

Formation of Polycyclic Compounds from Phenols by Fast Pyrolysis

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Abstract

An analytical pyrolysis gas chromatography mass spectrometry method has been used for investigation into the reaction mechanism leading to polycyclic compounds such as polycyclic aromatic hydrocarbons and heterocyclic compounds. Six phenols with different pendant groups were used in this study. The formation mechanism of producing naphthalene and dibenzofuran from phenol is proposed. In this mechanism, a cyclohexadiene-1-one radical was an important intermediate for the formation of these products. Three unique products were detected from m-cresol: 3,7-dimethyldibenzofuran, 1,7-dimethyldibenzofuran and 1,9-dimethyldibenzofuran. Cyclohexadiene-1-one radical was also found to be an important intermediate for dimerization reaction. Guaiacol pyrolysis yielded phenol as the major product, with a small amount of benzofuran. There arrangement of methoxyl group to methyl group and addition of methyl radical on phenoxy radical was a crucial route in this mechanism. From pyrocatechol, three indanone derivatives were produced via CO elimination with aromatic ring opening followed by pentadienone formation. After two proton donation, three pentanone biradicals were intra molecularly coupled to form indanones. From syringol pyrolysis, only benzofuran was produced, and from ethyl phenol, three types of benzofuran were detected containing different pendant groups such as methyl, ethyl and ethenyl groups. These results indicated that the phenol's ortho position is a vital reaction site for the formation of polycyclic compounds in pyrolysis.

Keywords: Phenols; Analytical pyrolysis; polycyclic compound; Formation mechanism

Introduction

Various polycyclic compounds, polycyclic aromatic hydrocarbons (PAHs) and other hetero-polycyclic compounds are generated from biomass combustion in residential stoves, fireplaces and manufacturing biomass boilers [1-3], and some are ubiquitous and toxic pyrolysis products [4,5]. PAHs and other organic compounds were detected in ash from biomass combustion [6]. This indicated that the analysis of PAHs content in ash is necessary when utilized as fertilizer. Fabri *et al.* [7] found that the PAHs content in a bio-oil from fast pyrolysis of poplar wood increased dramatically when pyrolysis was conducted over HZSM-5 zeolite. Carlson *et al.* reported that aromatics and polymer fragments are produced from catalytic fast pyrolysis of carbohydrate on solid acid catalyst [8].

Bio-oil produced from fast pyrolysis of biomass is considered a new resource and substitute for fuel oil or diesel in many static applications such as boilers, furnaces, engines and turbines for electricity generation and chemical production [9]. Many types of reactors have been examined for bio-oil production, and pilot plants have also been established worldwide [10,11]. Many agricultural crops and processes yield residues that can potentially be used for energy applications, in a number of ways. Several studies on pyrolysis conversion using residual plants and crops, such as softwood bark [12,13] hardwood [14], wheat straw [15], rice husk [16], tobacco residue

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[17], orange waste [18], giant cane [19], palm oil waste [20] and microalgae [21] have been reported. These plants consist of cellulose, hemicellulose and lignin. Therefore, bio-oil is a mixture of pyrolysates derived from these components. Lignin is the second most abundant natural biopolymer found in lignocellulosic plants, and it is a heterogeneous and complex polymer synthesized mainly from three p-hydroxycinnamyl alcohols differing in their degrees of methoxylation: p-coumaryl, coniferyl and sinapyl alcohol. Each monolignol gives rise to a different lignin type called the p-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) units, respectively, which together generate a variety of structures and linkages within the polymer [22-24]. Therefore, various phenols are generated from pyrolysis of biomass and lignin derivatives [25,26]. Some of these phenols can be further pyrolyzed to form more stable polycyclic structures such as benzofurans and PAHs. This hypothesis is supported by the following reports in which polycyclic compounds were generated from lignin model compounds. It was reported that pyrolysis of guaiacol and 2-ethoxyphenol yielded benzofuran and xanthene derivatives as well as from tars [27,28]. Britt *et al.* [29] found benzofuran and dehydrobenzofuran in the pyrolysate from β -alkyl aryl ether model compound pyrolysis. Faix *et al.* [30] also detected 9, 10-dihydrophenanthrene in addition to naphthalene from the pyrolysis products of lignin dimer models. These model phenols were induced from biomass pyrolysis as primary products, and some of the phenols are converted to polycyclic compounds by a radical coupling reaction. In this reaction pathway, lignin derivatives and biomass yielded polycyclic products. From Kraft lignin pyrolysis, polycyclic compounds such as naphthalene and 3-methoxy-2-naphthalenol were detected [31], and 2,3-dihydrobenzofuran was found from pyrolysate of moso bamboo meal [32] and switch grass [33]. Naphthalene and methylnaphthalene were also detected from the pyrolysate of alfalfa [34]. From pyrolysate of tobacco stem, benzofuran, 2,3-dihydrobenzofuran, indene, naphthalene and acenaphthylene were founded [35].

As mentioned above, many monomeric phenols were formed by pyrolysis of dimeric lignin models, isolated lignin and lignocellulose. These monomeric phenols consist of C6-C3, C6-C2, C6-C1 and a C6 structure. They are produced by primary pyrolytic degradation of lignin polymer and subjected to further homolytic reactions such as elimination of pendant groups and condensation. These low molecular primary products can be subjected to inter and/or inner condensation to produce polycyclic compounds as secondary pyrolysates. The bio-oil produced from pyrolysis of biomass consists of phenols; therefore, additional formation and emission of PAHs during combustion of bio-oil is of concern. In some cases, bio-oil may be used as an agricultural boiler fuel, and the possibility of contamination of crops by PAHs is to come out. This study evaluates the formation mechanism of polycyclic compounds such as PAHs and furans during a fast pyrolysis process and explores the possibility of the formation and emission during bio-oil combustion.

Materials and Methods

Six phenols were purchased from Wako Pure Chemical Industries, Ltd., Osaka, Japan as guaranteed grade. These samples were pyrolyzed with a Frontier Lab PY-2020iD pyrolyzer. Each dried sample cup was inserted into the pyrolyzer chamber, which was previously purged with helium gas. After pre-heating the furnace in the pyrolyzer (400-600°C), each sample was placed in the middle of the furnace for 0.2 min and then moved to the top of the furnace. The pyrolysates produced at these temperatures were separated and analysed using a GC/MS system coupled directly to the pyrolyzer. The GC/MS conditions are described below.

An Agilent GC/MS system consisting of an Agilent 6890 gas chromatograph and an Agilent 5975 inert MS selective detector was used to separate and obtain the MS spectra of the compounds derived from each sample. The samples were injected in split mode (100:1 ratio). The carrier gas was helium with a flow rate of 0.93 mL/min. The oven was initially maintained at 40°C for 5 min and ramped at a rate of 4°C/min up to 250°C, and then maintained at this temperature for 60 min. An Rtx-Wax cross-linked polyethylene glycol fused-silica capillary column (RESTEC, 60m \times 0.25mm i.d., 0.25 μ m film thickness) was used to separate the samples. The column was interfaced directly to the electron impact ion source of the MS. The ion source was operated at 70eV, and the injection port was set at 250°C. The separated peaks were identified using the NIST05 MS Library.

Results and Discussion

Formation of phenols and polycyclic compounds from Japanese cedar by fast pyrolysis

Area percentage, rather than the absolute area, was utilized as the dependent variable to eliminate any inconsistencies due to variations in the sample size and product carryover. It was confirmed that the contribution of the area for a given peak was statistically similar between experiments. As is common for pyrolysis-GC/MS, most of the pyrolysis products were identified by comparing their mass data with data in a widely used MS database. However, some of the products were not registered in this database. Therefore, these compounds were identified using the mass fragmentation method, their GC retention times and the MS database.

The total ion chromatograph (TIC) obtained from the Py-GC/MS of Japanese cedar at 600°C is shown in (Figure 1) Several pyrolysis products were produced from wood components such as lignin, hemicellulose and cellulose. Major pyrolysis products from lignin were pyrocathecol, 4-Ethylphenol, 2-methoxyphenol (guaiacol) and phenol. As minor products, naphthalene and 1-indanone were detected. The same results were obtained from pine wood [25], guayule [33] and tobacco stem [34]. To determine the relationship of these phenols and polycyclic compounds, six phenols were prepared and subjected to pyrolysis. The structures and abbreviations of these phenols are illustrated in (Figure 2)

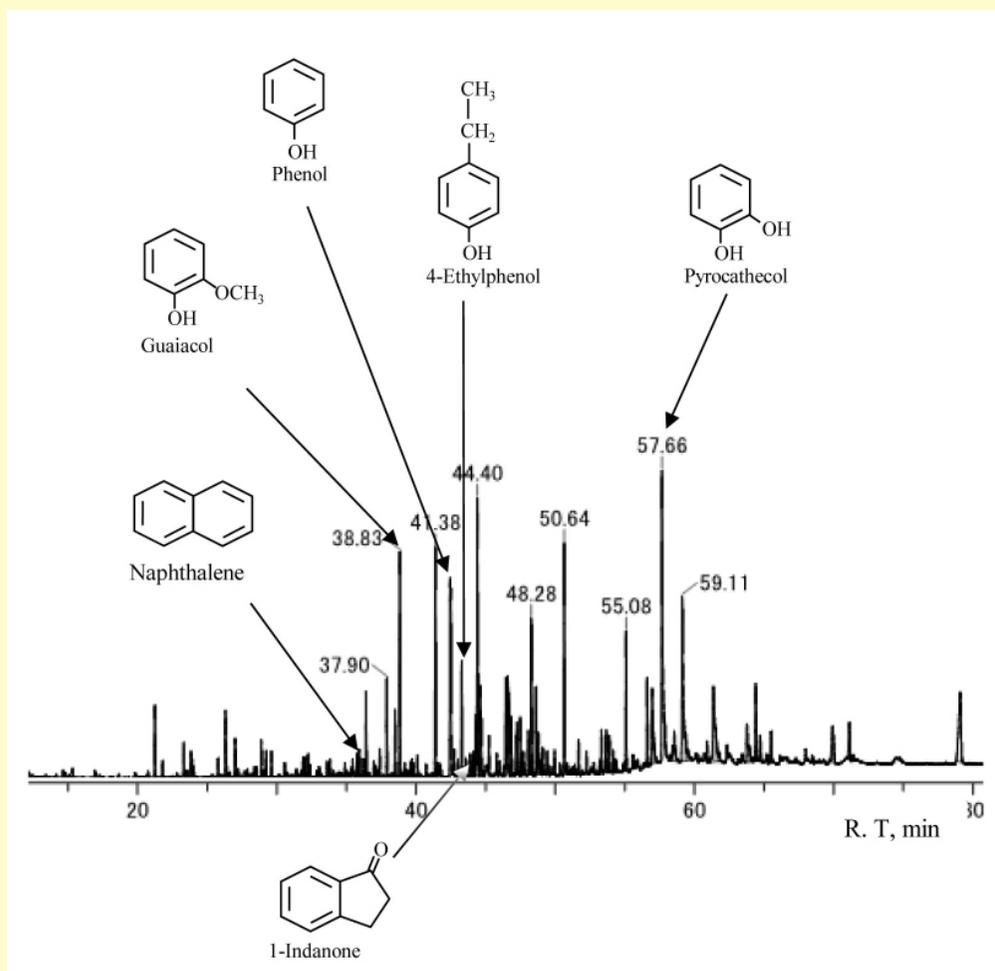


Figure 1: Total ion chromatograph for bio-oil from Japanese cedar at 600°C.

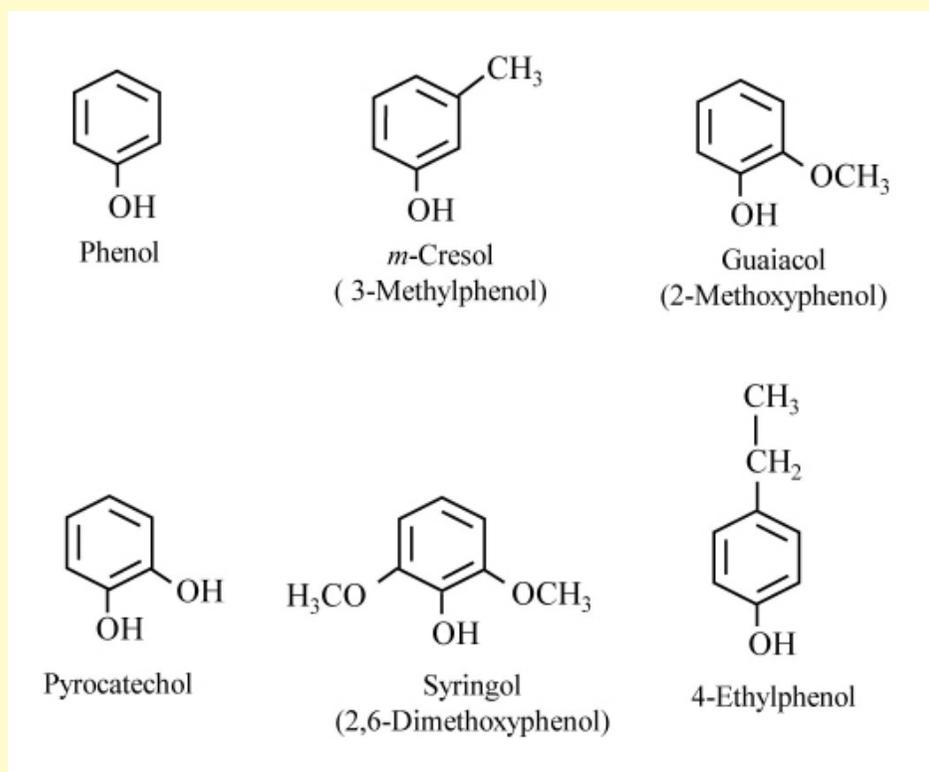


Figure 2: Phenols used in this study.

Pyrolysis of phenol

The TIC profile and MS spectra, with chemical structures of products (1) and (2) obtained from the Py-GC/MS of phenol at 600°C, are shown in (Figure 3). In this TIC profile, only two pyrolysis products and an unreacted starting material were detected. Generally, simple compounds (with low leaving group content) are considered more stable to thermal treatment than complex compounds with large numbers of leaving groups [35]. On the basis of their MS spectra, products (1) and (2) were identified as naphthalene and dibenzofuran, respectively.

The yields of products (1) and (2) increased with increasing pyrolysis temperature, from 400 to 600°C (Figure 4). This indicates that the formation reactions are accelerated at higher thermal conditions and both pyrolysis products are stable under the thermal condition without thermal degradation.

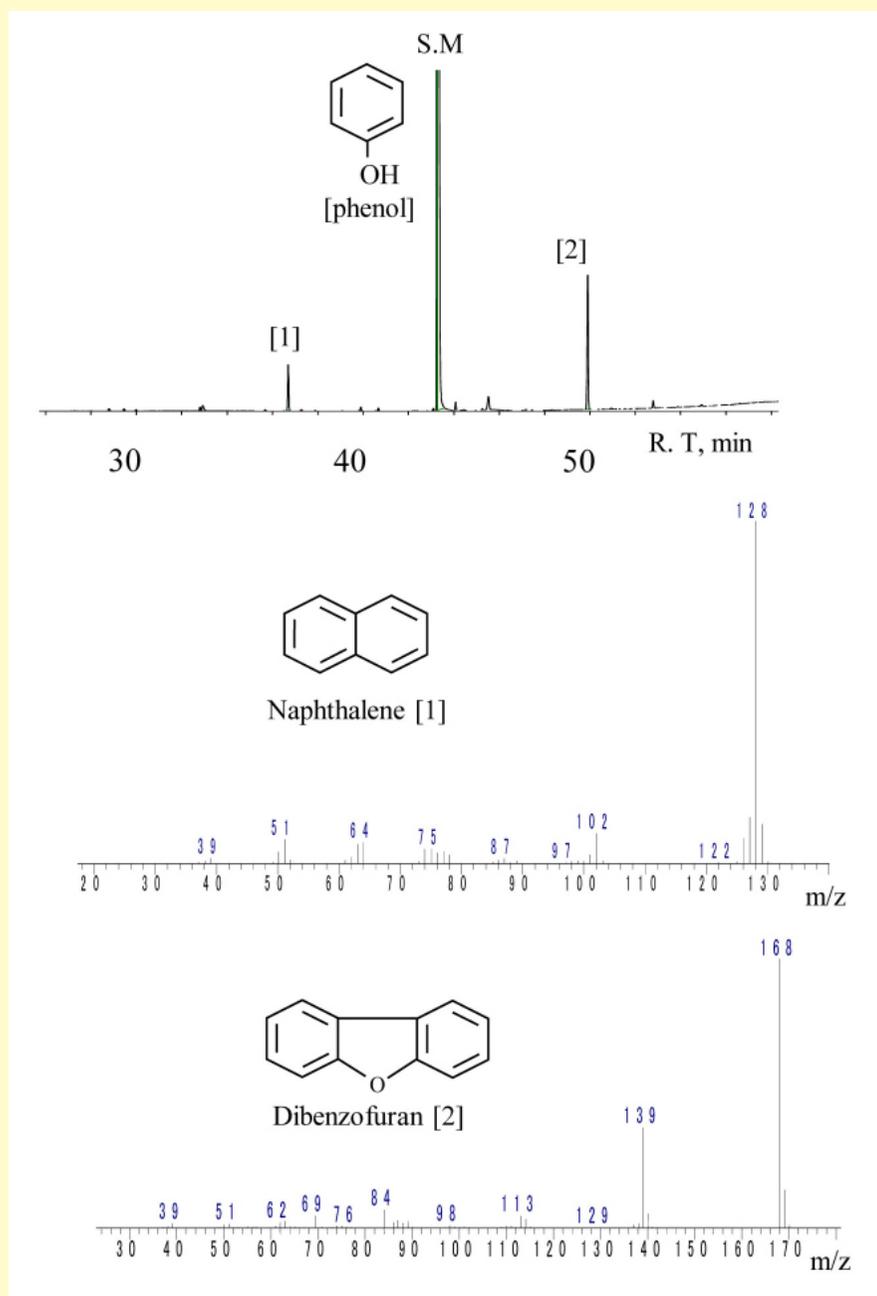


Figure 3: Total ion chromatograph for Py-GC/MS of phenol at 600°C and mass spectra of products (1) and (2).

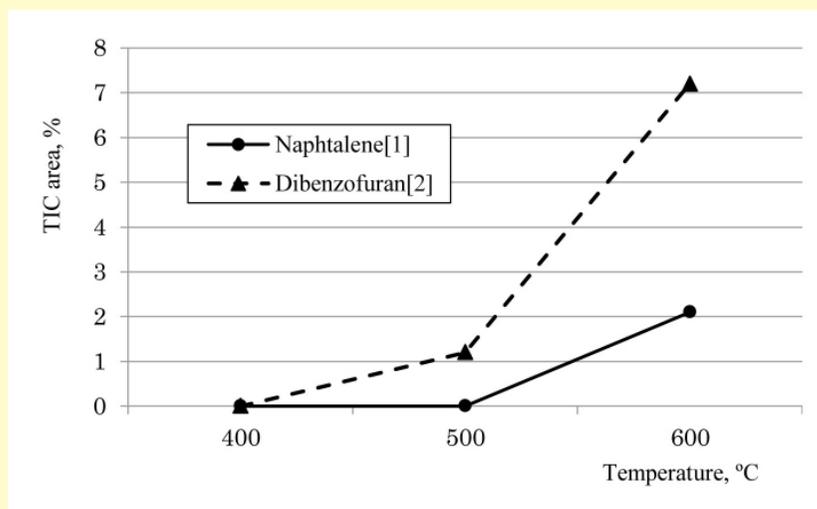


Figure 4: Effect of pyrolysis temperature on product yields of (1) and (2).

The proposed formation pathways of these products are illustrated in Figure 5. Cyclopentadiene is an important intermediate for the formation of naphthalene. The formation of the cyclopentadiene intermediate is initiated by the proton radical donation from the phenolic hydroxyl group of phenol followed by the radical transfer to the ortho quinone radical (route A). Then, elimination of CO from the ortho-radical occurs to yield the corresponding pentadienyl biradical and form cyclopentadiene. The unsaturated bond in this intermediate structure is subjected to homolytic electron transfer to form two pentenyl biradicals. These biradicals couple with each other to form a polycyclic product. Naphthalene is produced by the intermolecular arrangement associated with four proton radical releases (route B). This pathway was proposed by Egsgaard *et al.* [36]. Conversely, another formation mechanism was proposed by Evans *et al.* [37] and Melius *et al.* [38]. They reported that naphthalene is produced by a combination and rearrangement of two cyclopentadienyl radicals. The cyclopentadienyl radicals are formed from the elimination of a CO from phenol. The former pathway includes a two point coupling of biradical structures, and the latter pathway includes a one point coupling of radical structures. In both mechanisms, pentadienyl radical is a key intermediate as shown by Khachatryan *et al.* [39]. This compound is possibly carcinogenic to humans (Group 2B) and is a known product from biomass combustion [40].

Dibenzofuran is formed via radical coupling of two ortho radicals of phenol, and intermolecular condensation of a phenoxy radical with an aromatic carbon radical (route C). This formation mechanism has been proposed [37], and supported [41,42]. This compound has no serious effects on human health although it exhibits an irritating odour.

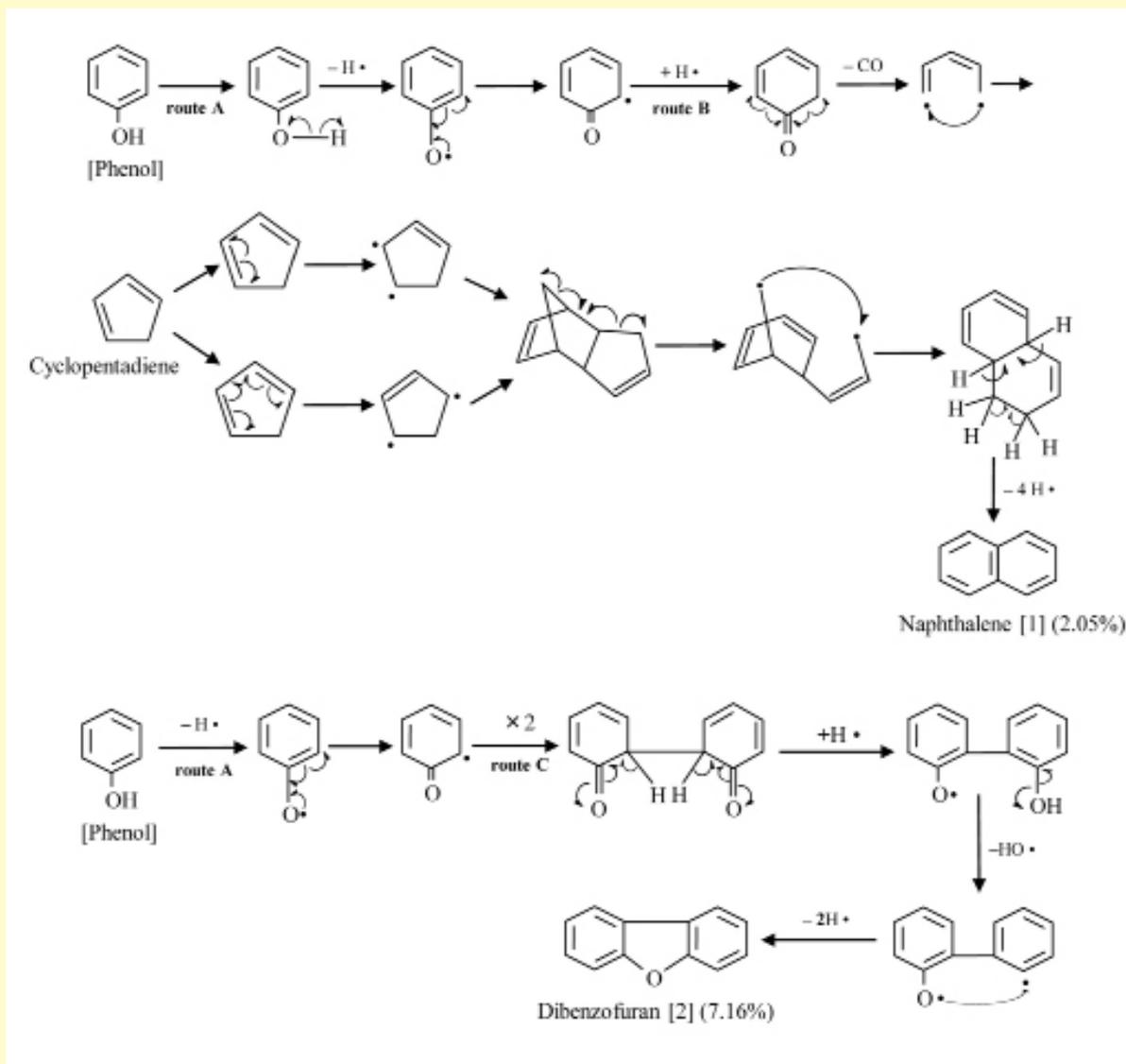


Figure 5: Proposed pathways for the formation of products (1) and (2).

Pyrolysis of m-cresol

The TIC profile and the MS spectra, with chemical structures of products (3), (4) and (5) obtained from the Py-GC/MS of m-cresol at 600°C , are shown in Figure 6. Product (3) was identified as phenol, and it is inferred that naphthalene and dibenzofuran were produced from this product in an undetectable amount with GC as shown in 3.2. On the basis of the MS spectra, products (4), (5) and (6) were identified as 1,7-dimethyldibenzofuran, 3,7-dimethyldibenzofuran, and 1,9-dimethyldibenzofuran, respectively. In the case of pyrolysis at low temperature (400 or 500°C), these products were not detected and the starting material remained without thermal degradation.

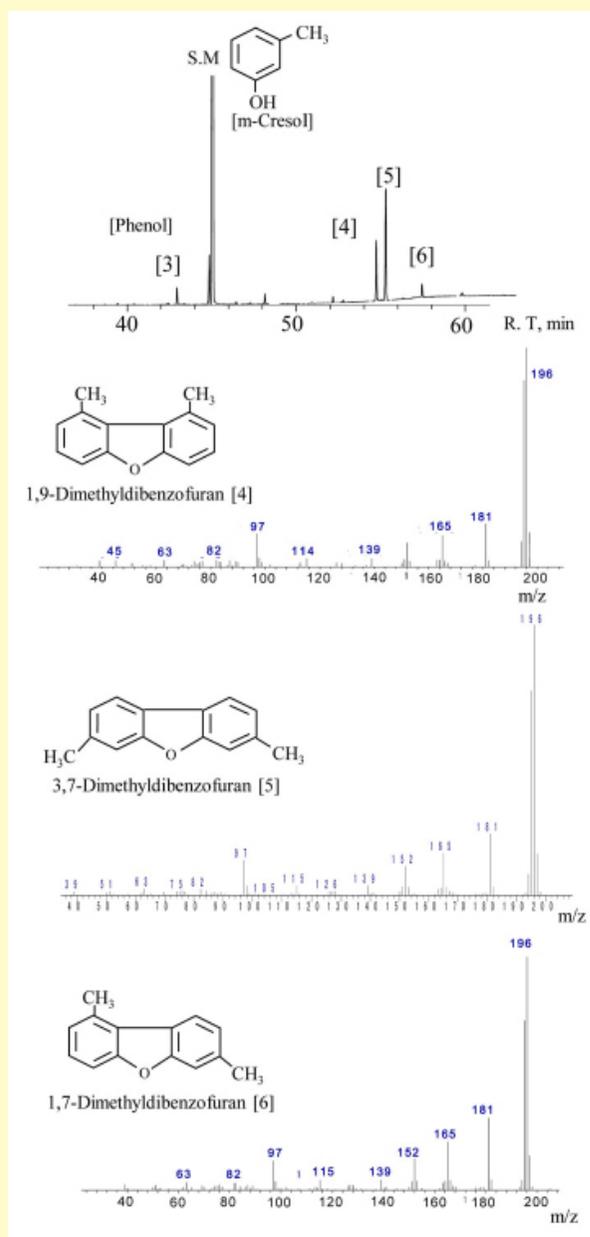


Figure 6: Total ion chromatograph for Py-GC/MS of m-cresol at 600°C and mass spectra of products (4) and (5).

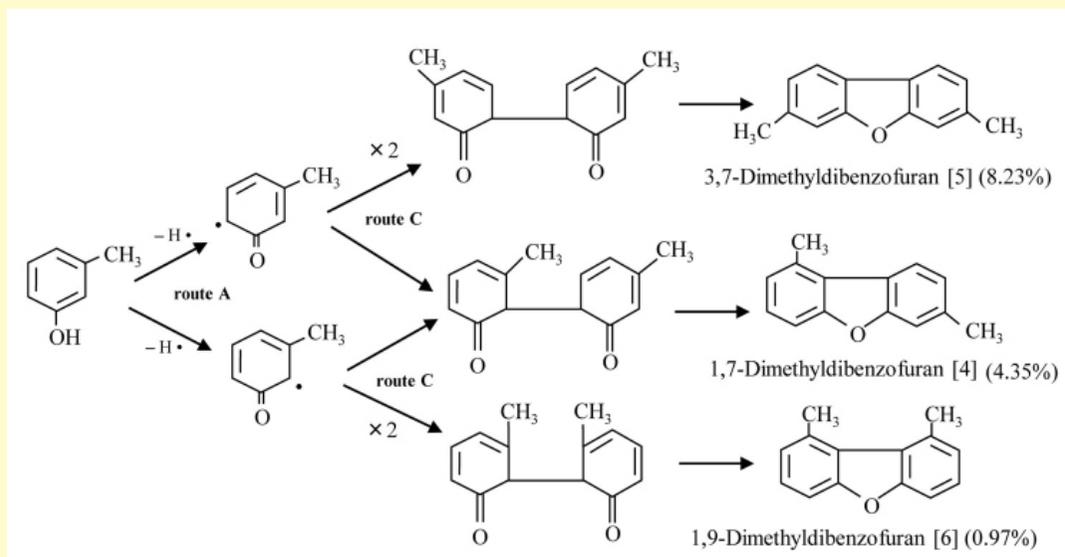


Figure 7: Proposed pathway for the formation of products (3)-(5).

The proposed formation pathways of these products are illustrated in Figure 7. In the first step of these pathways, two types of quinonemethide radicals (5-methyl-2,4-cyclohexadiene-1-one radical and 5-methyl-3,5-cyclohexadiene-1-one radical) are formed by proton radical donation from the hydroxyl group of m-cresol (the first half of route A). These radicals are considered to be important intermediates. Radical coupling with each other yields three kinds of dimers of 5-methyl-cyclohexadiene-1-one. These dimers are then subjected to intra molecular coupling (route C), as shown in Figure 5, to form 3,7-dimethyldibenzofuran, 1,7-dimethyldibenzofuran and 1,9-dimethyldibenzofuran.

Pyrolysis of guaiacol

The TIC profile and the MS spectra, with chemical structures of products (3) and (7) obtained from the Py-GC/MS of guaiacol at 600°C, are shown in Figure 8. Product (3) is the major pyrolysis product and identified as phenol, while product (7) was the minor product and identified as benzofuran.

The proposed formation pathway of product (7) is illustrated in Figure 9. Guaiacol, as a starting material, is subject to rearrangement of the methoxyl group to epoxide, which is initiated by proton radical donation from the methoxyl group. Then, the epoxide is opened by cleavage of the O-C (aromatic) bond to form the hydroxyl methyl group followed by elimination to form the o-cresol radical (route D). These reaction mechanisms are proposed by Asmadi *et al.* [28]. A proton radical donation at the hydroxyl group followed by addition of a methyl radical produces the biradical of 2-methylanisol. The radical undergoes intra molecular coupling to form benzofuran (route E). This compound was detected as the minor product. Therefore, this formation pathway may be an inconsequential reaction in guaiacol pyrolysis.

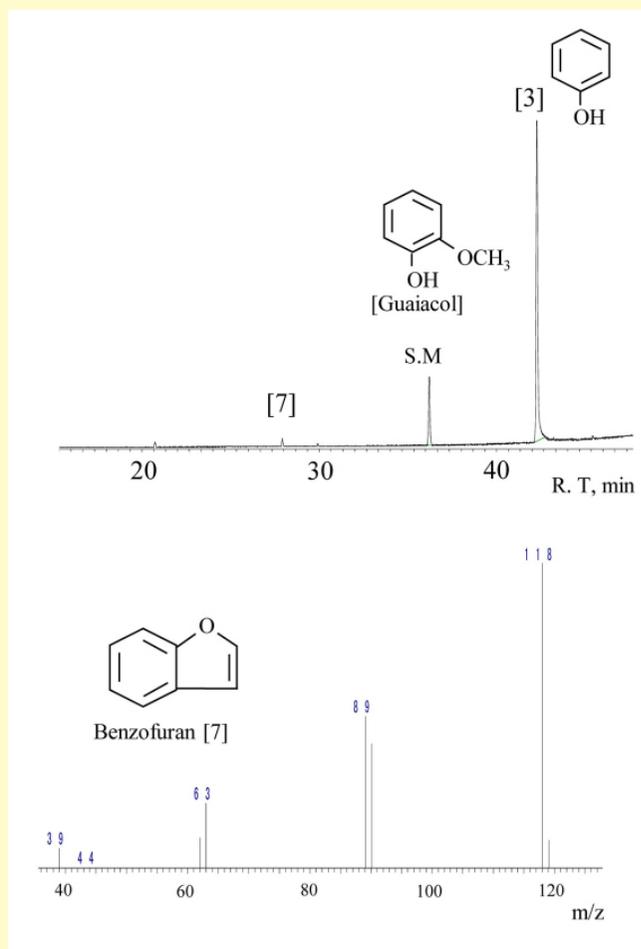


Figure 8: Total ion chromatograph for Py-GC/MS of guaiacol at 600 °C and mass spectrum of product (6).

Pyrolysis of pyrocatechol

The TIC profile and the MS spectra, with chemical structures of products (8), (9) and (10) obtained from the Py-GC/MS of pyrocatechol at 600°C, are shown in Figure 10. On the basis of their MS spectra, these products are assumed to have an indanone structure and products (8), (9) and (10) were identified as 2-indanone, 1-indanone and 1-dehydroindanone, respectively. Only product (8) was detected from the pyrolysate at 500°C, while the other products were not detected, as shown in Figure 11. The proposed formation pathways of these products are illustrated in Figure 12. The pyrolytic reaction is initiated by the formation of o-quinone from pyrocatechol, and CO elimination occurs to form a pentadienone biradical. Intra molecular radical coupling of the biradical produces cyclopentadienone as an important intermediate. The cyclopentadienone is subjected to two different electron transfers, forming two biradical structures: 3-cyclopentene-1-one (a) and 2-cyclopentene-1-one (b). Further reactions occur as two proton additions and an electron transfer occur in biradical structure (a) to form a new biradical structure (c). These biradical intermediates couple with each other and produce three indanone derivatives (route B). Coupling (a) with (c) and an electron transfer produces 2-indanone product (8), (route F). Coupling (a) with (b) and an electron transfer produces 1-dihydroindanone (product 10, route G). 1-Indanone is produced by two proton addition at the C1–C2 unsaturated bond of 1-dihydroindanone (product 9, route H).

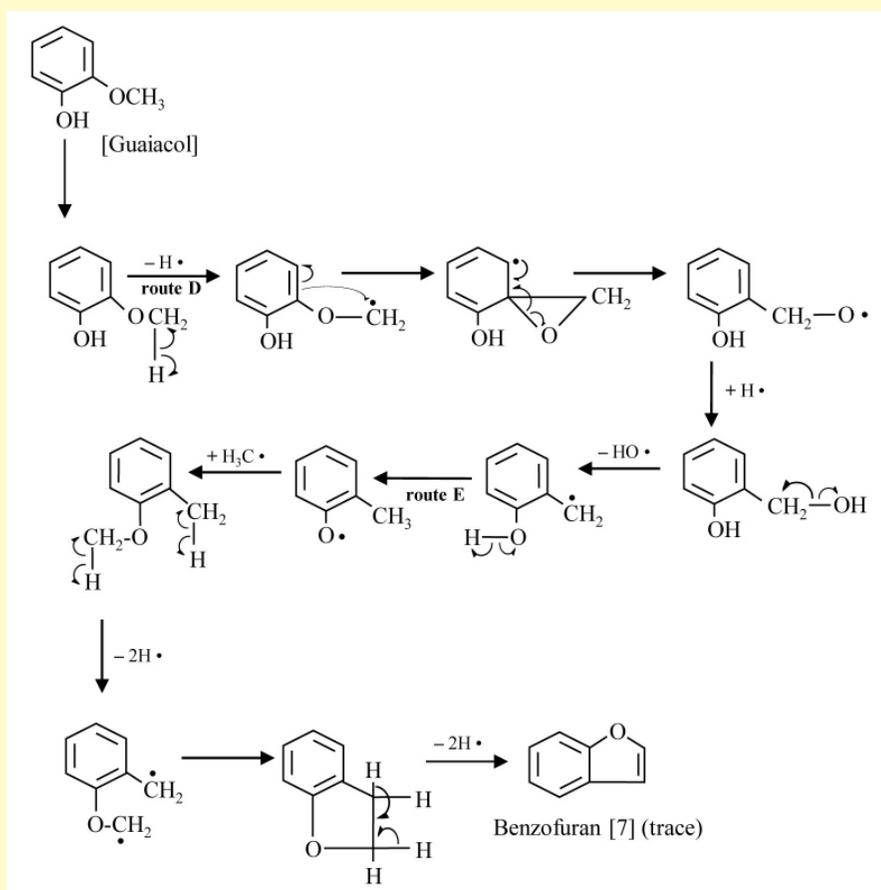


Figure 9: Proposed pathway for the formation of products (3) and (6).

Pyrolysis of syringol

The TIC profile and MS spectra, with chemical structures of products (7) and (11-15) obtained from the Py-GC/MS of guaiacol at 600°C, are shown in (Figure 13). Product (6) was identified as benzofuran and the only polycyclic compound obtained from syringol. Peaks 11-15 were identified as 1,3-dimethoxybenzene, guaiacol, o-cresol, 1,3-dimethoxyphenol and homovanillin, respectively. These compounds are formed by elimination of the methoxyl or hydroxyl groups and rearrangement of the methoxyl group to methyl or aldehyde groups. Benzofuran (product 6) is formed via a guaiacol intermediate in route E as shown in the pyrolysis of guaiacol section.

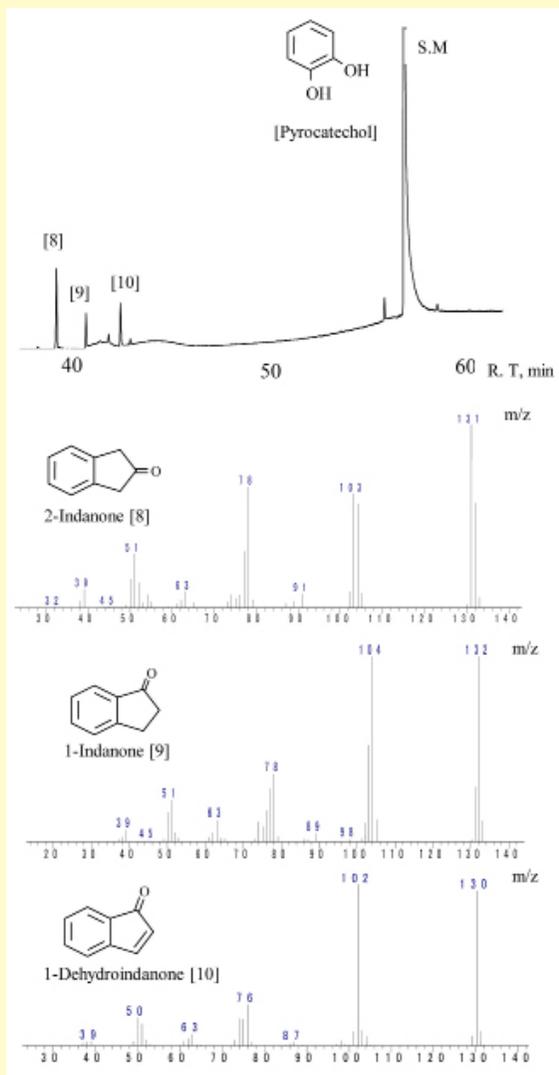


Figure 10: Total ion chromatograph for Py-GC/MS of pyrocatechol at 600 °C and mass spectra of products (7)-(9).

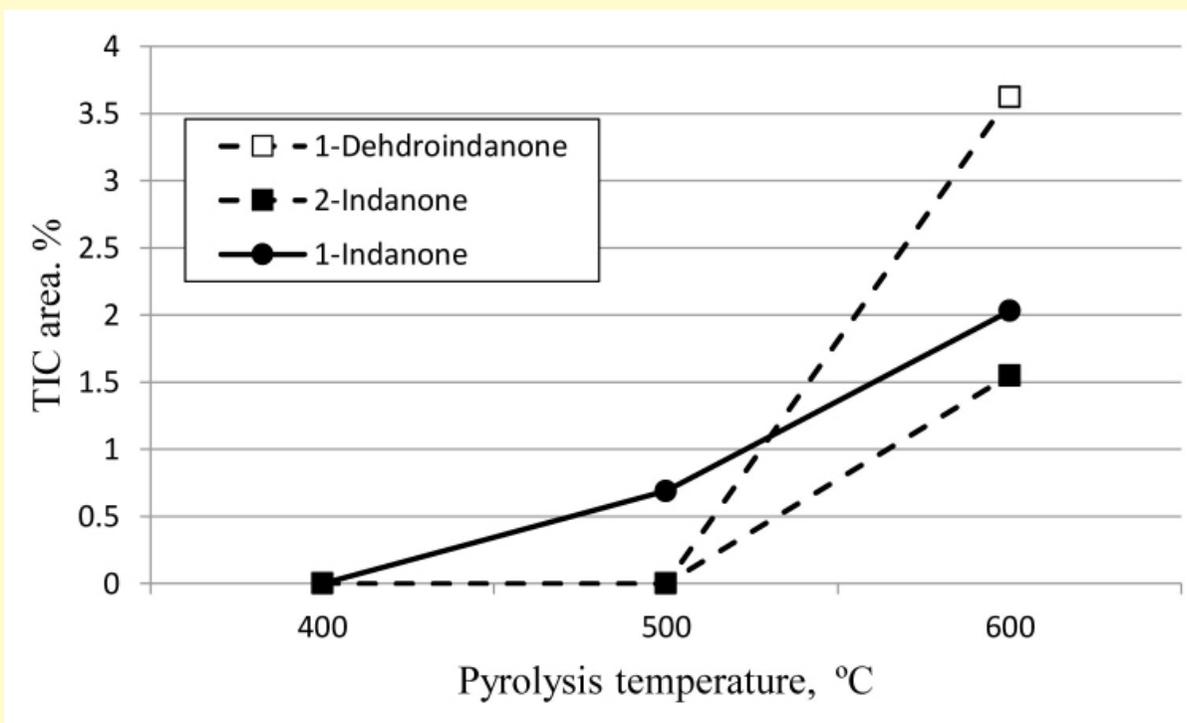


Figure 11: Effect of pyrolysis temperature on products yields of (7)-(9).

Pyrolysis of ethyl phenol

The TIC profile and MS spectra, with chemical structures of products (3), (7) and (16-21) obtained from the Py-GC/MS of guaiacol at 600°C, are shown in (Figure 14). Products (3), (16), (20) and (21) are not polycyclic compounds and are identified as phenol, 4-ethylanisol, p-cresol and 4-vinylnisol, respectively. These four polycyclic products were detected as benzofuran derivatives. Product (7) was identified as benzofuran, and products (17), (18) and (19) were identified as 5-methylbenzofuran, 5-ethylbenzofuran and 5-ethenylbenzofuran, respectively. The proposed formation pathways of these products are illustrated in (Figure 15). These benzofuran derivatives are formed in the same reaction route E, as shown in (Figure 9), except for ethyl radical addition. These radicals are induced from phenol, ethyl phenol and ethenyl phenol as well as o-quinonmetide. Addition of the ethyl radical to cyclohexadiene-1-one radicals followed by intra molecular radical coupling produced the dihydrobenzofuran radicals. Elimination of the two proton radicals resulted in products (7) and (17-19) (route I).

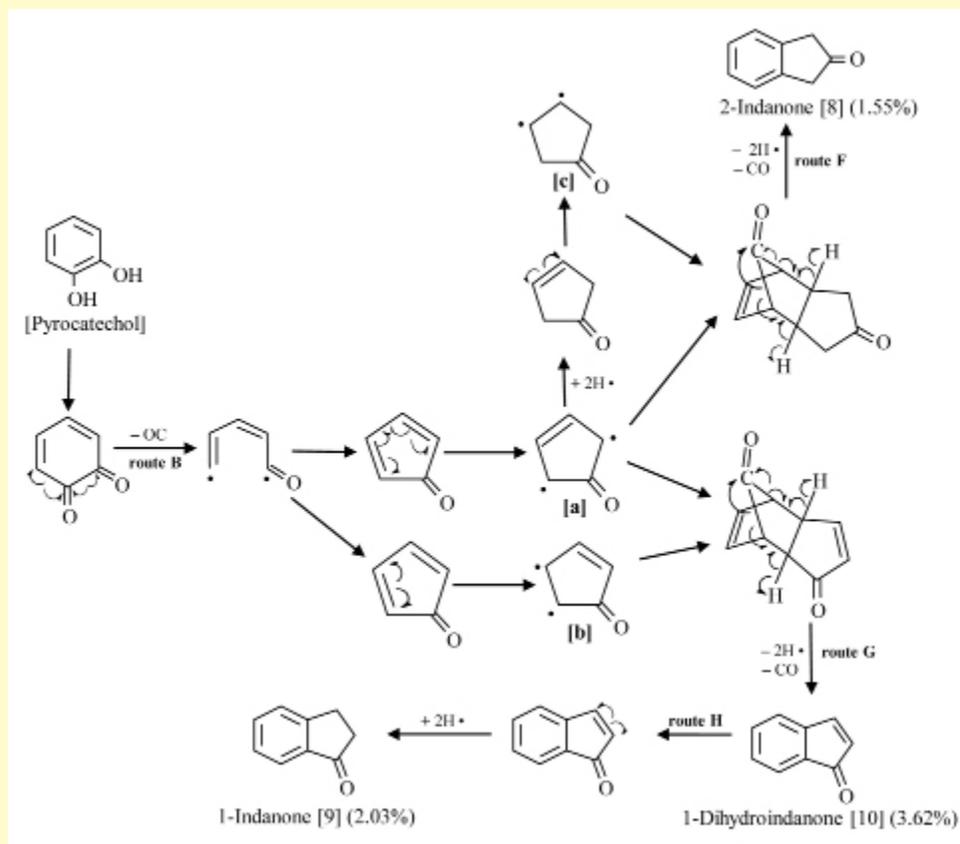


Figure 12: Proposed pathway for the formation of products (7)-(9) from pyrocatechol.

Conclusion

Six phenols with different pendant groups were used in this study for the investigation into the reaction mechanism leading to polycyclic compounds such as polycyclic aromatic hydrocarbons and heterocyclic compounds. The formation mechanism of producing naphthalene and dibenzofuran from phenol is proposed. In this mechanism, a cyclohexadiene-1-one radical was considered an important intermediate for the formation of these products. Three unique products were detected from *m*-cresol: 3,7-dimethyldibenzofuran, 1,7-dimethyldibenzofuran and 1,9-dimethyldibenzofuran. Cyclohexadiene-1-one radical was also found to be an important intermediate for the dimerization reaction. Guaiacol pyrolysis yielded phenol as the major product along with a small amount of benzofuran. In this formation mechanism, rearrangement of a methoxyl group to a methyl group and addition of a methyl radical on the phenoxy radical was a crucial route. From pyrocatechol, three indanone derivatives were produced via CO elimination with aromatic ring opening followed by pentadienone formation. After two proton donation, three pentanone biradicals were intramolecularly coupled to form indanones. From syringol pyrolysis, only benzofuran was produced, and from ethyl phenol, three types of benzofuran were detected containing different pendant groups such as methyl, ethyl and ethenyl group. From the results, it was determined that the ortho position of the phenol is considered an important reaction site for the formation of polycyclic compounds in pyrolysis. The polycyclic compounds detected in this study are formed easily from pyrolysis of phenols, and those phenols are abundant in the bio-oil. Therefore, incomplete combustion of bio-oil may lead to the emission of various polycyclic compounds.

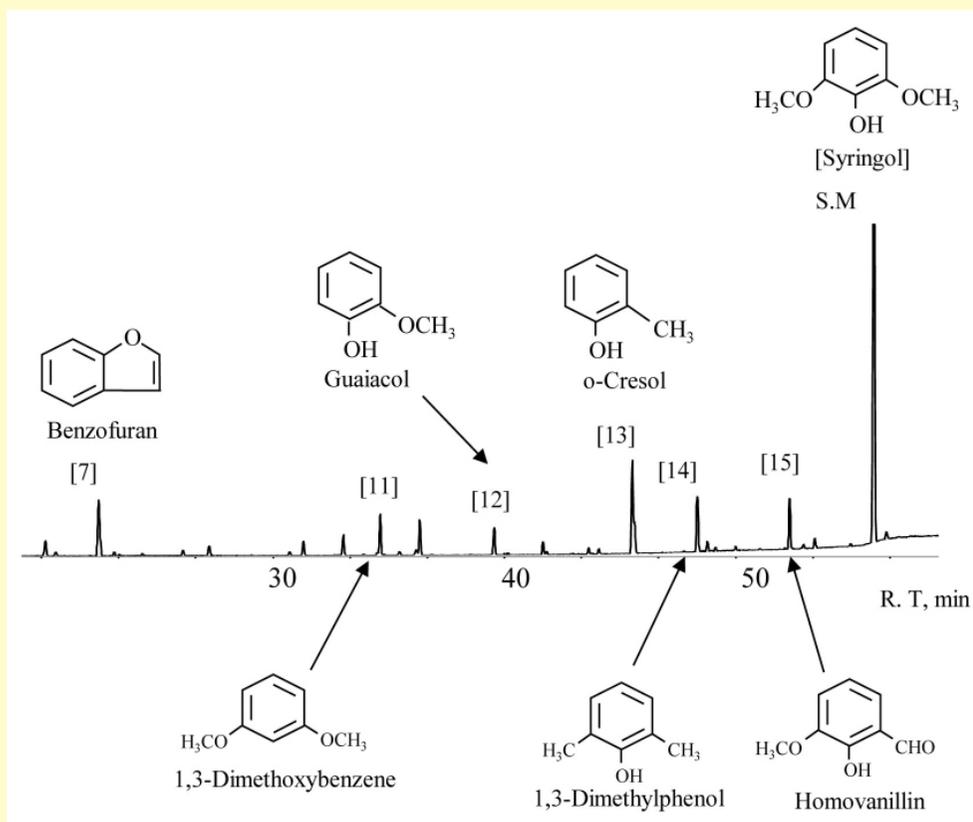


Figure 13: Total ion chromatograph for Py-GC/MS of syringol at 600 °C.

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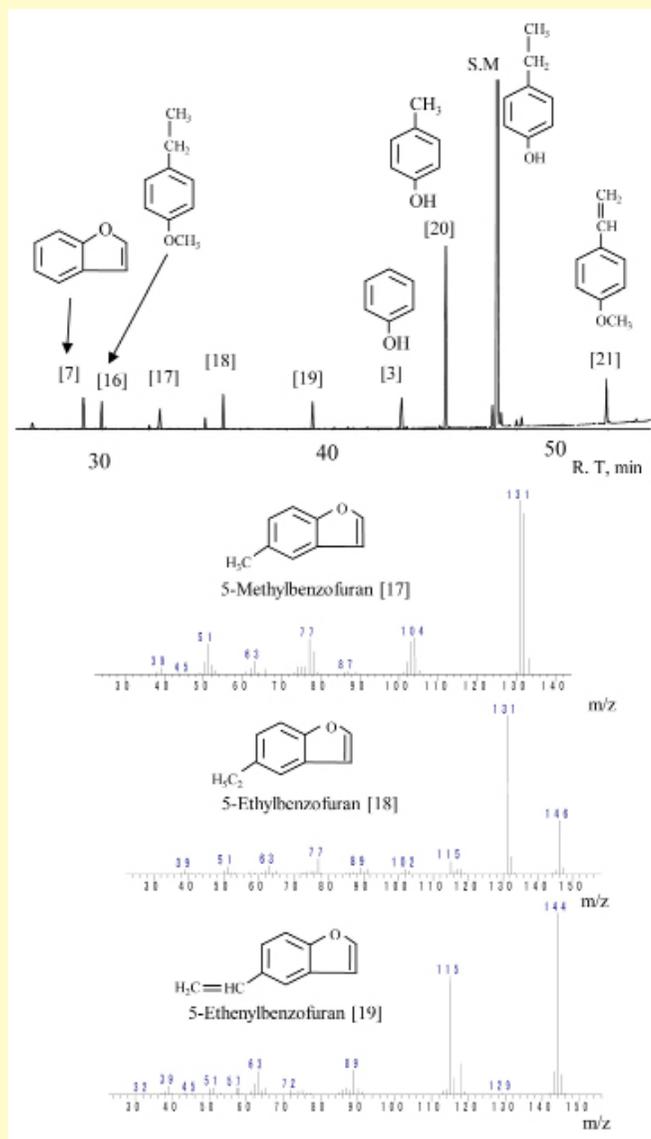


Figure 14: Total ion chromatograph for Py-GC/MS of 4-ethylphenol at 600 °C and mass spectra of products (16)-(18).

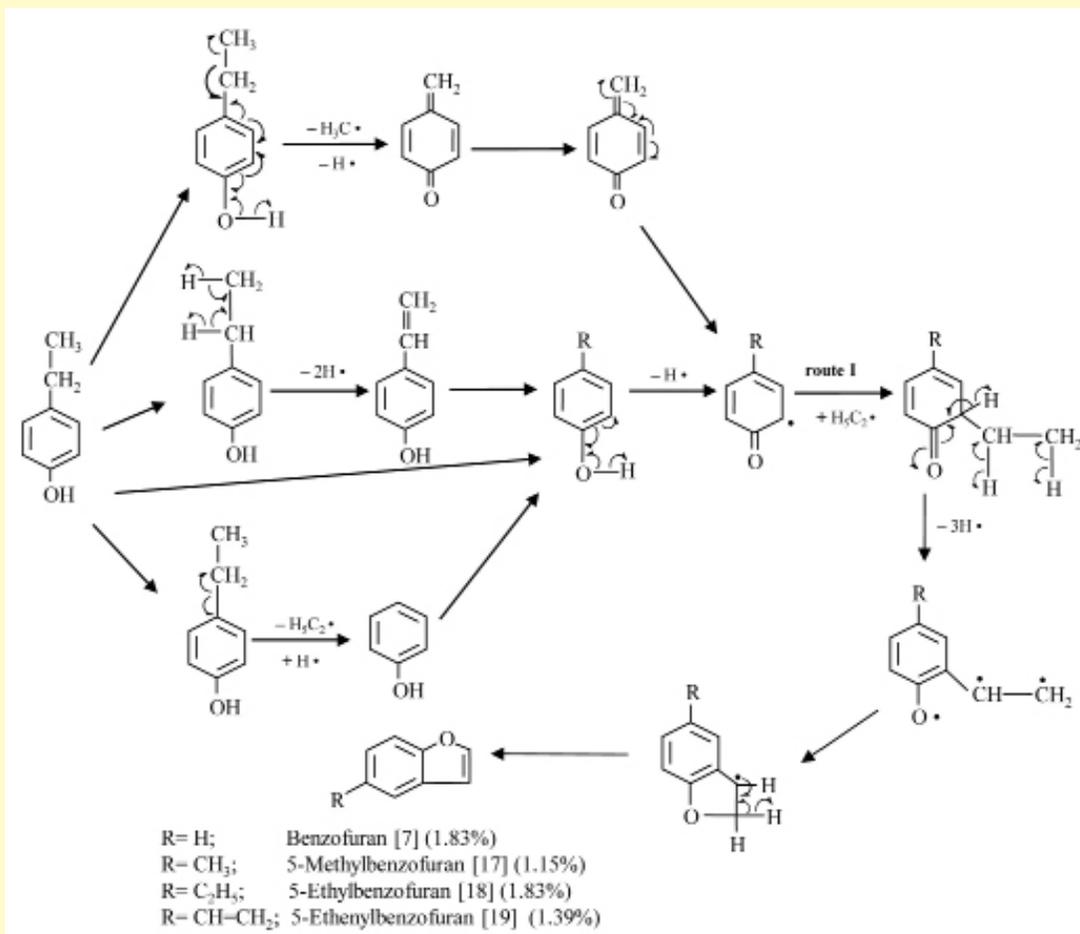


Figure 15: Proposed pathway for the formation of products (16)-(18).

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