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Evaluation of danger from fermentation-induced spontaneous ignition of wood chips

Xin-Rui Li *, Hiroshi Koseki, Michihiko Momota

National Research Institute of Fire and Disaster, 14-1 Nakahara 3-Chome, Mitaka-shi Tokyo 181-8633, Japan

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Abstract

Recently we conducted investigations in biological wastes because large pile-up storage of waste wood chips and others caused many fires in Japan. This paper shows the experimental results on wood chips with thermal analysis, by using a Thermogravimetry–differential thermal analysis (TG–DTA) and micro calorimeters, and as well with spontaneous ignition measurements, such as a UN wire mesh cube tester and a spontaneous ignition tester (SIT). Exothermic reaction of wood chips was observed during 45–60 °C only by the high sensitive microcalorimeters, TAM and MS 80. This reaction is far apart from the second major reaction by oxidation and is not easy to be recognized by the conventional detectors, like the TG–DTA and the wire mesh cube tester, because their sensitivity cannot meet the strict requirement. Correspondingly, experimental results under the adiabatic condition in the SIT confirmed this theory, in which the onset temperature of spontaneous ignition of wood chips was measured as 50–80 °C. This implies that the weak initial reaction at ambient temperatures mainly results from microbial fermentation in the presence of its inherent moisture and possibly gives rise to the further intense combustion sustained by a chemical reaction if the heat cannot be removed from the large scale storage of wood chips.

Keywords: Fermentation; Spontaneous ignition; Wood chips; Moisture; Low temperature reactions; Runaway; Combustion

1. Introduction

In order to reduce carbon dioxide emission for preventing global greenhouse effect, it is of importance to save forest resource. With the diversification of this industry, recycling of industrial and municipal wastes, which is mandated and guided by the environmental administration, is under great promotion in Japan. Meanwhile, it is a new technology and industry, which is in development without much care on safety, thus accidents in waste treatment and recycling process increasingly occurred over recent years. For example, fires occurred in the storage of automobile shredder residue, meat–bone–meal, activated carbon, wasted towel, household garbage in processing equipment, RPF (refuse plastics/paper fuel) and RDF (refuse derived fuel). A severe fire of wood chips also happened at Sakura-shi, Chiba Prefecture in August 2003 and lasted for more than 20 days, which was caused by the illegal storage of waste wood chips of 16 m high (about 65,000 m^3) coming from sawdust and chips of construction materials. Other fires of wood chips occurred successively. The frequent occurrences of such fires of various wastes have brought about severe impact on the society. In our previous research, investigations into meat–bone–meal and RDF were reported [1,2]. This paper aims to study the combustion from spontaneous ignition of wood chips.

Firstly it might be noted that the term ‘ignition’ tends to mean two different things [3]: (1) the ‘kindled ignition’ where a body is ignited by an external heat source such as flame, sparks or hot surface, and in general, the measurement of ignition point based on the ASTM is widely used [4]; and (2) the ‘spontaneous ignition’, ‘self-ignition’ or ‘non-flaming ignition’ where certain combustible materials can ignite as a result of internal heating which arises spontaneously if there is an exothermic process liberating heat faster than it can be lost to the surrounding. For the latter, spontaneous ignition is a possible cause of unwanted fire and in our concerns. It is a complex phenomenon of combustible materials ignited by their own heat of reaction. In particular the ignition of the wastes is still not fully understood. For example, there had earlier been much consensus about the minimum

* Corresponding author. Tel.: +81 422 44 8392; fax: +81 422 44 8392.
E-mail address: li@fri.go.jp (X.-R. Li).

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temperature needed for the ignition of wood chips due to the exothermic oxidation reaction at about 200–250, involving oxygen attack at reactive radical sites within the wood. Such ignition can be detected based on the UN recommendations [5], such as wire mesh cube, and then is necessarily extrapolated to large scale storage by the application of thermal explosion theory, as suggested by Frank-Kamenetskii and Thomas [6–8]. An ignition temperature or an ignition point is the temperature at which the fire starts without fire source. The UN or ASTM point usually only reported an ignition related to the chemical sources. However, in our experience, the common cause of the fire of the wastes results from some faint reactions, such as fermentation, decomposition, slow oxidation, absorption of water, or acidolysis at much lower temperatures than that the conventional methods can detect. Extremely small heat generation accompanied by such reaction, is accumulated in the pile-up and leads to a rise of the internal temperature. Therefore, the ignition point (the UN or ASTM) cannot often be applied to the cases of the thermal storage ignition of wastes. Microbiological heating source and its potential danger are underestimated. Except that Rothbaum [9] studied such source in wet grass, there are actually no other experimental data on the ignition of this mode of combustion. The objective of this paper is to investigate the nature of the reactions involved in the wood chips storage at low temperatures using calorimeters of high sensitivity and the conditions required for transition from the accumulation of such small heat generation to spontaneous ignition.

2. Experimental

2.1. Materials

Wood chips were sampled from the storage of the nearby fire sites, and then cut into the sizes fitted to be measured in the thermal apparatus. The water content was known either by the mass difference of the sample between virgin and dried in the ovens for 1 week or by the mass loss measurement during the following TG test.

2.2. Simultaneous thermogravimetry/differential thermal analysis (TG–DTA)

As a conventional thermal analyzer to examine the general thermal properties of the material in handiness and in a short time, a TG–DTA, Shimadzu thermal plus TG 8120, was used to perform the preliminary screening measurements of heat release and weight loss from the wood chips, at a scanning rate of 2 K/min. Sample mass was 20 mg. An open aluminum sample cell was used as reference. The atmosphere was air supplied with a flow rate of 80 ml/min.

2.3. Thermal activity monitor (TAM)

TAM 2277, Thermometric Co., Sweden, as one of the most sensitive thermometry, has two main functions: well control of isothermal conditions in the water thermostat and effective detection of thermal events. The TAM thermostat is stable to at 0.1 mK and a detect limit of 0.05 μW can be achieved. To figure out the thermal activities of wood chips more accurately, the isothermal measurement was carried out at relatively low temperatures like 30, 40, 50 and 70 °C. The sample of 0.7 g was filled into the ampoule of 4 ml. Most measurements were conducted in air, besides a comparable one in N_2 at 50 °C.

2.4. Heat flux calorimeter MS 80

The Calvet calorimeter, MS 80 was also used for precise determination of thermal activities of wood chips at extensive temperature range. In the Calvet calorimeter, two experimental vessels are stayed in a calorimeter block which imposes the temperature of the experiment as fixed or variable. Two symmetrical thermal flux meters composed of thermocouples connected in series surround the experimental vessels and thermally connect them to the calorimeter block. This enables Calvet calorimeters to provide high quantification of measurements and excellent sensitivity. The MS 80 has a detection threshold of 0.08 μW. A very low temperature ramp rate of 0.02 K/min, which is very close to the natural storage situation, was applied in this experiment. Under such conditions, a scanning throughout the whole temperature range was able to be conducted to clarify the reactions of wood chips at the full temperature range from the room temperature up to 200 °C. The sample of 1.4 g was filled into the stainless steel vessel of 12 ml.

2.5. Wire mesh cube test

This test is described in the UN Test N.4 [4] to measure the ability of a substance undergoing oxidative self-heating in a volume by exposure of it to air at certain constant environmental temperatures. Cubic sample containers was 100 mm side, made of stainless steel net with a mesh opening of 0.05 mm, with their top surface open. After the sample was filled, two chromel–alumel thermocouples of 0.3 mm diameter were inserted; one placed in the centre of the sample and the other between the sample container and the oven wall. In the measurements, temperatures of 90–190 °C, with 10 °C interval, were kept in a hot-air circulating type oven. The measurements were undergoing at least 1 week to see whether self heating took place at a certain surrounding temperature and whether further it could cause a spontaneous ignition.

2.6. Spontaneous ignition tester, SIT

To study the transition from self-heating to spontaneous ignition of wood chips, a more advanced detector is needed. The Shimadzu SIT, Spontaneous ignition tester, was used for measuring materials susceptible to spontaneous ignition under an adiabatic condition, in which heat loss to the surrounding can be reduced to the minimum and any possible heat liberation from exothermal reaction can survive and be used for self-heating. The schematic diagram of SIT is shown in Fig. 1. The sample cell is made of quartz. The thermocouples and the heaters are set around the sample cell and the adiabatic condition can be kept by comparing the sample cell temperature between inside

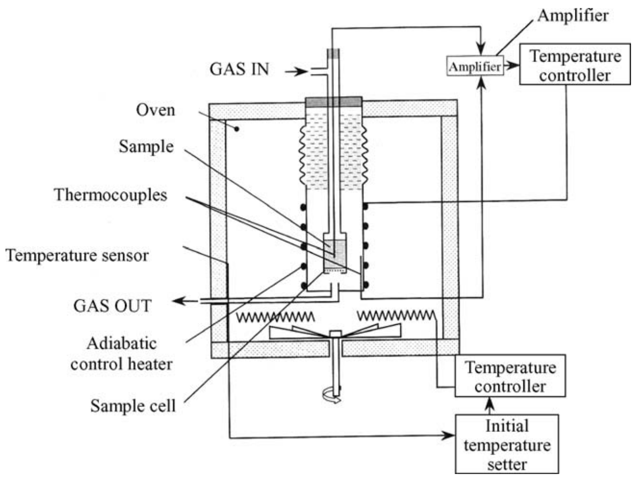

Fig. 1. Schematic diagram of the spontaneous ignition tester.

and outside. After an isothermal condition obtained, whenever any heat release from the specimen is detected, the furnace was then switched to the adiabatic mode, which allows the specimen to self-heat by its heat of reaction. During the adiabatic heating period the temperature surrounding the specimen is so controlled that there is no temperature difference between the center and the surrounding of the specimen. The onset temperatures of measurements can be set in the range from 10 to 300 °C. The SIT tests were conducted at a certain initial temperature between 40 and 150 °C in this paper, with the interval of 10 °C. In the furnace available at the SIT, about 1.4 g of sample was positioned in the tester and the specimen was then heated to a pre-selected temperature. The temperature of the specimen was recorded continuously until ignition occurred. During the SIT tests, air atmosphere of 5 ml/min was replenished after the isothermal condition of the test system was established.

3. Results and discussion

3.1. Reaction characteristics of wood chips at lower and higher temperatures

Fig. 2 shows the results of wood chips in the TG–DTA. First of all, the weight loss about 20% occurred gradually from the start of the measurement and visibly at 80 °C until 100 °C. Meanwhile a slight endothermic effect was observed. This is due to the evaporation of the moisture in the wood chips. The same moisture content in wood chips was also measured by the mass difference of the sample between virgin and dried in the ovens for 1 week. It seems that wood chips inherently contain about 20% in situ moisture. Only when 180 °C was reached, noticeable exothermic effect and heat loss were observed up to 350 °C as a result of major reactions. The rate of reaction was significant due to oxidation, which is a chemical reaction with the heat of reaction of about 18–22 kJ/g. The reactions at this stage are vigorous enough to lead to the combustion of wood chips, as reported in most previous studies. The curves of DTA and TG exhibited two stages of reactions, which might correspond to different combustion rates of cellulose and lignin. However, in the TG–DTA, no heat generation could be captured at temperatures lower than 100 °C, since the TG–DTA is a relatively insensitive device. It may not help to study the minor heat generation phenomenon at such low temperature.

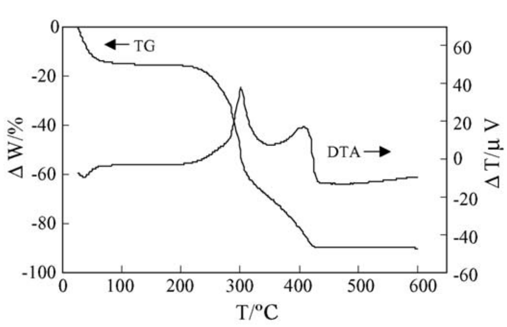

Fig. 2. TG–DTA results of wood chips, visible heat generation was observed above 250 °C (sample: 20 mg; heating rate: 2 K/min; electrostatic pressure ($\mu\upsilon$) was used in unit of DTA).

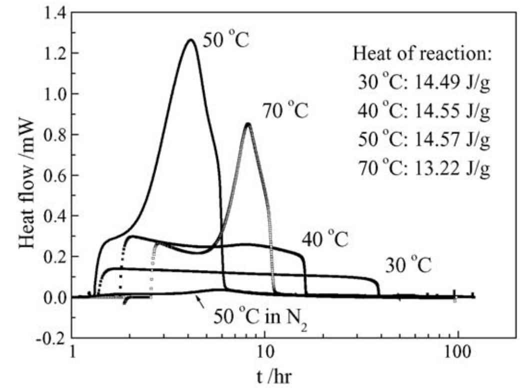

Fig. 3. Isothermal measurements of wood chips in the TAM (sample: 0.7 g).

In order to find out the mechanism that causes spontaneous ignition of wood chips at the lower temperature, the thermal analysis under more sensitive detectors and condition of no water vaporization are crucial. The TAM and MS 80 were used for this purpose because of their very high detect limits which are 0.05 and 0.08 μW, respectively. Fig. 3 is the results of heat flow versus time for wood chips when stored in the TAM at several isothermal temperatures like 30, 40, 50 and 70 °C. In comparison with the results in the TG–DTA, heat release from wood chips at near room temperature can be seen clearly in the TAM. The reaction underwent for about 40 h at 30 °C, 15 h at 40 °C and 5 h at 50 °C, respectively. Maximum heat flow at 50 °C, 1.3 mW, was the highest among these temperatures. Nonetheless, the heat generation is evaluated as 13–15 J/g at each temperature, with a little increase with the temperature rising (14.49 at 30 °C, 14.55 at 40 °C and 14.57 J/g at 50 °C). At 70 °C, heat flow and heat of reaction which was 13.22 J/g became smaller than those at 50 °C and a tiny endothermic peak due to evaporation was seen before the exothermic reaction. This indicates that the optimum temperature of the reaction for wood chips is about 50 °C and the reaction at this stage ascribes to the fermentation. Either the increase of temperature or the decrease of moisture makes the reaction lessen. Another measurement at 50 °C was done in the N_2, where the maximum heat flow is only 2% of that in air atmosphere, implying that the presence of oxygen favors the fermentation and aerobic micro-organism plays the main role of the fermentation.

To survey the available information on the nature of the reactions at a more extended temperature range, the temperature ramp mode from the room temperature to 200 °C in the MS 80 was performed by exposing the wood chips at a very low elevating temperature rate of 0.02 K/min. By this means, it ensured that temperature rising rate (outer heating) does not artificially affect or accelerate a self-sustained reaction and hence it can compatibly match a near nature storage condition during the measurement. As seen in Fig. 4(a), similar to the results in the TAM, heat generation of wood chips appeared around 25–70 °C, in which the most intense heat release was at 50–60 °C and thereafter there was no reaction occurring up to 100 °C. The heat of reaction during this stage is about 15 J/g, which is consistent with the measurement at each single temperature in the TAM. Above 100 °C a second significant but discontiguous reaction started. This shows that the first stage reaction is caused by fermentation, whereas the second stage reaction is caused by another mechanism, corresponding to vigorous oxidation of dry wood chips observed in the TG–DTA. As bacteria or fungi cannot survive at a temperature higher than 70 °C, the fermentation is inactive at this period and continuing temperature elevation above 100 °C to the ignition temperature is ascribe to oxidation. In Fig. 4(b), when the measurement was performed on the sample after being dried, the reaction at 50–60 °C did not appear, only the second reaction repeated. It confirmed the results in the TAM that the fermentation of wood chips is the major reaction at lower temperatures and the self-heating of wood chips at this stage starts with the fermentation by living cells and bacterial growth within the wood. This requires the proper amount of moisture. Micro-organism that causes fermentation cannot survive in the absence of moisture.

Wood is composed of three primary constituents—cellulose (about 47.5%), hemicellulose (about 23.7%) and lignin (about 28.8%). Cellulose and hemicellulose constituents, larger than lignin, are far more easily susceptible by enzymes to ferment the wood fibers. There are abundant cellulolytic bacterial species, existing substantially in forest soil, soil, mud, and other natural environments [10–12]. The growth temperatures are both mesophilic and thermophilic (growth optimum above 50 °C). The fermentation needs certain amount of moisture. As measured in the TG-TDA, about 20% of moisture inherently exists in the wood chips, which is typical for wood stackpiles exposed to the lands. Moisture can exist in wood in several forms: chemosorbed, physisorbed, bulk and surface. The presence of some available water is necessary for microbes to activate the fermentation, and as well the growth of bacterial species can be facilitated. Extra 20% water was added in the wood chips and the measurement at the same conditions in the MS 80 is shown in Fig. 4(c). This curve suggested that the exothermic peak at 50–60 °C was not as large as that when no additional water was in the samples. The heat of reaction in this sample was only

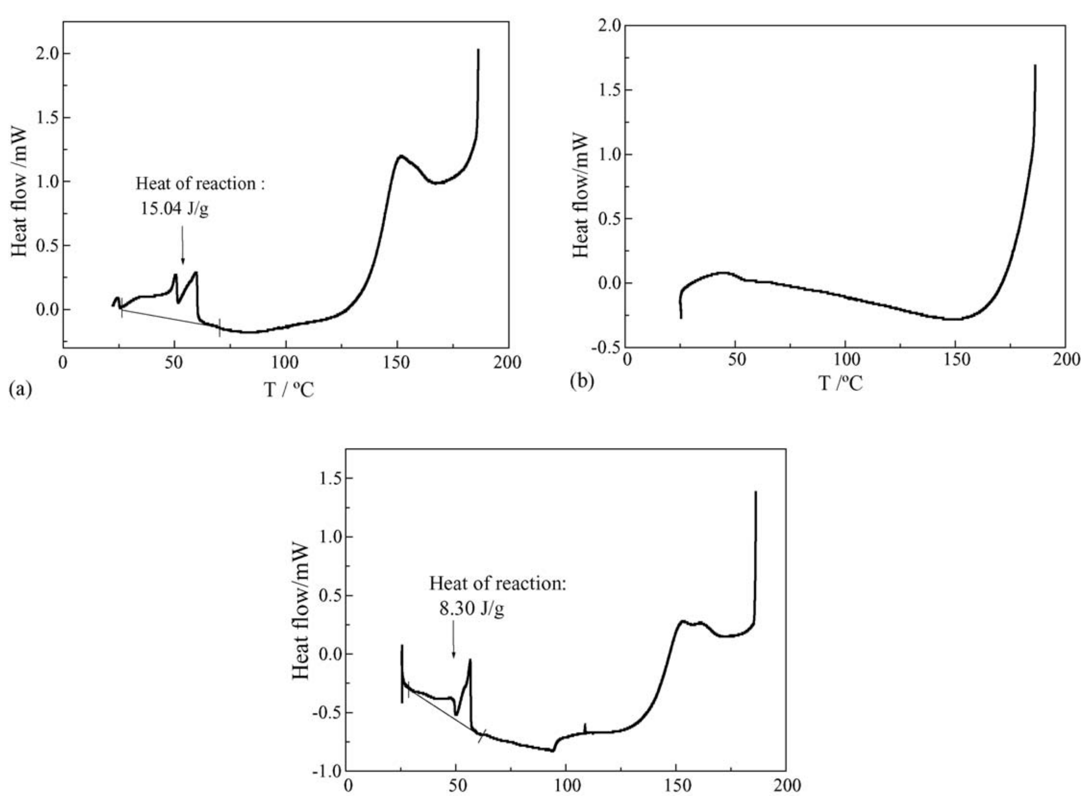

Fig. 4. Temperature ramp measurements of wood chips in the MS 80 (Sample: 1.4 g; heating rate: 0.02 K/min). (a) Fresh sample (fermentation occurred at room temperature ∼70 °C); (b) dried sample (no fermentation was observed); (c) sample with 20% extra water addition.

8.3 J/g. The effect of the amount of moisture on the rate of low temperature fermentation of wood chips is still not well understood. Perhaps the inherent 20% moisture is optimum to assist the fermentation. Short existing of extra water into the sample as in Fig. 4(c) does not help to cultivate the microorganism growth, but inversely may lead the endothermic effect from evaporation.

3.2. Spontaneous ignition of wood chips

The spontaneous ignition phenomenon of wood chips is normally transited from the heat accumulation in relatively large masses, and its principal characteristic is that combustion begins deep inside the stack where the effect of self-heating is adequate to overcome the heat loss. A small amount of wood chips does not lead self-heating, but when they are formed a huge pile, self-heating is a common problem. This is because that heat generation is proportional to the volume of the pile and this, in turn, is proportional to the third power of the radius; whereas, the heat loss is proportional to the surface area of the pile and this is proportional to the second power of the radius. On the other hand, direct measurements of self ignition from weak self heating in the laboratory scale were difficult and thus rare, limited by the small size of the sample, insensitive detection and the incomplete adiabatic condition. Therefore, the measuring condition is strict.

To clarify this point, the UN test N.4, which is the so-called wire mesh cube test, and the SIT test were carried out, as shown in Figs. 5 and 6, respectively. The UN test N.4 is an isothermal storage experiment, in which heat is readily lost by the conduction through the surface of the container and the convection with the environment. As the results in Fig. 5, up to 170 °C no self-heating of wood chips occurred over 24 h. At 180 °C, the inner temperature of wood chips started going up due to its self-heating after 8 h, but it went down after 15 h and no further ignition happened. Ignition of wood chips in the container occurred at 190 °C. These results are consistent with those observed in the TG–DTA. Self ignition occurs at a higher temperature, which is only triggered by an intense reaction like oxidation. It seems that the TG–DTA and the UN test N.4 do not help to investigate the long-term, low-temperature ignition in wood chips pile-up. Due to the low sensitivity or bad adiabaticity, such small heat

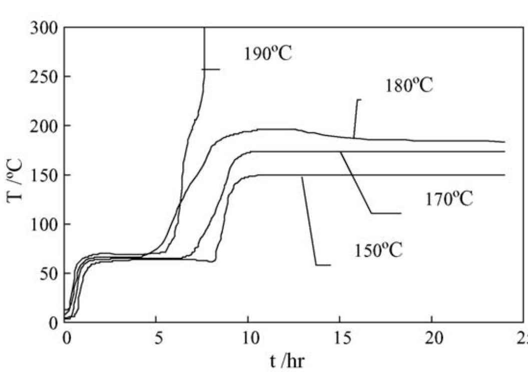

Fig. 5. Isothermal storage of wood chips in the wire mesh cube container (280 g sample in 1000 cm^3).

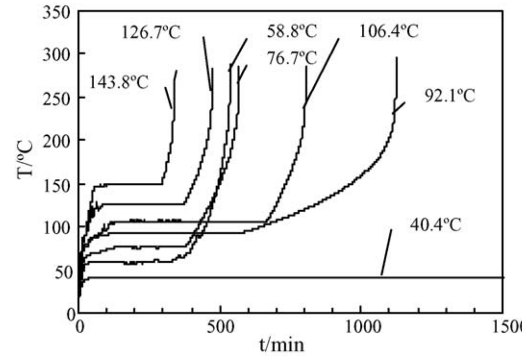

Fig. 6. Adiabatic storage of wood chips in the SIT (sample: 1.4 g; when heat generation was detected, the adiabatic condition worked).

generation accompanied by the fermentation of wood chips can hardly be detected by using these measurements. Normally, the ignition temperature was determined by extrapolating the results from such small scales to a huge one. The problem for wood chips is that it exhibits two stage reactions, fermentation and oxidation, and since they are not in the same mechanism, as discussed above, the reaction measured at higher temperature in small scale tests could not be taken as representative of the reaction at lower temperatures. So it may cause big excursion and hence is dangerous when it is used for extrapolating from high temperature ignition in a small scale tester to low temperature in a large scale storage.

Relatively, the adiabatic furnace method is technically and theoretically more advanced than the UN standard test for investigating materials susceptible to spontaneous ignition at lower temperature. The spontaneous ignition by the heat accumulation from slight reaction as fermentation was clarified under adiabatic condition in the SIT. During the adiabatic heating period there is no temperature difference between the center and the surface of the specimen, and thus faint heat generation could be survived and detected. In the SIT as in Fig. 6, wood chips initiated the ignition at much lower temperature than those in the wire mesh cube. The spontaneous ignition could be observed at 48.6 and 76.7 °C after 8 h holding wood chips in the SIT. Whereas at 90 °C the spontaneous ignition was observed after longer time, 18 h, and at 106.4 °C it occurs after 10 h. It again took less time to ignite the sample at 126.7 and 143.8 °C. This indicated that at 48.6 °C the spontaneous ignition of wood chips is more likely induced by the heat accumulation from fermentation, as confirmed by the TAM and MS 80. At this temperature, evaporation is small and the micro-organism is active. With the temperature rising up, the endothermic reaction of evaporation would counteract the exothermal reaction of fermentation. As a result, more moisture was lost at higher temperature due to its evaporation and fermentation becomes inactive. In contrast, the spontaneous ignition of wood chips at higher temperature like 90 °C is more likely induced by the heat accumulation from oxidation. There is no monotonous dependence of the induction time on the temperature rising, because of the different reaction mechanism between these temperatures.

Because the two reactions, fermentation and oxidation, are discontinuous from each other at the range of 70–90 °C, high surrounding temperature at the range of 70–90 °C does not sustain conditions for self heating of wood chips to take place. Moreover, the rate of reaction has no Arrhenius exponential temperature dependence throughout the range from room temperature to 200 °C. This makes the extrapolation difficult from small scale test to large scale test. The other problem is that some insensitive methods cannot find out the extremely weak reactions and the potential of transition from these reactions to a visible combustion. From the results of this paper, we can see that the reason for the initial temperature rise is microbiological in origin at the range of 50–60 °C. Under certain conditions this is capable of raising the temperature at a location within the stack as a worse heat conduction system and occasionally permitting microbial heating to steeply pass to chemical heating. The normal practice adopted to avoid self-heating and ignition of these materials is to make certain that the material is not damp when it stored and not in huge volume [6,8].

4. Conclusion

A number of accidents from wastes, biotechnology fuels and more complex wastes have increased, and we believed that it would increase along with the development of the recycling business in the future. For wood chips that is exposed to lower temperatures, self-heating is the dominant phenomenon. The concept of a fixed ignition temperature does not apply to a self-heating dependent strongly on the size of the specimen, and the method of extrapolation is invalid in this case.

Measurement in high-sensitivity calorimeters is needed to clarify an initial slight heat generation. Some of them were used to determine slight heat of the reaction of wood chips at the near ambient temperature and to confirm that it ascribed to aerobic fermentation. It appears that the presence of moisture enhances fermentation at the ambient temperature, in particular, at about 50 °C, and provides moderate condition for the growth of the cellulolytic bacterial species.

Fermentation plays a main role to cause spontaneous ignition of wood chips pile-up when the heat accumulation inside it exceeds the heat removal from the large volume of pile-up, as measured by an advance adiabatic tester, SIT in this paper.

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