APPENDIX A3.2.1-1

ASSESSMENT OF EHTP PERFORMANCE - PARTICLE SIZE REPORT

ASSESSMENT OF EHTP PERFORMANCE - COMBUSTION REPORT

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ANALYSIS of EHTP FEATURES with respect to BIOMASS/TOBACCO SMOKE FORMATION

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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 aerosol formed 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):

S1. what is the scientific definition of smoke?
S2. based on the compositional analysis of the aerosol generated from the Electric Heated Tobacco Product (EHTP), and scientific definition of "smoke", does the product produce "smoke" when used as intended?

In order to answer the above questions a literature search was carried out. An analysis and a critical discussion of different literature sources was then 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 and 3 report a detailed discussion of issues relevant to the questions raised, 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 two questions may be summarized as follows:

S1: Based on the analysis of the scientific literature that I conducted, the more comprehensive and correct definition of smoke is that given by the United States National Fire Protection Association (NFPA) standard 92B: smoke is composed of 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. This definition implies that smoke is not inherently associated to the combustion process, because pyrolysis and formation of volatiles may also cause the formation of smoke.

S2: The aerosol generated in EHTP operation is composed mainly (up to 98.3% by weight) of water and of products deriving from the vaporization, in the absence of chemical reactions, of substances present in the original tobacco substrate. Even applying the more comprehensive definitions of smoke (as discussed in Section 2), I can conclude that EHTS operation does not produce smoke. This conclusion is supported by:

1. the absence of combustion processes in the EHTP tobacco substrate, as discussed in detail in a separate report (Analysis of EHTP features with respect to tobacco/biomass combustion)
2. the very limited pyrolysis phenomena present in the EHTP tobacco substrate during EHTP operation, that 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 EHTP tobacco substrate.
3. the aerosol produced by EHTS operation is formed mostly by vaporization, as proven by the experimental data showing its chemical characterization

The aerosol generated in EHTS operation is very different in the chemical composition from the smoke formed in the self-sustained combustion of tobacco and more in general from smoke formed in combustion processes. Therefore, such aerosol should not be classified as smoke.

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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 aerosol formed during EHTS operation were the following:

S1. what is the scientific definition of smoke?

S2. based on the compositional analysis of the aerosol generated from the EHTP, and scientific definition of "smoke", does the product produce "smoke" when used as intended?

In the following an answer to questions **S1** and **S2** is provided.

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 question **S1** (what is the scientific definition of smoke generated from biomass/tobacco combustion), a literature search and analysis was carried out. Reference literature sources, both fundamental and specific with respect to smoke from 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 question **S2** (based on the compositional analysis of the aerosol generated from the EHTP, and scientific definition of "smoke", does the product

produce “smoke” when used as intended), 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 will assume the full responsibility of the experimental data included in the PMI report and in its integrations.

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 S1: What is the scientific definition of smoke?

2.1 Analysis of relevant scientific literature

During combustion processes, a cloud of black, gray, or white gases and dusts, named smoke, is often visible. Drysdale (2011), in his authoritative and well known book, uses for "smoke" the definition of Gross et al. (1967), who defines smoke as the gaseous products of burning organic materials in which small solid and liquid particles are also dispersed. The same author affirms that this definition is somehow more general than the common definitions which refer to smoke simply as the visible volatile products from burning materials.

The definition given in NFPA 92B is similar to the definition of Gross et al. (1967), but includes entrained air: smoke is 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.

Mulholland (2008), head of the Smoke Dynamics Research Group in the Center for Fire Research at the US National Bureau of Standards, defines smoke as the aerosol or condensed phase component of the products of combustion. The term aerosol is used in its proper significance, i.e. a mixture of solid or liquid particles in a gas.

Smoke aerosols vary widely in appearance and structure, from light colored, for droplets produced during smoldering combustion and fuel pyrolysis, to black, for solid, carbonaceous particulate or soot produced during flaming combustion. The most basic physical property of smoke is the size distribution of its particles.

The conditions under which the combustion process is taking place affect the phenomena that produce liquid and solid particles, thus affecting the amount and character of the smoke. Three main phenomena may result in smoke formation:

1. primary pyrolysis and formation of volatile species;
2. flaming combustion;
3. smoldering combustion.

Primary pyrolysis of solid fuels and volatile formation occur mainly at a fuel surface as a result of elevated temperatures (above 250°C). The vapors evolving from the surface may include fuel components vaporized due to the increasing temperatures, volatiles formed by the radical reactions ongoing in the solid substrate that constitute the pyrolysis process, and partially oxidized products. Depending on the temperature, radical pyrolysis reactions may affect also the gas-phase compounds generated. The overall process of primary pyrolysis and volatile formation is usually named "devolatilization" and the gas-phase compounds generated in this process are usually named "volatiles".

As volatiles leave the solid and move to lower temperature zones, the higher molecular weight and lower vapor pressure constituents of volatiles can condense, forming liquid droplets appearing as light-colored smoke.

Smoke from flaming combustion is different and consists almost entirely of solid (graphitic) carbon particles. Most are formed in the gas phase as a result of cracking reactions of volatiles formed in the primary pyrolysis. Cracking reactions are radical reactions induced by high temperatures in flame zones with low oxygen concentrations. In cracking reactions, high molecular weight organic volatiles break down to low molecular weight gases and to carbonaceous graphitic structures, that cluster to form particulate matter. The carbon particles formed from the gas phase are generally referred to as soot. Finally, hydrocarbon emissions (HC) result from the presence of unburned fuel (Liberman, 2008). The smoke emission from a flame thus represents a balance between growth processes in the fuel-rich portion of the flame and burnout with oxygen. A high concentration of particulate matter is manifested as visible smoke in the exhaust gases.

In contrast to flaming combustion, smoldering is a flameless form of combustion that occurs when oxygen reacts with the surface of solid fuels (Ohlemiller, 1995). The temperature during smoldering ranges typically from 300 °C to 850°C. Smoke from smoldering combustion is similar to that obtained when any carbon-based material is heated to temperatures at which there is chemical degradation and evolution of volatiles. The volatiles with higher molecular weight condense as they mix with cooler air, thus giving an aerosol, which consists of minute droplets of tar and high-boiling liquids. These will tend to coalesce under still air conditions to give a distribution of particle size with a mass median diameter of the order of 1 μm, and will deposit on surfaces to give an oily residue.

Finally it should be remarked that forced convection due to blowers (or to puffing) or natural convection caused by the combustion process may create a drag force that entrains, beside carbon-based solid particles, also fly ashes and unburned solid fuel particles in the smoke.

Smoke aerosols are dynamic with respect to their particle size distribution function. Smoke particles or droplets undergoing Brownian motion collide and stick together. The result of this behavior is that, in a fixed volume of smoke gas, the number of particles decreases, while the total mass of the aerosol remains unchanged. This process is known as coagulation.

With specific reference to tobacco and cigarettes, it is well known that the smoke is a very complex, multicomponent system, in which more than 4800 compounds have been identified by chromatographic techniques (Hoffmann et al., 2001). Consequently, the formation mechanism of smoke from tobacco self-sustained combustion is exceedingly complicated (Torikai et al., 2004). In general, we can say that mainstream smoke is tobacco smoke generated during puff-drawing in the burning cone of a tobacco product, which is inhaled directly before it is released into the surrounding air. Side-stream smoke is defined as a combination of: 1) smoke emitted into the air during burning of a tobacco product between puffs; 2) smoke escaping into the surrounding air during puffs; and 3) smoke components that diffuse through cigarette paper (Jaakkola et al., 1997).

Baker (2006) has published an important paper on this issue and gives a useful review on the overall phenomena occurring in a burning cigarette. Figure 2.1 reports a scheme of the phenomena involved in smoke formation. Smoke is generated both in the pyrolysis and combustion zone. However, the majority of smoke products are generated by a variety of mechanisms which are mainly endothermic. Hence, smoke is mostly related to the primary pyrolysis of the tobacco substrate, that leads to the formation of volatiles, whereas carbon monoxide and dioxide, and water, are produced in the oxidation zone.

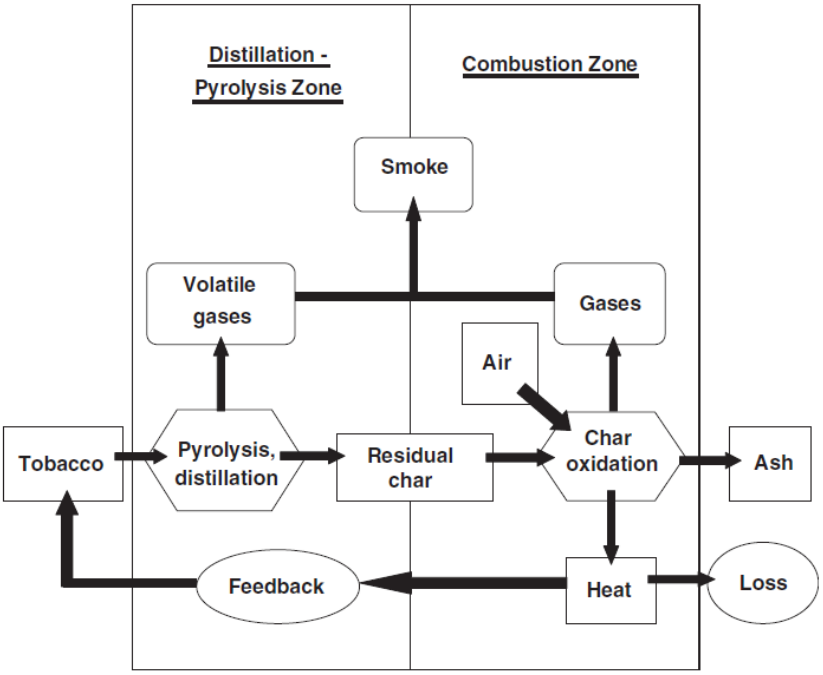


Figure 2.1: Schematic diagram of the major processes occurring during cigarette combustion, after Muramatsu (2005).

Thus, Baker suggests that smoke in tobacco self-sustained combustion is not related to the combustion reactions but more in particular to the pyrolysis and volatiles formation phenomena.

2.2 Answer to question S1

Different definitions are present in the scientific literature for smoke.

Based on the analysis of the scientific literature that I conducted, the more comprehensive and correct definition is that given by NFPA 92B: smoke is composed of 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.

This definition implies that smoke is not inherently associated to combustion, since pyrolysis and volatiles formation may also cause the formation of smoke.

Moreover, the above definition clearly remarks that smoke, as evident from the literature, may have a very different chemical and physical nature:

- from a physical point of view it may be composed of solid or liquid particles with different size distributions and concentrations;
- from a chemical point of view, smoke components may be: i) condensed, liquid combustion products (as water), and/or ii) condensed, liquid products of partial combustion (as high molecular weight and/or low vapor pressure organic liquids formed during fuel primary pyrolysis and volatile emission), and/or iii) solid combustion products (mainly graphitic carbon particles as soot, and inorganic fly ashes), iv) and/or unburned or partially oxidized solid or liquid fuel particles.

Smoke from tobacco combustion has specific features, as reported in reference publications (e.g. see Baker, 2006), and usually has a very complex composition, including all the above cited chemical components of smoke: condensed water, liquid drops of condensed volatiles (tar), soot, and ashes.

2.3 References for section 2

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

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3. Answer to Question S2: Based on the compositional analysis of the aerosol generated from the EHTP, and scientific definition of "smoke", does the product produce "smoke" when used as intended?

3.1 Characterization of Aerosol during simulated puffing

In order to assess if the EHTP produces smoke during operation, the aerosol formed during operation needs to be characterized and compared to that formed during cigarette and/or tobacco combustion.

A relevant attention was devoted in the technical and scientific literature to the characterization of smoke formed during cigarette puffing. Several internationally recognized standardized methodologies were developed and updated over many years and are summarized elsewhere (Darral, 1988; Thomsen, 1992; Baker, 2002), based on standardized smoking machine methods (e.g. see ISO 3308:2012, Health Canada, 1999).

Among others, two main reference methodologies are applied to simulate puffing: the International Organization for Standardization (ISO) smoking protocol (ISO 3308:2012, Directive 2001/37/EC) and the Health Canada Intense smoking protocol (Health Canada, 1999).

The analysis of smoke formed by these or other smoking protocols is then carried out by standardized methodologies.

Smoke is collected under a standard machine smoking regime and yields are measured from the collected smoke using prescribed ISO testing methods (ISO 4387:2000; ISO 10315:2013; ISO 10362-1:1999). Collection methods involve separation of the mainstream smoke into the fraction that is trapped on a filter pad (the Total Particulate Matter or TPM) and the fraction that is trapped after passing through the filter pad (the Gas Vapor Phase or GVP).

The main components measured in the TPM of cigarette smoke are water, nicotine and, by difference, the amount of Nicotine Free Dry Particulate Matter (NFDPM). ISO standard 4387 is normally used for the collection of TPM and the characterization of its main components (nicotine, water and NFDPM).

The total weight of TPM is measured by weighing the filter pad before and after smoking and then nicotine and water are measured by chemical methods to enable the calculation of NFDPM.

Since the characterization of TPM is crucial to assess the characteristics of the aerosol generated in EHTS operation, it is important to recall the main steps of the ISO 4387 procedure. Figure 3.1 shows the flow-chart of the standard procedure used for TPM collection and main component characterization, as well as possible further characterizations that may be carried out to identify specific components of the TPM.

As shown in the figure, a pad holder containing a Cambridge filter pad is positioned downstream to the smoking machine (e.g. a standard Borgwaldt machine) used for simulated puffing, so that the product stream generated in simulated puffing passes through the filter. Thus, the aerosol TPM in trapped on the Cambridge filter pad.

The figure evidences that the filter pad is weighed before and after the simulated puffing. Weight difference corresponds to the TPM determined by the ISO 4387 method.

In the following step, the ISO 4387 method requires to open the pad holder and to characterize the two main components of interest present in the TPM: nicotine and water.

As shown in the figure, the difference between the total amount of TPM and the weight determined for nicotine and water is defined as Nicotine Free Dry Particulate Matter (NFDPM). NFDPM is commonly referred to as "tar", since in conventional cigarette TPM it is mainly constituted by condensed volatile products formed in tobacco pyrolysis and combustion process.

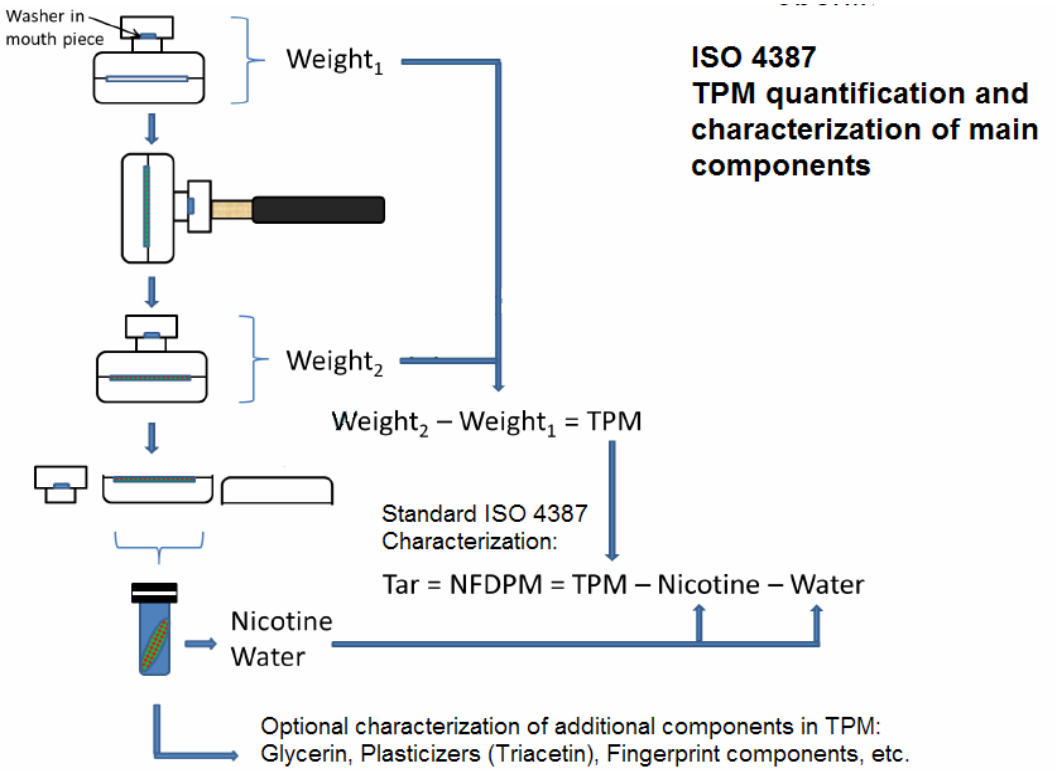


Figure 3.1: Flow-chart of the ISO 4387 procedure for TPM, water, nicotine and NFDPM quantification in cigarette smoke and, more in general, in the aerosol generated during operation of a standard smoking machine. Possibility of optional characterization of further TPM components, not required in the ISO 4387 procedure, is also evidenced.

Thus, the NFDPM fraction in TPM, usually named tar, applying the standard ISO 4387 procedure is calculated as:

"tar" = NFDPM = TPM - nicotine - water (3.1)

The ISO 4387 does not require any other characterization of the TPM. However, once the TPM has been recovered, as shown in Figure 3.1, optional characterizations may be carried out to quantify other components: e.g. glycerin, plasticizers, etc.

Since understanding the real nature of the NFDPM is crucial to assess the actual features of the aerosol generated, experimental data concerning the content of several components of the EHTP tobacco substrate that are vaporized (thus not generated by pyrolysis or combustion processes) during EHTP operation were carried out: e.g. glycerin, plasticizers, fingerprint components, etc. The results are reported in the PMI report and discussed in section 3.2.

Recent findings also evidenced that the ISO 4387 method may lead to an overestimation of the NFDPM fraction due to loss of water in the analytical procedure if a high quantity of water is present in the TPM (Ghosh and Jeannet, 2013).

Actually, in the ISO 4387 standard, errors in the amount of water determined (e.g. evaporation or absorption by components of the filter pad holder) lead to overestimate the amount of NFDPM determined by the method (more precisely, as shown in figure 3.1 any loss of water will increment NFDPM by an amount equal to the weight of the "lost" water). A modified procedure to overcome this problem was proposed by Ghosh and Jeannet (2013).

In order to assess if the EHTP produces smoke during operation, the data in the PMI report obtained from the characterization of the aerosol formed during EHTP operation using both the ISO and the HCI smoking regimes, and applying both the standard ISO 4387 procedure and the modified procedure suggested by Ghosh and Jeannet (2013) to TPM quantification were critically analyzed and discussed in the following.

3.2 Experimental data available for the aerosol formed during EHTP operation

The PMI report includes detailed data on the aerosol formed during EHTP operation, reporting the data concerning the characterization of the aerosol of EHTP and the comparison of such data to those obtained for a reference cigarette (see Table 3.1) under the Health Canada Intense (HCI) puffing regime. Data in Table 3.1 were obtained applying the standard ISO 4387 procedure for TPM quantification.

Table 3.1 reports the characterization of the TPM obtained from the HCI puffing regime using the standard ISO 4387 procedure. The results evidence that the gas outflow during EHTS operation is characterized by the presence of water, glycerin, nicotine and lower quantities of other high molecular weight components. The standard ISO 4387 analysis procedure used to obtain the data in Table 3.1 leads to detect also a relevant quantity of the fraction named "tar" in the TPM (comparable to that of a conventional cigarette).

However, the "tar" fraction in Table 3.1 was obtained applying the standard ISO 4387 procedure. Thus "tar" is actually the NFDPM fraction calculated by Eq.(3.1). Thus, it

should be remarked that although this fraction of the TPM is named "tar" in the table, its actual chemical nature was not characterized: it may be composed by tar, but also by other condensed products different from tar (e.g. other high molecular weight components vaporized during EHTP operation and condensed in the aerosol stream.

In particular, glycerin, that is added in relevant amounts to the EHTP tobacco substrate as an aerosol former and vaporized during EHTP operation, is actually included in the tar fraction in table 3.1 (see fig.3.1 and eq.(3.1)).

A separate determination of glycerin in TPM was thus carried out to assess the amount of glycerin included in the "tar" fraction in table 3.1. As evident from the table, about 25% of the "tar" fraction (or NFDPM) formed in EHTS operation and determined by the standard ISO 4387 procedure is actually glycerin, that is not a pyrolysis or combustion product.

Figure 3.2 reports a comparison of the total particulate matter (TPM) obtained for the EHTP operation and for a reference cigarette under the ISO regime. Figure 3.3 reports a comparison of the TPM obtained for the EHTP operation and for a reference cigarette under the HCI regime. In both figures, the TPM was analyzed by the modified ISO 4387 procedure developed by Ghosh and Jeannet (2013). In the figures, the "other" fraction was determined as follows:

$$\text{Other} = \text{NFDPM} - \text{glycerin} = \text{TPM} - \text{nicotine} - \text{water} - \text{glycerin} \qquad (3.2)$$

The actual condensed pyrolysis products that may be considered as tar are thus included in this fraction, named "other" in Figures 3.2 and 3.3.

As evident from Figure 3.2, the EHTP operation under the ISO puffing regime and the following characterization of the evolved product fractions leads to the identification of water as the main component of the TPM., while low amounts of "other" product fractions are detected. The comparison with the data obtained for a reference cigarette in the same experimental conditions clearly evidence relevant differences in the amount of the "other" fraction, that is the main component of the TPM for the reference cigarette.

Similar results are reported in Figure 3.3, that shows the characterization of the TPM obtained under the HCI puffing regime. The characterization of the evolved product fractions leads to the identification of water as the main component of the TPM, while low amounts of the "other" product fraction (that may include tar, if present in the TPM) are detected. The comparison with the data obtained for a reference cigarette in the same experimental conditions clearly evidence relevant differences in the amount of the "other" fraction, that also in this case appears as the main component of the TPM for the reference cigarette.

The differences among the data obtained for the amount of the "other" fraction in the ISO and HCI puffing regimes by the modified ISO 4387 procedure (Figures 3.2 and 3.3) with respect to the "tar" fraction determined by the standard ISO 4387 procedure (Table 3.1) are evident. As discussed above, this discrepancy derives from the error in water determination in the standard ISO 4387 procedure applied to obtain the data in Table 3.1. A comprehensive discussion of the issue is reported elsewhere (Ghosh and Jeannet, 2013). Thus, in the following, only data in Figures 3.2 and 3.3 will be considered to assess TPM composition.

Data in Figure 3.3 shows that in the HCI regime the modified ISO 4387 procedure leads to assess a total of 5.38mg/unit of "other" compounds in the TPM. In the absence of further characterization, this fraction and glycerin are usually attributed to NFDPM by the ISO 4387 procedure.

However, in order to better understand the actual nature and origin of this "Other" fraction, further analyses were carried out. Results are reported in Figure 3.4. As shown in the figure, 2.15mg/unit (40.0% of the 5.38mg of the "Other" fraction) of plasticizers (di-tri acetin) are actually found in the "other" TPM fraction. These are well known plasticizers present in the filter tow, used in the mouth piece filter of the EHTP. Thus their presence is reasonably not associated to pyrolysis or combustion, but only to the operating temperature of the EHTP that caused the vaporization of these substances from the filter tow material.

Other 2.27mg of the "Other" compounds in Figure 3.4 (42.2% of the 5.38mg of the "Other" fraction) were actually identified in the PMI report as "fingerprint" components, identified by a specific analytical methodology named "fingerprinting" (see PMI Report). Aerosol components identified using the fingerprinting method in the TPM collected at the end of the HCI regime simulated puffing are reported in Table 3.2. All the components listed in Table 3.2 are actually reported as components present in tobacco leafs (David and Nielsen, 1999; Rodgman and Perfetti, 2013). Thus, only 0.96mg of the "Other" fraction of TPM (17.8% of the 5.38mg of the "Other" fraction) were not characterized. Thus, actual tar (condensed volatiles formed in the primary pyrolysis of the EHTP tobacco substrate) if present, should be part of this product fraction. It should be remarked that such figure represents the maximum potential amount of tar: the actual tar quantity could in fact be lower or tars could even be absent, since other unidentified compounds derived from vaporization may still be present in this fraction.

If such results are reported on a general basis and are referred to the overall amount of TPM formed, Table 3.3 shows that a very different % (by weight) composition is obtained for TPM generated by EHTP operation with respect to that of a reference cigarette. In particular, the maximum amount of actual tar potentially formed by pyrolysis processes in the EHTP operation is around 1.7% by weight, more than 30 times lower than that formed in a conventional cigarette (45.3%).

Table 3.4 shows the results of ultimate analysis and of free water content before and after operation of the EHTP compared to those of a reference cigarette. The amount of water collected in the TPM under the HCI regime applying the modified ISO 4387 sampling method (44.65mg) is coherent with the amount of free water that is originally present in the sample.

Actually, as shown in Table 3.7, the weight of the EHTP before use is about 323mg, and the weight of EHTP after use about 212mg. Table 3.4 reports that free water content before use is about 14.4% by weight. This corresponds to 46.5mg of free water. The free water still present in the EHTP sample at the end of EHTP operation is 2.7% by weight, and the weight of the EHTP after use is about 212mg. Thus an amount of 40.8mg of free water is vaporized, in fair agreement with the amount collected in the TPM (44.65mg), also considering that data in Figures 3.2 and 3.3 were obtained from puffing with humid air, thus using air containing some water vapor.

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

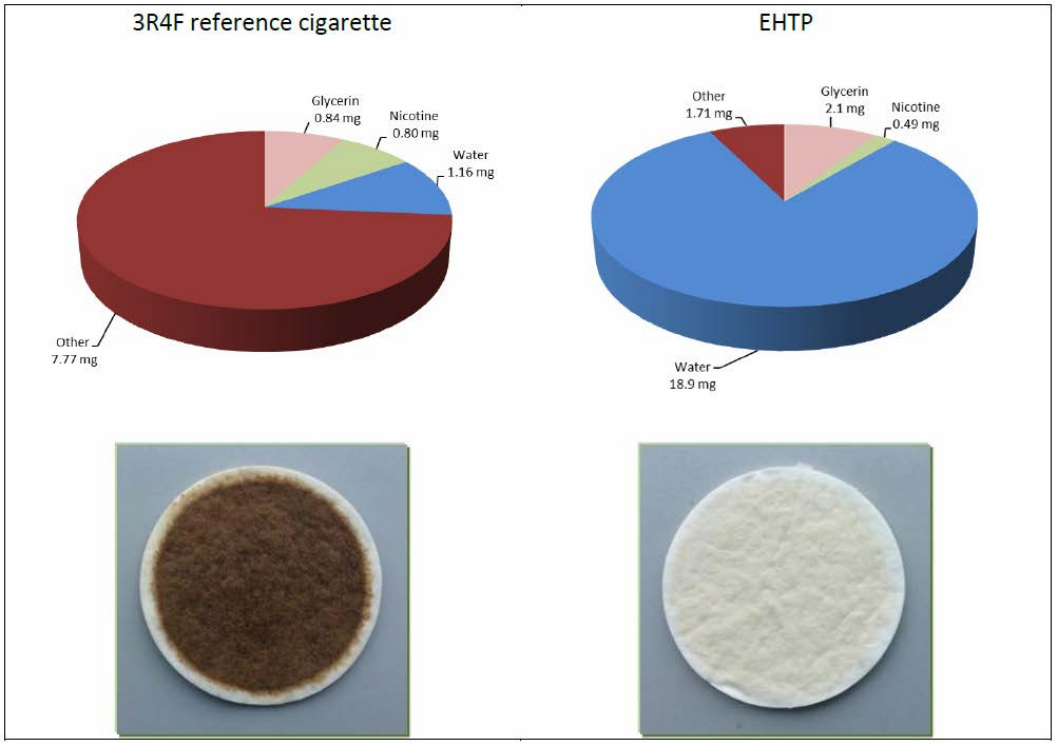


Figure 3.2: Relative composition of the TPM obtained from EHTS operation compared to that of a reference cigarette. The ISO smoking regime and a modified ISO 4387 procedure for product fraction sampling and quantification were applied. The photographs of the Cambridge filter pads after the collection of cigarette smoke (left) and EHTP aerosol (right) are also shown (from the PMI Report).

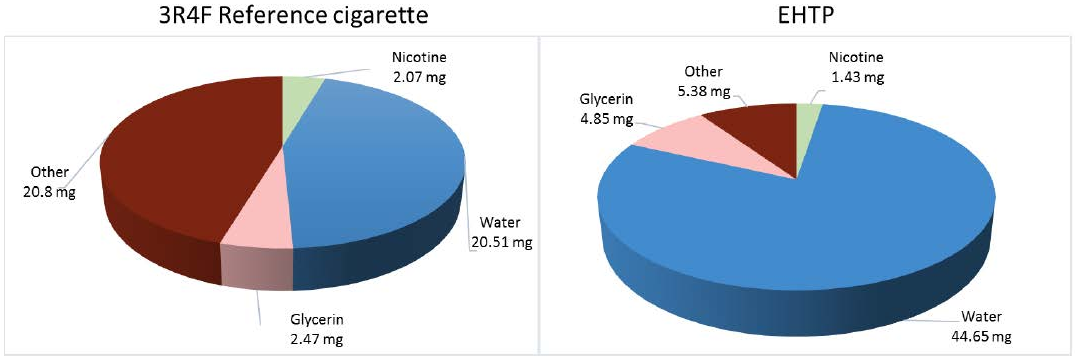


Figure 3.3: Composition of the TPM obtained from EHTS operation compared to that of a reference cigarette. The HCI smoking regime and a modified ISO 4387 procedure for product fraction sampling and quantification were applied (from the PMI report).

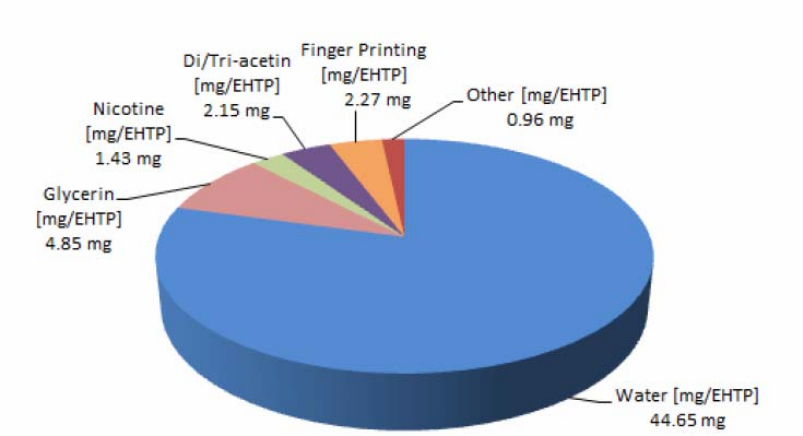


Figure 3.4: Composition of the TPM in the aerosol obtained from simulated EHTP operation under the HCI regime in humid air applying a modified ISO 4387 procedure for product fraction sampling and quantification, including the data concerning the detected amounts of finger printing components and plasticizers (from the PMI Report).

Methyl Formate	Neophytadiene
2,5-Dimethylfuran	Pyranone
Diacetyl	3-pyridinol
2-Pentanone	2,3'-Bipyridine
2,3-Pentanedione	HMF
Limonene	Benzeneacetic Acid
Acetol	Phytol
Acetic acid	Palmitic Acid
Propanoic acid	Cotinine
Formic Acid	Squalene
2-Furanmethanol	Stearic Acid
Solanone	Oleic Acid
3-methylpentanoic acid	D-Allose

Table 3.2: Components identified via the Fingerprinting method in the "other" fraction obtained by the modified ISO 4387 sampling procedure (see figure 3.3) applied to the HCI regime simulated puffing runs with the EHTP (from PMI Report).

	3R4F	**EHTP**
Water	44.7	79.3
Nicotine	4.5	2.5
Glycerin	5.4	8.6
Plasticizers	n.d.	3.8
Fingerprint compounds	n.d.	4.0
Tar	**45.3**	**1.7**

Table 3.3: TPM % (weight) composition from simulated puffings in the ISO regime. In the case of EHTP, the modified ISO 4387 sampling procedure was applied (Ghosh and Jeannet, 2013) and applied to the HCI regime simulated puffing runs with the EHTP (from PMI Report). In results for the 3R4F cigarette plasticizers and fingerprint components were not determined separately and were included in the "tar" fraction (n.d.: not determined). Data from PMI report.

	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 3.4: Ultimate analysis (CHN) and free water content of EHTP before and after operation compared to those of a reference cigarette (from PMI Report).

	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 3.5: Weight of EHTP and of a reference 3R4F cigarette before and after use (from PMI Report).

Based on the above discussion I can conclude that the chemical nature of the aerosol generated during the EHTS operation is very different from that formed in the combustion of tobacco in a cigarette. Both Table 3.3 and Figures 3.2 and 3.3 evidence that in EHTS operation the aerosol is mainly formed by water vapor and glycerin, while in tobacco combustion organic tar prevails.

The aerosol generated in EHTP operation is composed mainly (up to 98.3% by weight) of water and of products deriving from the evaporation, in the absence of chemical reactions, of substances present in the original tobacco substrate.

Thus, the definitions of smoke given by Drysdale (2011) [the gaseous products of burning organic materials in which small solid and liquid particles are also dispersed] or Mulholland (2008) [the aerosol or condensed phase component of the products of combustion] that explicitly refer to the solid and liquid particulates dispersed in gases (i.e. an aerosol) originated from combustion, do not apply to the EHTP aerosol, since no combustion phenomena are taking place (as evidenced also by a specific report concerning the absence of combustion phenomena in the EHTP).

Also the more comprehensive definition of NFPA 92B [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], which clearly refers also to pyrolysis as the potential cause of aerosol generation causing the formation of smoke, can hardly be applied to TPM obtained from EHTP operation. To be more specific: most of the aerosol in the EHTP operation process is generated by vaporization phenomena (water, glycerin, nicotine, plasticizers, fingerprint components), and only a minor part ("Other" in figure 3.2, 0.96mg and 1.7% by weight of the TPM) could possibly be originated by pyrolysis processes.

Thus, the aerosol produced by ETHS operation should not be considered smoke, due to the absence of combustion products and to the very limited amount of pyrolysis products potentially present in the TPM.

Indeed, some of the chemical species present in the aerosol formed during EHTS operation may be present also in cigarette smoke. However, these are largely reduced in absolute concentration, due to the extremely limited influence of pyrolysis phenomena on the EHTP aerosol formation.

3.3 Answer to question S2

The aerosol generated in EHTP operation is composed mainly (up to 98.3% by weight) of water and of products deriving from the evaporation, in the absence of chemical reactions, of substances present in the original tobacco substrate.

Even applying the more comprehensive definitions of smoke (as discussed in Section 2, I can conclude that EHTS operation does not produce smoke.

This conclusion is supported by:

1. the absence of combustion processes in the EHTP tobacco substrate, as discussed in detail in a separate report (Analysis of EHTP features with respect to tobacco/biomass combustion)
2. the very limited pyrolysis phenomena present in the EHTP tobacco substrate during EHTP operation, that 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 EHTP tobacco substrate.
3. the aerosol produced by EHTS operation is formed mostly by vaporization, as proven by the experimental data showing its chemical characterization

The aerosol generated in EHTS operation is very different in the chemical composition from the smoke formed in the self-sustained combustion of tobacco and more in general from smoke formed in combustion processes.

Therefore, such aerosol should not be classified as smoke.

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Annex I: Glossary

Aerosol

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

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.

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.

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.

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.

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.

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”

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Cover Page for the External Report

"Analysis of the EHTP Features with respect to Biomass/Tobacco Combustion"

Written by

Prof. Dr. Valerio Cozzani

This report contains important trade secrets and is strictly confidential

Prof. Dr. Valerio Cozzani

Draft

ANALYSIS of EHTP FEATURES with respect to BIOMASS/TOBACCO COMBUSTION

Bologna, April 4th, 2014

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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, concerning the features and classification of the process undergoing in the tobacco substrate during EHTS operation. 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 self-sustaining combustion process occurring in the tobacco product?

The answers 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 self-supported 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 data provided by the PMI report it is possible to exclude that a self-sustained combustion takes place in the tobacco substrate of the EHTP during EHTS operation.

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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 problems of interest were contained in a 1 page confidential 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 use/operation needed to better clarify the features and operation of the EHTP 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 self-sustaining 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 second part of question **C3**.

Answers are based on the updated PMI Report provided by PMI on March 26th, 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 a first timely 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 self-sustaining combustion occurring in the tobacco product), the content of the PMI integrated report, issued on March 26th, 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 and in its integrations.

The results of the activities carried out are not intended to assess health issues related to the EHTP aerosol and such issues will not be considered in the activities.

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 is commonly named pyrolysis and is referred to as 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).

The phenomenon of pyrolysis 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 thermal decomposition of the fuel, yielding the outflow of 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 usually 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 as oxygen.

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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, 1988). 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. Devolatilization, commonly named also pyrolysis or thermal degradation, producing a mixture of volatile combustible components. 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 devolatilization, 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). Volatile

combustion may take place separately or during devolatilization, depending on the specific features of the combustion system and process conditions.

4. Heterogeneous combustion of char: once devolatilization 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 devolatilization 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 devolatilization) 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 devolatilization 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 from these fuels 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 the devolatilization process includes pyrolysis reactions that occur mostly through solid-phase radical reactions generating volatiles, but also by gas-phase radical reactions. In gas-phase pyrolysis reactions taking place during devolatilization, 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, devolatilization, 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.

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, 1988). 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.

However, 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.

3.3 Answer to question C2

Biomass may undergo the combustion reactions either in the gas phase (due to the oxidation of fuels derived from the devolatilization/pyrolysis 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, devolatilization, 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, 1988). 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 devolatilization (distillation, pyrolysis).

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.

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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 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 314 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 (b) (4) (b) (4) .

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 50°C in the zone more near to the heating blade).

(b) (4)

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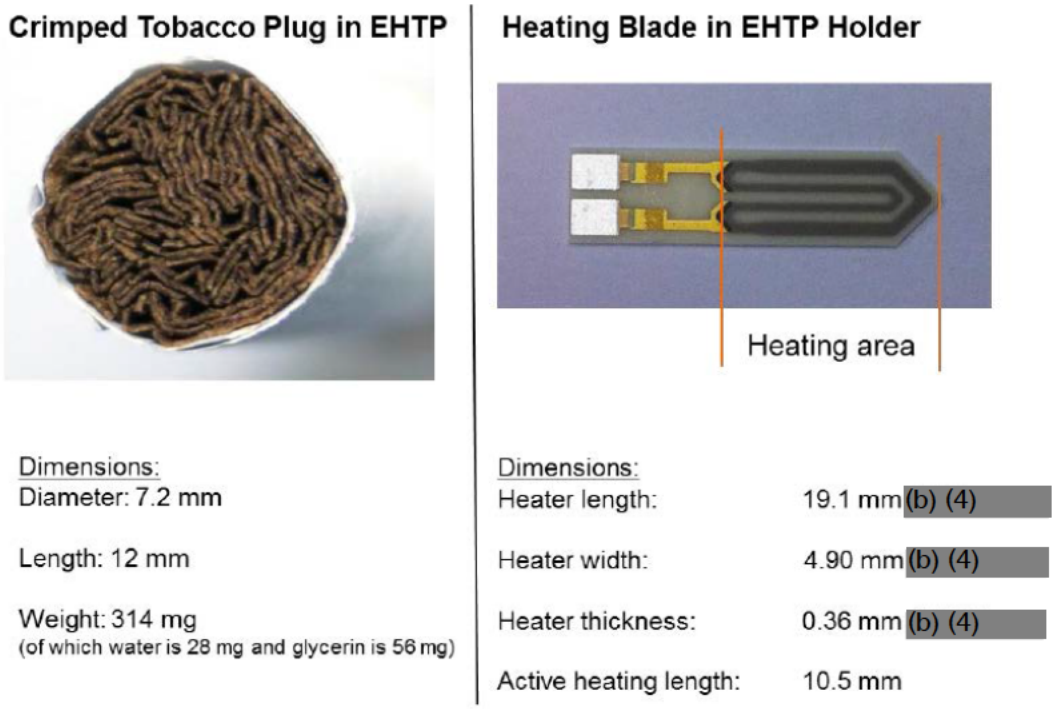


Figure 4.1: Details of the EHTP and of the heating blade of the EHTS (from PMI Report).



Figure 4.2: (b) (4) (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).

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 (volatilization) 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 (elemental analysis for the tobacco substrate in the EHTP, reported in Table 4.2, from the PMI report, shows an amount of nitrogen of about 2.5% 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. Eventually, it is impossible to distinguish if the three gases (H_2O, CO, NO_x) are formed due to i) devolatilization and/or nitrate decomposition in the case of NO_x; ii) low-temperature oxidation in the gas phase (of pyrolysis products with air), or iii) low-temperature oxidation on the surface of tobacco. Quite clearly, the last two phenomena, if present, should be related to combustion phenomena, despite the low temperature.

	EHTP						Cigarette				
	Replicate number	C [% w/w]	H [% w/w]	N [% w/w]	Total Ash [% w/w]		Replicate number	C [% w/w]	H [% w/w]	N [% w/w]	Total Ash [% w/w]
Before use	1	44.81	7.79	2.37	7.02	Before use	1	37	5.12	2.51	10.8
	2	38.46	6.78	2.06	7.12		2	37.29	5.64	4.17	10.4
	3	37.83	6.69	2.01	7.01		3	43.86	6.37	2.12	10.9
After use	1	45.93	5.97	2.56	9.43	After use	1	7.57	1.18	0.82	70.5
	2	46.00	5.80	2.54	10.6		2	6.89	0.59	0.95	69.8
	3	46.62	5.85	2.59	10.8		3	7.64	0.47	0.90	71.8

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

However, 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 carbon compounds, whose presence in the gas phase may be due either to pyrolysis or stripping of carbon compounds due to water evaporation, rather than to gasification.

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.

Finally it is worth to remark that the EHTP generates 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.

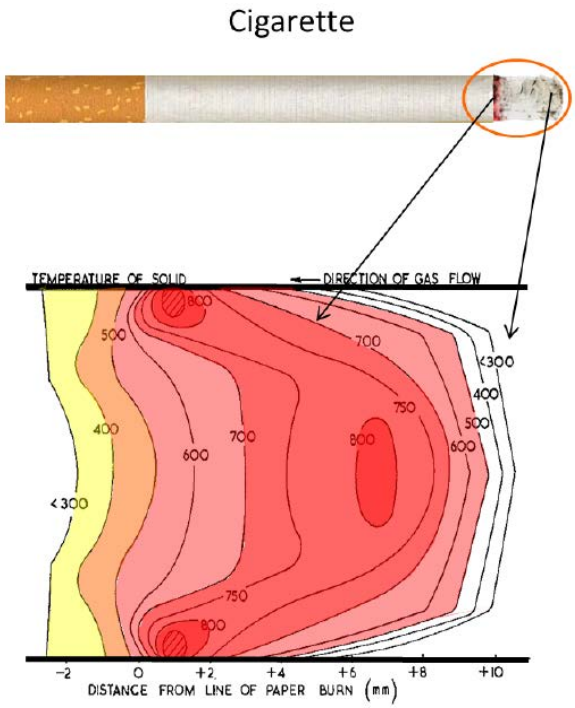


Figure 4.4: Tobacco temperature in a lit cigarette (Baker, 1975).

4.3 Tobacco self-sustaining 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 (314 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 (110-250°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 almost 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 fixed carbon in the exhaust EHTP tobacco substrate, while in the tobacco combustion

in a cigarette only a slight amount of fixed carbon (also considering the relevant weight loss) is present.

4.5 Answer to question C3

On the basis of the data provided by the PMI report it is reasonably possible to exclude that a self-sustained combustion takes place in the tobacco substrate of the EHTP during EHTS operation.

The above conclusion is supported by:

1. the 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. lack 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); 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.

In particular, conditions 1 and 3 are related to the unambiguous indicators of combustion, that are both negative.

While high temperature self-sustained combustion in the tobacco substrate of the EHTP during EHTS operation can be excluded on the basis of the data available for EHTS operation, the data present in the PMI report can not confirm the complete absence of any oxidation reaction in the gas or solid phase of the EHTP tobacco substrate during EHTS operation. Actually a very limited amount of carbon monoxide (about 4-5% that present in an ordinary cigarette, taking into account the different quantity of tobacco substrate) is detected in the gaseous products during EHTS operation in air (both synthetic and ISO), while no carbon monoxide is detected during operation in nitrogen. Carbon monoxide however may be formed by several different pathways and may not be assumed as an unambiguous indicator of a combustion process.

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.