Determination of kinetic rate of xylose decomposition in sub- and supercritical water

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SUMMARY
Reaction kinetics of xylose as a model compound of hemicellulose was studied in wide range of temperature covering subcritical and supercritical region. Retro-aldol condensation and dehydration products were found to be abundant in liquid intermediates. In addition, many kinds of organic acid were formed and suspected to be the final liquid intermediates that were decomposed to gas. Kinetic rate of each reaction was determined and the effect of temperature was discussed regarding of Arrhenius behavior.

1. Introduction
Supercritical water gasification (SCWG) is promising technology to convert biomass into energy because it has relatively high gasification efficiency and high gasification rate\textsuperscript{1-13}. Investigations of this technology for conversion of lignocellulosic biomass have been done by many researchers so far. However, most of them focus on studying behavior of cellulose and/or lignin in SCWG\textsuperscript{1-13}. Only few studies have investigated the behavior of hemicellulose in supercritical water. Thus, complete reaction network of xylose decomposition in sub- and supercritical water including organic acid species, the expected final intermediates to form gas products, is important. The purpose of this study is to elucidate the reaction network for xylose decomposition in supercritical water including organic acids, together with the reaction rate determination.

2. Experimental
The reactor scheme and operating procedure has been described elsewhere\textsuperscript{10}. The experimental conditions are shown in Table 1.

<table>
<thead>
<tr>
<th>Table 1 Experimental conditions</th>
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<tr>
<td>Material</td>
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<tr>
<td>Concentration</td>
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<tr>
<td>Feedstock : water</td>
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<tr>
<td>Temperature</td>
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<td>Pressure</td>
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<td>Residence time</td>
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The product yield of compound X, $Y(X)$, was evaluated based on the carbon amount using the equation

$$Y(X) = \frac{n_c(X)}{n_{c0}}$$  \hspace{1cm} (1)

where $n_c(X)$ and $n_{c0}$ denote the amount of carbon in product X and that in the xylose feedstock, respectively.

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3. Results and discussions

The intermediates found in the liquid product were xylulose, furfural, retro-aldol products (glyceraldehyde, glycolaldehyde, dihydroxy-acetone, formaldehyde), and organic acids (lactic acid, acetic acid, propionic acid and formic acid). The other products were treated as lumped product and named TOCs, which represented unknown products in the liquid phase. Detailed reaction network for decomposition of xyllose in supercritical water can be proposed as shown in Fig. 1.

Kinetic rate constants in the network were determined so that the values gave the best fitting between the calculated and experimental data, assuming the first order for all reactions. The least square of error (LSE) was the criterion for this calculation. If the reactions are radical reaction, it should follow the Arrhenius behavior. The radical reactions and their activation energy and pre-exponential factor could be determined as shown in Table 2. It was found that the total organic acids occupied the highest yield among the other intermediates. This shows the stability of these acids, and gasification of these acids could be the rate determining step of the total gasification reaction.

4. Conclusion

Reaction network for xyllose gasification reaction in sub- and super-critical water was proposed and the reaction rate parameters in the network were determined. The organic acids were stable and could be the rate determining step of xyllose gasification.

References

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