

### Method for calculating proton concentration.

In experiment (a), the proton concentration was estimated from the ion product of water and was  $2.0 \times 10^{-7}$  mol/L.<sup>S1</sup> In experiment (b) and (d), 0.01M nitric acid aqueous solution was loaded into the reactor instead of pure water to increase the proton concentration in the system. Nitric acid dissociates completely at ambient conditions. Chlistunoff et al.<sup>S2</sup> reported the dissociation constant of nitric acid in supercritical water and correlated the constant as the function of temperature and pressure. The dissociation constant of nitric acid estimated by their correlation was  $1.69 \times 10^{-4}$  mol/kg at 673 K and  $0.5 \text{ g/cm}^3$  of water density. Proton concentration at 673 K and  $0.5 \text{ g/cm}^3$  of water density, where 0.01 M nitric acid aqueous solution were loaded instead of pure water,  $3.6 \times 10^{-4}$  mol/L, and this value is about three orders of magnitude greater than that in pure water.

In experiment (c), water, phenol(PhOH), 2-isopropylphenol(iPr-PhOH) and 2-propylphenol(nPr-PhOH) should be dissociated as below, respectively.



The dissociation constant for each reaction can be expressed as

$$K_W = [\text{H}^+][\text{OH}^-] \quad (\text{S-5})$$

$$K_{\text{PhOH}} = [\text{H}^+][\text{PhO}^-]/[\text{PhOH}] \quad (\text{S-6})$$

$$K_{\text{iPr-PhOH}} = [\text{H}^+][\text{iPr-PhO}^-]/[\text{iPr-PhOH}] \quad (\text{S-7})$$

$$K_{\text{nPr-PhOH}} = [\text{H}^+][\text{nPr-PhO}^-]/[\text{nPr-PhOH}] \quad (\text{S-8})$$

The ionic compounds in this system are  $\text{H}^+$ ,  $\text{OH}^-$ ,  $\text{iPr-PhO}^-$ ,  $\text{nPr-PhO}^-$ . The electric charge balance is expressed as

$$[\text{H}^+] = [\text{OH}^-] + [\text{PhO}^-] + [\text{iPr-PhO}^-] + [\text{nPr-PhO}^-] \quad (\text{S-9})$$

Using eq S-9 and dissociation constants of  $K_W$ ,  $K_{\text{PhOH}}$ ,  $K_{\text{iPr-PhOH}}$ ,  $K_{\text{nPr-PhOH}}$ , eq S-10 is obtained

$$\begin{aligned} [\text{H}^+] = & K_W / [\text{H}^+] + K_{\text{Phenol}} [\text{Phenol}] / [\text{H}^+] \\ & + K_{\text{iPr-PhOH}} [\text{iPr-PhOH}] / [\text{H}^+] + K_{\text{nPr-PhOH}} [\text{nPr-PhOH}] / [\text{H}^+] \end{aligned} \quad (\text{S-10})$$

The proton concentration is expressed as

$$[H^+] = \sqrt{K_w + K_{\text{Phenol}}[\text{Phenol}] + K_{i\text{Pr-PhOH}}[i\text{Pr-PhOH}] + K_{n\text{Pr-PhOH}}[n\text{Pr-PhOH}]} \quad (\text{S-11})$$

The dissociation constants of 2-isopropylphenol and 2-propylphenol in supercritical water have not been reported. The dissociation constant of  $\beta$ -Naphthol in supercritical water is available from the literature.<sup>S3</sup> The dissociation constant ( $\text{pK}_a = -\log_{10}K$ ) of  $\beta$ -Naphthol at 298 K and 0.1 MPa is 9.31, while that of phenol at 298 K and 0.1 MPa is 9.82, which is the same order as that for  $\beta$ -naphthol.<sup>S4</sup> Recently, the dissociation constant of phenol in supercritical water were also reported.<sup>S5</sup> The dissociation constant of phenol at 673 K and 0.47 g/cm<sup>3</sup> of water density was  $1.0 \times 10^{-11}$  mol/kg-water. The dissociation constant of  $\beta$ -naphthol at the similar condition, namely, 673 K and 0.5 g/cm<sup>3</sup> of water density, was  $1.26 \times 10^{-11}$  mol/kg-water. The dissociation constant of phenol and  $\beta$ -naphthol were similar values, which indicates that dissociation constant of alkylphenols in supercritical water would be the same order.

Thus, we used the dissociation constant of  $\beta$ -naphthol ( $K_N$ ) for the estimation of  $[H^+]$  for phenol and alkylphenols (2-isopropylphenol, 2-propylphenol), and assumed that  $K_N = K_{\text{Phenol}} = K_{\text{IPP}} = K_{\text{PP}}$ . At 673 K, the dissociation constant increased from  $10^{-20}$  to  $10^{-11}$  mol/kg-water with increasing water density from 0.1 to 0.5 g/cm<sup>3</sup>. Since the phenol is mainly converted to 2-isopropylphenol and 2-propylphenol, the concentration of phenol, 2-isopropylphenol and 2-propylphenol is expressed as eq S-12.

$$[\text{Phenol}]_0 = [\text{Phenol}] + [i\text{Pr-PhOH}] + [n\text{Pr-PhOH}] \quad (\text{S-12})$$

Thus, from eq S-11 and S-12, the proton concentration is

$$[H^+] \cong \sqrt{K_w + K_N[\text{Phenol}]_0} \quad (\text{S-13})$$

Proton concentration at 673 K, 0.5 g/cm<sup>3</sup> of water density and  $[\text{phenol}]_0 = 0.33$  mol/L is  $1.4 \times 10^{-6}$  mol/L and this value is about two orders of magnitude lower than that in 0.01M nitric acid aqueous solution.

## References

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