

Review

Evaluation of Various Solid Biomass Fuels Using Thermal Analysis and Gas Emission Tests

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Abstract: Various recently proposed biomass fuels are reviewed from the point of view of their safety. Many biomass materials are proposed for use as fuels, such as refuse derived fuel (RDF), wood chips, coal-wood mixtures, *etc.* However, these fuels have high energy potentials and can cause fires and explosions. We have experienced many such incidents. It is very difficult to extinguish fires in huge piles of biomass fuel or storage facilities. Here current studies on heat generation for these materials and proposed evaluation methods for these new developing materials in Japan are introduced, which are consistent with measurements using highly sensitive calorimeters such as C80, or TAM, and gas emission tests. The highly sensitive calorimeters can detect small heat generation between room temperature and 80 °C, due to fermentation or other causes. This heat generation sometimes initiates real fires, and also produces combustible gases which can explode if fuel is stored in silos or indoor storage facilities.

Keywords: biomass fuel; thermal analysis; high sensitive calorimeter; gas emission test

1. Introduction

Because of increasing crude oil prices and environment aspects, such as reduction of CO₂ emissions, various biomass solid materials have recently been proposed for use as fuel [1,2]. These potential fuels include RDF (= refuse derived fuel), RPF (= refuse paper & plastic fuel), wood chips, coal-wood mixtures, chicken dung, *etc.* However all these fuels have high energy potentials and may cause fires and explosions [3–6]. We have experienced many incidents with these materials in Japan. It is very difficult to extinguish fires of these materials when they are stored in huge piles, or storage

facilities. We investigated these fires, and an evaluation method for these new developing materials was proposed. The method involves the use of highly sensitive calorimeters such as C80, MS80 or TAM which can detect small heat generation between room temperature and 80 °C, caused with fermentation or other reasons. This heat generation sometimes initiates real fires, and can also produce some combustible gases which may explode when fuel was stored inside silos, indoor storage or during indoor treating processes [7]. Because biomass fuels are developing, it is sometimes difficult to prepare enough amount of sample for tests. Therefore these tests have some advantages because they do not need large amounts of fuel [8].

2. Incidents in Japan

2.1. Some Examples of Biomass Fuel Incidents in Japan

2.1.1. RDF Explosions

RDF (Figure 1) is a cylinder type fuel, and its properties are listed in Table 1. Construction of RDF energy plants started in Japan around the early 2000s. RDF was used as fuel for these energy plants, but operation was poor because of a lack of knowledge. Huge amounts of RDF were stored in a silo and other storage facilities, where it sometimes generated heat and initiated fires. One explosion occurred during fire-fighting against heat generation in a RDF silo, and two firemen were killed in August 2003 by an explosion shown in Figure 2 [6,9]. The explosion occurred because methane was produced by anaerobic organisms. After this explosion, we started a cause investigation and study of biomass fuels, not only RDF. We clarified that RDF produces heat mostly by fermentation, which also produces methane in the absence of air.

Figure 1. Picture of RDF.



Table 1. Comparison between RDF and RPF [10].

	RDF (Refuse Derived Fuel)	RPF (Refuse Paper & Plastic Fuel)
Raw materials	Home waste	Industry waste
Heat of combustion, kJ / kg	12,600~16,800	25,000~42,000
Water content	Large, about 8%	Small

Figure 2. RDF silo explosion in August 2003.



2.1.2. RPF Fires

RPF has a similar profile as RDF (Table 1). However it does not generate heat like RDF because it consists of plastic and paper, and microorganisms cannot subsist in RPF. However sometimes it can cause fires when it is ignited by the heat generation produced from friction during transportation in a plant.

2.1.3. Wood Chip Fires

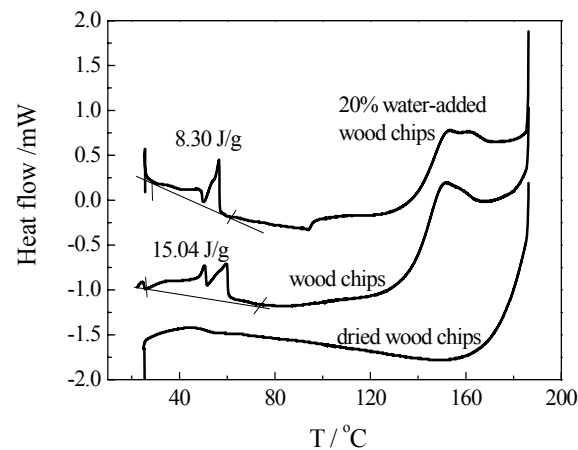
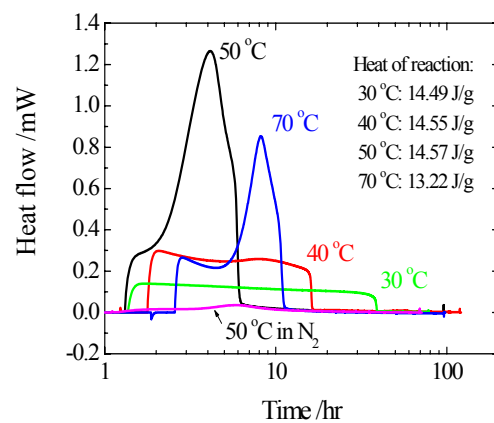
Recycle and reuse are recommended in the construction industry, but they have not worked smoothly, which led to the appearance in Japan of huge amounts of wood chip piles around 2002–2005. These piles sometimes caused fires that could not be extinguished easily. One example of such a fire occurred in Chiba, Japan, involving a 60,000 m³ pile of about 16 m height. The fire started in August 2003 and continued for several months. Three firemen were slightly injured. The cause of the fire is unknown, but heat accumulation in the pile was one of the possibilities. Aerobic organisms existed there and this led to heat generation, especially after rain [11].

3. Cause Investigation and Mechanism of Heat Generation

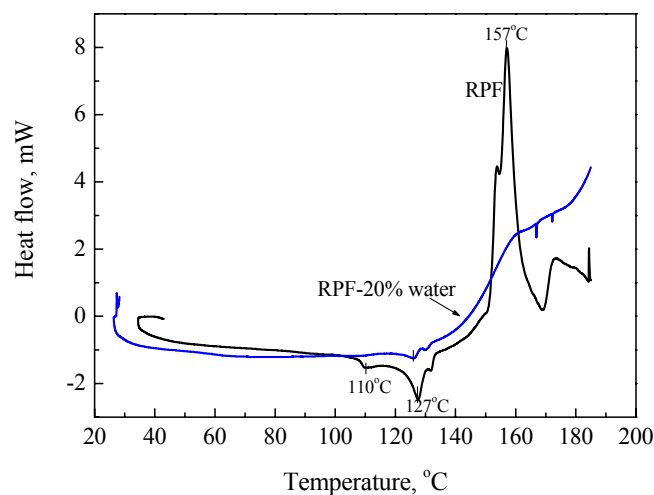
Based on the results of cause investigation of the above incidents, we studied the mechanism of combustion of these materials. There are three steps:

- (1) Faint heat generation between room temperature and about 60 °C;
- (2) Combustion of fatty acid esters in materials;
- (3) Combustion of cellulose or other organic materials.

The most important step was first one. It includes faint heat generation caused by fermentation of microorganisms which exist in the materials, and heat generation from water absorption on the surface of materials. Fermentation mostly occurred in the temperature range between 30 °C and 60 °C. When water was added to the material, much more active fermentation occurred. Microorganisms are classified into aerobic and anaerobic organisms. Heat generation was caused by first class at a relatively high temperature, under 80 °C, and methane and other combustible gas were produced mostly by the second ones at lower temperatures. Figure 3 shows heat generation by fermentation of wood chips in the MS80, and Figure 4 shows the TAM isothermal test experiments.

Figure 3. MS80 results of wood chips (sample: 1.4 g, heating rate: 0.02 K/min).**Figure 4.** TAM isothermal test results of wood chips (sample: about 2 g).

When under 100% N₂, there was nearly no heat generation, and heat generation was only occurred in the presence of air, producing a maximum peak value at around 50 °C. After they consumed oxygen, the reaction and heat generation stopped. Therefore heat generation at the various temperatures was within a similar value range, 13–15 J/g. MS80 experimental results of RPF are shown in Figure 5 [1].

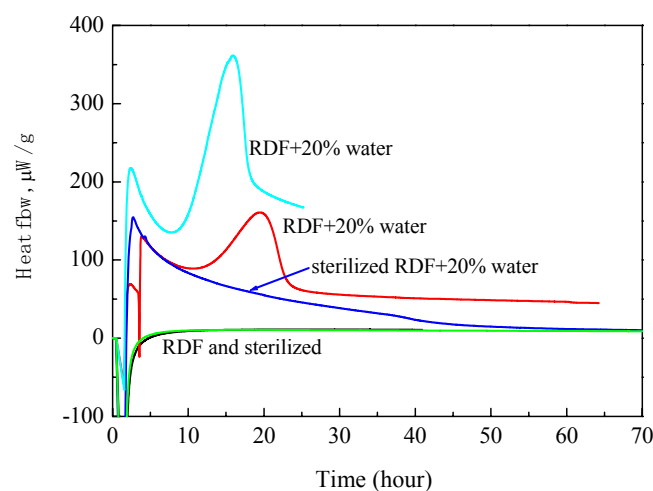
Figure 5. MS80 results of RPF with 20 wt% water added and no additional water (heating rate: 0.02 °C/min).

The results imply that RPF did not generate heat until about 130 °C with/without water, because it consisted of mostly paper and plastics. Even without additional water, it produced heat because of ignition of paper or plastic by friction or other reasons. The highly sensitive C80 and MS80 calorimeters are made by Setram Co. (France), and details are shown in our previous papers [1,9,12]. The TAM is made by Thermometric Co. (Sweden), and its details are shown in Section 4.2 of this article.

Absorption of Water and Chemical Reaction

When materials absorb water, they sometimes emit heat, at a faster rate than that of fermentation. Therefore we measured heat generation in various situations at 50 °C with the TAM unit [12] (Figure 6). Sometimes quick heat production was observed which might be due to water absorption, chemical reaction and/or fermentation. When it was sterilized, there was no heat generation by fermentation. When water was added to the sterilized RDF, it produced heat at the start of measurement, which might be due to absorption of water. Chemical reactions might occur that also result in heat generation. For example, reactions between acids and alkali might occur, because biomass fuel sometimes includes calcium compounds, and pH of water was sometimes lower than 7.

Figure 6. TAM results of RDF, at 50 °C.



The second step was more complicated, and Shimizu *et al.* [4] explained that peroxides were produced from fatty acid esters which might exist in RDF or another biomass fuels. This needs more research. The third one was a normal chemical reaction of wood at higher temperatures.

4. Experimental

4.1. Examples of Biomass Fuel

Various materials have been developing as biomass fuels, and Table 2 shows examples of biomass fuel and coal. Coal is a candidate of standard material for evaluation.

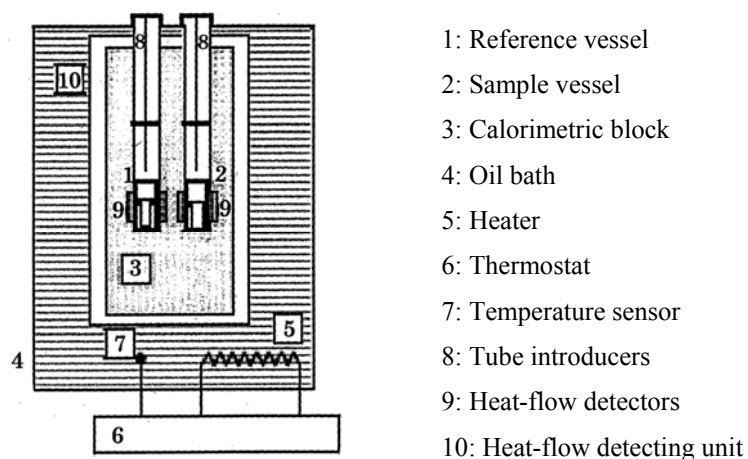
Table 2. Examples of biomass fuel and coal.

Fuel	Summary	Heat of Combustion, kJ/kg
RDF	Various domestic garbage materials exist (Figure 6)	16,800~21,800 * 12,600~16,800 ** [10]
RPF	Consists of paper and plastic	25,200~33,600 * 25,000~42,000 ** [10]
Wood-pellet (White)	Inner part of wood	19,700 *
Wood-pellet (Bark)	Outer part of wood, oily material exists	18,650 *
Chicken dung	Water content: about 40%	8000 *
Cow dung	Water content: less than 20%	6300 **
Coal-wood mixture	Water content: about 10%	21,500 *
Sewage sludge derived fuel	Various types are proposed	14,880~23,400 *
C-RPF	Char-Refuse Paper & Plastic Fuel	25,000 ** [10]
Fish meal	Water content 9.4%	23,500 ** [13]
Soy sauce residue	No water	22,000 ** [13]
Coal	Bituminous coal, standard material for evaluation [9]	29,800 *

* Measured by author; ** Examples (manufacturers information or references [10,13]).

4.2. The High Sensitive Calorimeter, TAM, MS80 and C80

The highly sensitive TAM calorimeter was used to find faint heat generation at 50 °C. Figure 7 shows a block diagram of the TAM, and details are shown our previous papers [2,9,12,14].

Figure 7. Block diagram of TAM.

Gram-sized samples were placed in a closed vessel and the temperature was measured, under isothermal conditions for 72 h, and nano-order heat generation (nano-watt/g) could be detected. When water was added samples were kept at about 50 °C, to detect heat production caused by fermentation (Figure 5). About 20% (weight) water was added to the fuel to establish the effect of water.

Both the C80 and MS80 are twin type highly sensitive calorimeters. The MS80 is much more sensitive than the C80. Sample amounts for measurements on both instruments were around one gram. Heat generation could be measured in the C80 from room temperature up to 300 °C, at a heating rate of 0.1 °C/min, and in the MS80 from room temperature up to 180 °C, at a heating rate of 0.02 °C/min [9].

4.3. Gas Emission Tests

When biomass fuels were kept in a closed vessel even at room temperature or slightly higher temperature, up to 50 °C for several days, carbon dioxide and methane were produced. Small amounts of hydrogen and carbon monoxide might also be produced. The produced gas was measured by a gas chromatograph. When water was added in sample, it produced more gases. The tests were conducted using about 10–20 g sample in one liter closed vessels.

5. Methods and Results of Evaluation of Biomass Fuels

The aim of the evaluation is to estimate heat generation and possibility of fire occurrence for new biomass fuels using small amounts of sample. Characteristics of coal were studied the same way because it might be considered a standard material [10].

5.1. Test Methods in the UN Recommendations

There is no standardized test method for evaluation of such biomass fuels. The wire mesh test, Division 4.2 in the UN Recommendations for the Transport of Dangerous Goods—Manual of Tests and Criteria [15], was used to evaluate self-heating substances. Here 1 L samples are used for each run. The Dewar vessel test, the Test H series in the UN recommendations [15], could be used for estimation of the self-accelerating decomposition temperature (SADT) of biomass fuels, but most of them do not have a SADT value. The flash point is one of the parameters often used to evaluate combustible materials, but most biomass fuels do not have low flash points. Therefore there is no method in the UN Recommendations for determining very small heat generation from fermentation or other heat generation routes which could be related with the causes of the fires.

5.2. Evaluation with Thermal Methods and Gas Emission Test

Test methods using the high sensitive calorimeters and measurement of gas emission were proposed by the National Research Institute of Fire and Disaster (NRIFD), Japan. Our understandings of the fire process is that faint heat generation inside the biomass fuel near room temperature, might cause fires when it existed under adiabatic conditions, such as huge piles, or inside storage facilities. Therefore the TAM, one of the most sensitive calorimeters available, was used for evaluation of biomass fuels after the screening test with the TG-DTA. These tests need only small amount fuel though most tests in the UN Recommendations need large amount of samples. The high sensitive C80 and MS80 calorimeters can also detect micro-order heat generation (micro J/g). Therefore the high sensitive calorimeters can be applied to materials which are under development. To measure the amount of gas emission it is also important to know possibility of gas explosion in indoor storage.

(1) Thermal analysis and high sensitive calorimeter:

- (i) TG-DTA: The thermal analysis, TG-DTA, is widely used for studying thermal properties of solid or liquid materials. In our evaluation process it was used for the screening tests of thermal properties with small amount of materials. Wood chips were measured in the TG-DTA, and results are shown in Figure 8. They did not produce any large heat generation until 200 °C. However there was not enough data to decide that wood chips did not produce small heat generation which was related with causing fires, so we should ascertain heat generation with the highly sensitive calorimeters.
- (ii) Highly sensitive calorimeters: Because the DTA and DSC do not have high sensitivity, we used high sensitivity calorimeters, C80, MS80 or TAM. Sample amounts of measurement of C80 and MS80 are about one gram, smaller than that of TAM. Heat generation can be measured in the C80 from room temperature up to 300 °C, at a heating rate of 0.1 °C/min, and in the MS80 from room temperature up to 180 °C, at a heating rate of 0.02 °C/min [9]. The TAM is a much more sensitive calorimeter than the MS80. It is used under isothermal conditions. Figure 5 shows results of RDF with/without water. When water was added to wood chips, heat generation was observed after several hours.
- (iii) Adiabatic tester, SIT and critical height in a huge pile: To verify ignition with small heat generation, we detected the heat with highly sensitive calorimeters. We used for this purpose the adiabatic testers, SIT and/or ARC. Figure 9 shows SIT test results for RPF. When RPF was held at higher than 160 °C, its temperature started increasing after several hours.

Figure 8. TG-DTA curves of wood chips (Sample: 20 mg; Heating rate: 2 K/min).

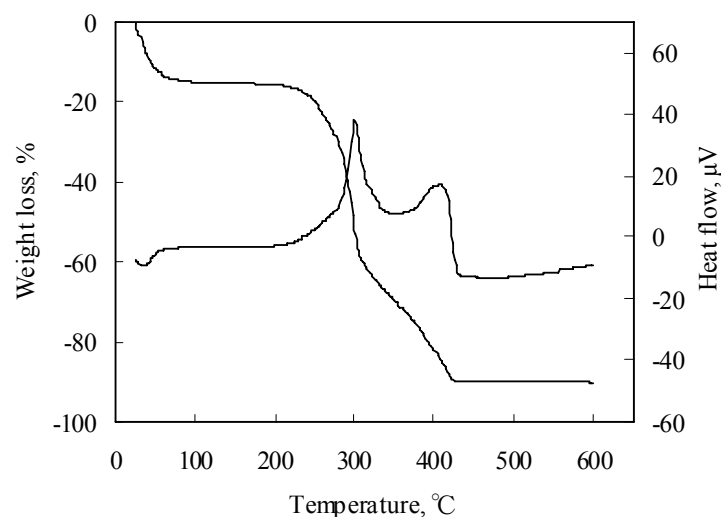
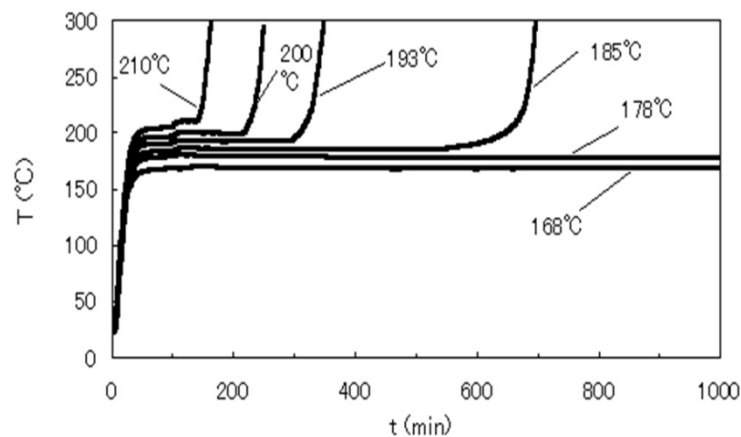


Figure 9. SIT results for RPF.

The reaction of RPF follows the Arrhenius law. The relationship of the induction time, Δt (min), and the spontaneous ignition temperature, T_s (K), in the SIT are shown in the following equation:

$$\Delta t = t_0 \cdot \exp(E/RT_s)$$

where E is the activation energy, R is the gas constant.

SIT data assure the critical height to increase its temperature and be ignited in a huge pile using the Frank-Kamenetskii equation. Heat generation and critical height is expressed with the following equation:

$$\delta_c = (\Delta H \cdot E \cdot r^2 \cdot A / \lambda R T_c^2) \cdot \exp[-E/RT_c]$$

where δ_c is the Frank-Kamenetskii parameter, T_c is the critical ignition temperature, λ is the thermal conductivity, E is the Activation energy, r is the critical height and A is a constant. Calculation results for RPF are shown in Figures 10 and 11. The activation energy, E is 53.8 kJ/mol, which is larger than that of most biomass fuels. That is, RPF is a safer material.

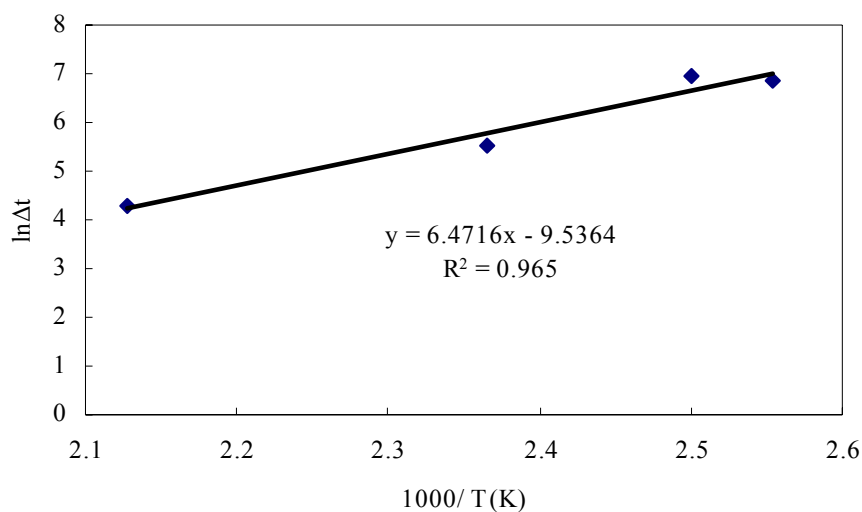
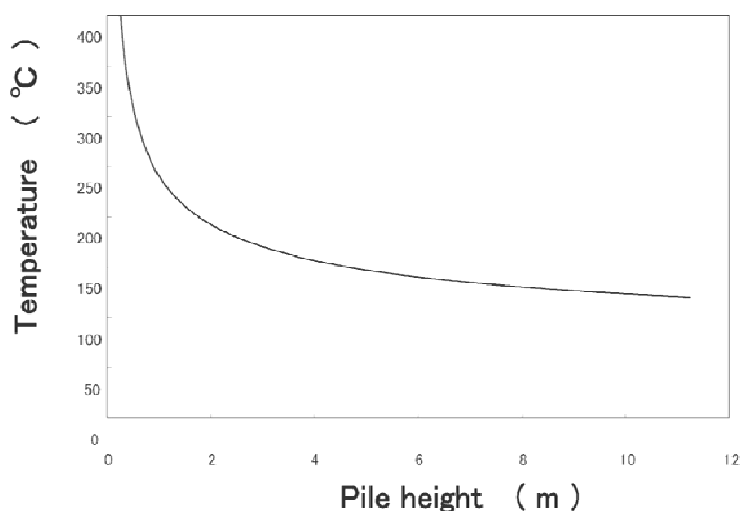
Figure 10. Correlation of induction time to ignition and temperature for RPF.

Figure 11. Calculation results for RPF.

(2) Gas emission tests

Tests using about 10–20 g sample in a 1 liter closed vessel were conducted. Samples were kept at 20 or 30 °C for 10 days. About 20% (weight) water was added to the fuel to find the effect of water. First mainly carbon dioxide (CO₂) was produced by aerobic organisms and then methane and CO₂ were produced by anaerobic organisms under low oxygen concentration circumstances. Methane was produced with aerobic fermentation, and might cause explosions when biomass fuel is stored in silos or indoor storage facilities. So the gas emission test might give the global gas emission characteristics of biomass fuels. Chicken dung gave the largest amount of gas with/without water, and RDF gave a large amount of gas, too.

6. Summary of Evaluation Results

In total about 20 biomass fuel samples were tested. Results of our evaluation are shown in Table 3. The heat generation and cause of fire hazard is divided into four ranks.

Table 3. Examples of evaluation test results.

Rank	Heat Generation*	Without Water	With 20% Water
A	>50 J/g		Chicken dung, Sewage sludge derived fuel A, RDF
B	10~50 J/g	Chicken dung, RDF, Sewage sludge derived fuel A	Wood-pellet (Bark, White)
C	5~10 J/g	Coal (Bituminous coal), Wood-pellet (Bark, White), Sewage sludge derived fuel B, Coal/wood mixture fuel , Cellulose A	Coal (Bituminous coal), Cellulose A, B, Coal/wood mixture fuel, Sewage sludge derived fuel B
D	<5 J/g	RPF, C-RPF, Cellulose B	RPF, C-RPF

* heat generation for 72 hours.

Chicken dung, RDF, and some of the sewage sludge derived fuels are the most hazardous (Rank A with water, Rank B without water). When water was added into these materials they produced much larger heat because of fermentation and water absorption. There are many types of sewage sludge derived fuel, and some of them can be ignited easily. Coal (Bituminous coal) can be used as a standard material, and belongs to Rank C, and the effect of water on heat generation of coal is small. The results of the gas emission tests and the calculation results with the Frank-Kammenetskii equation can be used for evaluation when the fuels are stored in silos or indoor storage facilities. Chicken dung and RDF gave huge gas emissions in both situations, with/without water. Based on the calculation result with the Frank-Kammenetskii equation, chicken dung should be kept at low temperatures.

7. Conclusions

Recent incidents of biomass fuel fires and the investigation of their causes are introduced. We found that water affected heat generation at near room temperature, and fermentation sometimes caused heat generation and caused a fire. After these incidents, we evaluated various biomass fuels under development, and we proposed test methods using thermal analysis using high sensitive heat flux measurements, and gas emission tests. The Frank-Kammenetskii equation can be useful for estimation of heat generation in piles of biomass fuel. Chicken dung, RDF and some sewage sludge derived fuels caused large heat generation, and might start fires. RPF, C-RPF did not generate heat until about 180 °C, which meant no fermentation or another chemical reaction occurred in these fuels, and they are safer. Results of the gas emission test shows that chicken dung, some sludge derived fuels, and RDF are most dangerous when stored in indoor facilities.

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