Thermochimica Acta 660 (2018) 101–109

Contents lists available at ScienceDirect

Thermochimica Acta

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

Studies on thermal decomposition behaviors of demineralized low-lipid microalgae by TG-FTIR

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ARTICLE INFO

Keywords:
Chlorella vulgaris
Pyrolysis
Dilute acid washing
TGA-FTIR

ABSTRACT

In this work, dilute acid washing of typical low-lipid microalgae has been performed to remove ash-forming inorganics for mitigating the negative consequences during pyrolysis process. In order to investigate the potential influence of demineralization, the kinetics and pyrolysis behaviors of pretreated *Chlorella vulgaris* was systematically studied using thermogravimetric analysis coupled by fourier transform infrared spectrometer (TG-FTIR). TG analysis showed that the temperatures corresponding to decomposition peaks for pretreated samples shifted to the low temperature zone. Comparing with the removal of inorganics, the physiochemical structure changes of microalgae played the dominant role in decomposition of carbohydrate and protein fractions. For evolved gas, acid washing suppressed the formation of CO_2 and increased the generation of C-H. It was noteworthy that the production of HCN by cracking of dipeptides was promoted clearly. HCl-5% had the lower average activation energy, residual mass (22.97%) and more desired gaseous products (pyrolysis effectiveness index $S = 0.32$).

1. Introduction

Due to energy crisis and global warming, the development of renewable energy is required to replace fossil fuels and reduce carbon emission. Microalgae is viewed as one of the next generation biofuel feedstock due to its fast growing rate, high photosynthetic efficiency, high productivity per culture area, and no competition for land with food agriculture [1,2]. Traditional algal biofuel production is mainly focused on costly extraction of lipids followed by transesterification to produce biodiesel, requiring the feedstock of high-lipid microalgal strains [3]. In contrast, pyrolysis is a key route to convert the entire microalgae to liquid fuels by thermal decomposition in absence of oxygen, which is more suitable to process low-lipid microalgae [4].

Comparing with fossil oil, bio-oil from pyrolysis of microalgae has higher oxygen and nitrogen contents with lower heating value, which limits its direct use in fuel applications [2]. Thus, zeolite catalysts have been applied to pyrolysis of microalgae, aiming to upgrade the quality of bio-oil via deoxygenation and aromatization reactions [5]. A high yield of aromatic hydrocarbon (~25 wt.%) was achieved in catalytic pyrolysis of *Chlorella vulgaris* (*C. vulgaris*) over HZSM-5 [6]. On the other hand, a reduction of oxygen content (from 30.1 to 19.5%) and an increase of heating value (from 24.4 to 32.2 MJ/kg) were noticed in bio-oil derived from catalytic pyrolysis of *Nannochloropsis* sp. [7]. In the practice of catalytic pyrolysis, catalyst deactivation occurs mainly due to the accumulation of coke and ash-forming inorganics on the surface of the catalyst or inside its pores, resulting in active site decay and pore blockage [8]. Ash-forming inorganics cannot be removed by catalyst regeneration process and the increasing amount of inorganic elements accumulated on HZSM-5 reduced the selectivity for the desired reaction products during catalytic pyrolysis [9]. It was reported that ash concentrations up to ca. 3 wt.% relative to the amount of pine wood fed could impact the stability of zeolite catalysts [10]. Moreover, these inorganics may cause ash fouling and agglomeration problems in thermal conversion systems [11].

The ash-forming inorganics such as K, Na, Mg and Ca are the nutrients of biomass necessarily required from the media during their growing process. Generally, the ash content is less than 1% in most terrestrial biomass [12]. Since microalgae grow in aqueous suspension, they have more efficient access to the nutrients [13]. The metal ions initially attached to the cell wall and then were slowly transported into the cell cytoplasm through the cell wall via membrane transport of the ion, leading to large amount of inorganics accumulated in the cells. Different species of microalgae contain various amounts of inorganics due to different size, shapes and cell wall compositions which affect their metal binding efficiency [14]. The ash content of high-protein and low-lipid microalgae such as Spirulina platensis is up to 9.6% [15]. Acid demineralization, which can be conducted under the conditions of room temperature and atmospheric pressure, is an effective and easy-

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https://doi.org/10.1016/j.tca.2018.01.001
Received 29 October 2017; Received in revised form 27 December 2017; Accepted 1 January 2018

to-operate way to remove the inorganics from biomass feedstock [16,17]. For lignocellulosic biomass, the removal of alkali and alkaline earth metals (AAEMs, e.g. K, Na, Ca and Mg) alters the reaction pathways and substantially increases the yield of anhydrosugars up to 10-fold [17–20]. Different from lignocellulosic biomass, algal biomass is mainly composed of not only carbohydrates but also proteins and lipids. Currently, the attention of demineralization of algae biomass has been mainly directed towards macroalgae which is characterized by higher ash content (up to 26%) and lower heating value [21]. Pretreatments of *Laminaria hyperborea* and *Fucus vesticulosus* with hydrochloric acid (HCl) [22] and *Cladophora socialis* with nitric acid (HNO_3) [16] have been reported to chemically change the samples by selective extraction of certain polymeric material (e.g. fucoidan, mannitol and laminarin), which were potential for production of fuel and chemicals by pyrolysis. However, to the best of our knowledge, there have been only few studies devoted to the demineralization of microalgae and especially the impacts on pyrolysis characteristics and evolved gas [23].

Compared to high-lipid microalgae, low-lipid microalgal species adapt easier to cultivation conditions with higher productivity, and can use wastewaters as culture medium instead of fresh water [24]. From this perspective, they seem to be the promising feedstock for biofuel production in the long term. In this study, *C. vulgaris* was selected and demineralized by sulphuric acid (H_2SO_4) and HCl with concentrations of 1 wt.%, 3 wt.% and 5 wt.%. The pyrolysis characteristics of pretreated samples were investigated by thermogravimetric analysis. Simultaneously, the fourier transform infrared spectrometer (FTIR) coupled with TGA were used to on-line detect the evolved gas from pyrolysis process. The results contribute to developing new strategies to reduce metal deposits during catalytic pyrolysis.

2. Materials and methods

2.1. Materials

The powder of *C. vulgaris*, purchased from Wudi Lv Qi Bioengineering, Shandong Province, P. R. China, was used after drying in an oven at 105 °C for 12 h. To leach the inorganics, the raw *C. vulgaris* was washed with dilute acid solutions. Specifically, 20 g of raw material was immersed into 200 mL of H_2SO_4 and HCl with concentrations of 1 wt.%, 3 wt.% and 5 wt.% at room temperature for 2 h under continuous-stirring condition by using magnetic stirrer. The pretreated samples were filtered, rinsed by deionized water until the pH value was neutral and then dried in an oven at 105 °C for 12 h. The raw and pretreated samples were labeled as RM, HCl-1%, HCl-3%, HCl-5%, H_2SO_4-1%, H_2SO_4-3% and H_2SO_4-5%. The proximate analysis of the samples was conducted according to GB/T 28731-2012, and the ultimate analysis was carried out by an elemental analyzer (Vario EL CUBE, Hanau, Germany). The content of crude protein was measured by Kjeldahl method according to China GB 5009.5-2010, and the crude fat content was determined after extraction with anhydrous diethyl ether using Soxhlet extractor followed by drying as described in GB/T 5009.6-2016 standards. The carbohydrate content was calculated as 100%-lipid-protein-ash.

0.2 g of raw and pretreated samples were weighted and digested by 10 mL HNO_3 (65 wt.%) reagent in a microwave digestion system, and then the digestion solutions were analyzed by inductively coupled plasma optical emission spectrometer (ICP-OES, Agilent 5100 SVDV) to quantify the inorganic contents of K, Na, Ca and Mg. Duplicate experiments for each test were performed, and the mean values were adopted with repeatability deviations less than 5%. The morphology of the samples was analyzed by scanning electron microscopy (SEM, Merlin S3700). To identify structural differences in solid phase, function groups of all the samples were characterized by a Nicolet iS 10 FTIR spectrometer. 2 mg of the samples were blended with KBr in a sample/KBr ratio of 1:100 in a mortar and pressed into tablets. Eight scans per sampling were made in the wavenumber range of 4000–500 cm^{-1} at a resolution of 4 cm^{-1}.

2.2. Thermogravimetric and TGA-FTIR analysis

A thermogravimetric analyzer (METTLER TOLEDO TGA/DSC1) was used to investigate the non-isothermal pyrolysis characteristics of the raw and pretreated *C. vulgaris* in an inert (N_2) atmosphere. The samples were preheated from 50 °C to 105 °C at a heating rate of 50 °C/min and then kept at 105 °C for 10 min to remove the moisture content. Subsequently, the samples were heated from 105 °C to 800 °C at different heating rates of 10, 20 and 40 °C/min. The flow rate of nitrogen was controlled at 80 mL/min. In order to enhance the comparability of the pyrolysis characteristic parameters, the initial sample mass was kept practically the same (10 ± 0.3 mg) for each run [25,26]. All the experiments were carried out at least twice to ensure the repeatable performance.

The pyrolysis evolved gas at heating rate of 20 °C/min was analyzed by FTIR (Nicolet iS 10 FTIR spectrometer). Measurements were carried out continuously at a time interval of 0.17 min when the heating temperature increased from 105 °C to 800 °C. FTIR spectra were recorded using 8 scans per sampling with a resolution of 4 cm^{-1} in the wavenumber range of 4000–500 cm^{-1}. The purge gas and the evolved gas from TGA pyrolysis furnace were transferred into the gas cell of FTIR through a heated transfer line. In all the experiments, the transfer line and gas cell were maintained at 215 °C in order to prevent the condensation of the evolved gas.

2.3. Kinetic analysis

Kinetic analysis provides thermal parameters of the pyrolysis behavior for the raw and pretreated samples. The rate of heterogeneous solid-state reactions can be described according to Arrhenius equation as following:

$$d\alpha/dt = k(T)f(\alpha) = A\exp(-E/RT)f(\alpha) \tag{1}$$

where α is fractional conversion of the sample, *t* is time, *T* is the reaction temperature (K), *k(T)* is the temperature dependence of rate constants, *f(α)* is the differential function of conversion depending on the reaction mechanism, *A* is the pre-exponential factor (s^{-1}), *E* is the activation energy (kJ/mol), *R* is the universal gas constant ($R = 8.314$ J/mol·K). The fractional conversion α is described by:

$$\alpha = (m_0 - m_t)/(m_0 - m_f) \tag{2}$$

where m_o and m_f are the initial mass and the final mass of the sample. m_t is the mass of the samples at time *t*. Eq. (1) can be transformed to Eq. (3) by introducing the linear heating rate ($\beta = dT/dt$) which is a constant.

$$\beta d\alpha/dT = A\exp\,(-E/RT)f(\alpha) \tag{3}$$

In this paper, both differential and integral isoconversional methods were applied for determination of apparent activation energy at three different heating rates. The Friedman method is the most commonly used differential isoconversional method based on Eq. (4) [27]:

$$\ln\left[\beta_i\left(\frac{d\alpha}{dT}\right)_{\alpha,i}\right] = \ln[f(\alpha)A_\alpha] - \frac{E_\alpha}{RT_{\alpha,i}} \tag{4}$$

Where the subscript α indicates isoconversional values, *i* identifies an individual heating rate. At each given α, the value of *Eα* can be obtained from the slope of straight line of ln $[\beta_i\,(d\alpha/dT)_{\alpha,i}]$ vs. $1/T_{\alpha,i}$.

The Kissinger–Akahira–Sunose (KAS) method is a popular integral isoconversional method to determine the value of *Eα* with high accuracy, which takes the form [25]: