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The impact of hydrothermal carbonisation on the char reactivity of biomass

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ABSTRACT

Hydrothermal carbonisation (HTC) is an attractive biomass pre-treatment as it produces a coal-like fuel, can easily process wet biomass and wastes, and lowers the risk of slagging and fouling in pulverised fuel (PF) combustion boilers. One of the major factors in determining the suitability of a fuel as a coal replacement for PF combustion is matching the char reactivity and volatile matter content to that of coals, as these significantly affect heat release and flame stability. The char reactivity of wood and olive cake biocoals and their respective drop tube furnace chars have been studied using thermogravimetric analysis in comparison to other biomass fuels and high-volatile bituminous coal. It was found that HTC reduces the reactivity of biomass, and in the case of HTC of wood pellets the resulting biocoal has a char reactivity similar to that of high-volatile bituminous coal. Proximate analysis, X-ray fluorescence analysis, and textural characterisation were used to show that this effect is caused primarily by removal of catalytic alkali and alkaline earth metals. Subsequent torrefaction of the wood biocoals was performed to tailor their volatile matter content to match that of sub-bituminous and high volatile bituminous coals without major impact on char reactivity.

1. Introduction

Utilisation of biomass as a partial or full coal replacement could be very useful in quickly lowering the carbon dioxide emissions of developing countries [1]. For biomass to be efficient as a coal replacement, it must have similar properties to coal, which is not the case with untreated biomass [2]. Coal is more energy dense, more friable, more hydrophobic, less reactive, and has lower concentrations of corrosive alkali and alkaline earth elements than biomass [3].

Pre-treatment can be used to alter the composition and properties of biomass to make it more suitable for use in pulverised fuel (PF) combustion boilers. Current popular pre-treatment technologies include torrefaction and leaching. Torrefaction of biomass results in a homogenous, friable fuel that has similar composition to coal in terms of fixed carbon and moisture content [2]. The main disadvantages of torrefaction as a pre-treatment are that it requires dry, high-quality biomass as a feedstock [2] and that it does little to remove alkali and alkaline earth metals from biomass [4], meaning PF combustion of torrefied biomass would still have slagging and fouling issues. Leaching uses biomass immersion in water or other solvents to significantly reduce the ash content of biomass. Leaching using strong acids is particularly effective, having been shown to be able to remove over 99% of potassium from a high alkali and alkaline earth metal biomass as well as effective removal of other alkali and alkaline earth metal species [5]. The main disadvantage of leaching is that it results in a product with a

very high moisture content that would be expensive to dewater [6].

Both pre-treatments improve certain aspects of biomass performance as a fuel, but neither alleviate all of them [7]. Hydrothermal carbonisation (HTC) is a pre-treatment process that can potentially do this. It can be considered a combination of torrefaction and leaching as it uses torrefaction conditions while employing water as a reaction medium [8]. The product of HTC, biocoal [9], is similar to torrefied biomass in that it has an increased fixed carbon content alongside decreased moisture and volatile matter contents [10]. HTC is also effective in removing alkali and alkaline earth metals from biomass [11], and biocoal is easier to dry than leached biomass due to being hydrophobic [12].

A key advantage of HTC is that it can process wet biomasses and wastes such as animal manures, sewage, and algal residues as no drying is needed prior to treatment [13]. In addition to this, it has been proven to be an environmentally friendly process due to low emissions and waste toxicity, and the favourable efficiency of the process has the potential to be further improved upon through process augmentation like utilising microwave heating [14].

One of the major factors in determining the suitability of a fuel as a coal replacement in existing PF boilers is matching the char reactivity and volatile matter content to coals, as these significantly affect heat release, and flame stability [15]. Alkali and alkaline earth metals catalyse combustion [16], so the removal of these from biomass could have an effect on the char reactivity. This study focusses on the impact

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of removal of these species on the char reactivity of biomass in comparison to other potential contributing factors, such as changes to the surface area and composition. The impact of post-treatment torrefaction of biocoal to reduce the volatile matter content is also investigated, as although HTC removes volatile matter from biomass the volatile matter content of biocoal is still higher than that of coal [10]. The novelty of this study is that it directly compares the char reactivity of biocoal to other biomass derived fuels and high-volatile bituminous coal, and that it aims to identify the primary determinant of char reactivity in biomass derived fuels.

2. Material and methods

2.1. Sample preparation

Four biocoals were produced, two using Brites soft wood pellets, and two using olive cake as a feedstock. These two biomasses were chosen as best- and worst-case scenarios in terms of the former having a low initial concentration of alkali and alkaline earth metals and the latter having a high initial concentration. The treatment was conducted on the feedstock on an as received basis in a 75 ml Parr reactor. The treatment parameters can be seen in Table 1. A slightly higher water to biomass was used for the olive cake HTC in an attempt to encourage alkali and alkaline earth metal removal.

Deionised water was used, and the moisture content of the biomass was taken into account in determining the volume of water to use. The reactor was then capped, sealed, and a pressure gauge was attached. A nitrogen atmosphere was established by flushing the reactor with and then injecting nitrogen at 1 bar pressure. The reactor was then placed in a sand bath pre-heated to the desired temperature, and the pressure gauge was checked to see if vapour pressure was established once heated. After the desired residence time the reactor was removed and cooled using compressed air. Once cooled to room temperature, the reactor was disassembled and the char was recovered by vacuum filtration. The char was washed thoroughly with deionised water before being dried at 105 °C. After drying the char was allowed to cool to room temperature before being weighed.

Torrefied wood pellets were produced using a horizontal tube furnace. Once the untreated wood pellets were placed in a ceramic boat and placed inside the furnace, the furnace was sealed and purged with nitrogen at a flow rate of 1 L min⁻¹ for 5 min. After this, the flow was maintained and the furnace was heated to 300 °C at a rate of 5 °C min⁻¹. Once the furnace reached the 300 °C the temperature was maintained for 2 h and then the furnace was turned off and allowed to cool to room temperature. The torrefied wood was then removed and weighed. This method was also used to adjust the volatile matter content of the biocoal, with the necessary torrefaction temperature calculated beforehand using devolatilisation studies using thermogravimetric analysis (TGA).

Acid leached olive cake was produced by immersing milled olive cake (0–75 µm) in 1 M hydrochloric acid, and stirring at 60 °C for 8 h. Once cooled the biomass was filtered using a Buchner funnel, and washed with DI water until the pH approached neutral. The biomass was then dried in an oven at 105 °C and then allowed to cool to room temperature.

A high-volatile bituminous coal was acquired for comparison with

Table 1

HTC process parameters used to produce the four biocoals.

Biomass	Temperature (°C)	Water:biomass ratio	Residence time (min)
Wood	200	4:1	60
Wood	225	4:1	60
Olive cake	200	6:1	60
Olive cake	225	6:1	60

the biomass derived fuels, originating from the Cerrejón mine in Colombia.

High heating rate chars were generated from all the samples using a drop tube furnace (DTF). The particle size of the feedstock was < 75 µm, the furnace temperature was 1300 °C, and the residence time was 600 ms. The devolatilisation was performed under nitrogen with 1% oxygen to avoid tarring by ensuring burn-off of volatiles.

All of the samples were ground so that they could pass through a 75 µm mesh sieve. The samples which were sufficient in quantity were ground using a ball mill, those which were not were ground using a pestle and mortar.

2.2. Analysis

2.2.1. Proximate analysis

Proximate analysis was conducted following the International Organisation for Standardisation method for coal (ISO 17246:2010) where the moisture content is determined at 105 °C; the volatile matter content at 900 °C; the ash content after burning at 500 °C and then 815 °C; and the fixed carbon content from the subtraction of the other three fractions from 100% [17]. The only alteration to this was that the ash content determination was performed solely at 550 °C as to avoid the loss of alkali and alkaline earth metals [18], which would inhibit further analysis of the ash. The moisture and ash contents were determined gravimetrically on an as-received basis using a muffle furnace, whereas the volatile matter was determined using TGA. The TGA measurements were performed in triplicate.

2.2.2. X-ray fluorescence (XRF) analysis

XRF analysis was performed on the ash samples using a Bruker S8 TIGER spectrometer running the semi-quantitative program ‘Quantexpress’, for a run time of 7 min. The ash was analysed as a loose powder behind Mylar film in a PTFE sample cup, and an 8 mm mask was used.

2.2.3. Textural characterisation

Textural characterisation of the drop tube chars was carried out using a Micromeritics ASAP 2420 surface area and porosimetry analyser using CO₂ as the adsorbate. Prior to analysis, approximately 0.1 g of sample was placed into a sample tube and degassed at 120 °C under high vacuum for 15 h. CO₂ isotherms were acquired at 0 °C, over an absolute pressure range of 0.004–1.190 bar. BET specific surface, micropore area and micropore volume were determined by applying the BET and Dubinin-Radushkevich models to the CO₂ isotherms.

2.2.4. Char reactivity analysis

Char reactivity was determined using TGA using a TA Q500 thermogravimetric analyser. The samples were completely devolatilised at 700 °C under nitrogen in the TGA before reducing the temperature to the desired burnout temperature and burning the sample. The char reactivity experiments were performed in triplicate and the burnout curves shown represent the average burnout. The average time taken to burn 90% of the char (t₉₀) at 475 °C was taken between 95% and 5% char remaining.

3. Results and discussion

3.1. HTC yield and proximate analysis

The yield of the HTC runs on an as received (AR) and dry-ash-free (DAF) basis are listed in Table 2. These values and are close to those found in literature [17–20], and a decrease in mass yield with HTC temperature would also be consistent with literature values [17]. This is confirmed in the olive cake HTC but in the case of wood pellets this decrease cannot be confirmed due to the yield for HTC at 225 °C being within the error of that of HTC at 200 °C.

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