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Catalytic gasification of oil-extracted residue biomass of *Botryococcus braunii*

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HIGHLIGHTS

- Catalytic gasification of oil-extracted residue of *Botryococcus braunii* was performed.
- Gas conversion of 91%-C without tar was attained at 1023 K by Ni–Fe/Mg/Al catalyst.
- Composition of product gas with high contents of H_2 and CO was suitable as syngas.
- H_2 yield of 74.7 mmol g-biomass^{-1} obtained was much higher than others reported.
- The residue biomass can be a superior renewable source of syngas or hydrogen.

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ABSTRACT

Catalytic gasification of the oil-extracted residue biomass of *Botryococcus braunii* was demonstrated in a laboratory-scale continuous feeding dual bed reactor. Steam gasification at 1023 K over Ni–Fe/Mg/Al catalyst can completely reform tar derived from pyrolysis of the residue biomass into C1 gases and hydrogen, and has achieved 91%-C conversion to gaseous product ($CO + CO_2 + CH_4$). Composition of product gas has higher contents of CO and H_2 with their ratio (H_2/CO) of around 2.4 which is slightly H_2-rich syngas. Maximum hydrogen yield of 74.7 mmol g-biomass^{-1} obtained in this work is much higher than that from gasification of other algal biomass reported in literature. The residue biomass of *B. braunii* can be a superior renewable source of syngas or hydrogen.

1. Introduction

Botryococcus braunii, a green colonial algae, is one of the most promising renewable energy sources, because it can produce hydrocarbon oils with higher productivity as compared to other lipid-producing algae as well as major oil crops (Yoshida et al., 2012; Watanabe and Tanabe, 2013). For achieving practical biofuel production from *B. braunii*, it should be crucially important to upgrade quality of products that are mainly extracted oils and residue biomass after oil-extraction. The hydrocarbon oils produced by the *B. braunii* are basically classified into heavy oil fractions, and can be converted into transport fuels by hydrocracking (Murata et al., 2014) or catalytic cracking (Yamamoto et al., 2014). On the other hand, our previous work (Watanabe et al., 2014) has recently shown that the oil-extracted residue biomass of *B. braunii* is classified as a hydrogen-rich solid fuel comparable to fossil fuel such as a coal rather than other algal and terrestrial biomass, and thus should be also a superior feedstock for biofuel production.

Thermochemical conversion of microalgal biomass into biofuel was recently reviewed (Chen et al., 2015), which included torrefaction, liquefaction, pyrolysis and gasification. Among these conversion technologies, gasification is one of the most economical and efficient technologies for conversion of lignocellulosic biomass (Lasa et al., 2011; Asadullah, 2014). Gaseous products from the biomass gasification have a wide variety of applications, such as (1) generation of electricity and heat by direct combustion of flammable gas produced, (2) production of liquid hydrocarbon fuels or methanol via syngas ($CO + H_2$) produced, and (3) production of hydrogen (Li et al., 2015). Catalytic gasification of algal biomass apart from *B. braunii* was recently reported: for instance, hydrogen production from lipid-extracted residue biomass of *Nannochloropsis oculata* via steam gasification with use of an iron

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catalyst (Duman et al., 2014); hydrogen-rich gas production from lipid-extracted residue biomass of *Scenedesmus almeriensis* by catalytic gasification (Diaz-Rey et al., in press). Li et al. (2015) have recently published a review paper on metal catalysts for steam reforming of tar derived from the gasification of lignocellulosic biomass. This includes recent development of the catalysts using metal of Rh (Tomishige et al., 2004) or Co (Li et al., 2013), alloys of Ni–Fe (Wang et al., 2011), Ni–Co (Wang et al., 2013) or Co–Fe (Wang et al., 2012), or Ni combined with CeO_2 (Tomishige et al., 2007) or MnO_x (Koike et al., 2013). Such supported-metal catalysts are often used for steam gasification of biomass, unless partial oxidative gasification without catalyst at high temperatures (Hirano et al., 1998).

In this work, catalytic steam gasification of the oil-extracted residue of an axenic strain of *B. braunii* (called BOT-22), of which growth ability and oil productivity are quite high (Sakamoto et al., 2012), has been demonstrated in a laboratory-scale continuous feeding dual bed reactor, with considering higher contents of hydrogen and carbon in the residue biomass as a potentially superior gas source. A high-performance Ni–Fe alloy catalyst prepared from hydrotalcite compounds, which was developed by a part of authors of this paper (Koike et al., 2012; Li et al., 2014), has been used in order to reform tar derived from pyrolysis of the residue biomass into gas products. Catalytic performance as well as effect of reaction conditions on gasification efficiency will be described in detail, and furthermore, energy conversion based on higher heating value (HHV) of feedstock and gaseous products and comparison of the gasification data to other algal biomass as well as lignocellulosic biomass will be discussed in this paper.

2. Methods

2.1. Biomass feedstock

Methods of preparation and characterization of oil-extracted residue biomass of *B. branii* (BOT-22 strain) are same as already described in our previous paper (Watanabe et al., 2014), and their outline is given as follows.

Culture broth of BOT-22 strain (Sakamoto et al., 2012) of *B. braunii* was concentrated by a centrifuge, and followed by drying at 333 K for overnight. The dried sample of the strain was soaked into *n*-hexane for extraction of hydrocarbon oils including a small amount of carotenoids. The oil-extracted residue biomass of the strain was milled and sieved, and then the size fraction from 106 to 500 μm was used for following analysis and gasification tests. Dry powder of cedar wood used in previous work (Li et al., 2011) was also employed as a reference of lignocellulosic biomass. Moisture content was measured as weight loss percentage of the residue biomass sample by heating at 380 K for 1 h (JIS Z7302-3) and ash content was measured as percentage of residual mass (ash) after heating the samples at 1088 K under ambient air atmosphere for 1 h (JIS Z7302-4). C, H and N contents in the biomass were measured using a CHN Elemental Analyzer (Perkin-Elmer 2400), where O content was deduced by difference: thus, $O = 100 - (C + H + N)$. Composition of biomass feedstock used in this work is summarized in Table 1.

2.2. Catalysts

Properties of catalysts used for the gasification tests in this work are summarized in Table 2. The details of preparation and characterization of the catalysts are available in each reference given in this table. Ni/Al_2O_3 catalyst was prepared by impregnation method using $Ni(NO_3)_2$ aqueous solution with α-Al_2O_3 support, and followed by drying at 383 K for 12 h and calcination at 773 K for 3 h under air atmosphere (Wang et al. 2011). Catalysts of Ni/Mg/Al (Li et al., 2011) and Ni–Fe/Mg/Al (Li et al., 2014) were basically prepared by co-precipitation of nitrates of Ni, (Fe), Mg and Al to synthesize a hydrotalcite-like compound, and drying at 383 K for overnight and calcination at 1073 K for 5 h under air atmosphere.

2.3. Thermogravimetry (TG) analysis

TG analysis of the biomass samples was carried out with using Shimadzu DTG-60. The sample of around 10 mg in a Pt pan was heated with a ramp rate 10 K min^{-1} up to 1073 K under nitrogen atmosphere with flow rate of 50 mL min^{-1} (Watanabe et al., 2014).

2.4. Catalytic steam gasification test

Experimental procedure for the gasification test is same as already described in our previous work (Watanabe et al., 2014), except for using catalysts in this work. The outline is given as follows.

Catalytic gasification test of oil-extracted residue biomass of the strain BOT-22 in presence of steam was demonstrated in a laboratory-scale continuous feeding dual bed reactor (Kimura et al., 2006). A schematic diagram of the reactor is given as a Supporting Information (Fig. S-1). The reactor consisted basically of co-axial double cylindrical tubes made of quartz glass, which was equipped with an infrared image furnace and connected with ports for introduction and effluent of gas. The biomass powder was continuously fed from a mechanically vibrating nozzle with nitrogen gas flow (A) into top part of the outer tube, where pyrolysis took place in presence of steam supplied by the evaporation of water fed by a microsyringe pump. The biomass powder was vertically falling within heating zone and pyrolyzed to form products such as solid and gas. The solid products (char (fixed carbon) and ash) accumulated onto a sintered glass plate on the bottom of the outer tube (primary bed). Another carrier gas flow (B) was supplied from below, and passing through the sintered glass plate to transport the gaseous product from biomass pyrolysis into the inner tube, of which lower end was set just above the glass plate. Catalyst bed was set in the inner tube end for steam reforming of biomass tar. The gaseous product flew upward within the inner tube and went out from heating zone of the reactor. Compounds with relatively higher boiling point were condensed together with unreacted steam (water) around outlet part of the reactor, and eventually those with relatively lower boiling point was collected by a bubbling trap into ice-cold 2-poropanol. Such condensable components produced from the pyrolysis of the biomass were named “tar” in this paper. A soap-film flow meter and gas-sampling ports for a syringe and a bag were set after the bubbling trap.

The gasification tests were performed under atmospheric pressure at temperature of 873, 923, 973 or 1023 K. Here, the temperature of the reactor was controlled by the thermocouple at the outer wall of the reactor as shown in Fig. S-1. The temperature measured was almost same as temperatures in both primary and secondary beds in the rector. It was experimentally confirmed that the temperature at the center of the reactor was slightly higher (typically ~15 K) than the temperature at the outer wall of the reactor, which was presumably due to characteristic of an infrared image furnace used in this work. The amount of the catalyst used was 0.3–1.0 g. Pre-reduction of the catalyst was carried out in the reactor with conditions as follows: under H_2/N_2 (30/30 mL min^{-1}) mixed gas at 1073 K for 0.5 h for Ni/Mg/Al (Li et al., 2011) and Ni–Fe/Mg/Al (Li et al., 2014) or at 773 K for 0.5 h for Ni/Al_2O_3 catalyst (Wang et al., 2011). After the pre-reduction, both biomass (45, 60 or 90 mg min^{-1}) and water (50 μL min^{-1}) were introduced with nitrogen carrier gas of 60 mL min^{-1} which was sum of 30 mL min^{-1}