



Analytical pyrolysis reaction characteristics of *Porphyra tenera*

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ABSTRACT

The non-isothermal pyrolysis of red algae (*Porphyra tenera*) was studied via thermogravimetric (TG) analysis in combination with two types of analytical pyrolyzer-gas chromatography/mass spectrometry (Py-GC/MS) techniques, namely, evolved gas analysis (EGA)-MS and multi-shot Py-GC/MS. The TG and model-free kinetic analyses revealed that the pyrolysis of *P. tenera* proceeded via the independent decomposition of carbohydrates, proteins, and lipids. Differential TG and EGA-MS indicated the existence of three decomposition temperature regions. In the first temperature region (< 300 °C), carbohydrates were mainly decomposed. Large amounts of pyrolyzates of proteins and lipids such as toluene, phenols, aromatic amino acids, and hexadecanoic acid were produced in the second temperature region (301–380 °C). In the third region (> 380 °C), large amounts of aromatic hydrocarbons and alkanes were obtained by the secondary cracking of the pyrolyzates of proteins and lipids.

1. Introduction

Technologies for the conversion of biomass to energy are being widely investigated as a potential strategy for alleviating worldwide issues such as fossil fuel depletion, environmental contamination, and climate change [1–5].

Among the various thermo-chemical conversion technologies, pyrolysis is considered as a promising method for the production of energy from biomass because larger amounts of bio-oil can be produced by this approach than can be achieved with gasification and fermentation, and less toxic compounds, such as dioxin, are generated than in the case of incineration [6]. Pyrolysis has been applied to various kinds of biomass, such as wood [7–9], citrus peels [10], and so on [11–16]. In contrast to land-based bio-fuel feedstocks like wood, algal biomass has attracted much attention as a potential resource for bioenergy production. Algae, classified as 3rd generation biomass, have higher productivity and a faster growth rates than lignocellulosic biomass, i.e., 2nd generation biomass, and do not require a wide harvesting area. The higher photosynthetic efficiency of algae (6–8%) relative to that of lignocellulosic biomass (1.8–2.2%) can also provide a high CO₂ fixing rate, suggesting

its potential to decrease atmospheric greenhouse gas [17–19].

A large amount of sea algae biomass (12 million tons of dry matter/year) is currently harvested for use as food or fertilizer and is considered as a potential biomass resource for the production of energy [11,17]. Several researchers are also trying to develop more efficient algal biomass for energy production [20,21]. Recently, extensive focus has been placed on the pyrolysis of micro- and macro-algae, where meaningful results demonstrate the potential for the production of large amounts of high-quality bio-oil [11,13,20,22–24]. Algal biomass consists of carbohydrates, lipid, and protein, however; lignocellulosic biomass is comprised of hemicellulose, cellulose, and lignin [8,17]. Therefore, pyrolysis properties and its product distribution are also different with those of lignocellulosic biomass. Owing to the presence of lipids and proteins in algae biomass, large amounts of fatty acids and nitrogen-containing pyrolyzates are produced from the pyrolysis of algae. Although their formation pathways from lipids and proteins have been reported, the formation of other chemicals that can be produced by the interaction between pyrolysis reaction intermediates of main components of algae were not discussed in prior literatures [11,12,16,20,23].

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The effect of inorganic metals on the pyrolysis of algae is also important because these metals can enhance catalytic effect on the pyrolysis reaction, however, they also can be an inhibition factor on plant operation [11,25]. Bae et al. [11] obtained the highest yield of bio-oil from the pyrolysis of different kinds of algae, *Undaria pinnatifida*, *Laminaria japonica*, and *Porphyra (P.) tenera*, at 500 °C and found that the large amounts of inorganic metals contained in the algae can act as catalysts for pyrolysis. High metal contents can make the catalytic effect on the decomposition of the tar vapor produced by pyrolysis of *P. tenera*, and this also encourages the pyrolysis of algae in the production of alternative energy from biomass [11,25]. Meanwhile, difficulty with the direct use of dried algae was also observed because high metal content in a macroalgae can cause operating problems such as a fouling and slagging during the combustion process [25]. Difficulty with the direct use of algae pyrolysis oil as a fuel due to the large amounts of nitrogen-containing compounds formed from the pyrolysis of proteins in the algae cells was also suggested by Bae et al. [11] and they emphasized that an additional catalytic upgrading process is necessary to decrease the nitrogen content in the final oil product.

Kim et al. [20,23] investigated the pyrolysis kinetics and analyzed the products generated from marine biomass, *Saccharina japonica* and *Sagarssum* sp., by using a thermogravimetric (TG) analyzer and a tubing reactor. Their combined interpretation of the pyrolysis kinetics and product analysis suggested that each algal species has different kinetic parameters and different selectivity toward bio-oil. Kebelmann et al. [22] performed TG analysis of lipids and proteins that were extracted from green microalgae, *Chlamydomonas reinhardtii* (CR), mutant CR, and *Chlorella (C.) vulgaris*, and found that both lipids and proteins had a wide decomposition temperature range from 150 to 600 °C. They also indicated that the major decomposition temperature of lipids was lower than that of proteins. Wang et al. [13] also decomposed the residue generated after the extraction of the lipids from *C. vulgaris* at 500 °C using a fluidized reactor and reported that the bio-oil (53 wt% of initial mass) had a complex composition consisting of aromatics, straight-chain hydrocarbons, amides, amines, carboxylic acids, and phenols. They also reported a high yield of biochar (31 wt%) that contained large amounts of potassium, phosphorous, and nitrogen, suggesting its potential as a soil fertilizer. Recently, Chagas et al. [26] investigated the pyrolysis of spirulina with high protein and low lipid contents at temperatures between 500 and 530 °C using a tail gas reactive pyrolysis (TGRP) process. They revealed that the amounts of aromatic hydrocarbons, phenols, and nitrogen-containing compounds produced using the TGRP process were larger than those generated by pyrolysis, and suggested possible pathways for formation of the chemicals produced by the TGRP process. As mentioned above, most investigations of the pyrolysis of algae were carried out by TG analysis for kinetic study and/or analysis of the product chemicals after isothermal fast pyrolysis. However, very few studies have focused on the detailed pathways for the reaction of each bio-polymer component of algae and their interaction during pyrolysis, though such studies are needed to obtain more details of the reaction properties and to determine the pathways for formation of the major chemicals from the pyrolysis of biomass. More reliable reaction pathway for biomass decomposition and its product formation during its pyrolysis can be studied by interconnecting the kinetic analysis results using TG analyzer and analytical pyrolysis technologies using a pyrolyzer-gas chromatography/mass spectrometry (Py-GC/MS), however, this approach was limited on the pyrolysis study of algae species.

In this study, non-isothermal pyrolysis of red macroalgae, *P. tenera*, is carried out to determine the detailed pyrolysis reaction pathway by TG analysis and Py-GC/MS. The kinetic analysis results obtained from a model-free kinetic analysis are used to understand the mechanism of the pyrolysis reaction, in conjunction with evolved gas analysis (EGA)-MS and multi-shot Py-GC/MS. By understating the combined results of TG and Py-GC/MS analysis, the main reaction pathways for the decomposition of *P. tenera* and formation of its products can be suggested

and will be able to be used as a fundamental data for the actual commercialization of algae pyrolysis process and the optimization of the process.

2. Experimental

2.1. Materials

P. tenera (Kjellman, 1897; AphiaID, 211507), purchased from a local market in Korea, was cryo-milled with liquid nitrogen using a milling machine. Before each experiment, the sample was sieved and the particles with sizes below 500 µm were isolated and dried at 105 °C for 4 h. The physico-chemical properties of the samples were determined by proximate and elemental analyses, and higher heating value (HHV) measurements were performed according to the previously reported procedures [7,8,27].

2.2. Kinetic analysis

A TG analyzer (Pyris Diamond, PerkinElmer Co.) was used for the kinetic analysis. *P. tenera* (6.0 mg) was pyrolyzed by raising the temperature from room temperature to 800 °C at three linear heating rates (10, 20, and 40 °C/min) under nitrogen at a flow rate of 120 mL/min. The Flynn-Wall-Ozawa (FWO) method (ASTM E698-11), a model-free kinetic analysis method, was used to determine the variation pattern of the apparent activation energy (E_a , kJ/mol) in terms of the conversion (X). Conversion, X, is expressed as Eq. (1).

$$X = \frac{(W_0 - W)}{(W_0 - W_\infty)} \quad (1)$$

where, W_0 is the initial mass of a sample, W is the mass of the pyrolyzed sample at a certain temperature, and W_∞ is the final mass after TG analysis.

2.3. Analytical pyrolysis using Py-GC/MS

Two kinds of analytical pyrolysis methods, EGA-MS and multi-shot Py-GC/MS, were carried out by using a pyrolyzer (EGA/Py-3003D, Frontier Laboratories Ltd.) coupled with GC/MS (7890A/5975C inert, Agilent Technologies) in order to acquire the thermal profiles of the products evolved from *P. tenera* during non-isothermal pyrolysis and the detailed distributions of each thermal zone. Schematic diagrams for the EGA-MS and multi-shot Py-GC/MS systems are presented in Fig. 1.

2.3.1. EGA-MS analysis

For the EGA-MS analysis, 2 mg of the sample in a deactivated stainless steel cup was heated from 100 °C to 800 °C at a heating rate of 20 °C/min in the pyrolyzer. The evolved gases and pyrolyzates generated from the sample during heating were swept away by a carrier gas through a deactivated metal tube (UA-DTM-2.5 N, 2.5 m length × 0.15 mm inner diameter), which had no stationary phase, and were transported to the MS detector. Thus, the pyrolyzates could be monitored in real time by EGA-MS without separation by a GC column; the GC oven temperature was 300 °C [27,28]. The detailed GC/MS operational conditions for EGA-MS analysis are given in Table S1 (Supplementary information). Extracted ion thermograms (EITs) for the typical pyrolyzates of each biomass component were also obtained by extracting the specific ions of each pyrolyzate from the total ion thermogram (TIT) obtained by EGA-MS analysis.

2.3.2. Multi-shot Py-GC/MS analysis

The total ion chromatogram obtained from the EGA-MS measurement also contains the decomposition peaks of each polymer in the sample, and the pyrolysis product of each polymer can be selectively analyzed by the multi-shot Py-GC/MS technique. Therefore, this multi-shot Py-GC/MS analysis was also used to determine the detailed

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