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Integrated Thermochemical Conversion of Microalgae for Sustainable Biofuel Production: An Overview

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Abstract

Microalgae have emerged as promising third-generation biomass feedstocks for renewable fuel production due to their high productivity, photosynthetic efficiency, carbon fixation capacity, and ability to grow on non-arable land and wastewater. However, conventional lipid-extraction-based biodiesel production utilizes only part of the biomass and requires energy-intensive processing. This review evaluates integrated thermochemical conversion of whole microalgal biomass, focusing on hydrothermal liquefaction (HTL), pyrolysis, and gasification. The effects of biochemical composition, moisture, ash, temperature, residence time, heating rate, reactor configuration, and catalysts on conversion performance and product quality are examined. HTL is particularly suitable for wet microalgae because it eliminates energy-intensive drying and produces bio-crude, aqueous products, hydrochar, and gases. Pyrolysis can further valorize hydrochar and residual biomass into bio-oil, biochar, and combustible gases, while gasification enables additional syngas and hydrogen production. Integration of these pathways with heat recovery, nutrient recycling, CO_2 utilization, catalytic upgrading, and co-product valorization can improve carbon utilization, energy efficiency, environmental performance, and economic viability. Nevertheless, catalyst deactivation, high-pressure operation, feedstock variability, product upgrading, and scale-up remain critical challenges. Future research should prioritize digitally optimized and demonstration-scale integrated algae biorefineries supported by advanced catalysts, process modelling, artificial intelligence, and comprehensive techno-economic and life-cycle assessment.

Keywords: microalgae; thermochemical conversion; hydrothermal liquefaction; pyrolysis; gasification; biofuel; integrated biorefinery.

1. Introduction

The global energy system is undergoing a profound transformation driven by climate change mitigation, energy security concerns, depletion of fossil fuel resources, and the increasing demand for sustainable energy carriers. Although petroleum, coal, and natural gas continue to dominate global primary energy consumption, their extensive utilization is associated with greenhouse-gas emissions, environmental degradation, and long-term resource constraints. Consequently, governments, industries, and researchers are increasingly investigating renewable energy technologies capable of delivering low-carbon

energy while maintaining economic competitiveness. Within this transition, biomass represents an important renewable carbon resource because, unlike intermittent renewable technologies that primarily generate electricity, biomass can provide carbon-containing fuels, chemicals, and materials through a range of biochemical and thermochemical pathways. The energy potential of biomass originates from the solar energy stored as chemical energy through photosynthesis, and its effective utilization can simultaneously support renewable fuel production, waste management, carbon recycling, and resource recovery [1, 2, 3]. The sustainability of biomass energy, however, depends strongly on feedstock selection, cultivation or collection systems, conversion efficiency, water requirements, and the extent to which carbon and nutrients are recovered within the production system [4,5].

Conventional biomass feedstocks such as corn, sugarcane, soybean, and palm oil have contributed substantially to biofuel development, but their large-scale utilization has generated concerns related to food security, land-use change, and competition with agricultural resources. These limitations have stimulated increasing interest in third-generation biofuels based on microalgae and other aquatic photosynthetic organisms. Microalgae offer several advantages over terrestrial energy crops, including rapid growth, high photosynthetic efficiency, the ability to utilize non-arable land, and potential cultivation using saline water, wastewater, or industrial effluents. Their cultivation can therefore be integrated with wastewater treatment, nutrient recovery, and carbon dioxide utilization, creating opportunities for coupling renewable fuel production with environmental remediation and circular resource management [5,6,7,8].

Microalgae also differ fundamentally from lignocellulosic biomass in their biochemical composition. Depending on species, cultivation conditions, and nutrient availability, microalgal biomass may contain substantial fractions of lipids, proteins, carbohydrates, pigments, and inorganic minerals. Some species can accumulate lipid contents exceeding 50% of dry biomass under nutrient-stress conditions, while simultaneously producing proteins, carbohydrates, pigments, antioxidants, and other value-added compounds. Nevertheless, large-scale algal production remains constrained by harvesting, dewatering, drying, cultivation infrastructure, and downstream processing costs. Consequently, whole-biomass conversion technologies have become increasingly important because they can utilize carbohydrates, proteins, lipids, and residual biomass without requiring extensive fractionation [2,8,9].

Historically, much microalgae biofuel research focused on biodiesel production through lipid extraction followed by transesterification. Although technically feasible, this route generally exploits only the lipid fraction and leaves a substantial quantity of residual biomass. Lipid extraction can also require drying, solvent consumption, cell disruption, separation, and purification, increasing energy and operating requirements. These limitations have encouraged the development of thermochemical pathways capable of converting whole microalgal biomass into liquid fuels, gaseous fuels, carbonaceous materials, and chemical intermediates. Thermochemical conversion includes pyrolysis, hydrothermal liquefaction (HTL),

gasification, and related processes, each characterized by different reaction environments and product distributions [8,10,11].

Among these technologies, HTL is particularly attractive for wet microalgae because it can process biomass directly in subcritical water without the energy-intensive drying required by conventional pyrolysis and gasification. Pyrolysis is attractive because of its relatively simple configuration and ability to produce bio-oil, biochar, and gases, while gasification can transform carbonaceous residues into syngas containing hydrogen, carbon monoxide, methane, and other combustible species. However, no single technology can efficiently utilize every fraction of microalgal biomass. This limitation has stimulated increasing interest in integrated thermochemical biorefineries in which different conversion technologies are sequentially or simultaneously combined to maximize carbon utilization and minimize energy and material losses [12,13,37].

A simplistic representation of microalgal based biorefinery system is shown in Figure 1.

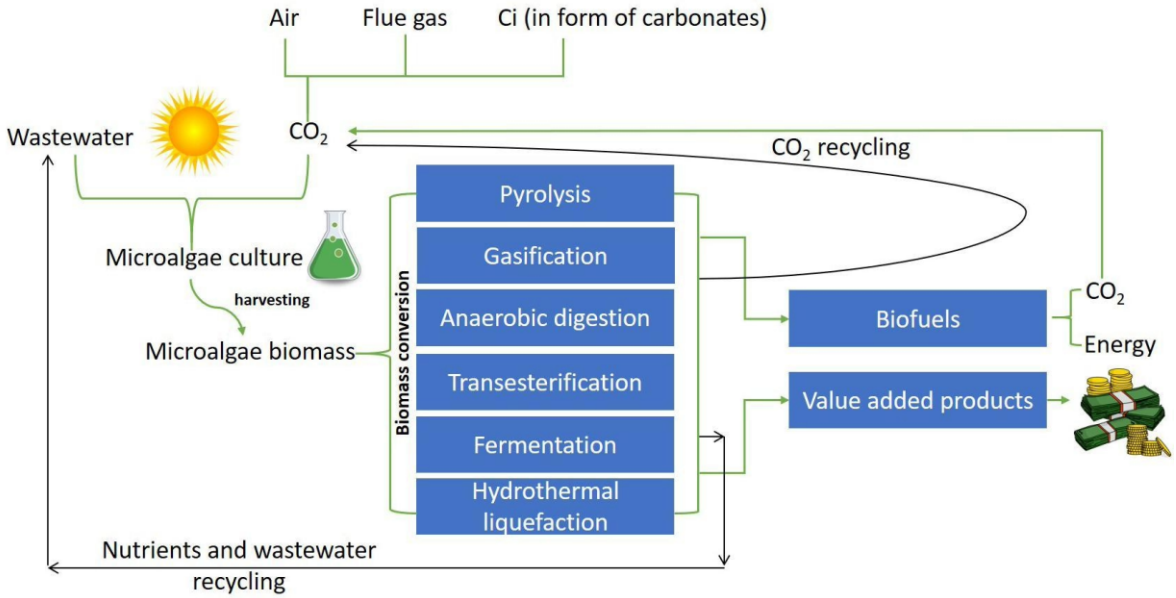

Fig.1. Microalgal based biorefinery system [39]

The central objective of this review is to critically examine the thermochemical conversion of microalgal biomass, emphasizing feedstock characteristics, pyrolysis, HTL, gasification, process integration, techno-economic performance, environmental sustainability, and future research directions. Particular attention is given to HTL–pyrolysis integration because HTL can process wet microalgae into bio-crude while producing hydrochar that can subsequently be converted through pyrolysis into additional bio-oil, biochar, and gases. Such integration provides a promising framework for increasing carbon utilization and energy recovery while supporting circular bioeconomy principles.

2. Microalgal Biomass Characteristics and Thermochemical Suitability

The suitability of microalgae for thermochemical conversion is primarily determined by their biochemical, proximate, and ultimate characteristics. Unlike terrestrial lignocellulosic biomass, which is dominated by cellulose, hemicellulose, and lignin, microalgae contain variable proportions of lipids, proteins, carbohydrates, pigments, and inorganic components. The relative abundance of these fractions strongly influences thermal degradation behavior and the distribution of liquid, gaseous, solid, and aqueous products. Lipid-rich biomass generally favors the production of energy-dense biocrude, whereas carbohydrate-rich biomass tends to produce oxygenated compounds and gaseous products. Protein-rich biomass is particularly challenging because protein degradation generates nitrogen-containing compounds that can reduce fuel quality and increase downstream upgrading requirements [14,15,9].

The proximate composition of microalgae includes moisture, volatile matter, fixed carbon, and ash, while ultimate analysis determines carbon, hydrogen, oxygen, nitrogen, sulfur, and other elemental concentrations. High volatile matter generally facilitates rapid thermal decomposition, whereas fixed carbon contributes to char formation and subsequent gasification or pyrolysis potential. A major distinction between microalgae and many lignocellulosic feedstocks is their relatively high ash and mineral content. These inorganic components can catalyze secondary reactions, influence char formation, cause slagging and fouling, and contribute to catalyst deactivation [10.9,11]

Moisture is another critical characteristic because freshly harvested microalgae commonly contain approximately 80–95% water. Conventional pyrolysis and gasification generally require relatively dry feedstock, meaning that dewatering and drying can become among the most energy-intensive stages of the process. Consequently, conventional thermal conversion of wet microalgae may suffer from poor energy balances unless drying is integrated with waste heat or low-energy dewatering technologies. HTL offers a fundamental advantage because water is retained as the reaction medium, allowing wet biomass to be processed [16,17,12].

Species selection is also important because microalgae exhibit different biochemical compositions and thermal degradation characteristics. *Chlorella vulgaris*, *Nannochloropsis oculata*, *Scenedesmus obliquus*, and *Spirulina platensis* have been widely studied as model feedstocks. Lipid-rich *Nannochloropsis* can favor biocrude formation during HTL, while differences in carbohydrate and protein composition can substantially affect gas, aqueous, and solid products. Studies of microalgal pyrolysis have similarly demonstrated that feedstock composition determines both product yield and chemical composition [18,19,20].

Thermal degradation occurs through overlapping reactions involving carbohydrates, proteins, and lipids rather than through independent decomposition of individual components. Fatty acids may undergo decarboxylation and cracking, while oxygenated intermediates may undergo dehydration, condensation, and polymerization. Consequently, feedstock composition and reaction mechanisms is

essential for designing conversion systems that maximize desired products while minimizing undesirable heteroatom-containing compounds [11,21,15].

3. Thermochemical Conversion Pathways

Thermochemical conversion involves the transformation of organic biomass through elevated temperatures under controlled reaction environments. Depending on oxygen availability, water content, heating rate, pressure, and reaction atmosphere, thermochemical processes can generate liquid bio-oil or biocrude, combustible gases, hydrogen-rich syngas, and carbonaceous solids. For microalgal biomass, the principal technologies are pyrolysis, HTL, and gasification. Hydrothermal carbonization and torrefaction can also improve the properties of solid residues, while supercritical water gasification provides a specialized pathway for hydrogen production from wet biomass [8,12].

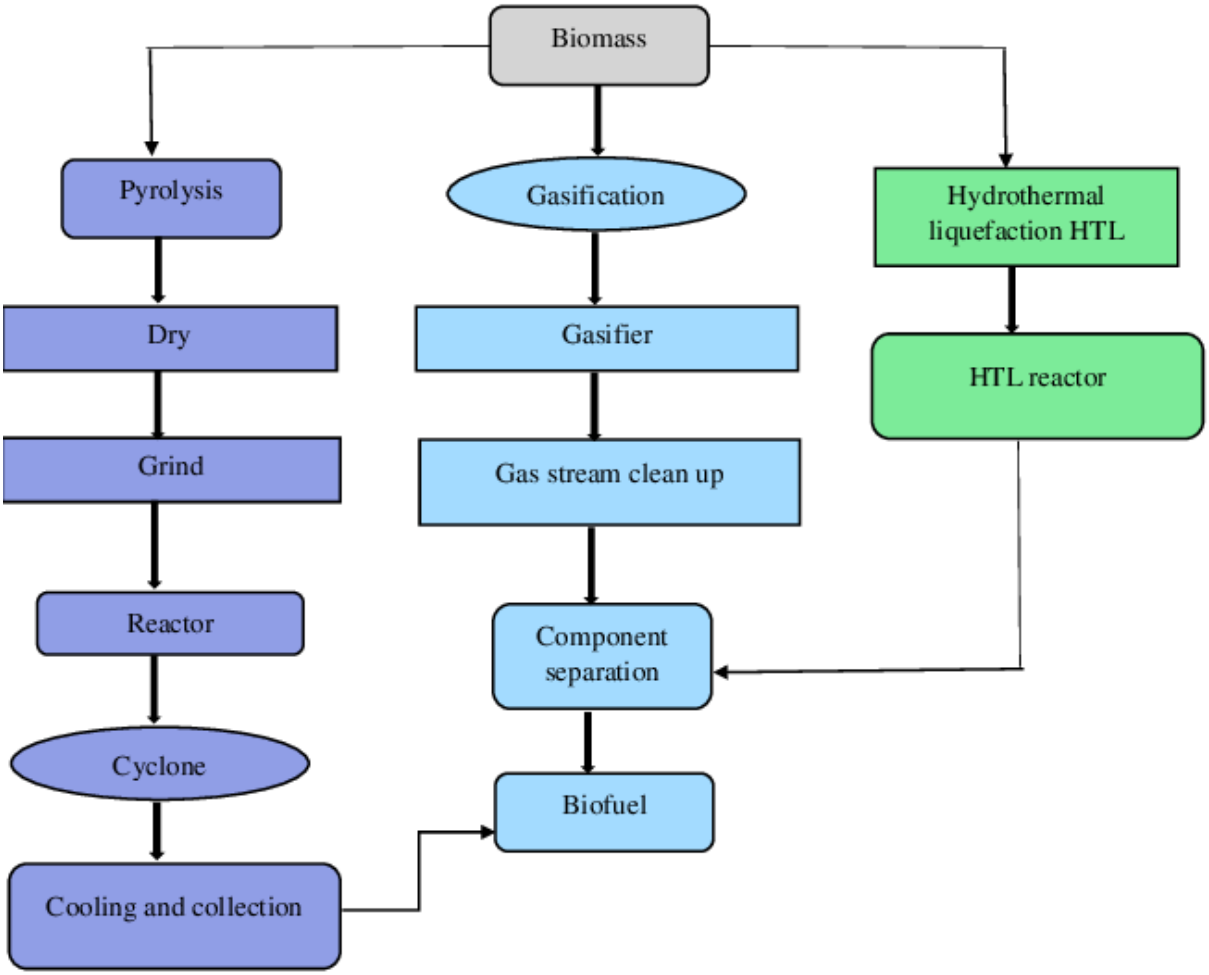

Fig 2. Thermochemical conversion process of biomass [40]

Pyrolysis is generally performed in the absence of oxygen and converts dry biomass into condensable vapors, non-condensable gases, and char. HTL uses high-temperature compressed water and is therefore particularly suited to wet feedstocks. Gasification operates at higher temperatures under partial oxidation and converts biomass into syngas. These technologies should not necessarily be regarded as competing alternatives. Instead, their different characteristics create opportunities for sequential integration in which the product of one process becomes the feedstock for another. Such cascading utilization is central to the development of integrated algae biorefineries [13,37].

4. Pyrolysis of Microalgal Biomass

Pyrolysis is one of the most extensively investigated thermochemical technologies for converting microalgal biomass into renewable liquid fuels. It involves thermal decomposition in the absence or near absence of oxygen, generally at approximately 350–700 °C, producing three principal product fractions: bio-oil, biochar, and non-condensable gases. Compared with biochemical conversion, pyrolysis offers rapid reaction times and can simultaneously utilize lipids, proteins, and carbohydrates without prior fractionation. Microalgae can produce relatively energy-dense pyrolysis oils because of their high volatile matter and hydrogen content. However, elevated nitrogen and oxygen contents can generate nitrogenous and oxygenated compounds that compromise fuel stability and increase upgrading requirements [15,9,22].

The fundamental mechanism involves a sequence of dehydration, devolatilization, fragmentation, cracking, cyclization, aromatization, condensation, and polymerization reactions. Carbohydrates, proteins, and lipids undergo overlapping thermal degradation, and their interactions generate complex secondary chemistry. Protein-derived nitrogen can react with carbohydrate-derived intermediates through Maillard chemistry, generating nitrogen-containing heterocycles and other undesirable compounds. These interactions explain why microalgal pyrolysis oil differs substantially from oil obtained from woody biomass [21,11].

Temperature is one of the most important parameters controlling pyrolysis product distribution. At lower temperatures, incomplete devolatilization can favor char formation. Increasing temperature generally enhances volatilization and liquid production until an optimum range is reached, commonly around 450–550 °C for many microalgal feedstocks. At still higher temperatures, secondary cracking of condensable vapors can increase non-condensable gas production and decrease liquid yield. However, the optimum temperature is strongly dependent on species composition, reactor configuration, heating rate, and vapor residence time [11,19,38].

Heating rate and vapor residence time are equally important. Fast pyrolysis uses rapid heating and short vapor residence times to minimize secondary cracking and generally maximize condensable products. Slow pyrolysis uses lower heating

rates and longer residence times, promoting char formation through secondary condensation and polymerization. Flash and microwave-assisted pyrolysis have received increasing attention because rapid internal heating can improve heat-transfer efficiency and reduce processing time. Nevertheless, microwave systems remain challenged by scale-up, reactor design, feedstock dielectric properties, and uniform energy distribution [22,23].

Reactor design determines heat transfer, mass transfer, mixing, residence time, and process scalability. Fixed-bed reactors are useful for laboratory kinetic studies because of their simplicity, but their heat-transfer limitations can become significant at larger scale. Fluidized-bed reactors are attractive for fast pyrolysis because of excellent mixing and heat transfer. Auger, ablative, entrained-flow, and rotating-cone reactors have also been investigated. Continuous feeding of fine microalgal particles remains an engineering challenge because agglomeration, poor flowability, and mineral accumulation can affect stable operation [22,8].

Raw microalgal pyrolysis oil generally has high viscosity, acidity, chemical instability, and significant oxygen- and nitrogen-containing compounds. Catalytic pyrolysis has therefore been investigated as a means of improving product quality during primary conversion. Zeolite catalysts, particularly HZSM-5, can promote cracking, deoxygenation, aromatization, and hydrocarbon formation. Metal-modified catalysts containing Ni, Co, Fe, Ga, or related active phases can further modify product distribution and heteroatom removal. However, coke deposition, mineral poisoning, pore blockage, and catalyst deactivation remain important obstacles to long-term operation [24,25].

Co-pyrolysis provides another route for improving product quality. Combining microalgae with lignocellulosic biomass, agricultural residues, waste plastics, or other carbonaceous materials can generate synergistic interactions through hydrogen transfer, altered radical chemistry, and modified volatile evolution. Such interactions may reduce undesirable oxygenated compounds and improve hydrocarbon selectivity. However, catalyst regeneration, feedstock variability, mineral contamination, and long-term stability remain major challenges for industrial implementation [25].

Despite its technological maturity, stand-alone microalgal pyrolysis faces substantial commercialization barriers. The high moisture content of harvested algae requires drying, while protein-rich species produce nitrogen-containing oils requiring extensive upgrading. Economic feasibility can therefore improve substantially when pyrolysis is incorporated into a biorefinery in which biochar and other co-products generate additional revenue. Integration with HTL is particularly attractive because HTL can process wet algae while the resulting hydrochar can subsequently serve as a pyrolysis feedstock [13,26,27].

5. Hydrothermal Liquefaction of Microalgae

Hydrothermal liquefaction has emerged as one of the most promising thermochemical pathways for converting wet microalgal biomass into renewable

liquid fuels because it eliminates the energy-intensive drying step required by conventional pyrolysis and gasification. HTL typically operates in subcritical water at approximately 280–370 °C and pressures sufficient to maintain water in the liquid phase. Under these conditions, water exhibits altered dielectric and ionic properties and functions simultaneously as solvent, reactant, and catalytic medium. Proteins, lipids, and carbohydrates undergo hydrolysis, depolymerization, dehydration, decarboxylation, deamination, cyclization, condensation, and repolymerization, ultimately producing an energy-dense biocrude fraction [28,16,12].

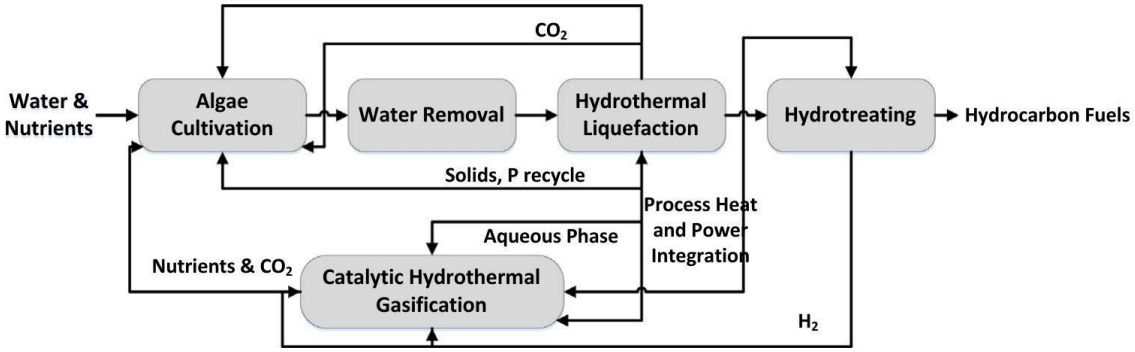

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Fig. 3. Process flow diagram of HTL process of algal biomass/wet biomass [14]

The major HTL products are biocrude, aqueous-phase products, gaseous products, and hydrochar. The biocrude yield depends strongly on biochemical composition and operating conditions. Lipid-rich microalgae generally produce higher oil yields because lipid-derived fatty acids readily undergo decarboxylation and related reactions. Carbohydrates tend to generate oxygenated products, while proteins contribute nitrogen-containing compounds. Consequently, biocrude yield alone is insufficient for evaluating HTL performance; product quality, carbon recovery, energy recovery, and upgrading requirements must also be considered [14,29,30].

Temperature is one of the dominant HTL parameters. At insufficient temperatures, hydrolysis and depolymerization may remain incomplete, producing substantial solid residues. Increasing temperature enhances conversion and typically improves biocrude production until an optimum range is reached. Excessively severe conditions can increase secondary cracking, gas formation, and repolymerization. For many microalgal feedstocks, temperatures around 300–350 °C provide a useful balance between conversion, biocrude yield, and energy recovery, although the optimum depends on species, solids concentration, residence time, and reactor configuration [16,18,28].

Residence time determines the extent of primary and secondary reactions. Short residence times can lead to incomplete conversion, whereas excessively long residence times promote condensation and repolymerization toward hydrochar and gases. Heating rate, biomass loading, particle size, and mixing intensity additionally

influence heat and mass transfer. Continuous-flow HTL systems are increasingly important because they offer opportunities for improved process control, heat recovery, and scale-up compared with batch systems [18,28].

Catalysts can modify hydrolysis, decarboxylation, hydrogenation, hydrodeoxygenation, and hydrodenitrogenation. Homogeneous bases such as sodium carbonate and hydroxides can improve conversion but introduce catalyst-recovery and wastewater-treatment challenges. Heterogeneous catalysts, including zeolites, activated carbon, metal oxides, nickel-supported catalysts, and noble-metal systems, offer opportunities for selective upgrading. Nevertheless, catalyst deactivation caused by coke, mineral fouling, and nitrogen-containing compounds remains a significant obstacle [29,31].

HTL-derived biocrude contains hydrocarbons, phenols, ketones, fatty acids, esters, amides, nitrogen heterocycles, and oxygenated compounds. Its heating value is considerably higher than that of raw wet biomass, but nitrogen and oxygen remain major quality constraints. Protein-derived nitrogen compounds can poison downstream catalysts, increase NOx formation, and complicate compliance with transportation-fuel specifications. Therefore, hydrotreatment, hydrodeoxygenation, and hydrodenitrogenation are generally required before biocrude can be converted into high-quality transportation fuels [30,31].

Importantly, the aqueous phase and hydrochar should not be treated simply as wastes. The aqueous phase can contain ammonium, phosphate, organic acids, amino acids, and other dissolved carbon compounds that may potentially be recovered or recycled following appropriate treatment. Hydrochar contains residual carbon and minerals and can be used as a solid fuel, carbon-material precursor, adsorbent, catalyst support, or secondary thermochemical feedstock. Such valorization is essential for improving overall carbon efficiency and reducing the environmental burden of HTL [12,13,32].

6. Gasification and Supercritical Water Gasification

Gasification is a high-temperature thermochemical process that converts carbonaceous biomass into combustible syngas through partial oxidation using controlled amounts of air, oxygen, steam, or carbon dioxide. Unlike combustion, which seeks complete oxidation, gasification aims to maximize CO, H_2, CH_4, and light hydrocarbon production. These gases can be used for electricity generation, hydrogen production, Fischer–Tropsch synthesis, methanol production, or ammonia manufacture. For microalgae, gasification is particularly attractive for utilizing residual biomass remaining after other conversion processes, thereby improving overall carbon utilization [11,9]

Conventional gasification generally operates at approximately 700–1000 °C. Drying, devolatilization, oxidation, reduction, reforming, water-gas shift, methanation, and Boudouard reactions occur simultaneously. Increasing temperature generally improves carbon conversion and hydrogen production while reducing tar formation, although excessive temperature increases energy demand

and can intensify ash melting, slagging, and reactor-material degradation.

The gasifying medium strongly influences syngas composition. Air gasification is relatively inexpensive but produces nitrogen-diluted syngas with lower calorific value. Oxygen gasification avoids nitrogen dilution but requires an energy-intensive oxygen separation system. Steam gasification can increase hydrogen production through reforming and water-gas-shift reactions. CO_2-assisted gasification is particularly interesting from a circular-carbon perspective because carbon dioxide can participate in the reverse Boudouard reaction, converting part of the carbon into carbon monoxide while potentially linking gasification with upstream microalgal cultivation.

Supercritical water gasification (SCWG) is especially attractive for wet microalgae because water above its critical point of approximately 374 °C and 22.1 MPa becomes a reactive medium capable of converting wet biomass without conventional drying. Under supercritical conditions, mass transfer limitations are reduced and rapid gasification can produce hydrogen-rich gas. Catalysts based on ruthenium, nickel, alkali compounds, and other active phases can enhance conversion and hydrogen production [33].

Catalytic gasification focuses on increasing gas yield and hydrogen selectivity while reducing tar. Nickel catalysts are widely studied because of their strong reforming activity, whereas ruthenium can provide superior catalytic performance at substantially higher cost. Dolomite, olivine, alkali catalysts, and modified metal oxides have also demonstrated potential for tar reduction. Catalyst deactivation caused by coke deposition, sulfur poisoning, sintering, and mineral accumulation remains an important challenge for continuous industrial systems.

Microalgal feedstock characteristics strongly influence gasification. High protein contents increase ammonia and hydrogen cyanide formation, requiring effective gas cleaning. High ash contents can promote slagging, agglomeration, and fouling. High moisture content reduces thermal efficiency in conventional gasification and makes direct processing of freshly harvested algae unattractive without efficient heat integration. Therefore, gasification is particularly valuable when applied to dried residues, hydrochar, or integrated systems in which waste heat is available.

7. Integrated Thermochemical Conversion and Algae Biorefineries

Recent research has shifted from optimization of individual thermochemical technologies toward integrated conversion systems. Instead of treating pyrolysis, HTL, and gasification as independent technologies, an integrated thermochemical biorefinery seeks to direct each biomass fraction toward the conversion route most suitable for its composition and energy content. HTL can convert wet algae into biocrude while producing hydrochar and an aqueous phase; hydrochar can subsequently undergo pyrolysis or gasification; and gases can supply process heat or hydrogen. Such cascading utilization addresses the limitation that no single technology can convert all biochemical fractions into high-value products [13,37].

HTL–pyrolysis integration is particularly promising. HTL eliminates the need to dry wet algae and produces hydrochar as a carbon-rich solid residue. Rather than disposing of or underutilizing hydrochar, secondary pyrolysis can transform it into bio-oil, biochar, and combustible gases. This approach increases the number of valuable product streams while improving overall carbon and energy recovery. The concept is consistent with the integrated HTL–pyrolysis framework in which hydrochar is explicitly investigated as a secondary feedstock and mass and energy balances are used to evaluate system-level performance.

HTL–gasification integration provides another pathway. Hydrochar or other carbon-rich residues can be gasified to generate hydrogen-rich syngas. The resulting hydrogen can potentially support hydrodeoxygenation and hydrodenitrogenation during biocrude upgrading, thereby reducing dependence on externally purchased hydrogen. Waste heat from gasification can also supply energy to upstream HTL, feed preheating, or separation processes. Such integration creates opportunities for internal heat and hydrogen recycling and can substantially improve system-level energy efficiency [13,33,37].

The aqueous phase produced by HTL can also become an important component of the integrated system. Rather than treating this stream solely as wastewater, ammonium, phosphate, dissolved carbon, organic acids, and other compounds can potentially be recovered for subsequent cultivation or further conversion. Nutrient recycling reduces fertilizer demand and wastewater treatment requirements, while organic compounds can potentially be directed toward additional energy recovery. The recovery of carbon and nutrients therefore links the thermochemical conversion stage back to biomass cultivation, creating a more circular system [7,13,32].

Heat integration is another essential element. HTL, pyrolysis, and gasification have different thermal requirements, allowing heat generated by high-temperature processes to be recovered for lower-temperature operations. Syngas cooling, combustion of selected gas streams, and thermal recovery from hot solids can provide energy for biomass preheating, HTL feed conditioning, and other unit operations. Consequently, integrated heat management can reduce external energy requirements and improve the net energy balance of the overall biorefinery [13,37].

Integrated conversion also aligns closely with the circular carbon economy. Carbon dioxide produced during gasification or combustion can potentially be recycled into microalgae cultivation, while nutrients can reduce dependence on synthetic fertilizers. Biochar generated through pyrolysis may provide long-term carbon storage and simultaneously function as a soil amendment, adsorbent, catalyst support, or material precursor. This combination of carbon capture, nutrient recovery, energy generation, and material production transforms algae utilization from a linear fuel pathway into a circular biorefinery system [8,13,26].

A broader concept of integrated thermochemical conversion system for microalgal biomass is illustrated in the figure 4.

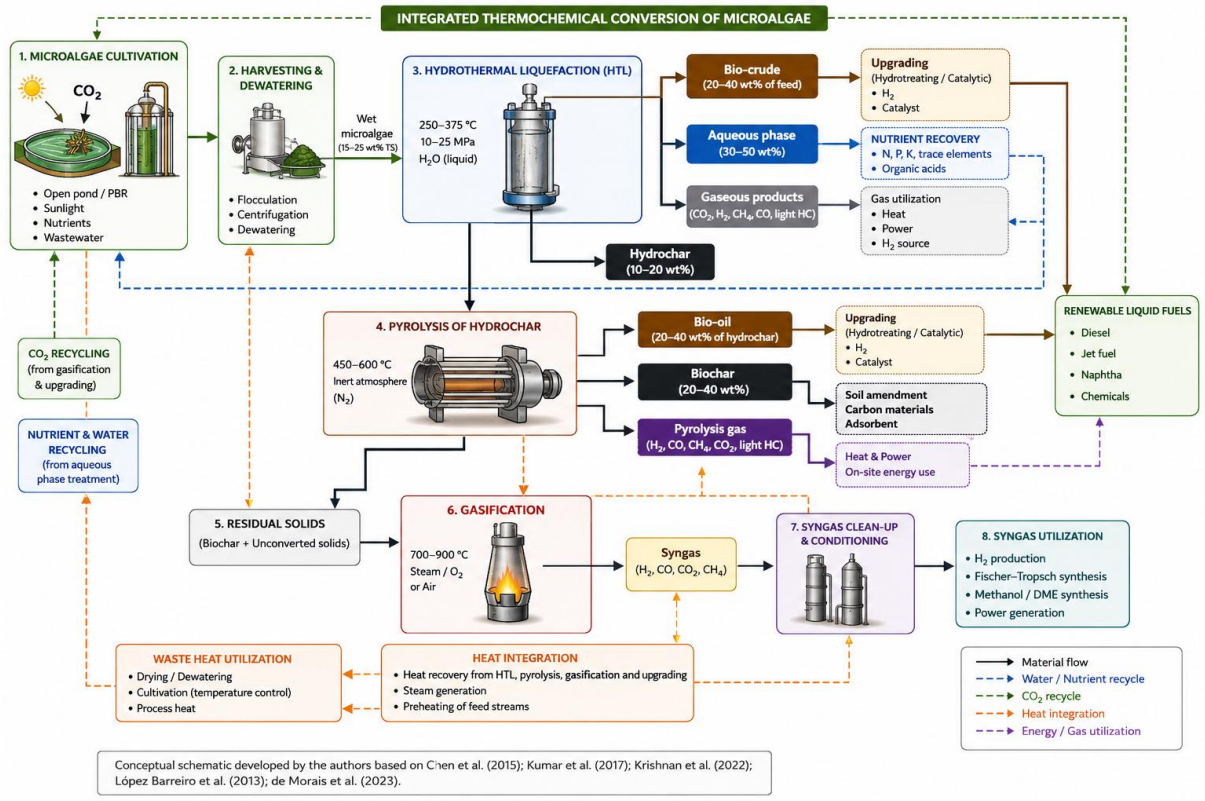

Fig.4. A concept of integrated thermochemical conversion system

The schematic illustrates an integrated thermochemical conversion pathway for microalgal biomass designed to maximize the recovery of fuels, chemicals, energy, water, nutrients, and carbon resources. The process begins with microalgae cultivation using sunlight, carbon dioxide (CO_2), nutrients, and potentially nutrient-rich wastewater as cultivation inputs. Following biomass production, the microalgae are harvested and dewatered through processes such as flocculation and centrifugation. Unlike conventional thermochemical routes that require extensive drying, the proposed configuration directs wet microalgal biomass to hydrothermal liquefaction (HTL), thereby reducing the energy requirement associated with biomass drying. Under elevated temperature and pressure conditions, HTL converts the major biochemical components of microalgae, including lipids, proteins, and carbohydrates, into several product fractions, primarily bio-crude, an aqueous phase, gaseous products, and hydrochar.

The bio-crude generated from HTL is subsequently subjected to upgrading, such as hydrotreatment or catalytic processing, to improve its physicochemical properties and reduce undesirable heteroatom-containing compounds. The upgraded bio-crude can potentially serve as a feedstock for renewable liquid fuels, including renewable diesel, sustainable aviation fuel, naphtha, and other value-added chemicals. Meanwhile, the HTL aqueous phase is considered a valuable resource rather than a waste stream because it contains dissolved nutrients and organic compounds. Following appropriate treatment and nutrient recovery, nitrogen, phosphorus, potassium, trace elements, and water can

potentially be recycled back to the microalgal cultivation stage. This establishes a circular pathway in which nutrients and water are recovered from the conversion process and reused for additional biomass production. The gaseous fraction generated during HTL can also be utilized for heat, power generation, or as a potential hydrogen source, depending on its composition and the effectiveness of subsequent gas treatment.

The hydrochar produced during HTL is further processed through pyrolysis to increase overall carbon and energy recovery. Pyrolysis generates additional bio-oil, biochar, and pyrolysis gases, with the bio-oil potentially undergoing further upgrading while biochar can be considered for applications such as carbon materials, adsorbents, or soil amendment, subject to its physicochemical characteristics and safety requirements. Residual carbonaceous solids can subsequently be directed to gasification, where high-temperature conversion produces syngas containing mainly hydrogen (H_2), carbon monoxide (CO), carbon dioxide (CO_2), and methane (CH_4). After syngas cleaning and conditioning, the gas can be utilized for hydrogen production, Fischer–Tropsch synthesis, methanol or dimethyl ether production, or power generation. Importantly, the integrated configuration also incorporates CO_2 recycling and heat integration. CO_2 generated from thermochemical conversion and upgrading may potentially be recovered and returned to microalgal cultivation, while waste heat from HTL, pyrolysis, gasification, and upgrading can be recovered for feed preheating, dewatering, steam generation, cultivation temperature control, and other process requirements. Consequently, the proposed system represents a circular microalgal biorefinery in which multiple thermochemical conversion pathways are interconnected to improve resource utilization and reduce waste, while simultaneously generating renewable fuels, chemicals, carbon-based products, hydrogen, heat, and power.

8. Techno-Economic Considerations

Although thermochemical conversion can substantially improve biomass utilization, economic feasibility remains one of the principal barriers to large-scale commercialization. Techno-economic studies consistently identify cultivation, harvesting, dewatering, drying, conversion, product upgrading, and capital-intensive equipment as major cost contributors. High-pressure HTL reactors, hydrogen production or supply, separation systems, and catalyst management can significantly increase capital and operating expenditures. Consequently, maximizing biocrude yield alone does not guarantee economic viability [5,26,34].

Integrated biorefineries offer a potential solution because production costs can be distributed across multiple products. Instead of depending exclusively on fuel sales, a facility can potentially generate revenue from bio-oil or upgraded fuel, biochar, proteins, pigments, specialty chemicals, recovered nutrients, electricity, hydrogen, and carbon-management services. The economic advantage of such integration arises from improved resource utilization and the ability to assign value to streams that would otherwise be considered waste [13,26].

Process integration can further improve economics by reducing external heat and hydrogen requirements. Internal syngas utilization, heat recovery, nutrient recycling, and aqueous-phase valorization can reduce operating expenditures. Aspen

Plus, process simulation, optimization, and mass–energy balance approaches are therefore increasingly important for evaluating alternative process configurations before expensive pilot-scale development.

The techno-economic challenge is especially relevant to HTL–pyrolysis integration. The integrated system requires additional equipment compared with stand-alone HTL, but the secondary conversion of hydrochar can generate additional fuel and carbon products. The economic question is consequently whether the incremental capital and operating requirements are outweighed by additional energy recovery, carbon utilization, and product revenue. This is precisely why system-level TEA should be combined with experimental optimization rather than evaluating each reactor independently. The research framework underlying the present study similarly identifies TEA as a key component for assessing economic feasibility and scalability.

9. Life Cycle Assessment and Environmental Sustainability

Life Cycle Assessment has become an essential methodology for evaluating the environmental sustainability of microalgae-based fuels. Unlike yield-based assessments, LCA evaluates environmental impacts across cultivation, nutrient supply, harvesting, dewatering, conversion, upgrading, transportation, and final utilization. Microalgae systems can provide environmental advantages when wastewater, renewable electricity, carbon dioxide recycling, and nutrient recovery are effectively incorporated. However, environmental performance remains highly sensitive to cultivation productivity, electricity sources, harvesting efficiency, reactor configuration, and hydrogen production pathways [5,34,35].

Co-product valorization can substantially improve environmental performance. Biochar can provide long-term carbon storage, while nutrient recovery can reduce the environmental burden associated with fertilizer manufacture. Therefore, environmental sustainability depends not only on the efficiency of fuel production but also on the extent to which every material and energy stream is utilized.

Integrated thermochemical conversion can potentially reduce greenhouse-gas emissions through heat recovery, internal hydrogen generation, nutrient recycling, and carbon utilization. However, integration does not automatically guarantee lower environmental impacts. Additional equipment, catalysts, hydrogen requirements, transportation, and energy consumption may introduce new burdens. Therefore, LCA should be conducted at the whole-system level and coupled with TEA to identify genuine sustainability improvements rather than relying solely on process-level indicators [26,35].

10. Research Gaps

Despite substantial progress, several important research gaps remain. First, most studies of HTL, pyrolysis, and gasification continue to be conducted at laboratory or pilot scale, while long-term continuous operation under industrial

conditions remains relatively limited. Second, catalyst deactivation caused by coke formation, mineral deposition, sulfur poisoning, and nitrogen-containing compounds is still insufficiently understood under prolonged operation. Third, standardized methodologies for comparing carbon recovery, energy recovery, fuel quality, environmental impact, and economic performance remain insufficient, making cross-study comparison difficult [12,15,27].

A particularly important research gap concerns the interaction between sequential thermochemical processes. Existing literature has extensively investigated individual HTL, pyrolysis, and gasification systems, but fewer studies systematically examine how upstream HTL conditions affect the physicochemical properties and subsequent pyrolysis behavior of hydrochar. The stored research framework similarly identifies the limited understanding of HTL-derived hydrochar conversion and the lack of systematic HTL–pyrolysis integration as research gaps.

Future studies should therefore move beyond maximizing individual product yields toward optimization of complete mass and energy flows. The performance of an integrated system should be evaluated using carbon utilization efficiency, energy recovery, net energy ratio, greenhouse-gas emissions, minimum fuel selling price, and co-product value. Such system-level indicators are more meaningful for commercialization than biocrude or bio-oil yield alone.

11. Future Research Directions

Future research should prioritize fully integrated and digitally optimized microalgae biorefineries. Artificial intelligence, machine learning, digital twins, computational fluid dynamics, and advanced process control can support reactor design, catalyst management, predictive maintenance, process optimization, and real-time monitoring. Process simulation platforms can also be coupled with TEA and LCA to identify optimal combinations of conversion pathways and operating conditions.

Biological innovations should be linked with thermochemical processing. Strain selection, metabolic engineering, and cultivation optimization could produce biomass with biochemical compositions specifically suited to downstream conversion. Rather than maximizing lipid productivity alone, future strains could be selected according to total carbon recovery, desired product distribution, reduced nitrogen content, mineral composition, and compatibility with HTL or pyrolysis. Such feedstock–process co-design could significantly improve integrated system performance [8,36].

The transition toward commercialization will also require stronger integration among technology development, policy, and industrial investment. Renewable fuel standards, carbon pricing, incentives for carbon capture and utilization, wastewater resource recovery, and support for demonstration-scale facilities could improve the competitiveness of algae-based fuels. Demonstration facilities should move beyond single-product production and demonstrate integrated production of renewable fuels, hydrogen, biochar, recovered nutrients,

electricity, and specialty chemicals.

A particularly promising future configuration is an integrated HTL–pyrolysis system in which wet microalgal biomass is first processed through HTL, the resulting biocrude is upgraded into transportation fuel, and hydrochar is subsequently converted through pyrolysis into additional bio-oil, biochar, and gas. The aqueous phase can be subjected to nutrient recovery, while process heat and gases can be internally recycled. Such a configuration directly addresses the central limitations of stand-alone conversion by reducing drying requirements, increasing carbon recovery, and assigning value to secondary product streams. The underlying research concept similarly targets improved energy recovery and carbon utilization through hydrochar valorization and integrated mass–energy analysis.

12. Conclusions

Microalgal biomass represents a promising renewable carbon resource for next-generation biofuel and biorefinery systems because of its rapid growth, flexible cultivation conditions, high photosynthetic productivity, and biochemical diversity. Nevertheless, the same biochemical characteristics that make microalgae attractive also create challenges during thermochemical conversion, particularly high moisture, ash, protein-derived nitrogen, and complex reaction chemistry.

The comparison of thermochemical conversion technologies for microalgae is shown in Table 1.

COMPARISON OF THERMOCHEMICAL CONVERSION TECHNOLOGIES FOR MICROALGAE

Parameter	Hydrothermal Liquefaction (HTL)	Pyrolysis	Gasification	Supercritical Water Gasification (SCWG)	Hydrothermal Carbonization (HTC)	Torrefaction
Process Principle	Thermochemical conversion of wet biomass in subcritical water (high temperature and pressure) to produce bio-crude.	Thermal decomposition of biomass in the absence of oxygen to produce bio-oil, biochar, and gas.	Partial oxidation of biomass with air/oxygen/steam/CO_2 at high temperature to produce syngas.	Oxidation of biomass in supercritical water to produce H_2-rich gas and CO_2.	Carbonization of biomass in hot compressed water (subcritical conditions) to produce hydrochar.	Mild heating of biomass at low temperature in the absence of oxygen to improve fuel properties.
Typical Operating Conditions	250–374 °C 10–25 MPa (subcritical water)	400–600 °C Atmospheric pressure or inert atmosphere	700–1000+ °C Atmospheric to several MPa (air/oxygen/steam)	374–700 °C 22–35 MPa (supercritical water)	180–250 °C 2–10 MPa (subcritical water)	200–300 °C Atmospheric pressure (inert atmosphere)
Feedstock Moisture Requirement	High (no drying required; wet biomass suitable)	Low (moisture <10–15% recommended)	Low (moisture <10–15% recommended)	High (wet biomass suitable)	High (wet biomass suitable)	Low to medium (moisture <15–20% recommended)
Main Products	Bio-crude, aqueous phase (organics), hydrochar, CO_2, gases	Bio-oil, biochar, syngas (non-condensable gas)	Syngas (H_2, CO, CH_4, CO_2, light hydrocarbons), tar, ash	Syngas rich in H_2 (H_2, CO_2), small amount of solid residue	Hydrochar, aqueous phase (organics), small amount of CO_2	Densified, hydrophobic solid (torrefied biomass), small amount of vapors and gases
Suitability for Wet Microalgae	Excellent (high moisture tolerance)	Moderate – Poor (drying required)	Moderate – Poor (drying required)	Excellent (high moisture tolerance)	Excellent (high moisture tolerance)	Poor – Moderate (drying recommended)
Technology Readiness Level (TRL)	TRL 6–7 (Demonstration)	TRL 8–9 (Commercial)	TRL 8–9 (Commercial)	TRL 4–6 (Pilot)	TRL 6–7 (Demonstration)	TRL 8–9 (Commercial)
Role in Integrated Biorefinery	Primary platform for converting wet microalgae to bio-crude and valuable co-products.	Valorization of hydrochar (from HTL/HTC) or residual biomass to produce bio-oil, biochar, and gas.	Production of syngas for heat, power, hydrogen, or chemical synthesis from char/residues.	Clean hydrogen production and energy recovery from wet microalgae.	Production of hydrochar for soil amendment, carbon sequestration, or as gasification feed.	Upgrading of low-quality biomass to improve energy density and facilitate handling and storage.
Key Advantages	• Can process wet biomass • High energy density oil • High carbon conversion • Co-production of chemicals and nutrients	• Simple technology • Flexible operation • Multiple products • Suitable for various scales	• High energy efficiency • Versatile syngas • Scalable technology • Suitable for power and chemicals	• High H_2 yield • No drying required • Fast reaction kinetics • Direct wet biomass conversion	• Wet biomass suitable • Useful, stable hydrochar • Lower severity conditions • Potential for nutrient and carbon recovery	• Improves fuel properties • Low-cost technology • Reduces moisture • Easy to integrate with existing systems
Key Challenges	• High pressure and cost • Corrosion and scaling • Complex upgrading • Catalyst deactivation	• Requires drying • Bio-oil needs upgrading • Catalyst deactivation • Heat transfer limitations	• Requires drying • Tar formation • High temperature materials and ash management	• Very high pressure • High capital cost • Corrosion issues • Limited large-scale experience	• Lower energy content • Dewatering of hydrochar • Limited bio-oil yield • Scale-up challenges	• Low energy yield • Does not produce liquid fuels • Volatile product loss
Typical End Uses	Liquid biofuels, chemicals, materials, nutrient recovery, energy.	Bio-oil for fuels/chemicals, biochar for soil or materials, energy.	Electricity, heat, hydrogen, Fischer–Tropsch fuels, methanol, ammonia.	Hydrogen production, energy, clean water, advanced fuels.	Soil amendment, activated carbon, gasification feed, carbon sequestration.	Solid fuel for combustion or co-firing, improved pellets, feedstock pre-treatment.

Note: Operating conditions may vary depending on microalgae species, composition, and reactor configuration.

Pyrolysis, HTL, and gasification each provide distinct advantages. Pyrolysis can generate bio-oil and carbonaceous materials but generally requires dry feedstock. HTL is particularly advantageous for wet microalgae because it eliminates the need for energy-intensive drying and generates biocrude together with hydrochar, aqueous products, and gases. Gasification can convert carbon-rich residues into hydrogen-rich syngas and therefore provides an important secondary conversion pathway. SCWG further expands the potential for direct conversion of wet biomass into hydrogen-rich gas.

The major opportunity lies in integrating these technologies rather than optimizing them independently. HTL–pyrolysis integration can utilize wet biomass efficiently while converting hydrochar into additional fuels and carbon materials. HTL–gasification can recover additional carbon and generate hydrogen and process heat. Aqueous-phase nutrient recovery, CO_2 recycling, and heat integration can further strengthen the circularity and sustainability of the overall system.

However, commercial implementation requires simultaneous optimization of technical, economic, and environmental performance. TEA and LCA should therefore be integrated with experimental studies to evaluate complete systems rather than isolated reactors. Future research should emphasize continuous operation, catalyst durability, digital process optimization, standardized performance metrics, and demonstration-scale integrated biorefineries.

Overall, integrated thermochemical conversion provides a promising pathway for transforming microalgal biomass from a single-purpose biofuel feedstock into a multifunctional circular-bioeconomy resource. The integration of HTL, pyrolysis, gasification, catalytic upgrading, heat recovery, nutrient recycling, carbon utilization, TEA, and LCA has the potential to substantially improve carbon efficiency, energy recovery, economic competitiveness, and environmental performance. In particular, the HTL–pyrolysis configuration offers a strong research direction for maximizing the utilization of hydrochar and establishing a more efficient and circular microalgal biofuel production platform.

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