The study of Lozano *et al.*[323] reported that the potential for emission reductions may be up to three times more beneficial when comparing HTL of sewage sludge for producing marine fuel and the pathway of sludge incineration for obtaining phosphate-rich ashes. However, one aspect that adversely affects any assessment is the transport of raw materials; for this reason, the study of Karka *et al.*[324] assumed decentralized stages during the HTL processing and central upgrading of products, thus obtaining GHG emission-savings in the range of 35% to 90% compared to the use of fossil diesel. Another relevant aspect is the cycle inventory, with the selection of the energy mix, water consumption, and delayed emissions having a significant impact on the estimated emissions.[325]

9 Conclusions

The HTL process has a great capacity to treat different types of biomass on a large scale. However, this advantage also limits its applicability due to the requirement to treat more than 100 tons of dried biomass per day to attain economic feasibility. Considering these high volumes of input materials, the technology application must be closely related to a mixture of wastes and raw materials capable of achieving high production rates in a localized zone. Despite all the extensive research, the technology is not close to commercialization and there are only a few demonstration plants worldwide. The complexity of the process and the high installation and operating costs are significant barriers unless the process can be successfully integrated into a conventional refinery to take advantage of shared processing units. Energy crops and wastes from a variety of sources appear to be the most logical combination of feedstocks to obtain biocrudes at a reasonable cost.

Data availability

Data supporting this manuscript has been included as part of the ESI.†

Author contributions

Iván Mazariegos: conceptualization, data curation, original draft, visualization. Silvial González-Rojo: review & editing, formal analysis. Ebtihal Abdelfatah-Aldayyat: data curation, visualization, editing. Xiomar Gómez: methodology, formal analysis, writing and supervision.

Conflicts of interest

There are no conflicts to declare.

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