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Phenols from pyrolysis and co-pyrolysis of tobacco biomass components

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HIGHLIGHTS

- The yields of phenols from the thermal degradation of tobacco biomass materials.
- Comparative analysis of char and phenols yields at different pyrolysis environment.
- A mechanistic explanation for the large reduction of phenols yields.

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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 and 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 from the thermal degradation 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.

1. Introduction

Various scientific and epidemiological studies have explicitly demonstrated that cigarette smoking is a risk factor for various degenerative diseases (Pryor et al., 1998; Halliwell and Poulsen, 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 (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 et al., 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 et al., 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

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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 toward 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 bio-polymeric 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, 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 (⩾ 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 (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, 2013;

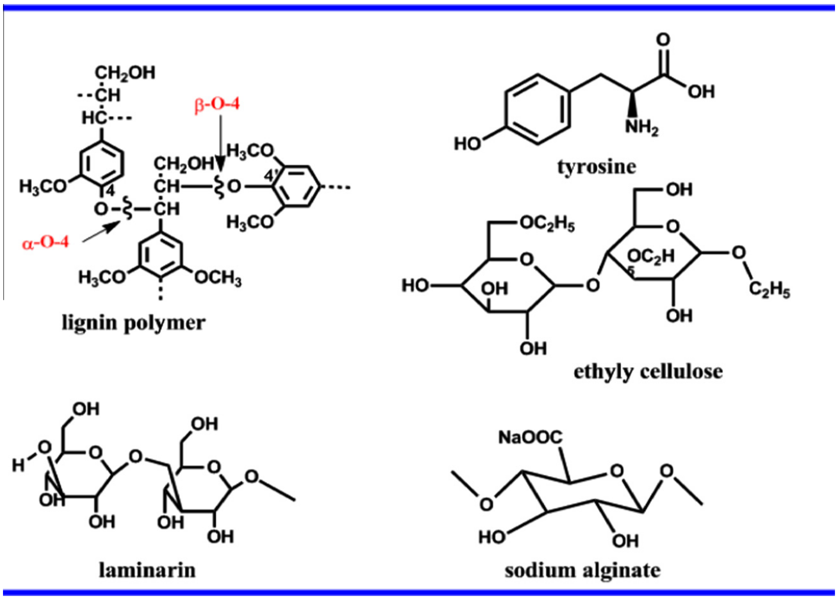

Fig. 1. Tobacco biomass materials investigated in this study.