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The influence of exogenous fiber on the generation of carbonyl compounds in reconstituted tobacco sheet

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ABSTRACT

In recent years, many efforts have been devoted to assessing the influence of saccharides on the toxicity of cigarette mainstream smoke. The primary goal of this paper was to investigate the influence of exogenous saccharides of hemp pulp (HP) and softwood pulp (SP) on the generation of carbonyl compounds (i.e., formaldehyde, acetaldehyde, acetone, acrolein, propanal, butenal, 2-butanone and butyraldehyde) in comparison with tobacco pulp (TP). The yields of carbonyl compounds in cigarette mainstream smoke of three reconstituted tobacco sheets (RTS) (TP-RTS, HP-RTS and SP-RTS) were studied under ISO standard smoking conditions. Thermogravimetric (TG) analysis and isothermal oxidative pyrolysis experiment in combination with high performance liquid chromatography (IOPy-HPLC) have been employed to indirectly investigate the influence of exogenous fiber on the generation of carbonyl compounds. The compositions of three fibers were analyzed by Ion chromatography (IC) and the monosaccharide was studied by IOPy-HPLC. Cigarette smoking results illustrated that, compared with TP-RTS, HP-RTS and SP-RTS generated significantly higher amounts of carbonyl compounds in cigarette mainstream smoke. TG results showed that the differences of thermal behavior between three RTS were mainly caused by the differences of three fibers. IOPy-HPLC results demonstrated that xylose (17.47 mg g^{-1}) generated significantly higher amount of carbonyl compounds than fructose (15.22 mg g^{-1}) and mannose (15.54 mg g^{-1}), and particularly than glucose (14.27 mg g^{-1}). Due to higher contents of xylose and lower contents of glucose, the exogenous fibers of HP and SP indeed generated higher amounts of carbonyl compounds than TP.

1. Introduction

Normally, during the processing and production of tobacco products, considerable amounts of tobacco stems and fines are produced. These tobacco wastes altogether constitute approximately one third of the raw material [1] and can not be incorporated directly into cigarettes. In order to comprehensively utilize these tobacco wastes, reconstituted tobacco sheet (RTS) has been developed by a papermaking process [2]. Due to its particular pyrolysis and combustion behavior, the reconstituted material decreased tar, nicotine and phenols yields in the particulate phase of tobacco cigarette mainstream smoke [3].

During the papermaking process, a certain proportion of exogenous plant fiber, commonly hemp pulp (HP) and softwood pulp (SP) [4], is historically added to stabilize the runnability of papermaking machine. These exogenous fibers are mainly attributed to the saccharides of hemicellulose and cellulose. In recent years, a host of studies have been conducted to investigate the influence of saccharides on the generation of carbonyl compounds. According to health concerns, carbonyl compounds of formaldehyde, acetaldehyde, acetone, acrolein, propanal, butenal, 2-butanone and butyraldehyde have been classified as toxic and carcinogenic constituents [5,6]. Baker et al. observed the formation of formaldehyde during the pyrolysis of brown sugar, white sugar, invert sugar, molasses and cellulose under the conditions that simulated a smoldering cigarette [7]. Tarora et al. [8] examined the pyrolysis of glucose, fructose, sucrose and cellulose on the generation of carbonyl compounds at 17 °C s^{-1} up to 800 °C. They found that these saccharides all generated formaldehyde, acetaldehyde, acetone and acrolein.

The above background information has illustrated that the saccharides studied by previous researchers were all found as tobacco components or used as tobacco ingredients. As exogenous fiber, the compositions of HP and SP, however, were greatly different from tobacco pulp (TP). For examples, mannan was the prevalent

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hemicellulose monomer for softwood pulp [9], while tobacco pulp mainly composed of glucose and fructose [10]. Nevertheless, the literature survey so far revealed that no publications have been done to investigate the influence of these exogenous fibers on the generation of carbonyl compounds.

In this study, TP-RTS, HP-RTS and SP-RTS were prepared by a papermaking process. The yields of eight carbonyl compounds in cigarette mainstream smoke were conducted by using smoking machine and high performance liquid chromatography (HPLC). The thermal behavior of RTS and exogenous fiber was studied by using thermogravimetric (TG) analysis. Isothermal oxidative pyrolysis experiment in combination with HPLC (IOPy-HPLC) was employed to pyrolyze the RTS. The compositions of three fibers were analyzed by ion chromatography (IC) and the monosaccharide was pyrolyzed using IOPy-HPLC.

2. Experimental

2.1. Materials

The raw materials of SP and HP were purchased from Tianjin Guangxian Tianfu Paper Products Co., Ltd, China. TP was manufactured by tobacco stem of which water-soluble fraction was removed. Acetonitrile with 99.99% purity was supplied by TEDIA reagents, Inc., USA. 2,4-Dinitrophenylhydrazine (DNPH) with AR purity was obtained from Adamas Reagent Co., Ltd, Switzerland. Perchloric acid with AR purity was provided by Shanghai Jinlu Chemical Reagent Co., Ltd, China. The standard reagents of eight carbonyl-DNPH compounds were purchased from Zhengzhou Tobacco Research Institute of China National Tobacco Corporation. The standard reagents of fucose, rhamnose, arabinose, galactose, glucose, xylose, mannose, fructose and ribose were obtained from Sigma–Aldrich Co., USA.

In order to remove sugar, pectin, starch, lipid and protein, the raw materials of TP, HP and SP were treated with 1.25% H_2SO_4 and then with 1.25% NaOH [11]. Hence, the saccharides of hemicellulose and cellulose were the major constituents of plant fiber. TP-RTS, HP-RTS and SP-RTS were manufactured by a papermaking process [2]. Strictly speaking, in the papermaking process, the water-soluble fraction of the tobacco fines, dust and stem was extracted with hot water followed by centrifugation, leaving behind a tobacco pulp and a tobacco extract. The ensuing tobacco pulp and 12% (w/w) plant fiber (dry weight) were mechanically beaten to fibrillate the cellulose and reduce its fiber length. Then, the refined cellulose was formed onto a web on the wire screen of a standard papermaking machine and dried by hot air and suction. In the parallel operation, the tobacco extract was condensed at about 30% soluble solid content. Finally, the cellulose web was impregnated with the condensed tobacco extract and then dried.

2.2. Measurements

2.2.1. Cigarette smoking analysis

Cigarettes manufactured by RTS were smoked by a machine (Borgwaldt RM200A) according to the selected smoking conditions (35 mL puff volume, 2 s duration, 1 puff min^{-1}) of International Standard (ISO) recommendations [12]. The carbonyl compounds in the cigarette mainstream smoke were collected onto a Cambridge filter pad already moistened by 5 mL DNPH acetonitrile solution. DNPH solution could be obtained as follows: 15.0 g DNPH was initially dissolved in 800 mL acetonitrile followed by addition of 2.0 mL perchloric acid and further dilution with acetonitrile to volume at 1000 mL. The carbonyl compounds in the mainstream smoke could be derived by DNPH due to its high reactivity and selectivity [13,14]. Finally, the derivatives of carbonyl-DNPH compounds on the pad were extracted with 100 mL 2% pyridine/acetonitrile (v/v) solution and detected by HPLC.

2.2.2. TG analysis

Thermogravimetric analysis was performed using thermogravimetric analyzer (Netzsch STA 449C) in the atmosphere of 10% oxygen in nitrogen (v/v) with a flow rate of 100 mL min^{-1}. Approximate 20 mg sample powder was put in a standard alumina crucible and heated at a rate of 40 K min^{-1}, with temperature varying from 30 to 1000 °C. All samples were dried at 40 °C for 4 h and grinded to pass through an 80 mesh screen.

2.2.3. IOPy-HPLC analysis

The continuous furnace pyrolyzer was illustrated in Fig. 1. A more detailed description of experimental set up and procedures were previously given elsewhere [5,6]. The isothermal oxidative pyrolysis was conducted in the atmosphere of 9% oxygen in nitrogen (v/v) with a flow rate of 200 mL min^{-1}. When the isothermal oxidative pyrolysis conditions in the tube reached the desired value, about 0.100 g sample placed in the quartz boat was rapidly pushed to the flat-temperature zone by the step-pushing pod. The residence time was 5 min. The gaseous products formed from the process of the experiment were transferred into 50 mL DNPH absorption solution. DNPH absorption solution could be obtained as follows: 0.500 g DNPH was dissolved in 800 mL acetonitrile initially followed by addition of 2.0 mL perchloric acid and further dilution with acetonitrile to volume at 2000 mL. The derivatives of carbonyl-DNPH compounds in the absorption solution were detected by HPLC.

2.2.4. Monosaccharide composition analysis

Ion chromatography (IC) was used to determine the monosaccharide composition of three kinds of fibers. After hydrolysis, neutralization, filtration and dilution, the hydrolyzed solution of pulp was injected and analyzed directly. The IC experimental procedures were carried out as follows. Chromatographic column: CarboPac PA20. Detection: pulsed amperometric detector. Column flow rate: 0.500 mL min^{-1}. Mobile phase A: H_2O; Mobile phase B: 250 mM NaOH. Mobile phase C: 1 M NaAc. Gradient conditions used: 98.2%A + 1.8%B (0 min), 98.2%A + 1.8%B (21.0 min), 93.2%A + 1.8%B + 5%C (21.1 min), 78.2%A + 1.8%B + 20%C (30.0 min), 20%A + 80%B (30.1 min), 20%A + 80%B (50.0 min). The content of monosaccharide was calculated using a linear calibration curve of standard solutions ranging from 0.1 to 10 mg mL^{-1}.

2.2.5. HPLC analysis

HPLC experiments were carried out in a Dionex Ultimate 3000 (Thermo Fisher Scientific Inc.) instrument. The HPLC experimental procedures were carried out as follows. Chromatographic column: Acclaim explosives (4.6 mm × 250 mm, 5 μm). Column temperature: 30 °C. Column flow rate: 0.900 mL min^{-1}. Injection volume: 5 μL. Detection: UV-DAD detector at 365 nm. Mobile phase A: 100% acetonitrile; Mobile phase B: 100% H_2O. Gradient conditions used: 50%A + 50%B (0 min), 50%A + 50%B (20 min), 60%A + 40%B (25 min), 60%A + 40%B (30 min), 80%A + 20%B (35 min), 90%A + 10%B (40 min), 50%A + 50%B (41 min), 50%A + 50%B (50 min). The yields of carbonyl compounds were calculated using a linear calibration curve of standard solutions ranging from 0.2 to 100 μg mL^{-1}. The data presented here were the average of three experimental determinations.

2.2.6. Statistical analysis

Factorial analysis of variance (AVOVA) was performed with IBM SPSS Statistics Version 19.0 software using t-Tukey test, and $p < 0.05$ was regarded as significant.