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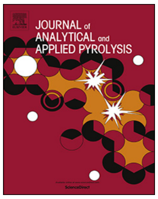

Contrasting effects of operating conditions and biomass particle size on bulk characteristics and surface chemistry of rice husk derived-biochars

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ABSTRACT

In this study, the slow pyrolysis of rice husk was conducted by using a split-tube furnace under a nitrogen environment to investigate the influence of various pyrolysis conditions and biomass particle sizes on products yield distribution as well as physicochemical characteristics and surface chemistry of produced biochars. Results revealed that temperature has a more pronounced influence on products yield compared to the other operational conditions. The biochar yield decreases from 57.13 ± 5.37% to 37.19 ± 2.05% and gaseous phase yield increase from 25.64 ± 0.93% to 42.50 ± 4.58% with temperature increase from 300 °C to 700 °C. The surface chemistry of produced biochar varies widely as the distribution of different functional groups on its surface influenced by operational conditions and biomass particle size; above 500 °C the intensity of FTIR vibrational peaks reduces abruptly. FTIR, SEM, elemental composition and surface area results indicate that biochar synthesized under higher pyrolysis temperature, extended retention time and, lower heating and gas flow rates with fine biomass particle size has utility as a potential C-sequestration and remedial agent to mitigate global climate change and adsorption of environmental pollutants, respectively. Furthermore, biochar has potential application as a renewable solid bio-fuel source due to higher calorific values. A cost-benefit analysis indicates that the viability of biochar saleable product system is more economical with an annual profit of 138,533$ for the low scenario, when the presumed unit processes 2500 tons y^{-1} of biomass. In a comparison to other presumed scenarios, this system is more feasible in areas where low-cost RH biomass waste is available abundantly such as in rice production and processing areas. The profitability of this system increases further by accounting pyrolysis-gas energy value that reduces operational cost. For the optimization of biochar economical yield with desired properties, this work provides insight knowledge.

1. Introduction

China is a leading rice producer country accounting ~35% of world production. Rice husk (RH) as a byproduct waste accounts about 20–22% of the rice bulk grain weight during industrial processing. Thus, on a global scale, 1.2 billion tons of RH waste is produced including 40 million tons from China [1,2]. Such a huge volume of biowaste is not used effectively and mostly dispose of by burning or landfilling, results in energy wastage, GHGs emission, and air pollution. RH biomass is primarily composed of lignocellulose and minerals mainly silica. Thus the production of biochar by using RH biomass as a feedstock has an additional benefit as silicon plays a substantial role in the resistance of plants to several biotic and abiotic stresses. Furthermore, it is the only element that excessively accumulates in plants without any damage [1]. Thus, pyrolysis of RH biomass yields biofuel and byproduct biochar that can be recycled effectively when applying as a soil amendment [2,3].

The systematic production of environmentally friendly clean energy and CO_2 emission reduction can be achieved simultaneously by applying the advanced biomass pyrolysis approach to yield biochar from rice husk as a soil amendment, in addition of the bio-syngas (BS) and bio-fuels as energy sources, emerged an auspicious pathway towards sustainability [4,5]. Pyrolysis is a thermo-chemical conversion process that involves the thermolysis of biomass materials structural

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components especially an organic one, in an inert medium at a moderate temperature for the production of solid charcoal (biochar) and non-condensable and condensable products [6]. The central concept behind the biomass pyrolysis elucidates that carbon in the biomass would be locked up in recalcitrant form and the resulting biochar comprising it can be persistent for a time scale of centennial to millennial [7]. The production and use of biomass energy have the vantage of the smaller volume of greenhouse gases (GHGs) discharge in comparison of the fossil fuels combustion, as the emission of CO_2 during the energy generation process is balanced by the photosynthesis process during the biomass regrowth [8,9]. This approach has potential applications for the reduction of greenhouse gases (GHGs) emission [10], sequestration of atmospheric carbon and mitigation of the climate change has been receiving attention worldwide [11,12]. On global scale, ~6.6 gigatons (Gts) of biomass is produced annually from different sources (crop stovers, waste woods, wheat and rice straws etc.), but such a huge amount is not used effectively [13]. Pyrolysis of such a gigantic volume of lingo-cellulosic biomass waste materials can transform it into valuable bioenergy-biochar products at gigaton (Gt) scale [7]. This approach worldwide can mitigate about 1.8 Pg (10^{15} g) CO_2-C greenhouse gas (GHG) annually, which is almost equal to 12% of the recent anthropogenic emissions [14]. Renewable fuel(s) procured by the biomass pyrolysis might be a propitious opportunity for attaining the clean energy/fuel goals according to the policy mandated by the European Commission-renewable energy directive (RED) [15] and renewable fuels standard (RFS) of the U.S. [16].

As, a by-product during pyrolysis process, biochar has complex porous aromatic structure, carbon enriched, higher specific surface area (SSA), the diverse chemistry of surface functional groups, higher adsorption affinity for cations and anions than the biomass feedstock [17]. Thus it can be used as an adsorbent, but notably utilized as soil conditioner due to its multi-functional benefits [18]. Recent evidences indicate that biochar from rice husk has garnered the significant attention for the betterment of soil quality by improving its physico-chemical and micro-biological characteristics [12,19]. When applied, it increases water and nutrient retention capacity, reduces the overall fertilizer requirement and improved the crop biomass productivity [11]. Further, the environmental positive aspects are the reduction of greenhouse gases (GHGs) emissions like CH_4 and N_2O, enhance carbon pool by trapping it in refractory organic form, increase sorption and decrease the bioavailability of organic and inorganic contaminants in soil and water system [11,20–22]. Additionally, many functional materials are also derived from the biomass which found applications in daily life such as energy storage devices, water purification system, construction material, fillers, resin, and drug delivery system [1].

Feedstock materials and operating conditions such as pyrolysis temperature, length of reaction time, heating rate (°C min^{-1}), reaction medium gas and particle size of biomass regulate the quantity and quality of products composition and heterogeneous structure of the engineered biochar [23]. Lignocellulosic biomass materials have a complex structure, due to different components (lignin, cellulose, hemicellulose, and extractives) they respond in a dissimilar fashion under varying thermo-chemical conversion processes, so there is a robust need for the chemical and structural characterization of the generated biochar. The selection of a particular biomass material may have a momentous role in the quality of biochar as well as for the economic feasibility of the pyrolysis process.

The distribution of pyrolysis products and the effects of a broad range of operating conditions on biochar properties simultaneously in a single study by using a single feedstock (rice husk) in relation to economic viability have not been reported until now in any previous study according to our knowledge up to date. The overall aim of this work was to investigate the different pyrolysis conditions and biomass particle size, which regulate the products yield distribution and characteristics of pyrolysis products (biochar, biooil, and gas). The more specific intentions were 1) to determine the synergistic effect of pyrolysis conditions i.e., temperature (300-700 °C), retention time (15–90 min.), heating rate (1–10 °C min^{-1}), gas flow rate (20–200 standard cm^3 min^{-1}) and biomass RH particle size (10 to < 200 mesh), on bio-oil, biochar and gas products yield distribution. 2) Optimization of operating for economical maximum bio-oil and biochar production in relation to desired characteristics. 3) Advanced characterization of biochar using a verity of analytical techniques to identify its potential applications as a soil amendment to sequester carbon, enhance crop productivity and remediation of contaminants as well as use as an energy source.

2. Materials and methods

2.1. Preparation of feedstock material

Feedstock material Rice husk (RH) (obtained from the Anhui province of China) was slightly washed by dipping in distilled water for 5–10 seconds to remove the dust particles, air-dried at room temperature and then dried in an oven with a constant supply of hot air at 105 ± 5 °C for overnight to remove moisture. Then, laboratory scale Thomas-Wiley mill (Model 4 Wiley® Thomas Scientific, USA) was used for the mechanical grinding of this dried biomass material. One portion of feedstock material was sieved by using 4 different types of sieves (10, 50, 100 and 200 mesh size) and other was used directly without particles size segregation for further process.

2.2. Pyrolysis experiment

The furnace (model BTF-1200C, AnHui BEQ equipment, technology Co., Ltd, China) integrated with digital PID controller (proportional-integral-derivative) to achieve a maximum working temperature of 1200 ± 1 °C with wide-ranging heating rates and retention times was used for pyrolysis purpose. The details of the pyrolysis process operational conditions (temperature, retention time, heating rate and nitrogen gas flow rate) and RH biomass particle size used in this experiment is provided in Table 1. Approximately 30 g of dried and ground biomass material (10–50 mesh size) was taken in an ultra-high purity quartz boat (100 mm L × 60 mm W × 40 mm H) and housed inside the center of the tube in the furnace. The residual air was purged by using a constant supply of nitrogen to provide the inert reaction

Table 1
Pyrolysis operation conditions and biomass particle sizes used during the experiment.

Test No	Temperature (°C)	Retention time (min)	Heating rate (°C/min)	Gas flow rate (sccm)	Particle size (mesh size)
T1	300	60	10	20	10–50
T2	400	60	10	20	10–50
T3	500	60	10	20	10–50
T4	600	60	10	20	10–50
T5	700	60	10	20	10–50
T6	500	15	10	20	10–50
T7	500	30	10	20	10–50
T8	500	60	10	20	10–50
T9	500	90	10	20	10–50
T10	500	60	1	20	10–50
T11	500	60	2	20	10–50
T12	500	60	5	20	10–50
T13	500	60	10	20	10–50
T14	500	60	10	20	10–50
T15	500	60	10	50	10–50
T16	500	60	10	100	10–50
T17	500	60	10	200	10–50
T18	500	60	10	20	10–50
T19	500	60	10	20	50–100
T20	500	60	10	20	100–200
T21	500	60	10	20	< 200