Applied Thermal Engineering 136 (2018) 9–15

Contents lists available at ScienceDirect

Applied Thermal Engineering

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

Research Paper

Microwave-assisted fast co-pyrolysis behaviors and products between microalgae and polyvinyl chloride

Minquan Dai, Hao Xu, Zhaosheng Yu*, Shiwen Fang, Lin Chen, Wenlu Gu, Xiaoqian Ma

School of Electric Power, South China University of Technology, 510640 Guangzhou, China
Guangdong Province Key Laboratory of Efficient and Clean Energy Utilization, 510640 Guangzhou, China
Guangdong Province Engineering Research Center of High Efficient and Low Pollution Energy Conversion, Guangzhou, Guangdong 510640, China

HIGHLIGHTS

- Microwave-assisted co-pyrolysis of microalgae and polyvinyl chloride was studied.
- Heating rate curves, yield of products, analyses of liquid and solid were investigated.
- Bio-oil yields was enhanced while aromatics proportion was reduced at 1000 W.
- Polyvinyl chloride can promote the production of aromatic hydrocarbons.

ARTICLE INFO

Keywords:
Microwave
Fast co-pyrolysis
Microalgae
Polyvinyl chloride
Oil yield

ABSTRACT

Microwave-assisted fast co-pyrolysis of microalgae (MA) and polyvinyl chloride (PVC) was investigated. The pyrolysis profiles, yields of three-phase, the chemical composition of liquid and the ultimate analyses of solid residues were studied. When the power increased from 800 W to 1000 W, the bio-oil yields increased significantly while the proportion of aromatics and the heating value of oil and char decreased. A remarkable synergistic effect between MA and PVC was achieved in terms of oil yield when MA to PVC ratios were 5:5 and 3:7 at 800 W and 5:5 at 1000 W, respectively. With the increase of PVC, the content of nitrogenous and oxygenous organic matter in oil decreased from 29.65% to 0.38% at 800 W. The yield of solid decreased, the HHV increased and the values of H/C had a wave change. According to the quantity and quality of liquid and solid, 30% percentage of PVC was the suitable ratio.

1. Introduction

With the development of economy and urbanization, the rapid increase in energy consumptions has brought about an energy crisis and environmental issues. The continuous increase of carbon dioxide emissions from the burning of fossil fuels necessitates a switch from conventional to renewable power sources. Biomass energy has become one of the most widely explored research fields, since it is sustainable, wide availability, CO_2 neutral [1,2]. And bio-oil is considered as an alternative to petroleum-based sources for a wide range of fuels and high value-added chemicals [3]. Under thermochemical conversion, biomass could be converted into gaseous, bio-oil and char products. Pyrolysis is conducted in the absence of oxygen or under an inert atmosphere and has the advantage of lower secondary pollution emissions and higher energy efficiency [4].

Microalgae (MA), known as the third generation of bio-energy, has the advantage over terrestrial crops, such as its wider source, shorter growing cycles, no land allocation requirement [5]. The main components of microalgae were lipid, protein and carbohydrate and it is acknowledged as the most potential alternative to fossil fuels. However, pyrolytic oil of algae has several disadvantages, such as low heating value, low stability, and high acidity, due to its high oxygen content and low hydrogen content [6]. To assess the relative hydrogen content of different samples, effective hydrogen index (EHI) is raised and can be expressed as [7]:

$$EHI = (H-2O-2S-3N)/C \quad (1)$$

The H, O, S, N and C in Eq. (1) are the moles of hydrogen, oxygen, sulfur, nitrogen and carbon, respectively. The EHI of MA is usually less than 0.3, indicating an extreme lack of hydrogen. It is important to find an effective utilization to improve the physicochemical properties. And co-pyrolysis of MA with other material with a higher EHI would be a

* Corresponding author at: School of Electric Power, South China University of Technology, 510640 Guangzhou, China.
E-mail address: zsyu@scut.edu.cn (Z. Yu).

https://doi.org/10.1016/j.applthermaleng.2018.02.102
Received 10 October 2017; Received in revised form 27 February 2018; Accepted 28 February 2018
Available online 01 March 2018

Table 1
The ultimate analyses and proximate analyses of MA, PVC and CA.

Samples	Ultimate analysis (dry basis, wt.%)					Calorific value	Proximate analysis (dry basis, wt.%)		
	C	H	O[a]	N	S	$Q_{net,d}$	Volatile	Ash	Fixed carbon[b]
MA	47.32	5.97	27.85	11.33	0.70	19.63	82.30	6.83	10.87
PVC	38.09	5.22	0	0	0	20.07	93.77	0.17	6.06
AC	72.18	2.17	20.92	4.28	0.09	25.12	8.66	7.86	83.48

[a] Calculated by difference, O (%) = 100-C-H-N-S-Cl (only for PVC, 54.37)-ash.
[b] By difference: Fixed carbon% = 100% − volatile% − ash%.

useful way to improve the oil quality. There could exist a hydrogen transfer and a synthetic effect during co-pyrolysis.

On the other hand, with the improvement of consumption level, plastics has become an indispensable part in daily life, and its worldwide demand is growing continuously [8]. Mainly used in packaging, cable, food and other industries [9], polyvinyl chloride (PVC) is a common available plastic type among municipal plastic waste, which would produce hazardous gas, such as hydrogen chloride (HCl) and dioxins, during its incineration. The effective treatment of PVC is urgent in the environment protection and the resources utilization. Since PVC seems to be a good hydrogen donor (EHI = 1.64) and pyrolytic residue obtained from MA might absorb chlorine volatiles of PVC, it is of great significance to combine the treatment process of MA and organics containing waste to find an efficient and low-pollution energy conversion.

At present, the studies of co-pyrolysis characteristics focus on biomass, coal [10], waste [11] and sludge. The microwave-assisted catalytic pyrolysis characteristics of lignin and low-density polyethylene (LDPE) were studied [12]. It was found that an obvious synergistic effect between lignin and LDPE was achieved in terms of bio-oil yield. And LDPE was proved to be a good hydrogen donor to improve the bio-oil quality. Xie [13] examined the production and characteristic of biodiesel from the co-pyrolysis of microalgae and scum, and found that a synergistic effect between algae and scum became significant only when EHI of feedstock was larger than about 0.7.

Microwave-assisted pyrolysis applies electromagnetic waves to interact with matters [14], which is volumetric and instantaneous. Therefore, biomass can be instantaneously heated to the desired temperature, with more energy efficient and less secondary reaction than conventional heating [15]. And fast microwave-assisted pyrolysis technology has been applied to produce biofuels successfully [16]. Shi [17] studied the microwave-assisted pyrolysis of bamboo for the production of hydrogen-rich syngas. It was found that microwave irradiation enhanced the cracking reaction and subsequently resulted in the formation of H_2-rich syngas. Hong [18] investigated microwave-enhanced pyrolysis of macroalgae and microalgae. Carbohydrate in algae led to higher gas yield whilst protein led to higher oil yield.

The conversion of waste into liquid oil and other valuable products by using pyrolysis is getting significant attention both as waste management and an alternative energy generation technology. Co-pyrolysis of MA and PVC is supposed to offer the advantages of energy recovery and production of high value-added chemicals, as well as low secondary pollution [19]. Nonetheless, to the best of our knowledge, microwave-assisted co-pyrolysis of MA and PVC has not been studied. The microwave devices and gas chromatography/mass spectrometry (GC/MS) were used to identify and quantify organic compounds present in bio-oil. The ultimate aim of this study was to improve the quantity and quality of pyrolysis liquid oil. The heating rate curves, the yields of gas, liquid and solid, the chemical composition of liquid and the ultimate analyses of solid under different microwave power and mixing ratios were studied. The synergistic effect between MA and PVC was evaluated by comparing the theoretical values and the experiment values, in term of the oil yield and the relative content of hydrocarbons in oil. This paper focused on the production and chemical component of oil, as well as the potential use of char. And further research about gaseous product remains to be done. This work would be expanded in the future to create a database for chlorella and tire treatment process.

2. Materials and methods

2.1. Samples

MA sample used in this paper was chlorella vulgaris, which was provided by Wudi lv Qi Bioengineering Co. Ltd. (Shangdong Province, China). PVC was collected from the rubbish recycle bin in South China University of Technology. All materials were dried in an oven at 105 °C for 24 h prior to milling to a size smaller than 200 μm (80 mesh). Thereafter, MA was mixed with PVC by a magnetic stirrer. The blending ratio of MA:PVC was 1:9, 3:7, 5:5, 7:3, 9:1, stirred for 2 h and then dried in an oven at 105 °C for 24 h. Activated carbon (AC), as microwave absorbent, was purchased from chemical reagent stores and was produced in Hongyan Reagent Factory (Tianjin Province, China). Ultimate and proximate analysis were performed using the elemental analyzer and GB/T 28731-2012, GB/T 212-2008 and ASTM D5373 standard method. And the results were displayed in Table 1.

2.2. Experimental device

The experimental device included the carrier gas bottle, suspended body flowmeter, thermocouple, flask with three necks, condenser system, liquid collecting system and computer. The temperature was determined by using a K-type thermocouple, with a deviation value of 1.5 °C. The system has two control modes, namely temperature control mode and power input control mode, which can control the microwave switch circuit. And the schematic diagram of experimental apparatus was shown in Fig. 1.

In each test, 50 ± 0.001 g sample was placed in the quartz reactor, with addition of 10% AC. Nitrogen at a flowrate of 300 mL/min was introduced to the reaction system for 10 min before each experiment to ensure an oxygen-free atmosphere. The pyrolysis time was set to 40 min

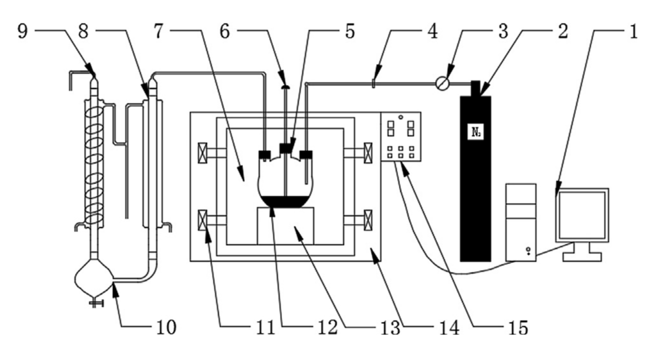

Fig. 1. Schematic diagram of microwave-assisted catalytic co-pyrolysis system. (1) data acquisition system; (2) N_2; (3) reducing valve; (4) flowmeter; (5) quartz flask; (6) thermocouple; (7) microwave oven; (8) the first level condenser; (9) the second level condenser; (10) collection funnel; (11) magnetron; (12) Samples; (13) quartz supports; (14) outer shell; (15) microwave control panel.