Applied Energy 114 (2014) 227–237

Contents lists available at ScienceDirect

Applied Energy

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

Kinetic analysis and thermal characterization of the microalgae combustion process by thermal analysis coupled to mass spectrometry

D. López-González, M. Fernandez-Lopez, J.L. Valverde, L. Sanchez-Silva *

Department of Chemical Engineering, University of Castilla-La Mancha, Avda. Camilo José Cela, 12, 13071 Ciudad Real, Spain

HIGHLIGHTS

- Combustion process of different microalgae was studied by TGA–MS.
- Heat released during microalgae combustion was evaluated by DSC.
- The kinetic analysis of the combustion process was modelled.
- CO, CO_2 and H_2O were the main products obtained together light hydrocarbons (CH_4).
- Nitrogen compounds were mainly released as NO_x, amines and HCN.

ARTICLE INFO

Article history:
Received 24 May 2013
Received in revised form 23 September 2013
Accepted 25 September 2013
Available online 18 October 2013

Keywords:
Microalgae
TGA-MS
DSC
Combustion
Kinetics

ABSTRACT

The thermal characteristics under oxidizing atmosphere of several species of microalgae: *Nannochloropsis gaditana* (NG), *Scenedesmus almeriensis* (SC) and *Chlorella vulgaris* (CV) was investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) coupled with mass spectrometry (MS). These microalgae were chosen according to their chemical composition. TGA results showed that microalgae combustion took place in two main stages: devolatilization and char oxidation, which were corroborated by DSC analysis. The former one could be related to the decomposition of their main microalgae components: carbohydrates, lipids and proteins. Samples SC and CV yielded the highest amount of ash, which implied that sample pre-treatment such as washing is required before being used in thermal applications in order to avoid operational problems. Sample NG showed the highest amount of combustion heat. Kinetics were evaluated assuming single separate reactions for each combustion stage. Additionally, the process was successfully modeled obtaining for sample NG a maximum error of ±3.1%. CO, CO_2 and H_2O were the main components obtained during the combustion process. The evolution of CH_4 at high temperatures was mainly attributed to lipid decomposition. Finally, it was noticed that nitrogen compounds (NO, NO_2 and HCN) were released in a higher proportion that sulfur ones (SO and SO_2).

1. Introduction

Biomass fuels are gaining particular attention as an energetic alternative to fossil fuels due to depletion of world petroleum reserves and environmental pollution [1]. Biomass can be converted into more valuable energy carriers via either biochemical or thermochemical conversion processes [2].

Algae are a very promising biomass for the following reasons: rapid growth rate, high yield per area, high efficiency in CO_2 capture and solar energy conversion and no competition with food agriculture. Among the different types of algae, microalgae have received more attention than others because they can be cultured in ponds or photobioreactors with supply of nutrients or wastewater [3].

The generic term microalgae refers to a large group of very diverse photosynthetic micro-organisms of microscopic dimensions. The knowledge of the biochemical composition of microalgae is of utmost importance because it provides information about the possibilities of their potential use as an alternative fuel source [4]. Generally, microalgae are mainly formed by proteins (6–52 wt.%), carbohydrate (5–23 wt.%) and lipid (7–23 wt.%). In this regard, Ross et al. [5] reported that microalgae with high lipid content could be a future source of third generation biofuels and chemicals.

Thermochemical conversion of biomass is considered as one of the most promising routes for biomass utilization. Thermochemical processes typically include: gasification, combustion, pyrolysis and liquefaction. These processes are employed for power

* Corresponding author. Tel.: +34 926 295300x6307; fax: +34 926 29 52 56.
E-mail address: marialuz.sanchez@uclm.es (L. Sanchez-Silva).

0306-2619/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.apenergy.2013.09.055

Nomenclature

$(dw/dT)_{max}$	maximum weight loss rate
$(dw/dt)_{max}$	maximum burning velocity
$(dw/dt)_{mean}$	average burning velocity
CCF	combustion characteristic factor
CV	*Chlorella vulgaris* microalgae
D_i	diffusion model
daf	dry and ash free basis
Dev. stage	devolatilization stage
DSC	differential scanning calorimetry
DTG	derivative thermogravimetric analysis
FTIR	Fourier transform Infrared Spectrometry
H_{comb}	heat of combustion
ICP	inducively coupled plasma spectrometry
MS	mass spectrometry
N_i	nucleation and growth model (Avrami–Erofeev eq.)
NG	*Nannochloropsis gaditana* microalgae
O_i	reaction order model
Oxid. stage	oxidation stage
PMSM	pseudo multi-component separate-stage model
P_i	power law model
R_i	phase boundary controlled reaction model
SC	*Scenedesmus almeriensis* microalgae
Sh	shoulder
T_b	burnout temperature
TGA	thermogravimetric analysis
T_i	Ignition temperature
T_p	peak temperature
A	pre-exponential factor
E	activation energy
$f(\alpha)$	hypothetical model of the reaction mechanism
$g(\alpha)$	integral function of conversion
k	reaction rate
m_o	mass at $t = 0$
m_f	final mass of the sample
m_t	mass at $t = t$
R	ideal constant gas
T	temperature
t	time
α	degree of conversion
β	heating rate

generation, production of liquid biofuels, chemicals and charcoal. Thus, a good understanding of the decomposition of microalgae during thermochemical conversion is important for developing efficient processing technology [6].

Combustion can be defined as the conversion of a fuel to energy in the form of heat in the presence of air or oxygen. Thermogravimetric techniques have commonly been used to investigate the thermochemical conversion of solid raw materials as coal and woods [7–9]. A large number of researches on microalgae pyrolysis have been carried out in recent years [10–13]. However, very few studies have been focused on the combustion of microalgae. Chen et al. [14] reported the combustion behavior of *Chlorella vulgaris* microalgae under different oxygen concentrations by thermogravimetric analysis (TGA). Furthermore, Tang et al. [15] investigated the combustion of *Chlorella protothecoides* microalgae in N_2/O_2 and CO_2/O_2 atmospheres by means of the same technique. Pane et al. [16] studied the effects of temperature in the combustion of marine algae.

Biomass characteristics and kinetics of biomass combustion are essential for modeling combustion processes at an industrial scale [17]. Furthermore, a knowledge of the kinetics of the process has great importance for a correct design of the industrial equipment where these kind of processes has to be performed and product yield control [18].

During the process of thermochemical conversion of biomass, the composition of the gas emissions should be determined before industrial application. In this sense, the evolution with time on stream of the volatile products evolved in the marine biomass pyrolysis or combustion processes has been carried out using the on-line combination of TGA and Fourier Transform Infrared Spectrometry (FTIR) [19] and thermal analysis-mass spectrometry (TA-MS) [20,21].

As aforementioned, thermogravimetric analysis coupled with mass spectrometry (TGA-MS) could be a useful technique to obtain information at real-time of mass loss and evolved gases for thermochemical processes.

The aim of this work was to study the thermal characteristics under oxidizing conditions of different species of microalgae by means of the TGA–DSC technique. Three different microalgae species were selected due to their different chemical composition analysis: *C. vulgaris*, *Nannochloropsis gaditana* and *Scenedesmus almeriensis*. Furthermore, the kinetics of biomass oxidation were evaluated by using different models, being the process properly reproduced. Finally, the main gaseous products released during the combustion process were analyzed by MS.

2. Materials and methods

2.1. Materials

Microalgae *C. vulgaris*, *S. almeriensis* and *N. gaditana* were purchased from Algaenergy company (Spain). These samples were dried in an oven for 5 h, milled and sieved to an average particle size between 100 and 150 μm.

The proximate analysis, ultimate analysis and composition of biomass samples are shown in Table 1. The proximate analyses were carried out according to the technical specifications UNE-EN, UNE-EN 14775:2010, UNE-EN 15148:2010 and UNE-EN 1474-2 for ash, volatile matter and moisture determination, respectively. The percentages of carbon, hydrogen, nitrogen, sulfur and oxygen (calculated by difference) of microalgae samples were determined after complete combustion of the sample using a CHNS/O analyzer (model LECO CHNS-932). Sulfamethazine was used as standard. Table 1 also lists the content of metals, chloride (Cl^-) and cyanide (CN^-). The mineral content was measured by using an inductively coupled plasma spectrometer (model Liberty Sequential, Varian) according to the procedure described by Cotillas et al. [22] (plasma emission spectroscopy). In order to evaluate the total metal concentration, microalgae samples were diluted to 50:50. v/v using 4 N HNO_3 in order to ensure the total solubility of the metal. Chloride content was measured by ion chromatography using Shimadzu LC-20A equipment column Shodex IC I-524A (mobile phase, 2.5 phthalic acid at pH 4.0, flow rate 1.0 ml/min). The cyanide content was determined by UV–visible spectrophotometry using a HACH equipment model DR2000.

2.2. Biomass selection

The conversion of biomass to different forms of energy mainly depends on its inherent properties, determining the conversion