Journal of Analytical and Applied Pyrolysis xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Journal of Analytical and Applied Pyrolysis

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

Comparative research on deoxy-liquefaction of marine and terrestrial biomasses

Jiping Wang, Bin Su, Yulin Xie, Min Du, Wenying Dai, Yuan Wen, Xiangyu Sun, Jinhua Li*

College of Chemistry and Chemical Engineering, Qingdao University, Qingdao 266071, China

ARTICLE INFO

Keywords:
Terrestrial biomass
Marine biomass
Deoxy-liquefaction
Liquid oil
Solid char

ABSTRACT

Marine biomass and terrestrial biomass have distinct compositions and structures. In order to understand the effect of feedstock difference on deoxy-liquefaction products, the experiments were performed with marine biomass (*Enteromorpha prolifera, Giant kelp, Undaria pinnatifida*) and terrestrial biomass (cotton stalk, sweet potato vine, plane leaves) for comparison of product yields and compositions. GC–MS results showed that the liquid oils from marine biomass were rich in alkanes (36.64–39.18%) and nitrogenous compounds (7.07–11.61%). While, the terrestrial biomass oils were rich in phenolic compounds (36.02–40.55%) and aromatic hydrocarbons (6.36–12.31%). The solid char properties were further characterized by FTIR, XRD and SEM analysis, respectively and their potential applications were also discussed. All the results suggested that the types of feedstock have a significant effect on the biomass deoxy-liquefaction products.

1. Introduction

Along with the rapid development of modern industry and society, the demand for energy is continuously increasing. Fossil fuels, providing approximately 80% of the energy for the world, are unevenly distributed and particularly non-renewable. Meanwhile, extensive use of fossil fuels will lead to environmental pollution due to the emissions of harmful gas (CO_x, SO_2, NO_x) [1,2]. Hence, it is imperative to find an environmentally friendly and renewable energy as an alternative energy source to replace fossil fuels [3]. In the past few years, some renewable energy including solar, wind, biomass, hydrogen and nuclear energy has been utilized and developed. Among them, biomass is the only sustainable source of organic compounds and has been proposed as the ideal alternative of petroleum because it can provide rich sources of sustainable commodity products, such as bio-fuels and chemicals which are primarily derived from petroleum now.

Biomass, as the highly oxygenated material, can be converted into products that are more stable and similar to currently used fuels *via* the thermochemical processing including gasification, pyrolysis and liquefaction [4]. These methods have been widely used to convert biomass feedstocks into bio-oil and chemicals, among which liquefaction is a promising technology to convert biomass into liquid fuels. For example, Zhu et al. [5] carried out the hydrothermal liquefaction of barley straw at different temperatures (280–400 °C), and obtained the bio-crude oil with the heating value of 28.4–29.4 MJ/kg and the oxygen content of 22.53–23.58%. Li et al. [6] investigated the liquefaction of the brown macroalgae (*Sargassum patens C. Agardh*) and the produced bio-oil had a heating value of 27.10 MJ/kg and the oxygen content of 22.04%; Zhou et al. [7] reported the liquefaction of green macroalge (*Enteromorpha prolifera*) and the results showed that the heating values of the bio-oil were 22–32 MJ/kg and the oxygen content was in the range of 16.5%–32.2%. In brief, those liquid oils contained large amount of oxygenous compounds such as aldehydes, ketones, acids, esters and ethers, which led to higher oxygen content and lower heating value. Such bio-oils can not be used as the conventional gasoline and diesel fuel because of their high oxygen content. Therefore, the more effective method must be developed to decrease the oxygen content of the bio-oils. Direct deoxy-liquefaction method which aims at removing oxygen from biomass has been proved to be effective to produce high-quality fuels from terrestrial biomass (Crofton weed, rice straw, corn stalk, wheat straw, and poplar leaves) [8–10] and marine biomass (*E. prolifera, Ulva lactuca, L. japonica and Gelidium amansii*) [11,12].

As mentioned above, terrestrial and marine biomasses are the dominant species of biomass, which have been widely reported. Interestingly, the obvious difference between them is the main components of terrestrial biomass (cellulose, lignin and hemicellulose) and marine biomass (polysaccharide, fat and protein), which causes different components of liquid oils from thermochemical conversion. Although extensive studies have been carried out on terrestrial biomass and marine biomass respectively, to the best of our knowledge, little information is available on the comparative liquefaction processing of these two kinds of biomass for liquid fuel production. In this study,

* Corresponding author.
E-mail address: jinhuali1978@126.com (J. Li).

https://doi.org/10.1016/j.jaap.2018.02.014
Received 27 January 2018; Received in revised form 13 February 2018; Accepted 13 February 2018
0165-2370/ © 2018 Elsevier B.V. All rights reserved.

terrestrial biomass (Cotton stalk, CS; Sweet potato vine, SPV plane leaves, PL) and marine biomass (*Giant kelp, GK; Enteromorpha prolifera, EP; Undaria pinnatifida, UP*) were selected as the feedstocks of the direct deoxy-liquefaction. The objective is to investigate the yields and compositions of liquid oils produced from different types of biomass by direct deoxy-liquefaction, and make a comparison with each other to reveal the relationship between feedstocks and products. The characterizations of the feedstocks and liquid oils were analyzed by using elemental analysis, Fourier transform infrared (FTIR) spectroscopy and gas chromatography-mass spectrometry (GC–MS).

2. Materials and methods

2.1. Raw material and pretreatment

GK, EP and *UP* were collected from Qingdao coast of Yellow Sea, China. CS, SPV and PL were collected from the countryside of Qingdao, respectively. The raw biomass feedstocks were washed with water to remove the impurities and then dried in an oven at 80 °C for 48 h. Subsequently, six kinds of feedstocks were milled to obtain 80-mesh powder by using a multi-functional grinder, and dried at 45 °C for experiments. The ash content of the feedstocks were measured at 600 °C and the C, H, O and N contents were determined by elemental analyzer Vario EL III.

2.2. Experimental procedure

The direct deoxy-liquefaction experiments were conducted in a stainless steel tubular reactor with the internal diameter of 20 mm and the length of 100 mm, equipped with an electrically heated furnace and a temperature controller. During each test, 20 g biomass feedstocks with 15 wt% distilled water were fed into the reactor. After that, the autoclave was tightened and heated to the liquefaction temperature (350 °C) at a heating rate of 15 °C/min and maintained at this temperature for 30 min. The reactor was cooled down to the room temperature and the volatile products in the reactor were firstly sampled into gas collecting bags. Then, the remains in the reactor were further distilled at normal pressure, with the temperature gradually raised from room temperature to 550 °C to produce the liquid oils. Water was also distilled out and the oil floated on the water. When distillation finished, water was separated by an injector. Finally, the solid char was removed and weighed at room temperature. At least three duplicate runs were conducted, and the maximum error under the same conditions was ensured within 5%. The yields of the products (gas, liquid oil and solid char) were calculated on the basis of the mass of feed according to the following equations:

$$\text{liquid oil (wt\%)} = W_{oil}/W_{feedstock} \times 100\% \quad (1)$$

$$\text{Char (wt\%)} = W_{char}/W_{feedstock} \times 100\% \quad (2)$$

$$\text{Water (wt\%)} = W_{water}/W_{feedstock} \times 100\% \quad (3)$$

$$\text{Gas (wt\%)} = 1 - \text{liquid oil (wt\%)} - \text{Char(wt\%)} - \text{Water(wt\%)} \quad (4)$$

where W_{oil} is the mass of the liquid oil; $W_{feedstock}$ is the mass of algae biomass fed into the reactor; W_{char} is the mass of solid residue after distillation; W_{water} refers to the difference of the mass between obtained and added water. It should be noted that the yield of gaseous products was obtained by difference; therefore, the contribution of some losses was also included.

2.3. Product analysis

The higher heating values (HHV) were obtained from calculation by Dulong's formula [13]

$$\text{HHV (MJ/kg)} = [338.2 \times \text{C wt\%} + 1442.8 \times (\text{H wt\%} - \text{O wt\%}/8)] \times 0.001 \quad (5)$$

Elemental analyses (C, H, and N) of the raw material, oil and char were performed on an elemental analyzer (Elemental Varian EL, Germany). The oxygen content was calculated by difference as follows:

$$\text{O (wt\%)} = 100 - (\text{C} + \text{H} + \text{N}) \text{ (wt\%)} \quad (6)$$

For characterization of the solid chars, the FTIR spectra were recorded using a Fourier-Transform Infrared Spectrometer (Varian 3100, America) over a range of 4000–400 cm^{-1}.

X-ray diffraction (XRD) patterns of the solid chars were carried out on a D8 Advance instrument (Bruker AXS, Germany) with Cu Kα radiation from 10° to 60° at a scanning rate 2θ of 2°/min.

Scanning electron microscope (SEM) images of solid chars were performed on a Zeiss merlin compact (Germany). The samples were previously sputter coated with gold for 30 s using a Neo coater.

The compositions of the liquid oils were analyzed on a Shimadzu gas chromatography and mass spectrometry (GC–MS) (QP2010S, Japan). The GC was fitted with a 30 m × 0.25 mm × 0.25 μm fused quartz capillary column and coated with TR-5MS as the stationary phase. Helium (99.999%) was used as carrier gas with a constant flow of 1.0 mL/min and split ratio was 50:1. The injector temperature was 250 °C. The oven temperature was programmed from an initial temperature of 50 °C (1 min) followed by a 10 °C/min to a final temperature of 250 °C and held for 10 min. After a solvent delay of 2 min, full scan mass spectra were acquired from 50 to 650 *m/z* with a scan rate of 0.4 s per scan. Compounds in the oils were identified by comparison with the mass spectra with the NIST (National Institute of Standards and Technology) 08 library, together with the literature data to obtain the highest likelihood of compound identification.

3. Results and discussion

3.1. Characterization of feedstock

The elemental and compositional characteristics of the feedstock samples on dry basis are shown in Table 1. The carbon contents of the terrestrial biomass samples are in the range of 40.83–45.85%, which are higher than those found in the marine biomass (27.65–30.68%).

Table 1
Characterizations of marine and terrestrial biomass feedstocks.

	EP	*GK*	*UP*	CS	SPV	PL
Ultimate analysis (%)						
Carbon	28.28	27.65	30.68	40.83	41.82	45.85
Hydrogen	4.51	4.80	5.32	5.81	5.86	6.37
Oxygen	63.86	65.59	61.40	52.12	51.04	46.77
Nitrogen	3.35	1.96	2.60	1.24	1.28	1.01
H/C molar ratio	1.91	1.65	2.08	1.71	1.68	1.67
O/C molar ratio	1.69	1.81	1.50	0.96	0.92	0.76
HHV (MJ/kg)	4.55	4.45	6.98	12.79	13.39	16.26
Proximate analysis (%)						
Crude protein	14.83	10.56	11.62			
Crude fat	1.53	0.55	0.32			
Crude fiber	6.24	6.65	9.78			
Carbohydrate	41.37	34.87	37.81			
Cellulose				38.83	43.23	22.61
Hemicellulose				23.53	25.31	20.24
Lignin				20.24	18.07	9.14
Ash	24.79	30.47	30.80	11.79	5.52	4.65
Element analysis (ppm)						
Na	22.20	24.85	23.18	5.46	2.70	1.74
K	15.50	41.47	19.36	11.03	3.80	1.90
Mg	20.27	33.01	10.08	6.52	5.08	7.62
Al	18.85	12.84	18.61	21.41	12.80	14.85
Fe	0.95	14.89	17.62	3.80	1.51	0.79
Ca	8.69	13.38	14.90	5.11	3.43	4.90
P	62.35	46.71	44.45	21.87	12.15	35.23

Download English Version:

https://daneshyari.com/en/article/7606320

Download Persian Version:

https://daneshyari.com/article/7606320

Daneshyari.com