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Investigation on spontaneous ignition of two kinds of organic material with water

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Abstract

A systematic investigation was performed to elucidate the cause of spontaneous ignition of Refuse Derived Fuel (RDF) and Meat Bone Meal (MBM). Heat generation in both RDF and MBM with addition of water liquid and vapor at room temperature was determined by isothermal calorimetry. Compared with water liquid, the heat of wetting by sorption of water vapor at 80% relative humidity and 25 °C was larger, which can raise the temperature of RDF and MBM more than 30 and 56 °C, respectively. Heat generation due to fermentation occurred and the temperature of RDF and MBM reached or exceeded 80 °C after 5 days for RDF and 4 days for MBM at 100% RH. The spontaneous ignition for RDF and MBM results from heat of wetting and fermentation at room temperature and a further exothermic reaction at higher temperature.

Keywords: Spontaneous ignition; Organic material; Calvet calorimeter; Heat of wetting; Fermentation

1. Introduction

Several fires from spontaneous ignition of organic materials such as Refuse Derived Fuel (RDF), Meat Bone Meal (MBM) and wood chips have occurred in recent years in Japan [1–3]. RDF is a fuel made of domestic combustible rubbish, pressed at 80–90 °C into cylinders 1.5–3.0 cm in diameter and 5–10 cm in length after desiccation at 130 °C. MBM, used as domestic animal food, is shaped into 2.5 mm granules after cooking at 130–135 °C and grinding at 60 °C. The compositions of RDF and MBM are listed in Tables 1 and 2.

Research on spontaneous ignition of RDF and MBM shows an exothermic reaction at higher temperature [2–4]. At room temperature, it was reported that heat generation in RDF was caused by fermentation [5]. However, moisture sorption also may have caused spontaneous ignition of RDF [6,7]. To clarify the cause of spontaneous ignition of RDF and MBM, the sorption of water liquid and vapor at ambient temperature was characterized by isothermal calorimetry and Dewar vessel. Exothermic reactions in RDF and MBM without sorption of water and vapor were examined by Spontaneous Ignition Tester (SIT).

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2. Experiments

2.1. Samples

The RDF samples were small chips from cylinders taken from a silo of RDF in Mie Prefecture, Japan. The MBM samples were 2.5 mm diameter granules from the Ministry of Agriculture, Forestry and Fisheries in Japan.

2.2. Calorimeters

The Calvet calorimeter experiments were carried out with C 80 and MS 80 (Setaram, France) calorimeters. The standard cell and membrane-mixing cell of C 80 were used. In the experiments with membrane-mixing cell, 1.50 g sample of RDF was placed above, and 2.00 g water under, a membrane made of stainless steel mesh with 0.05 mm pores. The heat generation, therefore, resulted from water vapor sorption by the sample. A 0.1 mm thick plastic membrane was used to obtain data with no vapor sorption.

A Thermal Activity Monitor (TAM) 2277 (Thermometric Inc., Sweden) isothermal calorimeter [8] with a 4 mL ampoule and a relative humidity control system was also used to study water liquid and vapor sorption. The air-

Table 1
Composition of Refuse Derived Fuel in mass% [4]

Water	5.38
Volatile	72.6–76.3
Carbon	46.2–51.8
Hydrogen	6.60–7.11
Nitrogen	1.11–1.30
Sulphur	0.48–0.59
Chloride	0.53–0.90
Calcium	2.1–2.7

Table 2
Composition of Meat Bone Meal [3]

Water (mass%)	4.54
Protein (mass%)	50.4
Fat (mass%)	10.6
Ash (mass%)	30.7
Calcium (mass%)	11.36
Chloride (wt%)	0.36
Iron (mg kg^{-1})	500
Zinc (mg kg^{-1})	500
Cobalt (mg kg^{-1})	9.6
Copper (mg kg^{-1})	8.5
Phosphorus (wt%)	5.74

flow rate was 40.8 mL h^{-1} at a relative humidity (RH) of 80%.

2.3. Dewar experiments

A spherical Dewar vessel of 1000 mL with an overall heat transfer coefficient of 0.1968 J m^{-2} s K was used to conduct the heat accumulation tests for RDF at room temperature and 50 °C. Water liquid was added from top of the Dewar vessel. Temperature was measured at three points in the Dewar (Fig. 1).

2.4. Experiments by SIT

The SIT (SIT-2, Shimadzu Co. Ltd., Japan) tests were carried out with air atmosphere at 5 mL min^{-1} after isothermal

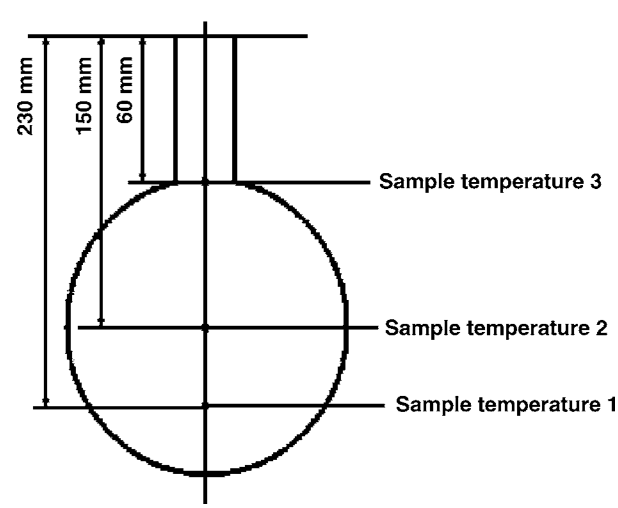

Fig. 1. Positions of thermocouples for the Dewar tests.

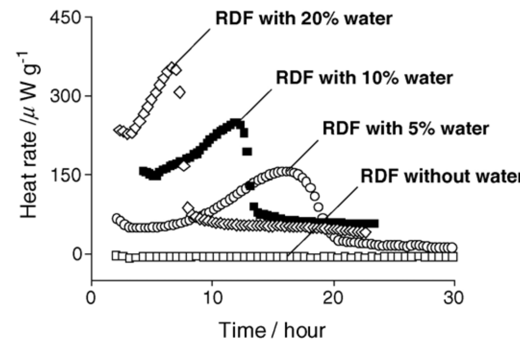

Fig. 2. Curves of heat rate vs. time for RDF with different water content at 27 °C by C 80 with standard cell.

conditions were established with nitrogen atmosphere. The sample mass was 1039–1071 mg for RDF and 800.3–808.8 mg for MBM.

3. Results

3.1. Results for RDF

3.1.1. Results by Calvet calorimeters

The curves of heat rate versus time in Fig. 2 show an exothermic peak at the beginning of the experiments for samples of RDF with addition of water liquid. The peak value of the second exothermic process increased with increasing water content. Tests by MS 80 validated the C 80 results. Heat generations for the samples of RDF by C 80 and MS 80 with standard cell are given in Table 3.

The experimental results by C 80 with special mesh membrane cell are shown in Figs. 3–5 and Table 4. The heat generation for the water vapor sorption test of RDF at 59 °C is given in Fig. 3. The maximum heat rate of the first exothermic process (AB) was 389 μW g^{-1} and total heat was 13.26 J g^{-1} at 1.07 days when heat rate equal zero, which can raise the temperature of RDF more than 9 °C if there is no heat loss. The fast increase of heat rate began 1.90 days later. Apparently, there was another exothermic process after 5.23 days. For the water vapor sorption test of RDF at 26.33 °C, there was no first exothermic peak compared with that at 59 °C (Fig. 4). Heat generation began after 2.27 days. The fast increase of heat rate began after 5.07 days. For the

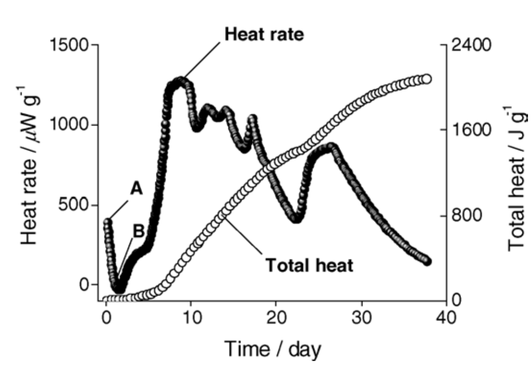

Fig. 3. Curves of heat rate and total heat vs. time for RDF by C 80 with mesh membrane cell at 59 °C.

Table 3
Results for RDF with different water content by Calvet calorimeters

Test No.	Sample mass (g)	Water mass (%)	Isothermal temperature (°C)	Maximum heat rate per gram of the sample (μW g^{-1})	Total heat (J g^{-1})	Calorimeter
1	4.50	0	27	–	–	C 80 (standard cell)
2	4.27	5	27	156	6.73 (30.72 h)	C 80 (standard cell)
3	4.07	10	27	250	8.75 (23.67 h)	C 80 (standard cell)
4	3.61	20	27	354	8.56 (22.89 h)	C 80 (standard cell)
5	2.26	0	Room temperature	–	–	MS 80
6	2.27	16.54	Room temperature	220	18.73 (75.66 h)	MS 80
7	2.24	34.50	Room temperature	276	14.95 (41.72 h)	MS 80

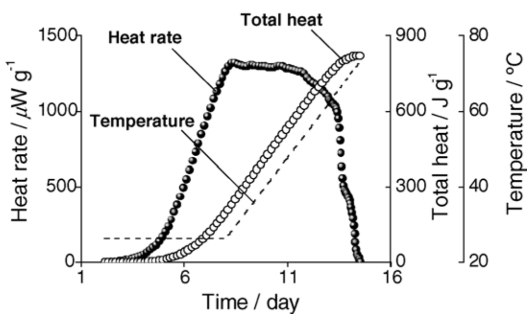

Fig. 4. Curves of heat rate and total heat vs. time for RDF by C 80 with mesh membrane cell at 26.33 °C.

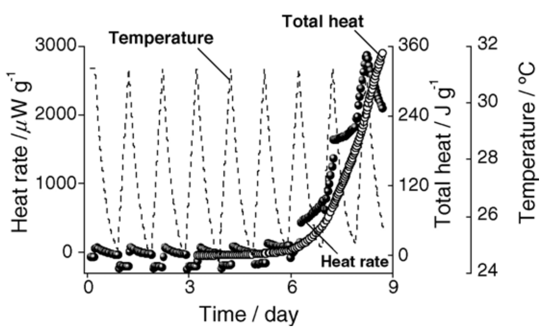

Fig. 5. Curves of heat rate and total heat vs. time for RDF by C 80 with mesh membrane cell in the temperature range of 24.4–31.2 °C.

water vapor sorption test of RDF at 78.8 °C (Table 4), there was first exothermic peak only comparable to that at 59 °C. Heat generation was detected immediately after the data collection began. The heat rate decreased to zero after 9 h, and continued to decrease to negative values. The total heat was 10.43 J g^{-1}, which can raise the temperature of RDF more than 7 °C. For the water vapor sorption test of RDF in the temperature range of 24.4–31.2 °C, similar results to those at 26.33 °C were obtained (Fig. 5). The heat generation increased very slowly in the first 5 days. At 5.87 days, a rapid exothermic process began.

3.1.2. Results by TAM

The exothermic process occurred in RDF with addition of water liquid while no heat generation was detected in RDF without additional water at room temperature (Table 5).

For the water vapor sorption test of RDF at 25 °C by TAM with RH control system, the heat generation from heat of water vapor sorption was detected at the beginning of the test (Fig. 6). Compared with the results by C 80 with mesh membrane cell, the heat generation by TAM was much less. When the experiment was ended at 8.89 days, the heat rate was stable at 44 μW g^{-1}.

3.1.3. Results by Dewar and SIT

In the Dewar tests, temperature in RDF rose continuously after addition of water liquid. This phenomenon was more significant at 50 °C (Fig. 7). No temperature rise was measured in RDF without addition of water even though the test lasted more than 230 h. The data in Table 6 show the temperature rise for sample temperature 3 was the highest among the three tempera-

Table 4
Total heat and adiabatic temperature rise for RDF by C 80 with mesh membrane cell

Testing time (day)	59 °C		26.33 °C[a]		78.8 °C		24.4–31.2 °C[b]	
	Total heat (J g^{-1})	Adiabatic temperature rise (°C)[c]	Total heat (J g^{-1})	Adiabatic temperature rise (°C)[c]	Total heat (J g^{-1})	Adiabatic temperature rise (°C)[c]	Total heat (J g^{-1})	Adiabatic temperature rise (°C)[c]
0.38 (9.11 h)	6.45	4.54	–	–	10.43	7.35		
1	13.22	9.31	–	–	–	–	–	–
3	19.52	13.75	0.33	0.23	–	–	0.37	0.26
5	54.57	38.43	11.94	8.41	–	–	2.71	1.91
8	250.17	176.55	198.34	139.68	–	–	199.74	140.66

[a] The temperature was heated to 80 °C by heating rate of 0.005 °C min^{-1} after the temperature had been kept at 27 °C for 8 days.
[b] The temperature change periodically from 32 to 22 °C in 12 h and then from 22 to 32 °C in another 12 h for 8.5 days after the temperature had been kept at 32 °C for 5 h.
[c] The heat capacity of RDF is 1.42 J g^{-1} K^{-1} [4].

Table 5
Results for RDF with different water content by TAM

Sample mass (g)	Water mass (%)	Isothermal temperature (°C)	Calorimeter	Maximum heat rate per gram of the sample ($\mu W\,g^{-1}$)	Total heat ($J\,g^{-1}$)
0.99	0	25	TAM	–	–
0.94	20	25	TAM	672.57	31.20 (45 h)
0.91	50	25	TAM	664.40	21.14 (45 h)
0.99	Vapor with 80% RH[a]	25	TAM-RH	97.46	43.99 (8.89 days)

[a] The test was carried out at 80% RH and with 40.8 mL h^{-1} of air flow rate.

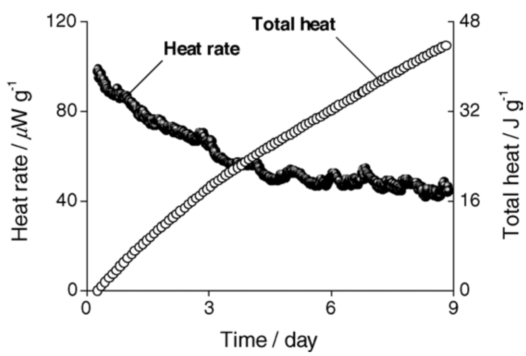

Fig. 6. Curves of heat rate vs. time for RDF by TAM with RH control system at 25 °C.

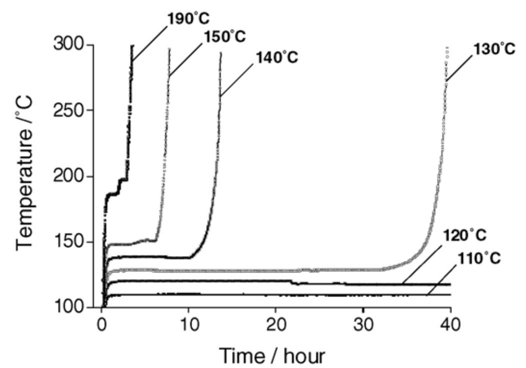

Fig. 8. Curves of temperature vs. time for RDF without additional water by SIT.

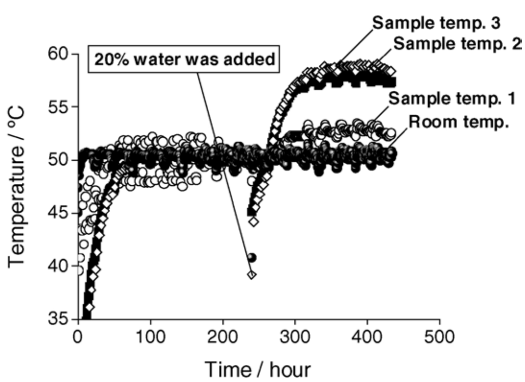

Fig. 7. Curves of temperature vs. time for RDF by Dewar at 50 °C.

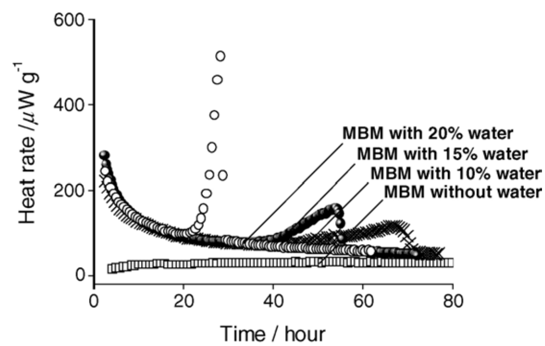

Fig. 9. Curves of heat rate vs. time for MBM with different water content by C 80 at 30 °C.

ture points and sample temperature 1 was the lowest, indicating the more water absorbed by RDF the more heat was produced.

The results by SIT suggest that the onset exothermic temperature for RDF without addition of water was higher than 130 °C (Fig. 8). According to the extrapolated results of the linear fitting for the relationship of induction time and temperature, the exothermic reaction for RDF would occur after 20 days if ambient temperature was 80 °C and 38.5 h at 120 °C.

3.2. Results for MBM

3.2.1. Results by C 80

For the experiments by C 80 with standard cell shown in Fig. 9, an exothermic peak appeared at the beginning of the experiments for samples of MBM with addition of water liquid. The peak value of the second exothermic process increased with increasing water content. There was no heat generation in MBM without addition of water. The total heat values for the samples of MBM by C 80 are given in Table 7.

Table 6
Temperature change in RDF with addition of water by Dewar vessel

Position of thermocouple	Temperature drop below 50 °C/ °C	Temperature rise rate ($°C\,d^{-1}$)	Temperature rise above 50 °C/ °C
1	3.0 °C	0.10	3.4
2	5.8 °C	0.22	8.0
3	12.2 °C	0.32	9.1

Table 7
Results for MBM with different water content by C 80

Sample mass (g)	Water content (%)	Isothermal temperature (°C)	Maximum heat rate per gram of the sample ($\mu W\,g^{-1}$)	Total heat ($J\,g^{-1}$)	Cell type
4.61	0	30	–	–	Standard
4.06	10	30	221.90	25.40 (77.28 h)	Standard
3.83	15	30	281.80	24.92 (77.28 h)	Standard
3.63	20	30	517.89	23.84 (77.28 h)	Standard
1.50	Vapor	22–32	1895.07	184.12[a] (6.30 d)	Membrane-mixing cell

[a] The total heat of 184.12 $J\,g^{-1}$ can raise the temperature of MBM more than 82.94 °C (the heat capacity of MBM is 2.22 $J\,g^{-1}\,K^{-1}$ [10]).

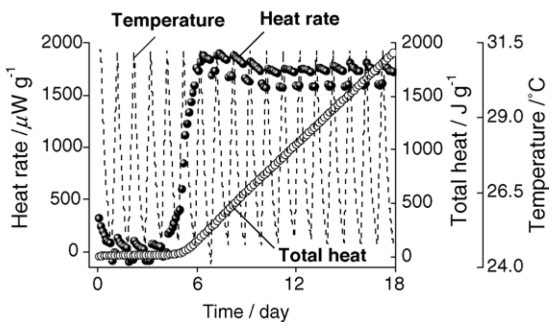

Fig. 10. Curves of heat rate and total heat vs. time for MBM by C 80 with mesh membrane cell in the temperature range of 22–32 °C.

For the water vapor sorption test of MBM from 24.1 to 31.3 °C, similar results to RDF were obtained (Figs. 5 and 10). Heat generation increased very slowly during the first 4 days, and at 4.23 days, a rapid exothermic process began.

3.2.2. Results by TAM and SIT

A similar phenomenon for MBM by TAM to that by C 80 with standard cell was observed. Compared with RDF, the total heat by water liquid sorption by MBM was a little less (Table 8). For the water vapor sorption test of MBM at 25 °C by TAM with RH control system, both the heat rate at the beginning of the test and total heat were larger than that of RDF. Similar to RDF, total heat for MBM by TAM was much less than that by C 80 with mesh membrane cell (Fig. 11). When the experiment was ended at 11.83 days, the heat rate was down to 57 $\mu W\,g^{-1}$. Obviously, the total heat for MBM by vapor sorption was larger than for RDF.

The results for MBM by SIT suggest that the onset exothermic temperature was higher than 180 °C [3]. The linear fitting for the relationship of induction time with temperature suggests the exothermic reaction for MBM would occur after 20 days at 150 °C.

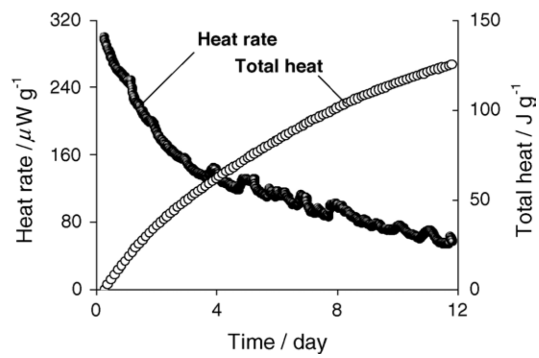

Fig. 11. Curves of heat rate vs. time for MBM by TAM with RH control system at 25 °C.

4. Discussion

4.1. Spontaneous ignition of RDF

The results show that heat generation occurred after water was added to RDF. The immediacy of the exothermic process shows this heat generation does not result from fermentation. According to Walker and Prunty [11,12], heat generation results from heat of wetting of RDF. Compared with water vapor, the data obtained by TAM suggest that the heat generation was small when liquid water was sorbed by RDF, but the heat of wetting of RDF by water liquid raises the temperature of RDF by several degrees. The results by Dewar vessel reveal that the temperature rise for RDF at 50 °C was 9.1 °C.

In the C 80 experiments with mesh membrane cell at 100% RH, the heat of vapor condensation was balanced by the heat of vaporization of water, and no exothermic process was detected at the beginning of the experiments at room temperature. A large heat generation occurred after 5 days. Assuming the vapor sorption rate is constant, then the final water content in theory can be calculated (Table 9). In fact, the water content is higher because

Table 8
Results for MBM with different water content by TAM

Sample mass (g)	Water content (%)	Isothermal temperature (°C)	Calorimeter	Maximum heat rate per gram of the sample ($\mu W\,g^{-1}$)	Total heat ($J\,g^{-1}$)
1.81	0	25	TAM	–	–
1.80	10	25	TAM	218.54	6.74 (45 h)
1.81	20	25	TAM	422.21	6.22 (45 h)
1.06[a]	Vapor with 80% RH	25	TAM-RH	299.71	125.41 (11.83 d)

[a] The test was carried out at 80% RH and with 40.8 $mL\,h^{-1}$ of air flow rate.

Table 9
Vapor sorption for RDF and MBM by C 80 with mesh membrane cell

Parameter	RDF				MBM
	59 °C	26.33 °C	78.82–78.88 °C	24.4–31.2 °C	24.4–31.2 °C
Total vapor sorption mass (g)	1.08 (38 d)	0.65 (15 d)	0.95 (7 d)	0.25 (8.71 d)	0.44(17.89 d)
Vapor sorption rate (g d^{-1})	0.028	0.043	–	0.029	0.024
Vapor sorption mass (g)	0.15	0.23	–	0.17	0.15
Water content in theory (%)	13.80 (5.23 d)	17.72 (5.23 d)	–	15.02 (5.87 d)	13.28 (6.30 d)

fermentation can be detected when water content in RDF was ≥35% while no gas generation occurred when water content was ≤23% [14]. The large heat generation in the experiments at 26.33 °C and 24.4–31.2 °C thus results from fermentation due to the high water content in RDF.

The experimental results at 59 and 78.8 °C by C 80 with mesh membrane cell further confirmed this. At 59 °C, there was a short exothermic process at the beginning of the experiment, and then a significant exothermic process after 5.23 days. At 78.8 °C, there was a short exothermic process at the beginning, but no second exothermic process. Thus, there is no fermentation process when temperatures ≥78.8 °C.

In the experiments by TAM with RH control system, the water vapor was supplied from outside the sample cell. When the water vapor condenses, heat is generated. A higher heat generation was therefore detected at the beginning of the TAM tests for both RDF and MBM (see Figs. 4, 6, 10 and 11). However, the water content in the RDF samples increased very slowly due to the lower RH of 80% compared with 100% RH in the C 80 tests with mesh membrane cell. The maximum mass of the vapor throughout the space of the sample cell was only 0.16 g. The heat generation due to fermentation was not detected in the experimental period of 9 days.

According to the Special Committee for Investigation on the Accident of Refuse Derived Fuel Power Station in Mie Prefecture in Japan, the hygroscopicity of RDF can increase the water content to 14–19% from less than 10% under 90% RH at 40 °C for 8 days [13]. Higher water content would be achieved after longer storage in the rainy season or with dew.

4.2. *Spontaneous ignition process of MBM*

Heat generation occurs in MBM with addition of water liquid. The second exothermic process occurred later than that of RDF and was not detected in the TAM. The oily property of MBM causes water to not be easily adsorbed. Compared with water vapor, the data suggest that the total heat is small when water liquid is sorbed.

When water vapor is sorbed, a large heat generation occurs. The large heat generation results from fermentation at high water content.

In the TAM with RH control, the heat rate for MBM was larger than that of RDF; however, the heat generation due to fermentation cannot be detected in a period of 11.83 days because of the lower water content in MBM.

5. Conclusions

The temperature rise for both RDF and MBM at room temperature first results from heat of wetting by sorption of water liquid and/or vapor. The total heat and the temperature rise of RDF depend on the storage conditions, i.e. temperature, water content and RH. Compared with liquid, the heat of wetting by sorption of vapor is larger, which can raise the temperature of RDF and MBM at 80% RH and 25 °C more than 30 and 56 °C, respectively. In the experiments by C 80 with mesh membrane cell lasting more than 5 days for RDF and 4 days for MBM at 24.4–31.2 °C and 100% RH, a large total heat due to fermentation occurs. The temperature for both RDF and MBM reaches or exceeds 80 °C. According to the results by SIT, a further exothermic reaction at higher temperature occurs subsequently.

The spontaneous ignition of RDF and MBM results from heat of wetting and fermentation at room temperature and a further exothermic reaction at higher temperature. To prevent fire accidents from occurring again, it is important to monitor relative humidity and temperature inside the organic materials, especially in rain and dew. Long-term storage should be avoided.

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