Reaction Mechanism of Tar Evolution in Biomass Steam Gasification for Hydrogen Production

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ABSTRACT:
Reaction mechanism of tar evolution in steam gasification of biomass was investigated with a continuous cross-flow moving bed type differential reactor, in which tar and gases can be fractionated according to reaction time. We estimated that time profile of tar and gas evolution in the gasification of cellulose, xylan, and lignin, and compared it with experimental product time profile of real biomass gasification. The experimental tar evolution rate is different from estimated tar evolution rate. The estimated tar evolution rate has a peak at 20 s. On the other hand, the experimental tar evolution rate at 20 s is little, and tar at initial stage includes more water-soluble and water-insoluble compounds. It can be concluded that in the real biomass steam gasification the evolution of tar from cellulose and lignin component was found to be precipitated by that from hemicellulose component.

KEYWORDS: Biomass gasification, Tar, Continuous Cross-flow moving bed type Differential Reactor

Introduction
The steam gasification of biomass is a promising technology for thermochemical hydrogen production from biomass. Since biomass is a renewable and clean energy resource, biomass hydrogen is essential for the sustainable hydrogen society. In addition, among biomass conversion processes, gasification is one of the most efficient ones [1]. On the other hand, biomass gasification has problems such as tar production. Tar is a complex mixture of condensable hydrocarbons such as aromatics. In biomass gasification process, a large amount of tar is produced, causing some trouble such as pipeline plugging, defluidization, and the reduction of thermal efficiency [2]. Thus, it is essential to elucidate the reaction mechanism of tar production in gasification for improvement in controllability and thermal efficiency of biomass gasifiers.

So far, many researchers have conducted the experimental studies about pyrolysis of biomass and its components [3-30]. Especially, cellulose has most been studied. Broido-Shafizadeh model (Fig. 1) was the initially proposed mechanism for the pyrolysis of cellulose [3-5]. This model consists of three coupled first order reactions. The first stage of pyrolysis involves no weight loss and leads to form intermediate called active cellulose. This is followed by a pair of competing reactions which produces either volatiles or char and gases with weight loss. This concept of active cellulose was inherited in many pyrolysis or gasification models of cellulose proposed later [6-11, 13,14]. Moreover, extensive efforts for intermediate and tar evolution had been reported [11-14, 16-20]. Boutin et al. [17-20] observed that the active cellulose is liquid at the reaction temperature but solid at ambient temperature. The active cellulose is completely soluble in water (anhydroy-oligosaccharides) and its calculated mean lifetime is 0.02 s at the reaction temperature [18]. Wooten et al. [16] found that final carbohydrate converts to aromatic carbons but not to aliphatic carbons when subjected to prolonged heating.

With regard to the pyrolysis of real biomass, many researchers has been studied and proposed reaction models [23-27]. Most of those assume that cellulose, hemicellulose, and lignin are pyrolyzed independently. Müller-Hagedorn et al. [23] proposed a parallel reaction model of 5 components (cellulose 1, cellulose 2, hemicellulose 1, hemicellulose 2, and lignin) and evaluated formal kinetic parameters. Miller and Bellan [24, 25] considered that kinetic scheme of cellulose pyrolysis is also adopted to hemicellulose and lignin (Fig. 2). They mentioned that pyrolysis of biomass can be explained based on a superposition of the three components.
However, in the conventional reactors for kinetic study of biomass gasification such as a thermobalance reactor, a drop tube reactor, a fixed bed reactor, and a fluidized bed reactor, it is impossible to investigate the time profile of tar and gas evolution during biomass gasification with differential method of kinetic analysis in continuous feeding condition. Thus, we have developed a continuous cross-flow moving bed type differential reactor (CCDR), in which biomass sample is continuously fed, and the products (tar, gas and char) can be fractionated from each compartment according to the reaction time. By using this apparatus, we previously researched the mechanism of pyrolysis of cellulose, and found that the dehydration of nascent char takes place after the devolatilization of tar is completed [8].

In the present study, the time profile of tar and gas evolution was investigated in steam gasification of biomass and its components: cellulose, xylan as hemicellulose, and lignin. The reaction temperature was kept at 673 K. The fractionated volatile matter and char were separated immediately and quenched. In this experimental condition, no secondary reaction between volatile matter and char takes place because of low temperature and short residence time. Based on the experimental results, we discuss on the reaction mechanism of tar evolution in biomass steam gasification.

**Experimental Apparatus**

Figure 3 shows the schematic diagram of a continuous cross-flow moving bed type differential reactor (CCDR). The reactor consists of a quartz glass half tube covered with a quartz glass plate and a belt conveyor system. The reactor is divided into six compartments (W90 mm×D80 mm×H40 mm) where gas flows are independent. The reactor is heated using an infrared gold image furnace (Ulvac Riko, Co. Ltd.). The heating zone of the furnace is divided into a preheat zone and three reaction zones. The temperatures of each zone are measured by K-type thermocouples and are controlled to be constant at 673 K independently. Biomass sample is fed out of a feeder onto the conveyor belt made of siliglass (SiO2 > 96%), which carries the sample across the six compartments, delivering produced char to a char sampling system. The initial time is defined as the time when sample is fed into the preheat zone. Tar and gases produced in each compartment are sampled with a carrier gas and fractionated according to reaction time. At the end of belt conveyor, char is collected using the char sampling system. By changing the belt speed, the residence time of each compartment can be varied in the range of 2.4 - 32 s.

A bowl feeder (model PEF-90AL; Sanki Co.) included in an acrylic feeder box was used to feed biomass...
sample continuously with an Ar carrier gas into the preheat zone through a SUS316 tube (6.35 mm, o.d.). The feed rate was calibrated by weighing fed sample within 1 min before and after experiment, and calculate the average feed rate using both weight of fed sample. Steam was generated in a steam generator and was fed into the reactor with an Ar carrier gas. Tar evolved in each compartment went through heated sampling lines, and then was collected separately in six tar traps that were cooled by ice. Water was also eliminated in CaCl2 columns. Although the six sampling lines were gathered in a gas sampler (EMT 4SC6MWE; Valco Instruments Co.), only one of the lines was connected to a micro gas chromatograph (M-200H; Hewlett Packard Co.), and the line to the micro GC was changeable. The flow rate of the effluent gas was measured with a mass flow meter. By using the micro GC we analyzed H2, O2, N2, CH4 and CO with an MS-5A column and Ar carrier gas; CO2, C2H4 and C2H6 with a Pora Plot column and Ar carrier gas.

Procedure
In this study, these are used as samples: Avicel microcrystalline cellulose (Merck Co. Ltd., < 160 μm, Avicel), xylan from birch wood (Sigma-Aldrich Co.), kraft lignin (Kanto Chemical Co. Ltd., 6.8-160 μm) and real biomass (Chilean eucalyptus). The elemental compositions of these samples are shown in Table 1. The sample was dried at 333 K in an oven for 12 h prior to the experiment. The sample was put in the feeder and the feeder box was purged with Ar. The reactor was also purged with Ar until the concentration of O2 declined below 1% and the flow rate of the carrier gas at each compartment was set to 400 cm3 min-1. The steam generator, steam feeding lines and sampling lines were heated at 523, 453 and 423 K, respectively, to avoid the condensation of steam and tar. After heating the reactor up to 673 K, steam (40 vol. %) and cellulose were fed for 60 min. The calibration of the sample feed rate from the feeder was carried out at room temperature. The sample feed rate was kept at 30-119 mg min-1 in this experiment. The belt speed was 750 mm min-1 and the reaction time of biomass sample was 38.4 s. Thus, the corresponding residence time of biomass sample in each compartment was 6.4 s.

Analysis of tar
After the experiment, distilled water was introduced into the reactor and sampling lines. Deposited tar was collected in the tar traps until the color of the solution became transparent. Acetone was also used as a solvent. Molecular weight of tar was also measured by a gel filtration chromatograph (pump: Waters 600E Multi Solvent Delivery System, column: Shodex AsahipakGS-220HQ, detector: Waters 2414 differential refractometer) while KCl was added to the solution in order to reduce the intramolecular ionic repulsion between hydroxyl groups. After evaporating solvent in the solution, the composition of dried tar was analyzed with a CHNS elemental analyzer (2400II CHNS/O; Perkin Elmer). A small amount of the dried tar was milled with KBr (0.1 g) and measured by FT-IR (FTIR-230; JASCO). The 4000-400 or 4600-400 cm-1 wave number rage with 16 scans was investigated.

In each compartment of CCDR the evolution rates of gas and tar were defined as the follows:

\[
evolution rate (\text{carbon molar basis}) = \frac{M_c}{M \cdot \tau}
\]

\[
evolution rate (\text{weight basis}) = \frac{M_G}{W \cdot \tau}
\]

where \( M_c \), \( M \), \( \tau \), \( M_G \), and \( W \) represent a molar amount of carbon in product in one compartment [mol], total molar carbon in fed biomass [mol], residence time in one compartment [s], molar amount of gases in product in one compartment [mol], and total amount of fed biomass [g], respectively.

Results and discussion
Trend of gas and tar evolution in gasification of each sample
Figure 4 shows the conversion rate to the gas, tar and char in steam gasification of cellulose, lignin, xylan and real biomass. The estimated biomass carbon conversion as a superposition of cellulose (50 %), lignin (27 %), and xylan (23 %) is also shown in Fig. 4. This ratio of three main
components of biomass is estimated with elemental analysis of biomass by the measure reported by Hasegawa et al. [31]. Figures 5-8 show the time profile of evolution rate of CO, CO$_2$ (weight basis) and tar (carbon molar basis) during steam gasification of these samples at 673 K for cellulose. Figure 9 shows the evolution rate estimated as a superposition of cellulose, lignin, and xylan. In these figures, abscissa represents the elapsed time after the sample is fed onto the quartz belt. Since the gas evolution rate of H$_2$, CH$_4$, C$_2$H$_4$, and C$_2$H$_6$ was smaller than 2% of that of CO$_2$ in any case, these gases are not represented in the figures.

In case of cellulose (Fig. 4), most of volatile was observed to be water soluble tar. It can be seen in Fig. 5 that the evolution of tar increased rapidly with reaction time to achieve a peak at 22.4 s. In addition, the evolution of gas was found to exhibit a peak at 28.8 s. These results are attributed to the existence of intermediates [8].

In case of lignin, about 70% of sample converted to char, and the amount of tar was very small as shown in Fig. 4. It was seen from Fig. 6 that the initial stage exhibits large evolution rates of tar and gas. With increasing time the evolution rates of tar and gas decreased. Most of tar was water insoluble. This was attributed to the composition of lignin which mainly consists of hydrophobic aromatic components.

For xylan, the amount of gas was observed to be larger than that of cellulose and lignin (Fig. 4). In Fig. 7 the time profile of gas evolution for xylan gasification was found to exhibit two peaks at the initial stage and 28.8 s. This result corresponds to the report by Müller-Hagedorn et
al. [23] which shows hemicellulose has two decomposition steps. The dominant tar evolution takes place at initial stage. The amount of tar in xylan gasification was smaller than that in cellulose gasification and larger than that in lignin gasification.

In case of biomass (Fig. 8), a similar trend for tar and gas evolution was observed with xylan gasification. The tar and gas evolution was found to exhibit two peaks at the initial stage and 28.8-35.2 s. As can be seen in Fig. 9, the estimated time profile of gas evolution was similar to that of experimental data. The gas evolution exhibits two peaks at the initial stage and 28.8 s.

In spite of similar trend for gas evolution, tar evolution was found to exhibit a different manner. In the initial stage of the large real biomass gasification, tar evolution rate was large and reduced with increasing time to a minimum at 22.4 s. On the other hand, tar evolution was found to be estimated to increase with time to reach a maximum at 22.4 s.

Figures 10 (a) and 10 (b) show the evolution time profiles of water-insoluble and water soluble tar for the experimental result and the estimation by means of the superposition of cellulose, lignin and xylan, respectively. In the experimental result, both water-soluble and water-insoluble tar evolved at initial stage, and then the ratio of water-insoluble tar decreased with reaction time. On the other hand, in the estimation of tar evolution most of tar was water-soluble because of small amount of tar from lignin and xylan, and most of tar evolved from cellulose was water soluble. These results suggest that, in biomass gasification, the amount of water-insoluble tar which mainly evolves from lignin increases and the evolution of water soluble tar which evolves from cellulose occurs earlier than in the cellulose gasification.

**Analysis of tar**

Figure 11 shows FT-IR spectra of water-soluble tar from cellulose, xylan, and biomass (3.2 s and 28.8 s). No significant change in FT-IR spectra of tar evolved from cellulose and xylan was observed with reaction time. Tar from cellulose has some peaks at 950 – 800 cm\(^{-1}\). These are considered to be assigned to α1-6 bond of levoglucosan, the main component of water-soluble tar from cellulose. Tar from xylan has a strong
peak at about 1400 cm\(^{-1}\). The tar from biomass gasification at 3.2 s after the beginning of reaction also has a comparatively strong peak at 1400 cm\(^{-1}\). Tar derived from biomass at 28.8 s has some distinct peaks at 950 – 800 cm\(^{-1}\). It is concluded that at initial stage in biomass gasification tar is mainly from xylan and at about 30 s later, tar derived from cellulose increases.

The FT-IR spectra of lignin and water-insoluble tar from biomass (3.2 s and 28.8 s) were shown in Fig. 12. The spectrum of lignin shows peaks assigned to aromatic ring at 1600, 1510, 1420 cm\(^{-1}\). Tar from biomass at 3.2 s also has these peaks.

Figure 13 shows the molecular weight distribution of water-insoluble tar from biomass (reaction time: 3.2 s and 28.8 s) measured by the gel filtration chromatography (GFC). Hasegasa et al. reported that the molecular weight distribution of tar derived from cellulose has peaks at about 150 and 300, and the MW of tar from lignin is distributed at about 1000 - 4000. The MW distribution of tar at 3.2 s of reaction time has a broad peak at 1000 – 3000. This suggests that the water-insoluble tar at initial stage of biomass gasification contains the component derived from lignin.

**Scheme of biomass gasification**

From the analyses of tar, the evolution mechanism of tar and gas in biomass gasification is summarized schematically in Fig. 14. Horizontal axis represents elapsed time from the beginning of gasification, and vertical axis shows the amount of produced gas and tar.

In cellulose gasification, tar and gas evolution rate increases with reaction time. The evolutions of tar and gas achieve a peak at about 20 s and 30 s, respectively. On the other hand, in biomass gasification, evolution of water-soluble tar showed peak early in the reaction. Thus, it can be considered that cellulose component of biomass releases tar earlier than pure cellulose.

Pure lignin releases gas at initial stage of gasification. With little tar evolution, most of lignin converted into char. In biomass gasification, however, at initial stage water-insoluble tar was produced much more than expected from the gasification of lignin alone. As this tar contained aromatic components derived from lignin, it is considered that the evolution of tar from lignin component of biomass was enhanced comparing with pure lignin gasification.

In case of xylan, the representative of hemicellulose, the evolution of gas shows two peaks at initial stage and 30 s later. Tar evolution occurs at the beginning of the reaction, and the amount is more than lignin but much less than cellulose.

As mentioned above, tar evolution of biomass gasification cannot be estimated by the superposition of cellulose, lignin, and hemicellulose. The increase in tar derived from lignin component in real biomass gasification is likely to be due to the effect of reaction of hemicellulose. Omori et al. [32] indicated that holocellulose (hemicellulose and α-hemilose) acts as hydrogen donor. Sagehashi et al. [33] reported that in biomass (Japanese cedar) gasification production of phenol and guaiacol surpassed the amounts predicted from the result of cellulose, xylan, and lignin. They considered that holocellulose which acts as hydrogen donor accelerates the pyrolysis of biomass. On the other hand, Müller-Hagedorn et al. [23] reported that inorganic salts promote pyrolysis reaction. In addition, some researchers have reported the catalytic effect of...
alkali and alkaline earth metallic (AAEM) species for biomass gasification [34, 35]. Thus, it is also likely that the inorganic salts like AAEM influences the tar evolution. Further investigation is needed to reveal the factor which influences the evolution of tar in biomass gasification.

Conclusions
By using a continuous cross-flow moving bed type differential reactor (CCDR), which can separate the volatiles according to reaction time, steam gasification of cellulose, lignin, xylan, and real biomass was investigated at 673 K. The fractionated tar was measured by weight and analyzed by FT-IR spectrometry, gel filtration chromatography, and elemental analysis. It is proven that in real biomass gasification the evolution rate of gas is similar to that of the predicted as superposition of cellulose, lignin, and xylan. On the other hand, the experimental tar evolution rate of real biomass is different from estimated tar evolution rate from each gasification result of the three components. The estimated tar evolution rate has a peak at 20 s, but experimental tar evolution rate has two peaks at the initial stage and 30 s. Tar derived from real biomass at initial stage includes more water-soluble and water-insoluble compounds.

From the analyses of tar, it is indicated that the composition of tar varies with reaction time. Tar at initial stage of gasification of real biomass includes both water-soluble tar derived from cellulose and hemicellulose, and water-insoluble tar from lignin. In addition, the main component of tar at 30 s of reaction time is water-soluble tar from cellulose.

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References:


