



Low temperature ignition of biomass



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ARTICLE INFO

Article history:

Received 17 October 2014

Received in revised form 13 February 2015

Accepted 17 February 2015

Available online 29 March 2015

Keywords:

Biomass

Ignition

Smouldering combustion

Spontaneous combustion

Self-heating

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 co-firing 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

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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while early harvested *Miscanthus* was supplied by Rothamsted Research, Harpenden, UK. The fuels were milled to a particle size of <212 μm prior to their analysis. Fuels were analysed for proximate analysis 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

Table 1
Proximate and ultimate analysis of the biomass fuels used in this study.

	Pine heartwood	Mesquite	Plane	Red berry juniper	Olive cake	Sunflower husk	<i>Miscanthus</i>
<i>Proximate analysis</i>							
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
<i>Ultimate analysis</i>							
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.

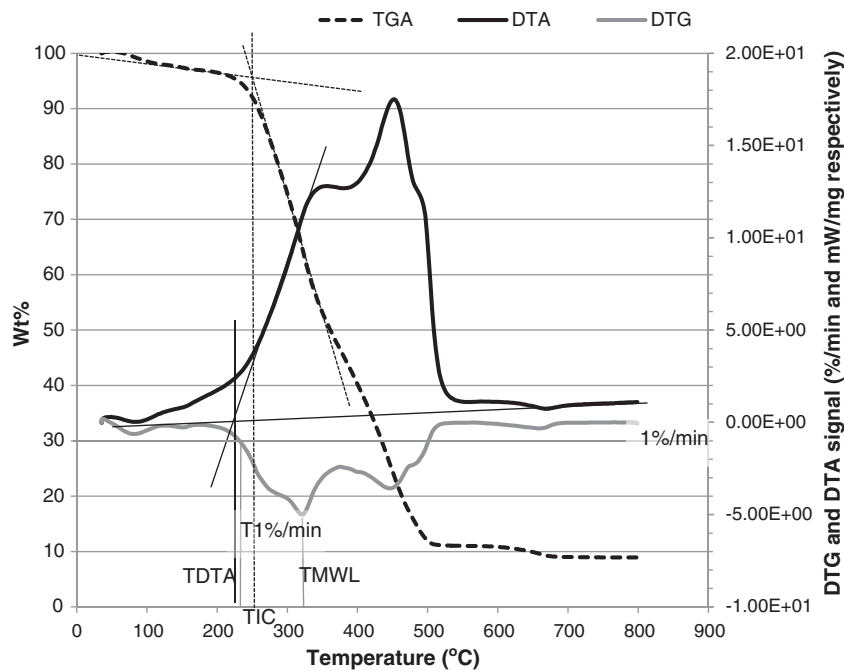


Fig. 1. Typical profiles from the STA experiments in air and illustration of how T_{DTA} (solid lines), T_{MWL} , $T_{1\%/min}$ (grey lines) and T_{IC} (dashed lines) are evaluated. This example is mesquite.

calculated from the estimated volatile compositions (Table 3) are very high (15–34%), because of the high concentration of inert components, mainly water vapour, present. Hence, the high LFL calculated here implies that ignition of the volatiles would be low risk in a well-ventilated area and in the absence of an ignition source. However, in practice, during some situations such as storage it is likely that water vapour would be absorbed by the surrounding biomass pile. In this case, the LFL reduces considerably to 6–8%, nearer to the LFL of methanol (6.7%) and thus volatile ignition risk increases. Also, in practice, biomass handling and utilization are often in an air atmosphere and the volatiles released during the pyrolysis process may be ignited. This in turn would have an effect on the devolatilization characteristics of biomass in a thermally accelerated process.

During dust layer experiments flaming combustion was never observed, only smouldering combustion. Thus, temperatures of the heated surface are insufficient for auto-ignition of the volatiles. For all the fuels studied here, the minimum temperatures for ignition within 30 min were in the range of 290 (olive cake) to 320 °C (pine). This is interesting, because at these temperatures, the pyrolysis rate of lignocellulose becomes rapid and in fact these temperatures are close to the T_{MWL} in

the TGA experiments (Table 2). For the dust layer and TGA experiments, these results point to a mechanism whereby pyrolysis evolves combustible products, highly diluted by reaction water vapour and CO_2 , which do not ignite. As devolatilization nears completion, air can diffuse to the highly reactive char product, which then reacts rapidly and exothermically.

Single particle experiments were conducted for three fuels, olive cake, *Miscanthus* and pine, and these also showed a similar ignition mechanism. A typical temperature–time profile for a suspended olive particle is given in Fig. 4. The temperature profiles for each particle were compared with the video footage, and each stage of combustion was visible. For all the fuels, the particles first pyrolyse (blackening of the particle and smoke production), followed by an ignition delay period, before the recording of an exotherm, and a concurrent visual observation of char combustion (a glowing red particle). Note that for large particles, moisture release will overlap with volatile release because of the temperature gradient through the particle. Ignition delay time was seen to increase as the temperature of the furnace decreased, and a logarithmic relationship was observed (see later).

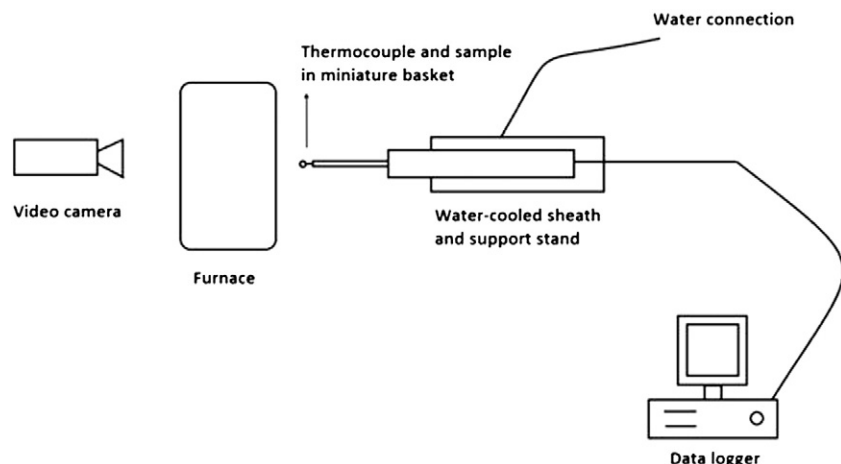


Fig. 2. Single particle combustion experiment.

Table 2

Onset of initial combustion temperatures (°C) evaluated by different methods during combustion, and kinetic parameters measured during pyrolysis.

Fuel	T _{IC}	T _{DTA}	T 1%/min	T _{MWL}	E _A (kJ/mol)	LnA (s ⁻¹)	k _{523K} (s ⁻¹)
Olive cake	192	170	183	295	37.26	1.0042	0.000530
Mesquite	246	209	233	310	81.17	10.97	0.000454
Sunflower husk	236	217	225	286	57.47	5.2126	0.000334
Miscanthus	244	219	223	286	63.80	7.1354	0.000532
Plane	239	224	237	323	72.13	8.4897	0.000304
Pine	271	236	236	330	56.39	4.9125	0.000317
Red berry juniper	269	239	230	325	65.40	6.8699	0.000283

Ignition delay times and critical temperatures were also recorded for two fuels (softwood chip and sunflower pellets) using the standard testing method for assessing spontaneous combustion in piles (BS EN 15188:2007). Critical temperature is the lowest temperature for which self-heating occurs in a biomass pile to a point where ignition happens. The larger the pile the lower the critical temperature and the longer the ignition delay period. Results can be interpreted based on the approach developed by Frank-Kamenetskii [9] from the work of Gray and Lee [17] and Boddington et al. [18]. According to this approach the activation energy for spontaneous combustion is measured as 139.1 and 206.8 KJ mol⁻¹ respectively for sunflower husk pellets and soft wood chip. This also demonstrates that sunflower husks are more reactive and have a higher ignition risk than wood pellets, as was observed in all other experimental tests.

4. Discussion

Fig. 5 combines data concerning ignition delay and set point temperature that have been measured on different biomass. This consists of both single particle tests, and dust layer tests, i.e. data is for samples close to or above the critical temperature. Data from basket tests are not included since this data was measured at the critical temperatures and much longer ignition delays are expected during these circumstances. This relationship enables an estimation of ignition delay at lower temperature and regardless of fuel type. For example, ignition delay times for fuels held isothermally at 70 °C or 150 °C are predicted to be 423 and 16 days respectively.

There is scatter on the data in Fig. 5 which results in a significant error in the predicted ignition delay. This is partly due to the different masses used, and partly due to the different types of biomass, and presumably also related to whether the test is close to the critical

Table 3

Mass yields (wt.%), lower flammability limits (LFL) and combustible fraction (CF) estimated from STA–FTIR analysis.

	Olive cake	Red berry juniper	Mesquite	Sunflower	Pine	Plane
Acetaldehyde	1.08	3.53	4.87	5.86	6.31	8.47
Acetic acid	0.02	0.93	2.03	2.86	1.54	4.84
Acetone	0.25	0.50	0.65	0.75	0.74	0.88
Ammonia	0.09	0.10	0.10	0.12	0.12	0.11
Carbon dioxide	4.66	4.64	4.36	3.61	3.45	5.07
Carbon monoxide	0.13	3.39	2.38	2.10	2.49	3.49
Char	28.33	24.27	31.22	26.30	22.93	23.10
Ethylene	0.06	0.08	0.09	0.12	0.10	0.11
Formaldehyde	0.05	0.63	1.25	1.87	1.07	2.60
Formic acid	0.27	0.71	1.07	1.11	2.15	1.18
Hydrogen cyanide	0.00	0.02	0.04	0.07	0.01	0.01
Methane	1.80	1.98	2.13	2.15	1.84	2.05
Methanol	0.40	0.88	0.86	0.80	0.97	1.32
Phenol	0.35	0.83	1.22	1.12	1.37	1.20
Tar ^a	45.44	37.55	26.35	28.22	34.44	23.53
Water	17.06	19.97	21.38	22.94	20.46	22.06
LFL (% in air) ^b	33.7	22.0	19.3	18.4	17.7	15.4
Combustible fraction ^b	0.316	0.384	0.383	0.368	0.388	0.457
LFL (% in air) ^c	7.75	7.03	6.31	5.97	6.08	6.16
Combustible fraction ^c	0.625	0.798	0.829	0.866	0.867	0.859

^a By difference.

^b Including dilution effect of reaction water vapour, excluding “tar”.

^c Excluding reaction water vapour and “tar”.

temperature for self-ignition. Nevertheless, the linear trend implies that a *similar ignition mechanism* is taking place for all test methods; i.e. char formation prior to heterogeneous ignition of the char. With this in mind, it can be assumed that the ignition delay is related to how long pyrolysis takes for each different type of biomass. As pyrolysis proceeds during the charring process, the evolving volatiles keep the oxygen from accessing the freshly formed char. Once pyrolysis nears its end, oxygen is able to diffuse to the char surface, and the oxidation rate is rapid enough to produce a rapid rise in temperature of the char particle as a result of the exothermic combustion. Thus, it seems sensible to predict the ignition risk from smouldering combustion from how long it would take the biomass to achieve a certain level of pyrolysis conversion. A figure of 90% was taken as an estimate of the point where the inward oxygen flux is on average greater than the efflux of volatiles. The biomass char produced has a high surface area and is

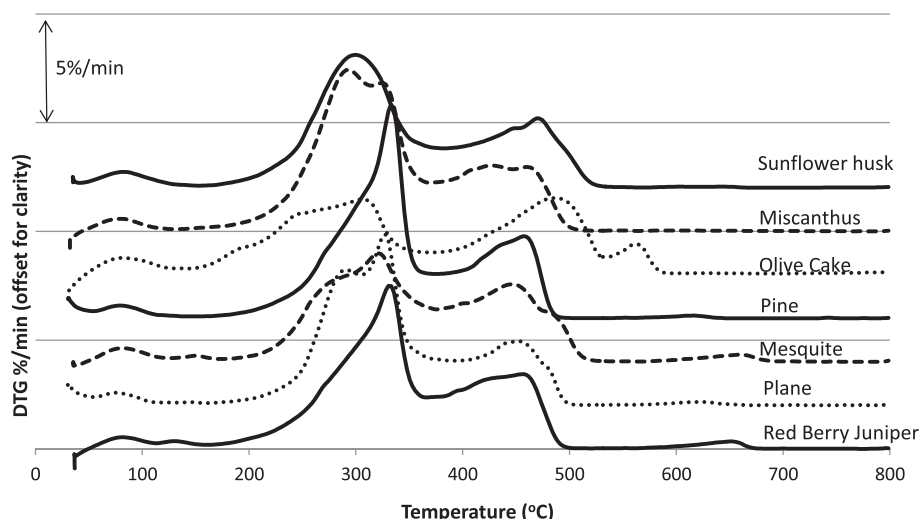


Fig. 3. DTG profiles for temperature programmed combustion at 10 K/min. Profiles have been offset for clarity.

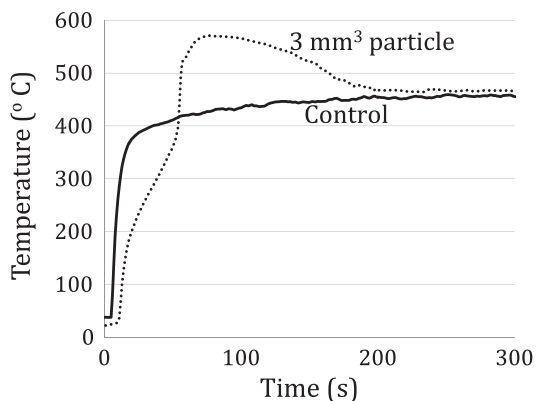


Fig. 4. Events observed during single particle combustion experiments [example is of an olive cake particle exposed to a furnace at 450 °C].

similar to an active carbon. Previously the role of a super reactive carbon has been suggested [19] and there is also evidence for this from the low spontaneous ignition temperatures reported for hydrocarbons adsorbed onto active carbons [20]. The ignition temperatures are about 300 °C.

The predicted conversion data calculated using the data in Table 2 (assuming 1st order) for selected fuels at 100 °C (isothermal) on this basis are shown in Fig. 6.

Other temperatures are tabulated in Table 4, based on the pyrolysis kinetics calculated for the main pyrolysis reaction (main peak), using the kinetics given in Table 2. Ignition delay predicted by the relationship in Fig. 6 fits better with this mechanism when extrapolated to low temperature, but overestimates it at elevated temperatures. Clearly more data is required to validate the empirical correlation.

In Table 4 we see the impact of activation energies on rates of reaction at low temperature. Those fuels with the highest activation energies (Plane, pine) are predicted as much more stable under slightly elevated temperature isothermal conditions. Olive cake, whose weight loss data relates to low activation energy is predicted to present the highest risk upon exposure to slightly elevated temperatures. From this data, it is clear that activation energy towards pyrolysis is a very important parameter when considering ignition risk. Ramírez [8] recognised this, and considered ranking fuels with respect to risk of spontaneous combustion according to their characteristic temperature (peak temperature during combustion in oxygen) and pyrolysis activation energy as shown in Fig. 7. Data from this work is also added to their data, but here, the temperature for maximum weight loss from combustion in air is used as the characteristic temperature. (In this work, TGA

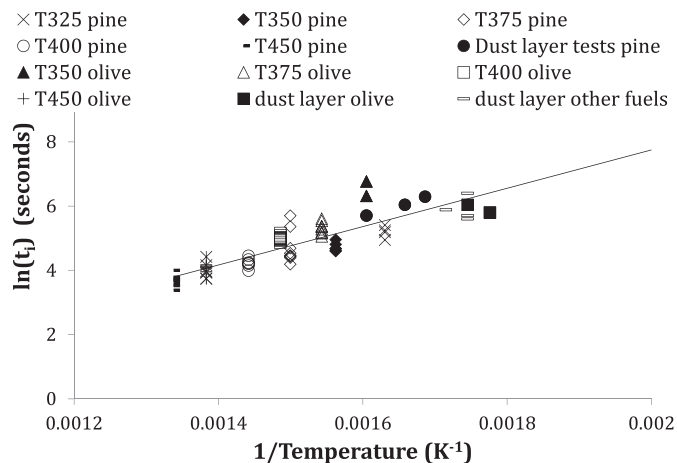


Fig. 5. Natural log (ignition delay) versus reciprocal set point temperature for single particle and dust layer measurements.

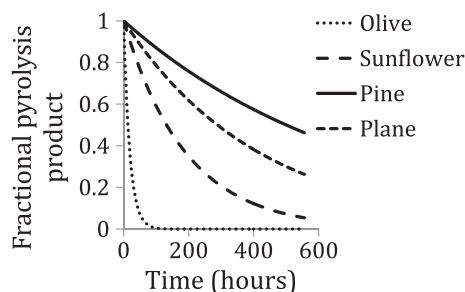


Fig. 6. Predicted pyrolysis product with time for fuels sitting at an isothermal temperature of 100 °C.

experiments were also attempted in oxygen following the method in [8], but only one fuel (Red Berry Juniper) gave a single characteristic peak; all others still showed well-separated devolatilization and char combustion events. Thus, T_{MWL} in air is used for our data in Fig. 7.) According to the approach used in Fig. 7, olive cake, sunflower husk and *Miscanthus* all fall into the “high risk” category, while the remaining woods fall into the medium risk category.

5. Conclusions

Ignition of seven biomass fuels has been evaluated using STA, single particle combustion, and dust layer experiments. Differences in the onset of combustion between the six fuels, and kinetic parameters were used to develop the evaluation tool for ranking ignition risk. Low temperature volatile release was observed for olive cake, which involved the low temperature evaporation and cracking of the vegetable oils, as confirmed using pyrolysis–GC–MS analysis. Further analysis of the volatiles by TGA–FTIR of the evolving volatile mixture identified fourteen volatile components whose lower flammability limits were in the range of 15–34% with dilution of reaction water, and 6–8% if it is assumed that reaction water is absorbed by surrounding biomass.

Single particle combustion and dust layer tests were developed. In both experimental arrangements ignition took place on the very reactive char particle formed after pyrolysis. Flaming combustion of volatiles was never observed. Thus, the ignition can be described as heterogeneous, and the combustion as smouldering. An ignition delay was observed (as the fuel pyrolysed), and ignition delay time increased exponentially as the isothermal temperature decreased. An empirical relationship was derived to estimate ignition delay times for low temperatures. Further validation of this equation is recommended to improve its robustness.

Ignition delays under isothermal conditions were estimated using the kinetics derived from the TGA data, and the calculated ignition delays are sensible based on available data. This approach does not account for the possible insulating effect of a heap of fuel where non-isothermal conditions occur.

An ignition risk rankings is assessed using kinetic parameters as well as characteristic temperatures. The residues and grasses, olive cake, sunflower husk and *Miscanthus* are predicted to have a high risk of

Table 4
Time to reach 90% conversion during low temperature pyrolysis (hours) [assuming isothermal conditions] assuming the kinetics given in Table 2.

Fuel	70 °C		100 °C		150 °C		200 °C
	h	day	h	day	h	day	h
Olive cake	132	5	44	2	10	0.4	3
Mesquite	25,312	1055	2565	107	116	4.8	10
Miscanthus	1970	82	389	16	44	1.8	8
Sunflower husk	2651	110	438	18	39	1.6	6
Pine	12,699	529	1661	69	106	4.4	12
Red berry juniper	1821	76	371	15	43	1.8	8
Plane	6058	252	958	40	79	3.3	11

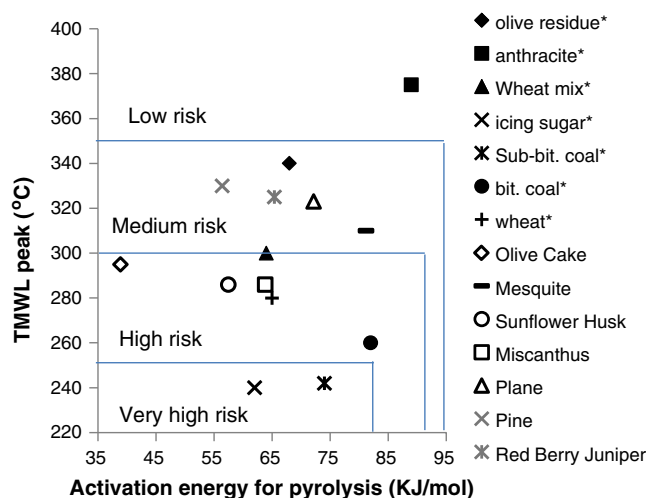


Fig. 7. Risk ranking, based on the approach of Ramirez et al. [8]. Asterisked data is from Ramirez et al.; all other data is from this work.

low temperature ignition. The woods, plane, mesquite, pine and red berry juniper, are predicted to have a medium risk of low temperature ignition.

Acknowledgement

This work was funded by BF2RA (Biomass and Fossil Fuel Research Alliance) grant #10. Funding from the EPSRC Centre for Doctoral

Training in Low Carbon Technologies (EP/G036608) is also gratefully acknowledged. Mr S Chilton is acknowledged for the data on Miscanthus in Fig. 3.

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