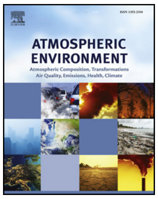
Atmospheric Environment 190 (2018) 218–225

Contents lists available at ScienceDirect

Atmospheric Environment

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



Production of biochar and bioenergy from rice husk: Influence of feedstock drying on particulate matter and the associated polycyclic aromatic hydrocarbon emissions

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ARTICLE INFO

Keywords:
Biochar
Pyrolysis
PM
PAH
Emissions
Air pollution

ABSTRACT

This study investigates the effect of feedstock drying on the emissions of polycyclic aromatic hydrocarbons (PAHs) associated with the particulate matter (PM) produced during the co-generation of biochar and bioenergy. Raw pyrolysis volatile mixtures were generated from the pyrolysis of rice husk at 400, 500, 600, 700, and 800 °C using a laboratory-scale continuous pyrolysis-combustion system and combusted at 850 °C. PM samples from the combustion were collected and analysed for 15 priority PAH species with a gas chromatography/mass spectrometer (GC/MS). It was found that the utilization of the as received (AR) rice husk resulted in significantly greater energy-based yields of PM$_{10}$ (1.2 times at 400 °C and 1.6 times at 800 °C) than the dried rice husk. The majority of the increase was of the PM$_{2.1\text{-}10}$ size fraction. The PM-bound PAH concentration was found to be 2.1 and 2.8 times higher for the AR rice husk at 400 and 800 °C, respectively. This resulted in a significant increase in the energy-based yield of PAHs over the entire volatile production temperature range for the AR rice husk. Nevertheless, the majority of the PM-bound PAH species generated from the AR rice husk consisted of 2 and 3 ring PAHs (naphthalene, acenapthylene, and acenaphthene) with relatively low toxicity. The concentration of 4, 5, and 6 ring PAHs was generally lower than that generated from the dried rice husk. This resulted in the benzo(*a*)pyrene-equivalent toxicity of the PM generated from the AR rice husk being lower than the dried counterpart.

1. Introduction

The co-production of biochar and bioenergy from agricultural by-products offers a potential approach for developing sustainable land-management practices with additional economic benefits (Roberts et al., 2010). The uptake of these feedstocks, however, often requires on-site utilization due to issues relating to the low-bulk density and decomposition during storage of wet biomass. The reduced throughputs of distributed systems suggests that it is often necessary to minimise the energy intensive drying processes in order to be economically viable. As such, this will result in the need to utilize feedstocks with as received (AR) moisture contents (Olave et al., 2017). One potential approach for the distributed co-production of biochar and bioenergy from agricultural by-products is through a combined pyrolysis and combustion process (hereafter named "pyrolysis-combustion") (Dunnigan et al., 2018; Roberts et al., 2010).

Pyrolysis-combustion involves combustion of the raw pyrolysis volatiles produced during the initial low temperature pyrolysis step of the process. The co-product of the pyrolysis reaction (biochar) is separated prior to combustion. These volatiles are a mixture of condensable (bio-oil) and non-condensable (pyrogas) fractions. The range of pyrolysis temperatures that typically favour biochar production (< 500 °C) also favour bio-oil formation over pyrogas. Recent study has suggested that it is beneficial to co-combust the two fractions for energy generation purposes (Dunnigan et al., 2018; Williams and Nugranad, 2000). The pyrolysis-combustion processes are especially advantageous for feedstocks with variable moisture contents, as the feedstock is dried in the pyrolysis process which volatilizes the fuel-bound moisture into vapor form prior to fuel combustion (Demirbas, 2004a). Therefore, the moisture variation in the AR feedstocks are less likely to induce the ignition and flame stability issues associated with direct combustion (McKendry, 2002).

Nevertheless, the utilization of agricultural by-products without prior drying may, however, present additional challenges for the pyrolysis-combustion system. The presence of moisture in the biomass results in decreased feedstock higher heating value (HHV) and higher

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https://doi.org/10.1016/j.atmosenv.2018.07.028
Received 14 March 2018; Received in revised form 11 July 2018; Accepted 12 July 2018

energy requirements for drying (Demirbas, 2007). The yield and composition of the bio-oil fraction of the volatiles has also previously been shown to be influenced by feedstock moisture (He et al., 2009; Wang et al., 2008). Bio-oil produced from AR biomass feedstocks is generally characterised by elevated water content and decreased HHV. The physical properties of the bio-oil are also affected by the presence of moisture, with increased density and decreased viscosity reported with elevated feedstock moisture content (He et al., 2009; Wang et al., 2008). The chemical composition of the bio-oil is also strongly influenced by the moisture content of the feedstock. Bio-oil with higher average molecular weights was found from feedstocks with reduced moisture contents (Demirbas, 2004b; He et al., 2009). In addition, elevated concentrations of acidic species (low pH) in the bio-oil produced from biomass with lower moisture contents have also been demonstrated (He et al., 2009). As a result, the physiochemical changes of the bio-oil resulting from the presence of moisture in the feedstock can strongly influence its fuel properties. This includes variations in both the required residence time for combustion and ignition delay (Shihadeh and Hochgreb, 2002). As such, it is plausible that the performance and the emission characteristics from the combustion of the raw pyrolysis volatiles produced from the AR feedstock may differ from the dried feedstock. Increased fuel moisture has previously been demonstrated to result in elevated yields of particulate matter (PM) during direct combustion (Sanchis et al., 2014; Shen et al., 2013). It has also been demonstrated that the polycyclic aromatic hydrocarbon (PAH) content associated with the emitted PM is greater without predrying of biomass fuels during direct combustion (Shen et al., 2013). Both these hazadous pollutant species are generally formed through incomplete combustion of the fuel (Nielsen et al., 2017; Zhang et al., 2018), the formation rate of which can be increased by the presence of moisture (Shen et al., 2013). In addition, elevated PM toxicity generated from the open burning of rice paddy wastes has been observed without prior drying of the biomass (Sanchis et al., 2014).

Despite the potential for pyrolysis-combustion processes to contribute to the global production of biochar and bioenergy, the emission characteristics of hazardous pollutants resulting from utilization of agricultural by-products with and without drying has not yet been established. This is of significant concern, as the potential for increased PM and PM-bound PAH emissions must be examined to allow for effective and sustainable land and waste management practices to be developed. There is currently no available information relating to the potential change in PM toxicity without prior drying. Assessment of PAH-related toxicity of the PM can be estimated through the application of a benzo(*a*)pyrene (BaP) - carcinogenic equivalency factor (TEF) to PAH concentrations (Jung et al., 2010). In order to investigate the influence of feedstock drying on the characteristics of the PM emissions, rice husk was chosen as a representative agricultural by-product. Rice husk is a widely available by-product that has traditionally presented challenges when attempting to increase utilization rates due to its poor fuel qualities and wide-spread availability (Fernandes et al., 2016).

The objectives of this study are therefore to determine the influence of rice husk drying on 1) the yields of primary pyrolysis products and raw pyrolysis volatiles HHV, 2) the energy-based yields of PM resulting from combustion of the raw pyrolysis volatiles, and 3) the energy-based yields of PM-bound PAHs and their associated toxicity.

2. Materials and methods

2.1. Feedstock proximate and ultimate analysis

The agricultural by-product used in this study was rice husk, which was provided by Beerbelly Brewing Equipment (Pooraka, South Australia). In order to examine the influence of rice husk drying both the AR and dried rice husk was used in the study. Drying was achieved following the oven-drying method (D4442), which was carried out at 105 °C for a minimum of 15 h. Both the AR and dried rice husk were then ground in a rotary mill and sieved to 420–500 μm. The proximate and ultimate analysis of the rice husk used in this study was previously presented in Dunnigan et al. (2018). The moisture content of the AR rice husk was found to be 9.2%.

2.2. Lab-scale pyrolysis-combustion process

The laboratory-scale pyrolysis-combustion process has been described in our previous work (Dunnigan et al., 2018). Briefly, N_2 carrier gas was first supplied at 0.25 l/min through the hopper. The rice husk was fed at 1.3 g/min from the hopper into the main screw reactor where the pyrolysis temperature (T_p) was maintained at 400, 500, 600, 700, or 800 °C by two cylindrical electrical heaters. It should be noted that T_p is used in this paper when considering biochar, bio-oil, and pyrogas. The term “volatile production temperature” (T_v) is used when considering the PM generated from combustion of the raw pyrolysis volatiles. The residence time for the pyrolysis reaction was approximately 16 min. After pyrolysis the solid biochar was collected in a char pot by gravity at the end of the main screw reactor. The recovered yield of biochar was calculated using the mass ratio of biochar collected and the mass of feed. The Boie equation (Boie, 1953) was used to estimate the HHV of the biochar from the result of ultimate analysis (Dunnigan et al., 2018). N_2 was also supplied above the char pot (0.1 l/min) in order to prevent stagnation of the combustible volatiles. The raw pyrolysis volatiles were then directed into a burner situated inside an enclosed quartz tube (0.15 m cm height x 45 mm I.D.) within a vertical 3-zone tube furnace (Carbolite®, GVC 12/1050). Auto-ignition of the volatile/air mixture was achieved by maintaining the furnace at 850 °C and supplying HEPA filtered air into the mixing chamber of the burner. The combustion temperature (T_c) of 850 °C was used in this study to represent the typical combustion temperature found in small-scale combustion systems (Miles et al., 1996; Obernberger, 1998).

2.3. Sampling of the raw pyrolysis volatiles

The pyrogas fraction of the raw pyrolysis volatiles was collected by attaching a Teflon sampling bag directly to the burner outlet. Once filled, the gaseous sample was drawn through a gas chromatograph (GC) with thermal conductivity detectors (Agilent, 490 Micro GC). The first channel of the GC was used to detect H_2, N_2, CH_4, and CO with a Molecular Sieve 5A column and the second channel to detect CO_2 with a Poraplot U column. The HHV of the pyrogas was calculated based on the heating values and concentrations of the individual species and their respective HHV. The mass of pyrogas produced was calculated by subtracting the combined mass of bio-oil and biochar from the mass of rice husk fed. It should be noted that there was negligible accumulation of any material along the length of the main pyrolysis screw reactor.

The bio-oil fraction of the raw pyrolysis volatiles was collected in a condensation train consisting of eight 50 ml test tubes connected by insulated piping and immersed in an ice/water mixture (≈ 0 °C). The condensation apparatus was connected to the burner outlet through a heated pipe (≈ 350 °C) to prevent condensation prior to the sampling tubes. After sampling was completed, the collected bio-oil was weighed in order to determine the yield. The HHV of the raw pyrolysis volatiles was calculated using an energy balance around the pyrolysis reactor with the yields of each of the products and the HHV values of the biochar and pyrogas. The yields and HHV of the primary pyrolysis products from the dried rice husk have previously been reported in Dunnigan et al. (2018).

2.4. Sampling of the PM

The PM generated from combustion at 850 °C of the raw pyrolysis volatiles produced between 400 and 800 °C was collected after diluting the flue gas in an air dilution tunnel (ADT) with HEPA filtered air (dilution ratio ≈ 8). This dilution ratio allowed the specific volumetric