

Research paper

The combustion characteristics of high-heating-rate chars from untreated and torrefied biomass fuels



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ABSTRACT

Torrefaction of biomass is of great interest at the present time, because of its potential to upgrade biomass into a fuel with improved properties. This study considers the fundamentals of combustion of two biomass woods: short rotation willow coppice and eucalyptus and their torrefied counterparts. Chars were prepared from the untreated and torrefied woods in a drop tube furnace at 1100 °C. Fuels and chars were characterised for proximate, ultimate and surface areas. Thermogravimetric analysis was used to derive pyrolysis and char combustion kinetics for the untreated and treated fuels and their chars. It was found that the untreated fuels devolatilise faster than their torrefied counterparts. Similarly, the chars from the untreated biomass were also found to be more reactive than chars from torrefied fuels, when comparing reaction rates. However, the activation energy value (E_a) for combustion of the untreated eucalyptus char was higher than that for the torrefied eucalyptus chars. Moreover, the eucalyptus chars were more reactive than the willow char analogues, although they had seen a lower extent of burn off, which is also a parameter indicative of reactivity. Similar trends in were also observed from their intrinsic reactivities; i.e. chars from the untreated fuel were more reactive than chars from the torrefied fuel and eucalyptus chars were more reactive than willow chars. Chars were also studied using scanning electron microscopy with energy-dispersive X-ray analysis. This latter method enabled a semi-quantitative analysis of char potassium contents, which led to an estimation of potassium partitioning during char formation and burnout. Results show a good correlation between potassium release and percent burnout. With respect to the effect of torrefaction on fuel-N, findings suggest that torrefaction would be beneficial for pf combustion in terms of nitrogen emissions, as it resulted in lower fuel-N contents and ~72–92% of the fuel-nitrogen was released with the volatile fraction upon devolatilisation at 1100 °C.

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1. Introduction

The use of biomass in UK power stations has increased considerably in recent years, either for co-firing with coal or for dedicated biomass burners. It has been estimated that approximately 2.9 million oven dry tonnes of solid biomass was used for electricity generation in the UK in 2011; with predictions that this usage will increase by 3–5.5 times the stated amount by 2020 [1]. Co-firing is also a popular technology for the reduction of carbon emissions in other European countries and North America. While biomass combustion has some similarities to coal combustion, there are significant differences in some aspects, e.g. the kinetics of devolatilisation and char burnout.

Torrefaction is a promising technology, as it has been shown to improve biomass properties and therefore has the potential to increase the usage of biomass in pulverised fuel (pf) combustion. During torrefaction the appearance and handling properties of the untreated wood are changed, and the resultant darker fuel has higher energy density, and improved hydrophobicity and grindability (e.g. Refs. [2–8]). Moreover, the chemical composition of the fuel is modified, resulting in differences in C, H and O contents, as well as a decrease in volatile matter due to partial or complete degradation of hemicellulose, and partial decomposition of lignin – and possibly even cellulose fractions – depending on the degree of processing [8–11]. These changes are expected to impact on the combustion behaviour of the pre-treated fuels, such as devolatilisation and char burnout reaction kinetics. Char burnout kinetic data of untreated biomass and torrefied biomass in relation to applications in power stations and in CFD modelling are scarce [12]. Previous studies on kinetics of biomass char burnout have

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mostly focused on the study of slow-heating rate chars, e.g. Refs. [13,14]. There have also been studies on the combustion and char burnout of torrefied biomass at high heating rates, such as those encountered in a drop tube furnace [12,15,16] and more recently, studies specifically on torrefied biomass high heating rate chars [17,18]. Nevertheless, still little is known about detailed surface areas of the resultant chars to enable intrinsic reaction rates to be determined.

Another unknown is the partitioning of potassium and nitrogen during high heating rate devolatilisation. Potassium is an important catalytic metal for both the pyrolysis stage and the char combustion stage [19–21], therefore its fate upon torrefaction and fast pyrolysis would also impact on the reactivity of the resultant char. Another critical impact of potassium is the deposition of its salts in boilers and furnaces, and so knowledge of potassium partitioning during combustion is extremely valuable. With respect to nitrogen oxides (NO_x), it is expected that the displacement of coal by biomass would result in a decrease in these emissions, since most biomass fuels have lower nitrogen concentrations than coals (usually <1%) [22]. In practice, findings are mixed since there are other factors that influence the formation of NO_x, such as burner configuration, flame temperature, char burnout and other process conditions. Hence, data on partitioning of fuel nitrogen between volatiles and char is needed for the development of a firing strategy that would assist in achieving low NO_x emissions. In such a scenario, it is necessary to understand the role of torrefaction and its effect on nitrogen behaviour upon devolatilisation and char formation.

The methodology used in this study was to prepare chars from short rotation willow coppice and eucalyptus, as well as from their torrefied counterparts at high heating rates and high temperature in a drop tube furnace, therefore comparable to those conditions encountered in industrial boilers. Chars were collected for examination and their reactivities were determined by means of thermogravimetric analysis (TGA). Kinetic parameters were also derived for the decomposition of the untreated and treated fuels from TGA data. Furthermore, the evolution of potassium and nitrogen during both torrefaction and char formation were also examined. The data obtained was then used to provide information on the behaviour of the fuels in high temperature combustion in pf flames.

2. Experimental

2.1. Samples

For this study two fuels sourced from local farms in Yorkshire, short rotation coppice willow (*Salix* spp.) and eucalyptus (*Eucalyptus gunnii*) and their torrefied counterparts, obtained from a previous study [10] were milled using a Retsch PM 100 ball mill at 250 rpm for 4 min and sieved to obtain a size fraction of 212–355 μm. The samples were then oven-dried at 80 °C for 24 h prior to the char preparation step. The torrefied samples were prepared under a nitrogen flow of 1.2 L min⁻¹ at a heating rate of 10 °C min⁻¹, with a drying step at 150 °C for 60 min. This was followed by programmed heating at a rate of 10 °C min⁻¹ to a final temperature of either 270 or 290 °C for either 30 or 60 min residence time, as follows: 270 °C for 30 min (Willow 270/30, Eucalyptus 270/30), 270 °C for 60 min (Willow 270/60) and 290 °C for 30 min (Willow 290/30, Eucalyptus 290/30). In this instance, the residence time is defined as the dwell at the final temperature. Detailed information about the torrefaction process and full characterisation of the untreated and treated samples can be found in Ibrahim et al. [10].

2.2. Drop tube furnace char preparation

High heating rate chars were prepared from each untreated and torrefied fuel in a drop tube furnace (DTF), for which a schematic is shown in Fig. 1. The DTF consists of an alumina tube of 1400 mm L × 65 mm i.d. inserted in an electrically heated vertical furnace (Elite Thermal Systems), with three independently heated zones and an isothermal reaction zone of 455 mm. The reaction gases consisted of pure nitrogen at a flowrate of 16 L min⁻¹ and entrained air in order to ensure an oxygen concentration of 1.0 ± 0.2%, which was continuously monitored using a Mitchell Instrument XTP601 paramagnetic analyser. The 1% oxygen was implemented to prevent the biomass chars sticking to the inside walls of the reactor. The gas flow rates used were found to result in Reynolds numbers that fell well within the laminar zone for the process temperature used. Furthermore, a vacuum pump ensured the gases flowed isokinetically through the reactor. All chars were prepared at a DTF temperature set at 1100 °C, with a residence time of ~0.5 s in the reaction zone—assuming the particles travel along the reactor centreline. The temperature profile measurements of the reaction zone, measured at seven points alongside the centreline of the reactor using a K-type thermocouple resulted in an average temperature of 1062 ± 33 °C. The inlet of the reactor consists of a water-cooled feeding tube to prevent the reaction of particles before the isothermal heating zone is reached. The chars

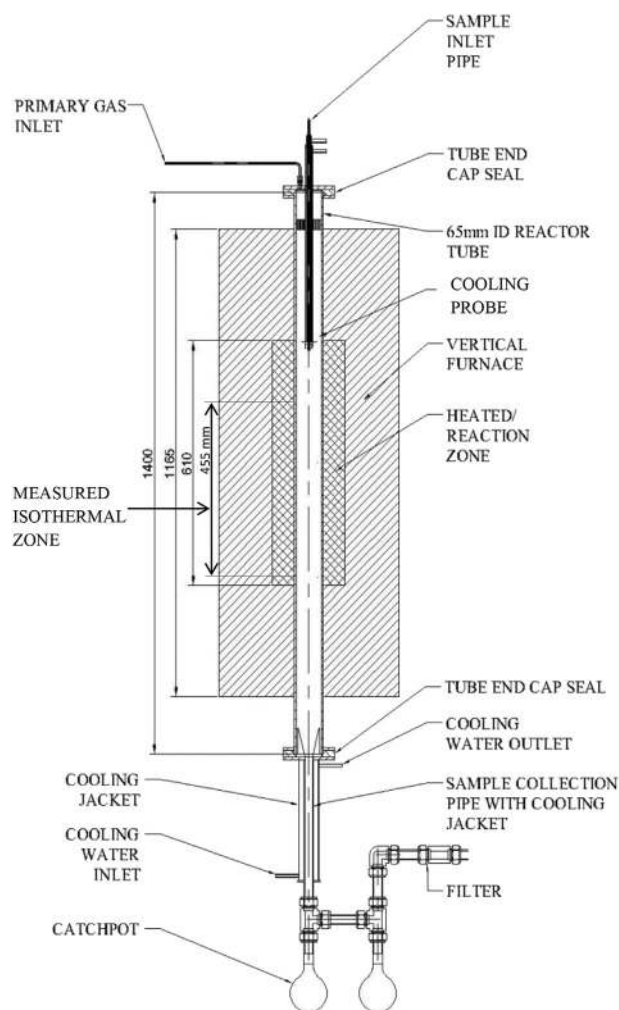


Fig. 1. Schematic of the drop tube furnace.

were prepared by manually feeding the fuel to the top of the reactor and collected via a water-cooled collection tube at the bottom end of the reactor and two catch pots.

2.3. Fuel and char characterisation

2.3.1. Proximate and ultimate analysis

The C, H, N and S contents of the fuel and chars were measured in duplicate using a CE Instruments Flash EA 1112 Series elemental analyser and average values are reported. Cl contents were determined by titration with HgNO₃ at the analytical laboratories in the Department of Chemistry, University of Leeds. The higher heating values (HHV) were estimated from the ultimate analysis in a dry basis, according to the approximation developed by Friedl et al. [23] and given in Equation (1):

$$\text{HHV} = 3.55\text{C}^2 - 232\text{C} - 2230\text{H} + 51.2\text{C}^*\text{H} + 131\text{N} + 20,600 \quad (1)$$

The moisture and ash content of the chars were estimated from pyrolysis and combustion thermogravimetric analyses using a TA Q5000 IR thermogravimetric analyser.

2.3.2. Surface area measurements

The BET surface area of the fuels and chars prepared were determined by adsorption of N₂ at –196 °C using a Quantachrome Instruments NOVA 2200 Multi-station Any-gas Sorption Analyser. Full adsorption/desorption isotherms were obtained for each sample from which the BET surface area was determined using a multi-point plot at relative pressures between 0.05 and 0.30. Prior to analysis, the samples were degassed at 300 °C under vacuum for a minimum of 6 h and then degassed further, if required, until no further mass loss was observed.

2.3.3. SEM/EDX analysis

Scanning electron microscopy (SEM) images of the fuels and (whole and ground) chars were obtained using a Carl Zeiss EVO MA15 SEM with Energy Dispersive X-ray analysis. Prior to analysis, <1 mg of fuel and chars were coated on an adhesive sticker on an aluminium stub. Scanning electron images were then obtained with an incident electron beam at 20 kV at varying degrees of magnification. The samples were then analysed using Electron-Dispersive X-ray analysis using AELEOS software to analyse for metals concentrations.

2.3.4. Metal analysis

ICP-MS analysis was employed to determine the metals content of the untreated fuels and torrefied counterparts in order to determine any changes in metals concentration upon torrefaction. For this, the samples were digested in nitric acid using an Anton Parr Multiwave 3000 microwave and diluted to ensure their concentrations fell within the detection limits of the instrument. The total metals concentration was then determined using a Varian 710-ES series inductively coupled plasma-Mass spectrometer (ICP-MS).

2.4. Fuel pyrolysis in a thermogravimetric analyser

Pyrolysis experiments were carried out on all the fuels using a TA Q5000 IR thermogravimetric analyser (TGA). For the TGA pyrolysis experiments, the untreated and torrefied fuels were milled to <90 μm using a Spex Freezer mill 6770 model. Approximately 5 mg of milled fuel was heated under flowing nitrogen (20 mL min⁻¹) at a heating rate of 10 °C min⁻¹ to a final temperature of 900 °C and a holding time of 15 min to ensure complete

reaction. A drying step at 105 °C for 10 min was included in the programme prior to pyrolysis.

2.5. Char combustion in a thermogravimetric analyser

Isothermal oxidation experiments were carried out on the chars using a TA Q5000 IR TGA. Approximately 2 mg of finely ground char was heated under nitrogen (20 mL min⁻¹) to 100 °C at a heating rate of 20 °C min⁻¹ and then held at this temperature for 20 min. The chars were then heated to a final temperature in the range 300–360 °C for the chars prepared from untreated fuel and a slightly higher range (320–400 °C) for the torrefied fuel chars. The chars were held at the final temperature for 30 min before the reaction gas was switched from nitrogen to air to allow isothermal combustion of the chars.

3. Results and discussion

3.1. Fuel and char characterisation

The proximate and ultimate analyses, calculated high heating values (HHV) and specific surface areas of the untreated and torrefied woods are given in Table 1. As expected, torrefied fuels have lower moisture, volatiles and oxygen contents, and higher ash and carbon contents. Furthermore, the more severe the torrefaction conditions, the larger these differences become. Since carbon is preferentially retained in the solid during torrefaction, HHV calculations result in higher values for the treated fuels when compared to their untreated counterparts. It can also be noted that both willow and eucalyptus are low nitrogen fuels. The sulphur contents of all fuels were below detection limits (<0.01%).

The moisture and ash contents and ultimate analyses of the chars from untreated and torrefied materials are given in Table 2. The data listed includes the char yields obtained and specific surface areas. As the fuels enter the DTF they undergo first moisture loss, then devolatilisation, then char burnout. From the ash content of the char it is possible to estimate the extent of char burnout, although this assumes that the ash is not volatilised during char combustion. This assumption will introduce a small error since it is well known that potassium vaporises during pyrolysis [20,24]. In the case of wood ash, it has been found that higher potassium losses can be expected when compared to straws, because formation of potassium silicates, like leucite (KAlSi₂O₆) in straw ash, results in retention of potassium in the slag [25]. The extent of char burnout was estimated for all the chars and the values obtained were listed in Table 2. Burnout was calculated using the ash tracer method [26]. The extent of char burnout will depend, among other factors, on the reactivity of the fuel, final temperature and the oxygen available for reaction with carbon—both from the reaction gases (in this case ~1%) and fuel-oxygen. It is noted that all chars in this study still have ~6–20% (DAF) oxygen in their structure. It can be observed that the effect of torrefaction is to slow down the char burnout (and the devolatilisation stage) such that the chars produced from the torrefied fuels have a lower extent of char burn-out. Also, the more severe the torrefaction conditions (i.e. higher final temperature and/or residence time), the lower the extent of char burnout. This indicates that the fuels have become less reactive upon torrefaction.

3.2. Char morphology

SEM images from the untreated and torrefied fuels 270/30 and 290/30 and their chars (×100 magnification) are shown in Figs. 2 and 3 for willow and eucalyptus respectively. It can be seen from these images that there are apparent changes in surface

Table 1
Proximate and ultimate analyses of untreated and torrefied willow and eucalyptus.

Parameters	Willow				Eucalyptus		
	Untreated	270/30	270/60	290/30	Untreated	270/30	290/30
Moisture (% ar) ^a	6.0	3.9	3.8	3.6	8.0	4.3	4.2
Volatile (% dry) ^a	84.4	73.4	72.4	63.2	79.6	67.9	60.3
Fixed carbon (% dry) ^a	15.1	26.1	27.6	36.8	18.8	19.6	39.7
Ash (% dry) ^a	0.5	0.5	0.7	1.1	1.6	1.6	2.2
C (% daf)	49.1	54.2	54.4	58.9	50.8	55.9	59.6
H (% daf)	5.8	5.5	5.5	5.4	5.4	5.3	5.1
N (% daf)	0.5	0.2	0.3	0.3	0.4	0.3	0.2
O ^b (% daf)	44.6	40.1	39.8	35.5	43.4	38.5	35.1
K (% dry)	0.23	NA	0.25	0.30	0.33	0.34	0.42
Cl (% daf)	ND	0.18	0.09	0.18	0.34	0.06	0.21
HHV (MJ kg ⁻¹) (daf)	19.6	22.3	22.9	24.4	19.6	23.5	28.5
Surface area (m ² g ⁻¹) ^a	3.8	3.4	3.1	1.9	1.1	NA	NA

^a Data from Ibrahim et al. [10].

^b O calculated by difference, ND-not detected, NA-not analysed.

morphology upon both torrefaction and char formation. The untreated fuels for both willow and eucalyptus appear more compact with bulky xylem tissues apparent relative to their torrefied counterparts. In turn, the treated fuels seem more brittle in structure, as evidenced by the deeper fissures on the surface.

The chars produced from the untreated fuel undergo a degree of structural changes with the pointed/sharp ends of biomass particles becoming more rounded; however they maintain their apparent elongated structure. In contrast, the chars produced from torrefied biomass undergo a more severe degree of transformation and are more rounded in structure—especially in the case of fuels treated at 270 °C for 30 min (270/30). Similar images were also obtained for the Willow 270/60 chars (not shown). The disparity between the chars produced from untreated and torrefied fuels can be attributed to the alteration of the biomass structure upon torrefaction. During torrefaction, there is degradation of the different lignocellulosic components in the biomass and the extent of degradation will depend on the severity of the process conditions. The hemicellulose fraction is most affected by the process, as it is the most reactive, but limited cellulose and lignin degradation may also take place. Melkior et al. [9] reported thermal degradation of lignin during torrefaction at temperatures as low as 200 °C, where demethoxylation of syringyl groups begin to occur. As torrefaction temperature increases, further chemical changes occur—with depolymerisation and demethoxylation of the guaiacyl groups occurring at 245 °C and 270 °C, respectively [9]. As the fuels in this study were torrefied at 270 °C and 290 °C, it can be assumed the thermal treatment the fuels have undergone will have a noticeable effect on the mechanical structure of the fuels and thus the

corresponding chars. It must be noted that the hemicellulose contents of both willow and eucalyptus were found to be comparable (19.0% and 19.6%, respectively). Eucalyptus was found to have higher lignin (Klason) contents (24.0%) than willow (21.6%).

In the case of the chars from torrefied fuels with a more rounded appearance, this transformation is reminiscent of that observed for high vitrinite bituminous coals during devolatilisation, whereby coal particles undergo transformation to cenosphere char particles that have melted and then resolidified [27]. Similar findings have been reported by other researchers, such as Tolaven et al. [28], who also observed a change in the appearance of torrefied particles upon pyrolysis in a DTF; the resultant char particles looked like droplets with an aspect ratio closer to one (relative to the original torrefied fuel prior to pyrolysis). Tolvanen et al. [28] suggested that formation of liquid intermediates by some of the components in the torrefied wood could be the reason for this behaviour.

In all the images of char particles, there is evidence of open pores on the surface, which were not visible on the fuels prior to devolatilisation in the DTF. These pores can be attributed to volatiles escaping from the particles due to the rapid heating and relatively high temperatures the particles have been exposed to. Upon heating the particles at high-rates and relatively high temperatures, there is rapid escape of volatile gases as a result of overpressure within the particles, and this results in the evolution of pores across the surface. From the SEM images, the chars produced from Willow 270/30 show pores which appear more macroporous in size, with evidence of particles with a hollowed out shell structure. Note that these chars have undergone a higher degree of burnout than the most severely torrefied biomass chars.

Table 2
Analysis of the untreated and torrefied biomass chars.

Parameters	Willow				Eucalyptus		
	Untreated	270/30	270/60	290/30	Untreated	270/30	290/30
Moisture (% ar)	1.4	1.39	1.47	1.6	2.0	1.6	1.8
Ash (% dry)	20.1	7.4	6.7	4.3	15.0	7.8	8.0
C (% daf)	80.1	84.4	87.9	84.4	87.8	89.4	87.9
H (% daf)	3.0	1.2	1.4	1.0	2.7	1.3	1.4
N (% daf)	1.4	0.3	0.4	0.4	1.1	0.3	0.2
O ^a (% daf)	15.6	18.8	19.9	20.5	8.4	6.5	20.5
Char burn-off (%) ^b	84	73	62	34	51	36	31
Char yield ^b	3.0	7.1	10.5	24.4	10.0	20.4	27.5
Surface area (m ² g ⁻¹)	57	80	17	49	94	66	10
Fuel-N in char (%)	7.9	12.7	8.7	26.7	27.8	16.9	18.9
Fuel-N in volatiles (%)	92.1	87.3	91.3	73.3	72.2	83.1	81.1

^a Oxygen by difference.

^b Estimated from ash tracer method.

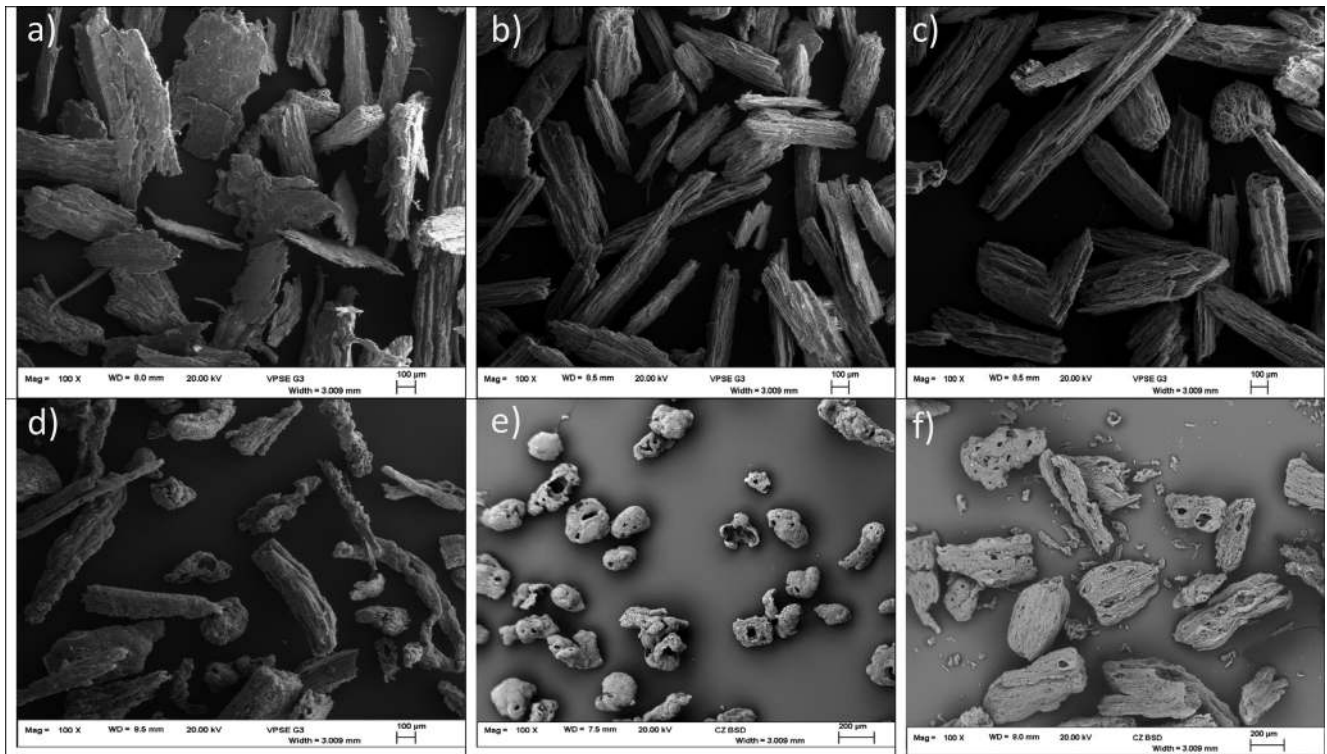


Fig. 2. Scanning electron micrographs $\times 100$ magnification of willow fuels and chars, where: a) Untreated Willow, b) Willow 270/30, c) Willow 290/30, d) Untreated Willow char, e) Willow 270/30 char, f) Willow 290/30 char.

The chars produced from willow torrefied under more severe conditions (290 °C and 30 min) show less evidence of hollowed out structure, but a more uniform coverage of pores of varying size can be observed instead. A similar trend is observed for eucalyptus chars. These differences in surface morphology upon fast pyrolysis for untreated and torrefied fuels are in agreement with Fisher et al.

[17], who also observed similar changes in torrefied fuels at high heating rates.

The BET surface areas for the fuels and chars are also listed in Tables 1 and 2, respectively. Upon torrefaction, willow shows a slight decrease in surface area, which becomes more significant at the more severe process conditions (290/30); this increase was

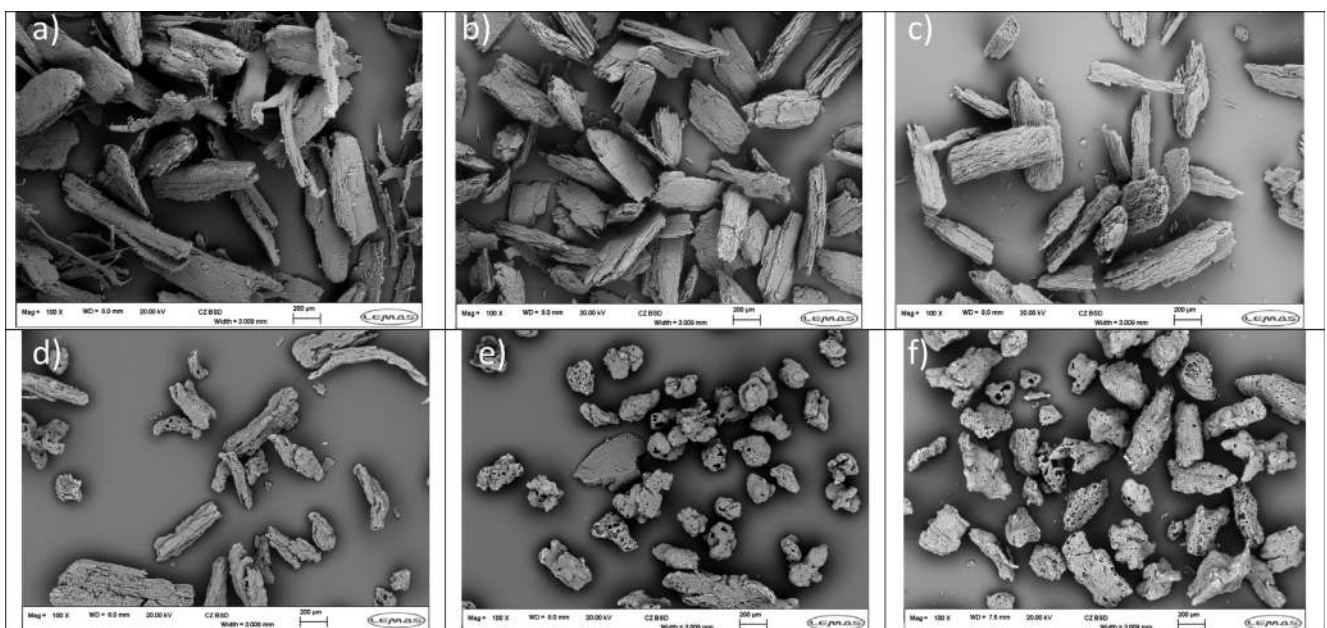


Fig. 3. Scanning electron micrographs $\times 100$ magnification of the eucalyptus fuels and chars, where: a) Untreated Eucalyptus, b) Eucalyptus 270/30, c) Eucalyptus 290/30, d) Untreated Eucalyptus char, e) Eucalyptus 270/30 char, f) Eucalyptus 290/30 char.

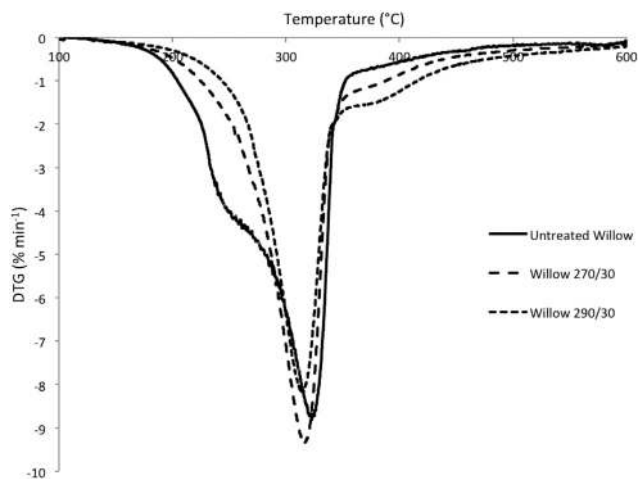


Fig. 4. Derivative of the mass loss-time curve during pyrolysis of untreated and torrefied willow.

unexpected, since the opposite effect has been reported previously by other researchers (e.g. Refs. [2,29]) In the case of the chars (Table 2), whilst for eucalyptus chars the surface area decreases as the torrefaction temperature increases (up to ~ 10-fold in reduction is observed with respect to the parent fuel char), for willow chars, the surface area decreases in the order Willow 270/30 > Untreated Willow > Willow 290/30 > Willow 270/60. The surface areas of the willow chars do not appear to follow any trends, due to the values obtained for the Willow 270/30 and Willow 270/60, but it should be noted that the chars have different degrees of burnout, as discussed below.

The development of pores across char particles upon heating, which will develop the exposed surface area of chars, are strongly affected by the pyrolysis conditions in which the chars are prepared—with heating rate being a key factor [30]. It is observed that for the chars produced from both untreated and torrefied willow and eucalyptus, the morphology and particle structure transforms significantly. This is particularly clear in the case of chars produced from all torrefied materials where the particles are clearly distinguishable from the parent fuel highlighting the impact fast-heating rates have on particle structure and specific surface

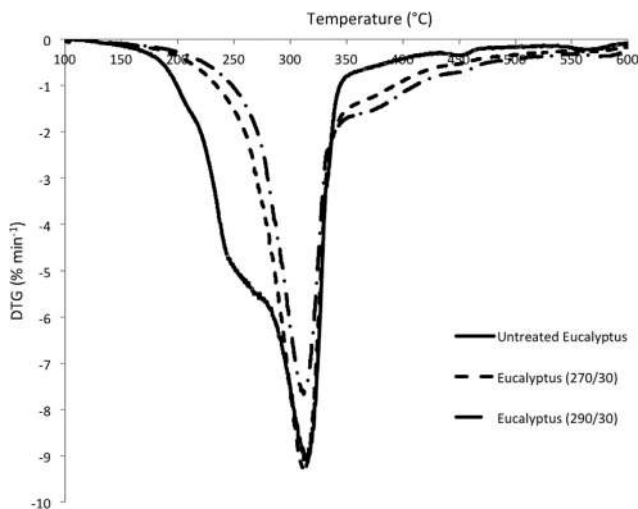


Fig. 5. Derivative of the mass loss-time curve during pyrolysis of untreated and torrefied eucalyptus.

area. Pyrolysis under slow-heating rates produce chars which differ in surface morphology to those produced under high heating rates, resulting in variations of surface area of 1–2 orders of magnitude when directly compared. In contrast to chars produced under high-heating rates, slow heating rates chars allow for escape of volatiles through ‘natural’ porosity and as a result often do not show notable changes in surface area from the parent fuel [15,17,31,32].

The magnitude of the surface area measured for biomass chars will vary depending on a number of factors such as temperature during pyrolysis, oxygen partial pressure and residence time, i.e. parameters which affect the degree of conversion [30]. In the case of chars produced from eucalyptus, the surface areas decrease with decreasing char burnout. Untreated eucalyptus contains more volatiles than its torrefied counterparts, which as an indicator of reactivity, thus could explain the increased degree of char conversion for this fuel. While this surface area trend is not shown by the chars produced from willow fuels, it should be noted that the highest surface areas reported for willow char is from the untreated fuel which undergoes the highest degree of char conversion. Additionally, because of the fibrous nature of biomass, a range of particles with varying diameters and lengths can be observed within the sieved fraction, and smaller particles will undergo a higher degree of burn off compared to larger particles leading to heterogeneity. In this study, a 1% oxygen environment was used during pyrolysis and various degrees of burnout are observed (Table 2). In general, a trend for a decrease in surface area as burnout decreases can be identified.

The surface area of the particles may also be affected by the annealing at high temperatures as a result of micropore coalescence [32]. At high temperatures, the biomass particles may begin to melt resulting in a loss of the cell wall structure [15]. As mentioned in Section 3.2, in the case of the Willow 270/30, Eucalyptus 270/30, and also Willow 270/60 chars, SEM images show the particles to be smaller and more rounded relative to the other chars. Since an unexpected lower surface area was measured in Willow 270/60 char, it is possible that this change in morphology could be due to annealing at high temperature.

In general, surface areas of chars from torrefied biomass were found to be lower than those produced from untreated biomass. It is interesting to note that accurate surface area measurements of biomass chars are difficult to perform with high confidence due to the nature of these materials. Biomass chars may still contain volatile matter which can slowly release during analysis leading to inaccurate measurements and so adequate outgassing prior to analysis is essential to avoid error as a result of this in surface area determination. For microporous carbons, nitrogen adsorption at cryogenic temperatures ($-196\text{ }^{\circ}\text{C}$) can be limited by the slow rate of diffusion of nitrogen molecules into the micropore structure, leading to an underestimation of the surface area of the particles [33]. This underestimation is especially evident when comparing measurements using a different adsorbing molecule such as CO_2 which is often used as the adsorbate in the case of biomass fuels and chars where micropores are prevalent. The figures reported using this latter method are often considerably higher than the measurements taken using N_2 [31]. For instance, Guerrero et al. [16] report very high surface areas of $528\text{ m}^2/\text{g}$ and $539\text{ m}^2/\text{g}$, for eucalyptus high heating rate chars from a fluidized bed reactor at $800\text{ }^{\circ}\text{C}$ and $900\text{ }^{\circ}\text{C}$, respectively using CO_2 adsorption. For the chars in this study however, adsorption with N_2 and the BET method was deemed appropriate as the presence of hysteresis loops characterised by type IV isotherms (as a result of capillary condensation in the mesopores) suggests the chars possess a mesoporous network structure. Measurement was still challenging and required long degassing periods and multiple repeats to give confidence in the results reported. Special care was taken during outgassing of the

biomass chars and the BET values reported show excellent linear correlation between 0.05 and 0.3 P/P₀ ($R^2 > 0.995$).

3.3. Potassium partitioning

The concentration of potassium (K) for untreated and torrefied fuels are shown in Table 1. It can be seen that the potassium tends to concentrate in the torrefied fuels, as its content increases with increasing torrefaction severity for both willow and eucalyptus; with the concentrations in the eucalyptus fuels higher than the willow fuels – for both untreated and torrefied. During torrefaction, it has been suggested that potassium existing as water soluble chlorides can react with functional groups on biomass such as carboxylic acids releasing HCl gas whilst incorporating potassium into the fuel matrix [34]. The chlorine concentrations of the untreated and torrefied fuels are shown in Table 1, where in the case of eucalyptus there is an observed decrease in chlorine concentration upon torrefaction which could be the result of these reactions taking place.

In the case of the chars, due to the small amounts produced owing to the very low char yields associated with fast-heating rate devolatilisation and high volatile matter contents of biomass-metal analysis by conventional methods, such as acid-digestion and ICP-MS (as performed on the parents fuels) was not an option. EDX analysis was employed instead to obtain information on the metal content of both fuels and chars. For this purpose, samples were ground in order to expose the internal structure of the char as the incident electron beam on to the surface of the particles penetrates around 1–2 microns in depth making it a semi-quantitative method of analysis-using the assumption that the entire particle is homogenous from centre to surface. From the char yields as listed in Table 2 and the potassium contents of the fuels and chars (average values calculated from a series of measurements taken using different particles from the same fuel or char), it was possible to obtain estimates of potassium partitioning, i.e. the split of potassium in the fuels between the char and volatiles upon reaction in the DTF. A plot of the fraction of potassium evolved with char burnout is shown in Fig. 6. It can be seen clearly from this plot that potassium evolves as the char combusts, and from the trend observed it can be reasonably assumed that it evolves monotonically with carbon.

3.4. Nitrogen partitioning

The partitioning of nitrogen between the volatiles and the remaining char during the devolatilisation process in the DTF was

calculated by a material balance from the nitrogen content of the fuel and that of the char. The results for nitrogen partitioning calculations for the willow fuels and their chars are shown in Table 2. In all cases, most of the nitrogen is released with the volatiles (>70%).

The nitrogen partitioning and type of nitrogen species obtained upon devolatilisation are fuel dependent, but they are also affected by the process temperature and residence time [35,36]. At low temperatures or very short residence times, nitrogen is more likely to be retained in the char, resulting in a nitrogen-enriched char, while at higher temperatures, nitrogen is released faster than the volatiles [35,37]. Werther et al. [36] have reported the release of nitrogen as being roughly proportional to the volatile matter in the fuel. In this instance, it can be observed that between ~8 and 28% of the fuel nitrogen was retained in the char, whilst ~72–92% entered the volatile fraction after the fuels have undergone devolatilisation at 1100 °C. These figures are comparable to the ones reported previously from pyrolysis of a range of untreated fuels (79–91%) [38], but higher than the ones obtained for untreated and torrefied willow (56–59%) [39] in a pyroprobe at 1000 °C. It is to be noted that in the present study, the fuels have been devolatilised at a higher temperature, which may have promoted further nitrogen release.

Furthermore, there is a reduction in nitrogen content of the fuels upon torrefaction (Table 1). Both lower fuel-N contents and the tendency to preferentially release fuel-N with the volatiles are beneficial for pf combustion in terms of potential lower NO_x emissions.

3.5. Fuel and char reactivity

3.5.1. Pyrolysis kinetics

Figs. 4 and 5 show a plot of the derivative of the mass loss with time curve (DTG) against temperature during the temperature programmed pyrolysis of (untreated and torrefied) willow and eucalyptus, respectively. Clearly shown in these plots is the impact of torrefaction on the hemicellulose fraction within the woods. In both untreated woods a shoulder is visible on the main decomposition peak; this shoulder is mainly attributed to hemicellulose decomposition, while the main peak is mainly attributed to cellulose decomposition, and lignin decomposition gives rise to the broad underlying peak. For the torrefied fuels, the hemicellulose decomposition shoulder is no longer present, and the lignin contribution to the curve has become more prominent; its relative concentration increases in the torrefied fuels as a result of the loss of hemicellulose [14]. The lignin concentration can be correlated to the fixed carbon content [40] which increases with increasing degree of torrefaction, as shown in Table 1.

Apparent pyrolysis kinetics were derived from the TGA data assuming a global first order reaction rate and the Arrhenius parameters are listed in Table 3. A rate constant calculated at 300 °C (k_{573}) demonstrates, firstly that eucalyptus decomposes more quickly than willow, and that pyrolysis becomes slower as the severity of torrefaction increases. The kinetic parameters obtained here are in agreement with previous work [41]. The relatively lower reactivity of the torrefied fuels compared to the untreated fuels has been observed previously by other researchers e.g. Refs. [5,14,41,42] and is also consistent with the results of extent of char burnout from the drop tube studies, i.e. a higher degree of burnout is experienced for the chars prepared from untreated fuels relative to the torrefied fuels at the same conditions and residence time. The extent of char burnout can be linked to the percentage of volatiles in the parent fuels and their oxygen concentrations. Untreated willow and eucalyptus fuel have volatile contents of 84.4% and 79.6%, respectively, which decrease upon torrefaction by around

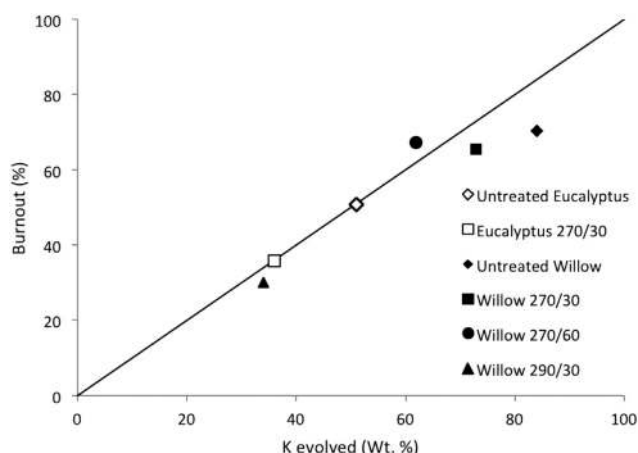


Fig. 6. Plot of the evolution of potassium with char burnout.

Table 3
Arrhenius parameters for pyrolysis and char combustion for untreated and torrefied fuels.

Parameters	Willow			Eucalyptus		
	Untreated	270/30	290/30	Untreated	270/30	270/30
Pyrolysis						
Ea (kJ mol ⁻¹)	60.7	61.3	72.2	58.5	65.8	78.5
Ln A (s ⁻¹)	6.5	6.5	8.6	6.5	7.3	9.8
k ₅₇₃ (s ⁻¹)	0.0020	0.0018	0.0013	0.0033	0.0015	0.0013
Char combustion						
Ea (kJ mol ⁻¹)	87.2	115.43	105.61	123.7	107.9	102.7
Ln A (s ⁻¹)	10.0	13.8	10.4	17.9	13.1	11.7
k ₈₂₅ (s ⁻¹)	0.067	0.049	0.009	0.918	0.068	0.0012

10% for willow and slightly more for eucalyptus 270/30 and by 20% for both fuels torrefied at 290 °C for 30 min, consistent with the reaction rate constants calculated above.

3.5.2. Char burnout kinetics

Kinetic parameters for the oxidative reaction of chars estimated from isothermal TGA experiments are also listed in Table 3. An example of the mass loss curves obtained from the isothermal combustion experiments is shown in Fig. 7, for the willow 290/30 char. Fig. 8 shows the plot of chemical reactivity (extrapolated to higher temperatures) against reaction temperature for the untreated and torrefied chars. The chemical reactivity plot also shows an outline of the data compiled by Di Blasi [43], who modelled the reactivity of a selection of biomass fuels pyrolysed at slow heating rates. For both willow and eucalyptus, the chars prepared from the untreated fuel are the most reactive, and a decrease in reactivity can be observed with increasing torrefaction severity for the DTF chars prepared at the same temperature and residence time. However, torrefaction appears to result in a bigger drop in reactivity for the eucalyptus chars than for the willow chars. Fisher et al. [17] reported on the reactivity of untreated and torrefied DTF chars and observe a similar effect of reduced reactivity for torrefied willow chars [17]. The difference in reactivity is also in agreement with single particle combustion measurements in a methane flame of untreated and torrefied willow undertaken previously by our group [39], where longer char combustion times were needed for the particles that had undergone torrefaction [2].

It is widely noted in the literature that the reactivity of fast heating rate chars are higher than those pyrolysed at low heating rates [16,17,31], and as such it would be expected that the behaviour of the chars from untreated fuels would dominate the top region of

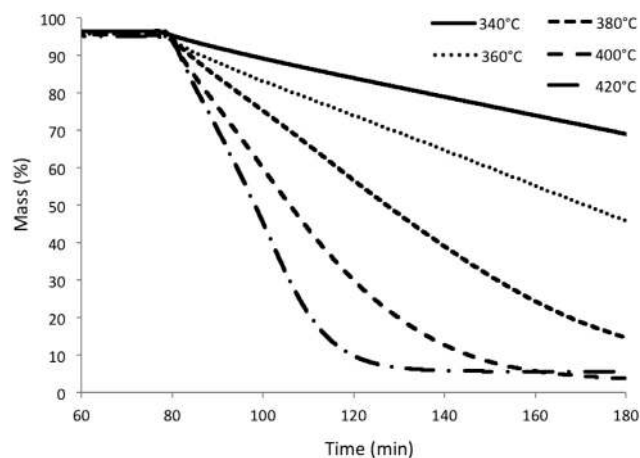


Fig. 7. Mass loss curves for the isothermal combustion of Willow 290/30 min char.

the Di Blasi outline. While untreated eucalyptus occupies this position, the chars from untreated willow exhibit considerably lower reactivities. The char combustion rate constants calculated at 552 °C (k₈₂₅) also listed in Table 3 predict that untreated eucalyptus chars would react considerably quicker than willow chars. Interestingly, the activation energy for the oxidation of char from untreated eucalyptus is an order of magnitude higher than the corresponding char from untreated willow; note that the measured surface area for eucalyptus char is also larger, which may account for an increased reactivity. During devolatilisation, the untreated willow fuel underwent a higher degree of burn-out than eucalyptus, 84% and 51% respectively, which may also account for the reduction in reactivity measured for the untreated willow chars. In the case of eucalyptus, the degree of disparity between the untreated and torrefied chars may be in part due to the reduction in

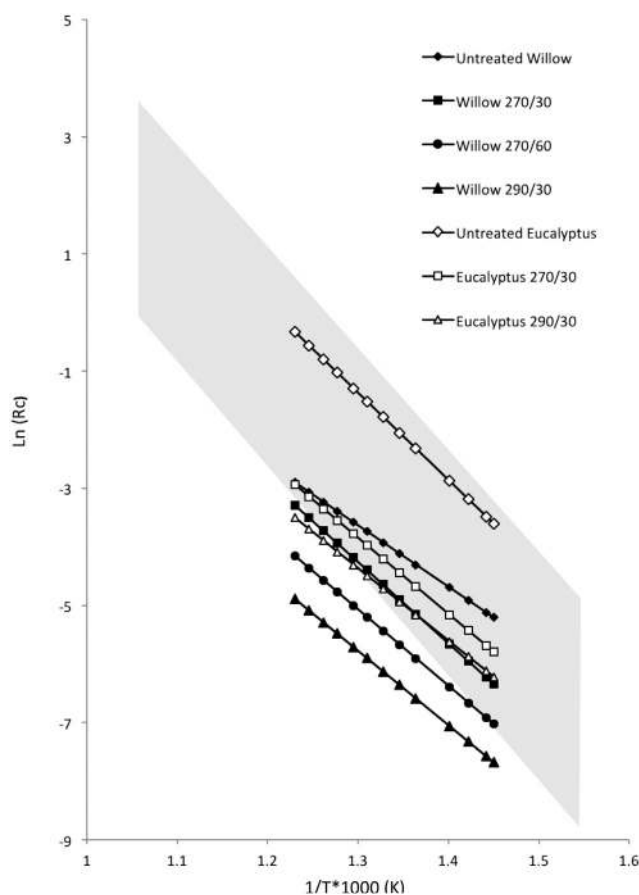


Fig. 8. Chemical reactivity plot for untreated and torrefied chars. Data from Di Blasi [43] outlined in the shaded area.

oxygen in these fuels during torrefaction. The mild torrefaction (270°C/30 min) for eucalyptus results in 10% reduction in oxygen concentration, while the most severe conditions (290°C/30 min) reduces the oxygen content by 20%. The reduction in oxygen content will have impact on the reactivity of the chars. In comparing the two sets of torrefied fuels, it can be noted that Eucalyptus 290/30 exhibits a similar reactivity to Willow 270/30. Potassium catalysis may be a factor here—as it is known potassium can affect reaction rates during pyrolysis and combustion [20,44]. It is to be noted that due to the lower extent of burnout on the eucalyptus chars, these appear to retain a larger fraction of potassium than willow chars (Fig. 6).

At present, there is limited information available in the literature that focusses on the oxidation characteristics of fast heating rate chars from torrefied fuels specifically. It must be noted that there are several factors that impact the reactivity of char oxidation, such as number of active sites, oxygen content of the fuel, film diffusion of the oxidising gases and diffusion of gases through the ash later and subsequent adsorption of gases on to the particle surface. Reactivity is further governed by the rate of chemical reactions taking place on the surface and the desorption of gases from the surface and through the particle into the ambient atmosphere [30,43]. The intrinsic reactivity, which can be defined as the reaction rate per unit area of pore surface in the absence of any mass-transfer limitations [45], can be obtained by normalising chemical reactivities for differences in surface areas and oxygen concentration of the reaction gas. A plot of the intrinsic reactivity of the untreated and torrefied chars against reaction temperature is shown in Fig. 9, alongside some data for bituminous coals from Jones et al. [46] and Smith [47], for comparison purposes. Similar to the chemical reactivities, the chars from untreated biomass are more reactive than the chars from torrefied fuels. The intrinsic reactivity of chars is a valuable approach when estimating the oxidative reactivity of chars in boilers and furnace. However, it is worth highlighting again, that the surface area of chars can vary considerably depending on the devolatilisation conditions and degree of burnout [30] and the method of surface area analysis. Essentially, Fig. 9 is not comparing “like with like”, since all the chars have different extents of burnout. Nevertheless, it is clear that chars from torrefied biomass are less reactive than those from untreated biomass, in spite of the former having higher surface area. This is consistent with findings from previous work [37].

4. Conclusions

In this study chars were prepared in a DTF from two biomass fuels: short rotation willow coppice and eucalyptus, and also from their torrefied counterparts. The fuels and chars were characterised for proximate, ultimate and surface areas and morphology by SEM/EDX. Furthermore, the pyrolysis and char combustion kinetics were estimated from TGA experiments. It was found that the torrefied fuels were less reactive for the pyrolysis stage than the untreated fuels. Similarly, the chars produced from the torrefied fuels were found to be less reactive than chars produced from the untreated materials. Differences between the combustion behaviour of the two types of wood studied were also observed. Eucalyptus chars were more reactive than willow char analogues, although they had seen a lower extent of burn off. Similar trends were also observed from their intrinsic reactivities -extrapolated to higher temperature ranges, which show that chars from the untreated fuel were more reactive than chars from torrefied woods, and in general, eucalyptus chars were more reactive than willow chars. Semi-quantitative EDX analysis analyses of the fuels and chars enabled the estimation of the partitioning of potassium during high heating rate pyrolysis. Results show a good correlation between potassium release and

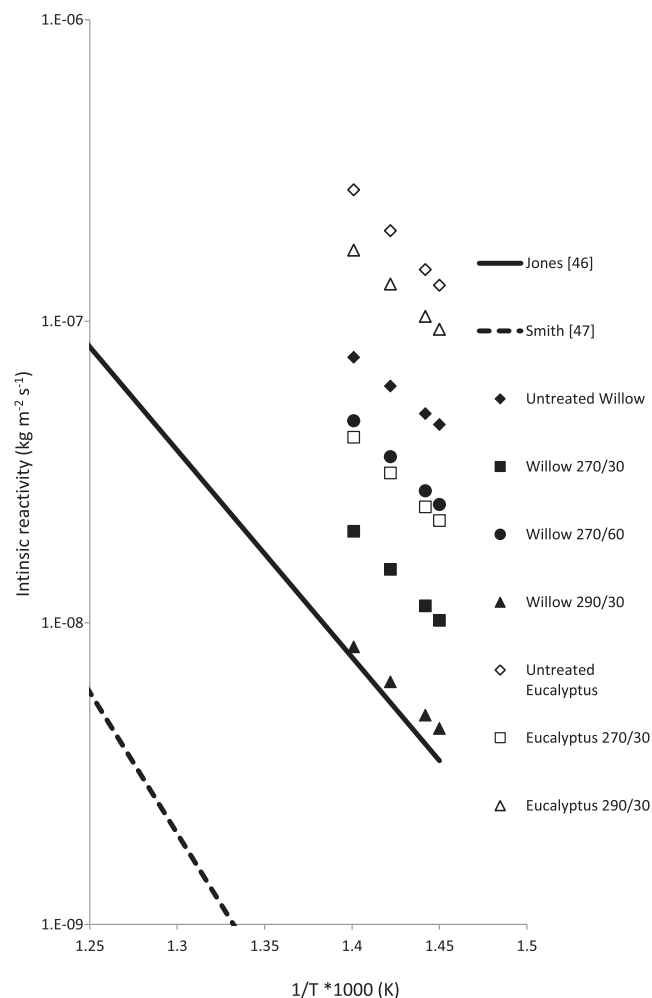


Fig. 9. Intrinsic reactivity for untreated and torrefied chars.

percent burnout. With respect to the effect of torrefaction on fuel-N, it was found that the process conditions used resulted in lower fuel-N contents for the fuels studied. Moreover, ~72–92% of the fuel-nitrogen was released with the volatile fraction upon devolatilisation at 1100 °C. Both findings suggest that torrefaction would be beneficial for pf combustion in terms of nitrogen emissions.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.biombioe.2015.05.016>.

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