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Determination of Spontaneous Ignition Behaviour of Biochar Accumulations

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Abstract: ***This study was conducted in order to determine the thermal susceptibility or spontaneous ignition behaviour of biochar accumulations so as to establish its critical values in terms of volume and temperature through Frank Kamenetskii theory of criticality and its respective methodology. Though biochar is considered a stable carbonaceous material, the fact that is often a very fine and light material, and contains a proportion of biochar 'dust' mixed with larger particles, makes it susceptible to spontaneous ignition and risk of explosion during storage, transport and handling and hence, this study. Conclusions are made that biochar is prone to spontaneous ignition and its behaviour is enhanced by increase in stockpile size and ambient temperature. The study establishes that at temperatures of 11°C and below, no self heating can occur to biochar samples even at maximum stockpile volumes and as temperature increases up to 40°C, each temperature range is associated with a specific critical volume and these critical volumes reduces with increase in temperature. The study further indicates that at any temperature above 40°C, spontaneous ignition is inevitable even at an accumulation of a smaller sample and therefore, a recommendation is made that temperatures for storage of biochar accumulations should be below 40°C, while observing that accumulations stored at temperature greater than 11°C, have specific critical volumes for a specific temperature range.***

Keywords: spontaneous ignition, biochar, critical volume, critical ambient temperature, Frank Kamenetskii theory

1. Introduction

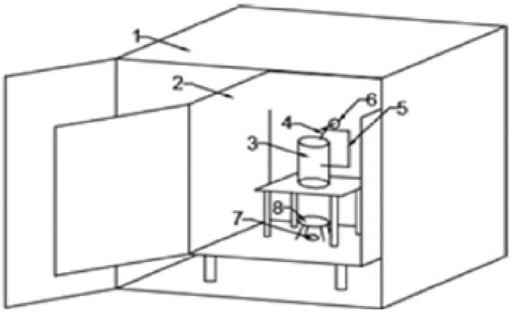
Self or spontaneous ignition is defined as the type of combustion which occurs in the absence of externally applied ignition source (Buggeln and Rynk, 2002). It is the type of ignition which its possibility of occurring, is influenced by favourable environment created for oxidation to occur in accumulations of various products, placed in stockpiles which are above their critical values in terms of temperature and volume (Hogland and Marques, 2002).

Biochar is defined as a solid material obtained from the carbonisation of biomass (Matovic, 2011). It is charcoal like material that is produced in an oxygen- reduced environment, through the process of pyrolysis in a reactor, by converting biomass and other feedstocks to charred product. This product is usually fine-grained, highly porous and has a stable chemical structure which is very difficult for microbes in the soil to break down; thereby preventing the carbon sequestered in the char to be released quickly back into the atmosphere once applied into the soil (Pereira, et al 2011, Matovic, 2011, Lehmann and Joseph,2009). Studies have reported the uses and importance of biochar to range from helping soils retain nutrients and water, thereby improving and enhancing soil functions, to reducing emissions from biomass that could otherwise naturally degrade to greenhouse gases and contribute to global warming and climate change (Dominic et. al., 2010, Cross and Sohi, 2011; Lehmann et al, 2011, Koide, et al, 2011). As an agricultural tool, biochar is becoming an important soil input for achieving increased crop yield and cropland diversity in areas with severely depleted soils, scarce organic resources, inadequate water and chemical fertilizer supplies (Warnock et al., 2007, Chan et al., 2007; Steiner et al., 2008).As a powerful simple tool to combat both food insecurity and Climate Change, sustainable biochar practices are likely to emerge and biochar is likely to be produced in large quantities; which translates to storage in stockpiles before use, thereby being susceptible to self heating or spontaneous ignition upon the critical volumes or critical temperatures being exceeded, despite biochar being a stable product in terms of degradation. Thus, Blackwell *et al* (2009) indicates that, the fact that "biochar is often a very fine and light material, or contains a proportion of biochar 'dust' mixed with larger particles";dusts tend to be highly flammable, and this can lead to a significant risk of explosion during storage, transport and handling. Thus, particle size is a critical factor as it has wide reaching consequences for how the product can be stored and applied, and the precautions which would need to be taken when handling it (Pauner et al, 2007).Van der Klashorst and Gore (1988) further reports that biochar fines or pellets produced require a binding agent to retain pellet integrity during transport and application and this pelleting and binding may increase the risk of spontaneous combustion or reducing the stability of the biochar to decomposition processes. Furthermore, Werther *et al (*2000) indicates that, fire hazards can also develop from the content of volatiles in the biochar (the higher the content of volatiles, the more subject to spontaneous combustion the product is), which is related to the biomass characteristics, temperature of biochar production and duration of pyrolysis. Hence, careful consideration is required as to the most suitable method for producing, storing and transporting biochar, considering that it is a potentially flammable product (García-Torrent et al, 2012; FAO, 1985). Furthermore, Naujoka (1985) reported that explosions are always possible when handling a dusty material that may contain combustible gases and vapors, and that fire hazard of charcoals (similar product as biochar) through spontaneous combustion has been there for almost a century. Thus, flammability being a significant concern for the handling, transportation and storage of biochar; and whilst a different product but of similar nature (i.e. charcoal) has already led to witnessing at least one major fire in the recent years when the Big K charcoal plant at Whittington in Norfolk was destroyed by fire (Lynn News, 2005); This study therefore, aims to determine the thermal susceptibility or spontaneous ignition behaviour of biochar accumulations, so as to establish its critical values in terms of volume and temperature through Frank Kamenetskii theory of criticality and its respective methodology.

2. Materials and Methods

Biochar samples in pellet form produced at 500°C and 20 minutes residence time were used. The apparatus used for this study were cubic gauze baskets of different side length sizes (5cm and 7.5 cm), thermocouples, thermo started oven, weight measuring scale, computer Pico-Log recorder Program and temperature recorder device.

Three thermocouples were prepared for each test. Two thermocouples were inserted and fixed tightly into the basket containing the sample to determine and enable recording of the temperature of the sample before and after being placed into the oven as well as behaviour of the sample towards a particular temperature it is exposed to. One thermocouple was placed at the centre of the oven connected to the computer using Pico-Log recorder program through a temperature recording device. This was done to ensure that critical ambient temperatures (CATs) are determined at different sample sizes for the same material and to enable comparison of initial and final mass after the reaction to provide evidence, if any combustion has occurred during the process. The mean of the oven temperature after subcritical and supercritical behaviour was calculated and taken into account to represent critical ambient temperature (Ta critical). The gauze baskets were selected for this study as opposed to any other baskets because they do not restrict entry of gases such as oxygen, carbon dioxide and so on, during combustion thereby allowing reactions to take place freely. This experiment was conducted at Fire Research laboratory in the school of Engineering, University of Edinburgh on biochar samples sourced from UK Biochar Research centre laboratory in the school of Geosciences, University of Edinburgh. A schematic diagram and the experimental set up are shown in figures 1 and 2.



1. Oven
2. Interior chamber
3. Basket with biochar sample
4. Thermocouple for measuring ambient temperature
5. Thermocouple for measuring sample temperature
6. Air inlet
7. Air outlet
8. Deflector

Figure 1: Schematic diagram of the experimental setup
Source: García-Torrent et al, 2012.

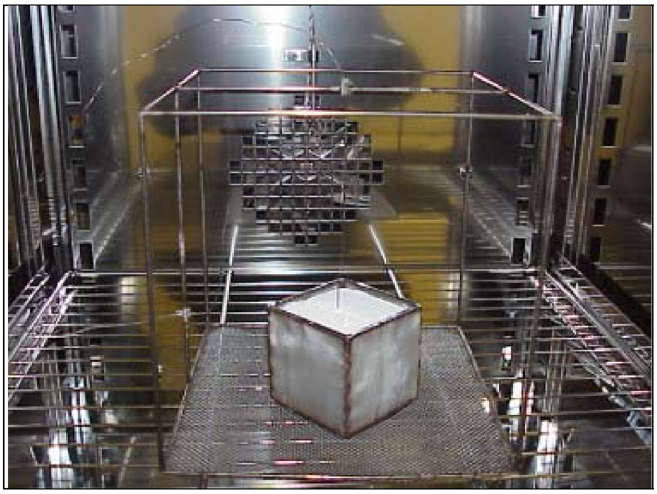


Figure 2: View of a filled basket inside a heating oven
Source: Janes et al, 2008.

Typical method of determining critical sizes at particular ambient temperatures as well as possibility of spontaneous combustion of material under oven basket method which follows Frank Kamenetskii theory of criticality was used for this study. According to the Frank-Kamenetskii's model, we can set a relationship between self-ignition temperature and storage size. Findings from this relation can help, to evaluate the critical size (maximum size) of storage for a specified temperature, which is particularly useful for low temperatures and the critical ambient temperature (maximum temperature) for specified size and geometry.

Through this method, an equation to allow the prediction of critical temperature is provided and through this equation, the equivalent scale relationship is derived. In this relationship, CATs and critical sizes for large scale bodies are calculated by means of smaller laboratory samples within defined geometries. The equation and its interpretation are presented below;

$$\ln [\delta\, critical T^{2} a, critical / r^{2}] = \ln [QEf(co)] - E/ RTa, critical$$

Where;
δcritical=A value dependant on the geometry of the body in question (as shown in table1)
Ta, critical= critical ambient temperature
r= Characteristic radius
Q= Heat of reaction per concentration of fuel
E= Activation energy of reaction
f(c)= Chemical reaction rate
R= Universal gas constant
k= Thermal conductivity

Through this theory and method as presented by Gray, (2002); subcritical behaviour is achieved if the oven temperature is close or far away from CAT of the sample, such that the sample temperatures usually surpasses the oven temperature by any temperature up to 40°C then decreases to equal it or just approaches the oven temperature. Supercritical behaviour on the other hand, is indicated by the rapid increase in temperature of the sample such that it surpasses the oven temperature by more than 40°C before declining. Therefore, in the experiments, trial and error approach was used on biochar samples in cubic basket using oven temperature to determine temperature at which highest subcritical and lowest supercritical behaviour of the sample was observed. If the observed behaviour was subcritical and the observed subcritical temperature is close to sample CAT, temperatures were being increased by 5°C, while ifthe observed subcritical behaviour is far from the sample CAT, more than 5°C oven temperature was being increased. This was repeated up until the lowest temperature at which supercritical behaviour was realised and determined. The critical ambient temperature (CAT) of the sample was then calculated by finding the arithmetic mean of the highest temperature that produced subcritical behaviour and the lowest temperature that produced supercritical behaviour. This trial process was then repeated for all samples to determine their CAT. We consider that the undertaking of the procedure described lead to an uncertainty of ±8.0 K (EN 15188) according to Janes(2006) on experiments related to this study.

After determining the CATs for each sample size, a graph of CAT (in Kelvin) against radius (half the side length of the container in which the sample was experimented on) was plotted. According to Frank Kamenetskii，the geometry of the body in which the material is contained, can be simulated by the relationship between critical ambient temperature (*Ta,critical*) and characteristic radius (ro) experimentally(Gray, 2002). Through this relationship, plotting a graph of *ln [*δ*criticalT*^{2}*a, critical / r*^{2}*]* against *1/Ta, critical*, can result to a straight line with gradient –E/R (as shown in Table 1) which intercept the Y axis at *ln (QEf(co)/kR*δ*critical).* The known data points on the graph were then extrapolated in excel beyond the known data points and through the extrapolation, realistic critical values for large biochar stockpiles were determined through correlation of the data points and using formula of a straight line graph.

3. Results and Discussion

3.1 Relationship between CAT (K) and Sample Size

Criticality was reached at lower temperatures with larger container and attained lower critical ambient temperature as compared to smaller container as indicated in table 1. This implies that as the size of material increases, the ambient temperature at which it should be stored should be lower than the size of the material when it is smaller in order to avoid critical values being exceeded and hence, self-ignition. From the results, it can also be observed that values for CAT obtained in this study and the known radius (m); as shown in Table 1;generated astraight line relationship upon a graph being plotted.These results are consistent with those implied by the theory which states that in order to derive Frank Kamenetskii equivalent scaling relationship, CAT and radius (m) relationship has to follow a straight line. These results are then used to make calculations of Frank Kamenetskii parameters (i.e. 1/ Ta,crit (K^-1) and ln [δ*crit*T^2a, *crit*/ r^2]) for derivingtheir relationship and through extrapolation using a straight line graph formula.

Table 1: Critical ambient temperatures in relation to container and sample size

Container side length(2r in cm)	Container radius (m)	Sub critical temp (^{0}C)	Super critical temp (^{0}C)(Ta critical)	CAT (^{0}C)
5	0.025	120.7	126.7	123.7
7.5	0.0375	106.9	110.9	108.9

From the values of CAT of each sample size and the known radius (m), the relationship between 1/ Ta,crit (K^-1) and ln [δ*crit*T^2a, *crit*/ r^2] is plotted in a graph and the extrapolation of the figures from the graph is performed as shown in Table 2.

Table 2: Calculations of values for deriving Frank Kamenetskii equivalent scaling relationship

Container side length(cm)	*Sub critical temp (^{0}C)*	*Super critical temp (^{0}C)*	*CAT (^{0}C)*	*CAT, Ta,crit(K)*	*1/Ta, crit(K^-1)*	*δcritTa, crit*	*2r (cm*	*r(m)*	*Ln[δcritT^{2}a, crit/r^2]*
5	*120.7*	*126.7*	*123.7*	*396.7*	*0.0025*	*396574.64*	*5*	*0.025*	*20.27*
7.5	*106.9*	*110.9*	*108.9*	*381.9*	*0.0026*	*367535.98*	*7.5*	*0.0375*	*19.38*

3.2 Relationship between critical volumes and ambient temperatures

Gray, (2002) indicates that Critical volumes are calculated based on assumed atmospheric or ambient temperature according to Frank Kamenetskii equivalent scaling relationship (Figure 3).This was considered in the study and the assumptions of the ambient temperatures in this study are based on average realistic temperature values experienced in different countries and regions, as they are considered important for application. However, higher ambient temperatures are also considered in the analysis. The radius(R) was calculated using values from ln [δ *crit*T^2a, *crit*/ r^2], obtained through equation of a straight line graph and extrapolation. R (m) values are then used to calculate the critical volume (Table 3).

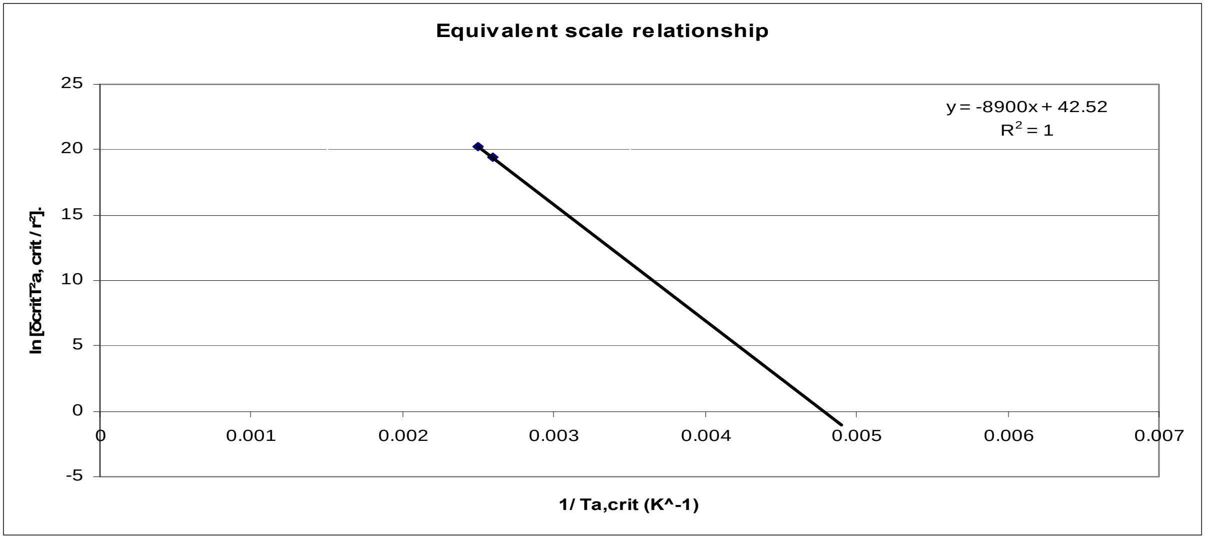


Figure 3: Frank Kamenetskii equivalent scaling relationship.

Table 3: Relationship between assumed ambient temperatures and critical volume

Assumed ambient temp.(^{0}C)	*Temp. (K)*	*Critical Volume (m^3)*
10	283	49.42
15	288	22.96
20	293	10.96
25	298	5.37
30	303	2.7
35	308	1.38
40	313	0.73
45	318	0.39
50	323	0.21
55	328	0.12
60	333	0.07
65	338	0.04
70	343	0.02
75	348	0.01
80	353	0.01
85	358	0.01
90	363	0
100	373	0

The relationship between ambient temperatures and critical volume produced an inverse trend where temperature increase was associated with decreasing critical volume and vice versa. From (Table4), it is further indicated that at 90°C ambient temperatures and above, critical volume is zero, implying that any temperature from 90°C, is associated with ignition even at very small stockpiles such that if the material is exposed to oxidizing agents or any ignition drivers, spontaneous ignition can definitely occur. This implies that at low temperature ranges i.e. 0-11°C, maximum stockpile volumes can be accommodated for storage or transportation before the critical conditions to cause ignition are reached (Figure 4). However, as temperatures increases from 11°C, specific ambient temperatures are associated with critical volumes (such that at a particular ambient temperature, exceeding specific stockpile volumes can lead to heat build up and hence, cause ignition) and this follows an inverse trend too. Conversely, these results are consistent with results reported by (Buggeln and Rynk, 2002) on investigation of self heating of yard trimmings as well as the theory of spontaneous ignition of solids. The results by (Buggeln and Rynk, 2002) indicated that volume of material and ambient temperature demonstrates an inverse relationship that can lead to spontaneous combustion with low temperatures being associated with larger stockpile volumes before critical conditions for spontaneous ignition are reached.

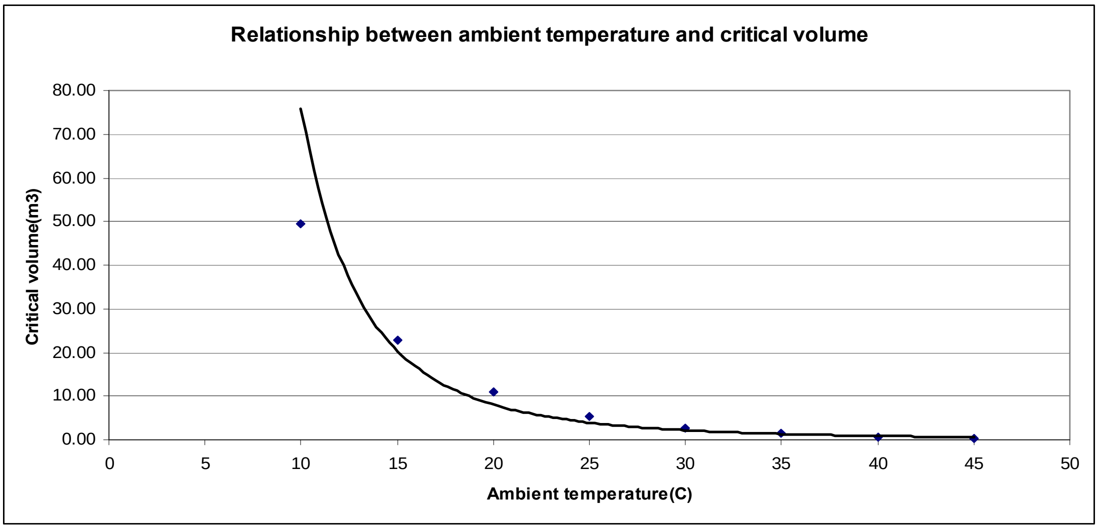


Figure 4: Relationship between ambient temperature and critical volume

Critical values established by this study are compared with other studies in which Frank Kamenetskii method was also used to predict critical ambient temperatures and critical volumes for spontaneous ignition of various “biomass related” fuels. A study on behaviour to spontaneous ignition of wood pellets by (Pauner and Bygjerg, 2007) was investigated for comparison. From these studies, results from charcoal were almost similar as observed in this study; with an inverse relationship between ambient temperatures and critical volumes being established. Maximum stockpile volumes were also predicted for ambient temperatures between 0-11°C (before critical conditions for ignition are reached) with specific critical volumes being defined on temperatures above 11°C. However, charcoal had higher critical volumes at same temperature than observed in biochar; for instance, at 15°C ambient temperature, critical volume of 400m^3 was predicted for charcoal as compared to 22m^3 predicted for biochar. On the other hand, results on wood pellets indicated a critical ambient temperature of 60°C for a cube with 7m side length (i.e. 60°C for 343m^3); while at the same temperature, biochar had 0.07m^3. Therefore, in comparing results from other studies with this study, an observation is made that, charcoal and wood pellets critical values are higher than observed in biochar.

From the results of these studies, it can be noted that wood pellets are more stable than charcoal produced in traditional kiln and biochar; with biochar being the least stable in terms of being susceptible to spontaneous ignition. This can be attributed to mass of volatiles and levels of cellulose within the material due to pre-treatment conditions (Liodakis, et al., 2002,). Through a study on “ignition characteristics of forest species in relation to thermal analysis data”, Liodakis, et al., (2002), indicated that ignition behaviour in biomass, is influenced by “mass changes related to cellulose decomposition” with high temperatures of 320°C-370°C being responsible for large scale cellulose decomposition and hence, ignition. It is further indicated that at temperatures between 120°C-160°C during pre-treatment, more mass of volatiles evolve and this has significant effect on ignition. Biochar used in this study was pre-treated at 500°C (which is at higher temperature) hence, had its cellulose largely decomposed and volatile matter evolved leading to its susceptibility to ignition even at lower temperatures and stockpile volumes than other materials.

From the result obtained (Table 3 and Figure 4), it can be deduced that at any ambient temperature 40°C and above, the critical volumes for biochar are less than 1m^3, such that at any ambient temperature, stockpiling material above the specified critical volumes indicated in the table, can cause heat build-up and hence ignition upon exposure of material to oxidizing agents

5. Conclusions

From this study, conclusions are made that biochar is prone to spontaneous ignition though is regarded as a stable product and its behaviour towards this is enhanced by increase in stockpile size (volumes) and ambient temperature. The study establishes that at temperatures of 11°C and below, no self heating can occur to biochar samples even at maximum stockpile volumes and as temperature increases up to 40°C, each temperature range is associated with a specific critical volume and these critical volumes reduces with increase in temperature. The study further indicates that at any temperature above 40°C, spontaneous ignition is inevitable even at an accumulation of a smaller sample and therefore, a recommendation is made that temperatures for storage of biochar accumulations should be below 40°C or more. Furthermore, if the temperature of biochar storage accumulations is greater than 11°C, the specific critical volumes for a specific temperature range should be observed.

6. Future Scope

Future work should involve testing the thermal susceptibility of biochars made from different feedstocks and/ or conditions and more than two container radius/ sizes have to be used, so as to validate the critical values.

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