An Experimental Study on the Formation of Polycyclic Aromatic Hydrocarbons during the Pyrolysis and Oxidation of Catechol[ortho-Dihydroxybenzene]-A Model Compound Representative of Structural Units in Coal, Wood, and Biomass

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AN EXPERIMENTAL STUDY ON THE FORMATION OF POLYCYCLIC AROMATIC HYDROCARBONS DURING THE PYROLYSIS AND OXIDATION OF CATECHOL [ORTHO-DIHYDROXYBENZENE]—A MODEL COMPOUND REPRESENTATIVE OF STRUCTURAL UNITS IN COAL, WOOD, AND BIOMASS

A Dissertation

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in

The Department of Chemical Engineering

By
Shiju Thomas
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Dedication

To my parents...
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Abstract

Polycyclic aromatic hydrocarbons (PAH) formed during the pyrolysis and combustion of solid fuels like coal, wood, and biomass are widespread environmental pollutants. Since some PAH are known to exhibit carcinogenic and mutagenic activity, understanding the chemical reactions responsible for PAH formation is of utmost importance.

To better understand the reactions leading to the formation of PAH from complex solid fuels, pyrolysis and oxidation experiments have been performed in an isothermal laminar-flow reactor, using the model fuel catechol (ortho-dihydroxybenzene), a phenol-type compound representative of structural entities in coal, wood, and biomass. Catechol pyrolysis experiments have also been performed in the presence of: (1) acetylene, a major growth species in combustion environments, and (2) 1,3-butadiene, a major product of the pyrolysis of coal, wood, and biomass. Experiments have been conducted over a temperature range of 500-1000 °C and at a fixed residence time of 0.3 s.

The pyrolysis products are analyzed by high-pressure liquid chromatography with diode-array ultraviolet-visible absorbance detection and mass spectrometric detection, by gas chromatography with flame-ionization and mass spectrometric detection, and by nondispersive infrared analysis. Analysis of the catechol pyrolysis products has led to the identification of 13 C$_1$-C$_6$ non-aromatic species, 5 one-ring aromatics, 7 oxygen-containing organics, and 104 PAH. Of these, 50 (including 47 PAH) have never before been reported as products of catechol or any phenol-type fuel. A new set of “rules” has been developed for the identification of methylene-bridged PAH. Employing these “rules,” two C$_{25}$H$_{14}$ methylene-bridged PAH have been identified that have never before been reported as products of any fuel.
Product quantification reveals that catechol’s relatively labile O-H bond and capacity for generating oxygen-containing radicals accelerate both fuel conversion and the pyrolysis reactions leading to 1- and 2-ring aromatics and PAH. Among the C₁-C₅ species, 1,3-butadiene appears to be the most important intermediate in PAH formation from catechol. The results are consistent with the C₂ and C₄ radicals being the dominant growth species. Reactions responsible for the formation of the C₁-C₁₀ products from catechol, under pyrolytic and oxidative conditions, are discussed. A tentative PAH formation mechanism during catechol pyrolysis is presented.
Chapter I. Introduction

1.1. Background and Motivation

Combustion of solid fuels like coal and biomass is one of the major sources of energy. Coal is the primary fuel used worldwide for electricity generation and accounts for 43% of the world’s electricity generation [1,2]. Coal also accounts for 26% of the global primary energy needs [2]. In fact, coal is used to generate roughly half of the electricity in the United States [1-3]. According to the Energy Information Administration (EIA) [2], coal’s share of the world energy consumption is going to increase to 28% by 2030. Though the share of biomass in the world energy consumption is only 14%, it accounts for 35% of primary energy consumption in developing countries [4]. In most of these developing nations, wood is directly burned as a source of heat. Since it is estimated that by the year 2050, 90% of the world population will live in developing countries [5], the consumption of biomass as a source of energy is expected to increase.

One of the main issues in the use of solid fuels as a source of energy is the formation of pollutants during combustion. Among the various pollutants produced during the combustion of solid fuels, polycyclic aromatic hydrocarbons (PAH) are unique due to their adverse effects on health [6-13]. PAH are produced primarily due to incomplete combustion of organic fuels. The combustion environment of these fuels is associated with high-temperature, oxygen-deficient zones where pyrolysis reactions are dominant. In combustion systems, pyrolytic reactions are known to be the primary source of polycyclic aromatic hydrocarbons (PAH) [14]. The formation and fate of PAH are of concern due to environmental as well as health reasons. PAH are widespread environmental pollutants and are precursors to soot [15-18]. PAH are also a major contributor to fine particles responsible for heart and lung diseases [11-13]. Also, some
compound of this class are known to have carcinogenic [6-8] and mutagenic [9,10] activity. In addition to the health effects, soot formation is also undesirable in the practical application of solid fuels involving catalysts as soot deposits can lead to catalyst deactivation [19,20]. Therefore, an understanding of the formation and fate of PAH and soot would be helpful in the development of cleaner combustion equipments.

There are two main interlinked aspects to the study of PAH and soot formation from solid fuel pyrolysis and combustion: (1) characterization of the products, and (2) study of product formation mechanisms. The characterization of products includes the isomer specific identification of products, product quantification, particle size distribution, particle morphology etc. The study of formation mechanisms includes determination of intermediates and reaction mechanisms, calculation of thermodynamic and kinetic parameters, effects of temperature and residence times, study of transformation of PAH into soot etc. While both of these aspects are equally important and are useful in gaining mechanistic understanding into PAH and soot formation reactions, the variation [9,10] in the biological activity across different PAH isomers and PAH structural classes warrants more emphasis on full characterization of product components.

Wise et al. [21,22] and Fetzer and Biggs [23] have stated that the large number of isomers, non-availability of reference standards, and poor resolution on conventional gas and liquid chromatographs [21,23,24] makes it extremely difficult to identify and quantify PAH and PAH isomers. In spite of these difficulties, several studies [25-33] have reported the identification of PAH from a variety of fuels and experimental conditions. The synthesis of authentic reference standards [23,34-43] have made it possible to identify many PAH including cyclopenta-fused and ethynyl-substituted PAH [34,35,37,40,41,43]. PAH for which reference standards are not commercially available can be identified by matching their unique ultraviolet-
visible (UV) spectra with those published in literature for these compounds. PAH for which UV spectra and reference standards are not available can be identified by using Clar’s annellation theory principles [44,45] and ultraviolet-visible (UV) and mass spectral information as demonstrated by various investigators [46-49].

Identification of PAH is important from both a mechanistic point of view as well as to assess the biological activity of the combustion product mixture. For example, the identification of ethynyl-substituted and cyclopenta-fused PAH—both thought to be the products of acetylene addition to aryl radicals [50]—among combustion products suggests that the hydrogen-abstraction/acetylene-addition (HACA) mechanism [17,50-53] is the dominant PAH formation mechanism in the combustion environment. The identification of large PAH (C > 25) would be useful to get better mechanistic understanding into soot formation as the larger PAH have a higher propensity to form soot [54,55]. In addition to mechanistic clues, the isomer-specific identification is also important as PAH carcinogenicity and mutagenicity is sensitive to structure [9,10,56]. Hence, the presence or absence of certain PAH can determine the biological activity of a PAH mixture as not all PAH are carcinogenic or mutagenic [9,10]. Among the different isomer classes of PAH, the C_{24}H_{14} PAH are of particular concern due to their relatively high biological activity [9,10]. Since not all C_{24}H_{14} PAH are carcinogenic or mutagenic [6,9,10,57], special attention must be given to the isomer specific identification of the C_{24}H_{14} PAH. Another class of PAH that warrants more careful attention during analysis are the methylene-bridged PAH [6,58-60]. In addition to the widely accepted diol-epoxide metabolic activation mechanism for PAH [14,61], the methylene-bridged PAH can undergo metabolic activation through an alternate mechanism [62,63].

In order to better understand PAH formation mechanisms, the quantification of product yields is as important as the identification of PAH products. In the practical combustion of solid
fuels like coal, wood and biomass, oxygen is absent on the immediate surface and pores of the solid fuel particles where pyrolysis reactions are dominant. The pyrolytic reactions produce volatiles containing light fuel fragments as well as high-molecular weight fragments, which in turn can undergo further thermal decomposition leading to PAH formation. The combustible volatiles are then driven out of the particle through the particle pore structure where they encounter oxygen and undergo oxidation reactions. Therefore, the generalized solid fuel combustion model [64,65] consists of the following steps—(1) fuel particle drying and heating to pyrolysis reaction temperature; (2) solid particle pyrolysis to produce combustible volatiles (low molecular weight hydrocarbons as well as PAH) and carbonaceous char; (3) combustible volatiles oxidation and heterogeneous char oxidation. Thus, oxygen plays a very important role in solid fuel combustion.

In addition to oxygen that plays a very important role in the thermal decomposition of solid fuels and formation of PAH, the C1-C6 products formed during fuel decomposition are known to be precursor species in the formation of small aromatics [66-74]. The formation of small aromatics is considered to be the rate limiting step in the formation of large PAH and soot [73,75,76]. Therefore, special attention should be given to the identification and quantification of these precursor species during solid fuel pyrolysis and combustion. Among the C1-C6 products, acetylene is considered to be an important growth species for PAH buildup reactions. Various studies [17,50-53] have attributed the formation of PAH to the hydrogen-abstraction/acetylene-addition (HACA) reactions. Therefore, the role of the C2 species in the formation of PAH under solid fuel pyrolysis and combustion conditions needs to be investigated. Equally important is the role of four-carbon conjugated free radicals in PAH formation that has been implied by various investigators [77,78]. Quantitative data on the C1-C6 products and PAH form solid fuel pyrolysis and combustion can be employed to get a better fundamental understanding into the processes
involved in PAH and soot formation. In addition, qualitative and quantitative data on the role of C₂ and C₄ species in PAH formation would be helpful in refining PAH growth models [79,80].

**Figure 1.1:** Representative structures of coal [81] and biomass [82].

Solid fuels have very complex structures [81,82], as shown in Figure 1.1. Though solid fuels like coal and biomass themselves can be used to study PAH formation, the complex nature of these fuels makes it extremely difficult to attribute certain products to certain reactant molecules or reaction pathways. In order to establish reaction pathways, it would be helpful if the identities of the reactants as well as the products are known. To overcome this difficulty, various studies [16,25,83-92] have used model compounds representative of structural entities in solid fuels to study fuel decomposition and product formation mechanisms. These model compounds are either prominent structural units in solid fuels or major primary pyrolysis products of solid fuels. Sakuma et al. [93] have demonstrated the use of chlorogenic acid and rutin, two major polyphenols in tobacco, as model compounds to understand the formation of PAH from tobacco. Britt et al.[94,95] have used methoxy-substituted lignin model compounds to get mechanistic insight into the reaction pathways in biomass pyrolysis. Since these compounds are much simpler than the actual fuels, products can be much more easily attributed to a reactant or reaction pathway.
Catechol (*ortho*-dihydroxybenzene) is one such model compound used by Wornat et al. [96-99] in their investigation into PAH formation from complex solid fuels like coal and biomass. The structure of catechol is presented in Figure 1.2. As a prominent structural entity of coal [100] and lignin (a major component of wood [101])—as well as a major component in biomass tars [102]—catechol is a suitable model compound for investigating solid fuel combustion. Catechol is also a structural unit in tobacco [103] and a major component of tobacco smoke [104]. Since tobacco smoke is a major source of environmental PAH [14,105], catechol studies are also relevant to tobacco. Moreover, the relevancy of catechol as a model compound to study solid fuels like coal, wood, and biomass has been demonstrated by Wornat et al. [96,106]. Therefore, catechol is an ideal model compound to study PAH formation from solid fuels like coal and biomass and is employed in this study.

![Figure 1.2: Model fuel compound catechol.](image)

To better understand the formation of PAH from solid fuels, Wornat and co-workers [96-99] performed pyrolysis experiments with catechol as a model fuel. In addition to five oxygen-containing organics, these previous catechol pyrolysis studies led to the identification of 10 C₁-C₅ species [98], 5 single-ring aromatics [96-99], and 54 individual PAH [96,97,99] products. Figure 1.3 presents the reversed-phase HPLC chromatogram reproduced from Wornat et al. [96] of 61 of these products of catechol pyrolysis at 1000 °C and 0.4 sec residence time: 3 oxygen-containing organics, 2 single-ring aromatics, and 54 PAH. Figure 1.3 reveals that there are a
number of unidentified peaks in the chromatogram. For PAH, the number of theoretically possible isomers increase with increasing molecular weight [48]. As mentioned earlier, the large number of isomers, limited availability of reference standards, and poor resolution on conventional gas and liquid chromatographs [21,24] have made it extremely difficult, over the years, to identify and quantify PAH [21,22].

Figure 1.3: Reversed-phase HPLC chromatogram of products of catechol pyrolyzed at 1000 °C, 0.4 sec. Reproduced, with permission, from Wornat et al. [96]. The isomer specific structures of the products are presented in Appendix A.

The identification of PAH in Figure 1.3 is based on matching the UV spectra of each product component with the UV spectra of appropriate reference standards. The unidentified peaks in the UV spectra most likely are products for which reference standards are not available. For PAH for which reference standards or published UV spectra are not available, identification
can be made simpler if mass spectral information is available. The mass spectrum obtained establishes the $C_xH_y$ formula and molecular mass of the product component and thus narrows down the possible candidates to one isomer class. Further structure elucidation can be achieved by using predictive tools like Clar’s annellation theory [44,45] and HPLC elution behaviors (e.g. planarity and length-to-breadth (L/B) ratios [85,107-109]). One of the objectives of the present study is to use the above tools to fully characterize the products from catechol pyrolysis.

The previous catechol pyrolysis studies by Wornat and co-workers [97-99] have also reported extensive quantification of product yields from catechol pyrolysis and calculated global kinetic rate parameters for PAH formation. The results from these studies provide strong evidence for PAH growth by successive ring buildup reactions involving $C_1$-$C_5$ species [97-99]. The results are also consistent with the HACA mechanism for PAH formation and growth [98,99]. These studies also reveal that acetylene and 1,3-butadiene are produced in particularly high abundance from catechol pyrolysis [98]. As mentioned earlier, the $C_2$ and $C_4$ species are thought to play a major role in PAH formation. The high yields of acetylene and 1,3-butadiene and the high abundance of PAH during catechol pyrolysis warrants more careful analysis of the role of these two species in PAH formation. Thus, another one of the objectives of the present study is to delineate the roles of $C_2$ and $C_4$ species in PAH formation.

The catechol pyrolysis studies by Wornat and co-workers have demonstrated the relevancy of catechol as an ideal model compound to study solid fuels like coal, wood, and biomass. Since oxygen is naturally present in the environment of a burning fuel, the present study further extends the catechol pyrolysis study to better understand the effects of oxygen on PAH formation reactions. The role of acetylene and 1,3-butadiene—two major catechol pyrolysis products—in PAH formation reactions is also investigated. In addition to these, the
present study also attempts to perform a more detailed analysis of the catechol pyrolysis products to identify products.

1.2. Structure of the Dissertation

Chapter II describes the experimental equipments and procedures. The catechol pyrolysis experiments are performed in an isothermal laminar flow reactor system. The products are collected and analyzed using non-dispersive infrared analyzers, gas chromatography with flame ionization and mass spectrometric detection, and high-pressure liquid chromatography with ultraviolet-visible diode array detection and mass spectrometric detection. The reactor system, experimental procedure, sample collection, and product analysis are described in detail.

Chapter III reports the identification of previously unidentified PAH products of catechol pyrolysis. The identity of all the products obtained from catechol pyrolysis would be helpful in evaluating the carcinogenicity and mutagenicity of the product mixture. Recent improvements in chemical analysis methods have prompted a more detailed examination of the products. Special emphasis is given to the identification of methylene-bridged PAH and $C_{24}H_{14}$ PAH due to their relatively high biological activity [6,7,9,10,59,60,110]. Also discussed is the development of a set of “Rules” for the identification of the methylene-bridged PAH for which reference standards are not available. In addition to the methylene-bridged PAH and $C_{24}H_{14}$ PAH, Chapter III also describes the identification of several large PAH ($C > 25$). The PAH products are identified by matching their unique UV spectra with those of authentic reference standards or the UV spectra published in literature for these compounds. A few compounds for which reference standards or published UV are not available are identified employing Clar’s annellation theory principles [44,45], and by using UV and mass spectral information. 50 new PAH products have been identified in the present study raising the total number of PAH products from catechol pyrolysis to 111. Portions of this chapter have been accepted for publication as a journal article [111].
Chapter IV discusses the effects of oxygen on the yields of the C1-C6 products of catechol pyrolysis. The C1-C6 products are of particular importance as they act as growth species for PAH buildup reactions [66-74]. Yield/temperature profiles of twelve C1-C5 species and five single-ring aromatic products are obtained at nine different temperatures over the temperature range of 500-1000 °C, a fixed residence time of 0.3 s, and at four different oxygen ratios ranging from 0 (pure pyrolysis) to 0.92 (near stoichiometric oxidation). Reactions responsible for the formation of the C1-C5 and single-ring aromatic products from catechol, under pyrolytic and oxidative conditions, are discussed. The work described in this chapter has been published as a journal article [112].

Chapter V describes the effects of oxygen on the yields of PAH products produced during catechol pyrolysis. Catechol pyrolysis produces 91 PAH products, ranging in size from two to ten fused aromatic rings, and falling into eight structural classes: bi-aryls, benzenoid PAH, indene benzologues, fluoranthene benzologues, cyclopenta-fused PAH, ethynyl-substituted PAH, methyl-substituted PAH, and vinyl-substituted PAH. Of the 91 PAH products of catechol pyrolysis, 43 are produced in quantities sufficient for reliable quantification. Yield/temperature profiles of these 43 PAH products are obtained at nine different temperatures over the temperature range of 500-1000 °C, a fixed residence time of 0.3 s, and at four different oxygen concentrations ranging from zero to near stoichiometric. The effects of oxygen on PAH yields are discussed and tied to the effects of oxygen on the yields of the C1-C8 thermal decomposition products discussed in Chapter IV. The yield/temperature data described here represent one of the most extensive quantifications of the effects of oxygen on PAH produced during the pyrolysis of any fuel. The work described in this chapter has been published as a journal article [113].

Chapter VI delineates the effects of acetylene addition on the C1-C10 products of catechol pyrolysis. The catechol pyrolysis experiments are conducted at a residence time of 0.3 s, at
temperatures of 500 to 1000 °C, with acetylene added as a dopant. Yield/temperature profiles are obtained for the C1-C10 products of catechol pyrolysis in the presence of acetylene dopant at nine different temperatures and compared with the yield/temperature profiles of each of the C1-C10 products of catechol pyrolyzed in the absence of the dopant. The role of acetylene in the formation of C1-C10 products of catechol pyrolysis are discussed with particular emphasis on the formation of 1- and 2-ring aromatics. The work described in this chapter has been published as a journal article [114].

Chapter VII describes the effects of 1,3-butadiene addition on the C1-C10 products of catechol pyrolysis. The catechol pyrolysis experiments are conducted at a residence time of 0.3 s, at temperatures of 500 to 1000 °C, with 1,3-butadiene added as a dopant. Yield/temperature profiles are obtained for the C1-C10 products of catechol pyrolysis in the presence of 1,3-butadiene dopant at nine different temperatures and compared with the yield/temperature profiles of each of the C1-C10 products of catechol pyrolysis in the absence of the dopant. Since various studies have shown that C1-C10 products are produced from 1,3-butadiene pyrolysis, 1,3-butadiene-only pyrolysis is also performed at a residence time of 0.3 s, at temperatures of 500 to 1000 °C, to better delineate the role of 1,3-butadiene in the formation of PAH. In addition to the effects of 1,3-butadiene addition on the yields of C1-C10 products of catechol pyrolysis, the formation of C1-C10 products from 1,3-butadiene pyrolysis is also discussed. The work described in this chapter will be submitted for publication as a journal article [115].

Chapter VIII uses the results from the previous chapters and examines the role of acetylene and 1,3-butadiene in PAH formation during catechol pyrolysis. Separate catechol pyrolysis experiments are performed with acetylene and 1,3-butadiene added as a dopant to the catechol pyrolysis environment. Yield/temperature profiles are obtained for the 43 quantifiable PAH products at nine different temperatures from catechol/dopant pyrolysis experiments and
compared against the yield/temperature profiles of each of the respective PAH obtained from catechol-only pyrolysis experiments. Portions of this chapter have been submitted for publication as a journal article [116].

Chapter IX summarizes the conclusions drawn from this work, highlights important contributions to the field, and suggests avenues for possible future work.
Chapter II. Experimental Equipment and Procedures

2.1 Reactor System

The catechol pyrolysis experiments are performed in a reactor system [50,96-99] shown in schematic form in Figure 2.1. The reactor system consists of a fuel vaporizer, isothermal quartz flow reactor, Balston Teflon filter, and product collection system. Each of the components—the fuel vaporizer, the reactor, and the product collection system—is described below.

![Schematic diagram of reactor system](image)

**Figure 2.1:** Reactor system for homogeneous pyrolysis of catechol with added gas-phase dopants. Adapted from Ledesma et al. [98].

2.1.1 Fuel Vaporizer

For the pyrolysis experiments, solid catechol particles (>99.5% pure, purchased from Aldrich Chemical Co.) are loaded as a fixed bed into a Pyrex tube capped at both ends by a stainless steel mesh that prevents the solid materials from being entrained in the carrier gas flow.
The Pyrex tube is placed vertically within an isothermal oven (the fuel vaporizer) held at 85 °C for slight vaporization of catechol. The fuel tube is connected to the inlet of the quartz reactor tube, as shown in Figure 2.1. The vapor-phase catechol is picked up by a flowing stream of ultrahigh purity (grade 6.0) nitrogen carrier gas, resulting in a 0.65 mole-% carbon loading in the reactor feed gas. Gas chromatographic analyses of samples taken from the vaporizer exit stream, both before and after each pyrolysis experiment, ensure the consistency of the 0.65 mole-% carbon loading in the reactor feed gas (Appendix B). The fuel vaporizer has a bypass line, also shown in Figure 2.1, so that fuel-free nitrogen can be run through the reactor before and after an experiment.

For the pyrolysis of catechol in the presence of added dopant, the nitrogen carrier gas is doped, in separate experiments, with known amounts of a gas-phase dopant. The dopants used in the present study are oxygen, acetylene, and 1,3-butadiene. The experimental procedures for catechol pyrolysis in the presence of each of the added dopants oxygen, acetylene, and 1,3-butadiene, are explained in detail in Chapters IV, VI, and VII, respectively. For the dopant pyrolysis, the nitrogen carrier gas doped with the gas-phase dopant is passed through the bypass line so that no fuel is picked up. The pyrolysis experiments with the dopant acetylene and 1,3-butadiene are explained in detail in Chapters VI and VII, respectively.

2.1.2. Reactor

The reactor is a 1.22-m long, 2-mm I.D. quartz tube supported in the centerline of an electrically heated Lindberg/Blue M tube furnace. The electric power is supplied in three independent zones along the length of the furnace, each separately regulated to ensure a uniform temperature throughout the reactor length. As shown in Figure 2.1, the fore end of the reactor tube passes through a heated insulating plug, into the adjacent fuel vaporizer; the other end passes through a heated insulating plug and attaches to the collection system. The furnace has
been calibrated between 500 and 1000 °C with a thermocouple placed at various locations along the centerline to ensure that the temperature profile is uniform and drops off sharply at both ends; thus the reaction zone is well characterized (Appendix B). The design of the reactor is such that laminar flow is maintained and the flow conditions inside the reactor meet Lee's criteria [117] for idealized plug flow. This allows specific residence times to be attributed to the products exiting the reactor without the need for any corrections due to mixing. Residence time is controlled by varying the flow-rate of nitrogen between 79 and 100 standard cm$^3$ per minute, allowing a residence time of 0.3 second for the temperature range of 700 to 1000 °C. (Due to practical limitations of the reactor system, the experimental runs at 500 °C and 600 °C are performed at a residence time of 0.4 s and 0.36 s, respectively. The residence time calculations are shown in Appendix B.)

2.1.3. Product Collection

Earlier experiments [97-99] have indicated that in order to accurately quantify the full range of products, it is necessary to run a given experiment twice—once with the collection system optimized for volatile (C$_1$-C$_6$) products collection, and a second time with the collection system optimized for heavier (>C$_6$) products that condense at room temperature. The heavier (>C$_6$) aromatic products are collected in a condensed-phase product collection system, which consists of three parts in series: an unheated, removable quartz arm in which the majority of products condense, a Balston Teflon filter on which some lighter products and any particulates are collected, and a dichloromethane (DCM) solvent trap intended to capture the lightest condensed-phase products. For the volatile (C$_1$-C$_6$) gas-phase products, the DCM solvent trap is replaced by a Teflon gas-sampling bag. While the condensed phase products are trapped on the Balston filter, the gaseous products flow through the filter into the gas-sampling bag for subsequent compositional analysis.
2.2. Sample Collection Procedures

2.2.1. Condensed-Phase Products

A pyrolysis experiment for the condensed-phase products consists of heating the reactor to the desired temperature while flushing thoroughly with nitrogen, then switching the fuel vaporizer flow from the bypass to the fuel chamber. The residence time of gases in the reactor is maintained at 0.3 s by adjusting the flow rate of the nitrogen carrier gas with a mass flow controller. Fuel is fed into the reactor for 75 minutes, followed by five minutes of nitrogen purge. Exiting the heated zone of the furnace, the reaction products are quenched to room temperature (quench time, approximately 0.028 s), collected on a Balston filter, and dissolved in DCM. At the conclusion of the experiment, the three components of the product collection system—the quartz arm, Balston filter, and DCM trap—are removed and thoroughly flushed with DCM. The quartz arm is also sonicated in DCM; the filter is three times filled with DCM, sonicated, and flushed. All of the DCM extracts from these steps are consolidated, and concentrated in a Kuderna–Danish evaporator. (GC analysis of standard solutions of one- and two-ring aromatics before and after concentration in a Kuderna–Danish evaporator confirms no loss of volatile compounds during the concentration step.) After concentration, 10 % of the total volume (representing 10 % of the total products collected) is set aside for GC analysis. The remaining 90 % is prepared for HPLC analysis by solvent exchange into dimethyl-sulfoxide (DMSO), a solvent compatible with the solvents used in the reversed-phase HPLC method. During the solvent exchange procedure, volatile species such as benzene and toluene are at least partially lost to vaporization as the DCM is evaporated away under a stream of nitrogen. Hence the one- and two-ring aromatics are quantified by gas chromatography of the reserved DCM solution (representing 10 % of the total products collected). However, both HPLC and GC have been employed for the identification of the one- and two-ring aromatics.
2.2.2. Gas-Phase Products

A pyrolysis experiment for the gas-phase products consists of heating the reactor to the desired temperature while flushing thoroughly with nitrogen, then switching the fuel vaporizer flow from the bypass to the fuel chamber. The residence time of gases in the reactor is maintained at 0.3 s by adjusting the flow rate of the nitrogen carrier gas with a mass flow controller. Fuel is fed into the reactor for 35 minutes, followed by five minutes of nitrogen purge. Exiting the reactor, the catechol reaction products are quenched at room temperature, and the condensed-phase products are trapped on the Balston filter. The gaseous products are allowed to bypass the sampling bag for seven minutes and then collected in the gas-sampling bag for 25 minutes by manually switching from bypass to the sampling bag. The gas-phase products collected in the gas-sampling bag is analyzed by GC.

2.3. Analytical Procedures for the Identification and Quantification of Products

Catechol pyrolysis produces a range of products including C$_1$-C$_6$ gas-phase products, light one- and two-rings aromatics, as well as large PAH products. While the identification of the C$_1$-C$_6$ gas-phase products and light one- and two-ring aromatics can be easily achieved by gas chromatography or gas-phase spectroscopy, the low volatility of PAH makes their analysis difficult with gas chromatography or gas-phase spectroscopy. Therefore, analysis of PAH mixtures, especially those containing large PAH, can be more easily performed in the condensed-phase. HPLC is a suitable analytical technique for analysis of condensed-phase products [22, 90, 96, 118, 119]. Though HPLC coupled to mass spectrometric detector can be used for PAH analysis, the large number of PAH isomers makes mass spectrometry of limited use for isomer-specific identification. Isomer-specific identification of PAH is of utmost importance as the chemical and biological activity of PAH are dependent on their structure [9, 10, 56]. Since each PAH has a unique UV spectrum, a UV diode-array detector is ideal for PAH analysis. The
analytical instruments and procedures for the identification of the C₁-C₆ gas-phase products, light one- and two-rings aromatics, and large PAH products of catechol pyrolysis are discussed in detail in the following.

2.3.1. C₁-C₆ Hydrocarbon Products

To quantify CO and CO₂, a portion of the product gases collected in the gas sampling bag is pumped through two Horiba Model VIA-510 nondispersive infrared analyzers. The remaining product gases are then routed to an Agilent Model 6890/5973 gas chromatograph/flame-ionization detector/mass spectrometer (GC/FID/MS) for analysis of C₁-C₆ hydrocarbons. Separation of the hydrocarbon gases is achieved on a GS GASPRO capillary column of length, 30 m, and diameter, 0.32 mm. (Temperature program for the separation is presented in Appendix C.) Except for cyclopentadiene and vinylacetylene, identification of the hydrocarbon products is accomplished by matching the retention times and mass spectra of individual product components with those of reference standards, and product quantification is based on the calibration of the GC/FID with reference standards (Appendix D). Since a reference standard for cyclopentadiene is not commercially available, its identification in the catechol pyrolysis products is based on matching the product component’s GC retention index with that of cyclopentadiene generated from the pyrolysis of dicyclopentadiene [88,120] as well as by matching the product component’s mass spectrum with that of the reference standard in the NIST/EPA/NIH mass spectral library. The identification of vinylacetylene is based on matching the product component’s mass spectrum with that of the reference standard in the NIST/EPA/NIH mass spectral library. In addition, the identification of vinylacetylene among the thermal decomposition products of catechol is consistent with the thermal formation of vinylacetylene from acetylene [121] and 1,3-butadiene [122-124]—two of the highest-yield hydrocarbon products present in the catechol pyrolysis environment.
2.3.2. Light (< 3-rings) Aromatic Products

Gas chromatographic analysis of the condensed-phase catechol pyrolysis products for the identification and quantification of light (< 3-rings) aromatics is performed on the Agilent Model 6890/5973 gas chromatograph/flame-ionization detector/mass spectrometer (GC/FID/MS). A sample of 2 µL is injected by syringe, through a split injector, onto a HP-5 fused silica capillary column of length, 30 m, diameter, 0.25 mm, and film thickness, 0.1 µm. The column temperature is programmed to hold at 40 °C for the first 3 minutes; it is then ramped at 4 °C/min to 300 °C, where it is held for 15 minutes. The one- and two-ring aromatic products are identified by matching retention times and mass spectra with those of reference standards. The identities of the 2-ring aromatics indene and naphthalene have also been confirmed by matching their HPLC retention times and ultraviolet absorption spectra with those of respective reference standards. The product quantification is based on the calibration of the GC/FID with reference standards (Appendix D).

2.3.3. PAH Products

To identify the PAH products, two separate aliquots of the PAH/dimethylsulfoxide solution are injected into two separate high-pressure liquid chromatographs—one, a Hewlett-Packard Model 1050 chromatograph, coupled to a diode-array ultraviolet-visible absorbance detector (HPLC/UV); the other, an Agilent Model 1100 chromatograph, coupled to a diode-array ultraviolet-visible absorbance detector in series with a mass spectrometer (HPLC/UV/MS).

Each HPLC uses a reversed-phase Restek Pinnacle II PAH octadecylsilica column (particle size, 5 µm; pore size, 110 Å; inner diameter, 4.6 mm; and length, 250 mm) to achieve the separation. The product components are separated by gradient elution. The HPLC/UV employs a sample injection volume of 25 µL, a mobile-phase flowrate of 1.5 mL/min, and a
time-programmed sequence of mobile phases that begins with 60:40 water:acetonitrile (ACN), ramps to pure ACN in 40 minutes, holds isocratic in ACN for 20 minutes, and then ramps to 100 % dichloromethane (DCM) in 40 minutes. The HPLC/UV/MS employs an injection volume of 20 µL, a flowrate 1.0 mL/min, and a time-programmed sequence of mobile phases that begins with 50:50 water:methanol (MeOH), ramps to pure MeOH in 40 min, holds isocratic in MeOH for 60 min, ramps to 100 % DCM in 40 minutes, and holds isocratic in DCM for 40 minutes. (The HPLC/UV/MS uses MeOH, instead of ACN, for better component mass spectra.)

After separation by either HPLC instrument, the catechol pyrolysis products in the eluent pass through a UV diode-array detector, which is set to simultaneously monitor five absorbance channels: 328-332 nm, 335-345 nm, 275-285 nm, 236-500 nm, and 190-520 nm. UV absorbance spectra, covering the range of 190-520 nm, are taken every 0.8 s at a resolution of 2 nm in the HPLC/UV and every 0.4 s at a resolution of 1 nm in the HPLC/UV/MS.

In the HPLC/UV/MS, products exiting the UV detector are introduced directly into a PhotoMate atmospheric-pressure photo-ionization (APPI) source. The APPI is equipped with a krypton discharge lamp, emitting 10.0 eV and 10.6 eV photons perpendicularly to the vaporized effluent. The ions are detected by a high-energy dynode detector, which operates in the positive-ion, full-scan mode and monitors mass-to-charge ratios up to 700. With these operating parameters and the water/MeOH, MeOH, and DCM solvent program employed, products eluting exhibit mass spectra whose primary ion is at M+H, where M is the molecular weight of the product component. The reason for the M+H peak is that MeOH, through photo-ionization in the MS, is able to ionize components through proton (H) transfer, yielding an M+H peak in the mass spectrum.[125]

The mass spectrum obtained from the HPLC/UV/MS establishes the CₓHᵧ formula and molecular weight of the PAH identified in the present study. The UV spectrum establishes the
exact aromatic structure of each product component, since UV spectra are isomer-specific. Thus, the products of catechol pyrolysis are unequivocally identified by matching each product component’s UV absorbance spectrum with that of the appropriate reference standard.

The reference standards used for our analyses include PAH that are commercially available as well as specially synthesized PAH that have been generously donated to us by the scientists who synthesized these compounds and documented their syntheses and structures in the literature: benz[f]indene [42]; dibenzo[cd,lm]perylene [23,36]; aceanthrylene [43]; acephenanthrylene and cyclopent[h]acephenanthrylene [37]; cyclopenta[cd]fluoranthene [35]; cyclopenta[cd]pyrene [39]; dicyclopenta[cd,mn]pyrene and dicyclopenta[cd,jk]pyrene [40]; benzo[ghi]cyclopenta[cd]perylene and cyclopenta[bc]coronene [38]; 2-ethynylnaphthalene, 1-ethynylacenaphthylene and 5-ethynylacenaphthylene [35]; 2-ethynylantracene, 2-ethynylphenanthrene and 3-ethynylphenanthrene [34,41]; benzo[a]fluoranthen and phenanthreno[2,3-a]pyrene [126,127].

Since all the reference spectra (from authentic reference standards) used in this study are obtained with the water/ACN, ACN, and DCM solvent program (on the HPLC/UV), all the UV spectral matches presented here for the identification of catechol pyrolysis product components for which reference standards are available to us are also obtained with the water/ACN, ACN, and DCM solvent program (on the HPLC/UV).

Some PAH for which reference standards are not available commercially, so their identifications are based on matching their unique UV absorbance spectra with those published in the literature for these compounds. The identities of a few PAH, for which reference standards and UV absorbance spectra are not available, have been achieved by using UV and mass spectral evidence and Clar’s annellation theory principles [44,45,48]. The identifications of methylene-bridged naphtho[2,1-a]pyrene and methylene-bridged naphtho[2,3-a]pyrene, for
whiсh reference standards and UV absorbance spectra are not available, have been achieved by comparing their respective UV absorbance spectra with the UV absorbance spectra of the parent PAH naphtho[2,1-a]pyrene and naphtho[2,3-a]pyrene, and by the use of Clar’s annellation theory principles [44,45]. These identifications are explained in detail in Chapter III.

For most of the PAH quantified in this study, the UV absorbance detector has been calibrated with known concentrations of the respective reference standards (Appendix D). Response factors of structurally similar compounds (Appendix D) have been used for the few products for which reference standards are not available, as negligible error is introduced [128]. The HPLC/UV is used for product quantification but with one change. The reversed-phase Restek Pinnacle II PAH octadecylsilica column is replaced with a reversed phase Vydac 201-TP octadecylsilica column (particle size, 5 µm; inner diameter, 4.6 mm; length, 250 mm), to be consistent with earlier quantification studies [97,99]. For the HPLC sample preparation method and the HPLC parameters of this study, the above techniques can detect products at yields as low as 0.0005 % of the mass of fed catechol.

Separate catechol pyrolysis experiments have been carried out at nine different temperatures over the temperature range of 500-1000 °C and a residence time of 0.3 s, under pure pyrolysis conditions, and with added dopants. Separate pyrolysis experiments with acetylene and 1,3-butadiene as fuels are also performed at nine different temperatures over the temperature range of 500-1000 °C and a residence time of 0.3 s. The yields obtained from HPLC and GC analyses of products from repeat experiments at the same temperature give very reproducible results. The collective mass of carbon obtained from the gas-phase products and the condensed-phase products—including PAH and oxygenated organics as well as any unconverted fuel—accounts for all of the carbon fed to the reactor as fuel. A carbon balance is thus closed on this reactor system (Appendix E).
Chapter III. PAH Product Identification

3.1. Introduction

The combustion of solid fuels like coal, wood, and biomass is associated with high-temperature, oxygen-deficient zones where pyrolytic reactions dominate. In combustion systems, pyrolytic reactions are known to be the primary source of polycyclic aromatic hydrocarbons (PAH) and soot. The formation of PAH as well as their subsequent release into the environment are of concern for both environmental and health reasons, due to the inherent carcinogenicity [6-8] and mutagenicity [9,10] of some members of this compound class.

Of the many PAH produced during solid fuel pyrolysis and combustion, not all PAH are carcinogenic or mutagenic. The PAH of the C_{24}H_{14} isomer class are of particular interest as they exhibit a relatively high level of biological activity [6,7,9,10,57,110,129-141]. The C_{24}H_{14} PAH (molecular weight 302 PAH) are found throughout the environment: in petroleum products [142,143], coal and wood combustion emissions [24,28,30,144-148], coal tar [22,132,140,149], carbon black [150,151], diesel exhaust [119,152,153], urban aerosols [22,154,155], sediments [132,140,156], tire fire products [157], vegetable oils [158], smoked meat and fish [159-161], asphalt [162], fly ash [163], and cigarette smoke [104,164-166].

The C_{24}H_{14} PAH also exhibit high biological activity [6,7,9,10,57,110,129-141]. The C_{24}H_{14} PAH benzo[b]pyrene, dibenzo[b,k]fluoranthene, naphtho[1,2-k]fluoranthene, naphtho[2,3-b]fluoranthene, naphtho[1,2-a]pyrene, naphtho[2,3-e]pyrene, dibenzo[a,e]pyrene, naphtho[2,1-a]pyrene, naphtho[2,3-a]pyrene, dibenzo[a,i]pyrene, dibenzo[a,h]pyrene, dibenzo[a,e]pyrene, and dibenzo[e,l]pyrene are reported to have mutagenic activity [9,10,30,129,133,141]. Naphtho[1,2-b]fluoranthene, naphtho[2,1-a]pyrene, dibenzo[a,i]pyrene, naphtho[2,3-a]pyrene, dibenzo[a,e]pyrene, and dibenzo[a,h]pyrene are reported to have
carcinogenic activity [6,57,134-136,138-140,167]. The C_{24}H_{14} PAH dibenzo[a,l]pyrene is one of the most carcinogenic and genotoxic PAH ever tested [10,110,131,133]. In addition, various studies [168-171] have shown that weak or non-carcinogenic PAH within a complex mixture can either increase the carcinogenicity of the mixture by acting as co-carcinogens or decrease the carcinogenicity by inhibiting the carcinogenic activity of strong carcinogens present in the mixture. Since not all PAH are carcinogenic or mutagenic [9,10], the distribution of PAH within a complex mixture determines the biological activity of the PAH mixture. Therefore, isomer-specific identification of PAH, C_{24}H_{14} isomers in particular, among the products of solid fuels is of great importance.

Another class of PAH that are widespread environmental pollutants [6,58,59] and exhibit carcinogenic activity are the methylene-bridged PAH [6,14,60-63,142,172-174]. Methylene-bridged PAH are a class of nonalternant PAH containing a five-membered ring containing a methylene carbon and are produced during the combustion of organic fuels. Many of these methylene-bridged PAH have been identified in coal tar [28,149,175], carbon black [176], cigarette smoke [164,175,176], soil and sediment samples[175], crude petroleum [177], used engine oil [175], and automobile exhaust condensates [142,174].

The formation and fate of methylene-bridged PAH has generated interest due to the demonstrated tumorogenic and carcinogenic potency of 4H-cyclopenta[def]chrysene [60,172,173] (methylene-bridged chrysene). 11H-benz[bc]aceanthrylene (methylene-bridged benz[a]anthracene) has been found to be a moderately potent tumor-initiator [60,173]. In addition, studies by Grimmer et al. [6,142,174] have revealed that the fraction containing methylene-bridged PAH contribute significantly towards the carcinogenicity of automobile exhaust condensate. Harvey and co-workers [14,61-63] have suggested that the methylene-bridged PAH can potentially undergo metabolic activation through two different pathways: (1)
the well established bay-region diol epoxide pathway [14,61], and (2) enzymatic hydroxylation on the relatively acidic bridge site followed by the formation of reactive acetate, sulfate or phosphate ester intermediates that are capable of forming DNA adducts [62,63]. Since methylene-bridged PAH have a higher propensity to undergo metabolic activation and have been previously identified among the products of solid fuel combustion [28,149,164,176], special attention must be paid to the analysis of combustion products to identify this unique class of PAH and understand their formation during solid fuel pyrolysis and combustion.

Unlike C_{24}H_{14} PAH or methylene-bridged PAH, large PAH (C > 25) have been considered to have low biological activity due to their low solubility. However, Lacassagne et al. [178] have demonstrated the carcinogenicity of the large PAH dibenzo[cd,lm]perylene. In addition to their possible biological activity, the formation of large PAH is also of concern due to their role in the formation of soot [15,16], a major contributor to fine particulates responsible for heart and lung diseases [11,12]. The formation of soot is also of concern in the practical applications of solid fuels as it can clog fuels lines [54] and can lead to catalyst deactivation [19,20]. Hence the identification of large PAH would be helpful in understanding soot formation mechanisms.

For solid fuels like coal, wood, or biomass, that have very complex structures, the understanding of chemical pathways leading to PAH formation has been greatly facilitated by the use of model fuel compounds that are representative of structural moieties in these fuels [16,25,83,85-92,179]. For our experimental investigations into the formation of PAH during solid fuel pyrolysis and combustion, we have chosen catechol (ortho-dihydroxybenzene) as a model fuel for the following reasons: (1) catechol is a prominent structural entity in coal [100], tobacco [103], and lignin (a major component of wood [101]); (2) catechol is a major component in biomass tars [102] and tobacco smoke [104]; (3) catechol is a structural unit in flavonoids
such as rutin and quercetin, as well as in chlorogenic acid, a common component of the leafy plant materials that make up some biomass fuels [103,180]; (4) catechol’s relevancy is further strengthened by the demonstrated [96] similarity between PAH product distributions obtained from catechol pyrolysis and coal volatiles pyrolysis. Hence, catechol is a suitable model compound for investigating PAH formation from solid fuels.

Previous catechol pyrolysis studies [96,99] have led to the identification of 54 individual PAH products ranging in size from two to seven fused aromatic rings including some large PAH and C_{24}H_{14} PAH using high-pressure liquid chromatography with diode-array ultraviolet-visible absorbance detection (HPLC/UV). HPLC/UV is an ideal technique for PAH identification provided the appropriate reference standards are available, as each PAH has a unique UV absorbance spectrum. But the large number of isomers, particularly for the C_{24}H_{14} PAH and large PAH (C > 25), and the limited availability of reference standards can make PAH identification difficult. The 65 theoretically possible C_{24}H_{14} PAH isomers [24,44] include 10 benzologues of pyrene, 21 benzologues of fluoranthene, 2 benzologues of perylene, 19 benzologues of aceanthrylene, 12 benzologues of acephenanthrylene, and zethrene. As stated by Wise et al. [21,22], the large number of isomers, limited availability of reference standards, and poor resolution on conventional gas and liquid chromatographs [21,24] have made it extremely difficult, over the years, to identify and quantify the C_{24}H_{14} PAH isomers. The same is the case for large PAH as pointed out by Fetzer [47,48]. Despite these difficulties, 3 of the 10 C_{24}H_{14} pyrene benzologues—dibenzo[α,ι]pyrene, naphtho[2,1-a]pyrene, and naphtho[2,3-a]pyrene—have been identified in previous catechol pyrolysis studies [96,97]. These studies have also led to the identification of some large PAH like dibenzo[cd,lm]pyrene, phenanthro[2,3-a]pyrene, and cyclopenta[bc]coronene [96]. Though methylene-bridged PAH have not been identified in these catechol pyrolysis studies, they have been identified in coal tar [28,149,175]
and in cigarette smoke [164,175,176]. Since catechol is a model compound representative of coal and tobacco, the pyrolysis of catechol has the potential to produce methylene-bridged PAH. The detection of C_{24}H_{14} PAH and large PAH among catechol’s pyrolysis products, the high biological activity of the C_{24}H_{14} PAH and the methylene-bridged PAH in general, and recent improvements in chemical analysis methods have prompted these new catechol pyrolysis experiments and a more detailed examination of the products for these PAH.

In the following, we describe the catechol pyrolysis experiments and present the analytical evidence supporting the identification of twelve new C_{24}H_{14} PAH, eight methylene-bridged PAH, and thirteen large PAH (C > 25). The catechol pyrolysis experiments are carried out in an isothermal laminar-flow reactor at 1000 °C and a residence time of 0.3 s. The PAH products are analyzed by high-pressure liquid chromatography (HPLC) with diode-array ultraviolet-visible (UV) absorbance detection and mass spectrometric detection. The UV spectral matches confirming the 15 C_{24}H_{14} PAH product identifications (12 newly identified and 3 previously identified) are presented. Literature findings on the identification of these 15 C_{24}H_{14} PAH in other fuel mixtures and environmental samples, as well as findings on their carcinogenicity and mutagenicity are also summarized. The UV spectral matches confirming the identifications of six of the eight methylene-bridged PAH products of catechol pyrolysis for which reference standards or published UV spectra are available are presented. Also presented are a set of “rules” for the identification of methylene-bridged PAH developed based on the UV spectra of available methylene-bridged PAH reference standards/UV spectra. These “rules” have been employed for the identification of two additional methylene-bridged PAH for which no reference standard or published UV spectrum is available. In addition, the UV spectral evidence confirming the identifications of 13 large (C > 250) PAH are presented.
3.2. Experimental Equipment and Procedures

3.2.1 Reactor System

As detailed elsewhere[96-99], the catechol pyrolysis experiments are performed in a laminar-flow reactor system that consists of a fuel vaporizer, isothermal quartz flow reactor, and product collection system. Catechol pyrolysis experiments are performed by loading solid catechol particles (>99.5% pure, purchased from Aldrich Chemical Co.) as a fixed bed into a Pyrex tube placed vertically inside the fuel vaporizer, an isothermal oven maintained at 85 °C for slight vaporization of catechol. The vapor-phase catechol is entrained in a flowing stream of ultrahigh purity (grade 6.0) nitrogen carrier gas, resulting in a 0.65 mole-% carbon loading in the reactor feed gas. The pyrolysis reactions take place at 1000 °C and at atmospheric pressure inside the isothermal laminar-flow reactor, which consists of a 2-mm (inner diameter) quartz tube insulated at both ends and maintained at isothermal conditions by a three-zone electrically heated furnace. The residence time for each experimental run is 0.3 s. The PAH products exiting the reactor are quenched to room temperature and collected with a condensed-phase product collection system (consisting of a Balston Teflon filter and dichloromethane solvent trap). The products dissolved in dichloromethane are concentrated with a Kuderna-Danish apparatus and exchanged into dimethylsulfoxide for subsequent analysis by HPLC.

3.2.2. Product Analysis

To analyze the PAH products, two separate aliquots of the PAH/dimethylsulfoxide solution are injected into two separate high-pressure liquid chromatographs—one, a Hewlett-Packard Model 1050 chromatograph, coupled to a diode-array ultraviolet-visible absorbance detector (HPLC/UV); the other, an Agilent Model 1100 chromatograph, coupled to a diode-array ultraviolet-visible absorbance detector in series with a mass spectrometer (HPLC/UV/MS). Each HPLC uses a reversed-phase Restek Pinnacle II PAH octadecylsilica column (particle size, 5
μm; pore size, 110 Å; inner diameter, 4.6 mm; and length, 250 mm) and gradient elution to achieve component separation. The HPLC/UV employs a sample injection volume of 25 μL, a mobile-phase flowrate of 1.5 mL/min, and a time-programmed sequence of mobile phases that begins with 60:40 water:acetonitrile (ACN), ramps to pure ACN in 40 minutes, holds isocratic in ACN for 20 minutes, and then ramps to 100 % dichloromethane (DCM) in 40 minutes. The HPLC/UV/MS employs an injection volume of 20 μL, a flowrate 1.0 mL/min, and a time-programmed sequence of mobile phases that begins with 50:50 water:methanol (MeOH), ramps to pure MeOH in 40 min, holds isocratic in MeOH for 60 min, ramps to 100 % DCM in 40 minutes, and holds isocratic in DCM for 40 minutes. (Methanol is used in the solvent program of the HPLC/UV/MS since better mass spectra result. Acetonitrile generally gives better UV spectra, so it is used in the solvent program of the HPLC/UV. Of the fifteen product component spectra presented in this paper, thirteen are from the water/ACN/DCM program of the HPLC/UV. Two are from the water/MeOH/DCM program of the HPLC/UV/MS since these two components are better resolved with this solvent program.)

After separation by either HPLC instrument, the catechol pyrolysis products in the eluent pass through a UV diode-array detector, which is set to simultaneously monitor five absorbance channels: 328-332 nm, 335-345 nm, 275-285 nm, 236-500 nm, and 190-520 nm. UV absorbance spectra, covering the range of 190-520 nm, are taken every 0.8 s at a resolution of 2 nm in the HPLC/UV and every 0.4 s at a resolution of 1 nm in the HPLC/UV/MS.

In the HPLC/UV/MS, products exiting the UV detector are introduced directly into a PhotoMate atmospheric-pressure photo-ionization (APPI) source, which is equipped with a krypton discharge lamp, emitting 10.0 eV and 10.6 eV photons perpendicularly to the vaporized effluent. The ions are detected by a high-energy dynode detector, which operates in the positive-ion, full-scan mode and monitors mass-to-charge ratios up to 700.
The mass spectrum obtained from the HPLC/UV/MS establishes the C<sub>x</sub>H<sub>y</sub> formula and molecular mass of each product component. The UV spectrum establishes the exact aromatic structure of each product component, since UV spectra are isomer-specific. Thus, the products of catechol pyrolysis are unequivocally identified by matching each product component’s UV absorbance spectrum with that of the appropriate reference standard injected onto the HPLC/UV.

The reference standards include commercially available compounds as well as those that have been specially synthesized and generously donated to us by the scientists who synthesized these compounds and documented their synthesis in the literature [23,44,119,181-183]. Reference standards for some of the methylene-bridged PAH and some large PAH identified here are not available commercially. Hence, their identification is based on matching each components’ unique UV absorbance spectrum with that published in literature for these compounds [44,46,48,49,54,142,183-188]. The identification of methylene-bridged naphtho[2,1-a]pyrene and methylene-bridged naphtho[2,3-a]pyrene, for which reference standards and UV absorbance spectra are not available, have been achieved by comparing their respective UV absorbance spectra with the UV absorbance spectra of the parent PAH naphtho[2,1-a]pyrene and naphtho[2,3-a]pyrene, and by applying Erich Clar’s annellation theory principles [44,45,48].

3.3. Results and Discussion

Figure 3.1 presents the HPLC chromatogram showing all the products produced from catechol pyrolysis at 1000 °C and 0.3 s. Ranging in size from one to ten fused aromatic rings, the catechol pyrolysis products in Figure 3.1 fall into 8 structural classes. Included in the chromatogram are the structures (color-coded by structural class) of 111 products of catechol pyrolysis: 47 benzenoid PAH, in black; 14 indene benzologues, in green; 13 fluoranthene benzologues, in dark blue; 10 cyclopenta-fused PAH, in red; 8 ethynyl-substituted species (triacetylene and 7 ethynyl-substituted aromatics), in purple; 10 methylated aromatics, in light
blue; 2 bi-aryls, in gray; and 7 oxygen-containing aromatics, in brown. The names and structures of all 111 products are presented, by class, in Table A.1 in Appendix A.

**Figure 3.1.** HPLC chromatogram of the products of catechol at 1000 °C and 0.3 sec. The rise in baseline at 63 minutes corresponds to a change in mobile-phase composition to UV-absorbing dichloromethane. Identified products are color-coded according to structural class: benzenoid PAH (black), indene benzologues (green), fluoranthene benzologues (dark blue), cyclopenta-fused PAH (red), ethynyl-substituted species (purple), methylated aromatics (light blue), bi-aryls (gray), and oxygen-containing aromatics (brown). The names and structures of all products are presented, by class, in Table A.1 in Appendix A.

Of the 111 products of Figure 3.1, 61 have been reported as products of catechol pyrolysis in an earlier study [96], and the UV spectral matches documenting the identifications of 11 of these 61 PAH that required specially synthesized reference standards have been presented [96]. The remaining 50 products in Figure 3.1 (47 PAH; 3 oxygen-containing aromatics) have never before been reported as products of the pyrolysis of catechol or any other phenol-type fuel. The isomer-specific identification of C_{24}H_{14} PAH, methylene-bridged PAH, and large PAH is the primary focus of what follows in this chapter.
3.3.1. Identification of the C$_{24}$H$_{14}$ PAH

![HPLC chromatogram of products of catechol pyrolysis (1000 °C and 0.3 s) eluting from 40 to 75 min in the solvent program of the HPLC/UV. The rise in the baseline at ~63 min corresponds to a change in HPLC mobile phase composition to UV-absorbing dichloromethane. Shown in red, the identified C$_{24}$H$_{14}$ PAH product components, in order of elution from left to right, are: naphtho[1,2-e]pyrene, naphtho[1,2-b]fluoranthene, naphtho[2,3-e]pyrene, naphtho[1,2-a]pyrene eluting with dibenzo[a,e]pyrene, naphtho[1,2-k]fluoranthene, benzo[k]pyrene, dibenzo[e,l]pyrene, dibenzo[b,k]fluoranthene, naphtho[2,3-b]fluoranthene, naphtho[2,1-a]pyrene, dibenzo[a,i]pyrene, naphtho[2,3-a]pyrene, naphtho[2,3-k]fluoranthene, and dibenzo[a,h]pyrene. Three of these C$_{24}$H$_{14}$ PAH—naphtho[2,1-a]pyrene, dibenzo[a,i]pyrene, and naphtho[2,3-a]pyrene—have been identified in a previous catechol pyrolysis study [96].

Figure 3.2. HPLC chromatogram of products of catechol pyrolysis (1000 °C and 0.3 s) eluting from 40 to 75 min in the solvent program of the HPLC/UV. The rise in the baseline at ~63 min corresponds to a change in HPLC mobile phase composition to UV-absorbing dichloromethane. Shown in red, the identified C$_{24}$H$_{14}$ PAH product components, in order of elution from left to right, are: naphtho[1,2-e]pyrene, naphtho[1,2-b]fluoranthene, naphtho[2,3-e]pyrene, naphtho[1,2-a]pyrene eluting with dibenzo[a,e]pyrene, naphtho[1,2-k]fluoranthene, benzo[k]pyrene, dibenzo[e,l]pyrene, dibenzo[b,k]fluoranthene, naphtho[2,3-b]fluoranthene, naphtho[2,1-a]pyrene, dibenzo[a,i]pyrene, naphtho[2,3-a]pyrene, naphtho[2,3-k]fluoranthene, and dibenzo[a,h]pyrene. Three of these C$_{24}$H$_{14}$ PAH—naphtho[2,1-a]pyrene, dibenzo[a,i]pyrene, and naphtho[2,3-a]pyrene—have been identified in a previous catechol pyrolysis study [96].

Figure 3.2 presents the portion of the HPLC chromatogram (from the HPLC/UV) in which the C$_{24}$H$_{14}$ PAH products of catechol pyrolysis (at 1000 °C and 0.3 s) elute. Shown in red in Figure 3.2 are the chemical structures corresponding to the 15 catechol pyrolysis products whose mass spectra designate them as C$_{24}$H$_{14}$ PAH and whose UV spectra have permitted determination of their exact isomer-specific identities. In order of elution in Figure 3.2, the C$_{24}$H$_{14}$ PAH products of catechol pyrolysis at 1000 °C and 0.3 s are: naphtho[1,2-e]pyrene,
naphtho[1,2-\textit{b}]fluoranthene, naphtho[2,3-\textit{e}]pyrene, naphtho[1,2-\textit{a}]pyrene co-eluting with dibenzo[\textit{a,e}]pyrene, naphtho[1,2-\textit{k}]fluoranthene, benzo[\textit{b}]perylene, dibenzo[\textit{e,l}]pyrene, dibenzo[\textit{b,k}]fluoranthene, naphtho[2,3-\textit{b}]fluoranthene, naphtho[2,1-\textit{a}]pyrene, dibenzo[\textit{a,i}]pyrene, naphtho[2,3-\textit{a}]pyrene, dibenzo[\textit{a,h}]pyrene, and dibenzo[\textit{a,e}]pyrene.

Except for the three noted in an earlier paper [96], none of the 15 C$_{24}$H$_{14}$ PAH have ever before been identified as products of catechol or any phenol-type fuel. In addition to the 15 C$_{24}$H$_{14}$ PAH products, Figure 3.2 shows in black the chemical structures of the 23 other PAH products of catechol pyrolysis that elute in the 40- to 75-min range of the HPLC chromatogram. The identifications of 12 of these 23 PAH have been reported in a previous catechol pyrolysis study [96]. The spectral evidence for the identifications of the 11 remaining PAH products will be presented in Sections 3.3.2, 3.3.3, and 3.3.4.

The 15 identified C$_{24}$H$_{14}$ PAH products of catechol pyrolysis belong to three structural classes: perylene benzologues, fluoranthene benzologues, and pyrene benzologues—each of which will be discussed separately. Figure 3.3 presents the UV spectral match unequivocally establishing the identity of the perylene benzologue; Figure 3.4, those of the five fluoranthene benzologues; Figures 3.5 and 3.6, those of the nine pyrene benzologues. Although three of the C$_{24}$H$_{14}$ pyrene benzologue products have been previously reported [96] (naphtho[2,1-\textit{a}]pyrene, dibenzo[\textit{a,i}]pyrene, and naphtho[2,3-\textit{a}]pyrene), the UV spectral matches confirming those identifications were not reported, due to the large number of compounds identified in that study [96]. They are included here for completeness. All of the catechol pyrolysis product component spectra in Figures 3.3-3.6 and 3.6a have been obtained with the water/ACN/DCM solvent program on the HPLC/UV; those in Figures 3.6b and 3.6c, for naphtho[1,2-\textit{a}]pyrene and dibenzo[\textit{a,e}]pyrene, have been obtained with the water/MeOH/DCM solvent program on the HPLC/UV/MS.
3.3.1.1. Perylene Benzologues

Figure 2 presents the UV spectrum of the catechol pyrolysis product component eluting at 50.8 min in Figure 3.2, along with that of a benzo[b]perylene reference standard. Some very minor spectral interference from the co-eluting product $1H$-benzo[$ghi$]cyclopenta[$pqr$]perylene [189] is evident in the two small peaks at 288 and 300 nm in the spectrum of the catechol pyrolysis product component. The otherwise very close match between the two spectra in Figure 2, however, confirms this product component’s identity as benzo[b]perylene.

![UV spectrum of benzo[b]perylene and catechol pyrolysis product component](image)

**Figure 3.3.** UV absorbance spectra of the reference standard of benzo[b]perylene (dashed line) and of a catechol pyrolysis product component (solid line) eluting at 50.8 min in Figure 3.2. Some spectral interference from co-eluting $1H$-benzo[$ghi$]cyclopenta[$pqr$]perylene is evident at 288 and 300 nm in the spectrum of the catechol pyrolysis product component.

As indicated in Table 3.1, benzo[b]perylene has been previously identified in a hard-coal flue-gas condensate [24] as well as in extracts of coal tar (SRM 1597) [132], urban air particulates (SRM 1648) [132], urban dust (SRM 1649a) [132], marine sediments (SRM 1941) [132], diesel particulates (SRM1650a) [152,153], wood soot [145], and carbon black [150]. Experimental carcinogenicity data are not available for benzo[b]perylene, but Durant et al. [10] have demonstrated benzo[b]perylene to be a human-cell mutagen, as indicated in Table 3.2.
<table>
<thead>
<tr>
<th>Compounds</th>
<th>Previously identified in</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>coal tar extract (SRM 1597)</td>
</tr>
<tr>
<td></td>
<td>urban dust particulates (SRM 1649a)</td>
</tr>
<tr>
<td></td>
<td>marine sediment (SRM 1941)</td>
</tr>
<tr>
<td></td>
<td>diesel particulates (SRM 1650a)</td>
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<tr>
<td></td>
<td>cigarette smoke condensate</td>
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<tr>
<td></td>
<td>urban aerosols</td>
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<tr>
<td></td>
<td>contaminated coal-fired residential furnaces</td>
</tr>
<tr>
<td></td>
<td>tire fire products</td>
</tr>
<tr>
<td></td>
<td>carbon black</td>
</tr>
<tr>
<td></td>
<td>coal soot extracts</td>
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<td></td>
<td>asphalt</td>
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<tr>
<td></td>
<td>fly ash</td>
</tr>
<tr>
<td></td>
<td>coal-fired residential stoves</td>
</tr>
<tr>
<td></td>
<td>motor vehicle exhaust condensate</td>
</tr>
<tr>
<td></td>
<td>tar-coke</td>
</tr>
<tr>
<td></td>
<td>wood soot extracts</td>
</tr>
<tr>
<td></td>
<td>hard wood combustion</td>
</tr>
<tr>
<td>Benzo[b]pyrene</td>
<td>X(^{[132]})</td>
</tr>
<tr>
<td>naphtho[1,2-b]fluoranthene</td>
<td>X(^{[132]})</td>
</tr>
<tr>
<td>naphtho[1,2-k]fluoranthene</td>
<td>X(^{[132]})</td>
</tr>
<tr>
<td>dibenzo[b,k]fluoranthene</td>
<td>X(^{[132]})</td>
</tr>
<tr>
<td>naphtho[2,3-b]fluoranthene</td>
<td>X(^{[132]})</td>
</tr>
<tr>
<td>naphtho[2,3-k]fluoranthene</td>
<td>X(^{[132]})</td>
</tr>
<tr>
<td>naphtho[1,2-e]pyrene</td>
<td>X(^{[132]})</td>
</tr>
<tr>
<td>naphtho[2,3-e]pyrene</td>
<td>X(^{[132]})</td>
</tr>
<tr>
<td>dibenzo[a,e]pyrene</td>
<td>X(^{[132]})</td>
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<tr>
<td>naphtho[1,2-a]pyrene</td>
<td>X(^{[132]})</td>
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<tr>
<td>dibenzo[e,l]pyrene</td>
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<tr>
<td>naphtho[2,1-a]pyrene</td>
<td>X(^{[132]})</td>
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<tr>
<td>dibenzo[a,i]pyrene</td>
<td>X(^{[132]})</td>
</tr>
<tr>
<td>naphtho[2,3-a]pyrene</td>
<td>X(^{[132]})</td>
</tr>
<tr>
<td>dibenzo[a,h]pyrene</td>
<td>X(^{[132]})</td>
</tr>
</tbody>
</table>

Superscript number in brackets indicates the number of the reference reporting that product’s identification.
Table 3.2. Literature Findings on the Carcinogenicity and Mutagenicity of Catechol’s C$_{24}$H$_{14}$ Product PAH

<table>
<thead>
<tr>
<th>Compound</th>
<th>Mutagenic*</th>
<th>Carcinogenic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzo[b]perylene</td>
<td>Yes [10]</td>
<td>Not available</td>
</tr>
<tr>
<td>naphtho[1,2-b]fluoranthene</td>
<td>No [10]</td>
<td>Yes [167]</td>
</tr>
<tr>
<td>naphtho[1,2-k]fluoranthene</td>
<td>Yes [9]</td>
<td>Not available</td>
</tr>
<tr>
<td>dibenzo[b,k]fluoranthene</td>
<td>Yes [9]</td>
<td>No [137,138]</td>
</tr>
<tr>
<td>naphtho[2,3-b]fluoranthene</td>
<td>Yes [9]</td>
<td>Not available</td>
</tr>
<tr>
<td>naphtho[2,3-k]fluoranthene</td>
<td>No [9]</td>
<td>Not available</td>
</tr>
<tr>
<td>naphtho[1,2-e]pyrene</td>
<td>No [129]</td>
<td>Not available</td>
</tr>
<tr>
<td>dibenzo[a,e]pyrene</td>
<td>Yes [9,10]</td>
<td>Yes [6,57,134-136,138-140]</td>
</tr>
<tr>
<td>naphtho[1,2-a]pyrene</td>
<td>Yes [129,141]</td>
<td>Not available</td>
</tr>
<tr>
<td>dibenzo[e,l]pyrene</td>
<td>Yes [10]</td>
<td>No [6,7,135,138,140,190]</td>
</tr>
<tr>
<td>dibenzo[a,i]pyrene</td>
<td>Yes [10]</td>
<td>Yes [6,57,134-136,138-140]</td>
</tr>
<tr>
<td>dibenzo[a,b]pyrene</td>
<td>Yes [10]</td>
<td>Yes [6,57,134-136,138-140]</td>
</tr>
</tbody>
</table>

* References [4] and [5] use a mutagenicity assay based on human h1A1v2 cells, and references 34 and 46 use a mutagenicity assay based on *S. typhimurium* TA 100.

3.3.1.2. Fluoranthene Benzologues

Figure 3.4 presents the UV spectra of the five C$_{24}$H$_{14}$ fluoranthene benzologue products of catechol pyrolysis, along with the UV spectra of the respective PAH reference standards: Figure 3.4a, naphtho[1,2-b]fluoranthene; Figure 3.4b, naphtho[1,2-k]fluoranthene; Figure 3.4c, dibenzo[b,k]fluoranthene; Figure 3.4d, naphtho[2,3-b]fluoranthene; and Figure 3.4e, naphtho[2,3-k]fluoranthene. The C$_{24}$H$_{14}$ fluoranthene benzologue products of catechol pyrolysis are produced in very small amounts (each < 30 μg/g of fed catechol), so they exhibit very small peaks in Figure 3.2. In some cases, the C$_{24}$H$_{14}$ fluoranthene benzologues also elute close to other product components. There are thus some slight discrepancies, between the components’ and standards’ UV spectra of Figure 3.4, in a few of the peak heights (e.g., at 308 nm in Figure 3.4c and at 255 nm in Figure 3.4d), and the component spectrum in Figure 3.4b even exhibits a peak at 260 nm that is due to an unidentified co-eluting compound. Nevertheless, the matching HPLC retention times of each of the component/standard pairs of Figure 3.4, the qualitative agreement in the UV spectral patterns, and the matching wavelengths of UV absorption for each pair—all substantiate the identifications of the catechol pyrolysis product components of Figures 3.4a,
3.4b, 3.4c, 3.4d, and 3.4e, as naphtho[1,2-\textit{b}]fluoranthenes, naphtho[1,2-\textit{k}]fluoranthenes, dibenzo[\textit{b,k}]fluoranthenes, naphtho[2,3-\textit{b}]fluoranthenes, and naphtho[2,3-\textit{k}]fluoranthenes, respectively.

As demonstrated in Table 3.1, all five fluoranthene benzologues identified here as catechol pyrolysis products have been previously identified in the extracts of coal tar (SRM 1597) [132], urban air particulates (SRM 1648) [132], urban dust (SRM 1649a) [132], marine sediments (SRM 1941) [132], and urban aerosols [154]. Four of the five, in different combinations, have also been found in diesel particulates (SRM1650a) [152,153], tire fire products [157], and coal-tar-contaminated sediments [140]. Naphtho[1,2-\textit{k}]fluoranthenes and dibenzo[\textit{b,k}]fluoranthenes have been identified in carbon black [150] and wood soot extracts [145], respectively. Table 3.1 further indicates that two of the C\textsubscript{24}H\textsubscript{14} fluoranthene benzologue products have been identified in coal soot extracts [30], and three have been identified in a hard-coal flue-gas condensate [24]. The fact that the C\textsubscript{24}H\textsubscript{14} fluoranthene benzologue products of catechol pyrolysis are also present in the products of practical fuels/environmental samples helps to corroborate catechol's relevancy as a model fuel for the study of PAH formation.

As evident in Table 3.2, Durant et al. [9,10] have tested the human cell (h1A1v2 cells) mutagenicity of the five C\textsubscript{24}H\textsubscript{14} fluoranthene benzologue products identified in the present study. They found the mutagenicity of dibenzo[\textit{b,k}]fluoranthenes comparable to that of benzo[\textit{a}]pyrene. Naphtho[1,2-\textit{k}]fluoranthenes and naphtho[2,3-\textit{b}]fluoranthenes were moderately mutagenic but less mutagenic than benzo[\textit{a}]pyrene. Naphtho[1,2-\textit{b}]fluoranthenes and naphtho[2,3-\textit{k}]fluoranthenes were inactive in these bio-assays [9,10]. Naphtho[1,2-\textit{b}]fluoranthenes, however, has been reported to be moderately carcinogenic by Weyand et al. [167]. In literature studies [137,138], dibenzo[\textit{b,k}]fluoranthenes did not exhibit carcinogenicity. Experimental carcinogenicity data for the other three C\textsubscript{24}H\textsubscript{14} fluoranthene benzologue products of catechol pyrolysis are not available.
Figure 3.4. UV absorbance spectra of the reference standard (dashed line) / catechol pyrolysis product component (solid line) pairs of the C_{24}H_{14} fluoranthene benzologues: (a) naphtho[1,2-b]fluoranthene and catechol pyrolysis product component eluting at 45.5 min in Figure 3.2; (b) naphtho[1,2-k]fluoranthene and catechol pyrolysis product component eluting at 49.5 min in Figure 3.2 (Some spectral interference from an unidentified co-eluting compound is evident at 260 nm in the spectrum of the catechol pyrolysis product component); (c) dibenzo[b,k]fluoranthene and catechol pyrolysis product component eluting at 55.8 min in Figure 3.2; (d) naphtho[2,3-b]fluoranthene and catechol pyrolysis product component eluting at 57.1 min in Figure 3.2; (e) naphtho[2,3-k]fluoranthene and catechol pyrolysis product component eluting at 73.5 min in Figure 3.2.
3.3.1.3. Pyrene Benzologues

Figures 3.5 and 3.6 present the UV spectra of the nine C\textsubscript{24}H\textsubscript{14} pyrene benzologue products of catechol pyrolysis, along with the UV spectra of the respective PAH reference standards: Figure 3.5a, naphtho[1,2-e]pyrene; Figure 3.5b, naphtho[2,3-e]pyrene; Figure 3.5c, dibenzo[e,l]pyrene; Figure 3.5d, naphtho[2,3-a]pyrene; Figure 3.5e, dibenzo[a,h]pyrene; Figure 3.5f, naphtho[2,1-a]pyrene; Figure 3.6a, dibenzo[a,i]pyrene; Figure 3.6b, naphtho[1,2-a]pyrene; Figure 3.6c, dibenzo[a,e]pyrene. As with the C\textsubscript{24}H\textsubscript{14} fluoranthene benzologues, the C\textsubscript{24}H\textsubscript{14} pyrene benzologue products of catechol pyrolysis are produced in small amounts (each < 20 µg/g of fed catechol). Figure 3.2 also reveals that—even though two of the nine C\textsubscript{24}H\textsubscript{14} pyrene benzologue products, naphtho[2,1-a]pyrene and dibenzo[a,i]pyrene, elute cleanly as pure components—five of the nine elute very close to other product components, and two (naphtho[1,2-a]pyrene and dibenzo[a,e]pyrene) even co-elute in the water/ACN/DCM solvent program of Figure 3.2. Hence, for the five C\textsubscript{24}H\textsubscript{14} pyrene benzologue products eluting close to other components, spectral interference from the near-eluting components causes some minor discrepancies between the product components’ and standards’ UV spectra in Figure 3.5: at 210 nm and 272 in Figure 3.5b, at 260 nm and 360 nm in Figure 3.5e, and, more markedly, at 282 nm in Figure 3.5a and at 240 nm in Figure 3.5c. Despite the interference from the near-eluting compounds, however, the closely matching UV spectra in Figure 3.5 and the matching HPLC retention times of each of the component/standard pairs confirm the identifications of the catechol pyrolysis product components of Figures 3.5a, 3.5b, 3.5c, 3.5d, and 3.5e, as naphtho[1,2-e]pyrene, naphtho[2,3-e]pyrene, dibenzo[e,l]pyrene, naphtho[2,3-a]pyrene, and dibenzo[a,h]pyrene, respectively.
Figure 3.5. UV absorbance spectra of the reference standard (dashed line) / catechol pyrolysis product component (solid line) pairs of C_{24}H_{14} pyrene benzologues: (a) naphtho[1,2-e]pyrene and catechol pyrolysis product component eluting at 42.1 min in Figure 3.2; (b) naphtho[2,3-e]pyrene and catechol pyrolysis product component eluting at 47.2 min in Figure 3.2; (c) dibenzo[e,l]pyrene and catechol pyrolysis product component eluting at 50.5 min in Figure 3.2; (d) naphtho[2,3-a]pyrene and catechol pyrolysis product component eluting at 72.1 min in Figure 3.2; (e) dibenzo[a,h]pyrene and catechol pyrolysis product component eluting at 74.5 min in Figure 3.2; (f) naphtho[2,1-a]pyrene and of a catechol pyrolysis product component eluting at 64.2 min in Figure 3.2. Some spectral interference from an unidentified co-eluting compounds is evident in the spectrum of the catechol pyrolysis product component in (a) at 282 nm and (c) and 240 nm.
**Figure 3.6.** UV absorbance spectra of the reference standard (dashed line) / catechol pyrolysis product component (solid line) pairs of the C_{24}H_{14} pyrene benzologues: (a) dibenzo[α,i]pyrene and catechol pyrolysis product component eluting at 70.5 min in Figure 3.2; (b) naphtho[1,2-a]pyrene and catechol pyrolysis product component eluting at 70.8 min in the solvent program of the HPLC/UV/MS and at 48.3 min in Figure 3.2, from the solvent program of the HPLC/UV; (c) dibenzo[α,e]pyrene and catechol pyrolysis product component eluting at 71.2 min in the solvent program of the HPLC/UV/MS and at 48.3 min in Figure 3.2, from the solvent program of the HPLC/UV. Some spectral interference from unidentified co-eluting compounds (molecular mass 276 and 288) is evident at 242, 262, and 325 nm in the spectrum of the catechol pyrolysis product component in (c).

The two C_{24}H_{14} pyrene benzologue products eluting at 64.2 and 70.5 min in Figure 3.2 are not affected by other components, so the UV spectral matches for these two products, in Figures 3.5f and 3.6a, respectively, are very clear—establishing the identities of these components as naphtho[2,1-a]pyrene and dibenzo[α,i]pyrene, respectively.

The two remaining C_{24}H_{14} pyrene benzologue products of catechol pyrolysis, co-eluting at 48.3 min in the water/ACN/DCM solvent program of Figure 3.2, are better resolved by the
water/MeOH/DCM solvent program on the HPLC/UV/MS. Therefore, Figures 3.6b and 3.6c, present the UV spectra of these two C_{24}H_{14} pyrene benzologue products (eluting at 70.8 min and 71.2 min, respectively, in the water/MeOH/DCM solvent program), along with the UV spectra of the respective PAH reference standards. As with the other C_{24}H_{14} products, the effects of low product concentrations and co-elution are evident in the spectra of the catechol pyrolysis product components in Figures 3.6b and 3.6c. Figure 3.6b shows slight discrepancies in the peak heights (at 232 nm, 267 nm, and 308 nm) between the UV spectrum of the naphtho[1,2-a]pyrene standard and that of the catechol pyrolysis product component. The UV spectrum of the catechol pyrolysis product component in Figure 3.6c exhibits peaks at 242, 262, and 325 nm that are due to un-identified co-eluting components. Despite these spectral interferences, the UV spectra of the catechol pyrolysis product components in Figures 3.6b and 3.6c are in agreement with both the spectral patterns and the wavelengths of peak absorbance in the UV spectra of the respective reference standards. This agreement, along with the matching HPLC retention times of the component/standard pairs, confirms the identities of the C_{24}H_{14} product components of Figures 3.6b and 3.6c as naphtho[1,2-a]pyrene and dibenzo[a,e]pyrene, respectively.

As evident in Table 3.1, the nine C_{24}H_{14} pyrene benzologue products of catechol pyrolysis have also been identified in the same four environmental reference materials shown to contain the one C_{24}H_{14} perylene benzologue and the five C_{24}H_{14} fluoranthene benzologue products of catechol pyrolysis: coal tar extract (SRM 1597) [132], urban air particulates (SRM 1648) [132], urban dust (SRM 1649a) [132], and marine sediment (SRM 1941) [132]. As also shown in Table 3.1, however, the C_{24}H_{14} pyrene benzologue products of catechol pyrolysis have been reported in a higher number and broader range of fuel product mixtures than either of the other two classes of C_{24}H_{14} PAH.
As evident in Table 3.2, the literature reports several studies on the biological activity of the C$_{24}$H$_{14}$ pyrene benzologues. Table 3.2 shows that except for naphtho[1,2-e]pyrene [129], all of the C$_{24}$H$_{14}$ pyrene benzologue products of catechol pyrolysis have been found to be mutagenic [9,10,129,141]. Also, dibenzo[a,e]pyrene, dibenzo[a,i]pyrene, dibenzo[a,h]pyrene, naphtho[2,1-a]pyrene, and naphtho[2,3-a]pyrene have been reported to be carcinogenic [6,57,134-136,138-140]. However, various studies [6,7,135,138,140,190] have found that naphtho[2,3-e]pyrene and dibenzo[e,l]pyrene are not carcinogens, and experimental carcinogenicity data for naphtho[1,2-e]pyrene and naphtho[1,2-a]pyrene are not available.

3.3.2. Identification of the Methylene-Bridged PAH

Shown in Figure 3.7 is the portion of the HPLC chromatogram (from the HPLC/UV) in which the eight identified methylene-bridged PAH products of catechol pyrolysis elute. The chemical structures corresponding to the eight methylene-bridged PAH products of catechol whose mass spectra and UV spectra have permitted determination of their exact isomer-specific identities are shown in red in Figure 3.7. In order of elution in Figure 3.7, the methylene-bridged PAH products of catechol pyrolysis at 1000 °C and 0.3 s are: 4H-cyclopenta[def]phenanthrene, 11H-benz[bc]aceanthrylene, 4H-cyclopenta[def]chrysene, 11H-indeno[2,1,7-cde]pyrene, 4H-benzo[def]cyclopenta[mno]chrysene, 1H-benzo[ghi]cyclopenta[pqr]perylene, 5H-dibenzo[a,mno]cyclopenta[def]picene, and 5H-dibenzo[b,mno]cyclopenta[def]chrysene.

None of the eight newly identified methylene-bridged PAH have ever before been identified as a product of catechol or any phenol-type fuel. Two of the methylene-bridged PAH, 5H-dibenzo[a,mno]cyclopenta[def]picene and 5H-dibenzo[b,mno]cyclopenta[def]chrysene, have never before been identified as a product of any fuel. In addition to the eight methylene-bridged PAH products, shown in black in Figure 3.7 are the chemical structures of the 78 other products of catechol pyrolysis that elute in the 19- to 83-min range of the HPLC chromatogram. The
identifications of 43 of these 78 products have been reported in our previous catechol pyrolysis studies [96,111]. Identifications of the remaining 22 products will be reported in Sections 3.3.2, 3.3.3, and 3.3.4. Figure 3.7 also reveals that the parent benzenoid PAH corresponding to each of the eight methylene-bridged PAH—phenanthrene, benz[a]anthracene, chrysene, benzo[e]pyrene, benzo[a]pyrene, benzo[ghi]pyrene, naphtho[2,1-a]pyrene, and naphtho[2,3-a]pyrene—are also produced during catechol pyrolysis. The identification of these parent benzenoid PAH have been reported in a previous catechol pyrolysis study [96].

Figure 3.7. HPLC chromatogram of products of catechol pyrolysis (1000 °C and 0.3 s) eluting from 19 to 83 min in the solvent program of the HPLC/UV. The rise in the baseline at ~63 min corresponds to a change in HPLC mobile phase composition to UV-absorbing dichloromethane. Shown in red, the identified methylene-bridged PAH product components, in order of elution from left to right, are: 4H-cyclopenta[def]phenanthrene, 11H-benz[bc]aceanthrylene, 4H-cyclopenta[def]chrysene, 11H-indeno[2,1,7-cde]pyrene, 4H-benzo[def]cyclopenta[mno] chrysene, 1H-benzo[ghi]cyclopenta[pqr]pyrene, 5H-dibenzo[a,mno]cyclopenta[def]chrysene, and 5H-dibenzo[b,mno]cyclopenta[def]chrysene. Shown in black are 76 other PAH products and two oxygenated products of catechol pyrolysis.
Reference standards and/or published UV spectra are available for six of the eight methylene-bridged PAH identified in the present study. We first present the UV spectral matches unequivocally establishing the identity of these six methylene-bridged PAH for which reference standards/published UV spectra are available. We then compare the UV spectra of these six methylene-bridged PAH to the respective parent benzenoid PAH to examine the effect of methylene-bridging on the UV spectrum of a benzenoid PAH. Based on these UV spectral comparisons, Clar’s annellation theory principles [44,45,48], and mass spectral information, we then develop a general set of “Rules” to predict the UV spectral features of methylene-bridged PAH. Finally, we use these “Rules” to identify two more methylene-bridged PAH products of catechol pyrolysis for which reference standards or published UV spectra are not available.

### 3.3.2.1. UV Spectral Matches for Methylene-Bridged PAH

Figure 3.8 presents the UV spectra of six methylene-bridged PAH products of catechol pyrolysis eluting in the 20- to 51-min range of the HPLC chromatogram, along with the UV spectra of the respective PAH reference standards: Figure 3.8a, 4H-cyclopenta[def]phenanthrene (methylene-bridged phenanthrene); Figure 3.8b, 11H-benz[bc]aceanthrylene (methylene-bridged benz[a]anthracene); Figure 3.8c, 4H-cyclopenta[def]chrysene (methylene-bridged chrysene); Figure 3.8d, 11H-indeno[2,1,7-cde]pyrene (methylene-bridged benzo[e]pyrene); Figure 3.8e, 4H-benzo[def]cyclopenta[mno]chrysene (methylene-bridged benzo[a]pyrene); and Figure 3.8f, 1H-benzo[ghi]cyclopenta[pqr]perylene (methylene-bridged benzo[ghi]perylene). The UV spectral matches in Figures 3.8a and 3.8c are based on authentic reference standards. Since reference standards are not available for 11H-benz[bc]aceanthrylene, 11H-indeno[2,1,7-cde]pyrene, 4H-benzo[def]cyclopenta[mno]chrysene, and 1H-benzo[ghi]cyclopenta[pqr]perylene, the UV spectral matches in Figures 3.8b, 3.8d, 3.8e, and 3.8f are based on UV spectra published in the literature [142,184] for these compounds.
Figure 3.8. UV absorbance spectra of the reference standard (dashed line) / catechol pyrolysis product component (solid line) pairs: (a) cyclopenta[def]phenanthrene and catechol pyrolysis product component eluting at 22.6 min in Figure 3.7; (b) 11H-benz[bc]aceanthrylene [184] and catechol pyrolysis product component eluting at 34.6 min in Figure 3.7; (c) 4H-cyclopenta[def]chrysene and catechol pyrolysis product component eluting at 35.2 min in Figure 3.7; (d) 11H-indeno[2,1,7-cde]pyrene [142] and catechol pyrolysis product component eluting at 39.7 min in Figure 3.7; (e) 4H-benzo[def]cyclopenta[mno]chrysene [142] and catechol pyrolysis product component eluting at 43.7 min in Figure 3.7; (f) 1H-benzo[ghi]cyclopenta[pqr]perylen [142] and of a catechol pyrolysis product component eluting at 50.7 min in Figure 3.7. Some spectral interference from an unidentified co-eluting compounds is evident in the spectrum of the catechol pyrolysis product component in (c) at 241, 287, and 343 nm, and (e) at 260 and 380 nm.
Figure 3.7 reveals that except 4H-cyclopenta[def]chrysene and 1H-benzo[ghi]cyclopenta[pqr]perylene (that co-elute with benzo[a]fluoranthene and benzo[b]perylene, respectively), all the other four methylene-bridged PAH of Figure 3.7 elute cleanly as pure components. Hence, the UV spectral matches in Figures 3.8b, 3.8d, 3.8e, and 3.8f are all very clear. The UV spectral matches in Figure 3.8a and 3.8c, however, show some minor discrepancies between the product components’ and standards’ UV spectra: at 241 nm, 287 nm, and 343 in Figure 3.8a, and at 260 nm and 280 nm in Figure 3.8c. Despite the spectral interference from the near-eluting compounds, however, the closely matching UV spectra in Figures 3.8a and 3.8c, the matching HPLC retention times of each of the component/standard pairs, and the mass spectra confirm the identifications of the catechol pyrolysis product components of Figure 3.8a and 3.8c as 4H-cyclopenta[def]chrysene and 1H-benzo[ghi]cyclopenta[pqr]perylene, respectively.

3.3.2.2. Effects of Methylene-Bridging on the UV Spectra of PAH

The UV absorbance spectrum is a very important feature in the identification of PAH, and an understanding of the UV spectral characteristics is very helpful especially in the identification of PAH for which reference standards are not available. Having unequivocally established the identities of six methylene-bridged PAH products of catechol pyrolysis, we now examine the effects of methylene-bridging on the UV spectral characteristics of PAH. Figure 3.9 presents the UV spectra of parent benzenoid PAH (dashed curve) and the corresponding methylene-bridged PAH (solid curve): Figure 3.9a, phenanthrene and 4H-cyclopentaphenanthrene; Figure 3.9b, chrysene and 4H-cyclopentachrysene; Figure 3.9c, benzo[e]pyrene and 11H-indeno[2,1,7-cde]pyrene; and Figure 3.9d, benzo[a]pyrene and 4H-benzo[def]cyclopenta[mmn]chrysene. For each of the four examples in Figure 3.9, the UV spectrum of the methylene-bridged PAH (solid curve) closely matches the UV spectrum of the
respective parent benzenoid PAH (dashed curve) in general shape and intensity, but is shifted to longer wavelengths with reference to the UV spectrum of the parent benzenoid PAH. In addition to the four examples shown in Figure 3.9, the UV spectra (not shown here) of both $11H$-benz$[bc]$aceanthrylene (methylene benz$[a]$anthracene) and $1H$-benzo$[ghi]$cyclopenta$[pq]$perylene (methylene benzo$[ghi]$perylene) also show similar effects of methylene-bridging as the four examples in Figure 3.9. The observed spectral shifts are also consistent with those reported by R.N. Jones [191] for methylene-bridging on benz$[a]$anthracene and dibenz$[a,h]$anthracene, and by Harvey et al. [192] for methylene-bridging on picene.

Figure 3.9. UV absorbance spectra of parent PAH (dashed curve) and the corresponding methylene-bridged PAH (solid curve): (a) phenanthrene and $4H$-cyclopentaphenanthrene; (b) chrysene and $4H$-cyclopenta $\beta$ chrysene; (c) benzo$[e]$pyrene and $11H$-inden $\beta$ benzo$[2,1,7-cde]$pyrene; and (d) benzo$[a]$pyrene and $4H$-benzo$[def]$cyclopenta$[mno]$chrysene. The UV absorbance spectra of $11H$-indo $\beta$ benzo$[2,1,7-cde]$pyrene and $4H$-benzo$[def]$cyclopenta$[mno]$chrysene are those published in the literature [142] for these compounds. All the other UV absorbance spectra are from authentic reference standards.
Having established that methylene-bridging preserves the general shape and intensity of the UV spectra but shifts the spectra to longer wavelengths, we now examine the UV spectra in terms of the shifts in the UV spectral bands. In general, the UV spectrum of a PAH contains a number of well defined peaks occurring in three groups known as the $\beta/\beta'$-bands, the $p$-bands, and the $\alpha$-bands. It is well documented that an alkyl-substitution on a PAH does not affect the shape and intensity of the UV spectrum of the parent compound but shifts the entire UV spectrum of the parent compound by 2-3 nm to longer wavelengths [48,191]. A close examination of the UV spectra in Figure 3.9 reveals that unlike the small (2-3 nm) bathochromic shift in the UV spectrum in the case of alkyl-substitution [48,191], the shift in the UV spectrum in the case of methylene-bridging is not the same for the different wavelength bands and is more pronounced for the $p$-band peaks (∼10 nm for the terminal $p$-band peak).

Another important aspect of the UV spectra of PAH that is helpful in predicting the structure of an unknown PAH is Clar’s annellation theory [44,45,48]. For benzenoid PAH, annellation theory [44,45,48] predicts the position of the wavelength of maximum absorption (terminal $\beta$- and $p$-band peaks) of an unknown PAH from the UV spectrum of a known PAH differing by a single aromatic ring. Based on the location of the added aromatic ring, and whether or not the added ring increases the number of aromatic sextets (rings containing 6 $\pi$ electrons and drawn with three alternate double bonds), annellation theory [44,45,48] predicts the shifts in the terminal $\beta$- and $p$-band peaks. Since methylene-bridging on a benzenoid PAH only shifts the UV spectral bands to longer wavelengths and preserves the overall shape and intensity of the UV spectrum of the parent benzenoid PAH, it would be interesting to examine if annellation theory principles are applicable to the methylene-bridged PAH. In the following, we examine the effects of methylene-bridging on UV spectra.
Figure 3.10. Effects of aromatic ring addition on the UV absorbance spectra: (a) UV spectra of phenanthrene (dashed curve) and chrysene (solid curve); (b) UV spectra of phenanthrene (dashed curve) and benz[a]anthracene (solid curve); (c) UV spectra of 4H-cyclopentaphenanthrene (dashed curve) and 4H-cyclopentachrysene (solid curve); and (d) UV spectra of 4H-cyclopentaphenanthrene (dashed curve) and 11H-benz[bc]aceanthrylene (solid curve). The UV absorbance spectra of 11H-benz[bc]aceanthrylene is from the present study.

Examples of various types of aromatic ring additions and their effects on the UV spectra of PAH have been reported in the literature [44-46,48,49]. Figures 3.10a and 3.10b present examples of a ring addition to an aromatic sextet of phenanthrene at positions “a” and “b,” respectively: Figure 3.10a, UV spectra of phenanthrene (dashed curve) and chrysene (solid curve); and Figure 3.10b, UV spectra of phenanthrene (dashed curve) and benz[a]anthracene (solid curve). Figure 3.10a reveals that the addition of an aromatic ring to phenanthrene at
position “a” results in benzene rings annellated in a zig-zag way to give chrysene. A comparison of the UV spectra of phenanthrene and chrysene reveals a shift of 16 nm in the terminal $\beta$-band and 27 nm in the terminal p-band. An aromatic ring addition to phenanthrene at the position “b” results in linearly annellated benzene rings to give benz[a]anthracene. The shifts in the terminal $\beta$-band and p-band in this case are 35 nm and 66, respectively. In both cases, the ring addition does not increase the number of sextets. These observations are consistent with annellation theory predictions [44,45,48] that a ring addition to an aromatic sextet shifts the p-bands of the UV spectrum substantially to longer wavelengths provided there is no increase in the number of sextets.

The shifts in the UV spectrum of methylene-bridged phenanthrene when an aromatic ring is added to a sextet at positions “a” and “b,” respectively, are shown in Figures 3.10c and 3.10d: Figure 3.10c, UV spectra of $4H$-cyclopentaphenanthrene (dashed curve) and $4H$-cyclopentachrysene (solid curve); and Figure 3.10d, UV spectra of $4H$-cyclopentaphenanthrene (dashed curve) and $11H$-benz[bc]aceanthrylene (solid curve). As in the case of “phenanthrene to chrysene” in Figure 3.10a, Figure 3.10c reveals that the addition of an aromatic ring to $4H$-cyclopentaphenanthrene at position “a” to give $4H$-cyclopentachrysene results in a very similar shift of 15 nm in the terminal $\beta$-band and 27 nm in the terminal p-band of the UV spectrum. In addition, Figure 3.10d reveals that the shifts of 36 nm in the terminal $\beta$-band and 67 nm in the terminal p-band of the UV spectrum when an aromatic ring is added at position “b” of $4H$-cyclopentaphenanthrene to give $11H$-benz[bc]aceanthrylene are virtually the same as the shifts in the UV spectrum for the case of an aromatic ring addition to phenanthrene to give benz[a]anthracene (Figure 3.10b). Thus, for a ring addition to an aromatic sextet, the methylene-bridged PAH show the exact same annellation effects as their benzenoid counterparts.
Figure 3.11. Effects of aromatic ring addition on the UV absorbance spectra: (a) UV spectra of benzo[e]pyrene (dashed curve) and benzo[ghi]perylene (solid curve); (b) UV spectra of chrysene (dashed curve) and benzo[a]pyrene (solid curve); (c) UV spectra of 11H-indeno[2,1,7-cde]pyrene (dashed curve) and 1H-benzo[ghi]cyclopenta[pqr]perylene (solid curve); and (d) UV spectra of 4H-cyclopentachrysene (dashed curve) and 4H-benzo[def]cyclopenta[mno]chrysene (solid curve). The UV absorbance spectra of 11H-indeno[2,1,7-cde]pyrene, 1H-benzo[ghi]cyclopenta[pqr]perylene, and 4H-benzo[def]cyclopenta[mno]chrysene are from the literature [142] for these compounds. All the other UV absorbance spectra are from reference standards.

Figure 3.11 depicts another example of an aromatic ring addition to a PAH. Figures 3.11a and 3.11b present the effects of an aromatic ring addition to a bay-region: Figure 3.11a, UV spectra of benzo[e]pyrene (dashed curve) and benzo[ghi]perylene (solid curve); and Figure 3.11b, UV spectra of chrysene (dashed curve) and benzo[a]pyrene (solid curve). Figure 3.11a shows that the addition of an aromatic ring to the bay-region of benzo[e]pyrene gives benzo[ghi]perylene and results in a shift of 12 nm in the terminal β-band and 50 nm in the
terminal p-band of the UV spectra. Addition of an aromatic ring to the bay-region of chrysene gives benzo[a]pyrene and a shift of 29 nm in the terminal β-band and 64 nm in the terminal p-band of the UV spectra as shown in Figure 3.11b. These shifts are consistent with the annellation theory predictions [44,45,48] that a ring addition to the bay-region that adds an isolated π bond, but not an aromatic sextet, shifts the terminal p-bands in the UV spectra to longer wavelengths.

The effects of an aromatic ring addition to the bay-regions of the methylene-bridged PAH 11H-indeno[2,1,7-cde]pyrene and 4H-cyclopenta[def]chrysene are presented in Figures 3.11c and 3.11d, respectively: Figure 3.11a, UV spectra of 11H-indeno[2,1,7-cde]pyrene (dashed curve) and 1H-benzo[ghi]cyclopenta[pqr]perylene (solid curve); and Figure 3.11b, UV spectra of 4H-cyclopenta[def]chrysene (dashed curve) and 4H-benzo[def]cyclopenta[mno]chrysene (solid curve). As with the examples in Figure 3.10, Figure 3.11 shows that the shifts in the UV spectrum for the “11H-indeno[2,1,7-cde]pyrene to 1H-benzo[ghi]cyclopenta[pqr]perylene” ring addition and “4H-cyclopenta[def]chrysene to 4H-benzo[def]cyclopenta[mno]chrysene” ring addition are exactly the same as the shifts in the UV spectrum for the corresponding ring additions to parent benzenoid PAH benzo[e]pyrene and chrysene, respectively. Hence, for all the 4 examples shown here, Figures 3.10 and 3.11 demonstrate that the amounts of the shifts in the terminal β- and p-bands—when an aromatic ring is added to a methylene-bridged PAH—are virtually the same as the respective shifts in the terminal β- and p-bands for an aromatic ring addition to the parent benzenoid PAH. Thus the methylene-bridged PAH exhibit the exact same annellation effects as the corresponding parent benzenoid PAH.

To summarize, methylene bridging on a benzenoid PAH conforms to three rules: (Rule 1) preserves the general shape and intensity of the UV spectrum but shifts the UV spectral bands to longer wavelengths, the shift being more pronounced for the p-bands (∼10 nm for the terminal
p-band); (Rule 2) does not affect the amounts of the shifts in the terminal β- and p-bands of the UV spectrum for an aromatic ring addition; and (Rule 3) does not affect Clar’s annellation theory predictions for the shifts in the UV spectrum for an aromatic ring addition. Having established these three “Rules” for methylene-bridging on a benzenoid PAH, we now employ these “Rules” to identify the structures of the two remaining catechol pyrolysis product components eluting at 75.5 min and 82.1 min in Figure 3.7. For clarity, we will denote these two components eluting at 75.5 min and 82.1 min in Figure 3.7 as component A and component B, respectively.

3.3.2.3. Identification of C_{25}H_{14} PAH: Methylene-Bridged Naphtho[2,1-a]pyrene

![Figure 3.12](image-url)

**Figure 3.12.** (a) Mass spectrum of a catechol pyrolysis product component eluting at 75.5 min in Figure 3.7. (b) UV absorbance spectrum of a catechol pyrolysis product component eluting at 75.5 min in Figure 3.7.

Figure 3.12a and 3.12b, respectively, present the mass spectrum and UV spectrum of catechol pyrolysis product component A eluting at 75.5 min in Figure 3.7. The mass spectrum in Figure 3.12a shows the primary [M+H] ion at 315, confirming that component A has a molecular mass of 314. For PAH, a molecular mass of 314 corresponds to a molecular formula of C_{25}H_{14}. The UV spectrum of component A in Figure 3.12b shows well defined peaks. Also, the p-bands in the UV spectrum of component A contain peaks that increase in intensity with increasing wavelength. These UV spectral features are characteristic of a benzenoid PAH [45,48].
Figure 3.13. UV absorbance spectra of the reference standard of naphtho[2,1-\(\alpha\)]pyrene (dashed curve) and of a \(\text{C}_{25}\text{H}_{14}\) catechol pyrolysis product component (solid curve) eluting at 75.5 min in Figure 3.7.

For PAH, the molecular formula \(\text{C}_{25}\text{H}_{14}\) corresponds to a methyl-substitution on a \(\text{C}_{24}\text{H}_{12}\) PAH or a methylene-bridging on a \(\text{C}_{24}\text{H}_{14}\) PAH. (Both \(\text{C}_{24}\text{H}_{12}\) and \(\text{C}_{24}\text{H}_{14}\) PAH have been identified as products of catechol pyrolysis [96].) Therefore, component A is most certainly either a methyl-substituted \(\text{C}_{24}\text{H}_{12}\) PAH or a methylene-bridged \(\text{C}_{24}\text{H}_{14}\) PAH. Collectively, the \(\text{C}_{24}\text{H}_{12}\) PAH and \(\text{C}_{24}\text{H}_{14}\) PAH have 72 theoretically possible isomers that can potentially lead to a \(\text{C}_{25}\text{H}_{14}\) PAH. Figure 3.12b provides strong evidence that component A has the base structure of a benzenoid PAH. Since both methyl-substitution and methylene-bridging preserves the UV spectral features of the parent benzenoid PAH, we can eliminate all the non-benzenoid isomers of \(\text{C}_{24}\text{H}_{12}\) and \(\text{C}_{24}\text{H}_{14}\) PAH. Of the 72 isomers of molecular formula \(\text{C}_{24}\text{H}_{12}\) and/or \(\text{C}_{24}\text{H}_{14}\), only 11 are benzenoid. Coronene, the only benzenoid \(\text{C}_{24}\text{H}_{12}\) PAH can be easily eliminated by comparing the UV absorbance spectrum of the coronene reference standard with that of the catechol pyrolysis product component A. Moreover, 1-methylcoronene—the only possible methylcoronene—elutes at 71.9 min (Figure 3.7).

All the 10 benzenoid \(\text{C}_{24}\text{H}_{14}\) PAH isomers have a bay-region and hence can form a \(\text{C}_{25}\text{H}_{14}\) methylene-bridged PAH. To check for “Rule 1” established in Section 3.3.2.2., we
compare the UV absorbance spectra of the reference standards of each of the 10 C_{24}H_{14} PAH isomers with that in Figure 3.12b for catechol pyrolysis product component A. Of the 10 C_{24}H_{14} PAH isomer, only the UV spectrum of naphtho[2,1-a]pyrene closely matches the UV spectrum of component A shown in Figure 3.12b. Figure 3.13 presents the UV spectrum of catechol pyrolysis product component A (solid curve) along with the UV spectrum of naphtho[2,1-a]pyrene reference standard (dashed curve). The closely matching UV spectral features and the 13 nm shift in the terminal p-bands of component A with reference to that of naphtho[2,1-a]pyrene reference standard confirm that component A is a methylene-bridged naphtho[2,1-a]pyrene.

The structure of naphtho[2,1-a]pyrene has two bay regions, and methylene-bridging can occur at either one of these two bay-regions yielding the structures A1 or A2. To establish the location of the methylene-bridging in component A, we turn to “Rule 2” and “Rule 3” established in Section 3.3.2.2. We first consider the structure A1.

Both “Rule 2” and “Rule 3” developed in Section 3.3.2.2 are based on Clar’s annellation theory predictions. Annellation theory is based on the comparison of UV spectra of PAH differing by a single aromatic ring. One of the structures that is one aromatic ring less than A1 but still retains the location of the methylene-bridging in A1 is the structure I or 4H-benzo[def]cyclopenta[nnn]chrysene. Structure I has two aromatic sextets, and addition of a ring to I at position “a” (which is an isolated π-bond on a moving sextet) yields A1 and increases the
number of aromatic sextets. This is analogous to an aromatic ring addition to II (the benzenoid counterpart of I) to form III (the benzenoid counterpart of AI). For this type of ring addition, annellation theory predicts that the p-bands of the UV spectrum of III (naphtho[2,1-a]pyrene) will show little or no shift with reference to the p-bands of the UV spectrum of II (benzo[a]pyrene) [44,45,48]. Since Section 3.3.2.2 established that the methylene-bridged PAH follow annellation theory (“Rule 3”), the “I to AI” ring-addition should show the same annellation effect as “II to III” ring-addition. Also, “Rule 2” predicts that the shifts in the terminal β-band and the terminal p-band of the UV spectra for the “I to AI” ring-addition should be virtually the same as the respective shifts in the terminal β-band and the terminal p-band of the UV spectra for the “II to III” ring-addition.

Figure 3.14a presents the UV spectra of II (dashed curve) and III (solid curve). As predicted by annellation theory [44,45,48], an addition of an aromatic ring to the isolated π-bond in benzo[a]pyrene (II) to form naphtho[2,1-a]pyrene (III) produces no shift in the p-bands: the p-bands of both II and III are virtually identical. The terminal β-band of naphtho[2,1-a]pyrene, however, is shifted 13 nm to longer wavelength with reference to that of benzo[a]pyrene. Figure 3.14b presents the UV spectra of I (dashed curve) and catechol pyrolysis product component A (solid curve). Figure 3.14b reveals that the p-bands of A are located at exactly the same wavelengths as that of I (4H-benzo[def]cyclopenta[mno]chrysene). In addition, as with the shift in the terminal β-band in the UV spectra in Figure 3.14a for the “II to III” ring-addition, Figure
3.14b reveals that the terminal $\beta$-band of catechol pyrolysis product component A is shifted by almost the same amount (by 14 nm) to longer wavelength with reference to the terminal $\beta$-band of I. Thus, the UV spectrum of the component A satisfies “Rule 2” and “Rule 3” for an aromatic ring addition on 4$H$-benzo[def]cyclopenta[mno]chrysene (I). Thus, the UV spectrum of A in Figure 3.12b is consistent with the structure A1.

![UV spectra](image)

**Figure 3.14.** UV absorbance spectra of: (a) benzo[a]pyrene (dashed curve) and naphtho[2,1-a]pyrene (solid curve); and (b) 4$H$-benzo[def]cyclopenta[mno]chrysene (dashed curve) and a C$_{25}$H$_{14}$ catechol pyrolysis product component (solid curve) eluting at 75.5 min in Figure 3.7. The UV spectrum of 4$H$-benzo[def]cyclopenta[mno]chrysene is from the present study.

We now consider the structure A2. As in the case of A1, we consider the structure IV (13$H$-dibenz[bc,j]aceanthrylene) which is one aromatic ring less than A2 but still retains the methylene-bridging in IV (13$H$-dibenz[bc,j]aceanthrylene). The “IV to A2” ring-addition is another example of an aromatic ring addition to the bay-region (similar to those in Figure 3.11)
and annellation theory predicts a substantial shift in the p-bands to longer wavelengths [44,45,48]. In addition, “Rule 2” predicts that the shift in the terminal β-band and p-band of the UV spectra for the “IV to A2” ring-addition should be virtually the same as the respective shifts in the terminal β-band and p-band of the UV spectra for the “V to VI” ring-addition.

Figure 3.15. UV absorbance spectra of: (a) dibenz[a,h]anthracene (dashed curve) and naphtho[2,1-a]pyrene (solid curve); and (b) 13H-dibenzo[bc,j]aceanthrylene (filled circles) and a C_{25}H_{14} catechol pyrolysis product component (solid curve) eluting at 75.5 min in Figure 3.7. The UV spectrum of 13H-dibenzo[bc,j]aceanthrylene is from R.N. Jones [191].

Figure 3.15a presents the UV spectra of V (dashed curve) and VI (solid curve). The spectral features of V and VI are consistent with the annellation theory predictions for an aromatic ring addition to a bay-region. Figure 3.15b presents the UV spectra of IV (filled circles) and catechol pyrolysis product component A (solid curve). Since a complete UV spectrum for IV is not available, we have used the UV spectral data (filled circles) from R.N. Jones [191]. Figure 3.15b reveals that the spectral features of IV and catechol pyrolysis product component A are also consistent with the annellation theory predictions for an aromatic ring addition to the bay-region. But the shift of 38 nm in the terminal p-bands for the “IV to A” ring-addition is 7 nm longer than the shift (31 nm) for the “V to VI” ring-addition (Figure 3.15a) and hence is not consistent with “Rule 3” predictions. Hence, we conclude that the UV spectrum of component A

\[ \text{Absorbance} \]
\[ \text{Wavelength (nm)} \]

\[ \text{Absorbance} \]
\[ \text{Wavelength (nm)} \]
in Figure 3.12b is not consistent with structure A2. Thus, we conclude that component A is 5H-dibenzo[a,mno]cyclopenta[def]chrysene (A1).

3.3.2.4. Identification of C_{25}H_{14} PAH: Methylene-Bridged Naphtho[2,3-a]pyrene

![Mass spectrum and UV absorbance spectrum](image)

**Figure 3.16.** (a) Mass spectrum of a catechol pyrolysis product component eluting at 82.1 min in Figure 3.7. (b) UV absorbance spectrum of a catechol pyrolysis product component eluting at 82.1 min in Figure 3.7. The higher intensities of the p-bands at 413 nm and 439 nm as compared to the terminal p-band at 465 nm in the spectrum of the catechol pyrolysis product component is most likely due to spectral interference from co-eluting dibenzo[cd,lm]perylene.

We now examine the spectral features of catechol pyrolysis product component B eluting at 82.1 min in Figure 3.7. Figure 3.16a and 3.16b, respectively, present the mass spectrum and UV spectrum of catechol pyrolysis product component B eluting at 82.1 min in Figure 3.7. As with component A, the mass spectrum in Figure 3.16a confirms that component B also has a molecular mass of 314 and hence is a C_{25}H_{14} PAH. Figure 3.7 reveals that the catechol pyrolysis product component B is produced in very low amounts and elutes very close to dibenzo[cd,lm]perylene. Thus, the UV spectrum of component B in Figure 3.16b shows spectral interference at 413 nm and 439 nm. Even though the peaks in the UV spectrum of component B in Figure 3.16b are not as well defined as that of component A in Figure 3.15b and the p-bands in the spectrum of component B do not show an increase in intensity with increasing wavelength, we are confident that component B is a benzenoid PAH. Since the p-bands of co-eluting
dibeno\[cd,lm\]perylene (which is produced in higher amounts from catechol pyrolysis as compared to component B) are located at 389 nm, 413 nm, and 439, the higher intensities of the p-bands in the UV spectrum of catechol pyrolysis product component B at 413 nm and 439 nm with reference to the terminal p-band at 465 nm (Figure 3.16b) can be attributed to spectral interference from co-eluting dibeno\[cd,lm\]perylene.

**Figure 3.17.** UV absorbance spectra of the reference standard of naphtho[2,3-\(a\)]pyrene (dashed curve) and of a C\(_{25}\)H\(_{14}\) catechol pyrolysis product (solid curve) component eluting at 82.1 min in Figure 3.7.

As with component A, a comparison of the UV spectrum of component B with the UV spectra of the reference standards of each of the 11 C\(_{24}\)H\(_{14}\) benzenoid PAH isomers reveals that the UV spectrum of component B matches the UV spectrum of naphtho[2,3-\(a\)]pyrene in general shape and intensity. Figure 3.17 presents the UV spectrum of catechol pyrolysis product component B (solid curve) along with the UV spectrum of naphtho[2,3-\(a\)]pyrene reference standard (dashed curve). The closely matching UV spectral features and the 11 nm shift in the terminal p-band of component B with reference to the terminal p-band of naphtho[2,3-\(a\)]pyrene reference standard suggests that component B is a methylene-bridged naphtho[2,3-\(a\)]pyrene (from “Rule 1”).
Since naphtho[2,3-a]pyrene has only one bay-region, the likely structure of component B is as shown above. To test for “Rule 2” and “Rule 3,” we consider the structure I that is one aromatic ring less than component B. Unlike the “I to A1” ring addition that increases the number of aromatic sextets, a ring addition to I at position “b” gives B and does not increase the number of aromatic sextets. This is analogous to the “II to VII” ring addition and annellation theory predicts a substantial shift in the p-bands for this type of ring addition [44,45,48].

![Diagram showing the structures of I, B, II, and VII](image)

Figure 3.18. UV absorbance spectra of: (a) benzo[a]pyrene (dashed curve) and naphtho[2,3-a]pyrene (solid curve); and (b) 4H-benzo[def]cyclopenta[mno]chrysene (dashed curve) and a C$_{25}$H$_{14}$ catechol pyrolysis product component (solid curve) eluting at 82.1 min in Figure 3.7. The UV spectrum of 4H-benzo[def]cyclopenta[mno]chrysene is from the present study.

Figure 3.18a presents the UV spectra of II (dashed curve) and VII (solid curve). The spectral features of II and VII are consistent with the annellation theory predictions that an aromatic ring addition to a ring with a high degree of aromaticity preserves the basic appearance of the UV spectrum but shifts the p-bands substantially to longer wavelengths [44,45,48,49].

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Figure 3.18a also reveals that the “II to VII” ring additions brings about a 36 nm shift in the terminal $\beta$-band and 74 nm shift in the terminal p-band of the UV spectrum. Figure 3.18b presents the UV spectra of I (dashed curve) and catechol pyrolysis product component B (solid curve). Figure 3.18b reveals that the “I to B” also follows annellation theory predictions and brings about the exact same shifts in the terminal $\beta$-band and the terminal p-band of the UV spectrum as with the “II to VII” ring addition. The UV spectrum of component B in Figure 3.16b is consistent with “Rule 2” and “Rule 3.” Hence, we conclude that component B is $5H$-dibenzo[b,mno]cyclopenta[def]chrysene (B). Thus, employing the three “Rules” developed in this study for predicting the structure of methylene-bridged PAH, we have identified two C$_{25}$H$_{14}$ methylene-bridged PAH for which reference standards or published UV spectra are not available. This is the first ever identification of these two C$_{25}$H$_{14}$ PAH as products of any fuel.

3.3.3. Identification of Large PAH

In addition to the carcinogenic and mutagenic C$_{24}$H$_{14}$ PAH and methylene-bridged PAH, catechol pyrolysis also produces 16 large PAH (C > 25). Figure 3.19 presents the portion of the HPLC chromatogram (from the HPLC/UV) in which the large PAH products of catechol pyrolysis (at 1000 °C and 0.3 s) elute. Shown in red in Figure 3.19 are the chemical structures corresponding to the 16 large PAH products of catechol pyrolysis whose mass spectra and UV spectra have permitted determination of their exact isomer-specific identities. In the order of elution in Figure 3.19, the 16 large PAH products of catechol pyrolysis at 1000 °C and 0.3 s are: benzo[a]indeno[1,2,3-cd]pyrene, dibenzo[b,ghi]perylene, phenanthro[2,3-a]pyrene, dibenzo[e,ghi]perylene, cyclopenta[bc]coronene, naphtho[8,1,2-bcd]perylene, benz[a]anthanthrene, benzo[a]coronene, dibenzo[cd,lm]perylene, benzo[ghi]naphtho[8,1,2-bcd]perylene, benzo[pqr] naphtho[8,1,2-bcd]perylene, tribenzo[cd,ghi,lm]perylene, benzo[c]picene, naphtho[8,1,2-abc]coronene, ovalene, and benzo[cd]naphtho[1,2,3-lm]perylene. Except for phenanthro[2,3-
a]pyrene, cyclopenta[bc]coronene, and dibenzo[cd,lm]perylene [96], none of the remaining 13 large PAH of Figure 3.19 have ever before been identified as products of catechol or any phenol-type fuel. In addition to the 16 large PAH products, Figure 3.19 shows in black the chemical structures of the 7 other PAH products of catechol pyrolysis that elute in the 65- to 100-min range of the HPLC chromatogram. The identifications of 6 of these 7 PAH products have been discussed in Section 3.3.1 and Section 3.3.2. Identification of the one remaining PAH will be discussed in Section 3.3.3.

**Figure 3.19.** HPLC chromatogram of products of catechol pyrolysis (1000 °C and 0.3 s) eluting from 65 to 100 min in the solvent program of the HPLC/UV. Shown in red, the identified large PAH product components, in order of elution from left to right, are: benzo[a]indeno[1,2,3-cd]pyrene, dibenzo[b,ghi]perylene, phenanthro[2,3-a]pyrene, dibenzo[e,ghi]perylene, cyclopenta[bc]coronene, naphtho[8,1,2-bcd]perylene, benz[a]anthanthrene, benzo[a]coronene, dibenzo[cd,lm]perylene, benzo[ghi]naphtho[8,1,2-bcd]perylene, benzo[pqr]naphtho[8,1,2-bcd]perylene, tribenzo[cd,ghi,lm]perylene, benzo[c]picene, naphtho[8,1,2-abc]coronene, ovalene, and benzo[cd]naphtho[1,2,3-lm]perylene. Shown in black are 7 other PAH products of catechol pyrolysis whose identifications have been presented earlier.
Of the 13 newly identified large PAH, authentic reference standards are available for benzo[a]coronene, benzo[pqr]naphtho[8,1,2-bcd]perylene, naphtho[8,1,2-abc]coronene, and ovalene. Six of the remaining nine have published UV spectra available in literature: benzo[a]indeno[1,2,3-cd]pyrene [44], benzo[b,ghi]perylene [185], dibenzo[b,pqr]perylene [44], naphtho[8,1,2-bcd]perylene [44], benzo[c]picene [186], and benzo[cd]naphtho[1,2,3-bm]perylene [48,183]. Identification of the remaining three are based on Clar’s annellation theory principles [45,48]. The UV spectral matches for the ten large PAH for which reference standards/published UV spectra are available are presented first.

![UV absorbance spectra of the reference standard (dashed line) / catechol pyrolysis product component (solid line) pairs: (a) benzo[a]coronene and catechol pyrolysis product component eluting at 81.2 min in Figure 3.19; (b) benzo[pqr]naphtho[8,1,2-bcd]perylene and catechol pyrolysis product component eluting at 86.0 min in Figure 3.19; (c) naphtho[8,1,2-abc]coronene and catechol pyrolysis product component eluting at 92.0 min in Figure 3.19; (d) ovalene and catechol pyrolysis product component eluting at 95.8 min in Figure 3.19. Some spectral interference due to the low concentrations of products is evident in the spectrum of the catechol pyrolysis product components.](image)

Figure 3.20. UV absorbance spectra of the reference standard (dashed line) / catechol pyrolysis product component (solid line) pairs: (a) benzo[a]coronene and catechol pyrolysis product component eluting at 81.2 min in Figure 3.19; (b) benzo[pqr]naphtho[8,1,2-bcd]perylene and catechol pyrolysis product component eluting at 86.0 min in Figure 3.19; (c) naphtho[8,1,2-abc]coronene and catechol pyrolysis product component eluting at 92.0 min in Figure 3.19; (d) ovalene and catechol pyrolysis product component eluting at 95.8 min in Figure 3.19. Some spectral interference due to the low concentrations of products is evident in the spectrum of the catechol pyrolysis product components.
Figure 3.21. UV absorbance spectra of the reference standard (dashed line) / catechol pyrolysis product component (solid line) pairs: (a) benzo[a]indeno[1,2,3-cd]pyrene [44] and catechol pyrolysis product component eluting at 68.2 min in Figure 3.19; (b) dibenzo[b,ghi]perylene [185] and catechol pyrolysis product component eluting at 69.9 min in Figure 3.19; (c) dibenzo[e,ghi]perylene [44] and catechol pyrolysis product component eluting at 72.5 min in Figure 3.19; (d) naphtho[8,1,2-bcd]perylene [44] and catechol pyrolysis product component eluting at 74.9 min in Figure 3.19; (e) benzo[c]picene [186] and catechol pyrolysis product component eluting at 89.5 min in Figure 3.19; (f) benzo[cd]naphtho[1,2,3-lm]perylene [48,183] and catechol pyrolysis product component eluting at 99.1 min in Figure 3.19. Except (f), the solvent used in the reference standard is different from the solvent of the catechol pyrolysis product components (ACN/DCM). Both spectra of (f) are in MeOH/DCM.
Figure 3.20 and Figure 3.21, respectively, present the UV spectra of four large PAH products of catechol pyrolysis, along with the UV spectra of the respective PAH reference standards (from HPLC/UV), and the UV spectra of six large PAH products of catechol pyrolysis, along with the UV spectra of the respective reference standards (from literature [44,48,183,185,186]): Figure 3.20a, benzo[a]coronene; Figure 3.20b, benzo[\textit{pqr}]naphtho[8,1,2-\textit{bcd}]perylene; Figure 3.20c, naphtho[8,1,2-\textit{abc}]coronene; Figure 3.20d, ovalene; Figure 3.21a, benzo[a]indeno[1,2,3-\textit{cd}]pyrene; Figure 3.21b, dibenzo[b,ghi]perylene; Figure 3.21c, dibenzo[\textit{e,ghi}]perylene; Figure 3.21d, naphtho[8,1,2-\textit{bcd}]perylene; Figure 3.21e, benzo[c]picene; Figure 3.21f, benzo[\textit{cd}]naphtho[1,2,3-\textit{lm}]perylene. The large PAH products of catechol pyrolysis are produced in very small amounts (each < 20 µg/g of fed catechol), so they exhibit very small peaks in Figure 3.19. In some cases, the large PAH also elute close to other product components. Hence, there are some slight discrepancies, between the components’ and standards’ UV spectra of Figures 3.20 and 3.21, in a few of the peak heights (\textit{e.g.}, at 260 nm and 280 nm in Figure 3.20b and at 260 nm and 295 nm in Figure 3.21d), and the component spectrum in Figure 3.21b even exhibits a peak at 308 nm that is due to an unidentified co-eluting compound.

The UV spectra of catechol pyrolysis product components in Figures 3.21a, 3.21b, 3.21c, 3.21d, and 3.21e show slight shifts in comparison to the UV spectra of the respective reference standards. The UV spectra of the reference standards in Figure 3.21 are from the literature and [44,185,186] and are obtained using solvent different from those of Figure 3.19. It has been demonstrated by Kundt [193] and by Bayliss and McRae [194] that a difference in the solvent can result in shifts in the UV spectral bands. Oña and Wornat [187,195] have linked these solvent-associated shifts in the UV spectrum to the differences in the solvent’s index of refraction. Hence, the slight shifts in the UV spectra in Figures 3.21a, 3.21b, 3.21c, 3.21d, and
3.21e are due to the difference in solvents used to obtain the UV spectra. The UV spectrum of catechol pyrolysis product component of Figure 3.21f has been obtained using the same solvent (MeOH/DCM) as that of the reference standard. Hence, the UV spectrum of catechol product component does not show a shift in comparison to the reference standard. Figure 3.22 presents the UV spectral match for the catechol pyrolysis product component in Figure 3.21b adjusted for the difference in the refractive index of the solvents using the method developed by Oña and Wornat [187,195].

Figure 3.22. UV absorbance spectra of the reference standard of dibenzo[b,ghi]perylene (dashed line) adjusted for difference in solvent’s index of refraction and of a catechol pyrolysis product component (solid line) eluting at 69.9 min in Figure 3.19.

In spite of these small discrepancies caused by solvents, co-elution, and the small yields of products, the matching HPLC retention times of each of the component/standard pairs of Figures 3.20, the mass spectra (not presented here), the qualitative agreement in the UV spectral patterns, and the matching wavelengths of UV absorption for each pair in Figures 3.20 and 3.21—all substantiate the identifications of the catechol pyrolysis product components of Figures 3.20a, 3.20b, 3.20c, 3.20d, 3.21a, 3.21b, 3.21c, 3.21d, 3.21e, and 3.21f, as benzo[a]coronene, benzo[pqr]naphtho[8,1,2-bcd]perylene, naphtho[8,1,2-abc]coronene, ovalene, benzo[a]indeno[1,2,3-cd]pyrene, dibenzo[b,ghi]perylene, dibenzo[e,ghi]perylene, naphtho[8,1,2-bcd]perylene, benzo[c]picene, and benzo[cd]naphtho[1,2,3-lm]perylene, respectively.
Reference standards or published UV spectra are not available for the remaining three large PAH products of catechol pyrolysis in Figure 3.19. Using Clar’s annellation theory principles [44,45,48], mass spectral information, and the correlation between the HPLC retention time and the length to breadth (L/B) ratio, Oña et al. identified benz[a]anthanthrene [188] among the products of supercritical pyrolysis of a Fischer-Tropsch synthetic jet fuel. Using the same techniques, McClaine et al. [46,49] identified benzo[ghi]naphtho[8,1,2-bcd]perylene and tribenzo[cd,ghi,lm]perylene among the products of supercritical pyrolysis of toluene and a Fischer-Tropsch synthetic jet fuel. The HPLC solvent program used in the studies of Oña et al. [188] and by McClaine et al. [46,49] is the same as the one used for the present study. Hence, the identifications of these three large PAH among the products of catechol pyrolysis were achieved by matching the UV spectra of the catechol pyrolysis product components to those obtained by Oña et al. [187,188] and by McClaine et al. [46,49] from the supercritical pyrolysis of toluene and a Fischer-Tropsch synthetic jet fuel.

Figure 3.23 presents the UV spectra of three remaining large PAH products of catechol pyrolysis, along with the respective reference UV spectra from the supercritical pyrolysis of a Fischer-Tropsch synthetic jet fuel (obtained on the HPLC/UV [46,49,188]): Figure 3.23a, benz[a]anthanthrene; Figure 3.23b, benzo[ghi]naphtho[8,1,2-bcd]perylene; Figure 3.23c, tribenzo[cd,ghi,lm]perylene. As with the large PAH in Figures 3.20 and 3.21, the large PAH products of catechol pyrolysis in Figure 3.23 are also produced in very small amounts (each < 20 µg/g of fed catechol) and exhibit very small peaks in Figure 3.19. Hence, the UV spectra of the catechol pyrolysis product component in Figure 3.19 show slight discrepancies (e.g., 330 nm and 380 nm in Figure 3.23a and 280 nm in Figure 3.23c). Nevertheless, the mass spectra (not presented here), the qualitative agreement in the UV spectral patterns, and the matching wavelengths of UV absorption for each component/reference pairs (reference spectra are
obtained from the supercritical pyrolysis of a Fischer-Tropsch synthetic jet fuel) of Figures 3.23—all substantiate the identifications of the catechol pyrolysis product components of Figures 3.23a, 3.23b, 3.23c, and 3.23d, as benz[a]anthanthrene, benzo[ghi]naphtho[8,1,2-bcd]perylene, and tribenzo[cd,ghi,lm]perylene, respectively.

![Absorbance spectra](image)

**Figure 3.23.** Reference UV absorbance spectra obtained from the supercritical pyrolysis of a Fischer-Tropsch synthetic jet fuel (dashed line) and UV absorbance spectra of the respective catechol pyrolysis product component (solid line) with same retention time: (a) benz[a]anthanthrene [188] and catechol pyrolysis product component eluting at 76.6 min in Figure 3.19; (b) benzo[ghi]naphtho[8,1,2-bcd]perylene [46] and catechol pyrolysis product component eluting at 82.8 min in Figure 3.19; (c) tribenzo[cd,ghi,lm]perylene [49] and catechol pyrolysis product component eluting at 88.3 min in Figure 3.19.

### 3.3.4. Other PAH

In addition to the 12 C_{24}H_{14} PAH, 8 methylene-bridged PAH, and 16 large PAH, the remaining 17 newly identified products of catechol pyrolysis are: 2-naphthol, benzanthrone, 6H-benzo[cd]pyren-6-one, 3-methylphenanthrene, 1-methylantracene, 2-methylantracene, 1-
methylpyrene, 2-methylpyrene, 4-methylpyrene, 1-methylcoronene, benzo[b]fluorene, dibenz[a,c]anthracene, benzo[c]chrysene, naphthacene, pentaphene, dibenzo[a,h]fluorene, and 8H-dibenzo[a,jk]pyrene.

Of these 17 PAH products, 2-naphthol, benzanthrone, 6H-benzo[cd]pyren-6-one, 1-methylnanthracene, 2-methylnanthracene, 1-methylpyrene, benzo[b]fluorene, dibenz[a,c]anthracene, benzo[c]chrysene, and pentaphene are identified by matching their UV spectra with the UV spectra of the respective reference standards. 3-methylphenanthrene, 2-methylpyrene, 4-methylpyrene, naphthacene, and 8H-dibenzo[a,jk]pyrene are identified by matching their respective UV spectra with those published in the literature for these compounds [44,196]. The UV spectral evidence confirming these identities is presented in Appendix F.

Reference standards or published UV spectra are not available for 1-methylcoronene and dibenzo[a,h]fluorene. Identification of 1-methylcoronene is based on mass spectral information and by comparing the UV spectra of the catechol pyrolysis product component with that of coronene reference standard. Since neither a reference standard nor a published UV spectrum is available for dibenzo[a,h]fluorene, the identification of dibenzo[a,h]fluorene is based on mass spectral information and by comparing the UV spectrum of the catechol pyrolysis product component with that of a methyl-substituted dibenzo[a,h]fluorene published by Somers et. al. [197]. The UV and mass spectral evidence confirming the identities of 1-methylcoronene and dibenzo[a,h]fluorene, respectively, are presented in Figures F.5 and F.6 in Appendix F.

3.3.5. Comparison with Coal Products

Wornat et al. [96] have previously demonstrated the remarkable similarity in product distribution obtained from catechol pyrolysis to that obtained from coal volatiles pyrolysis. Of the 61 products identified from catechol pyrolysis, 56 were present among the products of coal volatiles pyrolysis. The identification of 50 additional products from catechol pyrolysis in the
present study prompted a re-analysis of the coal volatiles products chromatogram using the improved analytical techniques. Of the 111 products of catechol pyrolysis, 84 have been identified as products of coal pyrolysis [198]; further confirming the assertion that catechol is an ideal model compound to study solid fuels.

3.4. Summary and Conclusions

In order to better understand the formation of PAH during the pyrolysis and combustion of solid fuels, we have performed pyrolysis of the model fuel catechol in a laminar-flow reactor at 1000 °C and 0.3 s. The products collected have been analyzed by HPLC with UV and mass spectrometric detection. Product analysis reveals that catechol pyrolysis produces 111 products ranging from one to ten fused aromatic rings and falling into 8 different structural classes: 47 benzenoid PAH, 14 indene benzologues, 13 fluoranthene benzologues, 10 cyclopenta-fused PAH, 8 ethynyl-substituted species (triacetylene and 7 ethynyl-substituted aromatics), 10 methylated aromatics, 2 bi-aryls, and 7 oxygen-containing aromatics. Of the 111 products, 61 have been identified in a previous catechol pyrolysis study [96]. The 50 newly identified products of catechol pyrolysis have never before been identified as products of catechol or any phenol type fuel. Among the products are 15 C_{24}H_{14} PAH and 8 methylene-bridged PAH—two PAH product classes that are known to contribute significantly towards the carcinogenicity and mutagenicity of PAH mixtures [6,7,9,10,60,110,129-133,142,172-174]. Catechol pyrolysis also produces 16 large (C > 25) PAH.

A new rule was developed and demonstrated for the identification of methylene-bridged PAH using annellation theory principles and UV spectral characteristics. Employing these rules, two molecular weight 314 PAH were identified as 5H-dibenzo[a,mno]cyclopenta[def]chrysene and 5H-dibenzo[b,mno]cyclopenta[def]chrysene. These two compounds have never before been synthesized and their existence has never been documented.
The relevancy of catechol as a model fuel is further confirmed by the remarkable similarity in the product distribution obtained from catechol pyrolysis to that obtained from coal pyrolysis. Since the isomer specific identification of the PAH is critical to the development of chemical pathways leading to their formation, the present study will be helpful in understanding the formation of PAH during solid fuel pyrolysis and combustion.
Chapter IV. Effects of Oxygen Addition: Yields of the C$_1$-C$_8$ Thermal Decomposition Products*

4.1. Introduction

Combustion of solid fuels like coal, wood, and biomass is associated with high-temperature oxygen-deficient zones within the immediate vicinities of the burning fuel particles. Solid-fuel pyrolytic reactions dominate in these zones, producing volatiles that contain light-gas fuel fragments as well as high-molecular-weight fragments [199,200], which in turn can undergo further pyrolytic reactions to form polycyclic aromatic hydrocarbons (PAH). The combustible volatiles are driven out of the particle through the particle pore structure, where they encounter oxygen and undergo oxidation reactions. In such diffusion-flame configurations, incomplete combustion can result, and incomplete combustion of fuels is by far the major contributor to environmental PAH [14]. Because of the inherent carcinogenicity [6-8] and mutagenicity [9,10] of some members of this compound class, and their relative stability once released into the environment, the formation and fate of PAH are of concern. PAH are also precursors to soot [15,16], a major contributor to fine particulates responsible for heart and lung diseases [11,12]. Therefore, an understanding of chemical pathways and product yields from reactions relevant to PAH formation under solid fuel pyrolysis and combustion conditions would be helpful to the development of detailed kinetic models for solid fuel combustion.

Although the literature reports several studies [25-28] on the identification and quantification of PAH from solid fuel pyrolysis and combustion, and generalized models of solid fuel combustion are available [64,201], no study has yet reported a detailed mechanistic investigation and kinetic parameters for PAH formation from solid fuels like coal, wood, and biomass. The complex nature of these fuels makes it extremely difficult to attribute products to

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certain reaction pathways. Therefore, most of the mechanistic studies on PAH formation have focused on examining the thermal decomposition of model compounds representing these fuels [16,25,83,85-92,179].

For our investigations into the decomposition of solid fuels and formation of PAH, we have chosen catechol (ortho-dihydroxybenzene) as a model fuel compound. As a prominent structural entity of coal [100], tobacco [103], and lignin (a major component of wood [101])—as well as a major component in biomass tars [102] and tobacco smoke [104]—catechol is a suitable model compound for investigating solid fuel combustion. Moreover, the aromatic ring structure of catechol is more likely to contribute to PAH than are the aliphatic constituents of solid fuels. Catechol’s relevancy is further strengthened by the demonstrated [96] similarity between PAH product distributions from catechol pyrolysis and coal volatiles pyrolysis.

In combustion systems, pyrolytic reactions are identified as the primary source of PAH. Hence, previous studies in our research group have examined in detail the homogeneous gas-phase pyrolysis of catechol in an isothermal laminar-flow reactor [50,96-99] at temperatures of 700-1000 °C, to gain fundamental insights into the formation of PAH from catechol decomposition. Three key observations from that work provide strong evidence that thermal decomposition products are major participants in reactions of PAH formation and growth: (1) The catechol pyrolysis environment contains a high abundance of C₂-C₅ species [98], and a decrease in the yields of the C₃-C₅ species at higher temperatures corresponds to an increase in PAH yields [98,99]. (2) At a given pyrolysis condition, PAH of smaller ring number are produced in higher yield than those of larger ring number [97,99], but increasing the pyrolysis temperature or residence time produces PAH products of higher ring number [99]. (3) Calculated global kinetic rate parameters for the formation of PAH from catechol show an increase in activation energy with increasing PAH ring number [97]. These three observations are consistent
with a mechanism for PAH growth involving successive addition of C₂-C⁵ species to initially single-ring compounds. In addition, the high abundance of ethynyl-substituted PAH and cyclopenta-fused PAH [99]—both thought to arise from acetylene addition to aryl radicals [50]—and the abundance of C₂ compounds among the catechol pyrolysis products [98] suggest that the hydrogen-abstraction/acetylene-addition (HACA) mechanism [17,52,53,202] may play a major role in the formation of PAH during the pyrolysis and fuel-rich oxidation of catechol.

Since oxygen is naturally present in the environment of a burning fuel, the effects of oxygen addition on the thermal decomposition of catechol and the formation and destruction of PAH during pyrolysis and fuel-rich oxidation conditions is a primary focus of our research. In addition to PAH, the pyrolysis of catechol produces a range of C₁-C₅ species, single-ring aromatic hydrocarbons, as well as oxygen-containing organics. The effects of oxygen addition on the yields of PAH and oxygen-containing organic products of catechol will be addressed in forthcoming papers. In the present study, we report the effects of oxygen addition on the yields of the C₁-C₅ species and single-ring aromatics—the primary building blocks of PAH—under pyrolysis and fuel-rich oxidation conditions. The catechol pyrolysis and fuel-rich oxidation experiments are carried out in an isothermal laminar-flow reactor at temperatures of 500-1000 °C, and the products are analyzed by gas chromatography and nondispersive infrared analysis.

In combustion systems, C₁-C₅ species are known to play a major role in PAH formation [66-74]. Also, the formation of single-ring aromatics has been reported to be the rate-controlling step in the formation of larger PAH and soot [73,75,76]. Therefore, here we present the yields, as functions of temperature, of twelve C₁-C₅ species and five single-ring aromatics produced during the pyrolysis and fuel-rich oxidation of catechol over a range of oxygen concentrations. We expand the set of reactions—previously proposed [98] to account for the C₁-C₅ and single-ring
aromatic products from catechol pyrolysis—to include reactions taking place in the presence of oxygen. Finally, we relate the results to the formation and fate of PAH in the context of solid fuel combustion.

4.2. Experimental Equipment and Procedures

4.2.1. Reactor System

The reactor system for catechol pyrolysis and oxidation experiments is shown in schematic form in Figure 2.1 and is described in detail elsewhere [50,96-99]. The reactor system consists of a fuel vaporizer, isothermal quartz flow reactor, Balston Teflon filter, and product collection system. The gaseous products are collected in a Teflon gas-sampling bag, and the condensed-phase products are collected, in separate experiments, in a condensed-phase product collection system. For the pyrolysis experiments, solid catechol particles (>99.5% pure, purchased from Aldrich Chemical Co.) are loaded as a fixed bed into a Pyrex tube placed vertically inside the fuel vaporizer, an isothermal oven maintained at 85 °C for slight vaporization of catechol. The vapor-phase catechol is entrained in a flowing stream of ultrahigh purity (grade 6.0) nitrogen carrier gas, resulting in a 0.65 mole-% carbon loading in the reactor feed gas. (GC-FID analyses of samples taken from the vaporizer exit stream, both before and after each pyrolysis experiment, ensure the consistency of the 0.65 mole-% carbon loading in the reactor feed gas.) The pyrolysis reactions take place in a high-temperature laminar-flow reactor, which consists of a 2-mm (inner diameter) quartz tube insulated at both ends and maintained at isothermal conditions by a three-zone electrically heated furnace. The reactor is operated at temperatures of 500-1000 °C and a residence time of 0.3 s.

For the fuel-rich oxidation experiments, the nitrogen carrier gas is doped, in separate experiments, with known quantities of oxygen. The oxygen ratios (OR) for the separate experiments are set to 0.0 (pyrolysis), 0.22, 0.58 and 0.92. The OR is defined as the mass feed
rate of oxygen to the mass feed rate of catechol (for that experiment), divided by the oxygen-to-catechol mass ratio required for stoichiometric oxidation.

4.2.2. Product Analysis

The catechol pyrolysis products exiting the reactor are quenched to room temperature (quench time, approximately 0.028 s), and the condensed-phase products are trapped on a Balston filter. The C$_1$-C$_5$ gas-phase products along with benzene, the most volatile of the aromatic products, flow through the filter and are collected in a Teflon gas-sampling bag for subsequent compositional analysis. The rest of the single-ring aromatic products are collected, in a separate experiment, using a condensed-phase products collection system (consisting of a Balston Teflon filter and dichloromethane solvent trap) and dissolved in dichloromethane for subsequent identification and quantification using gas chromatographic analysis.

A portion of the product gases collected is pumped from the sampling bag through two Horiba Model VIA-510 nondispersive infrared analyzers to quantify CO and CO$_2$. The remaining product gases are then routed to an Agilent Model 6890/5973 gas chromatograph/flame-ionization detector/mass spectrometer (GC/FID/MS) for analysis of C$_1$-C$_6$ hydrocarbons. Separation of the hydrocarbon gases is achieved on a GS GASPRO capillary column of length, 30 m, and diameter, 0.32 mm. Except for cyclopentadiene and vinylacetylene, identification of the hydrocarbon products is accomplished by matching the retention times and mass spectra of individual product components with those of reference standards, and product quantification is based on the calibration of the GC/FID with reference standards. Since a reference standard for cyclopentadiene is not commercially available, its identification in the catechol pyrolysis products is based on matching the product component’s GC retention index with that of cyclopentadiene generated from the pyrolysis of dicyclopentadiene [88,120] as well as by matching the product component’s mass spectrum with that of the reference standard in the
NIST/EPA/NIH mass spectral library. The identification of vinylacetylene is based on matching the product component’s mass spectrum with that of the reference standard in the NIST/EPA/NIH mass spectral library. In addition, the identification of vinylacetylene among the thermal decomposition products of catechol is consistent with the thermal formation of vinylacetylene from acetylene \([121]\) and 1,3-butadiene \([122-124]\)—two of the highest-yield hydrocarbon products present in the catechol pyrolysis environment.

The condensed-phase catechol pyrolysis products are also analyzed on the Agilent Model 6890/5973 GC/FID/MS. A 2-\(\mu\)L aliquot of the product solution is injected by syringe, through a split injector, onto a HP-5 fused silica capillary column of length, 30 m, diameter, 0.25 mm, and film thickness 0.1 \(\mu\)m. The column temperature is programmed to hold at 40 °C for the first 3 minutes; it is then ramped at 4 °C/min to 300 °C, and held at 300 °C for 15 minutes. The single-ring aromatic products are identified by matching retention times and mass spectra with those of reference standards.

The PAH products are quantified by a Hewlett–Packard Model 1050 high-pressure liquid chromatograph (HPLC) \([96,99]\), coupled to a diode-array ultraviolet-visible absorbance detector. The results of the HPLC analyses are reported in Chapter V and in a paper \([113]\) that addresses the effects of oxygen on individual PAH yields. In the present chapter, we report the effects of oxygen on the yields of \(C_1\)-\(C_5\) hydrocarbons and single-ring aromatics, which are analyzed by GC.

Separate experiments have been carried out at nine different temperatures over the temperature range of 500-1000 °C and a residence time of 0.3 s, under pure pyrolysis conditions \((OR = 0.0)\) and fuel-rich oxidation conditions \((OR = 0.22, 0.58, 0.92)\). The yields obtained from HPLC and GC analyses of products from repeat experiments at the same temperature give very reproducible results. The collective mass of carbon obtained from the gas-phase products and the
condensed-phase products—including PAH and oxygenated organics (not reported here) as well as any unconverted catechol—accounts for all of the carbon fed to the reactor as catechol. A carbon balance is thus closed on this reactor system.

4.3. Results and Discussion

Previous studies in our research group have reported the identification of $10 \text{ C}_1$-$\text{C}_5$ species [98], 5 single-ring aromatics [96-99], as well as 54 individual PAH [96,97,99] from catechol pyrolysis. Due to improved analysis techniques, in the present study, we have been able to identify an additional $\text{C}_4$ product, vinylacetylene, from catechol pyrolysis. A mechanism for catechol decomposition and formation of the $\text{C}_1$-$\text{C}_6$ thermal decomposition products under pyrolysis conditions (with no oxygen added) has been presented in a previous study [98].

Oxygen is naturally present in the environment of a burning fuel. Hence, here we extend our studies to pyrolysis in the presence of oxygen. The addition of oxygen can lead to two competing effects on pyrolysis product yields: (1) The Radical Enhancement Effect stems from an oxygen-induced increase in the number of free radicals, which leads to higher rates of pyrolysis reactions and increases in pyrolysis product yields. (2) The Oxidative Destruction Effect stems from an increase in oxidizer concentration, which increases rates of pyrolysis-product oxidation reactions, leading to decreases in pyrolysis product yields. The roles of these two competing effects will be examined in the results to follow on the effects of oxygen on catechol’s pyrolysis product yields. We first consider oxygen’s effects on catechol conversion.

4.3.1. Catechol Conversion

Figure 4.1 presents the yield/temperature profiles for unreacted catechol under pyrolysis ($\text{OR} = 0.0$) and fuel-rich oxidation ($\text{OR} = 0.22, 0.58, 0.92$) conditions. Figure 4.1 shows that, at all conditions studied, the yields of unreacted catechol follow a similar trend of decreasing with increasing temperature, as catechol conversion rapidly increases to 100% at temperatures $\geq 850$
°C. Figure 4.1 also reveals that in the temperature range 500-850 °C, catechol conversion increases with increasing OR (more oxygen available). Therefore, the presence of oxygen appears to increase the rate of catechol conversion.

![Diagram of catechol conversion vs temperature and oxygen ratio]

**Figure 4.1.** The yield of unreacted catechol as a function of temperature and at different oxygen ratios (OR), during the pyrolysis and fuel-rich oxidation of catechol at 0.3 sec residence time.

In a previous catechol pyrolysis study, Ledesma et al. [98] have proposed the scission of the O-H bond as the initiation reaction for catechol decomposition. Following initiation, catechol consumption under pyrolytic conditions proceeds via reactions with H and OH radicals [98]. Under oxidative conditions, however, the reactions involving oxygen and oxidative radicals must also be included. By analogy to the phenol oxidation studies of Brezinsky et al. [88], the following reactions will be relevant in catechol consumption under oxidative conditions (in addition to the reactions [98] involving H and OH radicals):
These additional reactions involving oxygen and peroxo radical apparently increase the rate of catechol conversion in our system, since Figure 4.1 shows that catechol conversion increases with increasing OR at temperatures ≤ 850°C.

4.3.2. C₁-C₅ and Single-Ring Aromatic Products

All the 11 C₁-C₅ species, including vinylacetylene, and the 5 single-ring aromatics observed in the pyrolysis experiments are also present under fuel-rich oxidation conditions. CO₂ is produced as an additional product in the presence of oxygen. The C₁-C₅ species identified and quantified in this study include CO, CO₂, methane, ethane, ethylene, acetylene, propyne, propylene, propadiene, 1,3-butadiene, vinylacetylene, and cyclopentadiene. Phenol, benzene, toluene, styrene, and phenylacetylene are the single-ring aromatics identified and quantified in the present study.

Figures 4.2a and 4.2b, respectively, present the summed yields of C₁-C₅ hydrocarbons and the summed yields of single-ring aromatic hydrocarbons, as functions of temperature and at different OR. In the temperature range of 500-800 °C, Figures 4.2a and 4.2b reveal corresponding increases in the summed yields of C₁-C₅ hydrocarbons and of single-ring aromatics with both increasing temperature and increasing OR. This temperature range is also the
one exhibiting increases in catechol conversion with increasing temperature or $OR$, as shown in Figure 4.1, and the oxygen-induced enhancements in the yields of the C$_1$-C$_5$ hydrocarbons and the single-ring aromatics can be attributed to the oxygen-induced enhancement of the free-radical pool. Therefore, the Radical Enhancement Effect appears to dominate in the lower temperature range of 500-800 °C.

**Figure 4.2.** Summed yields of products, as functions of temperature and at different oxygen ratios ($OR$), from the pyrolysis and fuel-rich oxidation of catechol at 0.3 sec residence time: (a) summed yields of C$_1$-C$_5$ hydrocarbons, and (b) summed yields of single-ring aromatic hydrocarbons. For the C$_1$-C$_5$ hydrocarbons, the yields presented are the sum of the individual yields of methane, ethane, ethylene, acetylene, propane, propadiene, propyne, 1,3-butadiene, vinylacetylene, and cyclopentadiene. For the single-ring aromatic hydrocarbons, the yields presented are the sum of the individual yields of benzene, toluene, styrene, and phenylacetylene.

In contrast to the lower temperature range, at temperatures $\geq$ 900 °C, catechol conversion is $\sim$100%, and the summed yields of C$_1$-C$_5$ hydrocarbons (Figure 4.2a) and of single-ring...
aromatics (Figure 4.2b) show dramatic decreases with increasing OR. Hence, the Oxidative Destruction Effect appears to be dominant in this high temperature range. The temperature range 800-900 °C appears to be a transition region, where the Radical Enhancement Effect and Oxidative Destruction Effect are both apparent. The similar trends shown by the \( OR = 0 \) and \( OR = 0.22 \) curves, suggest that pyrolytic reactions are dominant at \( OR = 0.22 \) but that as temperatures approach 900 °C, the decrease in yields is due to the emerging dominance of oxidative destruction. Further evidence, in Figures 4.2a and 4.2b, of the competition between the Radical Enhancement and Oxidative Destruction Effects is found in the shift, with increasing \( OR \), of the temperatures of peak yield to lower temperatures.

In combustion systems, the C\(_1\)-C\(_5\) hydrocarbons are known to be precursors to single-ring aromatics [78,202-209] and growth species in PAH buildup reactions [66-74,202,206]. Therefore, an understanding of the effects of oxygen on the individual C\(_1\)-C\(_5\) hydrocarbons as well as the single-ring aromatics is essential to interpret and understand PAH formation during solid fuel combustion. Figures 4.3-4.9 present the yield-temperature profiles of the individual C\(_1\)-C\(_5\) species and the single-ring aromatics formed during the pyrolysis and fuel-rich oxidation of catechol.

4.3.2.1. Phenol, Benzene and Cyclopentadiene

According to the catechol decomposition mechanism proposed by Ledesma et al. [98], phenol is a major intermediate in catechol pyrolysis and leads to the formation of both benzene and cyclopentadiene. Due to the ring structures in benzene and cyclopentadiene, we believe that benzene and cyclopentadiene play major roles in the formation of PAH from catechol. Figures 4.3a, 4.3b, and 4.3c, respectively, present the yield/temperature profiles of phenol, benzene, and cyclopentadiene at different \( OR \). Similar to the summed yields of Figures 4.2a and 4.2b, the yields of phenol, benzene, and cyclopentadiene in Figure 4.3 exhibit increases with increasing
temperature or $OR$, at temperatures $\leq 800 \, ^\circ C$. These increases in yield are consistent with the earlier observation that the Radical Enhancement Effect is dominant in the lower temperature range. At temperatures $\geq 900 \, ^\circ C$, the yields of phenol, benzene, and cyclopentadiene show decreases with increasing $OR$—the decreases being more dramatic for higher $OR$. The Oxidative Destruction Effect is thus dominant at the higher temperatures, especially at higher oxygen ratios. Above $900 \, ^\circ C$, Figure 4.3c also reveals that the cyclopentadiene yields at $OR = 0.22$ are comparable to pyrolysis yields. The comparable yields are likely due to competing effects of reactions leading to oxidative destruction of cyclopentadiene, and formation of cyclopentadiene by oxidative attack on aromatic products such as phenol [88] and benzene [210].

The consumption of phenol, benzene and cyclopentadiene under oxidative conditions will most likely involve O, O$_2$ and OH addition reactions as well as radical reactions with O and HO$_2$. Phenol consumption under oxidative conditions has been reported in detail by Brezinsky et al. [88]. The oxidative consumption of cyclopentadiene has been studied by various investigators, and a detailed mechanism is available in the literature [120,211]. A mechanism for the oxidation of benzene and the phenyl radical is detailed by Brezinsky [210].

As mentioned in our previous study, the negligible yields of phenol and the high yields of benzene at higher temperatures suggest that reactions other than the displacement of OH from phenol by H atom [98] may contribute to benzene formation at higher temperatures. The most likely reactions cited in the literature for benzene formation involve addition of acetylenic species to C$_4$ radicals [78,202,203,206] and the propargyl radical self-addition reactions [204,205,207-209]. Since C$_2$-C$_4$ species are present in high abundance in the catechol pyrolysis and oxidation environment [98], these reactions [78,202-209] may be relevant in contributing to our high yields of benzene, especially at higher temperatures.
Figure 4.3. Yields, as functions of temperature and at different oxygen ratios (OR), of: (a) phenol, (b) benzene, and (c) cyclopentadiene. The catechol pyrolysis and fuel-rich oxidation experiments are performed at a residence time of 0.3 sec.
4.3.2.2. Propylene, Propadiene and Propyne

Figures 4.4a, 4.4b, and 4.4c, respectively, present the yield/temperature profiles at different *OR* of the three C₃ hydrocarbon products—propylene, propadiene and propyne—formed during catechol pyrolysis and fuel-rich oxidation. The C₃ hydrocarbon yields show a uniform behavior with respect to temperature and oxygen ratio. Consistent yields show a uniform behavior with respect to temperature and oxygen ratio. Consistent with the summed C₁-C₅ hydrocarbon product yields (Figure 4.2a), the yields of all three C₃ compounds show increases with increasing temperature or *OR* at temperatures ≤ 800 °C. Above 900 °C, the yields at *OR* = 0.22 are comparable to those under pyrolysis conditions (*OR* = 0.0); but at higher oxygen ratios (*OR* =0.58, 0.92), the yields of all three C₃ compounds show a rapid decline to zero at the higher temperatures (>900 °C). Therefore, just as with the other products so far examined, the C₃ product yields reflect the dominance of the Radical Enhancement Effect in the lower temperature range and the Oxidative Destruction Effect at the higher temperatures.

As with the summed product yields in Figure 4.2, Figure 4.4 reveals that the temperatures of peak yield for the three C₃ products shift to lower temperatures with increasing oxygen ratio (*OR*). In a previous study in this series, Ledesma et al. [98] have proposed the formation of the C₃ species from the thermal decomposition of the cyclopentadienyl radical. The similarities between the C₃ yield profiles and that of cyclopentadiene (Figure 4.3c)—the stable form of the cyclopentadienyl radical—supports the assertion [98] that the C₃ compounds form from the thermal decomposition of cyclopentadiene. Though the yields of the C₃ products are not very high, the stability of the propargyl radical with respect to pyrolysis [212] and the slow reaction with O₂ [213,214] may lead to relatively high concentrations of the propargyl radical in the catechol pyrolysis and oxidation environment.
Figure 4.4. Yields, as functions of temperature and at different oxygen ratios ($OR$), of: (a) propylene, (b) propadiene, and (c) propyne. The catechol pyrolysis and fuel-rich oxidation experiments are performed at a residence time of 0.3 sec.
4.3.2.3. 1,3-Butadiene

**Figure 4.5**: Yields of 1,3-butadiene, as functions of temperature and at different oxygen ratios (OR), from the pyrolysis and fuel-rich oxidation of catechol at 0.3 sec residence time.

Figure 4.5 shows the yield of 1,3-butadiene as a function of temperature and at different oxygen ratios. As is evident from Figure 4.5, 1,3-butadiene appears to be the product whose yields are affected most by the presence of oxygen—the yields showing a significant oxygen-induced decrease, even at $OR = 0.22$, for all temperatures studied. Unlike the other hydrocarbons, the 1,3-butadiene yields decrease with increasing oxygen ratio at virtually all temperatures studied, and the temperature of peak yield remains constant at 850 °C for all oxygen ratios (except at $OR = 0.92$, where it shifts to 800 °C). The dramatic oxygen-induced decrease in the yield of 1,3-butadiene and the unique behavior exhibited by 1,3-butadiene under oxidative conditions indicates a more complex chemistry than for the other hydrocarbons. 1,3-butadiene’s unique oxidation behavior, coupled with its very high yields, also suggests that 1,3-
butadiene formation involves a reaction pathway entirely different from the phenol and cyclopentadiene decomposition pathways that are largely responsible for the formation of the C1-C3 hydrocarbons during catechol pyrolysis [98].

**Mechanism I (as proposed by Ledesma et al. [98]):**

\[
\begin{align*}
\text{OH} & \quad \xrightarrow{+ CO} \quad \text{OH} \\
\text{HO} & \quad \xrightarrow{+ CO} \quad \text{HO}
\end{align*}
\]

\[
\begin{align*}
\text{H} & \quad \xrightarrow{+ CO} \quad \text{CH}_2=\text{CH}-\text{CH}=\text{CH}\cdot + \text{CO} \\
\text{CH}_2=\text{CH}-\text{CH}=\text{CH}\cdot + \text{H} & \quad \xrightarrow{+} \quad \text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2
\end{align*}
\]

**Mechanism II (analogous to reactions in phenol studies of Cyprès and Bettens [215]):**

\[
\begin{align*}
\text{OH} & \quad \xrightarrow{2\text{CO}} \quad \text{O} \\
\text{O} & \quad \xrightarrow{2\text{CO}} \quad \text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2 + 2\text{CO}
\end{align*}
\]

Though various studies have reported the formation of 1,3-butadiene from the oxidation of aromatic fuels like benzene [210], phenol [88], and toluene [216], very little has been reported on 1,3-butadiene formation during the pyrolysis of an aromatic fuel. In a previous study, Ledesma et al. [98] proposed a mechanism (Mechanism I) for the formation of 1,3-butadiene...
during catechol pyrolysis. In order to better understand the formation of 1,3-butadiene from catechol, however, it is worthwhile to examine phenol pyrolysis studies. The high-temperature studies of Cyprès and Bettens [215], using isotope-labelled phenol, indicate the formation of a keto-form during the decomposition of phenol to cyclopentadiene and CO. Horn et al. [89] have also hypothesized that the dominant initiation step in phenol decomposition is the direct molecular elimination of CO from phenol—after internal rearrangement of the phenol molecule to a keto-form—to form cyclopentadiene. An analogous mechanism (Mechanism II) can be hypothesized for catechol and is presented.

Since the hydroxy-substituted phenoxy radical should be present in high abundance in the catechol pyrolysis environment [98], Mechanism I (Reactions 1-4) appears to be the dominant pathway for 1,3-butadiene formation. Our GC/MS analyses present evidence, however, of the presence of an isomer of cyclopentenone, which can be an intermediate in Mechanism II (Elimination of one CO molecule from the keto-form of catechol formed in Reaction 5 can lead to cyclopentenone.). Also, \textit{ab initio} calculations show that the $\Delta H_{\text{rxn}}$ of catechol decomposition to the keto-form is lower than $\Delta H_{\text{rxn}}$ of catechol decomposition to the hydroxy-substituted phenoxy radical. Though more experiments need to be carried out to ascertain the pathway(s) leading to 1,3-butadiene under catechol pyrolysis conditions, both of the above decomposition mechanisms (Mechanisms I and II) ultimately lead to the same stable products, 1,3-butadiene and CO.

Under oxidative conditions, the consumption of 1,3-butadiene most likely involves O atom addition reactions as well as H abstraction by H and OH radicals. Various investigators have studied the consumption of 1,3-butadiene under oxidative conditions, and a detailed mechanism is available in the literature [78,122,124,217].
4.3.2.4. Vinylacetylene

**Figure 4.6.** Yields of vinylacetylene, as functions of temperature and at different oxygen ratios (OR), from the pyrolysis and fuel-rich oxidation of catechol at 0.3 sec residence time.

The yield/temperature profiles of vinylacetylene at different oxygen ratios are presented in Figure 4.6. Figure 4.6 reveals that at temperatures ≤ 800 °C, vinylacetylene yields in the presence of oxygen (OR = 0.22, 0.58, 0.92) are higher than those in its absence (OR = 0), so the Radical Enhancement Effect appears to be active in this lower temperature regime. At temperatures > 800 °C, the Oxidative Destruction Effect becomes evident: vinylacetylene yields at OR = 0.22 and OR = 0 are comparable, but yields at OR = 0.58 and 0.92 are dramatically reduced. Accordingly the temperature of peak yield shifts from 850 °C at OR = 0.22, to 800 °C at OR = 0.58 and 0.92.

In considering how vinylacetylene would form from catechol, it is helpful to examine the yield/temperature profiles of 1,3-butadiene and vinylacetylene under pyrolysis conditions.
Figures 4.5 and 4.6 reveal that the yields of 1,3-butadiene and vinylacetylene follow a similar trend with respect to temperature under pyrolysis conditions \((OR = 0)\), indicating a link between the two \(C_4\) compounds. The most likely precursor to both the \(C_4\) compounds is the 1,3-butadienyl radical formed by Reaction 3. Various studies [78,122-124] have identified vinylacetylene as a product of 1,3-butadiene pyrolysis and have reported the H-abstraction from 1,3-butadienyl radical as the likely source of vinylacetylene. The high yields of 1,3-butadiene in the catechol pyrolysis environment, and the similarity (at \(OR = 0\)) in the yield profiles of 1,3-butadiene and vinylacetylene with respect to temperature, suggest that H-abstraction from 1,3-butadienyl radical (Reaction 7) is a very likely route to vinylacetylene under catechol pyrolysis conditions.

\[
\begin{align*}
\text{CH}_2=\text{CH-CH=CH}^+ & \rightarrow \text{CH}=\text{C-CH}=\text{CH}_2 + \text{H} & (7) \\
2\text{CH}=\text{CH} & \rightarrow \text{CH}=\text{C-CH}=\text{CH}_2 & (8)
\end{align*}
\]

In addition to Reactions 1-4 above, oxidative attack on the cyclopentadienyl radical can also lead to the 1,3-butadienyl radical [120,211,216] under oxidative conditions. However, the increase in vinylacetylene yields and the decrease in 1,3-butadiene yields, in the presence of oxygen and at temperatures < 850 °C, suggest that the formation of vinylacetylene (by hydrogen abstraction) from the 1,3-butadienyl radical is favored over the formation of 1,3-butadiene under oxidative conditions.

The polymerization of acetylene (Reaction 8) is another mechanism reported in the literature [121] for vinylacetylene formation. The presence of triacetylene [96] among the catechol pyrolysis products and the high yields of acetylene at the higher temperatures suggest that this mechanism may be relevant at the higher temperatures in the catechol reaction environment.
4.3.2.5. Ethylene and Acetylene

Figure 4.7. Yields, as functions of temperature and at different oxygen ratios (OR), of: (a) ethylene, and (b) acetylene. The catechol pyrolysis and fuel-rich oxidation experiments are performed at a residence time of 0.3 sec.

Previous work on the thermal decomposition products from catechol pyrolysis [98] has shown the abundance of C₂ species in the catechol pyrolysis environment. Figures 4.7a and 4.7b present the yields of ethylene and acetylene as functions of temperature and at different OR. The two C₂ products show similar behavior in the presence of oxygen: the yields increase with increasing OR at temperatures ≤ 800 °C and decrease with increasing OR at temperatures ≥ 850 °C. The effects are more dramatic at the higher oxygen ratios (OR = 0.58, 0.92). The oxygen-induced decreases, at temperatures ≥ 850 °C, in the C₂ product yields are consistent with the oxygen-induced decreases in the yields of cyclopentadiene and 1,3-butadiene, the two likely sources of the C₂ species [98]. Figures 4.7a and 4.7b also reveal that for both ethylene and
acetylene, the effects of temperature on product yields at $OR = 0.22$ are very similar to those at $OR = 0$—the yields peaking at 950 °C for ethylene and 1000 °C for acetylene. At higher oxygen ratios ($OR = 0.58, 0.92$), both C$_2$ products’ temperatures of peak yield shift to lower temperatures as the yields drop to zero at higher temperatures. All of the observed effects of oxygen and temperature on the two C$_2$ product yields are consistent with those exhibited in Figure 4.2a for the summed yields of C$_1$-C$_5$ products—all of them illustrating the dominance of the Radical Enhancement Effect in the lower-temperature regime and the Oxidative Destruction Effect in the higher-temperature regime.

**4.3.2.6. Methane and Ethane**

Figures 4.8a and 4.8b present the yield/temperature profiles of methane and ethane at different $OR$. The two alkanes show increases in yields, with increasing $OR$, at temperatures $\leq 850$ °C—consistent with the dominance of the Radical Enhancement Effect at the lower temperatures. As with the other products, Figures 4.8a and 4.8b reveal that both for methane and for ethane, the yield/temperature profiles at $OR = 0.22$ are similar to their respective ones at $OR = 0$ (pyrolysis). Unlike the other hydrocarbon products, however, the yields for methane and ethane at $OR = 0.22$ are higher than pyrolysis yields at all temperatures studied—suggesting that, at $OR = 0.22$, the Radical Enhancement Effect is dominant over the entire temperature range studied. At the higher oxygen ratios ($OR = 0.58, 0.92$) and higher temperatures ($> 850$ °C), the yields of both compounds decline rapidly with increasing temperature, due to the Oxidative Destruction Effect. As with the other products, the temperatures of peak yield shift to lower temperatures with increasing $OR$, in accordance with the competition between the Radical Enhancement and Oxidative Destruction Effects.
Figure 4.8. Yields, as functions of temperature and at different oxygen ratios (OR), of: (a) methane and (b) ethane. The catechol pyrolys is and fuel-rich oxidation experiments are performed at a residence time of 0.3 sec.

4.3.2.7. CO and CO$_2$

Figures 4.9a and 4.9b, respectively, present the yields of CO and CO$_2$ as functions of temperature and at different OR. For ease of comparison with Figures 4.1-4.8, the yields of CO and CO$_2$ in Figures 4.9a and 4.9b are reported as “mass percent of fed catechol.” For the OR = 0 experiments, the only source of oxygen in the CO and CO$_2$ is the oxygen supplied in the molecular structure of catechol itself; consequently, the yields of all products plus unreacted catechol all sum up to 100% for the OR = 0 case. For OR > 0, however, oxygen supplied in the carrier gas can be incorporated as O in CO and CO$_2$; hence product yields reported on the chosen basis of “mass percent of fed catechol” will sum up to > 100% for OR = 0.22, 0.58, and 0.92. The amounts in excess of 100%, however, are solely attributable to the incorporation of carrier-gas oxygen into the products and in no way signify a spurious source of carbon.
Figure 4.9. Yields, as functions of temperature and at different oxygen ratios (OR), of: (a) CO and (b) CO$_2$. For purposes of comparison with hydrocarbon yields, the yields of CO and CO$_2$ are reported as mass percent of fed catechol. It is recognized that when reported on this basis, CO and CO$_2$ yields can exceed 100% for the higher values of OR—since oxygen from the carrier gas can be incorporated into CO and CO$_2$. At OR = 0, the only source of oxygen is that in the molecular structure of catechol itself, so CO and CO$_2$ yields will of course be well below 100%.

As with the other products, Figure 4.9a reveals that, at temperatures $\leq 850$ °C, the yields of CO increase with increasing temperature or OR. This increase in yield of CO in the lower-temperature regime is consistent with the dominance of the Radical Enhancement Effect. At higher temperatures, the CO yields at OR = 0 level off at $\sim$50%, corresponding to complete conversion of the oxygen in the catechol to CO. As oxygen is increased to OR = 0.22 and then OR = 0.58 at higher temperatures, oxygen from the carrier gas becomes incorporated into the product CO, and CO yields increase with temperature and OR for OR $\leq$ 0.58. CO yields greatly drop at OR = 0.92 for the higher temperatures, however, as CO is oxidized to CO$_2$.
Figure 4.9b reveals that CO\textsubscript{2} is not produced at \( OR = 0 \), as pyrolytic reactions dominate. In the presence of oxygen, however, CO\textsubscript{2} yields increase with increasing \( OR \) and temperature, as the oxidative destruction of the hydrocarbon products takes place. Figure 4.9b shows that CO\textsubscript{2} yields are particularly high for temperatures \( \geq 900 \, ^\circ\text{C} \) at \( OR = 0.92 \)—signifying the oxidation of CO to CO\textsubscript{2}, as evident from Figure 4.9a. Under oxidative conditions, the combined yields of CO and CO\textsubscript{2} at the higher temperatures (\( \geq 950 \, ^\circ\text{C} \)) correspond to complete conversion of the total oxygen supplied to the reactor—both the oxygen in the catechol and the oxygen in the carrier gas—to CO and CO\textsubscript{2}.

4.3.2.8. Single-Ring Aromatic Hydrocarbons

The single-ring aromatics identified and quantified in this study include benzene, toluene, styrene, and phenylacetylene. The yield/temperature profiles of benzene at different \( OR \) are presented in Figure 4.3b, and those of toluene, styrene, and phenylacetylene at different \( OR \) are presented in Figure 4.10. As with benzene, Figure 4.10 reveals that all the single-ring aromatic hydrocarbons show increases in yields with increasing temperature and increasing \( OR \) in the temperature range 500-800 \, ^\circ\text{C}—consistent with the dominance of the Radical Enhancement Effect. As with the C\textsubscript{1}-C\textsubscript{5} hydrocarbon products in Figures 4.4-4.8, the effects of temperature on the yields of the single-ring aromatic products (Figure 4.10) at \( OR = 0.22 \) are very similar to those at \( OR = 0 \). In addition, Figures 4.10a and 4.10b reveal that, at temperatures \( \geq 850 \, ^\circ\text{C} \), the yields of both toluene and styrene at \( OR = 0.22 \) are comparable to their respective yields at \( OR = 0 \) (pyrolysis). Those of benzene (in Figure 4.3b) and phenylacetylene (in Figure 4.10c), however, show measurable decreases at \( OR = 0.22 \), compared to their respective yields at \( OR = 0 \). At higher oxygen ratios (\( OR = 0.58, 0.92 \)) and at temperatures > 800 \, ^\circ\text{C}, the yields of benzene, toluene, styrene, and phenylacetylene show significant decreases with increasing \( OR \)—the decrease being more dramatic for phenylacetylene—as the Oxidative Destruction Effect
Figure 4.10. Yields, as functions of temperature and at different oxygen ratios (OR), of: (a) toluene, (b) styrene, and (c) phenylacetylene. The catechol pyrolysis and fuel-rich oxidation experiments are performed at a residence time of 0.3 sec.
dominates. The similarity in the oxidation behavior of the single-ring aromatics and the C\textsubscript{1}-C\textsubscript{5} hydrocarbons supports the assertion that the C\textsubscript{1}-C\textsubscript{5} hydrocarbons play a major role in the formation of the single-ring aromatic hydrocarbons in the catechol pyrolysis and fuel-rich oxidation environment.

4.3.3. PAH Formation

Previous studies [97,99] in our research group have provided strong evidence of PAH growth by successive buildup reactions involving addition of thermal decomposition products. Figure 4.11 presents the summed yields of PAH formed during the pyrolysis and fuel-rich oxidation of catechol as functions of temperature and at different OR. Figure 4.11 reveals that PAH formation becomes significant only at temperatures $\geq 800$ °C. Figure 4.11 also shows that the PAH yields decrease dramatically with increasing OR. This decrease in yields is consistent with the oxidative destruction of the C\textsubscript{1}-C\textsubscript{5} hydrocarbons (Figure 4.2a) and the single-ring aromatics (Figure 4.2b) at higher temperatures—underlining the role of C\textsubscript{1}-C\textsubscript{5} hydrocarbons and the single-ring aromatics in PAH formation under catechol pyrolysis and fuel-rich oxidation conditions. The decrease in PAH yields in the presence of oxygen is consistent with the findings in a previous study from our research group on coal tar pyrolysis and fuel-rich oxidation [28].

The acetylene-addition/hydrogen-abstraction (HACA) reaction scheme is considered to be one of the main PAH formation and growth mechanisms in combustion systems, and it has been proposed [50] to account for the high abundance of ethynyl-substituted and cyclopentane-fused PAH we have observed among the products of catechol pyrolysis [96,99]. The high yields of benzene and acetylene and the similar oxidation behavior of benzene (Figure 4.3b) and phenylacetylene (Figure 4.10c) support this assertion.

Acetylene is not the only C\textsubscript{1}-C\textsubscript{5} hydrocarbon important in the formation of PAH from catechol, however. The dramatic reductions in the yields of the major hydrocarbon product, 1,3-
butadiene (Figure 4.5), and the corresponding decrease in the yields of PAH in the presence of oxygen suggest that 1,3-butadiene chemistry plays a significant role in PAH formation in our catechol reaction environment. The effects of 1,3-butadiene addition on the yields of individual PAH formed during the pyrolysis of catechol will be covered in detail in a forthcoming paper.

Figure 4.11. Summed yields of PAH, as functions of temperature and at different oxygen ratios ($OR$), from the pyrolysis and fuel-rich oxidation of catechol at 0.3 sec residence time. The yields presented here are the sum of individual yields of two- to eight-ring PAH formed during the pyrolysis and fuel-rich oxidation of catechol.

4.4. **Summary and conclusions**

In our effort to better understand the formation of PAH during the pyrolysis and combustion of solid fuels, we have performed pyrolysis and fuel-rich oxidation experiments in a laminar-flow reactor, using the model fuel catechol. The products collected have been analyzed and quantified by gas chromatographic analysis and nondispersive infrared analysis. Yield/temperature profiles for the C$_1$-C$_5$ species as well as single-ring aromatic products at
different oxygen ratios \((OR = 0.22, 0.58, 0.92)\) have been obtained and compared with pyrolysis yields \((OR = 0)\) to delineate the effects of oxygen on these products.

In the temperature range 500-850 °C, where the catechol conversion rapidly increases to ~100%, increases in \(OR\) generally bring about an increase in the rate of conversion of catechol and a complementary increase in the yields of the single-ring aromatics and the C\(_1\)-C\(_5\) hydrocarbons except 1,3-butadiene. At higher temperatures (> 850 °C), catechol conversion is 100%, and increases in \(OR\) bring about decreases in the yields of the C\(_1\)-C\(_5\) hydrocarbons and the single-ring aromatic products—the decreases being more dramatic at higher oxygen ratios \((OR \geq 0.58)\). The 1,3-butadiene yields decrease dramatically with increasing \(OR\) at all temperatures studied, suggesting a more complex chemistry. The coincident decrease in PAH yields with increasing \(OR\) suggests that 1,3-butadiene is a major intermediate in PAH formation under catechol pyrolysis and fuel-rich oxidation conditions.

The similar effects of temperature on the yields of the products under \(OR = 0\) (pyrolysis) and \(OR = 0.22\), along with the low yields of CO\(_2\) at \(OR = 0.22\), indicate that pyrolytic reactions are dominant at \(OR = 0.22\). At temperatures < 850 °C, the increase in product yields with increasing \(OR\) suggests an increase in the rates of formation of the products due to the Radical Enhancement Effect. At temperatures ≥ 900 °C, however, the product yields decrease with increasing \(OR\), as the products are rapidly oxidized to CO and CO\(_2\) due to the Oxidative Destruction Effect.

The data produced by this study contribute significantly towards delineating the effects of oxygen on the formation and fate of PAH from the pyrolysis of catechol. Since no kinetic model is currently available for catechol decomposition and PAH formation from catechol, the results obtained here and in previous catechol pyrolysis studies [25,50,96-99], collectively, will be helpful in the development of a detailed kinetic model for PAH formation during catechol
pyrolysis and fuel-rich oxidation. Since catechol is a model fuel representative of solid fuels like coal, wood, and biomass, the present work should be helpful towards understanding PAH formation during the burning of solid fuels.
Chapter V. Effects of Oxygen Addition: Yields of Polycyclic Aromatic Hydrocarbons*

5.1. Introduction

The formation of polycyclic aromatic hydrocarbons (PAH) during the burning of solid fuels like coal, wood, and biomass is of concern due to the inherent carcinogenicity [6-8] and mutagenicity [9,10] of some members of this class of compounds. During the practical combustion of solid fuels, high-temperature, oxygen-deficient zones exist in which pyrolytic reactions are dominant, and pyrolytic reactions are known [16,200,218] to be the primary source of PAH during combustion. The PAH thus produced can act as precursors to soot [15,16] and/or contribute to fine particle emissions that are associated with increased incidences of heart and lung diseases [11,12]. Therefore, it would be helpful to determine both qualitatively and quantitatively the formation and fate of PAH from complex solid fuels under pyrolysis and fuel-rich oxidation conditions.

Solid fuels like coal, wood, and biomass have complex structures that consist of aliphatic as well as aromatic units and produce a plethora of species upon initial pyrolysis. Due to this complexity of chemical structure, it is extremely difficult to assign specific reaction pathways to specific products or product classes produced during solid fuel pyrolysis and combustion. Therefore, most of the mechanistic studies on PAH formation have made use of model compounds [16,25,83,85-92,179] that represent entities in these fuels. For our investigations into the effects of oxygen on the formation of PAH during solid fuel combustion, we have chosen catechol (ortho-dihydroxybenzene) as a model fuel compound. As a prominent structural unit in coal [100], tobacco [103], and lignin (a major component of wood [101])—as well as a major component in biomass tars [102] and tobacco smoke [104]—catechol is a suitable model

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compound for investigating solid fuel pyrolysis and combustion. Moreover, aromatic structures such as catechol are more likely to contribute to PAH than are the aliphatic constituents of solid fuels. The demonstrated [96] similarity between PAH product distributions from catechol pyrolysis and coal volatiles pyrolysis further strengthens this assertion.

Previous studies in our research group [50,96-99] have reported in detail the identification and quantification of numerous PAH products as well as the C$_1$-C$_5$ and single-ring aromatic products produced during catechol pyrolysis in the absence of oxygen. Since oxygen is naturally present in the environment of a burning fuel, however, it is also important to know how the reactions leading to these products are affected when oxygen is present. Chapter IV and a companion paper [112] examine the effects of oxygen on the yields of the C$_1$-C$_5$ hydrocarbons and the single-ring aromatics produced during catechol pyrolysis. It is the purpose of the present paper and chapter to examine the effects of oxygen on the formation and growth of PAH during the pyrolysis and fuel-rich oxidation of catechol. To this end, we have performed pyrolysis and fuel-rich oxidation experiments with catechol in an isothermal laminar-flow reactor at temperatures of 500-1000 °C.

Since the C$_1$-C$_5$ hydrocarbons and single-ring aromatics are known to play a major role in PAH formation [66-74], it is worth noting here the key observations from our companion paper [112] that are of particular relevance to the present study on PAH formation and growth: (1) At temperatures < 850 °C, the addition of oxygen brings about an increase in the yields of the C$_1$-C$_5$ hydrocarbons and single-ring aromatics, due to an oxygen-induced enhancement of the free radical pool. (2) In the temperature range 850-1000 °C, where PAH production becomes significant, the addition of oxygen brings about drastic decreases in the yields of virtually all C$_1$-C$_5$ hydrocarbons and single-ring aromatic products, due to oxidative destruction reactions. (3) The effects of temperature on product yields at $OR = 0.22$ are very similar to those at $OR = 0$
indicating that reactions similar to those under pyrolytic conditions are dominant at $OR = 0.22$. (The $OR$ is defined as the mass feed rate of oxygen to the mass feed rate of catechol, divided by the oxygen-to-catechol mass ratio required for stoichiometric oxidation.)

In the following, we report the effects of oxygen addition on the yields of 21 individual PAH products produced during the pyrolysis and fuel-rich oxidation of catechol. The catechol pyrolysis and fuel-rich oxidation experiments are performed in an isothermal laminar-flow reactor at a fixed residence time of 0.3 s, at temperatures of 500-1000 °C, and over a range of oxygen concentrations from zero to near stoichiometric. The products are analyzed by gas chromatography (GC) and high-pressure liquid chromatography (HPLC) with diode-array ultraviolet-visible (UV) absorbance detection. After quantifying product yields, we discuss the effects of oxygen on PAH yields and relate the results to our study [112] on the effects of oxygen on the yields of the C$_1$-C$_8$ thermal decomposition products produced during catechol pyrolysis. By accounting for the effects of oxygen, we hope to further extend the relevancy of our work with catechol to the practical combustion of solid fuels.

5.2. Experimental Equipment and Procedures

5.2.1. Reactor System

The reactor system for catechol pyrolysis and oxidation experiments has been presented in schematic form and explained in detail elsewhere [112]. The reactor system comprises a fuel vaporizer, isothermal quartz flow reactor, Balston Teflon filter, and product collection system. The pyrolysis experiments are performed by loading solid catechol particles (>99.5% pure, purchased from Aldrich Chemical Co.) into a Pyrex tube placed vertically inside the fuel vaporizer, an isothermal oven maintained at 85 °C to facilitate vaporization of small amounts of catechol. A flowing stream of ultrahigh purity (grade 6.0) nitrogen carrier gas is passed through the Pyrex tube, picking up vaporized catechol, resulting in a 0.65 mole-% carbon loading in the
feed gas that enters the reactor. The catechol decomposition takes place inside the high-
temperature laminar-flow reactor, which consists of a 2-mm (inner diameter) quartz tube
insulated at both ends and maintained at isothermal conditions by a three-zone electrically heated
furnace. The reactor is operated isothermally at temperatures of 500-1000 °C and at a fixed
residence time of 0.3 s.

The fuel-rich oxidation experiments are performed by doping the nitrogen carrier gas, in
separate experiments, with known quantities of oxygen. The oxygen ratios \( OR \) for the separate
experiments are set to 0.0 (pyrolysis), 0.22, 0.58 and 0.92. The \( OR \) is defined as the mass feed
rate of oxygen to the mass feed rate of catechol (for that experiment), divided by the oxygen-to-
catechol mass ratio required for stoichiometric oxidation.

5.2.2. Product Analysis

The catechol pyrolysis products exiting the reactor are quenched to room temperature
(quench time, approximately 0.028 s), and the PAH products are collected with a condensed-
phase products collection system described in detail elsewhere [99]. The collected products are
dissolved in dichloromethane and concentrated in a Kuderna-Danish evaporator. After
concentration, a portion of the product solution is withdrawn for GC analysis, which achieves
[97,99] the identification and quantification of the light PAH products (\( \leq 3 \) rings). The remainder
of the product solution is exchanged into dimethylsulfoxide for analysis by HPLC.

The light PAH products (\( \leq 3 \) rings) are analyzed on the Agilent Model 6890/5973
GC/FID/MS. A 2-μL aliquot of the product solution is injected by syringe, through a split
injector, onto a HP-5 fused silica capillary column of length, 30 m, diameter, 0.25 mm, and film
thickness 0.1 μm. The column temperature is programmed to hold at 40 °C for the first 3
minutes; it is then ramped at 4 °C/min to 300 °C, and held at 300 °C for 15 minutes. The light
PAH products are identified by matching retention times and mass spectra with those of reference standards.

The heavier PAH products (> 3 rings) are analyzed by injecting a 25-µL aliquot of the PAH/dimethylsulfoxide solution into a Hewlett-Packard Model 1050 high-pressure liquid chromatograph, coupled to a diode-array UV absorbance detector. The chromatographic separation method [16,85,96] utilizes a reversed phase Vydac 201-TP octadecylsilica column (particle size, 5 µm; inner diameter, 4.6 mm; length, 250 mm) with time-programmed mobile phases of water/acetonitrile, acetonitrile, and dichloromethane (1.5 mL/min). The individual PAH products are unequivocally identified by matching each component’s retention time and UV absorbance spectrum with those of the appropriate reference standard. The HPLC/UV evidence establishing the identities of the PAH products of catechol pyrolysis is documented in a previous work [96] from our research group.

For most of the PAH quantified in this study, the GC-FID and UV-absorbance detectors have been calibrated with known concentrations of the respective reference standards. Response factors of structurally similar compounds have been used for the few products for which reference standards are not available, as negligible error is introduced [128].

Products are collected and analyzed from separate experiments at nine different temperatures, over the temperature range of 500-1000 °C, and at a residence time of 0.3 s. Experiments are performed under pure pyrolysis conditions (OR = 0.0) and fuel-rich oxidation conditions (OR = 0.22, 0.58, 0.92). Product yields obtained from repeat experiments under the same conditions give very reproducible results. The collective mass of carbon obtained from the C1-C8 species (reported elsewhere [112]), PAH products, and any unconverted catechol accounts for all of the carbon fed to the reactor as catechol. A carbon balance is thus closed on this reactor system.
5.3. Results and Discussion

The catechol pyrolysis studies in our research group have led to the identification of 11 C$_1$-C$_5$ species [98,112], 5 single-ring aromatics [96-99,112], 5 oxygen-containing aromatics [96], as well as 54 individual PAH [96,97,99]. In our companion study [112], we have presented the effects of oxygen addition on the yields of the C$_1$-C$_5$ species and single-ring aromatics formed during the pyrolysis and fuel-rich oxidation of catechol. The effects of oxygen addition on the yields of PAH formed during the pyrolysis and fuel-rich oxidation of catechol are the principal focus of the present study.

Most of the PAH formed under pyrolysis conditions are also produced during fuel-rich oxidation conditions. Of the 54 PAH identified among the catechol pyrolysis products [96,97,99], 45 are also detected when some oxygen is present. 43 of the 54 PAH are produced in amounts sufficient for reliable quantification, and it is these 43 PAH whose yields are reported here, collectively and/or individually, as functions of temperature, under pyrolysis and fuel-rich oxidation conditions. These 43 quantified PAH, listed in Table 1, fall into six structural classes: benzenoid PAH, indene benzologues, fluoranthene benzologues, cyclopenta-fused PAH, ethynyl-substituted PAH, and methyl-substituted PAH.

As demonstrated in our study [112] of the C$_1$-C$_5$ species and single-ring aromatics, the addition of oxygen can lead to two competing effects: (1) The Radical Enhancement Effect stems from an oxygen-induced increase in the number of free radicals, which leads to higher rates of pyrolysis reactions and increases in pyrolysis product yields. (2) The Oxidative Destruction Effect stems from an increase in oxidizer concentration, which increases rates of pyrolysis-product oxidation reactions, leading to decreases in pyrolysis product yields.

The relative importance of the Enhancement and Destructive Effects is highly dependent on temperature, as evident in Figure 5.1. Figure 5.1 presents the summed yields of PAH, as a
function of OR, obtained from catechol pyrolysis at 750 °C and 900 °C. The yields are expressed as mass percent of fed catechol and include the summed yields of the 43 individual PAH listed in Table 1. Consistent with our companion study [112], Figure 5.1 reveals that the PAH yields increase with increasing OR at 750 °C due to the Radical Enhancement Effect and decrease with increasing OR at 900 °C due to the Oxidative Destruction Effect. These two competing effects are a focus of our consideration as we examine, in the following, the effects of oxygen addition on the yields of PAH produced during catechol pyrolysis. First, we examine the effects of oxygen on the yields of the different structural classes of PAH, then on PAH grouped according to ring number.

![Graph](image)

**Figure 5.1.** Summed yields of PAH, as a function of OR, from the pyrolysis and fuel-rich oxidation of catechol at 750 °C (◊) and 900 °C (■) and at 0.3 sec residence time. The yields presented are those summed for the 43 individual PAH in Table 1.
5.3.1. **Effects of Oxygen on the Yields of Different Structural Classes of PAH**

Figure 5.2 presents the yield/temperature profiles of the five different structural classes of PAH—benzenoid PAH, indene benzologues, fluoranthene benzologues, cyclopenta-fused PAH, ethynyl-substituted PAH, and methyl-substituted PAH—at different OR. The yields are based on the mass of fed catechol and represent the yields of individual PAH summed by structural class. The members of each structural class that are included in the sums are listed in Table 1 and their structures along with the structures of all the identified products of catechol pyrolysis are presented in Appendix A.

**Table 5.1. Quantified PAH products of catechol pyrolysis and fuel-rich oxidation**

<table>
<thead>
<tr>
<th>PAH Structural Class</th>
<th>PAH Products</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Fluoranthene Benzologues</strong></td>
<td>Fluoranthene, Benzo[a]fluoranthene, Benzo[j]fluoranthene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Indeno[1,2,3-cd]pyrene.</td>
</tr>
<tr>
<td><strong>Ethynyl-Substituted PAH</strong></td>
<td>2-Ethynynaphthalene, 1-Ethynylacenaphthylene, 5-Ethynylacenaphthylene, 2-Ethynylphenanthrene, 2-Ethynylantracene</td>
</tr>
<tr>
<td><strong>Methyl-Substituted PAH</strong></td>
<td>1-Methylnaphthalene, 2-Methylnaphthalene.</td>
</tr>
</tbody>
</table>
Figure 5.2. Summed yields of PAH, as functions of temperature and at different oxygen ratios (OR), from the pyrolysis and fuel-rich oxidation of catechol at 0.3 sec residence time: (a) benzenoid PAH, (b) indene benzologues, (c) fluoranthene benzologues, and (d) cyclopenta-fused PAH. The yields presented are those for the individual PAH products shown in Table 1 summed by structural class (Figure continued on next page).
Several observations can be made from Figure 5.2. First, PAH production becomes significant only at temperatures $\geq 800$ °C. Second, the benzenoid PAH in Figure 5.2a are the highest-yield PAH at $OR \leq 0.22$; whereas at $OR \geq 0.58$, the indene benzologues in Figure 5.2b are the highest-yield PAH. Third, for each structural class, the effects of temperature on the summed PAH yields at $OR = 0.22$ are very similar to those at $OR = 0$ (pyrolysis)—indicating that reactions similar to those occurring under pyrolytic conditions are in effect at $OR = 0.22$. For all 5 classes of PAH in Figure 5.2, the $OR = 0.22$ and $OR = 0$ curves exhibit similar temperature behavior, but the yields at $OR = 0.22$ are significantly lower than those at $OR = 0$—signifying the
emerging dominance of the Oxidative Destruction Effect. At higher oxygen concentrations, $OR \geq 0.58$, the Oxidative Destruction Effect dominates for all of the structural classes in Figure 5.2, and the yields of PAH decrease dramatically, in comparison to those at $OR = 0.22$. In contrast, Figures 5.2a and 5.2b reveal that at temperatures $< 800 ^\circ C$, the yields of the benzenoid PAH and indene benzologues both show increases with increasing $OR$, due to the Radical Enhancement Effect. The similar behavior shown by the cyclopenta-fused PAH in Figure 5.2e and ethynyl-substituted PAH in Figure 5.2f with respect to temperature and $OR$ is consistent with the acetylene addition mechanism [15,17,50,52,53] for the formation of these two classes of PAH.

The decreases in PAH yields, observed in Figure 5.2 for an increase in $OR$ at temperatures $> 800 ^\circ C$, directly correspond to our observed [112] decreases in the yields of the $C_1$-$C_5$ hydrocarbons and single-ring aromatics—strengthening our earlier assertion [112] that the $C_1$-$C_5$ hydrocarbons and single-ring aromatics play important roles in the formation and growth of PAH during the pyrolysis and fuel-rich oxidation of catechol.

### 5.3.2. Effects of Oxygen on the Yields of PAH Grouped by Ring Number

Figure 5.3a and 5.3b present the summed yields of PAH, as functions of the number of aromatic rings, at different $OR$ and at 750 °C and 900 °C, respectively. The yields are based on the mass of fed catechol and represent the summed yields of the individual PAH (shown in Table 1) of each ring number. Figures 5.3a and 5.3b reveal that for all values of $OR$, PAH yields decrease dramatically with increasing ring number. The inset in Figure 5.3b presents the percentage decrease in the yields for 2- to 6-ring PAH when $OR$ is increased from 0 to 0.22 and reveals that the oxygen-induced decreases in PAH yields become increasingly more pronounced as the number of rings increases. These observations, consistent with our earlier results [97,99] from catechol pyrolysis, support PAH growth by successive ring buildup reactions.
Figure 5.3. Summed yields of PAH, as functions of the number of rings and at different oxygen ratios \((OR)\), from the pyrolysis and fuel-rich oxidation of catechol at: (a) 750 °C and 0.3 sec residence time, and (b) 900 °C and 0.3 sec residence time. The yields presented are those for the 43 individual 2- to 6-ring PAH of Table 1, summed according to ring number. The percentage decrease in PAH yields at 900 °C and 0.3 sec residence time, when \(OR\) is increased from 0 to 0.22, is presented in the inset of (b).

At 750 °C, Figure 5.3a reveals that an increase in \(OR\) brings about dramatic increases in the yields of 2-ring PAH. The increase in the 2-ring PAH yields at 750 °C corresponds to the increase in overall PAH yields as revealed in Figure 5.1. Figure 3b, however, shows that an increase in \(OR\) at 900 °C brings about dramatic decreases in the yields of the 2-ring PAH. The decrease in the yields of the two-ring PAH at 900 °C corresponds to the decrease in overall PAH yields (Figure 5.1). At 900 °C and \(OR = 0.58\), no PAH of > 4 rings are observed; at 900 °C and \(OR = 0.92\), no PAH are observed, as catechol and PAH precursors are rapidly oxidized to CO and CO\(_2\) [112].

In combustion systems, the formation of small (< 3-ring) aromatic products is considered to be the rate-determining step in the formation of large PAH [73,75,76]. Our previous results
from catechol pyrolysis in the absence of oxygen have provided strong evidence of PAH growth by successive buildup reactions involving C$_1$-C$_5$ species and small (< 3-ring) aromatic products. We now see that this finding is corroborated by our results from catechol pyrolysis in the presence of oxygen, as Figure 3b reveals that the oxygen-induced decreases in PAH yields are increasingly more drastic with increasing PAH ring number. In addition, the decreases in the yields of the 2-ring compounds and PAH, with increasing $OR$, at 900 °C—and the increases in the yields of the 2-ring compounds and PAH, with increasing $OR$, at 750 °C—also show consistency with the notion that PAH growth takes place by successive buildup reactions involving the smaller species.

5.3.3. Effects of Oxygen on the Yields of Individual PAH

Different PAH of a given ring number or within a given structural class may have different formation mechanisms. Also, since PAH mutagenicity is sensitive to structure [9,10,56], it is the isomer-specific product distribution that determines the mutagenicity of a mixture of PAH. Therefore, in our studies, it is important to examine the effects of oxygen addition on the yields of individual PAH produced during catechol pyrolysis and fuel-rich oxidation. Of the 43 quantifiable PAH formed during catechol pyrolysis and fuel-rich oxidation, we have chosen 18 individual PAH (ranging in size from two to seven fused aromatic rings and falling into five different PAH structural classes) to illustrate the effects of oxygen addition. Figures 5.4-5.8 present the yield-temperature profiles of these 18 individual PAH formed during the pyrolysis and fuel-rich oxidation of catechol at different $OR$: Figure 5.4, individual benzenoid PAH; Figure 5.5, individual indene benzologues; Figure 5.6, individual fluoranthene benzologues; Figure 5.7, individual ethynyl-substituted and cyclopenta-fused PAH; Figure 5.8, individual methyl-substituted PAH.
5.3.3.1. Benzenoid PAH

Figure 5.4 presents the yield/temperature profiles of the six chosen benzenoid PAH—naphthalene, phenanthrene, chrysene, benzo[a]pyrene, benzo[ghi]perylene, and coronene—at different $OR$. As the figures show, the yields of the five 3- to 7-ring benzenoid PAH become significant only at temperatures $> 800 \, ^\circ\text{C}$. At temperatures $< 800 \, ^\circ\text{C}$, the only benzenoid PAH produced in appreciable amounts are naphthalene and phenanthrene. The insets in Figures 5.4a and 4.4b, respectively, reveal that at these lower temperatures ($< 800 \, ^\circ\text{C}$), the naphthalene and phenanthrene yields show a slight increase with increasing $OR$, due to the Radical Enhancement Effect. At temperatures $> 800 \, ^\circ\text{C}$, however, Figure 5.4 shows that the yields of all six of the benzenoid PAH decrease dramatically with increasing $OR$, due to the Oxidative Destruction Effect.

Figure 5.4 also reveals that for all six benzenoid PAH, the effects of temperature on product yields at $OR = 0.22$ are very similar to those at $OR = 0$, but that the yields themselves at $OR = 0.22$ are significantly lower than those at $OR = 0$. At higher oxygen concentrations ($OR \geq 0.58$), the yields of all PAH in this class decrease drastically, and naphthalene is the only benzenoid PAH with an appreciable yield at $OR = 0.92$—a result of the domination of the Oxidative Destruction Effect at these higher oxygen ratios. In addition, Figure 4 reveals a trend, among the benzenoid PAH, of oxygen-induced yield decreases of increasingly greater magnitude as the PAH ring number is increased. This observation for the benzenoid PAH is consistent with the trends observed in Figure 5.3a and 5.3b for the PAH of all structural classes. Among the benzenoid PAH, naphthalene, the smallest PAH in this structural class, is the highest-yield product at all $OR$. 
Figure 5.4. Yields, as functions of temperature and at different oxygen ratios (OR), of: (a) naphthalene, (b) phenanthrene, (c) chrysene, and (d) benzo[a]pyrene. The yields are from the pyrolysis and fuel-rich oxidation of catechol at 0.3 sec residence time (Figure continued next page).
Figure 5.4 (continued). (e) benzo[ghi]perylene, and (f) coronene. The yields are from the pyrolysis and fuel-rich oxidation of catechol at 0.3 sec residence time.

5.3.3.2. Indene Benzologues

Figure 5.5 presents the yields of the four chosen indene benzologues—indene, fluorene, benz[f]indene, and benzo[a]fluorene—as functions of temperature and at different $OR$. As with the benzenoid PAH, only the 2-ring compound, indene in this case, is produced in appreciable amounts at temperatures $< 800$ °C. The inset of Figure 5.5a reveals that at temperatures $< 800$ °C, indene yields increase with increasing temperature or $OR$. This increase in yield, similar to that for naphthalene in Figure 5.4a, is consistent with our earlier study [112] that the Radical Enhancement Effect is dominant in the lower-temperature range. At temperatures $\geq 800$ °C, the indene yields show decreases with increasing $OR$—the decreases being more dramatic for higher $OR$. 
Figure 5.5. Yields, as functions of temperature and at different oxygen ratios (OR), of: (a) indene, (b) fluorene, (c) benz[f]indene, and (d) benzo[a]fluorene. The yields are from the pyrolysis and fuel-rich oxidation of catechol at 0.3 sec residence time.
Figure 5.5 shows that for the other three indene benzologue products, the yields become significant at temperatures $\geq 800 \, ^\circ C$ and show dramatic decreases with increasing $OR$. At $OR \geq 0.58$, the yields of all three of these PAH are $< 0.001\%$ of fed catechol at $OR \geq 0.58$. We thus see that for the indene benzologues—as for the benzenoid PAH in Figure 5.4 and the C$_1$-C$_5$ species and single-ring aromatics [112]—the Oxidative Destruction Effect is dominant at temperatures $> 800 \, ^\circ C$. As with the benzenoid PAH, the indene benzologues follow the same trend of oxygen-induced yield decreases of increasingly greater magnitude as the PAH ring number is increased. Also as with the benzenoid PAH, it is the smallest compound within the structural class, in this case indene, which is the highest-yield indene benzologue product at all $OR$.

5.3.3.3. Fluoranthene Benzologues

Figure 5.6 presents the yields of the three chosen fluoranthene benzologues—fluoranthene, benzo[$b$]fluoranthene, and indeno[$1,2,3-cd$]pyrene—as functions of temperature and at different $OR$. The production of fluoranthene benzologues becomes significant only at temperatures $> 800 \, ^\circ C$. Figure 5.6 reveals that the yields of all three fluoranthene benzologues decrease dramatically in the presence of oxygen. At $OR \geq 0.58$, the yields of the three PAH in this class are each $< 0.004\%$ of fed catechol—signifying the dominance of the Oxidative Destruction Effect at the higher $OR$, as has been seen for the benzenoid PAH and indene benzologues at temperatures $> 800 \, ^\circ C$. Also, as with these two other classes of PAH, the oxygen-induced decreases in the yields of the fluoranthene benzologues become more pronounced as the PAH ring number increases. In addition, fluoranthene, the smallest compound in this structural class, is the highest-yield product at all values of temperature and $OR$—just as naphthalene and indene have been shown to be among the benzenoid PAH and indene benzologues, respectively.
Figure 5.6. Yields, as functions of temperature and at different oxygen ratios (OR), of: (a) fluoranthene, (b) benzo[b]fluoranthene, and (c) indeno[1,2,3-cd]pyrene. The yields are from the pyrolysis and fuel-rich oxidation of catechol at 0.3 sec residence time.
5.3.3.4. Ethynyl-Substituted and Cyclopenta-Fused PAH

![Graphs of yields as functions of temperature and oxygen ratio](image)

**Figure 5.7.** Yields, as functions of temperature and at different oxygen ratios (OR), of: (a) 2-ethynynaphthalene, and (b) 1-ethynylacenaphthylene. The yields are from the pyrolysis and fuel-rich oxidation of catechol at 0.3 sec residence time.

The yields of the two chosen ethynyl-substituted PAH, 2-ethynynaphthalene and 1-ethynylacenaphthylene, as functions of temperature and at different $OR$ are presented in Figure 5.7. The yields of the ethynyl-substituted PAH become significant only at temperatures $> 800$ °C. Similar to the other PAH examined so far, the two ethynyl-substituted PAH in Figure 5.7 show dramatic decreases in yield when oxygen is present, due to the Oxidative Destruction Effect. Also consistent with the other PAH, the oxygen-induced decreases in the yields of the ethynyl-substituted PAH are more pronounced for the larger-ring-number compounds. The largest member of this class, 2-ethynylphenanthrene, is detected only when oxygen is absent ($OR = 0$) [96]. The other two ethynyl-substituted PAH, 2-ethynynaphthalene and 1-
ethynylacenaphthylene, are detected when oxygen is present, but their yields are negligible at $OR \geq 0.58$, when oxidative destruction reactions dominate.

**Figure 5.8.** Yields, as functions of temperature and at different oxygen ratios ($OR$), of: (a) acenaphthylene, and (b) acephenanthrylene. The yields are from the pyrolysis and fuel-rich oxidation of catechol at 0.3 sec residence time.

Figures 5.8 and 5.9 present the yields of the three chosen cyclopenta-fused PAH—acenaphthylene, acephenanthrylene, and cyclopenta[$cd$]pyrene—as functions of temperature and at different $OR$. At temperatures $< 800^\circ C$, the only cyclopenta-fused PAH produced in appreciable amounts is acenaphthylene. The inset in Figure 5.8a reveals that at these lower temperatures ($< 800^\circ C$), acenaphthylene yields show a slight increase with increasing $OR$, due to the Radical Enhancement Effect. At temperatures $> 800^\circ C$, however, the yields of all of the cyclopenta-fused PAH become significant—just as has been shown for the benzenoid PAH, fluoranthene benzologues, and ethynyl-substituted PAH. Figures 5.8 and 5.9 reveal that the three
cyclopenta-fused PAH show dramatic decreases in yield in the presence of oxygen—the decrease being more dramatic at higher $OR$ and for the larger-ring-number members of this structural class. This evidence of the Oxidative Destruction Effect is further borne out by the observation that at $OR = 0.92$, only the three-ring compound acenaphthylene, the highest-yield cyclopenta-fused PAH at all $OR$, is produced in measurable amounts.

![Figure 5.9](image.png)

**Figure 5.9.** Yields of cyclopenta[$cd$]pyrene, as functions of temperature and at different oxygen ratios ($OR$), from the pyrolysis and fuel-rich oxidation of catechol at 0.3 sec residence time.

The ethynyl-substituted and cyclopenta-fused PAH are both thought to arise from acetylene addition to aryl radicals [50,96]. The similarity in the overall behavior of the two compound classes (Figures 5.2d and 5.2e), with respect to temperature and $OR$—and the dramatic decreases in the yields of acetylene [112] and the ethynyl-substituted and cyclopenta-fused PAH at higher $OR$ in Figures 5.8 and 5.9—provide further evidence that the acetylene-
addition mechanism [15,17,50,52,53] is important in the formation of the ethynyl-substituted and cyclopenta-fused PAH.

5.3.3.5. Methyl-Substituted PAH

**Figure 5.10.** Yields, as functions of temperature and at different oxygen ratios (OR), of: (a) 1-methylnaphthalene, and (b) 2-methylnaphthalene. The yields are from the pyrolysis and fuel-rich oxidation of catechol at 0.3 sec residence time.

Figure 5.10a and 5.10b, respectively, present the yields of 1-methylnaphthalene and 2-methylnaphthalene, as functions of temperature and at different OR. Besides indene, naphthalene and acenaphthylene, the methylnaphthalenes are the only PAH produced in appreciable amounts at temperatures < 800 °C when oxygen is present. Figures 5.10a and 5.10b show that at temperatures ≤ 800 °C, the yields of both methylnaphthalenes increase with increasing temperature or OR. This behavior is consistent with the dominance of the Radical Enhancement Effect in the lower-temperature regime, as observed for naphthalene and indene, in Figure 5.4a and 5.5a, as well as for the C1-C5 and single-ring aromatic products [112]. At temperatures > 800
³C, the yields of 1-methylnaphthalene at \( OR = 0 \) and \( OR = 0.22 \) are comparable, but those of 2-methylnaphthalene are lower at \( OR = 0.22 \) than at \( OR = 0 \). At higher \( OR (\geq 0.58) \), the yields of both methylnaphthalenes show dramatic declines at temperatures \( > 800 \) °C, due to the dominance of the Oxidative Destruction Effect.

**5.4. Summary and Conclusions**

To better understand the reactions responsible for the formation of PAH during the pyrolysis and combustion of solid fuels, we have performed pyrolysis and fuel-rich oxidation experiments in a laminar-flow reactor, using the model fuel catechol. The products have been analyzed and quantified by GC and HPLC analyses. The PAH product yields, as functions of temperature and at different oxygen ratios (\( OR = 0.22, 0.58, 0.92 \)), have been determined and compared with pyrolysis yields (\( OR = 0 \)) to delineate the effects of oxygen on these products.

During the pyrolysis and fuel-rich oxidation of catechol, PAH production becomes significant only at temperatures \( > 800 \) °C. At temperatures \( < 800 \) °C, only two-ring aromatics are produced in appreciable amounts. In this low-temperature regime, increases in oxygen concentration bring about measurable increases in yields of the 2- and 3-ring aromatics indene, naphthalene, 1-methylnaphthalene, 2- methylnaphthalene, phenanthrene, and acenaphthylene due to the higher reaction rates that result from the oxygen-induced enhancement of the free-radical pool. At temperatures \( > 800 \) °C, increases in oxygen concentration significantly reduce the yields of all PAH products—the decrease being more dramatic at higher oxygen concentrations (\( OR \geq 0.58 \)), as the oxidative destruction reactions dominate. These observations on PAH yields are consistent with our findings [112] for the C\(_{1}-C_{5}\) hydrocarbon and single-ring aromatic products yields: that the Radical Enhancement Effect is dominant in the lower-temperature regime, and the Oxidative Destruction Effect prevails in the higher-temperature regime. The coincident oxygen-induced decreases in the yields of the PAH, C\(_{1}-C_{5}\) hydrocarbons, and 1- and 2-ring
aromatics at higher temperature and the oxygen-induced increases in the yields of these same products at lower temperature underscore the important role of the thermal decomposition products in the formation and growth of PAH during the pyrolysis and fuel-rich oxidation of catechol.

An earlier study from our research group [99] has shown that PAH of smaller ring number are produced in higher abundance than those of larger ring number, during catechol pyrolysis in the absence of oxygen. The present study shows that this preference for the smaller-ring-number PAH also holds during the fuel-rich oxidation of catechol. All the different classes of PAH examined in this study exhibit a trend of enhanced oxygen-induced decreases in yield as PAH ring number is increased. These observations regarding PAH ring number, from the fuel-rich oxidation experiments with catechol, fully support our finding [97-99] from catechol pyrolysis in the absence of oxygen: that PAH formation and growth occur by successive ring-buildup reactions involving the C_1-C_5 and single-ring aromatic products of catechol’s thermal decomposition.

Most kinetic modeling studies on PAH formation have employed data from premixed laminar flames of light hydrocarbon fuels [79,80]. No kinetic model is currently available for catechol decomposition or PAH production from catechol under pyrolytic or oxidative conditions. The results presented here and in previous catechol pyrolysis studies [25,50,96-99,112], collectively, should be helpful in the development of a detailed kinetic model for PAH formation during catechol pyrolysis and oxidation. Since catechol is a model fuel representative of entities in solid fuels like coal, wood, and biomass, it is anticipated that the results from these catechol studies will be directly applicable to fuel-conversion processes involving actual solid fuels.
Chapter VI. Effects of Acetylene Addition: Yields of the C$_1$-C$_{10}$ Thermal Decomposition Products*

6.1. Introduction

During combustion, solid fuels like coal, wood, and biomass are burned in a diffusion-flame configuration, involving high-temperature, oxygen-deficient zones. Pyrolytic reactions dominate in these high-temperature zones, leading to the formation of polycyclic aromatic hydrocarbons (PAH). Since some members of this compound class have been shown to exhibit carcinogenic [6-8] and mutagenic [9,10] activity, the formation of PAH and their subsequent release into the environment are of concern. In addition, PAH are precursors to soot [15,16], a major contributor to fine particulates responsible for heart and lung diseases [11,12].

Hydrogen-abstraction/acetylene-addition reactions [17,50-53] have been considered to be one of the major pathways leading to PAH formation during combustion. Therefore, the role of the C$_2$ species in the formation of PAH under solid fuel pyrolysis and combustion conditions needs to be investigated. Since the formation of 1- and 2-ring aromatic compounds has been shown to be the rate-controlling step in the formation of larger PAH and soot [73,75,76], the reactions leading to the 1- and 2-ring aromatics like benzene, indene, and naphthalene under solid fuel pyrolysis and combustion conditions also need to be considered.

Although it is possible to perform experiments with solid fuels like coal, wood, or biomass, the complex nature of these fuels makes it extremely difficult to attribute certain products to certain reaction pathways. To overcome this difficulty, most of the mechanistic studies on PAH formation have focused on examining the pyrolysis of model compounds representing structural moieties in these fuels [16,25,83,85-92,179].

We have chosen catechol (ortho-dihydroxybenzene) as a model fuel compound for our investigations into the formation of PAH during solid fuel decomposition. As a prominent

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structural entity of coal [100], tobacco [103], and lignin (a major component of wood [101])—as well as a major component in biomass tars [102] and tobacco smoke [104]—catechol is a suitable model compound for investigating certain aspects of solid fuel pyrolysis and combustion. The demonstrated [96] similarity between PAH product distributions obtained from catechol pyrolysis and from coal volatiles pyrolysis further strengthens our assertion that catechol is an ideal model compound for our studies.

Previous studies [50,96-99,112,113] in this series have examined in detail the homogeneous gas-phase pyrolysis and fuel-rich oxidation of catechol in an isothermal laminar-flow reactor at temperatures of 500-1000 °C, to gain fundamental insights into the formation of PAH during catechol pyrolysis. Collectively, these studies have led to the identification, among the products, of 11 C_1-C_5 species [98,112], 5 single-ring aromatics [96,97,112], 5 two- and three-ring oxygen-containing organics [96], as well as 54 individual PAH [96,97]. Several key observations from our previous work provide strong evidence that the C_1-C_5 thermal decomposition products play a major role in the formation of PAH during the pyrolysis and fuel-rich oxidation of catechol: (1) The catechol pyrolysis environment contains a high abundance of C_1-C_5 species [98,112], and a decrease in the yields of the C_3-C_5 species at higher temperatures corresponds to an increase in PAH yields [98,99,112]. (2) C_2 species, acetylene in particular, are present in high yields in the catechol pyrolysis environment [98,112]. (3) Ethynyl-substituted PAH and cyclopenta-fused PAH [99,113]—both thought to arise from acetylene addition to aryl radicals [50]—are produced in particularly high abundance during catechol pyrolysis. (4) Acetylene, benzene, and phenylacetylene each show very similar behavior under oxidative pyrolysis conditions: the yields of all three compounds increase with increasing oxygen concentration at temperatures ≤ 800 °C, and decrease with increasing oxygen concentration at temperatures > 900 °C [112]. (5) At a given pyrolysis condition, PAH of smaller ring number are
produced in higher yield than those of larger ring number [97,99,113], and increasing the pyrolysis temperature or residence time produces PAH products of higher ring number [99,113]. (6) Calculated global kinetic rate parameters for the formation of PAH from catechol show a trend of increasing activation energy with increasing PAH ring number [97]. Observations (1), (5), and (6) are consistent with a mechanism for PAH growth involving successive addition of C$_2$-C$_5$ species to initially single-ring compounds. Observations (2)-(4) provide strong evidence that hydrogen-abstraction/acetylene-addition (HACA) reactions [17,52,53,202] are likely to play a major role in the formation and molecular growth processes of PAH during the pyrolysis and fuel-rich oxidation of catechol.

To better understand the role of C$_2$ species in PAH formation and growth, we have carried out catechol pyrolysis experiments in the presence of acetylene added as a dopant. The pyrolysis experiments are carried out in an isothermal laminar-flow reactor at temperatures of 500-1000 °C, and the products are analyzed by gas chromatography (GC), nondispersive infrared analysis, and high-pressure liquid chromatography (HPLC). The effects of acetylene addition on yields of the PAH and oxygen-containing organic products of catechol will be addressed in Chapter VIII. The present chapter and corresponding paper [114] report the effects of acetylene addition on the yields of the C$_1$-C$_5$ species and 1- and 2-ring aromatic products formed during catechol pyrolysis. The C$_1$-C$_5$ species are known [66-74,204,207,208,219-221] to play major roles in the formation of 1- and 2-ring aromatics and can add to these same aromatic products to form PAH and soot [17,52,73,220].

In the following, we present the effects of acetylene addition on the yield/temperature profiles of eight C$_1$-C$_5$ hydrocarbons and seven 1- and 2-ring aromatic products of catechol pyrolysis. We then discuss reaction pathways for the formation of the 1- and 2-ring aromatic products. Since several studies [205,222-224] relevant to solid fuel combustion have highlighted
the roles of resonantly-stabilized radicals (e.g., propargyl, cyclopentadienyl, benzyl, and C₄H₃ radicals) in the formation of 1- and 2-ring aromatics, our discussion considers the participation of these resonantly-stabilized radicals in the formation of the 1- and 2-ring aromatic products of catechol pyrolysis.

6.2. Experimental Equipment and Procedures

6.2.1. Reactor System

Three sets of pyrolysis experiments are performed: Set 1, pyrolysis of catechol; Set 2, pyrolysis of catechol in the presence of acetylene dopant; Set 3, pyrolysis of acetylene. For all three cases, the pyrolysis experiments have been performed in an isothermal laminar-flow reactor system [96-99] depicted in schematic form in Figure 2.1. The reactor system consists of a fuel vaporizer, isothermal quartz flow reactor, and product collection system. The pyrolysis reactions take place inside the isothermal quartz flow reactor, which consists of a 2-mm (inner diameter) quartz tube insulated at both ends and maintained at isothermal conditions by a three-zone electrically heated furnace. The reactor is operated at temperatures of 500-1000 °C, at atmospheric pressure, and at a residence time of 0.3 s. The gaseous products are collected in a Teflon gas-sampling bag, and the condensed-phase products are collected, in separate experiments, in a condensed-phase product collection system.

The three sets of experiments differ by the reactor feed gas composition. For the Set 1 experiments, solid catechol particles (>99.5% pure, purchased from Aldrich Chemical Co.) are loaded as a fixed bed into a Pyrex tube placed vertically inside the fuel vaporizer, an isothermal oven maintained at 85 °C for slight vaporization of the catechol. The vapor-phase catechol is entrained in a flowing stream of ultrahigh purity (grade 6.0, 99.9999 %) nitrogen carrier gas, resulting in a 0.65 mole-% carbon loading in the reactor feed gas. The feed to the reactor for the Set 1 experiments is thus nitrogen with vapor-phase catechol (0.65 mole-% carbon).
The Set 2 experiments are conducted in the same manner as those of Set 1, except for one difference. For the Set 2 experiments, the pure nitrogen used as the carrier gas in the Set 1 experiments is replaced by nitrogen containing 1379 ppm of acetylene. As it passes through the vaporizer, the nitrogen/acetylene carrier gas in the Set 2 experiments picks up the same amount of vapor-phase catechol as the nitrogen carrier gas in the Set 1 experiments, so the catechol-to-acetylene molar feed ratio is fixed at 0.785 for the Set 2 experiments. The feed to the reactor for the Set 2 experiments, therefore, is nitrogen with vapor-phase catechol (0.65 mole-% carbon) and acetylene (0.276 mole-% carbon).

In the Set 3 experiments, no catechol is used; acetylene is the only fuel pyrolyzed. Therefore, the same nitrogen/acetylene carrier gas is used in the Set 3 experiments as in the Set 2 experiments. This time, however, the carrier gas is passed through the by-pass line in the fuel vaporizer (Figure 1) so that no catechol is picked up. The feed to the reactor in the Set 3 experiments, therefore, is nitrogen with acetylene (0.276 mole-% carbon).

For each of the three sets of experiments just described, samples are taken from the vaporizer exit stream, both before and after each pyrolysis experiment, and analyzed by GC, to ensure the consistency of each reactor feed-gas composition.

6.2.2. Product Analysis

Exiting the heated zone of the reactor, the pyrolysis products are quenched to room temperature and the condensed-phase products are trapped on a Balston Teflon filter. The C₁-C₅ gas-phase products along with benzene, the most volatile of the aromatic products, flow through the filter and are collected in a Teflon gas-sampling bag for subsequent compositional analysis. The condensed-phase products (1- and 2-ring aromatics and PAH) are collected, in a separate experiment, with a condensed-phase products collection system (consisting of a Balston Teflon
filter and dichloromethane solvent trap) and dissolved in dichloromethane for subsequent identification and quantification by gas chromatographic analysis.

A portion of the product gases collected is pumped from the sampling bag through two Horiba Model VIA-510 nondispersive infrared analyzers to quantify CO and CO$_2$. (No CO$_2$ is produced in the experiments reported here.) The remaining product gases are then routed to an Agilent Model 6890/5973 gas chromatograph/flame-ionization detector/mass spectrometer (GC/FID/MS) for analysis of C$_1$-C$_6$ hydrocarbons. Separation of the hydrocarbon gases is achieved on a GS GASPRO capillary column of length, 30 m, and diameter, 0.32 mm. Except for cyclopentadiene and vinylacetylene, identification of the C$_1$-C$_6$ gas-phase products is accomplished by matching the retention times and mass spectra of individual product components with those of reference standards, and product quantification is based on the calibration of the GC/FID with reference standards. Since a reference standard for cyclopentadiene is not commercially available, its identification in the catechol pyrolysis products is based on matching the product component’s GC retention index with that of cyclopentadiene generated from the pyrolysis of dicyclopentadiene [88,120] as well as by matching the product component’s mass spectrum with that of the reference standard in the NIST/EPA/NIH mass spectral library. The identification of vinylacetylene is based on matching the product component’s mass spectrum with that of the reference standard in the NIST/EPA/NIH mass spectral library. In addition, the identification of vinylacetylene among the thermal decomposition products of catechol is consistent with the thermal formation of vinylacetylene from acetylene [121] and 1,3-butadiene [122-124]—two of the highest-yield hydrocarbon products present in the catechol pyrolysis environment.

The condensed-phase catechol pyrolysis products are also analyzed on the Agilent Model 6890/5973 GC/FID/MS. A 2-µL aliquot of the product solution is injected by syringe, through a
split injector, onto a HP-5 fused silica capillary column of length, 30 m, diameter, 0.25 mm, and film thickness 0.1 \( \mu \)m. The 1- and 2-ring aromatic products are identified by matching retention times and mass spectra with those of reference standards. (The identities of the 2-ring aromatics indene and naphthalene have also been confirmed by matching their HPLC retention times and ultraviolet absorption spectra with those of respective reference standards.)

The PAH products are identified and quantified by analysis [96,99] on a Hewlett-Packard Model 1050 high-pressure liquid chromatograph coupled to a diode-array ultraviolet-visible absorbance detector. The results of the HPLC analyses for PAH yields will be reported in Chapter VIII; the present chapter reports the yields of the C\(_1\)-C\(_5\) hydrocarbons and 1- and 2-ring aromatics, which are determined by GC.

For each set of experiments (Set 1, Set 2, and Set 3), pyrolysis products are collected from separate experiments at each of nine different temperatures, over the range 500-1000 \(^\circ\)C, and at a fixed residence time of 0.3 s. The collected products are analyzed by GC, HPLC, and non-dispersive infrared analysis. The product yields obtained from repeat experiments under the same conditions demonstrate that the flow reactor system, sample preparation procedures, and product analysis techniques all give very reproducible results. The collective mass of carbon obtained from the gas-phase products and the condensed-phase products (including any unconverted catechol) accounts for all of the carbon fed to the reactor as catechol and/or acetylene. A carbon balance is thus closed on this reactor system.

### 6.3. Results and Discussion

Figures 6.1-6.11 present the yields, as functions of temperature, of the reactants and C\(_1\)-C\(_{10}\) hydrocarbon products from the pyrolysis of catechol in the absence of acetylene dopant (Set 1) and in the presence of acetylene dopant (Set 2). The products of catechol in Figures 6.4-6.6 are also products of acetylene pyrolysis alone, so Figures 6.4-6.6 include results of the Set 3
(acetylene-only pyrolysis) experiments, and Figure 6.3 (acetylene yields) includes yields of unreacted acetylene from the Set 3 experiments. To facilitate comparisons between the three sets of experiments, all yields in Figures 6.1-6.11 are reported as “mass-percent of fed catechol.” The catechol-to-acetylene molar feed ratio of 0.785 used in the Set 2 experiments translates into an acetylene-to-catechol mass feed ratio of 0.301, so the product yields from the acetylene-only (Set 3) pyrolysis experiments, initially determined as “mass-% of fed acetylene,” are multiplied by the acetylene-to-catechol mass feed ratio of 0.301 (for the Set 2 experiments) to obtain these yields in terms of “mass-% fed catechol” equivalent. Before discussing the product yields, we first consider the effect of acetylene addition on catechol conversion.

6.3.1. Catechol Conversion

![Figure 6.1](image_url)  
**Figure 6.1.** The yields, as functions of temperature, of unreacted catechol collected from catechol pyrolysis in the presence of acetylene dopant (◊) and in the absence of acetylene dopant (■).
Figure 6.1 presents the yield/temperature profiles of unreacted catechol collected in the products from the Set 1 experiments without acetylene dopant and from the Set 2 experiments with acetylene dopant. Figure 6.1 shows that the yields of unreacted catechol from the catechol pyrolysis experiments with the acetylene dopant are indistinguishable from those without the acetylene dopant. In both cases, the yields show a decrease with increasing temperature, as catechol conversion rapidly increases to 100 % at temperatures $\geq 850$ °C. Therefore, acetylene addition does not appear to affect catechol conversion.

6.3.2. CO Yields

![Graph showing CO yields as a function of temperature]

**Figure 6.2.** The yields, as functions of temperature, of CO from catechol pyrolysis in the presence of acetylene dopant (◊) and in the absence of acetylene dopant (■).

As demonstrated elsewhere [112], CO is the highest-yield product of catechol pyrolysis—its yield increasing dramatically with temperature in the 750-900 °C range and leveling off at ~50 mass-% of fed catechol, at the highest temperatures. Figure 6.2 presents the
yields, as functions of temperature, of CO produced from the catechol pyrolysis experiments without acetylene dopant (Set 1) and with acetylene dopant (Set 2). As revealed in Figure 6.2, our Set 1 and Set 2 experiments show no effect of acetylene dopant on CO yields, and the Set 3 experiments do not produce CO since there is no source of oxygen.

6.3.3. Acetylene Yields

![Acetylene Yield Graph](image)

Figure 6.3. The yields, as functions of temperature, of unreacted acetylene collected from acetylene pyrolysis (○), from catechol pyrolysis in the presence of acetylene dopant (◇), and from catechol pyrolysis in the absence of acetylene dopant (■). As explained in the text, the catechol-to-acetylene molar feed ratio of 0.785 used in the Set 2 experiments corresponds to an acetylene-to-catechol mass feed ratio of 0.301. The amount of acetylene in the reactor feed gas in the Set 2 and Set 3 experiments thus corresponds to a value of 30.1 % on the y-axis of this figure.

Figure 6.3 presents the yields, as functions of temperature, of acetylene collected in the products from the catechol pyrolysis experiments without acetylene dopant (Set 1) and with acetylene dopant (Set 2). Also presented in Figure 6.3 is the yield/temperature profile of unreacted acetylene (open circles) collected in the products from the acetylene pyrolysis
experiments (Set 3). The catechol-to-acetylene molar feed ratio of 0.785 used in the Set 2 experiments translates into an acetylene-to-catechol mass feed ratio of 0.301, so the amount of acetylene fed to the reactor in the Set 2 and Set 3 experiments corresponds to a value of 30.1 % on the y-axis of Figure 6.3. Therefore, on the chosen basis of “mass-percent of fed catechol,” an acetylene yield of 30.1 % for the Set 2 and Set 3 experiments corresponds to no conversion of the acetylene fed to the reactor.

The Set 3 curve of Figure 6.3 shows that no acetylene is converted in the acetylene-only pyrolysis experiments at temperatures ≤ 800 °C. At temperatures > 800 °C, however, ~3-4 % of the acetylene fed to the reactor in the Set 3 experiments is converted, so the yields of unreacted acetylene at these temperatures are ~96 % of fed acetylene, which corresponds to ~29 mass-% of fed catechol on the y-axis of Figure 6.3. Therefore, when expressed on this same y-axis basis, the amount of acetylene consumed in the acetylene-only Set 3 pyrolysis experiments at temperatures > 800 °C is ~1 % fed catechol equivalent. Analysis of the acetylene pyrolysis products shows that they are all C1-C6 hydrocarbons and that vinylacetylene is the one produced in highest yield (maximum yield 0.93 mass-% of fed acetylene; 0.28 mass-% of fed catechol equivalent). The yields of the C1-C6 products from acetylene pyrolysis are all small, compared to those from catechol, but are included in Figures 6.4-6.6, expressed in terms of “mass-percent of fed catechol” equivalent, for easy reference and comparison.

Figure 6.3 shows that at temperatures < 800 °C, acetylene is not produced from the pyrolysis of catechol (Set 1). In addition, the yields of acetylene from the Set 2 experiments in this low temperature range remain constant at 30.1 %, corresponding to no conversion of the acetylene fed to the reactor. Therefore, at temperatures < 800 °C, acetylene is neither produced nor consumed in the Set 2 or Set 3 experiments.
At temperatures > 800 °C, however, acetylene becomes a factor in the catechol pyrolysis reactions. The Set 1 curve of Figure 6.3 reveals that at temperatures > 800 °C, acetylene is produced from the pyrolysis of catechol and that the yield of acetylene rises rapidly with temperature as temperature is increased to 1000 °C. The Set 2 curve for Figure 6.3 also shows that when catechol is pyrolyzed with acetylene dopant, acetylene yields rise with temperature, from 800 to 1000 °C, but the magnitude of the rise for the Set 2 experiments is not as great as the one for the Set 1 experiments. In fact the Set 2 curve in Figure 6.3 reflects a synergistic effect when catechol and acetylene are pyrolyzed together at temperatures > 800 °C. In the absence of a synergistic effect, the acetylene yields from the Set 2 experiments at 800-1000 °C would equal the sum of the acetylene yields from the Set 1 (catechol-only pyrolysis) experiments plus the acetylene yields from the Set 3 (acetylene-only pyrolysis) experiments. However, since the acetylene yields obtained from the Set 2 experiments at 800-1000 °C are lower than this sum (by an amount of ~2-3 mass-% of fed catechol), we conclude that at temperatures > 800 °C, more acetylene is consumed when it is in the catechol pyrolysis reaction environment than when it is not. The rich pool of free radicals in the catechol pyrolysis reaction environment apparently facilitates acetylene consumption by obviating the need for an ethynyl C-H scission (a high-energy process) initiation step. The enhanced consumption of acetylene could have significance with regard to the formation of 1-ring aromatic products and PAH.

6.3.4. C₁-C₅ Hydrocarbon Products

Figure 6.4 presents the yield/temperature profiles of the C₁-C₅ hydrocarbon products from the pyrolysis of catechol in the absence of acetylene dopant (Set 1) and in the presence of acetylene dopant (Set 2). Figures 6.4a, 6.4b, 6.4c, 6.4d, and 6.4e, respectively, show that the yields of methane, ethylene, 1,3-butadiene, vinylacetylene, and cyclopentadiene obtained from catechol pyrolysis in the absence of acetylene dopant (Set 1) are comparable to those obtained in
the presence of acetylene dopant (Set 2). In the cases of methane, ethylene, and cyclopentadiene—which are produced in extremely low amounts from acetylene-only pyrolysis—the virtual equivalence of the Set 1 and Set 2 experimental yields suggests that the reactions producing methane, ethylene, and cyclopentadiene from catechol are not affected by acetylene’s presence. However, the fact that the Set 2 experiments’ yields for 1,3-butadiene (in Figure 6.4c) and vinylacetylene (in Figure 6.4d) are lower, at 850 °C and 900 °C, than their respective sums from the Set 1 and Set 3 experiments suggests that the consumption of both of these C₄ species is enhanced when acetylene is present.

![Graph](image_url)

**Figure 6.4.** The yields, as functions of temperature, of: (a) methane, (b) ethylene, (c) 1,3-butadiene, (d) vinylacetylene, and (e) cyclopentadiene. Experiments: acetylene pyrolysis (○); catechol pyrolysis in the presence of acetylene dopant (◊); catechol pyrolysis in the absence of acetylene dopant (■). The catechol-to-acetylene molar feed ratio of 0.785 used in the Set 2 experiments translates into an acetylene-to-catechol mass feed ratio of 0.301, so the product yields from the acetylene-only (Set 3) pyrolysis experiments, initially determined as “mass-% of fed acetylene,” are multiplied by the acetylene-to-catechol mass feed ratio of 0.301 (for the Set 2 experiments) to obtain the yields in terms of “mass-% of fed catechol” equivalent (Figure continued next page).
Figure 6.4 (continued). (c) 1,3-butadiene, (d) vinylacetylene, and (e) cyclopentadiene. Experiments: acetylene pyrolysis (○); catechol pyrolysis in the presence of acetylene dopant (◊); catechol pyrolysis in the absence of acetylene dopant (■).
For both of the C₄ species, the most likely channels of the additional consumption are reactions with acetylene to produce benzene[79,206,225] and/or reactions with propargyl radical to produce toluene—since the yields of benzene and toluene from catechol pyrolysis are both enhanced in the presence of acetylene dopant, as Figures 6.6 and 6.8 reveal.

![Graph showing the yields of propadiene and propyne as functions of temperature.](image)

**Figure 6.5.** The yields, as functions of temperature, of: (a) propadiene, and (b) propyne. Experiments: acetylene pyrolysis (○); catechol pyrolysis in the presence of acetylene dopant (◇); catechol pyrolysis in the absence of acetylene dopant (■). The basis used for the reported yields is explained in the caption of Figure 6.4.

In contrast to the products of Figure 6.4, however, Figure 6.5 reveals that at temperatures > 800 °C, the addition of acetylene increases the yields of the C₃ products: the yields of propyne and propadiene from catechol pyrolysis in the presence of acetylene dopant (Set 2) are higher than their respective yields in the absence of acetylene dopant (Set 1). The amounts of these increases at temperatures > 850 °C are higher than just the amounts of these C₃ products formed by acetylene pyrolysis alone, as Figures 6.5a and 6.5b show. Therefore, with regard to the C₃
products, acetylene addition appears to cause another synergistic effect. Since propyne and propadiene are the stable forms of the resonantly-stabilized propargyl radical—an important growth species in the formation of 1- and 2-ring aromatics like benzene [204,205,207,208,220,221], toluene [78,225,226], indene [66], and naphthalene [219]—the increases in the yields of the two C₃ products of catechol pyrolysis likely signify an increase in propargyl radical, which could translate into increases in the yields of the 1- and 2-ring aromatics as well as PAH.

6.3.5. One-Ring Aromatic Products

![Figure 6.6](image-url)

**Figure 6.6.** The yields, as functions of temperature, of benzene. Experiments: acetylene pyrolysis (○); catechol pyrolysis in the presence of acetylene dopant (◇); catechol pyrolysis in the absence of acetylene dopant (■). The basis used for the reported yields is explained in the caption of Figure 6.4.

Figures 6.6-6.9 present the yields, as functions of temperature, of the 1-ring aromatic products from catechol pyrolysis in the absence of acetylene dopant (Set 1) and in the presence
of acetylene dopant (Set 2). The 1-ring products phenol, benzene, and toluene are of particular importance due to their potential roles in the formation of indene [66,222,227] and naphthalene [17,52,67,202,219]. Styrene and phenylacetylene are reported to be important intermediates in the formation of naphthalene by the HACA mechanism [17,52,202].

Figure 6.6 presents the yields, as functions of temperature, of benzene produced from the pyrolysis of acetylene (Set 3) and from the pyrolysis of catechol in both the absence (Set 1) and presence (Set 2) of acetylene dopant. Figure 6.6 reveals that at temperatures > 800 °C, the addition of acetylene brings about an increase in the yields of benzene from catechol pyrolysis—an increase whose magnitude is significantly greater than what the added amount of acetylene would produce on its own (the Set 3 curve in Figure 6.6). This experimentally observed increase in benzene production can be associated with some of the C_2-C_4 products of catechol. First, as we mentioned in the discussion of Figures 6.4c and 6.4d, reaction of acetylene with the two C_4 major products, 1,3-butadiene and vinylacetylene, could account for at least some of the extra benzene at 850 and 900 °C. A second potential source of the additional benzene—which could cover the full temperature range of 800 to 1000 °C—is propargyl radical self-addition [204,205,207,208,220,221], one of the most cited benzene formation mechanisms in the literature. The acetylene-induced increases in the yields of propadiene (Figure 6.5a) and propyne (Figure 6.5b), the stable forms of the propargyl radical, indicate that propargyl radical self-addition could contribute to the higher yields of benzene during catechol pyrolysis in the presence of acetylene dopant (Set 2). Lastly, a third possible source for the higher yields of benzene in the presence of acetylene dopant is the polymerization of acetylene [228-230]. Even though the Set 3 curve of Figure 11 indicates that benzene is produced in only small yields by acetylene pyrolysis alone, the rich radical pool of the catechol pyrolysis reaction environment could facilitate acetylene’s reaction with itself. Both vinylacetylene (Figure 6.4d) and
triacetylene [96], two acetylene polymerization products, are produced during catechol pyrolysis, and our Set 3 experiments show that vinylacetylene and benzene, respectively, are the highest- and third-highest-yield products of acetylene pyrolysis.

![Figure 6.7](image.png)

**Figure 6.7.** The yields, as functions of temperature, of phenol. Experiments: acetylene pyrolysis (○); catechol pyrolysis in the presence of acetylene dopant (◊); catechol pyrolysis in the absence of acetylene dopant (■).

In contrast to benzene, none of the other one-ring aromatics of Figures 6.6-6.9 are produced by acetylene pyrolysis alone. Figure 6.7 shows that the yields of the one-ring product phenol from catechol pyrolysis in the absence of acetylene dopant (Set 1) are virtually indistinguishable from those produced in the presence of acetylene dopant (Set 2). Since the addition of acetylene does not affect catechol conversion (Figure 6.1), the comparable yields of phenol are consistent with our proposed mechanism [98] for phenol formation by the displacement of an OH from catechol by H atom. Also, the comparable yields of cyclopentadiene (Figure 6.4e) produced from catechol pyrolysis in both the absence and presence of acetylene
dopant support our earlier assertion [98,112] that during catechol pyrolysis, cyclopentadiene is formed from phenol by the unimolecular decomposition of the phenoxy radical.

Figure 6.8 presents the yield/temperature profile of toluene from catechol pyrolysis in the absence of acetylene dopant (Set 1) and in the presence of acetylene dopant (Set 2). Figure 6.8 reveals that the addition of acetylene increases the yields of toluene in the temperature range 800-950 °C, the increase being more dramatic at 850 and 900 °C. In combustion systems, there are multiple routes to toluene that involve the C1-C5 species [78,226,231-233]. One of the most cited toluene formation mechanisms is propargyl addition to the butadienyl radical [78,225,226].

The acetylene-induced decreases in the yields of 1,3-butadiene (representative of the butadienyl radical) at 850 and 900 °C in Figure 6.4c and the acetylene-induced increases in the yields of the two C3 species (representative of the propargyl radical) in Figures 6.5a and 6.5b suggest that

Figure 6.8. The yields, as functions of temperature, of toluene. Experiments: acetylene pyrolysis (○); catechol pyrolysis in the presence of acetylene dopant (◇); catechol pyrolysis in the absence of acetylene dopant (■).
propargyl addition to butadienyl radical could contribute to the experimentally observed increases in toluene yields at 850 and 900 °C. Alternative routes to toluene, involving methyl addition to benzene [232,233] and acetylene addition to cyclopentadiene [231], cannot be ruled out, however. Toluene is the stable form of the resonantly-stabilized benzyl radical. Like other resonantly-stabilized radicals, the benzyl radical can build up to high concentrations in our catechol pyrolysis environment. Hence, an increase in the benzyl radical, as evident in the increase of toluene yield (Figure 6.8), can potentially have a significant effect on PAH formation, as benzyl radical reactions can lead to 2-ring aromatics like indene [222] and naphthalene [219].

Figure 6.9. The yields, as functions of temperature, of: (a) styrene, and (b) phenylacetylene. Experiments: acetylene pyrolysis (○); catechol pyrolysis in the presence of acetylene dopant (◇); catechol pyrolysis in the absence of acetylene dopant (■).
Figures 6.9a and 6.9b, respectively, present the yield/temperature profiles of styrene and phenylacetylene from catechol pyrolysis in the absence of acetylene dopant (Set 1) and in the presence of acetylene dopant (Set 2). Both styrene and phenylacetylene can result from acetylene addition to benzene [52,202]. Figure 6.9a, however, shows that the yields of styrene from catechol pyrolysis in the presence of acetylene dopant (Set 2) are only slightly higher than those in the absence of acetylene dopant (Set 1). Therefore, HACA reactions are not likely to be the dominant styrene formation mechanism in our catechol pyrolysis environment.

Fahr and Stein [234] have suggested a mechanism, based on their high temperature studies, for styrene formation by vinyl radical addition to the phenyl radical. This mechanism was used in the RRKM analysis of Yu and Min [235] and gave a good fit for the experimental results obtained by Fahr and Stein [234]. This vinyl-plus-phenyl mechanism [234] for styrene shows consistency with our experimental observation that—when acetylene is added to the catechol pyrolysis environment—an increased yield of benzene (representative of phenyl) in Figure 6.6 and an unaffected yield of ethylene (representative of vinyl) in Figure 6.4b correspond to a slightly increased yield of styrene in Figure 6.9a. Alternative routes to styrene, involving propargyl addition to cyclopentadienyl radical, butadienyl addition to vinylacetylene [78], or vinylacetylene self-addition, cannot be ruled out, however.

Figure 6.9b reveals that, at temperatures > 800 °C, the yields of phenylacetylene from catechol pyrolysis in the presence of acetylene dopant (Set 2) are significantly higher than those produced in its absence (Set 1). This acetylene-induced increase in phenylacetylene yields, along with the high abundance of ethynyl-substituted PAH in our catechol pyrolysis environment [96,99,113], provides strong evidence that HACA reactions are chiefly responsible for the formation of phenylacetylene and the other ethynyl-substituted aromatics produced during catechol pyrolysis.
6.3.6. Indene

Figure 6.10. The yields, as functions of temperature, of indene. Experiments: acetylene pyrolysis (○); catechol pyrolysis in the presence of acetylene dopant (◊); catechol pyrolysis in the absence of acetylene dopant (■).

Figure 6.10 presents the yield/temperature profiles of indene from catechol pyrolysis in the absence of acetylene dopant (Set 1) and in the presence of acetylene dopant (Set 2). Figure 6.10 reveals that at temperatures > 800 °C, the yields of indene increase dramatically when acetylene is added as a dopant. This experimentally observed increase in indene yields and the implied [72,236] role of indene as a precursor species for PAH formation and growth warrant more careful examination of indene formation mechanisms. Three possible reaction schemes that can lead to indene formation in combustion environments and that are relevant to our catechol pyrolysis environment are: cyclopentadienyl radical addition to cyclopentadiene [227,237], propargyl addition to phenyl radical [66], and acetylene addition to benzyl radical [222]. These three mechanisms are presented in schematic form in Table 6.1.
The first of the indene formation schemes, cyclopentadiene self-addition (Scheme 1 in Table 6.1), was proposed by Manion and Louw [237], and the potential energy surface for this mechanism has been calculated by Wang et al. [227]. Although Figure 6.10 shows that our yields of indene, the first product of Scheme 1, increase dramatically when acetylene is added as a dopant, Figures 6.4a and 6.4e show that our yields of methane, the stable form of the other Scheme 1 product, and of cyclopentadiene, a reactant in Scheme 1, do not. Therefore, Scheme 1 in Table 6.1, cyclopentadiene self-addition, cannot be the dominant indene formation mechanism in our catechol pyrolysis environment.

The second indene formation scheme involves propargyl radical addition to the phenyl radical (Scheme 2 in Table 6.1). The potential energy surface of this mechanism has been
computed by Vereecken et al. [66] The coincidental increases in our yields of benzene (representative of the phenyl radical) in Figure 6.6, propadiene in Figure 6.5a, propyne in Figure 6.5b, and indene in Figure 6.10—when acetylene is added as a dopant—are all consistent with the Scheme 2 formation of indene by propargyl radical addition to the phenyl radical in our catechol pyrolysis environment. Also, the effects of temperature on the yields of propadiene (Figure 6.5a) and propyne (Figure 6.5b) are very similar to those on the yields of indene (Figure 6.10)—all three compounds showing peak yields at 900 °C. In addition, GC-MS analysis of our catechol pyrolysis products reveals a product component of molecular weight 116, consistent with the intermediate formed in Scheme 2 in Table 6.1. Therefore, the indene formation Scheme 2 in Table 6.1 shows consistency with the results from our catechol pyrolysis experiments.

Bittner and Howard [17] have proposed a HACA mechanism for indene formation, involving acetylene addition to the benzyl radical (Scheme 3 in Table 6.1). The increase in the yield of toluene (Figure 6.8), when acetylene is added as a dopant, and the corresponding increase in the yield of indene (Figure 6.10) suggest that this mechanism may also contribute to indene formation during catechol pyrolysis. The effects of temperature on the yields of toluene (Figure 6.8) are very similar to those on the yields of indene (Figure 6.10), suggesting a link between these two compounds. In addition, the detection, by GC-MS, of a catechol pyrolysis product component of molecular weight 118 (the molecular weight of the stable form of the intermediate in Scheme 3 in Table 6.1) is consistent with the Scheme 3 HACA mechanism for indene formation in Table 6.1.

Granata et al. [238] have found Scheme 3 in Table 6.1 to be the major indene formation mechanism in 1,3-butadiene flames. Since 1,3-butadiene and acetylene are the highest-yield hydrocarbon products from our catechol pyrolysis experiments—and since yields of the C_3 products (associated with Scheme 2) are roughly an order of magnitude lower—we believe that
the Scheme 3 HACA mechanism in Table 6.1 is also the dominant indene formation route in our catechol pyrolysis environment.

6.3.7. Naphthalene

Figure 6.11 presents the yield/temperature profiles of naphthalene from catechol pyrolysis in the absence of acetylene dopant (Set 1) and in the presence of acetylene dopant (Set 2). Figure 6.11 reveals that except for the highest temperature of 1000 °C, acetylene addition has virtually no effect on the yield of naphthalene from catechol pyrolysis.

![Graph of naphthalene yield vs temperature]

**Figure 6.11.** The yields, as functions of temperature, of naphthalene. Experiments: acetylene pyrolysis (○); catechol pyrolysis in the presence of acetylene dopant (◊); catechol pyrolysis in the absence of acetylene dopant (■).

Since naphthalene is an important species in the formation of larger PAH [73,75,76], it is important to consider the mechanisms that could lead to naphthalene formation in our catechol pyrolysis environment. Two of the most cited naphthalene formation mechanisms in the literature are presented as Schemes 1 and 2, respectively, in Table 6.2: the cyclopentadienyl
radical self-addition mechanism proposed by Melius et al. [67] and the HACA mechanism proposed by Frenklach and Wang [52,202] and by Bittner and Howard [17]. Two other less-cited mechanisms are included in Table 6.2 as Schemes 3 and 4.

Table 6.2. Mechanisms for Naphthalene Formation

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<thead>
<tr>
<th>Scheme 1: Cyclopentadienyl Radical Self-Addition Mechanism (Melius et al.[67])</th>
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<tr>
<th>Scheme 2: Hydrogen-Abstraction/Acetylene-Addition Mechanism (Frenklach and Wang [52,202])</th>
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<td><img src="image" alt="Scheme 2: Hydrogen-Abstraction/Acetylene-Addition Mechanism (Frenklach and Wang [52,202])" /></td>
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<th>Scheme 3: Propargyl Addition to Benzyl Radical (Marinov et al. [219])</th>
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<td><img src="image" alt="Scheme 3: Propargyl Addition to Benzyl Radical (Marinov et al. [219])" /></td>
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<tr>
<th>Scheme 4: Vinylacetylene Addition to Phenyl Radical (Bittner and Howard [17])</th>
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<td><img src="image" alt="Scheme 4: Vinylacetylene Addition to Phenyl Radical (Bittner and Howard [17])" /></td>
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We first consider naphthalene formation by cyclopentadienyl radical self-addition [67] mechanism, Scheme 1 in Table 6.2. Like the naphthalene yields from catechol pyrolysis in Figure 6.11, the yields of cyclopentadiene in Figure 6.4e are unaffected by the addition of
acetylene. Therefore, our results are consistent with naphthalene formation by the
cyclopentadienyl radical self-addition mechanism. Also, since the cyclopentadienyl radical is a
resonantly-stabilized radical, it can build up to high concentrations in our catechol pyrolysis
environment and contribute to naphthalene formation. The formation of naphthalene by
cyclopentadienyl radical self-addition has been experimentally demonstrated by Friderichsen et
al. [239] in their anisole pyrolysis study. Since our proposed mechanism for the thermal
decomposition of catechol [98,112] is very similar to that of anisole [239-241], it is logical that
naphthalene formation would occur by the same mechanism in the two systems.

Figures 6.6 and 6.9b, respectively, show that acetylene addition increases the yields of
benzene, the stable form of the phenyl reactant in Scheme 2 of Table 6.2, and of
phenylacetylene, the major intermediate in Scheme 2 (naphthalene formation by the HACA
mechanism). Since our naphthalene yields from catechol pyrolysis are unaffected by acetylene
addition, our experimental results at temperatures of 500 to 950 °C are inconsistent with
naphthalene formation by the HACA mechanism. However, the HACA mechanism cannot be
ruled out at 1000 °C, where acetylene addition brings about a slight increase in naphthalene
yield.

The naphthalene formation mechanism [219] in Scheme 3 in Table 6.2, propargyl
addition to the benzyl radical, is also not consistent with our experimental results for catechol
pyrolysis: Figure 6.11 shows that the acetylene-induced increases in the yields of the C_3
products (the stable forms of the second reactant in Scheme 3) in Figures 6.5a and 6.5b and of
toluene (the stable form of the first reactant in Scheme 3) in Figure 6.8 are not accompanied by
an increase in the yield of naphthalene, the product of Scheme 3.

Another reaction scheme that could lead to naphthalene during catechol pyrolysis is
vinylacetylene addition to the phenyl radical [17], Scheme 4 in Table 6.2. Catechol pyrolysis
experiments with C₄ species as dopant would need to be performed and kinetic parameters calculated, however, to ascertain the role of C₄ species in naphthalene formation.

6.4. Summary and Conclusions

In order to delineate the role of acetylene in the formation of PAH during the pyrolysis and combustion of solid fuels, we have performed pyrolysis of the model fuel catechol—a phenol-type compound representative of structural entities in coal, wood, and biomass—in a laminar-flow reactor, with acetylene added as a dopant. The products collected have been analyzed and quantified by high-pressure liquid chromatography with ultraviolet-visible absorbance detection and by gas chromatography with flame-ionization and mass spectrometric detection. Yield/temperature profiles for the C₁-C₁₀ species produced from catechol pyrolysis in the absence of acetylene dopant (Set 1) have been obtained and compared with product yields obtained in the presence of acetylene dopant (Set 2).

The addition of acetylene dopant to the catechol pyrolysis environment does not change the conversion of catechol or the yields of most of the C₁-C₅ products. Acetylene addition does, however, increase the yields of the C₃ products and facilitate consumption of the C₄ products. As for the 1- and 2-ring aromatics, acetylene addition brings about increases in the yields of benzene, toluene, phenylacetylene, and indene. The observed effects of acetylene addition are consistent with acetylene addition to benzyl radical [17] being the dominant pathway for indene formation in the catechol pyrolysis environment.

Even though the addition of acetylene brings about increases in the yields of benzene and phenylacetylene, the yields of naphthalene from catechol pyrolysis are not affected by the addition of acetylene. Therefore, the results are not consistent with an acetylene-addition mechanism being responsible for naphthalene formation in our catechol pyrolysis environment. The yields of cyclopentadiene, however, prove to behave similarly to those of naphthalene: they
are unaffected by the addition of acetylene. Our findings therefore are consistent with the formation of naphthalene by the cyclopentadiene self-addition mechanism [67].

The effects of acetylene addition on the yields of PAH from catechol pyrolysis will be reported in a forthcoming paper. The quantification of the effects of acetylene addition on all of the product yields from catechol pyrolysis contributes significantly towards a better understanding of the role of acetylene in the formation of benzene, indene, and naphthalene, as well as larger PAH. More experiments need to be performed and kinetic parameters calculated to ascertain the roles of the C3-C5 species in PAH formation. The results obtained from these future experiments along with those obtained from the present study should be helpful in ascertaining the reaction pathways responsible for the formation of PAH during catechol pyrolysis.
Chapter VII. Effects of 1,3-Butadiene Addition: Yields of the C$_1$-C$_{10}$ Thermal Decomposition Products

7.1. Introduction

When used as a source of energy, solid organic fuels like coal, wood, and biomass are burned in a diffusion-flame configuration, leading to high-temperature, oxygen-deficient zones. Pyrolytic reactions dominate in these oxygen-deficient zones, leading to the formation of polycyclic aromatic hydrocarbons (PAH). The formation and fate of PAH are of concern due to the carcinogenicity [6-8] and mutagenicity [9,10] of some members of this compound class. PAH are also widespread environmental pollutants and precursors to soot [15,16], a major contributor to fine particulates responsible for heart and lung diseases [11,12]. Hence, their formation and subsequent release into the environment is of concern.

The role of four-carbon conjugated free radicals in the formation of PAH has been implied by various studies [77,78,242]. Mestres and Sola [243] and Wang et al. [244] have reported that C$_4$ cyclo-additions can lead to larger PAH. Catallo et al. [245] have identified large PAH in the combustion residues from 1,3-butadiene. In addition, various investigators [78,122-124,217,233,246-252] have studied 1,3-butadiene pyrolysis and combustion and have reported C$_1$-C$_8$ hydrocarbons as the products—C$_2$ species being the major products. Since these C$_1$-C$_8$ hydrocarbons are considered to be precursors to PAH [66-74], and C$_2$ species are major growth species in PAH formation reactions [17,50-53], qualitative as well as quantitative studies on the role of C$_4$ species (1,3-butadiene in particular) in PAH formation reactions during solid fuel pyrolysis will be helpful in refining PAH growth models.

Solid fuels like coal, wood, or biomass, can themselves be used as a starting material to study PAH formation. But the complex nature of these fuels makes it extremely difficult to
attribute certain products to certain reaction pathways. To overcome this difficulty, most mechanistic studies on PAH formation have focused on examining the thermal decomposition of model compounds representing structural moieties in these fuels [16,25,83,85-92,179].

For our investigations into the formation of PAH during solid fuel decomposition, we have chosen catechol (ortho-dihydroxybenzene) as a model fuel compound. As a prominent structural entity of coal [100], tobacco [103], and lignin (a major component of wood [101])—as well as a major component in biomass tars [102] and tobacco smoke [104]—catechol is a suitable model compound for investigating solid fuel combustion. The demonstrated [96] similarity between PAH product distributions obtained from catechol pyrolysis and from coal volatiles pyrolysis further strengthens our assertion that catechol is an ideal model compound for our studies.

Previous catechol pyrolysis studies in our research group [50,96-99] have examined in detail the homogeneous gas-phase pyrolysis and fuel-rich oxidation of catechol in an isothermal laminar-flow reactor at temperatures of 500-1000 °C to gain fundamental insights into the formation of PAH during catechol decomposition. Collectively, these studies, along with one [112] more recent, have led to the identification of 11 C1-C5 species [98,112], 5 single-ring aromatics [96,97], as well as 54 individual PAH [96,97]. Several key observations from these studies provide strong evidence that the C2-C5 species, 1,3-butadiene in particular, play major roles in the formation of PAH during the pyrolysis and fuel-rich oxidation of catechol: (1) 1,3-butadiene is the highest-yield hydrocarbon product produced during catechol pyrolysis at temperatures ≤ 850 °C [98,112]. (2) A decrease in the yields of 1,3-butadiene at higher temperatures corresponds to an increase in the yields of PAH and of the PAH precursor species acetylene and benzene [98,99,112]. (3) A decrease in the yields of 1,3-butadiene in the presence of oxygen corresponds to a decrease in PAH yields [112]. (4) At a given pyrolysis condition,
PAH of smaller ring number are produced in higher yield than those of larger ring number [97,99], and increasing the pyrolysis temperature or residence time produces PAH products of higher ring number [99]. (5) Calculated global kinetic rate parameters for the formation of PAH from catechol show a trend of increasing activation energy with increasing PAH ring number [97]. Observations (1)-(3) provide strong evidence that 1,3-butadiene is a major intermediate in the formation of PAH and of PAH precursor species during catechol pyrolysis. Observations (4) and (5) are consistent with a mechanism for PAH growth involving successive addition of C₂-C₅ species to initially single-ring compounds. In addition, our catechol pyrolysis study in the presence of acetylene dopant (in Chapter VI and the corresponding paper [114]) has revealed that the addition of acetylene to the catechol pyrolysis environment facilitates the consumption of C₄ species and increases the yields of the 1- and 2-ring PAH precursor species. These observations warrant a more careful examination of the role of C₄ species in PAH formation reactions.

In order to better delineate the role of C₄ species in PAH formation reactions, we have performed catechol pyrolysis experiments in the presence of 1,3-butadiene added as a dopant. The catechol pyrolysis experiments are carried out in an isothermal laminar-flow reactor at temperatures of 500-1000 °C, and the products are analyzed by gas chromatography, nondispersive infrared analysis, and high-pressure liquid chromatography (HPLC). Previous catechol pyrolysis studies [96,98,99,112] have revealed that in addition to a range of PAH, the pyrolysis of catechol produces several C₁-C₁₀ species, as well as oxygen-containing organics. The effects of 1,3-butadiene addition on the yields of PAH and oxygen-containing organic products of catechol will be addressed in Chapter VIII and forthcoming papers. In the present study, we report the effects of 1,3-butadiene addition on the yields of the C₁-C₁₀ products formed during catechol pyrolysis. Quantitative data on the C₁-C₁₀ species are helpful in refining PAH
growth mechanisms as these species are known [17,52,66-74,204,207,208,219] to play major roles in the formation of PAH.

The effects of 1,3-butadiene addition on the yield/temperature profiles of eight C_{1-5} species and seven 1- and 2-ring aromatic products produced during the pyrolysis of catechol is the main focus of what follows in this chapter. We then incorporate the findings from the present study to refine our proposed mechanism [98,112,114] for the formation of the C_{1-5} and 1- and 2-ring aromatic products of catechol pyrolysis.

7.2. Experimental Equipment and Procedures

7.2.1. Reactor System

Three sets of pyrolysis experiments are performed: Set 1, pyrolysis of catechol (same as in Chapter VI); Set 4, pyrolysis of catechol in the presence of 1,3-butadiene dopant; Set 5, pyrolysis of 1,3-butadiene. For all three cases, the pyrolysis experiments have been performed in an isothermal laminar-flow reactor system [50,96-99] depicted in schematic form in Figure 2.1. The reactor system consists of a fuel vaporizer, isothermal quartz flow reactor, and product collection system. The pyrolysis reactions take place inside the isothermal quartz flow reactor, which consists of a 2-mm (inner diameter) quartz tube insulated at both ends and maintained at isothermal conditions by a three-zone electrically heated furnace. The reactor is operated at temperatures of 500-1000 °C, at atmospheric pressure, and at a residence time of 0.3 s. The gaseous products are collected in a Teflon gas-sampling bag, and the condensed-phase products are collected, in separate experiments, in a condensed-phase product collection system.

The three sets of experiments differ by the reactor feed gas composition. For the Set 1 experiments, solid catechol particles (>99.5% pure, purchased from Aldrich Chemical Co.) are loaded as a fixed bed into a Pyrex tube placed vertically inside the fuel vaporizer, an isothermal oven maintained at 85 °C for slight vaporization of the catechol. The vapor-phase catechol is
entrained in a flowing stream of ultrahigh purity (grade 6.0) nitrogen carrier gas, resulting in a 0.65 mole-% carbon loading in the reactor feed gas. The feed to the reactor for the Set 1 experiments is thus nitrogen with vapor-phase catechol (0.65 mole-% carbon).

The Set 4 experiments are conducted in the same manner as those of Set 1, except for one difference. For the Set 4 experiments, the pure nitrogen used as the carrier gas in the Set 1 experiments is replaced by nitrogen containing 1300 ppm of 1,3-butadiene. As it passes through the vaporizer, the nitrogen/1,3-butadiene carrier gas in the Set 4 experiments picks up the same amount of vapor-phase catechol as the nitrogen carrier gas in the Set 1 experiments, so the catechol-to-1,3-butadiene molar feed ratio is fixed at 0.83 for the Set 4 experiments. The feed to the reactor for the Set 4 experiments, therefore, is nitrogen with vapor-phase catechol (0.65 mole-% carbon) and 1,3-butadiene (0.52 mole-% carbon).

In the Set 5 experiments, no catechol is used; 1,3-butadiene is the only fuel pyrolyzed. Therefore, the same nitrogen/1,3-butadiene carrier gas is used in the Set 5 experiments as in the Set 4 experiments. This time, however, the carrier gas is passed through the by-pass line in the fuel vaporizer (Figure 2.1) so that no catechol is picked up. The feed to the reactor in the Set 5 experiments, therefore, is nitrogen with 1,3-butadiene (0.52 mole-% carbon).

For each of the three sets of experiments just described, samples are taken from the vaporizer exit stream, both before and after each pyrolysis experiment, and analyzed by GC, to ensure the consistency of each reactor feed-gas composition.

7.2.2. Product Analysis

Exiting the heated zone of the reactor, the pyrolysis products are quenched to room temperature, and the condensed-phase products are trapped on a Balston Teflon filter. The C₁-C₅ gas-phase products, along with benzene, the most volatile of the aromatic products, flow through the filter and are collected in a Teflon gas-sampling bag for subsequent compositional analysis.
The condensed-phase products (1- and 2-ring aromatics and PAH) are collected, in a separate experiment, with a condensed-phase product collection system (consisting of a Balston Teflon filter and dichloromethane solvent trap) and dissolved in dichloromethane for subsequent identification and quantification by gas chromatographic analysis.

A portion of the product gases collected is pumped from the sampling bag through two Horiba Model VIA-510 nondispersive infrared analyzers to quantify CO and CO$_2$. (No CO$_2$ is produced in the experiments reported here.) The remaining product gases are then routed to an Agilent Model 6890/5973 gas chromatograph/flame-ionization detector/mass spectrometer (GC/FID/MS) for analysis of C$_1$-C$_6$ hydrocarbons. Separation of the hydrocarbon gases is achieved on a GS GASPRO capillary column of length, 30 m, and diameter, 0.32 mm. Except for cyclopentadiene and vinylacetylene, identification of the C$_1$-C$_6$ gas-phase products is accomplished by matching the retention times and mass spectra of individual product components with those of reference standards, and product quantification is based on the calibration of the GC/FID with reference standards. Since a reference standard for cyclopentadiene is not commercially available, its identification in the catechol pyrolysis products is based on matching the product component’s GC retention index with that of cyclopentadiene generated from the pyrolysis of dicyclopentadiene [88,120] as well as by matching the product component’s mass spectrum with that of the reference standard in the NIST/EPA/NIH mass spectral library. The identification of vinylacetylene is based on matching the product component’s mass spectrum with that of the reference standard in the NIST/EPA/NIH mass spectral library. In addition, the identification of vinylacetylene among the thermal decomposition products of catechol is consistent with the thermal formation of vinylacetylene from acetylene [121] and 1,3-butadiene [122-124]—two of the highest-yield hydrocarbon products present in the catechol pyrolysis environment.
The condensed-phase catechol pyrolysis products are also analyzed on the Agilent Model 6890/5973 GC/FID/MS. A 2-µL aliquot of the product solution is injected by syringe, through a split injector, onto a HP-5 fused silica capillary column of length, 30 m, diameter, 0.25 mm, and film thickness 0.1 µm. The 1- and 2-ring aromatic products are identified by matching retention times and mass spectra with those of reference standards. (The identities of the 2-ring aromatics indene and naphthalene have also been confirmed by matching their HPLC retention times and ultraviolet absorption spectra with those of respective reference standards.)

The PAH products are identified and quantified by analysis [96,99] on a Hewlett-Packard Model 1050 high-pressure liquid chromatograph coupled to a diode-array ultraviolet-visible absorbance detector. The results of the HPLC analyses for PAH yields will be reported in Chapter VIII and a forthcoming paper [116]; the present chapter reports the yields of the C_1-C_5 hydrocarbons and 1- and 2-ring aromatics, which are determined by GC.

For each set of experiments (Set 1, Set 4, and Set 5), pyrolysis products are collected from separate experiments at each of nine different temperatures, over the range 500-1000 °C, and at a fixed residence time of 0.3 s. The collected products are analyzed by GC, HPLC, and non-dispersive infrared analysis. The product yields obtained from repeat experiments under the same conditions demonstrate that the flow reactor system, sample preparation procedures, and product analysis techniques all give very reproducible results. The collective mass of carbon obtained from the gas-phase products and the condensed-phase products (including any unconverted catechol) account for all of the carbon fed to the reactor as catechol and/or 1,3-butadiene. A carbon balance is thus closed on this reactor system.

### 7.3. Results and Discussion

The yield/temperature profiles of the reactants and C_1-C_10 hydrocarbon products from the pyrolysis of catechol in the absence of 1,3-butadiene dopant (Set 1) and in the presence of 1,3-
butadiene dopant (Set 4) are presented in Figures 7.1-7.9. Except for phenol in Figure 7.7, all the other C_1-C_{10} hydrocarbon products of catechol in Figures 7.4-7.9 are also products of 1,3-butadiene-only pyrolysis, so Figures 7.4-7.9 include results of the Set 5 (1,3-butadiene-only pyrolysis) experiments, and Figure 7.3 (1,3-butadiene yields) includes yields of unreacted 1,3-butadiene from the Set 5 experiments. To facilitate comparisons between the three sets of experiments, all yields in Figures 7.1-7.9 are reported as “mass-percent of fed catechol.” The catechol-to-1,3-butadiene molar feed ratio of 0.83 used in the Set 4 experiments translates into a 1,3-butadiene-to-catechol mass feed ratio of 0.59, so the product yields from the 1,3-butadiene-only (Set 5) pyrolysis experiments, initially determined as “mass-% of fed 1,3-butadiene,” are multiplied by the 1,3-butadiene-to-catechol mass feed ratio of 0.59 (for the Set 4 experiments) to obtain these yields in terms of “mass-% fed catechol” equivalent. Before discussing the product yields, we first consider the effect of 1,3-butadiene addition on catechol conversion.

7.3.1. Catechol Conversion

The yields, as functions of temperature, of unreacted catechol collected in the products from the Set 1 experiments without 1,3-butadiene dopant and from the Set 4 experiments with 1,3-butadiene dopant are presented in Figure 7.1. Figure 7.1 reveals that the yields of unreacted catechol from the catechol pyrolysis experiments with the 1,3-butadiene dopant and those without the 1,3-butadiene dopant are virtually indistinguishable. In both cases, the yields show a decrease with increasing temperature, as catechol conversion rapidly increases to 100 % at temperatures \( \geq 850 \) °C. Therefore, 1,3-butadiene addition does not appear to affect catechol conversion. Results from Chapter VI showed that the addition of acetylene to the catechol pyrolysis environment also does not affect catechol conversion. This is due to the lower energy catechol decomposition initiation step (breaking of the O-H bond) as compared to the high energy initiation step for 1,3-butadiene and acetylene (breaking of the O-H bond).
Figure 7.1. The yields, as functions of temperature, of unreacted catechol collected during catechol pyrolysis in the presence of 1,3-butadiene dopant (●) and in the absence of 1,3-butadiene dopant (▼).

7.3.2. CO Yields

Chapter IV and the corresponding paper [112] have shown that CO is the highest-yield product of catechol pyrolysis—its yield increasing dramatically with temperature in the 750-900 °C range and leveling off at ~50 mass-% of fed catechol, at the highest temperatures. Figure 7.2 presents the yields, as functions of temperature, of CO produced from the catechol pyrolysis experiments without 1,3-butadiene dopant (Set 1) and with 1,3-butadiene dopant (Set 4). Figure 7.2 demonstrates that the Set 1 and Set 4 experiments in the present study show no effect of 1,3-butadiene dopant on CO yields; the Set 5 experiments do not produce CO since there is no source of oxygen.
Figure 7.2. The yields, as functions of temperature, of CO from catechol pyrolysis in the presence of 1,3-butadiene dopant (♦) and in the absence of 1,3-butadiene dopant (■).

7.3.3. 1,3-Butadiene Yields

The yields, as functions of temperature, of 1,3-butadiene collected in the products from the catechol pyrolysis experiments without 1,3-butadiene dopant (Set 1) and with 1,3-butadiene dopant (Set 4) are presented in Figure 7.3. Also presented in Figure 7.3 is the yield/temperature profile of unreacted 1,3-butadiene (solid circles) collected in the products from the 1,3-butadiene pyrolysis experiments (Set 5). The catechol-to-1,3-butadiene molar feed ratio of 0.83 used in the Set 4 experiments translates into a 1,3-butadiene-to-catechol mass feed ratio of 0.59, so the amount of 1,3-butadiene fed to the reactor in the Set 4 and Set 5 experiments corresponds to a value of 59% on the y-axis of Figure 7.3. Therefore, on the chosen basis of “mass-percent of fed catechol,” a 1,3-butadiene yield of 59% for the Set 4 and Set 5 experiments corresponds to no conversion of the 1,3-butadiene fed to the reactor.
Figure 7.3. The yields, as functions of temperature, of unreacted 1,3-butadiene collected during 1,3-butadiene pyrolysis (●), collected from catechol pyrolysis in the presence of 1,3-butadiene dopant (◆), and from catechol pyrolysis in the absence of 1,3-butadiene dopant (■). The calculated sum (Δ) of Set 1 and Set 5 yields is presented as “Set 1 + Set 5 (Summed).” As explained in the text, the catechol-to-1,3-butadiene molar feed ratio of 0.83 used in the Set 4 experiments corresponds to a 1,3-butadiene-to-catechol mass feed ratio of 0.59. The amount of 1,3-butadiene in the reactor feed gas in the Set 4 and Set 5 experiments thus corresponds to a value of 59% on the y-axis of this figure.

The Set 4 and Set 5 curves of Figure 7.3 reveal that the yields of unreacted 1,3-butadiene from the catechol pyrolysis experiments with the 1,3-butadiene dopant are indistinguishable from those from the 1,3-butadiene-only pyrolysis. The Set 4 and Set 5 curves of Figure 7.3 show that 1,3-butadiene undergoes no conversion at temperatures ≤ 600 °C. At temperatures > 600 °C, however, both the Set 4 and Set 5 yields decrease rapidly with increasing temperature, as 1,3-butadiene conversion increases to ~98% (corresponding to ~1 mass-% of fed catechol on the y-axis of Figure 7.3) at temperatures ≥ 950 °C. It must be noted that when expressed on the same
y-axis basis of “mass-% of fed catechol,” the amount of 1,3-butadiene consumed in the Set 4 and Set 5 pyrolysis experiments at temperatures $\geq 950 \, ^\circ\text{C}$ is 58 % catechol equivalent.

The equivalence of the Set 4 and Set 5 curves of Figure 7.3 could initially appear to suggest that the presence of catechol does not effect the conversion of 1,3-butadiene. The Set 1 curve of Figure 7.3, however, reveals that 1,3-butadiene is produced from catechol pyrolysis at temperatures $> 700 \, ^\circ\text{C}$—the yield of 1,3-butadiene increasing rapidly with temperature, showing peak yield at $850 \, ^\circ\text{C}$, and then declining rapidly as 1,3-butadiene is consumed at temperatures $> 850 \, ^\circ\text{C}$. Thus, the equivalence of the Set 4 and Set 5 yields of Figure 7.3 reflects a synergistic effect when catechol and 1,3-butadiene are pyrolyzed together (Set 4) at temperatures $> 700 \, ^\circ\text{C}$. In the absence of this synergistic effect, the 1,3-butadiene yields from the Set 4 experiments at 700-1000 $^\circ\text{C}$ would equal the sum of the 1,3-butadiene yields from the Set 1 (catechol-only pyrolysis) experiments plus the 1,3-butadiene yields from the Set 5 (1,3-butadiene-only pyrolysis) experiments. This calculated sum of the Set 1 and Set 5 yields of unreacted 1,3-butadiene is presented as “Set 1 + Set 5” in Figure 7.3 (open triangles). Figure 7.3, however, shows that the 1,3-butadiene yields obtained from the Set 4 experiments at 700-1000 $^\circ\text{C}$ are lower than the calculated sum (open triangles) of the Set 1 and Set 5 yields of unreacted 1,3-butadiene. Therefore, we conclude that at temperatures $> 700 \, ^\circ\text{C}$, more 1,3-butadiene is consumed when it is in the catechol pyrolysis reaction environment than when it is not. The higher consumption of 1,3-butadiene is most certainly due to the enhanced free radical pool in the catechol pyrolysis reaction environment, which appears to facilitate the C-H scission initiation step in the consumption of 1,3-butadiene. Since previous catechol pyrolysis studies [98,112,114] have provided strong evidence that 1,3-butadiene is a major intermediate in PAH formation, the enhanced consumption of 1,3-butadiene could have significant effects on the formation of PAH.
7.3.4. C₁-C₅ Hydrocarbon Products

Figures 7.4-7.6 present the yields, as functions of temperature, of the C₁-C₅ hydrocarbon products from the pyrolysis of catechol in the absence of 1,3-butadiene dopant (Set 1) and in the presence of 1,3-butadiene dopant (Set 4). Also included in Figures 7.4-7.6 are the yields, as functions of temperature, of the C₁-C₅ hydrocarbon products from 1,3-butadiene-only pyrolysis (Set 5).

Figure 7.4. The yields, as functions of temperature, of: (a) methane and (b) ethane. Experiments: 1,3-butadiene pyrolysis (●); catechol pyrolysis in the presence of 1,3-butadiene dopant (●); catechol pyrolysis in the absence of 1,3-butadiene dopant (■). The calculated sum (Δ) of Set 1 and Set 5 yields is presented as “Set 1 + Set 5 (Summed).” The catechol-to-1,3-butadiene molar feed ratio of 0.83 used in the Set 2 experiments translates into an 1,3-butadiene-to-catechol mass feed ratio of 0.59, so the product yields from the 1,3-butadiene-only (Set 5) pyrolysis experiments, initially determined as “mass-% of fed 1,3-butadiene,” are multiplied by the 1,3-butadiene-to-catechol mass feed ratio of 0.59 (for the Set 4 experiments) to obtain the yields in terms of “mass-% of fed catechol” equivalent.
Figure 7.5. The yields, as functions of temperature, of: (a) ethylene, (b) acetylene, (c) propadiene, and (d) propyne. Experiments: 1,3-butadiene pyrolysis (●); catechol pyrolysis in the presence of 1,3-butadiene dopant (○); catechol pyrolysis in the absence of 1,3-butadiene dopant (■). The basis used for the reported yields is explained in the caption of Figure 7.4. The calculated sum (∆) of Set 1 and Set 5 yields is presented as “Set 1 + Set 5 (Summed).”
Figure 7.6. The yields, as functions of temperature, of: (a) vinylacetylene, and (b) cyclopentadiene. Experiments: 1,3-butadiene pyrolysis (●); catechol pyrolysis in the presence of 1,3-butadiene dopant (●); catechol pyrolysis in the absence of 1,3-butadiene dopant (■). The basis used for the reported yields is explained in the caption of Figure 7.4. The calculated sum (∆) of Set 1 and Set 5 yields is presented as “Set 1 + Set 5 (Summed).”

At temperatures > 750 °C, the Set 1 and Set 4 curves of Figures 7.4a, 7.4b, 7.5a, 7.5b, 7.5c, 7.5d, 7.6a and 7.6b show that the yields of methane, ethane, ethylene, acetylene, propadiene, propyne, vinylacetylene, and cyclopentadiene, respectively, obtained from catechol pyrolysis in the presence of 1,3-butadiene dopant (Set 4) are significantly higher than those obtained in the absence of 1,3-butadiene dopant (Set 4). At temperatures > 750 °C, the Set 5 curve of Figures 7.4-7.6 reveal that 1,3-butadiene-only pyrolysis produces very high yields of the C1-C5 hydrocarbons. In fact, on the chosen basis of “mass-% of fed catechol,” the yields of ethylene, acetylene, propadiene and propyne from 1,3-butadiene-only pyrolysis (Set 5) are significantly higher than their respective yields from catechol-only (Set 1) pyrolysis. Since both C2 and C3 hydrocarbons can be major growth species in PAH formation reactions [17,50-
53,66,78,204,205,207,208,219,226], the high yields of C$_2$ and C$_3$ species from 1,3-butadiene-only pyrolysis (Set 5) support our earlier observation (Chapters V and VI and the corresponding papers [112,114]) that 1,3-butadiene—a major product of catechol pyrolysis [98,112]—is a major intermediate and source of C$_2$ and C$_3$ growth species in our catechol pyrolysis environment.

The higher yields of C$_1$-C$_5$ hydrocarbon products from the pyrolysis of catechol in the presence of 1,3-butadiene dopant (Set 4) can be accounted for by the observed formation of C$_1$-C$_5$ hydrocarbon products from 1,3-butadiene-only pyrolysis (Set 5 curves of Figures 7.4-7.6). In a previous study in this series, Ledesma et al. [98] have reported the mechanisms leading to the formation of C$_1$-C$_5$ hydrocarbon products from catechol-only pyrolysis (Set 1). Figures 7.4-7.6 reveal that the effects of temperature on the yields of the C$_1$-C$_5$ hydrocarbon products from 1,3-butadiene-only pyrolysis (Set 5) are very similar to those on the yields of C$_1$-C$_5$ hydrocarbon products from catechol-only pyrolysis (Set 1), suggesting similar formation mechanisms for the C$_1$-C$_5$ hydrocarbon products during the Set 1 and Set 5 pyrolysis. Therefore, in addition to the mechanisms detailed in previous catechol pyrolysis studies from our research group [98,112,114] for the formation of C$_1$-C$_5$ hydrocarbon products, the formation of C$_1$-C$_5$ hydrocarbon products from 1,3-butadiene pyrolysis also must be considered.

Various investigators [78,122-124,217,233,246-252] have studied 1,3-butadiene pyrolysis and combustion and have reported formation mechanisms for C$_1$-C$_5$ hydrocarbon products. Bensen and Haugen [251] and Keifer et al. [247,248] have concluded that 1,3-butadiene undergoes decomposition through radical processes leading to two vinyl radicals, which can subsequently lead to the formation of ethylene and acetylene. Skinner and Sokoloski [252] and Rao et al. [250] have suggested a molecular dissociation leading to ethylene and acetylene. Thus, both the free radical and molecular mechanisms lead to ethylene and acetylene.
The 1,3-butadiene pyrolysis studies of Skinner and Sokoloski [252], Burke [253], and Colket [249] have all reported near equimolar yields of ethylene and acetylene at the lower temperatures and the yields of acetylene being higher than ethylene at higher temperatures. Our 1,3-butadiene-only pyrolysis also produces near equimolar yields of ethylene and acetylene at the lower temperatures and higher yields of acetylene at higher temperatures (Set 5 yields of Figures 7.5a and 7.5b). At high temperatures, acetylene can also form from the decomposition of the 1,3-butadiene pyrolysis products vinylacetylene [121] and cyclopentadiene [98,120,254]. In addition to the molecular pathway [250,252] and the radical pathway [247,248,251], Hidaka et al. [123] have included the high-temperature isomerization of 1,3-butadiene to 1,2-butadiene and subsequent decomposition to propargyl and methyl radicals in their shock tube and modeling study. The Set 5 yields of Figures 7.4a, 7.5c, and 7.5d, respectively, show that yield/temperature profiles of methane, propadiene, and propyne from our 1,3-butadiene-only pyrolysis are consistent with those reported by Hidaka et al. [123] for these same compounds. Hydrogen abstraction from 1,3-butadiene is the most likely route to the C₄ product vinylacetylene [123,247,250,251]. The most likely route to the C₅ product cyclopentadiene is the addition of acetylene to the propargyl radical [255]. Alternate pathways may involve methyl radical addition to 1,3-butadienyl [249] or C₄H₃ radicals. Both the propargyl and the C₄H₃ radicals are resonantly stabilized and can build up to high concentrations in our 1,3-butadiene pyrolysis environment.

Having considered the mechanisms for the formation of the C₁-C₅ hydrocarbon products, we now examine the synergistic effects when catechol is pyrolyzed in the presence of 1,3-butadiene. As with the 1,3-butadiene yields of Figure 7.3, the yields of C₁-C₅ hydrocarbon products of Figures 7.4-7.6 also show a synergistic effect when catechol is pyrolyzed in the presence of 1,3-butadiene dopant (Set 4). It was earlier observed that at temperatures ≤ 900 °C, the synergistic effect leads to higher consumption of 1,3-butadiene during catechol pyrolysis in
the presence of 1,3-butadiene dopant (Set 4). In the same temperature range of 500 to 900 °C, the yields of each of the C_1-C_5 hydrocarbon products obtained from the catechol pyrolysis experiments in the presence of 1,3-butadiene dopant (Set 4) are higher than the calculated sums of the yields for each of the C_1-C_5 hydrocarbon products from the Set 1 and Set 5 experiments (“Set 1 + Set 5” yields of Figures 7.4-7.6). At temperatures > 900 °C, however, the yields of all the C_1-C_5 hydrocarbon products (except methane) produced from the Set 4 pyrolysis experiments are lower than the calculated sum of the yields for each of the C_1-C_5 hydrocarbon products from the Set 1 and Set 5 experiments (open triangles in Figures 7.4-7.6). The lower yields of the C_1-C_5 hydrocarbon products from the Set 4 experiments as compared to the calculated “Set 1 + Set 5” yields at temperatures > 900 °C imply a higher consumption—due to the enhanced radical pool in the catechol pyrolysis environment—of C_1-C_5 hydrocarbon products at these high temperatures. Even though the methane yields from Set 4 experiments are always higher than the calculated “Set 1 + Set 5 (Summed)” yields, Figure 7.4a shows that the difference in the Set 4 and “Set 1 + Set 5(summed)” yields increase with increasing temperature except at temperatures > 900 °C—indicating a higher consumption of methane at temperatures > 900 °C. At all temperatures investigated, however, Figure 7.4b reveals higher consumption of ethane when catechol is pyrolyzed in the presence of 1,3-butadiene (Set 4) than when the two fuels are pyrolyzed separately (“Set 1 + Set 5” yields are higher than the Set 4 yields.). Since the C_1-C_5 hydrocarbon products are precursors to 1- and 2-ring aromatics, the higher consumption of the C_1-C_5 hydrocarbons during catechol pyrolysis in the presence of 1,3-butadiene dopant (Set 4) can lead to higher yields of the 1- and 2-ring aromatics.

7.3.5. One-Ring Aromatic Products

Figure 7.7 shows the yields, as functions of temperature, of phenol obtained from the pyrolysis of catechol in the absence of 1,3-butadiene dopant (Set 4) and in the presence of 1,3-
butadiene dopant (Set 1). The Set 1 and Set 4 curves of Figure 7.7 reveal that the yields of phenol produced from catechol pyrolysis experiments in the presence of 1,3-butadiene dopant (Set 1) are virtually indistinguishable from those produced in the absence of the dopant (Set 4). Phenol is not produced from the 1,3-butadiene-only pyrolysis (Set 5) since there is no source of oxygen. Since the addition of 1,3-butadiene does not affect catechol conversion (Figure 7.1), the comparable yields of phenol are consistent with the mechanism for phenol formation by the displacement of an OH from catechol by H atom [98]. Previous catechol pyrolysis studies from our research group [98,112] show consistency with the formation of cyclopentadiene from phenol. The higher yields of cyclopentadiene in the presence of 1,3-butadiene dopant (Set 4 curve of Figure 7.6b) and the formation of cyclopentadiene from the 1,3-butadiene-only pyrolysis (Set 5 curve of Figure 7.6b), however, provide strong evidence that cyclopentadiene is also produced from the major catechol pyrolysis product 1,3-butadiene.

**Figure 7.7.** The yields, as functions of temperature, of phenol. Experiments: catechol pyrolysis in the presence of 1,3-butadiene dopant (●); catechol pyrolysis in the absence of 1,3-butadiene dopant (■).
Figure 7.8. The yields, as functions of temperature, of: (a) benzene, (b) toluene, (c) styrene, and (d) phenylacetylene. Experiments: 1,3-butadiene pyrolysis (●); catechol pyrolysis in the presence of 1,3-butadiene dopant (♦); catechol pyrolysis in the absence of 1,3-butadiene dopant (■). The basis used for the reported yields is explained in the caption of Figure 7.4. The calculated sum (∆) of Set 1 and Set 5 yields is presented as “Set 1 + Set 5 (Summed).”
Figures 7.8a, 7.8b, 7.8c, and 7.8d show the yield/temperature profiles of benzene, toluene, styrene, and phenylacetylene, respectively, obtained from the pyrolysis of catechol in the absence of 1,3-butadiene dopant (Set 1) and in the presence of 1,3-butadiene dopant (Set 4). Also included in Figure 7.8 are the yields, as functions of temperature, of the benzene, toluene, styrene, and phenylacetylene obtained from 1,3-butadiene-only pyrolysis (Set 5). As with the yields of the C₁-C₅ hydrocarbon products of Figures 7.4-7.6, Figure 7.8 shows that at temperatures > 750 °C, the yields of benzene, toluene, styrene, and phenylacetylene obtained from catechol pyrolysis in the presence of 1,3-butadiene dopant (Set 4) are significantly higher than those obtained in the absence of 1,3-butadiene dopant (Set 1). At temperatures > 750 °C, the Set 5 curves of Figure 7.8 also reveal that benzene, toluene, styrene, and phenylacetylene are produced from 1,3-butadiene-only pyrolysis. The significantly higher yields of the 1-ring aromatic hydrocarbons from catechol pyrolysis in the presence of 1,3-butadiene (Set 4) are due to the collective effect of 1-ring aromatic hydrocarbons being produced from 1,3-butadiene-only pyrolysis (Set 5) and the experimentally observed higher consumption of the C₁-C₅ precursor species in the radical rich catechol pyrolysis environment.

Since 1,3-butadiene-only pyrolysis (Set 5) produces abundant amounts of 1-ring aromatic hydrocarbons, we now examine the reaction mechanisms responsible for their formation in the 1,3-butadiene-only pyrolysis environment. Previous catechol pyrolysis studies from our research group [98,112,114] have considered the roles of the C₁-C₅ hydrocarbon products in the formation of 1- and 2-ring aromatics. As detailed in our previous studies (Chapters IV and VI and the corresponding papers [112,114]), four pathways that may contribute to benzene formation in our catechol pyrolysis environment are: addition of acetylene to C₄ radicals [78,202,203], propargyl radical self-addition [204,205,207,208], acetylene polymerization [228,230], and the displacement of OH from phenol by H [88,89,98]. The first three mechanisms will be relevant in
the 1,3-butadiene-only pyrolysis environment since the C₂, C₃, and C₄ species, as well as benzene, are produced in high yields from butadiene-only (Set 5) pyrolysis. Since phenol is not produced in the 1,3-butadiene-only pyrolysis, the fourth mechanism involving phenol can be ruled out in the butadiene-only pyrolysis reaction environment. Also, the virtual equivalence of the Set 1 and Set 4 yields of phenol (Figure 7.7), the absence of phenol among the 1,3-butadiene-only pyrolysis products (Figure 7.7), the dramatic increase in benzene yields in the presence of 1,3-butadiene dopant (Set 4 yields of Figure 7.8a), and the high yields of benzene from 1,3-butadiene-only pyrolysis (Set 5 yields of Figure 7.8a) are all consistent with benzene formation from the reactions involving the C₂, C₃, and C₄ hydrocarbon products in our catechol pyrolysis environment. Our acetylene pyrolysis study (Chapter VI and the corresponding paper [114]) under the same pyrolysis conditions shows that acetylene undergoes little or no conversion and produces very low yields of benzene. Preliminary results from propyne pyrolysis (unpublished data) indicate that benzene yields become significant only at 1000 °C. The Set 5 curve of Figure 7.8a, however, show that benzene is produced in significant amounts at 800 °C from 1,3-butadiene-only pyrolysis and the yields increase dramatically at temperatures > 800 °C. Thus, the results from the present study are consistent with the addition of C₂ to C₄ radicals [78,202,203] as the dominant benzene formation mechanism in our 1,3-butadiene pyrolysis environment.

The formation of the other three 1-ring aromatic products from 1,3-butadiene-only pyrolysis can also be explained by the reactions involving the C₁-C₆ species. Figure 7.8b reveals that the effects of temperature on the yields of toluene from the catechol-only pyrolysis (Set 1) are very similar to those on the yields of toluene from 1,3-butadiene-only pyrolysis (Set 5), indicating a similar toluene formation mechanism. Our previous catechol pyrolysis study (Chapter VI and the corresponding paper [114]) show consistency with toluene formation by the propargyl addition to butadienyl radical [78,226]. Alternate mechanisms that likely contribute to
toluene formation in our 1,3-butadiene-only pyrolysis environment are methyl addition to benzene [232,233] and acetylene addition to cyclopentadiene [231]. There are multiple pathways that may lead to styrene in our 1,3-butadiene-only pyrolysis (Set 5) environment. The most likely mechanism to styrene formation is the 1,3-butadienyl radical addition to vinylacetylene [78,242]. Alternate mechanisms may involve vinyl radical addition to the phenyl radical [234], propargyl addition to cyclopentadienyl radical, or vinylacetylene self-addition. The fourth 1-ring aromatic product, phenylacetylene, is most likely a product of acetylene addition to benzene [52,202].

As with the other products, the yields of benzene in Figure 7.8a also reflect a synergistic effect. At temperatures > 850 °C, the Set 1 and Set 5 curves of Figures 7.4-7.6 reveal that the yields of C₂, C₃, and C₄ species, that are precursors to benzene, from 1,3-butadiene-only (Set 5) pyrolysis are higher than those from catechol-only (Set 1) pyrolysis. Figure 7.8a, however, shows that at temperatures > 850 °C, the yields of benzene from the catechol-only (Set 1) pyrolysis are higher than those from butadiene-only (Set 5) pyrolysis. As explained earlier, the rates of consumption of the C₂, C₃, and C₄ species during catechol pyrolysis in the presence of 1,3-butadiene (Set 4) appear to be higher than those in the 1,3-butadiene-only pyrolysis (Set 5) environment due to a synergistic effect caused by the enhanced radical pool in the catechol pyrolysis environment. Thus, higher consumption of the C₂, C₃, and C₄ species leads to higher yields of benzene from the Set 4 experiments as compared to the Set 5 experiments.

Figure 7.8 also reflects another synergistic effect. A comparison of the Set 4 yields and the calculated “Set 1 + Set 5” yields of Figure 7.8 reveal that the amounts of increases in the yields of each of the 1-ring aromatic hydrocarbons obtained from catechol pyrolysis in the presence of 1,3-butadiene dopant (Set 4) are higher than just the amounts of these 1-ring aromatic hydrocarbons formed by catechol pyrolysis (Set 1) and 1,3-butadiene-only pyrolysis (Set 5) separately. This synergistic effect stems from an enhanced radical pool available when
catechol and 1,3-butadiene are pyrolyzed together. As with the C₁-C₅ product yields in Figures 7.4-7.6, Figure 7.8 also reveals that at temperatures ≤ 900 °C, the difference in the Set 4 and the calculated “Set 1 + Set 5” yields increase with increasing temperature. Except for phenylacetylene, however, at temperatures > 900 °C, the difference in the Set 4 and the calculated “Set 1 + Set 5” 1-ring product yields decreases with increasing temperature—indicating a synergistic higher consumption of benzene, toluene, and styrene at higher temperatures. Our earlier study (Chapter VI and the corresponding paper [114]) has implied the importance of benzene and toluene in the formation of indene and naphthalene. Hence, a higher consumption of these two 1-ring aromatics can have a significant impact on the formation of two-ring aromatics and larger PAH.

Figure 7.8d reveals that the difference in the Set 4 and the calculated “Set 1 + Set 5” yields for phenylacetylene show a trend of increasing with increasing temperature throughout the temperature range studied. The most likely formation mechanism for phenylacetylene in our pyrolysis environment is by acetylene addition to benzene. Since both acetylene (Figure 7.5b) and benzene (Figure 7.8a) are produced in significantly high yields in the Set 4 experiments and both appear to get consumed at the higher temperatures, the trend shown by phenylacetylene reflects a higher temperature stability of phenylacetylene.

7.3.6. Two-Ring Aromatic Products

Figures 7.9a and 7.9b present the yield/temperature profiles of indene and naphthalene, respectively, obtained from the pyrolysis of catechol in the absence of 1,3-butadiene dopant (Set 1) and in the presence of 1,3-butadiene dopant (Set 4). Also presented in Figures 7.9a and 7.9b are the yields of indene and naphthalene obtained from 1,3-butadiene-only pyrolysis (Set 5). At temperatures > 750 °C, the Set 1 and Set 4 curves of Figures 7.9a and 7.9b reveal that the yields of indene and naphthalene, respectively, from catechol pyrolysis in the presence of 1,3-butadiene
dopant are significantly higher than those in the absence of the dopant. Also, the amount of the increases in the yields of indene (Figure 7.9a) and naphthalene (Figure 7.9b) in the presence of 1,3-butadiene dopant are far higher than the yields of these products from the 1,3-butadiene-only pyrolysis (Set 5)—as can be inferred by comparing the Set 4 and the calculated “Set 1 + Set 5” yields of Figures 7.9a and 7.9b. Therefore, with regard to indene and naphthalene, the addition of 1,3-butadiene appears to cause another synergistic effect.

**Figure 7.9.** The yields, as functions of temperature, of: (a) indene and (b) naphthalene. Experiments: 1,3-butadiene pyrolysis (●); catechol pyrolysis in the presence of 1,3-butadiene dopant (◆); catechol pyrolysis in the absence of 1,3-butadiene dopant (■). The basis used for the reported yields is explained in the caption of Figure 7.4. The calculated sum (Δ) of Set 1 and Set 5 yields is presented as “Set 1 + Set 5 (Summed).”

In a previous study in this series (Chapter VI and the corresponding paper [114]), we have considered the roles of the C₁-C₅ hydrocarbon products in the formation of 2-ring aromatics. The results were consistent with acetylene addition to benzyl radical being the dominant pathway for indene formation and with cyclopentadienyl radical self-addition being the
dominant reaction pathway for naphthalene formation in our catechol pyrolysis environment [114]. Since acetylene, cyclopentadiene, and benzene are also products of 1,3-butadiene-only pyrolysis, these two mechanisms can account for the formation of indene and naphthalene in our 1,3-butadiene-only pyrolysis (Set 5) environment, as well.

The experimentally observed increases in the yields of indene and naphthalene from catechol pyrolysis in the presence of 1,3-butadiene dopant can also be explained by the dramatic increases in the yields of the C_2-C_6 precursor species. The dramatic increases in the yields of acetylene in Figure 7.5b and toluene (the stable form of the benzyl radical) in Figure 7.8b during the pyrolysis of catechol in the presence of 1,3-butadiene dopant (Set 4) and the corresponding increases in the yields of indene in Figure 7.9a are consistent with our previous observation (Chapter VI and the corresponding paper [114]) that acetylene addition to benzyl radical is the dominant indene formation mechanism in our catechol pyrolysis environment. The increases in the yields of cyclopentadiene in Figure 7.6b during catechol pyrolysis in the presence of 1,3-butadiene dopant (Set 4) and a coincidental increase in the yields of naphthalene in Figure 7.9b further support our assertion (Chapter VI and the corresponding paper [114]) that cyclopentadienyl radical self-addition is the dominant reaction pathway for naphthalene formation in our catechol pyrolysis environment.

7.4. Summary and Conclusions

To better understand the role of four-carbon conjugated free radicals in the formation of PAH during the pyrolysis and combustion of solid fuels, we have performed pyrolysis of the model fuel catechol in a laminar-flow reactor, with 1,3-butadiene added as a dopant. Pyrolysis of 1,3-butadiene was also performed to better delineate the role of 1,3-butadiene in the formation of C_1-C_{10} species. The products collected have been analyzed and quantified by high-pressure liquid chromatography with ultraviolet-visible absorbance detection and by gas chromatography
with flame-ionization and mass spectrometric detection. Yield/temperature profiles for the C$_1$-C$_{10}$ species produced from catechol pyrolysis in the absence of 1,3-butadiene dopant (Set 1) have been obtained and compared with product yields obtained in the presence of 1,3-butadiene dopant (Set 4).

The pyrolysis of 1,3-butadiene (Set 5) produces a range of C$_1$-C$_{10}$ hydrocarbon products. The products include methane, ethane, ethylene, acetylene, propylene, propadiene, propyne, vinylacetylene, cyclopentadiene, benzene, toluene, styrene, phenylacetylene, indene, and naphthalene. The C$_2$ products ethylene and acetylene are produced in particularly high yields. Benzene is the highest yield aromatic product. The experimental results are consistent with previous 1,3-butadiene pyrolysis studies in the literature [123,247,248,251].

Addition of 1,3-butadiene as a dopant to the catechol pyrolysis environment does not change the conversion of catechol. 1,3-butadiene addition does, however, bring about dramatic increases in the yields of the C$_1$-C$_{10}$ products. The production of C$_1$-C$_{10}$ products from 1,3-butadiene-only (Set 5) pyrolysis is partly responsible for the higher yields of C$_1$-C$_{10}$ products from catechol pyrolysis in the presence of 1,3-butadiene dopant (Set 4). Another factor responsible for the higher yields of the C$_1$-C$_{10}$ products is the enhanced radical pool in the catechol pyrolysis environment that brings about higher conversion of 1,3-butadiene when it is in the catechol pyrolysis environment. The enhanced radical pool also leads to higher consumption of the C$_1$-C$_5$ products at higher temperatures, leading to higher yields of the 1- and 2-ring aromatic products. The observed effects of 1,3-butadiene addition are consistent with acetylene addition to benzyl radical [17] being the dominant pathway for indene formation and with the formation of naphthalene by the cyclopentadiene self-addition mechanism [67] in our catechol pyrolysis environment.
Since the C$_{1}$-C$_{10}$ hydrocarbon products are precursors to PAH, the higher yields of these products may have a significant effect on PAH formation. The effects of 1,3-butadiene addition on the yields of PAH from catechol pyrolysis and the formation of PAH from 1,3-butadiene-only pyrolysis will be reported in a forthcoming paper (Chapter VIII and the corresponding paper [116]). Quantified data on the effects of 1,3-butadiene addition on the products obtained from catechol pyrolysis will be helpful in refining PAH formation mechanisms and in delineating the role of four-carbon conjugated hydrocarbons in PAH formation.
Chapter VIII. Effects of Acetylene and 1,3-Butadiene Addition: Yields of Polycyclic Aromatic Hydrocarbons

8.1. Introduction

Within the diffusion flames of solid fuel combustion systems, pyrolytic reactions of fuel components and devolatilization products can lead to polycyclic aromatic hydrocarbons (PAH), an important class of environmental pollutants. Since some PAH are mutagenic [9,10,56] and/or carcinogenic [7,56] and since PAH are known precursors to soot [18], it is important to understand the pyrolytic reactions responsible for PAH formation.

Catechol (ortho-dihydroxybenzene) has emerged as a very useful model compound fuel to study the formation of PAH from solid fuels since: (1) catechol represents aromatic moieties within coal [100], wood [101], and other plant-based biomass fuels [103]; (2) catechol is a major component of biomass tars [102]; and (3) the PAH produced from catechol pyrolysis are compositionally very similar to those produced from coal volatiles pyrolyzed at similar conditions [96].

Previous studies on catechol pyrolysis [96,98,99,112] and fuel-rich oxidation [113] have investigated the effects of temperature, residence time, and oxygen concentration on catechol product composition and yields. The abundance of C\textsubscript{1} to C\textsubscript{5} species in catechol’s thermal decomposition products [98,112], the wide variety of compound classes represented in catechol’s product PAH [96,113], and the high dependence of mutagenic and carcinogenic activity on PAH structure [7,9,10,56] have prompted us to pursue three questions of relevance both to catechol pyrolysis and to solid fuel pyrolysis and combustion in general: (1) Which of the C\textsubscript{1}-C\textsubscript{5} thermal decomposition products are the most effective participants in PAH formation and growth? (2)
Are there linkages between particular growth species and particular structural classes of PAH?

(3) How does temperature influence the findings for (1) and (2)?

As a start in addressing these questions, we have performed catechol pyrolysis, catechol/acetylene co-pyrolysis, acetylene pyrolysis, catechol/1,3-butadiene co-pyrolysis, and 1,3-butadiene pyrolysis experiments. Acetylene (C₂H₂) was chosen for the following reasons: (1) The hydrogen-abstraction/acetylene-addition mechanism [17,50-53] is thought to be the major PAH formation mechanism in combustion environments; (2) C₂ species are present in high yields in the catechol pyrolysis environment [98,112]; (3) Ethynyl-substituted and cyclopenta-fused PAH [99,113]—both thought to arise from acetylene addition to aryl radicals [50]—are produced in particularly high abundance during catechol pyrolysis; (4) Acetylene, benzene, and phenylacetylene each show very similar behavior under oxidative pyrolysis conditions: the yields of all three compounds increase with increasing oxygen concentration at temperatures ≤ 800 °C, and decrease with increasing oxygen concentration at temperatures > 900 °C (Chapter IV and the corresponding paper [112]). The reasons for choosing 1,3-butadiene (C₄H₆) are also several-fold: (1) 1,3-butadiene is a product of the pyrolysis and/or combustion of biomass [256,257], wood [258,259], and coal [260,261]; (2) 1,3-butadiene is the highest-yield hydrocarbon product of catechol pyrolysis at temperatures < 900 °C [98]; (3) 1,3-butadiene is an important source of the C₂ growth species vinyl radical [247] as well as ethylene and acetylene [249,252]; (4) 1,3-butadiene has been reported as a major contributor to the formation of 1- and 2-ring aromatics [69,115,224] and PAH [69,262]; (5) Oxidative pyrolysis of catechol shows coincident decreases in yields of PAH and 1,3-butadiene with increasing oxygen concentration (Chapter IV and the corresponding paper [112]).

The catechol pyrolysis, catechol/acetylene co-pyrolysis, acetylene pyrolysis, catechol/1,3-butadiene co-pyrolysis, and 1,3-butadiene pyrolysis experiments are each conducted in an
isothermal laminar-flow quartz tube reactor at temperatures of 500 to 1000 °C and a fixed residence time of 0.3 sec. The products are analyzed by gas chromatography as well as high-pressure liquid chromatography (HPLC) with diode-array ultraviolet-visible (UV) absorbance detection, a technique ideally suited for the isomer-specific analysis of PAH. Chapters VI and VII report the results of these experiments for each of the C₁-C₁₀ products; this chapter presents the results for the PAH. In the following, we report the identities of the 111 individual products identified by HPLC and compare PAH product yields, as functions of temperature, for the different sets of experiments. Differences in PAH production for the co-pyrolysis experiments, in comparison to the pyrolysis experiments with the individual fuels, are discussed in terms of the fuels’ structures and products of decomposition. Effects on PAH of different ring number and structural class are also examined. Based on the results reported here and in previous chapters, a tentative mechanism for PAH formation from catechol is proposed.

8.2. Experimental Equipment and Procedures

The catechol pyrolysis (Set 1 experiments of Chapter VI), catechol/acetylene co-pyrolysis (Set 2 experiments of Chapter VI), acetylene pyrolysis (Set 3 experiments of Chapter VI), catechol/1,3-butadiene co-pyrolysis (Set 4 experiments of Chapter VII), and 1,3-butadiene pyrolysis (Set 5 experiments of Chapter VII) experiments are conducted in a reactor system (described in detail in Chapter II and in previous studies in this series [96,98,99,112-114]) that consists of a fuel vaporizer, isothermal laminar-flow quartz-tube reactor, and product collection system. Catechol pyrolysis experiments are carried out by loading catechol particles (> 99.5 % pure) into a Pyrex tube fixed within the vaporizer, a constant-temperature oven held at 85 °C, for slight vaporization of the catechol. A flowing stream of ultra-high purity nitrogen picks up the vapor-phase catechol, resulting in a 0.65 mole-% carbon loading in the reactor feed gas. Upon exiting the vaporizer, the vaporized catechol/nitrogen mixture enters the quartz tube reactor,
which is insulated at both ends and maintained at uniform temperature by a three-zone electrically heated furnace. The reactor is operated at temperatures of 600 to 1000 °C and at a fixed residence time of 0.3 sec.

The catechol/acetylene co-pyrolysis experiments are carried out exactly like the catechol pyrolysis experiments except instead of the pure nitrogen carrier gas, the carrier gas is nitrogen containing 1379 ppm of acetylene. As it passes through the vaporizer, the nitrogen/acetylene carrier gas in the catechol/acetylene co-pyrolysis experiments picks up the same amount of vapor-phase catechol as the nitrogen carrier gas in the catechol-only pyrolysis experiments, so the catechol-to-acetylene molar feed ratio is fixed at 0.785 for the catechol/acetylene co-pyrolysis experiments. The feed to the reactor for the catechol/acetylene co-pyrolysis experiments, therefore, is nitrogen with vapor-phase catechol (0.65 mole-% carbon) and acetylene (0.276 mole-% carbon). Thus, 70.2% of the total carbon fed to the reactor in the catechol/acetylene co-pyrolysis experiments is from catechol; 29.8% is from acetylene. (The catechol-to-acetylene molar feed ratio of 0.785 is chosen to ensure that the acetylene provided in the feed is several times the level produced by catechol during the experiments.)

In the acetylene-only pyrolysis experiments, no catechol is used; acetylene is the only fuel pyrolyzed. Therefore, the same nitrogen/acetylene carrier gas is used in the acetylene pyrolysis experiments as in the catechol/acetylene co-pyrolysis experiments. This time, however, the carrier gas is passed through the by-pass line in the fuel vaporizer (Figure 2.1 in Chapter II) so that no catechol is picked up. The feed to the reactor in the acetylene pyrolysis experiments, therefore, is nitrogen with acetylene (0.276 mole-% carbon).

The catechol/1,3-butadiene co-pyrolysis experiments are carried out exactly like the catechol pyrolysis experiments except instead of the pure nitrogen carrier gas, the carrier gas is nitrogen containing 1300 ppm of 1,3-butadiene. The feed to the reactor in this case is thus
nitrogen with 0.65 mole-% carbon loading from catechol and 0.52 mole-% carbon loading from 1,3-butadiene. Therefore 55.5% of the total carbon fed to the reactor in the co-pyrolysis experiments is from catechol; 44.5% is from 1,3-butadiene. (The corresponding ratio of moles of catechol to moles of 1,3-butadiene in the feed is 0.83, a level chosen to ensure that the 1,3-butadiene provided in the feed is several times the level produced by catechol during the experiments.)

The 1,3-butadiene pyrolysis experiments are carried out exactly like the acetylene pyrolysis experiments except for one difference. Instead of a nitrogen carrier gas that is doped with acetylene, the carrier gas is nitrogen containing 1300 ppm of 1,3-butadiene. The feed to the reactor in this case is thus nitrogen with 0.52 mole-% carbon loading from 1,3-butadiene.

For each of the pyrolysis experiments, the products exiting the reactor are quenched to room temperature. The gas-phase products are analyzed as described in Chapter II. The condensed-phase products are dissolved in dichloromethane, concentrated in a Kuderna-Danish evaporator, analyzed by gas chromatography with mass spectrometry (for the 1- and 2-ring aromatics) [112,113] and by HPLC with diode-array UV absorbance detection (for PAH of ≥ 3 rings). Details of the HPLC chromatographic separation method are given in Chapter II and in previous studies from our research group [96,113,259]. The individual PAH products are unequivocally identified by matching each component’s retention time and UV absorbance spectrum with those of the appropriate reference standard. Quantification of the identified PAH comes from extensive calibration of the HPLC/UV instrument with reference standards.

Product yields obtained from repeat experiments under the same conditions give very reproducible results. The masses of carbon quantified in the collected C_1-C_{10} products (reported in Chapter VI and VII and the corresponding papers [114,115]), PAH, oxygen-containing
aromatics, and unconverted fuel account for all of the carbon fed to the reactor. A carbon balance is thus closed on this reactor system.

8.3. Results and Discussion

Catechol pyrolysis (Set 1 experiments of Chapter VI), catechol/acetylene co-pyrolysis (Set 2 experiments of Chapter VI), acetylene pyrolysis (Set 3 experiments of Chapter VI), catechol/1,3-butadiene co-pyrolysis (Set 4 experiments of Chapter VII), and 1,3-butadiene pyrolysis (Set 5 experiments of Chapter VII) experiments have been conducted in the isothermal laminar-flow reactor at a fixed residence time of 0.3 sec and at nine temperatures within the range of 500 to 1000 °C. No PAH of > 3 rings are produced at temperatures < 700 °C. Hence, only the product yields in the temperature range 700 to 1000 °C are reported here.

All of the species identified by HPLC/UV in the condensed-phase products of the experiments in this study are present in the products of catechol pyrolysis at 1000 °C. The HPLC chromatogram of that product mixture from catechol pyrolysis appears in Figure 3.1 in Chapter III. All the 111 products shown in Figure 3.1 for catechol pyrolysis at 1000 °C are also produced from catechol/acetylene co-pyrolysis at 1000 °C and by catechol/1,3-butadiene co-pyrolysis at 1000 °C. In the following, we report identification of PAH products from acetylene pyrolysis, 1,3-butadiene pyrolysis, catechol/acetylene co-pyrolysis, and catechol/1,3-butadiene co-pyrolysis and examine the effects of each of acetylene and 1,3-butadiene on the PAH yields. We first consider the effects of acetylene addition.

8.3.1. Effects of Acetylene Addition

All the 111 products of catechol pyrolysis at 1000 °C (shown in Figure 3.1 of Chapter III) are also produced during catechol/acetylene co-pyrolysis at 1000 °C. Thus, the chromatogram for the 1000-°C catechol/acetylene co-pyrolysis at 1000 °C products looks similar to Figure 3.1 and is not presented here. HPLC chromatogram of the products from acetylene-only pyrolysis is
presented in Figure 8.1. Figure 8.1 reveals that acetylene pyrolysis produces only 13 of the 111 compounds produced from catechol pyrolysis. The largest compounds identified are 4-ring PAH. Also, the PAH products in Figure 8.1 were produced only at the highest temperature of our experiments (1000 °C) and are produced in very low amounts (~0.02 % of the fed carbon). This is an indication of the very low reactivity of acetylene under the conditions of this study.

![HPLC chromatogram of the products of acetylene pyrolysis at 1000 °C and 0.3 sec.](image)

**Figure 8.1.** HPLC chromatogram of the products of acetylene pyrolysis at 1000 °C and 0.3 sec. Identified products are color-coded according to structural class: benzenoid PAH (black), indene benzologues (green), fluoranthene benzologues (dark blue), cyclopenta-fused PAH (red), ethynyl-substituted species (purple), and methylated aromatics (light blue). The names and structures of all products are presented, by class, in Table A.1 in Appendix A.

To delineate the effects of acetylene addition, the yields of all the PAH products have been quantified for the catechol pyrolysis, catechol/acetylene co-pyrolysis, and acetylene pyrolysis experiments of this study. (The yield/temperature profiles for 26 individual higher-yield PAH appear in Figures G.1-G.7 of Appendix G.) For each pyrolysis temperature, the yields of all of the PAH of ≥ 3 rings have been summed, and the results are plotted, as functions of
temperature, in Figure 8.2 for each experiment set: catechol pyrolysis (filled squares), acetylene pyrolysis (filled circles), and catechol/acetylene co-pyrolysis (filled triangles). Because different fuels are used in the different experiment sets, the total PAH yields of Figure 8.2 are expressed as “% fed carbon as carbon in PAH of ≥ 3 rings.” For the catechol pyrolysis experiments, the “fed carbon” is the carbon in the fed catechol; for the acetylene experiments, it is the carbon in the fed acetylene; for the catechol/acetylene co-pyrolysis experiments, it is the carbon in the fed catechol and acetylene. The fourth symbol plotted in Figure 8.2 is the open triangle, which corresponds to a calculated “weighted sum,” for use in comparison to the catechol/acetylene co-pyrolysis experimental data. For any given temperature, the weighted sum is calculated from:

\[
\text{weighted sum} = 0.702 y_c + 0.298 y_a
\]  

(1)

where 0.702 and 0.298 are the fractions of the feed carbon in the catechol/acetylene co-pyrolysis experiment from catechol and acetylene, respectively, and \(y_c\) and \(y_a\) are the yield values from the catechol pyrolysis experiment (filled square) and acetylene pyrolysis experiment (filled circle), respectively. This weighted sum represents what the catechol/acetylene co-pyrolysis experiment would yield if the two fuels together simply behaved as a linear combination of the two fuels individually.

Acetylene-only pyrolysis produces PAH only at 1000 °C. Figure 8.2 reveals that the PAH yields from acetylene pyrolysis (filled circles) are very low (~0.02 % of the fed carbon). The extremely low yield of PAH from acetylene-only pyrolysis is consistent with the observed lower number of PAH products in Figure 8.1. In fact, Figure 8.1 reveals that acetylene pyrolysis produces only 9 PAH that are ≥ 3 rings and none > 4 rings. The observed low yield of PAH from the acetylene-only experiments is also consistent with the extremely low conversion of acetylene as reported in Section 6.3.3 in Chapter VI. To further explain the low yields of PAH from acetylene pyrolysis, we turn to the C₁-C₅ hydrocarbon products and the single-ring aromatic
hydrocarbon products that are the precursor species in the formation of PAH. The yields of these precursor species from catechol pyrolysis (filled squares), acetylene pyrolysis (filled circles), and catechol/acetylene co-pyrolysis (filled triangles) experiments are presented in Figure 8.3: summed C_{1}-C_{5} hydrocarbons, in Figure 8.3a, and summed 1- and 2-ring aromatic hydrocarbons, in Figure 8.3b. (The yield/temperature profiles of individual C_{1}-C_{5} hydrocarbons and 1- and 2-ring aromatic hydrocarbons as well as CO and phenol are presented in Chapter VI.)

![Figure 8.2](image_url)

**Figure 8.2.** Yields, as functions of temperature, of summed PAH of \( \geq 3 \) rings. Experiments: catechol pyrolysis (■); acetylene pyrolysis (●); catechol/acetylene co-pyrolysis (▲). Weighted sum values (Δ) calculated from Eq. (1).

The results from the acetylene-only pyrolysis experiments (filled circles in Figures 8.2 and 8.3) and the catechol-only pyrolysis experiments (filled squares in Figures 8.2 and 8.3) are considered first. Figures 8.3a and 8.3b, respectively, reveal that acetylene pyrolysis produces very low yields of C_{1}-C_{5} hydrocarbons and 1- and 2-ring aromatic hydrocarbons. The low yields of PAH and of the C_{1}-C_{5} hydrocarbons and 1- and 2-ring aromatic hydrocarbons from acetylene
pyrolysis are consistent with the low conversion of acetylene in the acetylene pyrolysis experiments (Set 3 curve of Figure 6.3 in Chapter VI). Catechol, however, undergoes complete conversion at temperature $\geq 900$ °C (Set 1 curve of Figure 6.1 in Chapter VI) and produces high amounts of C$_1$-C$_5$ hydrocarbons and 1- and 2-ring aromatic hydrocarbons, as revealed in Figures 8.3a and 8.3b. Consequently, catechol pyrolysis produces high yields of PAH.

![Graph](image)

**Figure 8.3.** Yields, as functions of temperature, of: (a) summed C$_1$ to C$_5$ hydrocarbons (excluding acetylene), and (b) summed 1- and 2-ring aromatic hydrocarbons. Experiments: catechol pyrolysis (■); acetylene pyrolysis (●); catechol/acetylene co-pyrolysis (▲). Weighted sum values (Δ) calculated from Eq. (1). Acetylene is excluded from (a) since it is supplied as one of the fuels to the experiments.

The co-pyrolysis of catechol and acetylene is examined next. Results from Chapter VI and the corresponding paper [114] show that when catechol and acetylene are pyrolyzed together, the catechol conversion/temperature profile is the same as when catechol is pyrolyzed alone. The results also show [114] that acetylene conversion is enhanced when acetylene is pyrolyzed in the presence of catechol, compared to when acetylene is pyrolyzed alone—and that
this enhancement begins at temperatures > 850 °C. As explained in Section 6.3.3 of Chapter VI, the rich pool of free radicals in the catechol pyrolysis reaction environment apparently facilitates acetylene consumption by obviating the need for an ethynyl C-H scission (a high-energy process [263-266]) initiation step.

The rich radical pool in the catechol/acetylene co-pyrolysis environment not only increases acetylene’s conversion in the co-pyrolysis environment, but it also marginally increases the consumption of the C₁-C₅ hydrocarbons, as revealed in the summed hydrocarbon product yield graphs of Figure 8.3. As figure 8.3a shows, the summed C₁-C₅ hydrocarbon yields from the catechol/acetylene co-pyrolysis experiments (filled triangles) are marginally lower than the weighted sum values except (open triangles) for the highest temperature. Figures 8.2 and 8.3b, respectively, reveal that the PAH yields and the 1- and 2-ring aromatic hydrocarbon yields from the co-pyrolysis experiments are higher (by a factor of 1.2 to 1.3) than the weighted sum values. In addition, the individual yields of the C₁-C₅ products (presented in Figure 6.4 of Chapter VI and the corresponding paper [114]) show a higher consumption of the C₄ species in the catechol/acetylene co-pyrolysis experiments. Thus, the increased consumption of the C₄ species and acetylene—due to catechol’s relatively labile O-H bonds and capacity to generate oxygen-containing radicals—results in an enhanced conversion of feed carbon to PAH carbon, whether the feed carbon is from catechol or acetylene. These observations from the acetylene addition experiments suggest that both the C₂ and C₄ species play an important role in PAH formation reactions.

Since catechol and acetylene produce ~1.3 times higher yields of PAH when they are pyrolyzed together than when they are pyrolyzed separately, it would be interesting to examine whether the synergism preferentially affects PAH of particular sizes or structural classes. Table 8.1 summarizes the effects of acetylene addition on the yields of PAH summed by ring number.
Table 8.1 shows that the ratios of the co-pyrolysis experiment yield to the weighted sum do not vary much with temperature or with ring number. (For the 3-ring PAH, the ratio is $1.5 \pm 0.3$; for the 4- and 5-ring PAH, $1.8 \pm 0.5$.) Thus, PAH of all ring numbers benefit fairly equally from the synergistic effects associated with pyrolyzing catechol and acetylene together.

<table>
<thead>
<tr>
<th>PAH by Ring Number</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>850</td>
</tr>
<tr>
<td>3-ring PAH</td>
<td></td>
</tr>
<tr>
<td>catechol and acetylene co-pyrolysis experiment (▲)^a</td>
<td>1.08</td>
</tr>
<tr>
<td>weighted sum (∆)^b</td>
<td>0.60</td>
</tr>
<tr>
<td>co-pyrolysis experiment / weighted sum (▲ / ∆)</td>
<td>1.79</td>
</tr>
<tr>
<td>4-ring PAH</td>
<td></td>
</tr>
<tr>
<td>catechol and acetylene co-pyrolysis experiment (▲)^a</td>
<td>0.18</td>
</tr>
<tr>
<td>weighted sum (∆)^b</td>
<td>0.08</td>
</tr>
<tr>
<td>co-pyrolysis experiment / weighted sum (▲ / ∆)</td>
<td>2.17</td>
</tr>
<tr>
<td>≥ 5-ring PAH</td>
<td></td>
</tr>
<tr>
<td>catechol and acetylene co-pyrolysis experiment (▲)^a</td>
<td>0.05</td>
</tr>
<tr>
<td>weighted sum (∆)^b</td>
<td>0.02</td>
</tr>
<tr>
<td>co-pyrolysis experiment / weighted sum (▲ / ∆)</td>
<td>2.17</td>
</tr>
</tbody>
</table>

^a Yields summed by ring number expressed as % fed carbon as carbon in PAH.

^b Calculated from Eq. (1).

Table 8.2 summarizes the effects of acetylene addition on the yields of PAH summed by structural class. Table 8.2 reveals that the PAH yields are highest for the cyclopenta-fused PAH—a PAH class that is thought to arise by the acetylene addition to aryl radicals [50]. Even though the yields are highest for the cyclopenta-fused PAH, the ratio of the co-pyrolysis experiment yield to the weighted sum, on average, is highest ($1.8 \pm 0.6$) for the fluoranthene benzologues, the lowest-yield product class. (These observations may have mechanistic implications, as described in section 8.3.3). Table 8.2 also shows that the ratio of the co-pyrolysis experimental yields to the weighted sum does not vary much with temperature for any of the PAH product classes.
Table 8.2. Effects of Acetylene Addition on PAH (of ≥ 3 rings) by Structural Class

<table>
<thead>
<tr>
<th>PAH by Structural Class</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>850</td>
</tr>
<tr>
<td><strong>Indene Benzologues</strong></td>
<td></td>
</tr>
<tr>
<td>catechol and acetylene co-pyrolysis experiment (▲) (^a)</td>
<td>0.24</td>
</tr>
<tr>
<td>weighted sum (Δ) (^b)</td>
<td>0.18</td>
</tr>
<tr>
<td>co-pyrolysis experiment / weighted sum (▲ / Δ)</td>
<td>1.35</td>
</tr>
<tr>
<td><strong>Benzenoid PAH</strong></td>
<td></td>
</tr>
<tr>
<td>catechol and acetylene co-pyrolysis experiment (▲) (^a)</td>
<td>0.27</td>
</tr>
<tr>
<td>weighted sum (Δ) (^b)</td>
<td>0.14</td>
</tr>
<tr>
<td>co-pyrolysis experiment / weighted sum (▲ / Δ)</td>
<td>1.98</td>
</tr>
<tr>
<td><strong>Fluoranthene Benzologues</strong></td>
<td></td>
</tr>
<tr>
<td>catechol and acetylene co-pyrolysis experiment (▲) (^a)</td>
<td>0.04</td>
</tr>
<tr>
<td>weighted sum (Δ) (^b)</td>
<td>0.02</td>
</tr>
<tr>
<td>co-pyrolysis experiment / weighted sum (▲ / Δ)</td>
<td>2.54</td>
</tr>
<tr>
<td><strong>Cyclopenta-Fused PAH</strong></td>
<td></td>
</tr>
<tr>
<td>catechol and acetylene co-pyrolysis experiment (▲) (^a)</td>
<td>0.61</td>
</tr>
<tr>
<td>weighted sum (Δ) (^b)</td>
<td>0.31</td>
</tr>
<tr>
<td>co-pyrolysis experiment / weighted sum (▲ / Δ)</td>
<td>1.98</td>
</tr>
</tbody>
</table>

\(^a\) Yields summed by structural class expressed as % fed carbon as carbon in PAH ≥ 3-rings.
\(^b\) Calculated from Eq. (1).

8.3.2. Effects of 1,3-Butadiene Addition

The HPLC chromatogram of the products of catechol/1,3-butadiene co-pyrolysis at 1000 °C is presented in Figure 8.4. Included in the chromatogram are the structures (color-coded by compound class) of the 111 products unequivocally identified by their UV spectra: 47 benzenoid PAH, in black; 14 indene benzologues, in green; 13 fluoranthene benzologues, in dark blue; 10 cyclopenta-fused PAH, in red; 8 ethynyl-substituted species (triacetylene and 7 ethynyl-substituted aromatics), in purple; 10 methylated aromatics, in light blue; 2 bi-aryls, in gray; and 7 oxygen-containing aromatics, in brown. The names and structures of all 111 products are presented, by class, in Table A.1 in Appendix A.
Figure 8.4. HPLC chromatogram of the products of catechol/1,3-butadiene co-pyrolysis at 1000 °C and 0.3 sec. The rise in baseline at 63 minutes corresponds to a change in mobile-phase composition to UV-absorbing dichloromethane. Identified products are color-coded according to structural class: benzenoid PAH (black), indene benzologues (green), fluoranthene benzologues (dark blue), cyclopenta-fused PAH (red), ethynyl-substituted species (purple), methylated aromatics (light blue), bi-aryls (gray), and oxygen-containing aromatics (brown). The names and structures of all products are presented, by class, in Table A.1 in Appendix A. Portions of the 1- and 2-ring products are lost by evaporation during the HPLC sample-preparation procedure, so these species are quantified by gas chromatography.

Of the 111 products of Figure 8.4, 61 have been reported as products of catechol pyrolysis in earlier catechol pyrolysis studies from our research group [96,113], and the UV spectral matches documenting the identifications of 11 of these 61 PAH that required specially synthesized reference standards have been presented [96]. The remaining 50 products in Figure 8.4 (47 PAH; 3 oxygen-containing aromatics) have never before been reported as products of the pyrolysis of catechol, catechol plus acetylene, catechol plus 1,3-butadiene, or any other phenol-type fuel. The UV spectra documenting the 47 new PAH product identifications are presented in
Chapter III and are the subject of three forthcoming papers: one on the C_{24}H_{14} PAH \[111\], one on the indene benzologues \[189\], and one on the large-ring-number PAH \[267\].

The 111 products shown in Figure 8.4 for catechol/1,3-butadiene co-pyrolysis at 1000 °C are the very same 111 products that are produced by catechol pyrolysis alone at this same temperature. The chromatogram for the 1000-°C catechol-only pyrolysis thus looks similar to Figure 8.4 and is presented in Chapter III (Figure 3.1). The catechol/1,3-butadiene co-pyrolysis chromatogram of Figure 8.4 shows higher peaks than the catechol-only pyrolysis chromatogram of Figure 3.1 in Chapter III. This is a sign of higher yields of PAH from the catechol/1,3-butadiene co-pyrolysis experiments.

Unlike acetylene-only pyrolysis, 1,3-butadiene-only pyrolysis produces a wide range of PAH products, and the HPLC chromatogram of the products of 1,3-butadiene pyrolysis at 1000 °C is presented in Figure 8.5. Figure 8.5 reveals that pyrolysis of 1,3-butadiene alone at 1000 °C produces only about two-thirds of the products shown in Figure 8.4 for catechol/1,3-butadiene co-pyrolysis (or catechol-only pyrolysis in Figure 3.1 of Chapter III) at this temperature. Since there is no source of oxygen in the 1,3-butadiene-only pyrolysis environment, the oxygen-containing products of catechol pyrolysis or catechol/1,3-butadiene co-pyrolysis, shown in brown in Figure 8.4, are not present in the 1,3-butadiene pyrolysis products of Figure 8.5 (The one oxygen-containing compound in Figure 8.5, phenalenone, represents the unstable C_{13}H_{10} reaction product phenalene, which oxidizes to phenalenone \[268,269\] as soon as the pyrolysis experiment is over and the collected quenched products are exposed to air and light.) Also, many of the larger-ring-number PAH in Figure 8.4, which are formed by catechol pyrolysis or catechol/1,3-butadiene co-pyrolysis at 1000 °C, are either not present or are present in much smaller amounts in the 1,3-butadiene pyrolysis products of Figure 8.5. This difference is a sign that, for a given temperature and residence time, the pyrolysis reactions leading to PAH
formation and growth in the catechol pyrolysis or catechol/1,3-butadiene co-pyrolysis environment progress to a much greater extent than they do in the 1,3-butadiene-only pyrolysis environment. A comparison of Figures 8.1 and 8.5, however, reveals that 1,3-butadiene is far more effective in producing PAH than is acetylene under the conditions of this study.

Figure 8.5. HPLC chromatogram of the products of 1,3-butadiene pyrolysis at 1000 °C and 0.3 sec. The rise in baseline at 63 minutes corresponds to a change in mobile-phase composition to UV-absorbing dichloromethane. Identified products are color-coded according to structural class: benzenoid PAH (black), indene benzologues (green), fluoranthene benzologues (dark blue), cyclopenta-fused PAH (red), ethynyl-substituted species (purple), methylated aromatics (light blue), bi-aryls (gray), and oxygen-containing aromatics (brown). The names and structures of all products are presented, by class, in Table A.1. The only oxygen-containing species in the chromatogram, phenalenone (the earliest-eluting species), actually represents the unstable C_{13}H_{10} reaction product phenalene, which oxidizes to phenalenone [268,269] as soon as the pyrolysis experiment is over and the collected quenched products are exposed to air and light. Portions of the 1- and 2-ring products are lost by evaporation during the HPLC sample-preparation procedure, so these species are quantified by gas chromatography.
To further explore the role of 1,3-butadiene in PAH formation, the yields of all of the PAH shown in Figure 8.4 have been quantified for the 1,3-butadiene-only pyrolysis and catechol/1,3-butadiene co-pyrolysis experiments. (The yield/temperature profiles for 26 individual higher-yield PAH appear in Figures H.1-H.7 of Appendix H.) For each pyrolysis temperature, the yields of all of the PAH of \( \geq 3 \) rings have been summed, and the results are plotted, as functions of temperature, in Figure 8.6 for each experiment set: catechol pyrolysis (filled squares), 1,3-butadiene pyrolysis (filled circles), and catechol/1,3-butadiene co-pyrolysis (filled triangles). Because different fuels are used in the different experiment sets, the total PAH yields of Figure 8.6 are expressed as “% fed carbon as carbon in PAH of \( \geq 3 \) rings.” For the catechol pyrolysis experiments, the “fed carbon” is the carbon in the fed catechol; for the 1,3-butadiene experiments, it is the carbon in the fed 1,3-butadiene; for the catechol/1,3-butadiene co-pyrolysis experiments, it is the carbon in the fed catechol and 1,3-butadiene. The fourth symbol plotted in Figure 8.6 is the open triangle, which corresponds to a calculated “weighted sum,” for use in comparison to the catechol/1,3-butadiene co-pyrolysis experimental data. For any given temperature, the weighted sum is calculated from:

\[
\text{weighted sum} = 0.555 y_c + 0.445 y_b
\]  

(2)

where 0.555 and 0.445 are the fractions of the feed carbon in the co-pyrolysis experiment from catechol and 1,3-butadiene, respectively, and \( y_c \) and \( y_b \) are the yield values from the catechol pyrolysis experiment (filled square) and 1,3-butadiene pyrolysis experiment (filled circle), respectively. This weighted sum represents what the catechol/1,3-butadiene co-pyrolysis experiment would yield if the two fuels together simply behaved as a linear combination of the two fuels individually.
Figure 8.6 reveals that the yields of PAH from 1,3-butadiene-only pyrolysis are more than 100 times higher than those produced from acetylene-only pyrolysis at 1000 °C. Thus, in the temperature range of this study, 1,3-butadiene is more reactive and far more effective in producing PAH. However, Figure 8.6 shows that—compared to catechol pyrolysis or catechol/1,3-butadiene co-pyrolysis—1,3-butadiene pyrolysis requires higher temperatures to produce PAH, but, even at the higher temperatures, produces a much lower amount of PAH. This observation is consistent with the observed lower proportion of larger-ring-number PAH in the 1,3-butadiene products of Figure 8.5. To explain these observations, we turn to the data on catechol and 1,3-butadiene conversion, in Figure 8.7.
**Figure. 8.7.** (a) Conversion, as a function of temperature, for catechol in the catechol pyrolysis experiments (■) and for 1,3-butadiene in the 1,3-butadiene pyrolysis experiments (●).

As before, just the results for the 1,3-butadiene-only pyrolysis experiments and the catechol-only pyrolysis experiments—represented by the circles and squares, respectively, in Figures 8.6 and 8.7—are considered first. As Figure 8.7 demonstrates, catechol conversion rises rapidly with temperature between 750 and 850 °C, reaching 87% at 850 °C and 100% at 900 °C. 1,3-butadiene conversion, in contrast, goes from 6% to 39% in the 750- to 850-°C temperature interval and requires temperatures in excess of 900 °C to achieve 90% conversion. We therefore see from Figure 8.7 that for any given temperature below 950 °C, the extent of catechol conversion in the catechol pyrolysis experiments is much higher than the extent of 1,3-butadiene conversion in the 1,3-butadiene experiments—a result consistent with the much higher production of PAH from catechol pyrolysis than from 1,3-butadiene pyrolysis, in Figure 8.6.

Since the main hydrocarbon product of catechol decomposition in the 750- to 850-°C temperature range (where catechol conversion dramatically rises) is 1,3-butadiene itself [112] and since the other C₁-C₆ hydrocarbon products of catechol pyrolysis—ethylene, acetylene, vinylacetylene, benzene, cyclopentadiene, propyne, propadiene, propene, and methane—are the
very C₁-C₆ products of 1,3-butadiene pyrolysis [114], the facilitated conversion of catechol, relative to that of 1,3-butadiene, must be linked to the oxygen that catechol contains in the form of its two hydroxyl groups. The bond dissociation energy (BDE) of the O-H bond in catechol, the weakest bond in the catechol molecule, is 81.2 kcal/mole [270], which is lower than 87.5 kcal/mole [271], the experimentally determined BDE for the weakest bond in 1,3-butadiene, the C-H bond of an internal C. Catechol’s lower BDE enables the radical-initiation step to take place at a lower temperature for catechol than for 1,3-butadiene. Furthermore, once catechol pyrolysis reactions start, OH and other vigorous oxygen-containing radicals are generated, further propelling the pyrolysis reactions that lead to 1- and 2-ring aromatics and eventually PAH. When 1,3-butadiene is not in the presence of catechol, not only does it have a higher energy threshold to overcome to initiate pyrolysis reactions, but there are also no oxygen-containing radicals around like OH, which are extremely effective at accelerating pyrolysis reactions. The 1,3-butadiene conversion curve of Figure 8.7 is therefore not only shifted to higher temperatures, relative to that of catechol, but it is also less steep in slope.

To further explain the lower proportion of PAH products from 1,3-butadiene pyrolysis with reference to catechol pyrolysis, let us now consider the data on the other hydrocarbon product yields: summed C₁-C₅ hydrocarbons, in Figure 8.8a, and summed 1- and 2-ring aromatic hydrocarbons, in Figure 8.8b. (Chapter VII and the corresponding paper [115] reports the yield/temperature behavior of each of the C₁-C₁₀ hydrocarbon products individually as well as of CO and phenol, two major products of catechol whose yields are unaffected by the addition of 1,3-butadiene to the catechol pyrolysis environment.)

As for the hydrocarbon products—since the 1,3-butadiene-only pyrolysis environment is void of the oxygen-containing radicals that accelerate the reactions leading to aromatic ring formation and growth—Figures 8.8a and 8.8b, respectively, show that: (1) the proportion of fuel
carbon ending up as C₁-C₅ hydrocarbons is roughly twice as high for 1,3-butadiene pyrolysis than for catechol pyrolysis and (2) the proportion of fuel carbon ending up as 1- and 2-ring aromatic hydrocarbons is roughly twice as high for catechol pyrolysis than for 1,3-butadiene pyrolysis at 850 to 950 °C (At temperatures ≥ 950 °C, it falls to less than twice, as the 1- and 2-ring aromatics from catechol become vulnerable to oxidation [112,113]. Since these 1- and 2-ring aromatics are the kernels for PAH formation and growth [224], catechol pyrolysis produces a much higher yield of PAH than does 1,3-butadiene pyrolysis, just as Figure 8.6 portrays.

![Figure 8.8](image-url)  

**Figure 8.8.** Yields, as functions of temperature, of: (a) summed C₁ to C₅ hydrocarbons (excluding 1,3-butadiene), and (b) summed 1- and 2-ring aromatic hydrocarbons. Experiments: catechol pyrolysis (■); 1,3-butadiene pyrolysis (●); catechol/1,3-butadiene co-pyrolysis (▲). Weighted sum values (△) calculated from Eq. (2). 1,3-butadiene is excluded from (a) since it is supplied as one of the fuels to the experiments.

Having considered the results from the catechol-only and 1,3-butadiene-only experiments, we now examine the co-pyrolysis of catechol and 1,3-butadiene. Results from Chapter VII show that when catechol and 1,3-butadiene are pyrolyzed together, the catechol
conversion/temperature profile is the same as when catechol is pyrolyzed by itself [114]. The results also show [115] that 1,3-butadiene conversion is enhanced when 1,3-butadiene is in the presence of catechol, compared to when 1,3-butadiene is pyrolyzed by itself—and that this enhancement begins at temperatures > 750 °C, the temperature at which catechol conversion really starts to “take off.” These observations are fully consistent with the oxygen-associated conversion-enhancement effects described above: Since catechol already contains the relatively labile O-H bond and is able to generate oxygen-containing radicals, adding 1,3-butadiene does not influence catechol conversion. Since 1,3-butadiene, however, has only higher-BDE bonds and no source of oxygen, adding catechol to its pyrolysis environment significantly increases 1,3-butadiene’s conversion.

The oxygen-containing radicals from catechol not only increase 1,3-butadiene’s conversion in the co-pyrolysis environment but they also permit the C₁-C₅ hydrocarbon products of 1,3-butadiene pyrolysis to participate as effectively as the C₁-C₅ hydrocarbon products of catechol in the reactions leading to the 1- and 2-ring aromatics and PAH. Evidence of this effect is found in the summed hydrocarbon product yield graphs of Figure 8.8—particularly in the comparison of the actual co-pyrolysis experiment yields (filled triangles) with the calculated “weighted sum” values (open triangles), which represent the hypothetical yields the co-pyrolysis experiments would produce if the two fuels together simply behaved as a linear combination of the two fuels individually. As Figures 8.8a and 8.8b show, the summed C₁-C₅ hydrocarbon yields from the catechol/1,3-butadiene co-pyrolysis experiments are lower than the weighted sum values in Figure 8.8a, and the 1- and 2-ring aromatic hydrocarbon yields from the co-pyrolysis experiments are much higher (by a factor of 1.3 to 1.6) than the weighted sum values in Figure 8.8b. The effect is even more dramatic for the PAH in Figure 8.6: At 850 to 1000 °C, PAH yields from the co-pyrolysis experiments are 2.1 to 2.5 times greater than the weighted sum
values. We therefore see—from comparison of the co-pyrolysis and weighted-sum values in Figures 8.6 and 8.8—that in the catechol/1,3-butadiene co-pyrolysis environment, catechol’s relatively labile O-H bonds and capacity to generate oxygen-containing radicals effectively facilitate conversion of feed carbon to PAH carbon, whether the feed carbon is from catechol or 1,3-butadiene.

The enhanced PAH production in the co-pyrolysis experiments is due not only to the reaction-promoting effects of the oxygen-containing radicals, however, but also to the effectiveness, as growth species, of the small hydrocarbons generated by catechol and 1,3-butadiene during pyrolysis. Of the C₁–C₅ hydrocarbons, it is the C₂ species ethylene and acetylene and the C₄ species 1,3-butadiene and vinylacetylene that, by far, are the most abundant in the catechol/1,3-butadiene co-pyrolysis environment [112,115]. The experiments with catechol/acetylene co-pyrolysis (Section 8.3.2) and catechol/ethylene co-pyrolysis (preliminary results), however, show that neither acetylene nor ethylene has any more than a modest effect in increasing PAH yields in the temperature range of this study (600-1000 °C). For example, at no temperature is the PAH yield from the catechol/acetylene co-pyrolysis experiment any more than ~23 % higher than the corresponding weighted sum for that system (Figure 8.2). Since, in contrast, PAH yields from catechol/1,3-butadiene co-pyrolysis are more than twice their corresponding weighted sum (Figure 8.6)—and since vinyl acetylene is produced in substantial amounts from both 1,3-butadiene pyrolysis [115] and catechol pyrolysis [112]—the present results provide strong evidence that it is the C₄ species, and not the C₂ species, that are the more effective growth agents in the catechol/1,3-butadiene co-pyrolysis environment—at least at temperatures up to 1000 °C, the maximum temperature of the experiments of this study. Consistent with the findings of the this study, several works [78,242,244,272] have cited C₄ as an important growth species for PAH.
Table 8.3. Effects of 1,3-Butadiene Addition on PAH (of ≥ 3 rings) by Ring Number

<table>
<thead>
<tr>
<th>PAH by Ring Number</th>
<th>Temperature (°C)</th>
<th>850</th>
<th>900</th>
<th>950</th>
<th>1000</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-ring PAH</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>catechol and 1,3-butadiene co-pyrolysis experiment (▲)(^\text{a})</td>
<td>1.16</td>
<td>3.05</td>
<td>5.25</td>
<td>5.86</td>
<td></td>
</tr>
<tr>
<td>weighted sum (Δ)(^\text{b})</td>
<td>0.48</td>
<td>1.52</td>
<td>2.68</td>
<td>2.75</td>
<td></td>
</tr>
<tr>
<td>co-pyrolysis experiment / weighted sum (▲ / Δ)</td>
<td>2.39</td>
<td>2.01</td>
<td>1.96</td>
<td>2.13</td>
<td></td>
</tr>
<tr>
<td>4-ring PAH</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>catechol and 1,3-butadiene co-pyrolysis experiment (▲)(^\text{a})</td>
<td>0.20</td>
<td>0.67</td>
<td>1.93</td>
<td>2.12</td>
<td></td>
</tr>
<tr>
<td>weighted sum (Δ)(^\text{b})</td>
<td>0.07</td>
<td>0.28</td>
<td>0.78</td>
<td>0.80</td>
<td></td>
</tr>
<tr>
<td>co-pyrolysis experiment / weighted sum (▲ / Δ)</td>
<td>2.98</td>
<td>2.37</td>
<td>2.46</td>
<td>2.66</td>
<td></td>
</tr>
<tr>
<td>≥ 5-ring PAH</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>catechol and 1,3-butadiene co-pyrolysis experiment (▲)(^\text{a})</td>
<td>0.04</td>
<td>0.21</td>
<td>0.72</td>
<td>1.32</td>
<td></td>
</tr>
<tr>
<td>weighted sum (Δ)(^\text{b})</td>
<td>0.02</td>
<td>0.08</td>
<td>0.34</td>
<td>0.50</td>
<td></td>
</tr>
<tr>
<td>co-pyrolysis experiment / weighted sum (▲ / Δ)</td>
<td>2.45</td>
<td>2.57</td>
<td>2.10</td>
<td>2.67</td>
<td></td>
</tr>
</tbody>
</table>

\(^{a}\) Yields summed by ring number expressed as % fed carbon as carbon in PAH.
\(^{b}\) Calculated from Eq. (2).

Having established that catechol and 1,3-butadiene produce more than twice the yield of PAH when they are pyrolyzed together than when they are pyrolyzed in the same amounts separately—let us now examine whether the synergism preferentially affects PAH of particular sizes or structural classes. When the yields of PAH from catechol/1,3-butadiene co-pyrolysis experiments are summed according to ring number and compared, at each temperature, with the corresponding weighted sums, the ratios of the co-pyrolysis experiment yield to the weighted sum are found (Table 8.3) not to vary much with temperature or with ring number. (For the 3-ring PAH, the ratio is 2.1 ± 0.2; for the 4- and 5-ring PAH, 2.5 ± 0.3.) This observation implies that PAH of all ring numbers benefit fairly equally from the synergistic effects associated with pyrolyzing the catechol and 1,3-butadiene together.

When the same type of data are compiled (Table 8.4) for the PAH grouped by structural class, however, two other observations emerge. First—similar to results from coal pyrolysis experiments [29]—PAH yields from the catechol/1,3-butadiene co-pyrolysis experiments are
highest for the cyclopenta-fused PAH and the benzenoid PAH, the two groups that contain the most potent mutagens produced in our experiments: cyclopenta[cd]pyrene, benzo[a]pyrene, dibenzo[a,i]pyrene, naphtho[2,3-a]pyrene, naphtho[2,1-a]pyrene [9,10]. Second, the ratio of the co-pyrolysis experiment yield to the weighted sum varies some with PAH structural class. For the benzenoid PAH and the indene benzologues, the ratio is constant at 2.3 ± 0.2, but it is a little lower for the cyclopenta-fused PAH (1.7 ± 0.2) and quite a bit higher for the fluoranthene benzologues (3.2 ± 0.4). A similar effect was also observed for the catechol/acetylene co-pyrolysis experiments (Table 8.2).

Table 8.4. Effects of 1,3-Butadiene Addition on PAH (of > 3 rings) by Structural Class

<table>
<thead>
<tr>
<th>PAH by Structural Class</th>
<th>Temperature (°C)</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>850</td>
<td>900</td>
<td>950</td>
<td>1000</td>
</tr>
<tr>
<td>Indene Benzologues</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>catechol and 1,3-butadiene</td>
<td>0.33</td>
<td>0.79</td>
<td>1.24</td>
<td>0.87</td>
</tr>
<tr>
<td>co-pyrolysis experiment</td>
<td>0.14</td>
<td>0.42</td>
<td>0.51</td>
<td>0.35</td>
</tr>
<tr>
<td>weighted sum</td>
<td>2.32</td>
<td>1.85</td>
<td>2.41</td>
<td>2.51</td>
</tr>
<tr>
<td>catechol and 1,3-butadiene</td>
<td>0.28</td>
<td>0.90</td>
<td>2.01</td>
<td>2.09</td>
</tr>
<tr>
<td>weighted sum</td>
<td>0.11</td>
<td>0.42</td>
<td>0.99</td>
<td>0.91</td>
</tr>
<tr>
<td>co-pyrolysis experiment / weighted sum</td>
<td>2.54</td>
<td>2.11</td>
<td>2.04</td>
<td>2.31</td>
</tr>
<tr>
<td>Benzenoid PAH</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>catechol and 1,3-butadiene</td>
<td>0.05</td>
<td>0.23</td>
<td>0.75</td>
<td>1.00</td>
</tr>
<tr>
<td>weighted sum</td>
<td>0.01</td>
<td>0.08</td>
<td>0.26</td>
<td>0.30</td>
</tr>
<tr>
<td>co-pyrolysis experiment / weighted sum</td>
<td>3.71</td>
<td>2.96</td>
<td>2.85</td>
<td>3.30</td>
</tr>
<tr>
<td>Fluoranthene Benzologues</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>catechol and 1,3-butadiene</td>
<td>0.37</td>
<td>1.27</td>
<td>2.61</td>
<td>4.05</td>
</tr>
<tr>
<td>weighted sum</td>
<td>0.24</td>
<td>0.76</td>
<td>1.57</td>
<td>2.06</td>
</tr>
<tr>
<td>co-pyrolysis experiment / weighted sum</td>
<td>1.55</td>
<td>1.66</td>
<td>1.66</td>
<td>1.96</td>
</tr>
<tr>
<td>Cyclopenta-Fused PAH</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>catechol and 1,3-butadiene</td>
<td>a</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>weighted sum</td>
<td>b</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>co-pyrolysis experiment / weighted sum</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a Yields summed by structural class expressed as % fed carbon as carbon in PAH ≥ 3-rings.
b Calculated from Eq. (2).

Even though these differences between structural classes are not huge, the lower ratio for the cyclopenta-fused PAH and higher ratio for the fluoranthene benzologues could be indicative of one or both of two types of reactions taking place. First, relative to other PAH, cyclopenta-
fused PAH demonstrate a greater facility for undergoing intramolecular rearrangement reactions that lead to fluoranthene benzologues [273,274]. For example, the C_{16}H_{10} cyclopenta-fused PAH acephenanthrylene and aceanthrylene convert to their isomer fluoranthene, but the reverse does not happen [274]. Second, the electrons composing the double bond between the two external carbons in the cyclopenta ring of cyclopenta-fused PAH are more localized than are the electrons composing the six-membered rings, rendering those two external carbons more vulnerable to reaction [275]. (Benish et al. [32] have suggested that this feature makes the cyclopenta-fused PAH important in soot growth processes.) Since either C_{2} or C_{4} radical addition to the two vulnerable carbons would result in fluoranthene benzologues (e.g., addition to acenaphthylene yielding fluoranthene)—and since C_{2} and/or C_{4} addition appears to be enhanced in our co-pyrolysis environment—the higher vulnerability to reaction of the external carbons in the cyclopenta ring could at least partially account for why the synergistic effects associated with the co-pyrolysis environment show a preference for the fluoranthene benzologues, at the expense, apparently, of the cyclopenta-fused PAH.

### 8.3.3. Mechanistic Implications

A mechanism for catechol decomposition and the formation of C_{1}-C_{6} species have been earlier proposed by Ledesma et al. [98]. This mechanism is analogous to the phenol decomposition mechanism proposed by Brezinski et al.[88]. Drawing from that phenol pyrolysis mechanism [88], results from our research group [96-99], and other relevant studies in the literature [17,50-53,67,202], Ledesma proposed [98, personal communication] a generalized reaction scheme, shown in Figure 8.9, for PAH formation from catechol with phenol as the most important intermediate.

According to this scheme, the initial decomposition of catechol forms phenol, and pyrolysis of phenol leads to cyclopentadiene, benzene, and naphthalene. Further ring growth and
PAH formation are largely based on the hydrogen-abstraction/acetylene-addition (HACA) reactions [17,50-53]. The above mechanism for PAH formation from catechol is based on several observations from the literature: (1) Both phenol [237,276] and cyclopentadiene [67,72] studies have reported PAH as products; (2) the yields/temperature data from catechol pyrolysis show a decrease in phenol yields at temperatures > 850 °C—the same temperature at which the PAH yields start to increase; (3) In the combustion environment, the HACA mechanism [17,50-53] is considered to be one of the major pathways leading to PAH formation; (4) In the catechol pyrolysis environment, acetylene is present in high abundance [98,112]; (5) Ethynyl-substituted PAH and cyclopenta-fused PAH [99,113]—both thought to arise from acetylene addition to aryl radicals [50]—are produced in particularly high abundance during catechol pyrolysis.

![Figure 8.9](https://example.com/figure89.png)

Figure 8.9. Generalized reaction scheme for PAH formation proposed by Ledesma. The reaction scheme draws from several studies [17,50-53,67,88,96-99,202].

The results from the present catechol/acetylene co-pyrolysis study, however, indicate that acetylene has only a modest effect (Figure 8.2) in increasing PAH yields in the temperature range of 600-1000 °C. The catechol/1,3-butadiene co-pyrolysis study reveals that 1,3-butadiene addition brings about dramatic increases in PAH yields (Figure 8.6). The conditions of this study
(600 – 1000 °C and 0.3 s residence time) are very similar to those of the earlier catechol pyrolysis studies [96-99]. For both co-pyrolysis experiments, the yields of phenol—the most important intermediate in the Scheme of Figure 8.9—from the co-pyrolysis experiments are the same as those from the catechol pyrolysis experiments (Figure 6.7 in Chapter VI and Figure 7.7 in Chapter VII). Hence, the increases in PAH in the co-pyrolysis study cannot be attributed to phenol. The catechol/acetylene co-pyrolysis results also reveal that the addition of acetylene to the catechol pyrolysis environment increases the consumption of the C₄ species (Chapter VI). Thus, the present study provides strong evidence that the C₄ species and/or the radicals produced from C₄ species are far more effective growth agents than acetylene in the catechol pyrolysis environment.

The present study also reveals that 1,3-butadiene-only pyrolysis, under the similar conditions, produces an range of PAH (Figure 8.5). Acetylene-only pyrolysis, however, produces very few PAH (Figure 8.1). Thus, comparison of Figures 8.1 and 8.5 further confirms that 1,3-butadiene is far more effective in producing PAH than acetylene in the temperature range studied. In addition, the yields of PAH from 1,3-butadiene-only pyrolysis (filled circles of Figure 8.6) is significantly higher than those from acetylene-only pyrolysis (filled circles of Figure 8.2). The bond dissociation energy (BDE) of the C-H bond in acetylene is 132 kcal/mole [263-266], which is higher than 87.5 kcal/mole [271], the experimentally determined BDE for the weakest bond in 1,3-butadiene, the C-H bond of an internal C. 1,3-butadiene’s lower BDE enables the radical-initiation step to take place at a lower temperature for 1,3-butadiene than for acetylene. Thus, as the temperature is increased from 700 to 1000 °C, acetylene undergoes little or no conversion but 1,3-butadiene undergoes almost complete conversion—the conversion of 1,3-butadiene is 98% at 1000 °C (Figure 8.7).
Since acetylene has only a moderate effect on the yields of PAH, the HACA mechanism does not appear to be the dominant PAH formation mechanism in the temperature range studied. The high conversion of 1,3-butadiene, high yields of 1,3-butadiene and vinyl acetylene from catechol pyrolysis, and the significant increase in PAH in the catechol/1,3-butadiene co-pyrolysis experiments all provide strong evidence that the C₄ species are the more effective growth agents in the catechol pyrolysis environment of this study. Thus, the reactions steps leading to PAH growth most likely involve radicals generated from 1,3-butadiene pyrolysis (e.g. C₂H₃, C₄H₅, and/or the resonantly stabilized C₄H₃ radicals). Consistent with our finding, the role of C₄ species in PAH formation has also been implied by various studies [78,242,244,272].

To further explore the role of 1,3-butadiene during the pyrolysis of catechol, let us now compare the yields of 1,3-butadiene produced from catechol pyrolysis with that of phenol—the most important intermediate in the scheme presented in Figure 8.9. The effects of temperature on the yields of phenol and 1,3-butadiene from catechol-only pyrolysis are very similar—the yields of both compounds peaking at 850 °C (Chapter IV). But yields of 1,3-butadiene are significantly higher than those of phenol at temperatures ≥ 850 °C. The similar temperature profiles and 1,3-butadiene’s ability to produce PAH suggest that 1,3-butadiene can also be an important intermediate in PAH formation.

Two alternated mechanisms for the formation of 1,3-butadiene from catechol are presented Chapter IV (Section 4.3.2.3). The mechanism proposed by Ledesma and presented in Figure 8.9 for catechol decomposition and PAH formation excluded 1,3-butadiene as an intermediate. The results from the present study, however, provide strong evidence that 1,3-butadiene is both an intermediate and a growth species in PAH formation reactions during catechol pyrolysis. Thus catechol decomposition may proceed through two alternate pathways, as presented in Figure 8.10.
Figure 8.10. Generalized reaction scheme for catechol decomposition routes.

Though both of these routes can independently lead to PAH, they are not mutually exclusive. Phenol pyrolysis produces benzene by the displacement of an OH by H [88,89] and 1,3-butadiene pyrolysis produces cyclopentadiene as shown in the present study (Figure 7.6 in Chapter VII). As discussed in Chapter VI, another important benzene formation mechanism in combustion environment is the propargyl radical self-addition [204,205,207,208]. But preliminary propyne (the stable form of the propargyl radical) pyrolysis experiments (Appendix I) reveal that the formation of benzene becomes significant only at temperatures > 900 °C. Since the C₃ products are produced in low yields from catechol pyrolysis, the propargyl radical self-addition mechanism may not be relevant in the formation of benzene. Propargyl radical may, however, play a role as a growth species in ring build-up reactions.

The phenol pathway will most likely lead to naphthalene by the cyclopentadienyl radical self addition reactions. The results presented in Chapter VI provide strong evidence for this pathway being the dominant naphthalene formation pathway. Further ring build-up may involve C₂ and C₃ radicals as well as the aryl aromatic addition reactions. The 1,3-butadiene pathway most likely involves C₄ radical reactions, in addition to the C₂ and C₃ radical reactions and the
aryl aromatic addition reactions. The HACA mechanism, though not the dominant PAH formation mechanism, may contribute to some PAH, particularly the ethynyl-substituted PAH, cyclopenta-fused PAH, and the indene benzologues.

Although the phenol pathway can lead to PAH, no experimental study on phenol or cyclopentadiene pyrolysis has reported PAH of > 4 rings. The complete absence of phenol at higher temperatures in the catechol pyrolysis environment also suggests that the phenol route is not likely to be the dominant PAH formation route. The present study demonstrates that the pyrolysis of 1,3-butadiene produces a range of PAH (Figure 8.5) and all the C₁⁻C₁₀ species (Chapter VII) that are precursors and/or growth species in PAH formation reactions. Since the products of 1,3-butadiene pyrolysis are very similar to those obtained from catechol pyrolysis, we conclude that the 1,3-butadiene route is the dominant PAH formation route during catechol pyrolysis. The absence of 1,3-butadiene among the products of phenol pyrolysis further strengthens this assertion [88]. Figure 8.11 presents a scheme for the formation of the C₁⁻C₆ products from catechol. A tentative mechanism for the formation of PAH from the C₁⁻C₆ thermal decomposition products of catechol is presented in Figure 8.12. The mechanism is based on the 1,3-butadiene route and draws from the results of catechol pyrolysis, acetylene pyrolysis, 1,3-butadiene pyrolysis, and the co-pyrolysis experiments. The C₂ and C₄ species are the main growth species. The intramolecular rearrangement reactions of cyclopenta-fused PAH that lead to fluoranthene benzologues [273,274] is also included.

**Figure 8.11.** Tentative reaction scheme for the formation of C₁⁻C₆ thermal decomposition products during catechol pyrolysis.
Since cyclopentadiene is a significant product of phenol pyrolysis [88], the phenol route would be significant in the formation of naphthalene. Pyrolysis of phenol or cyclopentadiene under conditions similar to catechol pyrolysis would provide answers to the role of the phenol-cyclopentadiene route in PAH formation during catechol pyrolysis.

8.4. Conclusions

Catechol’s relatively labile O-H bond and capacity for generating oxygen-containing radicals accelerate fuel conversion and the pyrolysis reactions leading to 1- and 2-ring aromatics and PAH. Since 1,3-butadiene has no such internal source of oxygen, for a given temperature, a much higher percentage of fed carbon is converted to PAH in the catechol-only pyrolysis experiments than in the 1,3-butadiene-only pyrolysis experiments. However, when the two fuels are pyrolyzed together, 1,3-butadiene and its decomposition products also benefit from the
reaction-promoting effects of the oxygen-containing radicals from catechol: For any given temperature, the percentage of the total fed carbon converting to PAH in the co-pyrolysis experiment is more than two times higher than the amount calculated for the hypothetical case of the two fuels together behaving as a linear combination of the two fuels individually. This elevated production of PAH from the co-pyrolysis experiments reflects not only the reaction-accelerating role of the oxygen-containing radicals but also the efficacy, as growth agents, of the C₂ and C₄ species abundantly present in the catechol and 1,3-butadiene pyrolysis environment. Since our catechol/acetylene co-pyrolysis and catechol/ethylene co-pyrolysis experiments produce PAH yields that are only slightly higher than those from catechol pyrolysis alone, we conclude that it is the C₄ species, and not the C₂ species, that are the more effective growth agents in the catechol/1,3-butadiene co-pyrolysis environment—at least at temperatures up to 1000 °C, the maximum temperature of our experiments. Since the hydrocarbons and oxygen-containing radicals produced during catechol pyrolysis experiments are also abundant in the reaction environments of actual solid fuels, the results presented here illustrate the kind of synergistic effects that can occur during PAH formation from solid fuel pyrolysis and combustion.

Based on the results from the pyrolysis experiments, a tentative mechanism for PAH formation from catechol is presented. The mechanism is based on 1,3-butadiene as the most important intermediate in the formation of PAH from catechol. The C₂ and C₄ species are the important growth species in our tentative PAH formation mechanism. Among the small aromatics, C₂ addition to C₄ radicals is the most likely mechanism for benzene formation and the cyclopentadiene radical self-addition mechanism is the dominant naphthalene formation mechanism in our catechol pyrolysis environment.
Chapter IX. Conclusions

9.1. Overview

This work is an experimental investigation into the formation of PAH during solid fuel pyrolysis and combustion using catechol as a model fuel representative of structural entities in solid fuels like coal, wood, or biomass. The work describes the identification and quantification of a range of PAH products and PAH precursor species from catechol pyrolysis as well as from the pyrolysis of acetylene and 1,3-butadiene—two of the major products of catechol pyrolysis. Products have also been quantified from catechol pyrolysis in the presence of oxygen as well as in the presence of each of the two major catechol pyrolysis products acetylene and 1,3-butadiene [98,112], to delineate their roles in PAH formation reactions.

Special attention is given to the identification of carcinogenic and mutagenic PAH like the C_{24}H_{14} PAH and methylene-bridged PAH. Since not all PAH are carcinogenic or mutagenic [9,10] and the biological activity of a PAH is structure dependent [277], a significant effort has gone into the isomer-specific identification of PAH. Particular attention has also been given to the identification of large PAH due to their implied role in soot formation [15,16]. The isomer-specific identification of PAH also provides mechanistic insight into PAH formation reactions.

The quantification of products from the combustion and pyrolysis experiments underscores the important role of the thermal decomposition products in the formation and growth of PAH during the pyrolysis and fuel-rich oxidation of catechol. The results are consistent with PAH formation and growth by successive ring-buildup reactions involving the C_{1}-C_{5} and single-ring aromatic products of catechol’s thermal decomposition. The combustion and pyrolysis results indicate that among the C_{1}-C_{5} products, 1,3-butadiene is the most important intermediate in PAH formation under catechol pyrolysis and fuel-rich oxidation conditions. The
results also demonstrate that catechol’s relatively labile O-H bond and capacity for generating oxygen-containing radicals accelerate fuel conversion and the pyrolysis reactions leading to 1- and 2-ring aromatics and PAH.

Though this study is far from providing answers to fully understand the formation of PAH during the pyrolysis and combustion of solid fuels, this study has made available exhaustive experimental data for advancement in the area of PAH formation. The data covers extensive analysis of products leading to the identification of many compounds that have never before been identified as combustion or pyrolysis products. The results also represent one of the most exhaustive examples of product quantification from any fuel.

9.2. Summary of Contributions to the Field

The present work includes extensive identification of PAH from the pyrolysis of the model fuel catechol, in an isothermal laminar-flow reactor at 1000 °C and 0.3 s. Product analysis reveals that catechol pyrolysis produces 111 products ranging from one to ten fused aromatic rings and falling into 8 different structural classes: 47 benzenoid PAH, 14 indene benzologues, 13 fluoranthene benzologues, 10 cyclopenta-fused PAH, 8 ethynyl-substituted species (triacetylene and 7 ethynyl-substituted aromatics), 10 methylated aromatics, 2 bi-arxls, and 7 oxygen-containing aromatics. Of the 111 products, 61 have been identified in a previous catechol pyrolysis study [96]. The 50 newly identified products of catechol pyrolysis have never before been identified as a product of catechol or any phenol-type fuel. Among the products are 15 C_{24}H_{14} PAH and 8 methylene-bridged PAH—two PAH product classes that are known to contribute significantly towards the carcinogenicity and mutagenicity of PAH mixtures [6,7,9,10,60,110,129,131-133,142,172,173]. This study has also led to the identification of 16 large (C > 25) PAH from catechol pyrolysis.
This study also describes the development of a new set of “Rules” for the prediction of the UV spectra of methylene-bridged PAH—an important class of PAH known to exhibit high biological activity [6,14,60-63,142,172,173]. These rules have been developed by comparing the UV spectrum of methylene-bridged PAH with the UV spectrum of the corresponding parent benzenoid PAH, and by using Clar’s annellation theory principles [44,45,48]. Employing these rules, two C_{24}H_{14} PAH (molecular weight 314) were identified as 5H-dibenzo[a,mno]cyclopenta[def]chrysene and 5H-dibenzo[b,mno]cyclopenta[def]chrysene. These two compounds have never before been identified as a product of any fuel. Also, these two compounds have never before been synthesized and their existence has not been documented.

A previous study [96] from our research group demonstrated the remarkable similarity in the product distribution obtained from catechol pyrolysis to that obtained from coal volatiles pyrolysis. Of the 61 products of catechol, 56 were also products of coal volatiles pyrolysis [96]. A preliminary re-analysis of the coal pyrolysis products shows that 28 of the 50 newly identified products of catechol pyrolysis are also present among the products of coal volatiles pyrolysis. Thus, 84 of the 111 catechol pyrolysis products have been detected among the products of coal volatiles pyrolysis. These 84 products include 14 of the 15 C_{24}H_{14} PAH products of catechol pyrolysis, 6 of the 8 methylene-bridged PAH products of catechol pyrolysis, and 10 of the 17 large PAH products of catechol pyrolysis. The product distribution from catechol pyrolysis is also very similar to that obtained from wood soot extracts [30,106]. This remarkable similarity in product distribution further confirms catechol’s relevancy as a model fuel for the study of solid fuels. In addition, the product distribution from 1,3-butadiene pyrolysis exhibits remarkable similarity to that obtained from catechol pyrolysis, implying the role of C_{4} species in PAH formation reactions. Since the isomer specific identification of PAH is critical to the
development of chemical pathways leading to their formation, the present study will be helpful in understanding the formation of PAH during solid fuel pyrolysis and combustion.

In addition to extensive product identification, this study also reports an exhaustive quantification of product yields from catechol pyrolysis, catechol oxidation, acetylene pyrolysis, 1,3-butadiene pyrolysis, catechol/acetylene co-pyrolysis, and catechol/1,3-butadiene co-pyrolysis. Yield/temperature profiles for the C_{1-5} species, single-ring aromatic products, as well as PAH products have been obtained at three different oxygen ratios and at nine different temperatures and compared with catechol pyrolysis yields in the absence of oxygen to delineate the effects of oxygen on these products. The coincident oxygen-induced decreases in the yields of the PAH, C_{1-5} hydrocarbons, and 1- and 2-ring aromatics at higher temperature and the oxygen-induced increases in the yields of these same products at lower temperature underscore the important role of the thermal decomposition products in the formation and growth of PAH during the pyrolysis and fuel-rich oxidation of catechol. Also, the different classes of PAH examined in this study exhibit a trend of enhanced oxygen-induced decreases in yield as PAH ring number is increased. These observations fully support findings from previous catechol pyrolysis studies [97-99] in the absence of oxygen: that PAH formation and growth occur by successive ring-buildup reactions involving the C_{1-5} and single-ring aromatic products of catechol’s thermal decomposition. Thus, this study is consistent with the implied [66-76,204,207,208,219-221] role of the thermal decomposition products (C_{1-10} species) in the formation and growth of PAH during pyrolysis and combustion of solid fuels. The oxidative pyrolysis results also indicate that 1,3-butadiene may have a major role in the formation of PAH during catechol pyrolysis and oxidation.

Yield/temperature profiles of the C_{1-5} species, single-ring aromatic products, as well as PAH products have also been obtained for acetylene pyrolysis, 1,3-butadiene pyrolysis,
catechol/acetylene co-pyrolysis, and catechol/1,3-butadiene co-pyrolysis at nine different temperatures. Each of these yields have been compared with catechol-only pyrolysis yields to delineate the effects of C₂ and C₄ species on PAH formation. Acetylene alone does not undergo much conversion, but acetylene addition to the catechol pyrolysis environment does increase the yields of the C₃ products and PAH, and facilitates consumption of the C₄ products. Unlike acetylene, 1,3-butadiene undergoes almost complete conversion in the temperature range of this study and produces all the C₁-C₅ species and single-ring aromatic products of catechol pyrolysis in addition to a range of PAH. The lower bond dissociation energy for the C-H bond in 1,3-butadiene (87.5 kcal/mol) as compared to acetylene (132 kcal/mol) leads to higher conversion of 1,3-butadiene in the temperature range of this study. The addition of 1,3-butadiene to the catechol pyrolysis environment brings about significant increases in the yields of all the products, including PAH. The increases in the yields of PAH from the catechol/1,3-butadiene co-pyrolysis experiments are significantly higher that those from the catechol/acetylene co-pyrolysis experiments, further strengthening our assertion that 1,3-butadiene is an important intermediate and/or growth species in the reactions leading to PAH formation. The results from both the co-pyrolysis experiments are consistent with acetylene addition to benzyl radical (suggested by Bittner and Howard [17]) as the dominant pathway for indene formation and cyclopentadiene self-addition mechanism (suggested by Melius et al.[67]) being the dominant naphthalene formation pathway in the catechol pyrolysis environment.

The results also suggest that catechol’s relatively labile O-H bond and capacity for generating oxygen-containing radicals accelerate fuel conversion and the pyrolysis reactions leading to 1- and 2-ring aromatics and PAH. A much higher percentage of fed carbon is converted to PAH in the catechol-only pyrolysis experiments than in the 1,3-butadiene-only pyrolysis experiments. However, when the two fuels are pyrolyzed together, 1,3-butadiene and
its decomposition products also benefit from the reaction-promoting effects of the oxygen-containing radicals from catechol, leading to elevated production of PAH. This elevated production of PAH from the catechol/1,3-butadiene co-pyrolysis experiments reflects not only the reaction-accelerating role of the oxygen-containing radicals but also the efficacy, as growth agents, of the C\textsubscript{2} and C\textsubscript{4} species abundantly present in the catechol and 1,3-butadiene pyrolysis environment. Since our catechol/acetylene co-pyrolysis and catechol/ethylene co-pyrolysis experiments produce PAH yields that are only slightly higher than those from catechol pyrolysis alone, we conclude that it is the C\textsubscript{4} species, and not the C\textsubscript{2} species, that are the more effective growth agents in the catechol/1,3-butadiene co-pyrolysis environment—at least at temperatures up to 1000 °C, the maximum temperature of our experiments.

Based on the results from this study, a tentative mechanism has been proposed for PAH formation from catechol. Since the results from this study provide strong evidence that C\textsubscript{4} species are the most important growth species in our catechol pyrolysis environment, the mechanism is based on 1,3-butadiene being the important intermediate that links catechol conversion and PAH production. The role of phenol as an intermediate cannot be ruled out though.

The present study is one of the most exhaustive quantifications of PAH and PAH precursor yields from any fuel. The data obtained from this study will contribute significantly towards delineating the effects of oxygen, acetylene, and 1,3-butadiene on the formation and fate of PAH from the pyrolysis of catechol. Most kinetic modeling studies on PAH formation have employed data from premixed laminar flames of light hydrocarbon fuels [79,80] and kinetic modeling studies for larger PAH (> 4 rings) are not available due to the lack of experimental data for these large PAH. Since no kinetic model is currently available for catechol decomposition and PAH formation from catechol, the results obtained here and in previous catechol pyrolysis
studies [25,50,96-99], collectively, will be helpful in the development of a detailed kinetic model
for PAH formation during catechol pyrolysis and fuel-rich oxidation. Since the hydrocarbons and
oxygen-containing radicals of the catechol pyrolysis experiments are also abundant in the
reaction environments of actual solid fuels, it is anticipated that the results from these catechol
studies will be directly applicable to fuel-conversion processes involving actual solid fuels.

9.3. Suggestions for Future Work

The present research has led to the identification of a large number of PAH from catechol
pyrolysis. However, there are still unidentified compounds among the catechol pyrolysis product
mixture. The identification of new products may provide clues to the identities of other products
that may be present but are not identified due to either the lack of reference standards and UV
spectra or due to very low yields. Hence, a more extensive analysis of the product mixture to
identify more products is of utmost importance. One approach in this direction would be to
synthesize compounds based on the structures of products already identified (e.g. that differ by a
single aromatic ring). The other approach is to further explore the scope of predictive tools like
Clar’s annellation theory principles and/or the rules developed in this study for identifying new
products. Also, a more detailed analysis of the UV spectra of available PAH may lead to new
rules for predicting UV spectrum of unknown compounds. The development of better solvent
programs (e.g. for the identification of oxygenated products) are also pertinent to PAH research.

The development of a comprehensive detailed mechanism for catechol pyrolysis and
oxidation is indeed one of the principal goals of our catechol research in general. Some work
[97,98] has already been done in this area and the yields/temperature data obtained in this study
would be helpful in refining the catechol decomposition mechanism proposed in a previous study
from our research group [98]. Once a catechol decomposition model is developed and tested, the
next step would be to test the extensive data from this study and from previous catechol pyrolysis
studies [97-99] against available solid fuel decomposition and PAH formation models. It is anticipated that such a modeling study would be helpful in refining the existing PAH formation models.

This study provides strong evidence that the C₄ radicals play an important role in PAH formation. Since these radicals are abundant in pyrolysis and combustion environment, the role of the C₄ radicals should be given more importance in future modeling studies on PAH formation. The modeling studies would also benefit from pyrolysis and co-pyrolysis studies with other C₁-C₅ compounds like propyne, ethylene, and cyclopentadiene. Studies with a mixture of these C₁-C₅ species in the presence or absence of catechol would be useful. Since the role of oxidative radicals, OH in particular, has been implied from the present results, introducing oxidative radicals to the 1,3-butadiene pyrolysis environment would be helpful in testing the results from this study.

Pyrolysis experiments with isomers of catechol—resorcinol (meta-hydroxybenzene) and hydroquinone (para-hydroxybenzene)—would be helpful in understanding catechol decomposition mechanisms as these differ only in the placement of the two OH group with reference to the aromatic ring. The product distribution from these experiments will be helpful in understanding the effect of this minor structural difference in fuel decomposition and product formation mechanisms.

In addition to aromatic and aliphatic hydrocarbon units, solid fuels like coal, wood, and biomass also contain inorganic matter [278-282] in elemental form (e.g. Ca, Mg, Fe, Ni) and/or as mineral matter (e.g. calcium carbonate, ammonia, pyrite, quartz, hematite, magnetite, calcite). Some inorganics are also introduced into the combustion environment of solid fuels for particular reasons (e.g. iron oxide to catalyze CO oxidation [283], calcium oxide during gasification [284,285]). Since these inorganics can have their own effects on hydrocarbon
products and/or can participate in gas-solid reactions during solid fuel pyrolysis and combustion [286,287], the effects of these inorganics on catechol decomposition and PAH formation also need to be addressed.
References


[249] Colket MB. Pyrolysis of 1,3-Butadiene in a Single-Pulse Shock Tube, The Combustion Institute, Easter States Section Fall Meeting, Providence, RI, 1983,


## Appendix A. Catechol Pyrolysis Products

### Table A1. Products of Catechol Pyrolysis in Figure 3.1.

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<thead>
<tr>
<th>Product Name (by Class)</th>
<th>Formula</th>
<th>Structure</th>
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</thead>
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<tr>
<td><strong>Benzenoid PAH (black structures in Figure 3.1)</strong></td>
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<tr>
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**Indene Benzologues (green structures in Figure 3.1)**

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| 1H-Benzo[ghi]cyclopenta[pqr]perylene | C$_{23}$H$_{12}$ | ![Structure](image1)
| 5H-Dibenzo[a,mno]cyclopenta[def]chrysene | C$_{25}$H$_{14}$ | ![Structure](image2)
| 5H-Dibenzo[b,mno]cyclopenta[def]chrysene | C$_{25}$H$_{14}$ | ![Structure](image3)

**Fluoranthenene Benzologues (dark blue structures in Figure 3.1)**

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<th>Structure</th>
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| Fluoranthenene$^a$ | C$_{16}$H$_{10}$ | ![Structure](image4)
| Benzo[a]fluoranthenene$^a$ | C$_{20}$H$_{12}$ | ![Structure](image5)
| Benzo[j]fluoranthenene$^a$ | C$_{20}$H$_{12}$ | ![Structure](image6)
| Benzo[b]fluoranthenene$^a$ | C$_{20}$H$_{12}$ | ![Structure](image7)
| Benzo[k]fluoranthenene$^a$ | C$_{20}$H$_{12}$ | ![Structure](image8)
| Indeno[1,2,3-cd]pyrene$^a$ | C$_{22}$H$_{12}$ | ![Structure](image9)
| Indeno[1,2,3-cd]fluoranthenene$^c$ | C$_{22}$H$_{12}$ | ![Structure](image10)
| Naphtho[1,2-b]fluoranthenene | C$_{24}$H$_{14}$ | ![Structure](image11)
| Naphtho[1,2-k]fluoranthenene | C$_{24}$H$_{14}$ | ![Structure](image12)
| Dibenzo[b,k]fluoranthenene | C$_{24}$H$_{14}$ | ![Structure](image13)
<table>
<thead>
<tr>
<th>Product Name (by Class)</th>
<th>Formula</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphtho[2,3-\textit{b}]fluoranthene</td>
<td>C$<em>{24}$H$</em>{14}$</td>
<td><img src="image1" alt="Structure" /></td>
</tr>
<tr>
<td>Naphtho[2,3-\textit{k}]fluoranthene</td>
<td>C$<em>{24}$H$</em>{14}$</td>
<td><img src="image2" alt="Structure" /></td>
</tr>
<tr>
<td>Benzo[\textit{a}]indeno[1,2,3-\textit{cd}]pyrene</td>
<td>C$<em>{26}$H$</em>{14}$</td>
<td><img src="image3" alt="Structure" /></td>
</tr>
</tbody>
</table>

**Cyclopenta-Fused PAH (red structures in Figure 3.1)**

<table>
<thead>
<tr>
<th>Product Name (by Class)</th>
<th>Formula</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acenaphthylene$^a$</td>
<td>C$<em>{12}$H$</em>{8}$</td>
<td><img src="image4" alt="Structure" /></td>
</tr>
<tr>
<td>Acephenanthrylene$^a$</td>
<td>C$<em>{16}$H$</em>{10}$</td>
<td><img src="image5" alt="Structure" /></td>
</tr>
<tr>
<td>Aceanthrylene$^a$</td>
<td>C$<em>{16}$H$</em>{10}$</td>
<td><img src="image6" alt="Structure" /></td>
</tr>
<tr>
<td>Cyclopent[\textit{hi}]acephenanthrylene$^a$</td>
<td>C$<em>{18}$H$</em>{10}$</td>
<td><img src="image7" alt="Structure" /></td>
</tr>
<tr>
<td>Cyclopenta[\textit{cd}]fluoranthene$^a$</td>
<td>C$<em>{18}$H$</em>{10}$</td>
<td><img src="image8" alt="Structure" /></td>
</tr>
<tr>
<td>Cyclopenta[\textit{cd}]pyrene$^a$</td>
<td>C$<em>{18}$H$</em>{10}$</td>
<td><img src="image9" alt="Structure" /></td>
</tr>
<tr>
<td>Dicyclopenta[\textit{cd,\textit{mn}}]pyrene$^a$</td>
<td>C$<em>{20}$H$</em>{10}$</td>
<td><img src="image10" alt="Structure" /></td>
</tr>
<tr>
<td>Dicyclopenta[\textit{cd,\textit{jk}}]pyrene$^a$</td>
<td>C$<em>{20}$H$</em>{10}$</td>
<td><img src="image11" alt="Structure" /></td>
</tr>
<tr>
<td>Cyclopenta[\textit{cd}]benzo[\textit{ghi}]perylene$^a$</td>
<td>C$<em>{24}$H$</em>{12}$</td>
<td><img src="image12" alt="Structure" /></td>
</tr>
<tr>
<td>Cyclopenta[\textit{bc}]coronene$^a$</td>
<td>C$<em>{26}$H$</em>{12}$</td>
<td><img src="image13" alt="Structure" /></td>
</tr>
<tr>
<td>Product Name (by Class)</td>
<td>Formula</td>
<td>Structure</td>
</tr>
<tr>
<td>-------------------------------------------------</td>
<td>----------</td>
<td>-----------</td>
</tr>
<tr>
<td><strong>Ethynyl-Substituted Species (purple structures in Figure 3.1)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phenylacetylene&lt;sup&gt;a&lt;/sup&gt;</td>
<td>C&lt;sub&gt;8&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt;</td>
<td><a href="#">Structure</a></td>
</tr>
<tr>
<td>2-Ethynynaphthalene&lt;sup&gt;a&lt;/sup&gt;</td>
<td>C&lt;sub&gt;12&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;</td>
<td><a href="#">Structure</a></td>
</tr>
<tr>
<td>1-Ethynylacenaphthylene&lt;sup&gt;a&lt;/sup&gt;</td>
<td>C&lt;sub&gt;14&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;</td>
<td><a href="#">Structure</a></td>
</tr>
<tr>
<td>5-Ethynylacenaphthylene&lt;sup&gt;a&lt;/sup&gt;</td>
<td>C&lt;sub&gt;14&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;</td>
<td><a href="#">Structure</a></td>
</tr>
<tr>
<td>3-Ethynylphenanthrene&lt;sup&gt;a&lt;/sup&gt;</td>
<td>C&lt;sub&gt;16&lt;/sub&gt;H&lt;sub&gt;10&lt;/sub&gt;</td>
<td><a href="#">Structure</a></td>
</tr>
<tr>
<td>2-Ethynylphenanthrene&lt;sup&gt;a&lt;/sup&gt;</td>
<td>C&lt;sub&gt;16&lt;/sub&gt;H&lt;sub&gt;10&lt;/sub&gt;</td>
<td><a href="#">Structure</a></td>
</tr>
<tr>
<td>2-Ethynylanthracene&lt;sup&gt;a&lt;/sup&gt;</td>
<td>C&lt;sub&gt;16&lt;/sub&gt;H&lt;sub&gt;10&lt;/sub&gt;</td>
<td><a href="#">Structure</a></td>
</tr>
<tr>
<td>Triacetylene&lt;sup&gt;a&lt;/sup&gt;</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;</td>
<td><a href="#">Structure</a></td>
</tr>
<tr>
<td><strong>Bi-aryls (gray structures in Figure 3.1)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Biphenyl&lt;sup&gt;a&lt;/sup&gt;</td>
<td>C&lt;sub&gt;12&lt;/sub&gt;H&lt;sub&gt;10&lt;/sub&gt;</td>
<td><a href="#">Structure</a></td>
</tr>
<tr>
<td>1-Phenylnaphthalene&lt;sup&gt;a&lt;/sup&gt;</td>
<td>C&lt;sub&gt;16&lt;/sub&gt;H&lt;sub&gt;12&lt;/sub&gt;</td>
<td><a href="#">Structure</a></td>
</tr>
<tr>
<td><strong>Methyl-Substituted Aromatics (light blue structures in Figure 3.1)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Toluene&lt;sup&gt;a&lt;/sup&gt;</td>
<td>C&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;</td>
<td><a href="#">Structure</a></td>
</tr>
<tr>
<td>1-Methylnaphthalene&lt;sup&gt;a&lt;/sup&gt;</td>
<td>C&lt;sub&gt;11&lt;/sub&gt;H&lt;sub&gt;10&lt;/sub&gt;</td>
<td><a href="#">Structure</a></td>
</tr>
<tr>
<td>2-Methylnaphthalene&lt;sup&gt;a&lt;/sup&gt;</td>
<td>C&lt;sub&gt;11&lt;/sub&gt;H&lt;sub&gt;10&lt;/sub&gt;</td>
<td><a href="#">Structure</a></td>
</tr>
<tr>
<td>3-Methylphenanthrene</td>
<td>C&lt;sub&gt;15&lt;/sub&gt;H&lt;sub&gt;12&lt;/sub&gt;</td>
<td><a href="#">Structure</a></td>
</tr>
</tbody>
</table>
Table A.1. (continued)

<table>
<thead>
<tr>
<th>Product Name (by Class)</th>
<th>Formula</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Methylanthracene</td>
<td>C\text{15}H\text{12}</td>
<td><img src="image1" alt="Structure" /></td>
</tr>
<tr>
<td>2-Methylanthracene</td>
<td>C\text{15}H\text{12}</td>
<td><img src="image2" alt="Structure" /></td>
</tr>
<tr>
<td>1-Methylpyrene</td>
<td>C\text{17}H\text{12}</td>
<td><img src="image3" alt="Structure" /></td>
</tr>
<tr>
<td>2-Methylpyrene</td>
<td>C\text{17}H\text{12}</td>
<td><img src="image4" alt="Structure" /></td>
</tr>
<tr>
<td>4-Methylpyrene</td>
<td>C\text{17}H\text{12}</td>
<td><img src="image5" alt="Structure" /></td>
</tr>
<tr>
<td>1-Methylcoronene</td>
<td>C\text{25}H\text{14}</td>
<td><img src="image6" alt="Structure" /></td>
</tr>
</tbody>
</table>

**Oxygen-Containing Aromatics (brown structures in Figure 3.1)**

<table>
<thead>
<tr>
<th>Product Name</th>
<th>Formula</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Naphthol\textsuperscript{a}</td>
<td>C\text{10}H\text{8}O</td>
<td><img src="image7" alt="Structure" /></td>
</tr>
<tr>
<td>2-Naphthol</td>
<td>C\text{10}H\text{8}O</td>
<td><img src="image8" alt="Structure" /></td>
</tr>
<tr>
<td>Dibenzofuran\textsuperscript{a}</td>
<td>C\text{12}H\text{8}O</td>
<td><img src="image9" alt="Structure" /></td>
</tr>
<tr>
<td>Phenalenone\textsuperscript{a}</td>
<td>C\text{13}H\text{8}O</td>
<td><img src="image10" alt="Structure" /></td>
</tr>
<tr>
<td>9-Fluorenone\textsuperscript{a}</td>
<td>C\text{13}H\text{8}O</td>
<td><img src="image11" alt="Structure" /></td>
</tr>
<tr>
<td>Benzanthrone</td>
<td>C\text{17}H\text{10}O</td>
<td><img src="image12" alt="Structure" /></td>
</tr>
<tr>
<td>6\textit{H}-benzo[\textit{cd}]pyren-6-one</td>
<td>C\text{19}H\text{10}O</td>
<td><img src="image13" alt="Structure" /></td>
</tr>
</tbody>
</table>

\textsuperscript{a} Identified in a previous catechol pyrolysis study [Wornat et al., 2001].

\textsuperscript{b} 6\textit{H}-Dibenzo[\textit{a,\textit{jk}}]pyrene has a methylene carbon and hence is not fully unsaturated.

\textsuperscript{c} Indeno[1,2,3-\textit{cd}]fluoranthene is an indeno-fused fluoranthene.
Appendix B. Characterization of the Reactor System

B.1. Vaporizer Calibration

The vaporizer calibrations are done using an Agilent Model 6890/5973 GC/FID/MS. A 2μL aliquot of known concentrations of catechol dissolved in dichloromethane is injected by syringe, through a split injector, onto a HP-5 fused silica capillary column (30m X 0.25 mm X 0.1μm). The calibration curve is shown in Figure B.1.

![Graph showing the calibration curve for catechol with the equation y = 3.1413E-09x and R² = 9.9781E-01](image)

Figure B.1. GC-FID calibration curve for catechol.

For the vaporizer calibration, sample is taken from the vaporizer exit stream before and after each pyrolysis run, dissolved in dichloromethane, and analyzed on the GC-FID. The calibration results for a few calibration runs are summarized in Table B.1

<table>
<thead>
<tr>
<th>CH₂Cl₂ (mL)</th>
<th>tₜ (min)</th>
<th>Temperature (°C)</th>
<th>Pressure (psi)</th>
<th>Flow (sccm)</th>
<th>Peak Area</th>
<th>Conc (mg/mL)</th>
<th>Mass (g)</th>
<th>Feedrate (g/s)</th>
<th>% C</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>30</td>
<td>85.00</td>
<td>15.00</td>
<td>90.00</td>
<td>42543859</td>
<td>1.34E-01</td>
<td>1.34E-02</td>
<td>7.42E-06</td>
<td>0.66</td>
</tr>
<tr>
<td>100</td>
<td>75</td>
<td>85.00</td>
<td>15.00</td>
<td>90.00</td>
<td>104981601</td>
<td>3.30E-01</td>
<td>3.30E-02</td>
<td>7.33E-06</td>
<td>0.65</td>
</tr>
<tr>
<td>100</td>
<td>30</td>
<td>85.00</td>
<td>15.00</td>
<td>100.00</td>
<td>46488929</td>
<td>1.46E-01</td>
<td>1.46E-02</td>
<td>8.11E-06</td>
<td>0.65</td>
</tr>
<tr>
<td>100</td>
<td>30</td>
<td>85.00</td>
<td>15.00</td>
<td>90.00</td>
<td>40456781</td>
<td>1.27E-01</td>
<td>1.27E-02</td>
<td>7.06E-06</td>
<td>0.63</td>
</tr>
<tr>
<td>100</td>
<td>75</td>
<td>85.00</td>
<td>15.00</td>
<td>100.00</td>
<td>118945328</td>
<td>3.74E-01</td>
<td>3.74E-02</td>
<td>8.30E-06</td>
<td>0.66</td>
</tr>
</tbody>
</table>
B.2. Temperature Characterization of the Reactor

The furnace has been calibrated between 500 and 1000 °C with a thermocouple (Omega; Model #: KMQXL-032U-40) placed at various locations inside the reactor with nitrogen gas flowing (0.3 s residence time). Table B.1 shows the thermocouple reading along the length of the reactor for the different temperature setting. The temperature drops off sharply at both ends. The heated length of the reactor is 22 in (55.88 cm).

Table B.2. Reactor Temperature Calibration

<table>
<thead>
<tr>
<th>Set Point (°C)</th>
<th>Distance from the End of Reactor (in inches)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>30</td>
</tr>
<tr>
<td>500</td>
<td>486</td>
</tr>
<tr>
<td>600</td>
<td>584</td>
</tr>
<tr>
<td>700</td>
<td>685</td>
</tr>
<tr>
<td>750</td>
<td>738</td>
</tr>
<tr>
<td>800</td>
<td>786</td>
</tr>
<tr>
<td>850</td>
<td>836</td>
</tr>
<tr>
<td>900</td>
<td>884</td>
</tr>
<tr>
<td>950</td>
<td>935</td>
</tr>
<tr>
<td>1000</td>
<td>986</td>
</tr>
</tbody>
</table>

B.2. Residence Time Calculations

Reactor radius = 0.1 cm
Reactor length = 55.88 cm
Reactor volume = 1.76 cm³
Room Temperature = 25 °C

Table B.3. Reactor Residence Time Calculation

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Flow (sccm)*</th>
<th>V (cm³/sec)</th>
<th>Residence Time (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>79</td>
<td>5.6246</td>
<td>0.3122</td>
</tr>
<tr>
<td>950</td>
<td>82</td>
<td>5.6088</td>
<td>0.3131</td>
</tr>
<tr>
<td>900</td>
<td>86</td>
<td>5.6419</td>
<td>0.3113</td>
</tr>
<tr>
<td>850</td>
<td>90</td>
<td>5.6527</td>
<td>0.3107</td>
</tr>
<tr>
<td>800</td>
<td>94</td>
<td>5.6411</td>
<td>0.3113</td>
</tr>
<tr>
<td>750</td>
<td>98</td>
<td>5.6070</td>
<td>0.3132</td>
</tr>
<tr>
<td>700</td>
<td>100</td>
<td>5.4418</td>
<td>0.3227</td>
</tr>
<tr>
<td>600</td>
<td>100</td>
<td>4.8826</td>
<td>0.3597</td>
</tr>
<tr>
<td>500</td>
<td>100</td>
<td>4.3233</td>
<td>0.4062</td>
</tr>
</tbody>
</table>

*Readout form the mass flow controller
Appendix C. GC and HPLC Methods

C.1. Temperature Programs for GC/FID/MS

The separation of the C<sub>1</sub>-C<sub>6</sub> hydrocarbon products and the light (< 3-rings) aromatic products is achieved on the Agilent Model 6890/5973 GC/FID/MS. The temperature programs for the C<sub>1</sub>-C<sub>6</sub> hydrocarbon products and the light (< 3-rings) aromatic products are presented in Figures C.1 and C.2, respectively.

![Figure C.1. Temperature program for C<sub>1</sub>-C<sub>6</sub> hydrocarbon products](image1)

**Figure C.1.** Temperature program for C<sub>1</sub>-C<sub>6</sub> hydrocarbon products

![Figure C.2. Temperature program for light aromatic products](image2)

**Figure C.2.** Temperature program for light aromatic products
C.1. Solvent Program for HPLC

PAH products are analyzed on a Hewlett-Packard Model 1050 chromatograph, coupled to a diode-array ultraviolet-visible absorbance detector (HPLC/UV). MS data are obtained from an Agilent Model 1100 chromatograph, coupled to a diode-array ultraviolet-visible absorbance detector in series with a mass spectrometer (HPLC/UV/MS). The solvent programs for the HPLC/UV and the HPLC/UV/MS are presented in Figures C.3 and C.4, respectively.

**Figure C.3.** Solvent program for HPLC/UV.

**Figure C.4.** Solvent program for HPLC/UV/MS.
Appendix D. Product Analysis: GC and HPLC Calibrations

D.1. Calibration of the GC/FID

The quantification of the C\textsubscript{1}-C\textsubscript{10} products is based on the calibration of the GC/FID with reference standards. For the C\textsubscript{1}-C\textsubscript{6} gas-phase products, a single point calibration was performed using a standard gas mixture. Since reference standards of cyclopentadiene and vinylacetylene are not available, an average value (average of benzene and 1,3-butadiene) was used for cyclopentadiene and the response factor for vinylacetylene is assigned the same value as 1,3-butadiene. The response factors and GC retention times for the C\textsubscript{1}-C\textsubscript{6} gas-phase products are presented in Table D.1.

**GC 6890 Conditions:**

<table>
<thead>
<tr>
<th>Column Flowrate (mL/min)</th>
<th>5.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>FID Temperature (°C)</td>
<td>250</td>
</tr>
<tr>
<td>Front Injection Temperature (°C)</td>
<td>150</td>
</tr>
<tr>
<td>Front Port Initial Head Pressure (psi)</td>
<td>14.5</td>
</tr>
<tr>
<td>Injection Volume (µL)</td>
<td>500.0</td>
</tr>
<tr>
<td>Split Ratio</td>
<td>5.0</td>
</tr>
</tbody>
</table>

**Table D.1. Response Factors and Retention Times for the C\textsubscript{1}-C\textsubscript{6} Gas-Phase Hydrocarbons**

<table>
<thead>
<tr>
<th>C\textsubscript{1}-C\textsubscript{6} Hydrocarbons</th>
<th>Response Factor (ppm / Area Units)</th>
<th>GC Retention Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>methane</td>
<td>4.537</td>
<td>1.2</td>
</tr>
<tr>
<td>ethane</td>
<td>2.482</td>
<td>1.8</td>
</tr>
<tr>
<td>ethylene</td>
<td>2.528</td>
<td>2.4</td>
</tr>
<tr>
<td>acetylene</td>
<td>2.170</td>
<td>3.9</td>
</tr>
<tr>
<td>propane</td>
<td>1.626</td>
<td>4.7</td>
</tr>
<tr>
<td>propene</td>
<td>1.646</td>
<td>8.2</td>
</tr>
<tr>
<td>propadiene</td>
<td>1.659</td>
<td>8.4</td>
</tr>
<tr>
<td>propyne</td>
<td>1.649</td>
<td>14.5</td>
</tr>
<tr>
<td>1,3-butadiene</td>
<td>1.298</td>
<td>15.3</td>
</tr>
<tr>
<td>vinylacetylene*</td>
<td>1.298</td>
<td>17.1</td>
</tr>
<tr>
<td>cyclopentadiene*</td>
<td>1.092</td>
<td>20.2</td>
</tr>
<tr>
<td>benzene</td>
<td>0.887</td>
<td>23.4</td>
</tr>
</tbody>
</table>

* Reference standards not available.

\[
\text{Conc. (ppm)} = (\text{Area}) \times (\text{Response Factor})
\]
For the light aromatic (≤ 3-rings) products, a five-point calibration was performed by preparing solutions of the reference standards of the light aromatics in dichloromethane at 5 different known concentrations. The response factors and the GC retention times for the light aromatic (≤ 3-rings) products are presented in Table D.2.

**GC 6890 Conditions:**
Front Column HP-5
Front Column Velocity (cm/s) 2.0
FID Temperature (°C) 300
Front Injection Temperature (°C) 280
Front Port Initial Head Pressure (psi) 9.1
Injection Volume (µL) 2.0

**Table D.2. Response Factors and Retention Times for the Light Aromatic Compounds**

<table>
<thead>
<tr>
<th>Light Aromatics</th>
<th>Response Factor (mg mL(^{-1}) / Area Units)</th>
<th>GC Retention Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>toluene</td>
<td>3.123E-09</td>
<td>3.8</td>
</tr>
<tr>
<td>2-cyclopenten-1-one</td>
<td>3.565E-09</td>
<td>5.4</td>
</tr>
<tr>
<td>ethylbenzene</td>
<td>2.316E-09</td>
<td>6.2</td>
</tr>
<tr>
<td>phenylacetylene</td>
<td>2.319E-09</td>
<td>6.7</td>
</tr>
<tr>
<td>benzaldehyde</td>
<td>3.03E-09</td>
<td>7.2</td>
</tr>
<tr>
<td>styrene</td>
<td>2.297E-09</td>
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<tr>
<td>anthracene</td>
<td>2.940E-09</td>
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</tr>
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</table>

\[
\text{Conc. (mg/mL)} = \text{(Area)} \times \text{(Response Factor)}
\]
D.2. Calibration of the HPLC/UV

For most of the PAH quantified in this study, the UV absorbance detector has been calibrated with known concentrations of the respective reference standards. A five-point calibration was performed by preparing solutions of 16 PAH reference standards in dimethylesulfoxide at 5 different concentrations. Figure D.1 shows a typical calibration curve for a PAH. The response of the UV detector is linear for lower concentrations (>0.05 mg/mL) and quadratic for higher concentration. Hence, two different equations are used for the calculation of product concentrations based on the calibration—a straight line fit (using the three lower concentrations data points) for low concentration and a quadratic fit for higher concentration. Thus, we have

\[
\text{Conc. (mg/mL)} = m \times \text{Area}; \text{ for low conc. (e.g. } A < 2000 \text{ for pyrene)}
\]

\[
\text{Conc. (mg/mL)} = m_1 \times \text{Area} + m_2 \times \text{Area}^2; \text{ for high conc. (e.g. } A > 2000 \text{ for pyrene)}
\]

![Calibration curve for pyrene](image)

**Figure D.1. Calibration curve for pyrene**

**HPLC/UV 1050 Conditions:**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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<tr>
<td>Column</td>
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<td>Column Flowrate (mL/min)</td>
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<tr>
<td>Injection Volume (µL)</td>
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</tr>
<tr>
<td>Temperature (°C)</td>
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</tr>
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</table>
Table D.3. Response Factors and Retention Times for Polycyclic Aromatic Hydrocarbons

<table>
<thead>
<tr>
<th>Polycyclic Aromatic Hydrocarbons</th>
<th>Conc. (mg/mL) = m1<em>A + m2</em>A^N</th>
<th>Conc. (mg/mL) = m*A</th>
<th>HPLC Retention Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>naphthalene</td>
<td>1.78E-05</td>
<td>2.54E-08</td>
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<tr>
<td>acenaphthylene</td>
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<td>phenanthrene</td>
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<td>anthracene</td>
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<td>fluoranthene</td>
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<td>1.24E-09</td>
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<tr>
<td>chrysene</td>
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<td>1.97E-09</td>
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<td>benzo[b]fluoranthene</td>
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<td>benzo[k]fluoranthene</td>
<td>1.46E-05</td>
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<td>benzo[a]pyrene</td>
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<td>6.64E-10</td>
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<td>dibenz[a,h]anthracene</td>
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<td>1.51E-09</td>
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<td>benzo[ghi]pyrene</td>
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<td>8.47E-10</td>
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<td>indeno[123-cd]pyrene</td>
<td>1.61E-05</td>
<td>4.82E-10</td>
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</table>

Compounds for which reference standards are not available, response factors (m, m1, and m2) of structurally similar compounds (surrogate compounds) have been used. Table D.4 lists these product compounds along with the respective surrogate compounds.

Table D.4. Surrogate Compounds for HPLC Calibration

<table>
<thead>
<tr>
<th>Product Compound</th>
<th>Response Factor from:</th>
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<td>2-Ethynynaphthalene</td>
<td>Naphthalene</td>
</tr>
<tr>
<td>1-Ethynylacenaphthylene</td>
<td>Acenaphthylene</td>
</tr>
<tr>
<td>5-Ethynylacenaphthylene</td>
<td>Acenaphthylene</td>
</tr>
<tr>
<td>Benz[j]indene</td>
<td>Fluorene</td>
</tr>
<tr>
<td>3-Ethynylphenanthrene</td>
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<tr>
<td>Acephenanthrylene</td>
<td>Phenanthrene</td>
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<tr>
<td>2-Ethynylphenanthrene</td>
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<td>Benzo[c]phenanthrene</td>
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<td>Triphenylene</td>
<td>Benz[a]anthracene</td>
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<td>Cyclopent[hi]acephenanthylene</td>
<td>Cyclopenta[cd]pyrene</td>
</tr>
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<td>Benzo[a]fluorene</td>
<td>Fluorene</td>
</tr>
<tr>
<td>Cyclopenta[cd]fluoranthene</td>
<td>Cyclopenta[cd]pyrene</td>
</tr>
<tr>
<td>Dicyclopenta[cd,mn]pyrene</td>
<td>Cyclopenta[cd]pyrene</td>
</tr>
<tr>
<td>Benzo[j]fluoranthene</td>
<td>Benzo[k]fluoranthene</td>
</tr>
<tr>
<td>Dicyclopenta[cd,jk]pyrene</td>
<td>Cyclopenta[cd]pyrene</td>
</tr>
<tr>
<td>Dibenz[a,j]anthracene</td>
<td>Dibenz[a,h]anthracene</td>
</tr>
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<td>Benzo[h]chrysene</td>
<td>Chrysene</td>
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<tr>
<td>Anthanthrene</td>
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<td>Picene</td>
<td>Chrysene</td>
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<tr>
<td>Coronene</td>
<td>Benzo[ghi]pyrene</td>
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## Appendix E. Carbon Balance

### Table E.1. Carbon Balance for the Catechol Pyrolysis and Oxidation Experiments

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Appendix F. Spectral Matches for PAH

Figure F.1. UV absorbance spectra of the reference standard (dashed line) / catechol pyrolysis product component (solid line) pairs: (a) 2-naphthol and catechol pyrolysis product component eluting at 5.8 min in Figure 3.1; (b) benzanthrone and catechol pyrolysis product component eluting at 19.7 min in Figure 3.1; (c) 6H-benzo[cd]pyrene-6-one and catechol pyrolysis product component eluting at 28.1 min in Figure 3.1; (d) 3-methylphenanthrene [Friedel, 1951] and catechol pyrolysis product component eluting at 23.5 min in Figure 3.1; (e) 1-methylanthracene and catechol pyrolysis product component eluting at 25.2 min in Figure 3.1; (f) 2-methylanthracene and catechol pyrolysis product component eluting at 29.1 min in Figure 3.1.
Figure F.2. UV absorbance spectra of the reference standard (dashed line) / catechol pyrolysis product component (solid line) pairs: (a) 4-methylpyrene [Friedel, 1951] and catechol pyrolysis product component eluting at 30.6 min in Figure 3.1; (b) 1-methylpyrene and catechol pyrolysis product component eluting at 31.0 min in Figure 3.1; (c) 2-methylpyrene [Friedel, 1951] and catechol pyrolysis product component eluting at 31.9 min in Figure 3.1; (d) benzo[b]fluorene and catechol pyrolysis product component eluting at 32.4 min in Figure 3.1; (e) dibenz[a,c]anthracene and catechol pyrolysis product component eluting at 37.8 min in Figure 3.1; (f) benzo[c]chrysene and catechol pyrolysis product component eluting at 37.9 min in Figure 3.1.
**Figure F.3.** UV absorbance spectra of the reference standard (dashed line) / catechol pyrolysis product component (solid line) pairs: (a) naphthacene [Freidel, 1951] and catechol pyrolysis product component eluting at 40.8 min in Figure 3.1; (b) pentaphene and catechol pyrolysis product component eluting at 41.8 min in Figure 3.1.

**Figure F.4.** (a) Mass spectrum of a catechol pyrolysis product component eluting at 58.2 min in Figure 1. (b) UV absorbance spectrum of a catechol pyrolysis product component eluting at 58.2 min in Figure 3.1 along with that of $8H$-dibenzo[a,jk]pyrene published in the literature [Clar, 1964]. The solvent used in the reference standard is different from the solvent of the catechol pyrolysis product sample (ACN/DCM), resulting in the slight shift in the UV spectrum of the reference standard with reference to the catechol pyrolysis product component. (The mass spectrum is obtained using the water/methanol/dichloromethane solvent program on the HPLC/UV/MS.)
**Figure F.5.** (a) Mass spectrum of a catechol pyrolysis product component eluting at 71.3 min in Figure 3.1. (b) UV absorbance spectrum of a catechol pyrolysis product component eluting at 71.3 min in Figure 3.1 along with that of coronene reference standard. The bathochromic shift towards longer wavelengths in the UV spectrum of the catechol pyrolysis product component is due to methyl-substitution on coronene. (The mass spectrum is obtained using the water/methanol/dichloromethane solvent program on the HPLC/UV/MS.)

**Figure F.6.** (a) Mass spectrum of a catechol pyrolysis product component eluting at 38.0 min in Figure 3.1. (b) UV absorbance spectrum of a catechol pyrolysis product component eluting at 38.0 min in Figure 3.1 along with that of methyl dibenzo[a,h]fluorene published in literature [Somers et al., 2007]. The bathochromic shift towards shorter wavelengths in the UV spectrum of the catechol pyrolysis product component is due to the absence of methyl-substitution. Thus the catechol pyrolysis product component is dibenzo[a,h]fluorene. (The mass spectrum is obtained using the water/acetonitrile/dichloromethane solvent program on the HPLC/UV/MS.)
Appendix G. Effects of Acetylene on the Yield/Temperature Profiles of PAH ≥ 3 Rings

Figure G.1. Yields, as functions of temperature, of: (a) phenanthrene, (b) pyrene, (c) chrysene, and (d) benz[a]anthracene. Experiments: catechol pyrolysis (■); acetylene pyrolysis (●); catechol/acetylene co-pyrolysis (▲). Weighted sum values (∆) calculated from Eq. (1) in Chapter VIII.
Figure G.2. Yields, as functions of temperature, of: (a) triphenylene, (b) benzo[a]pyrene, (c) benzo[ghi]perylene, and (d) anthanthrene. Experiments: catechol pyrolysis (■); acetylene pyrolysis (●); catechol/ acetylene co-pyrolysis (▲). Weighted sum values (Δ) calculated from Eq. (1) in Chapter VIII.
Figure G.3. Yields, as functions of temperature, of: (a) picene, and (b) coronene. Experiments: catechol pyrolysis (■); acetylene pyrolysis (●); catechol/acetylene co-pyrolysis (▲). Weighted sum values (Δ) calculated from Eq. (1) in Chapter VIII.
Figure G.4. Yields, as functions of temperature, of: (a) fluorene, (b) benz[f]indene, (c) 4H-cyclopenta[def]phenanthrene, and (d) benzo[a]fluorene. Experiments: catechol pyrolysis (■); acetylene pyrolysis (●); catechol/acetylene co-pyrolysis (▲). Weighted sum values (∆) calculated from Eq. (1) in Chapter VIII.
Figure G.5. Yields, as functions of temperature, of: (a) fluoranthene, (b) benzo[\(\alpha\)]fluoranthene, (c) benzo[\(k\)]fluoranthene, and (d) indeno[1,2,3-\(cd\)]pyrene. Experiments: catechol pyrolysis (■); acetylene pyrolysis (●); catechol/acetylene co-pyrolysis (▲). Weighted sum values (△) calculated from Eq. (1) in Chapter VIII.
Figure G.6. Yields, as functions of temperature, of: (a) acenaphthylene, (b) acephenanthrylene, (c) cyclopent[hi]acephenanthrylene, and (d) cyclopenta[cd]pyrene. Experiments: catechol pyrolysis (■); acetylene pyrolysis (●); catechol/acetylene co-pyrolysis (▲). Weighted sum values (∆) calculated from Eq. (1) in Chapter VIII.
Figure G.7. Yields, as functions of temperature, of: (a) 2-ethynlnaphthalene, (b) 1-ethynylacenaphthylene, (c) 5-ethynylacenaphthylene, and (d) 2-ethynylphenanthrene. Experiments: catechol pyrolysis (■); acetylene pyrolysis (●); catechol/acetylene co-pyrolysis (▲). Weighted sum values (△) calculated from Eq. (1) in Chapter VIII.
Appendix H. Effects of 1,3-Butadiene on the Yield/Temperature Profiles of PAH ≥ 3 Rings

Figure H.1. Yields, as functions of temperature, of: (a) phenanthrene, (b) pyrene, (c) chrysene, and (d) benz[a]anthracene. Experiments: catechol pyrolysis (■); 1,3-butadiene pyrolysis (●); catechol/1,3-butadiene co-pyrolysis (▲). Weighted sum values (Δ) calculated from Eq. (2) in Chapter VIII.
Figure H.2. Yields, as functions of temperature, of: (a) triphenylene, (b) benzo[a]pyrene, (c) benzo[ghi]perylene, and (d) anthanthrene. Experiments: catechol pyrolysis (■); 1,3-butadiene pyrolysis (●); catechol/1,3-butadiene co-pyrolysis (▲). Weighted sum values (Δ) calculated from Eq. (2) in Chapter VIII.
Figure H.3. Yields, as functions of temperature, of: (a) picene, and (b) coronene. Experiments: catechol pyrolysis (■); 1,3-butadiene pyrolysis (●); catechol/1,3-butadiene co-pyrolysis (▲). Weighted sum values (∆) calculated from Eq. (2) in Chapter VIII.
Figure H.4. Yields, as functions of temperature, of: (a) fluorene, (b) benz[f]indene, (c) 4H-cyclopenta[def]phenanthrene, and (d) benzo[a]fluorene. Experiments: catechol pyrolysis (■); 1,3-butadiene pyrolysis (●); catechol/1,3-butadiene co-pyrolysis (▲). Weighted sum values (Δ) calculated from Eq. (2) in Chapter VIII.
Figure H.5. Yields, as functions of temperature, of: (a) fluoranthene, (b) benzo[b]fluoranthene, (c) benzo[k]fluoranthene, and (d) indeno[1,2,3-cd]pyrene. Experiments: catechol pyrolysis (■); 1,3-butadiene pyrolysis (●); catechol/1,3-butadiene co-pyrolysis (▲). Weighted sum values (Δ) calculated from Eq. (2) in Chapter VIII.
Figure H.6. Yields, as functions of temperature, of: (a) acenaphthylene, (b) acephenanthrylene, (c) cyclopent[hi]acephenanthrylene, and (d) cyclopenta[cd]pyrene. Experiments: catechol pyrolysis (■); 1,3-butadiene pyrolysis (●); catechol/1,3-butadiene co-pyrolysis (▲). Weighted sum values (△) calculated from Eq. (2) in Chapter VIII.
Figure H.7. Yields, as functions of temperature, of: (a) 2-ethynlnaphthalene, (b) 1-ethynylacenaphthylene, (c) 5-ethynylacenaphthylene, and (d) 2-ethynylphenanthrene. Experiments: catechol pyrolysis (■); 1,3-butadiene pyrolysis (●); catechol/1,3-butadiene copyrolysis (▲). Weighted sum values (Δ) calculated from Eq. (2) in Chapter VIII.
Appendix I. Role of C$_3$ Species in Benzene Formation

The propargyl radical self-addition mechanism is thought to be the dominant benzene formation mechanism under pyrolysis and combustion conditions. Figure I.1 shows the yields/temperature profiles of benzene from: propyne pyrolysis (▲), 1,3-butadiene pyrolysis (♦), and catechol pyrolysis (■). Figure I.1 reveals that benzene formation from propyne pyrolysis becomes significant only at temperatures > 900 °C. This indicates that the propargyl radical self-addition mechanism is dominant only at higher temperatures. The high yields of benzene from 1,3-butadiene pyrolysis and the similar effects of temperature on the yields of benzene produced from 1,3-butadiene pyrolysis and from catechol pyrolysis suggest that the dominant benzene formation mechanisms in our catechol pyrolysis environment are the reactions involving C$_2$ and C$_4$ radicals.

![Figure I.1. Yields, as functions of temperature, of benzene from: catechol pyrolysis (■); 1,3-butadiene pyrolysis (♦); propyne pyrolysis (▲). Yields are expressed as mass-% of fed catechol.](image-url)
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Vita

Shiju Thomas was born in Cochin, India, in April of 1975. He completed his Bachelor of Technology with Honors from GEC Thrissur, University of Calicut, in the year 1998. Mr. Thomas worked as a Research Officer at Unilever Research India, Bangalore, India, from March of 1998 till August of 2002. His research involved structuring of multi-phase composites. He is the co-inventor in 5 Unilever patents. In the August of 2002, he joined the Department of Chemical Engineering at Louisiana State University as a doctoral student under the advisorship of Professor M.J. Wornat. The principal focus of his doctoral research is to gain mechanistic understanding into the formation and fate of polycyclic aromatic hydrocarbons produced during the pyrolysis and combustion of solid fuels, using model-fuel compounds. His works titled “The Effects of Oxygen on the Yields of the Thermal Decomposition Products of Catechol under Pyrolysis and Fuel-Rich Oxidation Conditions,” “The Effects of Oxygen on the Yields of Polycyclic Aromatic Hydrocarbons Formed During the Pyrolysis and Fuel-Rich Oxidation of Catechol,” and “Effects of Acetylene Addition on the Yields of C1-C10 Hydrocarbon Products of Catechol Pyrolysis,” have been published as research articles in peer-reviewed journals. His work titled “C_{24}H_{14} Polycyclic Aromatic Hydrocarbons from the Pyrolysis of Catechol” has been accepted for publication. Two of his recent works have been submitted for publication. He is expected to receive his doctorate degree in the spring of 2008.