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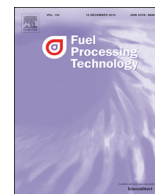
Full length article

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

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

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 CO_2 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. CO_2 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 CO_2 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 (t_{90}) 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.

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

Table 2
Mass yield of HTC of wood pellets and olive cake (AR and DAF basis).

Biomass	Temperature (°C)	Mass yield (AR) (%)	Mass yield (DAF) (%)
Wood	200	66.3 ± 3.0	68.5
Wood	225	65.7 ± 0.9	68.7
Olive cake	200	51.3 ± 2.0	56.8
Olive cake	225	47.1 ± 0.8	51.7

Table 3
Proximate analysis of the fuels.

Sample	Moisture (AR) (%)	Volatile matter (DAF) (%)	Fixed carbon (DAF) (%)	Ash (AR) (%)
Wood	5.4	86.1	13.9	0.61
Torrefied wood	3.3	39.2	60.8	1.2
Wood biocoal (200 °C)	2.6	82.1	17.9	0.22
Wood biocoal (225 °C)	1.5	75.1	24.9	0.12
Olive cake	6.3	81.6	18.4	9.5
Acid leached olive cake	1.8	79.6	20.4	3.0
Olive cake biocoal (200 °C)	1.3	75.1	24.9	5.5
Olive cake biocoal (225 °C)	1.7	73.3	26.7	5.0
Bituminous coal	3.4	40.8	59.2	5.2

The proximate analysis of the fuels is shown in Table 3. As described in literature, HTC increased the fixed carbon content of the biomass, while decreasing the moisture, volatile matter, and ash content [10]. This would result in an increase in the higher heating value (HHV) of the biomass [21]. These effects generally increase with increasing HTC temperature, as greater quantities of volatile matter and moisture are removed than fixed carbon. HTC is extremely effective in removing ash from the biomass, with all of the biocoals having ash contents significantly lower than their respective untreated biomass feedstock. Torrefaction does not remove ash from the biomass effectively, resulting in a concentration of the ash and therefore a higher ash content.

The biocoals have compositions between that of their respective untreated biomass feedstock and bituminous coal investigated, but are not particularly close to the coal in terms of volatile matter and fixed carbon content. The torrefied wood is much more similar to the bituminous coal in this regard. This is due to the harsher conditions of torrefaction removing more of the volatile matter. The composition of the acid leached olive cake is similar to olive cake in terms of volatile matter and fixed carbon, but the moisture content and ash content have both been reduced.

Table 5
Extent of total ash and alkali/alkaline earth metal removal by HTC.

Biomass	HTC temperature (°C)	Total ash removal (%)	Alkali/alkaline earth metal removal (%)			
			Na	Mg	K	Ca
Wood	200	76	81	82	95	81
Wood	225	87	89	93	97	92
Olive cake	200	70	N/A[a]	55	98	51
Olive cake	225	75	N/A[a]	66	98	41

[a] Concentration of sodium was too low to be detected.

3.2. XRF analysis

The concentrations of selected inorganic elements in the sample ashes are listed in Table 4; and the effect of HTC temperature on the extent of removal of total ash and alkali/alkaline earth metals is shown in Table 5. HTC is extremely effective in removing alkali and alkaline earth metals, with the values for the extent of removal being consistent with literature [11]. HTC is particularly effective in removing potassium, with over 95% removal in all cases. Some elements are less susceptible to removal by HTC, such as silicon, which concentrates in the ash. Increasing the HTC temperature results in further removal of inorganic content.

HTC is more effective in removing the alkali and alkaline earth metal content of the wood pellets than olive cake, especially in the case of calcium and magnesium. This leaves a significant concentration of potassium, calcium and magnesium in the biocoal ash. This could be due to the much larger proportions of these elements in the original olive cake ash in comparison to the wood ash. The effect of temperature on alkali and alkaline earth removal is also less pronounced in the case of HTC of olive cake, with there being very little difference in the alkali and alkaline earth metal concentrations in the two biocoal ashes.

Torrefaction is not particularly effective in removing alkali and alkaline earth metals in comparison to HTC. This is especially apparent in the case of potassium, which concentrates in the ash during torrefaction. Acid leaching was very effective in reducing the alkali and alkaline earth metal content of the olive cake, reducing the concentration of potassium and calcium much more than HTC.

3.3. Textural characterisation

The textural characterisation of the drop tube chars generated from the fuels is shown in Table 6. It shows that torrefaction, acid leaching, and HTC result in higher surface area DTF chars. Torrefaction increases the surface area significantly more than HTC, and HTC at higher temperatures results in a biocoal DTF char with higher surface area. As expected, coal DTF char has a surface area lower than that of wood DTF char, so HTC and torrefaction of wood makes this difference much

Table 4
Total ash content and concentration of selected inorganic elements in the fuel ash.

Sample	Total ash content (%)	Elemental composition of ash (g/g ash)					
		Na	Mg	Si	K	Ca	Fe
Wood	0.6	0.0066	0.0108	0.006	0.0906	0.1674	0.0096
Torrefied wood	1.2	0.0156	0.0204	0.012	0.3516	0.2136	0.0108
Wood biocoal (200 °C)	0.2	0.0018	0.0026	0.014	0.0064	0.045	0.0072
Wood biocoal (225 °C)	0.1	0.0009	0.001	0.0042	0.0035	0.0174	0.0023
Olive cake	9.5	N/A[a]	0.25	0.36	3.19	0.99	0.086
Acid leached olive cake	3.0	0.014	0.19	0.6837	0.047	0.021	0.053
Olive cake biocoal (200 °C)	5.5	N/A[a]	0.22	0.57	0.14	1.31	0.14
Olive cake biocoal (225 °C)	5.0	N/A[a]	0.18	0.41	0.16	1.27	0.12
Bituminous coal	5.2	0.0468	0.0364	1.0244	0.104	0.1092	0.364

[a] Concentration of sodium was too low to be detected.

Table 6
Textural characterisation of the DTF chars.

Sample	BET surface area (m^2/g)	Micropore surface area (m^2/g)	Limiting micropore volume (cm^3/g)
Wood DTF char	125 ± 8	91	0.036 ± 0.001
Torrefied wood DTF char	335 ± 1	475	0.19 ± 0.00
Wood biocoal (200 °C) DTF char	150 ± 2	189	0.075 ± 0.000
Wood biocoal (225 °C) DTF char	219 ± 2	268	0.11 ± 0.00
Olive cake DTF char	78 ± 1	91	0.037 ± 0.001
Acid leached olive cake DTF char	172 ± 1	230	0.092 ± 0.001
Olive cake biocoal (200 °C) DTF char	97 ± 1	110	0.044 ± 0.000
Olive cake biocoal (225 °C) DTF char	113 ± 0	145	0.058 ± 0.001
Coal DTF char	104 ± 7	61	0.025 ± 0.000
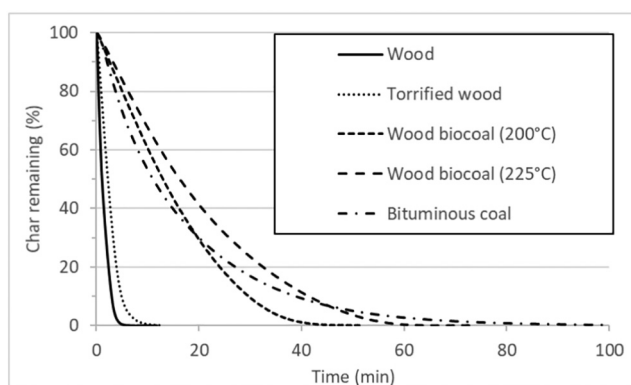
Fig. 1. Char burnout comparison of wood, torrefied wood, wood biocoals, and bituminous coal.

Fig. 3. Char burnout comparison of wood biocoals, olive cake biocoals, and bituminous coal.

larger. Olive cake DTF char has a lower surface area than that of the coal dtf char, with HTC resulting in olive cake biocoal DTF chars having similar surface areas to the coal dtf char.

3.4. Char reactivity analysis

The char burnout curves of the fuels are compared in Figs. 1, 2, and 3. The t_{90} values are listed in Table 7. They show that HTC greatly lowers the reactivity of the wood, and that increasing HTC temperature further decreases the reactivity of the resultant biocoal. The wood biocoals produced possessed similar char reactivity to the high volatile bituminous coal, with the higher HTC temperature biocoal being almost identical in this regard. Torrefaction of wood does slightly lower the reactivity of wood, but the effect is much smaller than in HTC.

In the case of the olive cake biocoal, the char reactivity is lower than that of untreated olive cake, but the reduction is not as great than what is seen in HTC of the wood. The resultant biocoals have a reactivity in
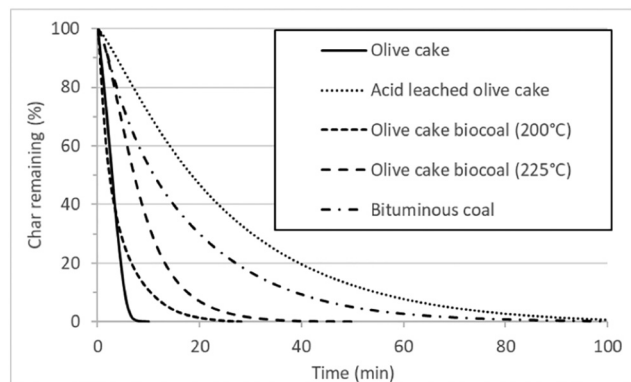

Fig. 2. Char burnout comparison of olive cake, acid leached olive cake, olive cake biocoals, and bituminous coal.
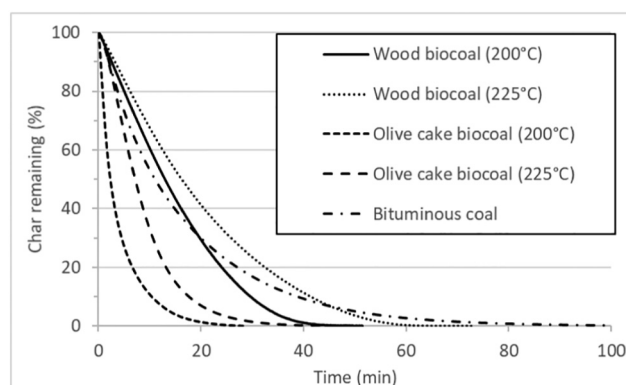
Table 7
t_{90} values of the fuels.

Sample	t_{90} (95–5%) (min)
Wood	3.2 ± 1.1
Torrefied wood	5.6 ± 0.8
Wood biocoal (200 °C)	32.2 ± 1.1
Wood biocoal (225 °C)	45.7 ± 3.0
Olive cake	5.3 ± 1.6
Acid leached olive cake	66.5 ± 5.5
Olive cake biocoal (200 °C)	13.5 ± 5.1
Olive cake biocoal (225 °C)	20.9 ± 0.9
Bituminous coal	44.4 ± 3.0

between that of the untreated olive cake and the bituminous coal. As with HTC of wood, increasing the HTC temperature results in a less reactive boicoal. Acid leaching of the olive cake results in a fuel which is less reactive than the coal.

The char burnout curves of the DTF chars made from the fuels are compared in Figs. 4, 5, and 6. The t_{90} values are displayed in Table 8. The DTF chars are generally more reactive than their respective TGA chars. The one exception to this is the acid leached olive cake, the char reactivity of which is left largely unchanged by DTF devolatilisation. In the case of the effect of DTF devolatilisation on the char reactivity of untreated wood, the extremely fast burnout at these burnout temperatures mean that there is a high associated error. This causes the error values of the two burnout curves to overlap considerably meaning that significant conclusions cannot be drawn.

Similar trends in reactivity of the fuels are present, with the biocoal and coal DTF chars having similar burnout profiles to their respective non-processed sample. This shows that the trends seen in the char burnout of the TGA chars are still true when the fuels are devolatilised under high heating rates representative of PF combustion. The only exception to this is the effect of HTC temperature on the char reactivity of olive cake biocoal DTF chars, where the char produced from the higher HTC temperature biocoal is more reactive than its lower HTC
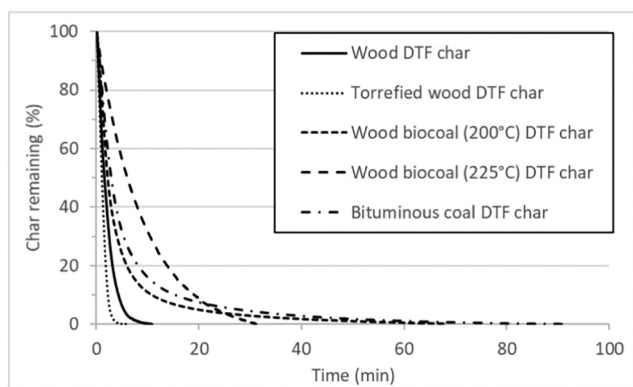
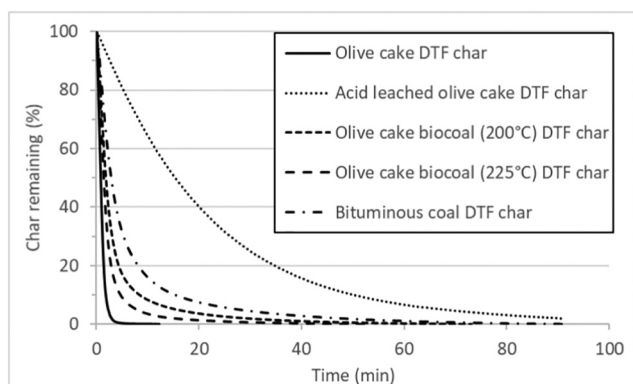**Fig. 4.** Char burnout comparison of DTF chars generated from wood derived fuels and bituminous coal.

Fig. 5. Char burnout comparison DTF chars generated from olive cake derived fuels and bituminous coal.
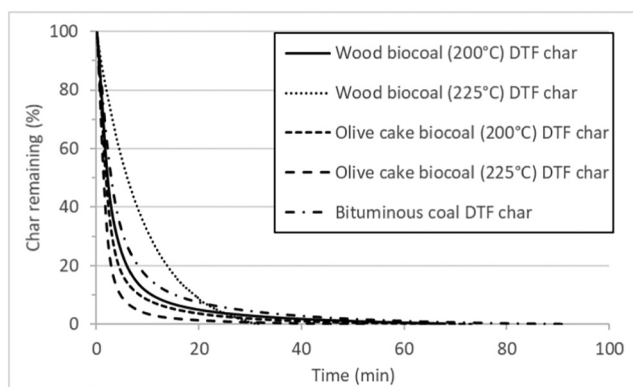

Fig. 6. Char burnout comparison of DTF chars generated from the biocoals and bituminous coal.

Table 8
t_{90} values of the DTF chars.

Sample	t_{90} (95–5%) (min)
Wood DTF char	4.6 ± 2.2
Torrefied wood DTF char	2.4 ± 0.4
Wood biocoal (200 °C) DTF char	19.2 ± 3.3
Wood biocoal (225 °C) DTF char	22.5 ± 5.0
Olive cake DTF char	2.2 ± 0.3
Acid leached olive cake DTF char	65.8 ± 7.6
Olive cake biocoal (200 °C) DTF char	15.4 ± 3.4
Olive cake biocoal (225 °C) DTF char	7.4 ± 3.2
Bituminous coal DTF char	27.3 ± 3.4

temperature counterpart. This is the reverse of what is seen in the olive cake biocoals that have not been devolatilised in the DTF.

The extent of alkali metal extraction by HTC shown in Table 5, alongside the known propensity of alkali and alkaline earth metals like potassium to catalyse combustion [16] clearly points to catalysis by alkaline and alkaline earth metals being the primary contributer to the char reactivity. The significant removal of alkali and alkaline earth metals and the increasing extent of removal with HTC temperature in the case of HTC of wood pellets match the trends seen. The intermediate char reactivity of olive cake biocoals also points to this, as there are still significant levels of alkali and alkaline earth metals in the ash, causing some catalysis of the combustion.

Changes to the composition of the fuels have a secondary effect on their char reactivity. This can be seen in the char reactivity of olive cake being reduced considerably more by acid leaching than the char reactivity of the wood through torrefaction. The proximate composition of the olive cake was not greatly changed by the leaching process and the leached olive cake had a higher surface area than the untreated olive cake, which would be expected to increase the char reactivity. This means that the only contributor to the reduction of char reactivity would be the removal of alkali and alkaline earth metals. The reduction of the char reactivity of wood by torrefaction would likely be solely due to the changing composition of the fuel through loss of high reactivity components [22] as torrefaction does not significantly remove the alkaline and alkaline earth metal content of biomass [4], and the surface area of the torrefied wood DTF char is significantly higher than that of the wood DTF char.

The effect of composition change on the reactivity of the biocoals can be seen in the case of olive cake biocoal. With the change in alkali and alkaline earth metal reduction between HTC temperatures being negligible and the surface area of the biocoals increasing with increasing HTC temperature, the lower reactivity of the higher HTC temperature biocoal would likely be the result of more aggressive conditions further altering the composition.

The effect of surface area on the reactivity of the biomass fuels is also secondary to that of alkali and alkaline earth metal catalysis. The main example of this it that the biocoal DTF chars have a higher surface area than their untreated biomass analogues. This would be expected to increase the reactivity, whereas all of the biocoal DTF chars are considerably less reactive than the untreated biomass DTF chars. This indicates that the effect of removing of alkali and alkaline earth metals is much larger than the effect of increasing surface area. In addition to this, in the case of wood biocoal DTF chars the effect of temperature on the char reactivity is the same as what is seen in the low heating rate chars. The further loss of alkali and alkaline earth metals is further reducing the char reactivity in spite of the surface area increasing with increasing HTC temperature.

As was seen in the case of composition changes affecting the char reactivity of olive cake biocoal, the similar alkali and alkaline earth metal content of the two biocoals allows for the effect of surface area to become significant in determining the char reactivity of the olive cake biocoal DTF chars. This is seen in the olive cake biocoal DTF char derived from the higher HTC temperature biocoal being more reactive than its lower HTC temperature counterpart. This is the reverse of the trend seen when the olive cake biocoal char reactivity was studied without DTF devolatilisation. This could be due to DTF chars having a considerably larger surface area than their slow heating rate analogues [23] and the extremely harsh devolatilisation conditions greatly altering the composition of the fuels. This would emphasise the effect of surface area and dampen the effect of composition seen at lower heating rates. This would suggest that the effect of fuel composition on char reactivity becomes even less significant when the fuel is subjected to high heating rates representative of PF combustion.

Table 9
Proximate analysis of coal and torrefied wood biocoals.

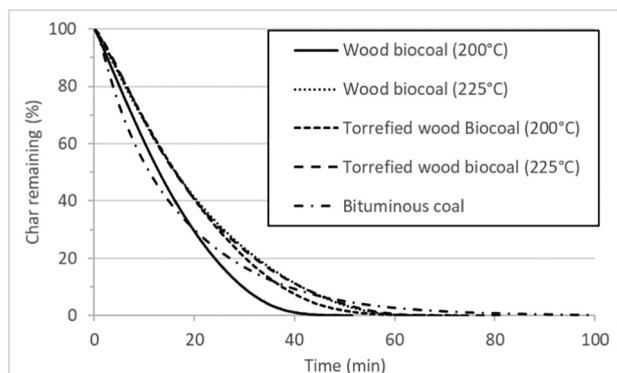| Sample	Moisture (AR) (%)	Volatile matter (DAF) (%)	Fixed carbon (DAF) (%)	Ash (AR) (%)
Bituminous coal	3.4	40.8	59.2	5.2
Torrefied wood biocoal (200 °C)	4.5	28.9	71.1	0.2
Torrefied wood biocoal (225 °C)	1.9	45.9	54.1	0.4

Fig. 7. Char burnout comparison of wood biocoals and torrefied wood biocoals.

Table 10
t_{90} values for wood biocoals, torrefied wood biocoals, and coal.

Sample	t_{90} (95–5%) (min)
Wood biocoal (200 °C)	32.2 ± 1.1
Wood biocoal (225 °C)	45.7 ± 3.0
Torrefied wood biocoal (200 °C)	40.5 ± 1.9
Torrefied wood biocoal (225 °C)	46.1 ± 3.1
Bituminous coal	44.4 ± 3.0

3.5. Generation of biocoal with volatile matter contents similar to coals

As shown in Table 3, the biocoals produced have a much higher volatile matter content than that of the bituminous coal studied. For biocoal to be an efficient coal replacement it must also match the composition of coal. As the wood biocoals had a similar char reactivity to the bituminous coal studied, they were subjected to torrefaction to lower their volatile matter content to produce a coal-equivalent fuel. Torrefaction was shown in Fig. 1 to have a minor effect on the char reactivity of biomass, so it was thought that the reactivity of the biocoals would remain in the region of the bituminous coal studied. The torrefaction temperature required to achieve a volatile matter in the region of high volatile bituminous coal was determined by stepwise devolatilisation by TGA. The biocoal produced at 200 °C was torrefed at a temperature of 370 °C, and the biocoal produced at 225 °C was torrefed at 290 °C. The proximate analysis of the torrefied biocoals in comparison to the bituminous coal is shown in Table 9. The torrefied biocoals have a DAF volatile matter content in the range of sub-bituminous and high-volatile bituminous coals, with the torrefied biocoal generated from the 225 °C biocoal having a volatile matter content similar to that of the bituminous coal studied. Both torrefied biocoals have a significantly lower ash content than the coal, which mean that ash deposition would be a more minor issue.

The char reactivity of the torrefied wood biocoals was compared to that of the non-torrefied wood biocoals and the coal to ensure that it had not been altered significantly by torrefaction. The char burnout curves of the torrefied biocoals, non-torrefied biocoals, and bituminous coal are compared in Fig. 7, and the t_{90} values are listed in Table 10. In the case of the biocoal produced at 200 °C, torrefaction results in a small decrease in reactivity, similar to what is seen when the wood pellets were torrefed. This would likely be due to changes to the composition of the fuel due to the harsh torrefaction conditions. This brought the char reactivity of this biocoal closer to that of the bituminous coal studied.

The biocoal produced at 225 °C saw virtually no change in char reactivity, with the char burnout curves of the biocoal and torrefied biocoal being almost superimposed on one another. This could be due to both the higher HTC temperature biocoal having already undergone greater composition change than the lower HTC temperature biocoal, and the torrefaction temperature being lower. In both cases, the resultant torrefied biocoal had a char reactivity similar to that of the bituminous coal studied.

4. Conclusions

HTC lowers the char reactivity of biomass primarily by removal of catalytic alkali and alkaline earth metals from the biomass, with the surface area and composition providing secondary effects. HTC of biomass with low alkali and alkaline earth metal content results in a fuel with a similar reactivity to that of high-volatile bituminous coal, whereas in the case of biomass with high alkaline and alkaline earth metal content the resulting biocoal has a reactivity between that of its untreated biomass feedstock and coal. These trends occur both in TGA chars produced under low heating rates, and more reactive DTF chars produced under high heating rates representative of PF combustion. Coal-equivalent fuel was generated from the wood biocoals by subsequent torrefaction. The torrefied biocoal had a DAF volatile matter content in the range of sub bituminous and high-volatile bituminous coal, with similar reactivity to high-volatile bituminous coal, and a very low ash content.

Acknowledgements

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