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Pyrolysis of microalgae residual biomass derived from *Dunaliella tertiolecta* after lipid extraction and carbohydrate saccharification

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HIGHLIGHTS

- *Dunaliella tertiolecta* residual biomass was further utilized by pyrolysis as a biorefinery concept.
- Effects of pyrolysis temperature and time on product distributions were investigated.
- The product bio-oil from pyrolysis of the biomass residue was analyzed by GC–MS.
- The pyrolysis reaction mechanism was studied using the lumped kinetic model.

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ABSTRACT

Microalgae (*Dunaliella tertiolecta*) are considered potential feedstock for production of biodiesel and bioethanol due to their high lipid and carbohydrate contents. To achieve complete utilization of microalgae in a microalgae biorefinery, residual biomass after conversion of lipids and carbohydrates into biodiesel and bioethanol can be converted into bio-oils by pyrolysis. *D. tertiolecta* residual biomass decomposed mainly between 200 °C and 550 °C at heating rates of 5–20 °C/min. The apparent activation energy increased from 163.12 kJ mol^{-1} to 670.24 kJ mol^{-1} with increasing pyrolysis conversion. Experimental results were consistent with the proposed lumped kinetic model, and the kinetic rate constant for *D. tertiolecta* residual → bio-oil (k_2) was the highest. This result indicates that the predominant reaction pathway of *D. tertiolecta* residual was **A** (*D. tertiolecta* residual) to **B** (bio-oil), rather than **A** (*D. tertiolecta* residual) to **C** (gas; C_1–C_4, CO, CO_2, H_2) or **B** (bio-oil) to **C** (gas; C_1–C_4, CO, CO_2, H_2).

1. Introduction

Biomass is considered to be a renewable feedstock for biofuel production and therefore an alternative to fossil fuels [1–5]. Among various biomasses, microalgae are a promising feedstock because they have several advantages compared to sugarcane, corn, and lignocellulosic biomass [6]. Microalgae can grow faster than plant crops, and are free of the controversy surrounding the use of food for fuel production. Furthermore, large-scale cultivation of microalgae can be implemented on non-arable land, such as deserts, or the ocean.

Microalgae are good feedstocks for biodiesel production because of their high oil content (up to 80% biomass) [7]. Many studies have been conducted to commercialize microalgae-based biodiesel production [8–10]. However, biodiesel production from microalgae is still too expensive to be commercialized at present [11]. To develop economically feasible processes for microalgae biofuels, whole components need to be used-up completely based on the microalgae biorefinery concept [12]. The main components of microalgae biomass are proteins, carbohydrates, and lipids. Residual biomass after oil extraction for biodiesel production is rich in proteins and carbohydrates. This residual biomass can be used as animal feed [6]. Carbohydrates in residual biomass could also potentially be exploited as feedstock for bioethanol production [13].

Previously, we developed a microalgae biorefinery for the sequential production of biodiesel and bioethanol. *Dunaliella tertiolecta* LB999 was cultivated in a photobioreactor using a semi-permeable membrane at a large-scale at a Korean coastal area [14]. Biodiesel was produced from the cultured *D. tertiolecta* biomass, and the fuel properties satisfied the fuel quality requirements of transportation fuel of the Korean Institute of Petroleum

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Management. Residual biomass after oil extraction was subjected to saccharification. More than 81% of the total carbohydrate content was saccharified by enzymes such as AMG 300L without any pretreatment. The saccharification cocktail was directly used for bioethanol fermentation using *Saccharomyces cerevisiae* with 82% yield [15].

To achieve complete utilization of whole cellular components, the materials that remain after biodiesel and bioethanol production can be subjected to pyrolysis to convert them into bio-oils. Ross et al. [16] performed pyrolysis of *Macrocystis pyrifera* at 500 °C using pyrolysis–GC–MS, and confirmed that degradation products were carbohydrates, proteins, or polyphenolics. Thangalazhy-Gopakumar et al. [17] reported catalytic pyrolysis of green algae for hydrocarbon production using HZSM-5 catalyst in a fixed bed reactor. They confirmed that certain negative attributes of algae bio-oil, such as its high nitrogen and oxygen content, were reduced by using HZSM-5 as a catalyst.

In the present study, we investigated the pyrolysis characteristics and kinetics of *D. tertiolecta* residual biomass obtained after lipid and carbohydrate utilization to obtain information regarding the types of fuel (gas, bio-oil, or bio-char) that can be generated. Thermogravimetric analysis was used to study the pyrolysis characteristics of *D. tertiolecta* residual and to obtain global kinetic parameters, including activation energy. Kinetic parameters from a lumped kinetic model were also calculated.

2. Experimental

2.1. Microlagae biomass sample preparation

D. tertiolecta LB999 was cultured in a 70 L plate-type photobioreactor with fluorescent lighting (60 μE/m^2 s) at 20–25 °C [14]. Residual microalgae biomass was obtained after lipid extraction and saccharification as follow: total lipids were extracted twice directly from dried cells using a 2:1 (v/v) methanol/chloroform mixture for 2 h at 65 °C [18]. For enzymatic saccharification, 5% (w/v) lipid-extracted microalgae biomass was treated using AMG 300L at pH 4.5 and 55 °C for 16 h [15].

2.2. Chemicals and analyses

Commercial cellulase (Celluclast 1.5L, Novoprime B957), amyloglucosidase (AMG 300L), and Viscozyme L were used for saccharification [15]. All other chemicals were of analytical or reagent grade and were used with no pretreatment. Lipid content of the dried biomass was determined using the Soxhlet method (method 920.39) [19]. Carbohydrate content was determined based on the methods of the National Renewable Energy Laboratory (NREL) [20]. Protein content was determined using a micro-Kjedahl method (method 976.05) [19].

2.3. Thermogravimetric analysis and tubing reactor

Moisture and ash contents of *D. tertiolecta* residual biomass were determined using ASTM E 1756 and ASTM E 1755, respectively [21]. Thermogravimetric analysis of *D. tertiolecta* residual biomass samples (25.0 ± 1.0 mg) was carried out using thermogravimetric analysis (TGA; TA Instrument Q50). Nitrogen was used as the carrier gas at a flow rate of 25 mL/min. Heating rates were controlled at 5, 10, 15, and 20 °C/min from 30 °C to 900 °C.

A tubing reactor was used to pyrolyze the *D. tertiolecta* residual biomass sample. The reactor was used to test the effect of residence time on the pyrolysis of *D. tertiolecta* residual biomass at a constant temperature. A sample mass of 2 g was used in each experimental run. Descriptions of the experimental apparatus and procedure are provided in our earlier publications [22,23]. Based on data from the differential thermogravimetric (DTG) curves, we selected pyrolysis temperatures of 410 °C, 420 °C, and 430 °C in the tubing reactor. Reaction time was varied from 1 to 5 min at each reaction temperature. After reaction, the reactor was removed from the molten salt and cooled to room temperature. Reaction products were analyzed by weighing gas, oil, and char products. Gas yield, defined as (gas weight) × 100/(feed weight), was obtained by weighing the tubing reactor before and after gas release. Other pyrolyzed products were separated into oil (acetone soluble) and char (acetone insoluble) using a solvent extraction technique [24]. Solid yield was defined as (weight of acetone insoluble) × 100/(weight of feed), while oil yield was defined as (100 − gas yield − char yield).

3. Results and discussion

3.1. Analysis of composition of D. tertiolecta LB999 after lipid extraction and carbohydrate saccharification

Cellular composition of *D. tertiolecta* LB999 after photoautotrophic culture was analyzed; results are shown in Table 1. Raw *D. tertiolecta* biomass sample consisted of lipid (22.0 wt.%), carbohydrate (40.5 wt.%), protein (27.2 wt.%), and ash (10.3 wt.%). For biodiesel production, lipids in the raw *D. tertiolecta* biomass sample were completely extracted using a solvent mixture of dimethyl carbonate and methanol. After lipid extraction, the residual biomass contained 51.9 wt.% carbohydrate, 35.0 wt.% protein, and 13.1 wt.% ash, without any trace of lipids (Table 1). This residual biomass was further utilized for saccharification using enzymes (AMG 300L) for bioethanol fermentation. After saccharification, a second residual biomass was obtained by separating supernatant containing various monosaccharides from bioethanol fermentation. As shown in Table 1, the second residual biomass obtained after lipid extraction followed by saccharification was composed mainly of protein (67.7 wt.%). To achieve complete utilization of the *D. tertiolecta* biomass sample, the second residual biomass was pyrolyzed to obtain valuable bio-oil.

The characteristics of the raw *D. tertiolecta* biomass and the second *D. tertiolecta* residual biomass samples are presented in Table 2. The ash content of the *D. tertiolecta* residual biomass was higher than that of the raw biomass, as inorganic materials were concentrated in the residual biomass during lipid extraction and saccharification. In general, the ash content of algal biomass is higher than that of lignocellulosic biomass. Bird et al. [25] produced algal biochar from macroalgae (seaweed) by pyrolysis of eight species of green tide algae. They reported that the ash content of raw algae was 10.5–33.8 wt.%, which is consistent with our findings.

The carbon (C) content of *D. tertiolecta* residual biomass was higher than that of other green tide algae such as *Cladophora linum* and *Cladophora coelothrix* that had C contents ranging from 20.5 to 32.1 wt.% [25]. The oxygen and nitrogen contents of *D. tertiolecta* residual biomass were 40.04 wt.% and 8.40 wt.%, respectively. The high content of nitrogen was likely due to the high protein content of 67.7 wt.% (Table 1). The higher heating values (HHVs) of the raw

Table 1
Analysis of composition of *D. tertiolecta* LB999 after lipid extraction followed by carbohydrate saccharification.

	Chemical composition (%)			
	Lipid	Carbohydrate	Protein	Ash
After culture	*22.0*	*40.5*	*27.2*	*10.3*
After lipid extraction	–	*51.9*	*35.0*	*13.1*
After saccharification	–	*15.5*	*67.7*	*16.8*