1. Introduction

Supercritical water (SCW) treatment of biomass is a promising technology for materials with high moisture contents. Lignin, a compound found in biomass, is an amorphous three-dimensional polymeric substance consisting of phenolic units and abundant aromatic rings. The composition of lignin polymers is unique to each species of plant. In addition, the structure of the polymers and the functional groups present in them are modified significantly depending on the method of isolating the polymers. Hence, the use of lignin in energy generation and chemical applications becomes particularly challenging. Among biomass compounds, lignin is the most difficult to convert to a gas, and although it can be gasified under hydrothermal conditions, char formation is significantly enhanced under supercritical conditions. This is a major complication since char formation is undesirable and an efficient pathway to gas production is hence in demand.

In our previous study\(^\text{1)}\), softwood lignin was decomposed in SCW at 390-450 °C and 25 MPa for very short residence times (0.5-10 s). Under these conditions, we concluded that lignin would be rapidly converted. Supercritical conditions resulted in a high yield of a solid, and char formation occurred at a residence time of 20 s and was enhanced with an increase in the temperature and residence time. Char formation from phenol and benzene competes with gas formation. Benzene decomposes in SCW, although the reaction is slower than the decomposition of phenol. The formation of resonance-stabilized phenoxy radicals is believed to play a key role in promoting its decomposition. In the supercritical water gasification (SCWG) of phenol, direct gasification occurring primarily through pyrolysis was more likely. However, in the SCWG of benzene, gasification occurred through two different pathways. Direct gasification mainly occurred through pyrolysis within the first few seconds, and ring opening of the aromatic compounds occurred during longer residence times, ultimately affording gaseous compounds through intermediates such as formic and acetic acid. The formation of phenol from benzene showed Arrhenius behavior, but benzene formation from phenol decreased with temperature in SCW (non-Arrhenius behavior). Based on the deduced mechanisms, we proposed reaction pathways for the decomposition of phenol and benzene in SCW.
matic groups in lignin, it is important to study monomeric model compounds such as phenol and benzene. Goodwin and Rorrer\(^2\) discussed the SCW decomposition of lignin to monomers that are based on similar phenolic structures as building blocks. Huelsman and Savage\(^3\) described phenol as one of the last hurdles to the complete gasification of biomass, because it is a ubiquitous and long-lived intermediate in SCWG.

Phenol is a major component of organic waste effluent and wastewater pollutants from pesticides, pharmaceuticals, pulp and paper manufacturing industries, the petrochemical industry, and municipal solid waste\(^6,9\). Benzene is a hazardous chemical and an environmental carcinogen; it is as ubiquitous as phenol and has a high degree of chemical inertness\(^9\). This single aromatic ring compound is identified as the building block for polyaromatic hydrocarbons (PAH) and substituted aromatic compounds\(^6\). Similar to phenol, benzene is widespread in nature, especially in wastewater, owing to its widespread industrial usage. The levels of benzene in the environment are further increased by its resilience to biochemical degradation. The aforementioned characteristics and complications associated with these two compounds emphasize the importance of investigating their decomposition behavior in SCW.

Studies of phenol and benzene decomposition in SCW, especially for short residence times and in a continuous-flow reactor, are limited. One of the earliest studies was performed by Xu et al. on the treatment of phenol in a continuous-flow reactor\(^7\). They observed that phenol was only partly decomposed at 600 °C. Huelsman and Savage\(^3\) conducted supercritical water gasification (SCWG) of phenol at three different temperatures (500-700 °C) in a mini batch reactor for long residence times of 8-60 min. Only 47 mol% of phenol was converted at 600 °C, but complete conversion was achieved at 700 °C. DiLeo et al.\(^3\) reported phenol SCWG at 600-700 °C with similarly long residence times of 5-60 min. They reported a slow decrease in phenol yields over time and the highest phenol conversion of 68 % after 60 min. However, both studies were conducted in batch reactors with long reaction times. The setup of the batch apparatus, which required a long heating time with the reactant in the system before the reaction temperature was reached, may have allowed for prior reactions to occur. Some phenol may have been converted once supercritical conditions were achieved, and some intermediates could have inhibited further phenol decomposition before the desired temperature was achieved. Goodwin and Rorrer\(^2\), on the other hand, utilized a continuous-flow system similar to that used in this study. They gasified phenol at 750 °C and for short residence times of 5.3-27 s. Although complete phenol conversion was achieved in 27 s, high temperatures (750 °C) were needed for the reaction. Hence, they concluded that gasification of phenol in SCW was difficult. Moreover, Weiss-Hortala et al.\(^5\) obtained phenol conversion of <50 % at 25 MPa, 500 °C, and for residence times of 0.06-0.23 min.

There are limited studies on the reaction of benzene in SCW owing to its low rate of decomposition. However, there are many studies on the supercritical oxidation (SCWO) of benzene in which the complete destruction of benzene is achieved\(^6,9,10\). Based on these studies, it can be concluded that the oxidation reaction in SCW proceeds through free-radical reactions. Some of the mechanisms in SCWO are similar to those in SCW, although the latter results in a much lower rate because of the absence of oxygen, which is the source of radicals in the SCWO reaction. Lee and Park\(^11\) observed that benzene underwent decomposition in SCW at 440-550 °C in their study on the decomposition of nitrobenzene under the same conditions. They further concluded that the benzene ring may rupture to form gaseous compounds. In addition, DiNaro et al.\(^6\) discussed benzene decomposition in SCW at 24.6 MPa with a 6 s residence time and temperatures ranging from 530 to 625 °C. Phenol was the only quantifiably detected hydrolysis product. Gaseous compounds (CO, CO\(_2\), CH\(_4\), C\(_2\)H\(_4\), C\(_2\)H\(_6\), and H\(_2\)) were also observed in their study.

All of these studies provide insights into the decomposition of phenol and benzene in SCW and hold the key to predicting the overall conversion pathways. Detailed mechanistic pathways could potentially be beneficial for understanding the decomposition behavior under supercritical conditions. To this end, we treated phenol and benzene in a flow reactor at specific temperatures for precise residence times and subsequently performed a quantitative analysis of the intermediates formed. A systematic study of this nature has not been previously reported.

2. Experimental

2.1. Experimental Procedure

A schematic of the experimental apparatus has been reported elsewhere\(^1\). Phenol and benzene decomposition under supercritical conditions was investigated in the temperature range 370-450 °C at 25 MPa and for short residence times (0.5-100 s) controlled using the feedstock flow rate. The initial concentration of phenol and benzene in the reactor was 0.1 wt%. In the continuous-flow system, the feedstock was mixed with preheated water and thus rapidly heated to the desired supercritical conditions. This apparatus set-up avoided slow heating, and thus, no intermediate reactions occurred before the desired reaction conditions were achieved. The total carbon balance (solid + liquid + gas) in this study was higher than 87 % for all of the experimental results discussed below.
Phenol and benzene obtained from Nacalai Tesque Inc. and Sigma-Aldrich Japan Co., respectively, were used as the feedstock in this experimental work. Deionized water (＜1 μS/cm; Organo water deionizer model BB-5A) was used in this study as the solvent. The chemical reagents used were catechol, naphthalene, acetic acid, and formic acid. Catechol was purchased from Tokyo Chemical Industry Co., Ltd; and naphthalene, acetic acid, and formic acid from Sigma-Aldrich Japan Co. Acetonitrile used in the preparation of the HPLC standard solutions were of analytical grade.

2.2. Analytical Methods
The liquid effluent was analyzed using a total organic carbon (TOC) analyzer to quantify the total carbon present in the liquid compounds (non-purgeable organic carbon) and in the dissolved gaseous products (inorganic carbon). The liquid constituents (phenol, catechol, benzene, and naphthalene) were quantified by high performance liquid chromatography (HPLC) using an RSpak DE-413L column (Shodex). The analytical conditions for the phenolic constituents (phenol and catechol) were as follows: flow rate, 0.7 mL/min and 0.4 mL/min; eluent, 0.005 M HClO4 aqueous solution/CH3CN = 50 : 50; oven temperature, 40 °C; ultraviolet detection wavelength, 220 nm. For benzene and naphthalene, the following analytical conditions were used: flow rate, 0.7 mL/min; eluent, 0.005 M HClO4 aqueous solution/CH3CN = 50 : 50; oven temperature, 30 °C; ultraviolet detection wavelength, 254 nm. For HPLC analysis of the acid content (acetic and formic acid), a Shim-Pack SCR-102H (Shimadzu Corp.) column was used under the following analytical conditions: flow rate, 0.7 mL/min; eluent, 0.005 M HClO4 aqueous solution; oven temperature, 40 °C; detector, refractive index detector (RID).

The gaseous products were analyzed using a gas chromatograph equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID). H2 was detected by GC-TCD with N2 as the carrier gas. CO2 and CO were detected by GC-TCD using He as the carrier gas, while CH4, C2H4, and C2H6 were detected by GC-FID with He as the carrier gas.

The solid product particles were trapped in the inline filter. These solid particles were subsequently removed using an ultrasonic cleaning device and placed in a porcelain crucible, and then dried overnight in a desiccator and weighed until a constant weight was attained. Elemental analysis of the char obtained from the experimental work was conducted using a Perkin Elmer Series II CHN/S/O Analyzer 2400. The char collected for the elemental analysis was from a number of experimental runs conducted under the conditions stated above. This is due to the small amount of char produced from each run. Therefore, the result of the elemental analysis of the char is the average value of the elemental composition under supercritical conditions.

2.3. Definition of Product Yield
Product yields from the experimental results were calculated on the basis of the carbon content in the feedstock:

\[ \text{Product yield} = \frac{\text{Carbon in product [mol-C/s]}}{\text{Initial carbon in feedstock [mol-C/s]}}, \quad (1) \]

In the case of hydrogen gas, the following definition was used.

\[ \text{Product yield} = \frac{\text{Hydrogen gas in product [mol-H2/s]}}{\text{Initial carbon in feedstock [mol-C/s]}}, \quad (2) \]

3. Results and Discussion
3.1. Phenol Decomposition in Supercritical Water
Figure 1 shows the yields of each compound during phenol conversion under supercritical conditions (370-450 °C, 25 MPa, 0.1 wt% phenol, and 0.5-100 s residence times). The phenol yields shown in Fig. 1(a) decrease slowly, and it is observed that phenol decomposition in SCW is relatively slow even at 450 °C. The highest degree of conversion achieved in this study was quite low at 68.0 %; however, this improved with temperature. This observation indicates that hydrothermal treatment at much higher temperature is needed for complete destruction of phenol, which is consistent with previous studies. Although full conversion was not achieved under the reaction conditions employed here, final products from its decomposition (char and gaseous compounds) were observed.

The mechanism of initial phenol decomposition in SCW can occur through two possible mechanisms: ionic or radical reactions. The preference for these types of reactions in SCW has been explained elsewhere. It is believed that the different mechanisms strongly influence the intermediates, and in turn, the final products, i.e., char and gaseous compounds.

As discussed by Sue et al. and Penninger et al., phenol dissociates in SCW to produce the phenolate anion and hydrogen ion (H+), as shown in Eq. (3). Hayashi et al. concluded that the high ionic products in water around the critical point enhance the dissociation of phenol, and the phenolate anion concentration is much higher in the vicinity of critical point (370 °C) than in the supercritical region. Furthermore, they found that reactions of phenolate anions with molecular oxygen were faster than those of neutral species with molecular oxygen. This is an important indication of the role of phenolate anions in the conversion of phenol to its intermediate products at near-supercritical temperatures.
However, phenol can also undergo a radical reaction to form the phenoxy radical and a hydrogen atom via the reaction shown in Eq. (3). Huesman and Savage suggested that, in the high-temperature SCWG of phenol, a free-radical mechanism dominates the overall reaction. Pyrolytic studies of phenol indicate resonance-stabilized phenoxy radicals readily form and play a key role in phenol decomposition. This suggests that phenoxy radicals play a vital role in the decomposition of phenol to its intermediate compounds at the elevated supercritical temperatures.

Gopalan and Savage reported that the phenoxy radical exists in three isomeric forms, which are shown in Eq. (5). The latter two structures are ketocyclohexadienyl radicals, with the radical site at the ortho and para positions. These isomeric forms are important in determining the subsequent reaction mechanism of radical coupling as well as the ring opening that leads to the formation of different intermediate products.

\[
\text{OH} + \text{H}_2\text{O} \rightarrow \text{O}^- + \text{H}^+ \quad (3)
\]

\[
\text{OH} \rightarrow \text{O}^- + \text{H}^+ \quad (4)
\]
made with the more likely to occur. High mole fractions of H2 and phenol structure, an formation of gaseous compounds. TOC yield with temperature is due to bonds in the increased phenol conversion. They deduced that as temperature increased, the bonds in phenol and intermediate products, being more easily broken as the temperature increases. This leads to two different reaction pathways: dimerization via radical coupling, which eventually leads to the formation of char, and ring opening to produce intermediates, which ultimately leads to the formation of gaseous compounds.

Several studies of the SCWG of phenol have been made with the main aim of understanding the underlying chemistry of the reaction in order to maximize the gas yield and to minimize undesirable char formation in this complex hydrothermal reaction. Huelsman and Savage\(^4\) reported that the molar yields of all gas species increased dramatically with temperature owing to the increased phenol conversion. They deduced that as temperature increased, the bonds in phenol and intermediate compounds were more easily broken, and the molecular transformation that resulted in H2 and CH4 production (e.g., steam reforming and methanation) was more likely to occur. High mole fractions of H2 and CH4 (33 % and 29 %, respectively) were obtained at 700 °C compared to 5 % and 0 % at 500 °C. In addition, CO and CO2 were produced from decarbonylation and decarboxylation of phenol and phenolic derivatives. DiLeo et al.\(^8\) showed that phenol could be directly gasified to H2 and CO2 under supercritical temperatures, although it was not the primary reaction at lower supercritical temperatures. Decomposition of phenol to form intermediate compounds that ultimately form gaseous compounds is believed to contribute significantly to the gasification efficiency.

The yield of gaseous carbon obtained in this study is shown in Fig. 1(c). All gaseous carbon observed in this study was in the form of CO2. Neither CH4 nor CO was produced under any of the experimental conditions. It can be clearly seen that the gaseous carbon yield was enhanced with temperature and residence time. The highest carbon gasification efficiency (CGE) obtained in this study was 10.75 %. Note that gaseous carbon is observed within a very short residence time of 5 s, which indicates that direct gasification of phenol is more dominant than degradation first to intermediate compounds and then to gas.

The trend of the CGE and the gaseous compositions offers insight into the phenol gasification mechanism. Goodwin and Rorrer\(^2\) suggested that phenol is initially hydrogenated to benzene, which is subsequently reformed in SCW to a mixture of CO and H2. CO is then converted to CO2 and additional H2 by the water-gas shift reaction. However, in our study, CO2 was produced within a residence time of 5 s; this result, in conjunction with the benzene yield obtained here (shown below), led us to believe that the mechanism proposed by Goodwin and Rorrer\(^2\) is not the main pathway for CO2 formation. Onwudili and Williams\(^4\) suggested that the early formation of CO2 from stable aromatic compounds such as phenanthrene must have resulted from the reaction between the pyrolysis gases and hydroxyl ions from water. This theory seems plausible for the SCWG of phenol and is also consistent with the conclusion of DiLeo et al.\(^8\) that phenol can be directly gasified under supercritical conditions. This mechanism agrees with our finding of the early formation of CO2.

It should be noted that the high temperature under supercritical conditions can lead to ring opening of the aromatic compounds to afford many of the intermediate compounds, which in turn form gaseous compounds\(^5\). The ring-opening mechanism has been discussed thoroughly in gasification pathways for the SCWO process. It has been suggested that phenol oxidation in SCW produces ring-opening products such as carboxylic acid, which eventually form CO2\(^6\). Gopalan and Savage\(^10\) suggested that CO cannot be the sole CO2 precursor in the phenol SCWO reaction on the basis of the high CO2 yields obtained in their study. It was subsequently deduced that a mechanism involving acid intermediates as sources of CO2, independent of CO, would be consistent with the larger amounts of CO2 relative to CO. Xu et al.\(^17\) concluded that acid, aldehydes, and ketones are formed by hydrolysis and/or free-radical reactions of phenol via the formation of the phenoxy radical and are then readily decomposed to gaseous compounds. Decarbonylation and decarboxylation of phenol and phenolic derivatives must thus play a key role in the gas formation pathway\(^3\).

To confirm the ring-opening mechanism in phenol conversion in SCW, the identification of acid compounds (formic and acetic acids) is necessary. These yields are shown in Fig. 2. Phenol decomposition in SCW produced acids similar to those obtained in studies of phenol SCWO. However, the yield was less than 0.015, indicating that the ring-opening mechanism is not dominant here. The fact that the CO2 yield, which is equal to the gaseous carbon yield in this study, is less than 0.167 also supports the idea that the hydroxyl group is the main CO2 precursor in phenol decomposition. The acid yield increases with the residence time and temperature, which suggests that the ring-opening pathways were favored by temperature, but the reac-

\[\text{O}^* \rightleftharpoons \text{O}^* \rightleftharpoons \text{O}^* \]

Figure 1(b) shows the TOC yield, which is the total carbon concentration of water-soluble liquid products, excluding phenolic compounds (catechol and phenol), benzene, and naphthalene, which are plotted separately. The TOC yield increases with temperature and with residence time, especially at 450 °C. The increase in TOC yield with temperature is due to bonds in the phenol structure, and subsequently in the intermediate products, being more easily broken as the temperature increases.
tions were relatively slow.

Figure 1(d) shows the char yield from phenol decomposition. Similarly to lignin, char formation from phenol also increases at higher temperatures. Char formation is observed within 5 s at these temperatures, which implies that char formation from phenol through cross-linking reaction occurs rapidly in SCW. In addition, this is consistent with our previous studies, in which it was established that polymerization of phenolic compounds forming char occurred rapidly under supercritical conditions for lignin and lignin model compounds such as guaiacol\textsuperscript{1).}

The results of the elemental analysis of the char obtained in this experiment are shown in Table 1. CHNS/O analysis of the phenol char indicated the amount of carbon to be 78.8 wt\% in comparison to that of phenol of 76.6 wt\%. This shows an increase in carbon in the solid content, suggesting that char from phenol is highly aromatic, which is similar to the char obtained from lignin and guaiacol decomposition under hydrothermal conditions. The elemental analysis also indicated an oxygen content of 14.2 wt\% in comparison to that of phenol (17.0 wt\%). The slight decrease in oxygen content in the char compared to that of phenol implies that oxygen atoms are involved in the linking of these aromatic compounds.

As discussed previously, under supercritical conditions, free-radical mechanisms are dominant and the formation of resonance-stabilized phenoxy radicals is believed to play a key role in the reaction of phenol. Polymerization through these highly reactive radicals combining with one another or with phenol is believed to be the key reaction in the early formation of char. This is consistent with the findings of Gopalan and Savage\textsuperscript{10),} who suggested that the initial coupling of phenoxy radicals through ether linkage is the main mechanism for dimerization. In addition, Huelsman and Savage\textsuperscript{3) suggested that radical coupling compounds such as dibenzofuran are the key precursors to the char formation pathways. Dibenzo-furan can readily participate in polymerization reactions to form char\textsuperscript{3).}

From this, we deduced that char formed from the de-

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Table 1 Elemental Analysis of Phenol and Char Obtained from Experiment (370-450 °C, 25 MPa, 0.1 wt% phenol, and 0.5-100 s residence times)

| Types of compounds | Elemental analysis [kg/kg-dry] |
|--------------------|--------------------------------|
| Phenol             | C: 0.766, H: 0.064, N: 0.000, S: 0.000, O: 0.170 |
| Char               | C: 0.788, H: 0.070, N: 0.000, S: 0.000, O: 0.142 |
composition of phenol under supercritical conditions consists mainly of aromatic compounds joined by ether linkages. This is consistent with the elemental analysis of the phenol char, as discussed earlier, where we found that the oxygen content in the solid phase differed only slightly from that of phenol. In addition, this is similar to observations from studies of real lignin and other lignin model compounds such as guaiacol under supercritical conditions. This is important for the understanding of the char formation pathway from phenolic compounds, especially in the case of lignin. Both gasification and char formation are enhanced at higher temperatures and compete with each other.

Figure 1(e) shows the hydrogen yield. It should be noted that the hydrogen yield increases with residence time. This high yield of hydrogen can be used for both acid production and benzene production, as discussed below.

Figure 3 shows the yields of benzene, catechol, and naphthalene. The yield of benzene shown in Fig. 3(a) is higher at low temperatures, especially in the vicinity of the critical temperature (370 °C), and then decreases as the temperature rises. This is an interesting observation and implies that benzene formation from phenolic decomposition is largely controlled by the dielectric constant and ionic product, which decrease dramatically as the temperature increases under supercritical conditions. This indicates that the formation of benzene from phenol is likely to occur via an ionic reaction, and not a radical reaction.

Two different mechanisms for the formation of benzene from phenol have been discussed in previous studies. In one of them, benzene is produced from the displacement of a hydroxyl group by an H atom liberated in the creation of the phenoxy radical, as shown in Eq. (6). The other mechanism, as discussed by Goodwin and Rorrer and Guo et al., postulates that phenol is hydrogenated by H₂ generated during phenol decomposition to produce benzene, as shown in Eq. (7).

\[
\text{OH} + \text{H} \rightarrow \text{C}_6\text{H}_6 + \text{OH} \quad (6)
\]

\[
\text{OH} + \text{H}_2 \rightarrow \text{C}_6\text{H}_6 + \text{H}_2\text{O} \quad (7)
\]

The yield of catechol is shown in Fig. 3(b). Unlike the decreasing yield of benzene with temperature, the catechol yield increased markedly with temperature, especially at 450 °C. Therefore, it is predicted that the reaction occurs through the addition of OH to the phe-
noxy radical, as shown in Eq. (8). Although it is possible that OH is added directly to phenol, it is not a likely source of catechol, especially at the elevated critical temperature, as hydrogen abstraction by OH to form phenoxy radicals and H$_2$O is preferred$^{10}$. 

$$\ce{O•} + \ce{•OH} \rightarrow \ce{O} \ce{H}$$  \hspace{1cm} (8)

Naphthalene is a polycyclic aromatic hydrocarbon that has been identified as a char precursor$^3$. Figure 3(c) shows the naphthalene yield from phenol decomposition. The formation of naphthalene from phenol increases with temperature, which is in good agreement with a previous study$^3$. Thus, it is likely that naphthalene formation goes via radical reaction. It should also be noted that the naphthalene yield was relatively small for short residence times and only increased notably when the residence time was longer than 50 s. Thus, it is highly likely that naphthalene is formed via benzene, which can form the phenyl radical before generating naphthalene$^{19}$.

3.2. Benzene Decomposition in Supercritical Water

Figure 4 shows the yield during benzene conversion under supercritical conditions (370-450 °C, 25 MPa, 0.1 wt% benzene, and 0.5-100 s residence times). The total carbon balances (solid + liquid + gaseous) across this entire set of experiments exceeded 90%.

Fig. 4 Benzene Decomposition and Product Distributions (TOC, gas, char, and H$_2$) under Supercritical Conditions (370-450 °C) at Different Residence Times (experimental conditions: 25 MPa, 0.1 wt% benzene)
Figure 4(a) shows the benzene decomposition behavior. Benzene degradation under supercritical conditions occurs at a slow rate, even at the highest temperature and for the longest residence time. The highest conversion was 44.8% at 450°C and for a 100 s residence time with a corresponding CE of 6.77%. The conversion and CE of benzene was lower than that of phenol (conversion 68% and CE 10.75%). This is an important indication that the hydroxy group in the aromatic structure increases the reactivity of phenol in the SCW treatment. However, formation of gaseous compounds and char within the 100 s residence time in this experimental work indicates that benzene was susceptible to degradation under SCW.

Benzene decomposition shows a slow reaction rate with minimal conversion even for extended residence times. However, temperature had a significant effect on its decomposition, especially at the highest temperature, which is consistent with Arrhenius behavior. More severe temperature treatment is required if higher degrees of conversion or complete destruction is desired. The mechanism of benzene decomposition in SCW has not been established, and two different mechanisms have been suggested. One mechanism predicts that benzene under supercritical conditions undergoes hydrogenation to produce cyclohexane, as shown in Eq. (9)\(^{21,15}\). The other predicts that the formation of the phenyl radical is important in the initial decomposition of benzene in SCWO, as shown in Eq. (10)\(^{6,20}\).

\[
\begin{align*}
\text{[} & + 3\text{H}_2 \rightarrow \text{[} \\
\text{[} & + \text{OH} \rightarrow \text{[} + \text{H}_2\text{O}
\end{align*}
\]

Figure 4(b) shows the TOC yield from benzene conversion in SCW. It can be seen that elevated temperature enhances the decomposition of benzene into its intermediate compounds. Ding et al.\(^{9}\) concluded that the substitution of hydrogen by the hydroxy group destabilizes the benzene ring. Further substitution results in the complete destabilization of the benzene ring and leads to ring opening, as observed in the case of phenol decomposition under the same experimental conditions\(^{9}\). Lee and Park\(^{11}\) also suggested the possibility of benzene ring opening in SCW to form intermediate compounds. These intermediate compounds could be further degraded to gaseous compounds such as CO and CO\(_2\). They predicted that the primary source of oxygen for the ring-breaking mechanism was SCW. Benzene can also undergo hydrogenation to form cyclohexane, as shown in Eq. (9).

The gaseous carbon yield during benzene decomposition is shown in Fig. 4(c). All gaseous carbon was in the form of CO\(_2\). The yield is much lower compared to the gasification of phenol under the same experimental conditions. The increase in gaseous carbon yield takes place in two steps: initial gas generation during 0-20 s and secondary gas generation after 20 s. Early formation of CO\(_2\) occurs directly from benzene. This is consistent with the work of Goodwin and Rorrer\(^{2}\), who suggested that benzene is reformed in SCW to a mixture of CO and H\(_2\). However, the yield was much lower compared to that of phenol SCWG, suggesting that the direct pyrolysis of benzene is not favorable and elevated temperatures are needed. The increase in carbon gas yield and its composition with extended residence times is indicative of another mechanism of CO\(_2\) formation. Similarly to phenol, a ring-opening mechanism is very possible in the case of benzene. As discussed in several studies\(^{8,10}\), benzene rings can rupture under supercritical conditions to produce intermediates that are decomposed further, before being reformed to yield CO\(_2\) and H\(_2\). Although it is slower than the first mechanism, this mechanism is believed to cause the increase in CE with residence time.

To further investigate the possibility of the ring-opening mechanism for benzene, it is important to quantify acid compounds (formic and acetic) present in the product yield, as they have been identified as precursors of gas formation. The yield of acid during benzene decomposition is shown in Fig. 5. Acid formation increased tremendously at 450°C, which is consistent with the higher CE obtained at the same temperature. This is an indication of not only a ring-opening mechanism for benzene under SCW but also of the formation of gaseous compounds from intermediate products. This was similarly observed in the SCWO of benzene, in which ring opening of benzene led to the formation of alcohols and acids that ultimately formed CO\(_2\) and H\(_2\)\(^{9}\). A similar mechanism to that of SCWO seems to be occurring here, although SCWO resulted in a higher CE because of the addition of oxygen.

Figure 4(d) shows the char yield during benzene conversion under supercritical conditions. Char formation from benzene is consistent with our previous study of lignin and its model compounds (guaiacol and phenol) in that polymerization of aromatic and phenolic compounds to form char occurs mainly through a radical reaction (Arrhenius behavior). The highest char yield from benzene was 12.57% (450°C and 100 s) in comparison to 24.29% from phenol decomposition under the same conditions. The lower yield of char formation from benzene compared to that from phenol is strongly indicative of the role of the hydroxy group in enhancing the polymerization of aromatic compounds to form char. The phenoxyl radical should enhance polymerization through the formation of ether linkages between aromatic rings.

Unlike phenol char, which is formed through the linkage of ether groups, char formation from benzene...
occurs mainly through ring combination, which ultimately forms a network of fused rings. However, polycyclic aromatic hydrocarbon precursors to char formation, such as naphthalene and anthracene, are thermally stable compounds, and therefore, elevated temperatures are needed for further polymerization to form char. This is in agreement with the study by Sharma et al.\textsuperscript{21}, who deduced that char consisting of a network of fused rings is only formed at around 400-500 °C. The aromaticity and the carbonaceous nature of the char increased with temperature and the char preferentially lost hydrogen as the temperature increased\textsuperscript{21}.

For confirmation of this prediction, we can examine the results of the elemental analysis of the char, as shown in Table 2. CHNS/O analysis of the benzene char showed that the carbon content was 95.2 wt%, while that of benzene was 92.3 wt%. This shows a significant increase in carbon in the solid content, suggesting that char from benzene is likely to consist of a network of fused rings\textsuperscript{21}. The increase in carbon content is consistent with the loss of hydrogen from the char structure (4.7 % in char compared to 7.7 % in benzene).

**Figure 4(e)** shows the hydrogen yield for benzene decomposition. Hydrogen is produced in the initial stages and is then consumed rapidly. Ring opening of benzene and cyclohexane production are associated with hydrogenation consumption, which can explain the hydrogen yield.

One of the main products from benzene decomposition in SCW is phenol, whose yield is shown in **Fig. 6(a)**. The formation of phenol from benzene shows Arrhenius behavior, with the yield increasing tremendously with temperature. This leads us to predict that hydroxylation of benzene to form phenol probably occurs through radical intermediates. As discussed previously for the conversion of phenol under the same conditions, benzene formation from phenol exhibits non-Arrhenius behavior with a higher yield at near-critical conditions, which leads us to predict that it occurs via an ionic reaction. However, interestingly, in the case of phenol formation from benzene, it is most

**Table 2** Elemental Analysis of Benzene and Char Obtained from Experiment (370-450 °C, 25 MPa, 0.1 wt% benzene, and 0.5-100 s residence times)

| Types of compounds | Elemental analysis [kg/kg-dry] |
|--------------------|-------------------------------|
|                    | C    | H    | N    | S    | O (balance) |
| Benzene            | 0.923 | 0.077 | 0.000 | 0.000 | 0.00 |
| Char               | 0.952 | 0.047 | 0.000 | 0.000 | 0.01 |
likely to be a radical reaction. Catechol and naphthalene yields are shown in Figs. 6(b) and 6(c), respectively. They are quantified in this study as representative structures of phenolic and dimerization products. The catechol yield is significantly smaller than that of naphthalene, indicating that dimerization is a more favorable pathway than hydroxylation for the formation of phenolic compounds under supercritical conditions. Formation of catechol from benzene occurs with phenol as the main intermediate compound, as discussed previously. In addition, benzene can form the phenyl radical, which in turn can undergo dimerization at high temperatures and pressures, leading to dimers such as naphthalene19).

The high yield of naphthalene comparable to char formation could explain the low char yield obtained in the case of benzene decomposition in SCW. As discussed previously, char from benzene consists of a network of fused rings. Therefore, dimerization to form naphthalene is the initial pathway. However, naphthalene, as with any other polycyclic aromatic hydrocarbon, is a thermally stable compound, and thus, elevated temperatures are needed for further polymerization to form char.

3.3. Proposed Reaction Pathways of Phenol and Benzene Decomposition in SCW

Overall, based on the product yields as shown in Figs. 1-3 and on the mechanism discussed, we can established the pathways of phenol decomposition under supercritical conditions into the major and minor ones. It is evident from Fig. 1 that the major pathways should be the formation of gaseous compounds and char, in addition to other unknown liquid constituents in the TOC. The minor pathways of phenol decomposition lead to the formation of benzene, catechol, and naphthalene. In addition, we further concluded that the direct formation of char and gas from phenol is possible due to its rapid formation within a very short residence time apart from the further conversion from TOC. The slow formation of naphthalene indicates that it is the secondary decomposition products from benzene instead of direct formation from phenol.

For the case of benzene decomposition in supercritical water as identified in Figs. 4-6, the major pathways are evidently towards naphthalene, gaseous compounds, TOC, and char. Other minor pathways are towards the formation of catechol and phenol. Similar to phenol, direct formation of char and gaseous compounds from benzene is possible apart from further degradation of the TOC constituents. In addition, similar to the case of naphthalene formation from phenol, naphthalene is formed preliminarily through benzene.

Based on the our experimental results for both phenol and benzene decomposition in SCW as discussed in Sections 3.1, and 3.2., the proposed reaction pathways are classified into major and minor pathways, and the resulting reaction network is shown in Fig. 7.
4. Conclusions

The decomposition of phenol and benzene was studied in SCW at 370-450 °C and 25 MPa for very short residence times (0.5-100 s). Under these conditions, we conclude that the decomposition of phenol and benzene is relatively slow although the formation of char and gas are observed in addition to other intermediate compounds such as catechol and naphthalene. Similarly to lignin and model compounds such as guaiacol, char formation pathways are in competition with gas production, especially for enhanced temperatures and residence times. Phenol decomposition is faster than that of benzene owing to the presence of resonance-stabilized phenoxy radicals, which are believed to play a key role in enhancing the rate of reaction of phenol in SCW. This study demonstrates the importance of the ring-opening mechanism in further degrading aromatic and phenolic compounds into intermediates that are ultimately polymerized to form char or degraded into gaseous compounds via acid precursors. In addition, the formation of phenol from benzene shows Arrhenius behavior. The formation of benzene from phenol, however, decreases with temperature in SCW (non-Arrhenius behavior). This implies that the reaction is strongly influenced by the dielectric constant and ionic product, which decrease tremendously as the temperature increases under supercritical conditions. From the deduced mechanisms, we have proposed reaction pathways for the decomposition of phenol and benzene in SCW.

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要  旨

超臨界水ガス化におけるフェノールとベンゼンの分解経路

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フェノールとベンゼンの超臨界水中における分解に及ぼす温度（370 〜 450 ℃）と滞留時間（0.5 〜 100 s）の影響を25 MPaで検討した。これらの分解温度は比較的低いが、滞留時間20 sでは炭素とガスの生成が進行し、温度と滞留時間とともにこれらの収率は増加した。フェノールならびにベンゼンからのチャーチャー生成はガス生成と競合していた。ベンゼンの分解速度はフェノールよりも遅く、共鳴により安定するフェノキシジカルの生成が分解に重要な役割を果たしていると考えられる。フェノールの超臨界水ガス化では、熱分解による直接ガス生成が進行していると考えられるが、ベンゼンの超臨界水ガス化については、ガス化は二つの異なる経路で進行していると考えられる。直接的なガス生成は反応初期の数秒間で進行し、芳香族の開環がより長い滞留時間で進行。キ酸やテクサを経由してガス化が進行していると思われる。興味深いことは、ベンゼンからのフェノール生成はアレニウス挙動を示したが、フェノールからのベンゼン生成は高温ほど遅く、非アレニウス挙動を示した。これらに基づいて、超臨界水中におけるフェノールとベンゼンの分解経路を提案した。

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