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Low temperature ignition of biomass

J.M. Jones ^{a,*}, A. Saddawi ^b, B. Dooley ^a, E.J.S. Mitchell ^a, J. Werner ^a, D.J. Waldron ^c, S. Weatherstone ^d, A. Williams ^e

^a Energy Research Institute, School of Process, Environmental and Materials Research, University of Leeds, Leeds LS2 9/T, UK

^b University of Lincoln, School of Engineering, Brayford Pool, Lincoln LN6 7TS, UK

^c Alstom Power, Excelsior Road, Ashby-de-la-Zouch, Leicestershire LE65 1BU, UK

^d E.ON, Technology Centre, Ratcliffe-on-Soar, Nottingham, Nottinghamshire NG11 0EE, UK

e Energy Technology Innovation Institute, School of Process Environmental and Materials Research, University of Leeds, Leeds LS2 9JT, UK

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ABSTRACT

Biomass is an especially reactive fuel. There have been large increases in the transportation and utilization of biomass fuels over the past 10 years and this has raised concerns over its safe handling and utilization. Fires, and sometimes explosions, are a risk during all stages of fuel production as well as during the handling and utilization of the product. This paper presents a method for assessing ignition risk and provides a ranking of relative risk of ignition of biomass fuels. Tests involved single particle measurements, thermal analysis, dust layer and basket ignition tests. In all cases, smouldering combustion was observed, whereby the fuels pyrolyse to produce a black char, which then subsequently ignites. Low temperature pyrolysis kinetics have been utilised to predict ignition delay times at low temperatures. A method for evaluating risk was explored based on the activation energy for pyrolysis and a characteristic temperature from TGA analysis. Here, olive cake, sunflower husk and *Miscanthus* fall into the high risk category, while the woods, plane, pine, mesquite and red berry juniper, fall into the medium risk category. This method is able to capture the impact of low activation energy for pyrolysis on the increased risk of ignition.

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1. Introduction

On a global scale, there is an increasing use of a wide variety of biomass fuels in power and heat generation [1]. Although biomass shares many properties with coal, there are some disadvantageous features, especially the heightened propensity for low temperature ignition during conveying and processing, and the hazard of spontaneous combustion associated with storage. Coal is far less hydrophilic than biomass; meaning that open-air storage is possible for coal whereas biomass must usually be stored in silos. The silos need adequate ventilation because biological and chemical processes cause the biomass to consume oxygen and release combustible gases such as methane and carbon monoxide. The friability of biomass means that dust layer ignition is an issue during milling and conveying, and dust accumulates on hot surfaces such as lamps and machinery. Biomass also has a higher burning rate than coal, meaning that any ignition flame will propagate much more quickly for biomass and with the larger mixture ratio of biomass in cofiring plants [2]. There have been several instances of explosions or fires during storage, milling or conveying [3]. Because of the risk of self-heating and low temperature ignition there have been many

E-mail address: J.m.Jones@leeds.ac.uk (J.M. Jones).

studies over the past 50 years [4–8] including the development of the underpinning theoretical understanding [9,10].

Within the lifetime of a particle or pellet of biomass being stored, transported, handled, milled etc. within a power station it will encounter a range of atmospheric conditions (humidity, temperature, oxygen concentration) and the biomass particle itself may vary in particle size. Some particles may form fine dust in hoppers, silos, or on and within plant equipment etc. Thus, situations where ignition is a hazard vary, and there is a great need for quick, laboratory methods for assessing risk of ignition, not just during storage, but during handling and conveying where dust layers on hot surfaces become a real hazard. Ramírez et al. [8] provided details of a number of laboratory methods for assessing ignition risk, and derived a risk ranking based on thermal analysis in oxygen; this technique is explored in the present work, together with other laboratory test methods. Thus, this paper considers approaches for assessing risk of ignition and provides an approach for evaluating relative ignition risk amongst biomass fuels.

2. Experimental

Seven samples of biomass were used for this study. Olive cake, mesquite, plane, pine heartwood, sunflower husk and red berry juniper were supplied in oven-dried form by industrial (BF2RA) members,

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^{*} Corresponding author. Tel.: +44 1133432477.

while early harvested *Miscanthus* was supplied by Rothamsted Research, Harpenden, UK. The fuels were milled to a particle size of <212 μ m prior to their analysis. Fuels were analysed for proximate an ultimate using British Standard Testing Methods (BS EN 14774-1:2009, BS EN 15148:2009 and BS EN 14775:2009) and fell in the expected range. That is, on an as received basis: 4–7% moisture, 2–6% ash except for olive cake at 11% ash, 60–70% volatiles; daf basis: 50–55% C, 6–6.5% H, 35–43%O. These are shown in Table 1.

Several methods were used to assess ignition risk, namely thermal analysis, single particle ignition measurements, dust layer ignition measurements, and basket ignition measurements.

Differential thermal analyses (DTA) were conducted in air to determine characteristic ignition temperatures of the fuels. The temperature of initial combustion (T_{IC}) and temperature of maximum weight loss (T_{MWL}) were assessed, and also the temperature at which the rate achieved 1%/min, and the temperature at which the process became exothermic from the DTA trace. The methods used to calculate each of these different characteristic temperatures are given in Fig. 1.

Combustion experiments used a TA Q5000 TGA with a heating rate of 10 K min⁻¹. Pyrolysis experiments used a Netzsch STA 449C Jupiter STA system interfaced with a Nicolet Avatar 370 FTIR spectrometer to examine evolved gases and volatiles. Kinetic parameters were determined using the reaction rate constant method based on an apparent first order reaction for the initial portion of the weight loss curve, as detailed in Saddawi et al. [11]. The STA–FTIR system was calibrated for 14 species i.e. peak area versus mass using a willow (short rotation coppice) for which the input files for the FG-Biomass model (AFR Inc.) had been evaluated previously. The calibration was used to estimate the mass per cent of these species evolved during pyrolysis of the fuels of interest. The lower flammability limits (LFLs) of each volatile mixture were evaluated using Le Chatelier's principle [12].

The low temperature ignition of single particles, 3 mm³ cubes of olive cake and pine, 3×3 mm needles of *Miscanthus*, was measured using the apparatus shown in Fig. 2. The particle was placed on a small basket at the end of a ceramic probe and a K-type thermocouple was placed just touching the surface of the biomass particle. A water-cooled sheath was slid in place to cover the particle and the whole assembly moved transversely into the centre position on the centre-line of a small tube furnace sitting at the desired set-point temperature. A data logger and camera were started simultaneously, the cooling sheath was retracted and the particle was exposed to the furnace and allowed to ignite and the ignition process recorded. Thus, the particle was not exposed to radiation from the furnace before the water-cooled sheath was retracted.

The dust layer ignition experiment was conducted according to the British Standard BS EN 50281-2-1:1999. The minimum temperature of a hot surface, which will result in the decomposition and/or combustion of a dust layer (100 mm diameter and 5 mm height, <212 µm particles)

was measured. The lowest temperature for ignition within 30 min, time to ignition, type of ignition seen and plate temperature were recorded.

Self-ignition temperatures and ignition induction times were measured for some of the fuels. The BS EN 15188:2007 standard method was used which utilizes different basket or heap sizes with the aim of extrapolating fuel behaviour to large volumes representative of industrial silos. For each biomass the experiment was repeated for three different sample volumes, namely 49, 286 and 3637 cm³. The critical ignition temperature was evaluated for each sample volume, and ignition delay times also were recorded. These were taken to be the time required for the sample temperature to exceed that of the oven by 60 °C.

3. Results

The characteristic temperatures obtained from the TGA temperature programmed combustion experiments in air are given in Table 2. For all biomass samples multiple peaks were observed during the devolatilization stage, followed at higher temperature, by a well-resolved char combustion peak, as illustrated in Fig. 3. Slightly different characteristic temperatures are evaluated using the different methods described later in this paper. In particular, the T_{IC} method is difficult to implement in cases where there is more than one volatile combustion peak, and T_{MWL} gives a poor indication of the ease of initial decomposition. We consider the T_{DTA} and $T_{1\%/min}$ to be better indicators of the on-set of combustion. On this basis, the general order of reactivity is olive > > sunflower husks, *Miscanthus* > red-berry juniper > mesquite > plane, pine. As discussed later, the reactivity of olive is high since there is evaporation of oil at low temperatures. Reactivity is also influenced by the presence of catalytic metals in the fuel, particularly potassium salts (e.g. [13,14]). Residues such as sunflower husks and grasses, such as Miscanthus can be high in these salts compared to woody biomass. For example, according to the ECN Phyllis database [15], sunflower husks have 21% K₂O in the ash, and Miscanthus can have up to 50% K₂O in the ash [16].

Fuels were also studied by TGA coupled with FTIR spectroscopy, which enabled evaluation of the apparent first order kinetics for pyrolysis given in Table 2 and an estimation of the volatile composition given in Table 3. Kinetics for the main pyrolysis process for the range of 96 to 86 wt.% were evaluated assuming apparent first order kinetics given in Table 2, and predict a reactivity order at 250 °C of olive cake \approx sunflower husks > mesquite > *Miscanthus* > red berry juniper > pine > plane. This is slightly different to the reactivity order predicted by the onset of combustion. The olive cake and sunflower husk kinetics still contain a contribution from the evaporation of oils, even at these values of alpha. Evaporation of fatty acids and esters was identified by PY-GC-MS at 250 °C but these results not shown here. Consequently rapid pyrolysis is predicted for these fuels at low temperature as discussed in the next section. Interestingly, the LFLs

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Proximate and ultimate analysis of the biomass fuels used in this study.

	Pine heartwood	Mesquite	Plane	Red berry juniper	Olive cake	Sunflower husk	Miscanthus
Proximate analysis							
Moisture (% ar)	7.4 ± 0.3	6.1 ± 0.2	6.86 ± 0.04	5.67 ± 0.07	6.40 ± 0.03	7.1 ± 0.5	4.70 ± 0.04
Ash (% ar)	2.1 ± 1.2	5.84 ± 0.08	2.84 ± 0.03	2.7 ± 0.4	11.0 ± 0.1	5.6 ± 0.3	3.0 ± 0.4
Volatiles (% ar)	68.3 ± 0.7	61.3 ± 0.7	68.3 ± 0.2	68.4 ± 0.7	59.79 ± 0.07	61.8 ± 0.5	69.59 ± 0.05
Fixed carbon (% ar)	22.23	26.77	21.96	23.20	22.78	25.47	22.67
Ultimate analysis							
C (% daf)	55.16 ± 0.07	54.40 ± 0.07	50.0 ± 0.2	52.0 ± 0.4	54.15 ± 0.04	54.84 ± 0.03	49.57 ± 0.03
H (% daf)	6.5 ± 0.1	6.07 ± 0.03	5.51 ± 0.05	5.9 ± 0.7	6.3 ± 0.7	6.4 ± 0.2	5.9 ± 0.7
N (% daf)	0.50 ± 0.01	1.51 ± 0.02	0.71 ± 0.05	0.45 ± 0.12	2.59 ± 0.15	2.56 ± 0.09	1.06 ± 0.27
O ^a (% daf)	36.93	36.98	42.80	40.82	35.50	35.01	42.84
$GCV (MJ kg^{-1}) (daf)$	22.80	21.95	19.96	20.88	21.90	22.57	19.12

^a By difference.

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