An experimental investigation into the operation of an electrically heated tobacco system

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ABSTRACT

An experimental investigation of the thermal processes taking place in the tobacco substrate of a recently developed multicomponent electrically heated tobacco product (EHTP) that is part of an electrically heated tobacco system (EHTS – also referred to as the Tobacco Heating System 2.2) was carried out. Temperature profiles in the tobacco substrate of the EHTP were characterized using thermocouples positioned at different distances from the heater surface. The average maximum temperature of the tobacco measured 0.2 mm from the heater's surface was < 260 °C, well below the temperature required for the self-sustaining smoldering combustion of the tobacco substrate to occur. The chemical composition of the aerosol generated from the EHTP when the EHTS was operated under oxidative and non-oxidative atmospheres was investigated. The aerosol derived from the controlled heating of the tobacco substrate is comprised principally of water, nicotine and glycerol that are evaporated from the tobacco substrate. No significant change in aerosol composition and in the amounts of CO, NO and NO_x were detected when comparing the aerosol formed under non-oxidative (where combustion processes cannot occur) and oxidative atmospheres.

1. Introduction

The presence of harmful and potentially harmful constituents (HPHCs) in the smoke resulting from burning tobacco is well known. A burning cigarette is a typical example of a self-sustaining smoldering (flameless) combustion process where temperatures of the tobacco in the burning tip of the cigarette can exceed 850 °C when air is drawn through the lit tip. The smoke aerosol produced from a lit cigarette is generated by complex combustion, pyrolysis, and pyrosynthesis processes that overlap with lower temperature distillation and sublimation processes. The composition of the smoke aerosol formed is a complex and dynamic mixture of gases, liquid droplets and solid particles suspended in air [1]. The self-sustaining smoldering combustion of the tobacco results in a region inside and behind the burning tip of the cigarette that is depleted in oxygen, where the (temperatures remain high enough (300–600 °C) to promote the thermal decomposition (pyrolysis) of unburned tobacco components. Directly behind the high temperature pyrolysis and the smoldering combustion regions of a burning cigarette, there is a much lower temperature region (< 300 °C) where volatile constituents native to tobacco evaporate due to the heat of the encroaching burning zone.

Of the more than 6000 chemical compounds that have been identified in cigarette smoke [2], public health authorities and others have proposed some 100 HPHCs [3–5]. The formation of HPHCs in a burning cigarette has been extensively studied and is influenced by a number of factors including the tobacco variety and high temperatures induced by the self-sustaining smoldering combustion process [6]. Different tobacco leaf constituents such as carbohydrates, biopolymers, waxes and proteins that decompose at different temperatures, release chemical compounds that form part of the cigarette smoke aerosol. A number of published studies contain information on the temperature of formation of selected HPHCs from different tobacco varieties, tobacco extracts and selected model tobacco plant components [7–20]. Most HPHCs result from the thermal decomposition of tobacco plant components at temperatures up to 850 °C [1,10,14].

Nicotine is naturally present in tobacco leaves and can be evaporated from tobacco at temperatures below 300 °C [21,22]. Obtaining a nicotine containing aerosol with a significant reduction in the levels of HPHCs may be achieved by heating rather than burning tobacco. This was the main driver for the development of heat-not-burn tobacco

products also referred to as Heated Tobacco Products (HTPs). HTPs use blended or processed tobacco substrates that contain an added aerosol former and operate by heating the tobacco substrate to temperatures sufficient to release nicotine and other volatile compounds naturally present in the tobacco leaf, but not to temperatures high enough to initiate high-temperature pyrolysis processes and the self-sustaining smoldering combustion of tobacco generating smoke. Early HTPs developed were reviewed by Baker [1] and Schorp et al. [23]. More evolved products, such as the recently developed Electrically Heated Tobacco System (EHTS) [24] by Philip Morris International (PMI), and *glo* [25] by British American Tobacco are now available.

Chemical and physical characterization of the EHTS aerosol has shown that it is very different in composition to cigarette smoke aerosols [26–42]. Indeed, examples of some of the assessments performed include aerosol chemistry [26–29], non-clinical (in-vitro and in-vivo), and clinical studies [26,29,32–35], which have all shown significant differences in the levels of emissions, toxicity and exposure to measured HPHCs in the EHTS aerosol compared with cigarette smoke. Other studies have investigated HTPs and e-cigarette aerosols for the presence/absence of liquid and solid particles, their size distributions, impact on indoor air quality, as well as performing passive exposure dosimetry simulations applying the multiple-path particle dosimetry model [36,42].

In such studies, significant differences have been reported between aerosols generated with and without the combustion of tobacco. As the aerosol formed in the EHTS is a function of the physical and chemical processes occurring in the tobacco substrate when heated during the operation of this HTP device, such information is of fundamental importance not only for the product investigated in this paper but also for other current and future products developed using heating methodologies in order to ensure that none can lead to the occurrence of tobacco combustion when used as intended.

When samples of biomass such as tobacco are heated to temperatures above 100 °C, a number of thermal processes occur that result in the formation of three main product fractions: gases, liquid condensate and a residual solid. Upon heating, a tobacco sample first undergoes a drying process, usually in a temperature range between 100 and 300 °C. In this initial stage, dehydration of the tobacco takes place with the release of water and the evaporation of volatile organic compounds such as nicotine. Between 200–300 °C, torrefaction (mild-pyrolysis) processes result in the formation of low levels of low-molecular-weight gases (such as CO, CO_2 and NH_3), aldehydes, ketones, low-molecular weight hydrocarbons and aromatics and the tobacco substrate itself starts to change structurally [43–46]. The liquid condensate generated at temperatures < 300 °C is primarily generated from the evaporation of water and other volatile and semi-volatiles naturally present in tobacco. At higher temperatures, more complex processes take place. Pyrolysis is the thermochemical decomposition of biomass into a range of products, either with a limited supply, or in the total absence of oxidizing agents [47–49]. High-temperature pyrolysis reactions result in the formation of a liquid condensate from the cooling and condensation of thermal degradation and depolymerization products from tobacco plant carbohydrates, fatty acids, waxes, phenolic compounds, lipids, alkaloids, proteins, peptides, amino acids, and organic salts. The residual solid that remains at temperatures > 250 °C appears black in color and is both aliphatic and aromatic in nature [44,45]. Heating to higher temperatures results in an increase in the aromaticity of the remaining solid with the evolution of light gases, aromatics and polycyclic aromatic hydrocarbons (PAHs), as well as oxygen and nitrogen-containing aromatics and PAHs [7,12,46].

At temperatures > 400 °C and in the presence of an oxidant (such as the oxygen in air), the residual solid phase "fuel" ignites and begins to burn (undergo a smoldering combustion and potentially a self-sustaining smoldering combustion processes) until the fuel is consumed [21,25]. The definition of a combustion process and its specific characteristics are very well known in the fields of combustion science and

fire safety and may be defined as an oxidative reaction of a fuel that occurs at a rate fast enough to produce heat and usually light in the form of either a glow or a flame [47–52]. The burning of tobacco in a cigarette is an example of a self-sustaining smoldering combustion process, where temperatures in the range of 500–700 °C are generated at the burning tip of the cigarette when the tobacco is lit with a match or lighter [53–59]. When air is drawn through the burning tip, temperatures rise above 850 °C. For other biomass materials such as wood, if the volatiles formed and released from the thermal decomposition of the sample ignite, combustion of volatiles occurs and an envelope or wake diffusive flame develops with a typical temperature in the region of 1500 °C.

While it is possible to have fully oxygenated stoichiometric combustion reactions occur in specialized laboratory equipment, everyday combustion reactions such as burning fossil fuels, wood, candles, and the tobacco in cigarettes are seldom a complete combustion process, and incomplete combustion products are formed [60]. However, incomplete or partial combustion should be distinguished from other thermal processes such as drying, torrefaction and pyrolysis, where oxygen is not necessary for these reaction processes to occur. Actually, it is impossible in practice to have biomass completely or even partially combust in the absence of lower thermal processes such as drying, torrefaction and pyrolysis. It is however possible to induce such processes in biomass materials without complete or partial combustion occurring.

The purpose of this study was to investigate the thermal reaction processes that are taking place in a tobacco substrate of a HTP when heated under controlled conditions. A specific device, the EHTS from PMI, was used to carry out experimental runs to characterize the temperature distribution in the tobacco substrate under an oxidative atmosphere. The aerosol emissions generated from this HTP when operated under both oxidative and non-oxidative atmospheres were collected and characterized using internationally recognized standardized methodologies. The final aim of the study is to shed some light on the physical and chemical processes taking place in the tobacco substrate when heated during the operation of this HTP device.

2. Experimental

A list of acronyms used through the manuscript is given in Table 1.

2.1. The EHTS

An EHTS device (also known as the "Tobacco Heating System 2.2″ – THS2.2) developed by PMI was used as an example of a HTP device for the experimental characterization of thermal processes that take place in the EHTS. It has three distinct components that perform different functions: (i) an *Electrically Heated Tobacco Product* (EHTP) - a multicomponent product containing a specially formulated tobacco substrate made from tobacco powder, water, glycerol, guar gum and cellulose fibers, (ii) a *Holder* into which the EHTP is inserted and that heats the tobacco portion of the EHTP by means of an electrically controlled heater, and (iii) a *Charger* that is used to recharge the battery in the Holder after each 360 s heating cycle or when 14 puffs have been taken, whichever comes first. A schematic of the EHTS and of the multiple

Table 1
List of acronyms used throughout the manuscript.

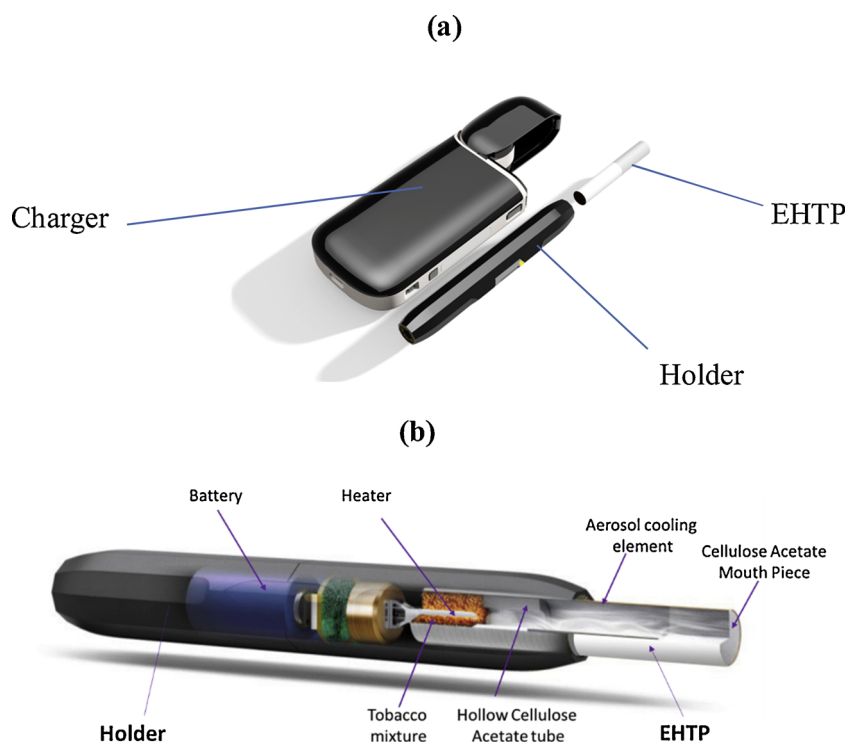|	
3R4F	Kentucky Reference Cigarette
EHTP	Electrically Heated Tobacco Product
EHTS	Electrically Heated Tobacco System
HCI	Health Canada Intense puffing regime
HPHC	Harmful and potentially harmful constituent
HTP	Heated Tobacco Products
NFDPM	Nicotine-free dry particulate matter
TPM	Total particulate matter

(a)

(b)

Fig. 1. (a) The three components of the Electrically Heated Tobacco System (EHTS) and (b) Schematic of the cross-sectional view of the Electrically Heated Tobacco Product (EHTP) and its components inserted into the Holder.

components in the EHTP are shown in Fig. 1-a and -b, respectively.

To operate the EHTS, an EHTP is inserted into the Holder (heating device) and a 360 s heating cycle is initiated. The Holder contains a ceramic-based heating blade (Heater) that heats the tobacco substrate in the EHTP from the center of the tobacco plug radially outwards (see Fig. 1-b). The airflow pathway through the Holder and EHTP when a puff is taken is shown in Fig. 2.

Air enters the Holder first through a gap between the outer and inner device walls, and then out through the components of the EHTP. The Heater consists of a platinum track encased in a glass coated ceramic substrate. Heat is supplied to the tobacco substrate for a fixed period of 360 s. After 360 s or after 14 puffs have been taken, the heater turns off. The temperature profile of the heater is electrically controlled and the energy supplied is continuously monitored by the EHTS Holder throughout the 360 s heating cycle. A photograph of the tobacco plug in the EHTP and of the Heater in the Holder are shown in Fig. 3-a and -b, respectively.

The Heater in the Holder, in contact with the tobacco substrate of the EHTP has a dual function. It heats the tobacco substrate by

adjusting the Heater power to maintain a pre-defined average temperature profile over the Heater's surface, and also monitors and regulates the Heater's temperature. The temperature of the Heater is determined by measuring the electrical resistivity over the Heater, which in turn is measured by monitoring the current and voltage of the system. The relationship between Heater resistivity and temperature measured in air was pre-established using an infrared camera [61]. The IR camera setup (see Supplementary materials section) was used only for the calibration of Heaters and not for the measurement of the tobacco substrate temperature as it would not allow to obtain a radial temperature distribution and evolution in the EHTS. The temperature evolution of the tobacco substrate was monitored using K-type thermocouples positioned at different distances for the Heaters surface as described in Section 2.2.1.

Software in a micro-controller regulates the electrical current supplied to the Heater to achieve the desired temperature profile during operation. The EHTS Holder features an over-heating protection mechanism that switches the device off if the measured temperature based on the power delivered is higher than the set-point.
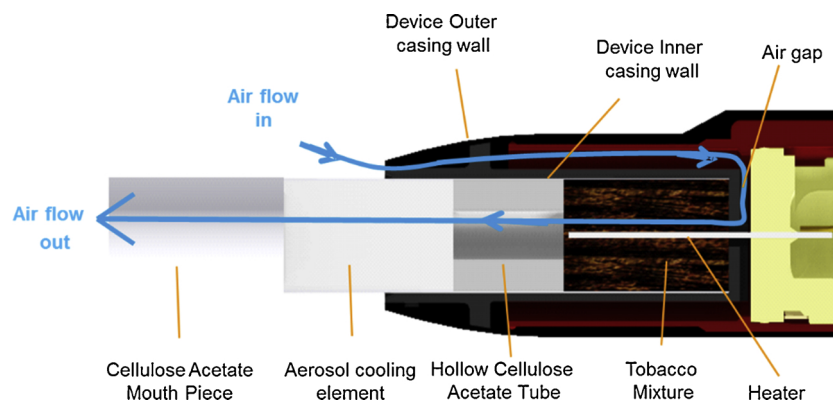

Fig. 2. Airflow pathway in the EHTP and Holder when air is drawn through the end of the mouth piece of the EHTP.
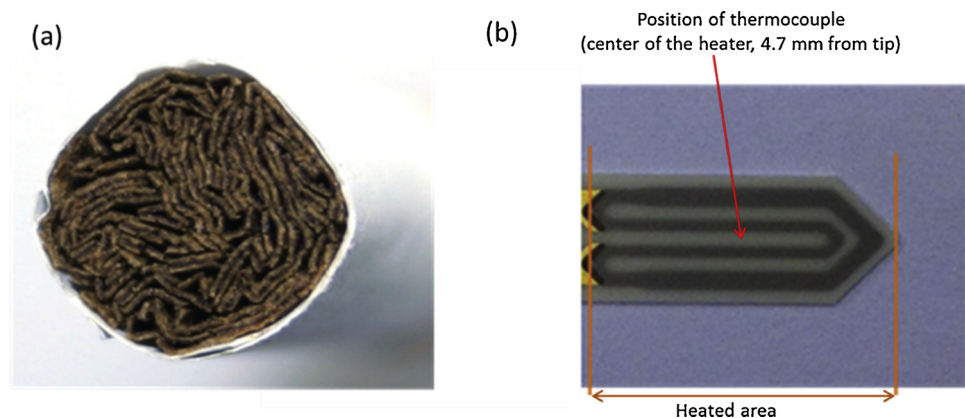
Fig. 3. Photographs of (a) crimped tobacco plug of the EHTP and (b) Heater in the Holder. The position of the thermocouple inside the Holder and relative to the tip of the heater is illustrated on the photograph.

2.2. Experimental procedures

2.2.1. Temperature measurements during EHTS operation

In order to investigate the thermal processes occurring in the tobacco substrate of the EHTP during its operation, specific experimental runs were carried out to measure the temperatures during operation. A 0.5 mm diameter hole was drilled into the side of the outer casing of the Holder to allow for a 0.25 mm diameter K-type thermocouple (standard accuracy ± 2.5 °C) to be inserted into the tobacco substrate. The location of the hole was selected to allow the thermocouple to be positioned towards the center of the heating blade (4.7 mm from the tip, as shown in Fig. 3-b). The thermocouple was mounted on a micrometer screw guide that allowed the thermocouple to be positioned in the tobacco substrate of the EHTP at different distances from the surface of the Heater. To allow a smooth insertion of the thermocouple into the tobacco substrate, a needle was used to pierce the tobacco substrate of the EHTP in the Holder prior to the insertion of the thermocouple. To measure the temperature at the surface of the Heater, the thermocouple was positioned in direct contact with the heater surface. This position was denoted by the radial distance (R) equal to 0.0 mm on the micrometer. The temperature variation with respect to time in the tobacco substrate during heating was measured (in separate experiments for each position) radially by positioning the thermocouple respectively at R = 0.2 mm, 0.5 mm, 1.7 mm and 3.4 mm, from the Heater's surface. After positioning the thermocouple in the Holder, the Holder was switched on and air was drawn through the EHTS after the pre-heating phase according to the Health Canada Intense (HCI) puffing regimen [62] (55 mL puff volume, 2 s puff duration, 30 s puff frequency) using a calibrated piston pump, to simulate user operating conditions. The temperature recorded by the thermocouple was monitored at time intervals of 0.1 s. Temperature measurements were performed under normal operating conditions, i.e. under a heating cycle of 360 s. Data recordings were stopped after 390 s, so that the change in temperature could be observed after the heating cycle had been completed. Five replicates at each thermocouple position were performed.

Additional temperature measurements were also performed to investigate the temperature of the tobacco substrate when the Heater of the device was switched off before the heating cycle had been completed. In an experimental run, the EHTS was operated under normal operating conditions for 300 s. The power to the Heater was then switched off, but the HCI puffing protocol was maintained. In a further experimental run, the EHTS Heater was switched on but no air was drawn through the EHTS for 300 s. The power input to the Heater was then switched off, and the HCI puffing protocol was initiated.

2.2.2. Optical characterization of the tobacco substrate in the EHTP

In order to investigate changes in the aspect and color of the tobacco

substrate as a function of temperature, samples were heated in an oven to 100 °C, 150 °C, 200 °C and 250 °C, respectively, for 360 s in air. The paper wrappers around the tobacco substrate plugs were not removed in order to maintain the tobacco substrate plug shape and physical integrity during heating and handling. A Jouan® laboratory oven, model EU1B from Astel S.A., was used and was preheated to the desired oven temperature. A tobacco substrate plug was inserted into an oven and heated for a total time of 360 s. Pictures of the tobacco substrate plugs upon cooling to room temperature were taken with a Canon EOS 100D (f/5, 1/500 s, ISO-800) camera. Three replicates were performed at each heating temperature.

To observe the actual changes in the aspect and color of the tobacco substrate in the EHTP before and after heating in the EHTS Holder, an EHTP was cut open before and after use and photographs of the tobacco substrate were taken with the same camera mentioned above. Three replicates were performed.

2.2.3. Mainstream aerosol generation and constituent analysis

In order to compare the composition of the EHTP mainstream aerosol generated under oxidative and non-oxidative atmospheres, the EHTS was operated under synthetic air and nitrogen, respectively. The synthetic air used was from a compressed cylinder, "extra dry", O_2 19.5–23.5%, H_2O < 10 ppm. The nitrogen gas used was from a compressed cylinder, grade 4.8, 99.998% purity, oxygen (O_2) < 5 ppm, water (H_2O) < 3 ppm. EHTP mainstream aerosol generation, collection and analysis under the HCI regimen [62] was performed by Labstat® International ULC, Ontario, Canada, and ISO 17025 accredited laboratory [63]. A photograph illustrating the experimental setup is reported in Fig. 4.

A 20 port Cerulean SM450 linear smoking machine (Cerulean, Milton Keynes, UK) was used for sample collections (with the exception of nitrogen oxides (NO_x), samples for which were generated using a Model RM1/G single port smoking machine (Borgwaldt Technik GmbH, Germany) coupled with a Model 8840 NO_x analyzer manufactured by Monitor Labs Inc. San Diego, USA). A Cerulean Model COA205 carbon monoxide (CO) analyzer, coupled to the 20 port Cerulean SM450 linear smoking machine was used for CO determinations. In accordance with the ISO standard 3402 [64], prior to aerosol generation, EHTPs were stored and conditioned for at least 48 h at 22 ± 1 °C and 60 ± 3% relative humidity for both experimental runs. Mainstream aerosol was generated under both synthetic air and nitrogen gas test conditions of 22 ± 2 °C and < 1% relative humidity. A 'blank' run where the heating cycle of the device was not initiated but air was drawn through the Holder (with no EHTP present) under the HCI regimen was also performed as part of the experimental design under the controlled room air environment (22 ± 2 °C and 60 ± 5% relative humidity).

Mainstream aerosol was collected from EHTPs heated in the EHTS
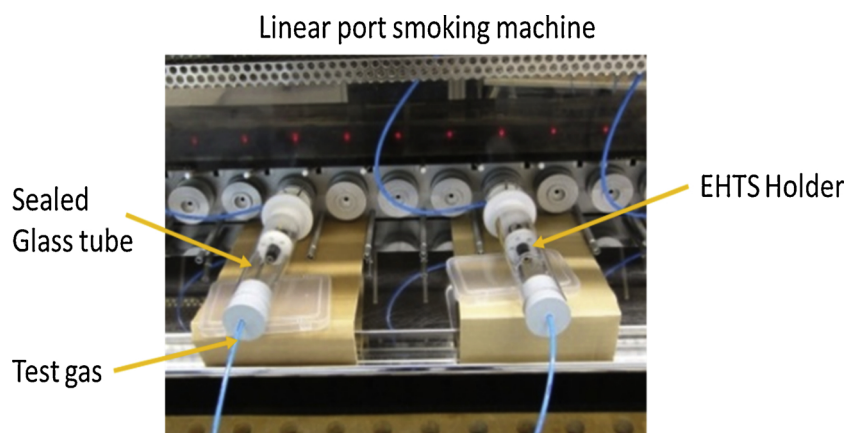
Linear port smoking machine

Fig. 4. Photo of aerosol generation setup for the collection of EHTS generated aerosol under oxidative (synthetic air) and non-oxidative (nitrogen) atmospheres.

Holder for a defined count of 12 puffs. The 12 puff count number is based on the fixed settings of the EHTS, which is programmed to finish heating after a maximum period of 360 s, and the 30 s puff interval of the HCI regimen [62]. Quantitative analysis of the EHTP mainstream aerosol for total particulate matter (TPM), water, glycerol, nicotine, nicotine-free dry particulate matter (NFDPM), CO, nitric oxide (NO) and NO_x, benzo[*a*]pyrene, semi-volatiles, phenolic compounds, carbonyls, aromatic amines and was performed using validated Labstat test methods (T-104, T-110, T-112, T-115/TMS/00115a, TMS-00120, TMS-00124, TMS-00128 and TMS-00139, respectively) [63].

To address the loss of water identified by Ghosh and Jeannet [65] using the standard ISO 4387 method [66] for aerosols of high water content, a modified ISO 4387 methodology [65] was used. Aerosol generation and compositional analysis were performed at PMI Research and Development facility, Neuchâtel, Switzerland. In addition to water, the TPM, nicotine, glycerol, CO and CO_2 content of the EHTP mainstream aerosol were also determined for the same experimental run. EHTP mainstream aerosol was generated during EHTS operation in air using a Borgwaldt linear smoking machine type LM20X (Borgwaldt KC GmbH, Hamburg, Germany). The HCI regimen [62] puffing conditions were used to draw air through the EHTP. Prior to testing, EHTPs were conditioned at 22 °C ± 1 °C and 60% ± 3% relative humidity in accordance with the ISO standard 3402 [55]. The laboratory conditions used for aerosol generation were 22 °C ± 2 °C and 60% ± 5% relative humidity. Mainstream aerosol was collected from EHTPs heated in the Holder using a bell-shaped puff profile for a defined puff count of 12 puffs.

The aerosol derived from the EHTP was collected on a Cambridge glass-fiber filter pad (44 mm in diameter). The gas flow leaving the filter was fed to a Borgwaldt CO/CO_2 Analyzer C25 (Borgwaldt KC GmbH, Hamburg, Germany) for CO and CO_2 online determination by Fourier Transform infrared spectroscopy (FTIR). TPM was determined gravimetrically (Mettler Toledo FACT 104/S, Mettler Toledo GmbH, Greiffensee, Switzerland) from the Cambridge filter pads. The NFDPM was calculated by subtracting the determined water and nicotine content of the aerosol from the measured TPM value.

The Cambridge glass-fiber filter pads were extracted applying the in-situ methodology [65] with 10 mL of isopropanol containing internal standards (ethanol for the water content analysis and n-heptadecane for nicotine and glycerol analysis) before removing the filter pad from the filter holder. The principle of the in-situ extraction methodology is to avoid any loss of water by flushing the extraction solvent through the sealed pad holder. For mass balance calculations it is essential to correctly quantify water in the TPM of aerosols with a high water content. The extracts were analyzed separately for nicotine, water, and glycerol.

Water was analyzed by gas chromatography (GC) using a thermal conductivity detector (TCD). A Thermo trace GC Ultra gas chromatograph (Thermo Electron S.p.A., Rodano, Italy) equipped with an

autosampler (CTC Analytics PAL system, CTC Analytics AG, Zwingen, Switzerland), a Haysep Q 80/100 mesh stainless steel column (8 feet long × 1/8″ OD ×2.1 mm ID, (BGB Analytik AG, Geneva, Switzerland), and a thermal conductivity detector was used. The column temperature was set at 170 °C (isothermal). The injector and the detector temperature were set at 200 and 250 °C, respectively. The concentration of water was calculated based on peak areas using linear regression of a five-point calibration curve prepared with ethanol as the internal standard.

Nicotine was analyzed by GC using a flame ionization detector (FID). A Thermo Trace GC Ultra gas chromatograph (Thermo Electron S.p.A., Rodano, Italy) equipped with an autosampler (CTC Analytics PAL system, CTC Analytics AG, Zwingen, Switzerland), a Restek 7% Carbowax 20 M/3% polyphenylether OS 138/2% KOH column (4 feet long, 1/8″ outer diameter (OD) × 2.0 mm inner diameter (ID) (Restek Corporation, Bellefonte, PA, USA) and a flame ionization detector was used. The column temperature was set at 170 °C (isothermal). The injector and the detector temperature were set at 200 and 250 °C, respectively. The concentration of nicotine was calculated from the peak areas using linear regression of a five-point calibration curve prepared with n-heptadecane as the internal standard.

Glycerol was analyzed by GC-FID. A PerkinElmer Clarus 500 GC (PerkinElmer Inc., Waltham, MA, USA) equipped with an autosampler. A DB-WAX column, 30 m × 0.53 mm ID, 1 μm film thickness (Agilent J &W Inc, Santa Clara, CA, USA) was used. The following oven temperature program was employed: 2 min at 100 °C, ramped to 150 °C at a rate of 10 °C/min, held for 1 min at 150 °C, ramped to 200 °C at a rate of 20 °C/min, and held for 3 min at 200 °C. The injector and the FID temperature were set at 200 °C and 300 °C, respectively. The concentration of glycerol was calculated based on peak areas using linear regression of a five-point calibration curve prepared with n-heptadecane as the internal standard. Further details of the quantitative analytical methodologies used can be found in Schaller et al. [26].

CO and CO_2 levels in the mainstream smoke of a 3R4F Kentucky reference cigarette were also determined for comparison purposes to the CO and CO_2 levels in the mainstream aerosol derived from heating the EHTP in the EHTS. Prior to cigarette mainstream smoke generation, 3R4F Kentucky reference cigarettes were conditioned under the same conditions (ISO 3402) [64] as described above for EHTPs. 3R4F mainstream smoke was generated during using a Borgwaldt linear smoking machine type LM20X (Borgwaldt KC GmbH, Hamburg, Germany). The HCI regimen [62] puffing conditions were used to draw air through the lit cigarettes. The laboratory conditions used for aerosol generation were 22 °C ± 2 °C and 60% ± 5% relative humidity. 3R4F Kentucky reference cigarettes were smoked to a butt length of 35 mm using a bell-shaped puff profile with 100% blocking of ventilation holes. The mainstream smoke from the 3R4F reference cigarette was collected on a Cambridge glass-fiber filter pad (44 mm in diameter) but

was not analyzed. The gas flow leaving the filter was fed to a Borgwaldt CO/CO₂ Analyzer C25 (Borgwaldt KC GmbH, Hamburg, Germany) for CO and CO_2 online determination by fourier transform infrared spectroscopy (FTIR).

2.3. Materials

The tobacco substrate of the EHTP is derived from high quality ground tobacco containing various tobacco types from different origins that is reconstituted into sheets of tobacco (termed cast-leaf) following the addition of water, glycerol, guar gum and cellulose fibers. The reconstituted tobacco cast-leaf used in the EHTP is fashioned into small plugs through a proprietary process known as '*crimping*'. The crimping progress allows for the same piece of tobacco cast-leaf to be folded upon itself many times. The formed tobacco plug can be considered as a porous medium with a void fraction of ~0.3. The weight of the tobacco plug in the EHTP used in the experiments was approximately 320 mg.

After their production, the EHTP samples were stored at 5 ± 3 °C with uncontrolled humidity conditions in the original packaging. Before experimental runs and experimental characterization, the EHTP samples were conditioned for at least 48 h at 22 ± 1 °C and 60 ± 2% relative humidity (RH), according to the International Organization for Standardization (ISO) method 3402 [64].

3R4F Kentucky reference cigarettes were obtained from the University of Kentucky (Lexington, KY, USA; http://www.ca.uky.edu/refcig/) and used as a reference cigarette in the present study. These cigarettes are produced solely for research purposes and are used for the development of analytical methods within a laboratory and to enable comparison of results between different laboratories. The 3R4F Kentucky reference cigarettes are designed to be representative of lit end cigarettes on sale in the United States and European markets.

Water content and ultimate analysis (carbon (C), hydrogen (H), nitrogen (N)) of the tobacco substrate in the EHTP and of the cut filler tobacco in the 3R4F Kentucky reference cigarette, before and at the end of experimental runs were performed by Solvias AG, Switzerland. Ultimate analysis was performed on samples as received, i.e. no conditioning. The water content of samples was determined by volumetric Karl Fischer titration.

3. Results

3.1. Temperature profile in the tobacco substrate in the EHTP during EHTS operation

Experimental runs applying the procedure described in Section 2.2.1 were carried out to investigate the temperature in the tobacco substrate during EHTS operation. The experimental runs also aimed to detect the occurrence of any net exothermic reaction processes in the tobacco substrate. Combustion reactions (flaming and non-flaming) are associated with the release of energy in the form of heat. Therefore, the occurrence of an overall exothermic heating process of the tobacco substrate is an important aspect to be assessed. This was investigated in the EHTS by measuring: (i) the temperature of the tobacco substrate in the EHTP during the heating cycle when heated in the EHTS Holder under simulated operating conditions, and (ii) switching off the Heater power supply and observing the temperature evolution in the tobacco substrate.

Fig. 5-a shows the pre-defined temperature profile (recorded by the device via the resistance of the heating element) used in all experimental runs and the power delivered to the heater during the experimental runs, measured at 2 s intervals. The Holder is programmed to turn the heating element off after 360 s. During experimental runs, the HCI puffing protocol was applied to draw air through the EHTP to simulate product operating conditions ("puffing"). The Heater, directly in contact with the tobacco substrate operated to maintain the pre-defined average temperature profile shown in Fig. 5-a. During the initial
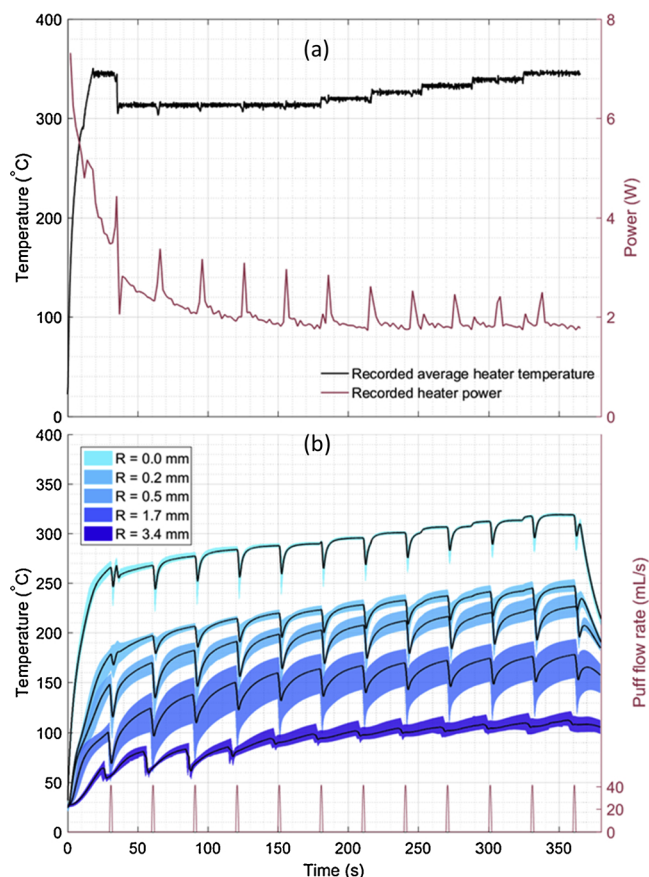

Fig. 5. (a) Average heater temperature and power absorption, and (b) tobacco substrate temperature measured at four different positions radially in the EHTP from the heater's surface: R = 0.0 mm, 0.2 mm, 0.5 mm, 1.7 mm and 3.4 mm, respectively, during 360 s heating cycle with simulated puffing. The air intake (or puff flow rate) is indicated on the secondary y-axis in Fig. 5(b). For each thermocouple measurement, the solid black line represents the average of 5 replicates and the colored region indicates the range between the minimum and maximum temperatures of the individual replicates.

heating phase, the power decreased quickly according to Ohm's law as the resistivity and therefore the temperature of the Heater increased towards the initial set point of 350 °C. When the initial heating phase was complete, as shown in Fig. 5-a, the temperature set-point of the heater changed from 350 °C to 320 °C, and the device switched off the output power for approximately 1 s to let the Heater reach the new set-point (as reflected by the negative trough at ~37 s). As air was drawn at regular intervals through the EHTP under simulated puffing using the HCI regimen, the measured temperature of the heater decreased during air inflow. To maintain the pre-defined Heater temperature profile, the power output of the Heater momentarily increased to compensate for the drop in temperature and then decreased again as the set point was attained.

The corresponding average temperature measured at the surface of the Heater (denoted as position R = 0.0 mm) and in the tobacco substrate of the EHTP at four different radial distances (R = 0.2, 0.5, 1.7 and 3.4 mm, respectively) from the Heaters surface, under simulated puffing, are plotted in Fig. 5-b. The average temperature profiles shown are when air was drawn through the EHTP at regular intervals under the HCI regimen.

The average temperature measured on the surface of the heater at R = 0.0 mm and in the tobacco plug at R = 0.2 mm, 0.5 mm, 1.7 mm and 3.4 mm, were 320 ± 4 °C, and 247 ± 4 °C, 226 ± 9 °C, 178 ± 15 °C and 108 ± 6 °C, respectively. As clearly shown in Fig. 5-b, the temperature of the tobacco substrate dropped during the air

Fig. 6. (a) Tobacco substrate temperature profile in the EHTP (measured R = 0.2 mm from the heater's surface) when the heater is turned off after 300 s. The Health Canada Intense puffing regime was used during the entire run and puffing continued after the heater was switched of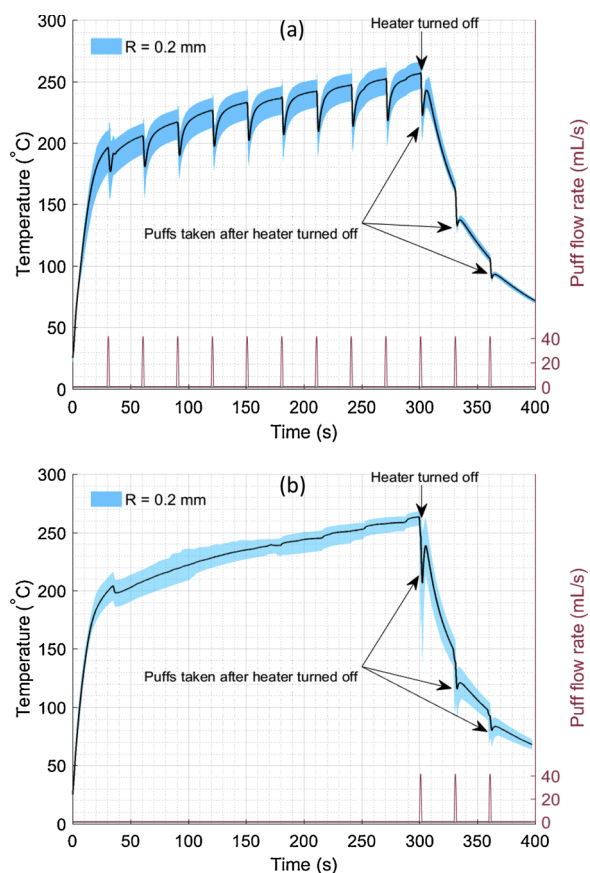f. (b) Tobacco substrate temperature profile in the EHTP (measured R = 0.2 mm from the heater's surface) when the heater is turned off after 300 s. The air intake (or puff flow rate) is indicated on the secondary y-axis. The solid black line represent the average of 5 replicates and the colored region indicate the range between the minimum and maximum temperatures of the individual replicates.

inflows. This is observed as troughs in the recorded temperature profiles. The temperature of the tobacco substrate significantly decreased as a function of the radial distance from the Heater's surface. When the Heater was switched off after 360 s, there was no recovery in the temperature of the system and as time passed the temperature of the tobacco substrate decreased.

Fig. 6 shows the results of a similar set of experimental runs, in which the Heater was switched off after 300 s and puffs were taken according to HCI regimen. Data acquisition was stopped after a total time of 390 s. The average temperature profile along with the minimum and maximum recorded for the tobacco substrate based on 5 replicates, measured at R = 0.2 mm from the surface of the Heater, is shown in Fig. 6-a. Similarly in this case, when the Heater was switched off, there was no recovery in the measured temperature and as time passed and additional air inflows were taken ("puffs taken"), a rapid decrease in temperature of the tobacco substrate was observed.

In Fig. 6-b the results of runs in which no air was drawn through the EHTP until 300 s after the start of the run (the time at which the heater was switched off) are shown for comparison. As there was no air drawn through the EHTP, a continual slow rise in the temperature of the tobacco substrate measured at R = 0.2 mm was observed and no troughs in the temperature profile were present before 300 s. When the Heater was switched off and air was immediately drawn through the system for the first time, there was a significant decrease in the temperature of the tobacco substrate. When additional air inflows were taken, a rapid decrease in temperature of the tobacco substrate was again observed.

3.2. Color change in the EHTP tobacco plug

The change in color of the tobacco substrate as a function of temperature after having been heated in an oven is shown in Fig. 7. For heating temperatures > 150 °C in air, the color of the tobacco substrate began to change from its initial color to dark brown at 200 °C to black by 250 °C. This change in color is due to the torrefaction of the tobacco and is well known for other biomass samples. One example of which is the color changes seen during the torrefaction of coffee beans [67].

The color of the tobacco plug of the EHTP before and after heating in the EHTS is also shown in Fig. 7 (vi and vii), respectively. After the 360 s heating cycle had completed and the tobacco plug was opened, a small portion of the tobacco material in the center of the tobacco plug that was close to the heater had changed from its original color (Fig. 7-vi) to a darker brown/black (Fig. 7- vii).

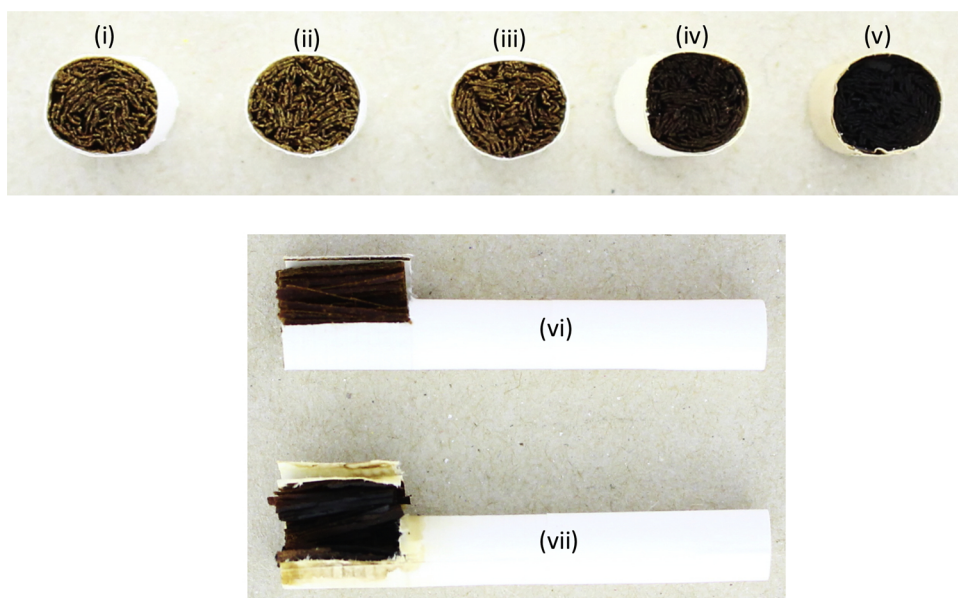**Fig. 7.** Change in color of the tobacco plug as a function of temperature (i–v) and in the EHTP before and after heating in the EHTS (vi-vii). Tobacco plugs with their outer paper wrapping were heated in an oven at set temperatures of 22 °C (i), 100 °C (ii), 150 °C (iii), 200 °C (iv), and 250 °C (v), respectively, for 6 min in air. The tobacco plug in the EHTP before (vi) and after (vii) heating in the EHTS.

Table 2
Levels of mainstream aerosol constituents obtained when operating the EHTP under oxidative and non-oxidative atmospheres.

Constituents	unit	EHTP in Nitrogen Average	Std. Dev.	EHTP in Synthetic Air Average	Std. Dev.	3R4F Cigarette Average	Std. Dev.	Blank Average	Std. Dev.	Method LOD	LOQ
TPM[a]	mg/unit	54.0	1.5	55.2	1.6	45.8	1.38	0.006	0.015	0.100	0.333
Water	mg/unit	34.7	4.3	37.3	3.8	16.3	0.94	BDL	BDL	0.064	0.213
NFDPM[†]	mg/unit	17.9	3.1	16.5	3.4	27.6	—	BDL	BDL	0.119	0.395
Glycerin	mg/unit	4.38	0.24	4.39	0.40	2.3	0.09	BDL	BDL	0.024	0.080
Nicotine	mg/unit	1.38	0.10	1.37	0.09	2.0	0.01	BDL	BDL	0.002	0.007
CO	mg/unit	< 0.530 but ≥0.159	—	0.54	0.16	33.4	0.54	BDL	BDL	0.159	0.530
NO	µg/unit	18.8	0.9	19.9	1.3	529	54	BDL	BDL	3.630	12.210
NOx (NO + NO$_2$)	µg/unit	19.5	1.0	20.8	1.4	581	54	BDL	BDL	7.009	18.229
Benzo[a]pyrene	ng/unit	0.60	0.09	0.61	0.11	17.3	0.9	BDL	BDL	0.106	0.354
1-3-Butadiene	µg/unit	0.3	0.03	0.3	0.02	98.2	8.4	BDL	BDL	0.029	0.095
Isoprene	µg/unit	2.6	0.4	2.3	0.1	913	79	BDL	BDL	0.041	0.135
Acrylonitrile	µg/unit	0.2	0.02	0.2	0.02	26.1	4.3	BDL	BDL	0.032	0.107
Benzene	µg/unit	0.5	0.07	0.6	0.06	90.7	12.5	BDL	BDL	0.017	0.056
Toluene	µg/unit	1.9	0.3	2.0	0.2	158	24	NQ	NQ	0.061	0.204
Pyridine	µg/unit	7.4	0.6	7.8	1.4	35.1	2.4	0.2	0.1	0.027	0.090
Quinoline	µg/unit	< 0.011 but ≥0.003	—	< 0.011 but ≥0.003	—	0.49	0.05	BDL	BDL	0.003	0.011
Styrene	µg/unit	0.8	0.3	0.7	0.2	18.2	1	0.1	0.01	0.012	0.039
Hydroquinone	µg/unit	7.4	0.7	7.0	0.2	92.5	0.6	BDL	BDL	0.062	0.207
Resorcinol	µg/unit	< 0.055 but ≥0.016	—	< 0.055 but ≥0.016	—	2.0	0.0	BDL	BDL	0.016	0.055
Catechol	µg/unit	14.7	1.1	14.3	0.5	84.2	1.2	BDL	BDL	0.026	0.086
Phenol	µg/unit	1.3	0.1	1.4	0.1	12.8	0.8	NQ	NQ	0.026	0.086
p-Cresol	µg/unit	0.07	0.01	0.07	0.01	8.14	0.3	BDL	BDL	0.010	0.034
m-Cresol	µg/unit	0.03	0.01	0.03	0.01	3.2	0.2	BDL	BDL	0.006	0.019
o-Cresol	µg/unit	0.07	0.01	0.06	0.01	3.9	0.2	BDL	BDL	0.008	0.026
Formaldehyde	µg/unit	6.1	1.2	9.1	1.4	87	3	1.7	0.2	0.361	1.204
Acetaldehyde	µg/unit	211	16	230	21	1656	26	NQ	NQ	0.973	3.244
Acetone	µg/unit	31.0	2.3	35.9	4.3	708	18	NQ	NQ	0.846	2.821
Acrolein	µg/unit	8.4	1.3	10.7	1.7	162	3	BDL	BDL	0.713	2.377
Propionaldehyde	µg/unit	13.7	1.1	14.9	1.9	125	4	BDL	BDL	1.001	3.336
Crotonaldehyde	µg/unit	< 3.292 but ≥0.988	—	< 3.292 but ≥0.988	—	54	1	BDL	BDL	0.988	3.292
Methyl Ethyl Ketone	µg/unit	7.0	0.6	7.6	0.8	197	6	BDL	BDL	1.099	3.664
Butyraldehyde	µg/unit	22.5	1.9	23.1	1.9	91	3	NQ	NQ	0.812	2.706
1-Aminonaphthalene	ng/unit	0.07	0.01	0.07	0.01	22.4	0.42	NQ	NQ	0.008	0.027
2-Aminonaphthalene	ng/unit	0.04	0.01	0.04	0.01	14.1	1.99	0.02	0.00	0.004	0.012
3-Aminobiphenyl	ng/unit	0.012	0.003	0.012	0.003	4.5	0.16	NQ	NQ	0.001	0.004
4-Aminobiphenyl	ng/unit	0.016	0.002	0.016	0.003	3.1	0.03	0.01	0.01	0.001	0.005

[a] Total Particulate Matter. Health Canada Intense puffing regime. ISO 4387 method "Determination of total and [†]nicotine-free dry particulate matter (NFDPM) using a routine analytical smoking machine" was used to determine TPM, nicotine, water and NFDPM values. BDL: Below the Limit of Detection, NQ: Below the Limit of Quantification (LOQ) but above Limit of Detection (LOD). Unit = EHTP.

This change in color is consistent with the temperatures measured and reported in Fig. 5-b and to the color change observed over the 200–250 °C temperature range (Fig. 7iv and v). Physical inspection of the tobacco substrate revealed that the original morphology was retained, and no macroscopic change in the fibrous substrate could be detected (e.g. no ash was visible).

3.3. EHTS aerosol composition and EHTP tobacco substrate ultimate analysis

The major constituents of the EHTP mainstream aerosol, including selected HPHCs determined by Labstat® are reported in Table 2. The table includes the results of experimental runs carried out in synthetic air and in pure nitrogen. The results of experiments performed under atmospheres of synthetic air and in nitrogen (where a combustion process cannot occur) yielded comparable levels of all the 36 measured analytes, including TPM, water, NFDPM, nicotine, glycerol, CO, NO, NO$_x$, benzo[a]pyrene, volatiles, phenolic compounds, carbonyls and aromatic amines.

The distribution of the main constituents detected in the EHTP mainstream aerosol when the EHTS is operated in air using the modified ISO 4387 methodology are summarized in Fig. 8. Water, glycerol and nicotine, accounted for ca. 90% of the total mass of mainstream aerosol collected. The full characterization of the mainstream aerosol using a combination of liquid chromatography coupled to high resolution accurate mass spectrometry (LC-HRAM-MS) and
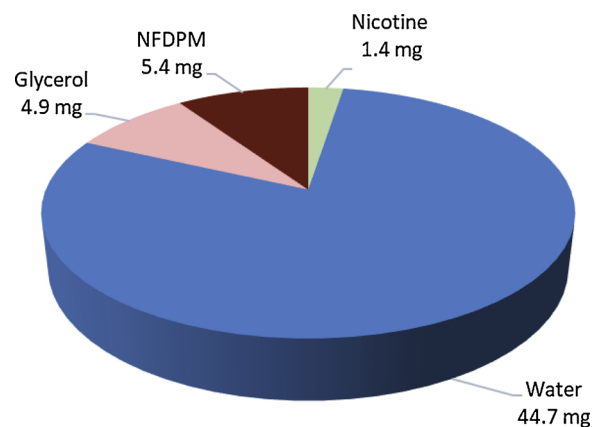

Fig. 8. Compositional analysis of the EHTP mainstream aerosol generated under the Health Canada Intense regimen for measuring emissions. Quantities are reported on a per unit EHTP basis. A modified ISO 4387 methodology that reduces water losses was used.

comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometry (GC × GC-TOFMS) analytical techniques lead to the identification of 99.7% of the total aerosol mass [68]. 97.8% w/w of the aerosol mass (based on the 50 most abundant compounds found in the mainstream aerosol) was comprised of compounds that are

Table 3

Elemental and Water Content Analysis of the EHTP tobacco plug and of a 3R4F Kentucky Reference Cigarette cut filler before and after experimental runs in air.

		Tobacco weight [mg]	C [% w/w]	H [% w/w]	N [% w/w]	Water Content [% w/w]
EHTP	Before Use	323.6 ± 14.5	38.4 ± 0.3	6.1 ± 0.2	2.0	14.3 ± 0.5
	After Use	212.0 ± 10.5	46.6 ± 1.2	5.4 ± 0.3	2.6 ± 0.2	2.8 ± 0.4
3R4F Cigarette	Before Use	817.0 ± 19.6	38.2 ± 0.8	5.9 ± 0.2	1.8 ± 0.3	13.2 ± 0.4
	After Use	381.4 ± 13.7	7.6 ± 0.9	0.8 ± 0.1	1.0 ± 0.2	1.9 ± 0.2

The percentage difference in weight lost by the tobacco plug of the EHTP and tobacco cut filler of the 3R4F reference cigarette was 34.5% and 53.4%, respectively. The nitrate content of the tobacco substrate in the EHTP ranged from 0.06 – 0.11% on a dry weight basis. Average and standard deviation reported are for 8 and 3 replicates, respectively, of the weight and elemental / water content analysis.

Table 4

CO and CO_2 levels in the EHTP mainstream aerosol and 3R4F Kentucky reference cigarette mainstream smoke when operating in air.

	EHTP		3R4F Cigarette	
	(mg/unit)	(μg/mg of tobacco)	(mg/unit)	(μg/mg of tobacco)
CO	0.5 ± 0.1	1.7 ± 0.3	31.4 ± 1.5	38.4 ± 1.9
CO_2	6.1 ± 0.6	18.7 ± 1.7	86.2 ± 2.9	105.5 ± 3.6

*Standard Deviation. Health Canada Intense puffing regime. Yields of CO and CO_2 are reported by unit EHTP and 34RF reference cigarette. Average and standard deviations reported are for 9 and 19 replicates, respectively, of the 3R4F Kentucky reference cigarette and EHTP.

known to be present in the multicomponent-EHTP before heating.

Ultimate analysis and water content for the tobacco substrate in the EHTP before and after experimental runs in air are reported for three replicates in Table 3. The weight lost by the tobacco substrate in the EHTP after the experimental runs are also given in Table 3. From this data, the weight loss was calculated to be 34.5%. Approximately 79% of the carbon was still present in the tobacco substrate of the EHTP after use. For comparison purposes, Table 3 also report the corresponding data obtained for a 3R4F Kentucky reference cigarette before and after burning. The elemental C, H, and N contents, as well as the water content of both tobacco samples were comparable before use. After use there was a significant difference is the elemental C, H and N content. In particular, a 53.7% weight loss was observed and only ~9% of the original carbon content was still present in the residual material of the 3R4F cigarette tobacco cut filler after use, due to the conversion of carbon to gaseous oxidized products via the smoldering combustion of the tobacco. Table 4 reports a comparison of the levels of CO and CO_2 in the EHTP mainstream aerosol and in the mainstream smoke of the 3R4F Kentucky reference cigarette.

As is evident from this Table, there was a significant difference in the levels of CO and CO_2 generated from the heating of the tobacco substrate in the EHTP compared to the smoldering combustion of tobacco in a 3R4F Kentucky reference cigarette. The CO and CO_2 levels in the EHTP mainstream aerosol were 98% and 93% lower, respectively, on a per unit basis, compared to the mainstream smoke of a 3R4F Kentucky reference cigarette under the HCI regimen. The significant reductions observed for CO reported in Table 4 were comparable to the reduction measured and reported by Schaller et al. [26].

4. Discussion

When the tobacco in a cigarette is ignited by an ignition source such as the flame from a lighter or match, a self-sustaining smoldering combustion process is initiated. Temperatures of between 500–700 °C are established at the tip of the cigarette and raise to above 850 °C when air is drawn into the burning cone [69]. The high temperatures, heat released, rapid rise in temperature and visible glowing upon puffing clearly evidence the overall exothermic nature of the smoldering combustion process [69–72]. The temperature onset of the combustion of tobacco samples, characterized by a rapid oxidation reaction (as

evidenced by a rapid loss in weight with a simultaneous large exothermic release of heat) has been reported to occur above 400 °C when investigated by thermogravimetric analysis coupled to differential scanning calorimetry [21,25].

Temperature data for the tobacco substrate in the EHTP when heated in the Holder (see Figs. 5 and 6) were significantly lower in comparison to the reported temperature of tobacco in the burning cone of a cigarette. The maximum temperature measured on the surface of the Heater (at R = 0.0 mm) was 320 ± 4 °C, well below the temperature required for the self-sustaining smoldering combustion of the tobacco substrate to occur (> 400 °C). In fact, the maximum temperature in the tobacco substrate measured 0.2 mm radially from the Heater's surface in all experiments reported here was < 260 °C. Simulated puffing (periodic air intakes) in the EHTP resulted in a decrease in the temperature of the tobacco substrate. The observed decrease in temperature of the tobacco substrate upon puffing was caused by the cooling effect of the flow of ambient temperature air through the EHTP. This effect clearly indicates that the heating process is endothermic and that no exothermic process occurred, and in particular that no self-sustained combustion process is ongoing in the tobacco substrate.

Another phenomenon that influences the temperature of the tobacco substrate is the continuous evaporation of volatile compounds such as water, glycerol and nicotine [73]. The evaporation process requires substantial energy. This, together with heat losses and the sequential cooling down of the tobacco when ambient air is drawn through the EHTP (due to gas-solid interfacial heat transfer), makes the tobacco temperature decrease rapidly in the radial outward direction from the Heater's surface [74]. This is in stark contrast to the rapid rise in temperature and heat release when air is drawn into the burning cone of a lit cigarette, caused by an increase in the rate of the combustion process.

Evidence for the absence of a self-sustaining combustion reaction is further provided by the drop in temperature of the tobacco substrate when power to the Heater is turned off during the heating cycle (see Fig. 6). As the Heater was turned off, there was no recovery in the temperature of the system and as time passed and additional puffs were taken, the temperature of the tobacco substrate continued to decrease. Yan and Fujita [75] used classical ignition theory calculations together with the experimentally measured temperature and thermal properties of the tobacco substrate in the EHTP to assess if ignition of the tobacco occurred in the EHTP. Their theoretical model confirmed that the temperature threshold for ignition of the tobacco substrate in the EHTP was not reached [21,25]. Additionally, the physical inspection of the EHTP upon completion of the programmed 360 s heating cycle in the EHTS revealed that its structural integrity was retained and that no ash was formed in the tobacco substrate after use (see Fig. 7-vii). The observed color change in the tobacco substrate close to the Heater is consistent with the temperatures reported in Fig. 5 and in Figs. 7-iv and -v).

The rapid decrease in temperature in the radial outward direction from the Heater shown in Fig. 5 can be explained by the layered morphology of the crimped cast-leaf tobacco substrate, and by the low effective thermal conductivity (ca. 0.09 W/m/K) and high thermal mass of the tobacco substrate (density of 990 kg/m^3 and a specific heat of

around 1400 J/kg/K [73]. The overall morphology of the tobacco substrate (shown in Fig. 3), due to the crimping process, resembles multiple layers of tobacco material. These layers are essentially flat rectangular channels and as air in drawn through the EHTP, i.e. when a puff is taken, these layers direct the flow of incoming air along the length of the tobacco plug. This anisotropy of the tobacco plug reduces flow related thermal dispersion in the radial direction, and ensures that the heat flux is governed primarily by heat conduction in the outward direction of the heating blade.

While CO and CO_2 are not unambiguous markers of combustion reactions (since they may be originated from lignocellulosic materials such as cellulose and hemicelluose by several low-temperature physical and chemical processes) [7,22,76] the levels of NO_x in the gas emissions can be used to provide evidence of the occurrence of exothermic reactions in the gas phase, or in the solid phase fuel due to combustion reactions. Operating the EHTS under both oxidative and non-oxidative atmospheres had very limited influence on the aerosol constituents detected in the mainstream aerosol, as shown in Table 2. The amounts of NO_x formed under both non-oxidative (nitrogen) and oxidative (synthetic air) atmospheres were $19.5 \pm 1.0\,\mu g/EHTP$ and $20.8 \pm 1.4\,\mu g/EHTP$, respectively. These yields are comparable and are small in absolute terms with respect to the total amount of tobacco "fuel" nitrogen (2.02% w/w) and the level of nitrates (ca. 0.1% w/w) naturally present in the tobacco substrate (see Table 3). The quantity of NO_x detected is also limited with respect to the amount of CO and CO_2 detected (0.5 mg/EHTP and 6.1 mg/EHTP, respectively – see Table 4) in the EHTP gas emissions, suggesting that exothermic reactions in the gas phase due to the oxidation of released compounds with air may be excluded. The low levels of NO_x reported in Table 2 support the absence of flaming phenomena or high temperature spots occurring in the gas phase, or in the solid phase, of the tobacco substrate in the EHTP.

Mainstream aerosol chemistry data for the EHTP was assessed to further explore the nature of the aerosol evolved from the tobacco substrate of the EHTP when heated in the Holder under simulated puffing. Smoke aerosols are generated when biomass materials undergo combustion or high temperature pyrolysis processes and are composed of solid particles, liquid droplets and gases suspended in air [47,77–79]. Tobacco undergoing smoldering combustion in a cigarette generates a complex smoke aerosol [1,80,81]. Smoke particulate matter is formed when products of combustion and high temperature pyrolysis products (e.g. hydrocarbons) reach supersaturation and condense to form droplets, or react together to form particles, or by the nucleation and growth of positively charged hydrocarbon ions resulting in the formation of soot particles [79]. In contrast to the smoke aerosol generated from burning tobacco leaves, the EHTP mainstream aerosol is formed when the electrically controlled Heater in the Holder raises the temperature of the tobacco substrate to a point that water, nicotine, glycerol (added to tobacco as an aerosol former) and tobacco flavors evaporate.

Fig. 8 and Table 2 report the main composition of the EHTP mainstream aerosol. Drying and evaporation dominate the low-temperature thermal processes that take place in the EHTP when heated in the EHTS. The change in the color of the tobacco substrate suggests that torrefaction (mild pyrolysis) occurred in a small portion of the tobacco substrate that resided close to the Heater surface. The EHTP mainstream aerosol generated is composed mainly of water and of products in the gas emissions derived from the vaporization/direct transfer of species (up to 97.8% by weight) present in the original EHTP. The amount of 44.7 mg of water collected under humid laboratory conditions using the modified ISO 4387 methodology [65] to minimize water loss and reported in Fig. 8 is consistent with the amount of free water that is transferred from the original tobacco sample (~41 mg considering the difference in the water content of the tobacco sample before and after heating – see Tables 2 and 3). The amount of unbound water contributed by the humid laboratory conditions was estimated to be 7.7 mg. Indeed, the total amount of water reported in Table 2 is

comparable under both oxidative and non-oxidative atmospheres, suggesting that no or very limited oxidation phenomena are responsible for the presence of water in the EHTP mainstream aerosol. As glycerol is added to the tobacco substrate to act as an aerosol former, and nicotine is naturally present in tobacco, the presence of these species in the gas emissions is due to vaporization processes.

A very specific aerosol, much different in composition from cigarette smoke aerosol, is thus formed in the EHTP [25,81,82]. The controlled low operating temperature range of the tobacco substrate in the EHTP leads to the generation of an aerosol not by the nucleation and condensation of either pyrolysis or combustion products, but rather by the condensation of glycerol, that forms nuclei, onto which water, nicotine and other constituents can condense. This aerosol formation mechanism was supported by Nordlund and Kuczaj [74], who modeled the aerosol nucleation process taking place in the EHTP numerically using an extended Classical Nucleation Theory (CNT) for multi-component gas substrates under the thermal conditions and gas yields present in the EHTP during heating in the Holder. The results from simulations performed demonstrated that droplets are formed only in the presence of an aerosol former [74,82] i.e. no aerosol droplets were generated when glycerol, water and nicotine were modelled as inert species.

With respect to higher molecular weight compounds such as B[a]P present in the aerosol, Table 2 shows that limited differences are present among the yields obtained in air and in nitrogen. PAHs, such as B[a]P are formed through the high temperature pyrolysis and incomplete combustion of biomass materials [1,12,15,16]. PAHs do not usually occur naturally in biomass, however their presence on tobacco leaves due to contamination can arise from the environment (during growing and curing) resulting from combustion sources [83]. When studying the PAH content of aerosols produced by different tobacco blends used in the EHTP [27], it was observed that the B[a]P content of aerosols was significantly lower (by an order of magnitude) than the amount originally determined on the tobacco blends before being heated in the EHTS. In fact, the actual amount of PAHs in the aerosol correlated with the PAH content of the tobacco varieties constituting the blends. These results strongly suggest that the B[a]P detected in the aerosol of the EHTP is most likely due to stripping caused by the gas stream [84].

Schaller et al. [26] reported aerosol chemistry results generated under the HCI regimen [62] for the EHTP in comparison to the mainstream smoke for a 3R4F Kentucky reference cigarette. The amount of NO_x ($537 \pm 43\,\mu g/3R4F$ cigarette) formed via the smoldering combustion of the tobacco in the 3R4F Kentucky reference cigarette is ~25 times higher with respect to the values reported in Table 2 for the EHTP. Similar differences, or even higher, were observed for CO, aldehydes, amines, aromatic and polycyclic aromatic hydrocarbon species. The lower amounts of NO_x, as well as the much lower amounts of CO, CO_2, aromatic compounds, aldehydes and amines present in the gas emissions of the EHTP are consistent with the lower operational temperatures reported in Fig. 5 for the tobacco substrate. The presence of low levels of NO_x in the EHTP mainstream aerosol, unaffected by operating the EHTS under oxidative and non-oxidative atmospheres, can be attributed to the thermal decomposition of nitrate salts originally present in the tobacco substrate [85].

A strong correlation between the nitrate content of different tobacco blends that where heated and the resulting NO_x determined in the aerosol was reported Schaller et al. [27]. This finding coupled with the absence of net exothermic processes occurring in the tobacco substrate of the EHTP during experimental runs, confirms the absence of combustion processes in the EHTP. The low levels of volatile organic compounds in the EHTP aerosol, the presence of unconverted carbon in the EHTP after heating, and the absence of ash provide additional evidence of the lower temperature processes occurring in the tobacco substrate of the EHTP compared to tobacco undergoing smoldering combustion in a burning cigarette.

5. Conclusions

The results of the experiments carried out show that the tobacco substrate in the EHTP, undergoes mainly drying, vaporization of volatiles, and torrefaction processes when used as intended in the EHTS Holder. Drying and evaporation dominate the low-temperature thermal processes. Torrefaction (mild pyrolysis) occurred in a small portion of the tobacco substrate that resided close to the Heater's surface. No evidence of self-sustained combustion processes were found. Moreover, in contrast to the smoke aerosol formed from the combustion and high temperature pyrolysis of tobacco in a cigarette, the EHTP aerosol is generated by the condensation of vaporized compounds originally present in the tobacco substrate, principally glycerol, water, and nicotine. The different processes taking place in the tobacco substrate during EHTS operation actually result in the formation of an aerosol that shows important qualitative and quantitative differences from the smoke aerosol formed from the self-sustained combustion of tobacco.

T. McGrath, B. Mahler, M. Nordlund, M. Smith, J.P. Schaller, and G. Zuber are Philip Morris International employees (PMI).

CRediT authorship contribution statement

V. Cozzani: Conceptualization, Writing - original draft, Writing - review & editing, Visualization. **F. Barontini:** Writing - review & editing. **T. McGrath:** Conceptualization, Writing - original draft, Writing - review & editing, Supervision. **B. Mahler:** Investigation, Validation. **M. Nordlund:** Formal analysis, Validation, Visualization, Writing - review & editing. **M. Smith:** Conceptualization, Writing - review & editing. **J.P. Schaller:** Conceptualization, Writing - review & editing. **G. Zuber:** Methodology, Investigation, Validation.

Declaration of Competing Interest

T. McGrath, B. Mahler, M. Nordlund, M. Smith, J.P. Schaller, and G. Zuber are Philip Morris International employees (PMI).

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.tca.2019.178475.

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