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Influence of Fe/HZSM-5 catalyst on elemental distribution and product properties during hydrothermal liquefaction of *Nannochloropsis* sp.

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ABSTRACT

Hydrothermal liquefaction (HTL) is a promising thermochemical technology to produce biocrude oil from algae; however, further improvement of the process efficiency is still required. In this study, we used a cost-effective catalyst (Fe/HZSM-5) during HTL of microalgae *Nannochloropsis* sp. The highest biocrude oil yield (38.1 ± 3.2%) was achieved at 365 °C with the inclusion of Fe/HZSM-5, which improved the biocrude oil yield by 25% compared with the non-catalyzed group. In addition, Fe/HZSM-5 showed a positive effect on influencing element migration during the HTL process. An increase of carbon in the biocrude oil and increase of nitrogen in the aqueous phase were observed, which would benefit downstream processing, including biocrude oil upgrading and nutrients recovery. Furthermore, the presence of low-molecular weight ketones, acids, amides and phenols in the biocrude oil indicated improvement of the oil quality. Hence, Fe/HZSM-5 could be a promising catalyst for the HTL of algae, enhancing biocrude oil production and regulating the distribution of carbon and nitrogen in the product fractions.

1. Introduction

Hydrothermal liquefaction (HTL) is a promising technology for energy production from wet waste biomass, operating at high temperatures (250–400 °C) and pressures (5–20 MPa) [1,2]. A distinct advantage of HTL over other thermochemical technologies is that it can utilize wet biomass and avoid the energy-intensive drying step in comparison to other thermochemical conversion routes, e.g., direct combustion and pyrolysis [3]. Algae are an aquatic organism with a fast growth rate and high biomass productivity. It is also a suitable HTL feedstock due to the fact that algae can be grown to consist of a high content of lipids and proteins [4–7]. Through HTL, algae can decompose into four kinds of products: biocrude oil, solid residue, aqueous phase and gas [8,9]. Biocrude oil with a higher heating value (30–40 MJ/kg) can be used as a biofuel, which is a promising potential route for algae utilization [10–12]. However, one issue is that part of the carbon (30–40 wt%) will inevitably migrate from the biomass to the aqueous phase [13–16]. Moreover, the high oxygen and nitrogen content of the biocrude oil hinder the application of biocrude oil as a fuel [2,17].

The implementation of a catalyst is a particularly prominent pathway that affects the characteristics of the HTL products [18]. The use of catalysts in the HTL process is conducted through two main strategies: direct introduction of catalysts into the HTL process (referred to as the one-pot method) or application of catalysts to upgrade the original biocrude oil obtained from direct HTL (referred to as the two-step method) [19,20]. Due to the low energy consumption and simple operation associated with the one-pot method, an abundance of studies have been conducted in recent years utilizing this method [19,21]. The manner in which shape-selective catalysts like zeolites impact the HTL process has been extensively investigated [2,20,22]. Duan et al. reported an increase of biocrude oil yield by 47% when a zeolite catalyst was used during the HTL of *Nannochloropsis* sp. [23]. Further studies revealed that the utilization of zeolite catalysts increased the carbon, hydrogen and hydrocarbon content of the oil [2,20]. To further improve the performance of zeolite catalysts during catalytic HTL, research focusing on synthetic zeolite catalysts has been gaining increasing attention. Zn/HZSM-5 was reported to have improved the quality of biocrude oil by accelerating decarbonylation, decarboxylation and dehydrogenation reactions of biomass during the HTL process

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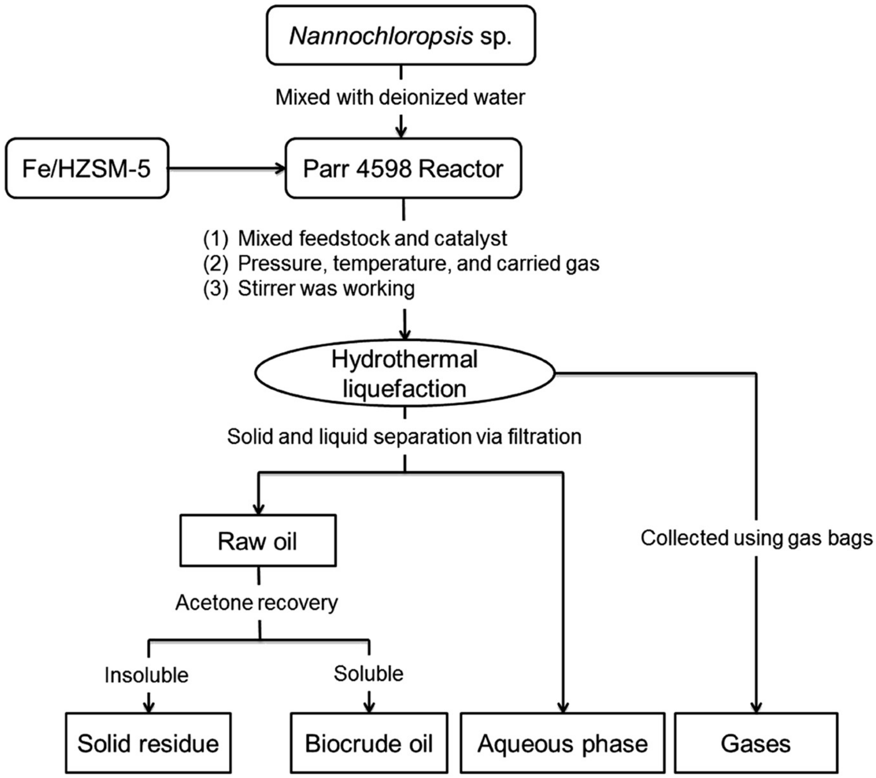

Fig. 1. Procedure for the HTL of *Nannochloropsis* sp.

[2]. Zeolite catalysts involving the incorporation of Ni also played a significant role in increasing the oil yield and hydrocarbon content in the oil by promoting cracking and hydrodeoxygenation reactions [24]. Xu et al. found that Ce/HZSM-5 induced better catalytic cracking effects than HZSM-5 during HTL of *C. pyrenoidosa*, leading to a higher oil yield and HHV in comparison to HZSM-5 [25].

However, the cost of the loaded metal is one of the key limitations for the application of synthetic zeolite catalysts in HTL. Fe, as an abundant and inexpensive metal, has been previously used in catalytic HTL. Zerovalent Fe has been employed in the HTL of oil palm empty fruit bunches, and the results demonstrated that the catalyst enhanced the production of bio-oils containing water-soluble and water-insoluble compounds [26]. Another study revealed the catalytic influence of $FeSO_4$ on the HTL of sludge. The application of a catalyst in this study achieved biocrude oil with the highest energy recovery (69.84%), total liquefied conversion (70.64%) and HHV (35.22 MJ/kg) [27]. Further tests have been conducted with MCM-41 assembled with Fe_2O_3 for the HTL of *Chlorella*. The results of this study demonstrated that inclusion of a catalyst led to the production of biocrude oil with a less complicated chemical composition and a higher HHV. Selective upgrading of palmitic acid and methyl palmitate into pentadecane in the oil was also enhanced [28].

In this study, we used Fe/HZSM-5 as catalyst to improve the performance of *Nannochloropsis* sp. during HTL. The effect of Fe/HZSM-5 on the biocrude oil production, and carbon and nitrogen elements distribution in the products were investigated. The purpose of this work was 1) to study the feasibility of Fe/HZSM-5 to improve the HTL of microalgae *Nannochloropsis* sp.; 2) to uncover how Fe/HZSM-5 impacts the yield and quality of biocrude oil; and 3) to investigate the influence of Fe/HZSM-5 on carbon and nitrogen elements distribution in the HTL products.

2. Experimental section

2.1. Materials

HTL experiments were carried out using *Nannochloropsis* sp., which was supplied by ENN Science & Technology Co., Ltd. (Lang Fang, China). The fresh feedstock was stored at −20 °C prior to use. The ultimate analysis results of the feedstock have been described in previous studies [10,14]. The proximate and chemical analyses of the feedstock were conducted. The main biochemical components of the feedstock were crude protein (52.36%), crude lipids (14.01%) and crude fiber (5.25%). The results illustrated that the feedstock possessed a high content of protein. Meanwhile, the ash content was relatively low (6.34%). The fresh feedstock contained a high content of moisture (71.64%). The HZSM-5 zeolite catalyst (SiO_2/Al_2O_3 molar ratio of 50) used in this study was purchased from Shanghai Shen Tan Environmental New Materials Co., Ltd., China. Analytical reagent grade acetone was used without any purification.

2.2. Catalyst preparation

The impregnation method is widely used to load metals onto supports, e.g., zeolite, active carbon, and carbon material [29,30]. By doing so, synthesis methods can be simplified. Microwaving was also carried out to promote the loading and dispersion of Fe nanoparticles on the surface and internal structure of the zeolite [31,32]. The Fe/HZSM-5 catalyst was prepared with HZSM-5 and $Fe(NO_3)_3$ using the impregnation method. The impregnation process included adding 10 g of HZSM-5 (with a particle size of 840 nm, an elliptical pore size of 0.53–0.58 nm, and a Si/Al ratio of 50) to 1000 mL of 0.5 M $Fe(NO_3)_3$ solution. The solid-liquid mixture was then placed in a microwave oven at a temperature of 80 °C and stirring time of 2 h. When the ion-exchange reactions finished, the demineralized catalyst was filtered with deionized water and then dried at 120 °C. Finally, the catalyst was heated in an oven at 600 °C for 3 h. The regular porous zeolite structure