The influence of additional hemicellulose on Japanese cedar based pre-carbonized solid biofuel properties

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Abstract

The global carbon dioxide emissions issue is the main hindrance of the Paris agreement goals. Biomass has been effectively utilized as a renewable energy in the household heating and the electricity generating sector. However, it is unsuited for use in the heavy industry. Due to the limitation of biomass applied in the steel industry, the pre-carbonized solid biofuel (Kindai Bio-coke) has been developed and studied throughout the years. This research studied the effect of hemicellulose (glucomannan powder from the Konjac tuber) on Japanese cedar base bio-coke apparent density, heating value, and compressive strength at room temperature and 973 K. The bio-coke samples were produced by the vertical laboratory scale compression machine connected with 12 mm mold by loading cell. The mixture of dried glucomannan powder, with 0, 2, 5, 8, 10 and 15 wt. % and Japanese cedar powder are the raw materials in this research. The production conditions were controlled following the trial experiments done by Bio-Coke Research institute. It shows that hemicellulose has blended in with Japanese cedar particles and has increased the bio-coke apparent density significantly. However, the heating value of bio-coke decreased by 3 % with 15 wt. % of hemicellulose. The maximum compressive strength at room temperature results show an open end downward parabola with peak at 5 to 8 wt. %. Bio-coke containing 10 wt. % of hemicellulose has the highest maximum compressive strength at 973 K.

Keywords: Kindai Bio-coke, Hemicellulose, Japanese cedar, Heating value, Compressive strength

1. Introduction

The most recent update on global carbon dioxide emissions, published by NOAA in January 2019, shows that the emission trends are increasing constantly. Biomass is an important renewable resource that has been used instead of fossil fuels to prevent the increase of carbon dioxide emissions in the global atmosphere. In Japan, bioenergy covers about 36% of the total primary renewable energy supply and over 88% of this number is solid biofuel (Japan – 2018 update, Bioenergy policies and status of complementation). The report shows that solid biofuels such as wood chips and wood pellets are mostly used in electricity production and heating. However, in order to counter the carbon dioxide emission crisis, the industrial sector remains a problem. The expansion of the crude steel industry in 2018 increased the coal demand by 0.4%, which negatively affected the emission problem (Economic and Energy Outlook of Japan through FY2018). A viable replacement for coal for the steel industry is still under development. The strength of solid biofuel, not only at room temperature but also at furnace operating temperatures, is one of the most important properties that needs to be researched.

This present research focuses on the pre-carbonized and densified solid biofuel called Kindai Bio-coke (BIC), invented by Ida et al. in 2005. The method utilizes very low temperatures (~ 473 degrees Kelvin) and low loading pressures (about 21 MPa). Unlike the terrified solid biofuels that form in the semi-carbonize region, BIC is a non-pyrolyzed process which form under pre-carbonized stage. The BIC product is a suitable alternative to coal coke in the steel industry because of its high physical and mechanical characteristic. It is currently utilized in the heavy industry as
a replacement for coal up to a rate of 35%. Fugigami et al., 2016, reported that BIC is suitable as a renewable energy in the industry and by using one ton of BIC, carbon dioxide emissions can be reduced by 2.16 tons. There are many factors that affect BIC characteristics such as moisture content, forming temperature, type and size of raw materials, and raw material components etc. Over a decade, various types of biomass raw materials have been used for BIC and major characteristics have been studied. Researchers studied the relationship between mold temperature and moisture content of raw material, and maximum compressive strength at room temperature of BIC made from persimmon, plum, broccoli, mango seed, and cherry leaf. The results show that BIC product has high maximum compressive strength, 40 to 120 MPa (Sawai et al., 2009, Mizuno et al., 2011). The moisture content has an effect on BIC, also depending on type of materials. According to Mizuno et al., 2013, the size of BIC made from green tea leaves effects the compressive strength under high temperature (973 K). This characteristic is a key to study the strength of solid biofuel, applied in steel manufacturing, (blast and Cupola furnace). Moreover, the apparent density of BIC was reported at about 1.35 g/cm³. Another important factor that influences BIC characteristics is the lignocellulose component, consisting of cellulose, hemicellulose and lignin, which is contained in organic materials. Tagami et al., 2018, studied the structural component relationship between trunk and bark of conifers, bagasse and rice straw, and its BIC products’ compressive strength. The result shows that cellulose content of materials directly affects the maximum compressive strength, and shows as open downward parabola curve for hemicellulose content.

Japanese cedar (Cryptomeria japonica) is a softwood species, commonly used in the furniture and siding industry. The annual report on forest and forestry shows that Japanese cedar had the largest production volume (round wood) in 2017. Sequentially, Japanese cedar residue is used as biomass material both directly (wood chips) and densified (wood pellets, torrefied) (Yoshida et al., 2015, Yoshida et al., 2017, Sawai et al., 2017). Meanwhile, hemicellulose is a carbohydrate in plant cell wall fractions (C5 and C6 sugars). It is extracted from biomass and converted into bioethanol as well as cellulose (P. Chandrakant et al., 2008, A.K. Chandel et al., 2018).

This research aims to investigate the physical, mechanical, and thermal characteristics of bio-coke produced from Japanese cedar with additional hemicellulose powder (glucomannan), and its relationship. The greater comprehension of characteristics, chemical reactions and its effect during BIC transformation would benefit in upgraded properties of BIC and densified biofuel.

2. Methodology
2.1 Raw materials and Bio-coke production

Japanese cedar (JC) used in this study is a residue from the furniture industry, collected from Gobo City, Wakayama, Japan. The wood chip residue, 80% of trunk and 20% of bark (approximately), was ground into powder and delivered to the Bio-Coke research institute. After the sieving process, Japanese cedar powder size 53-150 µm was used as the base raw material of bio-coke. A standards ultimate analysis and a quantitative determination of lignocellulose component (Tagami and Ida, 2018) of JC powder is shown in Table 1. Cellulose is a dominant component among a lignocellulose in JC.

<table>
<thead>
<tr>
<th>Ultimate Analysis (mass %)</th>
<th>Lignocellulose Component (dry wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>49.92</td>
<td>6.21</td>
</tr>
</tbody>
</table>

Moisture content of the cedar powder was adjusted at 10 wt. % and kept in a sealed container. Glucomannan powder from the Konjac tuber representing hemicellulose, was dried overnight in a 80 degrees Celsius oven. The adjusted moisture content cedar and 0, 2, 5, 8, 10 and 15 wt. % of dried glucomannan powder was mixed then fed into 12 mm BIC mold (laboratory scale). Production process starts with heating the BIC mold by electric furnace to 463 K, sustained for 225 seconds. The mold was then cooled down by fan until it returned to room temperature. The BIC samples production conditions are shown in table 2. The weight of the raw materials varied depending on the BIC characterization testing, which are 2 g for the compression testing and 1 g for the heating value testing. Each various condition has been reproduced 9 times, divided into two groups, six samples of 2 g and three samples of 1 g. The number of measurement repetitions is 3 times for the same experiment condition.
2.2 Bio-coke Characterization

2.2.1 Apparent density and heating value

Apparent density and heating value of solid biofuel are two major parameters that define the qualities of densified biomass (Tumuluru et al., 2010). Apparent density (g/cm$^3$), also known as particle density, of samples is a factor which impacts storage and transportation costs. Moreover, this factor also influences the combustion behavior in terms of solid biofuel efficiency. The apparent density of BIC samples was measured right after the production process.

Table 2 BIC production conditions

<table>
<thead>
<tr>
<th>Particle size [µm]</th>
<th>53-150</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hemicellulose ratio [wt. %]</td>
<td>0, 2, 5, 8, 10, 15</td>
</tr>
<tr>
<td>Initial moisture [wt. %]</td>
<td>10±0.3</td>
</tr>
<tr>
<td>Loading pressure [MPa]</td>
<td>21.7</td>
</tr>
<tr>
<td>Mold temperature [K]</td>
<td>463</td>
</tr>
<tr>
<td>Retention time [s]</td>
<td>225</td>
</tr>
</tbody>
</table>

A calorific value (MJ/kg) is a term which determines the amount of energy contained in fuel. The calorific value is collected by measuring the difference of water temperature during fuel combustion via bomb calorimeter. The calorific value of biomass varies depending on the chemical component, and forming conditions. An auto-calculating bomb calorimeter, CA-4AJ (Shimadzu) was used as an apparatus in this study.

2.2.2 Compressive strength

Compressive strength is another important characteristic that shows the ability of BIC to withstand compression. It is important to understand the compressive strength of BIC in order to apply as an alternative to coal coke in the steel industry. This research divides the compressive strength experiment into two parts by using the same SHIMADZU (UHF2000KNA) compression machine, the first experiment performed at room temperature, and the other was at 973 K. The machine is connected to TRAPEZIUM X software which allows the collection of real time Young’s Modulus of the test samples. The maximum compressive strength of samples are collected from the relationship between stress and strain. Figure 1 shows the compression experiment schematic. In the case of compressive strength at 973 K experiment, the inside of the heating chamber is covered by N$_2$ gas to simulate BIC burning circumstances in blast or Cupola furnace. The test sample is under a constant load at 0.1 MPa in the heating zone, shown in Fig. 1 (a). The compression test starts after the chamber temperature reaches 973 K.

![Fig. 1 Schematic of compression experiment (a) timing chart (b) testing system](image-url)
3. Results and Discussion

3.1 Apparent density and heating value

BIC samples were successfully produced from a mixture of Japanese cedar and additional hemicellulose (glucomannan powder from Konjac tuber) under all various conditions. The results of linear regression analysis, (Fig. 2a) shows that the apparent density is affected by additional hemicellulose ratio with 0.985 of Pearson’s correlation. The highest and lowest apparent density of BIC in this research is at 1.435 g/cm³ and 1.416 g/cm³ respectively, from 15% of additional hemicellulose. This result is explained by the softening behavior of hemicellulose, the softening temperature of dried hemicellulose has been reported at 423 K by Goto et al., 2012 and Tagami et al., 2019. The softening behavior of Japanese cedar was reported by Tagami et al., 2019 at approximately 460 K. Since the forming temperature of this research is 463 K, the increasing of additional hemicellulose results in greater reaction between materials particles. Hemicellulose has the lowest molecular weight among the biomass three main components. For this reason, the additional hemicellulose particles increase the reactions in the molecular levels between the JC main components and additional hemicellulose during the transformation process. The molding temperature softens and causes bonding mechanism, such as the hydrogen bonding. Additional hemicellulose could bond with cellulose molecule at the reducing end, at the amorphous region, increases lignin-carbohydrate complex or reacts with the additional particle itself. This result in the higher apparent density of BIC product.

![Graphs showing apparent density and calorific value](Image)

Figure 2 (b) shows the relationship between calorific value and additional hemicellulose ratio. The calorific value of BIC appears to decrease as the percentage of additional hemicellulose increases, with a Pearson’s correlation of -0.971 (solid line). The highest calorific value of BIC is at 19.6 MJ/kg from 100% JC. It has slightly decreased until 15 wt. % of hemicellulose mixture, 19.0 MJ/kg. The low calorific value of glucomannan powder reduces the value of BIC samples by 3%. The calorific value of raw materials were 19.5 MJ/kg for JC and 14.9 MJ/kg for glucomannan powder from Konjac tuber. Dot line in Fig. 2 (b) show the calculate value base on the calorific value of raw materials percentage which lower than the BIC calorific value. The reason is because calorific value is an energy release per weight. A high apparent density characteristic of BIC, which is calculated from the weight per volume, result in higher calorific value.

3.2 Compressive Strength

BIC made from JC with 5 wt. % and 8 wt. % of additional hemicellulose have the highest maximum compressive strength at room temperature which are 169.0 and 168.9 MPa. As shows in Fig. 3 (a), the maximum compressive strength results fit almost perfectly with the estimate Gauss curve (non-linear curve fit) which calculated following Eq. (1) where $\sigma_c$ is maximum compressive strength at room temperature and $x$ is the additional hemicellulose ratio with Reduced
Chi-squares of 0.055 and Residual Sum squares of 0.109. This result support the conclusion of Tagami and Ida, 2018, that shows the approximate quadratic curve relationship between maximum compressive strength and hemicellulose content. From the estimate Gauss equation, the highest value would be at around 6 wt. % of additional hemicellulose. Figure 4 shows the maximum compressive strength and total hemicellulose content of BIC, where Beta hemicellulose ($\beta_H$) is the total hemicellulose in BIC samples. Raw materials with approximately 33 to 35 wt. % of total hemicellulose have the highest maximum compressive strength which is close to the estimation (30 %) in Tagami and Ida, 2018 works.

$$\sigma_c = 141.217 \pm 6.557 + \left( \frac{664.198 \pm 251.506}{18.990 \pm 2.792 \sqrt{\pi^2}} \right) e^{-0.5969 \pm 0.0056}$$

(1)

![Graph showing maximum compressive strength vs. additional hemicellulose ratio](a)

![Graph showing maximum compressive strength vs. Beta hemicellulose content](b)

Fig. 3 Maximum compressive strength at various additional hemicellulose ratio (a) and Beta hemicellulose (b)

The change in maximum compressive strength value is also explained by the softening behavior of biomass. The softening region of raw material affects the macroscopic properties of solid biofuels (Kaliyan et al., 2010). The forming temperature of BIC at 463 K in this study is in the softening region of Japanese cedar (for the initial moisture content at 10 wt. %) and 20 K greater than glucomannan powder (Tagami et al., 2019). As mentions earlier about the reaction during the BIC transformation process in the molecular level, the additional hemicellulose react and bond with the molecules JC components. However, the higher hemicellulose content weakens the products strength. These bonds might decrease the cellulose crystalline region which is held together by the interchain bonding and cause the decreasing of the products maximum compressive strength. Another considerable factor is the initial moisture value which would affect the maximum compressive strength, and also the apparent density. In solid biofuels process, the moisture content of raw materials is an important factor in binding mechanism. It varies depending on the type of material, such as hardwoods, softwoods, and glasses. According to Tagami and Ida, 2019, which conducted the experiment on the solidification characteristics and maximum compressive strength, the higher initial moisture content the lower maximum compressive strength. In this case, the higher moisture content of mixtures could negatively affect the product strength.

The results of maximum compressive strength at 973 K shown in Fig. 4, which are 2.9, 3.3, 2.7, 4.8, 6.8, and 3.7 MPa, divided into 3 zones. The green line is the estimate linear line of 0 to 5 wt. % of additional hemicellulose. In this zone there is no significant change, because the bonding mechanism between JC particles remains in the same level. On the other hand, at the red line zone (5 to 10 wt. % of hemicellulose), the maximum compressive strength increases sharply with Pearson’s correlation of 0.995. Hemicellulose particles improve the chemical reaction between JC particles and also the reaction between JC and hemicellulose particles. The highest result of maximum compressive strength at 973 K (10 wt. % of hemicellulose) is about two times lower than the result of coal coke. Coal coke (48 mm diameter) has dominantly high maximum compressive strength at 973 K of about 14 MPa. This means that the chemical bonding of hemicellulose and biomass particles might be the key to improve the strength of solid biofuels application in the melting furnace. However, the maximum compressive strength at 973 K has decreased with 15 wt. % of hemicellulose, which mean the reaction between the hemicellulose particles itself decreases the strength of BIC. Hemicellulose is reported to be decomposed by thermal around 453 to 573 K. According to Tagami et al., 2019, glucomannan powder used in this study
starts to decompose at 443 K. The additive glucomannan particles could transform into different structures such as furfural or O-acetyl during the BIC production, results in improvement of the product with 5 to 10 wt. % of hemicellulose. Meanwhile, at 15 wt. % hemicellulose content, the additive particles are not able to bond with JC particles and remain the same. Under the high temperature atmosphere before and during the compressive experiment (at 973 K), the remaining hemicellulose was decomposed and reduced the maximum compressive strength result.

Figure 5 show how the maximum compressive strength at room temperature and 973 K relate to each other with the estimate lines. The change at 0 to 5 wt. % of hemicellulose, only occurs in room temperature strength. It increase about 5 MPa, but dominated almost the same for the strength at 973 K. Meanwhile, from 5 to 10 wt. % of hemicellulose, the positive influence is significant for the 973 K, but not major for the strength at room temperature. Both strength show the dramatically drop at 15 wt. % of additional hemicellulose. Based on qualitative binding mechanism, cellulose, hemicellulose, and lignin are bonded together create a micro fibrils structures of wood cell walls. These components is bound together during the BIC transformation. The additional hemicellulose increases the total hemicellulose content of BIC products and decreases the content of cellulose and lignin at the same time. At 5 to 10 wt%. of additional hemicellulose, the ratio between total hemicellulose and lignin became greater. At the same time the ratio between hemicellulose and cellulose became smaller. The ratio of total hemicellulose and lignin between 5 to 10 wt%. is almost two times difference, and conversely for cellulose. It creates the binding mechanism that responsible for the strength at high temperature. Under the high temperature environment, the binding mechanism that causes by the increasing amount of hemicellulose, occurs at the inner part of BIC remains enduring enough to withstand the compressive loading. The further study of quantitative binding mechanism related to the 3 mains component of biomass, such as the micro structure via FT-IR and NMR, of BIC needs to be conducted in order to express more in details.

The results of study show that Japanese cedar base BIC with additional hemicellulose higher than 15 wt. % has the lowest thermal and mechanical properties. Even though it has the highest apparent density, its mechanical strength at room and 973 K has decreased about 5 % and 45 % respectively comparing to 10 wt. % of hemicellulose mixture. The apparent density of BIC with 10 wt. %, 1.429 g/cm³, is considered as a high apparent density solid biofuel. Thus, it is not necessary to add hemicellulose more than 10 wt. % in the JC base BIC.

![Fig. 4 Japanese cedar BIC maximum compressive strength at 973 K value at various additional hemicellulose ratio](image)

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4. Conclusion

The operating conditions of this study are suitable to produce Japanese cedar bio-coke. The bio-coke characteristics studied are concluded in following points.

1) Additional hemicellulose has influenced as linear regression in case of apparent density and calorific value of bio-coke. It increased the bio-coke apparent density sharply, average of 1.428 g/cm³, but slightly decreased the calorific value by 3%.

2) Bio-coke contained 5 to 8 wt. % of additional hemicellulose have the highest maximum compressive strength at room temperature with 169.0 MPa because of the softening behavior of Japanese cedar and hemicellulose.

3) At 10 wt. % of additional hemicellulose bio-coke presented in ultimate maximum compressive strength at 973 K which is 6.7 MPa (about 2 times higher than pure Japanese cedar bio-coke).

4) Bio-coke with 15 wt. % of additional hemicellulose shows the poorest quality in all characteristics studied, except for the apparent density.

More study needs to be conducted in order to conclude the maximum compressive strength at furnace operating temperature, for example, the change in macro and micro structure during the bio-coke reaction.

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