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Effect of the addition of zeolites and silicate compounds on the composition of the smoke generated in the decomposition of Heet tobacco under inert and oxidative atmospheres

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ABSTRACT

Five potential additives, three zeolites and two silicates, have been studied for reducing the amount of compounds generated when smoking Heet tobacco. Pyrolysis-gas chromatography-mass spectrometry experiments (Py-GC/MS) show that this type of tobacco generates large amounts of nicotine and glycerol and compounds such as phenol, acetaldehyde, acetone and formaldehyde that are classified as harmful components and potentially harmful (HPHC). USY and SBA-15 are the additives that present major reductions in inert and oxidative atmosphere, being these reductions greater for SBA-15. These results have been confirmed by smoking experiments that show significant reductions for SBA-15, especially in the total particle matter (TPM) where a reduction of more than 40% is obtained for most of the compounds, being for several compounds even higher than 60%. These additives may further reduce the toxicity of Heet tobacco.

1. Introduction

The plant known as tobacco, or Nicotiana tabacum, is a member of the genus nicotiana, a close relative of the poisonous nightshade and previously could only be found in the Americas. Tobacco was introduced in Europe by the Spanish, and thanks to smoking sailors became an ingrained habit in Spain and Portugal in a short time. Cigarettes appeared in the 19th century and became most popular during the First and Second World Wars. Tobacco companies sent millions of packs of cigarettes to soldiers at the front lines, thus creating hundreds of thousands of loyal and addicted consumers.

Today it is known that cigarette smoke contains more than 8000 different compounds [1], resulting from the distillation, evaporation, combustion, pyrolysis and pyrosynthesis that take place during smoking, where temperatures of up to 900 ºC are reached. At least 250 of these compounds are harmful, including hydrogen cyanide, carbon monoxide and ammonia, and about 70 compounds have confirmed carcinogenic activity in humans [2]. Therefore, smoking is a preventable health risk factor that causes numerous diseases and deaths in society [3].

However, in recent years, tobacco industries have started to sell new tobacco-related products, such as electronic cigarettes (e-cigarettes) and non-burning tobacco (HNB) as less harmful alternatives to health [4]. Electronic cigarettes use a battery to heat a cartridge containing a liquid that may or may not contain nicotine, which generates vapor (that is, no combustion smoke is generated [5]). HNB tobaccos (as IQOS, for instance: "I Quit Smoking Regularly"), involve an electronic device that heats tobacco leaves or derived products (different types of reconstituted tobaccos) in a stick to low temperatures and the user inhales the generated aerosol instead of the smoke from the combustion [6].

Actually, the interest in HNB cigarettes has grown, which an increase in publications on this topic. These works range from the study of the impact of the consumption of this tobacco [7–9], to the study of different compounds produced in smoke when smoking at low temperatures, as the nicotine levels and emissions in HNB [10–12] or the harmful and potentially harmful constituents (HPTC) in mainstream emissions [13,14] or the particulate matter and HPHC in second hand emissions [15,16].

Micro and mesoporous zeolites and alumino-silicates have shown their ability to reduce the amount of most of the tar components of conventional tobacco, helping to eliminate carbonyl, aromatic compounds [17–21] and nitrosamines [22]. Nevertheless, we have no found studies of the effect of potential catalysts for reducing the generation of toxic compounds when smoking these type of HNB tobaccos.

Thermogravimetric analysis (TGA) and Pyrolysis gas chromatography mass spectrometry (Py-GC/MS) are powerful techniques, widely

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Table 1
Characteristics of the additives studied.

Material	Pore Size[a] (nm)	S_{BET}^{b} (m^2/g)	V_t^c (cm^3/g)	SiO_2/ $Al2O_3$ ratio (% w)[d]	Weak Acidity (mmol/g)[e]	Total Acidity (mmol/g)[e]
ZSM-5	0.51 × 0.55	341	0.18	22	1.2	2.1
USY	0.74	614	0.35	4.8	2.1	0.0
Beta	0.66 × 0.67 0.56 × 0.56	510	0.17	25	1.1	2.1
SBA-15	6.2	680	0.79	100% Si	0	0
SiF	6.78	217	0.44	100% Si	0	0

a pore diameter BJH method applied to the desorption branch; b BET surface area; c total pore volume at P/P0 = 0.995; d FRX; e TPD of NH3.

used for the study of the decomposition of tobacco. TGA shows the different mass loss processes that occur when tobacco is heated [23–25], and Py-GC / MS allows pyrolyzing different types of samples under different atmospheres and heating regimes. The evolved gases are introduced into a GC / MS that allows the separation of the generated compounds and their identification. In previous papers we have studied by this technique the behaviour of the 3R4F tobacco under inert and oxidative atmospheres at high temperatures, as well as the effect of different catalysts at high temperatures [26,27].

In a previous work [28] we studied the compounds generated when heating two HNB tobaccos (Heet and Neo) and a conventional tobacco (3R4F) in N_2 and air atmosphere at 250, 300, 350 and 400 ∘C. The results showed that these types of tobaccos generate larger amounts of nicotine and glycerol than conventional tobacco. Moreover, compounds as phenol, acetaldehyde, acetone and formaldehyde classified in FDA's HPHC list were generated at these low temperatures (i.e.: 250–400 ºC). We concluded that these HNB tobaccos are less harmful to health than conventional cigarettes, though they are not exempt of risk. The present work studied the effect of several additives, three zeolites and two silicates, mixed with a HNB tobacco (Heet tobacco) at 300 ºC under inert and oxidative atmosphere with the aim of further reducing the toxicity of this type of tobacco.

2. Materials and methods

2.1. Additives

Three commercial zeolites were chosen: ZSM5, USY and Beta. ZSM5 and USY were provided by GRACE-Davison, Beta was provide by Süd-Chemie Inc. Two silicate, SBA-15, with a fibre-like morphology and Silica Fumed (SiF) were selected for this study. SBA-15 was synthesised according to the procedure described by Zhang et al. [29], Silica Fumed (SiF) was provided by Sigma-Aldrich. The textural properties of these additives were obtained from the N_2 adsorption isotherms at 77 K, measured in an automatic Quantachrome AUTOSORB-6. The isotherms were recorded and the surface area was obtained according to the BET method, the pore size distributions were obtained applying the BJH model with cylindrical geometry of the pores. The total volumes were determined from the N_2 adsorbed at P/P_0 = 0.965. Temperature-programmed desorption (TPD) of ammonia was performed in a Netzsch TG 209 thermobalance to determinate the acidity of the

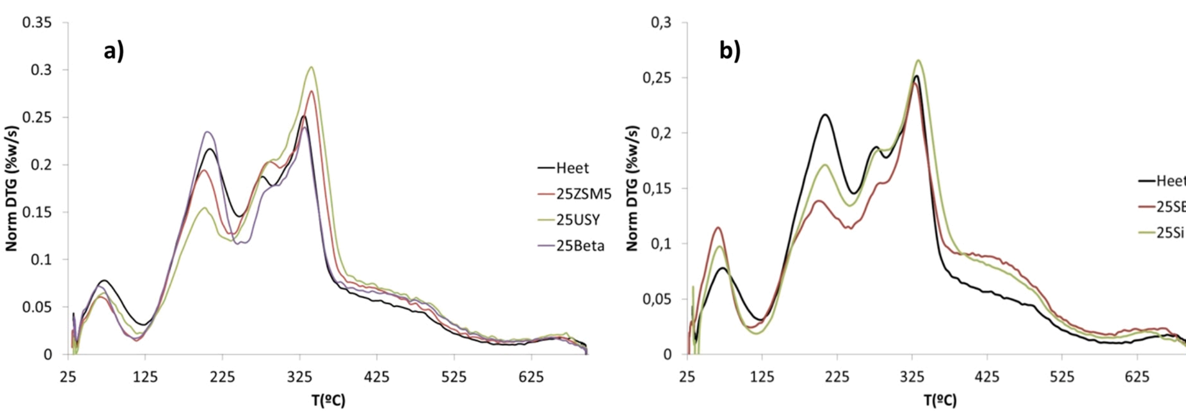

Fig. 1. Normalized DTG curves under inert atmosphere from Heet tobacco and: a) mixture with 25% w/w of the different zeolites, b) mixtures with 25% w/w of the different silicates.

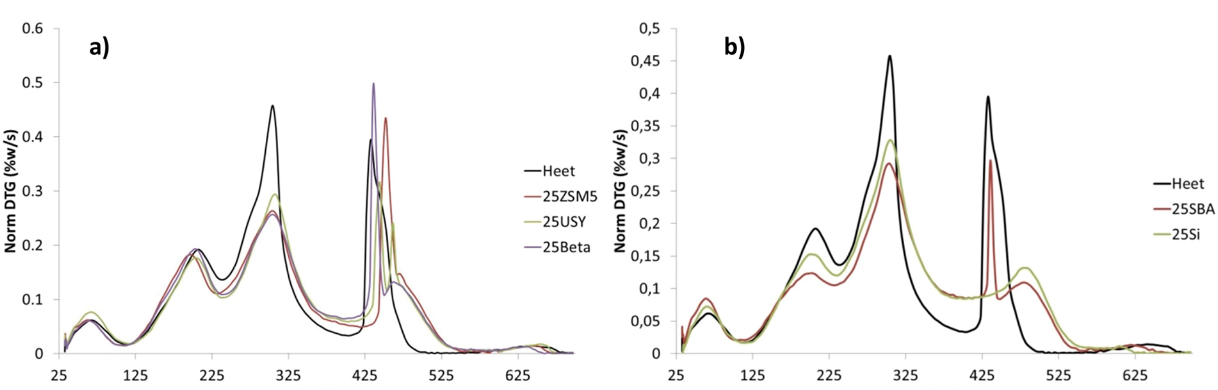

Fig. 2. Normalized DTG curves under oxidative atmosphere from Heet tobacco and: a) mixture of 25% w/w of the different zeolites, b) 2 mixtures with 5% w/w of the different silicates.

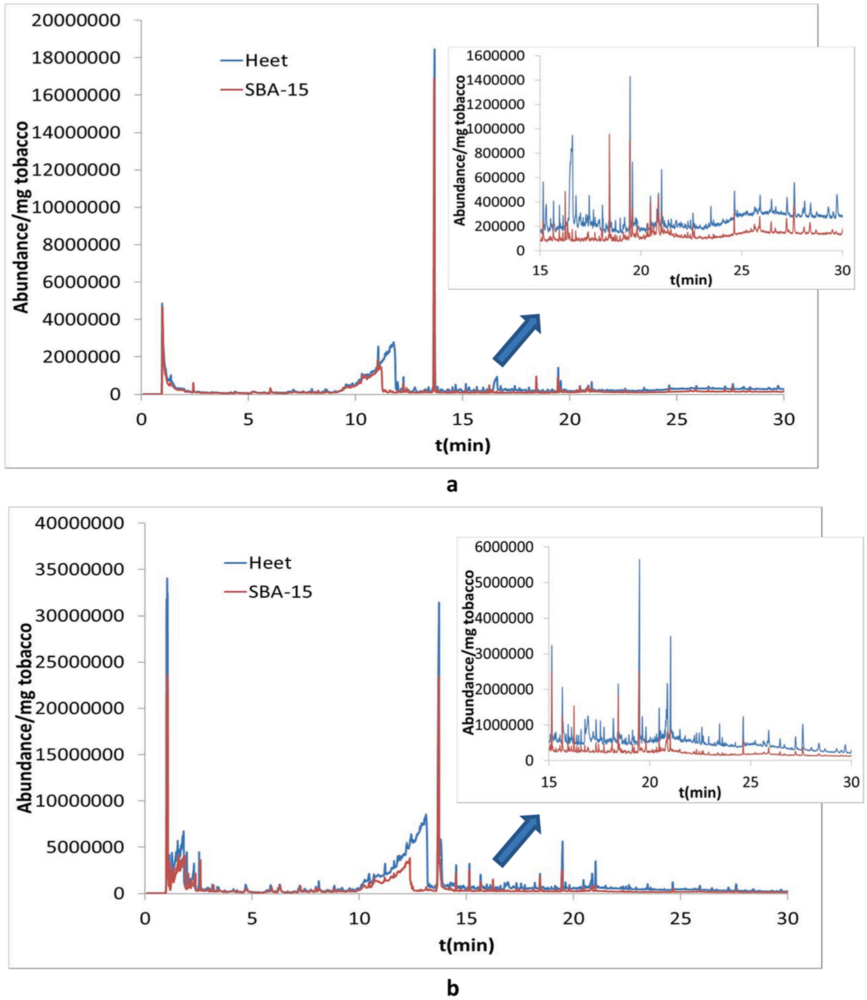

Fig. 3. Pyrogram obtained by Py-GC/MS from decomposition of Heet tobacco in absence and in presence of 25% w/w SBA-15: a) under inert atmosphere, b) under oxidative atmosphere.

additives. The samples were previously outgassed in a N_2 flow of 45 ml/min by heating to 500 °C with a rate of 10 °C/min, maintaining this temperature for 30 min. After cooling to 100 °C, the acid sites were saturated by treatment with an ammonia flow of 35 ml/min for 30 min. The physisorbed ammonia was removed by passing a N_2 flow of 45 ml/min for 60 min at 100 °C. Finally, the TPD measurements were carried out by heating the sample in the N_2 flow at a rate of 10 °C/min up to 900 °C. The acidity of the additives was calculated using the weight loss observed in the thermobalance at each TPD stage. The relation of SiO_2/AlO_2 was determined by FRX. The results of the characterization are show in Table 1. Zeolites are crystalline compounds while silicates are amorphous materials. As can be seen in Table 1, silicates show higher pore sizes than zeolites. In addition, the presence of aluminium atoms in the crystalline structure of zeolites gives them a negative defect of charge that must be compensated by protons generating acidity.

Heet tobacco "amber selection" was selected for this study, and was acquired in a smoke shop in the area. The tobacco was ground and mixed with the additives with a concentration of the 25% w/w in presence of water to obtain a homogeneous paste. This paste was dried at low temperatures (60ºC) to obtain thin sheets of the resulting mixtures. Parts of the slides were subsequently sieved through a 300 µm sieve to be analyzed by thermogravimetry analysis (TGA) and Py-GC / MS.

2.2. Equipment

Initial analyses of the decomposition of Heet tobacco in absence and presence of the different additives were run in a thermobalance Metller Toledo TGA/DSC1 under inert and oxidative atmospheres (N_2 and Air). Experiments were carried out under dynamic conditions were the sample was heated from 30° to 700°C at 35 °C/min under a flow of 80 ml min^{-1} (STP).

The compounds generated during the decomposition of Heet tobacco were analysed in a multi-shot pyrolyser (EGA/Py-3030D, Frontier Laborato-ries Ltd.), which was attached directly to a GC/MS (6890 N GC/5973 inert MSD, Agilent technologies). The different compounds generated were introduced into the GC separation capillary column and analysed by MS. About 400 µg of the tobacco and tobacco+ 25% w/w of additive were heated at 300 ºC during 1 min, under inert atmosphere (helium) and oxidative atmosphere (Air). This temperature was selected because it is an intermediate temperature used by commercial devices to heat HNB tobacco (260–350ºC). The reaction products were introduced into the GC separation column (HP-5MS UI, 30 m × 0.25 mm i.d.×0.25 µm film thickness, Agilent Technologies) with a split ratio of 50:1 (column flow rate: 2 ml min−1) using helium as carrier gas. The separated compounds were detected by MS (the temperature of the GC/MS transfer line was 280 °C and the MS source and MS Quad temperature were 230 and 150 °C, respectively). The mass spectrometer was operated in electron-impact mode at 70 eV at scan range of 15–350 amu. The compounds were identified by the NIST 08 library (National Institute of Standards and Technology, USA) and/or Wiley7n library (Wiley Registry of Mass Spectral Data, 7th Edition).

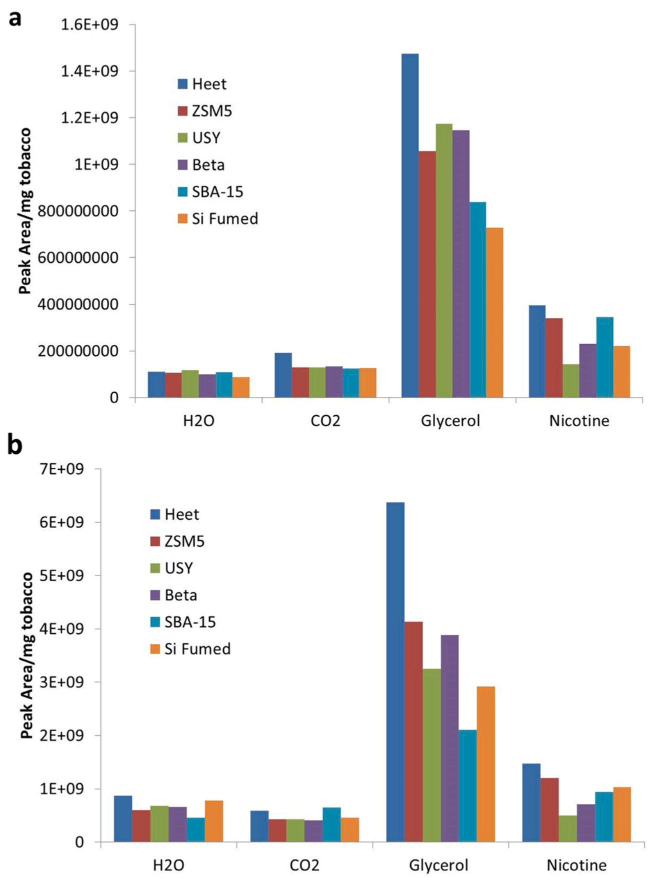

Fig. 4. Principal compounds obtained by Py-GC/MS from the decomposition of Heet tobacco in absence and presence of additives: a) under inert atmosphere, b) under oxidative atmosphere.

Table 2
Reductions (%) obtained by Py-GC/MS in the chemical families from the decomposition of Heet tobacco in presence of additives.

Famlily Inert Atmosphere	ZSM5	USY	Beta	SBA-15	SiF
Acid	17.9	12.7	19.8	17.6	28.5
Carbonyl	25.7	34.3	38.0	59.5	53.0
Alcohol	-53.6	-36.5	-33.7	41.5	32.1
Furan	-5.7	16.6	10.1	26.8	29.9
Aromatic	-8.5	11.3	4.8	59.0	50.6
Nitrogenated	-33.3	38.0	20.9	45.3	53.1
Aliphatic	-8.6	22.8	26.2	34.4	32.5
Not assigned	7.3	0.3	20.3	50.4	28.0
Oxidative Atmosphere					
Acid	10.1	29.5	25.0	41.2	11.6
Carbonyl	26.0	29.7	26.5	27.9	16.4
Alcohol	46.9	14.8	26.5	61.8	61.5
Furan	-8.8	15.5	-5.8	36.9	12.1
Aromatic	32.9	25.9	21.7	36.3	5.8
Nitrogenated	36.7	53.9	56.4	54.3	22.0
Aliphatic	20.7	37.8	18.7	55.5	41.1
Not assigned	40.4	42.5	27.2	38.9	37.2

2.3. Smoking experiments

Smoking experiments were performed following the ISO/TR 19478–1:2014 “ISO and Health Canada intense smoking parameters”. The machine, designed and built by the research group, consists of five steel tubes, surrounded by five resistances, where the cigarettes are inserted. The resistance controlled the temperature inside the tube, in this case 300ºC. Five cigarettes were simultaneously smoked and 8 puffs were always taken in each experiment. At least two replicates were carried out being the dispersion of the results less than 10% for most compounds. The not condensed products of tobacco smoke were collected in a Tedlar bag and analyzed by CG/TCD (CO and CO_2) and GC/FID (rest of compounds) in an Agilent 6890 N chromatographer with a GS-GASPRO column. The total particulate matter (TPM) condensed in the trap located before the Tedlar bag was extracted with isopropanol following the ISO4387 standard and analyzed by GC/MS in an Agilent 6890 N chromatographer with a HP-5-MS column. The identification of the different compounds was done by comparison with the Wiley MS library.

3. Results and discussion

3.1. Thermogravimetric analysis

Fig. 1 shows the normalized derivative thermogravimetry curves (NDTG) obtained from the normalized values of weight loss (NTGA) of Heet tobacco with and without additives. Weight loss curves were normalized between 100% and 0% to eliminate the effect of additive mass. NTGA values where calculated as (w – wf)/(w0 – wf), where w = weight of sample at time t, w0 = weight of sample at t = 0, and wf = final weight, obtained in the thermobalance as the weight of the residue at the final temperature. Fig. 1a shows the curve of Heet tobacco and its mixtures with the different zeolites under inert atmosphere, and Fig. 1b shows the tobacco and its mixtures with the two silicates testes. All mixtures were prepared with 25% w/w additive. This amount of additive was used to allow a better observation of the effects of the additive in the decomposition of Heet tobacco. Heet tobacco presents the same decomposition steps than a conventional tobacco, i.e.: evaporation of moisture at temperatures lower of 100 ºC; evaporation of glycerol and other volatile compounds in the range 120–240ºC; two overlapped processes in the range 210–375 ºC, probably corresponding to decomposition of hemicellulose and cellulose respectively; pyrolysis of lignin in a wide range of temperature at around 450ºC; dehydrogenation and aromatization of char and/or decomposition of endogenous inorganic compounds at around 650ºC. Moreover, the proportion of the different decomposition steps obtained in a conventional tobacco and Heet tobacco changes, being remarkable the great increase on the peak associated with the elimination of glycerol at 205 ºC [28] and it is in accordance with the manufacturer specifications that indicate that Heet tobacco is a mixture of 70% tobacco 30% glycerol [30], while for example 3R4F tobacco contain 2.7% glycerol [31].

As can be seen in Fig. 1, the peaks associated with the evaporation of glycerol and other volatile compounds (120–240ºC) and the decomposition of hemicellulose (250–300ºC) decrease in the presence of the additives, especially in the case of the SBA-15. The peak of decomposition of cellulose (300–380 ºC) is similar to tobacco from SBA-15 and Beta zeolite, but increase for the rest of additives. Lignin peak increases for all additives, especially for SBA-15. Finally, the peak associated with the dehydrogenation and aromatization of char and/or decomposition of endogenous inorganic compounds at around 650ºC are similar in all cases.

Fig. 2a shows the NDTG curves obtain under oxidative atmosphere for Heet with and without zeolites, and Fig. 2b shows the NDTG of Heet in presence and absence of the two silicates. As can be seen the main difference with Fig. 2a appears at the combustion peak (430–550 ºC). However, this range of temperature is higher than those used by HNB devices. In the pyrolysis zone, under 400 ºC, the principal differences with the curves obtained under inert atmosphere can be observed in the double peak associated with the decomposition of hemicellulose and cellulose. As can be seen, in oxidative atmosphere, these two decompositions peaks overlap and practically a single decomposition peak is observed. When Heet tobacco was mixed with the different additives these peaks decreased, especially for ZSM5, Beta and SBA-15. As in inert atmosphere, the peak corresponding to glycerol is clearly affected by

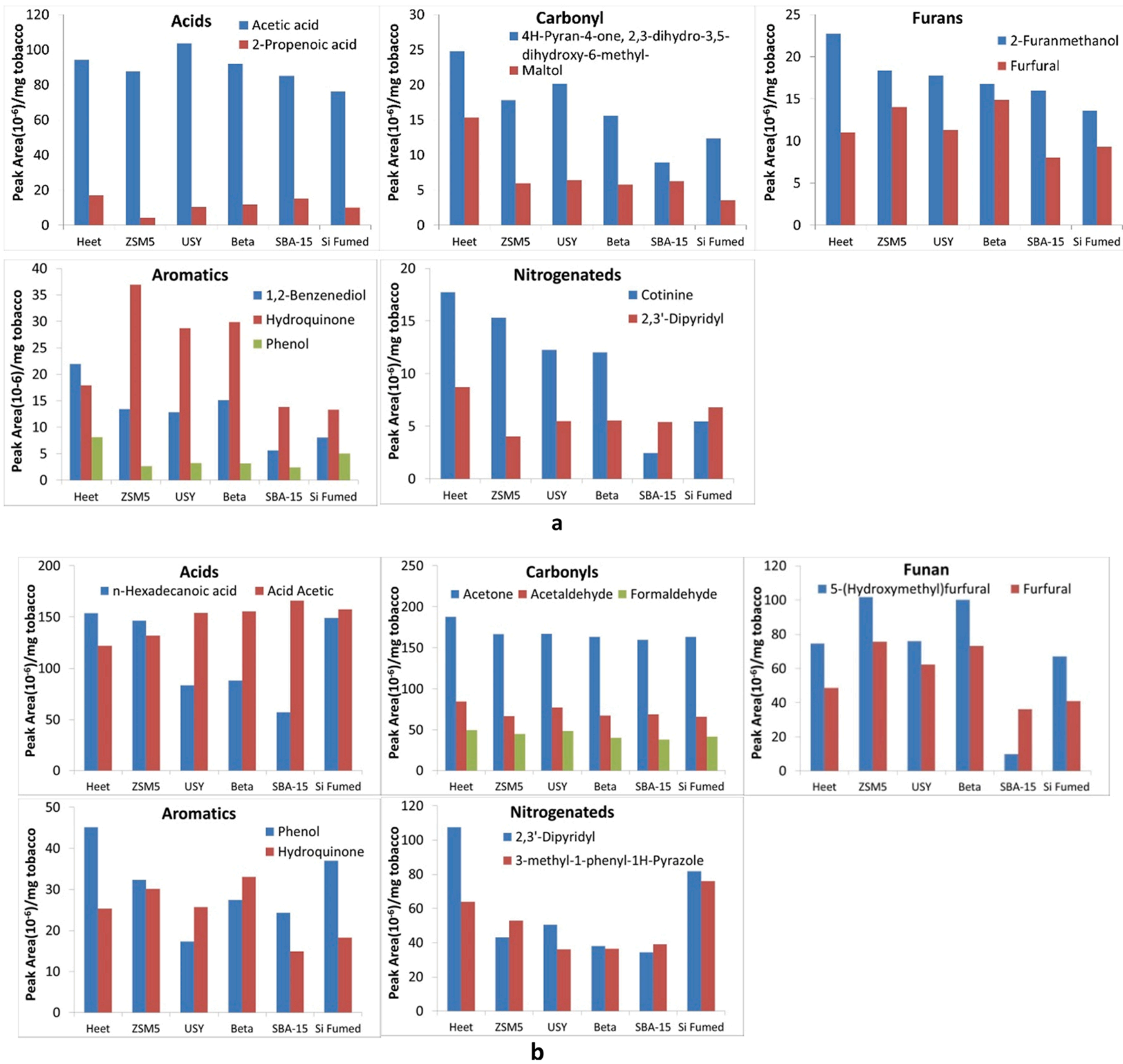

Fig. 5. Major compounds obtained by Py-GC/MS in the different chemical families from the decomposition of Heet tobacco in absence and presence of additives: a) under inert atmosphere, b) under oxidative atmosphere.

Table 3
Yield and reductions in total gases, TPM, CO_2, CO and Nicotine obtained in smoking experiment.

	mg/cigarette		%
	Heet	Heet+SBA-15	Reduction
Total Gases[a]	1.19	0.98	17.3
CO	1.29	1.19	7. 5
CO_2	12.12	9.51	21.5
TPM	24.22	13.12	45.8
Nicotine	0.64	0.40	38.0

[a] Obtained by GC/FID

these additives being silicates those that show major reductions, especially SBA-15.

3.2. Analysis of the products of decomposition of HNB: inert and oxidative atmosphere

Py-GC/MS analysis was carried out to identify and semi quantify the products obtained in the decomposition of Heet tobacco. In order to avoid the influence of the mass of sample, the peak area was normalised by dividing it by the mass of tobacco analysed. Experiments were replicated three times to secure the reproducibility of the results.

Fig. 3 shows one of the pyrograms obtained from the decomposition of Heet tabacco in absence and presence of one of the additives studied, SBA-15, under inert (Fig. 3a) and oxidative atmosphere (Fig. 3b), as well as a magnification of the pyrograms between 15 and 30 min. As can be seen, the decomposition of tobacco presents a complex pyrogram formed by a large number of small peaks. A first look reveals important reductions of the intensity of most peaks due to the presence of the SBA-15. Three important peaks/zones can be observed. The first zone, at times less than 2 min, is due to CO_2 and water and other compounds. The second zone, between 9 and 14 min, where a wide peak is observed, is mainly due to glycerol. Finally, around 13.6 min, a sharp and intense peak appears, that is due to the nicotine. Average peak areas of all the compounds analysed are shown in the supplementary material (Tables A1-A2).

Fig. 4 shows the four principal compounds generated in the heating of Heet tobacco (CO_2, water, glycerol and nicotine) under inert (Fig. 4a) and oxidative atmosphere (Fig. 4b) in absence and presence of the different additives. As can be seen in Fig. 4a, the amount of water obtained is similar for tobacco with and without additives, while CO_2 is reduced in similar proportion by all zeolites and silicates. Moreover, under inert atmosphere the quantity of glycerol decreases in presence of the additives studied, as was seen in the NDTG figures (Fig. 1), with

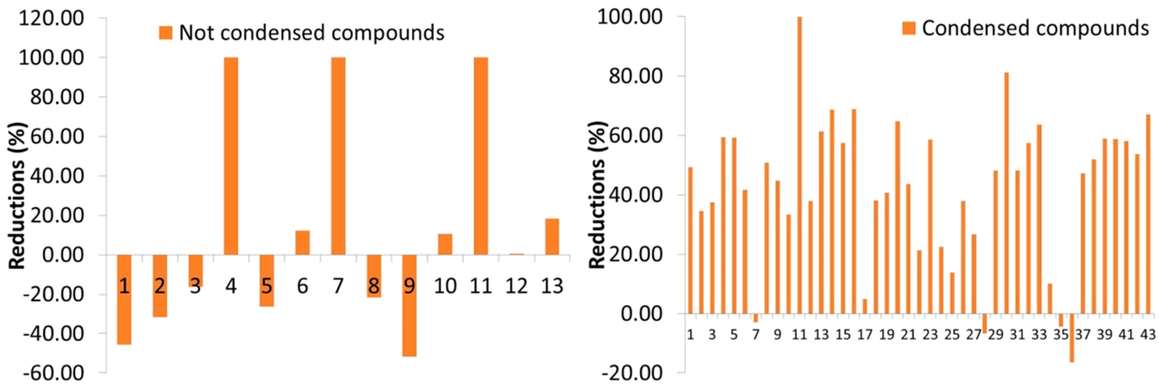

Fig. 6. Reductions (%) obtained in smoking experiment in presence of SBA-15 in not condensed and condensed compounds.

Table 4
Yield and reduction (%) of the products included in the FDA's HPHC list obtained in smoking experiment.

	mg/cigarette		%
	Heet	Heet+SBA-15	Reduction
Benzene	0.021	0.021	0.3
Acetaldehyde	1.061	0.866	18.3
Phenol	0.014	0.009	33.4
Nicotine	0.637	0.395	38.0

greater reductions when using the amorphous additives, SBA-15 and SiF. Moreover, the additive that shows a major reduction in the nicotine is the zeolite USY, while SBA-15 and ZSM5 show values similar to Heet tobacco, though somewhat lower. Similar behavior can be observed in Fig. 4b under oxidative atmosphere, where all additives reduce the glycerol peak, being SBA-15 the one that presents the greatest reductions. Moreover, zeolite USY in the additive that presents the greatest reductions in nicotine. It should be mentioned that under oxidizing atmosphere all compounds are generated in greater quantities.

The rest of the compounds generated in the decomposition of Heet tobacco with and without additives obtained by Py-GC/MS were grouped by functional groups families: Acids, Carbonyl, Furans, Alcohols, Aromatics, Nitrogenated, Aliphatics and Not Assigned, where glycerol was not included in Alcohols family and nicotine in the Nitrogenated one. It should be mentioned that furans have been grouped in a separate category from Carbonyls because they are compounds that normally have high toxicity. All compounds detected but not identified were grouped in Not Assigned family. Table 2 shows the reductions obtained in the different chemical families under inert and oxidative atmosphere. As can be seen, under inert atmosphere, SBA-15 and SiF present reductions in all the families, and a high reduction in Aromatics and Nitrogenated compounds. The zeolites USY and Beta show minor reductions that silicate compounds in all families, and increases the formation of Alcohols. ZSM5 only presents reductions in Acid and Carbonyls compounds and shows increases in the yield of the rest of the families. Under oxidative atmosphere all additives present better results than under inert atmosphere, and only ZSM5 and Beta show a slight increase in Furan compounds. In this atmosphere, SBA-15 presents the best reductions, followed by the SiF material, observing reductions above 50% for Alcohol, Nitrogenated and Aliphatic compounds.

Fig. 5 shows the principal compounds obtained by Py-GC/MS in the chemical families from the decomposition of Heet tobacco in absence and presence of the additives, under inert atmosphere (Fig. 5a) and oxidative atmosphere (Fig. 5b). As can be seen in Fig. 5a, acetic acid is the main compound under inert atmosphere. The rest of the majority compounds show similar trends. This compound may be generated by the decomposition of hemicellulose that is rich in acetyl group [32,33]. The effect of the additive changes according to the different compound generated. Acetic acid shows major reduction in presence of silicates, while 2-Propenoic acid was more reduced in presence of ZSM5. The main carbonyls generated are maltol and 2,3-dihydro-3,5-dihydroxy-6-methyl-4 H-pyran-4-one and are formed by pyrolysis of 1-deoxy-1-(L-prolino)-D-fructose and another sugar-amino acid (Amadori) compounds [34]. Both compounds present high reductions in presence of the silicates and zeolites only shows reductions in the formation of maltol. Furans show similar tendency, and the silicates present the major reductions. Within the Aromatic family, all additives reduce the formation of 1, 2-benzenediol, but hydroquinone shows a significant increase in the presence of zeolites. Phenol is a respiratory toxicant and cardiovascular toxicant compound and in classified in the group 3 (not classifiable as to its carcinogenicity to humans) in the FDA's HPHC list. As can be seen, all the additives studied reduce its formation, being the SBA-15 the additive that shows the major reductions. The main Nitrogenated compounds generated are alkaloids derived from nicotine decomposition [35], and all additives studied reduce their formation, being ZSM5 the additive that presents the best results for 2, 3′-dipyridyl, and SBA-15 for cotinine.

Under oxidative atmosphere (Fig. 5b), major yield of products was generated in all the chemical families, and the product distribution changes markedly. For example, within the Carbonyls compounds the most abundant compounds in oxidative atmosphere are acetone and acetaldehyde. In addition, several major compounds were detected in both atmospheres, i.e. acetic acid, furfural, and phenol.

In this atmosphere, acetone is the most abundant compound, followed by n-hexadecanoic acid. As can be seen, n-hexadecanoic acid is reduced by all the additives, especially by SBA-15, moreover the presence of the zeolites and silicates increases the formation of acid acetic. The principal carbonyls obtained were acetone, acetaldehyde and formaldehyde. These compounds are included in the FDA's HPHC list. Acetone is considered as a respiratory toxicant. Acetaldehyde, the second in abundance, is considered carcinogen, respiratory toxicant and addictive, and is listed by the international agent for Research on Cancer (IARC) within group 2B (possible carcinogenic to humans) and carcinogen. Formaldehyde is considered carcinogen and respiratory toxicant within group 1 (carcinogenic to humans). As can be seen, all additives, zeolites and silicates, slightly reduce the formation of these compounds in similar proportion, being SBA-15 the material that present better results. Within the Aromatic family, phenol is the majority compound, and as mentioned above, it is a respiratory and cardiovascular toxicant compound. As can be seen, all the additives reduce its formation, being USY zeolite and SBA-15 the two additives that present major reductions in oxidative atmosphere. In addition, hydroquinone is only reduced by silicate compounds. SBA-15 shows again the major reduction in the aromatics compounds.

Table A1
Compounds obtained by Py-GC/MS from the decomposition of Heet tobacco under inert atmosphere.

Peak	tr (min)	Compound	Area (10^{-7})/mg tobacco					
			Heet	Heet+ZSM5	Heet+USY	Heet+Beta	Heet+SBA-15	Heet+SiF
1	0.979	H_2O	11.16	10.71	11.89	10.07	10.92	8.80
2	0.992	CO_2	19.23	13.05	12.94	13.49	12.59	12.66
3	1.394	Acetic acid	9.43	8.75	10.36	9.21	8.51	7.62
4	1.725	2-Propanone, 1-hydroxy-	5.15	3.51	3.96	3.75	3.70	3.18
5	2.066	Acrylic acid	1.70	0.43	1.02	1.16	1.52	1.01
6	2.421	Propylene Glycol	1.06	1.63	1.45	1.42	0.62	0.72
7	2.614	Pyridine	1.47	0.00	1.01	1.13	1.11	0.62
8	3.292	Propanoic acid, 2-oxo-, methyl ester	0.57	0.38	0.00	0.34	0.43	0.00
9	4.128	Pentanoic acid, 2-methyl-	0.87	0.72	0.80	0.83	0.43	0.66
10	4.351	Furfural	1.10	1.40	1.13	1.49	0.80	0.93
11	5.167	2-Furanmethanol	2.27	1.84	1.77	1.68	1.60	1.36
12	5.989	2-Cyclopentene-1,4-dione	1.50	0.79	1.24	1.12	1.58	1.06
13	6.815	2(5 H)-Furanone	1.71	1.02	1.54	1.24	0.96	0.85
14	7.072	2-Cyclopenten-1-one, 2-hydroxy-	1.86	1.27	1.44	1.77	1.24	1.31
15	7.525	2-Furancarboxaldehyde, 5-methyl-	0.74	1.11	0.53	0.54	0.61	0.59
16	8.411	Phenol	0.81	0.27	0.32	0.32	0.24	0.51
17	8.562	1,2-Cyclohexanedione	1.01	0.63	0.58	0.53	0.36	0.43
18	8.629		1.08	0.91	0.96	0.70	0.52	0.61
19	9.204	1,2-Cyclopentanedione, 3-methyl-	0.00	0.38	0.00	0.25	0.21	0.00
20	9.404		0.52	0.43	0.77	0.44	0.17	0.46
21	10.03	Phenol, 4-methyl-	0.55	0.50	0.26	0.28	0.00	0.00
22	10.145		0.73	1.03	0.92	0.82	0.26	0.62
23	10.284	4 H-Pyran-4-one, 2,3-dihydro-3,5-dihydroxy-6-methyl-	1.51	0.56	0.77	0.84	0.41	0.45
24	10.284	Glycerol	147.40	105.59	117.43	114.72	83.87	72.77
25	10.573	Maltol	1.53	0.60	0.64	0.58	0.62	0.35
26	11.019	4 H-Pyran-4-one, 2,3-dihydro-3,5-dihydroxy-6-methyl-	2.48	1.78	2.02	1.56	0.90	1.24
27	11.889	1,2-Benzenediol	2.20	1.35	1.28	1.51	0.56	0.81
28	12.899	Hydroquinone	1.79	3.69	2.87	2.99	1.39	1.33
29	13.67	(S)-Pyridine, 3-(1-methyl-2-pyrrolidinyl)	39.66	34.15	14.36	23.05	34.42	22.23
30	14.513	1 H-Indole, 3-methyl-	0.77	3.31	0.34	1.44	0.67	0.54
31	15.14	Pyridine, 3-(3,4-dihydro-2 H-pyrrol-5-yl)-	1.58	3.37	0.88	0.79	0.96	0.63
32	15.652	2,3′-Dipyridyl	0.87	0.40	0.55	0.55	0.54	0.68
33	16.586	4-Methyl-2,5-dimethoxybenzaldehyde	8.84	8.49	4.63	4.25	0.40	3.16
34	17.39	Cotinine	1.77	1.53	1.22	1.20	0.25	0.55
35	19.448	n-Hexadecanoic acid	2.95	2.90	2.39	2.07	1.91	2.81
36	22.576		0.95	0.67	0.60	0.65	0.67	0.67
37	24.633	LCA[a]	1.50	1.65	1.93	1.01	0.81	0.87
38	25.902	LCA	1.46	1.41	0.88	1.11	1.05	0.90
39	27.239	LCA	1.92	2.17	1.18	1.34	1.19	1.29
40	27.599	LCA	2.73	3.04	1.89	2.17	1.95	2.08

[a] LCA= Long chain alkane

3.3. Smoking experiments

SBA-15 was selected due to the good results shown by Py-GC/MS in both atmospheres and smoking experiments have been carried out with this additive. Heet tobacco and Heet tobacco with an 25% SBA-15 w/w was smoked at 300 ºC and the not condensed fraction and the TPM obtained have been analyzed. Table 3 shows the yield and reductions obtained in the total gases analyzed by GC/FID, TPM, as well as the reduction obtained in CO, CO_2 (GC/TCD) and Nicotine. As can be seen, SBA-15 presents significant reductions in TPM, and nicotine, and lower reductions are observed in total gases.

Table A3 in the supplementary material shows the peak area, the assigned compound and a number, that is used in the abscissa of Fig. 6 for identifying the corresponding compound. As can be seen in Fig. 6 and Table A3, in not condensed fraction analyzed by GC/FID, some compounds as methane (peak 1) and isoprene (peak 9) were favored in presence of SBA-15, while others compounds as propane and butane (peaks 4 and 7 respectively) disappear. In TPM fraction significant reductions are observed in practically all compounds generated.

Between the not condensed products detected by GC/FID two products are included in the FDA's HPHC list, benzene and acetaldehyde. Benzene in considered carcinogen, cardiovascular toxicant and reproductive or developmental toxicant, and acetaldehyde, the more abundant compound in this fraction, is considered carcinogen, respiratory toxicant and addictive. Inside the TPM fraction, only two dangerous products were detected, phenol and nicotine, where phenol is a respiratory and cardiovascular toxicant compound and nicotine is addictive and is considered reproductive or developmental toxicant. Both compounds are among the most abundant in this fraction, with nicotine being the second most abundant compound and phenol being the tenth. Table 4 shows the reductions obtained for these compounds included in the HPHC list. It can be seen how nicotine, phenol and acetaldehyde are strongly reduced by the presence of SBA-15, with significant reductions of over 30%.

Comparing the compounds obtained in the smoking experiments with those obtained in the Py-GC/MS experiments (Tables A1, A2 and A3 in additional material), it can be seen that not all compounds are obtained with both techniques. For example 2-furanmethanol, phenol and hydroquinone were detected in smoking experiments and in inert and oxidative atmosphere in Py-GC/MS experiments. However, cotinine was only obtained in smoking experiments and in Py-GC/MS experiments under inert atmosphere and acetaldehyde was obtained in the smoking experiments and in Py-GC/MS under oxidative atmosphere. In addition, new products appear in smoking experiments that were not detected in Py-GC/MS experiments as for example neophytadiene or farnesol. This highlights the complexity of the reactions that occur during tobacco smoking that are modified according to the equipment used, the experimental conditions and the atmosphere used.

Table A2
Compounds obtained by Py-GC/MS from the decomposition of Heet tobacco under oxidative atmosphere.

Peak	tr (min)	Compound	Area (10^{-7})/mg tobacco					
			Heet	Heet+ZSM5	Heet+USY	Heet+Beta	Heet+SBA-15	Heet+SiF
1	1.061	CO_2	58.80	43.14	43.28	41.32	65.25	36.77
2	1.085	Formaldehyde	4.97	4.49	4.87	4.02	3.82	4.21
3	1.139	Acetaldehyde	8.49	6.68	7.74	6.75	6.90	6.59
4	1.273	Acetone	18.77	16.67	16.72	16.34	15.97	16.37
5	1.457		25.56	15.09	16.18	21.35	15.98	22.46
6	1.543	2,3-Butanedione	26.79	15.98	16.84	14.40	16.67	38.85
7	1.886	H_2O	86.77	60.42	67.94	66.02	45.64	80.82
8	2.102	Formic acid	10.35	9.34	8.84	9.99	8.74	9.27
9	2.455	Acetic acid	12.21	13.18	15.42	15.56	16.60	15.85
10	2.675	2-Propanone, 1-hydroxy-	4.66	3.46	4.50	6.45	4.17	3.29
11	3.06	Toluene	0.85	0.76	0.87	1.41	0.80	1.11
12	3.114	Glycidol	1.59	0.84	1.36	1.17	0.61	0.61
13	3.287	2-Butanone, 4-hydroxy-3-methyl-	1.49	1.17	1.58	1.67	1.47	6.11
14	3.507	Pyridine	0.62	2.74	1.21	1.29	1.10	0.15
15	4.272	Propanoic acid, 2-oxo-, ethyl ester	1.77	1.23	1.25	1.49	0.83	2.48
16	4.751	Furfural	4.88	7.56	6.24	7.31	3.62	4.11
17	5.973	2-Furanmethanol	4.80	3.34	2.95	3.30	3.93	3.80
18	6.3	2-Cyclopentene-1,4-dione	6.28	3.91	3.53	4.03	6.52	4.49
19	7.281	2(5 H)-Furanone	4.77	2.89	2.77	4.05	3.89	4.66
20	7.991	Benzaldehyde	2.88	2.50	2.87	2.62	2.37	3.02
21	8.126	2-Furancarboxaldehyde, 5-methyl-	5.51	5.88	3.62	4.34	3.69	5.32
22	8.856	Phenol	4.51	3.23	1.73	2.74	2.43	3.71
23	10.266		5.00	4.04	1.91	2.08	4.33	1.21
24	10.474	Glutaraldehyde	5.44	2.99	0.88	3.12	2.01	2.61
25	11.206	4 H-Pyran-4-one, 2,3-dihydro-3,5-dihydroxy-6-methyl-	4.44	5.07	0.97	2.84	1.64	2.63
26	11.618	Ethanone, 1-(4-methylphenyl)-	1.89	1.15	0.89	1.55	0.87	0.50
27	12.227	1,2-Benzenediol	5.07	0.00	3.75	2.42	2.78	3.26
28	12.425	5-(Hydroxymethyl)furfural	7.46	10.17	7.59	10.01	0.99	6.72
29	13.023	Glycerol	637.48	413.10	324.71	388.75	210.12	311.02
30	13.282	Phenol, 2,3,5,6-tetramethyl-	2.40	2.74	1.73	1.81	1.76	3.29
31	13.727	Pyridine, 3-(1-methyl-2-pyrrolidinyl)-, (S)-	147.21	120.22	49.66	71.13	111.16	103.94
32	14.073	Hydroquinone	2.53	3.01	2.57	3.30	1.49	1.80
33	14.525	Pyridine, 3-(3,4-dihydro-2 H-pyrrol-5-yl)-	9.51	4.93	2.69	3.14	4.03	6.59
34	15.142	1 H-Pyrazole, 3-methyl-1-phenyl-	6.39	5.29	3.62	3.65	3.91	7.64
35	15.663	2,3′-Dipyridyl	10.76	4.32	5.04	3.81	3.44	8.27
36	18.17	1,2,3,4-Tetrahydro-1-methyl-2,3-dioxoquinoxaline	3.30	2.02	1.80	1.52	1.70	1.75
37	18.429	Bicyclo[3.1.1]heptane, 2,6,6-trimethyl-, (1.alpha.,2.beta.,5.alpha.)-	4.73	4.43	3.56	4.88	2.93	3.38
38	19.484	n-Hexadecanoic acid	15.37	14.65	8.34	8.81	5.73	15.00
39	20.463		3.59	1.10	1.78	2.77	1.56	3.60
40	27.599	Eicosane	13.67	10.23	6.98	8.74	4.32	8.64
41	20.872	9,12,15-Octadecatrienoic acid, (*Z,Z,Z*)-	10.18	8.50	4.26	3.35	1.84	8.23
42	21.03	Octadecanoic acid	2.37	1.47	1.21	1.27	0.75	1.02
43	22.575		2.09	1.85	1.16	1.28	0.53	0.54
44	23.457	Hexadecanoic acid, 2-hydroxy-1-(hydroxymethyl)ethyl ester	3.49	2.60	2.19	2.83	1.42	2.18
45	24.625	LCA[a]	3.59	2.26	1.70	2.43	1.37	2.13
46	25.895	LCA	3.37	2.16	2.06	2.53	1.33	1.57
47	27.225	LCA	4.74	4.36	2.88	3.54	1.81	2.76

[a] LCA= Long chain alkane

4. Conclusions

HNB tobacco cigarettes are less harmful than conventional tobacco because they are heated at lower temperatures. Nevertheless, the results obtained in the study in Py-GC/MS show that Heet tobacco generates large amounts of nicotine and glycerol and various compounds as phenol (under inert and oxidative atmosphere), acetaldehyde, acetone, formaldehyde and phenol (under oxidative atmosphere) classified in FDA's HPHC list, at this low temperature.

The effect of five potential additives, three commercial zeolites (ZSM-5, USY, and Beta) and two silicates (SBA-15 and SiF), for reducing the amount of toxic compounds in the tobacco smoke has been studied. Zeolites showed minor reductions, especially under inert atmosphere, being ZSM5 the additive that shows the worst performance. However, silicates are more effective reducing the amount of all the families of compounds analysed by Py-GC/MS, highlighting the role of the SBA-15 material, which is the additive that presents the best textural properties, a large pore size, a large BET area and high total pore volume.

Smoking experiments confirm that SBA-15 permits reducing the toxicity compounds generated when smoking Heet tobacco, and reduce the formation of CO, nicotine and most of the condensed products of the TPM, including those on in FDA's HPHC list. Therefore, it can be concluded that this material, as well as the silica fumed, are very interesting candidates to add to the Heet tobacco for further reducing its toxicity.

CRediT authorship contribution statement

Deseada Berenguer: Visualization, Methodology, Investigation, Validation, Data curation, Writing – original draft preparation. **Antonio Marcilla:** Conceptualization, Methodology, Supervision, Writing – review & editing, Project administration. **Isabel Martinez**: Resources, Methodology.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Table A3
Yield and reductions (%) in not condensed and condensed products obtained in smoking experiment.

Peak	Not Condensed Compounds	Heet mg/ cigarrete	Heet+SBA-15 mg/ cigarrete	Reductions (%)
1	Methane	0.0109	0.0159	-45.6
2	Ethane	0.003	0.004	-31.8
3	Ethylene	0.0068	0.0079	-16.3
4	Propane	0.0018	0	100.0
5	Propene	0.0053	0.0066	-26.3
6	Chloromethane	0.0474	0.0416	12.2
7	Butane	0.0014	0	100.0
8	Isobutene	0.0032	0.0039	-21.7
9	Isoprene	0.008	0.0122	-51.7
10	Hexane	0.0026	0.0023	10.5
11		0.0177	0	100.0
12	Benzene	0.0109	0.0159	-45.6
13	Acetaldehyde	0.003	0.004	-31.8
Peak	**Condensed Compounds**	**Heet mg/ cigarrete**	**Heet+SBA-15 mg/ cigarrete**	**Reductions (%)**
1	Furfural	0.0076	0.0038	49.3
2	2-Furanmethanol	0.0091	0.006	34.5
3	2-Propanone, 1-(acetyloxy)-	0.0095	0.006	37.5
4	4-Cyclopentene-1,3-dione	0.0026	0.0011	59.4
5	2(5 H)-furanone	0.0027	0.0011	59.2
6	2(3 H)-furanone, 5-methyl-	0.0056	0.0033	41.7
7		0.002	0.002	-3.0
8	Butanoic acid, 3-methyl-	0.0055	0.0027	50.8
9	Furfural, 5-methyl-	0.0038	0.0021	44.7
10	Phenol	0.0136	0.009	33.4
11	2-isopropylfuran, 1 H-Pyrrole-2-carboxaldehyde	0.0014	0	100.0
12	2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	0.0055	0.0034	38.0
13		0.033	0.0127	61.3
14	Glycerol	4.23	1.33	68.7
15	2,3-Dihydro-benzofuran, 1,2-Benzenediol	0.0309	0.0131	57.4
16	2-furancarboxaldehyde, 5-(hydroxymethyl)-	0.0114	0.0036	68.8
17	Hydroquinone	0.0205	0.0194	5.0
18	Nicotine	0.6374	0.3952	38.0
19	2,3′-Bipyridine	0.0089	0.0053	40.6
20		0.0045	0.0016	64.7
21	Megastigmatrienone	0.0058	0.0033	43.7
22	Diethyl phatalate	0.0045	0.0036	21.4
23		0.0051	0.0021	58.5
24	Cotinine	0.003	0.0023	22.4
25	Benzenesulfonamide, N-butyl-	0.0077	0.0066	13.8
26	NEOPHYTADIENE	0.014	0.0087	37.9
27	Farnesol	0.0038	0.0028	26.7
28	Ethyl ester, hexadecanoic acid	0.0019	0.0021	-6.7
29		0.0099	0.0051	48.2
30	n-Hexadecanoic acid	0.0128	0.0024	81.2
31		0.0079	0.0041	48.2
32		0.0068	0.0029	57.4
33		0.0035	0.0013	63.6
34	9-Octadecenamide, (Z)	0.0196	0.0176	10.1
35		0.0067	0.007	-4.3
36	Pentadecane	0.0016	0.0018	-16.5
37	LCA*	0.002	0.0011	47.2
38	Docosano	0.0144	0.0069	51.9
39	Tricosane	0.0096	0.0039	59.0
40	Heptacosane	0.0061	0.0025	58.7
41	Octacosane	0.0093	0.0039	58.1
42	Triacontane	0.0223	0.0103	53.8
43	Tocopherol	0.0081	0.0027	67.0

* LCA= Long chain alkane

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See appendix

Table A1, Table A2, Table A3.

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