Energy 64 (2014) 567–574

Contents lists available at ScienceDirect

Energy

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

Microwave plasma studies of Spirulina algae pyrolysis with relevance to hydrogen production

Kuang C. Lin [a], Yuan-Chung Lin [b,*], Yi-Hsing Hsiao [b]

[a] Department of Mechanical and Electro-Mechanical Engineering, National Sun Yat-Sen University, Kaohsiung 804, Taiwan
[b] Institute of Environmental Engineering, National Sun Yat-Sen University, Kaohsiung 80424, Taiwan

A R T I C L E I N F O

Article history:
Received 9 May 2013
Received in revised form
18 July 2013
Accepted 24 September 2013
Available online 1 November 2013

Keywords:
Microwave plasma
Spirulina algae
Pyrolysis
Hydrogen production

A B S T R A C T

Growth of the hydrogen market has motivated increased study of hydrogen production. Understanding how biomass is converted to hydrogen gas can help in evaluating opportunities for reducing the environmental impact of petroleum-based fuels. Using an atmospheric-pressure microwave plasma reactor coupled with species-selective analysis, experiments are conducted at microwave power levels of 800, 900 and 1000 W, a reactant flow rate of 12 slm, and 1 g of dry Spirulina algae in nitrogen. At the absorbed microwave power levels used in this experiment, hydrogen gas produced is in the range of 36.75–45.13% volume fraction, 13.42–15.48 mg per minute, and 12.37–31.46 mg per gram of Spirulina algae consumed. Moreover, the selection of power levels demonstrates that 20.62–52.43% hydrogen atom mass content in dry algae is converted to hydrogen gas. In general, the effect of reaction temperatures on the gas product formation is qualitatively consistent with those produced from other biomass materials reported in literature. Overall, these results will help to expand our knowledge concerning Spirulina algae and hydrogen yield on the basis of microwave-assisted pyrolysis and reaction temperatures, which will inform the study and design of hydrogen production technologies.

1. Introduction

The widespread use of fossil fuels as a primary energy source has led to critical societal issues, namely fuel security and greenhouse-gas-related climate change [1,2]. The relentless growth in demand for energy has increased the severity of these issues and has thus driven a search for sustainable alternatives to fossil fuels. One attractive option is hydrogen gas, which is an environmentally friendly energy carrier and has a high-energy content per unit weight [3]. This carbon-free fuel produces mainly water as an emission in thermal combustion [4] or fuel-cell systems [5]; however, due to the fact that hydrogen is not readily available in nature like fossil fuels, one of the main challenges for hydrogen-fueled power systems is the development of clean and efficient technologies to produce this fuel. Consequently, hydrogen production has been a subject of interests for many researchers over the last decades [6].

Currently, there are two main categories of hydrogen production processes available in industry, fuel processing and non-reforming hydrogen production [7]. The former one produces gaseous hydrogen by converting a hydrogen containing material, such as hydrocarbon fuels [8,9], coal [10], methanol [11] and ethanol [12], to gas products. The latter one uses renewable resources, such as biomass [13], biodegradation waste [14], municipal waste [15] and water [16], to form gaseous hydrogen. Although fossil fuel reforming for hydrogen generation has been thoroughly studied in recent years, the main drawbacks are the considerable energy required for mining and the need for desulfurizing hydrocarbon stocks obtained from petroleum processing, as well as the existence of CO_2 (carbon dioxide) during hydrogen production [7]. Among the feedstock choices, biomass is particularly attractive as an alternative energy source as it can be derived from a variety of crops [17] and is able to produce useful products like gas, oil and solid char used as a fuel or a feedstock for petrochemicals and other applications [18]. Moreover, as carbon dioxide is consumed in the growth of the requisite feedstock, biomass use can also mitigate environmental issues associated with climate change. Thus, the potential renewability and reduction of CO_2 emissions are two important factors that drive the development of the biomass industry.

Recently, the utilization of microalgae biomass for production of biofuels [19–24], has attracted much attention because of its recognized benefits to biomass production and harvesting. Intrinsic

* Corresponding author. Tel.: +886 7 5252000x4412; fax: +886 7 5254412.
E-mail addresses: yuanchung.lin@gmail.com, yclin@faculty.nsysu.edu.tw (Y.-C. Lin).

0360-5442/$ – see front matter Crown Copyright © 2013 Published by Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.energy.2013.09.055

advantages of microalgae over terrestrial crops are all year round production, reduction of freshwater inputs, and being able to be cultivated in brackish water on non-arable land. Conversion technologies that have been currently used to generate syngas from microalgae biomass include gasification, pyrolysis and photobiology [21]. Among these different approaches, microalgae pyrolysis has been studied most extensively due to its advantages such as product diversity, cheapness, safeness, simplicity and possibility to use in industry. Pyrolysis can be described as thermal decomposition of organic components in an-oxygen free atmosphere to produce bio-oil, syngas and charcoal [21]. Many studies have been carried out in recent years to characterize the pyrolysis behavior of microalgae biomass. Miao et al. [25,26] carried out fast pyrolysis experiments on cultivated microalgae (*Chlorella protothecoides* and *Microcystis aeruginosa*), using a fluidized bed reactor at a temperature of 773 K. They reported an approach that the amount of H_2 in the produced bio-oil can be increased by 33% by manipulating the metabolic pathway in microalgae through heterotrophic growth. Pan et al. [27] studied the direct pyrolysis and catalytic pyrolysis of Nannochloropsis in a fixed bed reactor. The authors observed 0.14–0.23 wt.% H_2 (hydrogen) in the produced biogas using different catalyst-to-material ratios at temperatures of 573–773 K. Grierson et al. [28] investigated the thermal behavior of six microalgae species (*Tetraselmis chui*, Chlorella like, *Chlorella vulgaris*, *Chaetocerous muelleri*, *Dunaliella tertiolecta* and Synechococcus) when converted to biogas, bio-oils and charcoal under slow pyrolysis conditions in a conventional oven at temperatures up to 1023 K. The authors found that the pyrolyzed microalgae release only 0.1–1.3 wt.% H_2 at the reaction temperature of 773 K. Babich et al. [29], using a fix-bed reactor, studied the pyrolytic conversion of Chlorella algae to liquid fuel precursor in the presence of a catalyst at temperatures of 573–723 K. The authors reported that gas yields are typically around 20 wt.% and GC (gas chromatography) analysis of the gas products showed mainly CO_2 and H_2O (water), traces of H_2 and CO (carbon monoxide) and light hydrocarbons. Maddi et al. [30] carried out experiments with algal and lignocellulosic feedstocks under similar reactor conditions for a comparison of bio-oil, gas and bio-char yields and compositions. The authors observed that Lyngbya species and Cladophora species produce hydrogen gas up to 48.7 and 29.8 molar percent in the product streams, respectively. Sanchez-Silva et al. [31] investigated the effects of the initial sample mass, particle size and gas flow on the pyrolysis, combustion and gasification of *Nannochloropsis gaditana* microalgae in a TGA (thermogravimetric analysis) from the temperature of 313 to 1473 K. The authors used TGA/DTG (differential thermogravimetric) plot to show the signal intensity of gaseous products during the reaction and the results indicated that the amount of H_2 released in the pyrolysis is relatively low compared to the other 11 gaseous products identified. Most recently, Hu et al. [32] studied the pyrolysis of blue-green algae blooms in a fixed-bed reactor and observed the prevailing yield of bio-oil. At the reaction temperature of 773 K and N_2 volume flow rate of 100 mL/min, where the maximum oil produced is observed, the mass fractions of bio-oil, gas and char are approximately 55, 26 and 21%, respectively. In summary, our review of the literature reveals that microalgae studies were mostly carried out in conventional pyrolysis processes, which result in less amounts of hydrogen present in gaseous products. For this reason, thermal plasma technology, which has been considered as a highly attractive route for the processing of waste-to-energy [33], may be an alternative to enhance hydrogen production from algae pyrolysis in the future.

Although hydrogen production from microalgae biomass for energy supply has received considerable attention lately from the scientific and engineering community, relatively little is known about the Spirulina algae pyrolysis characteristics. Ecologically, Spirulina algae grows naturally in tropical and subtropical lakes, whereas most cultivated Spirulina algae is produced in open channel raceway ponds [34]. Prompted by these considerations, in this study, we have examined the production rate and yield of hydrogen from dry Spirulina algae in a microwave plasma reactor at various microwave power levels. An atmospheric-pressure microwave plasma reactor coupled with species-selective analysis is used to measure product yield variations of three species: H_2, CO and CO_2. The measurements are compared with the previously published results of other hydrogen-containing materials and the chemical reaction pathways for hydrogen production are discussed. Therefore, the findings of this study provide information on thermal degradation of algae and extend the applicability of microwave plasma for production of hydrogen from biomass.

2. Experimental section

Fig. 1 shows the experimental setup comprising the electrode less microwave excited APS (atmospheric plasma system) and the product analysis system. Details of this experimental setup are described in Refs. [35–37]. Experiments in the present study are repeated at least three times to provide evidence of reproducibility.

2.1. Pyrolysis procedure

The pyrolysis experiments are conducted in an atmospheric-pressure microwave plasma reactor at applied microwave power of 800, 900 and 1000 W corresponding to the temperature of 1063, 1093 and 1121 K in the plasma zone. Approximately 1 g of dry Spirulina algae at room temperature is fed with axial flow into the reacting zone from upstream of the cavity resonator and N_2 (nitrogen) is used as a bath gas at a flow rate of 12 l min^{-1} (axial flow rate of 3 l min^{-1} and swirl flow rate of 9 l min^{-1}). The flow rate of N_2, supplied from compressed gas tanks, is kept constant. The reactor is made from a quartz tube of 35 cm length and an inner and outer, diameter of 2.9 and 3.3 cm, respectively.

2.2. Dry Spirulina algae and gas analysis

Both the pyrolysis characteristics and product distribution of Spirulina algae are analyzed in this study. Morphological changes of the Spirulina algae samples before and after pyrolysis are observed by an ESEM (environmental scanning electron microscopy). Elemental chemical analysis (C, H, N, S and O) of Spirulina algae and the residue after pyrolysis is performed on an Elementar Vario Micro Cube EA (elemental analyzer). Sampling is accomplished by continuously withdrawing gases from within the plasma zone using a micro-probe with a diameter of the order of hundred microns. A gas chromatography (GC), equipped with capillary columns (type: SUPELCO 13821), a TCD (thermal conductivity detector) and a RGA (residual gas analyzer), are used for stable species measurements. The RGA is used to monitor the hydrogen concentration produced over the entire pyrolysis history. For the H_2 analyzed in GC/TCD, the carrier gas is nitrogen and the detector oven and vaporizer temperatures are 513 and 383 K respectively. The GC oven temperature is set to 383 K for 10 min and ramped to 473 K at 288 K min^{-1} held for 14 min. For the CO and CO_2 analyzed in GC/TCD, the carrier gas is helium and the detector oven and vaporizer temperatures are 393 and 323 K respectively. The GC oven temperature is set to 333 K for 5 min and ramped to 498 K at 293 K min^{-1} held for 10 min.