Applied Energy 102 (2013) 24–31

Contents lists available at SciVerse ScienceDirect

Applied Energy

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

Characterization of microalga Chlorella as a fuel and its thermogravimetric behavior

Andrea Maria Rizzo, Matteo Prussi, Lorenzo Bettucci, Ilaria Marsili Libelli, David Chiaramonti *

CREAR and RE-CORD, University of Florence, via Santa Marta 3, 50139 Florence, Italy

HIGHLIGHTS

- ▶ Proximate and ultimate analysis of two microalgae (*Nannochloropsis* and *Chlorella* spp.).
- ▶ TGA of *Chlorella* spp. and *Nannochloropsis* investigated at 15 °C/min up to 800 °C.
- ▶ 1.2 kg of Chlorella pyrolyzed in a novel batch, intermediate pyrolysis pilot reactor at 450 °C.
- ▶ Bio-oil from Chlorella oil analysed and compared to pine chips fast pyrolysis oil.
- ▶ Bio-oil from Chlorella exhibited superior properties compared to lignocellulosic pyrolysis oil as intermediate energy carrier.

ARTICLE INFO

Article history:
Received 17 February 2012
Received in revised form 29 July 2012
Accepted 2 August 2012
Available online 13 September 2012

Keywords:
Chlorella
Microalgae
Thermogravimetric analysis
Pyrolysis oil

ABSTRACT

Microalgae are photosynthetic microorganisms living in marine or freshwater environment. In this study, samples of *Chlorella* spp. and *Nannochloropsis* from two different origins were analysed to settle a preliminary characterization of these microorganisms as intermediate energy carriers and their properties compared to a conventional lignocellulosic feedstock (pine chips). Both microalgae samples were characterized in terms of elemental composition (CHONS and P) and thermogravimetric behavior. This was investigated through non-isothermal thermogravimetric analysis in nitrogen atmosphere at heating rate of 15 °C min^{-1} and temperature up to 800 °C. Solid residues produced at 300 °C and 800 °C from TGA were also analysed to determine the ultimate composition of chars. Activation energy, reaction order and pre-exponential factor were calculated for the single step conversion mechanism of 1 g of *Chlorella* spp. and compared to literature data on *Chlorella protothecoides* and *Spirulina platensis*. Calculated kinetic parameters, given as intervals of several determinations, resulted to be: pre-exponential factor (A) 1.47–1.62E6 min^{-1}, activation energy (E) 7.13–7.92E4 J mol^{-1}, reaction order (n) 1.69–2.41. 1.2 kg of *Chlorella* spp. was then processed in a newly designed batch pyrolysis pilot reactor, capable of converting up to 1.5 kg h^{-1} of material, and pyrolysis liquid collected, analysed and compared with a sample of fast pyrolysis from pine chips. This preliminary investigation aimed at carrying out a first characterization of algae oil and optimise the operational aspects of the reactor, tested with the first time with this unconventional feedstock. The algae pyrolysis oil exhibited superior properties as intermediate energy carrier compared to pyrolysis oil from fast pyrolysis of pine chips, in particular higher HHV and carbon content and lower oxygen and water content. These data can potentially be used in the design and modelling of thermochemical conversion processes of microalgae.

1. Introduction

Microalgae are a diverse group of prokaryotic and eukaryotic photosynthetic and heterotrophic microorganisms. Microalgae cultivation, or *algaculture*, using sunlight can be carried out in open or covered ponds or closed photo-bioreactors, based on different designs [1] and in several aqueous media, from fresh to very salty water. Nowadays more than 40 different species of microalgae, isolated in different parts of the world, are cultivated as pure strains in intensive systems. Microalgae can be extremely efficient in terms of land-use, as the potential oil productivity per hectare is considerably higher than traditional seed crops [1] and total biomass production rate (productivities) achievable with reactors is estimated at around 60–70 ton ha^{-1} $year^{-1}$ [2], but the theoretical potential is assessed to be even higher [3].

Algaculture is performed to produce high added value commodities. Sometimes the entire alga is the final product, but more often several compounds are extracted. Some examples of these so-called "unique products" include oils, fats, vegetable protein, carbohydrates, bioactive compounds and chemicals as well as food, food-additives and health-food, feed for fish, shrimp and shellfish, dyestuff and omega-3-fatty acids [4,5].

* Corresponding author. Tel.: +39 055 4796243; fax: +39 055 4796342.
E-mail address: david.chiaramonti@unifi.it (D. Chiaramonti).

0306-2619/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.apenergy.2012.08.039

Nomenclature

HHV	higher calorific value
LHV	lower calorific value
NF	nitrogen factor
TGA	thermogravimetric analysis
PID	proportional-integral-derivative effect
Symbols	
h	hour
min	minute
Nl	normal-litre
s	second
t	time
T	temperature
α	conversion of reactant
Δ	uncertainty or finite difference
Abbreviations	
ar	as received
avg	average
dry	dry base
daf	dry ash free
i	index
v/v	by volume
wt.%	percentage by weight
x	measured value

Under normal growing many species of microalgae exhibit a lipid yield between 10% and 30% on dry weight, but under special conditions the lipid content can be even doubled [6], and some Authors reported to have obtained oil content up to 80% by weight of dry biomass [7–9]. Growing of microalgae depends on the nutrients in the water as well on the illumination that is available for photosynthesis. The intake of nutrients can modify the production and accumulation rate of lipids within the microalgae. For example, Rodolfi et al. [6] reported an increased productivity and almost doubling of the lipid content to 60% after switching to nutrient-deficient conditions in an outdoor pilot reactor.

The algal biomass is a valuable source of carbon, because its content can exceed 50% on dry weight [10] and some microalgae can produce larger amount of oil than the best dedicated energy-crop and can therefore represent a potential renewable source of oil for the biofuel chains.

Several possible pathways for microalgae biomass-to-energy have been investigated, and several reviews are available in literature (such as [12–14]). Process technologies for the conversion of microalgae biomass encompass two main categories: thermochemical and biochemical processes. Thermochemical pathway includes direct combustion, gasification, liquefaction and pyrolysis, whereas the biochemical pathway includes anaerobic digestion, alcoholic fermentation. Another process option is trans-esterification, where the fatty acids can be converted into biodiesel. The scheme of Fig. 1 summarizes some of the possible conversion processes and final products.

According to the definition given by the International Confederation for Thermal Analysis and Calorimetry (ICTAC), thermal analysis is amidst the "[...] techniques in which a property of the sample is monitored against time or temperature while the temperature of the sample, in a specified atmosphere, is programmed" [15]. In case of thermogravimetric analysis, the monitored property is the weight of the sample. Thermogravimetric analysis is used since the end of the XIX century for gaining knowledge on the solid state decomposition mechanism of substances because it is a tool that may provide insight regarding the kinetic workings of heterogeneous reactions, in spite of the lack of consistency among data sets that White et al. pointed out of in their paper [16]. Despite the literature on pyrolysis kinetic for many biomass species is abundant, and excellent review papers were published on the subject [17,18], only a limited number of studies involving the pyrolitic behavior of microalgae are reported in the open literature [19–22] and to date no studies were found reporting on the pyrolysis of algal biomass carried out on lab pilot scale reactors fed with sample sizes exceeding few grams.

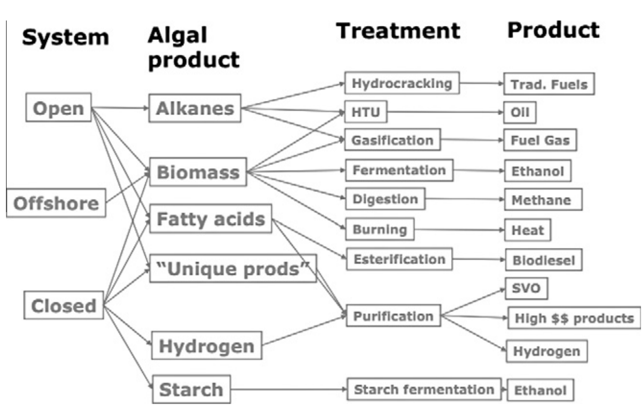

Fig. 1. Possible pathways for algae cultivation and valorisation [11].

This work aims at partially filling in the gap, by investigating the behavior of two samples of microalgae (*Chlorella* spp. and *Nannochloropsis*) during pyrolysis with a comprehensive approach. Both samples were characterized in their higher heating value (HHV) and content of carbon, hydrogen, nitrogen, oxygen, sulphur, phosphorous, moisture, ashes and their properties compared toward those of conventional lignocellulosic feedstock (pine chips). Both microalgae were then subjected to non-isothermal thermogravimetric analysis (TGA) in controlled atmosphere (nitrogen) and process condition (15 °C min^{-1}) in order to calculate kinetic parameters such as reaction order, activation energy and frequency factor, assuming the single step reaction model retained by other authors [21].

A significant amount (1.2 kg) of *Chlorella* spp. was then processed in a newly designed batch pyrolysis reactor at 450 °C and pyrolysis liquid collected, analysed and compared with a conventional sample of pyrolysis oil from fast pyrolysis of pine chips.

These data can potentially be used in the design and modelling of thermochemical conversion processes of microalgae.

2. Materials and methods

2.1. Microalgae culture and sample preparation

The microorganisms here investigated are two different batches of microalgae, *Chlorella* spp. and *Nannochloropsis*. The first sample (*Chlorella* spp.) was a proprietary strain supplied by Ingrepro B.V. (Netherland) in form of powder. The algae were grown outdoor in two separate periods of 2011 in algal ponds with 30 cm deep raceways and under outdoors climatic conditions, i.e. sunlight and natural day/night rhythm. The growing medium was enriched with potassium nitrate (KNO_3), nitrate, mono ammonium phosphate ($NH_4H_2PO_4$), phosphate, and sodium bicarbonate ($NaHCO_3$)