

Distribution of Oxygenated and Unoxygenated Aromatics from Phenol Pyrolysis at Low Temperatures

Yun Yang and James A. Mulholland, School of Civil and Environmental Engineering, Georgia Institute of Technology, Atlanta, GA 30332-0512 USA

Abstract

The gas-phase pyrolysis of phenol was studied to investigate the effect of temperature on the distribution of aromatic products. Experiments were conducted in a flow tube reactor over a temperature range of 400 to 700°C with a residence time of 20 seconds. Oxygenated and unoxygenated aromatic products were measured. The major oxygenated product was dibenzofuran, which peaked at 650°C. At low temperature, small amounts of 2- and 4-phenoxyphenol were observed. At high temperatures, small amounts of four C₁₆H₁₀O isomers hypothesized to be three benzonaphthofurans and benzoxanthene were observed, as well as two C₁₈H₁₀O₂ isomers hypothesized to be benzobisbenzofurans. Formation of oxygenated products can be explained by a pathway of phenoxy radical addition to aromatic structures followed by ring closure. The major unoxygenated products were benzene, naphthalene and indene. Yields of these and higher molecular weight polycyclic aromatic hydrocarbons increased with temperature.

Introduction

During incineration and other thermal destruction processes, a large number of organic combustion byproducts can be formed. Many of these byproducts, especially substituted aromatic compounds such as dioxin, are of significant environmental concern due to their toxicity and persistence. Although the formation of dioxin has been studied extensively, detailed mechanisms of the formation of specific product isomers are not well understood. We are studying aryl addition pathways to the formation of dioxin and polycyclic aromatic hydrocarbons (PAHs). As a first step, we have studied phenol pyrolysis at low and intermediate temperatures.

Phenol has been reported to be one of the most significant aromatic emissions of various waste incinerators.⁽¹⁾ While the high temperature (> 1000 K), short time scale (< 3 seconds) decomposition and oxidation products of phenol pyrolysis are well established,^(2,3) less is known about the distribution of gas-phase products at low temperatures (< 1000 K) and long residence times (> 10 seconds) typical of post-combustion gas streams. In this paper, we report the distribution of aromatic products from phenol pyrolysis as a function of temperature, and then postulate reaction pathways for the formation of these compounds. An understanding of this chemistry is needed to develop strategies for minimizing and predicting the formation of these byproducts. The results will also be used as a reference against which other effects, such as the presence of oxygen, water vapor and soot, can be compared.

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Experimental Methods

Experiments were conducted in an electrically-heated, quartz tube flow reactor (40 cm in length and 1.9 cm in diameter) over a temperature range of 400 to 700°C. A known amount of phenol was fully vaporized and swept into the reactor by helium carrier gas through a heated transfer line. The carrier gas flow rate was controlled to yield a reaction residence time of 20 seconds. At the outlet of the reactor, aromatic products were collected in a dichloromethane solvent trap cooled in ice. Product identification and quantification was accomplished using a Varian 3600/Saturn 2000 GC/MS system. A DB-5ms capillary column (30-m, 0.25- μ m film thickness, 0.25-mm i.d.) was used. Commercially available chemical standards were used, including phenol, benzene, indene, naphthalene, dibenzofuran, and 3- and 4-phenoxyphenol.

Results and Discussion

Aromatic products observed from the pyrolysis of phenol are grouped into two categories: oxygenated and unoxygenated products. Yields of product classes and unreacted phenol over the temperature range studied are shown in Fig. 1a.

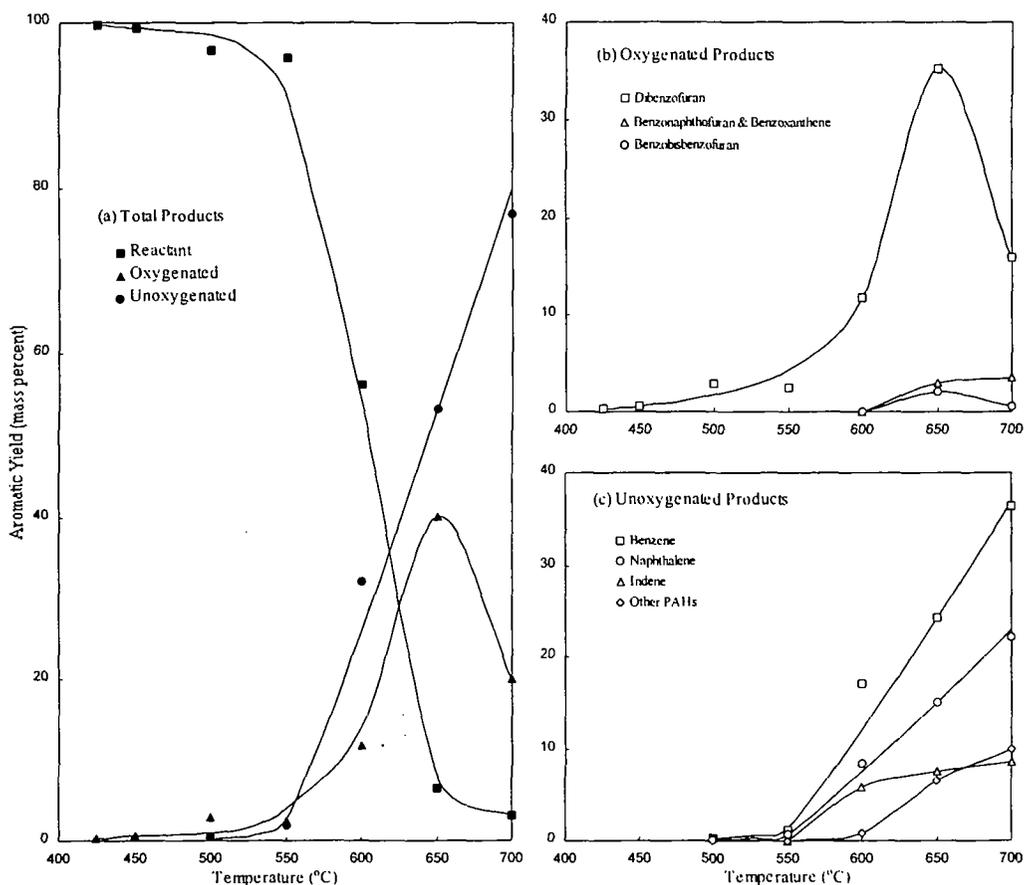


Figure 1. Aromatic product yields from phenol pyrolysis.

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Oxygenated aromatic products include dibenzofuran, four $C_{16}H_{10}O$ isomers hypothesized to be benzoxanthene and three benzonaphthofurans, and two $C_{18}H_{10}O_2$ isomers hypothesized to be benzobisbenzofurans. Product structures are shown in Fig. 2, with hypothesized structures in brackets. Unoxygenated aromatic products include benzene, naphthalene, indene, and higher molecular weight PAHs. Less than 5% of the phenol was reacted below $550^{\circ}C$; more than 95% was reacted at $650^{\circ}C$ and above. Oxygenated species were the major products below $550^{\circ}C$, with yields peaking at $650^{\circ}C$.

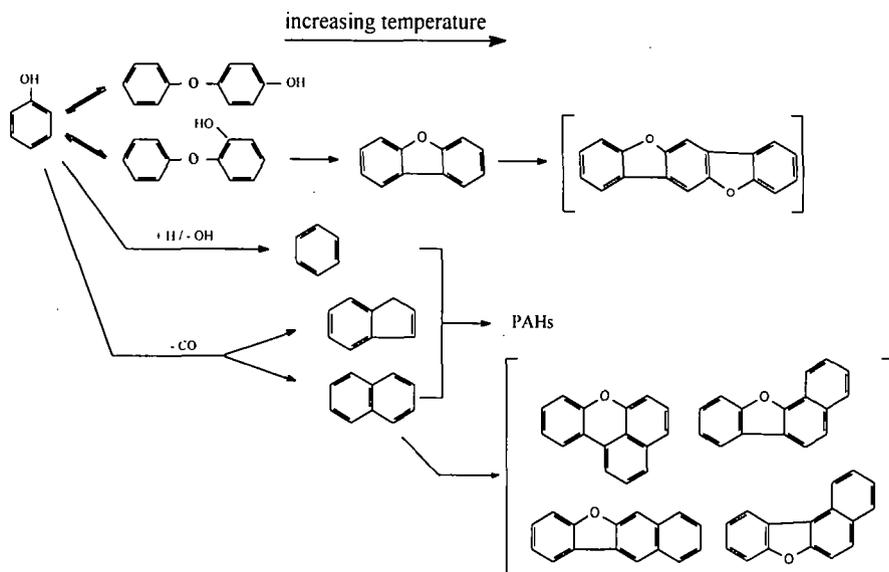


Figure 2. Phenol pyrolysis pathways.

The major oxygenated product at all temperatures was dibenzofuran (Fig. 1b). At $450^{\circ}C$, small amounts of 2- and 4-phenoxyphenol were observed; no 3-phenoxyphenol was detected. We postulate that phenol pyrolysis is initiated by the formation of the resonance-stabilized phenoxy radical through breaking of the relatively weak O-H bond.⁽⁴⁾ Phenoxy radical has been identified as important intermediate in a number of aromatic oxidation process.^(2,5) Once formed, phenoxy radical addition to phenol at the *ortho* and *para* sites produces the observed phenoxyphenols. The 2- and 4-phenoxyphenols were reported among the major multi-ring compounds formed from phenol oxidation in supercritical water at $380^{\circ}C$.^(6,7) Dibenzofuran formation is postulated to occur by ring closure of 2-phenoxyphenol with intra-molecular elimination of H_2O .

At $600^{\circ}C$ and above, other oxygenated products were observed. These products can be explained by phenoxy radical addition to naphthalene and dibenzofuran, followed by ring closure with H_2 elimination. Two $C_{18}H_{10}O_2$ isomers, hypothesized to be benzobisbenzofurans, are formed. Their peak yields occur at $650^{\circ}C$, corresponding to the peak in dibenzofuran. Four $C_{16}H_{10}O$ isomers, hypothesized to be benzoxanthene and three benzonaphthofurans, are also formed. The formation of these compounds corresponds to the formation of naphthalene (Fig. 1c). Phenoxy radical addition to the two unique sites of naphthalene and subsequent ring

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closure results in these four products. One of these products is produced in almost five times the yield of the other three products. Based on product energy considerations, we hypothesize that the benzoxanthene, which contains only six-member rings, is formed in greatest yield.

Of the unoxygenated aromatic products observed, benzene, naphthalene and indene were most abundant (Fig. 1c). This result is consistent with mechanisms for benzene and naphthalene formation proposed by Cypres and Bettens.⁽⁸⁾ Benzene is formed directly from the OH substitution by H-atom. Naphthalene formation is postulated to involve elimination of CO from phenol, followed by dimerization and cyclization. Indene is thought to form via CO elimination as well, followed by fragmentation and addition. There is evidence of both carbon fragment addition and aryl radical addition in further PAH growth based on the product structures observed.

The product pathways described above are summarized in Fig. 2.

Acknowledgment

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