Journal of Analytical and Applied Pyrolysis 107 (2014) 31–39

Contents lists available at ScienceDirect

Journal of Analytical and Applied Pyrolysis

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

Influence of heating temperature and holding time on biochars derived from rubber wood sawdust via slow pyrolysis

A. Shaaban [a], Sian-Meng Se [a,*], M.F. Dimin [a], Jariah M. Juoi [a], Mohd Haizal Mohd Husin [b], Nona Merry M. Mitan [c]

[a] Department of Engineering Materials, Faculty of Manufacturing Engineering, Universiti Teknikal Malaysia Melaka (UTeM), Hang Tuah Jaya, 76100 Durian Tunggal, Melaka, Malaysia
[b] Department of Automotive, Faculty of Mechanical Engineering, Universiti Teknikal Malaysia Melaka (UTeM), Hang Tuah Jaya, 76100 Durian Tunggal, Melaka, Malaysia
[c] Department of Plant and Maintenance, Faculty of Mechanical Engineering, Universiti Teknikal Malaysia Melaka (UTeM), Hang Tuah Jaya, 76100 Durian Tunggal, Melaka, Malaysia

ARTICLE INFO

Article history:
Received 2 November 2013
Accepted 30 January 2014
Available online 7 February 2014

Keywords:
Rubber wood sawdust
Slow pyrolysis
Biochar
Surface functional groups
BET specific surface area

ABSTRACT

Biochar samples were produced from rubber wood sawdust (RWSD), which is a by-product from sawmills, via slow pyrolysis. Biochar is a potential additive for agricultural soil as a soil amendment and for agronomics. The approach proposed in the current study considers the effects of heating temperature and holding time on the surface functional groups and morphologies of RWSD-derived biochars. The pyrolysis was performed in a vertical tube furnace heated at 5 °C/min from room temperature to maximum heating temperatures of 300 °C, 400 °C, 500 °C and 700 °C under nitrogen gas purging at a rate of 30 ml/min. Two sets of biochars were produced with holding times of (i) 1 h and (ii) 3 h. Proximate and ultimate analyses were performed on the raw RWSD using thermogravimetric analysis (TGA) and carbon–hydrogen–nitrogen (CHN) elemental analysis. The influence of heating temperature and holding time on biochar surface functional groups and porosities was investigated using X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy, Boehm titration, pH alkalinity, Brunauer–Emmett–Teller (BET) surface area analysis, scanning electron microscopy (SEM) and SEM with energy-dispersive X-ray (SEM–EDX) spectrocopy. The FT-IR spectra indicated the presence of acidic functional groups, such as carboxylic, phenolic and lactonic groups, and these groups were quantified by Boehm titration. The number of acidic functional groups decreased as the heating temperature and holding time increased. The maximum amount of acidic functional groups was determined to be 1.9 mmol/g at 300 °C for a 1-h holding time compared to 1.3 mmol/g for a 3-h holding time and 1.0 mmol/g with a 1-h holding time at 700 °C. All of the biochars produced at heating temperatures above 400 °C were alkaline, and the pH value increased as the heating temperature and holding time increased. The biochar produced at 300 °C with a 1-h holding time had a pH of 6.72 and the sample produced with a 3-h holding time had a pH of 7.67. In addition, the sample produced when the temperature was increased to 700 °C with a 1-h holding time had a pH of 11.44. The BET surface area analysis reported maximum values of 5.49 m^2/g, and the total pore volume was 0.0097 cm^3/g at a heating temperature of 700 °C with a 3-h holding time. SEM micrographs clearly showed the development of well-defined pores in the biochars, and the SEM–EDX spectra indicated localised carbon and oxygen content in all the samples. The results indicated that biochars produced from RWSD are potentially beneficial as soil amendments. However, an extensive study of biochar sustainability is worth investigating.

1. Introduction

Biochar is a stable carbon-rich form of carbon that can be applied to agricultural land as part of agronomic and environmental management. Biochar can be produced via the thermal pyrolysis of biomass using a pyrolysis reactor with little or no oxygen [1]. Agricultural and forestry by-products can be used as an inexpensive and renewable source for biochars. These by-products are lignocellulosic materials consisting of cellulose, hemicellulose and lignin [2]. Cellulose is a type of glucose polymer arranged in long chains with a well-ordered structure. Hemicellulose, which is an example of a polysaccharide, consists of sugar chains with a long branching arrangement. Lignin is composed of monomers that are linked together to form a long-chain molecule [3]. The composition of

* Corresponding author. Tel.: +60 6 3316069; fax: +60 6 3317075.
E-mail address: sianmeng@gmail.com (S.-M. Se).

0165-2370/$ – see front matter © 2014 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jaap.2014.01.021

hemicellulose and lignin vary from species to species. The carbon content of wood-based biomass varies from 47 wt% to 53 wt% due to variability in the lignin content. These waste materials are believed to have little or no economic value, and their disposal often becomes a major concern. Therefore, the conversion of these wastes into biochars would valuate these low cost by-products resulting in a profitable good [4,5]. In general, there are three types of pyrolysis processes (i.e., fast, moderate and slow pyrolysis) used to produce biochar. For fast pyrolysis, the biomass is heated rapidly for less than 1 min, but the holding time in slow pyrolysis is typically in the range of 30 min to 3 h. The yield composition for solid char, liquid bio-oil and non-condensable gases depends on the type of pyrolysis where fast pyrolysis yields more liquid (60–75 wt%) and less solid char (15–25 wt%) [6]. To yield higher percentages of solid char (35–50 wt%), slow pyrolysis was chosen for the current study.

The physical and chemical properties of biochar, such as specific surface area, pore structures and surface chemical functional groups, can be customised by varying the pyrolysis parameters, such as heating temperature, heating rate, holding time, type of gas and gas flow rate [7,8]. Among these parameters, the heating temperature and holding time are reported to significantly influence the final characteristics of the biochar due to the release of volatiles as well as the formation and volatilisation of intermediate melts [9,10]. Therefore, the heating temperature and holding time were investigated in this study. Incorrect production could be detrimental to agricultural production and the environment. Porosities created during pyrolysis are an important feature of biochar that affects its behaviour in soil, and the pores are divided into three categories according to their internal diameter (i.e., micropores (<2 nm), mesopores (2–50 nm) and macropores (>50 nm)) [11]. The internal structure and its large surface area are a preferred habitat for microbial activity in the soil [12]. The presence of macropores on biochar provides a suitably sized cluster for the growth and reproduction of microorganisms. In addition, the high porosity of biochar allows it to retain more moisture in soil and increases the water holding capacity [12,13].

Surface functional groups of biochar consist of carboxylic, lactonic and phenolic groups, which act as acidic sites, and carbonyl, quinone and pyranose groups, which act as base sites. Acidic sites on the biochar surface will deionised when applied to the soil resulting in the formation of a surface oxide, which is known as surface negative charge that may help to retain positively charge compounds, such as ammonium (NH_4^+) in the soil, and improve the cation exchange capacity (CEC) [13]. The base sites on the biochar surface enhance the interaction between biochar and acidic molecules in soil. This interaction may increase the anion exchange capacity (AEC) that aids in the reduction of the leaching of anion nitrogen nutrient compounds with negative charges, such as nitrite (NO_2^-) and nitrate (NO_3^-), to reduce the eutrophication [14]. In addition, biochar is also known as a doubly green revolution due to storage of carbon in the soil and reduction of carbon in the atmosphere, which causes global warming. This phenomenon is known as carbon sequestration [15]. Due to the potential of applications, the preparation and characterisation of biochar has received increasing attention by both academic and industrial researchers.

RWSD was chosen for this study due to its availability because it is one of the main plantation crops in South East Asia, especially in Malaysia with an estimated plantation area of 1.82 million hectares [16]. The current work focuses on (i) the production of biochars from RWSD and (ii) comparison of the surface porosities and surface functional groups of biochars produced at several heating temperatures (i.e., 300 °C, 400 °C, 500 °C and 700 °C) and holding times (i.e., 1 h and 3 h). The surface porosities and functional groups are important properties for nutrient retention and the water holding capacity when applied to soil.

2. Materials and methods

2.1. Raw materials

RWSD was obtained from a sawmill in Malacca, Malaysia. The RWSD was sieved to remove the large lumps, dried at 105 °C for 24 h and stored in a sealed container inside an incubator prior to the experiment. 0.1 N sodium hydroxide (NaOH) and 0.1 N hydrochloric acid (HCl) were purchased from Polyscientific Private Limited for the Boehm titration.

2.2. Proximate and ultimate analysis of RWSD

Prior to the pyrolysis process, a proximate analysis was performed according to a protocol adopted from ASTM D 3172-89 (2002) Standard Practice for Proximate Analysis of Coal and Coke [17]. The determination of ash content was performed according to Standard Biomass Analytical Methods (1994) [18]. For the determination of the ash content in biomass, the crucible was heated in a conventional furnace at 575 °C for 3 h and cooled in an incubator. The heating process was repeated until a constant weight was obtained. 1.0 g of dried RWSD was weighed and heated at 575 °C for 3 h with a heating rate of 10 °C/min. The step was followed by cooling and repeated heating until a constant weight was obtained.

Thermal stability analysis of RWSD was performed using thermogravimetric analysis (TGA) (Mettler Toledo Star SW901) under a nitrogen atmosphere with a gas flow rate of 10 ml/min. The sample was heated from room temperature to 700 °C at a heating rate of 5 °C/min. The TGA curve represents the mass change of RWSD as a function of temperature. The moisture content was calculated as the weight per cent lost when heated at 120 °C, the volatile matter was determined by the difference of the weight per cent lost between 150 °C and 450 °C, and the fixed carbon content was calculated as the total weight (100%) minus the ash content, moisture content and volatile matter [19,20].

The ultimate characterisation was performed with dried raw RWSD using a carbon–hydrogen–nitrogen (CHN) elemental analyser (Therma Finnigan EA 1112), and the sample was prepared by grinding the dried raw RWSD into smaller particle sizes using a lab-scale milling machine and sieved to 20 μm.

2.3. Pyrolysis of rubber wood sawdust

Pyrolysis of RWSD was performed using a stainless steel vertical tube furnace that was 1.0 cm in diameter and 50.0 cm length with 10.0 g of sample. Nitrogen gas was flowing at a rate of 30 ml/min during the pyrolysis. The heating rate was constant at 5 °C/min during the holding time (i.e., 1 h and 3 h). Then, the heating temperatures used were 300 °C (referred as BC 300-1 and BC 300-3), 400 °C (referred to as BC 400-1 and BC 400-3), 500 °C (referred as BC 500-1 and BC 500-3) and 700 °C (referred as BC 700-1 and BC 700-3).

2.4. Characterisation of biochars

The phase analysis of the prepared biochars was performed using X-ray diffraction (XRD) on a PANalytical X'Pert PRO MPD PW 3040/60 diffractometer using Cu$K\alpha$ radiation with a scan speed of 2.5°/min to determine the degree of crystallinity of the cellulose structures. The details for the calculation of the crystallinity index are provided in Section 2.4.1. Surface functional groups were analysed using FT-IR spectrocopy, and the test specimens were prepared by mixing the biochar with KBr at a fixed ratio to fabricate a translucent disc. The spectra were recorded in the range of 400–4000 cm^{-1} with a resolution factor of 4 cm^{-1}. The surface negative charge was determined using a titrimetric method based on