Thermal Properties of Biocoke for Safety Storage

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ABSTRACT

In order to get out from under global warming, expanding use of renewable energy is proposed in many countries. Although biomass is one of the renewable energy, it is not common because of its disadvantage of low transport efficiency from low density. Since Biocoke of which biomass is heated with compression has high density and high compressive strength, it is used as substitute of coal coke in several types of furnaces or considered as an effective method of volume reduction of gathered radioactive biomass generated by the Great East Japan Earthquake.

In Japan, Biocoke is determined as designated flammable goods in the same manner of Refuse-derived fuel, while it is reported that Biocoke is difficult to be ignited because of high density with little porosity. Although it is very important to know the thermal property while they are stored in other words, in the low temperature range, it has not investigated enough. So in this study, to investigate the possible origination of fire accidents, the generated heat from Biocoke made from bark and bark before making to Biocoke were measured by highly sensitive isothermal calorimeter in the condition of 50 °C, air packed atmosphere and for 3 days. The exothermic phenomenon which is caused by microbial fermentation was observed. Particularly, the sample with water addition appeared the large exothermal peak. In the both case with water addition and without water addition, the generated heat from Biocoke is less than that from bark. It is summarised that the storage of Biocoke is safer than that of raw material because microbial fermentation in the temperature range between 20 and 50 °C is inhibited by 130 °C heated in the Biocoke manufacturing process. In particular, Biocoke is much safer than raw material when stored in wet condition such as outdoor without roof.

Keywords: Biocoke, Safety storage, heat by fermentation, Recycled fuel, high sensitivity isothermal calorimeter

1. INTRODUCTION

At the 21st Conference of the Parties of the United Nations Framework Convention on Climate Change (UNFCCC) in Paris (COP21), the Paris Agreement was adopted by consensus by all of the 195 UNFCCC participating member states and the European Union. In this agreement, to keep a global temperature rise this century well below 2 °C and to drive efforts to limit the temperature increase even further to 1.5 °C above pre-industrial levels was set as main goal [1].

Before and during the Paris conference, countries submitted comprehensive national climate action plans which is called as Intended Nationally Determined Contributions (INDCs). The outline of Japan's INDC [2] is to reduce greenhouse gas (GHG) emissions at the level of 26.0% by fiscal year (FY) 2030 compared to FY 2013 (25.4% reduction compared to FY 2005) (approximately 1.042 billion t-CO₂ eq. as 2030 emissions). In order to achieve its target, expansion of the use of renewable energy that is solar, wind power, geothermal, hydropower and biomass is promoted.

Biomass power generation is important as a base-load power because it is capable of stable output that does not depend on the weather. It is estimated that power generation from biomass will constitute between 3.7% and 4.6% (between 39.4 and 49.0 billion kWh) of total power generation in FY 2030 (approx. 1065 billion kWh) [2]. For biomass power generation as of November 2014 is 17.7 billion kWh [3], it is necessary to construct more than twice the power plant in FY 2030. As described above, usage of biomass as energy is required to accomplish Japan's INDC.

On the other hand, biomass is lower energy density per volume as compared with fossil fuels so there is a problem that transport efficiency is low. Since the efficiency of the steam-power generation, which is the mainstream of biomass power generation, is improved as the power generation capacity increases, it is needed that the stable large amounts of biomass can be collected for a long time in order of power plant operation is economically justified. Therefore, the construction of the power plant is required to be in the vicinity of the biomass supply locations.

Biocoke (BIC) which is patented technology [4] is highly densified biomass fuel [5]. It is made from photosynthetic biomass in the manner of heating about lower than 200 °C with compressing about 20MPa and cooling with compression into lower than 60 °C. A commercial size plant was installed in 2011 in Takatsuki City, Osaka Prefecture [6] and some plants have been installed for 5 years [7-9]. The density of BIC is over 1200 kg/m³, so its transportation efficiency is higher than before BIC. It is considered that the amount of biomass usage increases by BIC technology. Actually BIC is used as substitute of coal coke in high temperature gasifying and direct melting furnace [10] and cupola furnace [11] as solid fuel, coupled with another advantage that has high compressive strength[12,13].

On the other hand, a lot of radioactively contaminated debris was generated by the Fukushima Daiichi nuclear disaster that was occurred on March 11, 2011. They are gathered and stored at temporal space. Because the bulk density of biomass is low, temporal space is filled with and there is no space to be carried in. So rehabilitation and reconstruction is not progressed smoothly [14]. In this situation, it has been investigated that gathered biomass is downsized by BIC technology to utilize temporal space efficiently [15,16].

Now in the Japanese Fire Service Act, BIC is determined as designated flammable goods in the same manner of Refuse-derived fuel (RDF), straw products and wood wool which will, once having caught fire, lead to the quick spread of the fire or make it extremely difficult to carry out fire extinguishing activities. In fact, it is reported that improper storage of RDF and wood chips makes fire accidents [17, 18]. The combustion mechanism starting from exothermic phenomenon from 20 to 50 °C by microbial fermentation was proposed [19]. Although BIC is considered to be difficult to burn because of high density with little porosity [20], the exothermic phenomenon of BIC at less than 50 °C have not been investigated so much. So the thermal property of BIC for safety storage that is very important in the both cases that are energy use and downsizing mentioned above is investigated in this study.

2. MATERIALS AND METHODS

2-1. Production of BIC

In this study, bark of wood that is also used as raw material in Takatsuki plant was used to produce BIC. Bark was dried to about 11% moisture in the laboratory kept at 25 °C. And it was cut under 1 mm size particle by cutter mill. BIC of diameters 4mm was shaped cylindrically under the same manufacturing conditions such as moisture and heating temperature. Loading force was determined to add the twice loading pressure in the case of over 8mm size BIC [13,21,22] because highly densified BIC was not produced if pressed at same pressure in the case of over 8mm size BIC. Retention time was set linearly with the diameter to see as a simple one-dimensional heat transfer model. Table 1 lists the production conditions, and Fig. 1 shows a schematic drawing of BIC of diameter 4mm producing device. Based



Fig. 1 Schematic drawing of BIC of diameter 4mm producing device

on Table 1 and Fig. 1, the production method of BIC starts with measuring the material weight. The measured material is stuffed into a cylinder and sealed with molds. Then, the top of the mold in the sealed cylinder is applied pressure at the foregoing setting conditions. After putting the top mold under the setting pressure, the cylinder is enclosed with an electric heating furnace, and a thermocouple is inserted into the cylinder to control the heating temperature. The set cylinder, in this condition, is heated

until it reaches production temperature. Afterward, the production temperature is held during the determined retention time. After waiting until a prescribed time, the furnace is taken off and the cylinder is cooled down to less than 30 $^{\circ}$ C with an electric fan.

Table 1 Production conditions of BIC									
Size of BIC Diameter	Moisture	Production Temperature	Weight	Loading Force	Retention Time				
(mm)	(%)	(°C)	(g)	(kg)	(sec)				
4.0	11	130	0.1	54	75				

2.2 Highly sensitive isothermal calorimeter

In order to evaluate the faint heat generation from the microbial fermentation, a highly sensitive isothermal calorimeter (2277 Thermal Activity Monitor (TAM), Thermometric) was used. Fig. 2 shows a schematic drawing of TAM. TAM that has a thermostatic bath that has been precisely temperature control (temperature drift over 24 hours of less than ± 0.0001 K) is one of the most sensitive, stable and flexible microcalorimeter systems for directly measuring this universal heat signal and, therefore, the quantitative thermodynamic and kinetic observation of any process such as the stability of various materials and material compatibility. It is a unique microcalorimeter system that is completely modular and combines the highest heat flow sensitivity with unmatched long-term temperature stability for measuring many processes that are undetectable by other techniques.

The sample, which was measured about 0.1 g, was packed with air into ampule. The bark that was cut and dried at room temperature, and cylindrical BIC of diameter 4mm were used. The samples were isothermally kept at 50.0 °C for about 3 days and measured the heat flow. The reason why set temperature is



Fig. 2 Schematic drawing of TAM

50 °C is because it is known that much of microorganisms are active in the temperature between 40 and 50 °C, and a lot of investigations measured at 50 °C were reported [19]. And the samples to which ion-exchanged water was added (20% of the sample's weight) were measured in order to examine the effect of moisture. The moisture content after water addition is calculated to be 26%. The measured samples are listed in Table 2.

Table 2 Sample measured in TAM							
Sample	Moisture	Shape	Weight	Size			
Bark	110/	Powder		<1mm			
BIC from bark	11%	Cylinder	0.1~	$\phi 4 \times \sim 5.5$			
Bark + water	26%	Powder	0.1g	<1mm			
BIC from bark+ water		Cylinder		$\phi 4 \times \sim 5.5$			

3. RESULTS AND DISCUSSION

3-1. Produced BIC

Pictures of the produced BIC are shown in Fig. 3. All specimens are blackened on all exposed surfaces (top, side, and bottom) which were brown color before produced. The density of BIC was shown in Fig.4. The density is in the range between 1.38 kg/m^3 and 1.41 kg/m^3 and its mean is 1.40 kg/m^3 with a standard deviation of 0.019 kg/m³. The real density that is defined, as the ratio of the dry specimen mass to the volume of its solid part is known about 1.50 kg/m^3 in the case of bark of wood [23]. The moisture

content of BIC is 11% so the calculated real density is 1.45 kg/m^3 . The calculated porosity in BIC is less than 5% by heated and compressed enough.



1.50

3.2 Highly sensitive isothermal calorimeter

The heat flux per 1gram sample without water is shown in Fig.5 and 6. Sample was set into TAM immediately after the measurement was started. All samples show rapidly exothermic behavior within a few minutes after the start of measurement and then heat flux decreased. Its peak of the sample with water addition is higher than without water addition. In the case of bark dried at RT (room temperature) with water addition, second exothermic peak was appeared about 20 hours after the start of measurement after peak and heat flux decreased gradually.



It is thought that this heat generation is occurred due to a biological activity that is fermentation, which is active in wet condition and active in the temperature range below 50 °C [19]. The first peak is appeared in the heating process in other words in the temperature range between 25 and 50 °C. So it is considered the fermentation by microorganisms, which is active below 50 °C, results in the first peak and subsequent decrease is caused that microorganisms become inactive because of too high temperature atmosphere for them. The second peak which is shown in the case of bark dried at RT with water addition is caused by fermentation by which microorganisms is active at 50 °C. In this study, sample was packed with air so the decrease of heat flux after second peak is result from consumption of oxygen by aerobic fermentation. It is considered that the sample without water addition does not generate heat because the moisture of sample is too low to ferment. Since BIC was produced by heating at 130 °C, it is considered that almost of microorganisms attached on sample was dead. So the generated heat from produced BIC is less than that from raw material.

The amount of generated heat per 1gram sample without water, which is found by graphical integration in Fig.5 and 6, and max heat flux are listed in Table 3. The integration range is from 0 to 24 hours, from 24 to 72hours and from 0 to 72 hours. The generated heat from BIC is decreased to 72%, 71% and 73% in the range of 0-24hours, 24-72 and 0-72 respectively compared with that from bark. In the case of water addition, the generated heat from BIC is decreased to 54%, 24% and 35% in the range of 0-

24hours, 24-72 and 0-72 respectively compared with that from bark. The max heat flux of BIC and BIC with water addition decrease to 87% and 45% respectively compared with that of bark and bark with water addition.

Table 3 Generated heat kept at 50 °C by TAM							
Sample	From 0 to 24 hrs	From 24 to 72 hrs	From 0 to 72 hrs	Max heat flux			
	J/g _{-dry}	J/g_{-dry}	J/g_{-dry}	$\mu W/J/g_{-dry}$			
Bark	0.81	1.44	2.25	112			
BIC from bark	0.58	1.26	1.84	97			
Bark + water	24.7	44.9	69.6	3735			
BIC from bark+ water	13.4	10.9	24.3	1681			

The combustion mechanism with the following steps has been proposed [19]. The first step occurred at from 20 to 50 °C by fermentation. When the temperature increased to from 60 to 80 °C, most microorganisms died from heating, which greatly inhibited aerobic heat generation. Generated heat accumulated up to 100 °C, after which the water content vaporized and the second stage of the process occurred. Fatty acid esters are present in plants, and may be oxidized, producing peroxide. The third step, in which cellulose and other organic materials start burning, occurred over 100 °C.

If the amount of generated heat is not enough to go next step, the fire accident does not occur. In the situation of storage, the fire accident does not occur if the accumulation of heat is less than sum of the release of heat from surface of pile and endothermic phenomenon such as vaporization of water.

As the results and discussion described above, we can say that storage of BIC is safer than that of raw materials because both the amount of generated heat and the peak heat flux of BIC is small compared to those of raw material. In particular, in the wet condition, for example outdoors storage with no-roof condition, storage of BIC is much safer than that of raw material. It is difficult to decide the safety standard of the heat flux in storage because the release of heat from surface of pile changes by the storage condition such as the amount of pile, coefficient of thermal conductivity and specific heat. And for totally risk assessment for fire accident, it is necessary to study the pyrolyzed flammable gas, spontaneous ignition and so on in addition to the above.

4. CONCLUSIONS

The heat flux of bark and BIC from bark with and without water addition was measured in the condition of 50 °C isothermally, air packed atmosphere and for 3 days by highly sensitive isothermal calorimeter (TAM), and the results were summarized as follows:

- 1) All samples show rapidly exothermic behavior within a few minutes after the start of measurement and then heat flux decreased. It is caused by the fermentation by microorganisms which is active below 50 $^{\circ}$ C.
- 2) The heat flux of bark and BIC with water addition was increased compared to with no water addition. It is because almost of microorganisms does not work in the moisture condition suitable for producing BIC that is about 11%.
- 3) The amount of generated heat and the peak heat flux of BIC are small compared to those of raw material. It is because almost of microorganisms attached on bark was dead while BIC was produced by heating at 130 °C.
- 4) It is revealed that the storage of BIC is safer than that of raw material because microbial fermentation in the temperature range between 20 and 50 °C is inhibited by 130 °C heated in the manufacturing process. In particular, BIC is much safer than raw material when stored outdoor with out roof.

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