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Energy recovery from microalgal biomass via enhanced thermo-chemical process

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ARTICLE INFO

Article history:
Received 8 March 2012
Received in revised form
20 May 2013
Accepted 31 January 2014
Available online 26 February 2014

Keywords:
Pyrolysis
Gasification
Microalgae
Biodiesel
CO_2

ABSTRACT

This work showed that microalgae having low lipid content has high potential for energy recovery via thermo-chemical processes. As an example, *Microcystis aeruginosa* (*M. aeruginosa*) was considered and tested. Specifically, this work verified that the growth rate of *M. aeruginosa* was extremely fast compared to other microalgae (as a factor of ~10). Moreover, this work investigated the CO_2 co-feed impact on thermo-chemical processes (pyrolysis/gasification) using *M. aeruginosa*. Introducing CO_2 in the thermo-chemical process as reaction media or feedstock can enhance the efficiency of thermo-chemical processes by expediting the cracking capability of condensable hydrocarbons (tar). The generation of CO was enhanced as a factor of ~2. Further generation of H_2 could be achieved in the presence of CO_2. Thus, utilizing CO_2 as reaction media or chemical feedstock can modify the end products into environmentally benign and desirable ones. The CO_2 co-feed impact on thermo-chemical processes with lingo-cellulosic biomass can be universally applied.

1. Introduction

Plants convert solar energy into chemical energy and store it in the form of structural components of biomass [1,2]. Biomass has been highlighted since it can be generated locally, thereby making any country self-sustainable when it comes to energy [3]. In other words, biomass offers a unique sustainable innovation pathway with potential for a variety of fossil energy and material feedstock alternatives[4,5]. Note, however, that the development of sustainable biomass production system on an industrial scale faces many challenges, e.g., competition with food production [6], degradation of biodiversity, land use management [7], and sustainable consumption of freshwater resources [8].

Biomass resources include wood [9], energy crop [10], aquatic plants [11], agricultural crops [12] and their waste byproducts, municipal wastes [13], and animal wastes [14]. Among these, microalgae have been suggested as a very good candidate, being a high-volume, cost-effective industrial solution [15]. Recently, many efforts have been put into producing fuel from microalgae. The production of biodiesel and gasoline through transesterification and catalytic cracking of lipid accumulated in algal cells have been investigated [4]; note, however, that the raw material for their methods is restricted to microalgae with high lipid content. Moreover, some microalgal strains do not have enough lipid contents for

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0961-9534/$ – see front matter © 2014 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.biombioe.2014.01.039

biodiesel production despite their sufficient ability to provide biomass (i.e., fast growth rate). Thus, the methodology for recovering energy from microalgae with low lipid content via thermo-chemical processes would be desirable.

Pyrolysis [16], the thermal decomposition of materials in the absence of oxygen, has been used to convert various feedstocks into a blend of solid, liquid, and gaseous products proportionally depending on the process variables [17]. In conventional slow pyrolysis, solid (char) is obtained; note, however, that the rapid heating of a carbonaceous feedstock (fast pyrolysis) results in liquid fuel, i.e., in the case of biomass pyrolysis, bio-oil, a complex mixture of compounds derived from depolymerization, is produced. The complex chemical composition of bio-oil depends on many factors [17,18], such as biomass type, feedstock pretreatment, and pyrolysis condition (temperature, heating rate, residence time, pressure, gaseous environment). As a result, the fuel properties of different bio-oils usually vary widely. Gasification [9,16,19], the transformation of the combustion value of solid fuel into gaseous energy carrier, is also an attractive technology for the production of syngas. The production of hydrogen from biomass is attracting increased attention, because the utilization of biomass to produce energy could contribute significantly to sustainable development and reduce greenhouse gas emissions (GHG).

Considerable work [18,20–25] has been documented with respect to the thermo-chemical process (pyrolysis/gasification) of conventional fuel, such as coal; note, however, that accessible information on unconventional fuel feedstock such as microalgae [26–28] is very limited. In addition, the impact of CO_2 on the pyrolysis/gasification process of microalgae has not been fully investigated[29,30]. The main objective of this work was to investigate mechanistically and evaluate the pyrolysis and gasification processes for microalgae, especially *M. aeruginosa*. In addition, the impact of CO_2 co-feed on the thermo-chemical process was studied for the enhancement or modification of products from the thermo-chemical process.

2. Materials and methods

2.1. Strain and sample preparation

The Korea Marine Microalgae Culture Collection Center (KMMCC) provided *M. aeruginosa, Chlorella vulgaris* F12 (*C. vulgaris*), *Scenedesmus* sp. F164, and *Chlorella protothecoides* (*C. protothecoides*) in pure form. Jaworski's Medium (JM) was used for the *M. aeruginosa and C. vulgaris* culture. Photosynthetic photon flux density (PPFD, $\mu mol\ m^{-2}\ s^{-1}$) was measured using a photometer (LI-250A, Biosciences, USA). A 100 $\mu mol\ m^{-2}\ s^{-1}$ of PPDF was employed during the 14-day culture period. The culture temperature was 25 °C. The growth rates for microalgae were physically measured on a dry basis. The membrane filter (Tokyo Roshi Karisha, Ltd., Japan, 3 μm) was used to collect the cultured microalgal samples; they were then weighed and dried at 95 °C for 12 h.

The lipid content was quantified using a Soxhlet extractor (Cole-Parmer, USA) with non-polar solvent, i.e., n-hexane (Sigma–Aldrich, St. Louis, USA) at temperature of 75 °C for 18 h. n-Hexane and the extracted lipid were separated using an evaporator (Cole-Parmer rotary evaporator system, EW-28615-06, USA). Acid esterification with sulfuric acid (H_2SO_4) was carried out at 60 °C for 65 h for the identification of fatty acids. Quantification was done using GC/MS (HP-7890A/5975C MSD), and FAME standards (Sigma–Aldrich, St. Louis, USA) were used for GC/MS calibration.

2.2. Experimental setup for the thermo-chemical process

All gases used in the experiments were of ultra-high purity and were obtained from Daesung Gas Ltd. All gas flow rates were set using the thermal mass flow controller (Brooks, Series 5800, USA). Steam flow rate was controlled using an HPLC pump (LabAlliance® Series II, USA), with the steam generated using a heat tape (Omega STR201-060) and a cartridge heater (Omega, CIR-1013/120V, USA) at temperature of 300 °C.

A Netzsch STA F1 Thermo-gravimetric Analysis (TGA) unit capable of different temperature analysis (DTA) measurements was used. TGA measures the weight changes in a material as a function of temperature (or time) under a controlled atmosphere. The TGA test was performed over temperature range of ambient ~1000 °C in N_2 and CO_2.

A tubular reactor (TR) made of 25.4 mm od quartz tubing (Chemglass CGQ-0800T-13) and 25.4 mm Stainless Ultra-Torr Vacuum Fitting (Swagelok SS-4-UT-6-400), was used to maintain airtight conditions. The required experimental temperature was achieved using a spit-hinged furnace (AsOne® tubular furnace, Japan) over temperature range of 500–1000 °C, with the temperature simultaneously compared with an S-type thermocouple reading to ensure that the target temperature had been reached. The sample was fed into the reactor using a customized screw feeder.

The gaseous effluent from the TGA unit and TR was sent to either μ-GC (Agilent 3000A) or GC/MS (HP-7890A/5975C MSD) using the transferred line for the identification and quantification of chemical species. The transferred heated line was heated at 300 °C to avoid adsorption onto the surface. A sampling pump (B19310TM5, Air Dimensions, Inc.) capable of 100 $mL\ min^{-1}$ was used.

3. Results and discussion

3.1. Evaluation of M. aeruginosa as feedstock of biodiesel

Recovering any form of energy from *M. aeruginosa* would be environmentally beneficial and desirable since *M. aeruginosa* is one of the most common microalgae in the world. *M. aeruginosa* (cyanobacteria) is a naturally occurring microalgae in the tidal fresh and low salinity areas. In addition, *M. aeruginosa* is one of the dominant plant species indicated the high degree of eutrophication. Thus, *M. aeruginosa* would not be restricted by regional area. In addition, many variants cyanobacteria produce multiple toxins, including the potent liver toxin, microcystin. Thus, utilizing *M. aeruginosa* for energy recovery would be desirable.

Recently, biodiesel derived from microalgal lipids has been highlighted. Thus, the feasibility of *M. aeruginosa* as lipid feedstock of biodiesel was considered. The dried sample of *M.*