Model Calculation of Heat Balance of Wood Pyrolysis

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Stoichiometric analysis and heat balance analysis of wood pyrolysis were conducted to improve a pyrolytic gasification system. Heat balance around a pyrolysis furnace was estimated by calculating heat of pyrolysis, sensible and latent heats of products and heat loss of a furnace. Using literature data, macromolecules were expressed by mean compositional formulas, and the heat of pyrolysis was obtained by the stoichiometric approach including the overall equation of pyrolysis. Pyrolysis was exothermic reaction at the range of 773 – 1373 K. Despite the exothermic nature of pyrolysis, heat balance calculation around a pyrolysis furnace showed that external heat was required to compensate heat consumption of the sensible and latent heats of products and heat loss of a pyrolysis furnace. When a feed contains moisture, additional external heat was required. To use charcoal as fuel for the external heating to a furnace, the required amount of charcoal was calculated.

Key Words
Wood pyrolysis, Heat balance, Stoichiometric theory

1. Introduction
Small-scale power generation through gasification of biomass has drawn attentions due to the higher efficiency than that of power generation by steam through wood combustion 1,2. There are two typical technologies in gasification, one is partial oxidation using air or oxygen-rich air or pure oxygen, and another is pyrolysis under an inert atmosphere giving flammable gas, liquid products and charcoal. Flammable gas is used as fuel for a power generator. Wood gasification through partial oxidation was widely conducted and it is a heat-generating process. Wood pyrolysis for flammable gas production has also drawn attentions because pyrolysis gas of the higher calorific value can be recovered, comparing to air-blown partial oxidation.

However, even in the fundamental nature of wood pyrolysis, there are conflicts between exothermic and endothermic reaction. There is a variety of heat flow within a wood pyrolysis system for power generation. There is a little known on the heat balance around a pyrolysis furnace, which is a core equipment of the system. It is a critical issue to evaluate how much energy generates and is consumed because a wood pyrolysis process is planned for the recovery of carbon-free energy. The precise examination of heat balance is needed both for the development and evaluation of an energy recovery system of biomass, considering heat of pyrolysis, heat of vaporization of the products and heat loss of a pyrolysis furnace.

For heat of pyrolysis, some researchers conducted micro-scale analysis of wood pyrolysis by thermogravimetric analysis to determine heat of pyrolysis 3,4. For the heat and material balances of macromolecular conversion, the authors proposed a new stoichiometric approach to analyze coal gasification 5,6, and, recently, it was applied to coal
gasification both on surface \(^7\) and in underground \(^6\). The stoichiometric theory was used to obtain theoretical heat of gasification, and adiabatic gasification temperature was also given rather than a simple matching of stoichiometric coefficients. Gasification temperature is of importance to estimate a theoretical rate of gasification, which helps to evaluate the performance of a gasifier such as treatment capacity of a gasifier and heat loss from it. Macromolecular feedstock such as coal and wood and some products such as char and tar are mixtures of various chemical species. In the new stoichiometric approach, a general notation of pyrolysis of macromolecules was used as follows.

\[
\text{CH}_{mO_n} \rightarrow \gamma \text{H}_2 + \delta \text{CO} + \epsilon \text{CO}_2 + \zeta \text{H}_2\text{O} + \eta \text{CH}_4 + \kappa \text{CH}_2\text{O}_3 + \phi \text{CH}_p\text{O}_q \quad (1)
\]

In Equation (1), macromolecules were expressed by “mean compositional formula” with one carbon atom, for example CH\(_{2}\text{O}_3\) as feed, CH\(_{2}\text{O}_3\) as char and CH\(_{2}\text{O}_3\) as tar. The mathematical derivation gives theoretical yields of H\(_2\) and CO and cold gas efficiency in terms of stoichiometric relationship.

In this report, the new stoichiometric approach was applied to wood pyrolysis to estimate heat of pyrolysis. Namely, wood pyrolysis was expressed as an overall pyrolysis formula using mean compositional formula, and heat of pyrolysis was obtained based on the results of gram-scale pyrolysis by Satonaka \(^9\). Heat of pyrolysis was calculated by using the detailed data of the composition and heating values of a feed and products, combining the new stoichiometric approach rather than the apparent data by TG-DSC including both heat of pyrolysis and heat of volatilization.

For the improvement of heat management of a power generation system, heat balance around a pyrolysis furnace was demonstrated in model calculations including heating values, sensible heats of the products, and heat loss from a furnace.

### 2. Methods of stoichiometric theory and heat balance calculation

#### 2.1 Experiments in a literature

In 1963, Prof. Satonaka reported the detailed experimental data of wood pyrolysis for charcoal production by using Mizunara oak (Quercus crispula) \(^9\). He took wood chip samples from the similar position (60 to 200 cm height from the groud) of Mizunara oak. The samples were cut in the size of \(1 \times 1 \times 7\) cm, in the direction of the right angle to a growth ring, tangential to a growth line, and in the vertical direction of a tree, respectively. The number of growth ring of each sample was ranging from 4 to 11. After drying of samples for two nights at 378 K, wood pyrolysis was conducted by increasing heating temperature at every 100 K during 15 min and keeping the temperature for 15 min. Elemental composition and calorific value were analyzed by using the resulting charcoal and the other products except tar.

#### 2.2 Notations of stoichiometric theory

In stoichiometric approach, unit compositional formula such as CH\(_{2}\text{O}_3\), CH\(_{2}\text{O}_3\) and CH\(_{2}\text{O}_3\) are used to express chemical formula of macromolecules. Similar to empirical formula in ultimate analysis, \(m, j \) and \(p\) are the ratios of the number of hydrogen atom to one carbon atom based on the elemental composition of the macromolecules. Similarly, \(n, k \) and \(q\) are determined as the ratios of oxygen atom to one carbon atom. In case the other component is examined, nitrogen or the other atoms or ash can be added to the unit compositional formula. For example, the mean compositional formula of a dry wood sample in Satonaka’s report can be determined as follows. The composition data is C: 48.86, H: 5.96, O: 44.85, Ash 0.33. Element ratios of C, H and O in weight can be converted into atom number ratios by dividing the weight percent by each atomic weight to give C: 4.068, H: 5.96, O: 2.803. Then dividing number ratio of C, H and O by 4.068 yields \(\text{CH}_{1.46}\text{O}_{0.69}\). It gives formula weight of 24.51 g/mol.

During wood pyrolysis, charcoal, tar, water and various gaseous products are produced. Fixing carbon atom of feed as one mol, wood pyrolysis can be depicted as Equation (1). Mean compositional formulas and reaction formula of pyrolysis can be expressed by determining elemental compositions and amounts of feed and products. Depending on the purpose of stoichiometric analysis, liquid and solid products can be expressed in the overall notation as mentioned in Equation (1) if their elemental composition and total heating values are available.

#### 2.3 Heat balance calculation around a pyrolysis furnace

Schematic flow of a power generation system by wood pyrolysis is shown in Fig. 1. Wood chips are supplied to a pyrolysis furnace, and undergo pyrolysis at a certain temperature, \(T\). The products are discharged from the furnace, and the temperature of each product is regarded as the same to the pyrolysis temperature. The whole portion of charcoal is stored in a receiver tank at the exit of the furnace. Gaseous products with vapor of H\(_2\)O and tar are cooled in a condenser or a scrubber to separate the liquid products. The resulting dry gas is used as a fuel for a power generator.

The core plant of the power generation system is a pyrolysis furnace, which should be examined in view
of chemical and thermal points of view for the higher performance in energy balance. Fig. 2 shows heat balance around a pyrolysis furnace. Heat input includes higher heating value (HHV) and sensible heat of dry feed. In model calculation, the feed is supplied at the standard temperature with the sensible heat of zero, not described in the figure.

Heat output includes HHVs, sensible heats of gaseous and liquid products and charcoal, latent heats of products, and heat loss of a furnace. The HHVs are the values under the standard ambient temperature and pressure (SATP). The temperature of each product that is discharged from the furnace is considered as the same to pyrolysis temperature. The total sensible heat $H_S$ of gaseous products is given by

$$H_S = \sum n_i \cdot C_{pm,i} \cdot (T_P - T_0)$$

where $n_i$, $C_{pm,i}$, $T_P$, and $T_0$ are molar amount of the product $i$, average heat capacity at constant pressure, temperature of the product $i$, and the standard ambient temperature (298 K), respectively.

Heat loss is the heat from the surface of a pyrolysis furnace to its surroundings by natural convection and radiation. The furnace has a certain treatment capacity. The total heat loss in joule per hour is divided by treatment capacity of molar feeding rate in mole per hour to give the heat loss per molar amount of feed in joule per mole of feed.

Heat of pyrolysis was obtained by the difference between HHV of feed (HHF) and the total HHV of products (HHP) at SATP. The heat of pyrolysis is consumed as sensible heats and latent heats of products and heat loss of a furnace. When heat of pyrolysis $(H_{HF} - H_{HP})$ is larger than the heat consumption $(H_{SP} + H_{LP} + H_L)$, pyrolysis can be autothermal one during operation. When the heat of pyrolysis is less than the heat consumption, an external heat to a furnace is required to maintain the pyrolysis temperature for compensating the sensible and latent heats of products and the heat loss of the furnace. Even if pyrolysis would be exothermic in a certain case, additional heat is required as an external heating to a furnace from outside. The external heat $H_E$ in joule per mole of feed was obtained by

$$H_E = H_{HF} + H_S - (H_{HP} + H_{SP} + H_{LP} + H_L)$$

where $H_{HF}$, $H_S$, $H_{HP}$, $H_{SP}$, $H_{LP}$, and $H_L$ are HHV of a feed, sensible heat of a feed, total HHVs of products, total sensible heats of the products, total latent heats of liquid products and heat loss of a pyrolysis furnace, respectively.

The external heat is supplied from a burner, and the amount of heat corresponds to the difference: (heat of fuel for a burner of the furnace) – (heat of flue gas carried away from the furnace).

3. Results and discussion

3.1 Material balance in pyrolysis of Mizunara oak

In this paper, stoichiometry and properties of feed and products in pyrolysis were referred from the comprehensive report by Satonaka. Mean compositional
formulas, formula weights of feed and charcoal, and molar yields of charcoal were obtained as in Table 1. As pyrolysis temperature increases, the mean compositional formula changed with pyrolysis temperature. The ratios of hydrogen and oxygen of charcoal in ultimate analysis decrease, and the calorific value of charcoal decreases with increasing pyrolysis temperature.

Table 2 summarizes the product distribution of charcoal and gaseous products in pyrolysis by Satonaka. In his report, hydrocarbons other than methane were expressed as CnHm. In this paper, CnHm was considered as ethylene in calculation. The report also lacks the elemental composition of liquid products.

As in Table 2, atom balances of C, H and O were calculated to obtain C, H and O in the liquid product that consists of tar and water. Using the product data of pyrolysis at 773 K in Table 3, the atom balance calculation is explained as follows. Pyrolysis of one mole of dry wood gives 0.491 mole of charcoal (CH_{0.431}O_{0.143}). The total amount of carbon atoms in CO, CH, C_{2}H_{4}, CO_{2} was 0.123 mol. The amount of carbon atom of the liquid products was 0.386 mol (= 1 – 0.491 – 0.123). The liquid products consist of tar and water. Tar in this paper is defined as the organic components of liquid products of both hydrophilic and hydrophobic organic compounds. The mean compositional formula of tar (CH_{0.801}O_{0.375}) was calculated from the data obtained in wood gasification by Yasuda et al. 10). The estimated HHV of tar was 21.68 kJ/g. Applying the formula weight of tar (18.82 g/mol) to the tar gave 408.0 kJ/mol (= 21.68 × 18.82).

Using this mean formula and 0.386 mol of carbon atom balance in the liquid product at 773K, the amounts of hydrogen and oxygen atoms of tar were determined as 0.309 (= 0.386 × 0.801) and 0.145 (= 0.386 × 0.375) mol/mol-feed, respectively. The amounts of hydrogen and oxygen atoms of water were determined as 0.908 (= 1.217 - 0.309).

### Table 1 Determination of unit compositional formula of wood and charcoal

| Pyrolysis temperature K | Ultimate analysis, % | Mean compositional formula | Mass yield of char wt% | Formula weight g/mol | Molar yield of char mol/mol-feed | HHV† kJ/mol |
|-------------------------|----------------------|----------------------------|------------------------|----------------------|----------------------------------|--------------|
| 378*                    | 48.86, 5.96, 44.85, 0.33 | CH_{1.46}O_{0.689}         | –                      | 24.51                | –                               | –            |
| 773                     | 80.66, 2.92, 15.34, 10.8 | CH_{1.46}O_{0.689}         | 29.5                   | 14.72                | 0.496*                           | –            |
| 873                     | 89.12, 2.54, 7.18, 11.6 | CH_{1.46}O_{0.689}         | 23.7                   | 13.31                | 0.816†                           | –            |
| 973                     | 92.06, 1.70, 4.99, 1.25 | CH_{1.46}O_{0.689}         | 25.8                   | 12.87                | 0.491                            | –            |
| 1073                    | 93.51, 1.19, 4.04, 1.26 | CH_{1.46}O_{0.689}         | 25.6                   | 12.70                | 0.495                            | –            |
| 1173                    | 94.39, 0.90, 3.05, 1.66 | CH_{1.46}O_{0.689}         | 25.1                   | 12.50                | 0.492                            | –            |
| 1273                    | 94.77, 0.58, 3.07, 1.58 | CH_{1.46}O_{0.689}         | 25.1                   | 12.46                | 0.493                            | –            |
| 1373                    | 96.18, 0.53, 1.87, 1.42 | CH_{1.46}O_{0.689}         | 24.7                   | 12.30                | 0.492                            | –            |

* Drying temperature of the original wood.
**Obtained by (24.51 g/mol×0.295 g/g-feed)/14.72 g/mol.
† Heat generation was expressed as a negative value.

### Table 2 Reaction formula of pyrolysis of Mizunara oak obtained by stoichiometric calculation

| Pyrolysis temperature K | Reaction formula for wood pyrolysis | Mass yields of the products per 100 g of feed, g (Total yield of the products, % in parentheses) |
|-------------------------|--------------------------------------|-----------------------------------------------------------------------------------------------|
| 773                     | CH_{1.46}O_{0.689} \rightarrow 0.490\text{CH}_{1.46}\text{O}_{0.689} + 0.002\text{H}_{2} + 0.046\text{CO} + 0.006\text{CH}_{4} + 0.006\text{C}_{2}\text{H}_{4} + 0.202\text{H}_{2}\text{O} + 0.386\text{CH}_{1.46}\text{O}_{0.689} | 29.5, 0.9, 5.3, 0.4, 0.1, 12.4, 21.3, 29.6 (98.6) |
| 873                     | CH_{1.46}O_{0.689} \rightarrow 0.500\text{CH}_{1.46}\text{O}_{0.689} + 0.007\text{H}_{2} + 0.055\text{CO} + 0.011\text{CH}_{4} + 0.002\text{C}_{2}\text{H}_{4} + 0.074\text{CO}_{2} + 0.326\text{H}_{2}\text{O} + 0.346\text{CH}_{1.46}\text{O}_{0.689} | 27.7, 0.1, 6.3, 0.7, 0.2, 13.3, 24.0, 26.8 (98.8) |
| 973                     | CH_{1.46}O_{0.689} \rightarrow 0.490\text{CH}_{1.46}\text{O}_{0.689} + 0.023\text{H}_{2} + 0.056\text{CO} + 0.019\text{CH}_{4} + 0.002\text{C}_{2}\text{H}_{4} + 0.075\text{CO}_{2} + 0.329\text{H}_{2}\text{O} + 0.345\text{CH}_{1.46}\text{O}_{0.689} | 25.8, 0.2, 6.4, 0.7, 0.2, 13.5, 24.2, 27.5 (98.8) |
| 1073                    | CH_{1.46}O_{0.689} \rightarrow 0.490\text{CH}_{1.46}\text{O}_{0.689} + 0.035\text{H}_{2} + 0.059\text{CO} + 0.025\text{CH}_{4} + 0.002\text{C}_{2}\text{H}_{4} + 0.076\text{CO}_{2} + 0.335\text{H}_{2}\text{O} + 0.341\text{CH}_{1.46}\text{O}_{0.689} | 25.6, 0.3, 6.7, 1.2, 0.2, 13.6, 24.6, 26.6 (99.0) |
| 1173                    | CH_{1.46}O_{0.689} \rightarrow 0.490\text{CH}_{1.46}\text{O}_{0.689} + 0.046\text{H}_{2} + 0.060\text{CO} + 0.027\text{CH}_{4} + 0.002\text{C}_{2}\text{H}_{4} + 0.076\text{CO}_{2} + 0.337\text{H}_{2}\text{O} + 0.341\text{CH}_{1.46}\text{O}_{0.689} | 25.0, 0.4, 6.9, 1.8, 0.2, 13.6, 24.8, 26.2 (99.0) |
| 1273                    | CH_{1.46}O_{0.689} \rightarrow 0.490\text{CH}_{1.46}\text{O}_{0.689} + 0.056\text{H}_{2} + 0.062\text{CO} + 0.028\text{CH}_{4} + 0.002\text{C}_{2}\text{H}_{4} + 0.076\text{CO}_{2} + 0.337\text{H}_{2}\text{O} + 0.337\text{CH}_{1.46}\text{O}_{0.689} | 25.1, 0.5, 7.1, 1.8, 0.2, 13.6, 24.8, 25.9 (99.0) |
| 1373                    | CH_{1.46}O_{0.689} \rightarrow 0.490\text{CH}_{1.46}\text{O}_{0.689} + 0.064\text{H}_{2} + 0.064\text{CO} + 0.029\text{CH}_{4} + 0.002\text{C}_{2}\text{H}_{4} + 0.076\text{CO}_{2} + 0.340\text{H}_{2}\text{O} + 0.335\text{CH}_{1.46}\text{O}_{0.689} | 24.7, 0.5, 7.3, 1.9, 0.2, 13.6, 25.0, 25.7 (99.0) |
and 0.290 (= 0.435 – 0.145) mol/mol-feed, respectively. From the atom ratio of water, the amounts of atoms are 0.904 mol of hydrogen and 0.452 of oxygen atoms on hydrogen basis, or 0.580 mol of hydrogen and 0.290 mol of oxygen atoms on oxygen basis. In this paper, oxygen basis was taken as the more accurate data as molar amount of water because of the smaller error in material balance. Then the amount of water was determined as 0.290 mol/mol-feed. These calculation results were summarized into the reaction formula of pyrolysis at 773 K as follows.

\[
\text{CH}_{1.46} \text{O}_{0.689} \rightarrow 0.491 \text{CH}_{0.431} \text{O}_{0.143} + 0.002 \text{H}_2 + 0.046 \text{CO} + 0.006 \text{CH}_4 + 0.001 \text{C}_2\text{H}_4 + 0.069 \text{CO}_2 + 0.307 \text{H}_2\text{O} + 0.386 \text{CH}_{1.08} \text{O}_{0.353} \tag{5}
\]

The similar stoichiometric calculations of pyrolysis data at 873 – 1373 K were performed, and the reaction formulas of pyrolysis with mass balance at each temperature were summarized in Table 3. Although the composition of tar varies with pyrolysis temperature\(^{11}\), the unit compositional formula of tar in this paper was approximated by the one averaged formula \(\text{CH}_{0.801} \text{O}_{0.375}\), which might be revised as temperature-dependent composition in further studies in order to reduce an error in heat balance estimation.

### 3.2 Heat of pyrolysis and heat consumption due to vaporization of pyrolysis products

The standard heats of pyrolysis were obtained by the difference between HHV of dry wood and the total HHVs of all products. For example, the heat of pyrolysis at 973 K was –78.9 kJ/mol-feed as shown in Table 4. Heat generation is expressed as a negative value.

As shown in Table 5, the heats of pyrolysis were obtained by using HHVs at SATP. Pyrolysis at 773 – 1373 K was exothermic reaction with the heats of pyrolysis at –70.4 to –82.8 kJ/mol-feed. Exothermic heats of pyrolysis and HHVs were expressed as negative values because of heat generation. The calculated values in the other categories were also expressed as negative values for keeping consistency with those heat-generation terms. The calculated value from the experiment by Yasuda et al.\(^{10}\) was used as the HHV of tar at all pyrolysis temperatures. When the HHV of tar at each temperature is available, the more accurate value of the heat of pyrolysis can be obtained.

During pyrolysis, products are discharged from a reactor in a pyrolysis furnace. Sensible heats of those products are brought out from the reactor. Additionally, heat balance calculation should include the latent heats of \(\text{H}_2\text{O}\) and tar, which are liquid at SATP. The total sensible heat of products is the sum of the sensible heats of gaseous and liquid products, calculated in the temperature ranges as follows:

\[
\text{C}_{\text{pet}} \text{ J/mol-K} \times \eta \text{ mol} \times (T_r – 298) \text{ K}
\]
\[
\begin{align*}
\text{H}_2\text{O} \text{ (gas): } & \ C_{\text{pm}1} \text{ J/mol} \cdot \text{K} \times n_1 \text{ mol} 	imes (T_p - 373) \text{ K} \\
\text{H}_2\text{O} \text{ (liquid): } & \ C'_{\text{pm}1} \text{ J/mol} \cdot \text{K} \times n_1 \text{ mol} 	imes (373 - 298) \text{ K} \\
\text{Tar} \text{ (gas): } & \ C_{\text{pm}2} \text{ J/mol} \cdot \text{K} \times n_2 \text{ mol} 	imes (T_p - 455) \text{ K} \\
\text{Tar} \text{ (liquid): } & \ C'_{\text{pm}2} \text{ J/mol} \cdot \text{K} \times n_2 \text{ mol} 	imes (455 - 298) \text{ K} \\
\end{align*}
\]

where \( C_{\text{pm}1}, C'_{\text{pm}1}, C_{\text{pm}2}, C'_{\text{pm}2} \) and \( n_1, n_2 \) are mean specific heat capacity of steam, mean specific heat capacity of water, molar amount of \( \text{H}_2\text{O} \), mean specific heat capacity of gaseous tar, mean specific heat capacity of liquid tar and molar amount of tar.

The specific heat capacity of tar was assumed as the same to that of phenol in each phase of liquid and gas. The calculated values of sensible heat and latent heat were shown in Table 5. Heat loss of a pyrolysis furnace was explained in Section 3.3, and Section 3.4 showed an example of the external heat required for pyrolysis at 1073 K.

### 3.3 Heat loss from a pyrolysis furnace

Heat loss will change depending on a furnace structure and operation temperature. A pyrolysis furnace with a screw conveyer was designed in the specifications of the furnace were designed as follows: treatment capacity, 50 kg/h dry wood; size of the furnace, 3100 mm length \( \times \) 1810 mm height \( \times \) 700 mm width; expected temperature of the outer surface of a casing 333 K at the environmental temperature at 298 K.

Heat loss, \( H_L \), is the sum of heat transfer by natural convection, \( h_c \), and radiation, \( h_r \), in Equation (6).

\[
H_L = h_c + h_r \quad (6)
\]

where \( h_c = (5.60 \times A_U + 4.33 \times A_V + 2.27 \times A_L) \times (333 - 298) \) K/W = 2682 W

\[
(8)
\]

Heat of radiation from a pyrolysis furnace can be estimated by Equation (8).

\[
where A_U, A_V and A_L are the area of upper surface (21.7 m²), vertical (13.8 m²) and lower surface (21.7 m²), respectively. And 5.60, 4.33 and 2.27 W/m²·K are the heat transfer coefficients that were calculated considering natural convection on each surface of the pyrolysis furnace.

The total surface area of the furnace is 18.1 m².

The total heat loss, \( H_L \), was 6755 W (= 24318 kJ/h). The feeding rate of the pyrolysis furnace was designed as 50 kg/h of dry wood, which corresponds to 204 kmol/h when the formula weight of wood (CH1.46O0.689) is 24.51 g/mol. When 1 mol of dry wood is processed in the furnace, the amount of heat required was 11.9 kJ/mol-feed (= 24318 kJ/h divided by 2040 mol/h) for compensating the heat loss due to natural convection and radiation.

The different heating temperature would give the different surface temperature if the insulation thickness of a furnace were fixed. In this paper, the constant surface temperature was assumed for convenience in calculation. Usually, the operation temperature is fixed and the surface temperature is assumed to be 333 K in each phase of liquid and gas.
temperature is designed considering operation safety.

3.4 Heat balance around a pyrolysis furnace

Heat balance around a pyrolysis furnace was calculated to estimate external heat, which is the required heat amount for heating a pyrolysis furnace. Despite the exothermic character of pyrolysis, autothermal pyrolysis is not known in wood pyrolysis without air supply. Heat balance around a pyrolysis furnace was examined to improve heat management and its performance.

As an example, Table 6 summarizes heat balance of a pyrolysis furnace operated at 1073 K. Following the ordinary description manner of a heat balance sheet, all values were expressed as positive values. The heat of pyrolysis was 79.8 kJ/mol-feed based on the difference between HHV of wood 474.8 and the total HHV of the products 395.0 kJ/mol-feed, indicating exothermic reaction. The total heat consumption was 119.9 kJ/mol-feed, which was the sum of sensible heats of products (78.8), latent heats of H₂O and tar (29.2) and heat loss of a furnace (11.9 kJ/mol-feed). Thus, despite 79.8 kJ/mol-feed of heat generation by exothermic pyrolysis, another 40.1 kJ/mol-feed of heat (= 1199 – 798) is required to supply to the pyrolysis furnace to compensate the heat consumption in order to maintain the reaction mixture at 1073 K during pyrolysis.

It should be noted that secondary reactions of the products such as water-gas shift reaction were ignored in heat balance calculation. If it is detected in experiments, heat of reaction and sensible heats of products should be corrected.

There are several papers on the heat of wood pyrolysis, which were typically measured by TG-DSC. It gives overall heats of reaction and phase transition including heat of fusion and volatilization of liquid products under isothermal or temperature-ramping conditions. The literatures reported the endothermic values 207 to 400 J/g or the varied data from exothermic to endothermic values, –221.8 to 363.5 J/g, depending on the type of plant and char yield.

Rath et al. mentioned an exothermic char formation process was competing with an endothermic volatile formation process. The total heat balance were

| Table 6 Heat balance around a pyrolysis furnace of at 1073 K |
|-------------------------------------------------------------|
| **Heat input per 1 mol of dry wood pyrolysis**              |
| **Category**   | **Amount, mol** | **Heat amount, kJ** |
| HHV            | Wood            | 1                   | 474.8                         |
| **Heat output per 1 mol of wood pyrolysis at 1073 K**      |
| **Category**   | **HHV, kJ/mol** | **Amount, mol**     | **Heat amount, kJ**            |
| HHV            | Charcoal        | 412.3               | 0.495                         | 2041 |
|                | H₂              | 286.0               | 0.035                         | 100 |
|                | CO              | 283.1               | 0.059                         | 16.7 |
|                | CH₄             | 890.8               | 0.025                         | 22.3 |
|                | C₅H₆            | 14117               | 0.002                         | 2.8 |
|                | Tar             | 408.0               | 0.341                         | 139.1 |
|                | **Subtotal**    |                     | 395.0                         |
| **Sensible heat** | **Amount, mol** | **Heat amount, kJ** |
| Wood           | 1               | 0                   |
| **Latent heat** | **Amount, mol** | **Heat amount, kJ** |
| H₂O (gas)      | 37.91           | 0.335               | 8.89                          |
| H₂O (liquid)   | 75.40           | 0.335               | 24.9                          |
| Tar (gas)      | 203.3           | 0.342               | 42.8                          |
| Tar (liquid)   | 199.8           | 0.342               | 10.7                          |
| **Subtotal**   |                 |                     | 78.8                          |

**External heat required 40.1**

Total 514.9

Heat loss 11.9

Total 514.9
endothermic values in most cases. Our model calculation of the heat balance around a furnace showed exothermic overall reactions and heat consumption consisting of sensible and latent heats of products with heat loss of a furnace. The calculation results showed the similarity to their paper in the point of heat generation in the reactions and heat consumption in volatilization of the products.

3.5 Effects of moisture in a feed

Dry feed was assumed in the heat balance calculations that were already examined. In reality, some amounts of moisture are accompanied with a feed. Considering 20 wt% of moisture in wet basis, the additional heats required for pyrolysis were calculated. One mole of the unit compositional formula of dry wood is 24.51 g. Moisture at 20 wt% on wet basis is 6.13 g (0.340 mol) of water per 1 mole of a wet sample (30.64 g).

Table 7 shows the calculated values to obtain the total external heat required for pyrolyzing wet wood with 20 wt% moisture. Because the HHVs of charcoal are heat generation terms expressed as negative values, all the other values were expressed as negative values to keep consistency with them. Moisture contamination in a feed increases the heat required for pyrolysis as a fuel amount supplied to a pyrolysis furnace. Heating the moisture to pyrolysis temperature requires the additional heat to the external heat in the case of dry wood. The additional heat corresponds to sensible and latent heat of H\textsubscript{2}O (liquid) and sensible heat of H\textsubscript{2}O (gas). The total external heat is the sum of the heat amount of external heating for dry wood pyrolysis and that of the additional heat for moisture. The total external heats required for pyrolysis were -39.3 to -160 kJ/mol-feed in the range of 773 – 1373 K.

Different from wood gasification using gasifying agents, pyrolysis of wood gives charcoal as a by-product, which has limited uses. Considering wood pyrolysis as a system for power generation using flammable gas products, charcoal combustion could be an economical solution for use as fuel to supply the required external heat. Table 7 shows the ratios of charcoal consumption as the fuel to charcoal yield in heating values. For example, at 973 K, charcoal yield was 0.491 mol/mol-feed, which gives –209 kJ/mol-feed (= 0.491 mol/mol-feed × –425.4 kJ/mol, in Table 1) as combustion heat. The total external heat was –54.4 kJ/mol-feed. Thus, the ratio was 0.26, which means that 26 wt% of charcoal will satisfy the required external heat to a furnace for pyrolyzing wood with 20 wt% moisture (wet basis), ignoring heat loss of a char combustion burner.

4. Conclusion

Heat balance is a critical issue to develop an energy recovery system from biomass. Wood pyrolysis generating flammable gas is considered as one of the effective systems for small-scale power generation. This report examined the heat balance around a pyrolysis furnace, considering heat of pyrolysis, sensible heat of products and heat loss of the

| Pyrolysis temperature, K | 773 | 873 | 973 | 1073 | 1173 | 1273 | 1373 |
|--------------------------|-----|-----|-----|------|------|------|------|
| Sensible heat of H\textsubscript{2}O (liquid)*2, kJ | -1.92 | -1.92 | -1.92 | -1.92 | -1.92 | -1.92 | -1.92 |
| Latent heat of H\textsubscript{2}O*3, kJ | -13.8 | -13.8 | -13.8 | -13.8 | -13.8 | -13.8 | -13.8 |
| C\textsubscript{pcm1}, J/mol\cdot K | -36.2 | -36.8 | -37.3 | -37.9 | -38.5 | -39.1 | -39.7 |
| Sensible heat of H\textsubscript{2}O (gas)*4, kJ | -4.92 | -6.26 | -7.61 | -9.02 | -10.5 | -12.0 | -13.5 |
| Additional heat for heating the moisture*5, kJ/mol-feed | -206 | -22.0 | -23.3 | -24.7 | -26.2 | -27.7 | -29.2 |
| External heat required for dry wood pyrolysis*6, kJ/mol-feed | -18.7 | -206 | -31.1 | -40.1 | -49.4 | -64.5 | -76.7 |
| Total external heat required for wet wood pyrolysis*7, kJ/mol-feed | -39.3 | -42.6 | -54.4 | -64.8 | -75.6 | -92.2 | -106 |
| HHV of charcoal produced*8, kJ/mol-feed | -227 | -228 | -209 | -204 | -196 | -197 | -193 |
| Ratio of the external heat required to HHV of charcoal produced, kJ/kJ | 0.17 | 0.19 | 0.26 | 0.32 | 0.39 | 0.47 | 0.55 |

*1 HHV of charcoal were expressed as negative values. To keep consistency among the calculated values, all the other values were also expressed as negative values. Additional amount of water as 20 wt%-moisture is 0.340 mol/mol-feed on wet basis.

*2 $75.4 \text{ J/mol\cdot K} \times 0.340 \text{ mol} \times (373 – 298) \text{ K}$.

*3 $40.67 \text{ J/mol\cdot K} \times 0.340 \text{ mol}$.

*4 $C_{pcm1} \times \text{ J/mol\cdot K} \times 0.340 \text{ mol} \times (T_p – 373) \text{ K}$.

*5 Sum of sensible heats of H\textsubscript{2}O (liquid and gas) and latent heat.

*6 Obtained in Table 5.

*7 Sum of the additional heat for heating the moisture and the external heat required for dry wood pyrolysis.

*8 Molar yield of char [mol/mol-feed] multiplied by HHV of char [kJ/mol] in Table 1.
furnace. Heat of wood pyrolysis was obtained by the new stoichiometric approach, in which macromolecules of feed, tar and charcoal were expressed as mean compositional formula. Based on the data by Satonaka, reaction formula of pyrolysis was described at the pyrolysis temperature 773 to 1373 K. The heats of pyrolysis of Mizunara oak were in the range of –70.4 to –82.8 kJ/mol-feed, which means that pyrolysis is exothermic reaction. The heat loss including that of natural convection and radiation was also estimated based on the specification of a pyrolysis furnace designed for a feeding rate at 50 kg/h.

Despite the exothermic nature of pyrolysis at SATP, the external heating to the furnace was required to compensate sensible heats of products (–47.8 to –115.4 kJ/mol-feed at 773 to 1373 K), latent heat of liquid products (–29.2 to –29.6 kJ/mol-feed at 773 to 1373 K) and heat loss from the surface of the furnace (–11.9 kJ/mol-feed). The external heat required for pyrolysis was –18.7 to –76.7 kJ/mol-feed. When a feed contains 20 wt%-moisture in wet basis, the total required heat was –39.3 to –106 kJ/mol-feed. The required heat amounts correspond to the combustion heat of 17 to 55 wt% of charcoal that produced in the pyrolysis temperature range of 773 to 1373 K.

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