Detailed gasification process of woody biomass-derived char with H\textsubscript{2}O and CO\textsubscript{2} gasifying agents

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Abstract
To effectively utilize renewable biomass resources, gasification technology is being actively developed. Many studies have been performed regarding the gasification of biomass-derived char (i.e., biochar), where the gasification rate varies greatly with experimental device and biomass type, even when the same gasification temperature is used. In addition, the pore development mechanism during gasification i.e., the relation between the gasification reaction rate and interface area, has been rarely studied. Herein, the gasification rate of wooden biochar with H\textsubscript{2}O and CO\textsubscript{2} gasifying agents using same experimental apparatus and char samples were investigated. The development of micro- and mesopores in the biochar during gasification with H\textsubscript{2}O and CO\textsubscript{2} agents was examined in detail. The results showed that (1) gasification rate constant of biochar was approximately 3–10 times higher under H\textsubscript{2}O gasifying agent than under CO\textsubscript{2} agent at 1073–1273 K; (2) this study reported the most typical values of frequency factor $A$ and activation energy $E$ on Arrhenius plot at high temperature region; and (3) the specific surface area of the micro and mesopores increased with proceeding H\textsubscript{2}O and CO\textsubscript{2} gasification, and the reaction rate is proportional to the interface area during the gasification process.

Keywords: Biomass, Gasification rate, BET specific surface area, Pore structure, Adsorption, Surface reaction, Char, Pyrolysis

1. Introduction
Most gasification processes including updraft/downdraft gasifiers and entrained flow gasifiers involve partial combustion, wherein the combustion heat (approximately 800–1100 °C) is used. In the reduction zone of gasifiers, biomass pyrolysis and biochar gasification proceed in the presence of the H\textsubscript{2}O vapor and heat, and CO\textsubscript{2} in the combustion area. (Thurner et al., 1981; Di-Blasi et al., 2001; Matsumoto et al., 2009; Guo et al., 2014; Ram et al., 2019.) Because the pyrolysis rate is much higher than the gasification rate of biochar, the overall conversion rate is controlled by the gasification rate of char. That is, the overall gasification rate is limited by the slow gasification rate of char. (Zhang et al., 2008; Okumura et al., 2009; Seo et al., 2010.) Many studies have been performed on the gasification of biochar. The gasification rate of biochar varies greatly with the experimental device and the type of biomass, even when the same gasification temperature is used. In addition, pore development in the biochar during gasification with H\textsubscript{2}O and CO\textsubscript{2} agents, especially the relation between gasification reaction rate and interface area, has been rarely studied.

The present study compared in detail the gasification rate of biochar in H\textsubscript{2}O gasifying agent with that in CO\textsubscript{2} gasifying agent at 1073–1273 K using the same experimental apparatus and the same char samples, under the same pyrolysis conditions. The results showed that the gasification rate constant of the biochar was approximately 3–10 times higher under H\textsubscript{2}O compared to the CO\textsubscript{2} gasifying agent. The specific surface area of woody biochar during H\textsubscript{2}O gasification was compared with that observed during CO\textsubscript{2} gasification. When the overall gasification rates were almost same, the increase in the specific surface area of the pores under the H\textsubscript{2}O atmosphere was similar to that processed under the CO\textsubscript{2} atmosphere i.e., no significant differences in pore development or physical shape were observed between the CO\textsubscript{2} and H\textsubscript{2}O gasifying agents.
2. Experimental Apparatus and Method

2.1 Preparation of the char sample (pyrolysis)

The chars were prepared using the middle heating rate (10 K/s) in an argon environment. After closing the outlet valve ⑤, a vacuum pump (rotary pump) was used to suck the air in the test section. (valve: ①－③ open) By opening valve ④, the gas in the experimental apparatus was completely replaced with Ar gas (99.9%). A raw biomass sample (Douglas fir: Pseudotsuga menziesii; 4.7～8.6 mesh; Table 1) was placed in a platinum cell (10 mm height, outer diameter 8 mm) and the biomass was heated using an infrared gold image furnace. The detailed pyrolysis conditions are listed in Table 2 (left side). When the maximum temperature of 1073 K was reached, the applied voltage was interrupted, stopping the heating, and the sample was then abruptly cooled. The pyrolysis duration was approximately 77 s. { (1073 [K] – 300 [K]) /10 [K/s] ≒ 77 [s] }

Table 1  Biomass properties.

|          | Douglas fir |
|----------|-------------|
| HV(d.b.) | 19600       |
| H/C      | 1.31        |
| Ultimate analysis (d.a.f.) |                     |
| C        | 52.10       |
| H        | 5.70        |
| O        | 42.1        |
| N        | 0.10        |
| S        | 0.006       |
| Proximate analysis (wt%) |                |
| VM       | 82.6        |
| FC       | 12.1        |
| ASH      | 0.3         |
| MOIST.   | 5.0         |

Table 2  Pyrolysis and gasification conditions.

|                  | Pyrolysis | CO₂ gasification | H₂O gasification |
|------------------|-----------|------------------|-------------------|
| Temperature (K)  | 1073      | 1073 - 1273      |                    |
| Atmospheric gas  | Ar (99.9%)| Ar → CO₂ (99.9%) | Ar → H₂O (water vapor 100%) |
| Sample weight (mg) | 50       | 10               |                    |
| Pressure (MPa)   | 0.1       | 0.1              |                    |

2.2 Gasification method and conditions

The chars produced by the pyrolysis described in Section 2.1 were gasified using the thermobalance, as shown in Fig. 1 (ALVAC 9600). The gasification rate was determined from the weight-loss curve of the biochar samples. The chars were sifted to obtain samples with nearly the same diameters (1.0～1.5 mm) and lengths (4.0 mm). In addition, all pyrolysis processes were set to 10 K/s and 1073K (Table 2), and the effect of pyrolysis conditions on gasification reactivity was eliminated. (Okumura et al., 2009.) Approximately 10 mg of the biochar samples were used for the gasification experiments. To obtain accurate gasification rates, the biochar particles were distributed independently. (hereinafter referred to as “single char particle distribution”: Kibria et al., 2019.)

After the biochar was heated and the atmospheric gas reached an isothermal temperature (Table 2), the atmospheric gas was changed from argon to the gasifying agent (CO₂ or H₂O), and the Douglas fir char was gasified. Any other carrier gas was not used, except the gasifying agents. The flow rate of the gasifying agent (mole fraction: 100%) was set at 400 mL/min using a flow meter/micro-feeder. A H₂O micro-feeder was used to supply a constant quantity of pure water vapor (H₂O), and vapor was generated using a heater to a predetermined temperature in a furnace. Subsequently, gasification experiments were performed in at least triplicate independently and under isothermal conditions at 800, 900, and 1000 °C.
(When H₂O is used, the steam is absorbed by the dry filter at the outlet of apparatus.) The temperature dependence of the gasification rate was determined using Arrhenius plots. In detail, the gasification rate was determined using Eq. (1), which is based on the random pore model. (Bhatia and Vartak, 1996.)

\[
\frac{dX}{dt} = K_p(1-X)\sqrt{1-\Psi \ln(1-X)}
\]  

Here, X represents the carbon conversion [-]. Solving Eq. (1) analytically, the following is obtained:

\[
X = 1 - \exp\left[-K_p t \left(1 + \frac{\Psi K_p t}{4}\right)\right]
\]  

Transforming Eq. (2) and taking logarithms on both sides of the transformed equation, Eq. (3) can be rewritten as:

\[
-\ln(1-X) = K_p + \frac{\Psi K_p}{4} t
\]  

The gasification rate constant \(K_p\) and pore structure parameter \(\Psi\) were derived by determining the intercept and gradient of the straight line of \(-\ln(1-X)/t\) versus t in Eq. (3).

2.3 Measurement of specific surface area

To measure the pore volumes, gaseous molecules were adsorbed on the solid particle surfaces and the specific surface area was obtained from the amount of gas adsorbed. For the surface area analysis, ASAP2020 (Shimadzu Co., Ltd.) was used. In the Brunauer-Emmet-Teller (BET) method, nitrogen was used as the adsorption gas and liquid nitrogen was used as the cooling medium. (Cross section of a N₂ molecule: 0.162 nm²) Using the BET equation (Eq. (4)) and the relationship between pressure (P) and adsorption amount (V), the monomolecular adsorption (\(V_m\)) was obtained. (\(P\) and \(P_0\) are the equilibrium and saturation pressures of adsorbates at the adsorption temperature, respectively.)

\[
\frac{P}{V(P_0-P)} = \frac{1}{V_m C} + \frac{(C-1)}{V_m C} \left(\frac{P}{P_0}\right)
\]  

C is the BET constant, where \(E_1\) is the heat of adsorption for the first layer, and \(E_i\) is that for the second and higher layers and is equal to the heat of liquefaction or heat of vaporization. (\(R\): gas constant, \(T\): absolute temperature)

\[
C = \exp\left(\frac{E_i - E_1}{RT}\right)
\]  

In addition, the specific surface area was measured by CO₂ adsorption method (cooling medium: ice water).  

3. Results and Discussion

3.1 Gasification rate with CO₂ gasifying agent

Figure 2 shows the results of a gasification experiment under a CO₂ atmosphere. The Douglas-fir char, which was in the pyrolyzed state \(X = 0.0\) at gasification initiation — 0 s, was changed into ash when the gasification was complete \((X = 1.0)\). As observed at \(T_{\text{gasific}} = 1273\) K (Fig. 2), the Douglas-fir char was completely gasified under CO₂ after 160–170 s. At 1173 K, the gasification time was approximately 800 s. Although not shown herein, at \(T_{\text{gasific}} = 1073\) K the time required for gasification was approximately 8000 s when CO₂ gasifying agent was used. The gasification rate increased with increasing gasification temperature. The gasification rate constant \(K_p\) exhibited an Arrhenius-type temperature dependence. (Later mention; in Section 3.2)

Fig. 2  The relationship between time and carbon conversion. (Gasification agent: CO₂; \(T_{\text{gasific}}=1073–1273\) K)

Fig. 3  The relationship between time and carbon conversion. (Gasification agent: H₂O, \(T_{\text{gasific}}=1073–1273\) K).
3.2 Gasification rate with H$_2$O gasifying agent

Figure 3 shows the gasification of Douglas fir char under a H$_2$O atmosphere. The dotted line represents the experimental data while the solid line represents the theoretical data (RPM: Eq.(1)). It is clear that the gasification rate increased with gasification temperature and the experimental data ($X$ - time) almost agreed with those in the calculation. At 1273 K, the time required for gasification was approximately 70 s under H$_2$O compared to 160–170 s under CO$_2$ (ref. Fig.2), therefore, the H$_2$O gasification rate was approximately 2–3 times higher than the CO$_2$ gasification rate at 1273 K.

Figure 4 shows the Arrhenius plots of the gasification rate constant $K_p$. At 1073–1273 K, the gasification rate constant exhibited an Arrhenius-type temperature dependence and the chemical reaction was rate determining. The gasification rate constant $K_p$ is larger by approximately 2.9, 5.6, and 10.0 times at 1273, 1173, and 1073 K, respectively, when H$_2$O gasifying agent was used. The difference is larger when the gasification temperature is lower, indicating that gasification using H$_2$O vapor accelerated char gasification at low temperatures. Table 3 shows the structure parameters where $\psi$ tends to be slightly higher at lower gasification temperatures. This indicates that the surface area of pores increases at lower temperature. Herein, the activation energy $E$ under H$_2$O gasifying agent was 170 (kJ/mol) and the frequency factor $A$ was $3.8 \times 10^5$ (1/s). The activation energy under CO$_2$ was 235 (kJ/mol) and the frequency factor $A$ was $8.0 \times 10^7$ (1/s). The increased value of the activation energy in CO$_2$ gasification than that in steam gasification can be explained by employing a gasification experiment using coals. (Essenhigh et al., 1981.) When the results of the gasification experiments were summarized using many types of coal, $K_p = 240–280$ kJ/mol for the C-H$_2$O reaction and $K_p = 200–400$ kJ/mol for the C-CO$_2$ reaction.

![Fig. 4 Comparison between H$_2$O and CO$_2$ gasification rate constant.](image1)

The data reported in this study is compared with previously reported experimental data in Figs. 5 and 6. The gasification rate constant $K_p$ varied greatly in previous studies because the experimental setups and char samples differed.
between studies. The gasification rate constants $K_p$ obtained herein ( ■ and the red line) were clearly compared with the those of many gasification experiments. The data in this study is positioned in middle of the previously reported data, and most probable values can be shown using the same experimental setup, same char samples, and same pyrolysis conditions in the accurate measurement (single char particle distribution: Kibria et al., 2019). Therefore, $A$ and $E$ and the differences in reactivity between H$_2$O and CO$_2$ gasifying agents were provided as typical values in previous data at high temperature region.

3.3 Examination on the gasification mechanism
3.3.1 Development of micro- and mesopores in the bio char during the gasification process

To elucidate the H$_2$O and CO$_2$ gasification mechanisms, pore development with gasification progress was examined. As shown in Fig. 4, at $K_p \approx 0.001$ (1/s), where the gasification rate constant between H$_2$O gasification ($T_{gasific} = 1073$ K) and CO$_2$ gasification ($T_{gasific} = 1173$ K) gave nearly the same values, then both gasification processes were compared. When the carbon conversion rate $X$ reached 0.2, 0.5, and 0.8, the gasification experiment was stopped, and the chars were collected. The gasification experiment was repeated ten times to collect the chars necessary for the surface area analysis by ASAP 2020 (Shimadzu Co., Ltd.).

Figure 7 shows the relationship between the BET specific surface area and carbon conversion. The measured value of the surface areas is provided in Table 4 in detail. The value in Fig. 7 was averaged from Table 4. The BET specific surface area of the char increased with gasification progress regardless of the gasification agent. During the first half of the reaction $X = 0.0$–0.5 (CO$_2$ gasification at 1173 K and H$_2$O gasification at 1073 K), no significant differences in pore development in the biochar were observed. During the second half of the reaction process ($X = 0.8$), the specific surface area was slightly larger under CO$_2$ gasifying agent compared to that under H$_2$O gasifying agent. From Fig. 8, the average diameter of the micropores remained unchanged with gasification progress. Using the CO$_2$ adsorption-medium the BET specific surface area was measured. (Fig. 9; the substance is equivalent to gasifying agent.) The BET specific surface area increased with gasification progress regardless of the gasification agent. The increase in BET surface area was confirmed by the adsorptions of two media.

Fig. 10 and Table 4 show the surface area of the mesopores determined by the BJH method. The mesopore surface area (2.0–50 nm) increased with gasification progress, similar to the BET specific surface area (cf. Fig. 7). Overall, the increased mesopores during H$_2$O gasification was similar to that during CO$_2$ gasification ($X = 0.0$–0.8). When the overall gasification rates were approximately the same, pore development (i.e., physical shape) was identical during both gasification processes. However, it is noted that the reactivity itself of the active sites on char surface with H$_2$O agent was much higher than that with CO$_2$ agent, because H$_2$O gasification was performed at a lower temperature (1073 K) than CO$_2$ gasification (1173 K). Herein, the specific surface area $S_{BET}$ in CO$_2$ gasification at $T_{gasific} = 1073$ K is referred in Fig. 7. (Ref. the dotted red line.) Comparing the BET specific surface area under H$_2$O gasifying agent at $T_{gasific} = 1073$ K, in the middle of gasification ($X = 0.5$), the $S_{BET}$ under CO$_2$ gasifying agent was larger than that under H$_2$O. Roughly, difference in the orders of magnitude of $S_{BET}$ was not observed, and the pores developed with increasing carbon conversion $X$.

![Fig. 7](image1.png) Relationship between the BET specific surface area and carbon conversion. (N$_2$ adsorption, Cooling medium: liquid nitrogen.)

![Fig. 8](image2.png) Relationship between the average micropore size and $X$.  

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Table 4: The specific surface area measured by the BET and BJH methods.
(N₂ adsorption, cooling medium: liquid nitrogen)

| Char sample | Gasifying agent and carbon conversion | Adsorption isotherm classification | BET method | BJH method |
|-------------|--------------------------------------|----------------------------------|------------|------------|
|             | BET surface area | Pore volume | Average pore diameter | Adsorption | Desorption | Mesopore volume | Mesopore area | Mesopore distribution average diameter | Mesopore volume | Mesopore area | Mesopore distribution average diameter |
|             | S_{BET} | V_{p} | d_{p} | S_{B} | V_{p} | S_{B} | d_{p,av} | V_{p} | S_{B} | d_{p,av} |
| DF-char     | 81,946 | 0.047 | 2.286 | 0.009 | 8.800 | 3.945 | 0.001 | 0.837 | 5.734 |
|             | 213,051 | 0.110 | 2.058 | 0.006 | 11.058 | 2.334 | - | - | - |
|             | 248,556 | 0.134 | 2.148 | 0.012 | 21.388 | 2.322 | 0.003 | 6.069 | 2.049 |
| H₂O gasific | 338,190 | 0.182 | 2.147 | 0.022 | 31.083 | 2.789 | 0.009 | 15.615 | 2.396 |
| (T_{gasific} = 1073 K) | 370,624 | 0.199 | 2.149 | 0.024 | 35.125 | 2.750 | 0.016 | 24.880 | 2.518 |
| H₂O gasific | 348,530 | 0.185 | 2.120 | 0.018 | 28.636 | 2.526 | 0.006 | 10.789 | 2.329 |
| (T_{gasific} = 1073 K) | 419,753 | 0.229 | 2.183 | 0.038 | 53.661 | 2.854 | 0.030 | 42.374 | 2.811 |
| H₂O gasific | 418,632 | 0.227 | 2.169 | 0.035 | 50.121 | 2.774 | 0.028 | 40.381 | 2.736 |
| (T_{gasific} = 1073 K) | 361,525 | 0.191 | 2.111 | 0.019 | 30.832 | 2.417 | 0.006 | 10.929 | 2.272 |
| CO₂ gasific | 390,051 | 0.166 | 2.149 | 0.010 | 32.472 | 2.697 | 0.010 | 17.870 | 2.314 |
| (T_{gasific} = 1173 K) | 377,389 | 0.202 | 2.140 | 0.024 | 37.100 | 2.637 | 0.014 | 23.408 | 2.637 |
| CO₂ gasific | 314,098 | 0.171 | 2.178 | 0.026 | 36.868 | 2.873 | 0.015 | 22.966 | 2.579 |
| (T_{gasific} = 1173 K) | 500,000 | 0.461 | 3.426 | 0.367 | 373.038 | 3.933 | 0.350 | 108.909 | 3.348 |
| CO₂ gasific | 430,811 | 0.234 | 2.174 | 0.037 | 52.712 | 2.793 | 0.028 | 41.025 | 2.748 |
| (T_{gasific} = 1173 K) | 366,929 | 0.201 | 2.192 | 0.034 | 46.182 | 2.905 | 0.025 | 35.159 | 2.794 |
| CO₂ gasific | 783,716 | 0.444 | 2.268 | 0.105 | 135.434 | 3.080 | 0.099 | 123.406 | 3.194 |
| (T_{gasific} = 1173 K) | 824,308 | 0.469 | 2.278 | 0.114 | 147.809 | 3.184 | 0.106 | 132.603 | 3.208 |
| DF-char     | 740,533 | 0.417 | 2.253 | 0.005 | 124.826 | 3.053 | 0.089 | 114.407 | 3.119 |

Fig. 9: Relationship between the BET surface area determined by CO₂ adsorption and carbon conversion X. (Cooling medium: Ice water)

Fig. 10: Relationship between the mesopore surface area determined by the BJH method and carbon conversion X.

3.3.2 Relation between the reaction rate and interface area

The random pore model was derived assuming that the gasification rate dX/dt is proportional to the development of the reaction interface area (i.e., Eqs. (6) and (7): Bhatia and Vartak, 1996).

\[
\frac{dX}{dt} = \frac{dX}{dt} \bigg|_{X=0} = \frac{S_B}{S_{B0}} = (1 - X)^{1 - \psi} \ln(1 - X)
\]

\[
S_B = S_{B0} (1 - X)^{1 - \psi} \ln(1 - X)
\]

Where S₀ is the surface area per unit volume (m²/m³) which contributes to the gasification rate and S₀ is the initial value of S₀ (m²/m³).
In Fig. 7, the BET surface area $S_{\text{BET}}$ is depicted in values per unit mass (m$^2$/g). If the pores are assumed to develop due to the gasification reaction but particle volume remains unchanged, the specific surface area can be converted into equivalent values per unit volume by multiplication by (1-$X$) (Kajitani et al., 2005). Figure 11 shows the relationship between the carbon conversion rate $X$ and $(1-X)S_{\text{BET}}$, while Fig. 12 shows the variation in non-dimensional gasification rate $(dX/dt)/(dX/dt)_0$ as a function of the carbon conversion rate. Comparing Fig. 11 with Fig. 12, the development of surface area i.e., $(1-X)S_{\text{BET}}$ is in good agreement with the non-dimensional reaction rate over the gasification process $(X=0.4 - 1.0)$, thus, the gasification reaction rate $dX/dt$ is proportional to the interface area. In the initial stage $(X=0-0.3)$, although $(1-X)S_{\text{BET}}$ increased by approximately 1.5 times, the non-dimensional gasification rate barely changed. The reason for this is that the development of mesopores was slower in the initial stage than in the latter half of the carbon conversion. (see the gradient in Fig. 10) In other words, it was difficult for a large amount of gasifying agent to enter the deep regions (interior) of the biochar in the initial stage. In Fig. 12, the curve is more convex than in the case of the volume reaction model (VRM), which is indicated by the alternating long and short dashed lines extending from the carbon conversion rate $X=0.0$ to $X=1.0$, (VRM: $dX/dt = K_v$, $(1-X)$, $K_v$: gasification rate constant). Previously, models such as the volume reaction and grain models have been applied to biomass gasification. (Billaud et al., 2016; Bhat et al., 2001; Kajita et al., 2010.) These figures (Fig. 11 and Fig. 12) suggested that the surface reaction model is more appropriate for gasification reaction of wooden biochar than the volume reaction model, and the gasification reaction rate is proportional to the interface area. It is considered that gasification modeling should be performed for wooden biomass-derived char using the surface reaction.

![Fig. 11 Changes in the equivalent value of surface area per unit volume calculated by the specific surface area with increasing carbon conversion X.](image1)

![Fig. 12 Relationship between the non-dimensional gasification rate and carbon conversion X. (experimental data)](image2)

4. Conclusion

The gasification rate under H$_2$O gasifying agent was compared to CO$_2$ gasifying agent at high temperature region (1073–1273 K). In addition, the development of micro-and mesopores with H$_2$O and CO$_2$ gasifying agents was clarified in detail. The results are as follows:

1. The gasification rate constant $K_p$ of biochar gasification was approximately 3–10 times higher under H$_2$O gasifying agent than CO$_2$ agent at 1073–1273 K. This study reported the most typical values of $A$ and $E$ by Arrhenius equation.

2. The specific surface area of the micro and mesopores increased with progressing gasification in any gasification agent. The non-dimensional gasification rate $(dX/dt)/(dX/dt)_0$ as a function of carbon conversion rate $X$ was approximately proportional to the interface area.

3. By measuring the increased surface area with progressing gasification under H$_2$O and CO$_2$ gasifying agents in detail, the reaction rate of wooden biochar in gasification process was related to the specific surface area of the solid reactant. Thus, the surface reaction model is more suitable than volume reaction model etc. for expressing the gasification phenomena of wooden biochar.
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