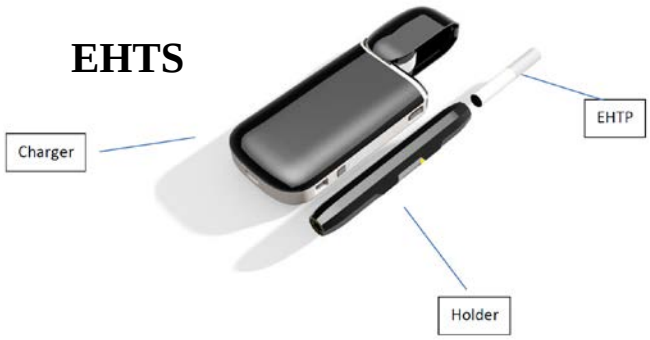
Source: PMIScience website

Philip Morris International (PMI) has developed a patented Electrically Heated Tobacco System (EHTS) that heats a specifically designed tobacco product (Electrically Heated Tobacco Product or EHTP). The EHTP contains tobacco[1] material in the form of a plug that undergoes a controlled heating process to produce a vapor (aerosol). The tobacco is only heated and is not burnt as happens in a lit cigarette.



PMI retained Professor Valerio Cozzani in an independent capacity to review and analyze scientific data on the thermal processes taking place in the EHTS during aerosol generation. Professor Valerio Cozzani is an expert in combustion (burning) and pyrolysis (thermal breakdown) of biomass (materials obtained from plants) and is a faculty member of the Chemical Engineering department at the University of Bologna, Italy,

Professor Cozzani issued two expert opinions:

1. The first addresses the scientific definition of combustion, indicators of tobacco combustion, and analyzes as to whether any combustion processes occur when the Holder heats the tobacco material in the EHTP.
2. The second addresses the scientific definition of smoke and analyzes whether the EHTS operation produces smoke when the Holder heats the tobacco material in the EHTP.

1. Expert Opinion on Combustion

To support his expert opinion, Professor Cozzani performed a literature search with respect to the scientific definition of combustion and the indicators of biomass and tobacco combustion. He then reviewed the operation of the EHTS and analyzed experimental data on the EHTS provided by PMI (that includes data generated by an independent analytical laboratory) to assess whether any combustion processes occur.

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[1] The EHTP does not contain tobacco cut-filler (tobacco leaf cut in small pieces found in cigarettes) or pipe tobacco. All of the tobacco in the EHTP is reconstituted (cast-leaf) tobacco made from tobacco powder, water, glycerin, guar gum and cellulose fibers.

The expert opinion of Professor Cozzani concludes that no combustion processes occur in the tobacco material when the Holder heats the EHTP to produce an aerosol.

Unlike a cigarette, where the combustion of tobacco at high temperature results in the formation of smoke and ash, the EHTS does not generate the conditions necessary to combust the tobacco material in the EHTP. The aerosol produced when an EHTP is heated results from vaporization of an aerosol former, water and some tobacco constituents.

Professor Cozzani's expert opinion is based on the following findings from his assessment:

- The temperatures reported for the EHTP during use are far below those required for the combustion of tobacco to occur;
- The key characteristics of combustion (e.g., the formation of relevant amounts of nitrogen oxides and the generation of heat) are absent in the EHTP.

2. Expert Opinion on Smoke

To support his expert opinion, Professor Cozzani performed a literature search with respect to the scientific definition of smoke. He then reviewed the operation of the EHTS and analyzed experimental data on the EHTS provided by PMI (that includes data generated by an independent analytical laboratory) to assess whether the EHTS operation produces smoke.

The expert opinion of Professor Cozzani concludes that the most comprehensive and accurate scientific definition of smoke is provided by Standard 92B of the US National Fire Protection Association and that the EHTS operation does not produce smoke.

Standard 92B defines that smoke is composed of airborne solid, liquid particulates and gases evolved when a material undergoes pyrolysis or combustion, together with a quantity of air that is entrained or otherwise mixed into the mass.

Professor Cozzani's expert opinion that the EHTS operation does not produce smoke is based on the following findings from his assessment:

- the aerosol produced by EHTS operation is formed principally by vaporization processes as proven by its chemical characterization
- the absence of combustion processes in the EHTP tobacco substrate
- very limited pyrolysis phenomena present in the EHTP tobacco substrate during EHTP operation, which do not have a relevant influence on the aerosol formed: less than 2% by weight of the aerosol components may derive from the pyrolysis of the tobacco substrate which would not be sufficient to characterize the aerosol as "smoke"

As a result of the above findings, Professor Cozzani determined that the aerosol produced is not derived from a smoke forming process and cannot be classified as smoke.

Environmental Analytical Chemistry

O'Connell et al., J Environ Anal Chem 2015, 2:5
http://dx.doi.org/10.4172/2380-2391.1000163

Short Communication Open Access

Heated Tobacco Products Create Side-Stream Emissions: Implications for Regulation

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Abstract

A number of tobacco manufacturers are promoting products where the tobacco is reportedly "heated" rather than burned. It has been claimed that certain heated tobacco products produce only mainstream and no side-stream emissions. In this study we investigated these claims for a commercially available heated tobacco product and, by using a simple experimental design, investigated whether the high temperature heating of the tobacco matrix during product activation and use results in the generation of side-stream emissions. By way of comparison, the Nicorette® inhalator and a leading e-cigarette brand were also investigated. Our findings indicated that a large number of different chemical compounds were released into the airspace around the heated tobacco product when switched on and during consumer use indicating the generation of side-stream emissions. As the public health community has concluded there is no safe level of exposure to tobacco-containing product emissions, this would be of concern and warrants further investigation. Based on our data showing side-stream emissions from the tobacco matrix, the use of heated tobacco products in indoor public places should fall under the same regulations as cigarettes.

Keywords: Heated tobacco; Heat-not-burn; E-cigarette; Nicorette; Side-stream emissions; Second-hand smoke; Nicotine; Tobacco

Introduction

It is well known that when tobacco burns, many thousands of chemicals are released from the tobacco matrix and are inhaled by consumers and bystanders [1,2]. It has been stated that the majority of smoking-related diseases are caused not by nicotine but by the generation of harmful or potentially harmful smoke constituents (HPHCs) from the burning of tobacco [3,4]. In response, a number of tobacco manufacturers are promoting products where the tobacco is reportedly "heated" rather than burned in an attempt to reduce HPHC emissions [5-7]. This is not a new concept, as cigarette-based heated tobacco products were first marketed in the USA in the 1980s and proved to be commercially unsuccessful. Heated tobacco products are now being revived and repositioned as an alternative for smokers who may not wish to replace conventional cigarettes with non-tobacco products such as electronic cigarettes (e-cigarettes). While some manufacturers claim heated tobacco products do not produce side-stream emissions, the major component of 'second-hand smoke', this has yet to be independently verified [8-12]. Since the World Health Organisation has stated "*there is no safe level of exposure to second-hand tobacco smoke*" [13] and the British Medical Association (BMA) has stated that "*almost 85 per cent of second-hand smoke is in the form of invisible, odourless gases*" [14], claims of an absence of side-stream emissions from heated tobacco products warrants investigation. To that end, we sought to investigate whether or not side-stream emissions were generated by a commercially available heated tobacco product. For comparative purposes, we also investigated the Nicorette® inhalator and a leading e-cigarette.

Experimental Section

The analytical technique Proton Transfer Reaction-Mass Spectrometry (PTR-MS) was used to sample and analyze for any side-stream emissions released to the airspace around an iQOS heated tobacco product with regular Marlboro *HeatSticks* (manufacturer, Philip Morris International) when activated by the user (but not puffed) and also during product use. Additionally, sampling was conducted for a Nicorette® inhalator (15 mg nicotine replacement aid; manufacturer, McNeil Consumer Healthcare Ltd) and Blu™ closed system e-cigarette (18 mg nicotine; manufacturer, Fontem Ventures B.V.) All products used in this study were used in accordance with manufacturer's instructions and consumed *ad libitum* i.e., there was no pre-defined consumption requirement. For each of the different products, a number of replicate puffs were made and representative data from a single puff is shown. In short, the PTR-MS instrument ionizes volatile organic compounds (VOCs) in the gas phase through their reaction with H_3O^+ to form protonated VOCs ($VOCH^+$) which can then be detected by a mass spectrometer [15]. This process can be run on air samples with or without dilution as normal air gases (e.g., N_2, O_2, CO_2) have a proton affinity less than water and thus are not ionized. Most VOCs have a proton affinity greater than water and therefore are readily ionized and detected [15]. Analyses with PTR-MS can be conducted in real-time and continuously without the need for sample preparation [15]. Airspace analysis was conducted by connecting the PTR-MS inlet to the test chamber and sampling directly. PTR-MS operating conditions were as follows: drift tube voltage, 500 V; drift tube pressure, 2.3 mbar; drift tube temperature, 120°C; drift tube length, 9.3 cm; *E/N* ratio, 130 Td (Townsends; where *E* is electric field and *N* is the number density of the gas in the drift tube; 1 Td=10^{-17} cm^2 V $molecule^{-1}$); inlet temperature, 120°C. The experimental set-up is outlined in Figure 1.

Results and Discussion

Qualitative characterization of side-stream emissions

Following activation of the iQOS heated tobacco product, as per the manufacturer's instructions, a large number of different VOC species across a range of masses were released into the airspace (Figure 2A). This clearly indicates the generation of side-stream emissions when the device is activated but not puffed by the consumer, which

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Received October 02, 2015; **Accepted** October 12, 2015; **Published** October 15, 2015

Citation: O'Connell G, Wilkinson P, Burseg KMM, Stotesbury SJ, Pritchard JD (2015) Heated Tobacco Products Create Side-Stream Emissions: Implications for Regulation. J Environ Anal Chem 2: 163. doi:10.4172/2380-2391.1000163

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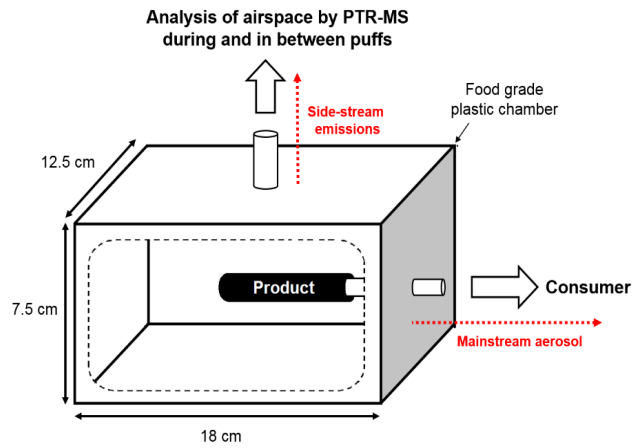

Figure 1: Schematic representation showing experimental set-up and the side-stream emissions capture chamber.

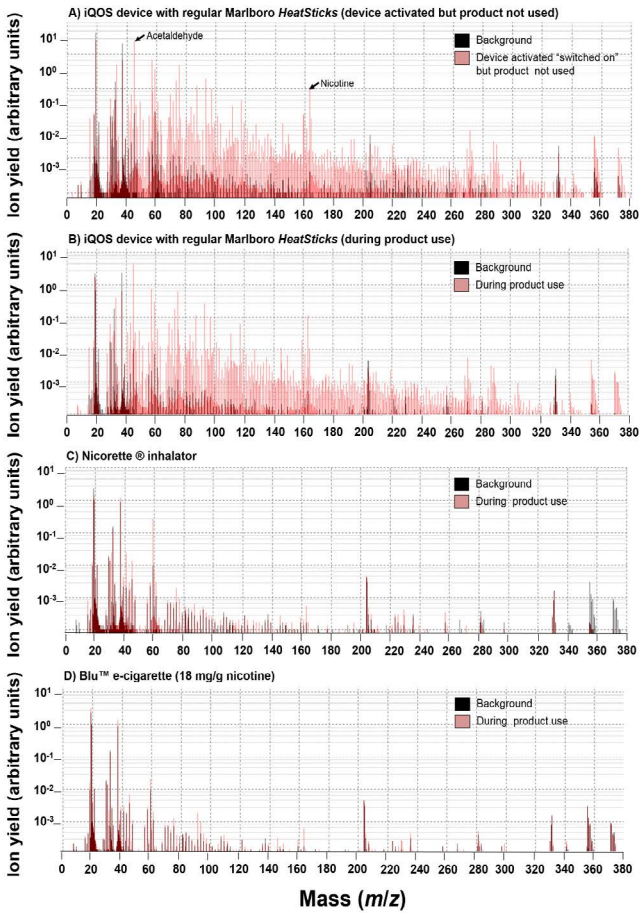

Figure 2: Representative PTR-MS mass spectra of the VOCs released to the airspace for (**A**) iQOS with regular Marlboro *HeatStick* when activated "switched on" but product not actively puffed and (**B**) during consumer use of the iQOS device with regular Marlboro *HeatSticks*; (**C**) during consumer use of the Nicorette® inhalator; and (**D**) during consumer use of the Blu™ e-cigarette. Specific compound (peaks) at *m/z* 45 is protonated acetaldehyde and *m/z* 163 is protonated nicotine and is labelled with arrowheads in (**A**).

would be released into the ambient air, raising potential concerns for bystanders. Furthermore, during active puffing on the heated tobacco product, side-stream emissions are also released (Figure 2B). These chemicals are being released from the high temperature heating of the tobacco matrix in the *HeatSticks*. Given the similarities of the Marlboro branded *HeatStick* used in the iQOS device to a conventional cigarette, the detection of side-stream emissions is perhaps not surprising even though it has been stated that such products produce no side-stream aerosol/smoke [8-12]. Given the findings presented in this pilot study, this requires further investigation.

The PTR-MS mass spectra of the VOCs in the airspace around the Nicorette® inhalator (Figure 2C) and the e-cigarette (Figure 2D) during product use are virtually indistinguishable. Moreover, the Nicorette® inhalator and the e-cigarette profiles are entirely distinct from that of the heated tobacco product, as may be anticipated given these products do not contain tobacco. The Nicorette® inhalator was selected as an appropriate comparator in this study as the UK Medicines and Healthcare products Regulatory Agency (MHRA) has indicated this should be used as a reference product, if manufacturers intend to license e-cigarettes as medicinal products [16].

Future investigations

PTR-MS is a one dimensional technique that characterizes VOCs via their mass; to enable identification of the chemicals in the side-stream emissions from the heated tobacco product it is necessary to further calibrate the machine for identification and quantification of compounds of regulatory interest e.g., HPHCs in tobacco products and tobacco smoke as developed by the US Food and Drug Administration (FDA) [17]. We will therefore determine the identities of the many different VOCs released to the airspace, and by extension to the bystander's breathing space, from the heated tobacco product when activated and used by the consumer. Moreover, it is also conceivable that differences in side-stream emissions may be observed under varying user consumption topographies. Further research in these areas will be informative.

Conclusions

The release of side-stream emissions from heated tobacco products has been observed by PTR-MS using the simple method presented here. These emissions are generated by the high temperature heating of the *HeatSticks* tobacco matrix inserted within the iQOS device.

The public health community has stated that there is no safe level of exposure to tobacco-containing product emissions [13,18], and so the side-stream constituents including nicotine, released during activation and use of the iQOS heated tobacco product can lead to exposure to bystanders; this would be of concern to public health authorities and warrants further investigation.

It is conceivable that based on these findings and the conclusions of public health community regarding tobacco product emissions, the use of heated tobacco products should be included in smoke-free legislation.

Conflicts of Interest

The work in this short communication was supported by Imperial Tobacco Group. Imperial Tobacco Group is the parent company of Fontem Ventures B.V., the manufacturer of the e-cigarette used in this study.

References

1. U.S. Department of Health and Human Services (2014) The health consequences of smoking—50 years of progress: A report of the surgeon general, Atlanta, GA: U.S.

2. U.S. Department of Health and Human Services (2010) How tobacco smoke causes disease: The biology and behavioral basis for smoking-attributable disease: A report of the surgeon general. Atlanta, GA: U.S.

3. UK National Institute for Health and Care Excellence (2013) Tobacco: Harm-reduction approaches to smoking. Public health guidance.
4. http://www.ash.org.uk/files/documents/ASH_715.pdf
5. PMI. Heat-not-burn. Accessed on: 10 August 2015.
6. BAT. Tobacco heating products (2015) Accessed on: 10 August 2015.
7. JTI. It's time to rethink tobacco (2013) Accessed on: 10 August 2015.
8. Frost-Pineda K, Zedler BK, Liang Q, Roethig HJ (2008) Environmental tobacco smoke (ETS) evaluation of a third-generation electrically heated cigarette smoking system (EHCSS). Regulatory toxicology and pharmacology 52: 118-121.
9. Tricke AR, Schorp MK, Urban HJ, Leyden D, Hagedorn HW, et al. (2009) Comparison of environmental tobacco smoke (ETS) concentrations generated by an electrically heated cigarette smoking system and a conventional cigarette. Inhalation toxicology 21: 62-77.
10. Ginglinger GC, Campelos P, Maeder S, Mitova M, Mottier N, et al. (2015) Indoor air chemistry comparative study between conventional cigarette and heat-not-burn technology. In Global Forum on Nicotine, Warsaw, Poland.
11. Ginglinger GC, Campelos P, Maeder S, Mitova M, Mottier N, et al. (2015) Indoor air chemistry comparative study between conventional cigarette and heat-not-burn technology. In Society of Toxicology Annual Meeting, San Diego, California, USA.
12. Ginglinger GC, Maeder S (2015) Indoor air chemistry (IAC) - comparative study between conventional cigarette and heat-not-burn technology. In Society for Research on Nicotine and Tobacco 21st Annual Meeting, Philadelphia, Pennsylvania, USA.
13. WHO (2007) Only 100% smoke-free environments adequately protect from dangers of second-hand smoke. Accessed on: 10 August 2015.
14. BMA (2002) Towards smoke-free public places. British medical association board of science and education and tobacco control resource centre.
15. Ellis AM, Mayhew CA (2014) Background, in proton transfer reaction mass spectrometry: Principles and applications. John Wiley & Sons, Inc., Chi Chester, UK.
16. MHRA (2013) Licensing procedure for electronic cigarettes and other nicotine containing products (NCPS) as medicines.
17. FDA (2012) Harmful and potentially harmful constituents in tobacco products and tobacco smoke; established list. Federal register: 20034-20037.
18. U.S. Department of Health and Human Services (2006) The Health Consequences of Involuntary Exposure to Tobacco Smoke: A Report of the Surgeon General. Rockville, MD: U.S.

Citation: O'Connell G, Wilkinson P, Burseg KMM, Stotesbury SJ, Pritchard JD (2015) Heated Tobacco Products Create Side-Stream Emissions: Implications for Regulation. J Environ Anal Chem 2: 163. doi:10.4172/2380-2391.1000163

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Indoor air quality and exhaled breath composition after use of nicotine delivery products

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SRNT-USA
26 February 2015

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1. Introduction

Electronic cigarettes (e-cigarettes) and heated tobacco (Heat-not-Burn) products are gaining acceptance with consumers as alternatives to traditional tobacco products. Consequently, there is a growing interest from regulators and public health organisations on whether the aerosol exhaled from such products has implications for the quality of air breathed by bystanders.

There is currently an absence of robust scientific evidence on the potential impact of exhaled aerosol on indoor air quality in everyday environments, like homes and offices. Nonetheless, there are calls, including by some by government bodies, to prohibit the use of e-cigarettes in workplaces and enclosed public spaces [1].

In the first part of our work we aimed to perform an assessment of indoor air quality by analysing the airborne concentrations of nicotine, propylene glycol and glycerol (the major components of e-cigarette liquids) before, during and after use of e-cigarettes in 'real-life' conditions. As there are no general indoor air quality guidelines or standards for nicotine, propylene glycol or glycerol, a comparison of the findings to UK workplace exposure limits (WELs) is made to provide an indication of potential bystander air quality [2].

As the quality of indoor air is influenced by the chemical composition of exhaled breath, in the second part of our work we aimed to determine whether Proton Transfer Reaction-Mass Spectrometry (PTR-MS) may be a suitable technique for the real-time analysis of chemicals released in exhaled breath following use of a range of nicotine delivery products. Please refer to our second SRNT-USA 2015 poster presented today for more information from our PTR-MS pilot studies [session 2; poster #54].

2. Air quality testing in an office before, during and after use of an electronic cigarette

An electronic cigarette (e-cigarette) air quality study was conducted by a leading independent UK accredited laboratory with recognised expertise in air quality measurements and analyses for Imperial Tobacco to assess the concentration of nicotine, propylene glycol and glycerol (the main components of e-cigarette liquid) in the ambient air before, during and after use of the Puritane™ 16 mg disposable e-cigarette (manufacturer Fontem Ventures B.V.) in an office environment.

A schematic representation of the office layout, the two independent sampling locations and the positions of the e-cigarette users and non-users is shown in ***Figure 1***. To investigate potential changes in indoor air quality, the ambient air was analysed before, during and after a 165 min vaping session. Sampling times are shown in ***Figure 2.***

The average puff rate over the three e-cigarette users during the 165 min vaping session was 3.2 puffs per minute. This level of product use may have been influenced by the no-vaping restriction during the first hour. Given the puffing frequency and 0.8 air changes per hour air exchange rate, it is likely that findings in this study may be an overestimate. ***Table 1*** summarises the results for airborne concentrations of nicotine, propylene glycol and glycerol before, during and after the vaping session.

As would be anticipated, the concentration of propylene glycol in the indoor ambient air, the major constituent of the e-liquid, was higher during the vaping session relative to the background and no vaping control period but remained within the workplace exposure limit (WEL) set for this chemical. Following cessation of vaping, there was a substantial decrease in the concentration of propylene glycol in the indoor ambient air. By contrast, there was no measurable increase in the airborne concentration of nicotine during use of the e-cigarette in the office space (limit of detection [LOD] for nicotine, 7 μg/m^3). Due to the LOD for glycerol (150 to 350 μg/m^3), glycerol was not detected in any of the samples taken, with the results being < 250 μg/m^3 for the vaping samples.

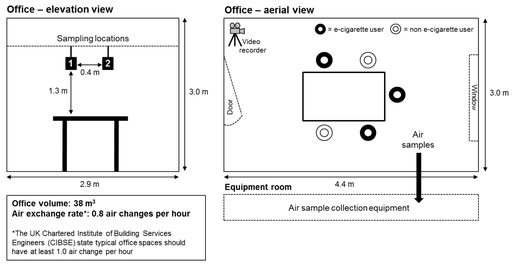

Figure 1 The layout of the office, the sampling locations and the positions of the e-cigarette users and non-users during the meeting.

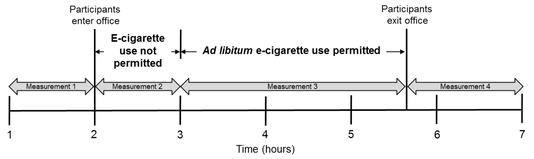

Figure 2 Timeline showing when participants entered and exited the office, when e-cigarette use was and was not permitted and the sampling times.

Table 1 Analysis of nicotine, propylene glycol and glycerol in indoor ambient air before, during and after a vaping session (average from the two sampling locations)

Chemical	Background (before participants enter room) [μg/m^3]	Room occupied (NO VAPING) [μg/m^3]	Room occupied (VAPING PERMITTED) [μg/m^3]	Room unoccupied (after participants leave room) [μg/m^3]	Workplace exposure limit (WEL) (8 h mean) [μg/m^3]	Comments
	Measurement 1	Measurement 2	Measurement 3	Measurement 4		
Nicotine	< LOD	< LOD	< LOD	< LOD	500	No measurable increase during vaping relative to background and no vaping control; below the WEL
Propylene glycol	< LOD	< LOD	204	10.2	474000 (total vapour and particulates)	Increase during vaping relative to background and no vaping control period; substantial decrease with cessation of vaping; below the WEL
Glycerol	< LOD	< LOD	< LOD	< LOD	10000	Glycerol not detected in any sample; due to large limit of detection, a more sensitive analytical method is required

Note: LOD, limit of detection

3. Analysis of VOCs released in exhaled breath following use of nicotine delivery products

The analytical technique PTR-MS (Proton Transfer Reaction-Mass Spectrometry) is a sensitive tool for the simultaneous real-time monitoring of volatile organic compounds (VOCs) with high sensitivity. PTR-MS is a tool that does not require sample preparation and so can be used for rapid determination of exhaled breath profiles e.g. in medical diagnostics.

We recently published an indoor air quality mathematical model to predict potential bystander exposures to exhaled e-cigarette aerosol constituents [3]. Here we identified 'quantity of chemical constituent exhaled' as the most important factor influencing indoor air quality and bystander exposure. Therefore, it is essential that precise measurements are made regarding the quantity of compounds exhaled by the e-cigarette user (e.g. nicotine) when determining potential bystander exposure. As the composition of the exhaled breath will influence the quality of indoor ambient air, PTR-MS may be used as part of an assessment scheme for indoor air quality.

In this proof-of-concept study we aimed to identify and determine the breath concentrations of nicotine following use of a range of nicotine delivery products. Representative data presented in ***Figure 3*** shows mass spectrometric profiles of exhaled breath following a single exhalation event after product use (red) and comparison with blank control breath (black). The peaks on mass 19 and 37 *m/z* (and their isotopes) represent the reagent ions (H_3O^+) and their clusters. The PTR-MS has been calibrated for nicotine (*m/z* 163; see arrowheads) [4]; all other red peaks correspond to compounds released following use of the specific nicotine delivery product; their identities remain to be determined in future work.

Following use of a conventional cigarette and heated tobacco product, a large number of different chemicals are released in the exhaled breath, as shown by the red spectra across a range of masses. With regards to exhaled nicotine, 1150 ppb (parts per billion) nicotine were detected in the exhaled breath following use of the conventional cigarette (**a**) and 1840 ppb nicotine following use of the heated tobacco device (**b**). In contrast, with the non-tobacco products, nicotine was detected in the exhaled breath at 7 ppb following use of the e-cigarette (**c**) and 1 ppb nicotine following use of the nicotine inhalator (**d**).

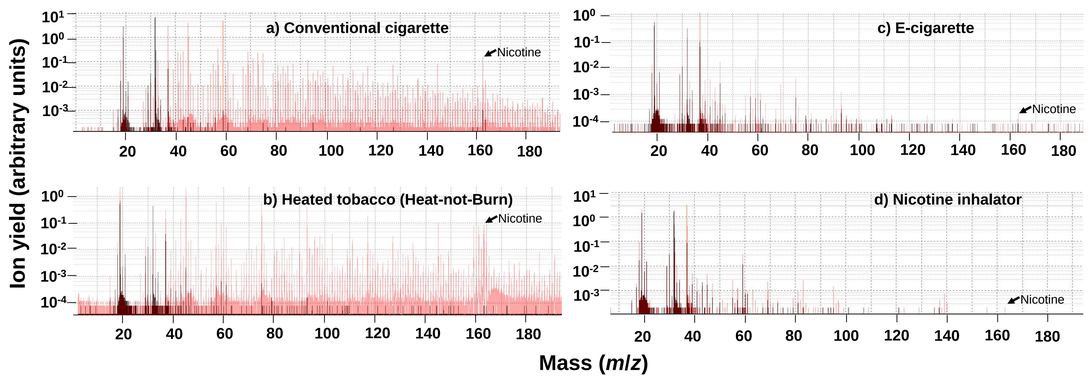

Figure 3 Representative PTR-MS mass spectra of VOCs released in a exhaled breath following use of (**a**) a conventional cigarette (0.6 mg nicotine [ISO smoking regime]), (**b**) heated tobacco device (Heat-not-Burn; iQOS with regular heatsticks) (**c**) electronic cigarette (20 mg/mL nicotine Puritane rechargeable e-cigarette device) and (**d**) 15 mg nicotine inhalator (Nicorette® Inhalator). Black peaks, VOCs released in normal exhaled breath (background control); red peaks, VOCs released in exhaled breath following product use. Results shown here are the output from a single exhalation event. Specific compound (ion trace) at *m/z* 163 is nicotine and is labelled with arrowhead. PTR-MS identification of nicotine at *m/z* 163 is shown elsewhere [4]. Three volunteers participated in this study and each volunteer used each of the four products described above. For each of the products tested: five blank breath measurements were taken directly before product use (background control) and following this the volunteer was given the product to use and become familiar with. Following this, the volunteer used the product *ad libitum* five times and exhaled into the PTR-MS each time allowing analysis on a per puff basis.

4. Conclusions & future work

During the use of the Puritane™ 16 mg disposable e-cigarette in the small office space indoor air quality study, the concentration of propylene glycol measured in the office air, and therefore breathed by bystanders, was significantly lower than the UK WEL. Exposure of bystanders to indoor ambient air following exhalation of this chemical at the levels seen in this study within the e-cigarette aerosol would not be anticipated to cause health problems, a conclusion in agreement with [5]. There was no measureable increase in the concentration of nicotine in the indoor ambient air during vaping. To explore this finding further, we aim to determine (i) the quantity of nicotine retained by the e-cigarette user (i.e. the fraction not exhaled into the ambient air); and (ii) whether any potential nicotine in the exhaled aerosol is deposited to various surfaces.

As may be expected from the tobacco basis of conventional cigarettes and heated tobacco (Heat-not-Burn), many more chemical components are detected in exhaled breath compared to simple electronic vapour products. Of note, substantially more nicotine is present in the exhaled breath following use of the tobacco based products. Due to the wide range of chemical species detected in the exhaled breath following use of the heated tobacco product, it is likely use of such products could impact indoor air quality in a similar way that has been reported for conventional cigarettes. As such, this is an important area for additional research.

The indoor air quality experimental design and methodology used in our work may be employed to evaluate the indoor ambient air quality assessment of other chemicals or particulates. Moreover, our proof-of-concept PTR-MS work showed the potential of this technology to be used as a technique to monitor the emissions from a range of nicotine delivery products and quantify released VOCs in real-time under a range of conditions and determine the impact on indoor air quality.

References

[1] WHO Conference of the Parties to the WHO Framework Convention on Tobacco Control. FTCT/COP/6.10. Sixth session. Provisional agenda item 4.4.2. apps.who.int/gb/gctc/PDF/cop6/FCTC_COP6_10-en.pdf
[2] UK Health and Safety Executive. EH40/2005 Workplace exposure limits. www.hse.gov.uk/pubns/books/eh40.htm
[3] Colard, S. *et al.* (2015) Electronic Cigarettes and Indoor Air Quality: A Simple Approach to Modelling Potential Bystander Exposures to Nicotine. *Int. J. Environ. Res. Public Health*. 12, 282-299
[4] O'Connell, G. *et al.* (2015) Real-time analysis of exhaled breath following the use of a range of nicotine delivery products by PTR-MS: proof of concept study. Technical Report. Access at www.imperialtobaccoscience.com
[5] McNeill, A. *et al.* (2014) A critique of a WHO-commissioned report and associated article on electronic cigarettes. *Addiction*. DOI:10.111/add.12730

Declaration

This project was supported by Imperial Tobacco Group. The e-cigarette used in this study was manufactured by Fontem Ventures, a fully owned subsidiary of Imperial Tobacco Group.

Heated Tobacco
Opportunity or Distraction?

FDA Workshop on E-Vapour Products

Dr Stephen Stotesbury
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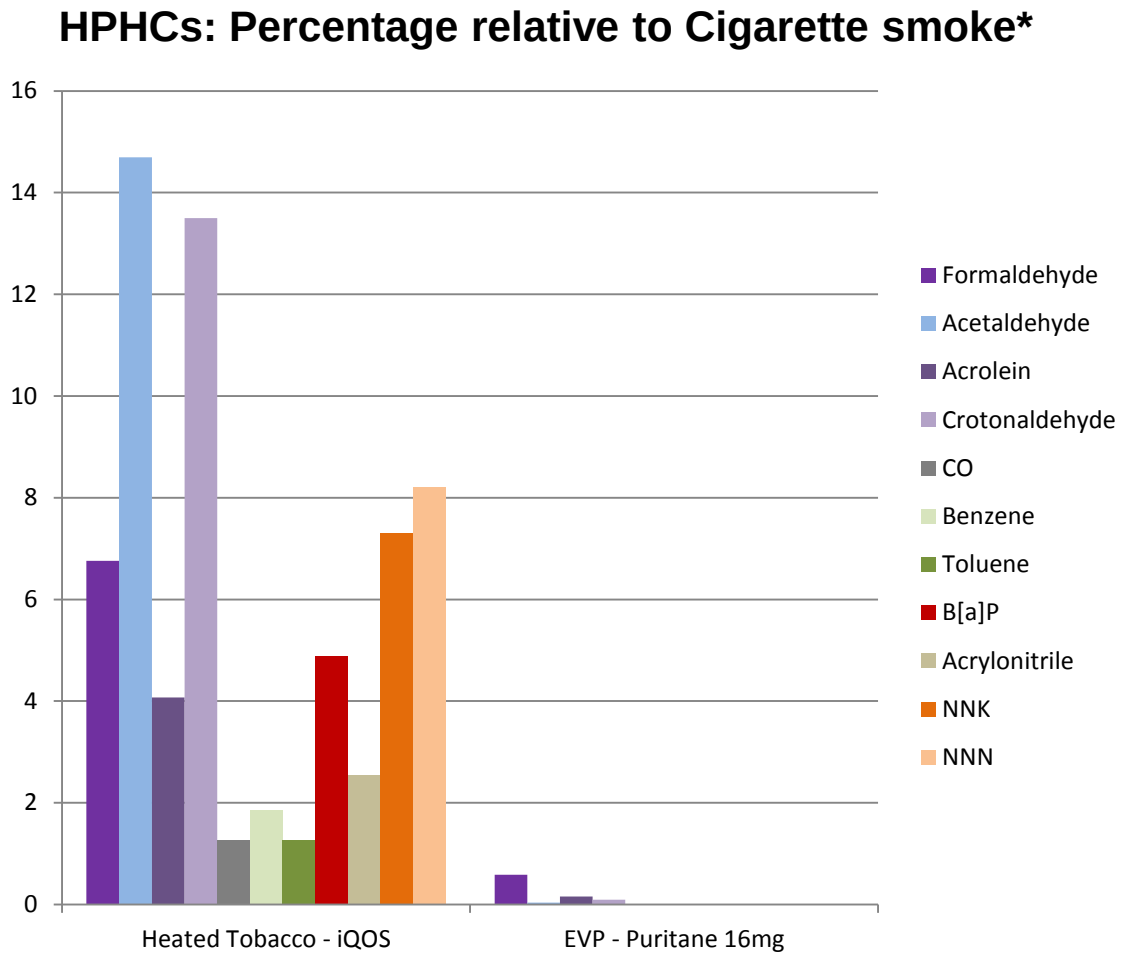
10 March 2015

Emissions from Heated Tobacco and E-Vapour

- EVP and Heated Tobacco both produce much lower emissions relative to cigarettes
- Products of combustion found in output from Heated Tobacco
- EVP emissions substantially different to and less than cigarette or Heated Tobacco
- E-Vapour is not smoke

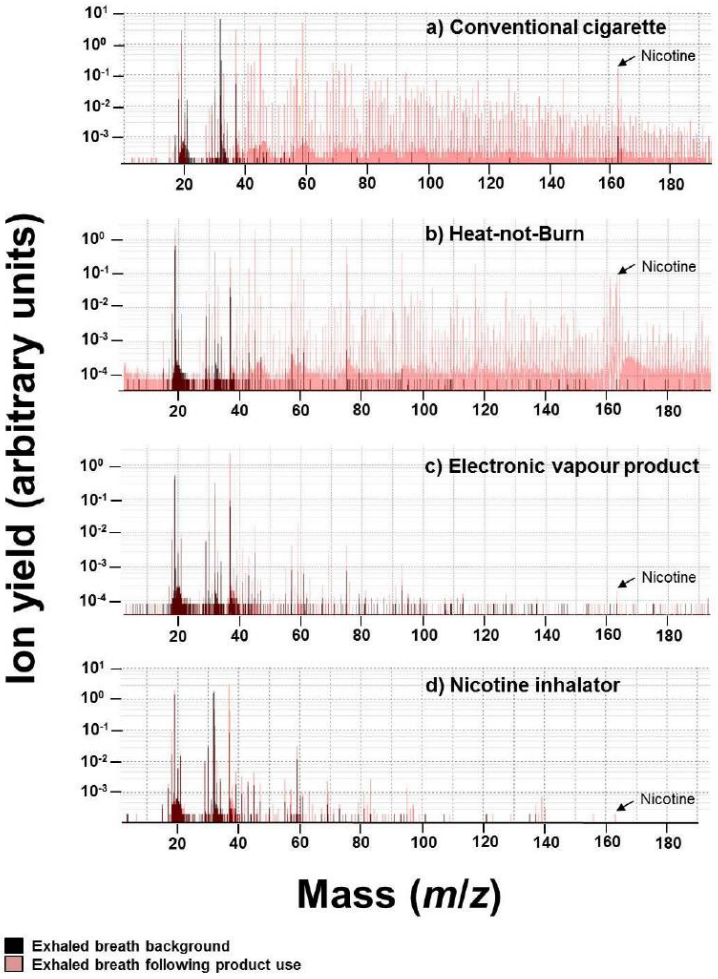


* 55ml puff every 30 seconds. 10 puffs each from EVP and Heated Tobacco.
Each HPHC presented as a percentage relative to quantity measured in cigarette smoke emissions (Marlboro Gold – Germany)

Impact on Indoor Air-Quality

Exhaled Air – PTR-MS study

- Substantially less chemicals from E-vapour
- E-vapour profile similar to Nicorette Inhalator®
- Exhalate from Heated Tobacco qualitatively similar to cigarette smoke



Real-time analysis of exhaled breath following the use of a range of nicotine delivery products by PTR-MS: proof of concept study, O' Connell, Burseg, Breiev, Colard and Pritchard http://www.imperialtobaccoscience.com/files/pdf/environmentaltobaccosmoke/Real-time_analysis_of_exhaled_breath_following_the_use_of_a_range_of_nicotine_delivery_products.pdf

Summary

- Claims for Heated Tobacco need to be critically evaluated
- Heated tobacco offers potential for reduced exposure – but does not eliminate exposure to smoke
- E-vapour has greatest potential for harm reduction

Real-time analysis of exhaled breath following the use of a range of nicotine delivery products by PTR-MS: proof of concept study

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1. Introduction

The analytical technique PTR-MS (Proton Transfer Reaction-Mass Spectrometry) is a sensitive tool for the simultaneous real-time monitoring of volatile organic compounds (VOCs) without sample preparation, with the potential to achieve parts per trillion detection levels.

The technique involves the chemical ionisation, by proton transfer, of a gaseous sample inside a drift tube under an electric field. The proton source is normally protonated water (H_3O^+). The chemical analyte and H_3O^+ ions are introduced into the drift tube, where proton transfer will occur for those VOCs with a greater proton affinity than water. On the basis of proton affinity, normal air gases (e.g. N_2, O_2, CO_2) show no reaction with H_3O^+ but many trace VOCs are readily protonated as shown: VOC + H_3O^+ → $VOCH^+$ + H_2O.

After passing through a drift tube to remove cluster ions, VOCs are then detected by the mass spectrometer. The mass spectrometer used in this work is a time-of-flight mass spectrometer that benefits from a mass resolution ($m/\Delta m$) >1000 Da and most significantly is able to observe all mass channels simultaneously.

PTR-MS has many applications in environmental and biological research, food flavour and fragrance science, indoor air quality, security and safety (detection of illicit substances) and in medical diagnostics. The fundamentals of PTR-MS and its applications have been reviewed elsewhere [1, 2].

PTR-MS has been established as a novel tool for a rapid determination of exhaled air profiles. However, no investigations have been carried out into the profile of exhaled air following use of nicotine delivery products as determined by PTR-MS. In this proof of concept study, we aimed to identify and determine the breath concentrations of nicotine following use of a conventional cigarette, a Heat-not-Burn (heated tobacco) device, an electronic vapour product (e-cigarette) and a nicotine inhalator.

2. Experimental setup

The PTR-ToF-MS 8000 used in this investigation has been described elsewhere (IONICON; [3]). As a modification to this original PTR-MS, a heated inlet system (120 °C) was used to prevent condensation and deposition of the analytes and to enable also a qualitative analysis of less volatile compounds. Exhaled air was sampled at a flow rate of 100 sccm (standard cubic centimetre per minute). Spectra were acquired at 0.8 cycle per second and the sampling time per channel in the TOF was 0.1 ns for a mass spectra ranging from m/z 1 to 280. The PTR-MS showed a count rate of the primary ions (H_3O^+ ions) of 6500 counts/s. The length of the drift tube of the PTR-ToF-MS was 9.3 cm, with an applied voltage of 600 V. The usual pressure in the drift tube was 2.2 mbar and the temperature was 120 °C. The ratio *E/N* (*E* is electric field and *N* is the number density of the gas in the drift tube) was at 100 Td (*Townsend*; 1 Td = 10^{-17} V.cm^2) which is the optimal value to avoid analyte fragmentation and to obtain high level of primary ions signal.

The following products were used in this study: conventional cigarette (0.6 mg nicotine [ISO smoking regime]), Heat-not-Burn (heated tobacco; iQOS with regular heatsticks), electronic vapour product (20 mg/mL nicotine Puritane rechargeable e-cigarette) and 15 mg nicotine inhalator (Nicorette® Inhalator). Three volunteers participated in this study and each volunteer used each of the four products. For each of the products tested: five blank breath measurements were taken directly before product use (background control) and following this the volunteer was given the product to use and become familiar with. Following this, the volunteer used the product *ad libitum* five times and exhaled into the PTR-MS each time allowing analysis on a per puff basis. Representative results shown here are the output from a single exhalation event.

To enable the identification and quantification of nicotine in the exhaled breath, the PTR-MS was calibrated with a liquid sample. A liquid calibration unit (LCU) was used to evaporate an aqueous nicotine standard (stock solution, 7.2% [v/v] nicotine in propylene glycol) into a gas stream, resulting in a gas flow containing nicotine at defined concentrations.

3. Identification of nicotine: *m/z* 163

To enable the identification and quantification of nicotine in the exhaled breath, the PTR-ToF-MS was calibrated by directly injecting liquid nicotine standards at a known rate into a dilution air stream. The key assumption of this approach is that the evaporation of the liquid standard into the air stream is complete, which is then homogenized in a mixing chamber. ***Figure 1*** shows the mass spectra of nicotine at *m/z* 163.123; confirming the expected exact mass of protonated nicotine.

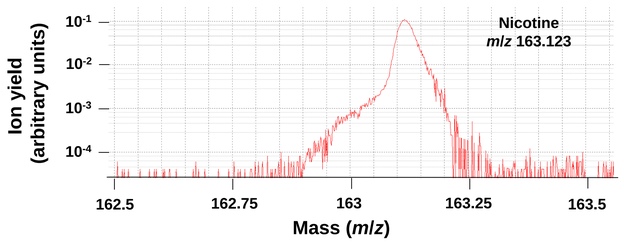

Figure 1 Calibration of PTR-ToF-MS for nicotine. Mass spectra of nicotine at *m/z* 163.123; the expected exact mass of protonated nicotine

4. Comparison of VOCs released in exhaled breath following use of a conventional cigarette, Heat-not-Burn device, electronic vapour product and nicotine inhalator product

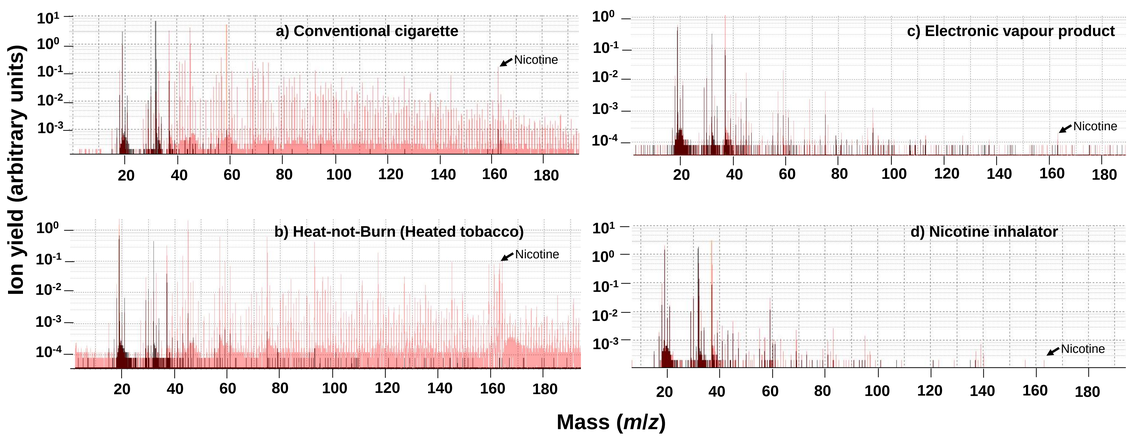

Figure 2 Representative PTR-MS mass spectra of VOCs released in exhaled breath following use of (**a**) a conventional cigarette, (**b**) a Heat-not-Burn [heated tobacco] device, (**c**) an electronic vapour product [e-cigarette] and (**d**) a nicotine inhalator. Black peaks, VOC released in normal exhaled breath (background control); red peaks, VOCs released in exhaled breath following product use. Specific compound (ion trace) at *m/z* 163 is nicotine and is labelled with arrowhead.

Representative data presented in ***Figure 2*** shows mass spectrometric profiles of exhaled breath following a single exhalation event after product use (red) and comparison with blank control breath (black). The peaks on mass 19 and 37 m/z (and their isotopes) represent the reagent ions (H_3O^+) and their clusters. The PTR-MS has been calibrated for nicotine (m/z 163; see arrowheads); all other pink peaks correspond to compounds released following use of the specific nicotine delivery product however their identities remain to be determined in future work

Following use of a conventional cigarette and a Heat-not-Burn product, a large number of different chemicals are released in the exhaled breath, as shown by the red spectra across a range of masses. When focussing specifically on exhaled nicotine, 1150 ppb nicotine were detected in the exhaled breath following use of the conventional cigarette (**a**) and 1840 ppb (parts per billion) nicotine following use of the heated tobacco device (**b**). In contrast, 7 ppb nicotine were detected in the exhaled breath following use of the electronic vapour product (**c**) and 1 ppb nicotine following use of the nicotine inhalator (**d**).

The exhaled breath following use of electronic vapour products appears chemically less complex compared to conventional cigarette and Heat-not-Burn and more similar to that of the nicotine inhalator.

The release of chemicals in the exhaled breath is likely to depend on the user topography (i.e. the way in which each individual uses the product)The components of the exhaled breath will also contribute to the quality of the indoor air, as we reported previously [4].

5. Conclusions & future work

In this study, many more chemical components were detected in the exhaled breath from users of conventional cigarettes and Heat-not-Burn (heated tobacco), compared to users of a simple electronic vapour product and a nicotine inhalator. This is not unexpected given that these are products based on tobacco. Substantially more nicotine was also found in the exhaled breath following use of the tobacco based products.

The large number of chemical species detected in the exhaled breath following use of the heated tobacco product might be indicative that the use of such products has the potential to impact indoor air quality in a similar way to that reported for conventional cigarettes. This is an important area for additional research.

Our proof-of-concept study presented here shows the potential of PTR-MS to be used as a technique to monitor the emissions from a range of nicotine delivery products and quantify released VOCs in real-time under a range of conditions.

PTR-MS mass spectra of complex aerosols, such as exhaled breath, requires careful interpretation, for example to appreciate that some overlap of certain compounds at a single mass-to-charge ratios can arise due to fragmentation.

PTR-MS is a one dimensional technique that characterises compounds only via their mass and is not sufficient for the diagnostic identification of 'unknowns' without prior calibration. Our next step will therefore be to determine the profiles and identities of VOCs in exhaled breath following use of a range of nicotine delivery products by a coupled PTR-MS/GC-MS study.

References

[1] Cappellin *et al*. (2013) PTR-MS in Italy: a multipurpose sensor with applications in environmental, agri-food and health sciences. *Sensors*. 13, 11923-11955.
[2] Schwarz *et al*. (2009) Determining concentration patterns of volatile compounds in exhaled breath by PTR-MS. *J. Breath Res*. 3, 1-15.
[3] IONICON, www.ionicon.com, accessed January 2015.
[4] Colard *et al*. (2015) Electronic cigarettes and indoor air quality: a simple approach to modelling potential bystander exposures to nicotine. *Int. J. Environ. Res. Public Healt*h. 12, 282-299.

Declaration

This project was supported by Imperial Tobacco Group. The electronic vapour product used in this study was manufactured by Fontem Ventures, a fully owned subsidiary of Imperial Tobacco Group.

Expert Report of Prof. Dr. Valerio Cozzani:

Analysis of EHTP Features with respect to Biomass/Tobacco Combustion

This appendix to the Philip Morris Products S.A. Technical & Scientific Dossier For the Electrically Heated Tobacco Product (EHTP) as part of the Tobacco Heating System (THS), Version 2.0, dated 27 May 2016, has been reformatted for publication on pmiscience.com.

Prof. Dr. Valerio Cozzani

ANALYSIS of EHTP FEATURES with respect to BIOMASS/TOBACCO COMBUSTION

Bologna, May 8th, 2014

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Professor of Chemical Engineering at University of Bologna

Executive Summary

The present document is intended to answer three questions related to the operation and features of an Electrically Heated Tobacco System (EHTS) patented by Philip Morris International (PMI), concerning the features and classification of the process undergoing in the tobacco substrate during EHTS operation. The questions were answered on the basis of technical details and specific experimental data on EHTS features and operation provided in a report issued by PMI (named as the "PMI Report" in the following).

The questions answered are the following:

C1. what is the scientific definition of combustion?

C2. what are unambiguous indicators of biomass/tobacco combustion?

C3. do the results of the experiments performed and reported in the "PMI Report" document support the absence of a combustion process occurring in the tobacco product?

In order to answer the above questions a literature search and analysis was carried out. An analysis and critical discussion of different literature sources was performed. The content of the PMI report, issued on April 11th, 2014, was then critically analyzed. In the present report, section 1 details the activities carried out. Sections 2, 3 and 4 report a detailed discussion of relevant elements, a list of relevant literature references and a complete answer to each question. Annex I reports a glossary and Annex II summarizes the relevant experience of the author.

The answers to the three questions may be summarized as follows:

C1: The term combustion refers to a particular redox chemical reaction where the reactant molecules, named "fuel" and "oxidant", are mixed and rearranged to become product molecules with the simultaneous release of heat. As in any chemical reaction, the presence of both the reacting species (the fuel and the oxidant, that usually is oxygen present in air) and an activation energy (ignition) are required for the combustion reaction to take place.

C2: Two indicators may be used to unambiguously detect biomass or tobacco combustion: i) the presence of relevant quantities of nitrogen oxides in the gaseous products, not formed from the decomposition of nitrates present in the original biomass/tobacco substrate; and ii) the clear evidence of an exothermic process. The two conditions should be simultaneously verified.

C3: On the basis of the analysis of the technical details and of the experimental data provided in the PMI report, I can exclude that a combustion process (including self-sustained combustion) takes place in the tobacco substrate of the EHTP during EHTS operation. This conclusion is supported by:

1. temperature profiles reported for the EHTP tobacco substrate during EHTS operation, that suggest that temperatures are far below those of self-sustained combustion of tobacco

2. no clear evidence of an exothermic process in the EHTP, as may be deduced by the temperature decrease during simulated puffing
3. limited amounts of NO_x formed during EHTP operation in comparison with CO. The amounts of NO_x formed are independent of the presence of oxygen, suggesting that their formation is governed by nitrate decomposition
4. Several other evidences of low-temperature processes during operation of the EHTS (very low amounts of high-molecular weight polyaromatic compounds formed, presence of unconverted fixed carbon in the EHTP residue, etc.) discussed in detail in Section 4.4.

Conditions 1 and 3 are related to the unambiguous indicators of combustion, that are accordingly both negative.

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1. Premise

1.1 Aims and Contents of the Report

On December 13th 2013 PMI asked for the assessment of some specific features of a newly developed "Electrically Heated Tobacco System" device (EHTS), based on the use of an "Electrically Heated Tobacco Product" (EHTP). The scientific issues of interest were contained in a memo (referred to as the "memo" in the following). Attached to the memo, an 8-page report titled "The Electrically Heated Tobacco System, the Electrically Heated Tobacco Product and Its Emissions" was also issued. This document will be referred to as the "PMI Report" in the following. The "PMI Report" was updated several times since January 2014, in order to include additional product design details and performance data, such as the temperature-time profiles in the tobacco plug of the EHTP during EHTS operation, needed to better clarify the features and operation of the EHTS device.

The questions concerning the processes taking place in the EHTP tobacco substrate during EHTS operation were the following:

C1. what is the scientific definition of combustion?

C2. what are unambiguous indicators of biomass/tobacco combustion?

C3. do the results of the experiments performed and reported in the "PMI Report" document support the absence of a combustion process occurring in the tobacco product? would additional data/experiments be required?

In the following an answer to questions **C1**, **C2**, and to first part of question **C3** is provided. A separate report was issued to answer the second part of question **C3**.

Answers are based on the updated PMI Report issued by PMI on April 11th, 2014.

1.2 Activities

In order to answer the questions reported in section 1.1, the following activities were carried out:

Activity 1: Literature search and analysis

In order to answer as far as possible the basic questions **C1** (definition of combustion) and **C2** (unambiguous indicators of biomass/tobacco combustion), a literature search and analysis was carried out. Reference literature sources, both fundamental and specific with respect to biomass and tobacco combustion were analyzed. An analysis and critical discussion of different literature sources was also carried out.

Activity 2: Analysis of data on EHTP performance provided by PMI

In order to provide an answer to the first part of question **C3** (do the results of the experiments performed and reported in the "PMI Report" document support the absence of a combustion process occurring in the tobacco product), the content of the PMI report, issued on April 11th, 2014, was analyzed also in the light of the results of activity 1.

1.3 Exclusions

PMI has the full and only responsibility of the data included in the PMI report.

The results of the activities carried out are not intended to assess health issues related to the aerosol formed during EHTS operation and such issues will not be considered in the present report.

2. Answer to Question C1: what is the scientific definition of combustion?

2.1 Analysis of relevant literature sources

It is well known that combustion is a particular chemical reaction producing heat. However, the combustion reaction is strongly associated to a number of physical phenomena (heat and mass transfer) and side processes (pyrolysis and gasification) that can hardly be separated from the overall combustion process, and that sometimes may create ambiguities in the definition of combustion.

As a starting point, it is important to define the chemical process of combustion. A fundamental definition of the combustion phenomenon, based on its chemical features, is given by Warnatz in his fundamental textbook (Warnatz et al., 2006).

Combustion is defined as a particular chemical reaction where the reactant molecules, namely the fuel and the oxidant, are mixed and rearranged to become product molecules, with the simultaneous release of heat.

The chemical reaction involved is defined as a process where the exchange and/or rearrangement of atoms between colliding molecules takes place. The term oxidant implies that the phenomenon must be intended as an oxidation-reduction (redox) reaction, i.e. a reaction in which electrons are transferred from one atom or molecule to another. Thus, the combustion phenomenon may be defined as a redox (an oxidation) reaction with the release of heat, where the reducing agent is named fuel and the oxidant (generally the oxygen of air) is the combustive agent.

This definition has the merit to leave out a number of side issues, usually associated to the chemical reaction in the discussion of the combustion process. In particular, this definition does not consider neither the reaction rate and the heat release rate, nor transport phenomena as the molecular or turbulent transport of mass and energy.

The thermochemistry of the reaction (i.e. the initial and final thermodynamic state of reactants and products) in the definition is considered self-consistent. Hence, the energy of combustion (or enthalpy) and maximum temperature reached by the products in adiabatic conditions are the only required parameters to define the combustion phenomenon.

This point of view, giving a basic definition of the combustion phenomenon, is essentially confirmed in all worldwide reference texts or lectures on combustion. Examples are: Peters (2010), who defines the phenomenon of combustion as a mass and energy conversion process during which chemical bond energy is transformed to thermal energy, or Turns (2000), who assumes as valid the basic definition given by the Webster's dictionary and considers the combustion phenomenon as a rapid oxidation generating heat, or both light and heat, however including slow oxidation accompanied by relatively little heat and no light, as e.g. the case of smouldering combustion, which is a slow, low-temperature, flameless form of combustion sustained by the heat evolved when oxygen directly attacks the surface of a condensed-phase fuel.

Many recent fundamental combustion books as those written by Glassman (2008), Williams (1985), and Law (2006), focused on the analysis of combustion processes, do not include a detailed definition of combustion reaction as that reported by Warnatz, assuming it as propedeutic to the analysis of the thermo-chemical aspects of combustion. Reference is explicitly given to the mainstream of previous scientific literature on combustion, and in particular to the Proceedings of the Combustion Institute. Most of this bulk of literature (including Semenov's Nobel lecture) cross-refer the pioneering work of Lewis and Von Elbe.

In the latest edition of their book, Lewis and Von Elbe (1985) refer to the combustion phenomenon of gaseous systems as a spontaneously accelerating chemical reaction associated to a large energy release.

This may have two alternative features:

- it may propagate as a wave (the flame) starting from a localized source of ignition (external ignition), or
- it may occur more or less simultaneously throughout the fuel and oxidant mixture (autoignition).

This definition, although related to gases, introduces several specific aspects of the combustion process and can be applied in general to any physical phase, including the solid phase.

The first key point introduced is that the chemical kinetics is essential for the detailed analysis of the chemical path of the fuel-oxidant reactive system: the combustion reaction accelerates spontaneously due to the Arrhenius' law under non-isothermal conditions, because the heat generated by the reaction itself increases the velocity of reaction.

The second key point introduced is that the combustion phenomenon can show itself as a flame, which may be defined as by Griffiths and Barnard (1995): a flame is a self-propagating exothermic reaction with (usually) a luminous reaction zone associated to it.

Finally, the occurrence of combustion needs an ignition source (a heat source or an electric spark which produce atoms and free radicals which may act as chain carriers in the chemical reaction) due to the large activation energy which characterizes the chemical kinetic of most fuel-oxidant mixtures. Else, the system should be homogeneously heated to a critical temperature, known as the "auto-ignition" temperature, above which radical reactions start.

The definitions introduced by Lewis and von Elbe refer explicitly to combustion processes (or combustion systems) as intended by mankind throughout its own history: a large, practical source of energy obtained burning fuels with air. To this regard, it is worth mentioning the definition given by Oppenheim (Oppenheim, 2008). A combustion process (or system) is defined as a confined field of a (compressible) fluid where the exothermic process of combustion takes place, subject to conditions imposed at its boundary. Energy is released by chemical reaction and deposited in the field. Both actions (chemical reaction and heat exchange with the system) are carried out simultaneously and are referred to as heat release.

In other words, following Griffith and Barnard (1995), the heat originates in the combustion reaction, but the exploitation involves heat transport processes and fluid motion.

Referring to combustion systems, Law (2006) affirms that in such processes chemical reactions frequently occur in highly localized regions, which are characterized by high temperature, high product concentrations, and low reactant concentrations. On the other hand, in regions away from these reaction fronts, the temperatures and products concentrations are low while the reactant concentrations are high. The existence of these temperature and concentration gradients will cause the transfer of energy and mass from regions of high values to regions of low values through the molecular process of diffusion. Mechanistically, the existence of diffusive transport is then crucial in many types of flames, since only through these processes fresh reactants can be continuously supplied to the flame, while the heat generated there is also being continuously removed, causing the heat up of reactants and the ignition of the fresh mixture.

Thus, since the combustion reaction can proceed only when its participating species can be brought to the neighborhood of a physical location and remain there for a period of time sufficiently long to allow their conversion in the reaction, a strong coupling between transport phenomena and chemical kinetics in determining the local reaction rate is to be expected.

2.2 Combustion processes and combustion of solid biomass

If considering combustion systems, the combustion process may thus be considered as a complex interaction of physical (fluid dynamics, heat and mass transfer) and chemical phenomena (chemical kinetics and thermodynamics). Hence, it is common to identify combustion categories based upon whether the fuel and the oxidizer are mixed first and burned later (premixed) or whether combustion and mixing occur simultaneously (non-premixed or diffusive). The phase of the fuel (gaseous, liquid or solid or even mixed phases) is also very important. Finally, the fluid dynamic conditions (laminar, turbulent) may affect the coupling between chemical kinetic and transportation properties. The combination of these physical parameters identifies specific combustion realms, whose specification is out of the scope of this analysis.

For the sake of this section, it is however crucial discussing the combustion process of solids. Actually, while the definition of the combustion phenomenon from a chemical point of view is not affected by the phase or physical state of the fuel, a number of chemical and physical phenomena are inherently associated to the combustion reactions and affect the overall combustion process.

As stated by Warnatz (2006), this type of combustion involves the heating of the solid substrate to a point where chemical decomposition reactions start (pyrolysis or thermal degradation), generating low molecular weight volatile compounds, that leave the substrate in gas phase and usually undergo a homogenous combustion process, and a residual solid, usually named “char” composed almost only by carbon and solid components not participating to the combustion process (inerts or “ashes”). The char usually undergoes a slow (in comparison to volatile combustion), flameless heterogeneous combustion process.

Hence, additional considerations concerning phase change and phase boundary are needed to describe solid combustion. When an organic solid substrate is introduced into a hot environment in the presence of an oxidant such as air, the substrate first undergoes a drying process, usually in a temperature range comprised between 100 and 300 °C. In this stage, exothermic dehydration of the biomass takes place with the release of water and low-molecular-weight gases as carbon monoxide and dioxide. Then the "devolatilization" process takes place (Law, 2006). This process consists of the pyrolysis of the original solid (usually indicated as "primary pyrolysis" in the scientific literature) forming products able to vaporize at the process temperatures (thus usually named "volatiles") and a residual solid, usually named char. The primary pyrolysis and volatile formation is thus the thermochemical decomposition of biomass into a range of products, either in the total absence of oxidizing agents or with a limited supply that does not permit gasification to an appreciable extent (Basu, 2010). During the "devolatilization" process, beside primary pyrolysis and volatile formation, the generated volatiles may undergo further gas-phase pyrolysis reactions, usually named as "tar cracking".

The phenomenon of primary pyrolysis and volatile formation produces a fuel vapor which, if ignited, results in either an envelope or wake diffusive flame. The gas-phase flame lasts for a while and then ends as the bulk of the substrate is pyrolyzed, and a solid char is formed. Char formed in the process is typically less than 20% of the original solid.

Char is a porous material, made up of carbon and mineral components. For most chars the carbon content ranges from about 50% to almost 97% of the combustible mass. When burning of char is activated, the temperature of the material is rapidly increased and carbon is gasified over the external and internal surfaces of the porous char while the gasified product (mostly carbon monoxide) can further react with air in the gas-phase. The presence of pores in the char particle allows for penetration of reactant species into the particle and therefore for much greater surface area for reactions than is associated with the external surface of the particle. The extent to which oxygen is able to utilize this additional surface area depends on the difficulty in diffusing through the particle to reach the pore surfaces and on the overall balance between diffusion control of the burning rate and kinetic control.

Self-sustained combustion refers to the combustion system based on the reiteration of this mechanism, starting from the drying of the adjacent particles. In the case of non-flaming combustion, the overall phenomena is often defined as smoldering combustion, which is the slow, low-temperature, flameless form of combustion sustained by the heat evolved when oxygen directly attacks the surface of a condensed-phase fuel (Drysdale, 2011).

The basic requirements for solid materials to be able to undergo self-sustained smouldering combustion are that they are porous and form a solid carbonaceous char when heated (Ohlemiller, 2008). Moussa et al. (1977) have examined the propagation of smouldering along horizontal, cylindrical cellulosic elements and have shown that the combustion wave has three distinct regions, which may be considered as common to all self-sustaining smouldering processes. The first zone is the pyrolysis region in which there is a steep temperature rise and an outflow of visible airborne products from the

parent material; the second zone is represented by a charred zone where the temperature reaches a maximum, and the evolution of the visible products stops and glowing occurs. Finally, the third zone is represented by a very porous residual char and/or ash which is no longer glowing and whose temperature is falling slowly. Heat is released in the second zone, where surface oxidation of the char occurs. There, the temperature reaches a maximum, typically in the region of 600°C for smouldering of cellulosic materials in still air. Heat is conducted from zone 2 into the virgin fuel and is responsible for the temperature rise observed in zone 1. This causes the pyrolysis of the fuel, yielding the outflow of volatile (gas phase) pyrolysis products and a residue of carbonaceous char. Temperatures higher than 250–300°C are required to accomplish this change in most organic materials. If there is a significant moisture content, there will be a delay in reaching zone 1 as the moisture is evaporated.

2.3 Answer to question C1

From the above, it may be concluded that the term combustion refers to a particular redox chemical reaction where the reactant molecules, named “fuel” and “oxidant”, are mixed and rearranged to become product molecules with the simultaneous release of heat.

As in any chemical reaction, the presence of both the reacting species (the fuel and the oxidant, that usually is oxygen present in air) and an activation energy (ignition) are required for the combustion reaction to take place.

The term combustion process (or combustion system) refers to a confined field of a fluid where the exothermic process of combustion takes place, subject to conditions imposed at its boundary. Heat or energy is generated by the chemical reaction and is deposited in the field; both actions are carried out simultaneously and referred to as heat release.

The fuel (solid, liquid, gas or multi-phase) and the oxidizer can be mixed first and burned later (premixed combustion or flame) or combustion and mixing can occur simultaneously (non-premixed or diffusive combustion or flame), either in laminar or in turbulent regime. In this framework, combustion science analyses the complex interaction of physical (fluid dynamics, heat and mass transfer) and chemical processes (thermodynamics, and chemical kinetics).

The combustion of an organic solid substrate, as a biomass, is inherently associated to several side processes and, in particular, to pyrolysis. Solid combustion usually involves, simultaneously or sequentially, both the gas-phase combustion of volatiles produced by the pyrolysis (i.e. the thermal decomposition and degasification of the heated solid), and by the gas-solid reaction occurring in the bulk of the residual solid (that may be named “char”) or at its interface. These phenomena are of fundamental importance in the combustion process of tobacco.

It is important to remark that, while it is impossible in practice to have biomass or tobacco combustion in the absence of pyrolysis, it is possible to induce pyrolysis reactions without combustion, since pyrolysis may take place at lower temperatures with respect to combustion and in the absence of oxidant species such as oxygen.

2.4 References for section 2

Basu P., Biomass Gasification and Pyrolysis - Practical Design and Theory, Academic Press, 2010.

Drysdale D., Introduction to Fire Dynamics, 3rd Ed., Wiley & Sons, UK, 2011

Glassman I., R.A. Yetter, Combustion, 4th Ed., Elsevier, 2008.

Griffiths J.F., J.A. Barnard, Flames and Combustion, 3rd Ed., CRC Press, 1995

Law C.L., Combustion Physics, Cambridge University Press, 2006.

Lewis B., G. Von Elbe, Combustion, flames, and explosions of gases, 3rd Ed., Academic Press, New York, 1985.

Moussa N.A., T.Y. Toong, C.A. Garris, Mechanisms of smouldering of cellulosic materials, Proceedings of the Combustion Institute, 16, 1447–1457, 1977.

Ohlemiller T.J., Smouldering combustion, in: SFPE Handbook of Fire Protection Engineering, 4th Ed. (Eds P.J. Di Nenno et al.), pp. 2.229–2.240. National Fire Protection Association, Quincy, MA, 2008.

Oppenheim A.K., Dynamics of Combustion Systems, Springer, 2nd Ed., 2008

Peters N., Combustion Theory, CEFRC Summer School of Princeton, 2010.

Turns, S.R., An introduction to Combustion: Concepts and Applications, 2nd Ed., McGraw-Hill Mechanical Series, New York, 2000.

Warnatz J., U. Maas, R.W. Dibble, Combustion, Physical and Chemical Fundamentals, Modeling and Simulation, Experiments, Pollutant Formation, 4th Ed., Springer-Verlag Berlin Heidelberg, 2006.

Williams F.A., Combustion Theory, 2nd Ed., The Benjamin/Cummings Publishing Company, Inc, California, 1985.

3. Answer to Question C2: what are unambiguous indicators of biomass/tobacco combustion?

3.1 Processes associated to Biomass combustion

The term *biomass* refers to any organic material derived from plants or animals. Solid carbonaceous biomasses, such as tobacco, may be classified according to two main features: their heating value (energy content, or more precisely the heat released in their combustion), and their proximate analysis.

Proximate analysis reports the moisture content, volatile matter, fixed carbon content, and ash or mineral content of a solid substrate following standard methodology (Flagan and Seinfeld, 1998). Definitions of volatiles, fixed carbon and ash are reported in the literature together with methods for their experimental determination (moisture content: ASTM E871, volatile matter: ASTM D3175, fixed carbon content: ASTM E870, ash or mineral content: ASTM E1755). However, since such concepts are crucial to answer question **C2**, a brief discussion of their definition is given in the following.

Moisture content is the free water adsorbed in the solid substrate. The volatile fuel content is the fraction of the original solid substrate that may evolve in the gas phase when the fuel is heated to high temperatures (at least above 250°C), whereas the fixed carbon is the organic fraction of the solid residue (almost only composed of carbon) after the volatiles have escaped. The ash content refers to the portion of the solid that remains when the fixed carbon has been fully oxidized, and is composed mostly of oxidized mineral compounds and inert solids (Glassman and Yetter, 2008).

In the answer to question **C1** the combustion process of an organic solid substrate was already described. Four main steps characterize the evolution of gas-phase compounds during the combustion process:

1. Drying and initial stage (100–300 °C). In this stage, the free moisture and some loosely bound water is first released at low-temperature. The free moisture evaporates, and the heat is then conducted into the biomass interior. After the drying mechanism, the exothermic dehydration of the biomass takes place with the release of water and low-molecular-weight gases as CO and CO_2. This step always takes place before combustion, but is not only associated to biomass combustion (e.g. it may take place during biomass heat-up in the absence of oxygen).
2. Primary pyrolysis of the solid fuel and formation of volatile combustible pyrolysis products. This step is also named “devolatilization” in the literature. Also this step always takes place before combustion, but is not only associated to biomass combustion (e.g. it may take place during biomass heat-up in the absence of oxygen). Primary pyrolysis starts at temperatures higher than 200°C (Basu, 2010).
3. Volatile combustion: the volatiles formed in the primary pyrolysis process, in the presence of an oxidant and of an ignition source, burn much more rapidly with a diffusive flame and forming, among other compounds, nitrogen oxides

(NO_x). Combustion of volatile products may take place separately or during prymary pyrolysis, depending on the specific features of the combustion system and process conditions.

4. Heterogeneous combustion of char: once prymary pyrolysis of the solid fuel is completed, a porous char substrate remains, composed mostly of carbon. Char burns through surface reactions of oxidizing species (O_2, H_2O, and CO_2), forming mostly CO as a product, and, to a lesser extent, H_2 if water vapor is present in the gas phase. In combustion environments (i.e. in the presence of the oxidant and with an ignition source) carbon monoxide formed in heterogeneous char combustion is converted to carbon dioxide in the gas phase. Hydrogen, if present, may be converted in part to methane or may oxidize to form water vapor, depending on gas-phase conditions (temperature and concentrations of oxygen and water). Heterogeneous combustion has usually a characteristic time longer than that of primary pyrolysis and of volatile combustion, thus when single fuel particles are considered, it usually takes place when steps 3 and 4 have ended. However, depending on system geometry, it may take place in a different zone of the solid.

3.2 Products formed in biomass/tobacco combustion

As clear from section 3.1, during the combustion of solid biomass and/or tobacco four different phenomena take place, all influencing the solid and gas-phase products of the combustion process. However, only two of these phenomena (volatile combustion and heterogeneous char combustion) are rigorously combustion reactions as defined in section 2, whereas the other two phenomena (drying and primary pyrolysis) are only induced by the heat generated by the combustion reactions.

Thus, in answering question **C2**, the point is if it is possible to define unambiguous indicators of these two phenomena among the products of the overall combustion process (that include products formed due to phenomena different from combustion).

The initial drying results in the release of water vapor followed, at slightly higher temperature (between 100 ° and 300 °C), by the dehydration of the biomass with release of water and low-molecular-weight gases like CO and CO_2 (Basu, 2010).

The primary pyrolysis results in the formation of volatiles and of char, independently on the occurrence of combustion reactions as it may occur also in the absence of oxygen. Indeed, the quantity and chemical composition of the volatile matter that is emitted is highly dependent on the nature of the original fuel structure, on the rate at which the particles are heated, and on the final temperature attained by the particles (Glassman and Yetter, 2008).

It should be remarked that besides the primary pyrolysis, that involves solid-phase radical reactions generating volatiles, also gas-phase radical reactions may be present. In gas-phase pyrolysis reactions taking place during volatile formation, the heavier molecular weight volatile products are cracked into smaller molecules of non-condensable gases such as low-molecular weight hydrocarbons, carbon monoxide and carbon dioxide. This stage typically occurs above 300°C (Reed, 2002). Hence, the presence of CO and CO_2 (together with H_2O) is not an unambiguous indicator of

combustion, since the presence of such species in the gas-phase may be caused as well by the drying and pyrolysis processes.

Char reactions with species present in the gas-phase during combustion processes, as O_2, H_2O and CO_2, are well known. However, while the exothermic reaction with oxygen producing mostly carbon monoxide and to a lesser amount carbon dioxide is the specific reaction that characterizes the heterogeneous combustion process, the endothermic reactions with H_2O and CO_2 may be associated to, but are not specific of, combustion phenomena. Such reactions, usually named as char gasification reactions, produce mainly CO, H_2, and CH_4 that may originate either from purely endothermic gasification reactions or from exothermic oxidative reactions of char (i.e. combustion-induced reactions).

Hence, the presence of carbon monoxide, carbon dioxide, water, volatile species and char cannot be an indicator of combustion occurrence, since such species may be formed in drying, primary pyrolysis, pyrolysis of volatile species, volatile combustion and char combustion processes.

This aspect has been further detailed in the authoritative study of Baker (2006). In this paper it is reported that 30% of carbon monoxide is formed in the pyrolysis of tobacco constituents, about 36% by combustion phenomena and at least 23% by the endothermic carbonaceous reduction of carbon dioxide due to high-temperature char gasification reactions.

3.3 Nitric oxides formed in biomass/tobacco combustion

In combustion processes, nitric oxides (in particular NO and NO_2, summarized as NO_x) are formed in three different reaction processes. The nitrogen oxides produced in these three different processes are commonly defined as thermal, prompt and fuel NO_x (Flagan and Seinfeld, 1998). Thermal NO_x are formed by the reaction between molecular nitrogen and oxygen present in air at high temperatures. The name “thermal” is used because the initial, rate-limiting steps (mainly the reaction: $O + N_2 = NO + N$) of the overall mechanism have a very high activation energy due to the strong triple bond in the nitrogen molecule (Warnatz et al., 2006). Hence high temperatures (usually above 1000°C) are needed for process initiation, such as those reached in full combustion regime.

Prompt NO_x are formed due to the fast reaction of very reactive intermediates (i.e. hydrocarbon radicals as CH produced in combustion processes involving hydrocarbon fuels) with molecular nitrogen present in air. Intermediate species formed in the reaction may undergo oxidation in the presence of sufficient concentrations of oxygen, forming NO_x. The prompt NO_x formation mechanism is active at lower temperatures than the thermal mechanism, although requiring relatively high temperatures for its activation (above 500°C) and relative abundance of oxygen.

Finally, fuel NO_x are formed from reactions of nitrogen contained in the fuel, that is oxidized to NO during the combustion process (Sarofim and Flagan, 1976). Fuel NO_x are formed in two steps: part of the nitrogen present in the fuel (usually about 75%) is released with the volatiles and may form NO_x during volatile combustion, while a

fraction is retained in the char and may contribute to fuel NO_x formation during char combustion.

At lower combustion temperatures (below 800°C), fuel bound nitrogen is a main source of NO_X emissions, while thermal and prompt NO_X are less relevant due to relatively lower temperatures of the process.

In fuel NO_x formation mechanism, fuel nitrogen is converted to intermediate components such as HCN and NH_i with i = 0, 1, 2 or 3. These can be oxidized to NO_X if oxygen is available, which is usually the case in a combustion process. If no oxygen is present, intermediates can interact in the reduction zone to form N_2 in reactions such as $NO + NH_2 = N_2 + H_2O$ (Nussbaumer, 2003).

The presence of NO_x due to the oxidation of fuel bound nitrogen or for the thermal and prompt oxidation of nitrogen of air indicates the occurrence of oxidation of nitrogen with air, hence a combustion reaction with the development of high temperature in the solid or gas phase.

3.4 Nitric oxides formation by nitrate thermal decomposition

In the case of some biomass species including some tobacco substrates, a further specific mechanism of fuel NO_x formation may be present. If the biomass substrate contains relevant quantities of nitrates, NO_x may be formed even at very low temperatures (250-400°C) from the decomposition of nitrates in the reducing environment created by the presence of the carbonaceous substrate (Norman et al., 1983; Im et al., 2003). In tobacco and cigarette combustion products, NO_x formation from low-temperature nitrate decomposition was reported as the more important mechanism of NO_x formation in the mainstream smoke (inhaled during puffing). In the sidestream smoke (smoke released to the environment during smoldering) NO_x concentrations may range up to about 4 to 12 times those in the mainstream NO_x and are clearly formed also from other mechanisms than from nitrates in the substrate (Im et al., 2003).

A specific study on NO formation, the main component in NO_x, in tobacco combustion products confirms that (Im et al., 2003):

- NO formation at low temperatures (275-375 °C) is independent of oxygen presence and mainly depends on nitrate ions decomposition;
- NO formation at higher temperatures (>400 °C) is strongly dependant on free oxygen

The sources for NO formation in the high-temperature range are the nitrogen-containing organic compounds, viz. amino acids and proteins. Before the NO formation at high temperatures, amino acids and proteins react at a temperature below 400°C to produce a nitrogen char. Subsequent combustion of this char at higher temperatures produces NO (Glarborg et al., 2003).

Thus it may be concluded that NO_x formation in tobacco combustion takes place at temperatures that are typically higher than 400°C, mainly by the fuel-NO_x mechanism. At lower temperatures, thermal decomposition of nitrates may cause limited formation

of NO_x due to decomposition reactions, that are not associated to combustion processes. Finally, it should be remarked that NO_x formation by nitrate decomposition is a process activated by temperature and is the only NO_x formation mechanism that does not require the presence of oxygen in the atmosphere surrounding the biomass or tobacco sample (Im et al., 2003). Thus, nitrate NO_x may be detected in experimental runs carried out heating the biomass or tobacco substrate in the absence of oxygen.

3.5 Answer to question C2

Biomass may undergo the combustion reactions either in the gas phase (due to the oxidation of fuels derived from the primary pyrolysis and volatile formation phenomenon) or in the solid phase (char gasification reactions).

The presence of large amounts of classical combustion products of hydrocarbon oxidation reactions (CO, CO_2, and H_2O) in the non-condensable gases may not be unambiguously imputed to the reaction of combustion. Indeed, these species may be formed as well, in a comparable amount, by phenomena as drying, primary pyrolysis and volatile formation, cracking and gasification reactions, and others.

The presence of NO_x due to the oxidation of fuel bound nitrogen (fuel NO_x) or from the oxidation of nitrogen in air (thermal and prompt NO_x) indicates the occurrence of an oxidation reaction of nitrogen in air.

The amount of thermal and prompt NO_x may be assessed considering the total nitrogen contained in the solid, which may be determined by *ultimate analysis (*Flagan and Seinfeld, 1998). If the resulting NO_x exceeds the corresponding molar content of fuel nitrogen, there is also a clear, though indirect, evidence of the occurrence of strong exothermic reactions in the gas or in the solid phase due to combustion reaction and to the development of high temperatures. If the moles of NO_x do not exceed the corresponding moles of fuel-bound nitrogen, but however the presence in the gas phase amount can be still observed in non-negligible amount with respect to the corresponding molar content of nitrogen in the biomass, the occurrence of an oxidation reaction in the solid phase of fuel-bound nitrogen with oxygen can be still recalled but temperatures higher than 400°C and the evidence of an overall exothermicity of the process are required to support the occurrence of combustion reaction.

Eventually, the presence of NO_x in the product gases, if associated with a clear assessment of the overall exothermicity of the process, can be considered an unambiguous indicator of combustion reactions.

In other words, two indicators may be used to unambiguously detect biomass or tobacco self-supported combustion:

1. the presence of relevant amounts of nitrogen oxides in the gaseous products, not formed from the decomposition of nitrates present in the original biomass/tobacco substrate;
2. the clear evidence of an overall exothermic process, despite the occurrence of endothermic reactions related to solid drying and primary pyrolysis/volatile formation.

In order to verify the first condition, a relevant positive value should be obtained for the difference between the overall quantities of NOx formed in the conditions of interest (e.g. EHTP operation in air) and NOx formed in the same conditions but in the absence of oxygen (e.g. in a pure nitrogen or helium atmosphere).

The two conditions reported above (NO_x formation in relevant quantities and overall exothermicity of the process) should be simultaneously verified and do not need the confirmation of the occurrence of self-sustained reaction, do not imply neither a fast kinetic of reactions, nor the velocity of the heat produced or adsorbed, nor the presence of light, nor the definition of flaming/non-flaming modality. Also the definition (and the presence) of smoke, char and ash is not needed.

3.6 References for Section 3

Baker R.R., Smoke generation inside cigarette: Modifying combustion to develop cigarettes that may be less hazardous to health, Progress in Energy and Combustion Science, 32, 373-385, 2006.

Basu P., Biomass Gasification and Pyrolysis - Practical Design and Theory, Academic Press, 2010.

Flagan R.C., J.H. Seinfeld, Fundamentals of air pollution engineering. Prentice-Hall, Inc. 1988.

Glarborg, P.; Jensen, J. E.; Johnsson, J. E. Fuel nitrogen conversion in solid fuel fired system, Prog. Energy Combust. Sci. 29, 89-113, 2003.

Glassman I., Yetter R.A., Combustion, 4th Ed., Elsevier, 2008.

Im H., Rasouli F., Hajaligol M., Formation of Nitric Oxide during Tobacco Oxidation, Journal of Agricultural and Food Chemistry, 51, 7366-7372, 2003.

Norman, V.; Ihring, A. M.; Larson, T. M.; Moss, B. L. The effect of some nitrogenous blend components on NO/NOx and HCN levels in mainstream and sidestream smoke. Beitr. Tabakforsch. Int., 12, 55-62, 1983.

Nussbaumer T., Combustion and Co-combustion of Biomass: Fundamentals, Technologies, and Primary Measures for Emission Reduction, Energy & Fuels, 17, 1510-1521, 2003.

Reed T.B., Encyclopedia of Biomass Thermal Conversion: The Principles and Technology of Pyrolysis, Gasification & Combustion (Hydrogen Generator Gas), 2002.

Sarofim A.F., R.C. Flagan, NOx Control for Stationary Combustion Sources, Progress in Energy Combustion Science, 2, 1-25, 1976.

Warnatz J., U. Maas, R.W. Dibble, Combustion, Physical and Chemical Fundamentals, Modeling and Simulation, Experiments, Pollutant Formation, 4th Ed., Springer-Verlag Berlin Heidelberg, 2006.

4. Answer to Question C3: Do the results of the experiments performed and reported in the "PMI Report" support the absence of a self-sustaining combustion process occurring in the tobacco product?

4.1 The EHTS and EHTP

The Electrically Heated Tobacco System (EHTS) patented by Philip Morris International has three distinct components that perform different functions:

(i) an Electrically Heated Tobacco Product (EHTP);

(ii) a Holder into which the EHTP is inserted and which heats the tobacco material by means of an electronically controlled heater;

(iii) a Charger that is used to recharge the Holder after each use.

The Electrically Heated Tobacco Product differs from a cigarette since:

1) There is no tobacco cut-filler (tobacco leaf cut in small pieces found in cigarettes). All of the tobacco is reconstituted (cast-leaf) tobacco made from tobacco powder, water, glycerin, guar gum and cellulose fibers.
2) There is a much smaller amount of tobacco in the EHTP compared to a cigarette because the weight of the tobacco plug in the EHTP is about 320 milligrams. In comparison, the weight of the cut filler in a standard cigarette rod ranging from 550 to 700 mg.
3) The reconstituted tobacco is formed into a small tobacco plug through a proprietary process known as "crimping".
4) Unlike a cigarette, the EHTP has two unique and independent filters: (1) a polymer-film filter which removes some aerosol constituents (primarily phenol) and (2) a low-density cellulose acetate mouthpiece filter.
5) The EHTP has a hollow acetate tube which acts as a mechanical spacer between the tobacco plug and the first filter.

Figure 4.1 shows the features of the EHTP tobacco plug and of the blade heater. Figure 4.2 shows further details of the set-up, of the position of the heating blade and of the air flow in the EHTS during puffing.

When used, the EHTP is inserted in the Holder of the EHTS and the user turns on the electronics by means of a switch. The heating blade in the EHTP Holder starts heating to a set-point temperature (between 310 and 350°C). The EHTP heating blade temperature is measured by the resistivity of the heating element, and is used to control the electric power supplied to the heating blade.

Figure 4.3, from the PMI Report, shows the temperature profile recorded for the heating blade in contact with the EHTP and for the EHTP tobacco substrate at three different

distances from the heating blade (respectively 0.5, 1.7 and 3.4mm) recorded by PMI during ETHS operation with simulated puffing (air intake by a pump, drawing 55 mL during 2 seconds). Temperatures in the crimped tobacco sample were recorded by thermocouples having a 0.25mm diameter inserted in the EHTP by drilled holes. The figure shows that the temperature of the heating element is oscillating around the set-point, and has a strong decrease when an air flow (inbreathing or "puffing") is induced inside the EHTP.

As shown in Figure 4.3, the temperature of the tobacco sample slowly raises (never exceeding 250°C in any point), but remains always far below that of the heating blade (comprised between 310 and 350°C). Higher temperatures are detected at lower distances from the heating blade. This suggests that a heat transfer from the hot surface of the heating blade takes place during EHTS operation, and that the EHTP is slowly heated up. During "puffing", the air flow causes the EHTP temperature to drop (even of about 30°C in the zone more near to the heating blade).

The electric power supply to the heating blade is always positive and comprised between 1.5 and 7W. After a transient in the first 30s, the power supply is almost constant but shows sudden increases (peaks) at regular time intervals, in correspondence to air intake due to simulated "puffing".

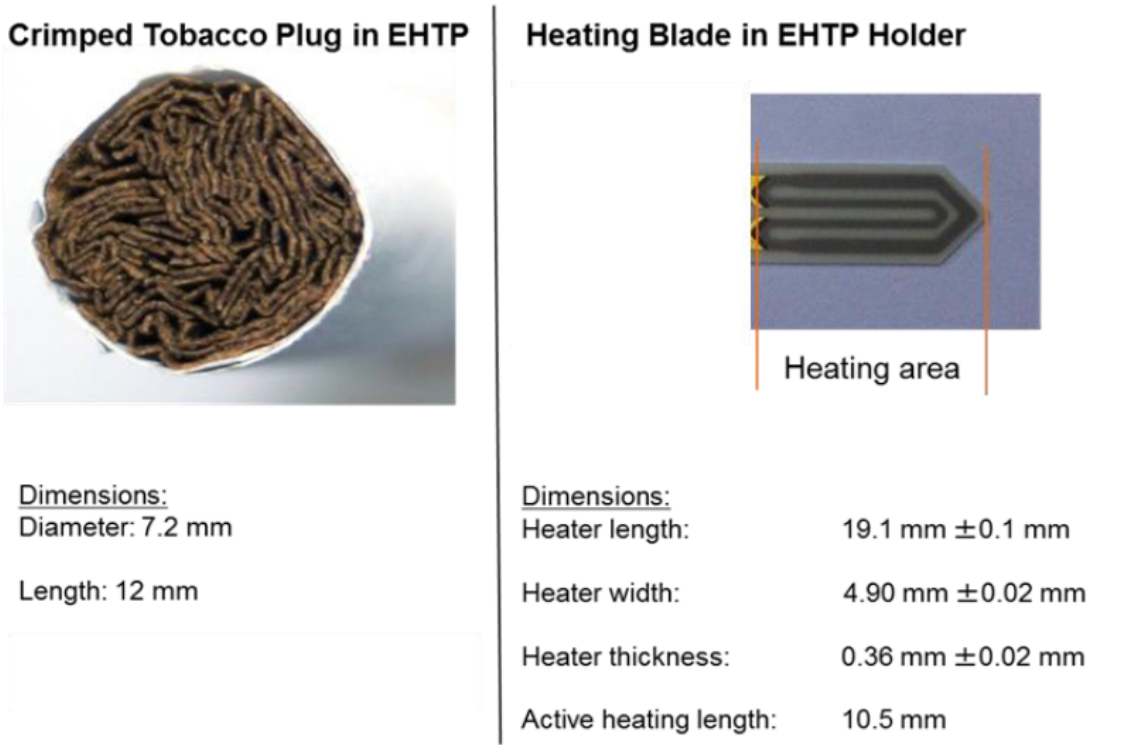

Figure 4.1: Details of the EHTP and of the heating blade of the EHTS (from PMI Report).

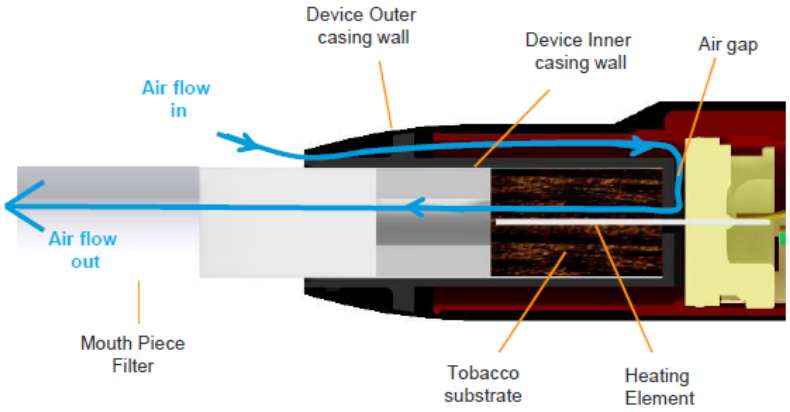

Figure 4.2: Air flow in the EHTP and EHTS holder during "puffing" (from PMI Report).

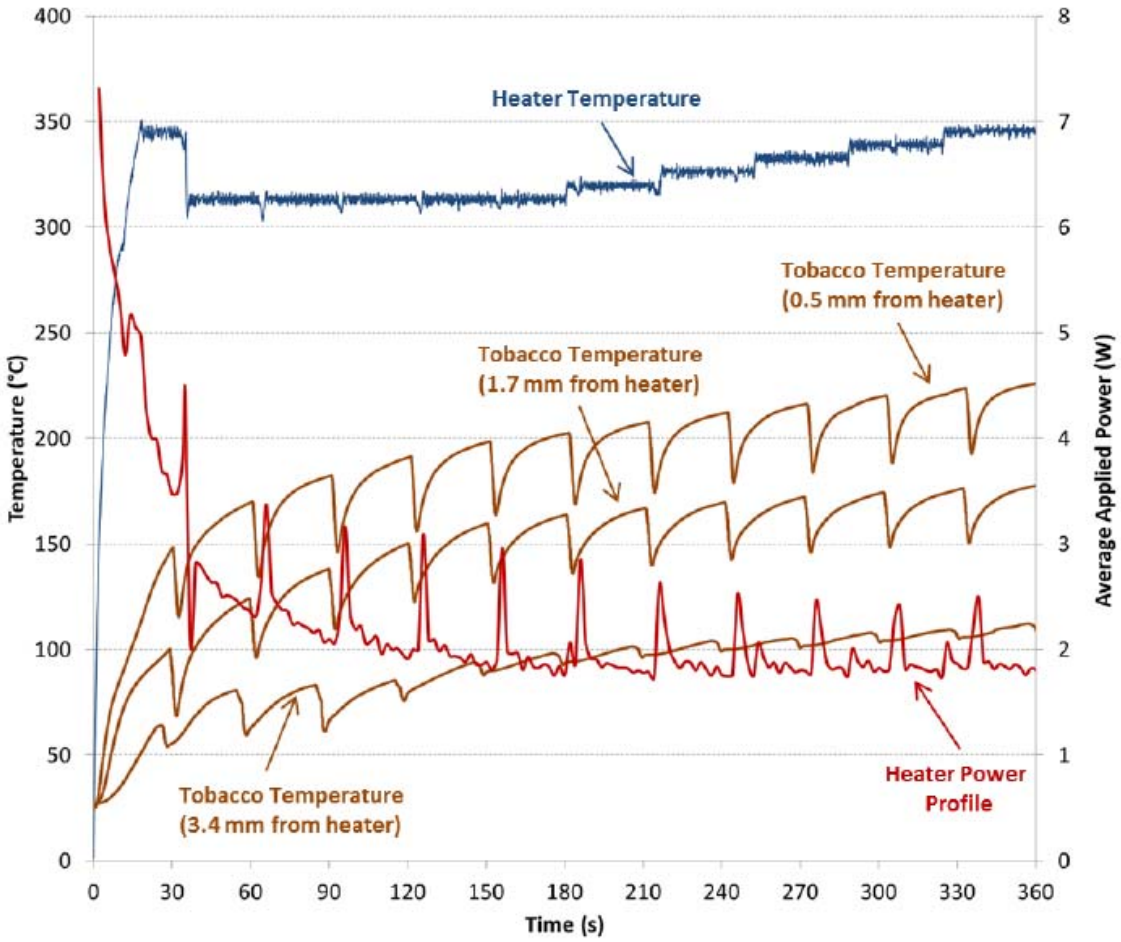

Figure 4.3: Temperature profile of the Heating Blade in the EHTP Holder (blue) and of the EHTP tobacco substrate at three different distances from the surface of the Heating Blade during operation with simulated puffing. The required power fed to the Heating Blade during operation is also reported (from PMI Report).

4.2 Products formed in EHTS operation

When operating the EHTS Holder, the EHTP Holder heating blade is heated to the selected operating temperature and an air flow passes through the EHTP at given intervals ("puffing"). The air flow sweeps away the gas-phase products formed from heating the EHTP, that are mixed to the air outflow shown in figure 4.2.

		Nitrogen		*Synthetic Air*		*Ambient ISO*		*Blank*	
Constituents	unit	Average	Std. Dev.	Average	Std. Dev.	Average	Std. Dev.	Average	Std. Dev.
*TPM	mg/unit	54.0	1.5	55.2	1.6	58.6	2.2	0.006	0.015
Water	mg/unit	34.7	4.3	37.3	3.8	40.9	2.9	BDL	BDL
Tar	mg/unit	17.9	3.1	16.5	3.4	16.3	3.9	BDL	BDL
Glycerin	mg/unit	4.38	0.24	4.39	0.40	4.44	0.27	BDL	BDL
Nicotine	mg/unit	1.38	0.10	1.37	0.09	1.37	0.11	BDL	BDL
CO	mg/unit	NQ	NQ	0.54	0.16	0.65	0.06	BDL	BDL
NO_x (NO + NO_2)	ug/unit	18.8	0.9	19.9	1.3	25.8	0.9	BDL	BDL
NO	ug/unit	19.5	1.0	20.8	1.4	26.8	0.9	BDL	BDL
Benzo[a]pyrene	ng/unit	0.60	0.09	0.61	0.11	0.66	0.15	BDL	BDL
1_3_butadiene	ug/unit	0.3	0.03	0.3	0.02	0.3	0.02	BDL	BDL
isoprene	ug/unit	2.6	0.4	2.3	0.1	2.8	0.1	BDL	BDL
acrylonitrile	ug/unit	0.2	0.02	0.2	0.02	0.2	0.01	BDL	BDL
benzene	ug/unit	0.5	0.07	0.6	0.06	0.7	0.07	BDL	BDL
toluene	ug/unit	1.9	0.3	2.0	0.2	2.0	0.3	NQ	NQ
pyridine	ug/unit	7.4	0.6	7.8	1.4	8.2	0.8	0.2	0.1
quinoline	ug/unit	NQ	NQ	NQ	NQ	NQ	NQ	BDL	BDL
styrene	ug/unit	0.8	0.3	0.7	0.2	0.8	0.2	0.1	0.01
Hydroquinone	ug/unit	7.4	0.7	7.0	0.2	7.6	0.3	BDL	BDL
Resorcinol	ug/unit	NQ	NQ	NQ	NQ	NQ	NQ	BDL	BDL
Catechol	ug/unit	14.7	1.1	14.3	0.5	14.8	0.8	BDL	BDL
Phenol	ug/unit	1.3	0.1	1.4	0.1	1.3	0.3	NQ	NQ
p-cresol	ug/unit	0.07	0.01	0.07	0.01	0.07	0.01	BDL	BDL
m-cresol	ug/unit	0.03	0.01	0.03	0.01	0.03	0.01	BDL	BDL
o-cresol	ug/unit	0.07	0.01	0.06	0.01	0.07	0.01	BDL	BDL
Formaldehyde	ug/unit	6.1	1.2	9.1	1.4	8.8	1.0	1.7	0.2
Acetaldehyde	ug/unit	211	16	230	21	250	11	NQ	NQ
Acetone	ug/unit	31.0	2.3	35.9	4.3	37.4	2.1	NQ	NQ
Acrolein	ug/unit	8.4	1.3	10.7	1.7	10.8	0.9	BDL	BDL
Propionaldehyde	ug/unit	13.7	1.1	14.9	1.9	16.0	0.8	BDL	BDL
Crotonaldehyde	ug/unit	NQ	NQ	NQ	NQ	NQ	NQ	BDL	BDL
Methyl Ethyl Ketone	ug/unit	7.0	0.6	7.6	0.8	7.9	0.4	BDL	BDL
Butyraldehyde	ug/unit	22.5	1.9	23.1	1.9	25.0	1.3	NQ	NQ
1_aminonaphthalene	ng/unit	0.07	0.01	0.07	0.01	0.07	0.004	NQ	NQ
2_aminonaphthalene	ng/unit	0.04	0.01	0.04	0.01	0.04	0.01	0.02	0.00
3_aminobiphenyl	ng/unit	0.01	0.00	0.01	0.00	0.01	0.002	NQ	NQ
4_aminobiphenyl	ng/unit	0.02	0.00	0.02	0.00	0.02	0.002	0.01	0.01

Table 4.1: Products detected in the gas outflow of simulated puffing runs with the EHTP (from PMI Report).

Thus, when operating, the EHTP generates gaseous products and an aerosol composed mainly of water, glycerin and nicotine. The EHTP aerosol is formed when the electronically controlled heater raises the temperature of the tobacco plug to a point at which distillation of nicotine and tobacco flavors takes place. Glycerin, which has been added to the tobacco as an aerosol former, aids the formation of the aerosol that is inhaled.

The EHTP use and puffing process were simulated by a specialized laboratory (Labstat), that carried out the analysis of the gas outflow from the EHTP in order to identify the volatile products formed during EHTP operation. The experimental runs were carried out using pure nitrogen, synthetic air, and an ISO standard "ambient air". A blank test (no tobacco substrate in the EHTP) was also carried out. The results are reported in table 4.1.

Water is not necessarily a combustion product but can be derived from the drying, dehydration/distillation phase. Indeed the total amount of water in table 4.1 is comparable in nitrogen or in dry air, suggesting that no or very limited oxidation or combustion phenomena are responsible for the presence of water.

As shown in the table, the gas used in puffing simulations (nitrogen, synthetic or humid air) has a very limited influence on the products detected in the gas outflow. However, some added water is produced in the presence of oxygen in standard ISO or dry air. Similar results are obtained for carbon monoxide. Provided that the tests are performed on standard EHTP units, the amount of CO is negligible in nitrogen atmosphere but, as for water, more CO is produced in the presence of air.

On the other hand the NO_x amount is almost the same in nitrogen and synthetic air, although showing a very limited increase in humid air. Nevertheless, the amount of NO_x present is very small in absolute terms with respect to nitrogen present in the sample (ultimate analysis for the tobacco substrate in the EHTP, reported in Table 4.2, from the PMI report, shows an amount of nitrogen of about 2.02% by weight of the tobacco substrate in the EHTP). The quantity of NO_x detected is limited also with respect to CO, thus excluding a relevant exothermic reaction in the gas phase due to the oxidation of pyrolysis gases with air.

	EHTP						Cigarette				
	Replicate number	C [% w/w]	H [% w/w]	N [% w/w]	Water Content [% w/w]		Replicate number	C [% w/w]	H [% w/w]	N [% w/w]	Water Content [% w/w]
Before use	1	38.06	5.97	2.02	14.7	Before use	1	37.92	5.76	1.99	13.3
	2	38.60	6.28	2.02	14.4		2	37.55	6.06	1.38	13.5
	3	38.50	5.99	2.02	13.7		3	39.15	5.96	1.91	12.7
After use	1	47.91	5.04	2.79	2.7	After use	1	6.87	0.69	0.74	1.8
	2	46.25	5.44	2.54	2.4		2	7.36	0.82	1.21	1.8
	3	45.58	5.60	2.48	3.2		3	8.68	0.76	1.04	2.1

Table 4.2: Ultimate analysis of EHTP and of a reference 3R4F cigarette (both samples "as received") before and after use (from PMI Report).

Moreover, flaming phenomena or high temperature spots in the gaseous phase and self-sustained combustion reaction (flaming or non-flaming) on the solid surface may be

excluded in the EHTP, as proved by the low amount of NO_x (hence low temperature in gaseous phase in the presence of air) and by the low amount of high molecular weight polycyclic aromatic compounds.

A final consideration concerning the NO_x detected in the gas phase is that no relevant difference in the quantities detected is present between runs in nitrogen and in air. This, together with the low operating temperatures of the EHTP shown in figure 4.3, suggests that these NO_x may be formed mainly by nitrate decomposition.

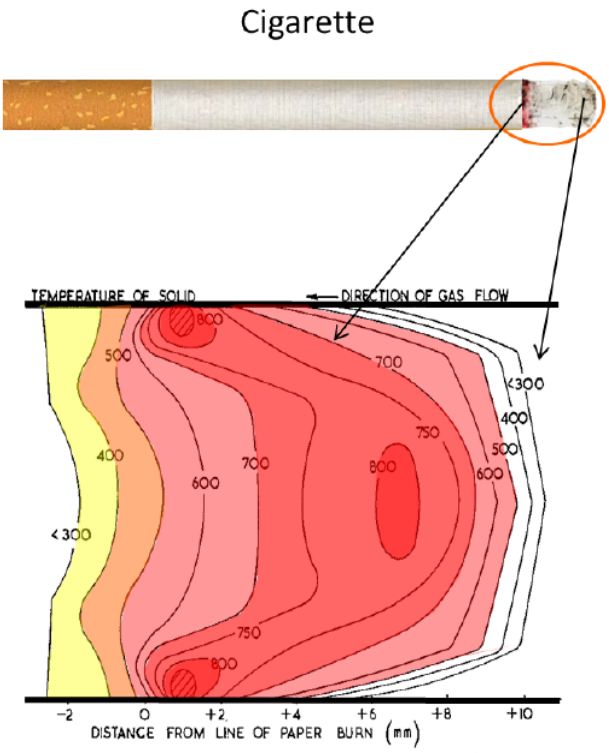

Figure 4.4: Tobacco temperature in a lit cigarette (Baker, 1975).

4.3 Tobacco combustion

Self-sustaining combustion of tobacco is the standard combustion process of tobacco in a cigarette. When a cigarette is lit, the combination of tobacco (fuel) and oxygen in the air generate a self-sustaining combustion process that consumes the tobacco. During the natural smolder period of a cigarette in between puffs, temperatures of between 600 to 800 °C occur in the center of the burning cone. During a puff the temperature increases to more than 900 °C at the periphery of the burning zone. The combustion of tobacco results in the formation of smoke (which contains a range of chemical compounds), heat and ash. Figure 4.4 shows a typical temperature profile in a lit cigarette during the self-sustaining combustion of tobacco.

The combustion of a lit cigarette is thus a high temperature process that causes the complete combustion of the tobacco (both volatile combustion and heterogeneous

combustion of the char), ending with the production of a relevant amount of ashes, as shown in Figure 4.5.

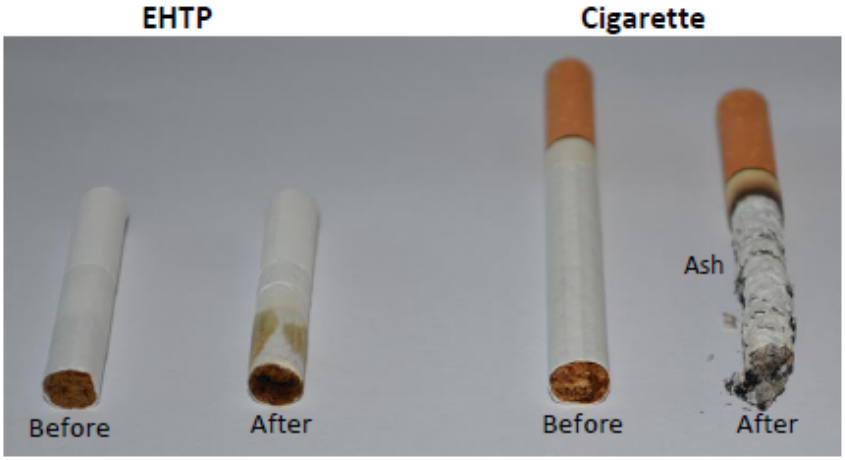

Figure 4.5: Final products of the combustion process of a lit cigarette compared to the residual solid produced from tobacco substrate after EHTS operation (from PMI Report).

Also the volatile products present in the outflow gas are very different. Table 4.3 shows a comparison among the products in the outflow gas detected by standard simulated puffing runs. As evident from the table, important differences are present in the products formed. Although the quantity of products formed is reported "per unit" and a very different quantity of tobacco substrate is present in the EHTP with respect to a cigarette (320 mg with respect to 550-700 mg), it is evident that quantities of nitrogen oxides, aldehydes, and aromatic species are far more different than the factor 2 difference present in the amount of tobacco substrate present in the units.

4.4 Comparison of experimental results for EHTP and reference cigarettes

In order to assess the presence of combustion reactions as defined in Section 2 using the unambiguous indicators of combustion identified in Section 3, it is important to compare the available data provided in the PMI report concerning the temperatures in the EHTP and the products in the EHTP outflow gas with respect to those available for the conventional self-supported combustion processes of tobacco. Results reported for reference cigarettes, also provided by the PMI report and discussed in Section 4.3 were considered for the comparison.

		3R4F Cigarette		EHTP	
Constituents	unit	Average	Std. Dev.	Average	Std. Dev.
*TPM	mg/unit	45.8	1.38	58.6	2.2
Water	mg/unit	16.3	0.94	40.9	2.9
Tar	mg/unit	27.6	--	16.3	3.9
Glycerin	mg/unit	2.3	0.09	4.44	0.27
Nicotine	mg/unit	2.0	0.01	1.37	0.11
CO	mg/unit	33.4	0.54	0.65	0.06
NO_x ($NO + NO_2$)	ug/unit	581	54	25.8	0.9
NO	ug/unit	529	54	26.8	0.9
Benzo[a]pyrene	ng/unit	17.3	0.9	0.66	0.15
1_3_butadiene	ug/unit	98.2	8.4	0.3	0.02
isoprene	ug/unit	913	79	2.8	0.1
acrylonitrile	ug/unit	26.1	4.3	0.2	0.01
benzene	ug/unit	90.7	12.5	0.7	0.07
toluene	ug/unit	158	24	2.0	0.3
pyridine	ug/unit	35.1	2.4	8.2	0.8
quinoline	ug/unit	0.49	0.05	NQ	NQ
styrene	ug/unit	18.2	1	0.8	0.2
Hydroquinone	ug/unit	92.5	0.6	7.6	0.3
Resorcinol	ug/unit	2.0	0.0	NQ	NQ
Catechol	ug/unit	84.2	1.2	14.8	0.8
Phenol	ug/unit	12.8	0.8	1.3	0.3
p-cresol	ug/unit	8.14	0.3	0.07	0.01
m-cresol	ug/unit	3.2	0.2	0.03	0.01
o-cresol	ug/unit	3.9	0.2	0.07	0.01
Formaldehyde	ug/unit	87	3	8.8	1.0
Acetaldehyde	ug/unit	1656	26	250	11
Acetone	ug/unit	708	18	37.4	2.1
Acrolein	ug/unit	162	3	10.8	0.9
Propionaldehyde	ug/unit	125	4	16.0	0.8
Crotonaldehyde	ug/unit	54	1	NQ	NQ
Methyl Ethyl Ketone	ug/unit	197	6	7.9	0.4
Butyraldehyde	ug/unit	91	3	25.0	1.3
1_aminonaphthalene	ng/unit	22.4	0.42	0.07	0.004
2_aminonaphthalene	ng/unit	14.1	1.99	0.04	0.01
3_aminobiphenyl	ng/unit	4.5	0.16	0.01	0.002
4_aminobiphenyl	ng/unit	3.1	0.03	0.02	0.002

Table 4.3: Products detected in the gas outflow of simulated puffing runs with the EHTP compared to those from a reference cigarette (from PMI Report).

Temperature data reported in Figure 4.3 for the EHTS Holder and heating element are strongly different from data in Figure 4.4 concerning temperatures in a lit cigarette. A comparison between Figure 4.4 and Figure 4.3 shows that the temperatures in the EHTS tobacco substrate are much lower (50-250°C with respect to 700-800°C). Even more important are the differences during simulated "puffs". Puffing induces an air flow in the tobacco substrate, thus creating ideal conditions for an intense self-supported combustion process. Experimental results (Baker, 1975) report that during puffing the temperatures in the tobacco substrate of a lit cigarette show an increase (up to 1000 °C), thus clearly evidencing the presence of an exothermic process.

On the contrary, simulated puffs in the EHTP produce a decrease in temperature, caused by the cooling due to the flow of ambient temperature gas in the EHTP.

Therefore, it may be concluded that the data in the PMI report support the absence of an exothermic process in the EHTP tobacco substrate.

The second important element to assess the nature of the process that takes place in the EHTP during EHTS operation comes from the data reported in the PMI report concerning the products detected in the gas outflow during simulated cigarette combustion and EHTS operation.

Table 4.3 clearly evidences important differences concerning the product yields detected for the different species in the gas outflow. In order to better understand the data in the table it should be considered that the table reports the amounts of the different species "per unit", and that the weight of the tobacco substrate in the EHTP is about half of the tobacco in a cigarette. Thus, the amounts reported for a cigarette should be divided by two for a correct comparison of product yields with those obtained for EHTP.

In spite of this, nitrogen oxides formed in the reference cigarette combustion are an order of magnitude higher with respect to those detected for the EHTP. Similar differences, or even higher, are present for carbon monoxide, aldehydes, amines and aromatic species.

The lower amounts of nitrogen oxides, as well as the much lower amounts of aromatic compounds, aldehydes and amines evidence that lower temperatures are present in the EHTP and that lower residence times of the volatiles may be supposed in high-temperature zones (if any) inside the EHTP. The latter conclusion comes from the evidence of a much lower formation of high molecular weight aromatic compounds due to pyrolysis reactions.

A further confirmation of the absence of relevant combustion phenomena in the EHTP comes from the low NO_x amount, that is unaffected by the presence or absence of air, and is very small in absolute terms with respect to CO, thus excluding a relevant exothermic reaction in the gas phase due to the oxidation of pyrolysis gases with air, and suggesting that detected NO_x are formed mainly due to the decomposition of nitrates in the EHTP tobacco substrate.

Finally, even if proximate analysis results for the EHTP tobacco substrate at the end of the EHTS operation are not available, Figure 4.5 and Table 4.2, reporting the results of ultimate analysis before and after use, show the presence of a relevant residual amount of carbon in the exhaust EHTP tobacco substrate. Actually, considering weight loss data

reported in Table 4.4 (34.7%), about 78.5% of carbon is still present in the EHTP after use. In tobacco combustion in a cigarette only a slight amount of carbon remains in the solid residue (also considering the relevant weight loss). Data for the 3R4F reference cigarette reported in Table 4.2, if combined with weight loss data in Table 4.4, show that only 8.8% of the original carbon content is present in the cigarette residue after use.

	Before use (mg)	After use (mg)
EHTP	813.1 ± 7.5	723.4 ± 7.1
EHTP - Tobacco Plug	323.6 ± 14.5	211.8 ± 12.0
Cigarette	1067.2 ± 11.5	475.6 ± 10.1
Cigarette - Cut Filler	817.0 ± 19.6	381.4 ± 13.7

Table 4.4: Weight loss of EHTP due to EHTS operation compared to weight loss of a reference cigarette (from PMI Report).

4.5 Answer to question C3

On the basis of the analysis of the technical details and of the experimental data provided in the PMI report, I can exclude that a combustion process (including self-sustained combustion) takes place in the tobacco substrate of the EHTP during EHTS operation.

The above conclusion is supported by:

1. temperature profiles reported for the EHTP tobacco substrate during EHTS operation, that suggest that temperatures are far below those of self-sustained combustion of tobacco (Figure 4.3)
2. no clear of evidence of an exothermic process in the EHTP, as may deduced by the temperature decrease during simulated puffing (Figure 4.3)
3. limited amounts of NO_x formed during EHTP operation in comparison with CO (Tables 4.1 and 4.3). The amounts of NO_x formed are almost independent of the presence of oxygen, suggesting that their formation is governed by nitrate decomposition
4. Several other evidences of low-temperature processes during operation of the EHTS (very low amounts of high-molecular weight polyaromatic compounds formed, presence of unconverted fixed carbon in the EHTP residue, etc.) discussed in detail in Section 4.4.

Conditions 1 and 3 are related to the unambiguous indicators of combustion, that are accordingly both negative.

4.6 References for section 4

Baker R.R., Temperature variation within a cigarette combustion coal during the smoking cycle, High Temp. Sci., 7, 236 – 247, 1975.

Annex I: Glossary

Aerosol

A fluid where solid or liquid particles are dispersed in a gas phase.

Arrhenius' law

The more common equation used to express the dependence of reaction rate with respect to temperature. The rate of a chemical reaction taking place at temperature T may be described as:

$$\frac{dC}{dt} = K(T) \cdot f(C)$$

where C is the concentration of the reactant of interest, t is time, f is a reaction-specific function, and K is the rate constant at temperature T. The Arrhenius' equation assumes the following dependence for the rate constant with respect to temperature:

$$K(T) = Ae^{-\frac{E_a}{RT}}$$

where E_a is the activation energy, A is a constant named pre-exponential factor, and R is the gas constant.

Adiabatic

Relating to or denoting a process or condition in which heat does not enter or leave the system concerned. A transformation of a thermodynamic system can be considered adiabatic when it is quick enough so that no significant heat is transferred between the system and the outside.

Biomass

The amount of living matter (as in a unit area or volume of habitat). In combustion science, carbon-based materials obtained from plants and animal waste, used as a fuel or a fuel source. Biomass covers a wide spectrum of species, from algae to grass to massive trees, from small insects to large animal wastes, and the products derived from such substrates.

Carbonaceous solid

A solid composed primarily of carbon. Solid carbonaceous fuels such as coal, biomass, and petroleum coke are widely used to provide heat and to generate electrical power through combustion processes. The ash content refers to the portion of the solid that remains when the fixed carbon has been fully oxidized, leaving behind oxidized mineral compounds.

Chemical kinetics

Chemical kinetics is the quantitative study of chemical systems that are changing with time. It deals with the experimental determination of reaction rates from which rate laws and rate constants are derived.

Combustion

The reduction-oxidation chemical reaction where the reactant molecules, namely the fuel and the oxidant, are mixed and rearranged to become product molecules with the simultaneous release of heat.

Combustion, Flaming

The combustion reaction of gaseous or vapor fuels with an oxidant. With reference to a solid fuel, the combustion reaction of gaseous vapors produced from the thermal decomposition of the fuel. The term may be also referred to the flame phenomenon: the self-propagating exothermic reaction with (usually) a luminous reaction zone associated to it. See also Smoldering Combustion.

Combustion Process

A confined field of a fluid where combustion reactions take place, subject to conditions imposed at its boundary. Heat and/or energy are generated by the chemical reactions and are deposited in the field. Both actions are carried out simultaneously and referred to as heat release. May be also referred to as a Combustion System.

Combustion, Self-Sustained

The occurrence of combustion reaction in the absence of external source of ignition. With reference to the combustion of solid, carbonaceous fuels, the combustion system based on the autonomous reiteration of the sequential mechanism of the thermal dehydration, thermal degradation (pyrolysis), and the slow, flameless combustion of char, which heats up the adjacent layer of un-burned solid.

Combustion, Smoldering

The slow, low-temperature, flameless form of combustion, sustained by the heat evolved when oxygen directly attacks the surface of a condensed-phase fuel or a char formed in a solid fuel devolatilization process.

Combustion, Solid

The combustion reaction of a fuel in the solid phase.

Cracking reactions

Thermal or catalytic pyrolysis reactions inducing the fragmentation of long-chain hydrocarbons.

Devolatilization

The overall process in which solid carbonaceous substances undergo a primary pyrolysis leading to the formation of lower molecular weight products and of a solid char residue. The lower molecular weight products formed in primary pyrolysis vaporize and are transferred from the solid to the gas phase (thus these species are named “volatiles”). The volatiles may undergo further gas-phase pyrolysis reactions, named “tar cracking” or “cracking” reactions during the devolatilization process. See also pyrolysis.

Diffusion control

A reaction regime in which the reaction rate is determined by the transport of the reactants through the reaction medium to the reaction zone. The transport of reactants takes place by diffusion, induced by differences in concentration of the diffusing species in the reaction medium.

Envelope flame

The boundaries (not necessarily visible) of an independent process that converts fuel and air into products of combustion. In heterogeneous combustion, the term envelope flame is often adopted for the combustion of a single drop of liquid fuel. If the drop is in a stagnant environment or moves slowly relative to the gas phase, then the drop will be surrounded by a thin, approximately spherical envelope flame. The flame will be centered on the drop, but will be present some distance away from its surface. A similar phenomenon may take place also during the combustion of solid particles, when an envelope flame forms due to the combustion of the volatiles formed in the primary pyrolysis of the solid. See also Wake diffusion flame.

Fluid dynamics

The branch of fluid mechanics dealing with the properties of fluids in motion.

Isothermal conditions

The condition for which a thermodynamic process is carried out at constant temperature.

Kinetic control

A reaction regime in which the reaction rate is controlled by chemical kinetics, not by the transport of the reacting species to the reaction zone.

Laminar

The highly ordered and deterministic flow of a viscous fluid at Reynolds numbers below the critical value for instability and transition to turbulence to occur. Such flows may be steady or unsteady, and include both periodic and transient behavior. In fluid mechanics, a flow condition in which the fluid travels smoothly or in regular paths, in contrast to turbulent flow, in which the fluid undergoes irregular fluctuations and mixing. In laminar flow, sometimes called streamline flow, the velocity, pressure, and other flow properties at each point in the fluid remain constant. Laminar flow over a horizontal surface may be thought of as consisting of thin layers, or laminae, all parallel to each other. See also turbulent.

Nicotine Free Dry Particulate Matter

Nicotine free dry smoke condensate (sometimes also referred to as “tar”): The dry particulate matter after deduction of its nicotine content.

Oxidation

A chemical reaction in which the removal of electrons from a chemical species takes place. The reducing agent (or reductant) is the electron donor; the oxidizing agent (or oxidant) is the electron acceptor. The electron transfer may be accompanied by other events, such as atom or ion transfer, but the net effect is the electron transfer and hence a change in oxidation number of an element. Oxidation is usually an exothermic reaction.

Proximate analysis

In chemistry, an analysis which determines the proximate principles of any substance, as contrasted with an ultimate analysis, which gives the composition with respect to the constituting elements. For biomass, coal or any other carbonaceous fuel, the proximate analysis consists of the partitioning of compounds obtained by separating moisture, volatile content, fixed carbon and inert components (ash).

Pyrolysis

The thermo-chemical decomposition of solid, carbonaceous substances into a range of products, either in the total absence of oxidizing agents or with a limited supply that does not permit gasification to an appreciable extent.

Smoke

The airborne solid and liquid particulates and gases evolved when a material undergoes pyrolysis or combustion, together with the quantity of air that is entrained or otherwise mixed into the mass.

Soot

Carbon particulate. Soot is not uniquely defined as a chemical substance, in that it may contain up to 10% (by moles) of hydrogen. The soot particle often consists of chain-like aggregates of nearly spherical particles.

Thermal decomposition

The production of gaseous substances (volatiles) from solids due to pyrolysis. The chemical decomposition of molecules at elevated temperatures.

Thermodynamics

Thermodynamics is the study of the transformations of energy.

Total Particulate Matter (TPM)

Crude smoke condensate: the portion of the mainstream smoke which is trapped in a smoke trap. Cigarette smoke TPM is generated by trapping the particulate matter from a machine-smoked cigarette onto a Cambridge filter pad and by extracting with a solvent.

Turbulent

In fluid mechanics, a flow condition in which local speed and pressure change unpredictably as an average flow is maintained. In turbulent flow, the fluid undergoes irregular fluctuations, or mixing, in contrast to laminar flow, in which the fluid moves in smooth paths or layers. Furthermore, the speed of the fluid at a point is continuously undergoing changes in both magnitude and direction.

Ultimate analysis

In chemistry, the ultimate analysis gives the percentage of constituent elements of a chemical substance. For biomass, coal or any other carbonaceous fuel, the ultimate analysis usually is limited to the composition in weight percentage of carbon, hydrogen, nitrogen and oxygen (the major components) as well as sulfur and chlorine. See also proximate analysis.

Vaporization

The phase transition opf a substance or mixture from the liquid phase to gas phase. Equivalent to evaporation, although usually evaporation is referred specifically to water or water solutions.

Wake diffusive flame

A wake is the region of recirculating flow immediately behind a moving or stationary solid body, caused by the flow of surrounding fluid around the body. The term wake diffusive flame is often adopted with reference to the combustion of a liquid fuel drop in a gas phase. If the drop is in a stagnant environment or moves slowly relatively to the gas phase, then the drop will be surrounded by a thin, approximately spherical envelope flame. The flame will be centered on the drop, but will exist some distance away from its surface. When the drop velocity is high relative to the gas phase velocity, a wake flame occurs, and combustion is confined to a region downstream of the drop. The velocity at which the transition from envelope to wake flame occurs increases with the square root of the drop diameter.

Annex II: Short CV of Prof. Valerio Cozzani

Valerio Cozzani was born in Pisa in 1968. He received a Bachelor and Master Degree (Laurea Quinquennale) in Chemical Engineering from the University of Pisa (Italy), in 1992, with honors. He received his Ph.D. (Dottorato di Ricerca) in Chemical Engineering from the Italian Ministry of Education, in 1997.

He was Visiting Scientist at the Industrial Hazards Unit, European Community Joint Research Centre, Ispra site (1/11/95-31/10/96). He then became Research Assistant (Tecnologo) at the National Research Group on Chemical and Environmental Risk of the Italian National Research Board (CNR), from 2/1/1997 to 25/11/1998. He was recruited as Lecturer at the Department of Chemical Engineering of Pisa University from 26/11/1998 to 30/9/2002. He was then Associate Professor at the School of Engineering of Bologna University from 1/10/2002 to 30/9/2006. He is now Professor of Chemical Engineering at the School of Engineering and member of the Department of Chemical Engineering at the University of Bologna since October 1st, 2006. He is also advocate lecturer at Steinbeis University, Berlin.

He is in charge of the undergraduate courses on "Unit Operations" and “Combustion Technologies”, and of the master courses of "Process Equipment and Plant Design", and "Process Analysis for Energy and Environment" at the University of Bologna. He gave several invited lectures on technologies for safety and environment in post-graduate courses at the Von Karman Institute for Fluid Dynamics, University of Stuttgart, Universities of Naples "Federico II", Pisa, Messina, and Seconda Università di Napoli.

He is Director of Studies in Chemical Engineering at University of Bologna and is Director of the post-graduate master program (Master di II livello) in "Design of up-stream oil&gas facilities", promoted by Bologna University and Eni group.

He is associate Editor of Safety Science and member of the Editorial Boards of the Journal of Hazardous Materials and of the Journal of Loss Prevention in the Process Industry. He is member of the executive board of the European Platform on Industrial Safety (ETPIS) and of the Italian working party on safety in the chemical and process industry (CISAP).

Prof. Cozzani has more than 15 years of research experience in the fields of safety of chemical plants, environmental technologies, and development of chemical processes. The specific subjects afforded in the research activity are the development of sustainable combustion and thermal conversion technologies, the study of pyrolysis and gasification processes for energy and material recovery from wastes, the development of innovative methodologies and models for hazard and risk analysis. The scientific activity is documented by more than 90 peer-reviewed publications. Prof. Cozzani participated and coordinated several national and international research projects, listed in detail in the following (period 2005-2014):

2005 MIUR (Italian Ministry of Education and Research), PRIN 2004: "Development of an integrated approach to safety, sustainability and environmental impact assessment of brominated flame retardants". Coordinator of the research unit at Bologna University.

2005 Tecnomare (Eni Group, Italy): “Development of a methodology for the assessment of missile impact hazard in O&G off-shore installations”. Responsible of the research grant and coordinator of the research group that carried out the activity at Bologna University.

2005 Shell Research (Chester, UK): "FREE: Fragmentation of Equipment Evaluation and assessment". Responsible of the research grant and coordinator of the research group that carried out the activity at Bologna University.

2006 Protezione Civile (Italian Government Agency for Civil Protection) - CONPRICI university consortium: “Safety and Security of sites handling or storing relevant quantities of hazardous substances”. Responsible of the research grant and coordinator of the research group that carried out the activity at Bologna University.

2007 Bologna University - Progetto strategico di ateneo: “Agroenergyfarm: pyrolysis and upgrading of biomass for liquid fuel production". Coordinator of the Chemical Engineering research unit.

2008 European Commission, VII Framework Program, Large-scale research project (80 partners): "Integ-Risk: Early Recognition, Monitoring and Integrated Management of Emerging, New Technology Related Risks". Coordinator of Sub-Project 2: "Emerging Risk Management Framework". Coordinator of CONPRICI university consortium research activities within the project.

2008 SEA Marconi: “Enhanced processes for the valorization of biomass by thermochemical processes”. Project coordinator.

2008 MIUR (Italian Ministry of Education and Research), PRIN 2007: "Development of Key Performance Indicators for the introduction of safety and sustainability drivers in process design". Project coordinator.

2009 European Commission, Joint Research Centre, IPSC, “Description of accident scenarios, failure frequencies, risk assessment data and separation distances for Land-Use Planning evaluations around Seveso plants”. Responsible of the research grant and project coordinator

2009 HERA: “Modeling the performance of De-NOx post-treatment in grid-combustors for the incineration of MSW”. Responsible of the research grant and project coordinator.

2012 Eni Exploration and Production: “Value at Risk of Oil Barrel” (Project Coordinator)

2013 European Commission, VII Framework Program: “TOSCA: Total Safety Management for Industrial Organizations”

2013 European Commission, VII FP: “EDEN: End-user driven DEmo for cbrNe”

Selected Relevant Peer-Reviewed publications:

V. Cozzani, L. Petarca, S. Pintus, L. Tognotti: “Ignition and Combustion of Single, Levitated Char Particles”. Combustion and Flame 103:181-193 (1995)

V. Cozzani, C. Nicolella, L. Petarca, M. Rovatti, L. Tognotti: "A fundamental study on Conventional Pyrolysis of a Refuse Derived Fuel". Industrial & Engineering Chemistry Research 34:2006-2020 (1995)

V. Cozzani, C. Nicolella, M. Rovatti, L. Tognotti: "Modelling and experimental verification of physical and chemical processes during pyrolysis of a Refuse Derived Fuel". Industrial & Engineering Chemistry Research 35:90-98 (1996)

V. Cozzani, C. Nicolella, M. Rovatti, L. Tognotti: "Influence of gas-phase reactions on the product yields obtained in the pyrolysis of polyethylene". Industrial & Engineering Chemistry Research 36:342-348 (1997)

V. Cozzani: "Characterization of Coke formed in the Pyrolysis of Polyethylene". Industrial & Engineering Chemistry Research 36:5090-5095 (1997)

E. Ranzi, M. Dente, T. Faravelli, G. Bozzano, S. Fabini, R. Nava, V. Cozzani, L.Tognotti: "Kinetic modeling of polyethylene and polypropylene thermal degradation". Journal of Analytical and Applied Pyrolysis 40:305-319 (1997)

V. Cozzani, M. Smeder, S. Zanelli: "Formation of hazardous compounds by unwanted reactions in industrial accidents". Journal of Hazardous Materials 63:131-142 (1998)

V. Cozzani, S. Zanelli: "Precursors of dangerous substances formed in the loss of control of chemical systems". Journal of Hazardous Materials 65:93-108 (1999)

V. Cozzani: "Reactivity in oxygen and carbon dioxide of char formed in the pyrolysis of refuse-derived fuel". Industrial and Engineering Chemistry Research 39:864-872 (2000)

F. Barontini, E. Brunazzi, V.Cozzani: "A novel methodology for the identification of azeotropic binary mixtures by TG-FTIR techniques". Thermochimica Acta 389:97-110 (2002)

J. Rath, M.G. Wolfinger, G. Steiner, G. Krammer, F. Barontini, V. Cozzani: "Heat of wood pyrolysis". Fuel 82:81-91 (2003)

F. Barontini, K. Marsanich, V. Cozzani: "The use of TG-FTIR technique for the assessment of hydrogen bromide emissions in the combustion of BFRs". Journal of Thermal Analysis and Calorimetry 78:599-619 (2004)

K. Marsanich, S. Zanelli, F. Barontini, V.Cozzani: "Evaporation and thermal degradation of tetrabromobisphenol A above the melting point". Thermochimica Acta 421:95-103 (2004)

F. Barontini, V. Cozzani: "Formation of hydrogen bromide and organobrominated compounds in the thermal degradation of electronic boards". Journal of Analytical and Applied Pyrolysis 77:41-55 (2006)

C. Gomez, E. Velo, F. Barontini, V. Cozzani: "Influence of Secondary Reactions on the Heat of Pyrolysis of Biomass". Industrial & Engineering Chemistry Research 48:10222-10233 (2009)

R. Sanchirico, G. Pinto, A. Pollio, M. Cordella, V. Cozzani: "Thermal degradation of Fenitrothion: characterization and eco-toxicity of decomposition products". Journal of Hazardous Materials 199:390-400 (2012)

M. Cordella, C. Torri, A. Adamiano, D. Fabbri, F. Barontini, V. Cozzani: "Bio-oils from biomass slow pyrolysis: a chemical and toxicological screening". Journal of Hazardous Materials 231-232:26-35 (2012)

F. Barontini, A. Tugnoli, V. Cozzani, J. Tetteh, M. Jarriault, I. Zinovik: "Volatile Products formed in the Thermal Decomposition of a Tobacco Substrate". Industrial and Engineering Chemistry Research 52:14984-14997 (2013)

ABSENCE OF COMBUSTION IN AN ELECTRICALLY HEATED TOBACCO SYSTEM - AN EXPERIMENTAL INVESTIGATION

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Introduction and Objectives

Combustion occurs when biomass such as tobacco is ignited by a heat source in the presence of an oxidant (oxygen in air). Biomass combustion involves, simultaneously or sequentially, the gas-phase combustion of volatiles produced by the thermal decomposition and degasification of the heated biomass and by the gas-solid reaction occurring at the interface or in the bulk of the residual solid. The tobacco in a lit cigarette undergoes smoldering combustion and burns at temperatures in excess of 600 °C [1]. A self-sustaining combustion process is established that consumes the tobacco forming ash and smoke. The latter containing more than 8,000 chemicals [2], a number of which have been classified by Regulatory bodies as harmful and potential harmful constituents (HPHCs) [3].

One approach to reduce the levels of HPHCs associated with cigarette smoke has been to generate an aerosol by heating, rather than burning, tobacco. Some of the earlier tobacco products developed using this approach have been briefly reviewed by Baker [1] and Schorp et al. [4].

A series of experiments were performed to investigate if combustion of a specifically designed tobacco substrate, referred to here as the Electrically Heated Tobacco Product (EHTP), occurs when used in a newly developed and patented electrically heated tobacco system‡.

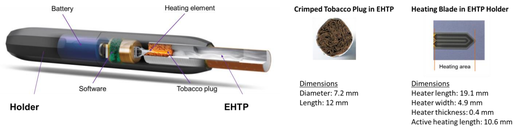
[1] R.R. Baker, Progress in Energy and Combustion Science 32, pp.373–385, 2006
[2] A. Rodgman, T.A. Perfetti, The chemical components of tobacco and tobacco smoke. CRC Press, Boca Raton. 2013.
[3] Federal Register Food and Drug Administration, 77, pp. 20034, 2012
[4] M. Schorp, A. Tricker, and R. Dempsey. Regul. Toxicol and Pharmacol. 64, pp. S1-S10, 2012.

Methods

- Temperature data for the tobacco in the EHTP at different distances from the heating blade was measured using a Class 2 K type thermocouple (diameter 0.25 mm). The position of the thermocouple was controlled using a micrometer and the thermocouples were inserted into the EHTP holder through a small drilled hole.
- Aerosol chemistry data for the operation of the EHTP under nitrogen and air in comparison to smoke from a 3R4F cigarette was generated by Labstat® International ULC, Canada. CO_2 and CO analysis was also performed by PMI R&D using a linear smoking machine type Borgwaldt LM20X. Puffs were drawn using the Health Canada Intense (HCI) puffing protocol [puff volume of 55 mL, puff duration of 2 s, puff frequency 30 s]. The laboratory conditions used were 22°C ± 2°C and 60% ± 5% relative humidity. The 3R4F cigarette is a standard reference cigarette used for research.
- Weight loss data for the tobacco material in the EHTP after use were compared to the 3R4F reference cigarette.
- Water and ultimate analysis (C, H, N, O) of the tobacco substrate in the EHTP and in the 3R4F reference cigarette before and after use was performed by Solvais AG, Switzerland.

Results

Temperature Measurements in Tobacco



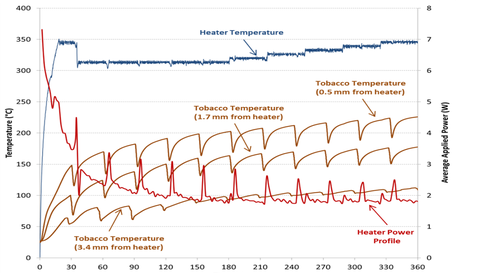


Figure 1. Average temperature and power profile of heating element in EHTP Holder, and average tobacco temperature (measured at three different positions from the heating element) during use. Average of 5 replicates.

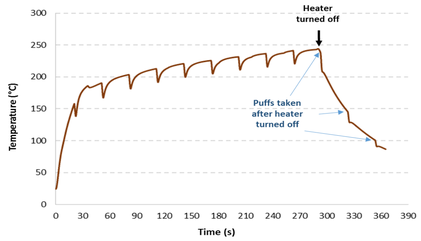


Figure 2. Average tobacco temperature (measured 0.5 mm from the heater) when the heater is turned off after the 10th puff during product use. Average of 3 replicates.

Aerosol Chemistry

Table 1. Levels of aerosol constituents obtained when operating the EHTP under atmospheres of air and nitrogen and compared to smoke from a reference cigarette

		EHTP in Nitrogen		*EHTP in Synthetic Air*		*3R4F Cigarette*		*Blank*	
Constituents	unit	Average	Std. Dev.	Average	Std. Dev.	Average	Std. Dev.	Average	Std. Dev.
TPM*	mg/unit	54.0	1.5	55.2	1.6	45.8	1.38	0.006	0.015
Water	mg/unit	34.7	4.3	37.3	3.8	16.3	0.94	BDL	BDL
NFDPM†	mg/unit	17.9	3.1	16.5	3.4	27.6	----	BDL	BDL
Glycerin	mg/unit	4.38	0.24	4.39	0.40	2.3	0.09	BDL	BDL
Nicotine	mg/unit	1.38	0.10	1.37	0.09	2.0	0.01	BDL	BDL
CO	mg/unit	<0.53 but ≥0.16	-----	0.54	0.16	33.4	0.54	BDL	BDL
NO	µg/unit	18.8	0.9	19.9	1.3	529	54	BDL	BDL
NO_X ($NO + NO_2$)	µg/unit	19.5	1.0	20.8	1.4	581	54	BDL	BDL
Benzo(a)pyrene	ng/unit	0.60	0.09	0.61	0.11	17.3	0.9	BDL	BDL
1_3_butadiene	µg/unit	0.3	0.03	0.3	0.02	98.2	8.4	BDL	BDL
isoprene	µg/unit	2.6	0.4	2.3	0.1	913	79	BDL	BDL
acrylonitrile	µg/unit	0.2	0.02	0.2	0.02	26.1	4.3	BDL	BDL
benzene	µg/unit	0.5	0.07	0.6	0.06	90.7	12.5	BDL	BDL
toluene	µg/unit	1.9	0.3	2.0	0.2	158	24	NQ	NQ
pyridine	µg/unit	7.4	0.6	7.8	1.4	35.1	2.4	0.2	0.1
quinoline	µg/unit	<0.011 but ≥0.003	----	<0.011 but ≥0.003	----	0.49	0.05	BDL	BDL
styrene	µg/unit	0.8	0.3	0.7	0.2	18.2	1	0.1	0.01
Hydroquinone	µg/unit	7.4	0.7	7.0	0.2	92.5	0.6	BDL	BDL
Resorcinol	µg/unit	<0.055 but ≥0.016	----	<0.055 but ≥0.016	----	2.0	0.0	BDL	BDL
Catechol	µg/unit	14.7	1.1	14.3	0.5	84.2	1.2	BDL	BDL
Phenol	µg/unit	1.3	0.1	1.4	0.1	12.8	0.8	NQ	NQ
p-cresol	µg/unit	0.07	0.01	0.07	0.01	8.14	0.3	BDL	BDL
m-cresol	µg/unit	0.03	0.01	0.03	0.01	3.2	0.2	BDL	BDL
o-cresol	µg/unit	0.07	0.01	0.06	0.01	3.9	0.2	BDL	BDL
Formaldehyde	µg/unit	6.1	1.2	9.1	1.4	87	3	1.7	0.2
Acetaldehyde	µg/unit	211	16	230	21	1656	26	NQ	NQ
Acetone	µg/unit	31.0	2.3	35.9	4.3	708	18	NQ	NQ
Acrolein	µg/unit	8.4	1.3	10.7	1.7	162	3	BDL	BDL
Propionaldehyde	µg/unit	13.7	1.1	14.9	1.9	125	4	BDL	BDL
Crotonaldehyde	µg/unit	<3.29 but ≥0.988	----	<3.29 but ≥0.988	----	54	1	BDL	BDL
Methyl Ethyl Ketone	µg/unit	7.0	0.6	7.6	0.8	197	6	BDL	BDL
Butyraldehyde	µg/unit	22.5	1.9	23.1	1.9	91	3	NQ	NQ
1_aminonaphthalene	ng/unit	0.07	0.01	0.07	0.01	22.4	0.42	NQ	NQ
2_aminonaphthalene	ng/unit	0.04	0.01	0.04	0.01	14.1	1.99	0.02	0.00
3_aminobiphenyl	ng/unit	0.01	0.00	0.01	0.00	4.5	0.16	NQ	NQ
4_aminobiphenyl	ng/unit	0.02	0.00	0.02	0.00	3.1	0.03	0.01	0.01

Labstat report numbers NS201 for EHTP and NS190 and NS179 for 3R4F Cigarette. Mainstream aerosol and smoke levels. *Total Particulate Matter. Health Canada Intense regime. ISO 4387 method "Determination of total and †nicotine-free dry particulate matter 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- above LOD but below LOQ. LOQ for quinoline, resorcinol, and crotonaldehyde = 0.011, 0.055 and 3.29 µg/unit, respectively. Unit = EHTP or 3R4F, respectively.

Table 2. CO and CO_2 Aerosol Levels

		EHTP		*3R4F cigarette*	
Constituents	unit	Average	Std. Dev	Average	Std. Dev
CO	mg/unit	0.54	1.5	31.4	1.5
CO_2	mg/unit	6.1	0.6	86.2	2.9

Yields are based on 12 puffs drawn using the Health Canada Intense (HCI) protocol. The number of replicates performed were 19 and 8, respectively, for the EHTP and 3R4F reference cigarette. Unit = EHTP or 3R4F, respectively.

Figure 3. Photograph of a EHTP and *3R4F reference cigarette

Table 3. Weight Loss and Ultimate Analysis Data

	EHTP - Tobacco Substrate					Cigarette - Tobacco Cut Filler				
	C	H	N	Water	Weight	C	H	N	Water	Weight
	[%w/w]	[%w/w]	[%w/w]	[%w/w]	[mg]	[%w/w]	[%w/w]	[%w/w]	[%w/w]	[mg]
Before	38.4 ± 0.3	6.1 ± 0.2	2.0	14.3 ± 0.5	324 ± 15	38.2 ± 0.8	5.9 ± 0.2	1.8 ± 0.3	13.2 ± 0.4	817 ± 20
After	46.6 ± 1.2	5.4 ± 0.3	2.6 ± 0.2	2.8 ± 0.4	212 ± 12	7.6 ± 0.9	0.8 ± 0.1	1.0 ± 0.2	1.9 ± 0.2	381 ± 14

Weight data: average and standard deviation values shown the number of replicates performed were 20 and 8, respectively, for the EHTP tobacco substrate and 3R4F reference cigarette tobacco filter.
Ultimate analysis: average and standard deviation values shown. 3 replicates were performed.

Discussion

Two indicators may be used to unambiguously detect biomass or tobacco combustion: (i) the presence of relevant quantities of nitrogen oxides in the gaseous products, not formed from the decomposition of nitrates present in the original biomass/tobacco; (ii) clear evidence of a self-sustaining exothermic process. The two conditions should be simultaneously verified.

Contrary to the increase in the temperature of tobacco that occurs when air is drawn through a lit cigarette [1], there is a significant drop in the temperature of the tobacco substrate in the EHTP when a puff is taken (Figure 1). The highest average temperature of the tobacco in the EHTS measured in close proximity to the heating blade is well below the temperature required for combustion of the tobacco substrate to occur[5]. Torrefaction and a darkening of the tobacco substrate occurs close to the heating element. Operation of the EHTP in an atmosphere of nitrogen (where combustion cannot occur) yields an aerosol that is substantially equivalent to that produced in air. Evidence for the absence of a self-sustaining exothermic reaction is also provided by the drop in temperature of the tobacco material when the heater is turned off (Figure 2).

While CO, CO_2, and H_2O are products of biomass combustion processes their presence in an aerosol are not unambiguous chemical markers that a combustion process has occurred. These chemical species can be generated from non-combustion, lower temperature thermal processes such as drying and torrefaction of biomass [6-8].

Further confirmation of the absence of combustion phenomena in the EHTP comes from the low level of NO_x in the aerosol, that is unaffected by the presence or absence of air. The presence of NO_x can be attributed to the decomposition of nitrates in the tobacco substrate [9].

The low levels of volatile organic compounds in the EHTP aerosol, the presence of unconverted fixed carbon in the EHTP after heating, and the absence of ash formation provide additional evidence of the lower temperature processes occurring in the EHTP compared to tobacco burning in a lit cigarette.

[5] Barontini, F., Tugnoli, A., Cozzani, V., Tetteh, J., Jarriault, M. Zinovik, I. Ind. Eng. Chem. Res. 52 (42),14984-14997, 2013
[6] Basu P., Biomass Gasification and Pyrolysis - Practical Design and Theory, Academic Press, 2010
[7] Baker, R. The formation of the oxides of carbon by the pyrolysis of tobacco, Beit. zur Tabak., 8, 1, 1976
[8] Senneca, O., Ciaravolo, S., Nunziata, A. "Composition of the gaseous products of pyrolysis of tobacco under inert and oxidative conditions." Journal of analytical and applied pyrolysis 79, 1, 234-243, 2007
[9] Im H., Rasouli F., Hajaligol M., Formation of Nitric Oxide during Tobacco Oxidation, Journal of Agricultural and Food Chemistry, 51, 7366-7372, 2003

Conclusions

The results of the experiments conducted confirm the absence of combustion occurring in the EHTP when used as intended. Due to the controlled operating temperature of the heater, the aerosol generated is formed principally by the evaporation of water, nicotine and glycerin from the tobacco substrate. The EHTP aerosol also contains substantially lower levels of harmful and potentially harmful compounds compared to smoke generated from a lit cigarette.

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9th - 12th of May 2016

ABBREVIATIONS: ‡ The Electrically Heated Tobacco System (EHTS) was developed by Philip Morris International. It is also referred to as the Tobacco Heating System 2.2 (THS 2.2).

The research described in this poster was sponsored by Philip Morris International