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RAW AND STEAM EXPLODED PINE WOOD: POSSIBLE ENHANCED REACTIVITY WITH GASIFICATION HYDROGEN

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Abstract

A commercial thermally treated biomass known as ‘steam exploded biomass’ or ‘black pellets’ was compared with the raw yellow pine wood feedstock to the process using the Hartmann dust explosion equipment. The aim was to investigate the difference in pulverised biomass reactivity and minimum explosible concentration, MEC. The reactivity was determined from the initial rate of pressure rise prior to the vent bursting in the Hartmann equipment. The flame speed in the vertical tube of the Hartmann equipment was also determined as a reactivity parameter. Steam exploded milled pellets (BP) was found to have a higher reactivity, leaner MEC and higher flame speed, than the raw pine. The enhanced reactivity of BP was due to the greater proportion of fine particles. Both raw pine and BP had a high reactivity for very rich mixtures and this was due to the gasification reactions in rich mixtures that released CO and hydrogen. The very lean MEC for both biomass also may have been enhanced by hydrogen release.

Keywords: Pulverised, Steam explosion, Flame speed, Explosibility, Reactivity, Renewable

1 INTRODUCTION

Concerns over global warming and the high CO_2 emissions from pulverised coal fired power plants are discouraging the use of coal as a fuel for electric power generation. Sustainable and consistent fuels need to be sourced to replace fossil fuels. Renewable pulverised biomass can be employed as a substitute for coal in existing coal fired electric power generation plants. Pulverised wood is increasingly being used for electric power generation as one way of meeting the mandated European renewable energy proportions of electricity supply. In 2014 5.8% of the UK’s supplied electricity was generated from pulverised biomass, mainly used in existing coal fired power stations. This was a 25.7% increase on 2013 and in 2014 was 19.69 mtoe [1]. It was the fastest growing renewable electricity source between 2013 and 2014.

Currently most wood used for power generation is raw wood, pulverised at source, dried and compressed into pellets. This pelletisation increases the density of the fuel and the drying improves its energy density so that more biomass energy can be shipped in the fixed volume of a ship's hold. The palletisation also enables the pulverised fuel to be transported with minimum dust generation and hence with lower explosion risk. At the power station the pellets are stored in silos from which they are fed to the coal mills, which break up the pellets into the pulverised biomass. The mills are not intended to pulverise the biomass further, all the pulverisation is done at the palletisation plant in the country from which the biomass originated. This work investigates a further development of the palletisation process that of steam exploded biomass which is a thermal treatment process that produces a more consistent pellet that is easily milled with a higher calorific value than the raw biomass pellets.

2 BIOMASS AND HYDROGEN PRODUCTION

Hydrogen production from steam methane reforming of methane is the current major source of commercial hydrogen, particularly for oil refinery use to reduce the aromatic content of diesel, the other main products are CO and CO_2 [2].. Steam reforming of coal and biomass can be used for the production of hydrogen and if the CO is converted to CO_2 and the total CO_2 solvent extracted and captured, then low carbon hydrogen can be generated from coal or biomass [3-5]. In the combustion of rich mixtures of biomass, as studied in this work, the equilibrium products are essentially those of a gasification process with high CO and H_2 [6]. Peak hydrogen formation is usually around an equivalence ratio of 3 and the present work has rich flames propagating with a relatively high reactivity for equivalence ratio >3. Both pyrolysis and gasification of biomass can result in hydrogen production [5, 7, 8] and the pulverised biomass propagating flame studied in the present work involve pyrolysis reactions due to flame heating of particles. For rich mixtures gasification reactions occur that produce hydrogen. For lean mixtures flame front pyrolysis of biomass will produce some hydrogen. It is known that the addition of hydrogen to hydrocarbons extends the lean limit and thus makes the mixture more reactive [9]. It is possible that the present very lean minimum explosible concentrations for biomass are contributed by the pyrolysis release of hydrogen in the flame front. A method for calculating the hydrogen produced in volatiles from the biomass heating is developed in this work and this shows that the proportion of hydrogen is relatively low, so that for lean mixtures the MEC enhancement would be low.

3 THERMAL TREATMENT OF BIOMASS

Thermal treatment processes such as torrefaction aim to break up the fibrous nature of woody biomass and make it more brittle so that it can be more easily milled alongside coal or on its own in the same mills as used for coal. These thermal treatment processes would be based at the source of the biomass alongside the pelletisation plant. They have the advantage of low water in the biomass, a higher pellet density and less tendency for the pellet to fracture and form dust clouds in transport. At present it is not clear whether the potential advantages of torrefied biomass outweighs the increased cost of manufacture, for power generation.

Biomass materials have a low bulk density, a fibrous structure and have low heating values [10, 11]. The cost of transporting raw biomass from source to the power generation plant for milling is too high. Thermal pre-treatment of the biomass potentially can reduce these transport costs. Torrefaction is one of the advanced and attractive pre-treatment that gives the following benefits [12, 13]: they are more compact (higher bulk density), have a higher heating value and are more easily pulverised as the biomass fibres are broken up by the thermal treatment. Torrefaction results in a significant loss of volatiles from the biomass depending on the torrefaction conditions; these are usually recycled to provide the heat for the torrefaction process. Thermally treated biomass materials are often referred to as bio coal as they are closer in some properties to coal than to the original biomass.

An alternative thermal treatment to torrefaction is ‘steam exploded biomass’ [14]. This is a commercial process at the pilot plant stage, that treats the woody biomass with pressurised hot water (1.2-1.7MPa, 170-250^{o}C) for a short time (up to 10 mins.) and then releases the pressure to flash vaporise the water. This process inside the woody biomass structure shatters the particles into finer fractions [15, 16]. These steam exploded biomass materials are transformed into pellets known as ‘Steam exploded pellets’ for the easiness of transportation. They are often referred to as ‘black pellets’ due to their black colour.

Black pellets have similar properties to that of torrefied biomass. The steam exploded biomass process has potentially a lower energy consumption than for torrefied biomass with a lower loss of volatiles. The steam exploded process is intended to have a lower tar formation and less cracking of the raw biomass material. The resultant pellets potentially have a higher proportion of the original biomass energy than for torrefied biomass.

The steam exploded biomass treatment and palletisation process produces a pellet with an externally sealed outer surface due to the treatment process. This leaves them less sensitive to absorb water than for torrefied biomass. The biomass fibres in the pellets are destroyed and the pellets are easily pulverised, which are similar to the benefits of torrefied biomass. Steam exploded biomass is potentially a lower cost product than torrefied biomass and a better product in terms of energy content as a proportion of the original biomass energy on a daf (dry ash free) basis [14]. However, until commercial scale production plants are available for both technologies the final cost of the two thermal treatment techniques is not known.

4 BIOMASS DUST EXPLOSION HAZARDS

Pulverised biomass, when mixed with air, may explode if there is an ignition source and the flame propagation is the same as that which occurs in pulverised biomass burners. Thus the study of biomass explosions has both safety and pulverised biomass flame propagation measurement applications. The high volatile content of biomass and thermally treated biomass and the oxygen bound into the structure of the biomass fibres make pulverised biomass very reactive [17-20]. Pulverised biomass samples have a lower MEC than pulverised coal [21-23] and are hence more reactive. The porous structure of biomass with higher volatile content makes them more reactive.

Dust fires or explosion are common in biomass plants [24] and a recent UK incident was the wood floor mill explosion at Bosley Mill near Macclesfield. This resulted in the loss of four lives and almost complete destruction of plant. Some recent incidents related to biomass dust explosions are given below as examples.

- **Krabi biomass power plant [April 8, 2015]**

  Two workers were injured due to massive fire. Damage was estimated at about Bt 100 million[25].

- **Biomass power plant managed by Eco Sustainable Solution Ltd. at Southampton dock [January 03, 2015]**

  No injury. 6m flame and thick clouds of billowing smoke due to the woodchip pile fire was seen. [25].

- **Fire and then explosion at Jaffrey, N.H., manufacturing plant, New England Wood Pellet LLC [October, 2011]**

  It took 100 fire fighters and 15 hours to put down the fire. The company had to pay fine of $100,000 [26].

- **Explosion at the RWE's 750,000 ton wood pellet factory, Georgia, USA [June, 2011]**

  An overheated roller/bearing assembly in a pelletizer sparked the blast at the factory [27].

The operation of a biomass burner involves the mixing of the biomass dust with air in close to stoichiometric proportions. For a flame to stabilise, the burner air and dust flow has to be greater than the burning velocity, else there will be a flashback that could reach the mill.

However, if the burner flow velocity is too high then there may be flame lift off and the generation of unstable flames, which in extreme circumstances can result in the boiler enclosed space undergoing a biomass dust air explosion. All industrial boiler flames of this type are turbulent, irrespective of the fuel, but pulverized biomass requires turbulent flow for the particles to remain suspended. This also applies to the basic laboratory investigation techniques, which differ in the way that turbulent clouds of dust and air are formed. In addition there are explosion hazards in biomass storage areas such as silos and on the conveyor belts that transfer biomass to mills and from mills to burners.

This work investigates the combustion properties of a steam exploded biomass sample from one of the pilot plants for this material. There is scarce data for the combustion properties of biomass and none at all for steam exploded biomass. In terms of the safe use of the product there is no fire and explosibility characteristics of pulverised steam exploded biomass. Evaluations of these properties before their application in power stations is necessary to determine any additional safety measures that may be required. The measurement of the flame speeds is also relevant to the design of burners as the propagation of pulverised flames and the structure of the flame front in burners is largely unknown at present.

5 EXPERIMENTAL TECHNIQUES

Raw biomass and steam treated samples were milled to a size fraction of less than 63µm prior to chemical characterisation. The elemental analysis of the samples was carried out using a Flash 2000 Thermo Scientific Analyser. It consists of a single reactor with temperature of 1800°C for the detection of Carbon, Hydrogen, Nitrogen and Sulphur (CHNS) with O found by subtracting the mass of CHNS from the original mass. At this extreme temperature, the material is converted into gas comprising carbon dioxide, water, nitric oxides and sulphur oxides. These combustion products are separated on a chromatographic column and detected using a Thermal Conductivity Detector (TCD).

Proximate analysis was carried out using a Shimadzu TGA-50 thermo gravimetric analyzer. It consisted of a mass balance attached to a ceramic sample pan in a furnace. It records the weight loss with time and temperature from which may be determined the moisture, volatiles, fixed carbon and ash contents. The sample was heated in nitrogen from ambient temperature to 110^{o}C at a rate of 10^{o}C/min and maintained at 110^{o}C for 10 minutes so as to completely dry the sample. The temperature was then increased to 910^{o}C at a rate of 25^{o}C/min and held for 10 min to stabilise the weight after the volatile loss. Then air was introduced at 910^{o}C to react with any fixed carbon. The mass loss was the fixed carbon content. The remaining material left was inert ash.

The minimum explosible concentration (MEC) or lean flammability that is an important parameter for defining the stability of the burner flame and also used for safety design was determined using the modified Hartmann explosion tube, shown in Fig. 1 The modifications to the original Hartmann tube were developed by Huéscar-Medina et al. (2013) [28] and Saeed et al., (2015) [29]. The Hartmann explosion tube is the most appropriate approach for biomass dust MEC measurement, as the dust is placed inside the vessel and dispersed with a blast of air. The standard ISO 1m^3 dust explosion vessel cannot easily measure the explosion properties of biomass, due to the difficulties in injecting pulverized woody biomass through the delivery tubes and the injector.

The Hartmann Perspex tube has 1 litre volume with 61mm internal diameter and is 322mm long. The continuous 4J spark arc was located 110mm above the dust injector. This was activated prior to the initiation of the dust injection and there was no ignition delay between the start of injection and the spark. A pressure transducer was added at the top of the tube just below the aluminium foil exit vent cover. Confinement of the initial explosion was provided by covering the top end of the tube with Aluminium foil of 0.020mm thickness, fixed with a locking ring. With the air blast injection into the Hartmann tube the aluminium foil does not break until there is an overpressure of 0.55 bar, as shown in Fig. 2. The air injection was from a 0.05 litre external container pressurized to 7 barg, which gives consistent repeatable MEC measurements [28].

Figure 1. Modified Hartmann tube

The air injection generates a pressure rise of 0.36 bar as shown in Fig. 2. The dust is placed over the mushroom shaped bowl at the bottom of the tube so that the incoming compressed air is directed onto the dust where a cloud of dust/air forms. The pressure transducer records the pressure rise as shown in Fig. 2 and the dust was flammable if the pressure rise was above that for the compressed air injection alone and the aluminium vent cover burst in the explosion.

Three Type K mineral insulated exposed junction thermocouples were placed above the spark at 50, 100 and 150mm to detect the arrival of flame propagation and to determine the flame speed. A typical record of the flame arrival time as a function of the thermocouple distance from the spark is shown in Fig. 3. This shows a uniform flame movement up the tube at a speed of 0.63 m/s.

The process for the determination of the minimum explosible concentration (MEC) using the Hartmann equipment was refined by Huescar-Medina et al. [28]. The minimum explosible concentration was defined as the concentration that gave a pressure rise of 100mbar and/or was detected by the thermocouples. This is in line with lean flammability limit determinations for gases where the limit is the leanest mixtures that will propagate 100mm from the spark in a vertical tube of similar size to the Hartmann tube [17, 29]. In dust explosion standards the MEC is vague and defined as a mixture that just does not burn, but the test requirements do not determine the MEC reliably as only mixtures of 750, 500, 250, 125, 60, 30 and 15 g/m^3 are required to be tested. If 60 g/m^3 explodes and 30 does not then the MEC is set at 30 g/m^3 and there is no requirement to determine the actual MEC. This is considered to be an inappropriate measurement procedure and the lean limit procedures used for gas explosions were followed in this work [29]. This requires the lean limit to be determined to better than 10% leaner than the last mixture that did burn [29], which for a hydrocarbon is a lean limit resolution of <0.05 equivalence ratio, Ø. For a hydrocarbon dust this is a resolution of <4 g/m^3 for hydrocarbon type dusts or <10 g/m^3 for a wood type dust with a stoichiometric A/F of typically 6/1. These are much closer resolution of the MEC than is given in the current procedures for dust flammability. The present procedures for MEC using the Hartmann equipment should enable the MEC to be determined with the same resolution of the gas flammability methods.

6 MEC EXPRESSED AS EQUIVALENCE RATIO

Dust flammability data is normally presented in terms of g/m^3 and Andrews and Phylaktou [17] showed that existing data, when converted into equivalence ratio, Ø, indicated that the published MEC for most dusts were very lean at ~0.2Ø for many HCO dusts compared with 0.4 for many hydrocarbon type dusts, which is close to the equivalent lean limits for gaseous hydrocarbons. It is considered that all data on dust explosions should be expressed in Ø terms, when this is done over the whole flammable range the Hartmann and ISO 1 m^3 explosion equipment results show that extremely rich mixtures are reported as flammable in the literature [23]. There is no reported rich limit for any dust explosion as all test equipment exceeds its capacity to inject more dust before there is any indication of a rich flammability limit. This rich burning phenomena does not occur for gases, which all have a defined rich flammability limit. The stoichiometric A/F on a mass basis can be calculated from the elemental composition of the biomass [17] and then converted to g/m^3 by using the density of the air (1200 g/m^3 at typical ambient conditions). A typical stoichiometric A/F for wood is 6/1 kg/kg and this converts to 200 g/m^3. The ratio of this stoichiometric A/F ratio to actual A/F is the equivalence ratio, Ø. By assuming the volatiles in dusts are CO, H_2 and CH_4 the elemental composition and the TGA proportion of volatiles can be used to determine the proportion of the three gases, as will be shown in this work.

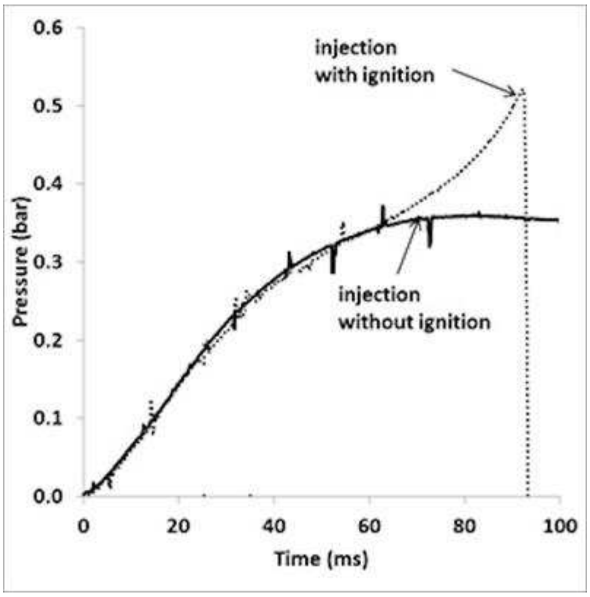


Figure 2. An explosion pressure record

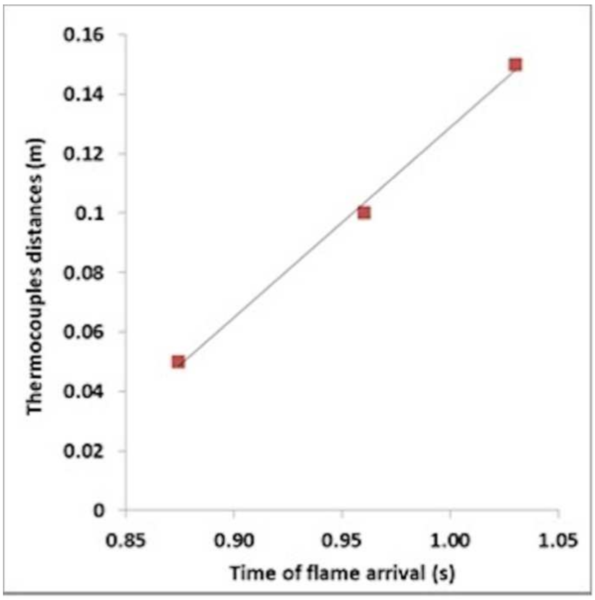


Figure 3. Example of Flame speed measurements

7 BIOMASS COMPOSITION

Biomass has a variable composition and the H/C v. O/C plot for a range of biomass investigated by the authors as shown in Fig. 4. This also includes the present yellow pine and the steam exploded yellow pine. Fig. 4 shows that the present biomass and thermally treated biomass falls within the range of other biomass. Fig. 4 also shows that the biomasses are quite different to coal. The steam exploded biomass, which is sometimes referred to as a biocoal, is not in the range of coal on the H/C and O/C plot and is still within the composition range of other biomass. The effect of the thermal treatment produced slightly lower O/C and H/C ratio as compared to its raw pine wood sample, as shown in Fig.4 and in Table 1, for the full composition of the present yellow pine and steam exploded pine. The steam exploded thermal treatment reduced the biomass volatiles by 4.5% compared with the original biomass. The fixed carbon increased after the steam explosion treatment. The steam exploded sample showed a small increase in the C-content and a small reduction in the H content.

Figure 4 also gives the H/C and O/C of cellulose, hemicellulose and lignin, which are the three main constituents of biomass. These are quite different and show that the variation of the H/C and O/C in different biomass is a reflection of their different proportions of cellulose hemicellulose and lignin. A low O/C in biomass indicates high lignin, high O/C indicates high hemicellulose and high H/C indicates high cellulose.

Figure 5 shows the variation of the calorific value with stoichiometric A/F by mass for the biomass and coal samples. The values for the two materials of the present work are also given in Table 1. This shows that there is a wide range of stoichiometric A/F for biomass, which has implications for burner control systems. There is also a wide variation of GCVs which is a reflection on the water and ash content as well as the O/C and H/C differences. Table 1 shows that the thermal treatment of the yellow pine had only a small change in the stoichiometric A/F. The CV was slightly increased by the thermal treatment, which was expected as CV normally increases with thermal processing of biomass. However, this thermal treatment process does not result in a major reduction in the water content and it increases the ash slightly, due to the lower volatile content.

The TGA analysis of the biomass volatile mass loss as a function of temperature, normalised to the total volatile mass, is shown in Fig. 6. The steam exploded biomass released more volatiles than the raw biomass at lower temperatures. This was unexpected as the thermal treatment process normally reduces the volatiles in the 300^{o}C region as this is the temperature at which these types of thermal treatment operate. It is likely that the change in the fibrous structure of the biomass with thermal treatment result in a reduction in the energy required to release the volatiles, so that more volatiles are released at lower temperatures [30].

At about 400-500°C, the rate of release of volatiles from the raw biomass was greater than the steam exploded biomass. This high temperature region is normally associated with lignin decomposition and this data would indicate that the thermal treatment did not reduce the lignin proportion of the biomass so that probably only the cellulose and hemicellulose structures were disrupted by the thermal treatment.

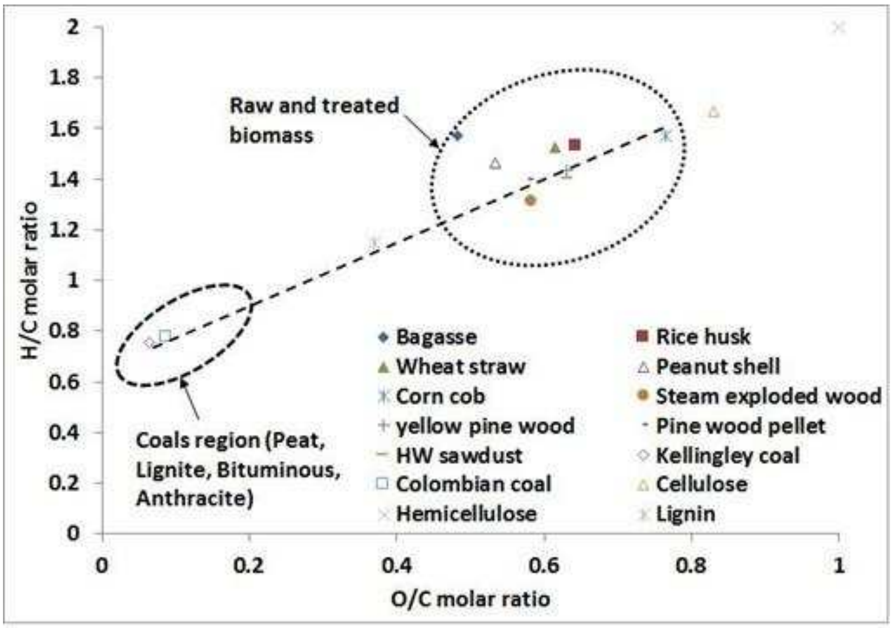


Figure 4. H/C vs. O/C in comparison to other biomass

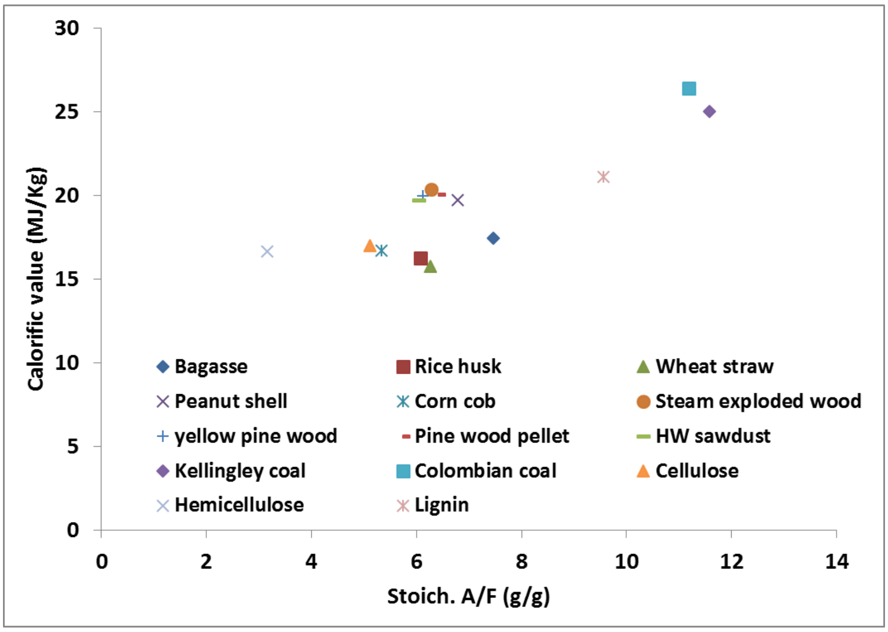


Figure 5 Fuel CV as a function of the Stoichiometric A/F for the biomass and other materials

Volatiles from biomass play an important role in their combustion characteristics and the higher volatile content is one of the factors that make biomass more reactive than coal. Also, the characterisation of these volatiles is necessary to understand the chemistry of the flame propagation. In the pulverised flame propagation, the heating rate and temperature of pyrolysis is extremely important. The higher the heating rate, the greater the release of volatiles with different compositional gases as compared to low heating pyrolysis. One of the unknowns at present in biomass combustion is the composition of the volatiles that are driven off the biomass at the low temperatures that Fig. 6 shows the volatiles are released.

In this work, simple elemental and proximate analyses were used for prediction of the composition of the volatiles gases in the low heating TGA analysis. The release of fixed carbon was assumed as pure carbon and it was deducted from the elemental carbon. The pyrolysis gases were assumed to be a mixture of CO, H_2 and CH_4. Elemental balances were carried out to determine the proportions of CO, H_2 and CH_4 that would occur if these were the only volatile gases. The results of this analysis are shown in Table 2. The red/negative values mean that an elemental balance could not be achieved and this indicates that there was the generation of other pyrolysis gases besides these gases. However, there were relatively few red/negative values and they were mainly for coal and steam exploded biomass.

For the biomasses the assumption that the volatile gases were CO, CH_4 and H_2 seems reasonable. Table 2 also shows the results that occur if the fixed carbon is assumed to be there because of the slow heating rates in the TGA. There is evidence of higher volatile release for higher heating rates and a limiting case has been calculated based on the fixed carbon being converted into CO or CH_4. However, due to the limited hydrogen in biomass an increase in CO is most likely if all the biomass apart from water and ash becomes volatile on rapid heating. This limited case is shown in Table 2 to reduce the number of cases where the assumed product gases could not balance the elemental analysis C, H and O. Also this limiting case predicts that the volatile gases would be mainly CO for all the biomass.

This analysis predicts that for coal methane would be the dominant volatile gas, but for fast pyrolysis, methane and CO would be of similar magnitude. It is often assumed in coal combustion modelling that the volatile gas driven off on heating is methane so that the initial flame can be modelled as a methane flame. For biomass this analysis shows that this would be an inappropriate model as there is insufficient hydrogen in the biomass to generate significant methane and the dominant volatile gas is likely to be CO.

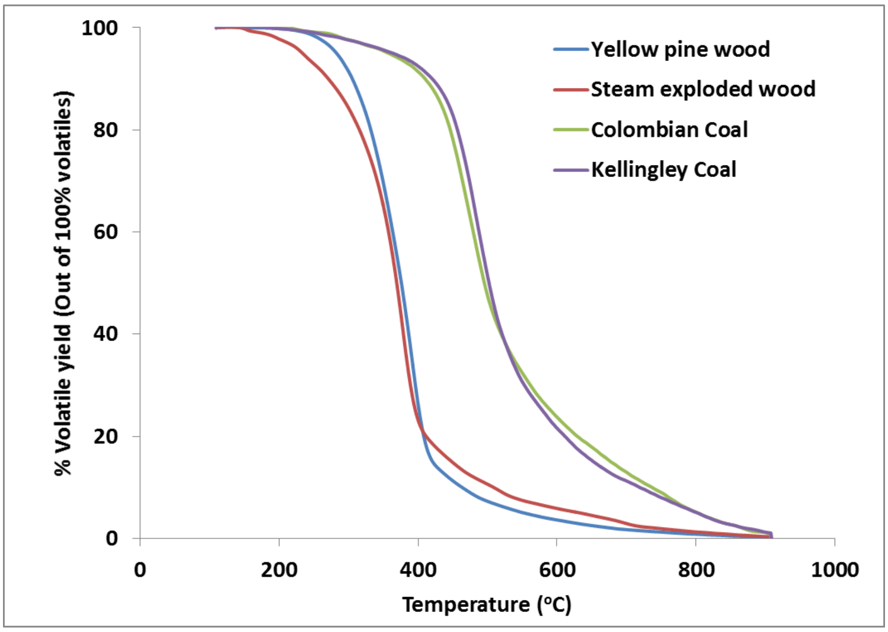


Figure 6. Volatile release vs. temperature of selected samples in comparison to coal

For yellow pine the results based on slow heating in the TGA and assuming that the fixed carbon does not form volatiles the predictions are that the composition of the volatiles is very similar for yellow pine and for steam exploded yellow pine with about 75% CO and 25% CH_4. However, if the fixed carbon is converted to volatile gases with rapid heating in a flame then the predictions are for more CO and less methane for yellow pine, but significantly more CH_4 and less CO for the steam exploded yellow pine. The authors are currently investigating the composition of the volatile gases that are released at the temperatures in Fig. 6 to see if the assumption of the main volatile gases is correct. There have been no analysis of the composition of biomass volatiles for slow heating rates that we have found in literature. Most work on the pyrolysis tars and gases from biomass and coal heating in nitrogen use much higher temperatures of around 900°C or higher. At higher temperature there are many high MW hydrocarbons (tars) as well as CO and the production of char. Initial results from our work using FTIR analysis of the volatiles released at 250 – 400°C in nitrogen indicate that their composition is more complex than has been assumed in this simple analysis.

8 PARTICLE SIZE DISTRIBUTION AND PARTICLE MORPHOLOGY

The size distribution of the raw milled yellow pine wood and the steam exploded thermally treated version of the same biomass were milled in the same rotary blade miller and the size distributions are summarised in Table 3 and shown as a distribution in Fig. 7. Table 3 compares the two biomass samples with two coal samples investigated by Huescar-Medina et al. [31] and the Kellingley coal size distribution is compared with that for the biomass in Fig. 7. Table 3 and Fig. 7 show that a key effect of the steam exploded biomass thermal treatment was to make the biomass more easily milled. Table 3 shows that the size fractions were much smaller for the steam exploded pine compared with the raw pine. Both particles were sieved through a 63µm sieve and yet the particles are very large for the raw biomass. This occurs because the particles are fibres that have a low diameter <63µm to pass vertically through the sieve, but long in the other direction. The action of the thermal treatment is to break up the biomass structure that makes the fibres resist cutting. The weak fibres are then easily milled to produce the smaller size. The laser light scattering size analysis technique gives a size that is the equivalent sphere that would generate the amount of scatter that was measured. Particle shape was investigated using SEM, as discussed below.

Comparison with the particle size for the two coals in Table 3 and one coal in Fig. 7 shows that the coal samples were finer than the present milled steam exploded yellow pine. However, the coal samples were delivered as milled at coal fired power stations and were substantially smaller than the present rotating blade miller that was used for the biomass. The reactivity of powders increase as the size is reduced so that direct comparison of the present biomass with coal reactivity is not purely due to their chemical differences.

The surface morphology of the milled yellow pine and the steam exploded yellow pine pulverised biomass was investigated using SEM imaging, as shown in Fig. 8. The raw biomass had fibrous particles with wide variation in the particle size distribution, whereas the steam exploded sample had less variation in the particle size distribution and the long cylindrical fibres had been destroyed. Both samples were milled and sieved to less than 63 µm, but the steam exploded biomass showed a greater fine fraction than the raw biomass as shown in Table 3 and Fig. 7. Fig. 8 shows that for the raw biomass there were particles of 150µm diameter and 500µm length present, but in the steam treated biomass the largest fibres were about 50µm diameter and 100µm long.

Table 1. Chemical characterisation of raw wood in comparison to its thermally treated wood

Biomass	**Raw yellow pinewood (YPW)**	**Steam exploded yellow pine wood (BP)**
C daf. (%)	51.0	52.8
H daf. (%)	6.1	5.8
N daf. (%)	0.0	0.4
S daf. (%)	0.0	0.0
O daf. (%)	42.9	41.0
H2O (%)	5.4	4.4
VM (%)	77.5	73.0
FC (%)	15.3	19.9
Ash (%)	1.7	2.7
OLS correlation CV (MJ/Kg)	20.0	20.4
Stoich. A/F daf. (g/g)	6.1	6.3
Stoich. Actual Conc. (g/m^3)	211.2	205.7

9 MINIMUM EXPLOSIBLE CONCENTRATION (MEC)

The MEC was determined using the Hartmann explosion tube using the method described earlier. The results are summarised in Table 4 where they are compared with other materials. The Colombian coal in Table 4 was tested on both the Hartmann explosion tube and on the ISO 1 m^3 dust explosion vessel, taking into account the unburnt dust in the determination of the burnt equivalence ratio, $Ø_{burnt}$. The results in Table 4 show good agreement between the Hartmann and 1 m^3 ISO explosion vessels. The leaner MEC for the steam exploded sample was due to the increase in the exposed surface area that resulted from the thermal treatment and the associated reduction in particle size, which increased the rate of heating of the biomass particles. This gave a faster release of volatiles which was responsible for the leaner MEC.

Table 2. Possible volatile composition based on the elemental and proximate analysis

Biomass	Including FC with the Volatiles					Volatile excluding FC				
	Formula	Stoich. A/F	CO	CH_4	H_2	Formula	Stoich. A/F	CO	CH_4	H_2
Rice Husk (RH)	$CH_{1.53}O_{0.64}$	6.15	76%	24%	0%	$CH_{2.10}O_{0.97}$	4.85	92%	2%	7%
Willow	$CH_{1.48}O_{0.68}$	5.82	78%	21%	1%	$CH_{1.76}O_{0.85}$	5.10	87%	9%	4%
Hardwood	$CH_{1.52}O_{0.76}$	5.38	83%	15%	2%	$CH_{2.15}O_{1.16}$	4.05	99%	-8%	9%
Softwood	$CH_{1.51}O_{0.76}$	5.38	83%	15%	2%	$CH_{1.85}O_{0.98}$	4.54	93%	1%	6%
Drax fine	$CH_{1.69}O_{0.64}$	6.34	75%	24%	1%	$CH_{2.01}O_{0.81}$	5.62	84%	11%	5%
Steam exploded wood (BP)	$CH_{1.31}O_{0.58}$	6.31	72%	29%	-2%	$CH_{1.46}O_{0.66}$	5.91	77%	22%	0%
Yellow pine wood	$CH_{1.44}O_{0.63}$	6.12	75%	25%	0%	$CH_{1.86}O_{0.86}$	5.18	87%	8%	5%
Pistachio nut shell	$CH_{1.53}O_{0.63}$	6.22	75%	25%	0%	$CH_{1.88}O_{0.84}$	5.27	86%	9%	5%
Corn flour	$CH_{2.0}O_{0.8}$	5.64	84%	12%	4%	$CH_{2.36}O_{0.98}$	5.03	91%	1%	8%
Kellingley Coal (K Coal)	$CH_{0.75}O_{0.06}$	11.59	13%	109%	-22%	$CH_{1.39}O_{0.39}$	8.07	56%	49%	-5%
Colombian Coal (C Coal)	$CH_{0.77}O_{0.09}$	11.18	17%	103%	-20%	$CH_{1.37}O_{0.40}$	8.01	56%	49%	-5%

Table 3. Particle size distribution (PSD) of the steam exploded pine, raw pine and two coals

Samples	d(0.1)	d(0.5)	d(0.9)
Steam exploded wood (BP)	13.3	51.9	151.8
Yellow pine wood (YPW)	30.7	198.3	629.6
Colombian Coal (C Coal)	6.8	28.1	85.2
Kellingley Coal (K Coal)	5.0	25.5	65.3

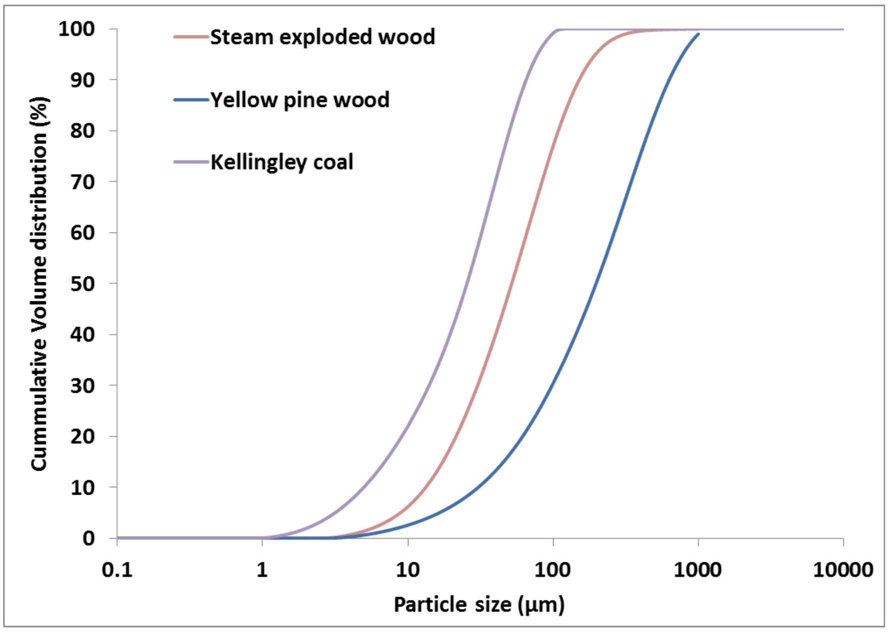
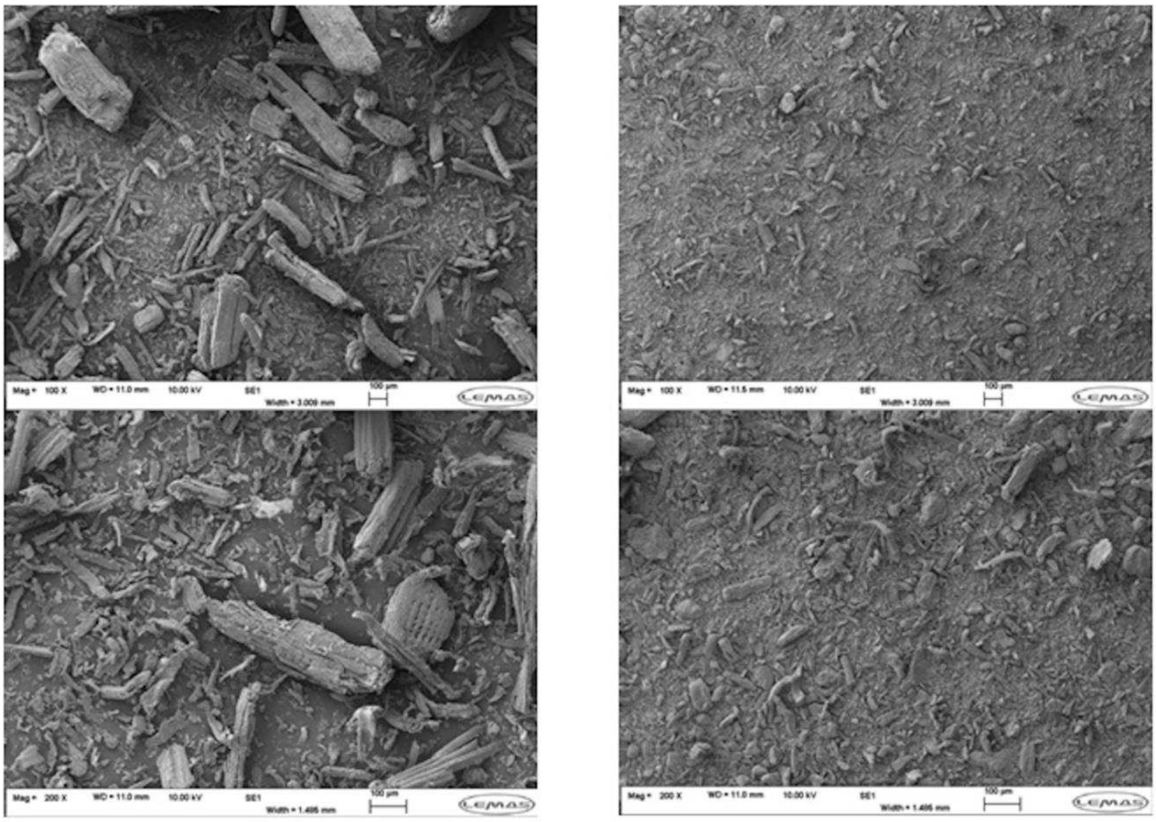


Figure 7 Particle size distribution by laser light scattering

Table 4 MEC Results for Yellow Pine and Steam Exploded Yellow Pine in comparison with a coal sample, polyethylene and propane [18, 31]

Material	A/F at Ø=1	g/m^3 at Ø=1	MEC Ø	MEC g/m^3	Method
Yellow Pine	6.1	196.7	0.39	76.7	Hartmann
Steam Exploded Yellow Pine	6.3	190.5	0.20	38.0	Hartmann
Columbian Coal	11.2	107.1	0.39	41.8	Hartmann
Columbian Coal	11.2	107.1	0.43	46.0	1 m^3
Polyethylene	14.8	81.1	0.37	30.0	Hartmann
Propane	15.7	76.4	0.43	32.9	EU Tube



Raw pinewood

Steam exploded wood

Figure 8. SEM images of raw pinewood and steam exploded wood for different magnifications, low resolution (top) and high resolution (bottom) for different parts of the samples.

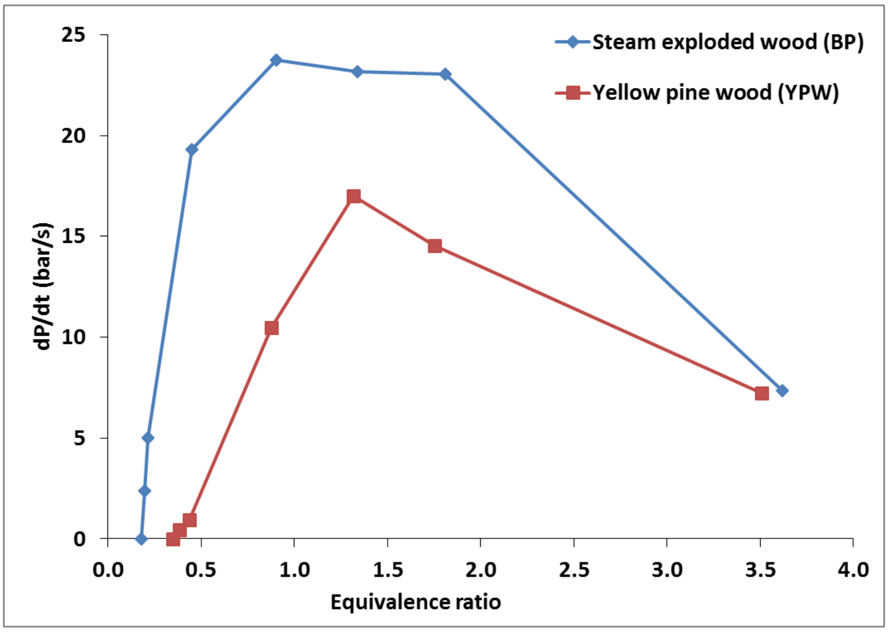


Figure 9. Rate of pressure rise of steam explosion wood in comparison to raw pinewood

Table 4 shows that the present MEC results for the raw pine biomass agree with the MEC for Columbian coal. This is a coincidence as the coal particle size was much lower which should make the MEC leaner and the volatile content was lower which should make the MEC richer. Comparison of the steam exploded biomass MEC with that for Columbian coal show a much leaner MEC for the steam exploded biomass, which indicates that it is more reactive in spite of the higher mean particle size for the thermally treated biomass. Steam exploded biomass, in spite of losing some volatiles in the thermal treatment process, was more reactive than Columbian coal due to more volatile yield, in spite of the larger particle size due to the opening of internal pores in the biomass as a result of transformation of the structure by the volatile outgassing, as shown in Fig. 8, and the related lower density and thermal mass of the particles. Table 2 shows that if the volatile release was a hydrocarbon as in polyethylene dusts or propane then a lean limit of ~0.4Ø (for 100% hydrocarbon volatile release) would be expected. However, Table 2 shows that the dominant volatile gas for low temperature heating of biomass, as in the TGA, would be CO and hydrocarbons would be lower and hydrogen relatively low. The MEC for hydrogen is 0.14Ø and for CO it is 0.41Ø [17]. Thus the volatiles being CO or hydrocarbons would not explain an MEC of 0.2 for the steam exploded biomass. The addition of hydrogen in the volatiles would help to explain the very lean MEC [9], but very high proportions of hydrogen in the volatiles would have to occur and there is insufficient hydrogen in the biomass for this to be the explanation of the very lean MEC.

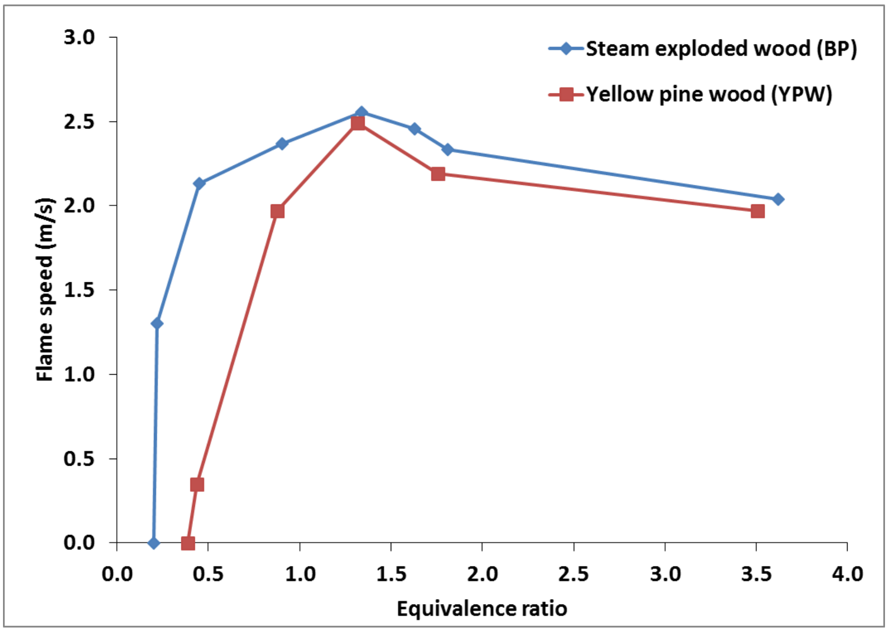


Figure 10. Flame speed of steam explosion wood in comparison to raw pinewood

These low MEC of ~0.2Ø have been reported by others in the literature [13, 17, 21, 29, 32] albeit in g/m^3 units and there is no explanation for such lean mixtures other than errors in the measurement procedure. The authors have shown [29] that the key problem is that on the Hartmann equipment with the spark on at the start of the test, for reactive dust (small particle size) the dust ignites immediately before the dust is mixed with the air. For less reactive mixtures (larger particle size or raw biomass in the present work) there is a delay between injecting the dust and ignition occurring and this allows a natural mixing time and may be the main reason that the MEC is closer to that expected for CO and HC gases for the raw yellow pine biomass.

For fine particles of polyethylene the authors [29] have shown that imposing an ignition delay of 150ms gives an MEC of 0.3Ø, compared with 0.10Ø for no ignition delay and 0.2 for 50 – 100ms delay. High speed video records of the explosion have shown that ignition occurs before the dust is mixed with all the air, so that a locally richer mixture is ignited. The effect of this is to extend the MEC to leaner mixtures. It is likely that a similar effect of ignition delay was responsible for the present very lean MEC for the steam exploded yellow pine, where the particles were finer than for the raw pine biomass. The alternative measurement method for MEC of the 1 m^3 also has measurement issues as the actual concentration that the flame propagates through is not reliably determined [29].

10 MIXTURE REACTIVITY MEASURED BY THE INITIAL RATE OF PRESSURE RISE IN THE HARTMANN

The Hartmann equipment was used to investigate the mixture concentration that had the highest reactivity using the initial rate of pressure rise just before the Hartmann explosion vent burst, which was measured as shown in Fig. 2. The results are shown in Fig. 9 which demonstrates that the raw yellow pine has a lower reactivity at all Ø than for the steam exploded yellow pine. The main reason for this was the finer particle size, due to the easier milling of the steam exploded pine, as shown in Fig. 7 and Table 3. The peak rate of initial pressure rise occurred at 1.3Ø, which is close to that expected for gas combustion (1.1Ø typically for gases [33]). For the steam exploded yellow pine with finer particle size distribution the mixture was more reactive with higher values of the initial rate of pressure rise. However, the variation of this reactivity parameter with Ø was different than for the raw yellow pine biomass. There was a peak value of the initial rate of pressure raise for 0.7Ø to 1.8Ø. This was an unusually wide peak reactivity range of Ø and is likely to be due to the use of the spark on at the start of dust injection. If only half of the dust is mixed with the air then an overall Ø of 0.5 is Ø=1 local mixture near the spark and hence would be very reactive. This is the cause of the broad peak in the mixtures that had a high reactivity. In contrast with the raw biomass the size distribution was much bigger and there was a natural ignition delay in which the raw biomass was mixing with the air and the distribution of reactivity is closer to that expected from gaseous explosions [33].

11 MIXTURE REACTIVITY DETERMINED BY THE FLAME SPEED

The flame speed was determined from the time of arrival at the three thermocouples, 50, 100 and 150mm above the spark on the tube centreline, as shown in Fig.3. The flame speed is shown as a function of Ø in Fig. 10 and for both the raw yellow pine and the steam exploded yellow pine the peak flame speed occurred at 1.3Ø, which is very similar to that found using the initial rate of pressure rise in Fig. 9. There was a clearer peak in the flame speed at 1.3Ø for the steam exploded biomass than was found for the initial rate of pressure rise in Fig. 9. The maximum flame speeds was measured as 2.5 m/s for the raw yellow pine biomass and 2.6 m/s for the steam exploded biomass at same equivalence ratio. This indicates a similar peak reactivity by rate of flame propagation at the same Ø for the two biomass. This is a different conclusion drawn from Fig.9 where the initial rate of pressure rise was significantly higher for the steam exploded biomass.

The similar flame speeds for the raw and thermally treated biomass indicate that the finer particle size for the steam exploded biomass did not lead to a significantly higher flame speed. For lean mixtures the finer steam exploded yellow pine had a significantly higher flame speed than for the raw biomass and this does indicate that the thermally processed pine was more reactive than the raw pine, as shown in Fig. 9 for the initial rate of pressure rise. The high speed videos showed that the flame speed measured for rich mixtures was not the initial flame speed before the vent burst, but the flame speed after air had flowed into the explosion tube post vent bursting. As the initial mixture was rich there was then a flammable mixture and a fast flame speed. Thus, it was concluded that the initial rate of pressure rise was a preferable parameter to base the mixture reactivity on, as this definitely occurred before the vent burst. The flame speeds by the thermocouple method were only valid for lean mixtures, where the measurements were made before the vent burst.

The flame speeds in Fig. 10 for lean mixtures indicate peak flame speeds in the 2 – 2.5 m/s region, which are close to those reported by others for flame propagation in a vertical tube [18]. This is not a fundamental flame speed as the flame is not spherical and there are burnt gas heat losses to the tube walls. However, the turbulent flame speed is lower than the laminar flame speed for spherical gaseous premixed flames [34], where for small explosion vessels the peak flame speed is 2.6 m/s for methane-air. As the Hartmann tube explosions occur in a turbulent mixture this means that the laminar flame speeds for the biomass dusts are well below those for gas flames. This has also been shown by the Sattar et al. [33] using the ISO 1 m^3 turbulent dust explosion vessel. This had peak spherical turbulent flame speeds in the range 6 – 12 m/s depending on the dust type with laminar burning velocities derived from this in the range 0.15 – 0.5 m/s depending on the dust.

12 CONCLUSIONS

The reactivity of yellow pine wood biomass and the effect of steam explosion thermal treatment was investigated. The steam explosion treatment only had small changes to the C/H and O/C ratios and was still within the spread of data for biomass. There was a small reduction in the proportion of volatiles with the thermal treatment and a corresponding increase in fixed carbon. However, the change in CV was minor. The main effect of the thermal treatment was to break up the fibrous natures of woody biomass and to make the biomass easier to mill. The particle size of the milled material was significantly smaller than that for the raw milled biomass, even though both materials had been sieved to <63µm.

If the composition of the volatiles given off in the TGA studies is assumed to be CO, CH_4 and H_2 then the proportion of these gases can be determined from the elemental analysis. Two scenarios were investigated: firstly where the fixed carbon did not contribute to the production of volatile and secondly where under rapid heating it was assumed that all the biomass C, H and O would be converted into gaseous volatiles. For both cases CO was the dominant gas in the volatiles and hydrogen release was predicted to be low for both cases. The very lean MEC measured for biomass was considered to be due to incomplete fuel and air mixing in the Hartmann for fine particles, rather than the participation of hydrogen released from heated biomass. For the present coarse particles there was an ignition delay that allowed more fuel and air mixing and more reliable MEC were determined. The measurement of MEC for dusts needs improving.

The steam exploded biomass was shown to be more reactive than the raw pine biomass due to the smaller particle size and the greater surface area created by the blow holes as the volatiles were released in the steam explosion treatment. Evidence for the increase in reactivity with the thermal treatment was provided by the MEC measurements, the initial rate of pressure rise and the flame speeds for lean mixtures.

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