**A Study of Physical Properties of High-Density Solid Biomass, Bio-coke, with Unutilized Biomass**

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**Abstract**

We produced high-density solid biomass (hereafter called Bio-coke) from broccoli, dead cherry tree leaves, and seed of mango based on our patent (PAT.-No.4088933) as one of the utilization methods of various unutilized biomass. The compressive strength of each kind of Bio-coke under room temperature was measured with a compression testing machine. The experimental results showed that the ultimate strength was related to the carbon content of broccoli, seed of mango, and dead cherry tree leaves, and the relations were close to linear.

**Key words**

Bio-coke, Initial moisture content, Processing temperature, Thermal analysis, Ultimate strength, Carbon content

1. Introduction

The regulation governing organic waste processing has been enforced in recent years. For example, the enforcement of food recycling and emission control of livestock industry wastes has resulted in about 30 million tons of organic wastes produced annually in Japan. This number however could be about 300 million tons if the non-processed biomass wastes are counted. These organic wastes such as sludge, domestic refuse, livestock waste, forestry waste, and so on are mainly unutilized biomass. It is estimated that the total combustion energy of organic wastes exceeds 10% of the annual total energy consumption in Japan [1]. However, it seems that the effective fraction of recycled organic wastes is currently 10% or less, and a large portion of the wastes is processed in landfills or by incinerations. It is shown in ‘Biomass Nippon Strategy’ adopted by the cabinet in 2002 that the utilization of waste biomass should be increased to about 80% by the year 2010[2].

In addition, the third session of the Conference of the Parties (COP3) to the United Nations Framework Convention on Climate Change held in Kyoto in 1997 had negotiations to address important global warming measures adopted in the Kyoto protocol. In the third article of the protocol, there is the provision that the parties must not exceed each emissions allowance estimated to reach a 5 percent reduction goal of the amount of CO₂ emissions for all parties by 2012 from 1990 levels. Under that protocol, Japan promised to reduce CO₂ emissions by 6 percent from 1990 levels by 2012.

There are not enough biomass utilization technologies to simultaneously achieve the two targets: the utilization of about 80% waste biomass and 6 percent reduction in the amount of CO₂ emissions. Thus, it is necessary to develop new technologies aimed at the utilization of unused biomass as energy and fuels to solve the problems of emission control of waste biomass and CO₂ emissions reduction. As a result, Bio-coke, the highly densified biomass briquette, was developed as a substitute for coal coke which is a fossil fuel. This new solidification technology enables the production of solid fuels from unutilized biomass and has the potential of becoming one of the methods to solve emissions control and environmental issues.

In this study, a solid biomass based fuel instead of coal coke was produced. One of the roles of coal coke is to keep the permeability of air and liquid in the blast furnace. Furthermore, a loading pressure of 0.1MPa is loaded on coal coke within the furnace [3]. Hence, coal coke requires hardness. As such Bio-coke requires hardness as well. The compressive strength of Bio-coke produced from broccoli, dead cherry tree leaves, and seed of mango are examined at room temperature and their physical properties are discussed. Also, the thermal decomposition of the raw materials was observed to obtain an optimum temperature range for the production of the Bio-coke. The relation between carbon content and ultimate strength derived by the compression test for each Bio-coke was also discussed.

2. Equipment and Procedure

2.1 Thermal analysis measurement

In order to assess the thermochemical characteristic of the raw biomass materials prior to the production of the Bio-coke, the measurements of yield of weight and exothermic / endothermic properties were performed with a differential thermal / thermogravimetry analyzer.

Table 1 shows the conditions of thermal analysis, and Fig. 1 shows a schematic drawing of TG / DTA device. Also, Fig. 2 shows an example of result obtained from a TG / DTA analysis. The left vertical axis in Fig. 2 shows the TG data, and the right vertical axis shows the DTA data. Also shown in Fig. 2 is an outline of the starting temperature of gasification, T₀, and the maximum gradient in gasification area. The maximum gradient indicates the gasification ratio and ignitability of raw biomass.

In this study, we observed the change in the thermal decomposition properties for each raw biomass material until the gasification region using the TG / DTA analyzer.

<table>
<thead>
<tr>
<th>Table 1 Conditions of thermal analysis</th>
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<tr>
<td>Sample weight [mg]</td>
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<tr>
<td>Gas flow rate [cm³/min]</td>
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<td>Gas atmosphere</td>
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<td>Maximum temperature [K]</td>
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<td>Heating rate [K/min]</td>
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Based on the values obtained for the thermal decomposition properties of the raw biomass materials, a range of temperatures for the production of Bio-coke from broccoli, dead cherry tree leaves, and the seeds of mango were determined.

### 2.2 Production and measurement of Bio-coke

This study is based on alternative coal coke technology which the authors developed [4, 5]. The method of production technology of Bio-coke follows our patent (PAT.-No.4088933) [6]. In this study, we used broccoli, dead cherry tree leaves, and the seeds of mango as unutilized biomass to produce Bio-coke. Under present circumstances, broccoli, dead cherry tree leaves and the seeds of mango don’t have possibility of utilization at all. Broccoli is discarded as the adjustment of production, and dead cherry tree leaves are the only things disposed of as waste every year. As with other the biomass materials, the seeds of mango are discarded as unutilized waste biomass in large quantity in Okinawa.

We adopted the same manufacturing conditions for Bio-coke produced from each material such as initial moisture content, processing temperature, loading pressure, and the duration time. Table 2 shows the manufacturing conditions and Fig. 3 shows the schematic drawing of molding device.

The method to produce Bio-coke is as follows: 50g of the material is loaded into the cylinder and sealed with the top and bottom molds. Pressure is applied to the sealed cylinder via the top mold using a piston as illustrated in Fig. 3. Thermocouples are inserted into the top mold to control the process temperature. The cylinder is then wrapped with an electric heating furnace. After the initial conditions are set, the sealed cylinder is heated until it reaches the pre-set process temperature. The process temperature is maintained at the pre-set value for 15 minutes. After 15 minutes, the electric furnace is removed from the sealed cylinder. The cylinder is then cooled using a fan until its temperature reaches room temperature.

Fig. 4 shows pictures of the Bio-coke specimens produced from broccoli, dead cherry tree leaves, and the seeds of mango. The apparent density of the Bio-coke is approximately 1.4 (g/cm³). This value is more than 2 times the value of the apparent density of the raw biomass material, which is in the range of 0.5~0.7 (g/cm³) [7]. The compressive strength of each Bio-coke produced is investigated at room temperature and their physical properties are discussed. The compressive strengths are determined at room temperature using the compression testing machine manufactured by SHIMADZU (SHIMADZU, UH-F2000KNA).
3. Results and Discussion

3.1 Pyrolysis characterization

Fig. 5 shows the result of TG analysis of broccoli, dead cherry tree leaves, and the seeds of mango as raw biomass material in an air-dry condition. The vertical axis gives weight reduction for each material. Similarly, Fig. 6 shows the result of DTA analysis for each raw material in an air-dry condition. The vertical axis indicates exothermic/endothermic properties.

The TG curves for all materials show an approximate weight reduction of 10% when the temperature was increased from 300K to 370K. The weight reduction in this region is caused by vaporization of external free water inside each biomass. Correspondingly in Fig. 6, the DTA curves for all materials also indicate that the endothermic reaction is caused by the phase change of external free water in this temperature region.

After the vaporization region of external free water, there is a temperature region in which there is only slight weight reduction and endothermic reaction on the TG and DTA curves for all materials [8]. Bio-coke is produced in this temperature region of minimal change of TG and DTA data. It was determined that the end of this region is equal to the start of gasification, where $T_b$ is 500K for broccoli, 530K for dead cherry tree leaves and 535K for the seeds of mango. Therefore, it is inferred that the optimum process temperature for Bio-coke productions for all materials falls in the range between 370K and 500K.

In the gasification region on the TG curves for each material, the maximum gradient, $M$, is $0.51 \times 10^{-2}$ (1/K) for broccoli, $0.38 \times 10^{-2}$ (1/K) for dead cherry tree leaves and $0.71 \times 10^{-2}$ (1/K) for seeds of mango. On the other hand, in the same region on the DTA curves, the initial gradient of exothermic reaction of volatile constituent, from highest to lowest, is seeds of mango, broccoli, and dead cherry tree leaves as well as the TG data. Thus, these results show that the seeds of mango are the most gasified biomass of the three materials, and consequently Bio-coke produced from this material seems to exhibit the highest ignitability.

Fig. 4 Appearance of Bio-coke produced from each biomass

Fig. 5 TG curves as comparison with broccoli, dead cherry tree leaves, and seed of mango

Fig. 6 DTA curves as comparison with broccoli, dead cherry tree leaves, and seed of mango

3.2 Physical properties of compressive strength

3.2.1 Evaluation for processing temperature

Figs. 7 to 9 show the ultimate strength for each processing temperature for Bio-coke produced from broccoli, dead cherry tree leaves, and the seed of mango. From Figs. 5 and 6, we targeted the range of infinitesimal change before gasification and determined the processing temperature in that region.

The main components of biomass which are cellulose, hemicelluloses, and lignin are used to produce Bio-coke. The skeletal structure of the Bio-coke is composed of cellulose and the high melting elements of lignin. Hemicellulose relatively softer at low temperature in comparison with cellulose and lignin is what fills the void in the skeletal structure of cellulose and lignin. Also, hemicellulose, which has adhesive properties, hardens the
skeleton of the Bio-coke. Consequently, this structure sustains external force and contributes to the hardness of Bio-coke. Furthermore, free water and temperature are significant to form the structure of Bio-coke. The free water and temperature are used in the softening of hemicelluloses and low melting elements included in lignin and control the reactivity of the main elements.

Fig. 7 shows that when the initial moisture content is increased for broccoli the highest ultimate strength is not affected by increased in the processing temperature. For example the optimum temperature with the highest ultimate strength is 413K for 5% and 7% initial moisture contents. An increased in the process temperature for these two lower moisture contents we see a reduction in the compressive strength. However, for higher moisture content of 10% there is little change in the compressive strength within the temperature range of 393K–433K. The highest ultimate strength is 130MPa for 5% initial moisture content, 116MPa for 7% initial moisture content, and 84MPa for 10% initial moisture content. In the case of the 5% initial moisture content, the result shows that the ultimate strength at 393K is lower than the ultimate strength at 413K and 433K. It is indicative that the Bio-coke formation reactions to solidify are not favorable at lower temperature with this moisture content. On the other hand, 453K has been determined as the highest process temperature condition for the production of Bio-coke. However, the Bio-coke ultimate strength at 453K is the lowest for 5% initial moisture content. Thus, the reaction at a higher temperature causes the softening of cellulose and the high melting biomass element of lignin in the Bio-coke. Consequently, in Fig. 7, the temperature range for Bio-coke production is established, and thus it is important to control the processing temperature within the range to ensure producing Bio-coke with high compressive strength. In addition, the result for 7% initial moisture content demonstrates similar results as in the case with 5% initial moisture content. However, the result for 10% initial moisture content is different from the other initial moisture contents. The ultimate strength for 10% initial moisture content for all processing temperature is approximately equal to 80MPa, except for the temperature of 453K. The highest ultimate strength of 10% initial moisture content is lower than the highest ultimate strength of the other initial moisture contents. This finding leads to a conclusion that the difference of initial moisture content for broccoli has considerably effects on the formation of Bio-coke. Furthermore, the initial moisture content range to produce Bio-coke must be established and controlled as well as the processing temperature both of which have significant effect on the quality of the Bio-coke produced.

Fig. 8 shows when the initial moisture content is increased for dead cherry tree leaves the highest ultimate compressive strength is not affected by increased in the processing temperature, thus showing similar behavior with broccoli. As with broccoli, the optimum temperature with the highest ultimate strength is 413K for the initial
The control of temperature and initial moisture content
Seed of mango has possibility to exhibit the highest stock affects the reaction in
Sing initial moisture content
The maximum gradient: M is 0.51×10⁻²
Chemical and physical evaluation
Temperature decreases with increase in temperature region in which
The weight reduction of approximately 10% is caused

However, the difference in the compressive strength between all initial moisture contents decreases with increasing processing temperature. At 453K there is only a very small difference in the compressive strength between 5%, 7% and 10% initial moisture contents. Thus, it is suggested that the optimum range for processing temperature as well as the initial moisture content is narrow for dead cherry tree leaves. Consequently, these results imply that dead cherry tree leaves are sensitive to both the initial moisture content and the processing temperature.

Fig. 9 shows that the optimum processing temperature with the highest ultimate strength for each initial moisture content decreases with increasing initial moisture content for seed of mango. The optimum temperature with the highest ultimate strength is 453K for 5% initial moisture content, 433K for 7% initial moisture content, and 413K for 10% initial moisture content. The highest ultimate strength is 57MPa for 5% initial moisture content and approximately 48MPa for 7% and 10% initial moisture contents. The trend showed for the seed of mango where the optimum processing temperature decreases with increasing initial moisture content is obviously different from the other two Bio-coke materials tested. This tendency exhibited by the seed of mango implies that free water included in biomass feedstock affects the reaction in the formation of the Bio-coke, thus creating higher hardness at lower temperature. This fact indicates that the optimum initial moisture content has the reduction effect of temperature on the production of Bio-coke from seed of mango.

3.2.2 Evaluation for carbon content
In terms of biochemical measurement, we do not have the facility to determine the fraction of the main elements of cellulose, hemicellulose, and lignin within the biomass. As a result the carbon content within the biomass was used as the quantitative evaluation of the various kinds of biomass tested. This is in addition to the compressive strength of each Bio-coke from strength of material point of view as a macroscopic evaluation.

Fig. 10 provides the plots of carbon content against ultimate strength for each Bio-coke produced from various materials. The ultimate strength for each Bio-coke decreases with increasing carbon content (negative correlation). This fact shows that the relation of carbon content and compressive strength is directly proportional without dependency on existing form of the main elements. It is indicated that the biochemical and physical evaluation seems to give a univocal relation despite the measurement of different characteristics.

Fig. 10 shows that broccoli and seed of mango have conflicting characteristics. Bio-coke can be produced from the mixed material such as blending broccoli with seed of mango. It is shown that we may be able to produce Bio-coke having higher carbon content than broccoli and higher compressive strength than seed of mango, which will be comparable to a blend of coffee + tea grounds in Fig. 10.

4. Conclusions
The following conclusions were derived from the results and discussion.
(1) The weight reduction of approximately 10% is caused by vaporization of external free water included in each material from 300K until 370K. After the region of vaporization, there is a temperature region in which there is only slight weight reduction and endothermic reaction occurrence on the TG and DTA curves for all materials up to 500K.
(2) The maximum gradient: M is 0.51×10⁻² (1/K) for broccoli, 0.38×10⁻² (1/K) for dead cherry tree leaves and 0.71×10⁻² (1/K) for seed of mango.
(3) Seed of mango has possibility to exhibit the highest ignitability because of the highest gasification ratio in all materials.
(4) The highest ultimate strength of broccoli, dead cherry tree leaves and seed of mango is 130MPa, 38MPa and 57MPa.
(5) The control of temperature and initial moisture content is significant for Bio-coke production owing to the
direct effect on compressive strength. Also, there is the range of optimum production temperature and initial moisture content for various kinds of biomass feedstock.

(6) About seed of mango, the optimum initial moisture content has possibility of the reduction effect for production temperature of Bio-coke.

(7) The ultimate strength for various kinds of Bio-coke decreases with an increase in carbon content, and this relation is direct proportion.

(8) To mix different kinds of biomass is effective to produce Bio-coke compatible with high carbon content and hardness.

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References


