Aquatic Biomass Conversion and Biorefinery for Value-Added Products

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Abstract The biorefinery concepts that merge technology and methods to transform aquatic biomass require the efficient utilization of most of the components. The presence of lipids, protein, and carbohydrates in aquatic biomass makes it a suitable feedstock for biofuel generation. Aquatic biomass's sugar and lignin components might be used to produce gas, heat, and bio-oil using thermochemical processes. The sugar component might be fermented to generate bio-butanol, bio-methanol, and bioethanol. The aquatic biomass lipid component could be used to manufacture biodiesel. Aquatic biomass might also be converted through biological processes into bio-methane and bio-hydrogen. Thermochemical processing (hydrothermal, pyrolysis, torrefaction) is a potential clean method for converting aquatic biomass and lignocellulosic materials to high-added value chemicals and bioenergy.

Keywords Aquatic biomass · Torrefaction · Pyrolysis · Biochar · Biogas · Bio-oil

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M. A. R. Lubis et al. (eds.), *Biomass Conversion and Sustainable Biorefinery*, Green Energy and Technology, https://doi.org/10.1007/978-981-99-7769-7_6

1 Introduction

Bioenergy is an environmentally conscious approach for minimizing reliance on oil, coal, and natural gas fuel. Energy is a commodity; hence a massive amount of feedstock is necessary. The search for innovative feedstocks for bioenergy production has been prompted by the rising energy demand and challenges associated with traditional feedstocks (Malode et al. 2022). In the recent past, researchers, policymakers, and the energy business have shown considerable interest in identifying and creating novel feedstocks. Current research focuses mainly on identifying acceptable feedstocks, creating effective conversion procedures, and reducing production costs overall. As biofuel feedstocks, lignocellulosic waste, municipal trash, microalgae, fungus, and other biomass have recently received considerable attention (Fakayode et al. 2023). These feedstocks have demonstrated biofuel production potential (Patel et al. 2021).

As a biofuel feedstock, aquatic biomass, including macro-, micro-algae, aquatic plants, and cyanobacteria, have the capacity to produce far more biomass per hectare than terrestrial crops; certain species produce fuel directly (Biller 2018). Advantages of such aquatic biomass include cultivating on the non-arable ground or even offshore and employing industrial carbon dioxide as a carbon source or wastewater as a fertilizer input (nitrogen and phosphorus). Aquatic biomass refers to energy crops that do not thrive with food crops for land or other resources. Numerous factors influence the productivity and composition of aquatic biomass, including nutrients, salinity, dark/light cycles, pH, irradiance levels, temperature, CO_2, and O_2 concentration. The composition of aquatic biomass includes proteins, lipids, carbohydrates, vitamins, and pigments, with lipids being the most interesting portion for biofuel production (Azwar et al. 2022). The practical implementation of regulating aquatic biomass as the raw material for diverse value-added products, as well as its biorefinery process (Fig. 1), has increasingly attracted the attention of researchers worldwide.

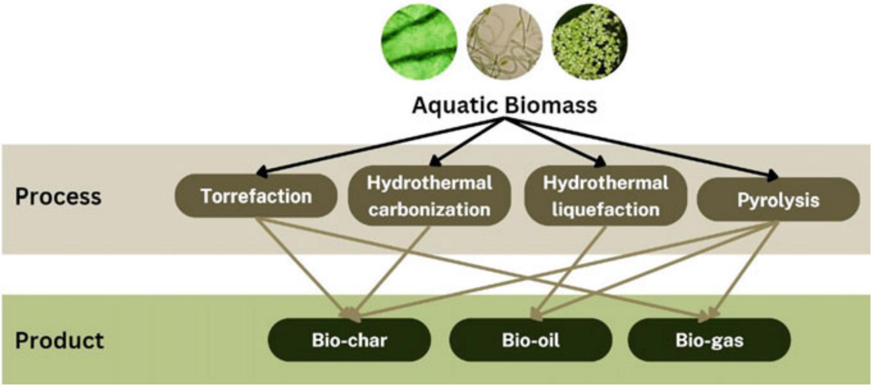

Fig. 1 The aquatic biomass biorefinery and its products

2 Aquatic Biomass as a Bioenergy Feedstock

Aquatic biomass has been identified as a viable renewable biomass feedstock in the production of bio-ethanol due to its high area-specific yields and photosynthetic efficiency. Microalgae have historically been explored for their potential high levels of lipids for biodiesel production (Ruiz et al. 2013). Among the significant benefits of microalgae versus terrestrial biomass is their elevated efficiency of photosynthetic to enhance CO_2 abatement and contributes to larger growth rates. Phototrophic and heterotrophic are the two functional classes of algae. Photoautotrophic algae absorb light and carbon dioxide for photosynthesis, while heterotrophic algae require oxygen and organic carbon sources.

Seaweed refers to a category of eukaryotic, photosynthetic marine organisms known as macroalgae (Alam et al. 2021). Both in terms of physical and biochemical properties, they differ significantly from microalgae. There are numerous species of them throughout the oceans and coastal waterways of the world. Aquatic weeds contain considerable levels of biofuel-convertible lignin, hemicellulose, and cellulose. The bulk of aquatic plant biomass is composed of lignin and carbohydrates. Lignin might be utilized to create combustible gases, bio-oil, and heat energy through thermochemical processes. The sugar component is immediately fermentable to produce bioethanol (Khammee et al. 2021). There is also a substantial opportunity to make bio-methanol and bio-butanol, among other alcohol molecules.

Additionally, aquatic weeds have lipids and a waxy covering composed primarily of modified fatty acids. Through the process of transesterification, these lipids may be converted into biodiesel. Through anaerobic digestion and biological processes, aquatic weeds can be used to produce biomethane and biohydrogen, respectively. Since aquatic weeds are fast-growing plants, they can provide greater biomass yields than most terrestrial energy crops. Macroalgae generally consist of a stipe, lamina or blade, and an anchoring and sustaining holdfast in marine conditions. Due to their size, the bulk of macroalgae must be ground before pumping. For instance, freshwater macrophytes are a diverse group of aquatic plants consisting of mono- or multi-cellular forms that frequently contain chlorophyll but lack genuine roots and stem in some cases. (Anyanwu et al. 2022). Algae and floating macrophytes (submerged, floating, and developing) are tiny, fast-growing plants typically found in watery habitat, and would not require agricultural land for agriculture, and several varieties are capable of living in freshwater, so preventing competing for water and land essential to produce food. Recent studies have revealed that the aquatic macrophyte *Ledermanniella schlechteri* (LS) and the green macroalgae *Ulva lactuca* (UL), prevalent throughout the Democratic Republic of the Congo, may be utilized to produce sustainable bioenergy (Mayala et al. 2022). Using biochemical methane potential (BMP) assays to evaluate how their anaerobic digestion functioned, it was revealed that the typical CH_4 levels for LS and UL are 262 and 162 mL gVS^{-1}, respectively. Moreover, LS's average HHV is 14.1 MJ kg^{-1} and UL's average HHV is 10.5 MJ kg^{-1}. Due to their negative ash behavior and high ash content, both biomasses would be challenging to convert thermally. The biochemical analyses revealed a high percentage of anaerobically digestible proteins and carbohydrates and a low quantity of lipids and lignin. The average biodegradability (BI) for LS was 76.5%, compared to 43.5% for UL.

Other kinds of aquatic biomass that are not algae but instead aquatic plants include water lettuce (Pistia stratiotes), water hyacinth (Eichhornia crassipes), cattail (Typha latifolia), salvinia (Salvinia molassis), and duckweed (Lemnaceae). Typically, all of those are invasive species that could colonize large bodies of water and prevent sunlight from reaching the bottom. They must be physically or mechanically removed from different rivers where they significantly damage the ecosystem to retain an intact biological system in many parts of the globe. These aquatic plants may also be grown expressly for biofuel generation; they use nutrients from wastewater and can generate approximately 20 tons (dry)/ha/year in only 24 h. As a result of its high moisture content, wet biomass cannot be burnt, making its disposal problematic and potentially expensive.

One kind of aquatic biomass, cyanobacteria, uses photosynthetic processes to convert carbon dioxide and solar energy into chemical compounds efficiently. Gram-negative photosynthetic bacteria called cyanobacteria are essential for global processes, including nitrogen fixation, carbon sequestration, and oxygen evolution. The natural cyanobacterial host system must often be better understood to boost goal output. In recent years, the accumulation of invaluable insights into the biochemistry and metabolism of cyanobacteria has propelled the development of cyanobacteria as cell factories for biochemical synthesis, including the synthesis of biofuels (Liu et al. 2022). Among the cyanobacteria that have been extensively examined for their ability to make biofuels are a marine species (*Synechococcus sp.* PCC 7002) and two freshwater species (*Synechocystis sp.* PCC 6803 and *Synechococcus elongatus sp.* PCC 7492) (Kumar et al. 2022).

That aquatic biomass (micro-, macro-algae, aquatic plants, and cyanobacteria) was processed through liquefaction, hydrothermal carbonization, hydrothermal torrefaction, and pyrolysis. The products from the process are summarized in Table 1.

2.1 Bio-Oil

A combination of several organic compounds known as "bio-oil" is often utilized as a raw material to manufacture pure chemicals like phenol, alcohol, organic acids, and aldehydes. Gasoline might be made from bio-oil via a processing step. Additionally, it contains chemicals that may be utilized for various applications at economically recoverable levels. Bio-oil has numerous manufacturing and selling benefits in the areas of combustion, preservation, transportation, adaption, and refurbishment. The literature is severely lacking in information on the creation of bio-oil from aquatic biomass. Several researchers have tried using thermochemical methods to extract bio-oil and other byproducts from aquatic biomass. Water hyacinth by pyrolysis method at 450 °C produced carboxylic acids, aldehydes, ketones, alkenes, quinines, alcohols, phenols, and aromatics, significant bio-oil components (Wauton and Ogbeide 2019).

Table 1 Value-added products from biomass refinery (Boro et al. 2022; Chacon et al. 2022)

Products	Properties	Limitations
Biogas (bio-methane and bio-hydrogen)	–Approximately consists of CH_4 (70%), CO_2 (25%), and other gases such as H_2S, NH_3 (5%) –Ignition temperature around 700 °C in anaerobic tanks –There is no smoke or residue produced during combustion (carbon neutral) –It can be utilized as cleaner fuel to generate electricity in the form of compressed natural gas (CNG) –Zero carbon dioxide and greenhouse gas emissions –Highly flammable and effective in producing energy –The only byproducts produced are water and heat	–Large bioreaction tanks increase the land area needed –Contain contaminants that, when used as fuel, might damage the engine systems of automobiles –Maintenance energy, optimal temperature, and a considerable amount of organic biomass are required –Foul odor –The production procedure is costly –Need compression due to its extremely low density
Bio-oil (bioethanol and bio-butanol)	–Utilized as an alternative fuel for automobiles by blending with gasoline –Must increase the combustion rate while cleaning the emissions –A transparent, colorless liquid –As a result of the low vapor pressure in comparison to gasoline, the rate of evaporation is low –Can utilize any substrate containing sugar; thus, agro-based lignocellulosic waste biomass usage is highly regarded for reducing challenges associated with the disposal of such waste –Nature-friendly and readily dilutable	–Low efficiency compared to gasoline –Implementation in vehicles necessitates engine modifications for older vehicles –Due to bioethanol's low vapor pressure, it is difficult to use it as a fuel at low temperatures, resulting in cold-start issues for vehicles –It has a high capacity to absorb moisture, which increases the risk of fuel pump corrosion
Biochar	–Enhance soil permeability –Increasing the water-holding capacity makes it simpler for plants to absorb water, nutrients, and oxygen –Boost soil pH levels	–Land loss due to erosion –Compaction of the soil during application –Elimination of crop residues

Moreover, duckweed at 350–700 °C of pyrolysis yields bio-oil around 35.5–45%, char around 30–50%, and gas around 11–20% (Djandja et al. 2021). Various aquatic plant biofuels' calorific value, such as Azolla (38.2 MJ kg^{-1}) and *Salvinia molesta* (39.73 MJ kg^{-1}), is more than that of biogas (30 MJ kg^{-1}), shown in Table 2 (Arefin et al. 2021).

In recent years, bioethanol has surpassed bio-oil as the primary alternative to fossil fuels, contributing up to 75% of global biofuel demand with an approximate extensive distribution rate of 86,000 kt/year. Aquatic biomass is handled using conventional hydrolysis techniques, much like any other bioethanol feedstock, and the resultant sugars are subsequently fermented to produce bioethanol. Aquatic vegetation is a favorable feedstock for bioethanol synthesis due to its richness of both cellulose and hemicellulose and the absence of lignin. *Limnocharis flava* was converted to bioethanol using several alkaline treatments (0% alkaline, 2% NaOH, and 1–2% CaO) to determine the most effective pretreatment for degrading cellulose, hemicellulose, and lignin to sugars fermentation. Significantly, 1% CaO resulted in a satisfactory total sugar, ethanol yield, and reducing sugar of 50.81, 0.72, and 28.88 g/L, respectively (Mejica et al. 2022). Prior research indicates the significance of NaOH for bioethanol in terms of Brachiaria mutica (Para grass) and Alternanthera philoxeroides (Alligator weed) (Aarti et al. 2022). In 12–96 h, the biomass from pre-treatment process showed that saccharification degree increased by 44.46 0.7%, 55.53 0.8%, 73.26 0.7%, 94.41 0.8%, and 73.3 0.7%. Bioethanol production from

Table 2 Aquatic biofuel properties comparisons with conventional fuel (Arefin et al. 2021)

Fuel properties	Aquatic plant biofuels					Conventional fuel		
	Azolla	Water hyacinth	Salvinia molesta	Water lettuce	Duckweed	Diesel	Gasoline	Biogas
Calorific value (MJ/kg)	38.2	35.8	39.73	24.93	21.7	45.5	45.8	30
Density (kg/m^3)	~880	834	792.23	952	800	850	715–780	1.15–1.25
Fire point (°C)	120	600–1370	300	–	–	210	280	650–750
Flashpoint (°C)	108	246	139	120	169	60	−43	−188
Pour point (°C)	3	−5	1.4	17	6	−2 to −12	−4 to −20	–
Cloud point (°C)	8	−1	1.5	–	–	−12	−22	–
Viscosity (cP)	4.3	9.85	3.657	26.4	~4.9	2.40	0.48	0.01–0.06
pH	3.5–10	2.93	6–7.7	6.6	7.8	5.5–8	5.9–6.8	6.8–7.2
Water	40	1.8	5	94.6	63.46	2	10	1–5

pre-treated aquatic weeds was evaluated utilizing yeast cells immobilized in sodium alginate for simultaneous saccharification and fermentation.

2.2 Biogas

Biogas in the aquatic biomass biorefinery comprises bio-hydrogen and bio-methane. Bio-hydrogen is seen as a feasible renewable energy source and an alternative to fossil fuels due to its higher energy content (122–142 $kJ\ g^{-1}$) in contrast to biomethane (56 $kJ\ g^{-1}$) and biodiesel (37 $kJ\ g^{-1}$). Biohydrogen can be produced at ordinary pressures and temperatures with low energy input, and its combustion simply creates water. Biohydrogen is already used in fuel cells, gasoline, and automobile engines (Yu et al. 2020). Currently, fossil fuels, which are expensive and inefficient, account for 96% of H_2 production. Single-celled algal species, including blue- and green algae such as *Chlorella sp*, *Platymonas subcordiformis*, and *Chlamydomonas reinhardti*, are typically used in H_2 production systems (enzymes such as the family Enterobacteriaceae). In anaerobic processes, the proton reduction by electronic hydrogenase of ferredoxin is necessary for biohydrogen production. The release of electrons from the breakdown of glucose to pyruvate leads to acetyl-CoA oxidation and carbon dioxide (Debowski et al. 2021).

One of the most flexible and clean-burning biofuels is biomethane, which is created through the anaerobic digestion of various feedstock materials (Zhang et al. 2021). Biomethane has advantages in easily transported and distributed by the same pipes as natural gas due to its easy storage after liquefaction. The byproduct of the manufacturing process may also be used on agricultural land as fertilizer. All types of biomass can be used to make biomethane, which offers advantages over other feedstocks, not just in terms of renewability but also in terms of waste management. Therefore, aquatic biomass has significant potential as a feedstock because it may be used immediately for biomethane production. AcD, also known as anaerobic co-digestion, is a promising strategy for boosting the biomethane manufacturing process's efficiency and overcoming the constraints of single digestion using catalysts. One of the AcD investigations found that adding Co_3O_4-NPs (3 mg/L) to water hyacinth (WH) increased biogas production by 27.2%. In addition, the production of methane (CH_4) was raised by 89.96% for the CD method and by 43.4% for the co-digestion method. The techno-economic analysis reveals that this method would generate 428.05 kWh of revenue based on the maximum net energy content of biogas, with such a sales revenue of 67.66 USD per m^3 of substrate (Ali et al. 2023).

2.3 Biochar

Biochar is black carbon or carbon-rich charcoal derived from organic matter through pyrolysis process; however, it can also be formed from a feedstock a feedstock via flash carbonization, torrefaction, or gasification (Janiszewska et al. 2021). Biochar has the capacity to hold carbon for millennia through enhancing water and nutrient retention and reducing greenhouse gas emissions from fertilized soils, hence enhancing the condition of the soils to which it is applied. As a feedstock for biochar, lignocellulosic (“woody”) biomass has been the subject of most of the study. This feedstock produces biochar with low mineral concentration and high fixed-C content. Marine and freshwater macroalgae are alternate feedstocks for biochar manufacturing. Algal biochar contains considerable amounts of macronutrients and essential trace elements, including nitrogen, phosphorus, calcium, magnesium, potassium, and molybdenum, while having less carbon than lignocellulosic biochar. Due to the nutrient retention effects of micronutrients (Mo) and macronutrients (Ca, N, Mg, P, and K) on the soil, algal biochar has the potential to produce more significant increases in the quantity of certain types of soil than lignocellulosic biochar. According to previous findings, the biochar of the freshwater macroalgae Oedogonium formed at 750 °C has the most resistant carbon and leaches the least amount of metal (Roberts et al. 2015). The retention of fertilizer nutrients (Mo, Ca, N, Mg, P, and K) and the growth of radishes are both boosted by 35–40% when this biochar is applied to poor-quality soil. Radishes grown in biochar-modified soil exhibited comparable or lower metal concentrations than radishes grown in unmodified soil but had significantly greater concentrations of essential macronutrients (Mg, K, and P) and trace elements (Mo).

3 Thermochemical Process of Aquatic Weeds

3.1 Torrefaction

Torrefaction, one of thermochemical processes with slow heating, has been utilized extensively to volatilize biomass and can be classified as dry and wet, with biocoal (biochar and hydrochar) as the main products (Yek et al. 2022). Without the use of solvents, dry torrefaction (DT) takes place in oxidizing (flue gas or air) or non-oxidizing (CO_2 or N_2) atmospheres between 200 and 300 °C. Compared to non-oxidative torrefaction, oxidative torrefaction has a quicker reaction rate and shorter torrefaction duration due to exothermic reactions in the biomass thermal breakdown (Viegas et al. 2021). Additionally, the ultimate separation of nitrogen and air is unnecessary for oxidative torrefaction. A large part of the ash content remained in the torrefied aquatic biomass following dry torrefaction pretreatment, leading to undesirable agglomeration, fouling, and slagging despite the good potential for biofuel production. Aquatic biomass has been pre-treated to lower its ash content before torrefaction. At a reactor temperature of 440 °C, the pyrolysis process was carried out after pretreatment of the water hyacinth biomass at 200, 250, and 300 °C. Torrefaction severity significantly impacted the yields of char classified as brown coal (high quality) or peat. ST-Raw non-torrefied sample had a char yield of

27.4%, whereas the ST-300, ST-250, and ST-200 torrefied samples had char yields of 59.4%, 51.2%, and 42.3%, respectively. However, when the torrefaction temperature increased, syngas and bio-oil yield declined. GC-MS and FTIR analyses both showed that the bio-oil acidity had significantly decreased and that the torrefaction temperature had increased. Torrefied bio-oils are therefore assured to be less corrosive than un-torrefied bio-oils (Parvej et al. 2022).

Water causes wet torrefaction (WT) when it is present at temperatures between 180 and 260 °C for 10–24 min (Das et al. 2021). When later wet torrefaction happens in a wet situation, the conventional pre-drying stage for thermal conversion processes may be avoided, particularly for highly moist biomass such as manure, sewage, and aquatic biomass. When water is heated to 180 °C, its properties (density, viscosity, ion products, and dielectric constant) change in a manner that is favorable for thermochemical conversion in the aqueous phase (Nazos et al. 2022). The dissolution of the ash's minerals in the liquid reduces the quantity of ash in the solid result. In addition, steam torrefaction can operate at greater temperatures (200–260 °C) with the assistance of a high-pressure steam explosion that expands the lignocellulosic components and separates individual fibers. Carbon content and calorific value of the biomass increase as low molecular weight volatiles are eliminated during the steam explosion, although the product's bulk density, equilibrium moisture content, and mean particle size decline. The lowest production costs (without carbon credits) were associated with grape pomace's dry and wet torrefaction, at 2.29 and 4.14 $/GJ, respectively. It is more difficult to create pellets from biochar than from raw biomass because biochar is more brittle, dry, and volatile. Because hydrochar has a higher concentration of oxygen functional groups than biochar, it has a higher water affinity (hydrophilicity) on the surface, which enhances the soil's ability to retain water when immersed (Akbari et al. 2020).

3.2 Hydrothermal Carbonization (HTC)

Hydrothermal carbonization (HTC) or wet thermal process takes place at pressures higher than 1 MPa and temperatures between 180 and 300 °C (Akbari et al. 2020). Although HTC has a shorter residence time and a lower temperature than HTL, both processes are carried out in subcritical water conditions. Furthermore, HTC produces hydrochar with the same yield and energy content as a torrefied solid product at far lower temperatures. Biomass/water ratio, temperature, and duration of 42 wt%, 232 °C, and 99 min, were determined to be optimal for producing high HHV (22 MJ/kg) and low char generation (47 wt%), respectively (Lynam et al. 2015). The carbonization processes quicken as the temperature increases, leading to quicker kinetics and less hydrochar generation. If the length of the stay is increased, the temperature may yet have a distinct impact. The HTC research with fresh aquatic plants such as cattail and water hyacinth use an autoclave reactor at 180–220 °C. Following HTC treatment at 220 °C, the carbon content of aquatic biomass (cattail and water hyacinth) increased by 30.2–41.7%. Greater H/C and O/C ratios in the feedstocks relative to the comparable hydrochars may have resulted from the dissociation of the dehydration and decarboxylation processes that occur throughout the HTC process. As the temperature rose, the H/C and O/C atomic ratios fell, and the 220 °C hydrochar sample exhibited peat-like characteristics (Poomsawat and Poomsawat 2021).

3.3 Hydrothermal Liquefaction (HTL)

Hydrothermal liquefaction (HTL) is among the most major advancement promising processes for aquatic biomass upgrading, which directly converts biomass into bio-oil (Guo et al. 2017). HTL has several advantages, including obtained bio-oil having lower oxygen content and not requiring drying as the required microalgae concentration is around 20 wt.% (Biller 2018; Biswas et al. 2021). The drying process was known as the main economic and energetic obstacle before further processing of aquatic biomass conversion into biofuel. However, in HTL, the cost of the drying process can be reduced because water functions as a solvent in the system (Biswas et al., 2021).

Various products, such as aqueous-phase product, bio-oil, volatiles, gas, and solid residual, are the primary constituents of the HTL process' hydrothermally decomposed biomass conversion (Guo et al. 2017). Species of feedstock and processing parameters, including temperature, residence time, and solvent, determine HTL product. Numerous studies have been investigating these various parameter effects on different aquatic biomass. Due to its potential lipid content and enhanced photosynthetic efficiency, aquatic biomass has been recognized as a possible renewable biofuel source (Biller 2018). Furthermore, aquatic biomass has a higher growth rate than terrestrial plant biomass with less demanding cultivation and land use (Biswas et al. 2022).

Some studies show that microalgae, as a species of aquatic biomass, had been utilized in the production of biofuel using HTL, such as *Chlorella, Nannochloropsis*, and *Sargassum* sp. (He et al. 2020; Moazezi et al. 2022). Microalgae with a high lipid content will be completely converted to bio-oil; therefore, algae species with a high lipid content will be more valued (Biller 2018). Table 3 demonstrates that Sargassum sp. is rich in lipid and protein; hence, it is more susceptible to being transformed into bio-oil. While, in *Nannochloropsis* sp., ash contents are much higher, mainly contributing to solid residue production (He et al. 2020). As shown in Table 4, the bio-oil yields of *Sargassum* sp. (16.3% wt.) were significantly less than those of *Nannochloropsis* sp. (39.0% wt.).

Table 4 also presents bio-oil yields for different biomass species and operational parameters. Temperature has an important influence on the production of bio-residues, gas, and bio-oil. At lower temperatures, the degradation of biomass will be incomplete and unreacted. Thus, the bio-oil formation will be suppressed while increasing the solid products. An increase in temperature should be beneficial for bio-oil formation due to the acceleration of biomass decomposition. The yield of

Table 3 Composition data of algal biomass used for hydrothermal liquefaction

Biomass	Component (%wt)									References
	Protein	Lipid	Cellulose	Hemicellulose	Lignin	Poly-saccharide	Carbo-hydrate	Moisture	Ash	
Sargassum sp	9.9	0.80	9.04	38.6	13.0	–	–	–	–	He et al. (2020)
Nannochloropsis sp.	45.6	6.20	0.30	0.91	0.52	–	–	–	–	
Sargassum sp	7.5	1.33	–	–	–	–	50.7		27	Ardiansyah et al. (2018)
Gracilaria corticata	22.8	7.07	–	–	–	49.6	8.30	8.40	8.10	Rosemary et al. (2019)
Azolla filiculoides	4.6	0.72	–	–	–	–	0.82	91.8	2	Bhaskaran and Kannapan (2015)
Azolla filiculoides	19.7	4.2	–	–	–	10.3	–	–	18.5	Datta (2011)
Chlorella vulgaris	58.0	11.5	–	–	–	–	19	5	6.5	Moazezi et al. (2022)
Chlorella vulgaris	45.0	20.0	–	–	–	5	20	–	10	El-Naggar et al. (2020)

Table 4 Bio-crude yields and properties of distinct aquatic feedstocks under various HTL conditions

Biomass	Description	Solvent	Operational parameter		Product (%wt)			References
			T (°C)	Reaction Time (min)	Solid	Liq	Gas	
Sargassum tenerrimum	Brown macroalgae	H_2O	260	15	61.2	11.5	11.6	Biswas et al. (2018)
			280	15	32.3	16.3	12.1	
			300	15	24.2	14.7	9.0	
Gracilaria corticata	Red macroalgae	H_2O	260	15	21.7	3.9	11.8	Fernandes et al. (2021)
			280	15	23.0	2.8	4.9	
			300	15	26.0	5.2	11.2	
		Methanol	300	15	–	8.2	–	
		Ethanol	300	15	–	14	–	
		Acetone	300	15	44.0	16.2	–	
		Ethanol–water	300	15	–	13.3	–	
Azolla filiculoides	Aquatic plants	H_2O	280	15	38.0	21.5	5.0	Biswas et al. (2021)
			260	30	47.0	13.6	12.4	
			300	60	39.0	15.2	6.9	
		Methanol	260	15	41.2	28.7	12.9	
			260	30	37.5	26.3	7.6	
			280	60	36.2	24.3	11.9	
		Ethanol	300	15	29.5	26.5	2.1	
			300	30	33.8	26.3	14.8	
			280	60	36.7	28.8	15.5	

(continued)

Table 4 (continued)

Biomass	Description	Solvent	Operational parameter		Product (%wt)			References
			T (°C)	Reaction Time (min)	Solid	Liq	Gas	
Chlorella vulgaris	High lipid, microalgae	H_2O	287	40	–	56.2		Moazezi et al. (2022)
Nannochloropsis sp.	Low lipid, microalgae	H_2O	260	30	11.0	39.1	15.9	He et al. (2020)
			280	30	6.7	43.5	18.8	
			300	30	4.8	45.3	23.9	
			320	30	3.1	54.1	20.8	
			340	30	4.39	41.73	36.97	
Sargassum sp.	Brown macroalgae	H_2O	260	30	40.04	3.11	22.22	He et al. (2020)
			280	30	36.36	5.99	22.39	
			300	30	36.12	6.93	23.96	
			320	30	32.08	8.43	25.38	
			340	30	32.04	9.49	26.20	

bio-residue and bio-oil decreases at the temperature above 280 °C, as shown in Table 4 (Biswas et al. 2018). The relationship between re-polymerization and hydrolysis has a substantial impact on the HTL process's temperature. Extensive depolymerization will occur at high temperatures to activate the bond-breaking activation energy. The bond-breaking increases free radicals and repolymerizes the pieces that have been degraded (Moazezi et al. 2022).

Based on bio-oil yield using *Gracilaria corticata* as biomass, the relative efficiency of solvent used during the HTL process could be reported as follows: water < methanol < ethanol-water < ethanol < acetone. Table 4 demonstrates that the type of solvent affects conversion yield. Organic solvents promote the solubility and stability of chemical intermediates due to their lower dielectric constants, resulting in a greater yield. Additionally, it will facilitate esterification and alkylation between intermediate molecules and solvents (Fernandes et al. 2021).

In addition to being affected by the type of biomass employed, the duration of reaction times can determine the products derived from HTL as well as the feedstock conversion rate. As indicated in Table 4, a relatively short reaction time is suited for efficient biomass breakdown since the HTL process rapidly hydrolyzes biomass. In a longer reaction period, liquid products will undergo greater decomposition and repolymerization, hence contributing to the creation of gaseous products and biochar (Moazezi et al. 2022).

3.4 Pyrolysis

The thermochemical conversion processes can be split into four categories based On the basis of operating features such as temperature, pressure, heating rate, and reaction environment: gasification, combustion/incineration, liquefaction, and pyrolysis (Vuppaladadiyam et al. 2022). Pyrolysis, often known as thermal decomposition in an inert atmosphere, has been widely used to transform biomass into products with added value (Gao et al. 2020). Pyrolysis is a type of thermolysis or carbonization that employs intense heat in a low or oxygen-free (O_2) atmosphere to thermally decompose biomass into a number of pyrolytic chemicals (Tripathi et al. 2016; Lee et al. 2020). This thermochemical conversion yields biochar, bio-oil, and bio-syngas as its principal by-products (Azizi et al. 2018). The features of the aquaculture biomass, the operational parameters, and the kind of pyrolysis reaction influence the number of products and the HHV (Chen et al. 2015).

Table 5 summarizes the experimental parameters for pyrolysis techniques. The pyrolysis process has been classified into 2 categories; conventional and advanced approaches (Lee et al. 2020), presented in Fig. 2. Conventional pyrolysis can be divided into three distinct types: slow pyrolysis, fast pyrolysis, and flash pyrolysis, depending on the operational parameters employed during the process. Slow pyrolysis is a crucial synthesis technique that is mostly used to produce biochar with byproducts such as syngas and bio-oil (Lee et al. 2017). Slow pyrolysis settings emphasize slow heating rates (30 °C/min), moderate temperatures (550–950 °C), and slow reaction time. According to Table XZ, the yields of biochar, bio-oil, and bio-syngas produced by pyrolysis at 600 °C in which bio-syngas is the dominant product obtained in this technique (Maddi et al. 2011). Fast pyrolysis, the counterpart of slow pyrolysis, is frequently utilized for biomass under the following pyrolysis conditions: rapid heating rate (>60 °C/min), high temperature (850–1200 °C), and brief pyrolysis period (0.5–10 s) (Campanella and Harold 2012; Ly et al. 2015). Fast pyrolysis aims to optimize bio-oil synthesis, readily stored, or transported, and contains less nitrogen and sulfur (Roddy and Manson-Whitton 2012).

To improve the pyrolysis process, advanced pyrolysis techniques are often modified to create new methods, e.g. co-pyrolysis, catalytic pyrolysis, and microwave-assisted pyrolysis, that make the pyrolysis process superior to conventional techniques and enhanced the yield, quality, and characteristics the pyrolysis products. Under a catalyst, catalytic pyrolysis is a directed control method for obtaining high-quality liquid fuel and high-value-added chemicals with a high yield (Qiu et al. 2022). In a fixed-bed reactor, *Pavlova* microalgae were pyrolyzed at various temperatures in the presence of titania-based catalysts. When Ni/TiO_2 (22.55 wt%) was present at 500 °C, the bio-oil output increased by 20% (Aysu et al. 2017).

In parallel to catalytic pyrolysis, co-pyrolysis (Duan et al. 2015; Uzoejinwa et al. 2018, 2019) and microwave-assisted pyrolysis (Beneroso et al. 2013; Hong et al. 2017) have been identified as a promising strategy for enhancing the performance of biomass pyrolysis processes through synergistic interactions. Co-pyrolysis is the process of heating together two or more organic materials in the absence of oxygen to produce the bio-oil, and it is also the synergistic effect in terms of gas, liquid, and solid product distribution and product composition modifications (Ma et al. 2022). (Duan et al. 2015) reported a good synergistic impact between the waste rubber tire (WRT) and microalgae. The largest synergistic impact value (37.8%) was recorded at a mass ratio of 1:1 R:M. During co-pyrolysis, the interaction between microalgae and WRT promoted denitrogenation and deoxygenation, hence enhancing the quality of the bio-oil. The heating values of bio-oils derived from the co-pyrolysis of microalgae and WRT were between 35.80 and 42.03 MJ/kg.

On the other hand, microwave-assisted pyrolysis is regarded as a straightforward processes with direct control (Zhang et al. 2016). Hong et al. found that porphyra was a more ideal raw material for syngas-rich gas production (85.6–87.1 wt%) by using microwave-assisted pyrolysis because of its high carbohydrate content (47.7 wt%), but spirulina and chlorella were more advantageous for oil production due to their higher protein levels. *Scenedesmus almeriensis* was also found to be an appropriate feedstock for microwave-assisted pyrolysis to create gas products (Beneroso et al. 2013). By reducing CO_2 and light hydrocarbons, it has been claimed that the maximum output of syngas at 800 °C with the highest H_2/CO ratio can approach 94% by volume.

The pyrolysis of algal biomass generates and disperses a variety of organic and inorganic chemicals. As pyrolysis fuel, the chemical components of aquatic biomass such as cyanobacteria, duckweed, micro- and macroalgae are acceptable. As measured by pyrolysis, they may affect the HHV values, viscosities, pH, densities, and product composition (Bharathiraja et al. 2015). By a significant margin,

Table 5 Biofuel production from different aquatic feedstocks under various conditions of pyrolysis

Algal biomass	Type of Pyrolysis	Operational reaction parameters				Product (wt.%)			HHV (MJ/kg)	References
		T (°C)	t (min)	Carrier gas flowrate (mL/min)	Heating rate (°C/min)	Solid	Liquid	Gas		
Lyngbya sp.	Slow	600	20	He: 200	30	17	12	44	Bio-char: 25.6	Maddi et al. (2011)
Cladophora sp.	Slow	600	20	He: 200	30	26	20	38	Bio-char: 22.7	
Saccharina japonica	Fast	350	2 s	N_2: 4500	–	34.2	45	20.8	Bio-oil: 24.8	Ly et al. (2015)
Green algae	Fast	500	1.5 s	N_2: 250	–	26	58.6	17.8	Bio-oil: 26.7	Campanella and Harold (2012)
Green-blue algae	Fast	500	1.5 s	N_2: 250	–	28.4	54	19.9	Bio-oil: 26.8	
Chlorella	Fast	500	1.5 s	N_2: 250	–	29	53.9	17.3	Bio-oil: 25.5	
Pavlova sp.	Catalytic (Titania)	450–550	60	N_2: 545	100	35.9–49.0	14.1–22.5	36.5–46.3	Bio-char: 4.8–6.9 Bio-oil: 33.3–37.1	Aysu et al. (2017)
Saccharina japonica	Fast catalytic (HZSM-5)	500	–	–	–	22.3	39.1	39.3	Bio-oil: 27.2	Ly et al. (2019)

(continued)

Table 5 (continued)

Algal biomass	Type of Pyrolysis	Operational reaction parameters				Product (wt.%)			HHV (MJ/kg)	References
		T (°C)	t (min)	Carrier gas flowrate (mL/min)	Heating rate (°C/min)	Solid	Liquid	Gas		
Enteromorpha prolifera	Co-pyrolysis (Rice Husk)	400–600	–	N_2: 100	5–25	22.8–31.4	39.2–47.2	28.7–31.4	Bio-char: 26.9–31.6 Bio-oil: 25.5–30.6	Uzoejinwa et al. (2018)
Chlorella pyrenoidosa	Co-pyrolysis (waste rubber tyre)	290–370	10–120	–	–	19–49.7	37.5–65.4	4.6–14	Bio-oil: 33.7–42.9	Duan et al. (2015)
Scenedesmus almeriensis	Microwave	400	30	He: 100	–	–	–	87.7 wt.%	Bio-syngas: 3.36 Wh/g	Beneroso et al. (2013)
Chlorella	Microwave	400	30	N_2: 100	–	8	8	84	Bio-syngas: 5.6	Hong et al. (2017)
Spirulina	Microwave	700	30	N_2: 100	–	10	6.3	83.7	Bio-syngas: 2.9	
Porphyra	Microwave	700	30	N_2: 100	–	10.4	2.5	87.1	Bio-syngas: 3.1	

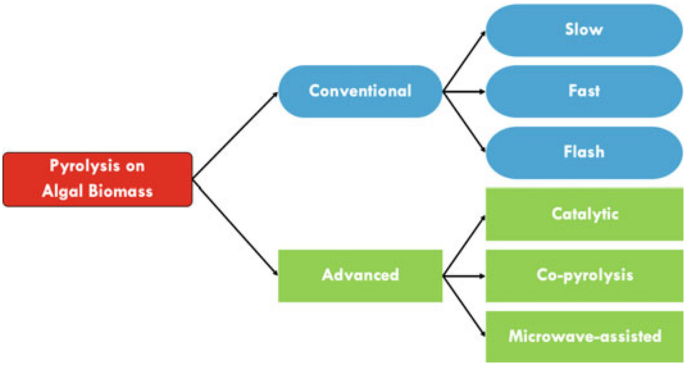

Fig. 2 The classification of the pyrolysis process in algal biomass

aquatic biomass confirms its suitability as pyrolysis feedstock for the eventual commercialization of energy-dense goods.

4 Conclusion

Aquatic biomass is emerging as a resource to produce biofuels and other goods with added value. Biomass derived from aquatic organisms offers significant potential for biomethane, bio-oil, and bioethanol production. However, the scientific community must address the following concerns.

- Research is necessary to develop an effective pre-treatment and conversion process.
- Collecting biomass, high processing costs for scaling up, poor hydrolysis, and conversion are challenges that must be overcome.
- Biological and other hybrid pretreatment approaches, as well as the intensification of the process, can be utilized to increase biofuel output.
- To achieve economic viability, the whole potential of aquatic weed biomass must be utilized.

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