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Catalytic hydrothermal liquefaction of microalgae using nanocatalyst

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HIGHLIGHTS

- Hydrothermal liquefaction was carried out for bio-oil production from microalgae.
- Nanocatalyst was applied to increase the bio-oil yield at low temperature.
- Catalytic hydrothermal liquefaction resulted in higher bio-oil yield.
- The highest bio-oil yield (30.0 wt%) was obtained at 250 °C by using Nano Ni/SiO_2.
- Nanocatalyst was recovered from the solid residue.

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ABSTRACT

Due to exhaustibility of fossil fuels and their adverse effects on the environment, bio-oil has been considered as an alternative energy source for fuel applications. Currently, there are two main processes for bio-oil production: pyrolysis and hydrothermal liquefaction (HTL). The hydrothermal liquefaction is defined as biomass-to-liquid conversion route carried out in the hot compressed water with or without the presence of a catalyst. The major concern in HTL is the high pressure of the process which results in high capital cost of equipment. Thus, the process pressure and temperature should be reduced, but at a lower temperature, bio-oil yield is not high enough to make HTL an economical process for sustainable fuel production. In this research, we investigated the applicability of a nanocatalyst (nano-Ni/SiO_2), an acid catalyst (synthesized zeolite), and an alkali catalyst (Na_2CO_3) to increase the bio-oil yield at low temperatures (210 °C, 230 °C, 250 °C). The major result of this work was higher bio-oil yields with the order of nano-Ni/SiO_2 > zeolite > Na_2CO_3 in hydrothermal liquefaction of microalgae *Nannochloropsis* sp.. The highest bio-oil yield (30.0 wt%) was obtained at 250 °C by using Nano-Ni/SiO_2. Moreover, applying catalyst resulted in a decrease in the oxygen and the nitrogen contents of the bio-oil and consequently an increase in its heating value. The results of this research also suggest the possibility of nanocatalyst recovery for 2–3 times.

1. Introduction

Recently, microalgae as a feedstock for biofuel production have drawn a great attention from both academia and industry. Using microalgae for biofuel production has several advantages over other types of biomass, including fast growth rate, higher lipid content, and ability to sequester carbon dioxide. Meanwhile, microalgae can be cultivated in non-arable or low-quality agricultural lands and/or saline water and does not have an overlap with food supply.

One approach to produce transportation fuels from microalgae is first lipid extraction and then conversion to biodiesel via esterification/transesterification reactions [1]. The other approach is bio-oil production from microalgae through thermochemical conversion processes (e.g. pyrolysis and hydrothermal liquefaction) and upgrading of the bio-oil to transportation fuels. Bio-oil production aims to break all biomacromolecules (i.e. carbohydrate, protein, and lipid) into an organic liquid phase named bio-oil or bio-crude oil. Bio-oil is known as a promising alternative for petroleum to produce transportation fuels, and extraction of valuable chemicals in a biorefinery [2].

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Currently, there are two main processes for bio-oil production: pyrolysis and hydrothermal liquefaction (HTL). Pyrolysis is typically defined as a thermochemical decomposition of biomass at medium to high temperatures (350–700 °C) in the absence of oxygen. Pyrolysis requires dried feedstock which increases the energy consumption of the process especially for naturally wet biomass. HTL is defined as the reaction of biomass in water at elevated temperature (200–370 °C) and high pressure (2–20 MPa) with or without using a catalyst. HTL does not require dewatering and drying steps, and therefore, it is suitable for processing aquatic biomass. The major concern in HTL is the high pressure of the process which results in high capital cost of equipment. Also more expensive and elaborated safety systems are required. As water is heated along its vapor–liquid saturation curve, the pressure is determined by setting the temperature. In order to reduce the process pressure, the process temperature should be reduced, but at a lower temperature, the bio-oil yield is not high enough to make HTL economical for sustainable fuel production.

Catalysts can be used to increase the bio-oil yield in the hydrothermal liquefaction of microalgae [3–11]. Duan et al. [3] investigated catalytic hydrothermal liquefaction of *Nannochloropsis* sp. in the presence of six different catalysts (Pd/C, Pt/C, Ru/C, Ni/SiO_2-Al_2O_3, CoMo/γ-Al_2O_3, and zeolite). Experiments were conducted at 350 °C. The major result was higher yields of the bio-oil. As an example, Ni/SiO_2-Al_2O_3 and zeolite increased the bio-oil yield from 35% up to 50% and 45%, respectively. Therefore, Ni/SiO_2-Al_2O_3 had better performance to increase the bio-oil yield compared to that of zeolite. Ross et al. [4] has studied the hydrothermal liquefaction of Chlorella vulgaris and Spirulina for bio-oil production. Experiments were performed at 300 °C and 350 °C. Catalysts were employed, including the alkali (KOH and Na_2CO_3) and the organic acids (CH_3COOH and HCOOH). The major result was higher yields of crude bio-oil with the order of CH_3COOH > HCOOH > KOH > Na_2CO_3. Their work showed that acid catalysts had better performance to increase the bio-oil yield, however, a part of acid catalysts were consumed during the reaction. Table 1 summarizes representative literature data on the catalytic hydrothermal liquefaction of microalgae. Although the bio-oil yield has increased, the mechanism of the catalytic liquefaction is still unknown. As it can be seen, most previous studies on catalytic HTL were conducted at temperatures higher than 250 °C, and more specifically higher than 300 °C. Meanwhile, no research work has been performed on the application of nanocatalysts in the HTL process.

Nanocatalysts have recently been used in different industries including fuel production from biomass. Nanocatalytic conversion of biomass to biofuel has been reported to improve the conversion yield [12]. In biomass gasification, the nanocatalysts have been used for tar removal and increasing the conversion yield under relatively mild conditions including nano-sized NiO [13] and Fe [14]. Nanocatalysts were also applied in biodiesel production including Cs/Al/Fe_3O_4 nanocatalyst [15], nanocrystalline MgO [16], and nanocrystalline CaO [17]. Due to the background of using nanocatalyst in bioenergy production, we utilized a nanocatalyst (nano-Ni/SiO_2) in the hydrothermal liquefaction of microalgae to investigate its effects on the yield and the composition of the bio-oil. Two other types of catalysts (synthesized zeolite, and Na_2CO_3) were also applied. Since most previous studies on catalytic HTL have been performed in temperatures higher than 250 °C, we conducted experiment at temperatures lower than 250 °C, and investigated the effects of the catalysts on the yield, the elemental composition, and the heating value. Meanwhile, recovery of the nanocatalyst was also investigated for the first time.

2. Experimental

2.1. Materials

2.1.1. Microalgae

Nannochloropsis sp. in dried powder form was purchased from Xi'an Lyphar Biotech Co., Ltd and was used as received. *Nannochloropsis* sp. was selected in this research because of its high lipid content, high growth rate, and the ability to grow in saline water. The lipid content, the protein content, the proximate and ultimate analysis, and the higher heating value (HHV) of the microalgae are listed in Table 2. The data of the lipid content (21.9%) and the protein content (40.5%) were provided by the manufacturer. The proximate analysis was carried out by the thermal gravimetric analysis (TGA) (TGA-50, Shimadzu) from the ambient temperature to 900 °C under 150 ml min^{-1} nitrogen flow. The temperature was raised from the ambient temperature to 105 °C at 25 °C min^{-1} and was kept constant for 30 min. Then, it was raised again until 900 °C at 50 °C min^{-1} and was kept constant for 20 min. Seven minutes after the temperature reached 900 °C, the oxygen valve was opened to start combustion using 150 ml min^{-1} oxygen flow. The ultimate analysis was performed by the elemental

Table 1
Representative literature data on the catalytic hydrothermal liquefaction of microalgae.

Catalyst	Species	Condition	Effects	Reference
Pd/C, Pt/C, Ru/C, Ni/SiO_2-Al_2O_3, CoMo/γ-Al_2O_3, Zeolite	*Nannochloropsis* sp.	350 °C, 60 min	Increased bio-oil yield from 35% to maximum 56% for Pd/C, increased heating value	[3]
CH_3COOH, HCOOH, KOH, Na_2CO_3	*Chlorella vulgaris*, *Spirulina*	300–350 °C, 60 min	Yield ranges from 6.4% to 19.5%, increased heating value, decreased boiling point	[4]
Na_2CO_3	*Dunaliella tertiolecta*	280–380 °C, 10–90 min	Increased bio-oil yield (highest bio-oil yield of 25.8 wt% at 360 °C with 5wt % Na_2CO_3)	[5]
Na_2CO_3	*Spirulina platensis*	300–350 °C, 30–60 min	Increased bio-oil yield from 39.9% to 51.6% at 350 °C and 60 min	[6]
NaOH	*Chlorella pyrenoidosa*	240–280 °C, 30 min	Increased bio-oil yield by 10%	[7]
Ce/HZSM-5	*Chlorella pyrenoidosa*	300 °C, 20 min	Increased bio-oil yield from 33% to 50%, increased C and H content Decreased N content	[8]
Na_2CO_3	*Microcystis viridis*	300–340 °C, 30–60 min	Increased bio-oil yield to 33%, decreased O content	[9]
Na_2CO_3	*Nannochloropsis*, *Pavlova*, *Isochrysis*	250–350 °C, 30–60 min	Increased bio-oil yield	[10]
H_2SO_4, CH_3COOH	*Enteromorpha prolifera*	230–290 °C, 20 min	Highest bio-oil yield of 28.4 wt% at 290 °C	[11]