Preparation of Coke from Hydrothermally Treated Biomass in Sequence of Hot Briquetting and Carbonization

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A sequence of briquetting of biomass solids (bamboo, larch and mallee) at temperature and mechanical pressure of 130–200°C and 114 MPa, respectively, and carbonization at 900°C produces coke with tensile strength (TS) of 5–19 MPa. Introduction of heat treatment in hot-compressed water (*i.e.*, hydrothermal treatment; HT) of the biomass prior to the briquetting increases TS up to 44, 57 and 42 MPa for the bamboo, larch and mallee, respectively. TS of coke is correlated well and positively with the coke/briquette bulk density ratio, and HT increases the ratio if operated under appropriate conditions. The efficacy of HT is attributed primarily to increase in the coke yield on a basis of the briquette mass. HT hydrolytically removes highly volatile cellulosic material (*i.e.*, cellulose and hemicellulose), transforms it into solid that contributes to coke as effectively as lignin, and thereby increases the mass yield of coke by a factor of 1.4 to 2.1. HT also enhances the plasticizability of the biomass during the briquetting by degradation of the lignin to reasonable extent, and then promotes particles' coalescence/fusion and densification of the briquettes. Applying mechanical pressure over a range of 12–114 MPa to the briquetting of a solid from HT of the bamboo at 240°C successfully results in production of coke with TS of 41–44 MPa.

KEY WORDS: biomass; hydrothermal treatment; coke.

1. Introduction

Use of low-grade carbonaceous resources is an important option for coke production in the future sustainable metallurgical industries. Lignite and biomass are the most promising resources in terms of abundance, but their common features; high porosity and no fusibility upon heating,[1)] prevent their application in conventional coke production. Properties of lignite as well as those of biomass such as fluidity and reflectance[1)] are out of the ranges of so-called MOF diagram.[2)] It is known that blending coal with biomass results in reduction of fluidity.[3,4)]

The present authors[5,6)] proposed sequences of hot briquetting and carbonization[5)] or hydrothermal treatment, hot briquetting and carbonization[6)] for production of coke from lignite. The briquetting of pulverized lignite at 100–200°C causes its thermomechanical plasticization while macromolecular relaxation occurs due to breakage of non-covalent bonds such as hydrogen ones. The plasticization leads to deformation and coalescence of particles and densification of resulting briquette. The briquette undergoes carbonization with no or insignificant softening/fusion, but transforms into coke that has tensile strength of 5–40 MPa.[5,6)] It was

also found for every type of lignite that the tensile strength of coke was correlated linearly with its bulk density, and this trend was consistent with general knowledge of mechanical strength of coke.[7)]

The sequential hot briquetting and carbonization can be applied to carbonaceous solid that has a propensity for plasticization under heating and mechanical pressure. There is no need of thermoplasticity during the pyrolysis, which is rather undesirable because of bubble formation. The present study focuses on biomass. It is known that woody biomass is plasticized by heating to temperature of 100°C or slightly higher with mechanical pressure of 200–450 MPa, and transformed into pellets or briquettes.[8)] The plasticization is generally attributed to softening or fusion of lignin and/or hemicellulose.[8)] Technical feasibility of such pelletization of woody biomass has already been demonstrated in commercial scales.[9)] Briquetting of biomass at higher temperature up to 210°C was investigated.[10)] Mechanical pressurization to 22 MPa produced briquettes of reed with compressive strength of 20–120 MPa.

It is expected from the above-mentioned knowledge that carbonization of biomass briquette enables to produce high strength metallurgical coke. However, the preparation of high strength briquette does not straightforwardly mean that of high strength coke, and this is because of much lower coke yield than that from lignite as well as coal. In general,

biomass consists of three major components; cellulose, hemicellulose and lignin. The pyrolysis of cellulose, which normally accounts for 50% or more of the biomass on a dry mass basis, produces coke but with yields lower than 10 wt%.[11,12] Such a highly volatile nature of the cellulose can substantially lower the density of coke unless shrinkage in bulk of the briquette catches up with the release of volatiles. Hemicellulose is less volatile than the cellulose during the pyrolysis, but the coke yield is around 25 wt%.[13] Lignin yields more coke (≈ 50 wt%) than the other two components,[13] although it is less abundant than the cellulose.[14]

The above-mentioned chemical and pyrolytic characteristics of biomass suggest necessity of modifying its chemical composition and/or structures of the individual components prior to the briquetting. It is believed that heat treatment of biomass in hot-compressed water, that is, hydrothermal treatment (HT), is a most reasonable way of such chemical modification in a practical sense because water is used as the only reactive solvent for hydrolytic decomposition of cellulose and hemicellulose into sugar monomers/oligomers,[15–17] but without any chemical reagents. The hydrolytic decomposition of cellulose and hemicellulose occurs at 180°C and 230°C, respectively, or even at lower temperatures.[15–17]

Lignin is less reactive in hot-compressed water than the other two components,[18,19] and its major portion is left in the residual solid. Knowledge on the mechanism of hydrothermal reactions of the lignin is much less compared with that for the cellulose and hemicellulose. Recent studies[18,19] showed simultaneous progress of depolymerization and polymerization[18] and formation of monomeric phenol derivatives.[19] HT is thus recognized to be a method to upgrade biomass to a lignin-enriched solid,[20] and it is therefore worth to study a sequence of HT, hot briquetting and carbonization examining the efficacy of HT in preparation of coke from the biomass. A potential problem of the lignin-rich solid is, even if prepared successfully by HT, is its propensity for foaming upon heating at temperature of 200–300°C. In a previous study on fabrication of carbon fiber from a type of lignin that was recovered by acid-catalyzed hydrolysis of woody biomass,[21] it was mandatory to stabilize fibers of the lignin by oxidation with air to prevent significant swelling during the carbonization.

The present study aimed to examine the efficacy of HT in the coke production through the hot briquetting and carbonization with consideration of changes in chemical/elemental composition of biomass, its briquettability, yield, density and mechanical strength of coke, and interdependency among them. Other important properties of coke represented by indices such as CRI (coke reactivity index) and CSR (coke strength after reaction) are not discussed in this paper but in future reports.

2. Experimental

2.1. Material

Three different types of biomass, moso bamboo (Japan), larch (Japan) and mallee (i.e., eucalyptus, Australia) were employed as the starting biomass samples. As received samples were dried in air at ambient temperature to moisture contents of about 10 wt%. **Table 1** lists ultimate analyses of

Table 1. Ultimate analyses of the samples. Unit; wt%-dry.

Biomass	C	H	O, N and S (by diff.)	ash
Bamboo	48.3	5.9	44.6	1.2
Larch	49.9	5.9	44.0	0.1
Mallee	52.3	5.2	42.4	0.1

the original samples.

2.2. Hydrothermal Treatment (HT)

The biomass sample (10 g-dry) and deionized water (90 g) were mixed, and charged in an autoclave (Taiatsu Techno®, TVS-N2). After closed, the autoclave was pressurized with N_2 (purity >99.9999 vol.%) to 1.0 MPa, and then immersed in a fluidized sand bath at 200–300°C. The heating rate of the content was ca. 7°C min^{-1}. The total period of heating was fixed at 60 min including the heating-up period. At the end of the heating period, the autoclave was immersed in 10 L iced water and quenched. The entire portion of the resulting slurry was recovered, and separated into the solid and liquid products by filtration under reduced pressure. A Teflon®-made membrane filter (pore size; 0.45 μm) was used for the filtration. The solid, which is hereafter referred to as HT solid, was dried at ambient temperature to moisture content of ca. 10 wt%. The solid from HT of biomass x at y°C will be denoted by x-y. HT at y°C will be abbreviated to HT-y.

2.3. Chemical Analysis of Original and Treated Biomass

The original biomass and HT solids were subjected to chemical analyses for determination of the contents of solvent-extractable matter, holocellulose (i.e., cellulose and hemicellulose) and lignin. The first analysis was solvent extraction with 2:1 (vol:vol) benzene:ethanol mixed solvent in a Soxhlet extractor for 6 h. The extract, i.e., the benzene:ethanol soluble matter (SOL), was recovered as solid after rotary evaporation of the solvents and subsequent vacuum drying at 40°C. The extraction residue was vacuum-dried at 30°C, and its portions were subjected to chemical analyses by means of Klason method[22] and aqueous-phase oxidation.[23] In the former analysis, the extraction residue was treated in an aqueous solution of sulfuric acid (concentration; 72 wt%) at 20°C for 4 h and then in another diluted one (3 wt%) at its boiling temperature (115°C) for 4 h. In these acidic media, the holocellulose (HCEL; i.e., cellulose and hemicellulose) underwent the acid-catalyzed hydrolysis and decomposed completely into water soluble material. The remaining solid was defined as Klason lignin (LIG) that is also called acid insoluble lignin.[23] An attention is needed for the content of LIG in the mallee. In general, mallee contains considerable amount of polyphenol[24] that is alkali soluble and can be distinguished from the Klason lignin. LIG defined in the present study involves such polyphenol. HCEL was quantified by treating the extraction residue in an aqueous solution of sodium hypochlorite and acetic acid at 75°C for 1 h with threefold or fourfold repetition, which was needed to complete the oxidative solubilization of the lignin. The mass of white or pale yellow solid was defined as that of holocellulose.[23] The total recovery of SOL, LIG

and HCEL was within a range of 98–102 wt% of the dry solid before the extraction.

2.4. Hot Briquetting and Carbonization

The original biomass and HT solids were briquetted at temperature (T_B) of 130 or 200°C. Details of the procedure are reported elsewhere.[5,6] In brief, 0.9–1.0 g of solid was placed in a 14.1 mm diameter mold and heated to 130 or 200°C. A mechanical pressure (P_B) of 12, 25, 55 or 114 MPa was then loaded for 8 min. After the pressure release, the mold was cooled down naturally to temperature lower than 40°C. The briquette, which had a size of 14.0 mm in diameter and *ca.* 5.0 mm thickness, was heated for the carbonization in atmospheric flow of N_2 at a rate of 3°C min^{-1} to 900°C where the temperature was held for 10 min.

2.5. Measurement of Mechanical Strength of Coke

The mechanical strength of carbonized briquette, *i.e.*, coke was measured at ambient temperature by means of diametrical compression test.[25] Details of the tests and the method of determining the tensile strength (TS) are reported elsewhere.[5,6] Compression strength was not employed because it depends on the shape (*i.e.*, aspect ratio of cylindrical specimen). Fractured surface of the coke was observed by scanning electron microscopy (SEM) on a micrograph (Keyence, model VE-9800).

3. Results and Discussion

3.1. Yield of Solid from HT

Figure 1 shows the yield of HT solid as a function of HT temperature (HTT). The solid yields from the bamboo and larch change from *ca.* 70 wt% to ca. 50 wt% as HTT increases from 200 to 300°C. The yield from the mallee is systematically higher than those from the bamboo and larch by *ca.* 10 wt%. This is ascribed mainly to the higher LIG content of the mallee, as evidenced later.

3.2. Change in Chemical Composition of Biomass by HT

Figure 2 illustrates change in the chemical composition of solid with HTT. The mass fractions of SOL, LIG and HCEL have been normalized by their total, *i.e.*, 100%. A common trend among the bamboo, larch and mallee is that

the fraction of HCEL (F_{HCEL}) decreases monotonously with HTT due to hydrolysis of cellulose and hemicellulose.[15–17] HT temperature of 250–260°C seems to be high enough to convert the major portion of HCEL. The decrease in F_{HCEL} is compensated by increases in the fractions of SOL (F_{SOL}) and/or LIG (F_{LIG}).

The mass fractions of SOL and LIG are shown on a basis of the mass of the dry biomass, that is, as net yields, in **Fig. 3**. HT at 200–220°C converts LIG of the bamboo to water-soluble material and/or SOL. Less noticeable but similar trends are seen for the larch and mallee. A portion of LIG is thus lost from the solid by HT at relatively low temperature. On the other hand, HT of the larch and mallee above 240°C give net LIG yields greater than the initial mass fractions of LIG. This is ascribed to the transformation of HCEL into material that is classified into the Klason lignin. Taken together with hydrolysis of HCEL at an early stage of HT (see Fig. 2), it is believed that water-soluble compounds from HCEL such as sugar monomers and oligomers undergo polymerization forming water-insoluble material that is classified into LIG and/or SOL. Recent studies on biomass processing such as steam explosion[26] noticed formation of cellulose- and/or hemicellulose-derived material that is not reactive with acid. Such material is termed lignin-like material or pseudo-lignin.[23]

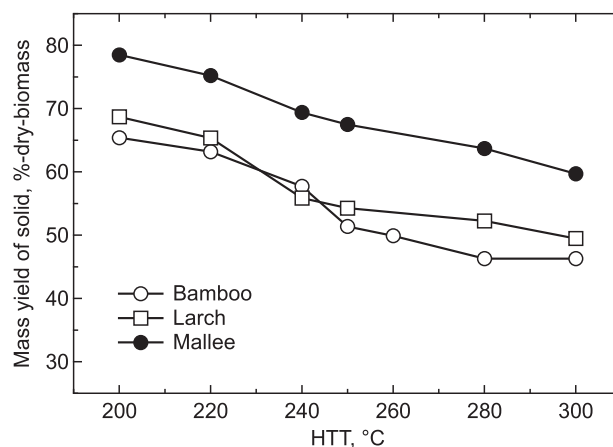The composition of SOL was further investigated. HT

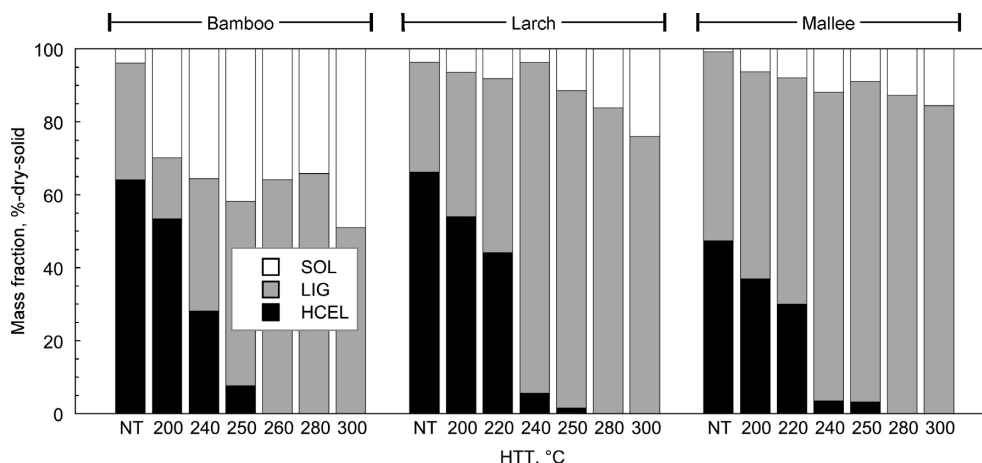**Fig. 1.** Change in the yield of HT solid with HTT.

Fig. 2. Changes in chemical composition of biomass with HTT. NT: no treatment before briquetting.
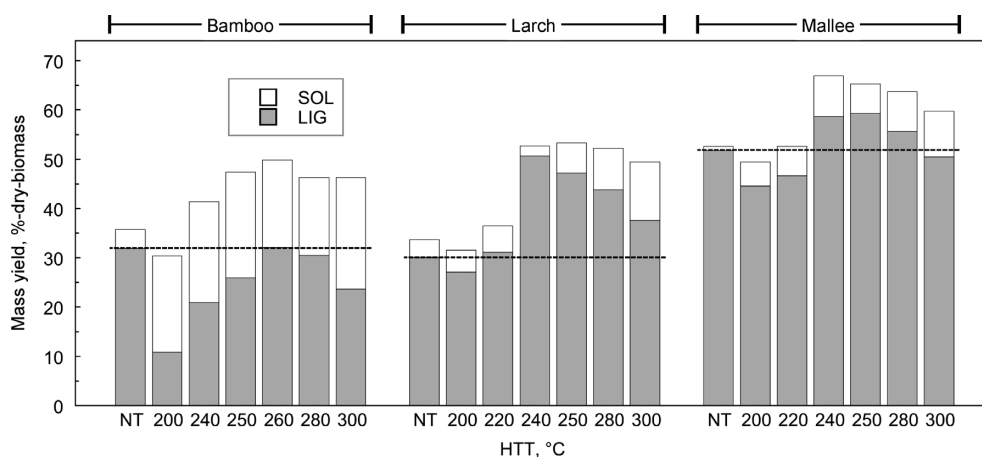
Fig. 3. Net yields of LIG and SOL. The dashed lines indicate the mass fractions of LIG in the initial dry biomass. NT: no treatment before briquetting.
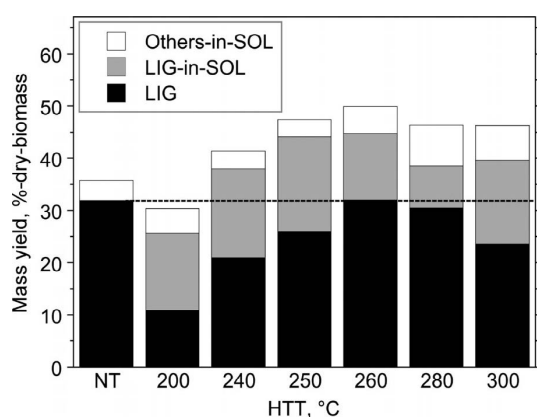

Fig. 4. The net yields of LIG, LIG involved in SOL (LIG-in-SOL) and the others in SOL from HT of bamboo. The broken line indicates the mass fraction of LIG in the dry bamboo. NT: no treatment.
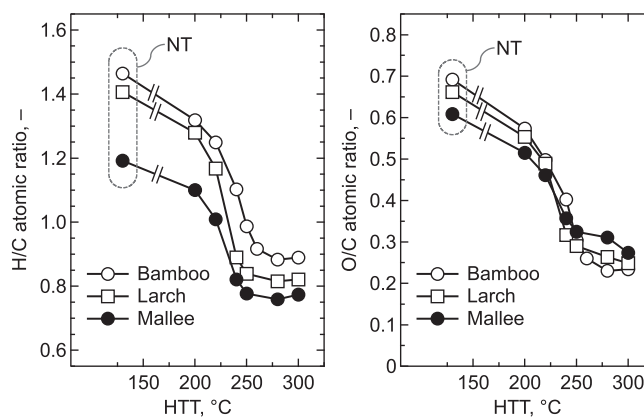

Fig. 5. Changes in atomic H/C and O/C ratios with HTT.

solids from the bamboo were subjected directly to the liquid phase oxidation without the benzene:ethanol extraction. This procedure made it possible to determine the total content of Klason lignin over the range of LIG to SOL. The result is presented in **Fig. 4**. It is seen that a substantial portion of SOL is contributed by the Klason lignin, which is indicated by LIG-in-SOL in the figure. Analyses of water from HT showed that the amount of lignin-derived phenolic monomers and oligomers was much less than that of LIG-in-SOL. It is also clear in Fig. 4 that the total yield of the net LIG and LIG-in-SOL exceeds the initial mass fraction of LIG. A major portion of LIG-in-SOL is thus represented by benzene:ethanol-soluble LIG. Analyses of HT solids from the larch and mallee drew similar conclusions, although details are not presented here.

The HT-solids were free or nearly free from HCEL when HTT was higher than 240°C. It was also confirmed that major portions, 85–100 wt%, of the HT solids consisted of LIG and LIG-in-SOL. Such high contents were due to transformation of HCEL into LIG as well as limited conversion of LIG into water-soluble material.

3.3. Elemental Composition of HT Solid

Figure 5 exhibits atomic H/C and O/C ratios of HT solid as functions of HTT. Both ratios decrease substantially in a range from 200°C (or lower temperature) to 250°C, but only slightly at higher temperature. The loss of carbon, hydrogen and oxygen from the solid, which are hereafter denoted by ΔC, ΔH and ΔO, respectively, can be calculated from the mass yield of solid and its elemental composition. As shown in **Fig. 6**, ΔH and ΔO change maintaining their ratio, $\Delta H/\Delta O$, around 1.64, regardless of the biomass type.

On the other hand, ΔC changes in a very different manner, as seen in **Fig. 7**. HTT up to 200°C seems to increase ΔC at a $\Delta H/\Delta C$ rate of around 1.75, but HTT at 200–250°C maintains or even decrease ΔC while ΔH and ΔO continue to increase. This cannot be explained only by the progress of the loss of HCEL that is clear at 200–250°C. The maintenance or slight decrease of ΔC thus suggests incorporation of water-soluble matter into the solid, in other words, retrogressive transformation of cellulose/hemicellulose-derived compounds, at a rate equivalent to or even greater than that of hydrolytic removal of HCEL. The retrogressive transformation is in agreement with the results shown in Figs. 2–4.

It is also estimated that HCEL-derived LIG has lower H/C and O/C ratios than HCEL. Further increase in HTT over 250°C restarts the loss of carbon together with those of hydrogen and oxygen. ΔC for the mallee is smaller than those from the bamboo and larch. This is explained reasonably by higher and lower contents of LIG and HCEL in the mallee, respectively, than those in the others. It was confirmed from analyses of product gases and water that ΔC consisted of losses of carbon by formation of gases (mainly
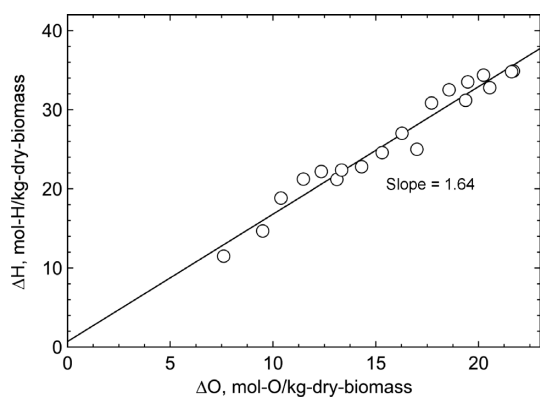
Fig. 6. Relationship between loss of hydrogen (ΔH) and that of oxygen (ΔO) from solid. Data for the bamboo, larch and mallee are not distinguished from one another.
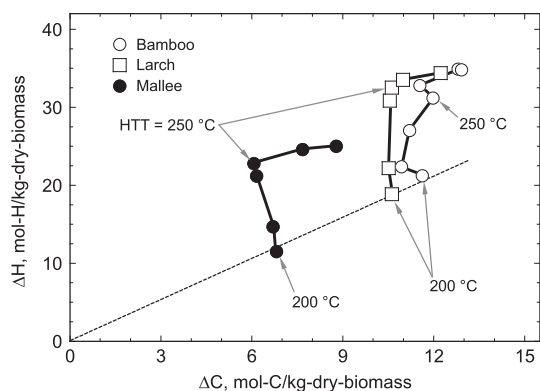

Fig. 7. Relationship between ΔH and ΔC. The slope of the broken line, *i.e.*, $\Delta H/\Delta C$, is 1.75.
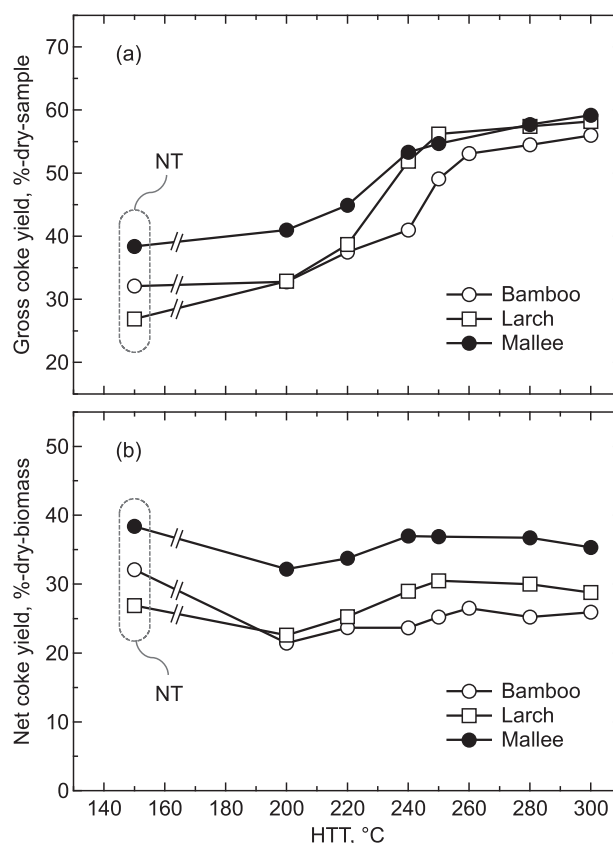

Fig. 8. Changes in (a) gross coke yield and (b) net coke yield. Conditions for briquetting: $P_B = 114$ MPa, $T_B = 200$°C.
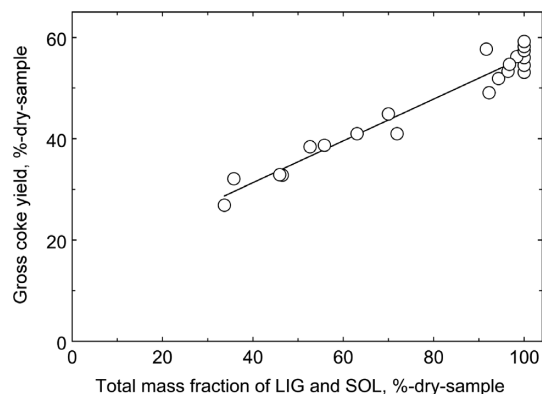

Fig. 9. Relationship between gross coke yield and total content of LIG and SOL. Data for bamboo, larch and mallee are not distinguished from one another.

CO_2, CO and CH_4) and dissolution of organic matter into water, the latter of which accounted for about 4/5 of ΔC.

3.4. Coke Yield

Figure 8(a) plots gross coke yields from briquettes of HT solids against HTT. T_B and P_B are 200°C and 114 MPa, respectively. Increasing HTT up to 250°C causes the coke yield increase significantly, and this is attributed mainly to removal of HCEL from the biomass. The coke yield further increases at HTT of 250–300°C, but only slightly. HT at 250–260°C increases the gross coke yields from the bamboo, larch and mallee by 21, 29 and 26 wt%-dry-sample, respectively. The gross coke yields from the HT solids with HTT $\geq$ 250–260°C are well above 50 wt%, and are as high as those from hot-briquetted lignites.[5,6] As seen in Fig. 8(b), HT at 240°C and higher temperatures give net coke yield that is equivalent to or even higher than that without HT in spite of substantial mass release during HT. This is a result that shows the importance of the retrogressive transformation of HCEL into LIG and/or SOL.

Effect of T_B on the gross coke yield was investigated, and it was found that the briquetting at 200°C gave coke yields higher than that at 130°C systematically by *ca.* 2 and 3 wt%-dry-sample for the HT solids (HTT $\geq$ 240°C) from the larch and mallee, respectively. No significant effect of T_B was, however, detected on the coke yield from the HT solids from the bamboo (HTT $\geq$ 240°C). On the other hand, when

HTT was 220°C or lower, the higher T_B gave greater coke yield than the lower T_B by 3–5 wt%-dry-sample. The effect of T_B on the carbonization of briquette will be discussed later.

3.5. Relationship between Chemical Composition of HT Solid and Coke Yield

The relationship between the gross coke yield and chemical composition of HT solid is considered. It is seen in **Fig. 9** that the gross coke yield is correlated well and linearly with the total content of LIG and SOL. These two components thus play similar roles of coke precursors. It is also suggested that the solubility or insolubility in benzene:eth-
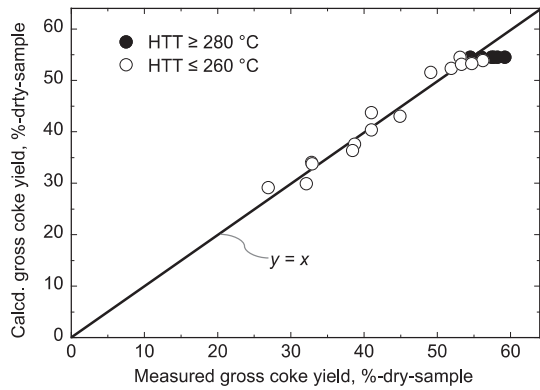
Fig. 10. Comparison between measured and calculated gross coke yields. Data for bamboo, larch and mallee are not distinguished from one another.

Fig. 11. Effect of HTT on the bulk density of briquette (ρ_B) of HT solid. Condition for briquetting: P_B = 114 MPa.

Fig. 12. Effect of HTT on the bulk density of coke (ρ_C). Condition for briquetting: P_B = 114 MPa.

anol is not important for such roles. Although not shown in the figure, correlation of the gross coke yield with either of LIG or SOL content was much less successful. Further numerical analysis reached calculation of the gross coke yield from the chemical composition, *i.e.*, the contents of HCEL, LIG and SOL in HT solid. **Figure 10** compares the measured gross coke yield with that given by

$$\text{Gross coke yield } [\%\text{-dry-sample}] = 0.545\left(F_{LIG} + F_{SOL}\right) + 0.163\,F_{HCEL} \quad\text{............ (1)}$$

The coke yields for HTT = 280–300°C are not considered in optimization of the coefficients of Eq. (1) because HCEL is absent in the HT solids with HTT = 280–300°C, and in addition, more or less changes in the elemental compositions of LIG and SOL were certain. Equation (1) demonstrates that the coke yields from LIG/SOL and HCEL are 55 wt% and 16 wt%, respectively, in other words, effectiveness of removing HCEL from the solid and then transforming it into LIG for increasing coke yield.

3.6. Bulk Density of Briquette and Coke

Our previous studies[5,6] revealed that the bulk density of briquette (ρ_B) was an important factor for preparing high-strength coke because greater ρ_B led to higher bulk density of resulting coke (ρ_C) and TS. It was then suggested that ρ_B was also an important property of briquette of HT solids in the present study because the briquettes from lignites and HT solids experience carbonization in the same or very similar fashions, *i.e.*, carbonization with no significant fusion during the carbonization.

Figure 11 shows combined effects of HTT and T_B on ρ_B. The bulk density is determined by the true density and porosity of solid. Increasing HTT greatly decreases the O/C ratio, and this must result in decrease in the true density of briquette. This seems to be consistent with the effects of HTT on ρ_B for the mallee. On the other hand, some HT solids from the bamboo have ρ_B greater than those for the original bamboo regardless of T_B. This must come from lower porosity of the formers than the latters. In other words, HT of the bamboo enables more degree of densification of solid during the briquetting. Some HT solids from the larch (T_B; 200°C, HTT; 200–220°C) have ρ_B equivalent to that for the original larch, suggesting a positive effect of HT on the den-
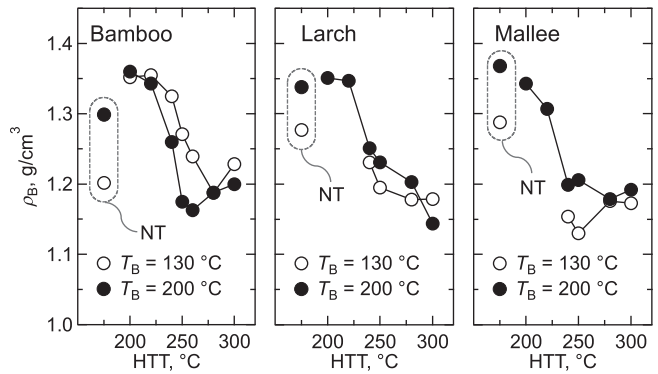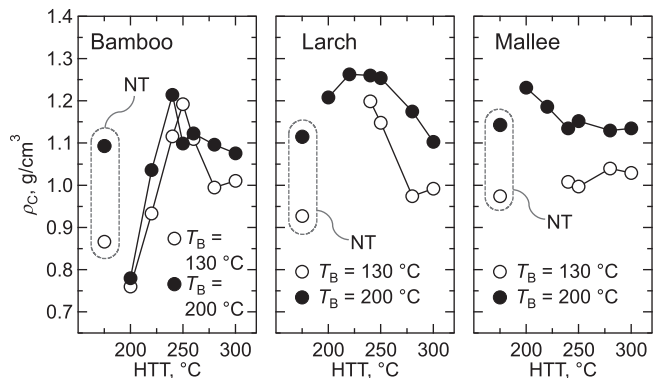
sification.

It should also be noted for the bamboo-derived HT solids that higher T_B results in smaller ρ_B at HTT = 220–280°C, unexpectedly. Our previous studies[5,6] showed that higher T_B was preferred to achieve greater ρ_B of lignite briquette, but the bamboo-derived HT solid is not the case. It is known that glass transition of organic polymer normally decreases the true density of the polymer increasing its free volume. This leads to a hypothesis of glass transition or a similar physical phenomenon with HT solids from the bamboo at temperature between 130 and 200°C under application of the mechanical pressure. In fact, lignin undergoes glass transition at 100–200°C.[21] This hypothesis will be examined in the future work.

Figure 12 displays the combined effects of HTT and T_B on ρ_C. There are certain ranges of HTT and T_B in which ρ_C from HT solid is higher than that of the original biomass, evidencing that HT leads to densification of coke. There are also HTT's that maximize ρ_C. More importantly, there seems to be neither clear nor simple relationship between ρ_C and ρ_B. The relationship between these two parameters will be considered later together with TS.

3.7. Tensile Strength of Coke

Figure 13 plots TS against HTT. TS is greater than 10 MPa even without HT while T_B = 200°C is needed. Introducing HT before briquetting clearly increases TS. Cokes from the bamboo, larch and mallee have maximum TS of 41, 50 and 32 MPa, respectively, at HTT of 240–250°C and
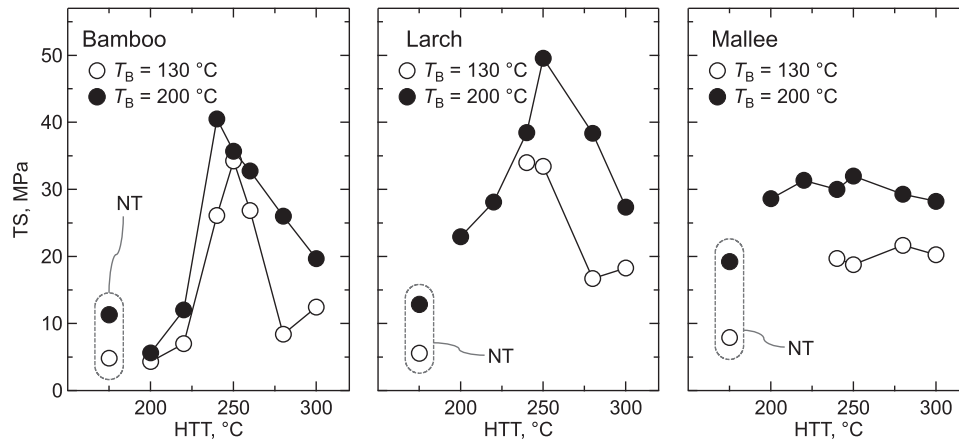
Fig. 13. Combined effect of HTT and T_B on TS. Condition for briquetting: $P_B = 114$ MPa.
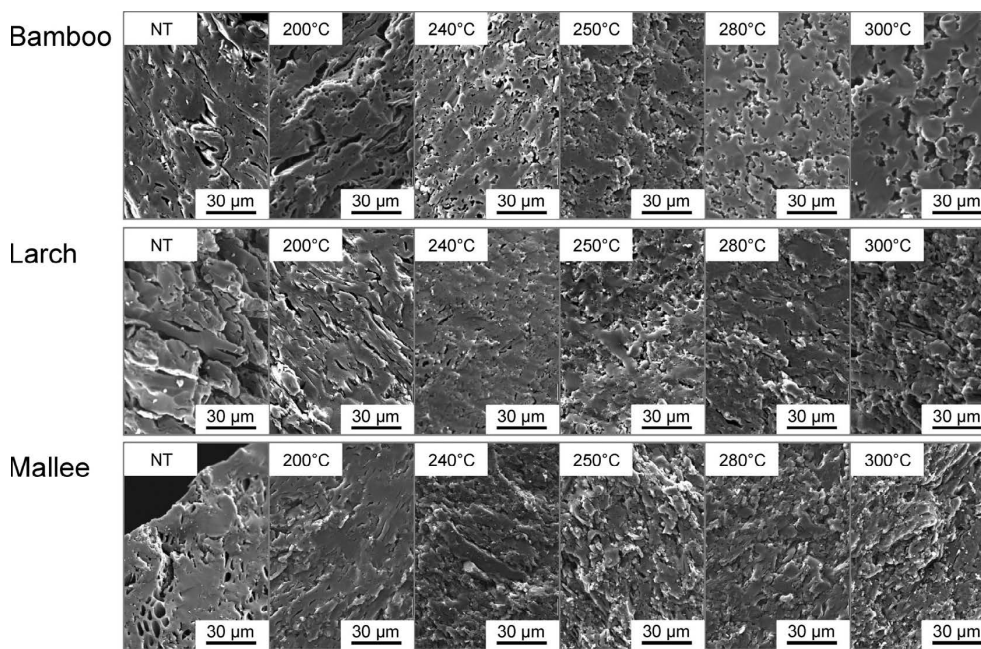

Fig. 14. SEM photographs of fractured surfaces of coke. NT: no treatment before briquetting. Condition for briquetting: $P_B = 114$ MPa, $T_B = 200°C$.

$T_B = 200°C$. TS of coke from the bamboo changes with HTT via a minimum at 200°C and then maximum at 240°C. This tendency is explained qualitatively based on the porous nature of coke, which is evaluated from the morphology of fractured surface, as displayed in **Fig. 14**.

The porosity and pore sizes for the coke from HT-200 are larger and more frequent, respectively, than those of the coke from the original bamboo. Increasing HTT to 240–250°C causes densification of the coke, but further increase results in the production of more porous coke. The substantial decrease in TS by increasing HTT beyond 260°C seems to be due to development of pores in population/size during the carbonization. HT-280 and HT-300 briquettes ($T_B = 200°C$) have greater ρ_B than those of HT250 and HT-260 ones (see Fig. 11). In other words, the former briquettes were densified more extensively than the latter ones. However, such greater ρ_B results in smaller ρ_C due to pore formation and/or growth in size during the carbonation. HT solids from the bamboo with HTT = 260–300°C contain SOL with mass fractions as large as 35–50 wt%. It is then

plausible that SOL experiences fusion and bubble formation in the briquette in an early stage of the carbonization, developing the porous structure. It is, however, difficult to explain the difference in the thermal behavior of HT solids between HTT of 240–250°C and 280–300°C because of no significant difference in the relative mass fractions of SOL and LIG. The physical behavior of SOL may thus be very sensitive to its detailed chemical structure (*e.g.*, distributions of functional groups and molecular mass).

It seems for the cokes from the larch that TS and the fractured surface morphology are consistent with each other. TS of the cokes from mallee are much less sensitive to HTT than those from the bamboo and larch. The fractured surfaces of the cokes from the mallee with HTT = 240–300°C are in fact similar to one another, and this is consistent with similarity in TS over the range of HTT from 200 to 300°C.

3.8. Correlation between TS and Coke/briquette Densities

Trials and error were made to reach best correlation

between TS and coke/briquette properties. Some of the correlations are provided in **Fig. 15**. It is difficult to say that TS is correlated well with ρ_C. The trends indicated by the solid and dashed lines are clearly different from each other. Though not shown in the figure, TS of the bamboo-derived coke was correlated well with ρ_C. On the other hand, TS *vs* ρ_C plots for the larch-derived cokes distributed over the full ranges between the solid and dashed lines. Much better correlations were found between TS and the coke/briquette density ratio, *i.e.*, ρ_C/ρ_B and also between TS and ΔSV that is the difference in the specific volume between the coke and briquette, *i.e.*,

$$\Delta SV = \frac{1}{\rho_B} - \frac{1}{\rho_C} \quad .... (2)$$

If $\rho_C = \rho_B$, ΔSV and ρ_C/ρ_B are 0 and 1, respectively. TS–ρ_C/ρ_B and TS–ΔSV relationships seem to be universal to the three different types of biomass. The results shown in Fig. 15 strongly suggest that the decrease in the density during the carbonization has a negative impact on TS. According to our previous study on the coke production from Victorian lignite,[5] the bulk density decreases up to temperature around 600°C (in other words, until completion of tar evolution) and then increases. Assuming that the bulk densities of the present biomass-derived briquettes change in the same fashion as those of the lignite, the followings may cause temporary or permanent decrease in the bulk density.

(1) *Pyrolysis of HCEL*: As established by Eq. (1), the pyrolysis of HCEL produces much more volatiles than LIG and SOL. More extensive release of volatiles tends to make the pyrolyzing solid more porous. Typical examples are the bamboo and larch without HT. For these solids, there are large differences between ρ_B and ρ_C.

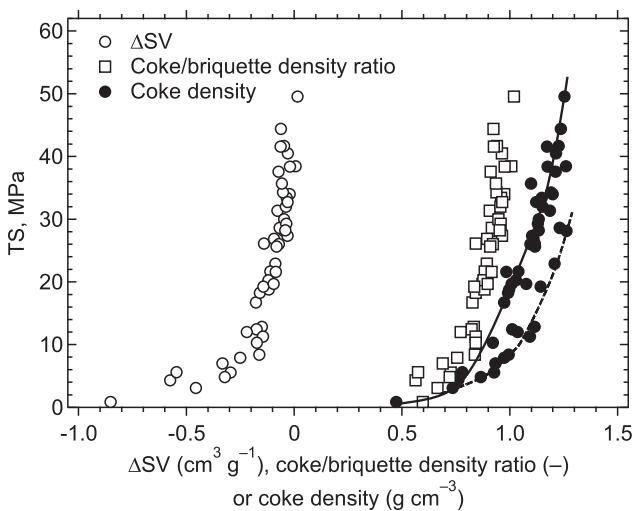(2) *Extensive depolymerization of LIG*: HT-200 converts more than half mass of the original LIG in the bamboo into SOL. HT-200 thus decreases the LIG content to only 16 wt%. SOL and/or well depolymerized LIG have propensities to fuse and generate bubbles in the early stage of carbonization, inhibiting densification in the later carbonization. Fusion of SOL is also suspected during the carbonization of HT solids from the bamboo with HTT > 260°C, the SOL contents of that are as high as 35–50 wt%. Depolymerization of LIG seems to be insignificant for HT of the larch and mallee, because HT even at 200°C increases TS of resulting cokes.

(3) *Polymerization of LIG during HT*: LIG undergoes not only depolymerization but also polymerization during HT.[18] HT of the larch and mallee at HTT > 260°C causes polymerization of LIG and then inhibits its plasticization and then particles' coalescence during the subsequent briquetting. The repolymerization of LIG can also suppress its flexibility during the carbonization and resultantly volumetric shrinkage responding to the volatile release.

(4) *Insufficient densification of briquette*: Briquetting at lower temperature (*i.e.*, 130°C) leaves more pores at particles' interfaces in the briquette. It is difficult to remove such pores during the pyrolysis unless the solid experience extensive softening. The carbonization with no or little fusion of the solid cannot promote particles' coalescence.

3.9. Effect of Briquetting Pressure on TS of Coke

It is suggested from the above discussion that HT solids from the bamboo have more plasticizability than those from the larch and mallee. **Figure 16** shows the effects of P_B on TS of coke for three selected HT solids; bamboo-240, larch-250 and mallee-250. TS of coke from the bamboo-240 with T_B = 200°C is nearly independent of P_B over the range of 12–114 MPa. In other words, P_B as small as 12 MPa successfully led to production of coke with TS over 40 MPa. Application of lower T_B (= 130°C) shows an optimum P_B of 55 MPa. Assuming that 130°C is not high enough to cause either extensive plasticization or glass transition, excess mechanical pressure may not only increase ρ_B but also induce residual stress in the briquette.[6] TS of cokes from the larch-250 and mallee-250 increase monotonously with P_B. This trend evidences that these HT solids have less plasticizability than the bamboo-250.

Another suggestion from the above discussion is control of the progress of depolymerization and polymerization of
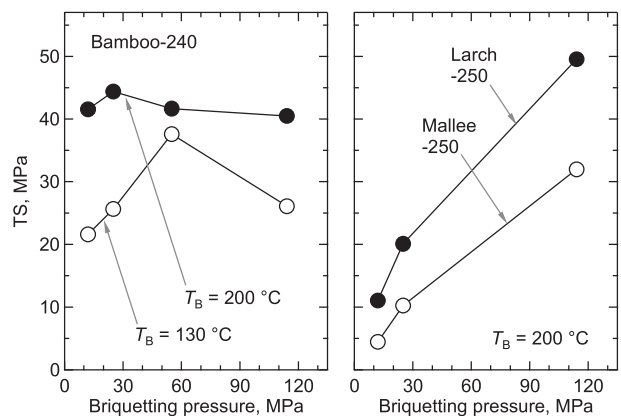
Fig. 15. Correlation of TS with three different single or combined properties of coke and/or briquette. ΔSV: difference between the specific volume between coke and briquette. Data for the cokes from the bamboo, larch and mallee are not distinguished from one another. Conditions for briquetting: T_B; 130 or 200°C, P_B = 114 MPa.

Fig. 16. Effects of P_B on TS of coke.

LIG. The larch and mallee were subjected to HT at 250°C while the heating periods were shortened from 60 to 30 min. This shortening resulted in increases in TS of cokes prepared at $T_B = 200$°C and $P_B = 114$ MPa from 50 to 57 MPa and from 32 to 42 MPa for the larch and mallee, respectively. It was expected for HT at 250°C that shorter period was preferred to suppress the polymerization of LIG of the larch and mallee.

4. Conclusions

The experimental results and numerical analyses in the present study draw the following conclusions.

(1)   HT has positive effects on TS of cokes for the all types of biomass investigated. The maximum TS for the bamboo, larch and mallee were 44, 57 and 42 MPa, respectively, at T_B; 200°C and P_B; 114 MPa, and these are greater than those from the corresponding original samples by factors of 3.9, 4.5 and 2.2, respectively.

(2)   HT not only hydrolytically removes HCEL but also incorporates it into a portion of LIG and/or SOL. These chemical events contribute to not only increase in the gross coke yield by 1.3–1.8 times but also make the net coke yield equivalent to that from the original biomass.

(3)   HT also causes depolymerization of LIG in the bamboo, enhancing its plasticizability. As a result of this, the briquetting the solid from HT-240 with P_B as small as 12 MPa leads to production of coke with TS equivalent to that for the briquetting with P_B of 114 MPa. Depolymerization of LIG in the larch and mallee is less extensive, and therefore TS of the cokes increases with increasing P_B.

(4)   TS of coke is well correlated with ρ_C/ρ_B and also with ΔSV regardless of the type of biomass.

(5)   The most appropriate HTT is 240–250°C if maximization of the gross/net coke yield and that of TS are desired simultaneously.

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