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 criticalT²a, critical / r²]* 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)/kRδ 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*T²a, *crit*/ r²]) 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 (^0C)	Super critical temp (^0C)(Ta critical)	CAT (^0C)
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*T²a, *crit*/ r²] 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 (^0C)*	*Super critical temp (^0C)*	*CAT (^0C)*	*CAT, Ta,crit(K)*	*1/Ta, crit(K^-1)*	*δcritTa, crit*	*2r (cm*	*r(m)*	*Ln[δcritT²a, crit/r²]*
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*T²a, *crit*/ r²], obtained through equation of a straight line graph and extrapolation. R (m) values are then used to calculate the critical volume (Table 3).

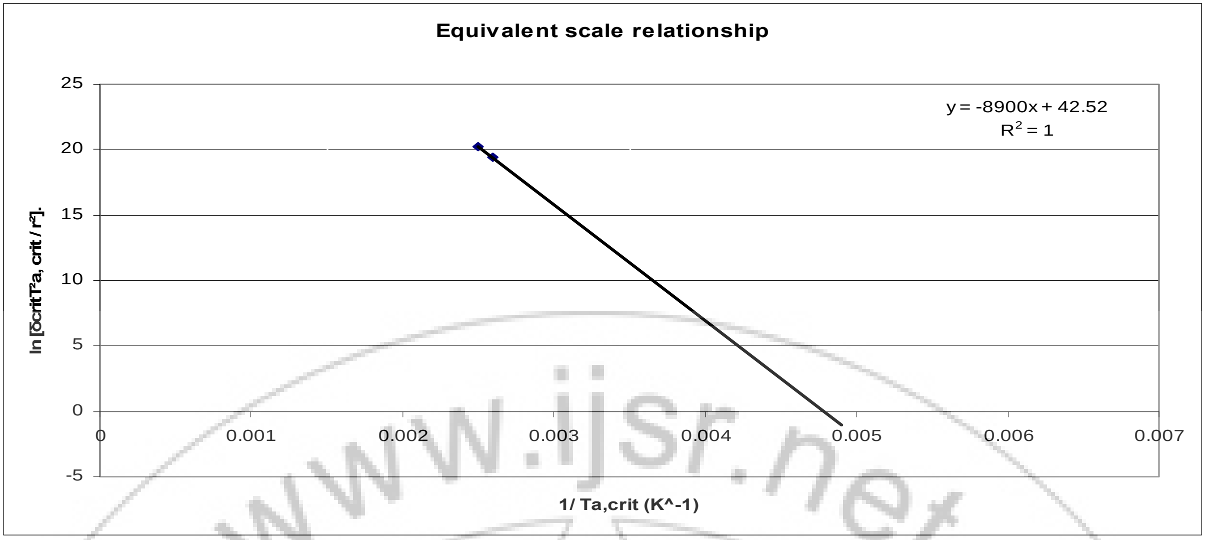

Figure 3: Frank Kamenetskii equivalent scaling relationship.

Table 3: Relationship between assumed ambient temperatures and critical volume

Assumed ambient temp.(^0C)	*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.

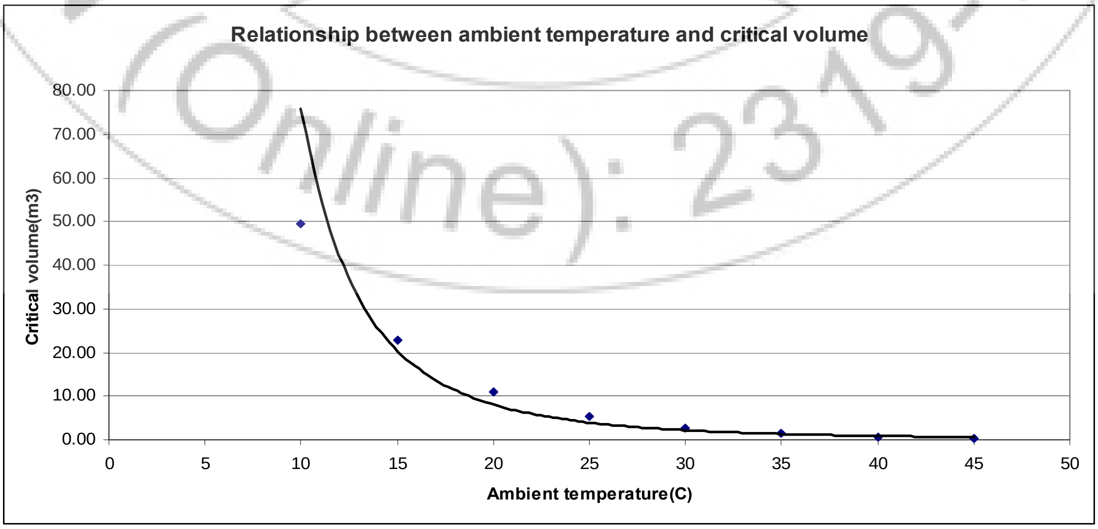

Figure 4: Relationship between ambient temperature and critical volume

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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