Bioresource Technology 229 (2017) 1–10

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

A study on growth and pyrolysis characteristics of microalgae using Thermogravimetric Analysis-Infrared Spectroscopy and synchrotron Fourier Transform Infrared Spectroscopy

Fanghua Li, Srikanth Chakravartula Srivatsa, Warren Batchelor, Sankar Bhattacharya *

Department of Chemical Engineering, Monash University, Wellington Rd, VIC 3800, Australia

HIGHLIGHTS

- High CO_2 (10%) concentration increased algae growth rate and total lipid content.
- Effects of temperature and heating rate in pyrolysis characteristics investigated.
- Nitrogen functional groups began to decompose at a temperature range of 250–300 °C.
- Lipid functional groups completely disappeared at a temperature range of 400–500 °C.
- Oxygen and nitrogen functional groups still remained at 550 °C.

ARTICLE INFO

Article history:
Received 2 December 2016
Received in revised form 4 January 2017
Accepted 5 January 2017
Available online 7 January 2017

Keywords:
Microalgae
Carbon dioxide
Pyrolysis
FTIR
TG-IR
Synchrotron

ABSTRACT

This two-part study firstly investigated *Tetraselmis suecica* grown in different CO_2 (0.04–15% v/v) concentration through indoor and outdoor cultivation systems. A high CO_2 concentration led to a high lipid content, and low nitrogen and oxygen content, which are desirable for transport fuel production. Pyrolysis characteristics were investigated by TG-IR and synchrotron IR microscopy. The results show *Tetraselmis suecica* grown in 10% CO_2 had the highest decomposition rate corresponding to more volatile products produced during the main thermal cracking stage and derived from protein-and lipid-corresponding functional groups. Moreover, a high reaction temperature and CO_2 concentration resulted in a low retention of surface functional groups. The nitrogen functional groups initially decomposed at a temperature range of 250–300 °C and still remained at 550 °C, while the lipid-corresponding functional groups completely disappeared at a temperature range of 400–500 °C. Besides, the decomposition of chemical components followed the order of carbohydrate, protein and lipid.

1. Introduction

Currently, there is a continuous increase in the consumption of fossil fuels around the world (Ehsani et al., 2016). Ninety-five percent of Australia's fuel needs is dependent on conventional petroleum (Hazrat et al., 2015). The dependence on fossil fuels is not sustainable in the long run. There is a need to develop technologies that can produce fuels locally, efficiently and inexpensively from renewable sources. This will reduce import bills and dependence on fossil fuels, while also partly mitigating CO_2 emissions. Carbon dioxide is used in multiple industries such as food, oil and gas industry, but the extent of utilization is far lower than the quantities generated. Hence, there is an increasing focus towards the conversion of CO_2 to alternative products. One such focus is the utilization of flue gas CO_2 for microalgae cultivation. Microalgae have a high photosynthesis efficiency, 10–20 times higher than terrestrial plants, resulting in a much faster biomass generation and CO_2 sequestration (Chiu et al., 2008). Microalgae can grow in various environments and do not compete with food crops for arable land. Even in the seawater, microalgae can remove carbon dioxide and phosphorous (Yeh et al., 2013). In addition, microalgal biomass can be helpful for wastewater treatment and used for the production of a broad range of fuels including methane, hydrogen, syngas, liquid fuels and chemicals (Chen et al., 2011; Krzemińska et al., 2015). Therefore, there has been a growing interest in microalgae as a promising candidate for biofuel production (Ross et al., 2009).

Despite these appealing advantages, microalgae-based fuel production remains outside the realm of economic feasibility. Depending on microalgae choice and growth conditions, the composition

* Corresponding author.
E-mail address: sankar.bhattacharya@monash.edu (S. Bhattacharya).

http://dx.doi.org/10.1016/j.biortech.2017.01.005
0960-8524/

of algae varies between 5–65% protein, 10–50% carbohydrate, and 3–50% lipid. Currently, lipids extracted from biomass are used for biodiesel production via transesterification (Babu et al., 2008), while carbohydrates can be used to produce bio-ethanol and butanol via enzymatic Saccharification (Kassim and Bhattacharya, 2015). However, these efforts have been hampered by energy-intensive extraction techniques and limitations in microalgae cultivation, dewatering, and processing. Most microalgae strains have thick cell walls, which make wall disruption and lipid extraction costly in terms of energy and cost. In addition, because of the high intrinsic protein content, microalgae cultivation requires large amounts of nitrogen fertilizer. As a result, there is a need to focus on microalgae conversion methods which can utilize the microalgae biomass fully and recycle nitrogen during the process.

Pyrolysis has been explored as a means to overcome these problems. Rather than separately processing the lipid fraction of microalgae, research is carried out to process whole microalgal biomass into chemical products. Ammonia released from microalgae pyrolysis can be used as fertilizer for algae cultivation. Fast pyrolysis occurs quickly and can be achieved at relatively low temperatures (300–600 °C) and atmospheric pressure. Microalgae pyrolysis generates bio-oil, bio-gas and bio-char, which all have downstream applications. Oils can be upgraded to transportation fuels, gases containing combustible species can be used to produce heat, and the char can be gasified to produce synthesis gas or chemicals.

There is a gap in the information on microalgae pyrolysis in open literatures. Pyrolysis bio-oils from microalgae have various compounds such as oxygen-containing compounds, whose presence reduces the heating value of the bio-oil. Additionally, the bio-oil with a high level of oxygen is not sufficiently stable, is immiscible and corrosive compared to petrofuels (Babich et al., 2011). Compared to lignocellulosic biomass based oils, microalgae based oils have an additional complexity due to the presence of nitrogen compounds from the decomposition of protein. The presence of nitrogen compounds will lead to the release of NO_x (a polluting gas) during combustion and is detrimental to the environment. These undesirable properties hinder the application of microalgal bio-oil as a potential source of transportation fuel.

Therefore, it is very important to understand the characteristics of the microalgae pyrolysis before large-scale processing for fuel production, such as (1) the properties of the raw material; (2) the evolution of oxygen and nitrogen-corresponding functional groups; (3) the roles of different chemical compositions in pyrolysis products; (4) the effect of pyrolysis parameters such as temperature and heating rate on the product distribution. Many investigations into the pyrolysis characteristics of microalgae are focused on the TGA analysis (Du et al., 2013; Thangalazhy-Gopakumar et al., 2012; Wang et al., 2013). The changes of surface functional groups through the initial stage of pyrolysis have been examined to clarify the formation of bio-oil compounds by in-situ FTIR (Liu et al., 2013; Zainan et al., 2015). To our knowledge, few studies have investigated the evolution of volatile products during pyrolysis of microalgae by the on-line combination of Thermogravimetric Analysis (TGA) and Fourier Transform Infrared Spectrometry (FTIR). In this paper, the technology of Thermogravimetric Analysis and Infrared Spectrometer (TG-IR), and Fourier Transform Infrared (FTIR) has been processed to analyze the pyrolysis characteristics of microalgae. The emphasis of current study is the pyrolysis characteristics of the harvested microalgae from the high concentration of CO_2.

In this work, we have selected *Tetraselmis suecica* as the microalgae for reasons listed below:

a) It is a marine green microalga and is able to tolerate a high range of salinity (25–30%), which makes it capable of growing in freshwater and seawater. It is possible to culture the microalgae near power plants which can utilize flue gas (carbon dioxide) emitted from boilers. Also, it is possible to recycle algal growth medium (Rodolfi et al., 2003).
b) It is a motile chlorophyte and oil-rich microalga. *Tetraselmis suecica* is considered to have a high-lipid productivity (Rodolfi et al., 2009) with an average lipid productivity of 32 $mg{\cdot}L^{-1}{\cdot}day^{-1}$ (Griffiths and Harrison, 2009), and a high potential for bio-oil production (Shen et al., 2015).

This research optimizes indoor cultivation conditions of *Tetraselmis suecica* by investigating several parameters – light intensity, temperature and different concentrations of CO_2. This study also compares the CO_2 capture capability of *Tetraselmis suecica* during outdoor cultivation under variable ambient temperature and natural sunlight with indoor cultivation when temperature and light intensity are kept constant.

To summarize, the aims of this study are to (a) investigate the optimum conditions for the cultivation of *Tetraselmis suecica*, (b) investigate the effect of CO_2 concentration, temperature, and heating rate on the profile of oxygen and nitrogen functional groups and volatile products.

2. Materials and methods

2.1. Microalgal cultivation

Tetraselmis suecica was obtained from the CSIRO Microalgae Research Centre (Hobart, Australia) and cultured at the Bioengineering Laboratory, Chemical Engineering Department of Monash University. All stock solutions (mainly five solutions) were made up in distilled water. The solutions were filtered (0.22 μm Millipore filter) and stored at 4 °C prior to use. An Aquarium Salt mix was used to produce a saline growth medium. It was added to distilled water (30.0 $g{\cdot}L^{-1}$) and stirred until the majority of the salt was dissolved. This solution was passed through a vacuum assisted filter to remove any undissolved salts and contaminates. All of the five nutrient solutions were added to the salt solution (1 $mL{\cdot}L^{-1}$ of each solution) and it was stirred once more to obtain a homogeneous solution. A combination of *Tetraselmis suecica* indoor and outdoor cultivation has been studied in this part.

(1) Microalgae indoor cultivation

The indoor microalgae were cultured in a Scott flask with 800 mL working volume. During microalgae indoor cultivation, each experiment was carried out in the triple. The growth of *Tetraselmis suecica* was measured at every 24 h interval and harvested during the stationary growth phase after 18 days of cultivation.

The following sets of experiments were completed.

a) Light irradiance was varied between 50 $\mu mol{\cdot}m^{-2}{\cdot}s^{-1}$ and 200 $\mu mol{\cdot}m^{-2}{\cdot}s^{-1}$ while holding temperature and CO_2 concentration constant at 30 °C and 0.04%, respectively.
b) Temperature was varied between 20 °C and 40 °C while holding light intensity and CO_2 concentration constant at 150 $\mu mol{\cdot}m^{-2}{\cdot}s^{-1}$and 0.04%, respectively.
c) CO_2 concentration was varied between 0.04% and 15% while holding light intensity and temperature constant at 150 $\mu mol{\cdot}m^{-2}{\cdot}s^{-1}$and 35 °C, respectively.

After the completion of each experiment, *Tetraselmis suecica* was transferred into another flask and incubated for 24 h to allow it to sediment at the bottom of the flask. The upper part of the flask containing of media was removed and the bottom part was used for centrifugation. *Tetraselmis suecica* was centrifuged at