

Review of Denitrogenation of Algae Biocrude Produced by Hydrothermal Liquefaction

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Abstract Recently, algae biocrude has drawn considerable attention as algae are considered to be one of the major fuel feedstocks of the future. Based on some impressive results achieved under appropriate conditions, the algae hydrothermal liquefaction (HTL) process has proven to be energy efficient. However, the HTL of biocrude is characterized by a high nitrogen content, which prevents its use in the field of transportation due to the associated nitrogen oxide emissions. Despite this toxicity, few research efforts have focused on the denitrogenation of algae biocrude. In this study, we review the effect of different strain-specific operation parameters and process upgrades with respect to the nitrogen content of biocrude. To achieve denitrogenation, chemical engineering may be required, although some improvements in biocrude properties have been achieved in a number of process upgrades. The use of similar successful pathways has the potential to improve the field of HTL biocrude denitrogenation. These methods, including the adsorptive and extractive denitrogenations of fossil fuels and the hydrodenitrogenation of the main nitrogen compounds, are helpful for developing a better understanding of the potential of denitrogenation for algae HTL biocrude. We also recommend the use of some available catalysts and corresponding operation parameters to promote continued research on denitrogenation.

Keywords Algae · Hydrothermal liquefaction · Biocrude · Upgrading · Denitrogenation

Abbreviations

HTL	Hydrothermal liquefaction
DCM	Dichloromethane
HDN	Hydrodenitrogenation
MOF	Metal organic framework
T_c	Critical temperature of water (°C)
P_c	Critical pressure of water (kPa)

Introduction

The twin challenges of climate change and the energy crisis, resulting from the unfettered energy demands of modern industry, have led to the development of biofuel production from biomass, which is associated with fewer emissions [1–3]. Biomass, as a renewable resource, fixes carbon dioxide in the atmosphere through photosynthesis during growth, and is regarded as an alternative feedstock for fuel. Biomass resources include terrestrial and aquatic plants, food materials, biowastes, algae and bacteria. Of these, algae grow in saline or fresh water and can be cultivated on non-arable lands. As such, they qualify as candidates because of their advanced photosynthetic efficiency, high biomass production, rapid growth speed, low environmental impact and low competition for food [4, 5]. Recently, the production of biocrude from algae biomass has been extensively investigated via processes of fermentation [6, 7], transesterification [8, 9], pyrolysis [10–13], gasification [14, 15], liquefaction [16–19], and carbonization [20, 21]. Of these methods, hydrothermal liquefaction (HTL) is considered to be a promising method for processing feedstock with high conversion efficiency

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and has the advantage of treating wet materials without the need for drying [22].

A typical HTL process is conducted around a critical point ($T_c = 373.95$ °C and $p_c = 22.064$ MPa) of water, and sometimes uses reducing gases such as H_2 and CO. A separation procedure is performed to recover biocrude from the product after liquefaction. After releasing gaseous products, organic solvents are added to dissolve the biocrude, followed by an organic phase that easily separates the aqueous and solid phases by decantation and filtration. These solvents typically include dichloromethane (DCM), chloroform, acetone, and toluene. Then, biocrude is obtained by evaporating the solvent after phase separation. In this paper, we base the calculated biocrude yields on dry algae if no specific description is provided.

The HTL of algae was first reported by Dote et al. [23] in 1994, followed by Minowa et al. [24] in 1995. In the years that followed, a growing number of studies and papers on the HTL of algae focused on the effects of operating parameters, algae types, and catalysts on biocrude's characteristics. For example, Matsui et al. [25] converted *Spirulina* into biocrude by various solvents over an iron catalyst. Some impressive results have been achieved under appropriate conditions. The co-liquefaction of algae with coal was also reported [26, 27], but is beyond the scope of this review. Besides HTL, we also address liquefaction processes in subcritical and supercritical alcohols in this review [28–30]. Table 1 summarizes the optimal conditions and results of existing studies.

During HTL, the proteins that abound in algae may also be converted into large amounts of nitrogenous heterocyclic compounds in biocrude, such as pyridine and quinoline, which affect smell, combustion, and various other properties. As such, understanding the degradation of proteins is important [31–33]. As shown in Fig. 1, nitrogen compounds are produced by Maillard reactions between sugars and amino acids [34]. Amino acids linked by peptide bonds are the building blocks of proteins. These peptide bonds are C–N bonds between the carboxyl and amine groups present in all amino acids, and are known to rapidly hydrolyze in hydrothermal systems [35]. In fact, differences in the chemical structures of amino acids yield divergent reaction paths. Since many amino acids contain the same peptide bonds, during HTL, they undergo similar decarboxylation and deamination reactions to produce carboxylic acids, aldehydes, carbonic acid, ammonia, and organic amines [36].

A biocrude that is high in nitrogen requires more extensive upgrading before it is suitable for use in the transportation industry or conventional refining, which increases the cost and energy inputs required to produce the final products [37]. Table 2 summarizes existing HTL research. To our knowledge, only a limited number of reviews have addressed the denitrogenation of algae

biocrude. In this review, we summarize the above-mentioned work to better understand this field. In addition, we present the latest achievements in the chemical engineering field in which denitrogenation has been successfully employed, including the hydrodenitrogenation (HDN) of nitrogen compounds and the adsorptive and extractive denitrogenations of fossil fuel.

Biocrude Production by HTL of Algae

The biochemical composition (lipids, proteins, and carbohydrates) in algae generally varies among species, and the growth of a given alga can be affected by different environments. Table 3 shows the typical compositions of four most investigated algae strains. Taking chlorella as an example, there are about ten major species (with varieties of up to 100 species) distributed across different regions of the world, each of which has different lipid and protein contents. More lipids can be induced in nutrient-deficient conditions, whereas more proteins can be produced in nutrient-rich conditions. Under specific conditions, *Chlorella pyrenoidosa* is a low-lipid and high-protein algae [38], and its counterpart, *Chlorella sorokiniana*, has the opposite characteristics [39].

The compositions of different algae strains have important influences on the composition of liquefied biocrude, as well as its reaction route [40, 41]. The biocrude production capability has the following order: lipids > proteins > carbohydrates [42]. Neveux et al. [43] studied six species of marine and freshwater green macroalgae that had been cultivated in outdoor tanks, and subsequently converted them to biocrude via HTL in a batch reactor. The authors then assessed the influence of the biochemical composition of the biomass on the biocrude yield. The results showed that freshwater *Oedogonium* (35.9%) and marine *Derbesia* (33.4%) had the highest biocrude yields of all species, based on their ash-free dry weight, as they had the highest proportion of lipids that are efficiently converted to biocrude through the rapid hydrolysis of triglycerides. Lopez et al. [44] analyzed the influence of strain-specific parameters (cell structure, biochemical composition and growth environment) on the HTL of microalgae. The authors found strain-specific parameters to play a role at higher temperature. In addition, the nitrogen content of algae can also vary significantly according to the species, environmental conditions, and post-harvest processing, so these parameters greatly influence the nitrogen content of the biocrude. Thus, the influences of different strain-specific and operational parameters on biocrude properties must be considered. In this section, we summarize these aspects and their biocrude upgrading results via HTL according to their algae strains.

Table 1 Summary of optimal experimental conditions and results of HTL of algae

Algae type	Conditions				Biocrude yield (%)	Nitrogen content (%)	HHV (MJ/kg)	References
	Temperature (°C)	Residence time (min)	Catalyst type	Extractant				
<i>Nannochloropsis</i>	350	60	Water only	DCM	43	3.9	39	[45]
	350	60	Pd/C	DCM	57	3.88	38.6	[46]
	350	60	Water only	Decane	39	4.44	NR	[47]
	350	60	Water only	DCM	34.3 (daf)	4.1	34.5	[48]
	350	30	Water only	Acetone	46	2.75	38.1	[49]
	600	1	Water only	DCM	66 (daf)	6.92	34.51	[50]
	300	60	Water only	DCM	40.6	6.59	39.6	[51]
	340	30	Ni-Mo/Al ₂ O ₃	DCM	78.5	4.88	37.53	[54]
	260	60	Water only	Acetone	55	5.4	31.5	[56]
<i>Chlorella</i>	350	60	Na ₂ CO ₃	DCM	27.3 (daf)	4.9	37.1	[58]
	280	120	Water only	Toluene	39.4	NR	35.4	[59]
	300	60	Water only	DCM	23.4	0.78	40.8	[39, 60]
	240	30	Ethanol	Acetone	71.3	NR	NR	[28]
	300	30	Ethanol	Acetone	NR	8.7	36.19	[28]
	350	60	Pt/Al ₂ O ₃	DCM	38.9 (daf)	5.6	37.9	[48]
	350	3	Water only	DCM	41.7 (daf)	7.7	33.8	[61]
	280	60	Water only	Toluene	42.8	NR	NR	[41]
	220	90	Water only	Acetone	82.9	0.3	34.9	[56]
	<i>Spirulina</i>	250	3	Water only	DCM	NR	3.5	30.7
350		60	Water only	Acetone	39.9	6.3	35.3	[64]
350		60	Water only	Acetone	39.93	6.2	31.5	[65]
300		30	Water only	DCM	32.6 (daf)	6.5	33.2	[62]
300		30	Water only	DCM	31	8.1	35.8	[63]
360		20	Water only	Acetone	NR	7.46	39.83	[57]
360		NR	FeS/ethanol	Ethanol	NR	9.64	37.13	[29]
310		30	Water only	Acetone	30	7.66	35.2	[49]
350		60	Na ₂ CO ₃	DCM	20 (daf)	4.6	34.8	[58]
<i>Dunaliella tertiolecta</i>		360	30	Water only	Chloroform	36.9	4.97	26.62
	360	50	Na ₂ CO ₃	Chloroform	25.8	3.71	30.74	[68]
	320	30	Ethanol–water	Chloroform	64.68 (daf)	5.35	34.96	[69]
<i>Enteromorpha prolifera</i>	300	30	Na ₂ CO ₃	DCM	23.0	5.76	29.89	[72]
	320	15	Ethanol	DCM	36.5	7.71	30.37	[30]
<i>Microcystis viridis</i>	340	30	Na ₂ CO ₃	Chloroform	33	7.1	31	[73]
<i>Sargassum</i>	340	15	Water only	Chloroform	32.1	2.45	27.1	[74]
<i>Desmodesmus</i>	375	5	Water only	DCM	49.4(daf)	6.3	35.4	[34]
<i>Laminaria saccharina</i>	350	15	Water only	DCM	19.3	4.9	36.5	[76]
<i>Golenkinia</i> sp.	300	60	Water only	DCM	31.2	6.56	37.0	[51]
<i>Tetraselmis</i> sp.	350	5	Water only	DCM	65	5	35	[71]

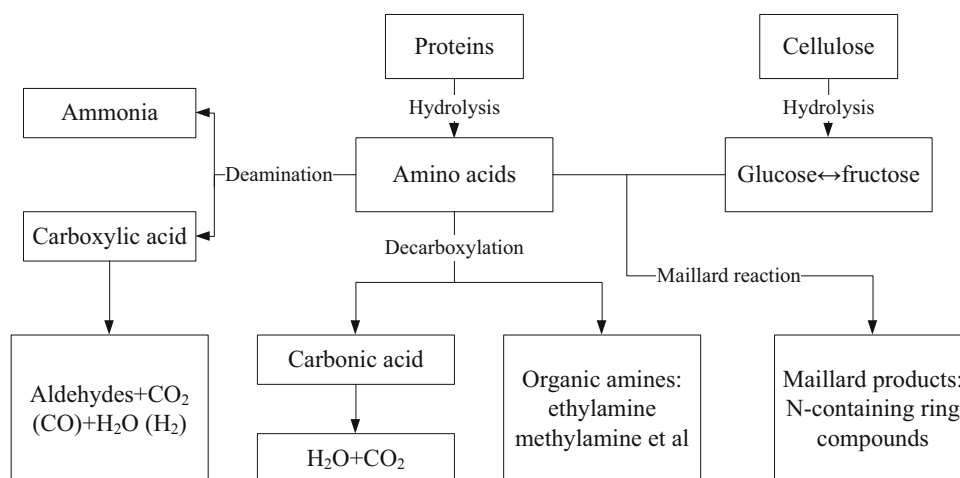
NR not reported, *daf* dry ash free basis

HTL of Algal Biomass for Biocrude

The liquefaction of *Nannochloropsis* has been extensively studied with respect to the production of biocrude [45–56] and some research results are provided as follows. Brown et al. [45–47] liquefied *Nannochloropsis* for producing

biocrude under various conditions. The authors achieved a maximum biocrude yield of 57% at 350 °C for 60 min with a 50% (daf) Pd/C catalyst, and the biocrude also contained the lowest nitrogen content (3.88%) of all their tests. It seemed to the authors that the Pt/C catalyst not only facilitated liquefaction but also supported denitrification.

Fig. 1 Fate of protein during HTL



Biller et al. [48] carried out the HTL of *Nannochloropsis oculata* at 350 °C for 60 min by several catalysts, including Co/Mo, Ni, and Pt, which were supported on γ -Al₂O₃. The nitrogen content was efficiently decreased by the Ni and Pt catalysts, and a higher heating value (HHV) was also achieved compared with the liquefaction process in which only water was used. Toor et al. [49] converted *Nannochloropsis salina* into biocrude using acetone as the extraction agent. Unlike Duan [46] and Biller et al. [48], the authors obtained biocrude at 350 °C for 30 min with a significantly low nitrogen content of 2.75%. This low nitrogen content might be attributed to the algae biomass whose nitrogen content was 2.9%. A fast liquefaction of *Nannochloropsis* was performed by Faeth et al. [50] who achieved a high biocrude yield of 66% for a 1-min reaction duration at a 600 °C set-point temperature. Unfortunately, this biocrude had a high nitrogen content (6.92%) and a low HHV (34.51 MJ/kg) due to its short reaction time. In the preparation process, large molecules were fully broken into small molecules, which required a longer processing time, and amino acids were converted into ammonia or water soluble compounds.

In many types of *Chlorellas*, the *Chlorella* sp. may be considered to be a high-lipid and low-protein microalgae (lipid 59.9%, protein 9.3%) under certain conditions, and the biocrude yield produced via HTL with the reducing gas H₂ reached 82.9% [56]. The HHV and nitrogen contents of biocrude by this process are 34.9 MJ/kg and 0.3%, respectively. Such a high yield may be attributed to the 220 °C reaction temperature since carbonization and coking were dominant at 300 °C during the HTL of *Chlorellas*, due to their higher lipid content and the more rapid hydrolysis process. Polymerization reactions are more active at higher temperatures [57]. The low biocrude nitrogen content could mainly be attributed to the low nitrogen content (1.9%) of the algae itself and the longer reaction time (90 min). Under these conditions, organic

nitrogen compounds can be fully transferred to a water phase or converted into gas products such as NH₃ or HCN [33].

Ross et al. [58] studied the HTL of *Chlorella vulgaris* with alkali and organic acids as catalysts. They produced biocrude with a higher yield, a higher HHV, and a lower nitrogen content using alkali catalysts instead of organic acid at high temperature. Biller et al. [48] also studied this process using metal catalysts that included Co/Mo, Pt, and Ni, which would imply that all the catalysts could significantly promote the reduction of biocrude's nitrogen content, especially Ni. Zhang et al. [28] also liquefied the same microalgae strain using ethanol as a solvent with heterogeneous catalysts. The lowest biocrude nitrogen content of 8.7% was achieved at 300 °C for 30 min in a hydrogen atmosphere. The big difference in nitrogen content achieved by Ross et al. [58] might be due to the fact that nitrogen could be removed more effectively as ammonia in water rather than in ethanol. Moreover, the higher biocrude yield may be attributed to the reaction of the algae biomass with ethanol.

Compared with *Nannochloropsis*, *Chlorella* is also an important raw material for the production of biocrude [59]. Chakraborty et al. [39, 60] developed a unique sequential hydrothermal treatment process for the extraction of polysaccharides from the green alga *Chlorella sorokiniana*, and the liquefaction of the extracted biomass to obtain biocrude. Interestingly, this biocrude had a very low nitrogen content of 0.78%, which is related to the low nitrogen content of the algae biomass (see Table 3). Jazrawi et al. [61] liquefied *Chlorella* at a continuous pilot-scale plant and obtained a maximum biocrude yield of 41.7% at 350 °C for 3 min. The nitrogen content and HHV of the biocrude were 7.7% and 33.8 MJ/kg, respectively. As with the results by Faeth et al. [50], the short retention time of this process possibly increased the biocrude nitrogen content due to the fact that transferring organic

Table 2 Summary of optimal experimental conditions and results of upgrading of algae

Algae type	Conditions				Biocrude yield (%)	Nitrogen content (%)	HHV (MJ/kg)	References
	Temperature (°C)	Residence time (min)	Catalyst type	Extractant				
<i>Nannochloropsis</i>	400	240	Pt/C	DCM	NR	2.24	43.0	[78]
	400	240	Pt/C	DCM	83	3.67	43.51	[79]
	530	360	Pt/C	DCM	NR	1.50	39.70	[80]
	400	240	HZSM-5	DCM	75	1.69	43.4	[81]
<i>Chlorella</i>	400	60	Pt/ γ -Al ₂ O ₃	DCM	79.8	4.7	33.0	[83]
	400	240	Ru/C + Ni	DCM	77.2	2.0	45.3	[86]
	400	240	Ru/ C + Mo ₂ C	DCM	51.5	2.87	43.30	[84]
	400	240	Ru/ C + Mo ₂ C	DCM	77.2	3.1	46.8	[85]

NR not reported

Table 3 Typical compositions of four most investigated algae strains

Algae	Elemental composition (%)					Biochemical composition (%)			References
	C	H	O	N	S	Carbohydrate	Lipid	Protein	
<i>Nannochloropsis</i>	43.3	6.0	25.1	6.4	0.5	12	28	52	[45–47]
	57.8	8	25.7	8.6	ND	8	32	57	[42, 48]
	55.16	6.87	33.97	2.73	1.27	33	12	37	[49]
	43.7	7.7	29.1	7.5	0.67	27.2	14.1	52.4	[56]
<i>Chlorella</i>	52.6	7.1	32.2	8.2	0.5	9	25	55	[42, 48]
	51.4	6.6	30.9	11.1	NR	22	0.1	71.3	[28, 38, 59]
	60.5	10.2	9.5	1.9	0.95	25.9	59.9	9.3	[56]
	50.4	7.9	37.4	2.9	0.2	45.6	24.7	16.8	[39, 60]
<i>Spirulina</i>	53.5	7.4	27.6	11.0	0.5	25	4	60	[61]
	45.2	6.4	37.8	9.8	0.80	20	5	64	[62, 63]
	42.96	8.49	39.19	8.87	0.49	22.4	8.2	69.4	[29, 57]
	42.26	5.86	47.26	3.47	1.15	19	6	60	[49]
<i>Dunaliella</i>	53.7	7.7	25.9	12.1	0.6	11	8	68	[61]
	39.0	5.4	53.0	2	0.6	21.7	2.9	61.3	[66, 68]

ND not detected, NR not reported

nitrogen into the aqueous phase as ammonia required a longer time.

Ross et al. [58] converted *Spirulina* to biocrude using alkali and organic acids. The biocrude yield followed the trend of sodium carbonate > acetic acid > potassium hydroxide > formic acid. In addition to Ross, other researchers have studied the liquefaction of *Spirulina* [29, 57, 61–65]. The results from Huang et al. [29] proved that the addition of FeS was helpful in improving its yield and reducing the nitrogen content. Jazrawi et al. [61] implemented this liquefaction process at a continuous pilot-scale plant, and obtained a low biocrude yield with a nitrogen content of 3.3% and an HHV of 30.7 MJ/kg at a low reaction temperature of 250 °C. These results indicate that most of the protein in the algae biomass might not be

converted into biocrude. Yuan et al. [57] performed this experiment using different organic solvents. Compared with 1,4-dioxane, liquefaction in alcohols produced higher biocrude yields for the same reason as that in Zhang et al. [28]. Also, the use of methanol resulted in the lowest nitrogen content of 7.46% and the highest HHV of 39.83 MJ/kg when compared with those of ethanol and 1,4-dioxane. The reduction of nitrogen fractions in biocrude was probably attributable to deamination reactions during liquefaction of the biomass, whereby methanol could act as a hydrogen-donor solvent and promote the formation of hydrogen-free radical and HDN reactions.

Zou et al. [66–68] converted *Dunaliella tertiolecta* into biocrude using a sodium carbonate catalyst. The authors found that the yield and nitrogen content of biocrude

declined with the addition of the catalyst, while the HHV of the biocrude increased. Chen et al. [69] liquefied *Dunaliella tertiolecta* in an ethanol–water mixture, and reported that a maximum biocrude yield of 64.68% was achieved at 320 °C for 30 min with a 40% (v/v) ethanol solution. This biocrude contained 5.35% nitrogen, which is only a little higher than that in water.

Other algae strains have also been liquefied into biocrude [30, 34, 51, 53, 70–76]. Zhou et al. [72] used sodium carbonate as a catalyst to liquefy *Enteromorpha prolifera* into biocrude and obtained 5.76% nitrogen content at 300 °C for 30 min with a 5% catalyst solution. In contrast to Zou [68], the biocrude yield increased with the addition of the catalyst. Zhou et al. [30] also performed this same liquefaction experiment in methanol and ethanol and produced biocrude with a high nitrogen content of 7.71%, which was later interpreted by Zhang et al. [28] and Chen et al. [69]. Compared with defatted *Scenedesmus* [63], biocrude with a higher yield and lower nitrogen content could be produced via the liquefaction of raw algae. Moreover, through a series of chemical processes such as transesterification, defatted algae was converted to green biodiesel. The shorter processing time, higher temperature, and sodium carbonate catalyst increased the biocrude yield from *Microcystis viridis* [73]. *Sargassum patens* [74] have also been liquefied into biocrude, yielding a nitrogen content of 2.45% under optimal conditions. This low nitrogen content was associated with an algae biomass whose nitrogen content was low. Torri et al. [34, 75] converted *Desmodesmus* into biocrude with a nitrogen content of 6.3% at a 375 °C reaction temperature and 5-min reaction time. For *Laminaria saccharina* [76], increasing the potassium hydroxide catalyst loading decreased the biocrude yield and nitrogen content, while a high temperature increased the biocrude yield and the

HHV, as well as decreased the nitrogen content. In addition, as revealed by mass spectrometry (MS) analysis [52, 55, 56], biocrude was obtained by the HTL of algae comprising thousands of compounds, for which it is difficult to efficiently control denitrogenation.

Upgrading Algae Biocrude

Raw biocrude has a high nitrogen content that must be reduced to meet transportation fuel standards. Recently, Cole et al. [77] systematically investigated the hydrothermal upgrading of *Oedogonium*. The results of this study represents a major breakthrough in the field of algal biocrude, with its emphasis on reducing the nitrogen content of the algal biomass and at each step of the production process, as shown in Fig. 2. With the addition of 10 wt% heptane, non-polar biocrude components selectively accumulate in the organic phase with the result being that the biocrude (after separation from the co-solvent) has a much lower nitrogen content (up to 50% less) than polar biocrude, which remains in the aqueous phase. After a series of operations including vacuum distillation, mixing with feed green and catalytic hydrotreating, the macroalgae can be converted to a renewable, high-quality liquid hydrocarbon fuel.

Other publications addressed the upgrading of HTL biocrude [78–87]. Duan and Savage [78, 79] conducted catalytic upgrading of crude biocrude that had been produced via the HTL of *Nannochloropsis* under various conditions. The authors realized a maximum upgraded yield of 83% at 400 °C for 240 min with a 20% Pt/C catalyst. However, this upgraded biocrude still contained a high nitrogen content of 3.68%. They also found that the transfer of nitrogen as ammonia into the aqueous phase was enhanced in a high-pressure hydrogen atmosphere. The

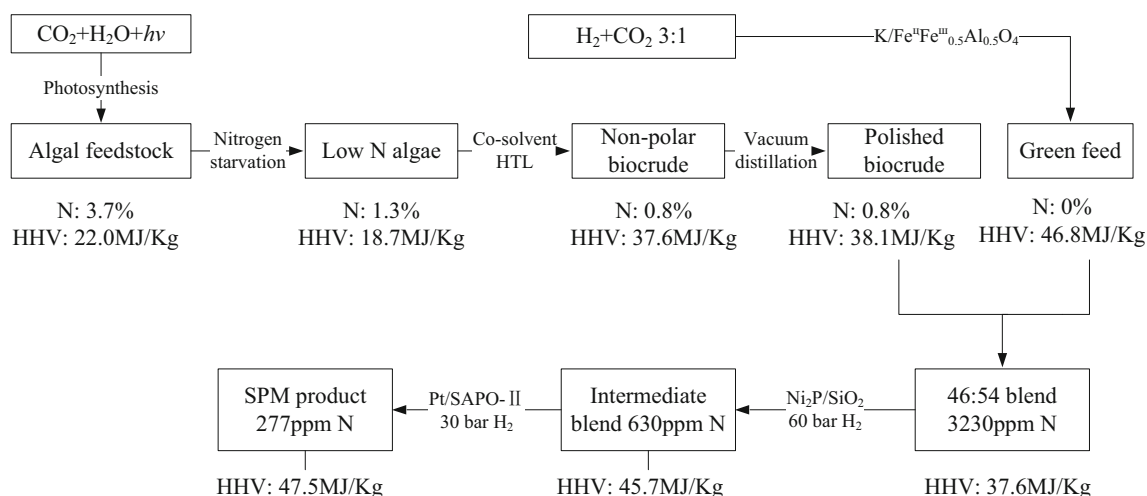


Fig. 2 Overview of each step in the conversion of *Oedogonium* into high-quality fuel [77]

nitrogen content decreased as the amount of catalyst increased. In another paper by the same authors [80], upgraded biocrude with the lowest nitrogen content of 1.50% was achieved at 530 °C for 360 min with a 10% Pt/C catalyst. Catalytic hydrotreatment was also effectively applied for the HDN of biocrude produced by the HTL of *Nannochloropsis* algae [88]. This upgrade process reduced the 4% nitrogen content to <0.25%. The effective reduction of nitrogen is particularly interesting as the level of nitrogen is much higher by this process than by typical petroleum hydrotreatment.

Li and Savage [81] carried out a similar upgrading process with an HZSM-5 catalyst in high-pressure hydrogen, and reported the production of upgraded biocrude with 1.69% nitrogen and 43.4 MJ/kg HHV. In addition, the investigation conducted by Patel et al. [82] demonstrated that denitrogenation can be achieved rapidly (in seconds) during the upgrading of algae paste, but requires more extreme reaction conditions.

Duan et al. [83] studied the upgrading of crude biocrude derived from *Chlorella pyrenoidosa* with a platinum catalyst supported on γ -Al₂O₃, which produced a maximum upgraded biocrude yield of 79.8% with a nitrogen content of 4.7%. This maximum yield might be caused by the reaction between the crude biocrude and formic acid. In general, the nitrogen content in biocrude decreased after upgrading, but this reduced nitrogen content is still above the required threshold of transportation fuel. In another paper [84], the authors compared different biocrude production methods from *Chlorella pyrenoidosa*, including HTL, Al (alcoholysis), Py (pyrolysis), and HPy (hydrolysis), and the catalytic hydrothermal upgrading of crude biocrude produced by these four conversion routes. Upgraded biocrude was obtained at 400 °C for 4 h with a 10 wt% (Ru/C + Mo₂/C) catalyst. The results showed that the nitrogen content was reduced from 7.05 to 2.87% by upgrading and the HHV increased to 43.30 from 37.42 MJ/kg, which further confirms that the properties of biocrude are seriously influenced by the reaction routes. Xu et al. [85] investigated the catalytic upgrading of pretreated algal biocrude with two-component catalysts and obtained a maximum upgraded biocrude of 77.2% with an HHV of 46.8 MJ/kg with Ru/C + Mo₂C. However, the nitrogen content of this upgraded biocrude was highest at 3.1%. Interestingly, the best denitrogenation result was achieved using the residue as the catalyst after upgrading. Bai et al. [86] developed a two-step process to upgrade the same crude biocrude. First, they pretreated the crude biocrude at 350 °C for 240 min in a hydrogen atmosphere and then upgraded the pretreated biocrude at 400 °C with various catalysts. The results showed that pretreatment can decrease the nitrogen content from 8.0% in crude biocrude to 4.1% in pretreated biocrude, and Raney-Ni generated the

best denitrogenation performance. The report showed that both Ru/C and Raney-Ni combined with upgraded biocrude can obtain good denitrogenation results, with a maximum biocrude yield of 77.2%, nitrogen content of 2.0%, and HHV of 45.3 MJ/kg, which could be attributed to the bimetallic synergy effect.

Summary

Previous studies have indicated that algae strains and liquefaction conditions can affect the properties of biocrude. As yet, the extent to which the nitrogen content of biocrude is related to algae types is open to question. Therefore, understanding protein behavior and its contribution to the properties of biocrude is vital, as algal biomasses having similar biochemical compositions give different product yields. Liquefaction with water generates nitrogen in the form of ammonia transferred to the aqueous phase, and liquefaction with alcohol can improve biocrude yield due to the reaction between alcohol and the biomass. However, it is difficult for liquefaction with alcohol to reduce the nitrogen content in biocrude. The limited residence time may increase biocrude's nitrogen content because transferring organic nitrogen into the aqueous phase likely requires a much longer time. In addition, a high liquefaction temperature can convert more proteins into biocrude, which also results in high-energy consumption problems and high biocrude nitrogen content. In conclusion, developing appropriate methods to improve biocrude yield and its characteristics is particularly important.

To improve the quality of biocrude, one route has received much attention and has been widely used in this field—catalytic hydrotreatment processing with homogeneous catalysts such as alkali catalysts or organic acids, and heterogeneous catalysts such as zeolite or supported metal catalysts. Some previous attempts to upgrade biocrude have shown only limited success, and the direct use of upgraded biocrude as transportation fuel remains unacceptable due to the significant amount of nitrogen oxides that would be released to the environment during combustion, thus causing air pollution. As such, the denitrogenation of algae biocrude requires further research.

Removal of Nitrogen from Biocrude

To produce a nitrogen-depleted biomass of *Oedogonium* for conversion to biocrude through HTL, the biomass was cultured in dechlorinated water without the addition of nutrients for seven days [77], as shown in Fig. 2. Research has shown that biomass nitrogen content was significantly reduced using the method of nutrient starvation. Such reduction is especially attractive because it is achieved

without the need for additional chemicals or complex processes. Nutrient starvation was also studied by Neveux et al. [89], which led to a reduction in the nitrogen content of 51–59%. The authors also analyzed the effect of washing the biomass on the quality and quantity of biocrude produced. Experimental results show that nutrient starvation of the cultures and washing of the biomass, either individually or combined, significantly affected the quality of the macroalgal feedstocks, and consequently, improved the quality of biocrude. Unfortunately, the yield and HHV of this biocrude is reduced by the lack of nutrients. While these pathways have a long way to go before producing satisfactory results, successful denitrogenation methods in the chemical engineering field may be forthcoming. Methods currently being explored include the adsorptive and extractive denitrogenations of fossil fuel and the HDN of the main nitrogen compounds, which are summarized in Table 4. These main compounds comprise aliphatic and cyclic compounds, including amides, nitriles, indoles, pyridines, pyrroles, pyrrolidines, pyrrolidinones, piperidines, carbazoles, pyrazines, and quinoline.

HDN of Main Nitrogen Compounds in Biocrude

Small-molecule aliphatic nitrogen compounds can be dissolved in water, while the remaining macromolecules remain in the biocrude. For these compounds, such as palmitamide, hexadecanenitrile and stearonitrile, HDN is an effectual means for converting them into hydrocarbons [90–92]. However, the rupture of C–N bond-breaking rings is very difficult to achieve in aromatic nitrogen compounds even under drastic conditions. Therefore, we investigated the HDN of these compounds with various catalysts, focusing primarily on the HDN of quinoline, which we selected as the model compound.

It is well documented that some phosphides exhibit catalytic activity in the HDN of quinoline, such as Ni₂P [93, 94], MoP [95], and Ni-rich bimetallic phosphides [96, 97], which were typically modified with a metallic oxide, such as TiO₂ and CeO₂. HDN is performed at high temperatures and high pressures with these catalysts and an abundance of the desired product propylcyclohexane has been produced. Unfortunately, some nitrogen compounds, like tetrahydroquinoline, have also appeared giving rise to further denitrogenation requirements.

Metallic oxides like MoO₃ and NiO [98, 99] have been used to catalyze the HDN of quinoline, and MoO₃ exhibited a synergetic effect with NiO in this process. In contrast to phosphides, the abundant product was propylbenzene, but some quinoline hydrides were retained in the hydrocarbons. The HDN of quinoline was also conducted with Pt/NaY and PtMo/NaY catalysts [100], but only about 35% of the quinoline was converted, and

propylcyclohexane and propylbenzene were produced with both catalysts.

Phosphide WP was employed in the HDN of pyridine [101]. Regrettably, not only was the conversion lower than 20%, but it also produced a great quantity of piperidine in the process. We can infer that phosphide shows better catalytic activity in the HDN of quinoline than pyridine although pentane was produced with a selectivity of 37.1% via the latter's HDN. Hydrothermal HDN of pyridine was performed using various catalysts [102], and we found Pt/ γ -Al₂O₃ to be the most active catalyst, achieving almost complete conversion under proper conditions. In these tests, its major products were butane and pentane as well as small amounts of methane, ethane, and propane. Deng et al. [103] reported the HDN pathway of pyridine with MoP (0 1 0), that is, the route pyridine → 4-monohydropyridine → 3,4-dihydropyridine → 1,3,4-trihydropyridine → 1,3,4,5-tetrahydropyridine → CH(CH₂)₃CHNH, followed by C–N bond rupture, and then NH₃ generation.

The HDN of piperidines was studied with Ni₂P/SiO₂ and Ni–Mo–S/Al₂O₃ catalysts [104], which yielded main products of hexane and 2-hexene. A high conversion of piperidines also appeared at high temperature with both catalysts. Given the piperidine produced from the HDN of pyridine with the WP catalyst, the combination of WP and Ni₂P catalysts might yield better performance in the HDN of pyridine.

The HDN of carbazole was performed with the phosphides Ni_{0.07}MoP [105] and NiB alloy [106], whose main product was bicyclohexane. The HDN of carbazole and light gas oil with supported Ni_xMoP catalysts were also investigated [107], and we found the highest conversion rate of carbazole and highest selectivity of bicyclohexane were obtained with Ni_{0.3}MoP/Al₂O₃, as well as the highest activity for the HDN of light gas oil.

This method consumes large amounts of hydrogen, and to achieve an ideal denitrification effect, in-depth hydrogenation is required, which leads to harsh reaction conditions (2.0–5.0 MPa, 300–500 °C) [108]. The input–output ratio of the energy production process greatly increases if we take into account the investment made in the purchase of hydrogen or hydrogen production and the energy consumption of the high-pressure reaction. Thus, finding new methods to achieve non-hydrogenation C–N bond rupture is important.

Adsorptive and Extractive Denitrogenations of Biocrude

In comparison to HDN, adsorptive and extractive denitrogenations have been researched extensively for the desulfurization and denitrogenation of petroleum to derive transportation fuel. There have been a number of recent

Table 4 Main nitrogen compounds produced from HTL of algae

Type	Compound	Chemical formula	References
Amides	Palmitamide	C ₁₆ H ₃₃ NO	[45–47]
Nitriles	Hexadecanenitrile	C ₁₆ H ₃₁ N	[28, 29]
	Stearonitrile	C ₁₈ H ₃₅ N	[57]
	2,4,6-Trimethyl-benzonitrile	C ₁₀ H ₁₁ N	[57, 62]
Indoles	Indole	C ₈ H ₇ N	[45, 46]
	1-Methyl-indole	C ₉ H ₉ N	[58]
	2-Methyl-indole	C ₉ H ₉ N	[72]
	3-Methyl-indole	C ₉ H ₉ N	[57]
	6-Methyl-indole	C ₉ H ₉ N	[46]
	7-Methyl-indole	C ₉ H ₉ N	[45]
	5,7-Dimethyl-indole	C ₁₀ H ₁₁ N	[57]
	5,6,7-Trimethyl-indole	C ₁₁ H ₁₃ N	[57, 74]
	2,3,7-Trimethyl-indole	C ₁₁ H ₁₃ N	[74]
Pyridines	5-Ethyl-2-methyl-pyridine	C ₈ H ₁₁ N	[57]
Pyrroles	1-Methyl-pyrrole	C ₅ H ₇ N	[47]
	1-Ethyl-pyrrole	C ₆ H ₉ N	[47]
	2,5-Dimethylpyrrole	C ₆ H ₉ N	[47]
	3-Ethyl-5-methylpyrrole	C ₇ H ₁₁ N	[29]
	2-Ethyl-3,5-dimethylpyrrole	C ₈ H ₁₃ N	[57]
	3-Ethyl-2,4,5-trimethylpyrrole	C ₉ H ₁₅ N	[28]
Pyrrolidines	1-Butyl-pyrrolidine	C ₈ H ₁₇ N	[58]
	1-Stearoyl-pyrrolidine	C ₂₂ H ₄₁ N	[67, 68]
	1-Ethyl-2-pyrrolidinone	C ₆ H ₁₁ NO	[45, 46]
	1-Butyl-2-pyrrolidinone	C ₈ H ₁₅ NO	[58]
	1-Propyl-2,5-pyrrolidinedione	C ₇ H ₁₁ NO ₂	[62]
Piperidines	1-Methyl-piperidine	C ₆ H ₁₃ N	[46]
	1-Pentyl-piperidine	C ₁₀ H ₂₁ N	[58]
	Piperidine-2,5-dione	C ₅ H ₇ NO ₂	[58]
	2,2,6,6-Tetramethyl-4-piperidone	C ₉ H ₁₅ NO ₃	[28]
Carbazoles	Carbazole	C ₁₂ H ₉ N	[45]
Pyrazines	2-Methylpyrazine	C ₅ H ₆ N ₂	[30]
	2,5-Dimethylpyrazine	C ₆ H ₈ N ₂	[72]
	3-Ethyl-2,5-dimethylpyrazine	C ₈ H ₁₂ N ₂	[72]
Quinolines	Quinoline	C ₉ H ₇ N	[45, 72]
	4-Methylquinoline	C ₁₀ H ₉ N	[72]

studies on the denitrogenation of model fuel [109–111] and light cycle oil [112, 113]. Unlike HDN, adsorptive and extractive denitrogenations have been mainly employed to remove aromatic nitrogen compounds.

The silica–zirconia co-gel adsorbent was shown to have a high capacity for selectively adsorbing nitrogen compounds from light gas oil at mild temperature and ambient pressure [114]. Moreover, the adsorption capacity of the adsorbent can be more fully recovered by regeneration carried out in methyl isobutyl ketone and methyl tertiary butyl ether.

Lithium-modified mesoporous silica adsorbent displayed a very strong adsorption affinity for nitrogen

compounds [115] and about 40% of the nitrogen compounds were removed under appropriate conditions. The adsorbent can be easily regenerated using methyl isobutyl ketone at a roughly constant readsorption capacity.

Heterogeneous cross-linking was also reported [116], in which the macroporous polymer poly (glycidyl methacrylate) was employed as the hydrophilic support coupled with tetranitrofluorenone to selectively remove neutral nitrogen compounds from heavy gas oil, and 6.7% of the nitrogen species were successfully removed. Reuse of this polymer showed consistency in the selective removal of nitrogen compounds, with a continuous and unchanging removal rate.

Some commercially available ion-exchange resins bearing pyridinium chloride functionality have exhibited much higher adsorptive capacity and selectivity for neutral nitrogen compounds [117]. The nitrogen concentration was greatly reduced in model fuel (dodecane–toluene mixture) and heavy gas oil. Regeneration of this sorbent is easily achieved using polar organic solvents like methanol.

Iron-nanoparticle-modified activated carbon was employed to remove nitrogen compounds (indoline and quinoline) in model diesel (mixture of decane and hexadecane containing sulfur compounds) [118]. This adsorbent demonstrates better affinity for indoline than quinoline.

Mesoporous molecular sieves (Ti-HMS, HMS, and MCM-41) have shown perfect performance in the adsorptive denitrogenation of model fuel (octane containing pyridine, quinoline, pyrrole, and indole) and commercial diesel [119, 120]. HMS and Ti-HMS exhibited higher adsorbability to indole, whereas MCM-41 showed better affinity with indole and quinoline. The adsorbent is easily regenerated by washing many times with ethanol and its performance may be maintained.

The metal organic framework (MOF) MIL-101 has long been used to remove nitrogen compounds from model fuel [121–123]. Although virgin MOFs have unsatisfactory properties, MOFs modified with ethylenediamine, phosphotungstic acid, or other compounds have exhibited remarkable performance. Modified MOFs, while promoting the adsorption of quinoline, have little influence on the adsorption of indole. In addition, they have exhibited good regenerative capacity when washed with acetone or ethanol, but adsorption capacity declines after a number of regeneration cycles.

Recently, Chen et al. [124] reported an extraction method for removing the nitrogen heterocyclic in algal biocrude using water as a solvent. This method is green, safe, and easily implemented, and the results show that nitrogen content in algal biocrude decreases from 6.83 to 5.75% with improved carbon and hydrogen contents. However, the authors also found that the nitrogen content remained too high to meet the requirements of the transportation fuel. The authors also discussed the potential for extracting protein from algae feedstocks prior to the conversion of the residual biomass to biocrude [125]. This is an interesting option for reducing nitrogen in algae and generating multiple products from a single feedstock.

The extractive denitrogenation of fossil fuel was widely researched using various ionic liquids [126–128]. Aromatic nitrogen compounds were more easily extracted than aromatic hydrocarbons when using ionic liquids. The solubilities of nitrogen compounds vary with the ionic liquids. Water dilution is used to regenerate ionic liquids

and the extraction efficiency after a number of regeneration cycles are nearly identical to those in the first cycle. In another study, researchers prepared supported liquid membranes using ionic liquids to separate organic nitrogen compounds from model fuel (heptane mixtures) at room temperature [129]. These organic nitrogen compounds (quinoline, isoquinoline, and pyridine) were more permeable than heptane, thus resulting in the purification of the fuel.

A new approach is needed to address this problem. For instance, nitrogenous substances that are harmful in biocrude could be used as raw materials for the pharmaceutical industry. Amino acids, as an intermediate product in the HTL of algae, have high commercial value (for use in feed, food, pharmaceuticals, and cosmetics) compared with most other biomass fractions. Some researchers [130, 131] have explored the potential of hydrothermal technologies for extracting amino acids from various protein-rich feedstocks. If the HTL reaction can be controlled, amino acids can be extracted during the process, thus making it possible to not only effectively utilize the protein in algae, but also to reduce the nitrogen content of the biocrude. This process is in the early stages and needs further research.

Summary

To improve the quality of biocrude by achieving lower nitrogen content, the cultivation of algae by starvation has been researched and has achieved tremendous results in reducing the hydrogen requirement for biocrude upgrading into a blendable fuel. Generally, the HDN of the main nitrogen compounds in fossil fuel has been conducted using pure substances and model fuel. Some impressive results have been achieved in appropriate conditions. However, given the complicated composition of biocrude, i.e., unsaturated compounds and moisture, the performance of these catalysts is still unknown with respect to the HDN of biocrude. Investigations are also needed regarding the deactivation properties and reusability of these catalysts.

Adsorptive and extractive denitrogenations have been carried out on biocrude, model oil, and fossil fuel, but mainly to achieve the further denitrogenation of fossil fuel, which contains nitrogen content at ppm levels. Aromatic hydrocarbons can also be adsorbed or extracted by some adsorbents and extraction agents, resulting in reduced biocrude yield. In addition, each nitrogen atom may be linked several or even dozens of times to carbon and hydrogen atoms, so after separation the remnant materials are very limited. Apart from fuel, biocrude can also be treated as feedstock for bulk chemicals. Cracking and catalytic pyrolysis methods were shown to be significant treatments for the utilization of biocrude [132].

Conclusions and Outlook

Based on extensive work in this field, the HTL of algae has been determined to be a very promising process for producing biocrude. Nevertheless, the associated high nitrogen content impedes its widespread adoption in the realm of transportation. Although the upgrading of algae biocrude has made some definite improvements, the direct use of these upgraded biocrudes in transportation remains unacceptable as yet. The HDN of nitrogen compounds retains some hydrogenated hydrocarbon in biocrude, as compared with adsorptive and extractive denitrogenations, while the harsh treatment condition impeded HDN's popularity. Also, the most active catalyst identified for the HDN of model compounds does not appear to have the best performance in denitrifying algal biocrude. Adsorptive and extractive denitrogenations can remove nitrogen compounds; however, their use likely results in a significant loss of biocrude yield. Moreover, adsorptive and extractive denitrogenations are usually performed in ultralow nitrogen content conditions.

In the near future, research attention should be focused on the following issues: (1) the selection of the appropriate catalysts and solvents to better control product distribution and to improve the properties of biocrude. The combination of two catalysts has been shown to perform better than either catalyst alone, which suggests that denitrogenation with two or more catalysts may be a productive avenue for further research; (2) the complex composition of algal biocrude often occurs in the presence of various components of a nitric heterocyclic compound, thus the denitrogenation mechanisms used on several model compounds cannot be used in biocrude in all cases. Therefore, it will be necessary to study dynamic behaviors to reap the desired product; (3) there are some disadvantages to the above-mentioned denitrification methods, such as the high-energy consumption of HDN and the poor selectivity of adsorptive and extractive denitrogenations. An optimal combination of chemical and physical denitrogenations may be more effective in generating biocrude that meets the needs of transport fuels without significantly reducing yield.

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