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Impact of torrefaction on the composition, structure and reactivity of a microalga residue

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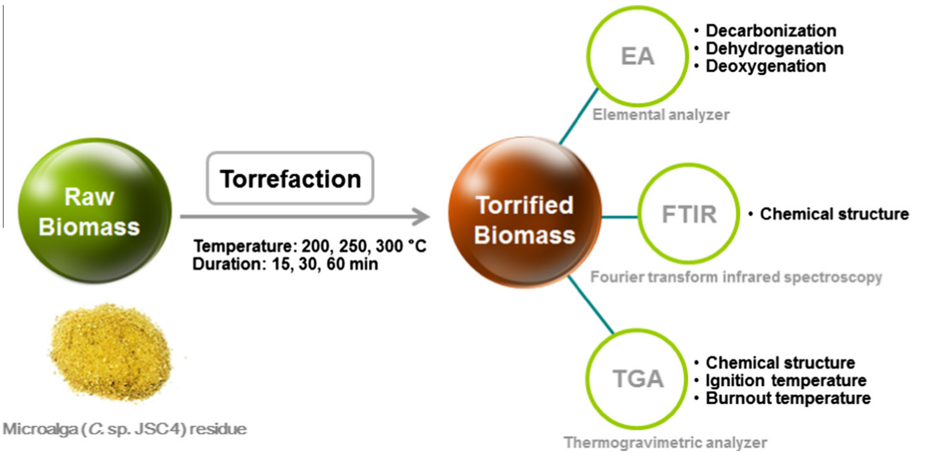
HIGHLIGHTS

- Composition, structure, and reactivity of a microalga residue after torrefaction are studied.
- Three indices of decarbonization, dehydrogenation, and deoxygenation are defined.
- Torrefied biomass is characterized by deoxygenation > dehydrogenation > decarbonization.
- Carbohydrate is first destroyed by torrefaction, followed by protein consumption.
- Ignition and burnout temperatures of biomass are raised when torrefaction severity rises.

GRAPHICAL ABSTRACT



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ABSTRACT

The impact of torrefaction upon the composition, structure, and reactivity of a microalga residue, which was obtained from *Chlamydomonas* sp. JSC4 (*C.* sp. JSC4) undergoing oil-extraction, is studied. Three indices of decarbonization (DC), dehydrogenation (DH), and deoxygenation (DO) are defined to account for the mass losses of carbon, hydrogen, and oxygen in the biomass from torrefaction. The results indicate that these indices are characterized by the order of DO > DH > DC, as a result of dehydration and devolatilization mechanisms occurred during biomass torrefaction, and the calorific value of torrefied biomass linearly increases with increasing the indices. The thermogravimetric analysis (TGA) and Fourier transform infrared (FTIR) spectra clearly suggest that carbohydrate is first destroyed with increasing torrefaction severity, followed by protein consumption. When the torrefaction degree is not severe, the ignition temperature of the biomass is governed by the thermal degradation of carbohydrate and is insensitive to the torrefaction severity. Once the residue is torrefied at 250 °C for 60 min or at 300 °C for 30 min, most of the carbohydrate and protein in the biomass are depleted, but part of the lipid is retained. As a result, the ignition and burnout temperatures of the biomass are raised to a certain extent, thereby reducing its reactivity. The obtained results have provided a useful insight into applications of using upgraded microalgae residues as fuels in industry.

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1. Introduction

Torrefaction is a promising technology to upgrade biomass for solid fuel production. Along the biomass surface, heat and mass transfer pertains to a counter-current pattern in nature. When biomass is pretreated in nitrogen at temperatures of 200–300 °C [1–3], heat transferred from the surrounding into biomass causes the liberation of water and light volatiles toward its environment and the thermal degradation of the treated material [4], especially in hemicellulose [5]. As a result, torrefied biomass has lower atomic H/C and O/C ratios and thereby a higher calorific value when compared to its parent biomass. The other advantages accompanied by torrefaction include improved grindability and promoted homogeneity of lignocellulosic materials as well as the conversion of hygroscopic biomass into hydrophobic one [1,3].

In the last decade, the impact of torrefaction upon biomass properties has been extensively investigated and much knowledge has been gained. When biomass is torrefied in a reactor, dehydration and devolatilization reactions are triggered [6]. This results in the release of condensable and non-condensable gases. The non-condensable gas comprises primarily CO_2 and CO [7], and small amounts of CH_4 and H_2 [8,9], while the main components in the condensed liquid include water, acids, alcohols, phenols, ketones, aldehydes, esters, and so forth [9–11]. On account of the liberation of hydrogen- and oxygen-rich species in the course of torrefaction, this thermal process is characterized by dehydrogenation, deoxygenation, and dehydroxylation processes [12,13], and, therefore, relative more carbon is retained in the torrefied biomass. In other words, the contents of low-energy H—C and O—C bonds are decreased, whereas the content of high-energy C—C bond is increased [14,15]. For this reason, the atomic H/C and O/C ratios in biomass are lowered and energy densification is achieved when torrefaction severity is raised.

To proceed farther into the recognition of the influence of torrefaction upon biomass, some researchers focused their attention on structure variation of biomass from torrefaction using FTIR as an analysis tool. Rousset et al. [16] investigated the structures of raw and torrefied bamboo, and found that the intensity of the OH bands around 3350 cm^{-1} decreased with increasing torrefaction severity. The partial disruption of hydroxyl groups in biomass reduced the formation of hydrogen bonding so that hydrophilic biomass was generated [1]. Chen et al. [17] torrefied coffee residue, sawdust, and rice husk, and examined the FTIR spectra of hemicellulose, cellulose, and lignin in the biomass. They concluded that most of the hemicellulose contained in the three wastes was consumed when the torrefaction temperature was 270 °C, and cellulose was partially depleted at the same temperature for 1 h torrefaction. On the other hand, it was difficult to identify lignin in the wastes, regardless of the raw or torrefied wastes. Li et al. [15] analyzed the functional groups in bamboo before and after torrefaction in carbon dioxide. Their results indicated that the intensity of the signal of aromatic and condensed structure increased as compared to the aliphatic ones at higher torrefaction temperatures, as a result of increased coalification degree. In another study [18] for bamboo in nitrogen suggested that the OH group at 3290 cm^{-1} shifted to a higher wavenumber in the torrefied samples, stemming from dehydroxylation and condensation reactions occurred in hemicellulose. The increase in torrefaction severity led to the weaker signal at 1723 cm^{-1}, which was due to the formation of acids, aldehydes, ether substances as well as CO and CO_2 from the decarboxylation, decarbonylation, and fracture of C=O groups. The relative increase of the signal for aromatic groups at 1610, 1510, and 1270 cm^{-1} compared to those for carbohydrates reflected the aromatization of bamboo and enrichment of lignin components.

In recent years, the commercialization of torrefaction has attracted more and more interest because of its potential applications in industry [19,20] such as combustion [21], gasification [22], ironmaking [23], and pyrolysis [12,24]. When torrefied biomass is used as a solid fuel for combustion, the recognition of fuel reactivity such as ignition and burnout is of the upmost importance. Bridgeman et al. [25] exposed raw and torrefied willow to a methane-air flame, and found that the latter was ignited more quickly. Pimchuai et al. [26] tested raw and torrefied rice husks in a spout-fluid bed combustor, and observed that the torrefied husks were ignited faster and the bed temperature was raised to a higher level. This improved reactivity is likely due to the low moisture content in torrefied biomass. Du et al. [27] torrefied and carbonized bamboo, oil palm, rice husk, sugarcane bagasse, and Madagascar almond, and examined their ignition temperatures by individually mixing these samples with sodium nitrite ($NaNO_2$). They found that an increase in pretreating temperature almost linearly increased the ignition temperature, resulting from less volatiles contained in the pretreated biomass which dominated the ignition temperature in their approach.

Reviewing literature suggests that torrefaction of lignocellulosic biomass has been extensively studied. In contrast, only a few studies were reported regarding algal biomass torrefaction [28–32], and they focused on torrefaction performance (e.g., solid and energy yields [28,31,32]) and its impact on biomass properties (e.g., appearance [32], elemental analysis [28,29,31,32], proximate analysis [28], calorific value [28,31,32], and grindability [28]), torrefaction kinetics [29], and energy analysis of a torrefaction system [31]. As described earlier, the torrefaction process involves dehydration and devolatilization reaction, which are related to the liberation of carbon, hydrogen, and oxygen. Instead of investigating conventional properties of raw and torrefied biomass, the present study addresses decarbonization, dehydrogenation, and deoxygenation processes of a microalga residue from torrefaction. The structure variation of the microalgal residue before and after torrefaction will be examined from Fourier transform infrared (FTIR) spectra. Moreover, the thermal degradation, ignition, and burnout characteristics of the biomass will be explored from thermogravimetric analysis (TGA). The aforementioned topics for microalga residue undergoing torrefaction have not been studied yet. From the compositional, structure, and reactivity analyses, the reaction mechanism, thermal degradation of carbohydrate, protein, and lipid, and ignition and burnout characteristics of the microalga residue from torrefaction can be figured out. Therefore, obtained results are able to provide a comprehensive insight into the applications of microalga residue torrefaction for solid fuel production in industry.

2. Experimental

2.1. Material

Microalgae have been thought of as important feedstocks for the production of third-generation biofuels such as biodiesel, bio-butanol, biohydrogen and bio-oils. After these biofuels are produced, microalgae residues become wastes. These wastes can be upgraded by torrefaction to produce solid fuels with better quality, and the secondary energy recovery from microalgae can be achieved. Consequently, a microalga residue was chosen as the feedstock and torrefaction was adopted as the thermochemical conversion method in this study. The microalga *Chlamydomonas* sp. JSC4 (*C.* sp. JSC4), which was isolated from freshwater in southern Taiwan, was an oil-rich biomass [33]. After the microalga was oil-extracted using a hexane/methanol co-solvent system, its residue was adopted as the raw material of torrefaction. Prior to