Experimental investigation of thermal decomposition of dihydroxybenzene isomers: catechol, hydroquinone, and resorcinol

Huamei Yang¹, Yuki Furutani¹, Shinji Kudo², Jun-ichiro Hayashi^{2,3}, and Koyo Norinaga^{*2}

¹*Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, Kasuga, 816-8580, Japan.*

²*Institute for Materials Chemistry and Engineering, Kyushu University, Kasuga, 816-8580, Japan.*

³*Research and Education Centre of Carbon Resources, Kyushu University, Kasuga, 816-8580, Japan.*

^{*} **Corresponding author:** Koyo Norinaga, Tel +81 92 583 7794, Fax +81 92 583 7793
email: norinaga@cm.kyushu-u.ac.jp.

Abstract

In this study, dihydroxybenzene isomers such as catechol, resorcinol, and hydroquinone were used as models of volatiles from solid fuels to better elucidate the mechanism of the thermochemical conversion of solid fuels. These isomers were pyrolyzed in a two-stage tubular reactor with a residence time up to 3.6 s and temperature ranging from 650 to 950 °C. In total, 51 products were identified by online gas chromatography. The product distribution from the pyrolysis of the three isomers was quite different. *p*-Benzoquinone was the primary product obtained from the pyrolysis of hydroquinone, while *o*-benzoquinone and *m*-benzoquinone were not detected from the pyrolysis of catechol and resorcinol, respectively. CO was the major final product formed from catechol, resorcinol, and hydroquinone, with maximum yields of 27.3 wt%, 19.4 wt%, and 20.0 wt%, respectively, whereas CO₂ (15.5 wt%) generated from resorcinol was significantly higher than those generated from hydroquinone (1.0 wt%) and catechol (0.8 wt%) at 950 °C and 0.3 s. Considering the mass selectivity of C₁–C₅ light hydrocarbons, the possible reaction pathways leading to CO and CO₂ were analyzed to describe the pyrolysis of catechol, resorcinol, and hydroquinone. Catechol mainly afforded CO and C₄ hydrocarbons by H-migration and ring-opening reactions. Hydroquinone mainly generated CO, C₂, and C₄ hydrocarbons, with the initial step being the formation of *p*-benzoquinone. During the pyrolysis of resorcinol, competition reactions occurred for the formation of CO and CO₂ with the production of C₁–C₅ hydrocarbons at a nearly equal mass selectivity. Compared with catechol and hydroquinone, resorcinol produced significantly more C₅ hydrocarbons, which suggested the intramolecular combination of aldehyde radical and ketone radical for explaining the large amount of CO₂ formed from the pyrolysis of resorcinol.

Keyword: Reaction mechanism, chemical kinetics, analytical pyrolysis, gas chromatography

1. Introduction

A large amount of energy and fuels is required to drive industrial and economic development. Solid fuels such as coal and biomass can be converted to afford chemicals, fuels, and electrical power by thermochemical conversion processes, such as liquefaction, pyrolysis, gasification, and combustion. Pyrolysis occurs at the initial step of gasification and combustion [1-3]. Commonly, the pyrolysis of solid fuels can be categorized into two stages: primary pyrolysis and vapor-phase cracking (secondary pyrolysis) [4-7]. Solid fuels are converted to volatiles and char during primary pyrolysis, and the cracking of volatiles occurs to yield both light-gas and high-molecular-weight compounds such as polycyclic aromatic hydrocarbons. Vapor-phase cracking is inevitable, which decides the distribution of the final products [1,4]. The complex nature of the solid fuels makes it difficult to gain insight into the vapor-phase reactions with a complex reaction network [2,3,8,9]. It is imperative to investigate the model compounds representing the structural moieties of solid fuels or volatiles derived from the solid fuels for understanding the reaction pathways of vapor-phase reactions during the pyrolysis of solid fuels, as these model compounds could simplify the reaction network.

Dihydroxybenzenes, such as catechol, resorcinol, and hydroquinone, are frequently included in the products obtained from the thermal degradation of solid fuels [10-13]. These compounds represent the simplest structure for investigating the pyrolysis behavior of phenolic compounds found in lignin and coal, and they are chosen as model compounds to obtain further insight into the pyrolysis of solid fuels [12-34]. Their decomposition plays an important role in the vapor-phase reactions of solid fuel conversion; furthermore, they always form polycyclic aromatic compounds, which inevitably result in the blocking and fouling of engines and turbines as well as environmental problems [14-16, 29, 31]. Thus far, the pyrolysis pathway of these isomers has been investigated by two methods: experimental investigation and theoretical calculation. Wornat *et al.* [13-16, 18, 21, 22, 24] have experimentally investigated the thermal decomposition of catechol, with main focus on the formation of polycyclic aromatic hydrocarbons. They have also reported the distribution of C₁–C₆ products generated from the pyrolysis of catechol at temperature ranging from 700 to 1000 °C. Khachatryan *et al.* have investigated the formation of persistent free radicals from the pyrolysis of catechol and hydroquinone by low-temperature matrix isolation electron paramagnetic resonance spectroscopy [17, 28, 32-34]. Truong and Lomnicki *et al.* have investigated the pyrolysis of catechol and hydroquinone for understanding the formation of dibenzofuran and dibenzo-p-dioxin [29, 31]. Altarawneh *et al.* [30] and Khachatryan *et al.* [32, 33] have theoretically investigated the decomposition pathways of catechol and have suggested that the initial step of the reaction involves the migration of hydroxyl H to a neighboring C–H group and the main channel for the decomposition of catechol is ring opening. Altarawneh *et al.* [30] have also calculated the thermochemical properties and

decomposition pathways of three isomeric semiquinone radicals [12]. The main pathway for the decomposition of *o*-semiquinone radicals involves the formation of *cyc*-C₅H₄OH and CO, and with increasing temperature, the formation of *o*-benzoquinone is promoted. The *p*-semiquinone radicals are mainly consumed to form *p*-benzoquinone. Moreover, for *m*-semiquinone radicals, they simply proposed the possible pathway for the formation of *cyc*-C₅H₄OH and CO, as few studies on the pyrolysis behavior of resorcinol, as well as very limited information on its product distribution, are available.

In fact, excluding the careful and detailed investigation for the pyrolysis of catechol by Wornat *et al.* [13-16, 18, 21, 22, 24] as mentioned above, there is limited information available on the pyrolysis behavior and product distribution of hydroquinone and resorcinol. Thus far, only Sakai *et al.* have briefly examined and compared 14 products generated by the pyrolysis of three isomers only at 600 °C [26]. In this study, for acquiring more information on the pyrolysis products under a wide range of conditions and gaining deeper insight into the pyrolysis reaction pathways of dihydroxybenzene isomers, the pyrolysis of catechol, resorcinol, and hydroquinone is investigated by a two-stage tubular reactor (TS-TR) equipped with GC. TS-TR exhibits a high heating rate, and the residence time can change up to 3.6 s at temperatures of 650–950 °C. In total, 51 products were quantified by GC. In addition, the distribution of products as a function of temperature (650–950 °C) at 0.3 s as well as a function of residence time (0.1–3.6 s) was compared in detail from the pyrolysis of catechol, resorcinol, and hydroquinone. The pyrolysis pathways of catechol, resorcinol, and hydroquinone were also discussed on the basis of the products identified.

2. Experimental

2.1 Sample

Three dihydroxybenzene isomers (catechol, resorcinol, and hydroquinone) with purities greater than 99.0% (Wako Pure Chemical Industries, Ltd.) were employed in this study.

2.2. Rapid pyrolysis in TS-TR

TS-TR was employed for investigating the rapid pyrolysis of catechol, resorcinol, and hydroquinone. As shown in Supporting Information Figure S1, TS-TR was employed for investigating the vapor-phase reactions of cellulose and lignin in our previous studies [35-37]. The TS-TR composed of quartz consisted of two zones divided by a quartz wool filter. The first zone was utilized for sample vaporization, while the secondary zone was utilized for vapor-phase pyrolysis reactions. The maximum temperature of the upper part of the TS-TR was less than 70 °C at which the sample was not vaporized. First, 1 mg of sample was wrapped by a 10 mm × 10 mm sheet of stainless (SUS316) wire mesh with a mesh opening of 45 μm. Next, after the lower part of the TS-TR and GC baseline were stabilized, the prepared sample was fixed at the upper part of the TS-TR. Second, the sample was dropped into the bottom of the first hot zone after the TS-TR temperature and GC baseline were stable. Third, volatiles were passed into the secondary zone with a carrier gas at 241 kPa. The residence

times of the volatiles (t_r) in the secondary zone were varied up to 3.6 s by adjusting the effectively heated volume of the second reactor, which can be achieved by moving the furnace. The TS-TR conditions were set at 650–950 °C with $t_r = 0.3$ s or at 750 °C with $t_r = 0.1$ –3.6 s. After passing the secondary zone, volatiles were directed into the GC column with the carrier gas and further identified by a GC detector. The volatile composition was directly measured by two GCs equipped with a thermal conductivity detector (TCD) and/or a flame ionization detector (FID). Inorganic products such as CO, CO₂ and H₂O were detected by TCD, while the other products were detected by FID. For detecting the products in detail, four columns were employed, and supporting information Table S1 lists the chromatographic conditions. Peak assignments were carried out based on the retention time matching with the known compounds. The quantifications of the products were conducted based on the external calibration method which uses response vs amount functions that are subsequently used to estimate amounts of analyte in a separately analyzed sample as long as the standard compounds for the target products and their calibration lines were available. The effective carbon number concept [38, 39] was also employed for estimation of the amounts of products of which standards were unavailable. Product yields were calculated based on the mass of the sample fed. The repeatability examinations for the analytical pyrolysis experiments revealed that the relative errors of the product yield generally within $\pm 10\%$.

3. Results and discussion

As introduced above, Ledesma *et al.* have reported the distribution of C₁–C₆ products generated from the pyrolysis of catechol at 700–1000 °C and 0.4 s [13]. However, thus far, the distribution of these products from resorcinol and hydroquinone has not been investigated in detail, and their pyrolysis pathways have still not been analyzed. In this study, catechol, resorcinol, and hydroquinone were pyrolyzed in the TS-TR equipped with online GC under the following pyrolysis conditions: (i) temperature ranging from 650 to 950 °C with $t_r = 0.3$ s, (ii) at 750 °C with t_r ranging up to 3.6 s. In total, 51 products were quantified by GC and were used to compare the pyrolysis behavior of catechol, resorcinol, and hydroquinone. All products were grouped into 10 chemical families as inorganic gases (IOGs), C₁–C₅ hydrocarbons, light oxygenated compounds (LOCs), aromatic hydrocarbons (AHs), benzoquinone, and phenols. Figure 1 shows the yields of these products and unreacted sample as a function of temperature at 0.3 s (upper) and as a function of t_r at 750 °C (lower). In this study, “yield” was defined as the ratio of the percent of the product mass to that of the sample-feed mass. Detailed information of each chemical family as a function of temperature at 0.3 s and as a function of t_r at 750 °C will be explained in detail in the following two sections.

3.1 Distribution of products as a function of temperature

Figure 1 (upper) shows the yields of products and unreacted sample at 650–950 °C with $t_r = 0.3$ s. The discrepancy in the mass balance, especially at high temperature, is attributed to

the formation of heavy-weight molecules such as polycyclic aromatic hydrocarbons with increasing temperature [14, 16, 19]. In this study, we focused on the decomposition of hydroquinone, catechol, and resorcinol; hence, the effort to detect the heavy-weight molecules or complex molecules is not included here. The yield of unreacted catechol sharply decreased at 750 °C, and its conversion rapidly increased to 100% at temperatures higher than 850 °C. The yields of unreacted hydroquinone and resorcinol significantly decreased more slowly than that of catechol, indicating that the decomposition of catechol is easier than that of hydroquinone and resorcinol.

As shown in Figure 1, *p*-benzoquinone was detected from the pyrolysis of hydroquinone, while *o*-benzoquinone and *m*-benzoquinone was not detected from the pyrolysis of catechol and resorcinol, respectively. This result is in agreement with those published in the studies by Truong and Lomnicki *et al.* [29, 31]. They reported that *p*-benzoquinone is formed by the pyrolysis of hydroquinone at temperatures as low as 250 °C and rapidly disappears at temperatures greater than 700 °C, while *o*-benzoquinone is not observed from the pyrolysis of catechol. In this study, *p*-benzoquinone was formed at 650 °C from the pyrolysis of hydroquinone, with its maximum yield obtained at 750 °C, as shown in Figure 1 (upper). Moreover at temperatures greater than 850 °C, *p*-benzoquinone was completely consumed. As shown in Figure 1, the yields of LOCs obtained from the pyrolysis of the three isomers were very low. The main LOC components were acraldehyde for catechol, 3-pentene-2-one for resorcinol, and 1,4-pentadiene-3-one for hydroquinone, and Figure 2 lists their yields. The maximum yield of LOCs was obtained at 800°C from the pyrolysis of all three isomeric compounds studied.

IOGs, such as CO, CO₂, H₂O, and H₂, are one of the main product groups generated from the three isomers. As shown in Figure 1, the total yield of IOGs increased with increasing temperature. Figure 3 (upper) and Figure 4 (upper) show the yields and oxygen conversions of CO, CO₂, H₂O, and H₂ as a function of temperature, respectively. Oxygen conversion is defined as the percent ratio of the oxygen content in IOGs to that in the feeding sample. CO is the main inorganic gas produced from the pyrolysis of catechol, hydroquinone, and resorcinol. CO was formed from the pyrolysis of catechol at 650 °C, and its yield rapidly increased to the maximum at 750 °C. CO was generated from hydroquinone and resorcinol at temperatures greater than 650 °C, and its yield increased with temperature. The maximum yields of CO produced from hydroquinone and resorcinol were similar, 19.4 wt% and 20.0 wt%, respectively, while the maximum yield of CO produced from catechol was higher than them, 27.3 wt%. The lower yield of CO from the pyrolysis of resorcinol should partially be attributed to the competition pathway for the formation of CO₂. As can be clearly observed in Figure 3 (upper), the pyrolysis of resorcinol generated CO₂ significantly more than that generated from catechol and hydroquinone within the entire temperature range. The yield of CO₂ formed from the pyrolysis of catechol and hydroquinone slightly increased to around 1.00 wt% with increasing temperature to 950 °C, while it is notable that the maximum yield of CO₂ generated from the pyrolysis of resorcinol was 15.5 wt% at 950 °C. As shown in

Figure 4, the oxygen conversion into CO from hydroquinone and catechol was significantly higher than that of CO₂, while the oxygen conversion into CO and CO₂ was similar from resorcinol over the entire range of temperature. Moreover, the yields of H₂ generated from the pyrolysis of the three isomers increased with temperature, as shown in Figure 3 (upper). The yield of H₂ obtained from the pyrolysis of hydroquinone was higher than those obtained from catechol and resorcinol at 650 °C, suggesting that the initial step in the pyrolysis of hydroquinone involves the formation of *p*-benzoquinone. As shown in Figure 3 (upper), the yield of H₂O formed from the pyrolysis of catechol at 650 °C was 0.61 wt%, at which H₂O was almost not formed from the pyrolysis of hydroquinone and resorcinol. The formation of H₂O from the pyrolysis of catechol, resorcinol, and hydroquinone was remarkably promoted between 750 and 800 °C. The generation of H₂O from catechol and hydroquinone (maximum yields of 3.70 wt% and 3.35 wt% at 950 °C, respectively) was significantly more than that from resorcinol (maximum yield of 1.80 wt% at 850 °C). The oxygen conversions into H₂O from hydroquinone and catechol (10.0 wt% and 11.5 wt%, respectively) were higher than that from resorcinol (4.8 wt%), as shown in Figure 4 (upper).

Figure 1 (upper) also summarizes the yields of methane (CH₄), C₂ hydrocarbons (C₂H_n), C₃ hydrocarbons (C₃H_n), C₄ hydrocarbons (C₄H_n), and C₅ hydrocarbons (C₅H_n) as a function of temperature at 0.3 s. The total yields of C₁–C₅ hydrocarbons from hydroquinone and resorcinol were significantly lower than that from catechol. The main hydrocarbon generated from catechol was clearly C₄H_n, appearing at temperatures as low as 650 °C and achieving its peak yield (29.5 wt%) at 750 °C. For better clarity, Figure 5 shows the mass selectivities of CH₄, C₂H_n, C₃H_n, C₄H_n, and C₅H_n. In this study, “mass selectivity” is defined as the percent ratio of the product mass to the sample-converted mass. The pyrolysis of resorcinol produced CH₄ in amounts greater than that produced from that of catechol and hydroquinone. C₂H_n detected in this study included ethane, ethylene, and acetylene, and their peak yields were obtained at 800 or 850 °C. For the three C₂H_n, their peak selectivity decreased in the order of hydroquinone >> catechol > resorcinol. C₃H_n include propane, propylene, allylene, and propadiene. Resorcinol produced C₃H_n with a mass selectivity higher than those of catechol and hydroquinone. In this study, C₄H_n includes 1,3-butadiene and 1-buten-3-yne, of which 1,3-butadiene exhibited a yield significantly higher than that of 1-buten-3-yne. The main compounds generated from the pyrolysis of catechol were C₄H_n (mainly 1,3-butadiene), and its selectivity from catechol was as high as 38.7 wt% even at temperature as low as 650 °C, which is significantly higher than those from other hydrocarbons. The maximum mass selectivity of C₄H_n decreased in the order of catechol >> hydroquinone >> resorcinol. Cyclopentadiene, 1,4-pentadiene, and 1,2-pentadiene were grouped as C₅H_n, of which cyclopentadiene exhibited a yield significantly higher than those of 1,4-pentadiene and 1,2-pentadiene. Cyclopentadiene produced from resorcinol was significantly greater than that produced from catechol and hydroquinone. As can be observed in Figure 5, light hydrocarbons are mainly C₄ hydrocarbons (1,3-butadiene) generated from catechol, C₂H_n and C₄H_n hydrocarbons generated from hydroquinone, while the selectivity of C₁–C₅

hydrocarbons generated from resorcinol is similar to those observed from catechol and hydroquinone. Compared with catechol and hydroquinone, resorcinol preferred to form C_3H_n and C_5H_n .

The total yields of AHs formed from the pyrolysis of catechol, resorcinol, and hydroquinone increased with increasing temperature to 950 °C (Figure 1). The peak yields of AHs from the pyrolysis of catechol, resorcinol, and hydroquinone were observed at 35.1 wt%, 33.0 wt%, and 28.5 wt%, respectively. Figure 6 (upper) shows the yields of the main AHs produced from the pyrolysis of catechol, resorcinol, and hydroquinone as a function of temperature at $t_r = 0.3$ s. The main AHs detected include benzene, toluene, styrene, indene, naphthalene, anthracene, and phenanthrene. The peak yields of toluene and styrene were observed at 850 °C. The yields of benzene and naphthalene increased with increasing temperature to 950 °C. The amount of naphthalene generated from the pyrolysis of resorcinol was more than those generated from the pyrolysis of catechol and hydroquinone, attributed to the higher yield of cyclopentadiene mainly formed by the combination of cyclopentadienyl radicals [13].

Figure 1 (upper) also displays the total yields of phenol and cresols produced from the pyrolysis of catechol, resorcinol, and hydroquinone as a function of temperature at 0.3 s. The peak yield of phenols was achieved at 850 °C. Phenol generated from hydroquinone exhibited a peak yield (14.7 wt%) higher than those generated from catechol (6.1 wt%) and resorcinol (6.5 wt%) at 850 °C. The H-substitution of OH contributes to the formation of phenol from the three isomers with the possibility of H_2O formation. Scheer et al. have proposed a pathway for the combination between radicals to produce phenol ($C_5H_4OH + CH_3 = C_6H_5OH + 2H$) during the pyrolysis of guaiacol [41]. The combination of cyclopenta-2,4-dienone with CH_3 possibly supports the formation of phenol from the three isomers. The formation of cyclopenta-2,4-dienone is the main pathway by which the decomposition of *p*-benzoquinone occurs, accounting for the higher yield of phenol from hydroquinone at 800 °C [12]. The yields of cresols were significantly lower than those of phenol, which are mainly *p*-cresol for hydroquinone, *o*-cresol for catechol, and *m*-cresol for resorcinol.

3.2 Distribution of products as a function of residence time

The effect of t_r on the product distribution was considered at 750 °C with t_r ranging up to 3.6 s. Figure 1 to 6 (lower) show the distributions of products. As shown in Figure 1 (lower), catechol was completely decomposed within 1.2 s, while the yield of unreacted resorcinol and hydroquinone decreased with increasing t_r to 3.6 s. Benzoquinone was not detected from the pyrolysis of catechol and resorcinol at 750 °C within the entire t_r range up to 3.6 s, while the yield of *p*-benzoquinone decreased with increasing t_r to 3.6 s. Figure 2 (lower) shows the yields of the main LOCs generated from the three isomers. The yield of 1,4-pentadien-3-one generated from the pyrolysis of hydroquinone reached its maximum at 0.3 s and then decreased with increasing t_r . The peak yields of acraldehyde and 3-pentene-2-one were observed at 1.2 s during the pyrolysis of catechol and resorcinol at 750 °C.

As shown in Figure 1 (lower), the yield of IOGs generated from resorcinol and hydroquinone increased with increasing t_r , while the yield of IOGs generated from catechol rapidly increased within 0.3 s and peaked at 1.2 s. Figure 3 (lower) shows the yields of each IOG. The CO yield clearly increased within 0.3 s during the pyrolysis of catechol and then was maintained constant at around 26 wt%, while the yields of CO obtained from the pyrolysis of hydroquinone and resorcinol increased to 12.8 wt% and 14.9 wt% with increasing t_r to 3.6 s, respectively. Besides CO, CO₂ is another main IOG generated from resorcinol, as shown in Figure 3 (lower). The yield of CO₂ produced from resorcinol increased to 11.1 wt% with increasing t_r to 3.6 s, while only a small amount of CO₂ was generated from the pyrolysis of catechol and hydroquinone.

The total yield of light hydrocarbons generated from catechol was significantly higher than those generated from hydroquinone and resorcinol, as shown in Figure 1 (lower), as the decomposition of catechol to light products was easier than that of hydroquinone and resorcinol. The peak yield of C₄H_n was as high as 29.5 wt% at 0.3 s, while the yields of other hydrocarbons were significantly lower and increased with t_r . Resorcinol and hydroquinone continuously produced light hydrocarbons, and the yield of C₁–C₅ hydrocarbons increased with t_r . Figure 5 (lower) shows the mass selectivity of each C₁–C₅ hydrocarbon from catechol, resorcinol, and hydroquinone. C₂H_n and C₄H_n are the two main groups generated from hydroquinone, with their peak selectivity at 1.2 s. C₄H_n was the main group generated from catechol, with its peak selectivity at 0.3 s. Resorcinol produced C₁–C₅ hydrocarbons at a nearly equal mass selectivity. The mass selectivity of C₃H_n, C₄H_n, and C₅H_n decreased with increasing t_r during the pyrolysis of resorcinol, and the mass selectivity of C₃H_n and C₅H_n from the pyrolysis of resorcinol was greater than those from catechol and hydroquinone.

As shown in Figure 1 (lower), the yield of AHs increased during the pyrolysis of three isomers with increasing t_r . Figure 6 (lower) shows the yields of the main AHs. The yield of the AHs increased with t_r . Benzene was the main AH generated from the three isomers, and its yield from catechol, resorcinol, and hydroquinone was 12.6 wt%, 7.5 wt%, and 9.1 wt% at 3.6 s, respectively. The yield of styrene from the pyrolysis of catechol within 0.3 s was higher than those from hydroquinone and resorcinol. As compared to hydroquinone and catechol, resorcinol generated more indene and naphthalene. Figure 1 shows the total yields of phenol and cresols as a function of t_r at 750 °C. The yield of phenol and cresol increased with t_r . It was obviously shown that hydroquinone yield much more phenol and cresol than catechol and resorcinol due to the same reason mentioned in section 3.1.

3.3 Pyrolysis pathway of the three isomers

Catechol, resorcinol, and hydroquinone are the simplest model isomers for phenolic units in solid fuels. As described in Sections 3.1 and 3.2, the distribution of products, especially CO, CO₂, and C₁–C₅ hydrocarbons, generated from the pyrolysis of catechol, resorcinol, and hydroquinone was very different as a function of temperature and t_r . The pyrolysis reaction pathway was suggested to be very different, attributed to the two hydroxyl groups located at

the ortho-, meta-, and para-position. Figure 7 to 9 show the reaction pathways leading to CO, CO₂, and C₁–C₅ hydrocarbons during the pyrolysis of catechol, resorcinol, and hydroquinone, respectively. Even the combinations of light hydrocarbons to form AHs are important reactions during the pyrolysis of the three isomers; however, these reactions were not shown.

Figure 7 shows the pyrolysis pathway of catechol to CO and hydrocarbons. Catechol was decomposed at a temperature lower than those of resorcinol and hydroquinone. The major products generated from the pyrolysis of catechol were 1,4-butadiene and CO. Altarawneh *et al.* [30] have compared six pathways for the decomposition of catechol based on quantum calculation. They found that the migration of hydroxyl H to a neighboring carbon, the RC₁ pathway, exhibits a lower energy barrier compared to the RC₆ and RC₁₀ pathway, and is the initial step for the decomposition of catechol below 727 °C [30, 32, 33], followed by the release of two CO and 1,3-butadiene via the RC₁–RC₄ pathway [30]. The intermediate IC₁ formed from the RC₂ pathway was not detected in this study, but it could be proved by the quantified acraldehyde, which would be formed from the decomposition of IC₁ via the RC₅ pathway, along with the formation of C₂H_n and CO. With increasing temperature, the pyrolysis of catechol results in the formation of *o*-benzoquinone (RC₆ pathway), which would be rapidly destroyed to cyclopenta-2,4-dienone or its derivatives (RC₇ pathway) [12, 30]. Cyclopenta-2,4-dienone was possibly decomposed to support the formation of C₂H_n or C₄H_n (RC₈ pathway). Cyclopentadiene formed during the pyrolysis of catechol is mainly attributed to the decomposition of phenol with the release of CO. The H-substitution of OH contributed to the formation of phenol and benzene from the pyrolysis of catechol via the RC₁₀ and RC₁₁ pathways with H₂O formation. As mentioned above, the combination of cyclopenta-2,4-dienone with CH₃ supports the formation of phenol via the RC₉ pathway.

Compared with the wide investigation of catechol [13-24], there is limited literature about the decomposition of hydroquinone to CO and C₁–C₅ hydrocarbons. As for hydroquinone, *p*-benzoquinone was the main product detected at a low temperature and short *t_r*, indicating that the formation of *p*-benzoquinone is the initial step in the pyrolysis of hydroquinone with the release of H radical, as shown in the RH₁ and RH₂ pathways of Figure 8. *p*-Benzoquinone decomposed to generate 1,4-pentadien-3-one via the RH₃ pathway with the release of CO. C₂H_n and C₄H_n were the two main hydrocarbon groups formed from the pyrolysis of hydroquinone. The breakage of 1,4-pentadien-3-one supports the formation of C₂H_n via the RH₄ pathway with CO formation. C₂H_n was also directly formed by the decomposition of *p*-benzoquinone via the RH₅ pathway with the release of CO. The combination of C₂H_n radicals could afford C₄H_n. C₄H_n was also produced from the decomposition of cyclopenta-2,4-dienone via the RH₇ pathway. Cyclopenta-2,4-dienone was formed from the decomposition of *p*-benzoquinone via the RH₆ pathway [41]. As in the case of the catechol pyrolysis, cyclopentadiene formed during the pyrolysis of hydroquinone was mainly generated from the decomposition of phenol via the RH₁₀ pathway with the release of CO. Phenol was mainly formed by H-substitution during the pyrolysis of hydroquinone with possible H₂O formation via the RH₈ pathway. As mentioned above, the combination of

cyclopenta-2,4-dienone with CH₃ supports the formation of phenol via the RH₁₁ pathway.

There are limited studies on the pyrolysis of resorcinol, and limited information is available about the light compounds generated from resorcinol. Figure 9 shows the pyrolysis pathway of resorcinol, which was built on the basis of the product distribution from the pyrolysis of resorcinol by TS-TR. *m*-Benzoquinone was not detected in this study; however, we suppose that *m*-benzoquinone is as an intermediate formed from the pyrolysis of resorcinol. It is unstable and can be rapidly decomposed as the enthalpies of formation of *m*-benzoquinone (2.11 kcal/mol) are significantly higher than those of *p*-benzoquinone (−25.20 kcal/mol) and *o*-benzoquinone (−17.40 kcal/mol)¹². Pent-3-en-2-one quantified from the pyrolysis of resorcinol herein would prove the supposed existence of *m*-benzoquinone to be reasonable as pent-3-en-2-one would be formed by the RR₁ and RR₂ pathways, as shown in Figure 9. Pent-3-en-2-one was decomposed and supported the formation of CH₄ and C₃H_n with the release of CO via the RR₃ reaction pathway. CO is one of the main IOGs obtained from the pyrolysis of resorcinol, which would be similarly formed by the pyrolysis pathways of hydroquinone and catechol. C₄H_n and C₂H_n were formed via cyclopenta-2,4-dienone via the RR₄–RR₇ reaction pathway from *m*-benzoquinone with the formation of CO. The decomposition of phenol could support the formation of C₅H_n and CO by the RR₁₀ reaction pathway. An obvious, a significant difference in the product distributions is the significantly higher yield of CO₂ from resorcinol than those from hydroquinone and catechol. CO₂ could be formed by the water-gas shift reaction (CO + H₂O = CO₂ + H₂). However, this reaction could not explain the high yield of CO₂ generated from resorcinol as the yield of H₂O from resorcinol was significantly lower than those from hydroquinone and catechol. Notably, indene and naphthalene obtained from the pyrolysis of resorcinol exhibited a yield higher than those from the pyrolysis of catechol and hydroquinone. The cyclopentadienyl radical is an important precursor for the formation of indene and naphthalene [37, 38]. The mass selectivity of C₅H_n during the pyrolysis of resorcinol was higher than those obtained from catechol and resorcinol. For explaining the formation of CO₂ from the pyrolysis of resorcinol, the RR₁₂–RR₁₆ reaction pathways with the IR₃ transition state shown in Figure 9 was suggested via the intramolecular combination of aldehyde and ketone radicals. It is difficult for this pathway to occur during the pyrolysis of hydroquinone because of a higher steric hindrance between the two oxygen atoms. As mentioned above, for catechol, the migration of a hydroxyl H to a neighboring carbon was the main and rapid reaction pathway, which gives few chances for the formation of IR₃ during the pyrolysis of catechol.

4. Conclusions

Three dihydroxybenzene isomers, catechol, hydroquinone, and resorcinol, were pyrolyzed in TS-TR for investigating the product distribution at 650–950 °C with *t_r* = 0.3 s and at 750 °C with *t_r* up to 3.6 s. Clear differences in the distribution of the vapor products were observed on the basis of the online analysis and GC quantification. C₄H_n (mainly 1,3-butadiene) constituted the main light hydrocarbons, with its mass selectivity as high as 38.7 wt% from

the pyrolysis of catechol. Catechol was pyrolyzed to light compounds by H-migration and ring-opening reactions to CO and C₄ hydrocarbons. *p*-Benzoquinone was the main product at temperatures lower than 800 °C, and C₂H₄ and C₄H₆ were the main light hydrocarbons, where the initial step involves the decomposition of hydroquinone, with the formation of *p*-benzoquinone, followed by the decomposition of *p*-benzoquinone to afford C₂H₄ and C₄H₆ with the release of CO. As compared to catechol and hydroquinone, resorcinol produced C₁–C₅ hydrocarbons at a nearly equal mass selectivity and generated more C₃ and C₅ hydrocarbons and naphthalene. Notably, CO₂ generated from the pyrolysis of resorcinol (15.8 wt%) was significantly greater than that generated from hydroquinone (1.0 wt%) and catechol (0.8 wt%). A reaction pathway including the intramolecular combination of aldehyde radical and ketone radical attached on cyclopentadiene was suggested for explaining the formation of the large amount of CO₂ from resorcinol.

Acknowledgement

This study was financially supported in part by MOST-JST, Strategic International Collaborative Research Program, SICORP and a Grant-in-Aid for challenging Exploratory Research (Grant No. 15K12266). H.-M.Y. is grateful to the China Scholarship Council (File No. 201206420006).

References:

- [1] H.E. Jegers, M.T. Klein, Primary and Secondary Lignin Pyrolysis Reaction Pathways, Ind. Eng. Chem. Process. (1985) 173–183.
- [2] T.J. Morgan, R. Kandiyoti, Pyrolysis of Coals and Biomass: Analysis of Thermal Breakdown and Its Products, Chem. Rev. 114 (2013) 1547–1607.
- [3] J.E. White, W.J. Catallo, B.L. Legendre, Biomass pyrolysis kinetics: A comparative critical review with relevant agricultural residue case studies, J. Anal. Appl. Pyrolysis. 91 (2011) 1–33.
- [4] J. Caballero, R. Font, A. Marcilla, Kinetic study of the secondary thermal decomposition of Kraft lignin, J. Anal. Appl. Pyrolysis. 38 (1996) 131–152.
- [5] J. A. Caballero, R. Font, A. Marcilla, Study of the primary pyrolysis of Kraft lignin at high heating rates: Yields and kinetics, J. Anal. Appl. Pyrolysis. 36 (1996) 159–178.
- [6] E.B. Ledesma, C. Campos, M.N. Ton, E. A. Dixon, D.J. Cranmer, B.L. Foytik, et al., Vapor-phase cracking of eugenol: Distribution of tar products as functions of temperature and residence time, Energy and Fuels. 27 (2013) 868–878.
- [7] S. Zhou, M. Garcia-Perez, B. Pecha, A.G. McDonald, S.R.A. Kersten, R.J.M. Westerhof, Secondary vapor phase reactions of lignin-derived oligomers obtained by fast pyrolysis of pine wood, Energy and Fuels. 27 (2013) 1428–1438.
- [8] M.A. Serio, D.G. Hamblen, J.R. Markham, P.R. Solomon, Kinetics of Volatile Product Evolution in Coal Pyrolysis : Experiment and Theory, Energy and Fuels. 1 (1987) 138–152.
- [9] A. V. Bridgwater, D. Meier, D. Radlein, An overview of fast pyrolysis of biomass, Organic Geochemistry. 30 (1999) 1479–1493.
- [10] E. Dorrestijn, L.J.J. Laarhoven, I.W.C.E. Arends, P. Mulder, Occurrence and reactivity of phenoxyl linkages in lignin and low rank coal, J. Anal. Appl. Pyrolysis. 54 (2000) 153–192.

442 [11] Z. Maskos, B. Dellinger, Radicals from the oxidative pyrolysis of tobacco, *Energy and*
443 *Fuels*. 22 (2008) 1675-1679.

444 [12] M. Altarawneh, B.Z. Dlugogorski, E.M. Kennedy, J.C. Mackie, Thermochemical
445 properties and decomposition pathways of three isomeric semiquinone radicals, *J. Phys.*
446 *Chem. A*. 114 (2010) 1098–1108.

447 [13] E.B. Ledesma, N.D. Marsh, A.K. Sandrowitz, M.J. Wornat, An Experimental Study on
448 the Thermal Decomposition of Catechol, *Proc. Combust. Inst.* 29 (2002) 2299–2306.

449 [14] M.J. Wornat, E.B. Ledesma, N.D. Marsh, Polycyclic aromatic hydrocarbons from the
450 pyrolysis of catechol (ortho-dihydroxybenzene), a model fuel representative of entities in
451 tobacco, coal, and lignin, *Fuel*. 80 (2008) 1711-1726.

452 [15] E.B. Ledesma, N.D. Marsh, A.K. Sandrowitz, M.J. Wornat, Global kinetic rate
453 parameters for the formation of polycyclic aromatic hydrocarbons from the pyrolysis of
454 catechol, a model compound representative of solid fuel moieties, *Energy and Fuels*. 16
455 (2002) 1331–1336.

456 [16] N.D. Marsh, E.B. Ledesma, A.K. Sandrowitz, M.J. Wornat, Yields of polycyclic aromatic
457 hydrocarbons from the pyrolysis of catechol [ortho-dihydroxybenzene]: Temperature and
458 residence time effects, *Energy and Fuels*. 18 (2004) 209-217.

459 [17] L. Khachatryan, J. Adoukpe, Z. Maskos, B. Dellinger, Formation of cyclopentadienyl
460 radical from the gas-phase pyrolysis of hydroquinone, catechol, and phenol, *Environ. Sci.*
461 *Technol.* 40 (2006) 5071–5076.

462 [18] S. Thomas, E.B. Ledesma, M.J. Wornat, The effects of oxygen on the yields of the
463 thermal decomposition products of catechol under pyrolysis and fuel-rich oxidation
464 conditions, *Fuel*. 86 (2007) 2581-2595.

465 [19] S. Thomas, M.J. Wornat, C(24)H(14) polycyclic aromatic hydrocarbons from the
466 pyrolysis of catechol. *Int J Environ. Anal. Chem.* 88 (2008) 825-840.

467 [20] S. Thomas, M.J. Wornat, The effects of oxygen on the yields of polycyclic aromatic
468 hydrocarbons formed during the pyrolysis and fuel-rich oxidation of catechol. *Fuel*. 87 (2008)
469 768-781.

470 [21] S. Thomas, M.J. Wornat, Effects of acetylene addition on yields of the C1-C10
471 hydrocarbon products of catechol pyrolysis, *Energy and Fuels*. 22 (2008) 976–986.

472 [22] S. Thomas, M.J. Wornat, Polycyclic aromatic hydrocarbons from the co-pyrolysis of
473 catechol and 1,3-butadiene, *Proc. Combust. Inst.* 32 I (2009) 615–622.

474 [23] M. Asmadi, H. Kawamoto, S. Saka, Thermal reactivities of catechols/pyrogallols and
475 cresols/xlenols as lignin pyrolysis intermediates, *J. Anal. Appl. Pyrolysis*. 92 (2011) 76–87.

476 [24] N.B. Poddar, S. Thomas, M.J. Wornat, Polycyclic aromatic hydrocarbons from the
477 co-pyrolysis of catechol and propyne, *Proc. Combust. Inst.* 33 (2011) 541-548.

478 [25] S. Thomas, N.B. Poddar, M.J. Wornat, Identification of Methylene-Bridged Polycyclic
479 Aromatic Hydrocarbon Products of Catechol Pyrolysis. *Polycyclic Aromatic Compounds*, 32
480 (2012) 531-555.

481 [26] T. Sakai, M. Hattori, Thermal Decarbonylation of Catechol, Hydroquinone and
482 Resorcinol. *Chem. Lett.* 1976 (1976) 1153-1156.

483 [27] J. Adoukpe, L. Khachatryan, B. Dellinger, Radicals from the gas-phase pyrolysis of
484 hydroquinone: 1. Temperature dependence of the total radical yield, *Energy and Fuels*. 22
485 (2008) 2986-2990.

486 [28] L. Khachatryan, J. Adoukpe, B. Dellinger, Radicals from the gas-phase pyrolysis of
487 hydroquinone: 2. Identification of alkyl peroxy radicals, *Energy and Fuels*. 22 (2008) 3810–

3813.

[29] S. Lomnicki, H. Truong, B. Dellinger, Mechanisms of product formation from the pyrolytic thermal degradation of catechol, *Chemosphere*, 73 (2008) 629-633.

[30] M. Altarawneh, B.Z. Dlugogorski, E.M. Kennedy, J.C. Mackie, Theoretical study of unimolecular decomposition of catechol, *J. Phys. Chem. A*. 114 (2010) 1060–1067.

[31] H. Truong, S. Loranicki, B. Dellinger, Mechanisms of molecular product and persistent radical formation from the pyrolysis of hydroquinone, *Chemosphere*. 71 (2008) 107-113.

[32] L. Khachatryan, J. Adoukpe, R. Asatryan, B. Dellinger, Radicals from the Gas-Phase Pyrolysis of Catechol: 1. o-Semiquinone and ipso-Catechol Radicals, *J. Phys. Chem. A*. 114 (2010) 2306-2312.

[33] L. Khachatryan, R. Asatryan, C. McFerrin, J. Adoukpe, B. Dellinger, Radicals from the gas-phase pyrolysis of catechol. 2. Comparison of the pyrolysis of catechol and hydroquinone, *J. Phys. Chem. A*. 114 (2010) 10110–10116.

[34] L. Khachatryan, J. Adoukpe, B. Dellinger, Formation of phenoxy and cyclopentadienyl radicals from the gas-phase pyrolysis of phenol, *J. Phys. Chem. A*. 112 (2008) 481–487.

[35] K. Norinaga, T. Shoji, S. Kudo, J.I. Hayashi, Detailed chemical kinetic modelling of vapour-phase cracking of multi-component molecular mixtures derived from the fast pyrolysis of cellulose, *Fuel*. 103 (2013) 141–150.

[36] K. Norinaga, H. Yang, R. Tanaka, S. Appari, K. Iwanaga, Y. Takashima, et al., A mechanistic study on the reaction pathways leading to benzene and naphthalene in cellulose vapor phase cracking, *Biomass and Bioenergy*. 69 (2014) 144–154.

[37] H.M. Yang, S. Appari, S. Kudo, J. Hayashi, K. Norinaga, **Detailed Chemical Kinetic Modeling of Vapor-Phase Reactions of Volatiles Derived from Fast Pyrolysis of Lignin**, 54 (2015) 6855-6864.

[38] Y.R. Huang, Q.Y. Ou, W.L. Yu, The Effect of Compound Structure on the Elemental Responses in Gas Chromatography-Microwave Induced Plasma Atomic Emission-Spectrometry, *J. Chromatogr. Sci.* 28 (1990) 584-588.

[39] J.T. Scanlon, D.E. Willis, Calculation of Flame Ionization Detector Relative Response Factors Using the Effective Carbon Number Concept. *J. Chromatogr. Sci.* 23 (1985) 333-340.

[40] A.M. Scheer, C. Mukarakate, D.J. Robichaud, M.R. Nimlos, G.B. Ellison, Thermal decomposition mechanisms of the methoxyphenols: Formation of phenol, cyclopentadienone, vinylacetylene, and acetylene, *J. Phys. Chem. A*. 115 (2011) 13381–13389.

[41] D.J. Robichaud, A.M. Scheer, C. Mukarakate, T.K. Ormond, G.T. Buckingham, G.B. Ellison, et al., Unimolecular thermal decomposition of dimethoxybenzenes., *J. Chem. Phys.* 140 (2014) 234302.

Figure Captions

Figure 1. Distributions of products obtained from the rapid pyrolysis of hydroquinone, catechol, and resorcinol as function of temperature ranging from 650 to 950 °C at 0.3 s (upper) and at a residence time of 0.1–3.6 s and 750 °C (lower).

Figure 2. Yields of the main light oxygenated compounds (LOCs) obtained from the rapid pyrolysis of hydroquinone, catechol, and resorcinol as a function of temperature ranging from 650 to 950 °C at 0.3 s (upper) and as a function of residence time ranging from 0.1 to 3.6 s and 750 °C (lower).

Figure 3. Yields of light oxygenated compounds (LOCs) from the rapid pyrolysis of hydroquinone, catechol, and resorcinol as a function of temperature ranging from 650 to 950 °C at 0.3 s (upper) and as function of residence time ranging from 0.1 to 3.6 s at 750 °C (lower).

Figure 4. Oxygen conversion of inorganic gases (IOGs) from the rapid pyrolysis of hydroquinone, catechol, and resorcinol as function of temperature ranging from 650 to 950 °C at 0.3 s (upper) and as a function of residence time ranging from 0.1 to 3.6 s at 750 °C (lower).

Figure 5. Selectivities of hydrocarbon groups from the rapid pyrolysis of hydroquinone, catechol, and resorcinol as a function of temperature ranging from 650 to 950 °C at 0.3 s (upper) and as a function of residence time ranging from 0.1 to 3.6 s at 750 °C (lower).

Figure 6. Distributions of AHs from the rapid pyrolysis of hydroquinone, catechol, and resorcinol as a function of temperature ranging from 650 to 950 °C at 0.3 s (upper) and as a function of residence time ranging from 0.1 to 3.6 s at 750 °C (lower).

Figure 7. Reaction pathways for the decomposition of catechol.

Figure 8. Reaction pathways for the decomposition of hydroquinone.

Figure 9. Reaction pathways for the decomposition of resorcinol.

■ Unreacted sample ■ Benzoquinon ■ Phenols ■ IOGs ■ AHs ■ LOCs
 ■ CH₄ ■ C₂H_n ■ C₃H_n ■ C₄H_n ■ C₅H_n

Figure 1. Distributions of products obtained from the rapid pyrolysis of hydroquinone, catechol, and resorcinol as function of temperature ranging from 650 to 950 °C at 0.3 s (upper) and at a residence time of 0.1–3.6 s and 750 °C (lower).

Figure 2. Yields of the main LOCs obtained from the rapid pyrolysis of hydroquinone, catechol, and resorcinol as a function of temperature ranging from 650 to 950 °C at 0.3 s (upper) and as a function of residence time ranging from 0.1 to 3.6 s and 750 °C (lower).

CO
 CO₂
 H₂O
 H₂

Figure 3. Yields of IOGs from the rapid pyrolysis of hydroquinone, catechol, and resorcinol as a function of temperature ranging from 650 to 950 °C at 0.3 s (upper) and as function of residence time ranging from 0.1 to 3.6 s at 750 °C (lower).

Figure 4. Oxygen conversion of IOGs from the rapid pyrolysis of hydroquinone, catechol, and resorcinol as function of temperature ranging from 650 to 950 °C at 0.3 s (upper) and as a function of residence time ranging from 0.1 to 3.6 s at 750 °C (lower).

Figure 5. Selectivities of hydrocarbon groups from the rapid pyrolysis of hydroquinone, catechol, and resorcinol as a function of temperature ranging from 650 to 950 °C at 0.3 s (upper) and as a function of residence time ranging from 0.1 to 3.6 s at 750 °C (lower).

Benzene
 Toluene
 Styrene
 Naphthalene
 Anthracene
 Phenanthrene
 Indene

Figure 6. Distributions of AHs from the rapid pyrolysis of hydroquinone, catechol, and resorcinol as a function of temperature ranging from 650 to 950 °C at 0.3 s (upper) and as a function of residence time ranging from 0.1 to 3.6 s at 750 °C (lower).

Figure 7. Reaction pathways for the decomposition of catechol.

Figure 8. Reaction pathways for the decomposition of hydroquinone.

Figure 9. Reaction pathways for the decomposition of resorcinol.