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Hydrothermal liquefaction of *Chlorella pyrenoidosa* for bio-oil production over Ce/HZSM-5

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HIGHLIGHTS

- An effective method for converting *Chlorella pyrenoidosa* into bio-oil is proposed.
- The bio-oil was produced over Ce/HZSM-5 using hydrothermal liquefaction.
- The liquefaction mechanism was disclosed.
- Ce/HZSM-5 enhances Lewis acid active center accelerating liquefaction.

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ABSTRACT

This paper investigated a novel hydrothermal liquefaction process of *Chlorella pyrenoidosa* catalyzed by Ce/HZSM-5. The chemical groups and components of the residues of *C. pyrenoidosa* were analyzed by Fourier transform infrared spectrometry and Gas Chromatograph–Mass Spectrometer. The crystal structure and micro surface topography of *C. pyrenoidosa* before and after catalytic liquefaction were characterized by X-ray diffraction and Scanning electron microscopy, respectively. The experimental results showed that the catalytic cracking effects of Ce/HZSM-5 were superior to that of HZSM-5 as a liquefaction catalyst of *C. pyrenoidosa*. Compared with HZSM-5, Ce/HZSM-5 has a significantly enhanced Lewis acid active center, smaller particle size, larger specific surface, and highly dispersed Ce_4O_7 with trivalent and tetravalent cerium in the zeolite skeleton channel that accelerate the catalytic liquefaction of *C. pyrenoidosa*. The rare earth modified zeolite Ce/HZSM-5 exhibits good potential and a beneficial nature for the preparation of bio-oil from microalgae with high efficiency.

1. Introduction

With the depletion of traditional fossil fuels, the exploration of alternative energies received much attention. Bio-oil has become one of the most promising substitutes for engine diesel fuels because it is renewable and carbon–neutral, with low fine particulate matter (PM2.5) emission (Pootakham and Kumar, 2010). Recently, bio-oil has attracted increasing concerns from scientific researchers, and has become the focus and frontier of global biomass energy studies (Mohan et al., 2006; Mortensen et al., 2011; Varuvel et al., 2012). Preparation methods of bio-oil include fast pyrolysis (Demiral et al., 2012; Volli and Singh, 2012) and high-pressure liquefaction (He et al., 2009). Fast pyrolysis technology is generally characterized by the rapid thermal decomposition of biomass to produce bio-oil, bio-char, and uncondensable gas under an oxygen-free condition, temperature of approximately 500 °C, extremely high heating rate, and a short vapor residence time (less than 2 s). Fast pyrolysis is an attractive technology in obtaining crude power oil or chemical extraction, albeit the resulting oil is high in oxygen content. High-pressure liquefaction refers to cutting the macromolecular of biomass into micromolecular in liquefied oil by using a solvent under high temperature and pressure solvate. Researchers popularized the use of high-pressure liquefaction method due to its the relatively low oxygen content and high heating value of bio-oil from this technology. Furthermore, the liquefaction temperature and pressure can be reduced through the selection of suitable catalysts during the hydrothermal liquefaction process and the wet biomass can be directly liquefied without drying (Sun et al., 2010). Thus, the hydrothermal liquefaction technology is an energy saving and highly promising prospects for application.

Microalgae as a biomass material for bio-oil offers many advantages, propagates rapidly, and does not occupy farmland (Konur, 2011; Li et al., 2012; Singh et al., 2011). Previous research focused

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on microalgae oil yield. Although the yield of bio-oil has increased, the catalytic liquefaction mechanism remained unclear, and has become the key issue hindering the quality and yield upgrades of bio-oil. Based on the previous work (Xu et al., 2010, 2011, 2012) and to provide a reference for the development of high grade microalgae biomass liquid fuels, *Chlorella pyrenoidosa* was selected as a representative of microalgae biomass, and hydrothermal catalytic liquefaction products and residues were analyzed, as well as the catalytic liquefaction mechanisms from the chemical structure and micromorphology of Ce/HZSM-5 catalyst were investigated.

2. Experimental

2.1. Material

C. pyrenoidosa power is a product of Wudi Luqi Biological Engineering Co. Ltd. The mass fractions of cellulose, hemicellulose, and protein of *C. pyrenoidosa* are 25.8%, 12.22%, and 52.32%, respectively. HZSM-5 was purchased from the Catalyst Plant of Nankai University (Si/Al = 28, average grain diameter is 27.79 μm) and Ce/HZSM-5 is prepared according to reference (Xu et al., 2012).

2.2. Catalytic liquefaction test

The catalytic liquefaction experiment was conducted according to reference (Xu et al., 2012). A typical detailed process is as follows: 7.00 g of *C. pyrenoidosa* powder was placed into an autoclave reactor with 70 ml of de-ionized water. After stirring, 0.35 g of Ce/HZSM-5 was added into the reactor. The system was sealed to displace the air with pure N_2 (99.999%). The reaction kettle was heated to 300 °C and maintained for 20 min. The system was rapidly cooled by using cooling water at room temperature. Noncondensable gas was released from the vent, and the solid–liquid mixed phase was collected and separated by filtration. The liquid phase was extracted using $CHCl_3$, and the $CHCl_3$ was removed by vacuum distillation, then the remaining dark brown viscous oil was collected and defined as bio-oil (marked as CBO_c). An equal amount of HZSM-5 was added in the control group, with or without a catalyst, and the bio-oil was marked as CBO_h and CBO_n. The solid residues (SR) were filtered, dried at 105 °C for 1 h, and marked as SR_c, SR_h, and SR_n, respectively. Each test sample under the same liquefying condition was repeated for three times to reduce the artificial errors and to obtain the statistical standard deviations.

According to the average results of the three times tests, the yield of the products was calculated by the following formula (Chumpoo and Prasassarakich, 2010):

$$\text{Bio-oil yield} = \text{mass of bio-oil mass of raw material} \times 100\%;$$

$$\text{SR yield} = \text{mass of solid residue/mass of raw material} \times 100\%;$$

$$(\text{Gas} + \text{loss})\ \text{yield} = 100\%\text{-bio-oil yield} - \text{SR yield}.$$

2.3. Analyze test

The elemental analysis and heating value of the bio-oils were tested by a EuroEA3000 Element Analyzer (Leman Ltd.) and a XRY-1B oxygen bomb calorimeter (Shanghai Changji Geological Instrument Co., Ltd.), respectively. The chemical structures of the solids including microalgae raw materials, liquefaction residues, and catalysts were analyzed by using a Spectrum 100 Fourier Transform infrared spectroscopy (FTIR, PerkinElmer Co.) with the KBr pellet technique. The components of the bio-oil were analyzed by a Gas Chromatograph–Mass Spectrometer (GC–MS) with a Finnigan Trace 2000-MS employing a Varian capillary CP-SIL 5CB GC column (30 m × 0.25 mm id, 0.25-μm film). Crystal structures of the raw materials and the residues were tested by using a D/MAX2500V X-ray diffraction system (XRD, Rigaku Co.) with a maximum power of 18 kW, voltage 40 kV, current 40 mA, Cu/K- alpha radiation, and scanning speed of $5^\circ \cdot min^{-1}$ of 2θ from 5° to 80°. Surface morphologies of residue and powder samples were observed by using a JSM-6490LV Scanning Electron Microscopy (SEM, JEOL Co.) at 20 kV.

3. Results and discussion

3.1. Effects of catalysts on the yield and components of bio-oil

Fig. 1 shows the effects of the catalyst on the product yield of *C. pyrenoidosa* liquefaction. As can be seen from the statistical analysis results of the figure, the bio-oil yields increased to 34.02% and 49.87% using the catalysts HZSM-5 and Ce/HZSM-5, respectively. Compared with the group without a catalyst, groups with catalyst produced higher bio-oil yield as well as lower gas and residues yields. Especially, Ce/HZSM-5 induced a better catalytic effect than HZSM-5, which shows that Ce modification not only enhances the acidic property of HZSM-5 but also affects the liquefied selectivity of low-carbon small-molecule (Bi et al., 2011).

The elemental composition and heating value of *C. pyrenoidosa* bio-oil are shown in Table 1. It indicate that the Ce/HZSM-5 can increase the contents of element C, H and decrease the element N of the bio-oil significantly, which may lead to the calorific values of CBO_n, CBO_h, and CBO_c are 19.01, 21.77, and 26.09 MJ/kg, respectively. Therefore, compared with bio-oil from traditional lignocellulose such as rice husk with calorific value of 17.11 MJ/kg (Xu et al., 2010), bio-oil from algal biomass *C. pyrenoidosa* exhibits more advantages as fossil fuel substitutes, and also the catalysts of Ce/HZSM-5 play an important role in upgrading the quality of the bio-oils.

The total ion current (TIC) of the bio-oils are tested by GC–MS, and the main components and components' contents of the bio-oils were analyzed using a NIST library. The analysis results are listed in Table 2 (CBO_n), Table 3 (CBO_h) and Table 4 (CBO_c), respectively. It can be found that there are C_4–C_{16} oxygen containing organics in CBO_n, including aldehyde, ketone, acid, ester and some nitrogen containing chemicals which comes from the protein in *C. pyrenoidosa*. The acid components decreased and hydrocarbons appeared in CBO_h. Furthermore, there are more hydrocarbons such as cyclanes derivative, benzene derivative and alkene derivative in

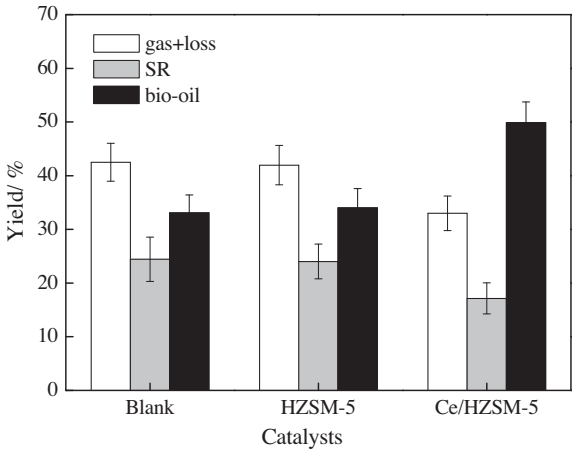

Fig. 1. Effects of catalysts on the product yield of *C. pyrenoidosa* liquefaction.