THERMAL BEHAVIOR OF SEWAGE SLUDGE DERIVED FUELS

by

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The utility of sewage sludge as a biomass fuel is taken as an approach to deal with global warming. Thermal characterization of this new type of fuel is a premise before it is practically used in real facilities. Four sludge derived fuels were examined by thermal calorimeters (TG-DTA, C80, and TAM) at temperature ramp and isothermal conditions. Heat generation at low temperature was found in some sludge species. The corresponding spontaneous ignition was measured in an adiabatic spontaneous ignition tester at 80 °C. The reason of the thermal behaviors of the sludge fuels was discussed. The critical temperature of large scale pile-up was predicted.

Key words: *biomass fuel, self heating, sewage sludge, thermal activity*

Introduction

Sewage sludge is unwanted residual solid wastes generated in wastewater treatment and its management is one of the most critical environmental issues of today. Four sludge disposal methods are currently used, *i. e*. recycling in agriculture, landfilling, dumping into sea, and incineration. The future trend presents the increasing role of sludge incineration [1]. More approach for utilization of biomass is also expected for prevention of global warming and creation of a recycling society by being making a solid fuel from drying or coal/blend sewage sludge to completely burn with oxygen in incinerator. Among lots of biomass, sewage sludge has an advantage that the generated amount and quality is almost constant throughout the year.

In addition to optimization of energy balance, the development objectives also include assurance of safety of produced sludge regarding self-heating, *etc*. [2]. Sewage sludge has calorific and fuel value but also has the risk of self-heatiging and spontaneous ignition which commonly exists in the storage of the products of biomass fuels, such as wood pellets, refuse derived fuels (RDF), refuse paper and platic fuels (RPF), and poultry manure. This phenomenon was widely studied for coals [3, 4]. Normally the vigorous heat release occurs at "higher" temperature by combustion above 200 °C, however, there is a risk of heat release from the materials at lower temperature below 100 °C. And generally in large scale pile up indoor or outdoor, there is a potential that a temperature rise occurs in the body when the rate of heat generation exceeds the rate of heat removal, even if the volume is surrounded by an environment at a low ambient temperature, for example 20 °C. Thus the knowledge of the heat source of self heating and its hazard of this new type of fuel should be gained before they are practically used in real facilities. Hazardous materials basically can be viewed as having two aspects of hazard: (1) determination of heat source of a self-heating process, in particular immeasurable by some conventional methods; and (2) the consequences of the self-heating. The aim of the present study was to evaluate the thermal properties of the sewage sludge derived fuels to determine their heat source in particular at low temperature, and to examine whether it leads to self-heating, and ignition of. For this purpose, measurements should be performed in sensitive calorimeters to find out the weak heat generation and adiabatic ignition tester to simulate the ignition occurrence at extreme condition if the heat is ineffectively dissipated, a hot spot may develop within a stockpiled storage and lead eventually to spontaneous ignition.

Experimental

Samples

The composition of sewage sludge is given in tab. 1. Four sewage sludges were used in this study, from A to D. They were treated by different ways, and hence vary in calorific value. In order to examine the effect of water, 20% water was added into these fuels for comparison.

Table 1. Composition of sewage sludge

Element analysis [wt.%]				Industrial analysis [wt.%]			
C, dry	Ht, dry	Nt, dry	St, dry	Moisture	Ash, dry	Volatilet, dry	Otherst, dry
32-38	0.8-2	2-4	0.2-0.4	0.1-1	46-60	6-8	330-360

Dry density: 0.49, wet density: 2.22

Thermal properties

The heat of combustion of the sludges was measured according to the JIS M8814-1976 [5]. Thermogravimetry-diferential thermal analysis (TG-DTA) was carried out for 10 mg sample in an aluminum pan at an extensive temperature range from the room temperature up to 500 °C at a heating rate of 2 °C/min. Heat flux was also measured in a Calvet calorimeter, C80, from the room temperature up to 300 °C at a heating rate of 0.1 °C/min., in which the sample of 1.5 g was filled into a 12 ml stainless steel vessel. Furthermore, isothermal measurement was carried out at 50 °C in a thermal activity monitor (TAM). In the measurement, the sample of 0.7 g was filled into a 4 ml ampoule.

Spontaneous ignition

A wire mesh cube test was used 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. The sample was kept in an 100 mm^3 container at a constant surrounding temperature in a hot-air circulating type oven. The measurement was undergoing at least one week to see whether self heating took place at this temperature and whether further it could cause a spontaneous ignition.

A Shimadzu spontaneous ignition tester (SIT), was used for measuring materials susceptible to spontaneous ignition under an adiabatic condition. 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. During the SIT test, air atmosphere of 5 ml/min. was replenished after the isothermal condition of the test system was established.

Gas generation at surrounding temperatures

Sludges with and without 20% water were stored in an 1000 ml closed glass bottle for 10 days at the room temperature and 60 °C. The bottle was then merged into water upside down and gases released from the bottle were collected by a tetoron bag and analyzed by gas chromatography.

Results and discussion

Thermal properties

The values of heat of combustion of the sludge fuels are given in tab. 2. This value is related to the energy and reactivity of the fuels. It is seen that the order of the energy is A < C < B < D. The heat of combustion of coal is 20-30 kJ/g.

Table 3 lists the results of the sludges in the TG-DTA. The onset temperature of heat release of the sewage sludge A was 283 °C, whereas the sewage sludge B and C were 120 °C. The sewage sludge D was the most unstable sample whose onset temperature was 99 °C. The mass loss of the sludges was 2-4% at 100 °C, that is mainly caused by evaporation of small quantity of moisture in the sludges.

Table 2. Heat of combustion of sewage sludges

Sample	Heat of combustion [kJ/g]
A	13.06
B	21.10
C	14.88
D	23.40

Table 3 Results of TG-DTA

Sample	DTA onset temp., [°C]	TG mass loss at 100 °C [%]
A	283	4.43
B	123	2.48
C	121	2.42
D	99	2.07

The heat flux of the sludges and the sludges in the presence of water at the full temperature range in the C80 are given in figs. 1-4. In contrast of the TG-DTA, weak thermal behavior is possibly observed in particular at low temperature regime due to the high sensitivity of the C 80. The sewage sludge A was a quite stable sample. It only had a minor heat generation peak which started from 50 °C. The sewage sludge B was similar to the sewage sludge A at low temperatures, but more active at the higher temperatures. The heat release of the other two sludges at the lower temperature range (around 50 °C) was more marked. This is because these two sludges retain much more energy.

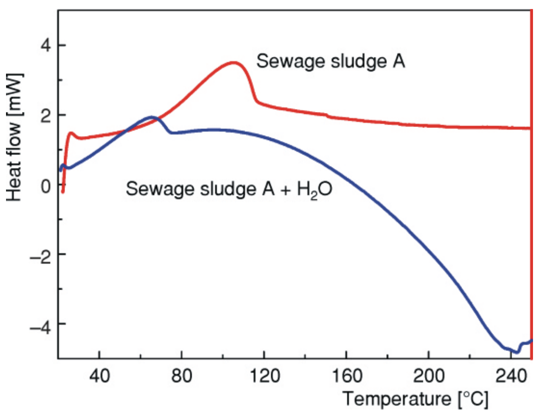


Figure 1. Heat flow *vs.* temperature of sewage sluge A in the C80

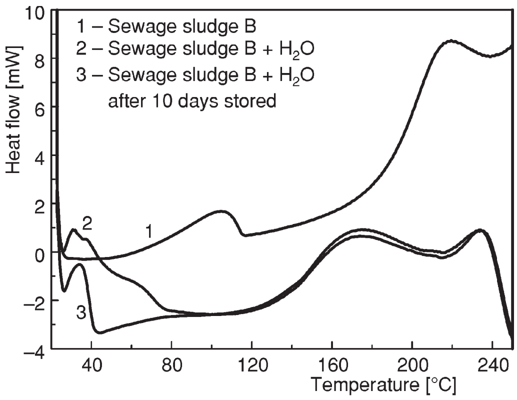


Figure 2. Heat flow *vs*. temperature of sewage sludge B in the C80

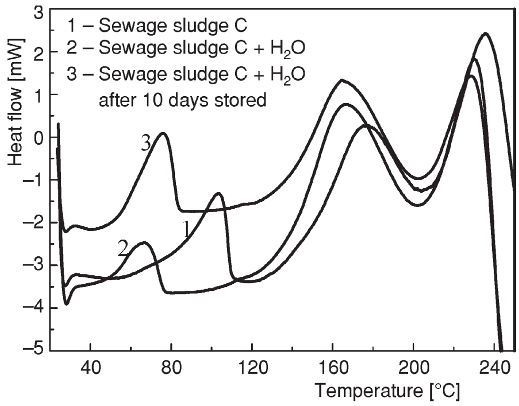


Figure 3. Heat flow *vs*. temperature of sewage sludge C in the C80

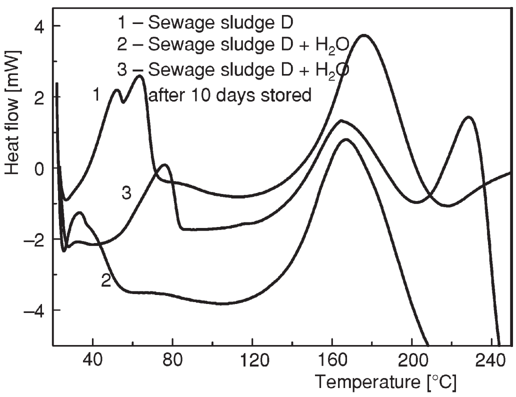


Figure 4. Heat flow *vs*. temperature of sewage sludge D in the C80

In the presence of water, the onset temperature of the first heat release peak tended to move to the room temperature. This is mainly caused by an initial adsorption of water by the sludges. After ten days of storage, the heat release became weaker for the sewage sludge B, but still remained slightly.

In order to better understand the thermal behavior at the low temperature range and the effect of water, the measurement in the TAM was performed at a typically optimum temperature of 50 °C. Figures 5-8 show the curves of heat flow *vs*. time for the sewage sludges in the TAM at 50 °C. It shows that the sludges had the similar behavior with and without wa-

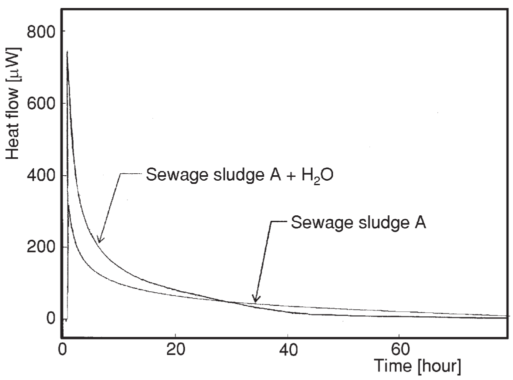


Figure 5. Heat flow *vs*. time of sewage sludge A at 50 °C in the TAM

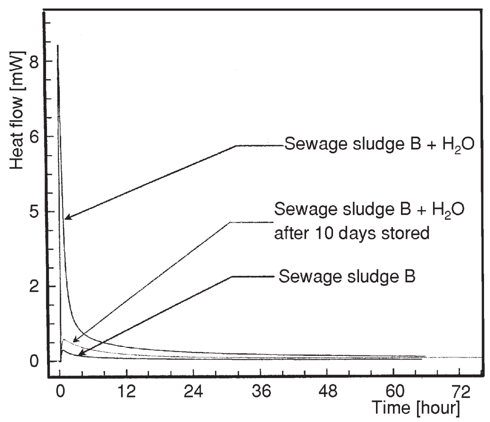


Figure 6. Heat flow *vs*. time of sewage sludge B at 50 °C in the TAM

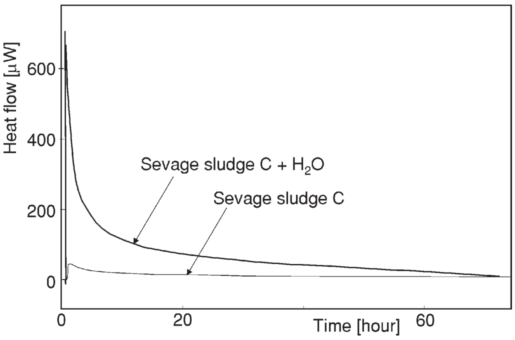


Figure 7. Heat flow *vs*. time of sewage sludge C at 50 °C in the TAM

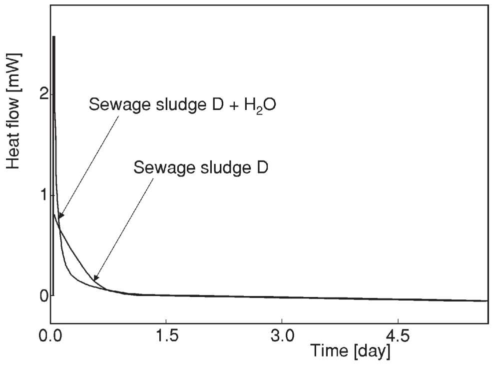


Figure 8. Heat flow *vs*. time of sewage sludge D at 50 °C in the TAM

ter. Heat release happened at the very beginning and then tapered off after one or two days. In the presence of water, the initial heat flow was more significant.

In more details, tab. 4 lists the heat generation from the sludges with and without water, measured in the TAM. It is seen that apart from the sludge D, the heat generation from the other three samples with water was much higher than those without water. It implies that the adsorption of water is the dominant heat source in these samples. Only the sewage sludge D presented a higher heat generation without water, suggesting that the other heat sources exist in the dry virgin sample. It indicates that the heat release increases with the increasing heat of combustion of the samples.

Table 4. Heat generation of sewage sludges in the TAM

Sample	Heat of reaction at 50 °C [J/g]		
	0~24 hour	24~72 hour	0~72 hour
A	17.74 (35.11)	11.14 (8.521)	28.88 (43.63)
B	7.526 (57.75)	4.590 (21.89)	12.12 (79.64)
C	3.147 (27.44)	2.977 (13.58)	6.124 (41.02)
D	89.4 (80.04)	6.369 (4.008)	95.77 (84.05)

Values in the ( ) are sludges with 20% water

Self-heating and spontaneous ignition

Figures 9-12 are the results of these four sewage sludge derived fuels in the wire mesh cube and figs. 13-16 in the SIT. Table 5 lists the results of the spontaneous ignition in the wire mesh cube and the SIT. The wire mesh cube can not capture the weak heat source because of its significant heat loss. It also does not help to remain water in the sample, for which heat source of biological activity is needed. By contrast, the adiabatic condition of the SIT can avoid these factors. Moreover, air is replenished during the measurement, and thus the oxidation if exists can be maintained. There was no difference for the ignition temperatures of sewage sludges A and B in the two containers (the sludge A was 130 °C in the SIT, 10 °C lower than in the wire

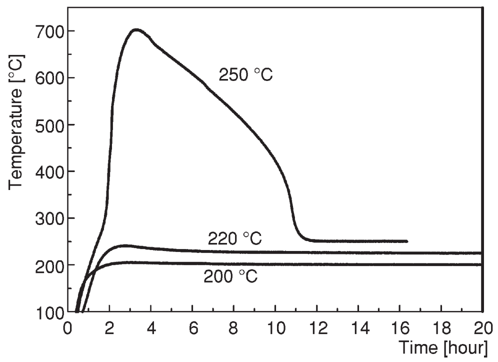


Figure 9. Self heating and ignition of sewage sludge A in the wire mesh cube

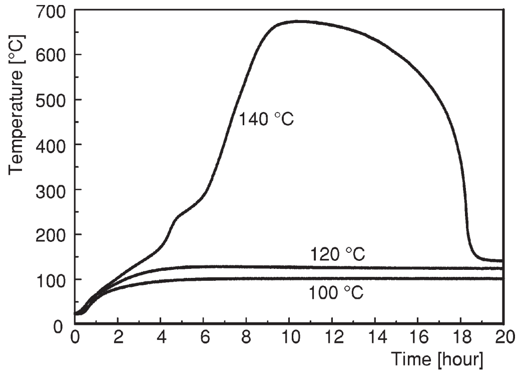


Figure 10. Self heating and ignition of sewage sludge B in the wire mesh cube

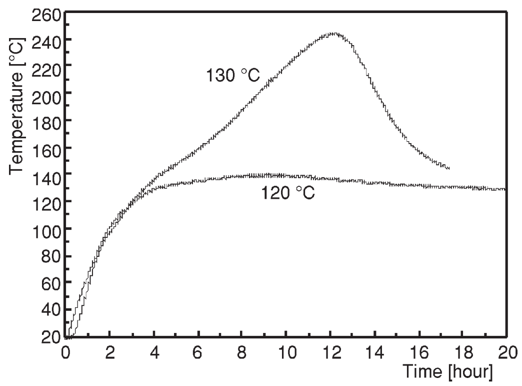


Figure 11. Self heating and ignition of sewage sludge C in the wire mesh cube

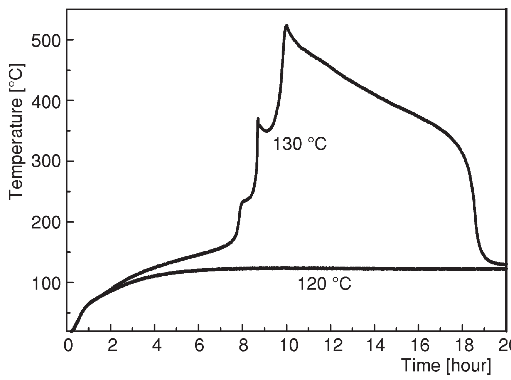


Figure 12. Self heating and ignition of sewage sludge D in the wire mesh cube

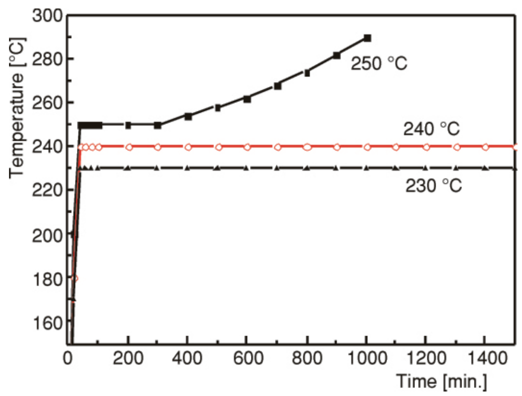


Figure 13. Self heating and ignition of sewage sludge A in the SIT

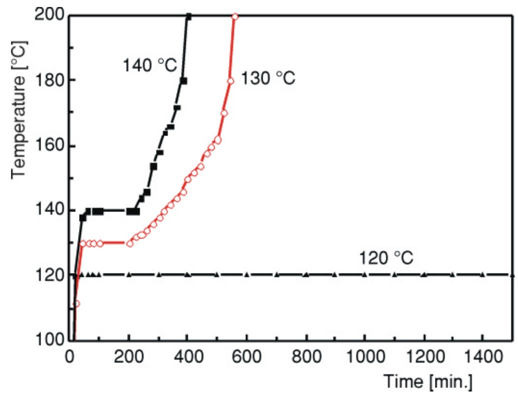


Figure 14. Self heating and ignition of sewage sludge B in the SIT

mesh cube). This indicates that heat sources from these two sludge species at lower temperature range below 100 °C are not sufficient to cause self heating and ignition. The ignition temperature of sewage sludges C and D was 130 °C in the wire mesh cube, whereas it was 80 °C in the

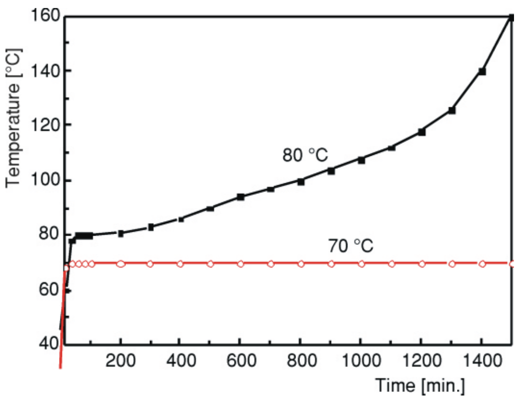


Figure 15. Self heating and ignition of sewage sludge C in the SIT

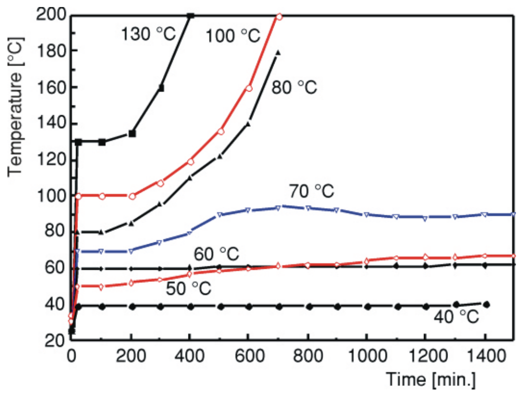


Figure 16. Self heating and ignition of sewage sludge D in the SIT

SIT. The heat sources occurring at low temperatures are responsible for the ignition in these samples. It implies that by conventional testing method, like the wire mesh cube, the ignition by such weak heat sources is not found. But the potential hazard exists and should not be neglected. Below the ignition temperature of each sample, only the sewage sludge D presents self-heating behavior at 50 and 70 °C.

The spontaneous ignition behaviors of the sludge fuels correspond to what happened in the TAM. It shows that sewage sludges C and D present more active reactions at the lower temperatures and thus more hazard than the other sludges.

Table 5. Spontaneous ignition temperature in the wire mesh cube (UN test) and SIT

Sample	Ignition temperature [°C]	
	Wire mesh cube	SIT
A	250	250
B	140	130
C	130	80
D	130	80*

* Only the sewage sludge D presents self-heating behavior, from 70 to 94 °C and 50 to 67 °C, respectively.

Gas generation

Table 6 is the gas generation from the sludge fuels after being stored 10 days at room temperature. It is seen that CO (about 0.5%) was released from the sewage sludge D with water. Hydrogen was released in this sample. CO_2 was released in the sewage sludge B and D and vigorously increased when in the presence of extra 20% water.

Table 7 is the gas generation from the sludge fuels after being stored 10 days at 60 °C. At this elevated temperature, some reactions tend to be active. As the results, the amounts of gaseous generation almost commonly increased greatly. Apart from the sludge A, CO, and H_2 increased in the other three sewage sludges. This greatly promotes the hazards of these fuels due to not only for heat release, but for flammable gas generation. CO_2 also universally increased, especially in the presence of water. The release of CO_2 does not directly lead to danger of flammable gas generation, however, it is a consequence of exothermic processes at the low temperature.

Table 6. Gas generation from biomass fuels storing 10 days at room temperature (26 °C)

Sample	CO	H_2	CO_2	Propane	Gasoline
A	No (No)	No (No)	0.49% (2.29%)	No (No)	0.02% (0.01%)
B	No (0.19%)	No (No)	0.22% (10.13%)	No (0.05%)	0.02% (0.04%)
C	No (0.09%)	No (No)	0.27% (1.53%)	No (No)	0.02% (0.01%)
D	No (0.48%)	247 ppm (59 ppm)	3.66% (13.15%)	0.03% (0.05%)	0.03% (0.06%)

Values in the ( ) are samples with 20% water

Table 7. Gas generation from biomass fuels storing 10 days at 60 °C

Sample	CO	H_2	CO_2	CH_4
A	No (No)	No (No)	5.92% (13.20%)	–(–)
B	0.28% (0.35%)	38 ppm (63 ppm)	2.02% (10.17%)	32 ppm (100 ppm)
C	0.12% (0.34%)	No (32 ppm)	2.12% (14.57%)	– (29 ppm)
D	0.51% (0.35%)	47 ppm (19 ppm)	8.56% (12.54%)	– (–)

Values in the ( ) are samples with 20% water

Mechanism of heat source

Considering the mechanism of the heat release, from the above results in the C80 and TAM, the dominant heat sources causing self-heating lie in:

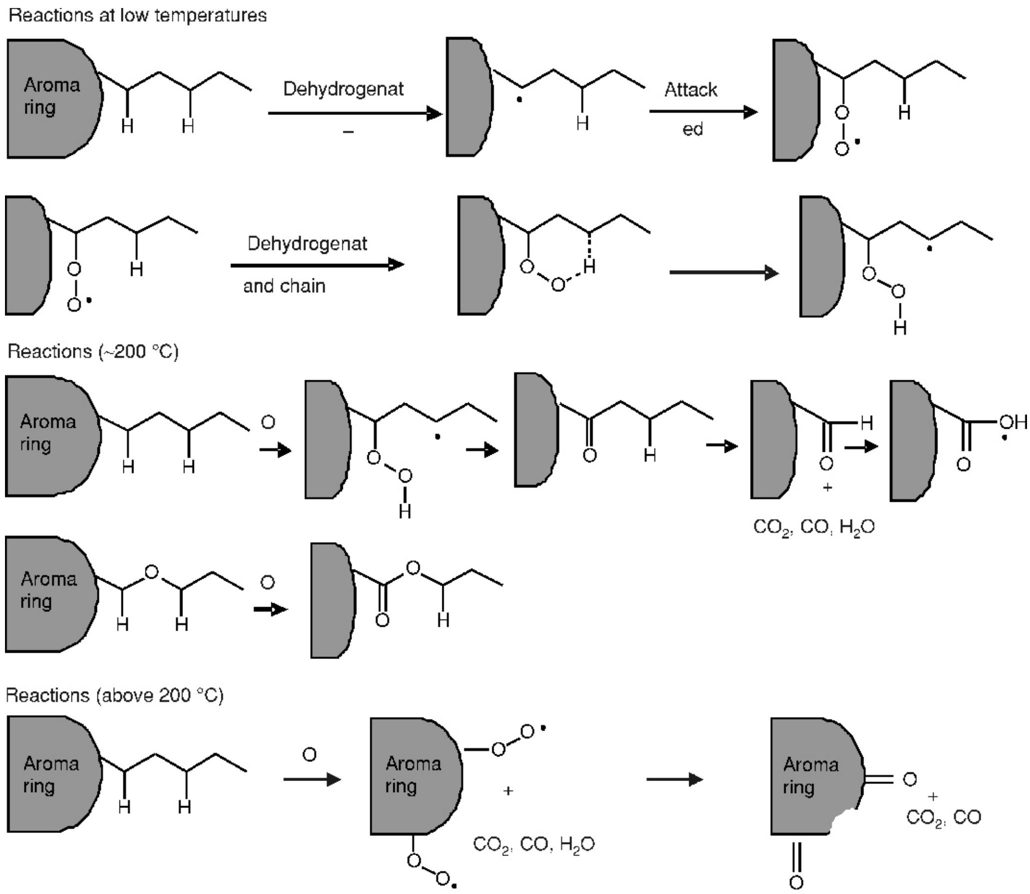
(1) The common one in self-heating is the adsorption of water. Many substances prone to self-heating tend to adsorb large amount of water. This physical process releases a significant amount of energy and is important with many practical products. Adsorption of water is not the sole cause of self-heating. When adsorption of water is occurring, other thermophysical effects also need to be considered [6].

(2) Biological activity: This occurs at the optimum 50 °C and was enhanced in the presence of water.

(3) Besides the active site of metal, surface free radicals such as of alkyl -CH_2, carbonyl -CO, and carboxyl -COO were found by FT-IR and XPS [7]. The main reason of heat release lies in the oxidation of these radicals. As shown in figure on the next page, oxidation at low temperatures present firstly that dehydrogenation takes place from the -CH_2 on the aromatic rings the produced radical is attacked by oxygen to form R-CO- and R-COOH. In addition the R-COOH and its adjacent -CH_2 chain-react.

At higher temperature, ketone is formed and spit and CO, CO, and HO are released. Above 200 °C, decomposition and more active oxidation are dominant.

The moisture content is 2-4 % for these sludge fuels. The heat release of sludge A, B, and C more relies on the presence of 20% water, whereas the heat release of sludge D is independent of water, implying that oxidation dominantly happens in this sludge.



Prediction of the critical size of large scale

The spontaneous ignition phenomenon of the materials 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. 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 predict the ignition at surrounding temperatures in large scale storage, the results in the SIT were used. According to the Arrhenius expression, the induction time has the relation with the temperature as:

$$t = t_0 \mathrm{e}^{\frac{E}{\mathrm{R}T}} \tag{1}$$

where t, t_0, E, R, and T are the induction time, the pre-frequency factor, the activation energy, the gas constant, and the absolute temperature, respectively. Figures 17 and 18 shows the relationship of ln (t) and $1/T$ of two sludges B and D. The value of E is obtained.

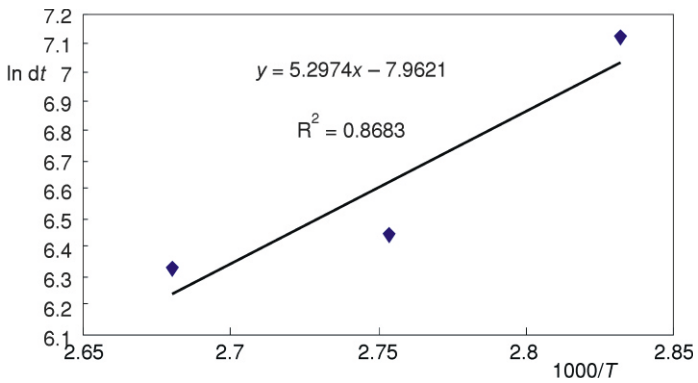


Figure 17. Correlation of induction time to ignition and temperature for the sludge B

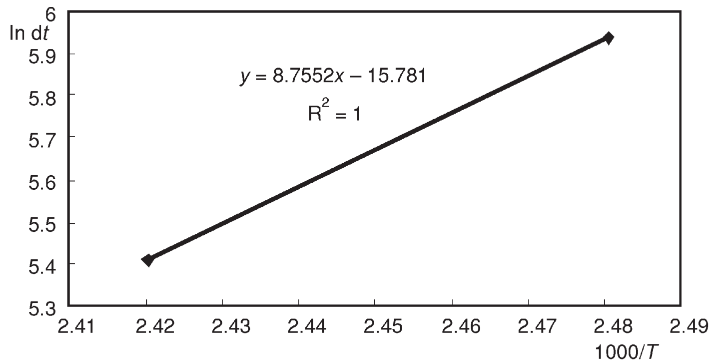


Figure 18. Correlation of induction time to ignition and temperature for the sludge D

Consequently, by inserting these data in the Frank-Kamenetskii equation, the critical size of sewage sludges was evaluated in respect of the spontaneous heating in a pile-up storage [8-11]. The Frank-Kamenetskii model expresses the critical condition in term of the parameter, δ_c:

$$\frac{E}{\mathrm{R}}\frac{r_0^2}{T_A^2}\Delta H\frac{A}{\lambda}\mathrm{e}^{\frac{E}{\mathrm{R}T_A}}\rho \quad \delta_c \qquad (2)$$

where T_A is the ambient temperature corresponding to δ_c. The critical condition for an ignition is $\delta > \delta_c$. Because of the space co-ordinates in the conduction part of the formulation, the value of δ_c depends upon the shape and for a cube it is assumed as 2.57, with half height of r_0.

Other parameters are:

R = 8.314 J/molK;

λ = 0.056 J/smK, measured by a thermal conductivity meter (THP-202, Tokyo Riko Co. Ltd);

ρ = 290 kg/m, from reference, and

δ_c = 2.52.

Figures 19 and 20 show the evaluated critical sizes of pile-ups for sewage sludge B and D. It shows that spontaneous ignition is easier to occur for a pile-up of the sludge D than for sludge B.

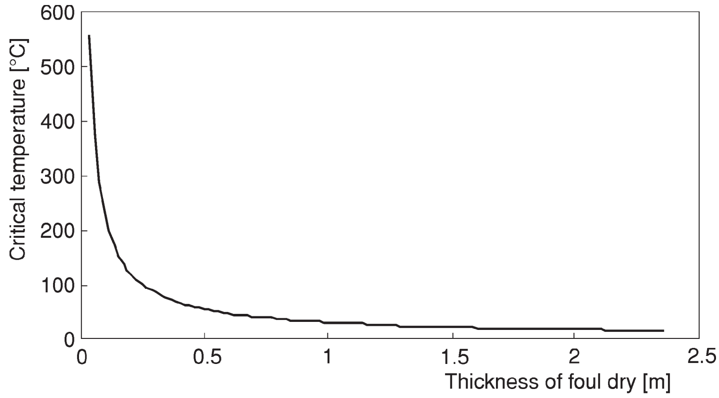


Figure 19. Relationship between the critical ignition temperature and the height of sludge B pile-up

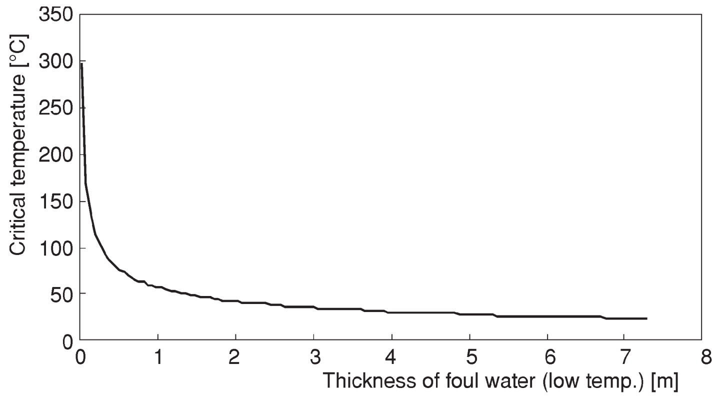


Figure 20. Relationship between the critical ignition temperature and the height of sludge D pile-up

Conclusions

This paper compared the thermal behavior and relevant spontaneous ignition of four sewage sludges at near surrounding temperature range. It implies that:

in high-sensitivity calorimeters, slight heat was observed to release from the sludges at the near ambient temperature and it ascribed to several weak reactions; the heat release increases with the increasing heat of combustion of the samples,

spontaneous ignition was induced at 80 °C in the adiabatic SIT for the dried sludges; whereas self heating was found at lower temperature in one species, and

in addition to heat release, gases were also generated during the storage of the sludges, which contribute the hazard of this kind of fuel.

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