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Review

From Heteroatom-Rich Biocrude Towards Drop-In Fuels: A Comprehensive Catalyst Review for Upgrading Algal HTL-Derived Bio-Oils

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Abstract

The upgrading of microalgal biocrude produced via HTL is essential for the production of refinery-compatible drop-in fuels. Despite the high energy density of HTL biocrude, its elevated nitrogen and oxygen content originating from protein and lipid fractions presents significant hurdles for downstream hydroprocessing. This review evaluates the performance and mechanisms of diverse catalysts, ranging from conventional sulfides and oxides to noble metals, TMCs, bifunctional and zeolitic catalysts. While noble metals consistently yield high-quality products with HHVs of 40–45 MJ kg^{-1}, their industrial application is restricted by high costs and vulnerability to nitrogen and sulfur poisoning. Conversely, TMCs, specifically Mo_2C, emerge as robust, cost-effective alternatives that resist deactivation while favoring hydrogen-conservative decarboxylation pathways. A critical analysis of catalyst architecture reveals that hierarchical zeolite pore structures are vital for overcoming mass-transfer limitations associated with bulky algal macromolecules. It is observed that achieving industrial-scale viability requires a shift toward feedstock-specific catalyst design, utilizing staged hydroprocessing and applying different catalyst structures to manage the complex heteroatom fingerprint of microalgal feedstocks.

Keywords: algal HTL biocrude; upgrading catalyst; advanced catalyst design; bifunctional catalyst; hydrodenitrogenation; hydrodeoxygenation; hydrodesulfurization

1. Introduction

The global transition toward sustainable energy systems has intensified the search for renewable liquid fuels capable of seamless integration into existing refinery infrastructures [1]. Within this context, HTL has emerged as a premier technology for the valorization of high moisture biomass, specifically microalgae, due to its ability to operate in subcritical water conditions (typically between 280 °C and 370 °C) and pressures of 10–25 MPa and residence times of 5–120 min [2–4]. By utilizing water as both a reactive medium and a solvent, HTL bypasses the energy-intensive drying requirements that traditionally hinder the economic viability of pyrolysis and gasification for aquatic feedstocks [5]. Recent performance data indicate that HTL can achieve biocrude yields ranging from 24 to 64 wt.% on a dry basis, with HHV typically spanning 28–38 MJ kg^{-1}, significantly exceeding those of lignocellulosic bio-oils [6,7].

Despite these promising yields, the chemical complexity of microalgal biocrude driven by its primary biochemical constituents (lipids, proteins, and carbohydrates) presents a

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formidable barrier to direct fuel application [8–10]. Microalgae are characterized by protein contents often exceeding 40 wt.%, which, during the HTL process, undergo extensive hydrolysis and Maillard reactions to form a suite of nitrogenous heterocycles, such as indoles, pyrroles, and quinolines [11–14]. Consequently, while petroleum crude typically contains <0.5 wt.% nitrogen, raw algal biocrude can exhibit nitrogen concentrations from 5 to 8 wt.%, oxygen levels from 10 to 15 wt.%, alongside sulfur levels from 0.5 to 1.5 wt.%. These elevated heteroatom levels, compared to conventional petroleum fractions (typically <2 wt.% each), necessitate more severe and selective upgrading strategies [15–17]. In this context, sulfided transition metal catalysts such as $NiMo/Al_2O_3$ and $CoMo/Al_2O_3$ are among the most widely studied systems due to their established performance in heteroatom removal; however, they remain susceptible to deactivation due to metal leaching during catalyst degradation [18]. Furthermore, the high concentration of nitrogen in algal feeds promotes accelerated coke formation and induces competitive adsorption at metal–sulfide active sites, thereby suppressing catalytic activity [19]. In response to these limitations, extensive research efforts have focused on the development of advanced catalytic systems. Noble metal catalysts such as Pt, Pd, and Ru supported on carbon or metal oxides have demonstrated superior hydrogenation activity and improved product quality, with upgraded oils achieving HHVs approaching 40–45 MJ kg^{-1} and significantly reduced oxygen content [20,21]. However, their widespread application is constrained by high cost, limited availability, and susceptibility to deactivation, particularly in nitrogen-rich environments where strong adsorption of basic compounds can poison active sites [22,23]. As an alternative, transition metal carbides, phosphides, and nitrides have emerged as promising alternatives, offering noble-metal-like electronic properties alongside improved resistance to sulfur and nitrogen poisoning [24,25].

Despite significant advances in catalyst development, critical challenges remain in designing robust catalyst systems capable of handling the highly variable and heteroatom-rich nature of HTL-derived algal biocrude, which particularly suffers from nitrogen species. Moreover, catalyst deactivation may limit process stability and long-term performance. In this context, the novelty of the present review lies in its catalyst-centered, multi-scale perspective, which systematically connects varied feedstocks with catalyst architecture, reaction pathways, and process conditions, linking these with the final product features. Accordingly, a wide range of catalyst formulations are deeply discussed including conventional sulfided and oxide catalysts, noble transition metal catalysts, transition metal carbides, zeolitic and bifunctional catalysts. This catalyst-focused approach clearly clarifies the structure–activity–stability relationships governing upgrading reactions and provides insights for the development of next-generation catalyst systems suitable for industrial-scale applications. In summary, this work distinguishes itself as a comprehensive and dedicated review of catalyst design and functionality in the upgrading of HTL-derived algal biocrude.

2. Composition and Challenges of Algal HTL Biocrude

HTL of microalgae has emerged as a promising route for converting wet biomass into energy-dense liquid intermediates. The process operates under subcritical—or supercritical—water conditions and enables the direct conversion of wet feedstocks into biocrude without the need for drying, offering significant energetic advantages over alternative thermochemical routes [26]. However, the resulting algal biocrude differs substantially from petroleum crude in both composition and reactivity, creating major challenges for downstream upgrading [27].

2.1. Chemical Complexity Beyond Conventional Bio-Oils

Algal HTL biocrude is a highly heterogeneous mixture formed through complex reaction pathways, including hydrolysis, dehydration, decarboxylation, and recombination reactions [26]. Unlike lignocellulosic pyrolysis oils, algal biocrude contains significant contributions from lipids, proteins, and carbohydrates, resulting in a broad spectrum of chemical compounds [27,28]. The conventional classification of HTL products based on feedstock fractions (lipid → hydrocarbons, protein → N-compounds) is overly simplistic; intermediate cross-reactions dominate the final chemical landscape yet remain poorly quantified.

Although lipid-derived compounds are often associated with hydrocarbon formation, several studies indicate that total biocrude yields frequently exceed lipid content, suggesting substantial contributions from protein- and carbohydrate-derived intermediates [27,28]. This behavior highlights the importance of cross-reactions and secondary polymerization pathways in determining final product composition. The major chemical classes in the final products include phenolic compounds and other oxygenated hydrocarbons, fatty acids and their derivatives (esters), long-chain aliphatic hydrocarbons, nitrogen-containing heterocycles such as pyridines, indoles and amides, sulfur-containing species, and trace inorganic elements including alkali and alkaline earth metals (Na, K, Ca, Mg, Fe) [29,30].

2.2. Heteroatom Enrichment and Its System-Level Impact

A key limitation of algal HTL biocrude is its high heteroatom content, particularly nitrogen and oxygen. Nitrogen levels typically range from 5 to 8 wt.%, significantly higher than in conventional bio-oils due to the protein-rich nature of microalgae [27–32]. Oxygen content remains substantial (10–20 wt.%), contributing to instability and reactivity issues [33].

While oxygen removal has traditionally been prioritized in upgrading processes, recent studies emphasize the dominant role of nitrogen compounds in catalyst deactivation. Nitrogen-containing species exhibit strong adsorption on catalyst active sites and inhibit hydrogenation and deoxygenation reactions [32].

The upgrading challenge of algal biocrude is not merely “high oxygen content” but rather a multi-heteroatom problem, where nitrogen often plays the dominant role in catalyst deactivation and process inefficiency [22,27,33].

2.3. Physicochemical Properties and Fuel Limitations

Algal biocrude exhibits high viscosity, acidity, and thermal instability, largely due to polar functional groups and heavy molecular fractions [34]. These characteristics complicate storage, transport, and refining processes; however, they also reflect the presence of reactive functional groups.

For instance, oxygenated species such as phenolics and ketones are often targeted for removal, yet they serve as key intermediates in catalytic upgrading reactions, particularly under hydrogenation conditions [35]. Furthermore, fractionation studies indicate that a significant portion of biocrude consists of lighter fractions below 350 °C, which can be effectively upgraded into fuel-range hydrocarbons [36].

Instead of viewing heteroatom-rich fractions solely as impurities, process design could leverage their reactivity through staged upgrading strategies, reducing hydrogen demand and improving carbon efficiency.

The compositional complexity of algal HTL biocrude is further reflected in its elemental distribution, physicochemical properties, and heteroatom content, as summarized in Table 1. These properties directly influence upgrading requirements, hydrogen consumption, and catalyst selection.

Table 1. Typical composition and physicochemical properties of algal HTL biocrude.

Property/Component	Typical Range	Origin/Description	Implication for Upgrading
Carbon (C)	70–80 wt.%	Lipid-derived hydrocarbons	High energy density
Hydrogen (H)	8–12 wt.%	Organic matrix	Determines H/C ratio
Oxygen (O)	10–20 wt.%	Alcohols, ketones, acids	Requires HDO (high H_2 demand)
Nitrogen (N)	5–8 wt.%	Proteins → N-heterocycles	Catalyst poisoning, HDN needed (high H_2 demand)
Sulfur (S)	0.5–1.5 wt.%	Nutrients, amino acids	HDS required, catalyst interaction
Higher Heating Value	30–35 MJ kg^{-1}	Energy content	Lower than petroleum fuels
Viscosity	High	Polar/heavy compounds	Poor flow properties
Acidity (TAN)	High	Carboxylic acids	Corrosion issues
Molecular weight	Broad distribution	Polymerization products	Refining difficulty
Boiling range	Wide (to >350 °C)	Heavy fractions	Requires fractionation
Metals (Na, K, Ca, Fe)	ppm-wt. trace	Growth medium residues	Catalyst fouling/poisoning

Note: Data compiled from multiple literature sources on algal HTL biocrude characterization and upgrading [27,28,33,34]. Values may vary depending on algal species, HTL conditions, and analytical methods.

2.4. Reaction Network in Biocrude Formation

The formation of algal HTL biocrude proceeds via a complex reaction network involving parallel and consecutive pathways, as illustrated in Figure 1. Lipids undergo hydrolysis to fatty acids followed by decarboxylation and hydrogenation to form long-chain hydrocarbons. Proteins are converted into amino acids and subsequently undergo deamination, cyclization, and condensation reactions to produce nitrogen-containing compounds such as amides, pyridines, and indoles. Carbohydrates are decomposed into sugars, which further undergo dehydration and fragmentation to yield oxygenated intermediates including ketones, aldehydes, and phenolics. These primary intermediates participate in secondary reactions such as polymerization, condensation, and aromatization, leading to the formation of heavy fractions and coke precursors [26,27,34,35]. In parallel, gas-phase products (CO_2, NH_3) and aqueous-phase compounds are generated. The complexity of these interconnected pathways governs the final composition and upgrading behavior of algal HTL biocrude.

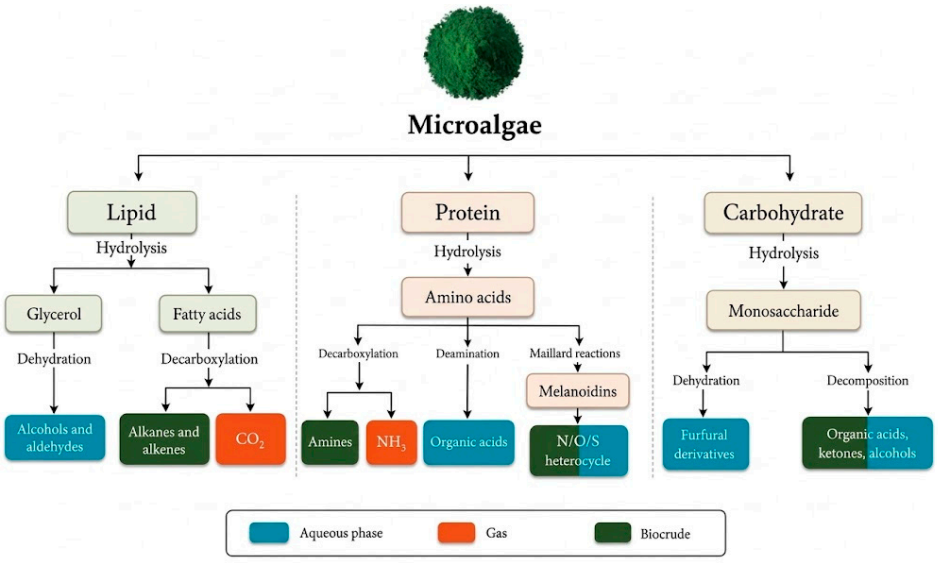

Figure 1. Schematic representation of reaction pathways during HTL of microalgae and the formation of biocrude (adapted from [32]).

2.5. Upgrading Requirements

The complex composition and physicochemical properties of algal HTL biocrude impose stringent requirements on upgrading processes. To produce transportation-grade fuels, algal HTL biocrude must undergo catalytic upgrading processes that address its unfavorable physicochemical properties. The key objectives of upgrading can be summarized as follows [26,37]:

- Reduction of heteroatoms (O, N, S): Essential for meeting fuel standards and preventing corrosion and emissions issues.
- Increase in H/C ratio: Achieved through hydrogenation reactions, improving fuel quality and calorific value.
- Improved volatility and stability: Necessary for compatibility with existing fuel infrastructure.
- Minimization of hydrogen consumption: Critical for economic feasibility, as hydrogen is a major cost driver.
- Maintaining catalyst lifetime: Requires mitigation of deactivation pathways such as coking, leaching, sintering and poisoning.

A primary objective is the reduction of oxygen, nitrogen, and sulfur contents through HDO, HDN, and HDS, respectively. However, the high nitrogen content of algal biocrude presents a particularly challenging constraint, as nitrogen-containing compounds strongly inhibit catalytic activity and often dictate overall process performance [22,27–29].

In addition to heteroatom removal, upgrading must target the reduction of molecular weight and viscosity through controlled hydrocracking, enabling the production of fuel-range hydrocarbons. At the same time, isomerization reactions are required to improve cold flow properties and fuel quality, particularly for diesel-range fractions [34,35].

There is an inherent trade-off between hydrogen consumption and carbon efficiency. While HDO pathways preserve carbon by producing water, alternative pathways such as decarboxylation and decarbonylation reduce hydrogen demand but lead to carbon loss in the form of CO_2 and CO [27,35]. For this reason, carefully controlling the selectivity among these reactions is key to making the upgrading process economically practical. In addition, catalyst durability remains a major concern, since coke formation, metal deposition, and poisoning by heteroatoms can quickly reduce catalyst activity and shorten its lifespan [22,34,35]. These challenges highlight the necessity of developing robust, multifunctional catalysts capable of operating under complex feed conditions. In general, upgrading strategies must be designed as integrated systems that balance heteroatom removal, hydrogen efficiency, carbon retention, and catalyst durability, rather than focusing on individual reaction pathways.

2.6. Knowledge Gaps in Composition–Reactivity Relationships

Despite extensive compositional analysis, a major limitation in the literature is the lack of direct linkage between molecular composition and catalytic behavior. Most studies rely on bulk characterization techniques, which fail to capture molecular interactions and competitive adsorption effects in complex mixtures [34]. There is a critical need for integrated molecular-level analysis linking composition, reaction pathways, and catalyst performance, particularly when treating realistic feeds under industrial conditions.

3. Catalyst Families for Algal Biocrude Upgrading

Following the compositional challenges discussed in Section 2, catalyst design plays a significant role in enabling efficient upgrading. Catalyst systems used for algal biocrude upgrading can be broadly classified according to their phase relative to the reaction medium. Homogeneous catalysts are soluble in the reaction phase and enable molecular-level in-

teractions, whereas heterogeneous catalysts exist as solid phases that operate through adsorption–desorption mechanisms on their surfaces, providing practical advantages such as easy separation, recyclability, and greater resistance to harsh operating conditions, which makes them the dominant technological option for industrial biocrude upgrading [38]. Furthermore, these solid catalysts offer the advantage of enabling multiple regeneration and reuse cycles, while their strong activity toward bond cleavage promotes the degradation of complex macromolecules and the conversion of oxygenated and nitrogenated compounds into higher-grade hydrocarbons, ultimately yielding biocrude with lower viscosity, higher HHV, and reduced nitrogen content [39]. Accordingly, heterogeneous catalysts are generally synthesized to provide a high density of active metal sites that facilitate hydrogenation reactions to achieve higher reaction rates and improved efficiency, particularly in sequential biomass conversion processes [40]. However, a significant technical barrier remains the gradual deactivation of heterogeneous catalysts during algal biocrude upgrading, which is primarily caused by coke deposition, poisoning by nitrogen- and sulfur-containing compounds, and structural changes in active metal sites under severe hydrothermal and hydrogenation conditions, ultimately reducing catalytic activity, selectivity, and long-term process stability [41–43]. Specifically for algal feedstocks, this challenge is exacerbated by the intrinsically high nitrogen content of algal biocrude (typically 4–8 wt.%), which can rapidly poison conventional hydrotreating catalysts and hinder efficient HDN reactions, as highlighted by several studies [15,44]. Consequently, current research has increasingly focused on the development of robust heterogeneous catalyst systems and engineered structures capable of achieving deep deoxygenation and denitrogenation while minimizing coke formation and undesired gas production, as discussed in the following subsections covering the major catalyst families employed for algal biocrude upgrading.

3.1. Transition Metal Non-Sulfides (Oxides)/Sulfides

Transition metal catalysts, specifically those based on molybdenum, cobalt, nickel, and tungsten, are the most widely explored materials for the catalytic hydrotreating of a wide range of biocrudes due to their established efficiency in industrial refinery processes [21,45–47]. The most common hydrotreating catalysts are CoMo, NiMo, and NiW systems, typically containing 1–4 wt.% Co or Ni, 8–16 wt.% Mo and 12–25 wt.% W, dispersed on high surface area supports such as γ-Al_2O_3 to enhance active site availability and catalytic performance [48]. In the literature, these catalysts are generally categorized into sulfided and non-sulfided (oxide) forms: sulfided catalysts such as Co-MoS_2 and Ni-MoS_2 represent the conventional benchmarks widely employed in hydrotreating and hydroprocessing reactions owing to their well-established activity for heteroatom removal [35]. However, these sulfided catalysts typically require the addition of sulfur sources to activate and maintain their catalytic activity during hydroprocessing, which may lead to an increased sulfur content in the upgraded fuel product [49]. Within this context, understanding the structural nature of these catalysts is essential for interpreting their performance in algal biocrude upgrading. Earlier, Topøse et al. [48] stated that in sulfided transition metal catalysts, the catalytically active phase is typically composed of metal sulfide slabs (e.g., MoS_2) promoted by cobalt or nickel, where the exposed edge sites serve as the primary active centers for heteroatom removal reactions during the hydroprocessing of heteroatom-rich feedstocks. Building on this understanding, the structural organization of these sulfided phases and the incorporation of promoter metals into the MoS_2 framework have been interpreted through a series of models developed over time, as summarized in Figure 2. The early monolayer model describes molybdenum species as highly dispersed oxide layers anchored to the alumina support through Mo-O-Al linkages, with a surface oxygen layer that is replaced by sulfur during activation. Although this model captures the

dispersion of molybdenum, it does not account for the role of promoter metals. To address this, the intercalation and pseudo-intercalation models proposed that cobalt or nickel atoms are incorporated within the MoS_2 structure, either between the layers or at their edges, thereby modifying the electronic properties of molybdenum and enhancing catalytic activity. In contrast, the contact synergy model suggests that MoS_2 and cobalt sulfide phases exist separately, and that their interaction occurs through hydrogen spillover rather than direct structural integration. The currently accepted Ni/Co-Mo-S model resolves these interpretations by describing a MoS_2-based structure in which promoter atoms are preferentially located at the slab edges, forming sites with reduced sulfur coordination. These edge-decorated configurations generate the active centers responsible for HDO, HDN, and HDS reactions, thereby directly linking catalyst structure to hydrotreating performance.

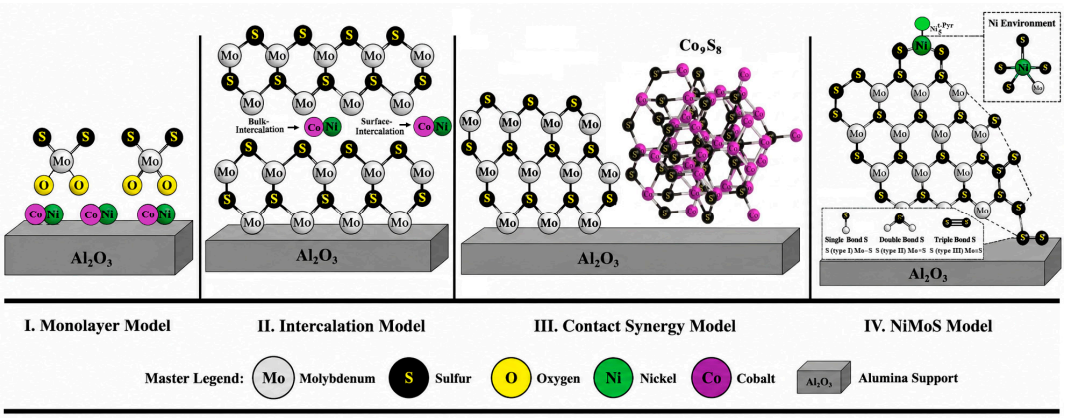

Figure 2. Structural model evolution and active phase distribution in Al_2O_3-supported CoMo/NiMo hydrotreating catalysts (created based on data from [48]).

During hydroprocessing, these catalysts—as with many catalysts—promote the cleavage of C-O, C-N, and C-S bonds through hydrogenation-dehydrogenation, allowing heteroatoms to be removed as H_2O, NH_3, and H_2S, as well as converting complex bio-oil molecules into more stable hydrocarbon products [50].

Building on this structural framework, the reaction network for catalytic upgrading of algal biocrude is governed by three principal hydrotreating pathways, namely HDO, HDN, and HDS, as illustrated in Figure 3. HDO primarily targets oxygenated compounds derived from lipids and other oxygen-rich fractions, proceeding through a combination of hydrogenation (C=O → C-OH), dehydration (C-OH → C-H), and direct HDO of C-O bonds, ultimately producing hydrocarbons and water (H_2O) [51,52]. In parallel, decarbonylation (R-C=O → R-CH_3 + CO) and hydrocracking (C-C cleavage) pathways also contribute to oxygen removal and influence the distribution of lighter hydrocarbon products [52]. Simultaneously, HDN is predominantly associated with nitrogen-containing compounds originating from the high protein content of algal biomass. This pathway involves sequential hydrogenation of nitrogen functionalities followed by C-N bond cleavage, leading to the formation of hydrocarbons and ammonia (NH_3) [53,54]. Similarly, HDS facilitates the removal of sulfur species via hydrogenation and hydrogenolysis reactions, where C-S bonds are cleaved to produce hydrocarbons and hydrogen sulfide (H_2S) [55].

Accordingly, within this catalyst class, sulfided transition-metal systems such as CoMo and NiMo supported on γ-Al_2O_3 are widely employed for hydrotreating and biocrude upgrading due to their high activity for heteroatom removal and HDO, HDN, and HDS reactions [43,56].

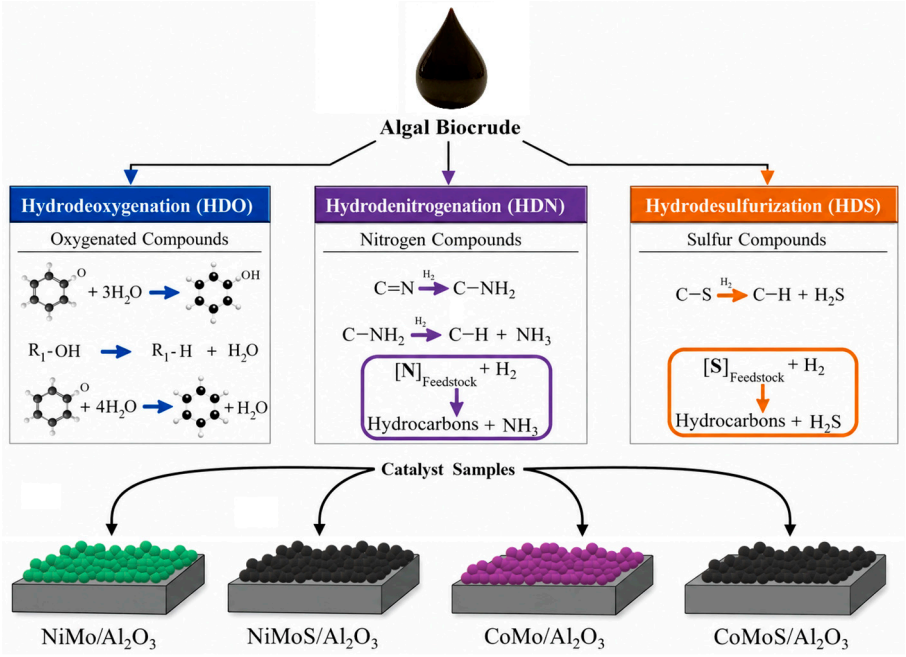

Figure 3. General hydrotreating pathways.

While these pathways define the fundamental chemistry of upgrading, their practical effectiveness is strongly governed by catalyst composition, synthesis, and reaction environment, as discussed in the following studies. Elliott et al. [57] reported the continuous hydrotreatment of algal biocrudes from four different microalgae in a bench-scale trickle-bed reactor over a high-metal-loading sulfided Co-Mo catalyst on a fluorinated alumina support containing 4 wt.% Co and 15 wt.% Mo. Under harsh conditions (405 °C and 13.6 MPa), they achieved oil yields of 80–85%, reducing the oxygen and nitrogen content to approximately 1.8–0.8 wt.% and 0.25–<0.05 wt.% respectively, resulting in the production of stabilized fuel with a higher heating value (HHV) of 46–47 MJ kg^{-1}. They also pointed out the difficulty of directly comparing continuous and batch systems due to equilibrium limitations in batch processes. In a comparative batch study, Biller et al. [58] investigated the performance of sulfided NiMo and CoMo catalysts supported on alumina for the upgrading of algal biocrude at 350 °C and 405 °C for 2 h under an initial H_2 pressure of 6.6 MPa. While high biocrude yields were obtained at 350 °C (89–93 wt.%), the product quality improved significantly at 405 °C, where the NiMo catalyst achieved the lowest nitrogen content of 2.4 wt.%. To ensure the formation and stability of the active sulfided phase, the authors implemented a rigorous catalyst sulfidation procedure using a 2 wt.% DMS solution in kerosene. This activation program involved a multi-step temperature ramp from 40 to 300 °C under a hydrogen atmosphere, which helped prevent the reduction of metal sites to their metallic form, thereby reducing susceptibility to coking and nitrogen poisoning in the presence of the highly polar compounds typically found in algal biocrude. These results suggest that continuous systems such as that employed by Elliott et al. [57] provide improved mass transfer and catalyst contact compared with batch reactors, which are often limited by equilibrium constraints. In a related investigation, Biller et al. [59] evaluated the catalytic upgrading of biocrudes derived from two microalgae species, *Chlorella vulgaris* and *Nannochloropsis occulata*, using several metal catalysts supported on Al_2O_3, including Ni, and CoMo. The catalysts were prepared through an IWI method with a metal loading of 20 wt.% for Ni, while Co was introduced at a lower loading of 6 wt.%. Catalytic processing was carried out at 350 °C for 1 h with a catalyst:water ratio of 1:9. The results showed that the bio-oil yield was strongly influenced by both the microalgae species and the catalyst composition. In the absence of catalysts, bio-oil yields of 36%

and 34% were obtained for *Chlorella* sp. and *Nannochloropsis occulata*, respectively. When catalysts were introduced, $CoMo/Al_2O_3$ slightly increased the bio-oil yield from *Chlorella* sp. to 39%, whereas Ni/Al_2O_3 reduced the yield to 30%. In contrast, all catalysts led to a decrease in bio-oil yield when processing *Nannochloropsis occulata*, with the Ni/Al_2O_3 catalyst producing the lowest yield of only 18%. Chromatographic analysis further revealed that the incorporation of $CoMo/Al_2O_3$ promoted the formation of paraffinic and aromatic hydrocarbons, which was attributed to enhanced C-C and C-O bond cleavage as well as more effective deoxygenation of oxygenated compounds compared with the Ni/Al_2O_3 catalyst.

A complementary perspective emerges when these catalysts are applied under hydrothermal upgrading conditions rather than conventional hydrotreating environments. Bai et al. [60] investigated this aspect through a comprehensive catalyst screening study for the upgrading of *Chlorella*-derived algal biocrude. In their work, sulfided $CoMo/Al_2O_3$ was evaluated alongside several other catalytic systems under supercritical conditions with added hydrogen at elevated temperatures (~400 °C). The authors observed that while CoMo-based catalysts maintained measurable activity for HDN, their HDO performance was comparatively limited in the aqueous hydrothermal environment, indicating that the catalytic behavior of conventional refinery hydrotreating catalysts may differ significantly when operating in water-rich upgrading systems. Specifically, $CoMo/Al_2O_3$ demonstrated denitrogenation activity comparable to several noble metal catalysts but showed lower efficiency in oxygen removal relative to catalysts such as Ru/C. This observation suggests that the catalytic functionality of Mo-based sulfides may be strongly influenced by the reaction medium and the complex molecular composition of algal biocrude, which contains nitrogen-rich heterocyclic compounds derived primarily from proteins and amino acids. The results highlight an important limitation in the application of conventional sulfided hydrotreating catalysts to algal feedstocks. While CoMo catalysts are well known for their efficiency in HDS and HDN in petroleum refining, the presence of water, polar oxygenates, and nitrogen-containing compounds in algal biocrude can alter adsorption behavior and active-site accessibility. Under hydrothermal conditions, competitive adsorption between water molecules and polar intermediates may reduce the effective availability of CUS located at the edges of the MoS_2 slabs, which are normally responsible for heteroatom removal reactions. Consequently, although CoMo catalysts remain active for denitrogenation reactions, their overall HDO efficiency may be suppressed compared with metal catalysts that favor hydrogenation pathways in aqueous media. These findings illustrate that the catalytic performance of Mo-based sulfides is not solely determined by the Mo active phase but also by the interaction between the promoter metal, support material, and reaction environment, particularly when upgrading nitrogen-rich algal biocrudes. Under more conventional hydroprocessing environments, however, the catalytic behavior of NiMo and CoMo systems can differ significantly, Haider et al. [16] investigated batch upgrading processes using commercial $NiMo/\gamma\text{-}Al_2O_3$ catalysts under high temperature hydrotreating conditions. Their results confirmed that significant removal of heteroatoms from algal biocrude requires relatively severe operating conditions, typically between 300 and 420 °C and hydrogen pressures ranging between 30 and 170 bar, in order to promote effective HDO and HDN reactions. The authors also noted that batch reactors tend to be equilibrium limited systems, which may require even higher temperatures to achieve substantial nitrogen removal compared with continuous hydrotreating systems. In the referenced experiments, hydrotreatment of microalgal biocrude with NiMo and CoMo catalysts resulted in substantial oxygen removal (up to ~86–91%) and moderate nitrogen reduction (~55–60%), indicating that although these catalysts are effective for deoxygenation, complete denitrogenation remains challenging due to the strong stability of nitrogen

containing heterocycles present in algal oils. The apparent differences in the dominant upgrading limitations reported in the literature can largely be attributed to variations in reaction environments and feedstock composition. In the hydrothermal upgrading system investigated by Bai et al. [60], the presence of excess water and the relatively low hydrogenation activity of sulfided CoMo catalysts under such conditions can suppress HDO, resulting in comparatively limited oxygen removal. In contrast, the batch hydrotreating experiments of Haider et al. [16], performed under hydrogen-rich hydroprocessing conditions using NiMo/γ-Al_2O_3 catalysts, demonstrated that deoxygenation can proceed efficiently at moderate temperatures, whereas the removal of nitrogen remains more challenging due to the high stability of heterocyclic nitrogen compounds derived from protein rich microalgae such as *Spirulina*. Consequently, these studies do not represent contradictory observations but rather illustrate that the rate-limiting upgrading step can shift between HDO and HDN depending on reaction medium, catalyst functionality, and the molecular structure of the heteroatom species present in algal biocrude. To overcome some of these limitations, Xu et al. [61] developed multimetallic catalysts (NiMoW, NiCoMo, CoMoW, and CoNiMoW) supported on γ-Al_2O_3, which leverage the synergistic effects of multiple active components. These catalysts were prepared via incipient wetness impregnation of γ-Al_2O_3 with aqueous metal precursors (10 wt.% MoO_3, 14 wt.% WO_3, and ~3 wt.% NiO and/or CoO), followed by drying at 100 °C, calcination at 400 °C, and activation through reduction under 2% H_2/98% argon at 500 °C rather than conventional sulfidation. Catalytic upgrading was performed in batch reactors at 400 °C with an initial H_2 pressure of 3.4 MPa and a water to biocrude ratio of 1:2. Under these conditions, the ternary CoMoW/γ-Al_2O_3 catalyst achieved the lowest oxygen content (6.31 wt.% after 1 h), while the quaternary CoNiMoW/γ-Al_2O_3 catalyst produced oil with the highest heating value (38.7 MJ kg^{-1}), the highest carbon content (78.6 wt.%), and reduced nitrogen (5.1 wt.%) and sulfur (0.18 wt.%) after 4 h. These improvements were attributed to synergistic Mo-W interactions that enhanced HDO and dehydration, significantly reducing organic acids and amides while increasing alkane formation, thereby demonstrating that multimetallic oxide catalysts can maintain strong deoxygenation activity in water rich environments where conventional bimetallic sulfides are often inhibited.

Beyond metal composition, catalyst support properties can also strongly influence upgrading performance. A further example highlighting this effect was reported in a study employing NiMo catalysts dispersed on mesoporous aluminosilicate supports [62]. In that work, NiMo catalysts supported on Al-SBA-15 with tunable Si/Al ratios were applied to the upgrading of *Chlorococcum*-derived biocrude under hydrogen at temperatures between 425 and 500 °C. The incorporation of NiMo significantly improved the production of liquid fractions compared with reactions conducted without catalysts, increasing the total product yield to approximately 65 wt.% and enhancing the formation of kerosene-range hydrocarbons (C12-C17) through hydrogenation and catalytic cracking pathways. Importantly, the catalyst promoted the stabilization of intermediate fragments, thereby inhibiting repolymerization reactions that normally lead to coke formation during thermal upgrading. Nevertheless, the study also demonstrated that the acidity of the Al-SBA-15 support strongly influenced product distribution, as highly acidic supports enhanced cracking and hydrogenation but simultaneously increased coking tendencies. As a result, the upgrading process achieved only partial nitrogen removal, typically reducing the nitrogen content by approximately half of its initial value, indicating that although NiMo-based systems can improve hydrocarbon formation and oil yield, the complete removal of nitrogen-containing heterocycles remains difficult when processing protein-rich algal biocrudes.

Further mechanistic insight into the behavior of Mo-based sulfide catalysts during *Botryococcus braunii*-derived biocrude oil upgrading was provided by Ren et al. [63]. The re-

sults showed that hydrotreated oils were composed predominantly of straight and branched hydrocarbons, representing more than 75% of the detectable product distribution after extended reaction times. Product analysis indicated that HDO was the dominant reaction, as long-chain fatty acids such as oleic acid was converted primarily into paraffinic hydrocarbons including octadecane and heptadecane. However, the study also demonstrated that nitrogen-containing compounds present in algal biocrudes can strongly influence catalyst performance. Amide species derived from proteins were found to compete for adsorption on the active sulfur vacancy sites of the CoMoS catalyst, which are responsible for Brønsted acidity and heteroatom removal reactions. This competitive adsorption limited the extent of hydrodecarboxylation (HDC) and HDN, resulting in residual oxygen and nitrogen species in the upgraded oil even after prolonged hydrotreating. These findings emphasize that although CoMo-based catalysts can effectively promote HDO reactions in lipid-rich algal oils, the presence of nitrogen-containing molecules can inhibit the availability of active sites and therefore reduce the efficiency of simultaneous HDN and HDS reactions.

Given the severe conditions often required for effective heteroatom removal, thermal instability and coke formation become important challenges during upgrading. To address this issue, Haider et al. [42] successfully implemented a two-stage batch hydrotreatment. By first stabilizing the oil at 350 °C to achieve complete deoxygenation before rising to 400 °C, they achieved up to 92.5% denitrogenation with significantly reduced Spirulina coke yields (1.0 wt.%) compared to direct processing at 400 °C (9.1 wt.%). In another related study, the same group explored the influence of reaction severity on heteroatom removal during the hydrotreatment of Spirulina-derived biocrude using a commercial Pre-sulfided $NiMo/Al_2O_3$ catalyst in batch autoclave systems [64]. Their parametric study revealed that while near-complete deoxygenation could be achieved at moderate conditions (350 °C and 8 MPa H_2), denitrogenation remained significantly limited, reaching a maximum of only 48% nitrogen removal. This behavior was attributed to the presence of stable nitrogen-containing structures inherent to algal biocrude, which require more severe hydrogenation conditions to enable C-N bond cleavage. Furthermore, the study demonstrated that increasing reaction severity promotes cracking and hydrocarbon formation, but does not proportionally enhance HDN efficiency, highlighting a fundamental limitation in the upgrading of protein-rich algal feedstocks. A comparison with sewage sludge-derived biocrude showed that, although similar paraffinic hydrocarbon distributions could be obtained, nitrogen removal from algal biocrude remained more challenging, reinforcing the critical role of feedstock composition in determining upgrading performance.

Further evidence of the limitations of conventional sulfided catalysts was reported by Silva et al. [65] who evaluated a CoMo catalyst supported on γ-Al_2O_3 for the upgrading of biocrude derived from wastewater-grown microalgae at 375 °C and 100 bar for 1 h. Although complete sulfur removal was achieved, the oxygen content of the upgraded oil remained relatively high (8.0 wt.% compared with 8.3 wt.% in the raw biocrude), while nitrogen decreased only from 5.5 wt.% to 3.7 wt.%. These results suggest that CoMo catalysts alone may be insufficient to achieve deep deoxygenation and denitrogenation without either more severe reaction conditions or longer residence times. This was done by Da Costa Magalhães et al. [46], who investigated the hydrotreatment of microalgal biocrude using a commercial sulfided NiW/Al_2O_3 catalyst at temperatures between 350 and 400 °C for 5 h in n-heptane solvent. Increasing the reaction temperature to 400 °C enhanced heteroatom removal and reduced the O/C and N/C ratios of the upgraded oil to near-zero values, while simultaneously improving the HHV to 46.4 MJ kg^{-1}. However, the oil yield decreased from approximately 70 wt.% to 58 wt.% as the reaction severity increased, illustrating the typical trade-off between heteroatom removal and liquid yield during catalytic upgrading. In a more recent study, Marangon et al. [1]. investigated one-

step catalytic HTL and upgrading of wastewater algae using NiMo/Al_2O_3 catalysts with loadings between 0 and 20 wt.% and applied response surface methodology to determine optimal operating conditions. Their analysis indicated that a reaction temperature of approximately 324 °C combined with a catalyst loading of about 15 wt.% provided a favorable balance between oil yield and sulfur removal. Nevertheless, the authors noted that the composition of wastewater-derived algal feedstocks can vary substantially depending on cultivation conditions and wastewater sources, which may influence the reproducibility of the predicted optimal parameters during scale-up and consequently affect the balance between product yield and fuel quality.

From a mechanistic standpoint, the performance of sulfided catalysts is closely linked to the structure of the MoS_2 active phase. Despite their high activity, the limitations of sulfided catalysts also include their dependence on the presence of CUS or sulfur vacancies within the MoS_2 structure, where the promoter (Co or Ni) facilitates electron donation to molybdenum to weaken the Mo-S bond [34]. Consequently, significant research efforts have been directed toward improving the efficiency of HDO, HDN, and HDS reactions through the design of promoted Mo-based catalysts [66–69]. In particular, the aforementioned recent studies have focused on understanding how catalyst synthesis methods, support interactions, and promoter incorporation influence the formation of active MoS_2 phases, the distribution of edge sites, and the stability of the catalytic structure under severe hydroprocessing conditions.

The studies discussed above demonstrate that Mo-based transition-metal catalysts promoted with Ni, and to a lesser extent Co, remain among the most widely investigated catalytic systems for algal biocrude upgrading due to their ability to achieve substantial heteroatom removal and improved fuel quality. Their ability to promote HDO, HDN, and HDS reactions has been demonstrated under a wide range of hydrotreating conditions. Nevertheless, the upgrading of algal oils remains particularly demanding due to the high concentration of protein-derived nitrogen compounds and the complex mixture of oxygenated intermediates present in these feedstocks. These species can compete for adsorption on active catalytic sites and may contribute to catalyst deactivation through coke formation or site blocking. As a result, although conventional sulfided catalysts remain effective for heteroatom removal, their performance can vary significantly depending on the reaction environment and feedstock composition. These limitations have motivated the exploration of alternative catalyst formulations and catalytic systems aimed at improving stability, selectivity, and resistance to deactivation during the upgrading of algal biocrudes.

3.2. Transition Metal Carbides (TMCs) and Two-Component Beds

TMCs formed by the incorporation of carbon into the lattices of early transition metals have recently attracted attention as alternative catalytic systems to conventional sulfided NiMo and CoMo catalysts because they exhibit metallic character and a modified electronic structure that enables catalytic properties comparable to those of noble metals, making them highly promising for hydroprocessing applications [25]. Scientifically, the density of states at the Fermi level for TMCs resembles that of platinum-group metals (PGMs), which allows carbides to facilitate hydrogenation, HDO, isomerization and methanation reactions [70]. From an economic and operational perspective, TMCs like molybdenum carbide (Mo_2C) are exceptionally attractive because they are roughly 290 times less expensive than platinum while offering high thermal stability and superior resistance to corrosion in harsh hydrothermal environments [71,72]. In contrast to PGMs, which are often susceptible to deactivation in the presence of sulfur and nitrogen containing species abundant in biocrudes, TMCs exhibit high structural stability, resistance to sulfur poisoning, and reduced tendency toward carbon deposition, enabling sustained catalytic performance

under severe upgrading conditions [73,74]. The development of TMC catalysts for biomass conversion has necessitated advanced synthesis protocols to overcome the limitations of conventional powder metallurgy, which typically yields materials with low specific surface areas [25]. As reviewed by Smith [75], common synthesis techniques such as TPR of metal oxides with light hydrocarbons (e.g., CH_4, C_2H_6) have been refined to produce well-dispersed nanoparticles with diameters between 1 and 5 nm. Further investigations into CHR have shown that Mo precursors undergo a sequential transformation from high valence oxides through intermediate oxycarbide phases (MoOxCy) before forming the stable β-Mo_2C phase, with an optimal treatment temperature of around 650 °C being critical to suppress particle agglomeration and the growth of graphitic filaments, thereby preserving a high density of accessible active sites [76].

For algal specific applications, Masoumi and Dalai [77] developed a synthesis route in which algal-derived hydrochar from *Nannochloropsis* was first activated with KOH to generate a high surface area (631 m^2/g), mesoporous carbon support, followed by co-impregnation with Mo and Ni precursors (~13 wt.% Mo and ~3.5 wt.% Ni), ensuring the formation of highly dispersed synergistic carbide phases. As a result, they reported that the NiMoC/AC system exhibits enhanced accessibility of active sites and improved hydrogen transfer dynamics, which translate into substantial heteroatom removal efficiency, with oxygen content reduced from ~15.3 wt.% in the raw algal biocrude to ~2.6 wt.%, nitrogen to ~3.9 wt.%, and a corresponding increase in HHV to ~42.8 MJ kg^{-1}, reflecting effective simultaneous HDO and partial HDN under relatively moderate hydrogen pressures. Figure 4 schematically illustrates the synthesis route of the NiMoC/AC catalyst from algal-derived hydrochar, including KOH activation of the hydrochar to produce a high-surface-area mesoporous carbon support, co-impregnation of Ni and Mo precursors, oxide-phase formation, and subsequent carbothermal reduction to generate highly dispersed NiMoC and Mo_2C active phases responsible for enhanced hydrodeoxygenation and hydrodenitrogenation performance. In comparison, earlier work by Duan and Savage [78], employing unsupported or less structured Mo_2C systems in SCW over a *Nannochloropsis* sp. paste highlighted that although carbide phases are intrinsically active for HDO, their performance is highly sensitive to catalyst loading and dispersion, with the catalyst type exerting a stronger influence on product composition than operational parameters such as time or temperature. While this study established that the intrinsic activity of Mo_2C phases is a primary driver for product composition, Masoumi and Dalai [77] advanced this by demonstrating that supporting these phases on high surface area, algal derived activated carbon significantly improves site accessibility and hydrogen transfer.

Similarly, Bai et al. [60] reported that Mo_2C-based systems can achieve significant *Chlorella p.* oil oxygen removal resulting in an upgraded oil with a higher heating value (HHV) of 43.3 MJ kg^{-1}. However, their effectiveness is often constrained by limited control over phase composition and surface functionality, particularly in hydrothermal environments where oxidation of active carbide phases or formation of oxycarbides (MoOxCy) can reduce HDO efficiency. They also noted that binary mixtures like Ru/C and Raney-Ni also exhibit superior performance, retaining 86% of the chemical energy of the original oil while achieving a high H/C ratio. These carbides are also capable of processing different biocrude fractions. For instance, Xu and Savage [79] upgraded the water-insoluble portion of *Nannochloropsis* sp. biocrude using Mo_2C, achieving a high carbon content of 80.9 wt.% and a heating value of 40.7 MJ kg^{-1} without the need for external solvents. Scientifically, the activity of these catalysts is often governed by the d-band filling and atomic radius of the metal, where the dissociation of oxygenated intermediates like butanol is identified as a critical rate-determining step [70]. These findings suggest that the future of industrial algal refining will likely involve hybrid catalyst configurations to manage the diverse nitrogen

and oxygen heterocyclic species found in the feedstock. In this context, the controlled formation pathway of Mo_2C in Masoumi and Dalai [77] work via co-impregnation and optimized carbothermal reduction offers a more stable catalytic surface with a higher proportion of active carbide species, thereby mitigating the deactivation pathways observed in earlier studies. Recent scientific advancements have focused on the synergistic potential of two-component catalyst beds to overcome the kinetic barriers of single-metal systems. Xu et al. [80] pioneered the use of a 1:1 mass ratio mixture of Ru/C and Mo_2C in supercritical water, which achieved a record upgraded *C. pyrenoidosa* oil recovery of 77.2 wt.% and reduced the oxygen content to a negligible 0.1 wt.%. This synergistic effect is scientifically vital because the presence of Mo_2C shifts the dominant reaction pathway from hydrogen-intensive HDO toward decarboxylation, where oxygen is removed as CO_2. They concluded that this mechanistic shift conserves expensive external hydrogen while producing an oil where nearly 99% of the material falls within the boiling point distribution of petroleum diesel.

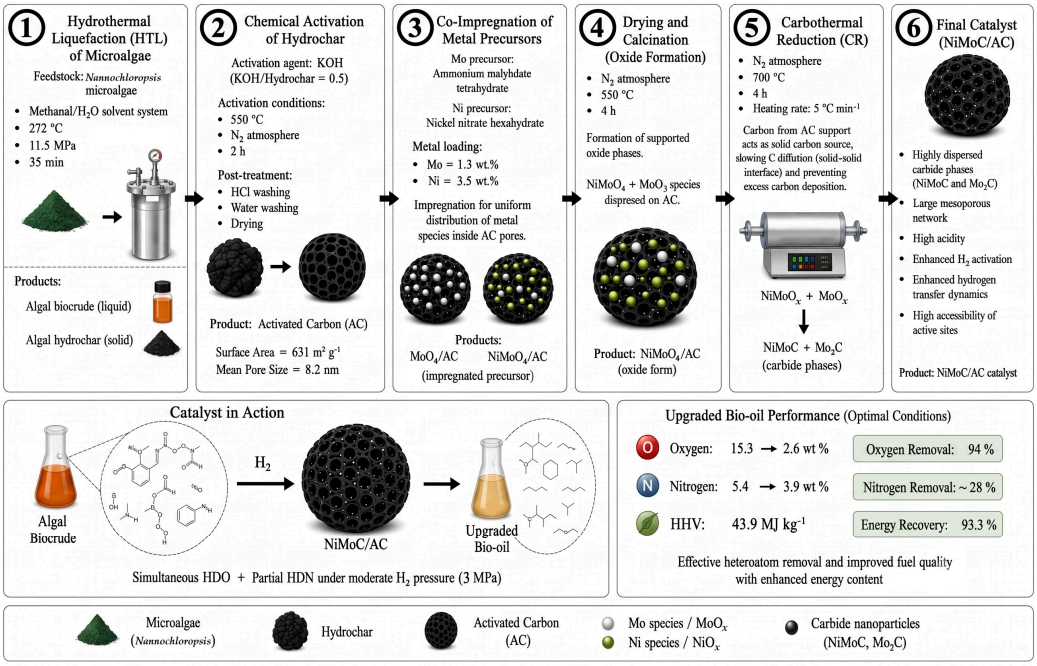

Figure 4. NiMoC/AC Catalyst Synthesis from Algal-Derived Hydrochar for HDO and HDN of Algal Biocrude (created based on the method described in [77]).

The scientific versatility of molybdenum carbide (Mo_2C) is further elucidated through comparisons with non-algal feedstocks based on the molecular architecture of the source material. In a study on duckweed biocrude (Lemna minor), Zhang et al. [81] achieved a robust upgraded oil yield of approximately 71.3 wt.% using Mo_2C, a result that compares favorably to the high yields seen in microalgal studies. However, a scientific divergence was noted regarding heteroatom removal, as they stated that while oxygen was significantly reduced, the nitrogen content in the upgraded duckweed oil rose from 4.7 wt.% to 5.6 wt.%. This suggests that nitrogen removal is considerably more recalcitrant in duckweed than in pretreated algal oils, a phenomenon this study attributed to the high concentration of stable aromatics in duckweed which act as competitive adsorbents and coke precursors, unlike the more aliphatic nature of some microalgal biocrudes. The impact of catalyst design parameters, particularly metal loading, is similarly emphasized in studies of lignocellulosic feedstocks. When upgrading bio-oils derived from corncob and agave bagasse, Ayala-Cortés et al. [82] demonstrated that increasing the Mo concentration on CNFs to 30 wt.% had a transformative effect on product yields, reaching up to 67.4%. This higher Mo density

was found to dramatically suppress secondary gasification reactions, reducing gas yields to as low as 0.5%, thereby conserving carbon within the liquid phase without compromising the quality of the upgraded oil. Furthermore, this study highlighted that while a 10 wt.% Mo loading is sufficient for high deoxygenation (up to 72%), higher loadings are essential for maximizing liquid recovery from phenolic-rich feedstocks like agave, which are prone to yield-reducing polymerization on the catalyst surface.

The stabilization of thermally unstable bio-oils presents another frontier where the acidic properties of Mo_2C are strategically utilized. Wang et al. [83] successfully implemented a two-step process to upgrade acidic bio-oils, leveraging the inherent surface acidity of Mo_2C to catalyze esterification at a mild 180 °C before the high-temperature HDO stage. This pre-stabilization step effectively converted reactive alcohols and organic acids into stable esters, which subsequently allowed for 69% HDO in the second stage while keeping coke formation below 3 wt.%. Besides providing results comparable to expensive noble metal catalysts such as Pd/C, this two-step methodology significantly enhances the processing capacity and lifetime of the carbide catalyst.

All these comparative studies underscore that while Mo_2C is an exceptionally versatile platform for biomass valorization, its success is predicated on tailoring the Mo loading and synthesis parameters to the specific chemical fingerprint of the biocrude. Our assessment suggests that the next generation of algal biorefining plants will most likely adopt these multi-stage strategies and high-loading carbide systems to manage the unique transition from aliphatic nitrogen species (common in algae) to the aromatic recalcitrance seen in other biomass sources. The probability of achieving refinery-grade specifications depends on this fundamental shift toward feedstock-specific catalyst engineering, ensuring that the high energy recovery and thermal stability of carbides are fully exploited across the diverse spectrum of renewable biocrudes. We also expect the next generation of algal upgrading will utilize heteroatom-doped carbides (e.g., Zr- or Nb-doped Mo_2C), which have been theoretically modeled to lower activation barriers for C-OH cleavage to as little as 0.58 eV, as reported in the study by Meena et al. [70], potentially allowing for deep denitrogenation at much milder temperatures than currently possible.

3.3. Noble/Precious Metal Catalysts for Algal Biocrude Upgrading

Noble metals—mainly Pt, Pd, and Ru—have received attention because they are highly active for hydrogenation and heteroatom removal under hydrothermal or hydrotreating conditions. More recent catalyst reviews still treat noble metals as benchmark materials for biocrude HDO, while also noting their economic penalty and sensitivity to deactivation [43].

Compared with many base-metal or acidic catalysts, noble metals typically offer three advantages in algal biocrude upgrading:

i. Strong hydrogenation activity, which helps saturate unsaturated compounds and stabilize reactive intermediates.
ii. Better heteroatom removal, especially oxygen and, to a lesser extent, nitrogen.
iii. Higher-quality upgraded oils, often with improved flow behaviour, lower acidity, and higher heating value.

This is especially important for algae-derived biocrude because algae are rich in proteins and lipids. Protein-derived HTL oils tend to carry substantial nitrogen-containing compounds, making HDN particularly challenging. Review literature emphasizes that nitrogen removal remains harder than oxygen removal even when noble metals are used [31].

The pioneering work of Duan and Savage showed that HTL *Nannochloropsis* sp. biocrude could be upgraded in supercritical water (SCW) using Pt/C with high-pressure hydrogen. Their work reported that SCW treatment already improved oil quality but adding Pt/C produced a more freely flowing oil with a higher abundance of hydrocarbons

and a higher heating value around 42 MJ kg^{-1}. The upgraded product also had lower fatty acids, O and N contents and was essentially sulfur-free. This study helped establish Pt/C as an early benchmark for catalytic upgrading of algae HTL biocrude and is important for two reasons. First, it showed that water itself can serve as an upgrading medium, creating conceptual compatibility with HTL. Second, it demonstrated that noble metals can do more than crack or reform molecules: they can also improve fuel-like handling properties, which is critical for downstream refining and blending [20].

Further studies have found that even in the absence of hydrogen, Pt/C can decarboxylate most of the lipids in *Chlorella* after 120 min at both 330 and 370 °C [84]. In another study Duan and Savage [85] reported the catalytic hydrotreatment of crude bio-oil, produced from the hydrothermal liquefaction of a microalga (*Nannochloropsis* sp.) over palladium on carbon (5% Pd/C) in SCW at 400 °C. Similarly, the Pd/C catalyst was found to be effective for improving biocrude oil properties. It was shown that longer reaction times and high catalyst loadings increased the H/C ratio of the upgraded oil while simultaneously decreasing the O/C and N/C ratios. Same authors also studied hydrothermal catalytic denitrogenation of pyridine between 250 and 400 °C. They found that Pt/γ-Al_2O_3 has the highest catalytic activity when compared to Pt/C, Pd/C, Ru/C, Rh/C, sulfided Pt/C, PtO_2, Mo_2C, MoS_2 and sulfided CoMo/γ-Al_2O_3 (a traditional HDN catalyst) [86].

Duan et al. reported the catalytic upgrading of crude oil, produced from the HTL of *Chlorella pyrenoidosa* over Pt/γ-Al_2O_3 in SCW. They determined the influence of catalyst loading, water density, and formic acid loading on the product yields and properties of the treated oil. Pt/C-Al_2O_3 showed good upgrading performance and increasing the catalyst loading produced a lower yield but higher quality treated oil. The highest HDO activity obtained with 40% catalyst loading [87].

Later catalyst screening studies were broadened to include algal HTL bio-crude [70]. Specifically, the catalytic activities of 5% Pt/C, 5% Pd/C, 5% Ru/C, sulfided 5% Pt/C, Mo_2C, MoS_2, alumina, sulfided CoMo/γ-Al_2O_3, Ni/SiO_2-Al_2O_3, HZSM-5, activated carbon, and Raney-Ni were evaluated for the hydrothermal HDO and HDN of pretreated algal oil produced from the HTL of *Chlorella pyrenoidosa*. Among these, Ru/C demonstrated the best performance for deoxygenation, yielding the highest hydrocarbon content and the highest HHV, whereas Raney-Ni was the most effective catalyst for denitrogenation. Consequently, a mixture of Ru/C and Raney-Ni catalyst yielded excellent results in both deoxygenation and denitrogenation of biocrude, achieving higher yields (77.2 wt.%) alongside lower gas and coke formation. These findings imply that upgrading utilizing multicomponent catalyst mixtures could be highly effective for the upgrading of algal crude bio-oil in SCW.

In their subsequent work, Xu et al. [80] conducted a research study to investigate the activity of various potential two-component catalyst mixtures for improving pre-treated algal oil in supercritical water. According to their results, two-component catalyst blends are a promising strategy for improving pre-treated algal oil in supercritical water. These catalyst blends not only produce improved oil with high yield and quality but also control coke formation under hydrothermal conditions. Among the catalyst blends tested, Ru/C + Mo_2C produced improved oil with the highest oil yield and energy recovery.

Another representative example for catalyst screening studies is Shakya et al. [88], who upgraded *Nannochloropsis*-derived HTL bio-oil using Ni/C, ZSM-5, Ni/ZSM-5, Ru/C, and Pt/C at 300 and 350 °C. Their results are particularly useful for literature synthesis because they show the classic trade-off between oil yield and oil quality. Ni/C gave the maximum upgraded bio-oil yield at 350 °C, but the best-quality oils came from the noble metal catalysts Ru/C and Pt/C, which produced lower acidity, higher heating values, and better nitrogen reduction. The upgraded oils reached 40–44 MJ kg^{-1}, and the nitrogen content dropped from 5.37 wt.% to as low as 1.29 wt.% under the best conditions.

As seen in algal upgrading studies in the literature, base metals may preserve or increase liquid yield, but noble metals usually deliver better deoxygenation/hydrogenation quality. For practical fuel production, that distinction matters because a high gross oil yield is less valuable if the oil still fails fuel-property or refinery-compatibility targets.

3.3.1. Effect of the Support: Carbon vs. Alumina and Related Systems

The active metal is a major part of the catalyst; however, support choice of the upgrading catalyst strongly affects dispersion, acidity, water tolerance, coke formation, and reaction selectivity. The literature on algal biocrude upgrading commonly uses carbon and γ-Al_2O_3 supports noble metals.

In a study by Patel et al. [21], commercially available Pt, Pd, and Ru supported on carbon and alumina, as well as NiMo/Al_2O_3, were investigated for hydro-treating algal bio-crude. The study reported upgraded biocrude yields above 60 wt.%, with the highest yield and HDN activity obtained using NiMo/Al_2O_3. However, it was observed that precious metals had higher oxygen removal activities and carbon weight percentages, which ultimately improved the overall oil quality. The same literature also states that alumina-supported Pt and Ru can perform better than their carbon-supported counterparts in some HDO reactions due to the beneficial acidity and metal-support interactions provided by the support material. Some results also show that the use of activated carbon as a supporting material contributes to the exceptional HDN properties of platinum metal sulfides [89].

This point is important for interpreting catalyst data: when a paper says, "Pt is better than Pd" or "Ru is better than Pt," the result may depend on support acidity, pore structure, water tolerance, and metal dispersion, not only on the identity of the noble metal itself. Recent HDO reviews explicitly stress that the best performance comes from balancing metal functionality and acid functionality [43].

3.3.2. Noble Metals for Water-Insoluble vs. Water-Soluble Fractions Upgrading

A useful refinement in the literature is the distinction between water-insoluble biocrude and water-soluble biocrude recovered from the HTL aqueous phase. These fractions behave differently during upgrading.

In a study conducted by Xu et al. [79], SCW upgrading was studied for both fractions from *Nannochloropsis*. For the water-insoluble biocrude, Pt/C gave the best performance among the tested catalysts, reaching 80.9 wt.% carbon, 10.6 wt.% hydrogen, a heating value of 41.6 MJ kg^{-1}, and lower N, S, and O contents than the alternatives. For the water-soluble fraction, upgrading also improved quality significantly, but the product remained more oxygenated and nitrogenous than the insoluble fraction.

This has a practical implication for catalyst development: a catalyst that performs well on the main oil phase may not be optimal for the more polar, heteroatom-rich soluble fraction. In other words, fraction-specific upgrading strategies may be better than a single universal catalyst.

The water-soluble fraction is often overlooked, but it may contain significant amounts of recoverable organic matter. He et al. explored catalytic upgrading of the water-soluble biocrude from Chlorella using Pt/C, Pd/C, Ru/C, Pt/C + Pd/C, and a multi-metallic non-noble catalyst. Even from the abstract-level source, this study is valuable because it shows that noble metals were still the reference catalysts for upgrading this chemically difficult fraction [90].

The broader lesson from this literature is that noble metals are not only useful for the heavy oil phase; they are also promising for the more reactive and polar aqueous-extract fraction, where their hydrogenation ability can stabilize intermediates and suppresses re-polymerization. That said, the economic case for applying Pt/Pd/Ru to dilute, highly

polar fractions are not yet fully convincing and remains an open techno-economic question. This last point is an inference based on catalyst cost and the more refractory chemistry of the water-soluble fraction.

3.3.3. Denitrogenation of Algae HTL Bio-Crude

Across the literature, nitrogen removal is consistently more difficult than oxygen removal for algae-derived biocrude. This is a central issue because algae contain substantial protein, and HTL converts protein into persistent amides, nitriles, indoles, pyridines, pyrroles, and other N-heterocycles. Even when noble metals improve overall product quality, the final nitrogen content often remains above the threshold desirable for refinery-compatible fuels.

The pyridine HDN activity of carbon-supported sulfides of Ru, Rh, Pd, Ir, and Pt were evaluated and compared with commercial NiMo/alumina and CoMo/alumina catalysts by Vit and Zdrazil [89]. The carbon-supported sulfides of platinum metals performed significantly better in HDN than the commercial bimetallic counterparts. The results demonstrated that while the selectivity of the Rh, Ru, and Pd catalysts was similar to those of the CoMo and NiMo systems, the Ir and Pt catalysts were highly selective for HDN. The denitrogenation review by Sun et al. [31] summarizes this problem well. It reports that Duan and Savage achieved high upgraded yields with Pt/C, but the upgraded biocrude still retained notable nitrogen. The same review points to studies where even more severe conditions or mixed catalysts still did not reduce nitrogen to truly fuel-grade levels.

This is why the following are increasingly discussed in the literature:

- two-stage upgrading,
- pretreatment or fractionation,
- multimetallic catalysts, and,
- coupling noble metals with acidic or oxygen-storage supports to improve HDN without excessive cracking or coke formation.

Among the noble metals, Ru is often highlighted as especially effective in hydrogenation/HDO under hydrothermal conditions. Although Pt is the most commonly used benchmark in early algal studies, later literature often treats Ru/C as a very strong competitor, sometimes superior depending on the feed and operating conditions. In the Shakya study, Ru/C and Pt/C were the best performers in product quality. Broader reviews of hydrothermal and bio-oil upgrading also repeatedly identify Ru, Pd, and Pt as the noble metals most frequently chosen for supercritical-fluid upgrading [74].

Ruthenium's advantage usually comes from strong hydrogenation activity and relatively good performance in deoxygenation, but it still cannot completely solve the full nitrogen problem on its own. In practice, Ru often appears most attractive when combined with a support or promoter that adds acidity or improves oxygen-storage/redox behavior.

3.3.4. Bimetallic and Promoted Noble Metal Catalyst Systems

The literature has gradually shifted from single-metal noble catalysts toward bimetallic or promoted systems. One example is Ni-Ru/CeO_2, reported by Xu et al. for catalytic hydrothermal upgrading of water-insoluble algal biocrude. Ni/CeO_2 catalyst was mixed with Ru as a promoter at a rate of 10% by weight, and the resulting Ni-Ru/CeO_2 catalyst was found to exhibit high HDS activity. Another direction is γ-Al_2O_3-supported multimetallic catalysts. The working principle of bimetallic catalysts can be explained as follows: noble metals provide excellent hydrogenation, while the second metal or support can improve C-O/C-N bond cleavage, suppress coke, or reduce cost per unit activity [27].

Recent general HDO reviews reinforce this trend by emphasizing that future catalyst design should focus on tuning the balance between metal sites and acid sites, not simply

increasing noble metal loading [43]. This is especially relevant for algae biocrude because excessive acidity can increase cracking and gas formation, while insufficient acidity can limit deep heteroatom removal.

3.3.5. Deactivation

Catalyst deactivation presents a significant challenge in the conversion of microalgae oil to biofuel production. Deactivation occurs when active sites on the catalyst are blocked, particularly due to coking.

The loss of active sites can result from:

- chemical poisoning by impurities such as sulfur and halogens,
- loss of active components through metal dissolution or migration,
- Structural distortion of the carrier due to phase transitions,
- Sintering of catalyst particles.

Various methods have been proposed to reduce deactivation, including raw material pre-treatment, design of stable carriers, and improvement of core–shell structures.

The deactivation rates of noble metals 1% Pt/Al_2O_3, 0.5% Rh/Al_2O_3 and sulfided $NiMo/Al_2O_3$ catalysts in the HDO of microalgae oil, were investigated by Zhou et al. They concluded that coke accumulation decreased in the order of sulfided NiMo > Pt > Rh. Additionally, coke formation on sulfided NiMo catalysts increased with time on stream, whereas no such time dependence was observed for Rh and Pt based catalyst. The highest hydrocarbon yield, 76.5%, was obtained over 1% Pt/Al_2O_3 catalyst which is 13.8% higher than that over NiMo catalyst [91].

3.3.6. Main Limitations of Noble-Metal Catalysts

Despite their strong catalytic performance, noble metal catalysts face several limitations:

- High cost. Pt, Pd, and Ru are expensive, which challenges scale-up for a low-margin fuel application.
- Deactivation. Algal biocrude contains heavy molecules, ash-derived impurities, sulfur, nitrogen compounds, and coke precursors. These can poison or foul catalyst surfaces. Recent reviews of biocrude HDO still list deactivation as a central barrier [43].
- Incomplete nitrogen removal. Even strong noble metal catalysts often leave residual N above desirable levels for transportation fuels.
- Hydrogen demand. Hydrotreating quality improves with hydrogen availability, but hydrogen supply adds cost and process complexity. Early Pt/C studies already showed the importance of high-pressure hydrogen.
- Feed variability. Catalyst behaviour is species-dependent and feed-dependent. The 2016 state-of-the-art review specifically noted species dependence in heterogeneous catalytic upgrading [34]

3.3.7. Future Research Direction and Outlook

The literature suggests that noble metals will likely remain benchmark catalysts for algal biocrude upgrading, but not necessarily the final commercial solution. Current work is moving towards:

- hybrid or bimetallic catalysts to reduce noble-metal loading,
- support design to improve activity and stability,
- fraction-specific upgrading for insoluble vs. soluble biocrude,
- two-stage processes to separate stabilization from deep deoxygenation/denitrogenation,
- integration with techno-economic and life-cycle analysis so that catalyst choice is judged not only by oil quality but also by hydrogen use, durability, and cost.

Overall, the literature supports a clear conclusion: Pt-, Pd-, and Ru-based catalysts are among the most effective materials for upgrading algal biocrude quality, especially for hydrogenation and deoxygenation, but persistent nitrogen removal, catalyst cost, and deactivation remain the key barriers to commercial deployment.

3.4. Bifunctional Catalysts for Algal Biocrude Upgrading

Within this field, bifunctional catalysts are especially important because they combine two catalytic functions in one material or catalyst pair. In practice, this usually means a metal function for hydrogenation/HDO/HDN and an acidic support function for cracking, isomerization, cyclization or aromatization. The reason these catalysts attract attention is that algal biocrude is chemically complex: nitrogen-containing compounds often need hydrogenation to become removable, while heavy oxygenates need cracking and deoxygenation at the same time. A single-function catalyst often cannot do both efficiently [88].

Bifunctional catalysts are particularly important for algae biocrude because microalgal HTL oils are often more nitrogen-rich than lignocellulosic bio-oils due to the protein content of algae. Nitrogen removal is notoriously difficult and usually demands severe hydrotreating conditions, including elevated temperature and hydrogen pressure. Severe conditions, however, also promote polymerization, condensation, coking, and catalyst deactivation. A bifunctional catalyst can reduce some of these drawbacks by combining hydrogenation capacity with controlled cracking and structural rearrangement, thereby improving the conversion of compounds without depending on harsher operating conditions [42].

This is a reason why two-stage upgrading has emerged as a rational process design. First, a milder stabilization stage suppresses the thermal instability of raw biocrude and removes the most reactive coke precursors, while a second, more severe stage performs deeper deoxygenation, denitrogenation, and hydrocarbon tailoring. The literature on highly nitrogenous HTL biocrudes reports that two-stage processing can enable very high heteroatom removal and may be the only practically viable route to drop-in fuel quality for some algae-derived feeds. In this broader process architecture, bifunctional catalysts can be especially valuable in the second stage, once the feed has been partially stabilized, and the catalyst is less exposed to the most aggressive deactivation pathways [42].

A bifunctional catalyst contains at least two different classes of active sites that cooperate during upgrading. In the context of biocrude hydrotreatment and hydrocracking, these are usually:

- Metal sites; responsible for hydrogen activation and hydrogenation/hydrogenolysis reactions.
- Acid sites; responsible for cracking, isomerization, dehydration, cyclization, and related carbocation-mediated transformations.

This dual functionality is especially valuable for HTL biocrudes because the feed contains both heteroatom-rich molecules that require hydrogen-assisted removal and heavy oxygenated/nitrogenous compounds that benefit from skeletal rearrangement or controlled cracking [39].

Mechanistically, the metal function first dissociates molecular hydrogen into reactive surface hydrogen species. These hydrogen atoms participate in saturation of unsaturated bonds, cleavage of C-O bonds, and HDO/HDN pathways. The acid function then converts partially hydrogenated intermediates through protonation-driven chemistry, including C-C bond scission and isomerization. In a well-designed bifunctional system, these two roles are coupled rather than independent: the metal sites stabilize reactive fragments generated on the acid sites, while the acid sites reduce the molecular weight and alter the structure of compounds that are difficult to upgrade by metal hydrogenation alone [92].

Bifunctional catalysts combine metallic hydrogenation sites with acidic supports such as transition metals on acidic oxides and noble metals on zeolites. These catalysts enable simultaneous hydrogenation and cracking but require careful balance to avoid excessive coke formation. Examples include Pt/HZSM-5, Pd/HZSM-5, Ni/HZSM-5, Pt/zeolite Y, NiO/SAPO-34, and more recently carbide- or phosphide-containing zeolitic systems. Zeolites are particularly attractive because their acidity can drive deoxygenation-related cracking and aromatization pathways, while their pore architecture can help shape selectivity. ZSM-5 is especially significant due to its tunable Si/Al ratio, adjustable acidity, and strong performance in deoxygenation, decarboxylation, and decarbonylation chemistry [39,93,94].

NiMo catalysts supported on acidic oxides (ZrO_2, TiO_2, Al-SBA-15, zeolite, etc.) are highly effective for upgrading bio-crude via HDO, reducing oxygen content while enhancing stability. They facilitate HDO by promoting C-O bond scission through Lewis's acid sites while maintaining hydrogenation capacity, with optimal performance achieved around 300–400 °C.

A useful example is the work on Ni/ZSM-5 for upgrading biocrude from *Nannochloropsis* HTL. In that study, Ni/ZSM-5 was chosen explicitly as a bifunctional catalyst to combine nickel hydrogenation activity with ZSM-5 cracking activity. The authors found that catalytic upgrading at 350 °C gave better-quality oils than at 300 °C, while Ni/C gave the highest upgraded oil yield and Ru/C and Pt/C gave better fuel quality. The study also reported substantial reductions in nitrogen content and total acid number, showing that bifunctional catalysts are promising but still compete with noble-metal systems in overall upgrading performance [88].

In a study by Peng et al. [95], Hβ zeolites were used as supports, and a bifunctional Ni/Hβ catalyst was obtained by impregnating Ni active sites into these supports. This catalyst, which showed exceptional activity in the HDO (hydrogenation and oxidation) of microalgal oil, specifically catalyzed the hydrogenolysis of fatty acid esters, the decarbonylation of aldehyde intermediates, and the hydrogenation of C=C bonds at its Ni centers. Simultaneously, the acidic sites of the Hβ zeolite facilitated the dehydration of alcohol intermediates, as well as the hydro isomerization and hydrocracking of alkanes.

Song et al. prepared bifunctional Ni/Hβ catalysts using four synthesis routes: impregnation, ion exchange/precipitation, DP, and a pre-synthesized Ni nanoparticle (Ni NP) grafting approach. The ion exchange/precipitation, DP, and Ni NP methods produced smaller and more uniformly distributed Ni particles (2–4 nm) than conventional impregnation (25 nm), resulting in significantly higher hydrodeoxygenation activity and improved catalyst stability during the deoxygenation of stearic acid and crude microalgal oil. In contrast, the impregnated Ni/Hβ catalyst exhibited the lowest activity but showed relatively higher selectivity toward *n*- and iso-C_{18} hydrocarbons because its higher Brønsted acidity promoted dehydration and isomerization reactions. The lower Brønsted acid site concentration observed for catalysts prepared by the ion exchange/precipitation and DP routes suppressed dehydration and isomerization pathways, thereby altering product selectivity [96].

Another important work looks at in situ or one-pot bifunctional upgrading during HTL, rather than only post-treatment of already produced biocrude. For example, bifunctional Ni/HZSM-5 systems have been used during HTL to improve product quality directly in the liquefaction step. Likewise, Wang et al. investigated the performance of five bifunctional catalysts (NiO/SAPO-34, NiO/ZSM-5, NiO/USY, NiO/γ-Al_2O_3, and NiO/SiO_2) for the HTL of *Spirulina* to produce high quality biofuel. Their findings demonstrated that the catalyst's structure, acidity, and pore architecture significantly affect both the yield and quality of the biocrude [97]. This supports a broader conclusion in the literature: metal–acid balance is one of the central design variables for algal upgrading catalysts. Too

little acidity limits cracking and deoxygenation pathways, while too much acidity increases coke formation and catalyst deactivation.

Peng and colleagues used ZrO_2-supported Ni catalysts to convert microalgal crude oil into diesel alkanes. The Ni-based catalyst enabled the hydrolysis of fatty acid lipids into fatty acids and the hydrogenation of these fatty acids to aldehydes via two parallel pathways. The synergistic interaction between Ni and ZrO_2 resulted in the formation of carboxylates through the adsorption of carboxyl groups into the oxygen vacancies of ZrO_2. Optimal catalytic performance was achieved under mild conditions (260 °C, 4 MPa H_2) with a 15% weight Ni loading, resulting in 100% selectivity for stearic acid conversion and 96% selectivity for C17 hydrocarbons [98].

The literature also shows that bimetallic and modified mesoporous catalysts can improve upgrading selectivity. For instance, Ni-Cu/ZrO_2 has been reported as an effective HDO catalyst for *Chlorella* and *Nannochloropsis* sp. algae bio-oils, with catalytic performance depending strongly on the Ni/Cu ratio. The highest performance was achieved using the 15.71Ni6.29Cu/ZrO_2 catalyst. Furthermore, it was observed that the HDO activity of the Ni-Cu/ZrO_2 catalyst was higher than that of the commercial S-Ni-Mo/Al_2O_3 catalyst and it also showed higher stability over 24 h periods [99].

A novel route was proposed by Li and coworker for microalgae biofuel production by catalytic upgrading of *Chlorella* HTL biocrude. Modified SBA-15-based catalysts such as CuO/Al-SBA-15, ZnO/Al-SBA-15, and CuO-ZnO/Al-SBA-15 have also been explored for hydrogen-free or low-hydrogen upgrading routes, where mesoporosity helps accommodate bulky biocrude molecules and the metal/acid combination promotes decarboxylation and hydrocarbon formation. The hydrocarbon yield was increased from 25.1 wt.% (thermal) to 65.7 wt.% on the CuO/Al-SBA-15. These studies suggest that bifunctionality is not limited to zeolites; it can also be engineered in mesoporous supports to reduce diffusion limitations [100].

A similar study was conducted by Dirgarini and colleagues [95]. They reported that biocrude obtained from *Chlorococcum* sp. algae was hydrotreated with Al-SBA-15 supports and NiMo/Al-SBA-15 catalysts having different Si/Al ratios and consequently different acidities. It was observed that the nitrogen content of biocrude was reduced by approximately half in all reactions, regardless of temperature, H_2 pressure, or the presence of a support/catalyst. Product aromaticity increased with reaction temperature. The presence of supports, especially those with lower acidity, reduced product yield due to severe coking. The addition of NiMo had a pressure-dependent effect on product yield. In reactions carried out at 425 °C, NiMo more than compensated for the coking effect of the support, increasing product yield by up to 65% and the proportion of liquid products in the kerosene boiling point range (C12–C17). Supports with higher acidity provided higher product yields, and this superiority was maintained when NiMo was added as metal phase [62,101].

Bifunctional heterogeneous SO_3H/SBA-15-NH_2 catalysts were synthesized and tested for microalgae (*Chlorella*) hydrothermal liquefaction and ex situ upgrading by Yu et al. [102]. The optimum catalyst, SO_3H-SBA-15-NH_2, was prepared by grafting -SO_3H and -NH_2 groups onto the clin/SBA-15 surface. The results showed that bifunctional catalyst increased the hydrocarbon yield by up to 68.34% and enabled the deoxygenation of bio-oil. High acid strength and a large number of acid and base sites improved the activity of Chlorella to fuel conversion under subcritical water.

A recent study was performed to investigate the catalytic activity of bimetallic nickel-zirconia catalysts supported on different support (zeolite BEA, zeolite ZSM-5 and Al_2O_3) in the hydrocracking reaction of spirulina platensis algal oil. The results showed that bimetallic Ni-Zr catalyst supported on zeolites exhibited high conversion of algal oil

and the highest conversion and selectivity towards the gasoil fraction were noted for bifunctional 5%Ni-5%Zr/BEA zeolite catalyst having the highest specific surface area, pore volume and average pore radius. Alumina supported Ni-Zr catalyst showed the highest selectivity towards gasoline and kerosene and the smallest selectivity towards gasoil compared with the catalysts supported on zeolites. This result indicates that support acidity is an important factor influencing the type of product formed during algal oil hydrocracking. Taken together, the literature suggests that the most promising bifunctional systems are those that carefully tune metal dispersion, acid strength, pore accessibility, hydrogen availability, and resistance to coking [103].

New work has also broadened the definition of bifunctionality beyond classical noble-metal/zeolite systems. For example, a recent study on HTL biocrude upgrading to sustainable aviation fuel reported high activity for Fe-Mo_2C/ZSM-5 nano catalysts, where the carbide-based hydrogenation/deoxygenation function was combined with the acidic zeolite framework. In that work, the catalyst improved oil H/C ratio and strongly reduced oxygen content relative to non-catalytic upgrading, illustrating how non-noble metal or carbide phases can be integrated with acidic supports to deliver bifunctional behavior at lower precious-metal dependence [104].

From a catalyst design standpoint, the support is not merely an inert carrier. The review by Duan et al. [91] emphasizes that support surface area, pore volume, and pore structure strongly influence catalytic performance, while zeolitic aluminosilicates are often preferred because oxide supports alone may provide acidity that is either too weak or difficult to tune precisely. Thus, the performance of a bifunctional catalyst depends not only on the identity of the metal but also on the balance, proximity, and accessibility of its metal and acid sites.

A major challenge in algal biocrude upgrading is nitrogen removal, because algal feedstocks are protein-rich and generate pyridines, indoles, pyrroles, amides, and nitriles. Zhao and co-workers addressed this in two influential studies. One reported two-stage upgrading of hydrothermal algae biocrude to kerosene-range biofuel, showing strong improvement in kerosene-range hydrocarbons after staged treatment. A follow-up study on low-nitrogen-containing biofuel analyzed compositions, intermediates, and reaction routes, highlighting how staged or guarded catalyst systems can improve denitrogenation performance. This is a critical point for bifunctional catalyst design: for algal biocrudes, HDN is often more difficult than HDO, so catalysts must be designed for both heteroatom chemistry and resistance to poisoning [105,106].

3.5. Acidic and Zeolitic Catalysts

Zeolites are scientifically distinguished as three-dimensional, microporous aluminosilicate materials characterized by exceptionally high surface areas and robust adsorption capacities [34,107]. Their catalytic efficacy in algal biocrude upgrading is primarily derived from their inherent Brønsted and Lewis acid sites, which facilitate complex reaction networks including cracking, dehydration, decarboxylation, and aromatization via a carbonium ion mechanism [39,108].

Within the broader context of upgrading catalysts, zeolites offer a distinctive advantage over transition metal sulfides by maintaining catalytic activity even in the absence of external hydrogen, although their performance can be further enhanced under reducing atmospheres to promote saturation reactions [108]. Lang et al. [109] further emphasized that zeolites combine industrial robustness with functional versatility, demonstrating resilience under harsh operating conditions while enabling efficient CO_2 management through predominantly physical adsorption mechanisms that reduce regeneration energy requirements. Moreover, their inherently fast adsorption kinetics and tunable microporous structures

allow for enhanced CO_2 selectivity via controlled framework modification, highlighting their adaptability for process-specific optimization. However, the same microporous structure that provides selectivity also promotes rapid coking and pore blockage, as bulky oxygenated and nitrogen-containing compounds in algal biocrude accumulate within the pores and limit access to active sites.

The fundamental performance of zeolites as standalone catalysts in the upgrading of algal oil has been widely demonstrated, particularly in their ability to drive substantial shifts in product composition and fuel quality. For instance, Li and Savage [108] investigated the upgrading of *Nannochloropsis*-derived biocrude over HZSM-5 (calcined at 550 °C for 4 h to obtain the protonic form) under water-free conditions. Their results revealed a strong temperature-dependent selectivity: operation at 400 °C produced a paraffinic oil (95 wt.% C and H) with a high heating value of 43.4 MJ kg^{-1}, whereas increasing the temperature to 500 °C shifted the product toward a freely flowing aromatic-rich liquid dominated by benzenes and naphthalenes. This behavior indicates that lower reaction temperatures favor the formation of diesel-range aliphatic hydrocarbons, while higher temperatures enhance the intrinsic aromatization functionality of the zeolite, highlighting its versatility as a platform for both fuel-oriented upgrading and the production of valuable chemical feedstocks. The performance of zeolites in algal oil upgrading is strongly influenced by both the biochemical composition of the feedstock and the reactor configuration. Barreiro et al. [34] demonstrated this clearly by comparing *Scenedesmus almeriensis* and *Nannochloropsis gaditana* biocrudes over HZSM-5 at 400 °C. Under dry conditions, the catalyst delivered an upgraded oil yield of 61.7 wt.% for *S. almeriensis*, comparable to Pt/Al_2O_3, whereas the yield for *N. gaditana* dropped to 50.4 wt.%, indicating a pronounced sensitivity to feedstock composition. The introduction of water further altered the reaction pathway: for *S. almeriensis*, the oil yield decreased sharply to 42.3 wt.%, accompanied by increased solid residue formation (17.2 wt.%) and significant mass losses, suggesting that water enhances contact between reactive intermediates and acid sites, thereby accelerating polymerization and coke formation. Despite these limitations, zeolites remain highly effective in improving oil quality through deoxygenation and selective cracking. In the wet upgrading of *S. almeriensis*, HZSM-5 achieved a remarkably low O/C ratio of 0.012, producing upgraded oils with heating values approaching 41–43 MJ kg^{-1}, comparable to petroleum diesel. However, nitrogen removal was less efficient and remained dependent on the feedstock; for *N. gaditana*, the nitrogen content decreased only from 4.8 wt.% to around 2.4–2.5 wt.%, showing limited improvement over non-catalytic conditions. Building on this limitation, further insight into nitrogen removal over zeolitic systems is provided by Hosseinpour et al. [110], who showed that the H/C ratio of upgraded bio-oil—an indicator of aromatization—follows a temperature-dependent trend, confirming that in the presence of H^+ZSM-5 higher temperatures favor aromatization over cracking, thereby enhancing molecular stability but making HDN more difficult. A key aspect of this behavior lies in both catalyst design and reaction environment. In this study, nano-sized H^+ZSM-5 was synthesized via a SCW route using a controlled precursor system, followed by an aging step (80 °C) and rapid crystallization (450 °C), then converted to the protonic form through NH_4^+ exchange and calcination. This approach yields highly dispersed crystals with increased surface area and acidity, improving active site accessibility compared to conventional zeolites. In parallel, the use of formic acid as an in situ hydrogen donor generates reactive hydrogen species that stabilize intermediates and suppress excessive condensation, partially mitigating coke formation. Within this framework, the upgrading performance reflects a balance between competing conditions: moderate temperatures (~400 °C) provide sufficient hydrogen availability and reaction activity, whereas lower temperatures limit

conversion and higher temperatures shift the system toward aromatization, consuming transferable hydrogen and reducing the effectiveness of nitrogen removal.

Extending this discussion, the limitations associated with purely microporous zeolites have prompted comparative evaluations of alternative frameworks with improved mass transport properties. In a comprehensive screening of nine zeolites, including Hβ, HZSM-5 (in three formulations), HY (in two formulations), MCM-41 (in two formulations), and SAPO-11, Duan et al. [111] reported that MCM-41 (100%Si) delivered the highest upgraded oil yield (54.5 wt.%) and hydrocarbon content (82.5%) for *Chlorella* biocrude. This superior performance was attributed to its mesoporous structure, which alleviates diffusion constraints and reduces coke accumulation compared to microporous systems such as HZSM-5, where pore dimensions are comparable to the size of coke precursors. These results explain that although microporous zeolites are superior in selectivity and aromatization, their restricted pore networks limit accessibility and accelerate deactivation. In contrast, mesoporous materials such as MCM-41 and SAPO-11 offer improved molecular transport and resistance to pore blockage, albeit sometimes at the expense of acidity. Several studies have addressed this trade-off, highlighting the growing importance of hierarchical (micro-mesoporous) catalyst design [112–115]. Figure 5, which aims to integrate strong acidity with enhanced diffusion pathways to simultaneously achieve high carbon recovery and effective heteroatom removal.

Figure 5. The combination between microporous zeolites and mesoporous materials for the formation of hierarchical zeolites.

Building on the limitations of purely acidic zeolites, introducing metal functionality has proven effective in improving upgrading performance. In this context, Shakia et al. [88] examined Ni-modified HZSM-5 for algal biocrude upgrading under hydrotreating conditions (300–350 °C, 69 bar H_2, 10 h, WHSV 0.51 g bio-oil gcat^{-1}·h^{-1}). The parent HZSM-5 delivered higher liquid yields (up to 74.69 wt.% at 300 °C), consistent with its strong cracking and aromatization behavior, but showed limited nitrogen removal (from 5.37 to 3.40 wt.%). In contrast, Ni/HZSM-5 significantly improved heteroatom removal, reducing nitrogen to 1.81 wt.% at 300 °C and reaching its best performance at higher temperature. A similar trend was observed for oxygen removal: while HZSM-5 tended to retain phenolic compounds, the Ni-modified catalyst facilitated more effective deoxygenation through combined hydrogenation and acid-catalyzed pathways. This difference reflects the contribution of metal–acid interactions, where Ni sites promote hydrogen activation and stabilize intermediates, while the zeolitic framework maintains cracking activity. Although both catalysts achieved comparable heating values (~40–43 MJ kg^{-1}), Ni/HZSM-5 produced oils with lower acidity and reduced heteroatom content. It is worth noting, however, that the relatively long reaction time (10 h) indicates remaining kinetic and diffusion limitations, suggesting that further improvements in catalyst design and process intensification are still required for practical application. A related approach was reported by Liu et al. [116]; different catalysts were prepared by wet impregnation of $Pd(NO_3)_2$ onto HZSM-5 and a mesoporous silica-coated variant (HZSM-5@MS), followed by drying and reduction at 400 °C to obtain well-dispersed metal sites. Under hydrothermal upgrading conditions (380 °C, 2 h, with formic acid as an in situ hydrogen donor),

the two catalysts showed clearly different roles. Pd/HZSM-5 reduced nitrogen content from 7.15 to 5.50 wt.%, indicating that accessible Brønsted acid sites remain important for nitrogen removal. However, its deoxygenation performance was limited, with relatively high oxygen content (19.85%), suggesting that strong acidity alone does not effectively promote HDO. In contrast, Pd/HZSM-5@MS showed almost no improvement in nitrogen removal, as the mesoporous silica layer partially covered the acid sites responsible for HDN. Yet, this same structural modification improved deoxygenation, lowering oxygen content to 14.62% (O/C = 0.16), increasing HHV to 32.65 MJ kg^{-1}, and reducing coke formation (8.56%). The improved HDO behavior is consistent with moderated acidity and better diffusion, which limits over-cracking and favor stabilization of intermediates. When compared with the previous systems, these results still indicate relatively high residual heteroatom contents. Reaction time appears to be a key factor: the shorter duration (2 h) likely restricts the extent of both HDN and HDO, whereas longer times, although beneficial for conversion, are not always practical from a process standpoint.

4. Reaction Pathways in Catalytic Upgrading of Algal HTL Biocrude

Algal HTL biocrude represents a highly complex and reactive intermediate, whose composition is governed by intricate interactions between lipid-, protein-, and carbohydrate-derived pathways [28,116]. The elevated heteroatom content, particularly nitrogen and oxygen, not only limits direct fuel applicability but also fundamentally alters catalytic upgrading behavior.

The reaction pathways involved in biocrude upgrading are strongly interconnected, where HDO, HDN, and HDS proceed simultaneously and compete for active sites and hydrogen. Among these, nitrogen-containing compounds emerge as critical inhibitors, often controlling the overall reaction network and catalyst performance [22,27,29].

Furthermore, secondary reactions such as polymerization, cracking, and condensation highlight that upgrading is not solely a matter of heteroatom removal, but also of controlling undesired pathways that lead to coke formation and catalyst deactivation.

Overall, a comprehensive understanding of the interplay between biocrude composition and reaction pathways is essential for developing efficient upgrading strategies. These insights underline the necessity of advanced catalyst design and process optimization, which will be addressed in the subsequent sections.

4.1. Hydrodenitrogenation (HDN)

$$R - NH_2 + H_2 \rightarrow R - H + NH_3$$

HDN is considerably more challenging than HDO due to the stability of nitrogen-containing heterocycles. These compounds require multi-step hydrogenation followed by C-N bond cleavage [31]. Nitrogen species strongly inhibit catalyst activity by competing for active sites and suppressing parallel reactions such as HDO [22,29].

As a result, HDN often acts as the rate-limiting step in upgrading processes involving nitrogen-rich algal biocrude.

4.2. Hydrodesulfurization (HDS)

$$R - S - R' + H_2 \rightarrow R - H + R' - H + H_2S$$

Sulfur should be treated as a dynamic process parameter rather than a passive impurity, particularly in sulfided catalyst systems. HDS removes sulfur in the form of H_2S and is necessary to meet fuel specifications.

Although sulfur content is relatively low, its impact on catalytic performance is significant. Sulfur compounds can lead to catalyst poisoning, but they are also required to

maintain the active phase of sulfided catalysts [35]. Therefore, sulfur plays a dual role in upgrading processes.

4.3. Hydrodeoxygenation (HDO)

$$R - OH + H_2 \rightarrow R - H + H_2O$$

HDO is the primary pathway for oxygen removal and is essential for improving fuel stability and energy density. It proceeds via hydrogenation, hydrogenolysis, and dehydration reactions [35]. Two main routes are typically observed: direct deoxygenation (DDO), producing aromatic hydrocarbons, and hydrogenation-dehydration (HYD), producing saturated hydrocarbons. The balance between these pathways is strongly influenced by catalyst structure, particularly the interplay between metal and acid sites.

However, HDO is associated with high hydrogen consumption, representing a major economic constraint in large-scale applications. Moreover, mechanistic conclusions derived from model compounds often fail to accurately describe real biocrude systems, where multicomponent interactions dominate and alter both kinetics and selectivity [27,31,33,39,56]. In addition to hydride, oxygenation, oxygen removal can also proceed via decarboxylation and decarbonylation pathways, which are discussed separately in the following section.

4.4. Decarboxylation and Decarbonylation

In addition to HDO, oxygen can also be removed from algal HTL biocrude via decarboxylation and decarbonylation pathways. Decarboxylation involves the removal of oxygen in the form of CO_2, while decarbonylation leads to CO formation. These pathways are particularly relevant for carboxylic acids and oxygenated intermediates derived from lipid and carbohydrate fractions.

Compared to HDO, these reactions require significantly lower hydrogen consumption, making them attractive from an economic perspective. However, they are inherently associated with carbon loss, which reduces overall liquid fuel yield and carbon efficiency [27,35].

Decarboxylation is commonly observed during the conversion of fatty acids to hydrocarbons, resulting in the formation of n-alkanes with one carbon atom less than the original molecule. Similarly, decarbonylation contributes to the formation of hydrocarbons through C-C bond cleavage and CO release. The relative contribution of these pathways depends strongly on catalyst properties, particularly acidity, metal dispersion, and reaction conditions [22,34].

Importantly, these reactions compete directly with HDO pathways, creating a trade-off between hydrogen consumption and carbon retention. Therefore, controlling the selectivity between HDO, decarboxylation, and decarbonylation is a key challenge in optimizing upgrading processes for algal HTL biocrude.

4.5. Hydrocracking and Isomerization

Hydrocracking and isomerization reactions play a critical role in the upgrading of algal HTL biocrude by improving fuel-range distribution and physicochemical properties. Hydrocracking involves the cleavage of C-C bonds in heavy molecules, leading to the formation of lighter hydrocarbons within the gasoline and diesel range [33,34]. This process is particularly important for reducing the high molecular weight fractions generated during HTL and secondary polymerization reactions [27,34].

Isomerization, on the other hand, enhances fuel quality by converting linear hydrocarbons into branched isomers, thereby improving cold flow properties and combustion characteristics [35]. These reactions are typically catalyzed by bifunctional catalysts possessing both metallic sites for hydrogenation and acidic sites for skeletal rearrangement [22]. However, hydrocracking is often accompanied by undesirable side reactions such as ex-

cessive gas formation and carbon loss, especially under high temperature and hydrogen pressure conditions [27,35]. Similarly, isomerization selectivity can be limited by competing cracking reactions, highlighting the importance of catalyst design and process optimization [22].

These reactions are strongly coupled with HDO and HDN pathways, as the removal of heteroatoms facilitates subsequent cracking and rearrangement reactions [27,34]. Therefore, hydrocracking and isomerization should not be considered as independent processes but as integral components of the overall upgrading reaction network.

The balance between hydrocracking and isomerization is crucial for maximizing liquid fuel yield while minimizing gas formation, which remains a key challenge in catalyst and process design [22,35]. Unlike non-selective thermal cracking reactions discussed in secondary pathways, hydrocracking refers to catalytic C-C bond cleavage under hydrogen atmosphere with controlled selectivity toward fuel-range hydrocarbons.

4.6. Secondary Reactions and Catalyst Deactivation

In addition to primary upgrading pathways, secondary reactions such as cracking, polymerization, and condensation significantly influence process performance. These reactions contribute to coke formation, catalyst deactivation, and carbon loss through gas formation [35].

Catalyst deactivation remains one of the primary challenges in HTL biocrude upgrading, driven by coke deposition, metal sintering, and heteroatom poisoning [22,35]. These reactions differ from controlled hydrocracking processes, as they are generally non-selective and contribute to undesirable product formation.

4.7. Reaction Coupling and Process Constraints

The simultaneous removal of oxygen, nitrogen, and sulfur leads to substantial hydrogen demand, which represents a major economic limitation. Furthermore, these reactions compete for active sites and hydrogen, creating complex interactions that are not adequately captured in simplified kinetic models [27,35,56].

There is a lack of integrated kinetic models describing multi-heteroatom removal under realistic conditions, which limits process optimization and scale-up.

5. Catalytic Process Selection and Integration

The translation of algal HTL biocrude into drop-in transportation fuels requires strategic decisions regarding upgrading process architecture, catalyst deployment, and system integration. This section examines the principal process configurations and evaluates their comparative performance, techno-economic implications and industrial deployment challenges. Understanding these trade-offs is essential for guiding research priorities and accelerating the pathway from laboratory demonstrations to commercial-scale algal biofuel production. In practice, the main process architectures can be grouped into: (i) single-stage catalytic HTL or one-pot liquefaction-upgrading, (ii) direct single-stage ex situ upgrading of raw biocrude and (iii) multi-stage upgrading in which stabilization and deep hydrotreatment are deliberately separated.

5.1. One-Pot Catalytic HTL and Upgrading

Single-stage catalytic HTL and upgrading represents an integrated approach in which catalytic reactions occur concurrently with or immediately following hydrothermal liquefaction, consolidating biocrude production and heteroatom removal into a single reactor or tightly coupled reactor system. This strategy is conceptually attractive and aims to simplify process and reduce capital investment via creating a process intensification; however, because the catalyst is exposed to the raw algal conversion environment, it operates

under more challenging conditions, which can accelerate catalyst deactivation and limit upgrading performance [27].

The fundamental concept involves performing catalytic upgrading under hydrothermal conditions, typically at temperatures of 200–370 °C and pressures sufficient to maintain subcritical phases (4–20 MPa). Under said conditions, water acts as both reactant and catalyst in hydrothermal liquefaction, providing unique hydrogen donor capabilities. Subcritical conditions help water maintain liquid state properties that enhance its effectiveness [1,117]. In situ catalytic HTL incorporates catalysts directly into the liquefaction reactor to shift product distributions toward higher-quality biocrude with reduced oxygen and nitrogen content, thereby simplifying downstream processing requirements.

Marangon et al. [1] examined wastewater-grown microalgae as feedstock for integrated one-step hydrothermal liquefaction and catalytic upgrading toward SAF precursors. The authors used a $NiMo/Al_2O_3$ catalyst in a batch reactor and systematically varied temperature (270–370 °C), reaction time (30–120 min), and catalyst loading (0–20 wt.%) using a response-surface design. Their core objective was to see how these variables affect bio-oil yield, composition, and heteroatom removal in a single combined step rather than in separate HTL and upgrading stages. The results revealed that an energy-dense, lower-sulfur bio-oil can be generated in a single hydrothermal step, with optimum performance near 320–324 °C. However, the resulting oil still requires downstream refining and catalyst stability under hydrothermal conditions remains unresolved.

Xu et al. [27] examine the studies where direct HTL or 2-stage (HTL + upgrading) was applied to algae. Overall, the comparison of the two methods indicates that direct catalytic HTL offers a simpler process configuration and relatively higher biocrude yield, whereas the two-step pathway provides superior upgraded-oil quality, reflected by higher C/H contents and HHV, lower heteroatom contents and lower molecular weight. The improved performance of the two-step route is attributed to the initial non-catalytic HTL step, which conditions the feed for subsequent upgrading by reducing solids and problematic species. Nevertheless, this quality advantage is achieved at the expense of lower liquid yield, greater process complexity, and likely higher energy demand.

As observed in most of the one-pot approaches presented above, current evidence suggests that single-stage catalytic HTL should be regarded primarily as a process intensification concept rather than a fully demonstrated industrial route. In situ catalytic HTL studies on microalgae have shown that catalysts can enhance carbon and hydrogen content, reduce oxygen and nitrogen levels, and improve the heating value compared to non-catalytic HTL. However, these findings are largely based on short-duration batch experiments and do not yet address key scale-up challenges, including catalyst recovery, long-term hydrothermal stability, ash and mineral tolerance and regeneration under realistic continuous operation conditions. Accordingly, one-pot catalytic HTL may be best suited for partial in situ upgrading or early-stage process simplification, rather than the complete production of drop-in fuels. The integrated configuration of one-pot catalytic HTL and in situ upgrading is schematically illustrated in Figure 6.

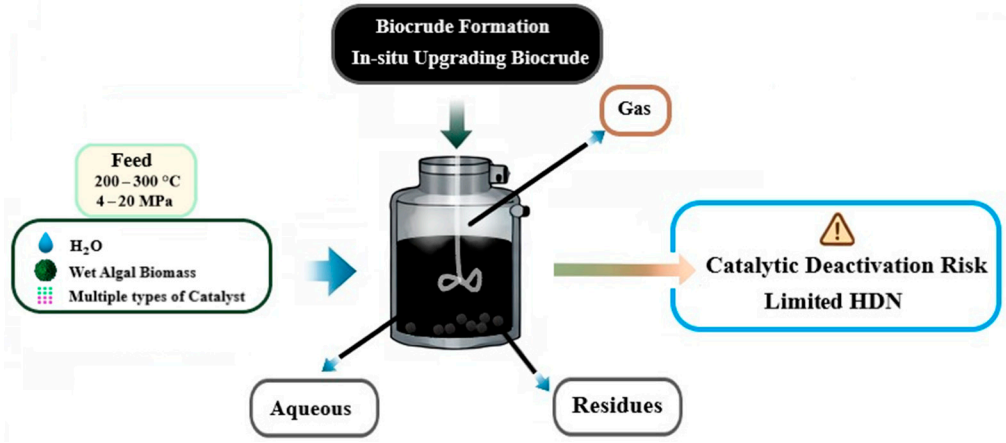

Figure 6. Schematic representation of one-pot catalytic HTL and in situ upgrading of algal biomass.

5.2. Direct Single-Stage Ex Situ Upgrading of Raw Biocrude

A more conventional route is to first produce and separate the algal HTL biocrude and then subject it to a single downstream hydrotreatment step. This configuration offers better control over hydrogen pressure, catalyst-to-oil contact and reactor severity than one-pot HTL-upgrading.

In an early benchmark study, Biller et al. [58], first produced *Chlorella* biocrude by continuous HTL, then subjected that separated biocrude to a single hydrotreatment step in a stirred batch reactor using sulfided CoMo and NiMo catalysts at 350 or 405 °C and operating at a constant pressure of 138 bar (initial H_2 pressure of 60–66 bar) [4] Temperature emerged as the most critical parameter, with higher temperatures dramatically improving nitrogen, oxygen and sulfur removal across all catalyst conditions, though at the cost of significantly reduced yields. At 405 °C, nitrogen removal reached 84% (though "60%" is emphasized in the abstract, possibly to represent a conservative, typical value) with NiMo catalysts, 69% with CoMo, and 58% without catalysts, while oxygen content dropped to just 1.0–1.5% compared to 4.2–5.0% at the lower temperature. However, this enhanced heteroatom removal came with substantial yield penalties, dropping from 89 to 95% at 350 °C to only 41–69% at 405 °C. Catalyst selection proved equally important, with NiMo demonstrating superior nitrogen removal capabilities, achieving the lowest final nitrogen content of 2.4%, while CoMo excelled in sulfur removal, completely eliminating detectable sulfur compared to NiMo's 20 ppm residual content. The study revealed that optimal heteroatom removal required higher temperatures but resulted in lower yields.

Batch hydrotreating study of Spirulina-derived HTL biocrude by Haider et al. [16], used a two-level factorial design to test three variables: temperature (250 or 350 °C), initial H_2 pressure (40 or 80 bar) and residence time (2 or 4 h) [5]. Under 350 °C, 80 bar H_2, 4 h, they achieved complete deoxygenation but only about 47% denitrogenation. They then pushed the severity higher, where at best, they reached about 60% denitrogenation at 375 °C, 70 bar, 3 h; and at 400 °C, denitrogenation was around 50–58%, so higher severity did not cleanly solve the nitrogen problem. The paper explicitly notes that although higher temperatures favor deeper N removal, fuel quality starts to decline at 400 °C, with lower H/C and HHV, which they attribute to cracking and likely coke formation/instability of the polar HTL biocrude. So, it was shown that deoxygenation is mainly driven by temperature, while denitrogenation depends more strongly on the interaction between temperature and hydrogen pressure. This distinction is crucial for algal biocrudes, for which HDN is often the rate-limiting upgrading function.

Patel et al. [21] investigated single-step catalytic hydrotreatment of algal biocrude produced by continuous-flow HTL (380 °C, 0.5 min) using commercially available Pt, Pd, Ru,

and NiMo catalysts supported on carbon or mesoporous γ-Al_2O_3. The upgrading achieved over 60 wt.% upgraded biocrude yield, with the highest yield obtained over NiMo/Al_2O_3. Product quality improved significantly: oxygen content decreased to ca.1.6–6 wt.% and maximum denitrogenation reached ca. 43%. An important finding was that product distribution analysis showed that hydrotreatment caused both cracking and polymerization, redistributing the gas-oil fraction into lighter and heavier fractions.

Castello et al. [64] hydrotreated *Spirulina* biocrude in a single catalytic step over sulfided NiMo/Al_2O_3 at different temperatures and H_2 pressures. They found that algal biocrude could be fully deoxygenated and converted toward jet-fuel-range branched paraffins, but deep denitrogenation remained challenging. A key process conclusion is that higher H_2 pressure was essential to limit coking and decarboxylation.

Guo et al. [118] subjected algal biocrude to catalytic upgrading using NiMo/Al_2O_3 and NiW/Al_2O_3 at 400 °C, which significantly improved fuel properties, with oxygen removal reaching >93%, nitrogen reduction of around 50% and sulfur removal up to 80%. Temperature was the dominant upgrading parameter, and interestingly promoting HDO and cracking at 400 °C while favoring repolymerization and decarboxylation at 250 °C. The gasoline, kerosene and diesel components increased from 18 wt.% to >30 wt.% after upgrading, with heating values reaching up to ca. 44 MJ kg^{-1}. NiMo catalyst excelled in deoxygenation/denitrogenation while NiW showed superior desulfurization performance, with catalyst reactivity being strain-dependent.

The main weakness of direct single-stage upgrading is that the severity required for deep denitrogenation has the potential to destabilize the raw biocrude, as shown in another study of Haider et al. [42]. For highly nitrogenous HTL biocrudes, direct processing at around 400 °C has been associated with substantial coke formation and low upgraded-oil yields, because reactive oxygenated intermediates undergo condensation and polymerization before they are fully stabilized. Haider and co-workers therefore showed that direct high-temperature hydroprocessing of nitrogen-rich HTL biocrudes is inherently prone to coking and potential reactor plugging. In that sense, single-stage ex situ upgrading is operationally simplest, but it is least forgiving when feedstocks contain high levels of oxygenates, basic nitrogen compounds, metals, or suspended solids [42].

Comparative analysis of single-step upgrading studies shows that this route can substantially improve algal HTL biocrude quality, particularly through strong deoxygenation, higher heating values, and increased light-fuel fractions. However, the literature consistently identifies a three-way trade-off among heteroatom removal, liquid-yield and feed stability. Temperature is the dominant upgrading variable: higher temperatures generally promote HDO, cracking and redistribution toward lighter boiling fractions, as shown by several researchers [21,58,118]. Yet severe conditions do not suppress all undesirable chemistry. Rather, around 400 °C, desired upgrading reactions and undesired condensation pathways can proceed in parallel. This explains why Guo et al. [118] observed that HDO and cracking were more strongly promoted at 400 °C, whereas Haider et al. [41] showed that similarly severe conditions could also intensify polymerization, coke formation, and yield loss in highly nitrogenous, thermally unstable biocrudes. These findings are therefore complementary rather than contradictory: 400 °C is chemically powerful but operationally risky, especially when the feed has not first been stabilized. A compare-and-contrast of the studies of Patel et al. [21] and Haider et al. [42] further supports this interpretation. High-temperature single-step hydrotreating can indeed improve fuel quality, but whether it remains practical depends on how well the feed tolerates severe conditions before stabilization. For less problematic or more upgradeable algal biocrudes, high temperature can be beneficial. For highly nitrogenous, thermally unstable HTL biocrudes, the same temperature window can trigger polymerization and coke formation faster than stabiliza-

tion reactions can suppress them, causing yield loss. A second consistent conclusion across the literature is that oxygen removal is significantly easier than nitrogen removal. Studies on *Spirulina*-derived biocrudes show that complete or near-complete deoxygenation can be achieved under conditions where denitrogenation remains only partial, indicating that HDN is the more demanding and often limiting upgrading function. Finally, catalyst performance is objective-specific rather than universal: NiMo-based catalysts generally provide the best overall balance between deoxygenation, denitrogenation, and fuel-quality improvement, whereas CoMo or NiW may outperform them in sulfur removal, and noble metals may enhance selected aspects of product quality at the expense of yield or cost.

Overall, the evidence suggests that single-stage upgrading is best regarded as a simple but severity-sensitive strategy: it is effective for partial-to-moderate upgrading, but its applicability narrows significantly as feed nitrogen content, thermal instability, and denitrogenation requirements increase. This in turn raises the question of whether two-stage upgrading can mitigate these limitations more effectively, as discussed in the following section. A schematic representation of the direct single-stage ex situ upgrading process is shown in Figure 7.

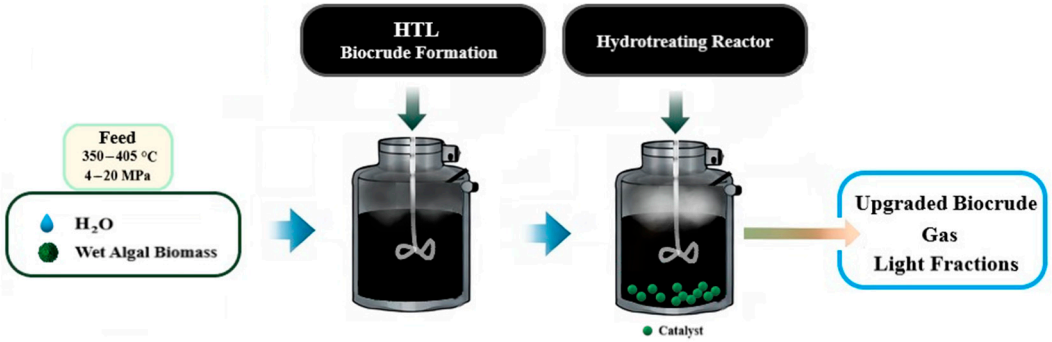

Figure 7. Process configuration for direct single-stage ex situ catalytic upgrading of algal biocrude.

5.3. Multi-Stage Upgrading Strategies

The findings discussed for "direct single-stage ex situ upgrading" provide the clearest rationale for moving toward staged processing. While single-stage hydrotreatment can markedly improve algal biocrude quality, the severity required for deeper denitrogenation may destabilize raw, highly nitrogenous feeds. In this sense, multi-stage upgrading does not represent a fundamentally different objective from single-stage upgrading, but rather a different process strategy for achieving it: instead of forcing stabilization, deoxygenation and denitrogenation to occur simultaneously under one severe condition set, these functions are distributed across sequential stages better matched to the chemistry of the feed. In this scheme, the first stage is operated at relatively mild conditions to hydrogenate reactive oxygenates, reduce thermal instability and in some cases remove part of the metals or other catalyst poisons. A second, more severe stage is then used for deep HDN, HDS, hydrocracking and product finishing.

The study of Haider et al. [42]—as mentioned under "direct upgrading", too—provides a clear bridge between these two approaches. Building directly on the problem observed in severe one-step upgrading, they showed that raw HTL biocrudes lack sufficient thermal stability at the approximately 400 °C conditions required for effective HDN. Their solution was a two-stage hydrotreatment strategy in which the first stage operates at lower temperature to stabilize the oil and remove reactive oxygen-containing compounds, while the second stage applies higher severity to accomplish deeper nitrogen removal. Importantly, the study showed that complete deoxygenation was already achieved in the first stage at 350 °C with limited coke formation, whereas the full two-stage configuration achieved

up to 92% denitrogenation with dramatically lower coke yields than direct processing at 400 °C. For Spirulina biocrude, coke decreased from 9.1% in direct 400 °C processing to 1.0% in the two-stage route, clearly demonstrating that staging suppresses the instability observed in severe single-step upgrading.

Haider et al. [119] showed that staged upgrading of *Spirulina* HTL biocrude can be implemented not only as separate reaction steps, but also as functional staging within a continuous graded-bed hydrotreater. The system combined a front-end, low-activity high-porosity Mo/γ-Al_2O_3 bed for HDM with a downstream NiMo/γ-Al_2O_3 bed for hydrotreating, operated under an optimized temperature profile at 100 bar and WHSV 0.5 h^{-1}. The continuous experiments were run at 200–340 °C and the resulting partially upgraded oils were then subjected to batch hydrotreatment at 400 °C to directly test how prior stabilization affects coke formation under severe conditions. The main mechanistic conclusion was that contaminant removal followed the order HDM > HDO > HDS > HDN, meaning that organometallics and oxygenates are removed more readily than nitrogen species. In the continuous runs, very mild treatment at 200 °C already achieved about 45% demetallization and 9.2% deoxygenation, while at 340 °C the process reached 100% deoxygenation, 97.5% desulfurization, but only 38.5% denitrogenation, confirming that HDN remains the most difficult upgrading function. A major contribution of the study is that it links staged stabilization directly to reactor operability. With the optimized graded-bed configuration, the authors achieved 335 h time-on-stream without pressure drop or plugging and the run ended only because the feed was exhausted. They further showed through batch tests at 400 °C that direct treatment of raw biocrude produced 10.2% coke, whereas prior partial upgrading reduced coke progressively to 3.1%, 1.9%, 0.8%, and finally 0.03% for feeds pre-treated at 200, 250, 300, and 340 °C, respectively. At the same time, oil yield increased from 62.3% for raw direct treatment to 86.2% after prior treatment at 340 °C. Thus, the study shows that the main value of multi-stage upgrading is not only improved heteroatom removal, but the creation of an operable process window in which severe downstream upgrading becomes feasible with greatly reduced coke formation.

Building on this process-stabilization perspective [119], Castello et al. [44] extended the analysis from preventing premature clogging to a more comprehensive understanding of continuous hydrotreating behavior for nitrogen-rich Spirulina biocrude. Whereas the earlier study established that mild front-end HDM/HDO treatment and an optimized graded-bed temperature profile are essential to stabilize the feed and suppress coke formation during continuous operation, the later study addressed the broader questions that remained open, namely how hydrotreating severity affects deoxygenation, denitrogenation, hydrogen consumption, and boiling-point distribution. In particular, it was shown that HDO can be achieved under relatively mild conditions, whereas deep HDN requires much more severe conditions, including temperatures around 400 °C, low space velocity, and high H_2 consumption. They further observed that mild hydrotreating favors diesel-range hydrocarbons, while increasing severity shifts the product distribution toward lower-boiling, gasoline-range fractions. Using advanced characterization, including FTICR-MS, the authors suggested that this shift is linked to the denitrogenation mechanism itself, since C-N bond cracking promotes fragmentation of larger molecules in the heavier biocrude fractions. Similarly, nitrogen removal showed strong temperature dependence: no visible removal until 50 °C, then progressive decrease from 7.6% (feed) to 4.2% (340 °C single-stage) to 0.8% (340 + 400 °C two-stage). Oxygen removal was rapid, completely removed at ≥300 °C. Sulfur removal was highly effective across all temperatures. Longer residence times significantly improved nitrogen removal at 340 °C, yet at higher temperatures (370 °C) reactions approached equilibrium. Pressure had minimal impact compared to other variables. More severe conditions (higher temperature, longer residence time) reduced upgraded biocrude

yields: from 99.2% (200 °C) to 77.3% (340 + 400 °C) [44]. The multi-stage upgrading strategy, highlighting sequential stabilization and deep hydrotreatment steps, is illustrated in Figure 8.

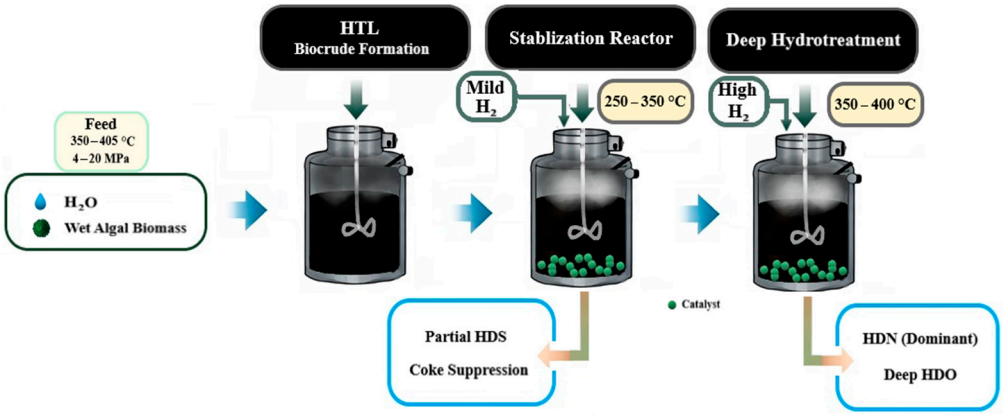

Figure 8. Multi-stage upgrading strategy for algal biocrude involving sequential stabilization and deep hydrotreatment.

Table 2 presents a comparison of different upgrading strategies mentioned so far. Overall, the three methods can be understood as occupying different positions on a trade-off spectrum. One-pot upgrading maximizes integration but remains least proven in terms of catalyst durability and full upgrading performance. Single-stage ex situ upgrading is simpler and already effective for substantial quality improvement but is highly severity-sensitive and often struggles with nitrogen-rich algal feeds. Multi-stage upgrading is the most intricate one and offers superior control over coking, catalyst deactivation and heteroatom removal, particularly for challenging feedstocks with high nitrogen content. However, these benefits come at the cost of increased process complexity, higher capital investment and potentially greater cumulative hydrogen consumption. Single-stage catalytic HTL and upgrading remain attractive for their simplicity and lower capital requirements, provided that catalyst formulations and reaction conditions can be optimized to manage deactivation and achieve acceptable product quality. The choice between these configurations depends on feedstock characteristics, target fuel specifications, hydrogen availability and cost and the relative importance of capital versus operating expenses in the overall techno-economic landscape.

Table 2. Comparison of different upgrading strategies.

Upgrading Strategy vs. Metrics	One-Pot Catalytic HTL and Upgrading Related Ref.: [1,27]	Direct Single-Stage Ex Situ Upgrading of Raw Biocrude Related Ref.: [16,21,42,58,64,118]	Multi-Stage Upgrading Related Ref.: [42,43,119]
Catalyst deactivation	High risk/insufficiently resolved. Catalyst is exposed directly to the harsh hydrothermal conversion environment, which can accelerate deactivation and limit long-term stability.	Moderate to high risk, feed-dependent. Better controllable than one-pot systems, but severe conditions can destabilize N-rich biocrudes and accelerate catalyst deactivation.	Lowest deactivation risk. By stabilization before severe HDN, catalyst exposure to the most reactive contaminants is reduced and continuous operability becomes much more feasible.

Table 2. *Cont.*

Upgrading Strategy vs. Metrics	One-Pot Catalytic HTL and Upgrading Related Ref.: [1,27]	Direct Single-Stage Ex Situ Upgrading of Raw Biocrude Related Ref.: [16,21,42,58,64,118]	Multi-Stage Upgrading Related Ref.: [42,43,119]
Coking tendency	Potentially significant. Batch studies indicate partial in situ upgrading, but coke behaviour under continuous operation remains largely unresolved.	Moderate. Ca. 400 °C, upgrading reactions and undesired polymerization can proceed; coking risk is severe for unstable, nitrogenous feeds.	Low. Mild stabilization suppresses coke precursors before exposure to severe conditions; coke is reduced relative to direct severe hydrotreating.
N/O/S removal	Moderate improvement, but limited depth. O and N contents can be reduced relative to non-catalytic HTL, but deep heteroatom removal is generally not shown in a robust way.	Strong HDO and often strong HDS, but HDN level can be limited. O removal can be complete or near-complete, sulfur removal can be high, but nitrogen removal often remains partial even at high severity.	Best for deep upgrading. Early stages remove metals, O and S; later stages target N more effectively; HDN remains the most demanding, but staged systems clearly outperform 1-stage severe processing for N-rich feeds.
Hydrogen consumption	Unclear to moderate. Process complexity may be reduced by integration, but incomplete upgrading usually still necessitates downstream refining, limiting the practical hydrogen advantage.	Moderate to high. Increases with severity, especially when HDN is targeted; pressure assists HDN, but high severity does not always translate into efficient nitrogen removal.	High overall, but more rationally utilized. Hydrogen demand increases across stages, yet staged severity avoids inefficient H_2 use under unstable conditions and better aligns H_2 input with contaminant reactivity.
Product quality and yield	Moderate quality with simpler flowsheet. Can yield a more energy-dense, lower-S biocrude, but typically far from drop-in fuel quality; best viewed as a process-intensification concept rather than a fully demonstrated route.	Can markedly improve HHV and increase lighter fuel fractions, but often at the expense of liquid yield. High temperature improves fuel quality, yet may reduce yield through cracking, gas formation and coke.	Best balance between quality, yield and operability. Enables deeper HDN and supports continuous processing; however, increasing severity in later stages may shift products toward lighter fractions and reduce yield.

5.4. Scale-Up Considerations and Process Integration

HTL crude bio-oil upgrading faces multiple interconnected challenges that can limit its scale-up to be used as transportation fuel. The primary issues include high heteroatom content compared to refinery crude, resulting in poor fuel quality and processing difficulties. Chemical instability at ambient conditions can lead to polymerization during storage and lower heating values compared to conventional fuels reduce energy content. Catalyst poisoning from high metal/salt content, particularly challenging nitrogen removal from algal feedstocks and poor miscibility with refinery fuels further complicate upgrading processes. Economic constraints include high capital expenditure requirements for standalone biorefineries and construction material issues due to corrosive properties.

These feedstock-dependent variations necessitate different upgrading strategies, making standardized processing approaches difficult to implement [120].

The comparison of one-pot, single-stage ex situ and multi-stage upgrading strategies becomes most meaningful when viewed through a scale-up lens. At scale, upgrading must be judged against catalyst lifetime, solids tolerance, pressure-drop stability, hydrogen efficiency, product consistency, integrability, continuous operability and compatibility with downstream refinery operations.

5.5. Batch vs. Continuous Operation

Most one-pot catalytic HTL studies and many direct ex situ hydrotreating studies remain batch-based, which is suitable for catalyst screening and reaction mapping but does not adequately capture long-term deactivation, metal deposition, pressure-drop development or feed variability. By contrast, continuous studies show that these issues quickly become decisive. In the report PNNL [121], algal HTL biocrude was upgraded in a continuous trickle-bed hydrotreater operated at around 100 bar with 350/400 °C temperature zones, giving hydrotreated oil yield containing ca. 23 wt.% jet-fuel-cut. However, the jet-fuel cut still contained 3200 ppm N, which led the report to assume a separate HDN polishing step in the full process design. This is a useful scale-up reminder: even when continuous hydrotreating is demonstrated, product upgrading may still need to become fraction-specific rather than reactor-wide.

Continuous operation also makes catalyst-poisoning mechanisms much more visible. Jarvis et al. [122] showed that iron porphyrin compounds in algal HTL biocrude can cause catalyst-bed plugging through iron deposition, which directly links algal feed chemistry to operability risk reactivity. Two-stage continuous hydrotreater can maintain long-time operation for nitrogen-rich microalgal biocrude, although HDN still remains much harder than HDO. So, it might be suggested that the scale-up challenge is not simply "continuous versus batch," but rather whether the continuous process is designed to manage metals, oxygenates, and nitrogen species in the order of their reactivity.

Most published studies are either batch hydrotreating investigations, useful for screening severity and catalyst effects or continuous hydroprocessing studies, which are more informative for operability and scale-up. The available evidence nevertheless suggests that continuous systems provide advantages not captured in batch tests, including steadier control of hydrotreating severity, the possibility of guard-bed and staged catalyst configurations and better management of metals, coke precursors and product fractionation.

5.6. Compatibility with Refinery Infrastructure

A second major issue is compatibility with existing refinery infrastructure. The compatibility of HTL algal biocrude with existing petroleum refinery infrastructure is generally higher than that of other biomass-derived feeds like pyrolysis-derived oils. However, significant technical hurdles arise mainly due to the fact that HTL-derived algal bio-crude exhibits lower oxygen content, HHV and reduced acidity and typically contains 60–75 wt.% carbon and 8–12 wt.% hydrogen, with oxygen content of 10–20 wt.% [123]. As categorized by Churchill et al. [124], the following compatibility issues are faced: (i) chemical instability and poor miscibility (particularly at concentrations higher than 10 wt.%) due to high levels of oxygen and nitrogen; (ii) corrosion and handling due to high viscosity and acidity leading to damage on the standard refinery equipment; (iii) catalyst poisoning due to nitrogen species particularly in FCC and hydrocracking processes; (iv) phase separation when directly blending with petroleum fuels.

Alvarez-Majmutov et al. [125] identified a critical physical bottleneck in co-refining: raw algal biocrude is inherently incompatible with VGO, forming heavy precipitates that

cause immediate equipment fouling and reactor plugging. To mitigate these operational risks, fractional distillation is established as a critical pre-upgrading step to remove the high-molecular-weight polar molecules and residual water responsible for this instability. By refining the biocrude into a compatible distillate, it achieves full miscibility with VGO, enabling stable, long-term co-hydroprocessing that successfully yields high-quality renewable drop-in fuels while preserving the integrity of standard refinery infrastructure. The study conducted a continuous pilot-scale test using a 10 wt.% distilled biocrude and 90 wt.% VGO blends over a commercial NiMo/Al_2O_3 catalyst and achieved high efficiency, with 99.7% nitrogen removal and 100% oxygen removal under optimal conditions, where the co-processed oil produced high-quality hydrocarbons within the boiling ranges of renewable diesel and jet fuel.

5.7. Techno-Economic and Sustainability Considerations

The economic and sustainability considerations for HTL algal biocrude upgrading involve several critical factors as identified by Ghadge et al. [120]. Economic considerations include the high CAPEX requirements for standalone bio-refineries versus the cost advantages of refinery integration options. The choice between standalone configurations (maximizing ATF/diesel or gasoline/diesel fractions) and refinery integration strategies (blending with fossil crude or FCC feed) significantly impacts capital expenditure. Sustainability aspects focus on by-product utilization, particularly the nutrient-rich HTL aqueous phase which can be recycled to algal ponds, though this requires careful management of inhibitory compounds like phenols and fatty acids. Alternative treatments like CHG and AD increase minimum fuel selling price by 11% and 2.9% respectively compared to direct recycle. Process integration challenges include catalyst poisoning from high metal/salt content in algal biocrude, necessitating desalters or guard beds and the need for ash removal systems for feedstocks yielding high-ash content oils [120].

From a techno-economic perspective, the main message of the broader literature is that upgrading cannot be evaluated in isolation from the rest of the HTL system. This indicates that process integration around upgrading -especially management of the aqueous phase, nutrients, and gas by-products- can matter almost as much as the hydrotreating reactor itself. Zhu et al. [126] showed that plant scale significantly impacts economics, with larger facilities (500 MT/d vs 50 MT/d) reducing minimum fuel selling price by 6.9% due to economy of scale effects. The integration of aqueous phase treatment methods creates important trade-offs between capital costs and energy efficiency—direct recycle eliminates treatment costs but requires higher natural gas consumption, while CHG and AD processes convert organics to useful methane but increase capital investment by 64% and 17% respectively. Process integration benefits include nutrient recycling (87–89% nitrogen, 81% phosphorus recovery) that reduces external fertilizer demands, and energy integration where biogas from aqueous treatment reduces natural gas requirements for hydrogen production. Sustainability considerations encompass carbon efficiency (47–52% overall) and energy efficiency (51–59% overall) improvements through integrated heat recovery and off gas utilization. The study emphasizes that conversion costs represent only 14–22% of total fuel costs, making feedstock cost optimization and yield improvements more critical than process intensification for commercial viability.

Saral et al. [127] demonstrates that biorefinery integration is essential for economic viability, with MSP ranging from minimum selling prices ranged between US$2.5–3.94 per GGE depending on pathway configuration, while total GHG emissions ranged from 59.2 to 147.4 g CO_2-eqMJ^{-1}, showing strong sensitivity to coproduct strategy and aqueous-phase management The analysis emphasizes that integrated biorefineries combining biochemical

and thermochemical processes with value-added co-products are crucial for competing with petroleum-based fuels.

6. Research Gaps and Future Perspectives

The transition of algal HTL biocrude from a laboratory-scale curiosity to a commercially viable energy carrier hinges on addressing several critical technical and fundamental bottlenecks. While significant progress has been made in demonstrating the chemical feasibility of hydrotreating, the following areas remain the primary frontiers for future research:

6.1. From Bulk Characterization to Molecular-Level Insights

A major limitation in the current literature is the lack of a direct, mechanistic linkage between the complex molecular composition of biocrude and its specific catalytic behavior. Most existing studies rely on bulk characterization techniques—such as CHNS analysis or simulated distillation—which provide a general overview but fail to capture the nuanced molecular interactions and competitive adsorption effects inherent in multi-component mixtures. There is a critical need for integrated molecular-level analysis that links specific functional groups and molecular architectures to reaction pathways and catalyst performance. Future work should prioritize in situ and operando studies under realistic feed conditions to understand how nitrogen-rich heterocycles and oxygenated species compete for active sites, thereby guiding the design of more resilient catalysts.

6.2. Next-Generation Catalytic Systems: Beyond Noble Metals

While noble metals (Pt, Pd, Ru) remain the benchmark for high-quality biocrude upgrading due to their superior hydrogenation activity, their high cost and susceptibility to nitrogen poisoning remain significant barriers to large-scale deployment. The research trajectory is increasingly shifting toward:

- Hybrid and Bimetallic Architectures: Developing catalysts that reduce noble metal loading through synergy with transition metals (e.g., Ni-Ru, Ni-Pd) or innovative support designs (e.g., carbon nanofibers, carbides) to enhance stability and activity.
- Targeted Nitrogen Removal: Moving beyond conventional NiMo and CoMo formulations toward advanced materials specifically engineered for C-N bond cleavage and resistance to basic nitrogen species.
- Fraction-Specific Upgrading: Recognizing that "one size fits all" catalytic strategies may be inefficient, future research should explore tailored upgrading for soluble versus insoluble fractions to optimize catalyst lifetime and hydrogen consumption.

6.3. Industrial Integration and the "Refinery Integration" Model

The path to industrial-scale deployment requires a strategic shift from demonstrating chemical feasibility to ensuring operational reliability. Future development should favor the Refinery Integration model, utilizing existing hydroprocessing infrastructure to offset the capital costs of standalone biorefineries. To succeed, the industry must focus on:

- Standardization of Pre-Upgrading Protocols: Ensuring feedstock miscibility with petroleum fractions (e.g., VGO) to prevent fouling and protect refinery hardware.
- Implementation of Graded-Bed Architectures: Utilizing continuous, multi-stage systems that manage the hierarchy of reactivity -removing metals and oxygen at mild conditions before subjecting stabilized oil to severe denitrogenation- thereby extending catalyst lifetimes.
- Circular Integration: Upgrading units should not operate in isolation. Future deployments must integrate aqueous phase treatment to recover nitrogen and phosphorus,

offsetting fertilizer costs for cultivation and producing renewable hydrogen to reduce the carbon footprint of the final fuel.

7. Conclusions

The catalytic upgrading of HTL-derived microalgal biocrude is essential for producing refinery-compatible drop-in fuels, yet it remains fundamentally challenged by the feedstock's complex chemical nature. While high energy density is achievable, elevated nitrogen and oxygen contents create severe bottlenecks for downstream hydroprocessing. Nitrogen-containing heterocycles, in particular, act as a definitive barrier; they strongly adsorb to catalyst surfaces, block active sites and accelerate coke formation.

Through a multi-scale, catalyst-centered perspective, this comprehensive study surveyed a remarkably broad array of catalyst systems for the upgrading process, providing extensive coverage of the structure–activity relationships that govern these reactions. This large-scale evaluation establishes that overcoming upgrading barriers requires moving beyond conventional sulfided and oxide catalysts, which are highly susceptible to metal leaching and rapid deactivation. Instead, successful integrated refining depends on the following advanced formulations and synergistic designs:

- Noble Metal Benchmarks: Metals such as Pt, Pd and Ru remain the standard for deep hydrogenation and maximum oxygen removal, consistently yielding high-quality products with HHVs approaching 40–45 MJ kg^{-1}. However, their industrial scalability is severely restricted by high costs and acute vulnerability to nitrogen poisoning.
- Transition Metal Carbides (TMCs): TMCs, specifically molybdenum carbide (Mo_2C), have emerged as highly robust, cost-effective alternatives. They mimic the electronic properties of noble metals while favoring hydrogen-conservative decarboxylation pathways, exhibiting superior thermal stability and resistance to nitrogen and sulfur poisoning in harsh hydrothermal environments.
- Zeolitic, Micropores, Mesopores or Hierarchical Architectures: Bridging the gap between micropores (for selectivity) and mesoporous channels (for mass transfer) via tunable zeolites or mesoporous supports (e.g., Al-SBA-15) is a critical breakthrough. This architecture overcomes mass-transfer limitations, allowing bulky protein- and lipid-derived macromolecules to reach active metal sites while inhibiting the rapid pore-plugging typical of conventional microporous catalysts.
- Bifunctional Synergy: The most effective modern systems leverage a dual-function approach, coupling metallic sites for hydrogen activation with acidic supports (like HZSM-5) for cracking and isomerization. Success in these systems relies on a precise metal–acid balance; insufficient acidity limits heteroatom removal, whereas excessive acidity exacerbates coking.

Ultimately, achieving industrial-scale viability requires moving toward feedstock-specific catalyst design and staged hydroprocessing strategies. For highly nitrogenous algal biocrudes, forcing deep nitrogen removal in a single stage triggers rapid catalyst deactivation and severe yield loss. Instead, process configurations must utilize sequential, multi-stage processing or continuous graded beds. Implementing a mild front-end stage over high-porosity metal oxide catalysts isolates and completely removes oxygenates and reactive metals, stabilizing the "intermediate upgraded/stabilized biocrude" before it reaches the second hydrotreating zone, which is specially optimized with advanced formulations such as heteroatom-doped transition metal carbides, zeolitic catalysts or highly selective noble metal sulfides designed specifically to break down and completely remove resistant cyclic nitrogen compounds. Building upon the extensive coverage of catalyst architectures established in this review, a subsequent study is warranted to provide a complete investigation of advanced final fuel characterization techniques. Furthermore,

future work must thoroughly explore the subsequent downstream processing steps such as secondary cracking, deep isomerization and fractional distillation that are essential for converting these upgraded intermediates into final ready-to-use drop-in fuels.

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Conflicts of Interest: The authors declare no conflicts of interest.

Abbreviations

The following abbreviations are used in this manuscript:

HTL	Hydrothermal Liquefaction
HHV	Higher Heating Value
HDN	Hydrodenitrogenation
HDO	Hydrodeoxygenation
HDS	Hydrodesulfurization
IWI	Incipient Wetness Impregnation
CUS	Coordinatively Unsaturated Sites
TMCs	Transition Metal Carbides
PGMs	Platinum-Group Metals
TPR	Temperature-Programmed Reduction
CHR	Carbothermal Hydrogen Reduction
CNFs	Carbon Nanofibers
SCW	Supercritical Water
DP	Deposition-Precipitation
DMS	Dimethyldisulfide
HDC	Hydrodecarboxylation
HDM	Hydrodemetallization
FTICR-MS	Fourier-Transform Ion Cyclotron Resonance Mass Spectrometry
WHSV	Weight Hourly Space Velocity
FCC	Fluid Catalytic Cracking

VGO	Vacuum Gas Oil
CAPEX	Capital Expenditure
MSP	Minimum Selling Prices
ATF	Automatic Transmission Fluid
CHG	Catalytic Hydrothermal Gasification
AD	Anaerobic Digestion
GGE	Gasoline Gallon Equivalent

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