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Catalytic hydrothermal liquefaction of algae and upgrading of biocrude: A critical review

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ABSTRACT

Over the last two decades, the hydrothermal liquefaction (HTL) of algae has emerged as a promising technology for producing liquid bio-oil to meet increasing energy demands and reduce environmental pollution. In this article, the present research status of the catalytic HTL of algae and the catalytic hydrothermal upgrading of biocrude (crude bio-oil) is systematically reviewed and analyzed. The corresponding catalytic characteristics (such as the catalytic effect on the biocrude yield and quality and the related influencing factors) and catalytic mechanisms (e.g., hydrogenation, deoxygenation, decarboxylation, denitrogenation and desulfurization) during algae HTL as well as the approaches for upgrading of biocrude are summarized and analyzed comprehensively. Another potential technological flow for bio-oil production from algae HTL is proposed, and a comparison between direct catalytic HTL and the two-step production method is presented for the first time. Moreover, contemporary problems and subsequent research directions are presented.

1. Introduction

The development and application of clean renewable energy is important because the excessive consumption of fossil fuels has led to a series of global problems, especially regarding environmental pollution. As a substitute for fossil fuel, liquid biofuel can decrease carbon dioxide emission in its whole life cycle and thus alleviating global warming, and it can also reduce energy import dependence to improve energy security [1–4]. The raw materials for producing liquid biofuels have evolved from food crops to lignocelluloses (straw and trees) and further to algae. The use of food crops and lignocelluloses is restricted because it consumes food, arable land and water resources, whereas algae have the best potential for biofuel production [5–7]. Compared with terrestrial plants, first of all, algae growth is not competitive with water resources and cultivated land for farming [1,8–11]. Second, the photosynthetic efficiency of algae is higher, which leads to a higher growth rate and a greater potential for CO_2 fixation [11,12]. Third, algae possess higher lipid contents, meaning that it has higher biofuel yields. With these advantages, liquid bio-fuel production from algae has been shown to be economically feasible and has become a significantly developed energy source [6].

Hydrothermal liquefaction (HTL) has higher energy recovery efficiency and lower energy consumption rates from processing algae in comparison to gasification and pyrolysis [13–16]. "Algae HTL" refers to the process of converting algae into liquid biocrude at 280–370 °C and 10–25 MPa for 5–120 min in the presence of water, with or without a catalyst [4,17–22]. The process generates four varieties of products simultaneously, including gases, an aqueous phase, biocrude (crude bio-oil) and solids [23–25]. HTL is a promising technology for converting algae into primary liquid biofuel with many advantages. First, it can directly convert wet algae into biocrude and thus avoids extra energy consumption during the drying process [19,26]. Second, the biocrude yield from HTL is higher than those of other methods (e.g., pyrolysis), because not only the lipids but also the proteins and carbohydrates in algae are mostly converted into biocrude [27,28]. Third, the nutrients (e.g., N, P and K) in algae are transformed into the corresponding water-soluble salts or acids in HTL, and they can be reused for algae growth by means of aqueous phase recovery and use [14,19]. Of course, the algae-derived biocrude also has some disadvantages, such as a high water content, high viscosity, high heteroatom content, and difficulty with upgrading.

Presently, the biocrude yield of algae HTL ranges from 24 to 64 wt %, and the higher heating value (HHV) of biocrude is 28–38 MJ/kg [12,13,21,29–32]. The influences of the operating parameters (e.g., the reaction temperature, residence time, reaction pressure, algae loading and extraction solvent) on the algae HTL have been reported extensively [18,29,33–35]. Undoubtedly, the yield and quality of biocrude can be improved to some extent by optimizing these operating

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parameters. However, the contents of heteroatoms (N, S and O) and the HHV of the biocrude directly obtained from algae HTL cannot meet the requirements for liquid biofuel [36]. Thus, the catalytic HTL of algae and the catalytic upgrading of biocrude are being investigated to a considerable extent to improve the yield and quality of biocrude [37–40]. The typical biocrude yield is approximately 40 wt% from algae HTL on a dry ash-free basis, but it can be increased to 50–60 wt% when using a proper catalyst [12]. The catalyst can also able to improve the biocrude HHV and decrease its viscosity and the fractions of N, S, and O. Non-catalytic HTL followed by catalytic upgrading is a very effective method for obtaining high-quality bio-oil [10,36,41,42]. Specifically, the catalyst type is helpful for improving the compound compositions of the upgraded biocrude, and catalyst loading has a great effect on its HHV and O/C ratio [41]. These catalysts can be classified into homogeneous and heterogeneous types. The homogeneous types include alkali compounds (carbonate or hydroxyl roots) [18,21,27,43,44], organic acids [45,46], inorganic acids [47], etc. The heterogeneous types largely involve metals [21], molecular sieves [48], insoluble inorganic salts [49,50] and others.

In this review, the present research status of catalytic algae HTL and the catalytic upgrading of the resulting biocrude are reviewed systematically. The catalytic performances of various catalysts on algae HTL and biocrude upgrading are presented and analyzed, and the catalytic reaction mechanisms of hydrogenation, deoxygenation, denitrogenation and desulfurization are summarized in detail. The characteristics of direct catalytic HTL and the two-step production method are compared, and a potential entire technological flow concerning bio-oil production from algae HTL is proposed, and subsequent research subjects on catalytic algae HTL and biocrude upgrading are recommended. This information is significantly valuable for further research on catalytic algae HTL and for following the catalytic upgrading of biocrude.

2. Catalytic hydrothermal liquefaction of algae

2.1. Catalysis of homogeneous catalyst

Homogeneous catalysts used in the algae HTL are water-soluble at room temperature and primarily include alkali salts (e.g., Na_2CO_3 and KOH) and organic acids (e.g.,CH_3COOH and HCOOH). They usually have positive effects on the liquefaction of algae by improving biocrude yield and reducing solid residue. Typically, Na_2CO_3 is the most frequently used homogeneous catalyst. Table 1 shows the catalytic characteristics of Na_2CO_3 on the biocrude yield of algae HTL. Overall, it can obviously improve the biocrude yield, which may promote the decomposition of carbohydrates [46]. It seems that the optional loading amount of Na_2CO_3 to obtain biocrude yield improvements is 5 wt%, which obtains the highest HHV as well [51]. However, this loading amount inevitably induces a higher pH value in the reaction liquid and a higher recovery cost for reusing the catalyst. Additionally, Na_2CO_3 has a negative effect on biocrude production from lipids and causes an increase in solid residue, because sodium aliphatate is likely to be formed from lipids through a saponification reaction in the presence of Na_2CO_3 and remains in the solid residue [46]. Other reports [26,52] also confirm that alkali catalysts can induce saponification reactions with lipids.

Na_2CO_3 promotes the fractionation of CO_2 probably because it improves the decarboxylation of organic acids or because it reacts with organic acids during HTL [26]. The alkali catalyst significantly reduces the fraction of organic acids, and thus the decarboxylation reaction is not the primary reason for the reduction in organic acids [52]. Therefore, the increased CO_2 fraction should be attributed to the reactions between Na_2CO_3 and organic acids. Moreover, Na_2CO_3 can also able to clearly improve the biocrude quality, which is reflected in the increased HHV and C, H contents and the reduced of the O, N, and S contents [23,26,46,49] through reactions involving denitrogenation, deoxygenation, desulfurization and decarboxylation, etc..

Notably, the catalytic performance of the alkali catalyst is significantly affected by the reaction temperature [45,46]. For example, compared with KOH, Na_2CO_3 leads to higher biocrude yields and quality at 300 °C but a lower biocrude quality at 350 °C [45], suggesting a significant temperature effect on the catalyst performance. The fractions of N and O heterocyclic compounds increased dramatically in the presence of Na_2CO_3 at 240 °C in contrast to the results at 280 °C [52]. A possible explanation is that the alkali catalyst primarily promotes the recombination or repolymerization reaction of organic acids at a relatively low temperature.

The organic acid catalyst decreases the biocrude viscosity and the fraction of high-boiling point compounds, and it increases the gas fraction. This type of catalyst may be decomposed into gases under hydrothermal conditions [45,46]. For example, the use of formic acid and acetic acid induce gas fractions of approximately 30 wt% and 16–22 wt%, respectively [45]. However, compared with the alkali catalyst, the organic acid catalyst is less efficient at removing the S, N and O contents of biocrude [45,46], and in particular the S content of biocrude was doubled [45]. Therefore, the organic acid catalyst seems to be unsuitable for use in algae HTL [21,53]. Ross et al. [45] confirm that the order of catalyst activity in terms of biocrude yield is $Na_2CO_3 > CH_3COOH > KOH > HCOOH$.

Overall Na_2CO_3 is most effective at improving biocrude yield and quality among known homogeneous catalysts. However, homogeneous catalysts based on carbonates, hydroxides and simple carboxylic acids are evaluated to have a low prospect for the hydrothermal conversion of algae, due to their low susceptibility to catalyze decarboxylation of fatty acids, isomerization and aromatization coupled with their non-recyclable nature [54]. The alkali catalyst and acidic catalyst have negative effects on the pH value of liquid products and cause strong corrosion in reaction equipment [55]. The organic acid catalyst has a relatively weak performance with respect to denitrogenation, deoxygenation and desulfurization. Moreover, the homogeneous catalyst is consumed during reactions to some extent and has a high recovery cost, so it is difficult to select its cyclic use [15]. These undesired aspects have brought great difficulty to the future industrial applications of

Table 1
Catalytic characteristics of Na_2CO_3 on the biocrude yield of algae HTL.

Algae	Primary reaction conditions	Biocrude yield	Ref.
Dunaliella tertiolecta	300 °C, 60 min, 5 wt% Na_2CO_3	From 34.3–42.0 wt%	[27]
Microcystis viridis	340 °C, 30 min, 5 wt% Na_2CO_3	From 25.5–33 wt%	[26]
Enteromorpha prolifera	300 °C, 30 min, 5 wt% Na_2CO_3	From 20.4–23.0 wt%	[23]
Dunaliella tertiolecta cake	360 °C, 50 min, 2.5–10 wt% Na_2CO_3	Slight increase	[51]
Porphyridium cruentum		From 21.2–27.1 wt%	[46]
Spirulina	350 °C, 60 min, 1 M base Na_2CO_3	Decrease	
Chlorella vulgaris			
Nannochloropsis oculata			
Spirulina platensis	350 °C, 60 min, 5 wt% Na_2CO_3	From 39.9–51.6 wt%	[49]
Chlorella pyrenoidosa	280 °C, 30 min, 5 wt% Na_2CO_3	From 39.0–44.0 wt%	[52]