Review

A Mini Review on Pyrolysis of Natural Algae for Bio-Fuel and Chemicals

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Abstract: The disposal and use of natural algae have recently been the subject of great interest, due to increasing concern for environmental protection and resource utilization. In this paper, a mini review of recent research on the pyrolysis of natural algae, especially the algae from water blooms, is presented. The chemical compositions of the natural algae are summarized, and the pyrolysis properties of different compositions are reviewed. Non-catalytic, catalytic, and integrated catalytic processes are reviewed. Different ideas and methods for the production of bio-fuel or chemicals are discussed. Apparently, deoxygenation and denitrogenation are highly necessary for algae-based bio-fuel and catalysts play an important role in these processes. In addition, the integrated catalytic process, which involves catalysis and other operation conditions aside from the thermal treatment under inert atmosphere, shows potential for the valorization of algae-based bio-oil. Based on the recent concept and progress, the research gaps are discussed, followed by the challenges and proposals to achieve high-value utilization of the natural algae.

Keywords: bio-based chemicals; bio-fuel; catalysis; natural algae; pyrolysis

1. Introduction

In recent years, many inland waters and oceans have suffered from water blooms, which cause damage to the environment and can even jeopardize the safety of drinking water. For example, about two thirds of the lakes in China suffer from eutrophication and about one third of them are at severe or extreme eutrophication levels [1]. Consequently, large-area water bloom algae have appeared frequently, typically in main freshwater lakes, such as Taihu, Chaohu, and Dianchi Lakes. Ecological, physical, and chemical methods have been used to eliminate the natural algae. However, there is no effective technology yet to dispose of natural algae, including their collection and conversion into harmless substances. Meanwhile, increasing concern over the growing global energy demand and the lack of fossil fuel resources has promoted the utilization of bio-based resources as a substitution.

It is believed that a suitable and reasonable concept for the disposal of natural algae is to regard them as a resource, not just a burden. Effects should be taken to transform the "secondary pollution" caused by water bloom algae into the "secondary utilization" of them [2,3]. Thus, the resource potential of water bloom algae can be released, which not only protects the environment, but also increases the amount of resources [4,5].

Because of their high lipid content and high productivity with short growth cycle, natural algae are an attractive precursor for third-generation biofuel [6,7]. As a renewable energy, bio-fuels have been commonly used in modern society. The demand for bio-fuels is increasing due to high oil prices, government policies, as well as advancing technologies. Bio-fuels have significant advantages over conventional fuels in terms of their renewability and low greenhouse gas emissions [8]. Under the stimulus of targets for "carbon peaking

and carbon neutrality" proposed by China in 2020, the development of bio-fuels is receiving more and more attention and is expected to achieve better development.

Thermo-chemical conversion technology can be used to obtain energy or matter by thermal decomposition of the organics in natural algae with low or high contents of lipids. The process of conversion mainly includes direct combustion [9], gasification [10], liquefaction [11], and pyrolysis [9,12]. Although thermo-chemical conversion technology is considered more suitable and widely used for the first-generation and second-generation of lignocellulose raw material processing, it is also applied to deal with dry and wet algae. When applied this way, pyrolysis is generally conducted in anaerobic or anoxic conditions, in which natural algae is decomposed under high temperature to generate gases and volatiles. The condensable component eventually condenses into liquid state and is collected, and is generally referred to as bio-oil. Compared to algae-based biodiesel produced by the transesterification of extracted lipids and butanol/bio-ethanol obtained by enzymatic saccharification, pyrolysis can directly convert algae into liquid, char, and gas without any pro-processing [13]. Moreover, all of the pyrolysis products have terminal applications (Figure 1): bio-oil can be used as automotive fuel after further refinery; bio-gas, which consists of many combustible substances, can be used to generate heat and power; and bio-char, which contains a considerable amount of C and N with porous structure, can be used as an adsorbent or fertilizer [14].
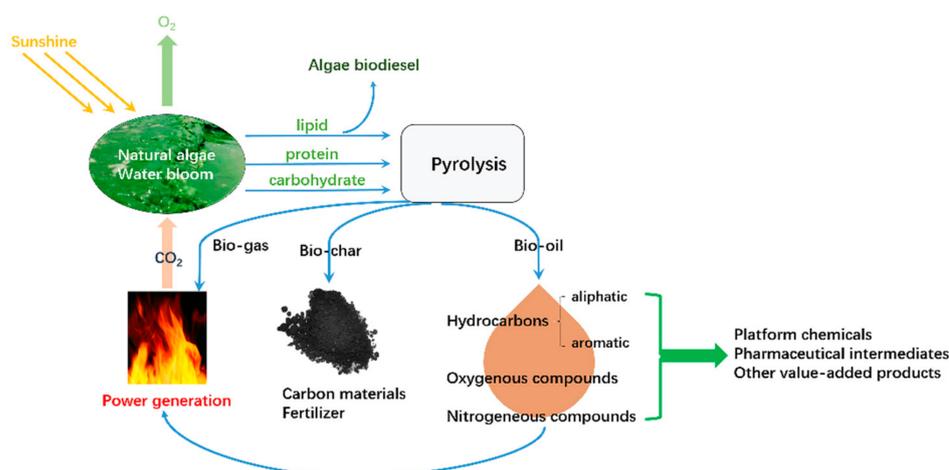

Figure 1. Pyrolysis of natural algae for valuable products.

Dehydration, cracking, polymerization, carbonation, rearrangement, and other complex reactions occur during the pyrolysis process. The bio-oils derived from the pyrolysis of algae contain large amounts of organic compounds, which usually can be catalogued into hydrocarbons (aliphatic and aromatic), and oxygenous and nitrogen-containing compounds [15]. Although the algae-based bio-oil is suitable as fuel in view of its elementary composition, the content of the oxygenous compounds may lead to the high acidity, corrosion, high viscosity and relatively lower high heat value (HHV) [16]. What is worse, unlike bio-oil derived from lignocellulosic biomass, the bio-oil obtained by algae, especially from high nitrogen-content species, contains 5–10% nitrogen, which may contaminate catalysts in the pyrolysis or refining process and produce NO_x during combustion [17]. To solve some of these problems, several studies have been devoted to reducing the oxygenous or nitrogenous compounds in algae-based bio-oil by using a catalytic process and optimizing the process parameters [18–20]. Taking a different perspective, some researchers take the advantages of the high nitrogen content and hope to obtain some value-added chemicals from the bio-oil. They suggest the idea that the pyrolytic bio-oil obtained from algae could be treated as feedstock to obtain platform chemicals though further treatment, rather than simply treated as fuel [21–23].

Considering the fact that algae blooms do damage water ecology and can be deposed by pyrolysis for some useful products, efficient conversion of algae is desirable. With the aforementioned description, this review is presented with the aim of providing a brief framework for the pyrolysis of natural algae to obtain future bio-fuels and value-added chemicals. Detailed descriptions and brief discussions are presented regarding the methods involved in the pyrolysis of algae, in association with their opportunities and challenges. The focus of this review is to summarize and discuss the technology for a more efficient and economic pyrolysis process for natural algae, and to provide recommendations for future work.

2. Chemical Composition of the Natural Algae

Natural algae, typically bloom-forming algae, are microorganisms that live in fresh and salt water. They usually proliferate and bloom in warm, stagnant, nutrient-rich waters. The compositions of some bloom-forming algae from water blooms are presented in Table 1. Although the bloom-forming algae are a mixture of algae, whose biological composition differs, their chemical composition is similar, mainly lipid, protein, and carbohydrate [11,24,25]. As a kind of algae grown in natural environments, bloom-forming algae contain relatively lower amounts of carbohydrates and lipids, but are rich in proteins. As a result, their nitrogen content was much higher than that in some lignocellulosic feedstock, especially those collected in the Chinese mainland. As a fuel, the bloom-forming algae contain a considerable amount of C and H of ~40% and ~6%, however, the relatively higher content of oxygen and nitrogen leads to the low HHV (<20 MJ/kg).

Table 1. Compositions of bloom-forming algae from water blooms [1].

Proximate Analysis (wt %)				Ultimate Analysis (wt %)					HHV [2] (MJ/kg)	Chemical Composition (wt %)			Source of the Algae	Reference
M_{ad}	A_{ad}	V_{ad}	FC_{ad}	C	H	O	N	S		Lipid	Protein	Carbohydrate		
3.38	5.62	75.04	15.96	46.37	6.73	37.39	8.71	0.8	19.77	5.12	60.02	21.08	Dianchi Lake, China	[11]
2.5	12.9	- [3]	-	43.7	6.4	28.9	8.1	-	18.3	8.4	28.9	15.4	Taihu Lake, China	[24]
9.78	12.12	53.94	24.16	42.26	6.27	43.07	7.88	0.52	16.0	-	-	-	Dianchi Lake, China	[26]
11.2	16.5	75.5	8.0	38.1	5.9	51.8	4.2	-	-	-	-	-	Puan shallow Lake, Argentina	[15]
3.5	28.2	-	-	43.3	6.2	-	8.7	-	18.3	13.6	-	16.0	Taihu Lake, China	[27]
2.4	25.7	55.6	16.3	37.3	5.8	26.2	4.2	-	15.6	1.39	29.9	13.25	Lake Erie, USA [4]	[25]
5.91	13.3	64.1	16.7	38.9	6.1	38.1	2.7	-	15.8	5.8	24.6	24.8		

[1] Based on dry powder. [2] Calculated value based on ultimate analysis. [3] "-" represents not provided in the ref. [4] Algae species collected from two distinct blooms.

Generally, protein, whose basic structural units are amino acids, is the most common form of most nitrogen in the algae. During the pyrolysis process, the nitrogen in protein may crack and transform into pyrrolic, quaternary, and pyridinic forms through such reactions as dehydrogenation, deamination, cyclization, dehydration, and dimerization [28]. This means most of the nitrogen remains in the bio-oil obtained [29]. In addition, although pyrolysis can improve the chemical composition to a certain extent, thus obtaining a higher HHV, the HHV still lags behind that of commercial fuels (e.g. heavy fuel oil).

For the pyrolysis of algae, the realities that we have to face are: on one hand, the natural properties of the bloom-forming algae make it a suitable and promising raw material for pyrolytic bio-oil. On the other hand, the high N content, which leads to the high NO_x emission, may limit the downstream application of the bio-fuel obtained and needs to be improved continuously. The organic nitrogenous compounds have to be removed to be used as fuel. However, because the organic nitrogenous compounds do contain certain amounts of high value-added products, the upgrading process leads to the inefficient use of nitrogen elements and the poor atomic economy.

3. Pyrolysis Process of Natural Algae

3.1. Non-Catalytic Pyrolysis Process

Because of its relatively higher efficiency and lower energy consumption compared to other processes, pyrolysis is considered as an economical method for converting algae to fuel [17,30]. Li et al. [12] found that the main components in algae decomposed sequentially: first carbohydrates, then proteins and finally lipids. Thermogravimetry analysis and differential thermogravimetry analysis (TG/DTG) results from Taihu Lake cyanobacteria obtained by Zhou et al. [31] indicated that the degradation mainly occurs at four temperature stages: room temperature to ~170 °C, ~170 to ~310 °C, ~310 to ~550 °C, and 550 to 800 °C. The weight loss of each stage are 6.7%, 23.7%, 32%, and 3.4%, respectively, with a solid residue of 34.3 %. The TG/DTG of blue-green algae blooms results obtained by Hu et al. [32,33] indicated that the pyrolysis process mainly has three stages according to the temperature. Moreover, the decomposition mainly occurs in the temperature range of 160–400 °C.

Based on the differences in heating rate and residence time, slow and fast pyrolysis are briefly classified for pyrolysis process. Generally, fast pyrolysis obtains higher oil yields than slow pyrolysis process since the high heating rate associated with short residence time prevents the secondary reactions and minimizes the formation of char. Generally, for the aim of maximizing the yield of liquid products or bio-oil, a relatively lower temperature andhigher heating rate as well as short gas residence time are preferred [34,35]. Unlike lignocellulosic biomass, the high content of lipids and proteins make the process and the preferred operation parameters for the pyrolysis of algae different [25]. It is recognized that primary and secondary reactions occur when algae are heated. First, the organic macromolecules in algae are fractured to form primary pyrolysis products and intermediates. Then the intermediates are further involved in the secondary reaction. The primary reactions mainly include dehydration and carbonization, while the secondary reactions are mainly the further decomposition and volatilization of intermediates.

3.1.1. Effects of Pyrolysis Temperature

Generally, a moderate temperature range of 400–550 °C leads to the highest yield of bio-oil. Once beyond this temperature range, the secondary cracking reaction intensifies, and the bio-oil and char are converted into gaseous products. In addition, decarboxylation and dehydration reactions increase when temperatures of >700 °C are used, therefore, the content of polycyclic aromatic hydrocarbons (PAHs) in the bio-oil increases, such as pyrene and phenanthrene.

Li et al. [36] presented a pyrolysis study of algae from lake blooms using a horizontal tubular reactor. The results showed that 500 °C was the optimum pyrolysis temperature, at which the maximum yield of 59% for the bio-oil was achieved. Compared to the pyrolysis of pine sawdust under the same conditions, the yields were similar, while the HHV obtained by algae was higher (21 vs. 18 MJ/kg). However, the bio-oil obtained from algae contains 26.8 times more nitrogen compared with that obtained from pine sawdust. The experimental results also suggested that higher pyrolysis temperature increased the HHV and the content of hydrocarbon, thus improving the quality of the bio-oil. However, nitrogenous compounds and PAHs formed with the temperatures above 600 °C. Demirbaş et al. [37] investigated the pyrolysis of moss and algae. They demonstrated that the amount of bio-oil obtained from the Cladophora fracta increased with the increase in temperature. Specifically, the yield increases and reached a plateau value of 46.8% at 775 K when the temperature increased from 525 to 875 K. The experimental results also indicated that similar tendencies of the yields of bio-oil as well as the gaseous products obtained from six different sources of moss and algae were present with the increase of temperature.

According to the research about pyrolysis of algae, whether natural or cultured, the results seemed to present a consensus: the higher pyrolysis temperatures could increase the

HHV and hydrocarbon content of bio-oil obtained, thus improving its quality. However, too-high temperatures might lead to the formation of contaminants.

3.1.2. Effects of Heating Rates

Heating rates present another important factor for the pyrolysis of algae, which can affect the composition as well as the properties of the final products. Generally, slower heating rates reduce the secondary cracking reaction and increase the solid coke. By contrast, higher heating rates prevent the restriction of heat/mass transfer, promoting the rapid fragmentation of biomass, thus producing more gases and less char/coke, which improves the yields of liquid and gaseous products. Moreover, the available time for such secondary reactions as tar cracking and re-polymerization decreases with the increase of heating rates, which also contributes to the increase in the yield of bio-oil [38].

Luo et al. [39] performed TG-DSC analysis of cyanobacteria, and the results showed that with the increase of the heating rate (10 to 40 °C/min), the weight loss temperature presented in TG curves shifted to higher temperature. In addition, the residual char decreased correspondingly, which indicated that a higher heating rate was conducive to the formation of gaseous and liquid products. On balance, the heating rate plays a significant role. Long periods of low heating rates can produce more bio-char, while short periods of high heating rates can produce more bio-oil [40].

3.1.3. Effects of Sweep Gases

Pyrolysis reactions of biomass are generally carried out in inert atmosphere, such as nitrogen and helium. The inert gases passing through reduce the residence time of gaseous phase intermediates, thus the possibility of re-coagulation and re-polymerization of the gases can be inhibited, and the yield of liquid products can be maximized. Relatively higher sweep gas flow rates with lower residence time of gas phase intermediates inhibit the formation of char and thus facilitate the high yield of bio-oil. Hu et al. [32] observed that the yield of bio-oil increased noticeably when the flow rate of N_2 increased to 100 mL·L^{-1}. However, with the further increase of the flow rates from 200 to 400 mL·L^{-1}, the yield of bio-oil decreased.

On the other hand, reactive gases were used recently as a substitution for sweep gases, which can further adjust the pyrolysis process [41]. Cho et al. [42] investigated the pyrolysis of algae in CO_2 environments and found that the effects of CO_2 initiate at temperatures above 530 °C, directly leading to increased syngas production. The influence of CO_2 atmosphere on the pyrolysis of Microcystis aeruginosa was presented by Jung et al. [43]. Their results showed that the role of CO_2 is mainly to promote the decomposition of volatile organic compounds, and to accelerate the reactions between them and CO_2. The experiment proved that the use of CO_2, which played a role in the reaction environment or as raw material, provided a new technical approach to control the ratio of syngas obtained. In addition, compared with the pyrolysis oil under N_2 environment, fewer substituted aromatics were detected than under CO_2 environment.

3.2. Catalytic Pyrolysis Process

Compared to the algae raw material, the composition and fuel performance of the bio-oil from the pyrolysis process do improve a lot (shown in Table 2). However, the bio-oils obtained by non-catalytic pyrolysis are still generally unsatisfactory, especially their qualities. The catalytic process is a promising and attractive approach to solve the problems of pyrolytic bio-oil, equally applied to the algae upgrades. The challenge is to design catalysts and a catalytic process that improve the quality of the bio-oil, as well as increase the amount of hydrocarbons, which can be realized by deoxygenation, aromatization, and denitrification reactions [44]. In some aspects, the effects of catalysts are consistent with those in catalytic pyrolysis of lignocellulosic materials.

Table 2. Properties of the pyrolysis bio-oil obtained from natural algae.

Species	Catalyst	Conditions	Elemental Composition (wt%)				HHV [1] (MJ/kg)	Reference
			C	H	N	O		
Blue-green algae blooms	None	final pyrolysis temperature: 500 °C, particle size: <0.25 mm, N$_2$ flow rate: 100 mL/min, heating rate: 40 °C/min	67.58	8.95	7.75	14.48	31.9	[32]
Algae from lake blooms	None	final pyrolysis temperature: 700 °C, particle size: <0.18 mm, N$_2$ flow rate: 300 mL/min	61.87	8.07	3.7	26.36	21.57	[36]
Cyanobacteria from lake blooms	HZSM-5 (mass ratio to algae: 0.5:1)	final pyrolysis temperature: 400 °C, particle size: <0.42mm, N$_2$ flow rate: 50 mL/min	73.6	8.3	7.4	10.7	36.6	[24]
Algal biomass (*C. vulgaris*)	H$^+$ZSM-5 (mass ratio to algae: 1:1)	final pyrolysis temperature: 800 °C, N$_2$ flow rate: 30 mL/min	51.4 ± 2.3	10.4 ± 0.4	12.4 ± 1.1	24.8 ± 1.6	18.6 ± 0.3	[45]
Algae (mainly *cyanobacteria*),	silica-supported nickel phosphide(mass ratio to algae: 1:1)	final pyrolysis temperature: 450 °C, H$_2$ flow rate: 100 mL/min	69.2	9.1	10.8	10.8	35.0	[27]
Natural algae (mainly *cyanobacteria*)	MgAl4-LDO/ZSM-5 (mass ratio to algae: 0.75:1)	final pyrolysis temperature: 550 °C, N$_2$ flow rate: 40 mL/min	71.19	9.683	10.597	8.530	37.164	[19]
Algae bloom	Ni$_2$P loaded zeolite (mass ratio to bi0mass: 0.8:1)	co-pyrolysis with water hyacinth (0.4:1), final pyrolysis temperature: 450 °C, N$_2$ flow rate: 100 mL/min,	- [2]	-	-	-	32.00 ± 0.08	[46]
Cyanobacteria	MgAl3-LDO/ZSM-5 (mass ratio to algae: 0.75:1)	final pyrolysis temperature: 550 °C, vaporized methanol flow rate: 66 mL/min, heating rate: 10 °C/min	-	-	-	-	37.47	[47]

[1] Calculated value based on ultimate analysis. [2] "-" represents not provided in the ref.

3.2.1. Performance of Zeolite Catalysts

Generally, zeolites benefit the reactions of cracking and dehydration [48]. ZSM-5 is the most commonly used zeolite [49,50]. Taking ZSM-5 as an example, the acidic site in ZSM-5 plays a catalytic role in accelerating carboxylation, decarbonylation, and deoxidation, while the shape-selective catalysis, due to the special porous structure, can lead to the formation of aromatics. All these effects facilitate the improvement of H/C ratio, thus leading to a bio-oil with higher heat value and higher stability, and simultaneously promoting the formation of more value-added components. Generally, the bio-oil obtained is made up of organics as acetonitrile, BTX (Benzene-Toluene-Xylene), epoxy, and other oxygenated compounds [51].

Casoni et al. [15] studied the production of bio-oil from the pyrolysis of Rhizoclonium sp. algae. It was found that the concentrations of aliphatic alcohols and some products with high molecular weight in the bio-oil were reduced by the SBA-15 or SBA-15-based catalysts. Therefore, the quantity of light products obtained increased with the use of catalysts. Du et al. [52] used three types of zeolite (H-Y, H-β, and H-ZSM-5) for the catalytic pyrolysis of Chlorella vulgaris. The results showed that, compared to the non-catalytic process, many more aromatic hydrocarbons were produced by catalytic pyrolysis. The total yield of aromatics dramatically increased and the pyrolysis catalyzed by H-ZSM-5 obtained a maximum yield of 18.12%. Deoxidation and denitrogenation are found in the ZSM-5 catalytic pyrolysis, and lead to a high carbon yield of aromatic hydrocarbons, especially the BTX molecules. By contrast, nitrogen, removed by the catalyst, is mostly distributed in the water-soluble and solid phase as a nitrogen fertilizer [53].

Denitrogenation is proved to be the key factor in upgrading algae-based bio-oil [54,55] and reducing the coking on zeolite catalysts [56]. However, denitrogenation is difficult, since the concentration of nitrogenous compounds is high and the energy of C-N bonds are high [57].

Li et al. [24] found that HZSM-5 could promote the further reactions of pyrolytic intermediates of natural algae Cyanobacteria, including dehydration, cracking, and aromatization. At the optimum dosage of HZSM-5 for fractional pyrolysis, the main compositions in bio-oil were indoles and phenols. In addition, the oxygen content was reduced to 9.4 wt.% with the HHV raised to 37.3 MJ/kg. Thangalazhy-Gopakumar et al. [45] investigated the fixed-bed and analytical pyrolysis of Chlorella vulgaris. The results showed that in the pyrolysis process catalyzed by HZSM-5, the carbon yield of aromatic hydrocarbons increased from 0.9 to 25.8 wt.%, while the mass ratio of catalyst/biomass increased from 0 to 9. The experimental results confirmed that a high dosage of ZSM-5 catalyst could reduce the contents of nitrogen and oxygen in bio-oil.

3.2.2. Performance of Catalysts Other Than Zeolites

The basic concept commonly adopted i improving the quality of the organic phase by hydrodeoxygenation and hydrodenitrogenation, or is oriented towards producing specific compounds through the regulation and control of the composition and properties of the catalysts. Thus, many kinds of catalysts other than zeolites have been used, such as metal oxides and composite catalysts based on zeolites or metal oxides, etc. [15].

Sabegh et al. [58] produced a multi-metal oxide catalyst (mainly Al_2O_3, CeO_2, and AuO_2 et al.) from the catalytic converter of a spent car for the pyrolysis of the C. glomerata. The results showed that the main function of the catalyst is deoxidizing nitrogenous compounds, promoting ketonization reaction, converting acid to ketone, and thus reducing the corrosiveness of the bio-oil. Zeng et al. [27] used Ni_2P/SiO_2 as a catalyst for bio-oil production from the pyrolysis of Cyanobacteria. Related experimental results suggested that catalytic pyrolysis could reduce the oxygen content in the bio-oil. In addition, the bio-oil seemed to be upgraded: and long-chained alkanes were the dominant component, with a content of 59.4%.

Typically, metal oxides and zeolites are often composited for the combination of the catalytic effects. Wang et al. [59] investigated the pyrolysis of Enteromorpha clathrata with the catalysis of Mg-Ce oxides supported on ZSM-5. It was found that the modified ZSM-5 catalysts, although they do not improve the yields of the bio-oil, exhibit promising performance in increasing the relative content of C5–C7 and decreasing that of acids. Gao et al. [19] presented a kind of Mg-Al layered double oxide/ZSM-5 composite, and investigated its catalytic performance on the pyrolysis of Cyanobacteria. They found that the MgAl-LDO/ZSM-5 catalyst with optimal composition could obtain bio-oil with higher yield and quality compared to the non-catalytic process and the catalytic process with zeolite or oxides alone.

3.3. Non-Catalytic Pyrolysis Process

An integrated process, which involves the catalysis and other operation conditions aside from the thermal treatment under inert atmosphere, such as co-pyrolysis [60], microwave-assisted pyrolysis [61], and pyrolysis under active gas atmosphere [16], has also been studied for the conversion of algae. The main intent and results focus on the integrated resource utilization of the waste or the preparation of specific components [23,62].

Wang et al. [60] investigated the co-pyrolysis of Enteromorpha clathrata and rice husk using ZSM-5 and MCM-41. The experimental results demonstrated that ZSM-5 presents stronger effects on the improvement the yield of bio-oil. Nevertheless, MCM-41 showed special synergetic effects for co-pyrolysis, as the content of a specific component (5-methyl-2-furancarboxaldehyde) increased significantly compared with that obtained solely from Enteromorpha clathrata. Li et al. [46] investigated co-pyrolysis of water hyacinth and algae from water-bloom. The effects of operation parameters, including CO_2-cofeeding and steam co-feeding, were investigated through both no-catalytic and Ni_2P-loaded zeolite catalytic pyrolysis. It was showed that both the hydrocarbon production and HHV of the bio-oil increased, when the catalyst/biomass ratio increased from 0 to 1. With the synergistic effects of catalyst, co-feeding of different kinds of biomass, CO_2, and steam, the

chemical composition of the bio-oil was affected and the carbon number distribution was at its maximum between 7–17. The highest yield of hydrocarbon of 70.23% was obtained under optimum conditions, and the supreme HHV was 35.72 MJ/kg. Zhang et al. [61] investigated the pyrolysis of water blooms enhanced by microwave. Under the optimum conditions of 20–50 mesh algae particle size, 600 W microwave power, and 10% of activated carbon, the maximum yields of bio-oil obtained were 49.1%, 51.7%, and 54.3% under N_2, 10% H_2/Ar, and CO_2 atmosphere, respectively. It was also found that H_2 atmosphere generated more hydrocarbons, while CO_2 atmosphere led to the production of more acids.

The deoxidation and denitrification of algae bio-oil are needed when they are used as fuel. However, another way of thinking is to take the advantage of the high nitrogen content, and realize valorization by converting the algae not into fuel, but into bio-oil rich in nitrogen-containing components [23], which show potential use value as main raw materials or precursors for fine chemicals and pharmaceuticals. Bai et al. [47] and Yang et al. [21] studied the catalytic pyrolysis of Cyanobacteria with vaporized methanol using metal oxides loaded with ZSM-5 and MCM-41, respectively. They found that the yield of bio-oil increased through the utilization of methanol. Typically, the organics phase obtained by Mg-Al hydrotalcite-derived oxides/ZSM-5 contained less nitrogenous and oxygenous compounds and more aromatic compounds [47].By contrast, about 25% of the nitrogen in the algae transferred into the bio-oil with the catalysis of Ni-Al layered double oxide/MCM-41, in which the content of nitriles dominated in nitrogenous compounds [21].

4. Conclusions

To summarize, pyrolysis of natural algae has been performed in different kinds of reaction conditions. Both inert and reactive atmospheres are used in the process. The results from the literature show that yields of bio-oil generally range between 20–50 wt.%. Meanwhile, it should be noted that some studies regard liquid products as bio-oil, while others further divide liquid products into an aqueous phase and oily phase; the oily phase is defined as bio-oil.

The catalytic process is widely used for the bio-oil used as fuel, which is mostly intended as the target for deoxygenation and denitrogenation. In general, long-chain hydrocarbon and aromatics are expected when using zeolites and metal oxide-based catalysts, and process intensification technologies such as co-pyrolysis and microwave-assisted pyrolysis can make the process more efficient. However, both the process and the catalysts should be further improved since the HHV and the nitrogen content still cannot meet requirements for green fuel oil. In addition, considering the energy consumption in pyrolysis process, the concept of algae-based bio-fuel is not that economically rational, since the nature of the process is to produce one type of energy from another type of energy. However, it is still worth studying in the view of global ecological balance and "carbon neutrality". Future research should focus on more energy-conserving and integrated technology aiming at large-scale application.

Beyond that, the recent concept of regarding the nitrogen-containing species as a feedstock for platform chemicals would be a good solution for the conversion of natural algae. The discovery and production of more value-added components from the disposal of algae can fill the gap of low economy that appears when the material is only used as fuel. Nonetheless, the design and coupling of the process and the catalyst are worth deep investigation for the conversion paths and mechanisms for the N-containing components, oriented towards the synthesis of specific chemicals. Unlike the common stoichiometric reaction in which we can usually obtain a specific product with specific raw materials and mechanism, the complexity of the pyrolysis itself and the integrated effects of catalyst and operation parameters may more or less lead to the uncontrollability of the process. The catalytic and integrated pyrolysis processes so far have provided some guidance in this respect, whereas the technology and method is still lacking. However, it is foreseeable that suitable and valuable products can be obtained if the common rules of the process could

be revealed by further research and induction, such as controlling of the cracking degree, nitrogen transfer pathways, and directional pyrolysis.

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