A Review of the Biofuel Yield in Hydrothermal Liquefaction of Different Microalgae

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Abstract. Among various biomass, microalgae has unique advantages such as fast growing, high efficient photosynthesis, no competition with crops etc. Hydrothermal liquefaction (HTL) is a potential technology for converting microalgae biomass into biofuel, with merits including higher biofuel yield than other methods and lower energy consumption etc. A review of the biofuel yield by HTL of different microalgae is presented here, summarizing the past research about the highest biofuel yield and corresponding conditions for various microalgae. Finally, based on the literatures above-mentioned, future directions in this field are suggested.

Introduction

A brief introduction of biofuel

With the development of world economy, more and more fuel is desired. However, traditional fossil fuels are non-renewable resource, pollute the environment and produce many green gases during combustion. Thus, searching an environmentally-friendly and renewable substitution for fossil fuels is necessary. Biofuel is environmentally-friendly, renewable and has excellent combustion performance. Microalgae has properties of short cultivation cycle, high photosynthetic efficiency, high biofuel yield, good quality of biofuel, which is considered a promising substitution for addressing the energy crisis and environmental issues associated with fossil fuel use [1], so microalgae-based biofuel has great potential applications.

Hydrothermal liquefaction reaction

There are many methods for converting microalgae to biofuel, including pyrolysis [2], transesterification of lipids [3] and hydrothermal liquefaction. Hydrothermal liquefaction (HTL) is considered as the most promising method. HTL is defined as an reaction process by physical-chemical change under the high-temperature and high-pressure water. It has a large number of advantages such as higher energy efficiency, excellent solubility of lower polarity organic molecules [4] and no phase-changing heat dissipation. Moreover, it can convert proteins and polysaccharides from feedstock into lipids, increasing the biofuel yield [5]. So HTL technology can be applied in all microalgae. And it also can improve the recycling of nitrogen, phosphorus, iron et al [6]. In all, HTL has wide applicability, higher biofuel yield and energy efficiency, which has potential development prospects.

The research on HTL of microalgae started in 1994, from Dote et al [7]. With more and more desire of renewable energy, more researchers has focus on it. They performed HTL of different microalgae and obtained the relations between microalgae and reaction parameters.

HTLs of different microalgae species

At present, the research on HTL of microalgae primarily was focused on Spirulina, Chlorella, Nannochloropsis, Dunaliella and others such as Desmodesmus, Scenedesmus and Phaeodactylum etc.

Spirulina

Spirulina is a kind of common microalgae with high proteins and carbohydrates [8], which is often considered as healthy food boosting the body's defenses. The research is shown in Fig.1. Jena et al [8] provided a comparison of Thermochemical Liquefaction (TCL) and slow pyrolysis processes for producing biofuel from algae, indicating that the highest biofuel yield can reach 40.7% and the higher heating value (HHV) was 34.21MJ/kg at 350 °C, 60 min and 20% solid concentration. In addition, he [9] investigated the optimum TCL operating conditions for biofuel from Spirulina at 200-380 °C, 0-120 min, and gained the highest biocrude yield of 39.9% at 350 °C, 60 min and 20% solids concentration. HTL of Spirulina with catalysts was also studied [10] and the highest biofuel yield was 51.6% at 350 °C, 60 min, 20% solid concentration and with 5% Na_2CO_3. Vardon et al [11] explored the influence of wastewater feedstock composition on HTL biofuel properties and physico-chemical characteristics at 300 °C, 10-12 MPa, 30 min reaction time and 20% solid concentration and finally obtained the highest biofuel yield for Spirulina was 32.6%, whose HHV was 33.2 MJ/kg. Moreover, he [12] compared HTL (300 °C and 10-12 MPa) with slow pyrolysis, and the highest biofuel yield for HTL was 31%. Toor et al [13] performed HTL of Nannochloropsis salina and Spirulina platensis at subcritical and supercritical water conditions (220-375 °C, 20-255 bar) and found that the optimal HTL condition for Spirulina appeared at 310 °C, 120 min, 25% solid concentration and 11.5MPa, when the highest biofuel yield was 38%. From Fig.1, we found that appropriate temperature for high biofuel yield is between 300 °C and 350 °C, time is about 60 min and solid concentration is about 20%, also Na_2CO_3 as a catalyst for HTL of Spirulina.

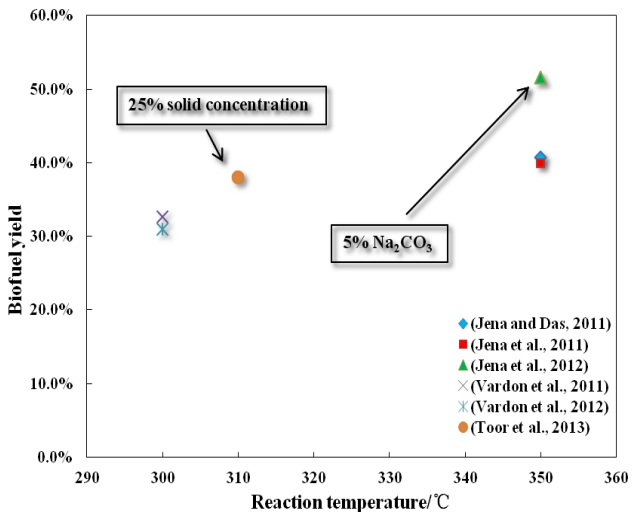

Fig.1 Research about Spirulina

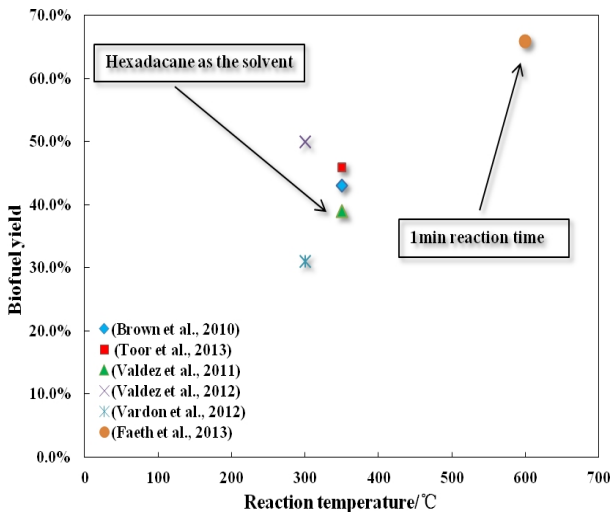

Fig.2 Research about Nannochloropsis

Nannochloropsis

Nannochloropsis sp. is a marine algae with high-lipid content [14]. There were many studies about it, shown in Fig.2. Brown et al [15] converted the Nannochloropsis sp. into biofuel via HTL from 200 to 500 °C with 60 min and obtained the highest biofuel yield was 43% at 350 °C, 5% solid concentration, with the HHV of 39 MJ/kg. Toor et al [13] gained the highest biofuel yield for Nannochloropsis salina in HTL was 46% at 350 °C, 30 min, 25% solid concentration and 17.5 MPa. Valdez et al [16] performed HTL of Nannochloropsis sp. at 350 °C, 60 min and 20% solid concentration by analyzing products and finally he found that the highest biofuel yield was 39±3% at hexadecane as the solvent. Also he [17] investigated HTL of Nannochloropsis sp. at 250-400 °C, 10-90 min, water densities

(0.3-0.5 g/mL) and biomass loadings (5-35%) and gained the highest biofuel yield was 50% at 300 °C, 10 min and 15% solid concentration. Faeth et al[5] studied the fast HTL of Nannochloropsis sp. at 1, 3, and 5 min and 300-600 °C and he found that the highest biofuel yield can reach 66±11% at 600 °C, 1 min reaction time and 15% solid concentration. From Fig.2, it is shown that appropriate temperature is between 300 °C and 350 °C, time range is 30-60 min (except fast HTL technology) and solid concentration is 15-20%, also hexadecane was active as the solvent for HTL of Nannochloropsis.

Chlorella

Chlorella is a green unicellular alga with low-lipid high-protein content, found in both fresh and marine waters usually [18] and it is also as food grade material. Guo et al [19] studied the effects of operating conditions on the distributions of carbon and nitrogen in HTL products and found that the highest biofuel yield was 39.4% at 280 °C, 120 min and 20% solid concentration. And he [20] investigated the effects of key operating parameters (reaction temperature, reaction time and initial pressure) on the oil product yields and found that the highest refined oil yield was 39.4%±1.2% of the total dry mass of algal feedstock, achieved under that condition of 280 °C reaction temperature and 120 min reaction time. Miao et al [21] compared the two-step sequential hydrothermal liquefaction (SEQHTL) with direct hydrothermal liquefaction (DHTL) and studied the effects of parameters (reaction temperature, reaction time and biomass/water ratio) on the product distribution. The result showed that the biofuel yield can be over 30% at 240 °C, 20min and 1:9 biomass/water ratio by SEQHTL after considering the operation cost.

Dunaliella

Dunaliella has proteins (32%), lipids (22%) and carbohydrate (20%) [22]. Zou et al [22] converted Dunaliella into biofuel through a sub- and supercritical water liquefaction process and studied the effects of parameters on the yields of the products. The results showed that the maximum biofuel yield was 36.9% at 360 °C, 30 min and a feedstock ratio of materials to water of 1:10. Zou et al [23] investigated HTL of Dunaliella under certain catalyst and obtained the maximum biofuel yield of 25.8% at 360 °C, 50 min using 5% Na_2CO_3 as a catalyst. Zou et al [24] studied TCL of Dunaliella in ethylene glycol acidified with H_2SO_4 as a catalyst and set up the mathematical model by a central composite rotatable design (CCRD) and response surface analysis (RSA). Finally, he obtained the highest liquefaction yield of Dunaliella was 97.05% under the optimized condition of 170 °C, 33 min and 2.4% H_2SO_4 added. Minova et al [25] studied the effects of reaction parameters on the biofuel yield and obtained the highest biofuel yield was 43.8% at 300 °C, 5 min, 25% solid concentration and no Na_2CO_3, differed from Zou [23], maybe due to difference of feedstock or processing. Moreover, Yang et al [26] investigated HTL of Dunaliella salina over solid acid catalyst and obtained the highest biofuel yield of Dunaliella was 72.0% under the condition of 200 °C, initial H_2 pressure 2.0 MPa, 60 min, 10% solid concentration and Ni/REHY as the catalyst.

Others

There are few research about other microalgae. Alba et al [27] converted Desmodesmus into biofuel by hydrothermal treatment (HTT) technology and the maximum biofuel yield (49%) was obtained at 375 °C and 5 min. Vardon et al [12] obtained the conclusion that raw Scenedesmus had the highest yield of HTL bio-oil (45%) and about defatted Scenedesmus (36%) during the experiments of comparing HTL with slow pyrolysis. Christensen et al [28] processed Phaeodactylum by HTL in order to assess the influence of reaction temperature and reaction time on the product and elemental distribution and found that the highest bio-oil yield can reach 39% under the condition of 350 °C and 15 min. Tian et al [29] focused on the HTL of harvested algae from Dianchi in China and obtained the highest biofuel yield (18.4%) at 300 °C, 60 min and 20% solid concentration. Hognon et al [30] found

that the highest biofuel yield was 71% at 230 °C, 60 min and 14% solid concentration for Chlamydomonas reinhardtii.

Conclusions and future directions

For microalgae feedstock, hydrothermal liquefaction is a very potential technology for producing biofuel. As far as we're aware, it can offer efficient conversion from microalgae to biofuel, avoid water phase-changing heat dissipation and improve the recycling process of nutrients and metal elements, in favour of follow-up use of them.

Microalgae is composed of proteins, polysaccharides and lipids primarily. Different microalgae differ from percentage compositions of these three substances. Although some microalgae are low-lipid but high-protein, the biofuel yield is not always lower than high-lipid species due to outstanding advantages of HTL above-mentioned. Therefore, different microalgae species may result in different optimal reaction parameters, biofuel yields, higher heating values (HHV) and distributions of products. The summary of HTL of different microalgae can provide a research overview for further investigation in the very potential field with rapid development.

In the future, the research about the cell structure of microalgae need to be studied deeper. Various microalgae produce different compositions of biofuel and aqueous products, which may be necessary to quantify for follow-up separation and processing. Also, the reaction kinetic research for feedstock and some intermediate products need to be devoted to the field to explore the reaction mechanism of HTL completely.

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