



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



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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.

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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

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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 Fig. 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 ±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. Fig. 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.

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