Preparation of Formed Coke from Biomass by Sequence of Torrefaction, Binderless Hot Briquetting and Carbonization

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This paper proposes a method of preparing high-strength formed coke from woody biomass without binder. Chipped and pre-dried Japanese cedar was heat-treated in an inert atmosphere (i.e., torrefied) at 225–325°C (Tt), pulverized to sizes in three different ranges, molded into briquettes (in the form of thick disk with diameter/thickness = 2.5) at temperature up to 200°C by applying mechanical pressure of 128 MPa. The torrefied/briquetted cedar (TBC) was then converted into coke by heating to 1 000°C in an inert atmosphere at normal pressure. This process sequence enabled to prepare coke having indirect tensile strength (St) of 8–32 MPa, which was much higher than that without torrefaction, below 5 MPa. The torrefaction greatly improved pulverizability of the cedar, which was further promoted by increasing Tt, St of TBC and that of coke both increased as the particle sizes of TBC decreased, but this explained only a minor part of significant effect of Tt on St of the coke. St was maximized at Tt = 275°C regardless of the degree of pulverization. The Tt effects on physicochemical properties of TBC and coke were investigated in detail. The difference in St of coke by Tt was mainly due to that in the increment of St along the carbonization at 500–1 000°C. Fracture surfaces of the coke had particular morphologies that had been inherited from the original honeycomb structure of the cedar.

KEY WORDS: woody biomass; torrefaction; formed coke; hot compression molding; tensile strength.

1. Introduction

Production of blast furnace coke from biomass is a potential technology in the future ironmaking with minimized or no emission of coal-derived CO2. So far, not few studies have been studied on this technology, as outlined below, under a common assumption of replacement of a limited portion of the current feedstock, i.e., coal, by biomass. Matsumura et al.1) added woody biomass to a slightly caking coal with addition rates of 0.5–2.0 mass% and carbonized mixtures at 1 000°C. The I-type strength of coke from the mixture was equivalent to that from the coal alone in the case that the biomass had been molded by hot compression at 200°C. But the coke strength decreased by adding the biomass without densification prior to mixing.

Montiano et al.2) investigated effects of addition of chestnut or pine sawdust to general coal blends on properties of coke from carbonization at 1 100°C, and obtained results similar to that of the previous study.3) They confirmed reduction of apparent density and strength by adding the sawdust, and attributed this mainly to loss of fluidity by adding the sawdust at a rate of 0.75–3.0 mass%. Diez et al.3) studied effects of adding woody biomass (sawdust), its particular components (cellulose, xylan and lignin) and charcoal to a coking coal (logarithm of maximum fluidity (logFmax) ≈ 2.5). They showed that logFmax decreased greatly to 0.5 by adding cellulose or sawdust at a rate of only 1–3 mass%, while slightly to 2.1 with 6–9 mass% addition of charcoal, lignin or xylan. These effects strongly suggested that the loss of fluidity was caused by a mismatch in the content of volatile matter or temperature range for its release. Such loss of the fluidity was also reported by Diaz et al.3) They found that heating rate as high as 180°C/min minimized the fluidity loss even at a biomass addition.
rate of 5 mass%, mainly due to promoted fluidity by rapid heating. Ueki et al.\textsuperscript{9} reported significant reduction of coke strength (on a tumbler strength index), by 5 mass% addition of sawdust (particle sizes < 0.15 mm), but also effectiveness of its semi-carbonization at 400–500°C, which minimized the loss of strength. These results are in broad agreement with those by Diez et al.\textsuperscript{23}

Very recent world-wide strategies of ‘decarbonization’ with zero emission of fossil-fuel-derived CO\textsubscript{2} from industries/societies by 2 050–2 060 may strongly restrict the use coal but encourage that of biomass as the main carbonaceous feedstock of coke as well as the main alternative to PCI fuel. Production of formed coke solely from biomass was studied by Kudo et al.\textsuperscript{7} who pretreated woody and herbaceous biomasses in hot-compressed water (HCW) at 200–300°C, dried, briquetted by hot-compression molding at 130–200°C, and then carbonized at 900°C. The resulting coke had a tensile strength of 20–50 MPa, which was several to ten times that of commercially available blast furnace coke. Such high strength of coke was attributed to high thermal plasticizability in the briquetting and no thermal swelling/fluidity in the subsequent carbonization, which gave highly densified briquette and high strength of coke, respectively. The implementation of the HCW treatment of biomass may be, however, difficult due to high capital and operational costs, unless the HCW treatment and subsequent processes produce high added-value products with substantial yields.

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Production of formed coke from biomass is potentially applicable if high-degree densification of biomass (or pretreated biomass) prior to carbonization with modestly suppressed volatile matter release is realized. Recent studies on production of formed coke from coal\textsuperscript{8–10} or lignite\textsuperscript{11–13} have given highly densified briquette and high strength of coke, which is supported well by the improved pulverizability\textsuperscript{15,16} due to physical embrittlement. Thus, the pulverizability and briquettability may be in a trade-off relationship. Torrefaction under optimized conditions potentially enables to convert biomass into high-strength coke by the pulverization, hot-briquetting and carbonization. There have so far been no studies on formed coke production from torrefied biomass alone.

The present authors studied production of formed coke from woody biomass by applying sequential torrefaction, pulverization, binderless hot briquetting and carbonization. This paper reports experimental data demonstrating preparation of high-strength coke, and also discusses the mechanisms for emergence of optimum torrefaction conditions and occurrence of coke strength.

2. Materials and Methods

2.1. Biomass Sample

Sawdust of a Japanese cedar (SD) with particle sizes smaller than 3.0 mm was supplied from The Iron and Steel Institute of Japan. SD was pulverized to sizes smaller than 100 μm in a cutter mill (Wonder Blender WB-1, Osaka Chemical) for a short period of ca. 1 min. The cutter milling of SD was necessary to prepare coke samples without torrefaction.

2.2. Torrefaction and Pulverization

A prescribed amount of SD (1.0 g) was heated in atmospheric flow of high-purity N\textsubscript{2} (flow rate; 300 mL-stp/min, purity; > 99.9999 vol%) in a horizontal tubular reactor, applying heating rate, peak temperature and holding time at the peak temperature of 5°C/min, 225–325°C and 60 min, respectively. The temperature for the torrefaction will be denoted by \(T_t\). The gaseous products ranging from H\textsubscript{2} up to C\textsubscript{4} hydrocarbons were collected in a gasbag, while the liquid products (pyrolytic water, light oil and heavy oil) on an aerosol filter (150°C) or in cold traps (0°C, −70°C) connected to the reactor in series. The entire portion of the liquid product (except water) was defined as tar. Details of the product collection, quantification and analysis were reported elsewhere.\textsuperscript{22} The solid left in the reactor, i.e., the torrefied SD was then recovered. Hereafter, the torrefied SD with \(T_t = x°C\) is referred to as TxD (\(x = 225, 250, 275, 300\) or 325). The yield, atomic composition and higher heating value (HHV) of SD and TSD are shown in Table 1.

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<table>
<thead>
<tr>
<th>(T_t), °C</th>
<th>Yield, kg/kg-dry-SD</th>
<th>H/C atomic ratio</th>
<th>O/C atomic ratio</th>
<th>HHV, MJ/kg-dry</th>
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<tbody>
<tr>
<td>SD</td>
<td>100</td>
<td>1.45</td>
<td>0.68</td>
<td>19.7</td>
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<tr>
<td>225</td>
<td>91.2</td>
<td>1.29</td>
<td>0.59</td>
<td>20.4</td>
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<tr>
<td>250</td>
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<td>1.29</td>
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<tr>
<td>275</td>
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<td>1.18</td>
<td>0.53</td>
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<tr>
<td>300</td>
<td>55.2</td>
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<td>325</td>
<td>42.2</td>
<td>0.86</td>
<td>0.28</td>
<td>24.6</td>
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were smaller than 100 μm, as shown later. The cutter-milled TSD was further pulverized by gentle ball milling for 10 or 20 h. Details of the ball milling were reported previously.9) The ball milling further decreased the particle sizes to smaller than 40 or 20 μm.

2.3. Briquetting by Hot-compression Molding

The pulverized SD and TSD were molded into a circular plate by hot-compression employing a mold with 15 mm inner diameter and 20 mm depth, and applying the following conditions: mass of SD or TSD; 1.0 g-dry, temperature (Tm); 40–200°C, mechanical pressure (Pm); 128 MPa, period of mechanical pressure loading; 8 min. These conditions followed the authors’ previous studies.9,10) No binder was used in the molding. The dimensions (diameter and thickness) of each circular plate were measured. In the cases of Tm = 200°C, the diameter was within a range of 14.0±0.1 mm, independent of both Tm and degree of pulverization, but these influenced the thickness within another range of 5.1–6.9 mm.

2.4. Carbonization

Four to eight specimens of TSD briquettes, which had been prepared from the same TSD and under the same conditions, were heated together in atmospheric flow of N2 (flow rate; 300 ml-stp/min, purity; > 99.9999 vol%) at a heating rate of 5°C/min to the peak temperature (Tp) of 1000°C with a 10 min holding time at Tp. The carbonization was followed by natural cooling of coke to ambient temperature in the same N2 flow as above, and its recovery. Cutter-milled SD and TSD were also carbonized under the same conditions as above, but without briquetting.

2.5. Characterization

Coke, TSD briquettes and SD briquettes were subjected to strength tests for measuring indirect tensile strengths (St). Details of the measurement were reported previously.9,10) Four to twelve specimens were tested for each coke or briquette. It was confirmed that the deviation of the measured St was within ±10% from the average. The fracture surfaces of cokes and briquettes were observed by scanning electron microscopy with a JEOL model of JSM-IT7001HR. The particle size and distributions of TSD were measured with an analyzer (Malvern Pananalytical, Morphologi 4). In each analysis, 55 000–74 000 particles were observed with a microscope, and the properties of the individual particles such as circle-equivalent (CE) diameter, solidity, aspect ratio and circularity were determined. The porosities of coke samples were measured by a mercury porosimetry over a range of pore size of 0.1 to 100 μm.9)

Figures 1(a) and 1(b) show the effects of Tp on the distribution of particle size (represented by CE diameter) for TSDs after the cutter milling and 10-h ball milling. It is seen that increasing Tp shifts both distributions toward smaller

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![Fig. 1](image.png)

Fig. 1. Particle size distributions of TSDs with different Tm of 225–325°C. (a) after cutter milling (CM), (b) after 10-h ball milling (BM10).
CE diameter side. This is also confirmed in Fig. 2(a) that demonstrates monotonous decreases in average CE diameter with increasing $T_t$. Figure 2(b) reveals that the solidity, circularity and aspect ratio all increase toward unity (theoretical maximum) as $T_t$ increases. The increasing aspect ratio and solidity result from more extensive disintegration of particles and grinding of their surfaces, respectively, and are both consistent with increasing circularity. The data shown in Figs. 1 and 2 thus demonstrate an improvement of pulverizability by increasing $T_t$. The improvement in pulverizability of SD is remarkable because SD was hardly pulverized by the ball milling.

Another important feature of torrefaction was found. It was spontaneous pulverization of SD during or after the torrefaction, which was induced thermochemically. Figure 3 exhibits typical SEM photographs of TSDs with $T_t = 225$, 250, 275 and 300°C. The torrefaction with higher $T_t$ results in smaller TSD particles even before the intentional pulverization.  

3.2. Strength of Briquette

Figure 4 shows the effect of $T_t$ on $S_t$ of briquette. $S_t$ is hardly influenced by $T_t$ at 225–275°C, but decreased by that at 300–325°C. This result is discussed by focusing on the size and thermomechanical properties of pulverized TSD before the briquetting. Figure 4 also shows that a smaller particle size is favored for greater $S_t$. This trend is well known in molding of particles to densified bulk material. In fact, for each TSD, the apparent density of briquette increases with decreasing particle size (Fig. 5(a)). Figure 5 expresses that the apparent densities of T300 and T325 briquettes depend more strongly on the particle size than those of T225–T275. Such dependency is probably related to the plasticity of TSD in the hot compression. It was believed that SD lost much of its original plasticity during the torrefaction at 300–350°C but less at 225–275°C. The remaining plasticity of particles allowed their deformation, inducing particles’ contact and bonding, leading to more degree of densification. The size was thus less important for particles with more plasticity. Figure 5(b) plots the logarithmic $S_t$ of T225–T325 briquettes against average particle size. The dependencies of $S_t$ of the briquettes on the particle size are similar to one another with respect to the slope of the lines drawn in the figure. Decrease in $S_t$ with increasing particle size is consistent with the trends seen in Fig. 5(a).

The above-discussed particle size effect is important for $S_t$ of briquette. It is, however, not reasonable to attribute the variation with $T_t$ of briquette’s $S_t$ only to the particle size effect. As mentioned previously, it was believed that a more or less portion of the original plasticity had been left in T225, T250 and T275, and that the plasticity helped particles’ contact/bonding and densification of briquette. The densification of T300 and T325 was not successful due to their less plasticity than T225–T275. The data shown in Figs. 4–5 thus demonstrate that the torrefaction under appro-
appropriate conditions greatly improve the pulverizability of SD with no or little loss of briquetatability (moldability). Though not shown in Figs. 4–5, $S_t$ of the briquette from SD was as low as 3.2 MPa. The torrefaction and subsequent milling even improved the briquette strength, which was reported by none of the previous works.

The effect of $T_t$ on the briquette $S_t$ is considered from a chemical viewpoint. Figure 6 illustrates change in the chemical composition of SD by the torrefaction. The cellulose (CL) seems to be stable up to $T_t = 275^\circ$C, while the hemicellulose (HC) is converted at $T_t \geq 250^\circ$C. The fraction of the lignin (LG) unexpectedly increases with $T_t$ of 225–300°C probably due to conversion of HC into components that undergo pyrolysis following kinetics very similar to that of LG. It is noted that the total fraction of the CL, HC and LG (including HC-derived LG) decreases but very slightly up to $T_t = 275^\circ$C. This is consistent with that the briquettes of T225, T250 and T275 had equivalent $S_t$. It is clear that the torrefaction at 300°C and that at 325°C respectively convert HC and CL completely, leaving LG, HC-derived LG and the secondary component. More importantly, the torrefaction at 300–325°C greatly increases the fraction of non-volatile matter, which is given by the difference between unity and the total fractions of CL, HC, LG and secondary component. This is clearly from the progress of polymerization and carbonization during the torrefaction. It is hence expected that the torrefaction at 300–325°C causes loss of the inherent plasticity of SD. The torrefaction at 300–325°C thus enhances the pulverizability but diminishing plasticity at the molding temperature (200°C). $S_t$ of T300 and T325 briquettes and their chemical compositions indicate that negative effect of plasticity loss on the briquette $S_t$ is more than the positive effect of enhanced pulverizability.

3.3. Strength of Coke from Carbonization with $T_c = 1000^\circ$C

This section presents and discusses the effects of $T_t$ on coke properties. The coke samples were prepared by the carbonization of briquettes that had been prepared with $T_m = 200^\circ$C. This temperature was decided based on preliminary results for the effects of $T_m$ on $S_t$ and apparent density of coke. Figure 7 shows that $S_t$ of coke increases greatly with $T_m$ within the range of 40–200°C, demonstrating the effectiveness of employing higher $T_m$ unless TSD undergoes pyrolysis. Such a positive effect of $T_m$ on $S_t$ is arisen mainly from greater apparent density of briquette with higher $T_m$. It is believed that TSD, regardless of $T_t$, is plasticized under the heating and mechanical pressure of 128 MPa.

Figure 8 illustrates the effects of $T_t$ on $S_t$ of cokes from the cutter-milled and ball-milled TSDs, showing some important features of the sequential processes of torrefaction, pulverization, hot briquetting and carbonization. Firstly, the coke from the cutter-milled TSD is greater than that from SD, 4.7 MPa, regardless of $T_t$. The torrefaction is thus necessary for not only improvement of pulverizability of SD but also production of high-strength formed coke with $S_t$ greater than 5 MPa. Secondly, more degree of pulverization leads to coke with greater $S_t$. This is in broad agreement with existing knowledge in formed-coke production.9,10) The maximum $S_t$ of the coke from the 20-h ball-milled TSD is as high as 32 MPa. Thirdly, regardless of the degree of pulverization of TSDs, $S_t$ is maximized at $T_t = 275^\circ$C. The effect of $T_t$ on $S_t$ of the coke is clearly different from that of the briquette. There is no significant effect of $T_t$ at 225–275°C on $S_t$ of the briquette, as seen in Fig. 4. For each of the cokes from cutter-milled (CM), 10-h ball-milled (BM10) and 20-h ball-milled (BM20) TSDs, the $S_t$ is maximized and minimized at 275°C and 325°C, respectively. The ratio of the maximum $S_t$ ($T_t = 275^\circ$C) to minimum $S_t$ ($T_t = 325^\circ$C) is 2.1, 2.0 and 2.8 for the cokes from CM, BM10 and BM20 TSDs, respectively.
3.4. Physical Properties of Coke from Carbonization with $T_c = 1\,000^\circ C$

The above-mentioned third feature is considered based on coke properties. Figure 9 plots the apparent density and porosity of coke against $T_t$. The density and porosity decrease and increase monotonously with $T_t$, respectively. As seen in Fig. 9(c), these properties are related linearly to each other. The straight dashed line drawn in this figure indicates a relationship if the density of coke, which is given by assuming that the density after elimination of the volume of macropores with sizes greater than 0.01 $\mu m$ (in other words, based on the total volume of mesopores, micropores and non-porous carbonaceous matrix) is 1.43 g/cm$^3$. The linearity suggests that the effects of $T_t$ on the true density and micro-/meso-porosity of coke were, if any, insignificant.

In general, $S_t$ of coke decreases with a decrease in the apparent density or an increase in the porosity, and these changes with $T_t$ may explain the magnitude relation of $S_t$ amongst the cokes from T275, T300 and T325 qualitatively, but not at all for the cokes from T225, T250 and T275. The coke from T275 has $S_t$ greater than those of T225 and T250, while smaller apparent density and greater porosity. Figure 9(d) shows that the apparent density of coke from the ball-milled TSD changes in somewhat different manners from that for the cutter-milled TSDs. Nevertheless, the effect of $T_t$ on the apparent densities can hardly explain the trend of $S_t$ at $T_t = 225–275^\circ C$.

Figure 10(a) illustrates the pore size distributions of the cokes from cutter-milled TSDs. The pore size ranges from ca. 0.1 to 2 $\mu m$ commonly for the cokes except for that from T325, of which pore size ranges ca. 0.1 to 3 $\mu m$. Mechanical strength of porous solid is generally affected negatively by the pore size. However, the magnitude relation of $S_t$ among the cokes with different $T_t$ cannot be explained by that of pore size distribution. As shown in Fig. 10(b), the porosity increases with the mean pore size. This trend cannot explain that $S_t$ of the coke from T275 is greater than those from T225 and T250.

Thus, the above-described consideration of the effects of $T_t$ on the coke properties is not successful in drawing the mechanism for maximization of $S_t$ at $T_t = 275^\circ C$. It is also difficult to attribute the difference in $S_t$ of coke with different $T_t$ to that of the density of the ‘non-macroporous’ part of coke because the density seems to be hardly influenced by $T_t$ (see Fig. 9(c)).

Figure 11 shows the net and gross coke yield on the bases of the mass of SD and TSD, respectively. The gross coke yield increases as $T_t$ increases, as expected. It is noted that the net coke yield is almost independent of $T_t$ as 225–300 $^\circ C$, which is primarily due to that more volatile matter yield in the torrefaction is compensated by less yield in the carbonization. The net coke yield from T325 is slightly lower than the others. This is because of the less extensive suppression of volatile matter release during the carbonization by the previous hot briquetting. As shown in Fig. 12, the hot briquetting suppresses the release of tar, while such an effect diminishes for $T_t = 300–325^\circ C$.

T325 has underwent more degrees of pyrolytic conversion, in other words, tar evolution and cross-linking (according to the yields of pyrolytic water and inorganic gases such as CO$_2$ and CO) than the other TSDs. The yields of pyrolytic water and CO/CO$_2$ are shown in Fig. S2. T325 has the smallest ability of evolving tar during the carbonization. Figure 12 suggests that the tar evolution in the torrefaction, if more than 20 mass%-dry-SD, results in less positive effects of hot briquetting on the coke yield. According to the net coke yield (Fig. 11), there is no significant effect of $T_t$ (225–275$^\circ C$) on the chemical nature of coke.
3.5. Occurrence and Development of Coke Strength during Carbonization

The physical and chemical properties of coke and characteristics of carbonization, discussed in the previous section are both insufficient to explain the \( T_t \) effect on the coke \( S_t \), in particular, those from T225, T250 and T275. In this section, changes in \( S_t \) of TSD along the carbonization over the range of \( T_c \) from 300 to 1000°C are shown and discussed for understanding how the effect of \( T_t \) on \( S_t \) of coke \( (T_c = 1000°C) \) occurs, and find out a main reason why \( T_t = 275°C \) leads to the maximum \( S_t \).

Figure 13 plots \( S_t \) against \( T_c \) for T225–T300. The plots at \( T_c = 200°C \) indicate \( S_t \) of briquettes before the carbonization for expedience. \( S_t \)s of cokes from the four different TSDs, which have different \( S_t \)s before the carbonization, converge into around 5 MPa at \( T_c = 420°C \), and then diverge at higher \( T_c \) to a range from 8.8 MPa (T225) to 16.9 MPa (T275). Thus, the effect of \( T_t \) on \( S_t \) diminishes in the early stage of carbonization at \( T_c \) up to 420°C, but grows at \( T_c = 500–1000°C \), where the H/C and O/C atomic ratios of T275 coke decrease from 0.43 to 0.02 and 0.11 to 0.03, respectively (Fig. S3). The apparent density and \( S_t \) of the
four cokes from T225–T300 were all within narrow ranges of 0.85–0.87 g/cm² and 4.8–5.1 MPa, respectively at $T_\text{c} = 420^\circ$C. It was also found that the relative mass of coke at $T_\text{c} = 1000^\circ$C to that at $T_\text{c} = 420^\circ$C was within a very narrow range of 0.80–0.81 regardless of $T_t$. $S_t$ of coke at $T_\text{c} = 1000^\circ$C was, nonetheless, influenced greatly by $T_t$. The effect of $T_t$ on $S_t$ of coke at $T_\text{c} = 1000^\circ$C was thus attributed to the increment of $S_t$ of coke during the carbonization at 500–1000°C. Thus, understanding the $T_t$ effect on the coke $S_t$ at $T_\text{c} = 1000^\circ$C requires explanation of that on the increment of the coke $S_t$ at $T_\text{c} = 500–1000^\circ$C. Such explanation is, however, difficult within the range of coke properties that have so far been measured.

3.6. Further Discussion on Coke Properties

The discussion on the coke $S_t$, developed in the previous section, encounters difficulty in considering the mechanism of occurrence of the strength only based on the bulk properties of coke. It is believed that the three-dimensional structure of coke and its change along the carbonization are necessary for approaching the mechanism of the occurrence and development of coke strength. Figure 14 compares the fracture surfaces of T225 and T300 after carbonization at $T_\text{c} = 420^\circ$C. Both surfaces were very similar to those of the corresponding briquettes before the carbonization. The fracture surface of T225 has a morphology that can be illustrated schematically in the pictures (a) and (b). The compressed honeycomb structures indicate flexibility and plasticity of T225 in the hot pressing. Similar morphologies were also observed on fracture surfaces of T250 and T275. On the other hand, that of T300 seems to consist of plates (as walls of honeycomb) that were probably formed by breakage of the honeycomb and stacking of plates during the hot pressing, as shown in the picture (c). This is
consistent of the loss of plasticity in the torrefaction with $T_t = 300$–$325^\circ$C, and also the lower $S_t$ of T300 and T325 briquettes that those of T225–T275 briquettes.

The above-mentioned morphologies were inherited to cokes with $T_c = 1000^\circ$C, as shown in Fig. 15 and also in Fig. S4. The compressed honeycomb structure is obvious on the fracture surface of the T225 coke, while such structure is hardly seen on that of the T300 coke. In a qualitative sense, the surfaces of T250 and T275 appear to be similar to those of T225 and T300, respectively. It is difficult to draw a main reason why the T275 coke has the greatest $S_t$, but a hypothesis occurs from the inheritance of the honeycomb structure. The honeycomb walls of T225 are flexible under the pressure in the hot pressing, and therefore compressed without their breakage. The compressed honeycomb structure is maintained during the carbonization, contributing to the coke strength. But meanwhile, such a structure hinders bonding of walls to those of other honeycombs during the carbonization because the walls are fixed in the honeycomb structure. On the other hand, the contribution of the honeycomb structure to the T300 coke strength is much smaller than that of T225. At the expense of this, plate-shaped walls are allowed to contact and to others, which leads to their bonding and occurrence of the coke strength. Thus, the breakage of the compressed honeycomb structure results in more frequent bonding of plates and an increase in the coke strength. In this hypothesis, the breakage of the honeycomb structure (during the hot pressing) causes both negative and positive effects on the coke strength. According to the effect of $T_t$ on $S_t$ of coke, the maximum $S_t$ of the coke from T275 is qualitatively explained as follows. The breakage of honeycomb structure of T275 occurs more frequently than those of T225–T250, while bonding of walls occurs more frequently during the hot pressing. The $S_t$ of T275 briquette is therefore as high as those of T225 and T250 briquettes. Thus, the honeycomb structure of T275 is ‘modified’ three-dimensionally with slight or no loss of $S_t$ in the hot pressing. Such bonding of plates is less frequent for T300 and T325, due to more loss of plasticity than T275. In the subsequent carbonization (at $T_c > 500^\circ$C) of T275, plate-to-plate bonding occurred obeying the mechanism similar to sintering, and its frequency is more than that in the carbonization of the T225 and T250 briquettes. $S_t$ of T275 coke therefore increases with $T_c$ more steeply than the T225 and T250 cokes. T300 undergoes such plate-to-plate bonding during the carbonization with a similar frequency to T275, and then its $S_t$ increases in a similar manner.

The above-mentioned hypothesis seems to explain the effect of $T_t$ on $S_t$ of coke at $T_c > 500^\circ$C, but not the convergence of $S_t$ at $T_c = 420$–$500^\circ$C (see Fig. 13). Then, examination of the hypothesis by more-detailed structural analyses of coke and briquette is necessary for understanding of the mechanism of coke strength occurrence over the entire range of torrefaction to carbonization in the future work.

4. Conclusions

The authors studied the sequence of torrefaction, pulverization, and binderless briquetting by the hot-press molding and carbonization, and have demonstrated its applicability to preparation of formed coke with $S_t$ of 8–32 MPa from the chipped cedar. Such large $S_t$ cannot be achieved without torrefaction. It has also been revealed that $S_t$ is maximized with $T_t = 275^\circ$C. $S_t$ is also increased by increasing the degree of pulverization. The torrefaction not only improves the pulverizability greatly but also induces the self-pulverization.

The inherent honeycomb structure of SD is compressed or broken forming plate-shaped honeycomb walls during the briquetting. The compressed honeycomb and broken honeycomb are more abundant in the torrefied cedar at lower and higher $T_t$, respectively, due to the loss of flexibility of honeycomb walls by increasing $T_t$. $T_t$ over $275^\circ$C induces a decrease in $S_t$ of briquette, due to collapsing of honeycombs and insufficient bonding of walls of broken honeycombs.

The effect of $T_t$ on $S_t$ of coke with $T_c = 1000^\circ$C is attributed mainly to increment of $S_t$ at $T_c = 500$–1 000$^\circ$C, where $S_t$ increases by 1.8–3.6 times. $S_t$ with $T_c = 420^\circ$C is almost independent of $T_t$. Different $T_t$ also results in a different relationship between $S_t$ of coke and its apparent density. The higher apparent density does not necessarily lead to greater $S_t$. 

Fig. 14. Fracture surfaces of T225 and T300 after carbonization at $T_c = 420^\circ$C.

Fig. 15. Fracture surfaces of cokes from T225–T300 for $T_c = 1000^\circ$C.
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Supporting Information

This material contains pyrolysis characteristics of the original and torrefied cedars, elemental composition of coke and SEM images of fracture surface of coke.

This material is available on the Journal website at https://doi.org/10.2355/isijinternational.ISIJINT-2022-013.

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