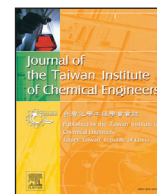




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Reactivity of solid residue from hydrothermal liquefaction of diatom in oxidizing atmosphere

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ABSTRACT

The reactivity of solid residue (char) derived from diatom (*Fistulifera* sp.) after hydrothermal liquefaction (HTL) reaction at 673 K, 10 MPa, 30 min was investigated during oxidation in air at 553–1073 K. Results indicate the derivative thermo-gravimetric (DTG) curve of HTL char showed very small peak below 600 K, indicating HTL reaction effectively decomposed lipid, carbohydrates and protein. The activation energies of the HTL char derived from diatom during combustion up to 1073 K by FWO and KAS methods was 120.0 and 115.3 kJ/mol, respectively, when the char conversion α is 0.2–0.5 (*i.e.* pyrolysis). At higher char conversion ($\alpha \geq 0.5$), the activation energy monotonically increased as combustion reaction proceeds. However, this increment of activation energy of HTL char derived from diatom during oxidation stage was much smaller than those of de-oiled microalgae char reported in the literature. The HTL char derived from diatom has porous structure (specific surface area: 293.2 m²/g and total pore volume: 0.672 cm³/g). It was found this porosity is derived both the silicon structure of diatom and remaining carbon after HTL reaction. The total amount of oxygen functional groups (OFG) substantially increased by oxidation at 553 and 573 K. By holding the reaction temperature at 553 K up to 60 min, the total OFG monotonically increased to 1.04 mmol/g. At 573 K, the amount of total OFG peaked 1.08 mmol/g at 30 min and decreased. The decomposition of carboxyl groups is dominant reaction for reduction in total OFG after 30 min at 573 K during oxidation. The tendencies of BET surface area and total pore volume of char agreed with these results of char during oxidation.

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1. Introduction

Microalgae have been attracting attention because of their advantages such as high lipid content, fast growth rate and non-competition with the food. Production of algal biofuel and biochemical includes following processes: cultivation and harvesting of algae, bio-oil extraction, and the bio-oil conversion into biofuel and biochemicals [1,2]. Solvent extraction method and hydrothermal liquefaction (HTL) method that is thermal decomposition of biomass in subcritical water at 473–623 K and 5–20 MPa, are usually used as the bio-oil extraction methods. It is considered that HTL is promising to produce bio-oil because HTL does not need the energy-intensive drying and distillation processes. However, in both methods, after the bio-oil extraction process, efficient utilization of solid algal residue is needed to reduce production of waste and improve process economics in large-scale biofuel and biochemicals production systems [3,4]. At present, utilization of

solid residue (1) by combustion to supply process heat, (2) as adsorbents to remove heavy metal ions, pigments and other cations, and (3) as soil amendment, are considered to be promising.

Research works have been conducted on pyrolysis and combustion of microalgae and de-oiled (or defatted) microalgae residue after bio-oil extraction as summarized in Table 1. In most of the studies, thermogravimetric analysis (TGA) was used to measure reactivity of microalgae [5–10] and de-oiled algal residue [11–13] in pyrolysis or oxidation reaction with different heating rates and then calculated activated energy of the reactions. Ferreira et al. [13] investigated the kinetics of three microalgae and their solvent extracted (ultrasound assisted) residue in TGA. They reported the calculated activation energy was similar for the raw and extracted microalgae [13]. Gao et al. [14] and Tahmasebi et al. [15] investigated reactivity of microalgae and coal blend in co-combustion and reported that the activation energy increased as the ratio of microalgae increased.

In the last decade, extensive research works on the utilization of biomass char by (1) activation to obtain activated carbon that has large specific surface area and/or (2) oxidation to increase the amount of oxygen functional groups (OFG) on the surfaces at

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Nomenclature

A	pre-exponential factor [s^{-1}]
E	activation energy [J/mol]
k	rate constant
m_f	final weight of char [g]
m_i	initial weight of char [g]
m_t	weight of char at time t [g]
R	gas constant [J/mol·K]
T	temperature [K]
t	time [s]

Greek alphabets

α	conversion of char [–]
β	heating rate [K/s]

Abbreviations

DTG	derivative thermo-gravimetric
FWO	Flynn–Wal–Ozawa
HTL	hydrothermal liquefaction
KAS	Kissinger–Akahira–Sunose
OFG	oxygen functional groups
TGA	thermogravimetric analysis

relatively low temperatures, have been conducted as summarized in Table 2 [16–30]. In some of these studies, these activated or oxidized carbon was used for adsorbents to remove metal cations and organic materials [18,19,25,26]. The activated carbon has been produced from microalgae and macroalgae [16–19]. Chang et al. measured properties of char derived from *Chlorella*-based microalgal residues after pyrolysis in N_2 and reported the *Chlorella*-based biochar has high-N (> 10%) and rich-mineral, and porous structure [16]. In the series of study [17], they conducted pyrolysis and activation of the char in N_2/CO_2 and reported the activated carbon still has significant nitrogen contents (3.6–9.6wt%) and lower carbon contents (54.6–68.4wt%) than those of commercial activated carbons [17].

Leng et al. conducted HTL of sewage sludge [28,29], microalgae and rice straw [29] in organic solvent and studied adsorption tests of dyes using the produced HTL chars. They reported that the surface area of the HTL char was very small. Chen et al. [30] conducted hydrothermal carbonization of glucose in water at 453 K for 24 h and produced HTL char. They then oxidized the HTL char in air up to 373–573 K for 5 h to use the oxidized solid residue as adsorbents for heavy metal ions. It was reported the amount of surface OFG is more important than the specific surface area of char for adsorption of ammonium ions, dyes and metal ions [27–31].

Recently, novel diatom *Fistulifera solaris* JPC DA0580 that can accumulate approximately 60wt% of lipid has been developed [32]. In our previous study, we carried out experiments of HTL of this diatom [33] and showed that HTL is promising to produce crude bio-oil and recover nutrients in the aqueous phase. However, the experimental studies and system design regarding the aftertreatment of the solid residue (char) after HTL of diatom has not been conducted. At present, we consider combustion of the solid residue to recover process heat is most feasible aftertreatment. However, no research on reactivity of the solid residue (char) derived from microalgae (diatom) obtained after HTL in sub-critical water has been conducted in combustion. In this study, we investigated the characteristics and kinetics of solid residue (char) of the diatom after HTL reactions 1) during combustion in air by using a muffle furnace and TGA up to 1073 K and 2) during oxidation of the char in air at 553–573 K.

2. Experimental

2.1. Microalga

A marine diatom *Fistulifera solaris* JPC DA0580 [32] was used. The diatom was pre-cultured in a flat 1.2 L culture vessel in 2-fold concentrated f medium (2f medium) [34] dissolved in artificial seawater [35] for 7 days and was then cultured in a photo bioreactor with the 2f medium for 12 days [36,37]. The concentration of the alga was measured by weight difference. After culturing, the concentration of the algal slurry was increased to 30 g-dry-algae/L with a centrifuge (himac CR7, Hitachi Koki Co., Ltd.). The sample was freeze dried and was kept in a deep freezer at 213 K prior to experiments. Details were described in our previous studies [33,35].

2.2. Hydrothermal liquefaction (HTL) in an autoclave reactor

The concentrated microalgal slurry (100 mL) was loaded into an autoclave HTL reactor (TPR-1, 300 mL, Taiatsu Techno® Corporation, Osaka, Japan). After closing a lid, the autoclave reactor was purged with 2.5 MPa Ar gas. The reactor was heated with an electric heater up to 573 K and maintained for 30 min. The reaction pressure was approximately 10 MPa.

After the reactor was cooled to room temperature, the water-soluble fraction was separated from bio-oil and solid products by using a filter paper. Because the bio-oil and solid residue attached strongly as if they were one solid phase, the water soluble fraction was able to be separated easily. The bio-oil and solids products remaining on the filter paper, inside of the reactor and an impeller was also recovered with acetone. The bio-oil was extracted from the solid product by using acetone for 30 min and then the acetone soluble fraction and the solids products were separated by filtration using a nylon-mesh. The HTL bio-oil was obtained after acetone was evaporated at 353 K. The remaining solid products on the nylon mesh were recovered and dried in a vacuum oven.

We have carried out the HTL experiments 24 times. The average bio-oil yield was 13.86wt% (standard deviation = 1.22 wt%) and the average solid residue yield was 28.32wt% (standard deviation = 5.47 wt%). The procedures of HTL reaction, and product separation and recovery were written in previous studies [33,38].

2.3. Combustion of solid products

2.3.1. Muffle furnace

The solid products were combusted in air by using a muffle furnace (F100, Yamato Science Co.Ltd., Tokyo, Japan). The reaction temperatures were 553–1073 K (holding time was 0 s) with a heating rate of 10 K/min. After combustion experiment using the muffle furnace, the remaining ash was quantified based on Japanese Industrial Standards (JIS) Z 7302-4 protocol [39]. Approximately 0.25 g of the ash was placed in the muffle furnace and heated up to 773 K for 60 min in air. The temperature was then increased to 1088 K for 45 min and maintained for 1 h in air. The sample was cooled in a desiccator for 15 min and weighed.

2.3.2. Thermogravimetric analyser (TGA)

The weight change during combustion of the solid residue after HTL was carried out by using a thermogravimetric analyzer (TGA-50, Shimadzu Corporation, Japan). The solid sample (ca. 2.1–2.7 mg) was placed in an alumina basket, which was suspended in a quartz glass reactor tube of which inner diameter was 18.7 mm. The temperature of the alumina basket was measured with a thermocouple placed just below the basket. Air was fed

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