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Ashman, JM, Jones, JM and Williams, A orcid.org/0000-0002-9841-3203 (2018) Some Characteristics of the Self-Heating of the Large Scale Storage of Biomass. Fuel Processing Technology, 174. pp. 1-8. ISSN 0378-3820

https://doi.org/10.1016/j.fuproc.2018.02.004

Some Characteristics of the Self-Heating of the Large Scale Storage of Biomass.

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Abstract

Increasingly large quantities of biomass are being transported and stored for use in bioenergy applications. This large storage of biomass is liable to undergo self-heating sometimes leading to ignition and fire. Numerous studies on both the laboratory scale and by using theoretical analyses have been made in order to predict their behaviour but these are made on the basis of a number of simplifying assumptions. It is clear from studies reported here of self-heating in 40 kt storage piles of wood pellets that the process is much more complex than the simpler models suggest since thermal waves are observed.

Keywords: biomass; large scale storage; self-heating

1. Introduction

Stored combustible fuels such as coal [1] and biomass [2-5] are liable to self-heat which can, under certain conditions, lead to ignition. This phenomenon has been known for many years and the first theoretical studies on the ignition of cellulosic materials [2-6] were based on earlier work relating to explosive ignition of gases; this work, particularly by Frank-Kamenetskii, is cited in these references. In view of these hazards, regulations have been developed in most countries to govern the transportation and storage of these materials, and appropriate testing methods established to estimate the fire risk eg. [7,8]. In recent years, biomass is being used in much larger quantities, particularly for power generation [9], than was envisaged when these test methods were developed and this poses a number of additional safety issues.

The technology for the safe handling of coal is well established, but this is not the case for the large scale transportation and storage of biomass. In addition there are a variety of types of biomass fuels which may be in the raw state, or processed into the form of pellets, or may be washed or torrefied. Although biomass shares many properties with coal, there remain many disadvantageous features such as a larger content of volatiles that can evolve at lower temperatures than for coal. In addition, the porous nature of biomass, particularly in the pellet form, permits the ingress of oxygen and moisture which can increase the susceptibility to bacterial attack; this in turn can increase the possibility of self-heating and ignition. As biomass stockpiles increase in size this becomes even more of an issue and there have been several instances of fires in storage silos. Consequently, there is a need to improve our knowledge of the underpinning chemistry and physics of these events.

Both experimental and theoretical approaches have been made of the ignition process which should be complementary, but often look at different aspects. In the former, self-ignition temperatures and associated ignition induction times have been assessed by a standard method which utilizes different basket or heap sizes with the aim of extrapolating fuel behaviour to large volumes representative of industrial silos or storage piles [7,8]. Thermogravimetric analysis techniques, which are less time intensive but use small samples, have been conducted and compared with this standard method to determine the relative ignition risks of different fuels [10-15].

The second approach is the use of theoretical studies which involve mathematical analysis of heat conduction and kinetic parameters in geometrically simple and isotropic systems [2,4,5]. More recently, detailed analyses have been made of large quantities using CFD methods [16-18]. These models, representing real situations are complicated by the fact that in addition to heat released by the oxidation of the fuel by the ingress of molecular oxygen, the role of moisture [19-21] and heat released by microbiological action have to be considered [19,22-27].

This paper aims to examine experimentally the pre-self-ignition behaviour of large scale (40 kt) storage units and to examine how it compares with theoretical analysis and laboratory tests.

2. Materials and methods

2.1 Materials used

Most of the experiments were undertaken using compressed pine wood pellets but some laboratory measurements were using agricultural residues (Miscanthus, wheat or barley straw), and torrefied pellets consisting of mixed wood materials. The proximate and ultimate compositions of typical wood pellets are given in Table 1. The moisture content is 4.8

wt%.The size range of the pellets used is that typically 97 wt% of the pellets are in the range of 6.3 to 10 mm with a diameter in the range 6-10 mm, and their compact density as received is 698 kg/m^3.

Table 1. Typical Data for Ultimate and Proximate analysis of wood pellets

	As received	Dry basis
Moisture %	4.8	
Ash %	2.5	2.5
Volatile matter %	76.8	80.7
Fixed carbon.%	16.1	16.8
Carbon %	48.87	51.33
Hydrogen %	5.61	6.1
Potassium %	0.12	0.13
Chlorine %	0.01	0.01
Nitrogen %	0.28	0.29
Sulphur %	0.02	0.02
Gross CV MJ/kg	19.76	20.76

2.2 Laboratory Studies

The temperature changes resulting from the addition of water to the samples of pellets were determined using a thermocouple and a FLIR Model 6 infrared camera. The biomass samples were weighed into 1L polyethylene vessels and water added up to 40% (w/v). After the addition of the water, images were taken with an infrared camera monitoring the heating profile in each sample vessel for a period of 2-4 h.

Measurements were made of the pH of water after it was added to the biomass. 10g of biomass samples were weighed into a 100mL glass beaker and 50mL of demineralised water (at 20^{o}C) was then added to the beaker. pH measurements were made for 520 min using a Mettler Toledo SevenMulti pH meter.

Thermogravimetric (TGA) analysis was undertaken using a Perkin Elmer STA6000 instrument. Samples of ground pellet (< 80 µm) were used, and the sample sizes used for the experiments were approximately 5mg. An initial temperature ramp of 2°C/min from 30-900°C was used in a stream of nitrogen gas and the sample was then held at 900°C for 30 min in an air stream. The results were plotted using derivative weight loss (% loss/min) giving the characteristic peak temperatures, and the estimation of apparent first order pyrolysis kinetics as previously described [13,14].

2.3 Studies with Large scale (40kt) Biomass Storage

Two large biomass stores, Pile A and Pile B, were studied each containing 40 kt of biomass but with slightly different depths (6-8 m and 10-13m respectively). A schematic aerial view of the geometrical shapes is shown in Fig. 1.

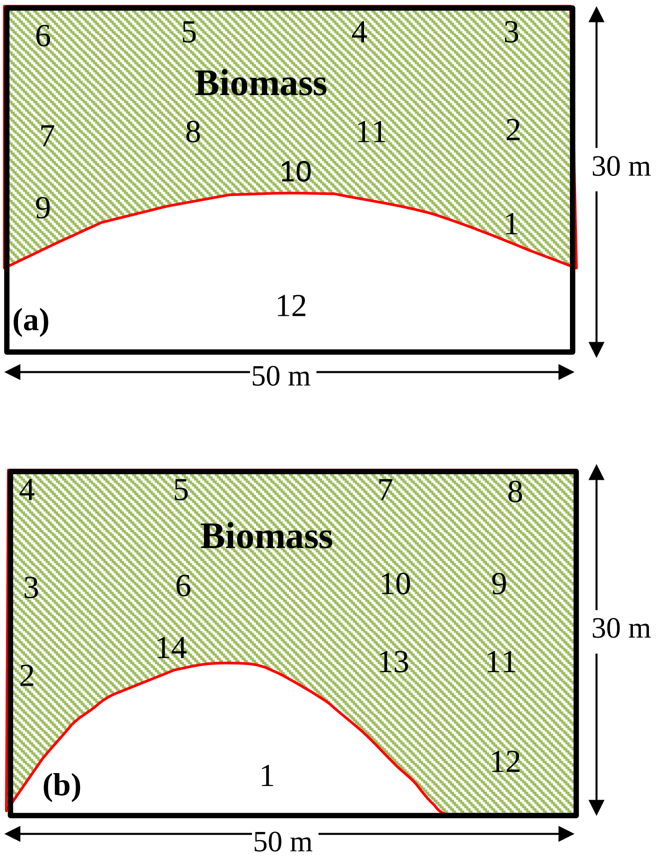


Fig. 1. Diagrammatic aerial view of the biomass stores. (a) Pile (A) depth: 6-8m over monitored area. (b) Pile (B) depth: 8-10m over monitored area. Numbers refer to sampling positions (in or above the bed).

The volume in each case is about 52,600 m^3 and the moisture content for these samples when loaded into the store was 7%. Both stores, which measured 30 m x 50 m, were filled to an even depth on three sides of the stores and take the natural angle of repose for biomass down to the base of the store (approx. 60°), the edge of the biomass is shown by the red line. Measurements of temperature and gas composition within the piles at varying depths were made by bundles of 5mm internal diameter PVC sampling tubes and K-type thermocouples. Temperature measurements were made from the floor (0 m) to the top of the pile at 1m intervals and gases at every 2 m intervals. Results are presented here from the sampling bundle, located in Pile A at location 11 and in Pile B at location 13, as shown in Fig 1. Samples were also taken above the bed at 1m intervals. The external ambient temperature was measured as were the relative Humidity and temperature at 1m above the bed.

Samples of the volatile organic compounds emitted from the two piles were measured above the surface and within the bed using the ppb RAE 3000 Gas Detector. The concentrations of CO, CO_2, O_2, SO_2 and flammable gases were analysed using a Drager Xam 7000 instrument. Volatile organic compounds (VOC) were analysed by sampling tubes for formaldehyde, acetaldehyde, n-pentanal, n-hexanal, furfural and glutaraldehyde at a flow rate of 0.3L/min for 45min, and charcoal sampling tubes for terpenes, acetone, and butanoic and octanoic acids at a flow rate 0.2L/min for 60 min.

The microbiological activity on spot samples of pellets taken at random from within Pile A and other Piles where heating was not observed were measured using dip slides. 10g of milled biomass sample was weighed with 40mL of demineralised water in a 50mL centrifuge tube at room temperature, and agitated for 2 min. The supernatant was then decanted on to the dip slides. Two types of were used, a sterile nutrient agar which grows bacteria, and a second which grows fungi, bacteria and yeasts. They were incubated for 48 hours (72 h for yeast) at 30^{o}C. The results are then compared visually with the growth guide supplied with the dip slides.

The microbiological contents in air samples taken 0.5 m above the centre of the wood Piles at location 11 in Pile A and location 13 in Pile B were determined using a Sartorius AirPort MD8 portable air sampler. The total viable bacteria count (TVC) was made using Tryptone Soya Agar (TSA) and fungi (Sabourguard) agar plates for sample collection. The samples were taken at 125 mL/min for 4 min. The plates were incubated at 22^{o}C for 3 days and provided information on the in-colony forming unit/plate for bacteria and the number/plate for fungi.

3 Experimental Results

3.1 Laboratory Studies

For the temperature-development studies the biomass samples were in the form of pellets, milled pellets, and pellet fines (dust) resulting from the pellet transportation. They were weighed into 1L polyethylene sample vessels and deionised water was added and the temperature rises were observed. The cases studied for the addition of 40% (w/v) of the samples are given in Fig. 2 and it was found that the temperature rises are similar for the different samples. The temperature rises observed are consistent with values calculated from the heat of wetting using the value of the heat of wetting given by Kajita et al. [21]. This experiment was repeated using straw but the temperature change in this case was very small and was not visible by the infra-red camera so are not shown here.

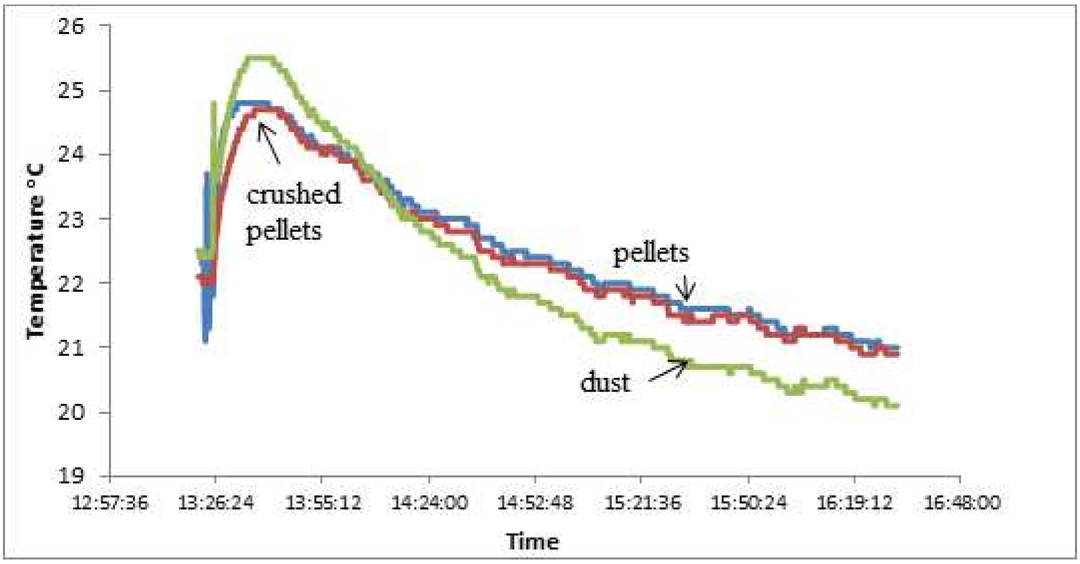


Fig. 2. Change in temperature when biomass samples from pellets, crushed pellets and biomass ‘fines’ (dust) are added to water.

It was observed there was a physical change in volume of the wood pellets due to water addition. Swelling of the pellets is seen with a 5%wt addition of water giving an increase of approximately 10% in volume; 40%wt water addition yields an approximate 80% increase in volume.

The pH values resulting from the addition of water were measured for a number of samples of wood pellets from Pile B as well as samples of Miscanthus and straw. The wood samples consist of two normal wood pellets, material from a ‘hot spot’, and from a projection on the surface of a Pile of a ‘chimney’ about 15 cm high which is thought to be due to moisture condensation. Similar ‘chimneys’ have been observed by others [27]. The data obtained are shown in Fig. 3.

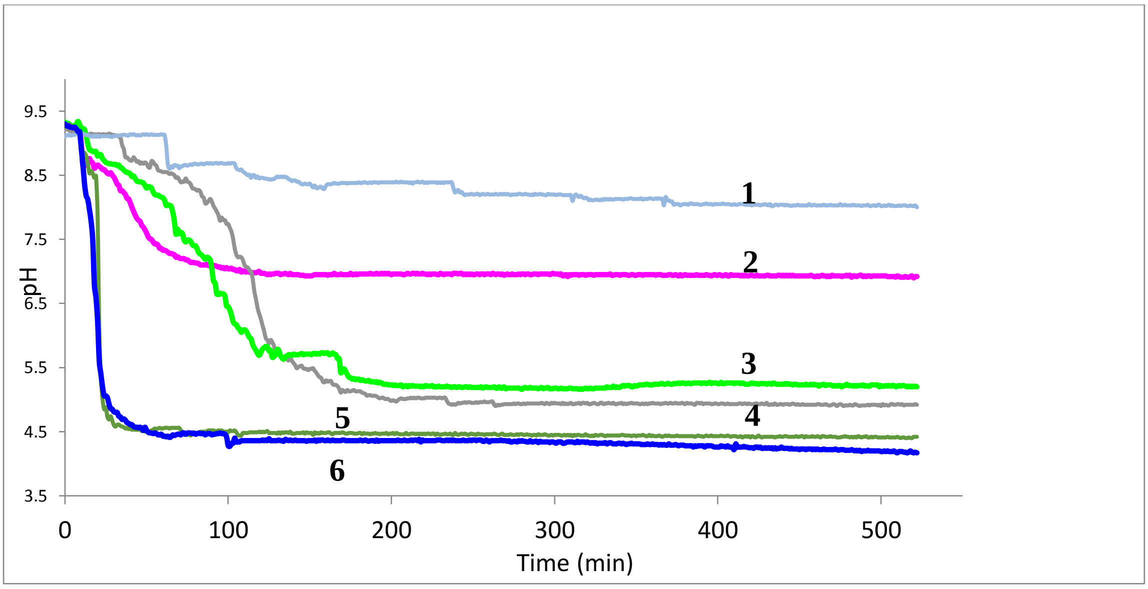


Fig. 3. Changes in pH when samples of wood, Miscanthus and straw pellets are added to water: 1, straw; 2, Miscanthus; 3, sample from hot spot in Pile B; 4, material from Pile B; 5, material from a ‘chimney’; 6, torrefied fuel.

There are significant differences between the values for the wood and the straw and Miscanthus samples, the increase in acidity being greatest for the woods, and interestingly the most acidic samples are the torrefied and the ‘chimney’ sample. This arises in part because of the solution of KCl from the biomass; dilute KCl solution has a pH of 7 and becomes moderately acidic as it becomes more concentrated, and this is seen in Fig 3. Additionally organic acids are produced from the decomposition of hemicellulose and are probably the major factor. The increase in acidity in turn has an influence on the level of microbiological activity [23]. The straws however contain 0.87 wt% dry basis of K and only 0.24 wt% Cl and this would result in the effect of the alkalinity of the KOH produced countering the acidity of the KCl and organic acid formation.

Thermogravimetric analysis (TGA) has been used as a means to examine the reactivity of fuels particularly in relation to self-heating. The activation energy, obtained using an apparent first order reaction, has been considered to be an important parameter to distinguish the spontaneous combustion tendency of coals [12] and has been used in a similar way with biomass [12-15]. In the case of biomass, TGA is a useful method to give an indication of the amounts of the major components, hemicellulose, cellulose and lignin in the sample.

Such TGA plots were obtained for pyrolysis under a nitrogen atmosphere for wood, torrefied wood, straw and Miscanthus and these are shown in Fig. 4. The major peaks for cellulose are apparent for all four fuels, but in the case of the torrefied fuel the hemicellulose peak is absent; this is because the temperature required for the torrefaction process results in the decomposition and loss of the of the hemicellulose.

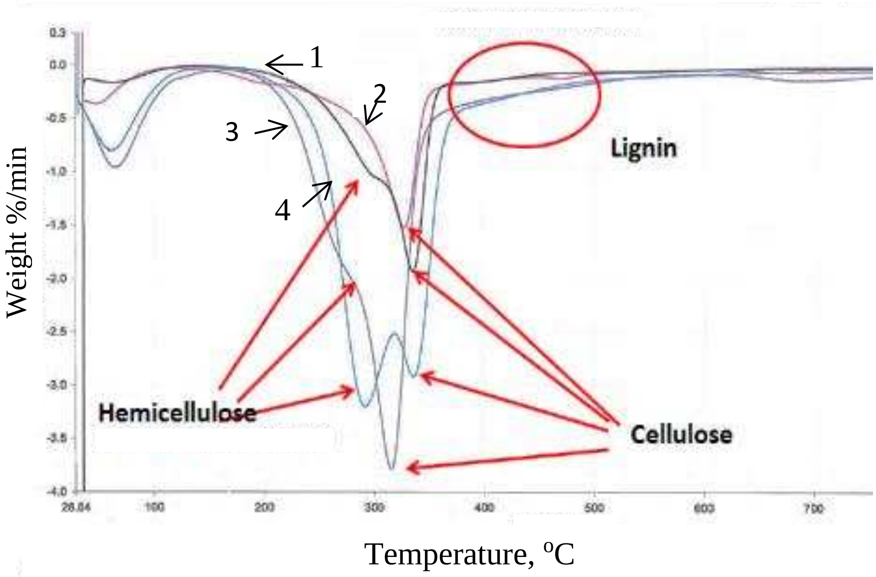


Fig. 4. TGA data, derivative weight (%/min) against temperature, for the decomposition of: (1) wood (black); (2) torrefied wood (pink); (3) straw (purple); (4) Miscanthus (blue).

Simultaneous thermal analysis of the wood sample was undertaken for 100 mol% air (79 mol% N_2, 21 mol% O_2) and a number of nitrogen/oxygen atmospheres (85 mol% N_2, 15 mol% O_2; 90 mol % N_2, 10 mol% O_2; 95 mol% N_2 ,5 mol%O_2) and 100 mol% N_2. The results for weight loss as a function of temperature are shown in Fig. 5 together with the DSC (differential scanning calorimetry) analysis of the heat flow showing the exothermic and endothermic regions.

The impact of ‘inerting’ with nitrogen gas on biomass oxidation and pyrolysis is seen from Fig. 5, where the weight loss is plotted against time to illustrate the effect on the reaction rates. The largest and earliest release of heat is given when air is used. Increasing the amount of nitrogen however does not have a significant effect, even with 95 mol% nitrogen there is still some oxidation presumably because the biomass contains chemically bound oxygen which results in the exothermic release of products on heating. Therefore nitrogen gas can only be used for control of fire and not for extinguishing it.

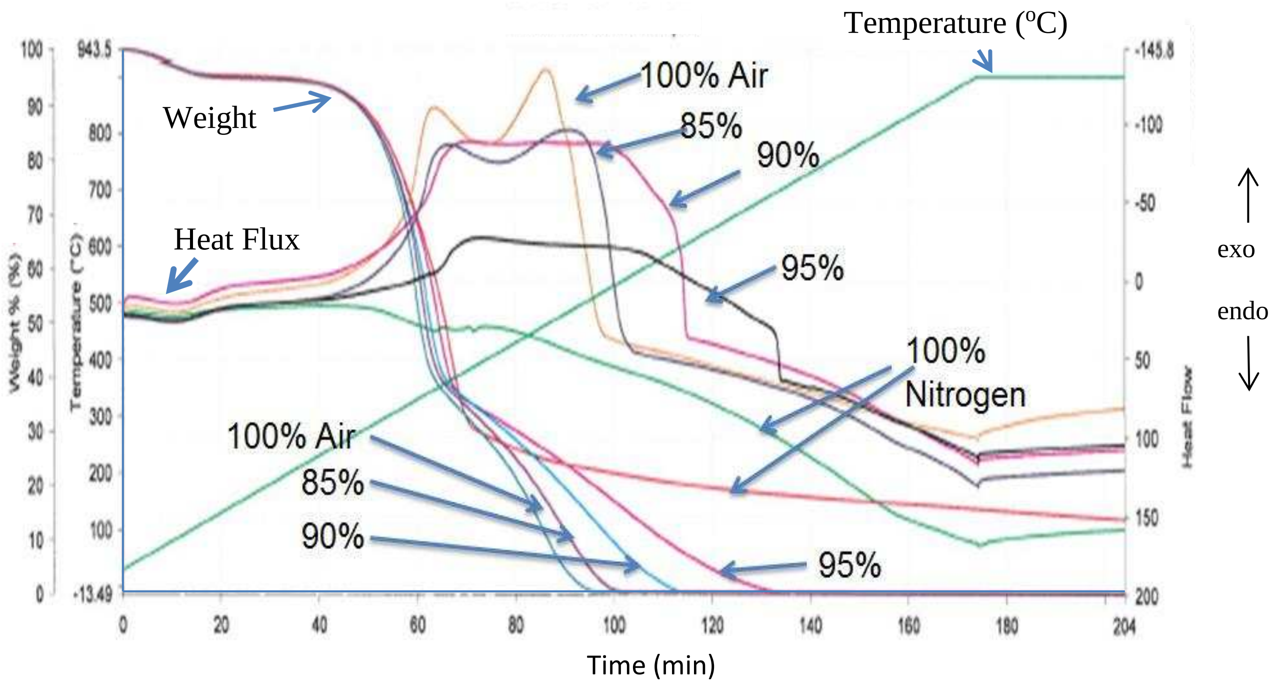


Fig. 5. Simultaneous thermal analysis (STA) plots of weight loss (%) against time and heat flux showing the reaction of wood in 100 mol% air, in ‘inerted’ nitrogen-oxygen atmospheres (85 mol% N_2, 15 mol% O_2; 90 mol % N_2, 10 mol% O_2; 95 mol% N_2 ,5 mol%O_2) and 100 mol% nitrogen. The linear change in temperature (5°C/min) is shown. The heat flux (mV/W) curves indicate the endothermic and exothermic reaction.

The first order apparent activation energies (Ea) for the early part of pyrolysis corresponding to hemicellulose decomposition were calculated and the results are given in Table 2. The values obtained range from 68.8 kJ/mol in 100% nitrogen to 75.4 kJ/mol in air with an error of ± 2kJ/mol.

The data obtained in air are consistent with data from other studies using the same method [13,14]; they are slightly higher than the values obtained by Guo et al. [24], but similar to earlier values obtained by this method as pointed out by these authors. The reaction rate constants, k, at 50°C and 100°C calculated from the data given in Table 2 are also given. The value for $k_{(50^oC)}$ are lower than that obtained by Guo et al. [24] although their values are for fresh pellet samples, the age of the pellets is an important parameter. The reaction rate constant with 100% N_2 is 14 times slower than with air and a similar ratio, 12, applies at higher temperatures (such as 100°C) given in Table 2 because of the similarity of the activation energies.

Table 2. Values of E and A for pellet wood pyrolysis under varying nitrogen concentrations

	E kJ/mol	A /s	Log $k_{(50^oC)}$ /s	Log $k_{(100^oC)}$ /s
100% N_2	68.8	1221	-7.39	-5.89
95% N_2/5% O_2	72.0	2524	-8.27	-6.73
90% N_2/10% O_2	73.6	3908	-8.36	-6.76
85% N_2/15% O_2	75.4	5878	-8.48	-6.84
100% air: 71%N_2/21% O_2	75.4	6138	-8.46	-6.82

3.2 Studies with the large scale (40kt) biomass storage piles

Schematic aerial views of the storage Piles are shown in Fig.1 and the stores are filled to an even depth on all three sides of the stores as described in section 2.3. Temperature profiles were made vertically through the two piles over an eight week period in Pile A and over a nine week period in Pile B. In Pile A, (8 m high pile) the maximum temperature increased from when the biomass was first delivered reaching a maximum temperature attained of 38.8°C at week 4 at a depth of 2 m from the bottom. It should be noted that the temperature of the top of the pile decreased due to a reduction in the ambient temperature. In Pile B (9 m high pile) the maximum temperature attained was 45.8°C after week 5 at a depth of 3m from the bottom. These results are shown in Fig 6.

Humidity measurements were made above the beds and in all cases they were between 50-60%. The control of humidity is an important control issue.

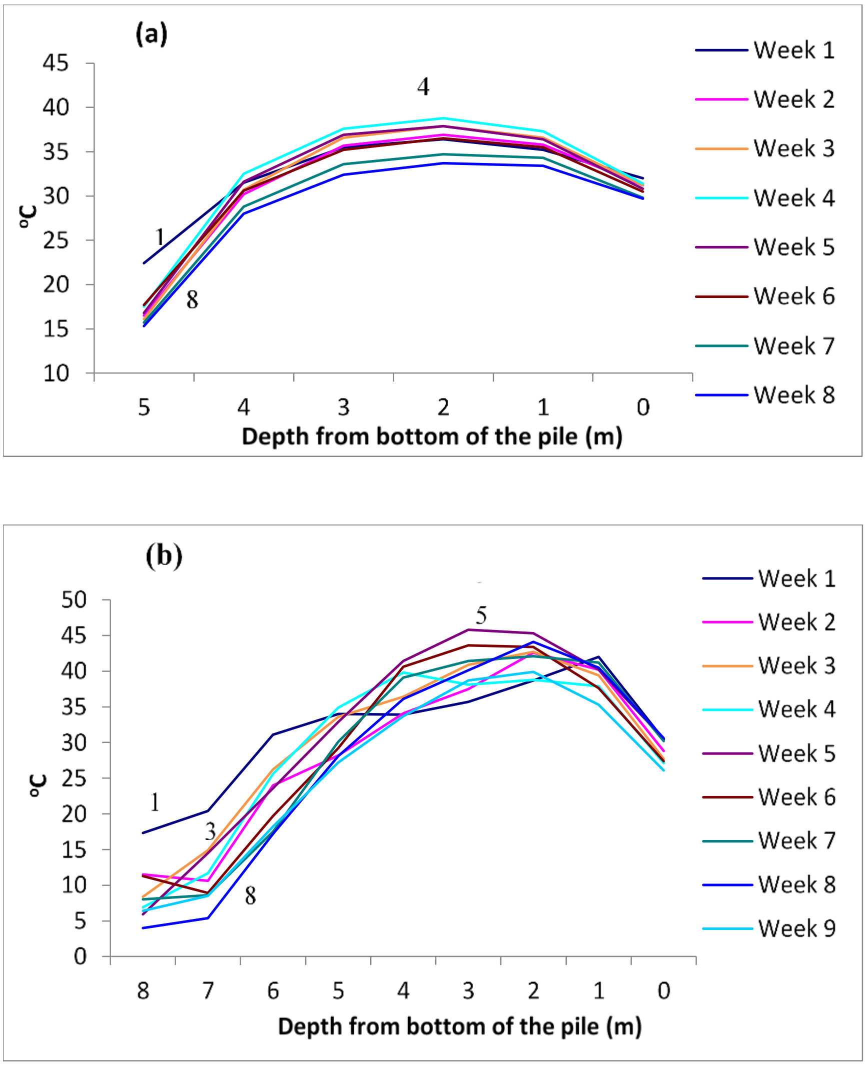
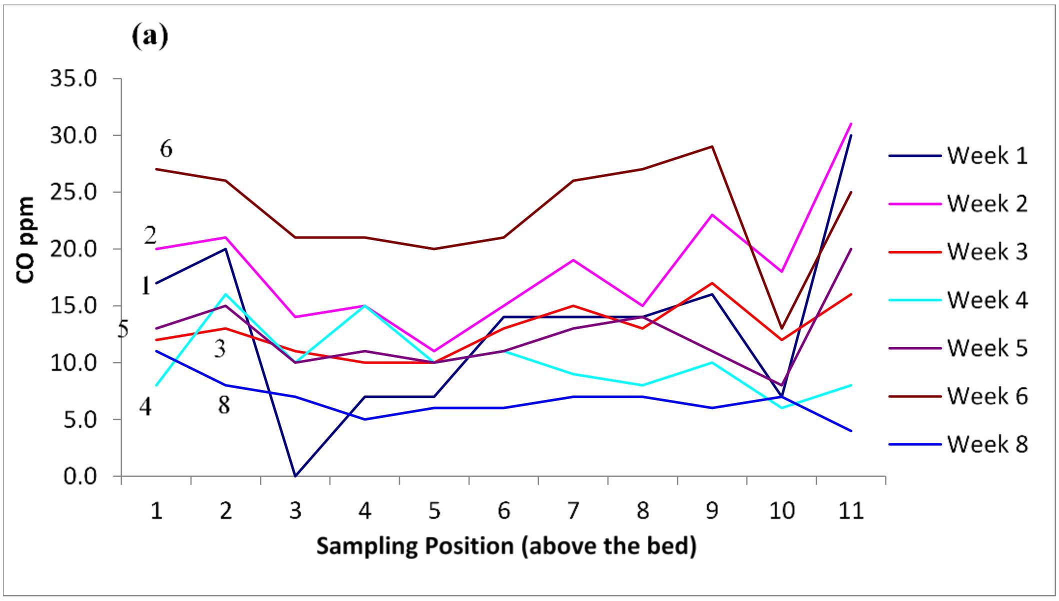


Fig. 6. Temperature profiles measured vertically through (a) Pile A and (b) Pile B at 1m intervals. The numbers refer to the number of weeks the biomass has been stored.

Measurements of the CO and CO_2 emissions were made immediately above the biomass bed for both piles at the sampling positions shown and the data for the CO emissions obtained are shown in Fig. 7 (a) and (b). In the case of Pile A, the CO results show a maximum value of about 25ppm for week 1 and, and after some slight variation, this decreases in all cases.



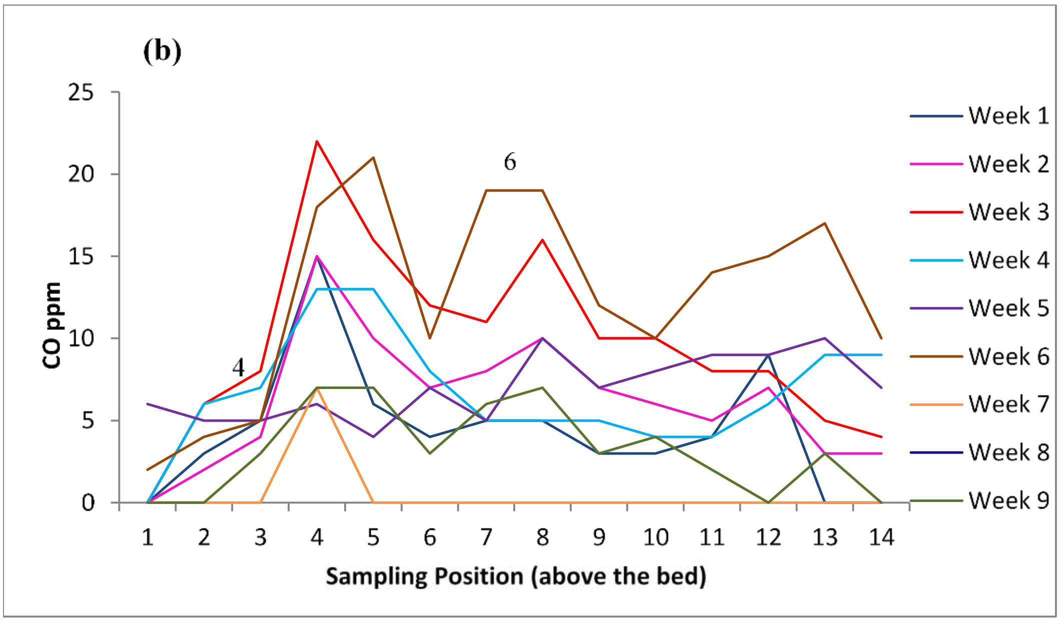


Fig. 7. Carbon monoxide measurements above (a) Pile A and (b) Pile B. The numbers on the plots refer to the number of weeks the biomass has been stored.

Pile B behaves differently in that the concentrations are not uniform and vary in a periodic manner with sampling position (that is, with the distance across the bed). This appears to signify a stratification effect with distance, and the position of maximum CO emission moves across the Pile with time after reaching a maximum. This is a similar pattern to the way the temperature changes: Pile A reaches a maximum temperature of 39°C after 4 weeks and Pile B reaching 46°C after 5 weeks, and then in both cases the temperature decreases, The CO emissions follow this trend with a time lag of about a week, presumably due to the slow reaction rate and thus the slow formation and release of CO.

The emissions of the volatile organic compounds (VOC) are shown in Fig 8. The VOC consist of aldehydes (mainly acetaldehyde) and ketones (mainly acetone) resulting from the microbiological breakdown of fatty acids on the wood pellets [24-26]. The experimental data given in Fig. (a) were obtained by sampling from above the Pile A at a number of locations which are defined in Fig 1(a). It is seen that in this case the VOC emissions approximately follow a pattern over the eight week period sampled irrespective of the position over Pile A. That is, after a brief peak at week 2 it then increases to a maximum in week 6 and then drops. It follows the same pattern as the CO release and also lags behind the temperature in the same way. It is linked to the extent of microbiological activity as discussed later.

The data shown in Fig 8(b) were obtained within Pile B at 2, 4, 6 and 8m depth. As might be expected the concentrations are very much greater within Pile B, and the highest concentrations are 2m from the top of the pile. The same pattern is seen as with CO emission from the pile, a maximum being reached and then a decline. This pattern is seen at all depths but is much smaller at the greater depths.

A second group of VOC are the terpenes (α-pinene, myrcene, limonene) which tend to follow the same pattern as the VOC, but are in very low concentrations and are thus not shown here. The terpenes are the volatile oils present in wood and are vaporized as the temperature rises without a chemical reaction being involved, although some may be formed by bacterial/fermentation processes. However, the terpene emission acts as a marker of the advancing thermal front and the CO acts as an indicator of the main reaction zone.

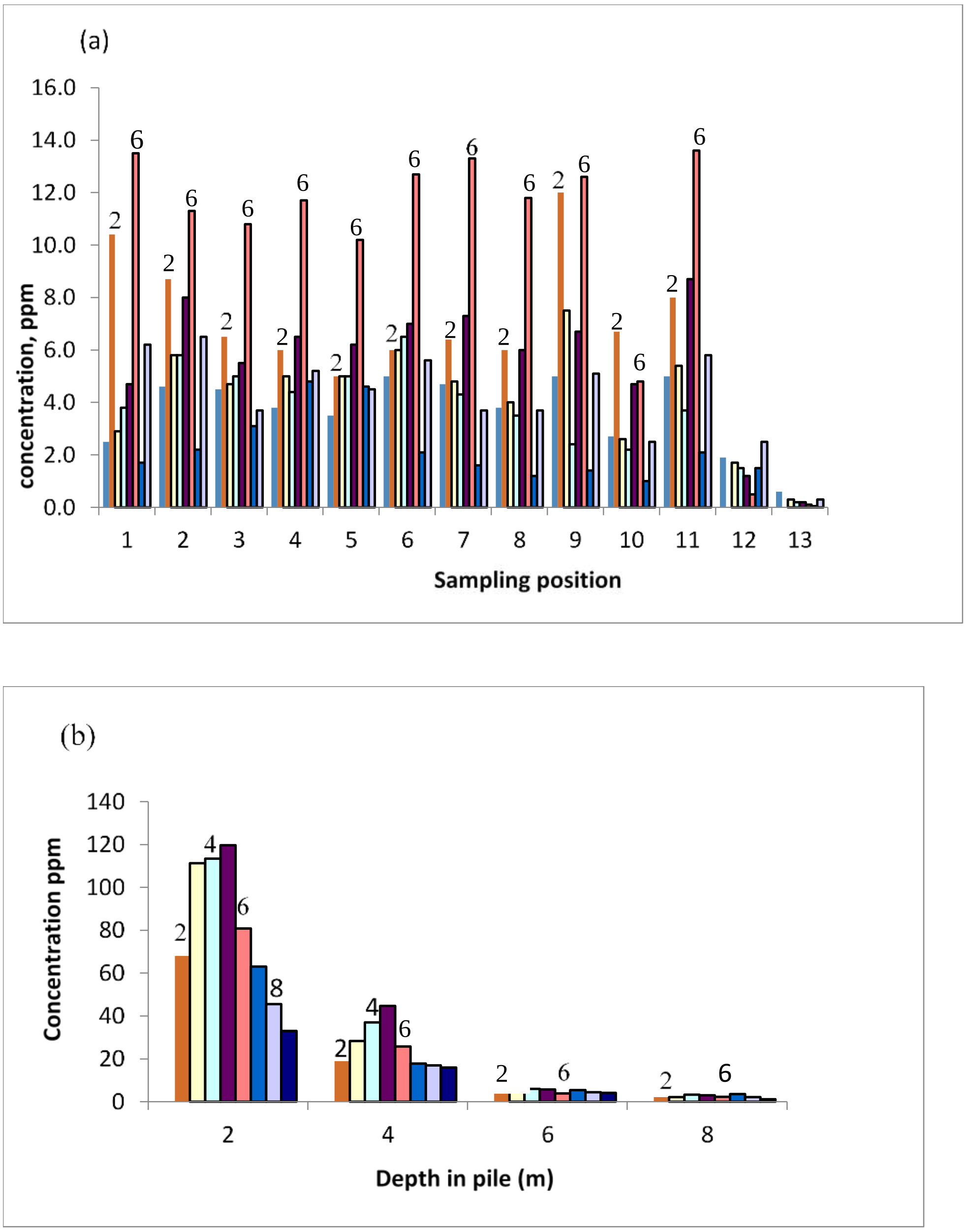
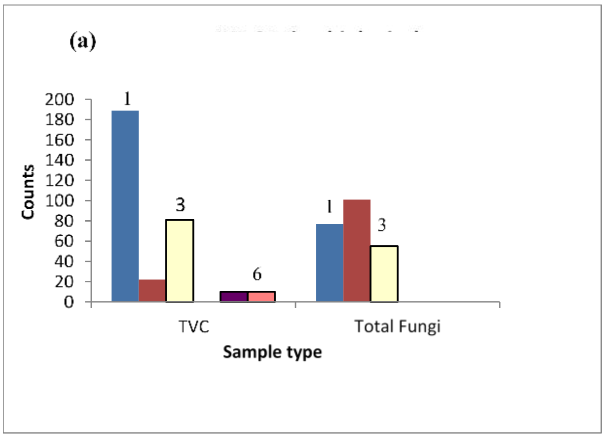


Fig. 8. Volatile organic compound concentrations as a function of time (the numbers refer to the number of weeks, but only some are indicated) in (a) above Pile A as a function of sampling position, and (b) in Pile B as a function of depth. Measurements were not made in week 1 in Pile B.

Studies have been made of the fungi present in biomass samples taken from within the Piles. Significant amounts of fungi (or moulds) are only found where heating of the Pile occurs, such as Pile B. But microbiological activity has been analysed on all conditions of pellets, although the extent may vary from load to load. The major fungi identified is Amorphotheca Resinae (also known as Cladosporium Resinae) and a number of strains were observed, namely: oidiodendron griseum, oidiodendron tenuissimum CBS=238.31, geomyces asperulatus, ovadendron sulphureoochraceum and pseudogymnoascus roseus. It is a common fungi and grows on glucose, glutamate or fatty acids present in biomass. Mesophilic fungi such as these are commonly found in piles at temperatures about to 20-30°C [22,23] and cause degradation with loss of dry mass as well as the release of CO_2 and CO.

Measurements have been made at 0.5m above Pile A and B of the Total Viable Count (TVC), that is, the total number of colony forming units which is a measure of the total amount of both bacteria and fungi, and the level of fungi present is also shown. These data are given in Fig 9 (a) and (b) and it is seen that the levels are highest in Pile B. The thermophilic reactions start at about 40-50°C resulting in the formation of CO. In this work the CO concentration was taken as a measure of microbiological activity because thermal oxidation is only significant above 80°C. The maximum temperatures reached in Piles A and B (39 and 46°C) do not reach the critical value leading to ignition.



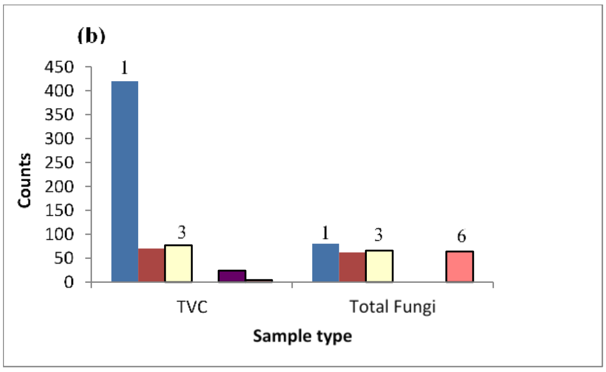


Fig. 9. Microbiological measurements above the bed: (a) Pile A, (b) Pile B. TVC is the Total Viable Bacteria Count. The numbers refer to the week the measurement was made; these were not made in all weeks and the measurements after week 6 are below the detection limit.

4. Discussion

4.1 General features of self-heating

The general features of the steps leading first to self-heating and then ignition are shown diagrammatically in Fig. 10. This diagram is based on a scheme given by Meijer and Gast [19] but with an added temperature rise which can result from the condensation of water, that is, if sufficient moisture is present. The next step is biological oxidation accompanied by the release of CO_2 and volatile organic species such as acids and aldehydes [19,22,23]. This can only take place if microorganisms are present in significant quantity, which is not always the case. Indeed many mathematical models omit this stage. Then biomass thermal oxidation starts with the release of CO, and finally, if the critical temperature is reached and if no preventative action is taken, the temperature would increase leading to ignition.

The wood pellet production process requires temperatures of about 110°C which would destroy the fungi and bacteria initially present, but the pellets can undergo ‘reinfection’ from fungi and bacteria during transportation. The rate of this process depends on the fines and moisture content of the pellets and thus the amount of microbiological action that can take place from batch to batch received by the biomass store will vary [22,23].

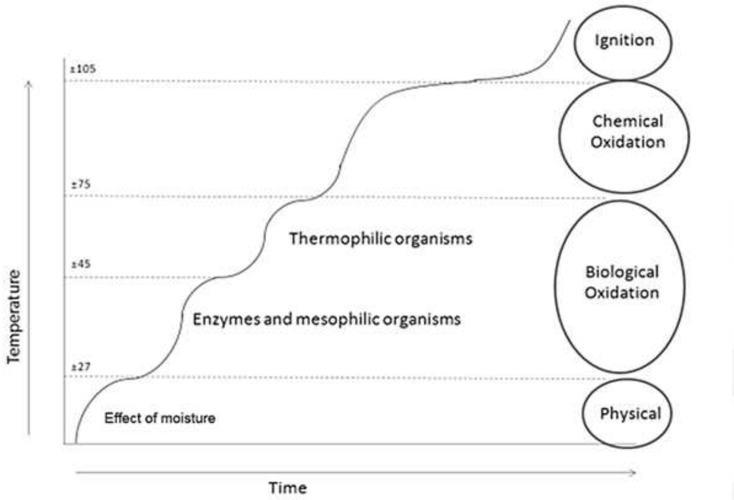


Fig. 10. Diagram showing the general features of ignition.

The processes shown in Fig. 10 can overlap and that the temperatures given on the vertical axis are indicative and may vary depending on the nature of the pellets and the reaction conditions. In particular the effects of moisture and the early stages of biological oxidation work in conjunction with one another. The level of microbiological activity could be deduced from the temperature rise in the biomass as well as from the carbon dioxide emitted from fatty acid oxidation and similar compounds on the woods or straws; a priori estimates are therefore difficult. It is known that as the temperature rise increases towards 75°C the thermal oxidation of biomass commences and in doing so kills off the microbial activity. The start of the thermal oxidation is marked by the release of carbon monoxide as well as carbon dioxide and flammable compounds such as formaldehyde, acetaldehyde, methanol and ethanol are produced as the temperature increases to about 105°C [14,15, 25,26]. The maximum temperatures reached in Piles A and B (39 and 46°C respectively) shows that rates of heat release does not reach the critical value leading to ignition, that is, the heat loss is greater than the heat generated. This is probably due to the heat required for the evaporation of water resulting from the control of humidity in the store; the other factor is probably the low level of thermophilic bacteria. Thus in terms of predicting the behaviour in a biomass pile it is necessary to understand the linked effects of moisture and the microbiological behaviour.

Once a critical temperature is reached rapid oxidation would occur, although this is not the case here, and its value depends on the 'ease of reaction' of the biomass. Various studies have been made to quantify what the critical temperature is for different biomass materials and the reactivity (or rate of reaction) after this point. These parameters would define risk of ignition bearing in mind that the crucial determining steps are the effects of moisture and the extent of microbiological action. The main predictors are the use of TGA [12-15] to measure reactivity, heated basket tests [7,8,13,16] and by direct thermochemical measurements [24, 25]. They only form part of the sequence of events leading to ignition since they do not take into account the thermal effects of microbiological heating and water condensation.

4.2 The use of TGA as a predictor

The experimental determination of the apparent first order activation energy, Ea, has been used to distinguish the spontaneous combustion tendency of coals which range from 70-90kJ/mol [12,15]. It was concluded in this work that this parameter is not so important for biomass since for most samples the values of Ea lie in a very small range, namely 63.5 kJ/mol to 68.3kJ/mol, as reported in their experiments [15]. These authors used a risk assessment [15] based on two parameters, the activation energy and a characteristic temperature based on the ignition of a sample in a TGA and using oxygen as the oxidant.

They studied a number of biomass fuels, and on this basis found that ‘straw’ is considered to have a medium risk and ‘wood chips’ have a high risk of self-heating [15].

Jones et al [14] have ranked the risk factors using similar method using air instead of oxygen that was used in reference [15], and leading to slightly to different values of activation energies. They show that ‘straw’ has a borderline high risk and ‘pine’ had a medium risk. This is the opposite conclusion to the previous work but both research groups used slightly different fuels with different preparation histories, different methods of determining the activation energy (and a slightly wider range of activation energies) and different criteria for the onset of ignition.

Most types of biomass materials (wood and straw) will have similar activation energies because the thermogravimetric method usually used measures a common feature to all untreated biomass, the decomposition of the hemicellulose. The activation energies obtained also depend on the exact mathematical manipulation of the data employed [28], and additionally, how the ‘onset of reaction’ is defined since this may be done in different ways. It seems that these techniques are best used on a comparative basis. In practice at Drax Power it has been found that pellets of “Agricultural Residues”, although stored in smaller quantities than the wood pellets, has shown greater potential to heat-up. But in these large scale stockpiles other effects also come into play such as the effect of moisture and microbiological activity. Also, on storage the pH in straw is reduced less than in woody biomass, probably due to the high potassium content as previously discussed. Additionally there is a potential influence of higher heavy metals concentrations and this may introduce toxicity effects on enzyme growth.

Kinetic data obtained from the TGA analysis using different nitrogen concentrations of 100, 95, 90 and 85 mol% show the increasing time for pyrolysis at different temperatures and under different atmospheres. These values are of significance in examining the impact of using an inert gas such as nitrogen on reducing the rate of biomass oxidative decomposition. Since biomass contains a significant amount of oxygen in its molecular make up it seems possible based on these results for the biomass to smoulder without the addition if significant amounts of molecular oxygen being present.

4.3 The use of small scale basket tests under hot conditions

The TGA method for risk assessment has limitations because of the small amount of sample employed. A more realistic test method is the British/European Standard Test Method

BS/EN 15188-2007 [7]. This uses a method based on small scale cube-shaped baskets heated in an oven environment permitting determination of ignition temperature and associated ignition delays and has been used in a number of studies [eg 13,16, 17]. In this the size of the biomass sample is defined by a characteristic dimension, which is defined as the volume to surface area ratio, V/A.

The ignition temperature and corresponding ignition delay are obtained by trial and error and this can be obtained for a number of sample basket sizes. But in the case of wood there are limited experimental data available and for chipped wood only and for small basket sizes. A plot of ‘characteristic dimension’ against a reciprocal of the ignition temperature have been made using results from our earlier publication [13] together with more recent work [17], and this is shown in Fig. 11. It is seen that there is good agreement between the two sets of results. Extrapolation of this data for a static pile suggests that the ignition for large stores is about 40°C or slightly above depending on the choice of experimental data.

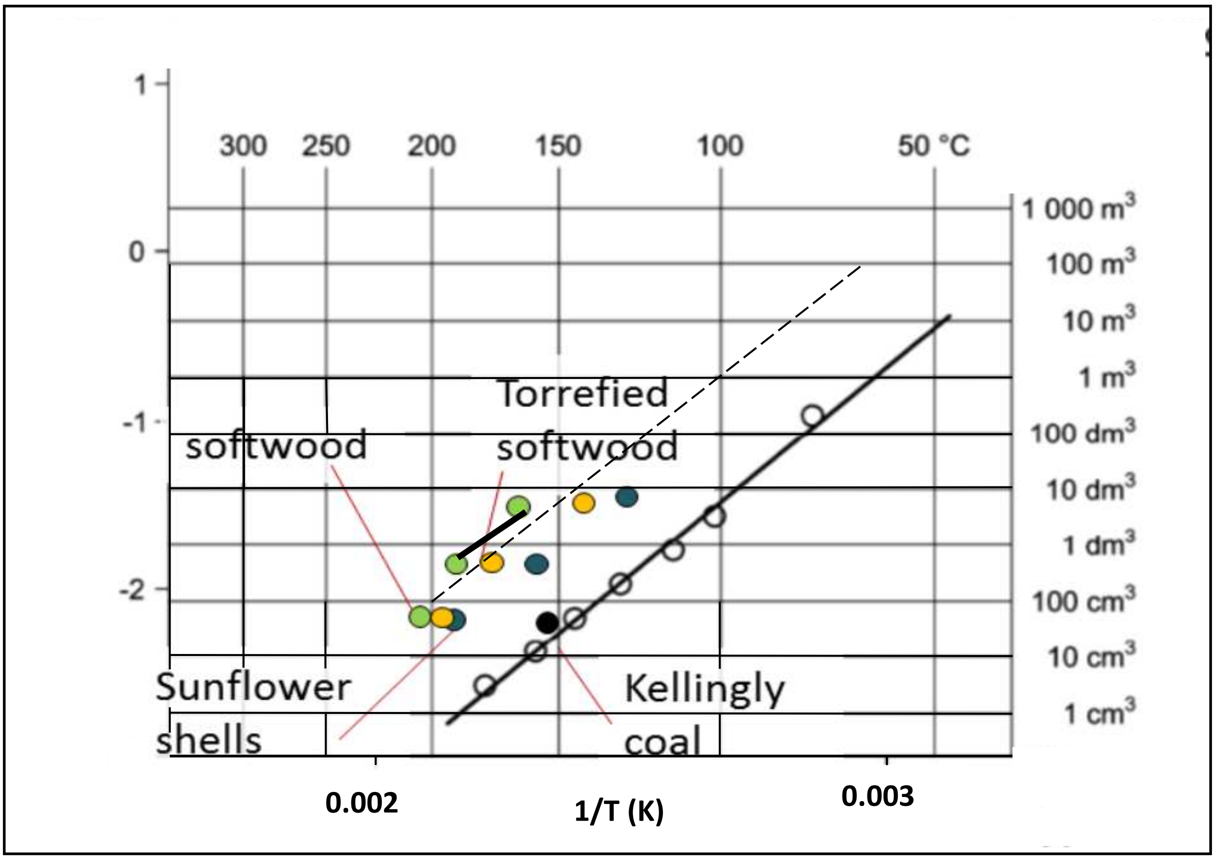


Fig. 11. Plot of characteristic dimension against reciprocal temperature (K) superimposed on the BS/EN line from BS EN 15188:2007. The experimental points are from

Saddawi et al. [13], the heavy black line is from Ferrero et al. for wood chips [16]. The dashed line is an average for the biomass results.

4.4 Studies of the Large scale Piles A and B

The extrapolation of the laboratory testing methods to the large scale industrial storage of wood pellets is a tempting hypothesis but the extrapolation is considerable and there is a major problem in estimating the contribution of self-heating due to biological action and the linked issue of moisture condensation. In both Piles the measured Relative Humidity above the beds are similar and are between 50-60%. The Relative Humidity, the bed temperature and the moisture sample in the bed are linked and these values are consistent with published data [25]. There is a considerable difference in the two piles, A and B. Pile A is 6m high and reaches a maximum temperature of 38.8 C 4m from the top, and Pile B is 9m high and reaches a maximum temperature of 45.8 C 5m from the top: both Piles have the same mass, 40kt. Their dimensions are indicated in Fig 1 and although Pile B is higher than Pile A there is a difficulty in determining the value of V/A accurately because of their irregular shape. Extrapolation of the plot in Fig 11of the volume/area ratio against the ignition temperature to Piles A and B would suggest that ignition would occur if stored long enough. This is not in accord with the observed temperature profiles. Indeed, in both case a maximum temperature is observed after six weeks and then the temperature through the piles decrease probably resulting from the control of humidity. The other factor is possibly the low level of thermophilic bacteria.

But an important difference is the position of the peak temperature in the larger, hotter Pile B which initially rises with time and then drops after the maximum temperature is reached; the rate of movement is approximately 5cm/h. There is also the non-uniform almost periodic emission of CO with distance across the larger Pile B (see Fig 7(b); here the movement of the peak concentration is about 1cm/h. The fact that this stratification occurs in the CO emission in the larger store is an interesting feature although it is not as clearly observed with the temperature. A possible explanation is that this arises from periodic evaporation and condensation of water. The water would catalyse the activity of the fungi and bacteria resulting in the release of CO. This suggests the coupled effect of change in temperature and reaction rate as expressed in CO emission (Fig.7) and VOC (Fig.8).

Thermal waves have been observed [27] to occur in a 4.6 kt silo containing wood pellets and these progressed with a velocity of 3cm/h, but in this silo that is subject to charge and discharge of the pellets. The charge/discharge operation would prevent the development of any significant periodic behaviour. The observed vertical movement of the hot region in Pile B in this work is about 5cm/h, but this biomass store is much larger than that studied by Larsson et al. [27]. However this periodic behaviour has been observed in other systems, for example in water emulsions with ammonium nitrate [29]. In the present studies there is an influence of evaporation and subsequent condensation, through the effect on temperature on competing exothermic reactions of biomass giving CO and endothermic reactions (pyrolysis) of biomass giving volatile gases. The scheme is set out in Fig.12. This can result in periodic thermal waves seen in Pile B.

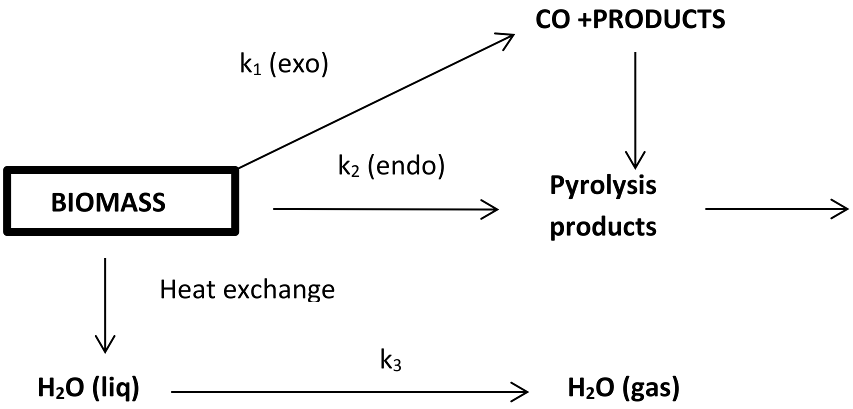


Fig. 12. Diagram of the competing exothermic and endothermic processes that can lead to ignition, based on [29].

4.5 Larger Piles: the 70kt domes at Drax Power Ltd, UK

Drax Power Station at Selby, UK has three pulverised biomass fired 660 MW boilers and the fuel store for this consists of four 70 kt storage units or domes. Each dome is 50m in diameter with a bed depth of about 50m and a storage volume up to 120,000m^3. The fuel used is pulverised wood pellets which have typical specifications given in Table 1. When the biomass is received into the store the maximum permitted temperature is 50^{o}C and the permitted range of moisture in the wood pellets is normally 4 to10 wt%, with a typical value of about 7%. The dome is constantly charged and discharged and is kept under reduced O_2 partial pressure.

It is clear that in large biomass stores the moisture level has to be controlled for the reasons already described in the experiments with the 40kt storage units. The domes are maintained with a low oxygen atmosphere by the use of dry nitrogen gas injected through the base of the dome and which percolates though the wood pellets. This controls the humidity and thus the moisture level in the wood pellets, and reduces the concentrations of the off-gases especially that of carbon monoxide in the space above the dome. These are monitored on a routine basis and together with temperature measurement through the pile form the basis of a control and fire prevention strategy. Since the condensation of moisture plays an important initial role in causing self-heating, the reduction of moisture within the pile has to be carefully controlled. Moisture migration has been tracked on the small scale test-rig and has been shown to have exited the pile. On the full scale dome, given the depth, this moisture might not exit the pile before it has condensed and this may result in higher concentrations of moisture in the upper levels of the biomass store. However the material in the Dome is not a static pile of biomass and there is constant movement, material is constantly added by the supply system and being removed for consumption by the boilers: at full load, each unit consumes 320 t/h, so assuming no deliveries, the storage facility has a maximum capacity of 12 – 13 days reserve for three units at full load on a 24/7 basis. This would prevent the build-up of hot regions in the dome resulting from the combined effects of moisture condensation and microbiological activity which could lead to the development of thermochemical oscillation; this is not observed in the domes. It is seen from the information available from heated basket experiments (as discussed in section 4.3 that the ignition delay for a static store of this size with the type of maximum temperatures reached would be about 6 months and possibly longer [13,16].

Finally it should be noted that from the TGA experiments that thermally pre-treated biomass (torrefied biomass) shows promise to alleviate some of the problems associated with biomass use such as moisture and microbial activity as well as the reduction of fines. The torrefied fuel also gave a low pH in contact with water (cf Fig 3). It could be possible that the pellet production parameters are intensified to provide some of the advantages of mild torrefaction.

5 Conclusions

In order to describe the self-heating of large scale storage of wood pellets it is necessary to take into account the influence of chemical oxidation, microbiological processes as well as the effect of the evaporation and condensation of moisture. Therefore to reduce the risk of ignition leading to fire, the moisture content has to be controlled, as well as monitoring the temperature and the emission of CO, VOC etc.

Whilst models describing steady state heating and conduction losses will apply to small piles of biomass, there is evidence that periodic behaviour occurs in large piles due to the interaction of the evaporation and condensation of water coupled with chemical reaction. This has to be included in detailed computer models that attempt to predict the onset of ignition.

The introduction of biologically active organisms should be minimised during transportation and the biomass temperature should be monitored in conjunction with CO emissions.

Acknowledgements

We wish to thank Drax Power Ltd. for some financial support and Laura Barlow for assistance with some of the experiments.

References

1 J.D. Davis, D.R. Reynolds, Spontaneous heating in coal, U.S. Bureau of Mines Tech. Paper. No, 409 (1928).

2 P.H. Thomas, On the thermal conduction equation for self-heating materials with surface cooling, Trans. Farad. Soc. 54 (1958) 60.

3 D. Gross, A.F. Robertson, Self-ignition temperatures of materials from kinetic reaction data, J. Res. Nat. Bureau Standards, 61 (5) (1958) 413-417.

4 T. Kinbara, K. Akita, An approximate solution of the equation for self-ignition, Combust. Flame 4 (1960) 173-180.

5 P.H. Thomas, P.C. Bowes, Some aspects of the self-heating and ignition of solid cellulosic materials, Br. J. Appl. Phys. 12 (5) (1961) 222-229.

6 P.C. Bowes, Thermal ignition in two-component systems. Part II-Experimental study. Combust. Flame 19 (1972) 55-69.

7 BS EN 15188-2007 Determination of the spontaneous ignition behaviour of dust accumulations BSI 2008.

8 UN Recommendations on the Transport of Dangerous Goods: Manual of Tests and Criteria. Sixth Edition United Nations, New York/Geneva, 2015.

9 IEA Bioenergy Task 40. Large Industrial Users of Bioenergy. Biomass 2013.

10 J.C. Jones, A. Puignou, On thermal ignition of wood waste, Trans. Inst. Chem.Eng. B: Process Saf. Environ. Protect. 76 (1998) 205–210.

11 T. Grotkjær, K. Dam-Johansen, A.D. Jensen, P. Glarborg, An experimental study of biomass ignition, Fuel 82 (2003) 825–833.

12 Á. Ramírez-Gomez, J. Garcia Torrent, A. Tascón, Experimental determination of self-heating and self-ignition risks associated with the dusts of agricultural materials commonly stored in silos, J. Hazard. Mater. 175 (2010) 920–927.

13 A. Saddawi, J.M. Jones, A. Williams, M. Aslam, X. Baxter, I. Hedges, Assessment of the self-Ignition characteristics of raw and processed biomass Fuel, Paper P2-89, Proc. European Combustion Meeting, Lund, June, 2013.

14 J.M. Jones, A. Saddawi, B. Dooley, E.J.S. Mitchell, J. Werner, D.J. Waldron, S. Weatherstone, A. Williams, Low temperature ignition of biomass. Fuel Process. Technol, 134, (2015), 372–377.

15 J.Garcia Torrent, Á. Ramírez-Gómez, N. Fernandez-Anez, L.M. Pejic, A. Tascón, Influence of the composition of solid biomass in the flammability and susceptibility to spontaneous combustion, Fuel 184 (2016) 503–511.

16 F. Ferrero, C. Lohrer, B.M. Schmidt, M. Noll, M. Mal, A mathematical model to predict the heating-up of large-scale wood piles, J. Loss Prevent. Process, 22 (2009) 439–448.

17 C.D. Everard, M. Schmidt, K.P. McDonnell, J. Finnan, Heating processes during storage of Miscanthus chip piles and numerical simulations to predict self-ignition, J. Loss Prevent. Process, 30 (2014) 188-196.

18 J. Zhang, T. Ren Y. Liang Z. Wang, A review on numerical solutions to self-heating of coal stockpile: mechanism, theoretical basis and variable study. Fuel 182 (2016) 80-109.

19 R. Meijer, C.H. Gast, Spontaneous combustion of biomass: experimental study into guidelines to avoid and control this phenomena. IEA working group meeting task 32. Biomass Combustion and Co-firing, Annex 5 (2007).

20 K. Miura, Adsorption of water vapor from ambient atmosphere onto coal fines leading to spontaneous heating of coal stockpile, Energy Fuels 30 (2016) 219-229.

21 H. Kajita, M. Yoneda, T. Koshijima, J. Mukudai, S. Yata, Heat of wetting of the constituents of wood in water, J. Soc. Mater.Sci. 26 (1977) No. 284 417-423.

22 J. Ryckeboer, J.Mergaert, K. Vaes, S.Klammer, D. De Clercq, J. Coosemans, H. Insam, J. Swings, A survey of bacteria and fungi occurring during composting and self-heating processes, Ann. Microbio. 53 (4) (2003) 349-410.

23 S. Krigstin, S. Wetzel, A review of mechanisms responsible for changes to stored woody biomass fuels, Fuel 175 (2016) 75–86.

24 W. Guo, K. Trischuk, X. Bi, C.J. Lim, S. Sokhansanj, Measurements of wood pellets self-heating kinetic parameters using isothermal calorimetry, Biomass Bioenergy, 63 (2014) 1-9.

25 N. Murasawa, H. Koseki, Investigation of heat generation from biomass fuels, Energies 2015, 8, 5143-5158.

26 S. Wang, X. Yuan, C. Li , Z. Huang, L. Leng , G. Zeng, H. Li, Variation in the physical properties of wood pellets and emission of aldehyde/ketone under different storage conditions, Fuel 183 (2016) 314-321.

27 S.H. Larsson, T.A. Lestander, D. Crompton, S. Melin, S. Sokhansanj, Temperature patterns in large scale wood pellet silo storage. Appl. Energ, 92 (2012) 322-327.

28 A. Saddawi, J.M. Jones, A. Williams, M.A. Wojtowicz, Kinetics of the thermal decomposition of biomass, Energy Fuels 24 (2013) 1274–1282.

29 K.J. Hughes, J. Brindley, A.C. McIntosh, Initiation and propagation of combustion waves with competitive reactions and water evaporation, P. Roy. Soc. A 469 (2013) 20130506.