Phenols from Pyrolysis and Co-Pyrolysis of Tobacco Biomass Components

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Abstract

Phenol and its derivatives (phenol, *o*-,*m*-, *p*-cresols, catechol, hydroquinone, methoxy substituted phenols etc. referred to as phenolic compounds or phenols) are well-known toxicants that exist in the environment and affect both human and natural ecosystems. This study explores, quantitatively, the yields of phenolic compounds from the thermal degradation (pyrolysis and oxidative pyrolysis) of common tobacco biomass components (lignin, tyrosine, ethyl cellulose, sodium alginate, and laminarin) as well as some mixtures (lignin/tyrosine, ethyl cellulose/tyrosine, sodium alginate/tyrosine) considered important in high temperature cooking, tobacco smoking, and forest fires. Special attention has been given to binary mixtures including those containing tyrosine -pyrolysis of binary mixtures of tyrosine with lignin and ethyl cellulose results in significant reductions in the yields of majority phenols relative to those of tyrosine. These results imply that the significant reductions of phenol yields in mixtures are not only dependent upon the mass fractions of the components but also the synergetic inhibition effect of biomass components on the thermal degradation of tyrosine. A mechanistic description of this phenomenon is suggested. The results may also be implied in tobacco industry that the cigarette paper (as ethyl cellulose derivative) may play a critical role in reducing the concentration of phenolic compounds released during tobacco burning.

Key Words: fractional pyrolysis/oxidative pyrolysis, tyrosine, lignin, ethyl cellulose, inhibition

1. Introduction

Various scientific and epidemiological studies have explicitly demonstrated that cigarette smoking is a risk factor for various degenerative diseases ([Pryor 1998](#), [Halliwell et al. 2006](#), [Ghosh et al. 2012](#)). Molecular phenolic compounds such as phenol, *p*-cresol, *o*-cresol, *m*-cresol, catechol, hydroquinone, and methoxy-substituted phenols are well-known threats to both environmental ecosystems as well as biological systems. Phenolic compounds found in cigarette smoke considered toxic are those believed to originate from the thermal degradation of lignin; one of the major components of tobacco ([Smith and Hansch 2000](#)). These phenols include 4-vinyl phenol, 4-vinyl guaiacol, syringol and vanillin ([D. Selassie et al. 1999](#), [Smith and Hansch 2000](#))([Kibet et al. 2012](#)). Substituted phenols bearing electron-donating substituents would therefore be expected to be more toxic ([Smith and Hansch 2000](#))([Kibet et al. 2013](#)). For instance, phenol affects liver enzymes, lungs, kidneys, and the cardiovascular system, while *m*-cresol attacks the nervous systems ([Talhout et al. 2011](#)). Phenoxy radicals produced from further degradation of phenol([Khachatryan 2008](#)), on the other hand can combine to form dibenzo-*p*-dioxin/dibenzofuran (DD/F) which is one of the most toxic environmental pollutants ([Berho and Lesclaux 1997](#), [Wiater et al. 2000](#), [Khachatryan 2003](#), [Evans and Dellinger 2005](#)). The *p*-hydroxyl phenoxy radical known in literature as neutral semi-quinone radical has been reported in cigarette smoke and shown to be highly active in generation of reactive oxygen species (ROS) in biological systems ([Pryor et al. 1998](#), [Dellinger et al. 2000](#)). ROS induces oxidative stress in living organisms which is currently considered a sure cause of health problems ([Dellinger et al. 2001](#), [Squadrito et al. 2001](#), [Hirakawa et al. 2002](#), [Maskos et al. 2005](#), [Cormier et al. 2006](#)). Once in the biological environment, phenols can be converted to quinones ([Bolton et al. 2000](#)). Quinones are a class of toxicological intermediates which are believed to create a variety of

hazardous effects *in vivo* including acute cytotoxicity, immunotoxicity, and carcinogenesis (Bolton et al. 2000). (DeCaprio 1999, Hirakawa et al. 2002). Quinones are highly redox active compounds which redox cycle with their respective semi-quinone radicals, resulting in the formation of reactive oxygen species. High yields of phenol have been detected from fractional pyrolysis / oxidative pyrolysis of tyrosine (one of the tobacco biomass components) reported from our laboratory (Kibet et al. 2013). Nevertheless, determining the toxicity of tobacco chemicals in general from available literature may not be an exact procedure but rather an estimation (Smith and Hansch 2000).

The quantitation of phenols (Wt% yield) from the pyrolysis and co-pyrolysis of biomass materials are critical towards understanding their evolution with temperature. This information is important in food processing, tobacco burning and other industries such as confectioneries. It would thus imply processing foods at certain optimum temperatures will be beneficial and minimize the formation of high yields of poisonous reaction by-products.

Accordingly, this study will explore in detail the formation of biologically important phenols such as phenol, *p*-cresol, *o*-cresol, *m*-cresol, catechol, hydroquinone, and methoxy-substituted phenols from selected tobacco biomass materials (lignin, tyrosine, ethyl cellulose, sodium alginate and laminarin – Fig. 1) and equimolar mass fractions of some mixtures such as lignin/tyrosine, cellulose/tyrosine, and alginate/tyrosine under various pyrolysis conditions. To the best of our knowledge, very few studies have been conducted on the co-pyrolysis of biopolymeric mixtures presented in this work.

Special attention has been given to binary mixtures especially those containing tyrosine. It has been postulated that the combined study of biomass and amino acids is the best approach to grasp a more comprehensive mechanism of nitrogen chemistry in biomass components (N-

Chemistry) ([Becidan et al. 2007](#)). While the pyrolysis of amino acids has been extensively studied, there is very little information on the product distribution from the co-pyrolysis of amino acids with other forms of biomass ([Li et al. 2007](#), [Ren et al. 2011](#)). Thus, this study attempts to bridge this gap in a more detailed manner. Since most of the elemental nitrogen is bound in proteins, co-pyrolysis of lignin + tyrosine, ethyl cellulose + tyrosine, and sodium alginate + tyrosine was conducted with the aim of finding features that are protein-specific ([Li et al. 2007](#))([Hansson et al. 2003](#), [Hansson et al. 2004](#)). Notably, the studies of the pyrolysis of some biomass constituents such as tyrosine, laminarin and sodium alginate are scarce in literature. This investigation primarily focuses on the formation of phenolic compounds from a broad range of biopolymers and selected mixtures.

2. Materials and Methods

2.1. Materials. The biomass samples; lignin, tyrosine, ethyl cellulose, sodium alginate and laminarin ($\geq 99.99\%$, purity) explored in this study were purchased from sigma Aldrich Inc. (USA) and used without further treatment. The lignin used in this study was hydrolytic, described in our earlier article ([Kibet et al. 2012](#)).

2.2. The system for thermal diagnostic studies (STDS). In order to avoid many experimental challenges associated with analysis of biomass pyrolysis ([Chiavari et al. 2001](#)), the system for thermal diagnostic studies (STDS) ([Rubey and Grant 1988](#)) was used in this work (SFig.1- Supplementary material), *vide infra*. The sampling of the reactor pyrolysate was done at the head of a GC column at - 60 °C using an in-line GC-MS. The experimental details for STDS are reported elsewhere ([Rubey and Grant 1988](#), [Evans and Dellinger 2005](#))([Kibet et al. 2012](#)). It is a well-established technique for analysis of a wide range of organic materials including amino acids ([Lawrence J. Marnett and Wilcox 1988](#)).

2.3. Fractional pyrolysis and fractional oxidative pyrolysis. The fractional pyrolysis technique applied in this study is an experimental procedure in which the same sample is continuously pyrolyzed at each pyrolysis temperature (Kibet et al. 2012)(Agblevor et al. 2010, Kibet et al. 2013). It is defined as a selective, *in situ* conversion of biopolymers to products (Kibet et al. 2013)(Agblevor et al. 2010). The benefits of this method are discussed elsewhere (Kibet et al. 2012)(Kibet et al. 2013).

The thermal degradation of biomass components was generally investigated in a tubular flow reactor over the temperature range of 200 °C to 800 °C at 1 atmospheric pressure, typically in 50 °C increments under two reaction conditions; pyrolysis in N₂ and oxidative pyrolysis in 4% O₂ in N₂ (SFig.1). The concentration of oxygen in the oxidative pyrolysis experiments was kept low to optimize the formation of phenolic products (Kibet et al. 2013). The gas flow rate was designed to maintain a constant residence time of 0.2 s. The sample, 30±0.2 mg, was loaded into a tubular quartz reactor (0.3 cm i.d. x 17.7 cm, volume 1.25 mL) and held in place by quartz wool to avoid being swept by carrier gas flowing through the reactor. The reactor used in this work is presented in SFig. 2. A summary flow chart outlining the steps taken during the determination of phenolic compounds from the thermolysis of bio-polymers is presented in SFig. 3. For co-pyrolysis experiments, equimolar mixtures of biopolymer/tyrosine were pyrolyzed in a reactor placed inside an electrically heated furnace whose heating rate was 10 °C s⁻¹ (SFig.1). After a total pyrolysis time of 3 minutes, the furnace was turned off and the sample cooled in flowing N₂ while exposing the reactor to a cooling fan (Kibet et al. 2012). The residence time with charred material was short enough (0.2 seconds) to minimize secondary reactions.

2.4. GC – MS characterization of phenols. The gas chromatography–mass spectrometry (GC-MS) analysis of the pyrolysate was conducted using an Agilent 6890N gas

chromatograph equipped with a 5973N mass selective detector (MSD) with an electron impact (EI) ion source set at 70 eV. A DB5-MS GC column (30m x 0.25mm x 0.25µm) was used (Kibet et al. 2012), SFig.1. The temperature program was typically: - 60 °C initial temperature; held for 3 min followed by heating at a rate of 15 °C/min to 130 °C; held for 1 minute at this temperature and heated to 300 °C at a heating rate of 25 °C/min (final temperature; held for 5 min). The injector and MSD detector temperatures were 250 °C and 280 °C, respectively. Ultra high pure (UHP, 99.999%) helium was used as the carrier gas at constant flow of 3.3mL/min. The mass spectrometer was operated in total ion current mode (TIC) over a mass scan range of 15 –600 amu. As discussed elsewhere (Kibet et al. 20123), the pyrolysis products (phenols) were determined using NIST library and by comparing retention times with those of pure compounds (standards). The experimental data presented in this study were averaged values from 2 or more replicates.

2.5. Calibration of Pyrolysis Products

A stock solution was prepared by weighing 0.1 g of each individual calibration compound and dissolved in a 10 mL volumetric flask containing analytical grade methanol. Aliquots of the 1000 µg/mL stock solution was then diluted to concentrations of 100, 500, 800, 1000, 1200, and 1500 µg/mL. 1µL was injected into the GC-MS and the peak area of each standard compound was then plotted against the mass of the compound in µg/mL solution and then linearly regressed to obtain the calibration curve of the compound. The R² value was greater than 0.98 for all standards. The weight percent yield of each compound was determined using the following formula:

$$Y = \left(\frac{\text{weight of product, } w}{\text{weight of sample, } W} \right) \times 100 \quad \text{Equation 1}$$

where Y is the yield of the pyrolysis product in Wt %.

The structural formulas of major products (phenols) and their weight % yields from the thermal degradation of tobacco components; lignin and tyrosine are presented in the supplemental information (Table S1, and Table S2 – Table S6, respectively).

3. Results and Discussion

3.1. Pyrolysis of lignin and co-pyrolysis of lignin/tyrosine mixtures

The quantitative release of common phenolic compounds from pyrolysis and co-pyrolysis of lignin and tyrosine was investigated experimentally and presented in Fig. 2. It was clear that some phenolic products overlapped while others were not detected under certain pyrolysis conditions. For instance, hydroquinone was detected only under oxidative conditions when lignin and tyrosine were co-pyrolyzed. The char yields (Fig. 2) decreased with increase in pyrolysis temperature. Interestingly, above 500 °C, the char yields and pyrolysis products decreased in a similar trend. This is because, above this region (500 °C) most of the pyrolysis products would be gaseous, mainly CO, CO₂, methane, and other small molecules including H₂.

From Fig. 3, it is evident that most phenolic compounds decreased during the co-pyrolysis of lignin and tyrosine compared to when tyrosine was pyrolyzed individually. For instance, phenol was decreased by nearly 30% during the co-pyrolysis of lignin and tyrosine (Fig. 3A) while for oxidative pyrolysis phenol decreased by about 25% (Fig. 3B). Majority of observed reaction products were methoxy substituted phenols: syringol, guaiacol, and 3-methoxy catechol. Other major phenols observed in this study were phenol, *p*-cresol, catechol, 4-ethyl phenol, 4-vinyl guaiacol, and eugenol. Pyrolysis of tyrosine generally gave rise to higher levels of phenol and *p*-cresol relative to that from the thermal degradation of lignin (Fig. 3).

Therefore, thermolysis of biomass rich in tyrosine is expected to give high yields of phenolic compounds especially phenol, *p*-cresol and *o*-cresol. However, the pyrolysis/oxidative pyrolysis of binary mixtures of lignin and tyrosine results in significant reduction in the yields of some phenols relative to those of tyrosine, Fig. 3A (*vide infra*, Table 1).

3.2. Pyrolysis of ethyl cellulose, and ethyl cellulose/tyrosine mixture.

Ethyl cellulose (EC) is a semi-synthetic cellulose derivative that has found widespread application in the food and cigarette paper industries (Guo and Gray 1994, Lai et al. 2010). The chemical structure of EC comprises chains of anhydroglucose units linked together by oxygen bridges, with the most commonly used materials having a degree of ethoxyl substitution between 43 and 50 % (Lai et al. 2010). The ethyl cellulose used in this study had an ethoxy substitution of 48 %. The co-pyrolysis of ethyl cellulose with tyrosine resulted in lower yields of phenolic products in comparison with the yields observed when tyrosine was co-pyrolyzed with lignin or when tyrosine was pyrolyzed individually, Fig. 4. However, it should be noted that during individual pyrolysis of tyrosine 30±2mg was used while for co-pyrolysis experiments equimolar quantities of sample was used i.e. 15 mg / 15 mg. As a result, phenol was decreased by 83 % while *p*-cresol was decreased by 87 % in comparison with experiments in which pure tyrosine was pyrolyzed. During oxidative co-pyrolytic experiments, phenol was decreased by 96 % while *p*-cresol was decreased by 94 %. Co-pyrolysis of tyrosine with ethyl cellulose yielded neither catechol nor hydroquinone, Table 1. A similar observation was noted when tyrosine was co-pyrolyzed with lignin.

3.3. Pyrolysis of tobacco minor components sodium alginate and sodium alginate/tyrosine mixture.

It is evident from Table S7 (supplementary information) that the co-pyrolysis of sodium alginate and tyrosine in a nitrogen atmosphere does not yield phenols at all, although some phenolic compounds were detected from sodium alginate pyrolysis. Laminarin being a minor component of tobacco ([Rioux et al. 2007](#), [Anastasakis et al. 2011](#)) was not considered for co-pyrolytic experiments with tyrosine. Nonetheless, lower amounts of common phenols (phenol, *p*-cresol, *o*-cresol) were observed from laminarin pyrolysis (oxidative pyrolysis did not yield any phenols).

3.4. Mechanistic explanation for the drastic reduction of phenol yields from co-pyrolysis/co-oxidation of biopolymer/tyrosine mixtures.

The co-pyrolysis experiments show large decrease in yields of phenols in comparison to the yields observed from tyrosine pyrolysis, Table 1, Fig. 4. For instance, the total yields of three major phenols from Table 1 (phenol, *p*- and *o*- cresols) depends differently upon mass fraction of biopolymer/tyrosine mixture (components' ratio = 1:1) i.e. at twice dilution of tyrosine by lignin or ethyl cellulose the total yields of phenol+*p*-cresol+*o*-cresol from tyrosine pyrolysis (~ 61 %) drops almost twice in case of Lig/Tyr pyrolysis (28.2 %) while it drops by a factor of ~ 5 during EC/Tyr pyrolysis (12.36 %). A drastic drop of the yields of the mentioned phenols also occurred during oxidative pyrolysis of Lig/Tyr (by a factor of 2.4) and EC/Tyr (by a factor ~ 15), Table 1. To examine more clearly the dilution effect on the reduction of the yields of phenolic compounds (phenol, *p*-cresol, and *o*-cresol), a multi-component mixture (at different mass fraction) pyrolysis was performed.

3.4.1. The Co-Pyrolysis of Lignin, Cellulose, Pectin, Tyrosine, and Glutamic Acid Mixture

A mixture of five tobacco components (Lig: EC : Pectin : Tyr : Glutamic acid) were pyrolyzed in a tubular flow reactor to mimic plant matter especially in tobacco. These

compounds were found to be the major fractions in tobacco (Schiffman and Leffingwell 1981,
Forehand et al. 2000). Whereas lignin, pectin, ethyl cellulose, and tyrosine are well known
components of tobacco, glutamic acid has been found to be one of the major components in
burley tobacco (Sharma et al. 2006). Their estimated percentages in tobacco model sample
normalized to tyrosine were; Lig: EC: pectin: Tyr: Glutamic acid = 5:10:12:1:2, i.e tyrosine was
diluted by a factor of 30. The predominant products observed in this study were mainly
oxygenated products with hydrocarbon products as the minor products. Most of the products
were peaked at between 400 and 500 °C with the exception of phenols which peaked at about
500 °C. Levoglucosan was exclusively the major pyrolysis product contributing nearly 50% of
the total products detected. Other major products included methyl alcohol and 5-(hydroxyl
methyl) furfural which were peaked at about 300 and 400 °C, respectively. The minor products
detected included vinyl acetylene, propene and propane. At higher temperatures ≥ 400 °C
benzene, toluene and a few aromatic hydrocarbons (indene, naphthalene and methyl
naphthalene) were detected in low quantities.

The phenolic compounds were detected surprisingly in much lower yields, Table 2.
While phenols are usually observed to form at lower temperatures (< 400 °C) during the
pyrolysis of individual biomass components such as lignin and tyrosine, phenolic compounds (cf.
Table 2) were observed to peak at higher temperatures (> 400 °C) when 5 component mixtures
were pyrolyzed together. This observation is similar to the pyrolysis of binary mixtures reported
in Fig. 2A, B and Fig. 3. It is clear from the data in Table 2 that the total yields of phenol+*p*-
cresol+*o*-cresol (0.28 % at 500 °C) dropped non proportionally to the dilution (60.84 % : 30 ~
2%) i.e. instead of the expected 2 % yield, 0.28% was found experimentally.

Naturally a synergetic inhibition may occur in the pyrolysis mixture if we consider the pathways of formation of phenol from tyrosine discussed elsewhere (Kibet et al. 2013). Phenol may form during pyrolysis via either direct decarboxylation and deamination (Fig. 5, left hand side) widely documented in literature (Basiuk 1998, Douda and Basiuk 2000, Chiavari et al. 2001, Sharma et al. 2004, Li et al. 2008) or in modified, radical assisted degradation pathways we discussed elsewhere (Kibet et al. 2013). In presence of tobacco biopolymers, (lignin or ethyl cellulose) which have plenty of end OH groups, tyrosine may easily associate with the biopolymer molecules through hydrogen bonding which may increase the energetic barrier for phenol formation through decarboxylation/deamination or may cause a steric hindrance for formation of phenol through radical degradation pathway, Fig. 5. As a result, the yields of phenols (phenol and cresols) are expected to decrease synergistically with dilution. Note that tyrosine (or similar compounds) may form intermolecular hydrogen bonding with complex molecules in solution and solid phases which is well-known in literature (Huang et al. 1996, Pace et al. 2001) (Kolev, 2007 #5459). For instance, most tyrosine OH groups contribute favorably through the intermolecular hydrogen binding to protein stability (Pace et al. 2001).

The same phenomenon may be observed during oxidative co-pyrolysis of biopolymer/tyrosine mixtures. It is known from our early research that *p*-tyramine is the major product from tyrosine oxidative pyrolysis and that *p*-tyramine may be a source for formation of phenol (Kibet et al. 2013), Fig. 5. Not only tyrosine, but also *p*-tyramine will be associated with biopolymers through hydrogen bonding thereby strongly inhibiting the formation of phenol during oxidative pyrolysis. The experimental fact that the reduction of phenol yields for EC/Tyr mixture pyrolysis is larger than in case of Lig/Tyr (Fig. 4) may be explained by much high concentration of the “end OH” groups in ethyl cellulose (43-48 %) vs (18-33 %) in lignin (Lai et

al. 2010). Based on the results obtained from this study, it is important to note that the use of ethyl cellulose as a cigarette paper decreases the yields of phenols significantly.

4.0 Conclusion

This work has explored in detail the formation of phenolic compounds from the thermal degradation of tobacco biomass materials such lignin, tyrosine, ethyl cellulose, sodium alginate, and laminarin) as well as some mixtures (lignin/tyrosine, ethyl cellulose/tyrosine, sodium alginate/tyrosine) that mimic plant matter. The main focus was directed towards the formation of phenols (phenol, *o*-,*m*-, *p*-cresols, catechol, hydroquinone, methoxy substituted phenols etc.) from bio-polymeric mixtures with tyrosine as the greatest producer of phenolic compounds in comparison to other biomass components. Moreover, the concept of dilution and synergic effect as factors affecting the yields of pyrolysis products (phenolic compounds) in bio-polymeric materials has been demonstrated in this study. Accordingly, a mechanistic explanation has been proposed to elucidate this observation.

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FIGURES

Fig. 1. Tobacco Biomass materials investigated in this study

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Fig. 2. Co-pyrolysis of lignin/tyrosine mixture (**A** and **B**) in N_2 and 4% O_2 in N_2 respectively, and pyrolysis of lignin (**C** and **D**) in N_2 and 4% O_2 in N_2 , respectively.

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Fig. 3. Comparison of phenols (in wt %) from pyrolysis (A) / oxidative pyrolysis (B) of lignin, tyrosine, and Lig/Tyr mixture.

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Fig. 4. Total wt % yields of phenol (brown line) and *p*-cresol (blue line) from pyrolysis of various biomass components in the temperature region from 200 °C to 900 °C.

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Fig. 5. Possible pathways for formation of phenol from pyrolysis of tyrosine through decarboxylation/deamination, radical assisted degradation (left hand side) and oxidative pyrolysis through participation of oxygen and hydroxyl radicals, right hand side.

Compound	Pyrolysis (Yield in Wt %)				Oxidative pyrolysis (Yield in Wt %)			
	Lignin	Tyrosine	Lig/Tyr	EC/Tyr	Lignin	Tyrosine	Lig/Tyr	EC/Tyr
phenol	3.71	31.89	17.12	8.64	1.45	16.36	8.70	0.90
<i>p</i> -cresol	2.02	24.03	11.08	3.07	0.61	10.34	3.45	0.65
<i>o</i> -cresol	nd	4.92	nd	0.65	nd	2.55	nd	0.46
catechol	3.07	nd	1.14	0.46	nd	0.81	nd	nd
ethyl phenol	1.87	nd	8.39	2.32	0.33	nd	0.33	0.47
hydroquinone	nd	0.64	0.06	3.10	nd	nd	0.65	nd
<i>p</i> -tyramine	-	1.61	2.45	2.30	-	6.14	nd	0.23
guaiacol	2.68	-	5.57	nd	1.30	-	2.45	nd
syringol	8.28	-	7.39	nd	2.32	-	3.26	nd
4-vinyl guaiacol	5.07	-	3.44	nd	1.69	-	4.07	nd
eugenol	4.39	-	5.42	nd	1.44	-	0.36	nd
3-methoxy catechol	2.27	-	1.63	nd	1.11	-	0.87	nd

Table 2. Quantified yields (Wt %) of Phenolic Compounds from Fractional Co-Pyrolysis of Lignin, Cellulose, Pectin, Tyrosine, and Glutamic Acid Mixture at different Temperatures in N₂ at 1 atm.

Quantified Yields	Pyrolysis Temperature (°C)							
	200	300	350	400	450	500	550	600
phenol	0.00	0.00	0.00	0.01	0.01	0.12	0.02	0.01
<i>o</i> -cresol	0.00	0.00	0.00	0.01	0.01	0.05	0.01	0.01
<i>p</i> -cresol	0.00	0.00	0.00	0.01	0.02	0.11	0.02	0.01
2,3-dimethyl phenol	0.00	0.00	0.00	0.01	0.02	0.05	0.02	0.01
<i>p</i> -ethyl phenol	0.00	0.00	0.00	0.01	0.03	0.08	0.03	0.02
catechol	0.00	0.00	0.00	0.01	0.03	0.04	0.02	0.01
Wt % Total	-	-	-	0.06	0.12	0.45	0.12	0.07