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The effect of the addition of SBA-15 to the slow pyrolysis of tobacco studied by heart-cutting GC/MC

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Abstract

The composition of evolved slow pyrolysis products under inert and oxidising atmospheres of reference tobacco from the University of Kentucky and its mixture with an SBA-15 mesoporous silica have been measured using a multishot pyrolyser attached directly to a gas chromatography/mass spectrometer. The results obtained show that under an inert atmosphere, the main decomposition rate occurs between 200 and 400 °C, with the evolution of nicotine and the generation of compound's characteristic of the decomposition of cellulose, hemicellulose, lignin and other constituents. The addition of SBA-15 to tobacco produces a reduction in most evolved gases at temperatures below 300 °C, markedly decreasing the formation of quinic acid, neophytadiene, nicotyrine and so on. In contrast, at temperatures above 300 °C, the opposite effect occurs and the generation of compounds is higher, increasing mainly the formation of acetaldehyde, chloromethane and aromatics. Under an oxidising atmosphere, at temperatures below 300 °C, almost all compounds are reduced when SBA-15 is added to tobacco, such as glycerol, neophytadiene and nicotine. The combustion processes occur between 400 and 500 °C with the generation of mainly CO_2 and H_2O. At temperatures above 300 °C, there is also a significant reduction in the evolved gases like acid acetic, acetonitrile and some aromatics. The application of this type of material could be interesting for heat-not-burn tobaccos to further reduce their toxicity for the consumer.

Keywords Tobacco · Pyrolysis · SBA-15 · Py-GC/MS · Mesoporous silica

Introduction

Tobacco is a herbaceous plant that contains over 8000 compounds and is composed of biopolymers such as cellulose, pectin, hemicellulose and lignin, and non-polymeric and inorganic compounds [1]. The chemical composition of tobacco varies with the tobacco type depending on its origin and cultivar variability. The biopolymeric components of tobacco make up 40–50% of the tobacco mass and usually contain ~ 10% each of cellulose and hemicellulose, 6–12% pectin and 4–5% lignin. Between 5 and 10% of the tobacco mass is attributed to inorganic components, while 30–40% is composed of non-polymeric compounds. The distribution of non-polymeric compounds in tobacco is very diverse. Starch and sugars (sucrose, fructose and glucose) range from 10 to 20% of the tobacco mass, the nicotine content is ~ 1.5%, and carboxylic acids such as citric, oxalic, malonic and malic could contribute ~ 10%. Waxes and resins may contribute between 0.2 and 8.0%.

Tobacco companies have recently developed a new generation of cigarettes known as "heat not burn" (HNB), in which the tobacco is heated by means of a device to temperatures between 200 and 350 °C. There are therefore no combustion or pyrolysis reactions at high temperatures, and the aerosol aspirated by smokers has a simpler chemical composition. Studies carried out by tobacco companies show a reduction of ~ 90% in toxic and potentially toxic compounds while maintaining nicotine levels [2].

Tobacco smoke has been studied by several techniques, with pyrolysis being one of the most used [3–5]. The study of tobacco pyrolysis is used to obtain information about

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the behaviour of the cigarette smoking process and the smoke generated. The system of a burning cigarette is very complex, where several chemical and physical processes take place. Several works have focused on modelling and simulating the processes of pyrolysis and combustion that occur in the tobacco smoking process [6–9]. The objective of these works is to obtain information concerning the cigarette smoke chemistry and toxicity through knowledge of the composition of the compounds contained in the tobacco smoke. Therefore, the experimental conditions of pyrolysis and combustion should simulate, as far as possible, those occurring during the tobacco smoking process; because in other case, false predictions could be obtained [4, 10]. A thermogravimetric (TG) balance coupled to Fourier transform infrared spectroscopy (FTIR) is commonly used for the quantification of products formed in thermal degradation [11–13]. This technique can monitor the processes of mass loss and identify the functional groups of the generated volatile species and their corresponding release temperature range. However, TG–FTIR cannot measure homodiatomic species [14], and it is also difficult to distinguish the generation of compounds with similar functional groups. In contrast, the combination of evolved gas analysis, trap-and-purge sampling of desired portions of the evolved fraction and gas chromatography–mass spectrometry (GC–MS) characterisation can be a potent method to investigate complex biomass materials, as information can be obtained on the compounds generated, rather than their functional groups.

Recently, different studies have been carried out by applying microporous and mesoporous catalysts to tobacco, either added to the filter or directly mixed with tobacco, for the reduction of toxic compounds generated by combusting tobacco [15, 16]. An example is the use of mesoporous silicates such as SBA-15 or zeolites to selective capture tobacco-specific nitrosamines [17–19]. The main advantage of mesoporous materials in the catalytic decomposition of tobacco is the easier accessibility of large molecules to active sites through their large pores (2–50 nm). Nevertheless, we have not found studies of the effect of such catalysts under conditions such as those in HNB products (i.e. at low temperatures).

The present study focuses on the evolution patterns of volatiles and the pyrolysis products evolved from a reference tobacco blend and its mixture with a mesoporous catalyst, SBA-15, under slow heating rate, covering the low-temperature range typical in HNB applications, conditions similar to those present in previous TG experiments [11]. Heart-cutting gas chromatography/mass spectrometry (HC-GC/MS) was used for the semiquantitative determination of individual compounds formed. Inert and oxidising atmospheres are used to study the pyrolysis and oxidation reactions.

Table 1 Composition of the cigarette reference 3R4F

Blend summary	3R4F/%
Flue-cured	35.41
Burley	21.62
Maryland	1.35
Oriental	12.07
Reconstituted (Schweitzer process)	29.55
Glycerin (dry-mass basis @ 11.6% OV)	2.67
Isosweet (sugar)	6.41

Table 2 Characteristics of catalyst

Catalyst	BET area[a]/m^2g^{-1}	Pore volume[b]/ cm^3g^{-1}	Pore size[c]/nm
S (SBA-15)	728	0.954	6.091

[a] N_2 adsorption isotherms, BET method

[b] N_2 adsorption isotherms, measured at $P/P_0 = 0.995$

[c] N_2 adsorption isotherms, BJH method

Materials and methods

Materials

A 3R4F tobacco reference from the Reference Cigarette Program of the College of Agriculture of the University of Kentucky was used for the experiments. The composition of the reference cigarettes, as well as other characteristics, is reported by the supplier (Table 1) [20, 21]. The proximate analysis of this tobacco provides the following results: 8.2% moisture, 69.9% volatiles, 10.3% fixed carbon and 11.9% ashes. The reference tobacco was grinded (particle size lower than 70 µm) to avoid heterogeneity associated with different tobacco fibres, which is very important for taking into account the small amount of sample that the experimental equipment allows processing of.

The mesoporous catalyst SBA-15 (S) has been synthesised according to the standard procedures described by Zhang et al. [22], where Pluronic P123 was dissolved in a HCl 2 M, and then, TEOS was added and the solution was agitated at 38 °C during 20 h. Finally, it was recovery by filtration, dried and calcined at 550 °C to remove the template. The result suspension was aged at 80 °C during 24 h. Table 2 shows the textural properties, obtained from the N_2 adsorption–desorption isotherms at 77 K on an automatic AUTOSORB-6 supplied by Quantachrome. The surface area parameters were obtained according to the BET method. The pore size distributions were determined by applying the BJH model, using a cylindrical geometry for the pores and the de Boer equation for determining the adsorbed layer thickness (*t*) and external surface area. Figure 1 shows the XRD patterns where the peaks (100), (110) and (200) are observed confirming the typical 2D hexagonal (p6mm) structure of this type of materials [23]. Figure 2 shows the SEM imagens with a fibre-like morphology.

As in previous thermal studies [11], mixtures of 15% (w/w) SBA-15 and tobacco were prepared. This amount was selected to be high enough to magnify its effect and enable a more precise observation. About 5% of water was added drop by drop and agitated vigorously when mixing the tobacco with the catalyst, to improve the degree of contact between them. Samples were conditioned under the standard conditions before the experiments in a 60% relative humidity environment. For comparison, the same amount of water was added and thoroughly mixed with tobacco when tobacco samples without catalyst were studied.

Experimental apparatus

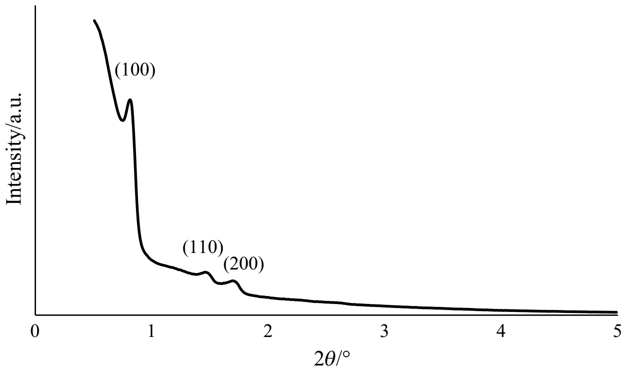


Fig. 1 Low-angle XRD pattern of the synthesised SBA-15

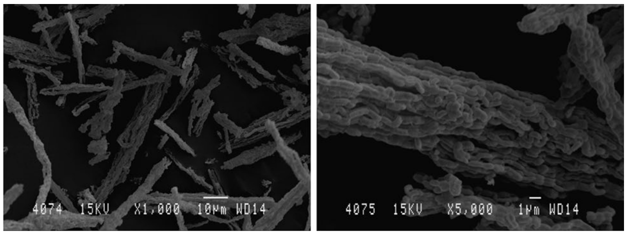


Fig. 2 SEM images of the synthesised SBA-15

The pyrolysis measurements were carried out using a multi-shot pyrolyser (EGA/Py-3030D, Frontier Laboratories Ltd.), which was attached directly to the GC/MS system (6890 N GC/5973 inert MSD, Agilent technologies). The setup for a typical heart-cutting GC/MS is shown in Fig. 3; the pyrolysates eluting from the tobacco sample at each temperature range are introduced selectively into the GC separation capillary column and analysed by MS. About 400 µg of the tobacco and about 500 µg of the mixture were pyrolysed at a heating rate of 35 °C min^{-1}, and the pyrolysis thermal zones were divided into 100 °C intervals, for both atmospheres, from 100 to 600 °C. The reaction products were vaporised from the sample holder during the heating program of each thermal region, were introduced into the GC separation column (UA-5, 30 m × 0.25 mm i.d. × 0.25 µm film thickness, Frontier Laboratories Ltd.) and were cryo-focused at the front part of the column by liquid nitrogen (− 196 °C) during the pyrolysis time. The product vapours were also split in the GC inlet (300 °C) at a split ratio of 50:1 (column flow rate: 2 mL min^{-1}). After the cryo-focusing time, the products were separated using the GC oven program from 45 °C (hold time of 5 min) to 285 °C (hold time of 5 min) at a heating rate of 12 °C min^{-1}. The separated pyrolysates 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).

Results and discussion

Heart-cutting GC/MS analysis was carried out to identify and semiquantify the products of the reference tobacco pyrolysis and combustion formed at each temperature range. In order to avoid the influence of the mass of sample pyrolysed, the peak area was normalised by dividing by the initial mass of tobacco loaded (without catalyst). Several experiments replicated three times showed that the reproducibility of the results (i.e. the peak area/amount of tobacco loaded) is better than 10% for all compounds detected. The different compounds have been grouped by chemical families (acid, alcohol, aliphatic, aromatic, carbonyl, furans, nitrogenous and phenolic) to facilitate the analysis. In all graphs, the dotted bars correspond to the tobacco catalyst mixture results.

The results of the peak areas (Tables A and B) and the chromatograms (Figure A and B) are found in the supplementary material.

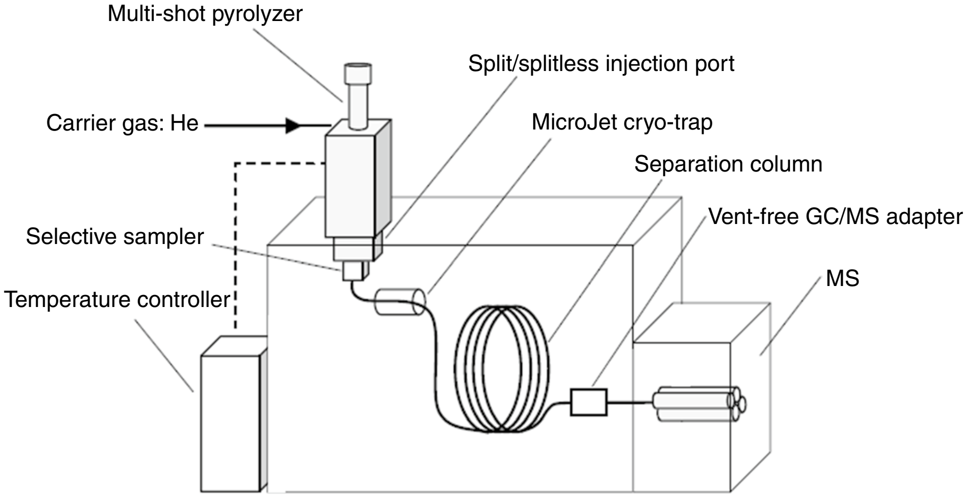


Fig. 3 Instrument setup for a heart-cutting analysis

Inert atmosphere

Water, carbon dioxide, nicotine and glycerol are individually represented in Fig. 4 because they are the main evolved compounds. Most of the nicotine is produced between 100 and 300 °C and it is the main evolved product in the 100 and 200 °C thermal range. The nicotine is produced by distillation, always occurring with some degradation of the tobacco [4]. In contrast, large amounts of carbon dioxide and water were observed over the entire temperature regions, as can be seen in Fig. 4, both compounds peaking in the 200–400 °C temperature range. Yang et al. [24] found that the release of carbon dioxide was mainly caused by the cracking and reforming of carboxyl (C=O) and COOH functional groups; therefore, the generation of CO_2 and H_2O is likely to be caused by the cracking and reforming of the carboxyl, carbonyl and carboxylic acid functional groups of hemicelluloses, cellulose and lignin. Moreover, glycerol is an additive of tobacco and undergoes evaporation in the range of 100–300 °C.

The presence of SBA-15 has different effects depending on the decomposition temperature range. At low temperatures, in the 100–300 °C thermal zone, a reduction effect can be seen in nicotine, CO_2 and water, and this is particularly prevalent at 100–200 °C range. On the other hand, an increment in the generation of CO_2 and nicotine between 300 and 400 °C is observed due to the catalyst. In the range 400–500 °C, the catalyst has almost no effect, and at higher temperatures, there is an increase in the production of CO_2 and water, which means that the SBA-15 favours the decomposition of the residue at this temperature range. SBA-15 produces a marked reduction in evaporated glycerol, which may indicate that the catalyst retains it. The retained glycerol could react at higher temperatures (300–500ºC) and form different aldehydes.

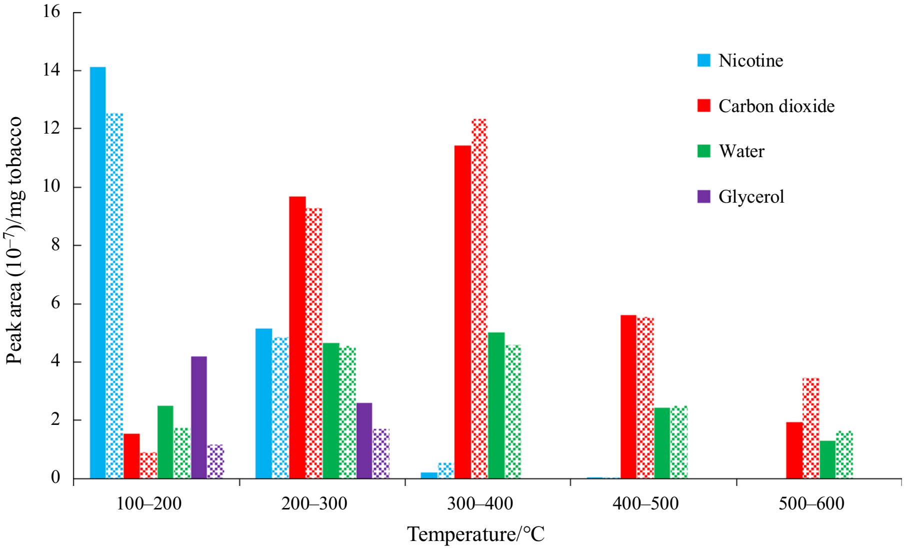


Fig. 4 Carbon dioxide, water and nicotine peak areas evolved from the pyrolysis of the reference tobacco under an inert atmosphere

Figure 5 shows the peak areas of the chemical families (acid, alcohol, aliphatic, aromatic, carbonyl, furan and nitrogenated) evolved from the pyrolysis of the reference tobacco and its mixtures with SBA-15 under an inert atmosphere for each temperature range, while Fig. 6 shows the peak areas of the major chemical compounds generated for each chemical family. Families such as aliphatic and carbonyl, have been divided into two figures due to the more significant amount of compounds generated.

The chemical families mainly evolved from the thermal zone of 100–200 °C are aliphatic, alcohol and carbonyl, whereas the nitrogenated compounds are evolved to a lesser extent.

In the carbonyl family, as seen in Fig. 6a, the main compound is 2,3-dihydro-3,5-dihydroxy-6-methyl-4*H*-pyran-4-one, which according to Baker [4] can be formed by pyrolysis of 1-deoxy-l-(*l*-prolino)-ᴅ-fructose and another sugar-amino acid (Amadori) compounds at temperatures below 300 °C and as can be seen, there is a diminution in the generation due to the catalyst.

The main aliphatic compound is the neophytadine that probably occurs in tobacco leaf through the degradation of chlorophyll, and it is almost eliminated by the effect of the addition of SBA-15. This result is interesting because reducing the neophytadiene also reduces the PAHs formed during combustion. Schmeltz et al. [25] estimated that ~ 0.1% of the tobacco neophytadiene is converted during the smoking process to PAHs in the mainstream smoke.

Finally, a brief generation of nitrogenated compounds is evolved, such as nicotyrine and myosmine, which are eliminated by adding the catalyst.

In the zones 200–300 °C and 300–400 °C, there is an increase of almost all chemical families. The principal decomposition of tobacco occurs between 300 and 400 °C under an inert atmosphere and the products obtained are related to the pyrolysis of cellulose, hemicellulose and pectin [11].

The carbonyl compounds (Fig. 5) are the most evolved at 300 and 400 °C. The carbonyl compounds mainly formed (Fig. 6a) are acetol, acetone, acetaldehyde, 2-pentanone and pentanal. The main carbonyl compound evolved is acetol, which could be due to cellulose pyrolysis, and is believed to be generated from the cleavage of the C_2 and C_3 bonds in glucose and the opening-loop of the hemiacetal group of cellulose [26, 27]. Furthermore, Collard and Blin [28] observed that the many reactions of depolymerisation in cellulose pyrolysis also lead to the formation of some unstable compounds containing new functional groups such as carbonyl and carboxyl groups. These compounds undergo dehydration or fragmentation reactions, explaining the high production of H_2O, CO_2 and small chain compounds (glycolaldehyde, acetaldehyde and acetol) in this temperature range. The addition of SBA-15

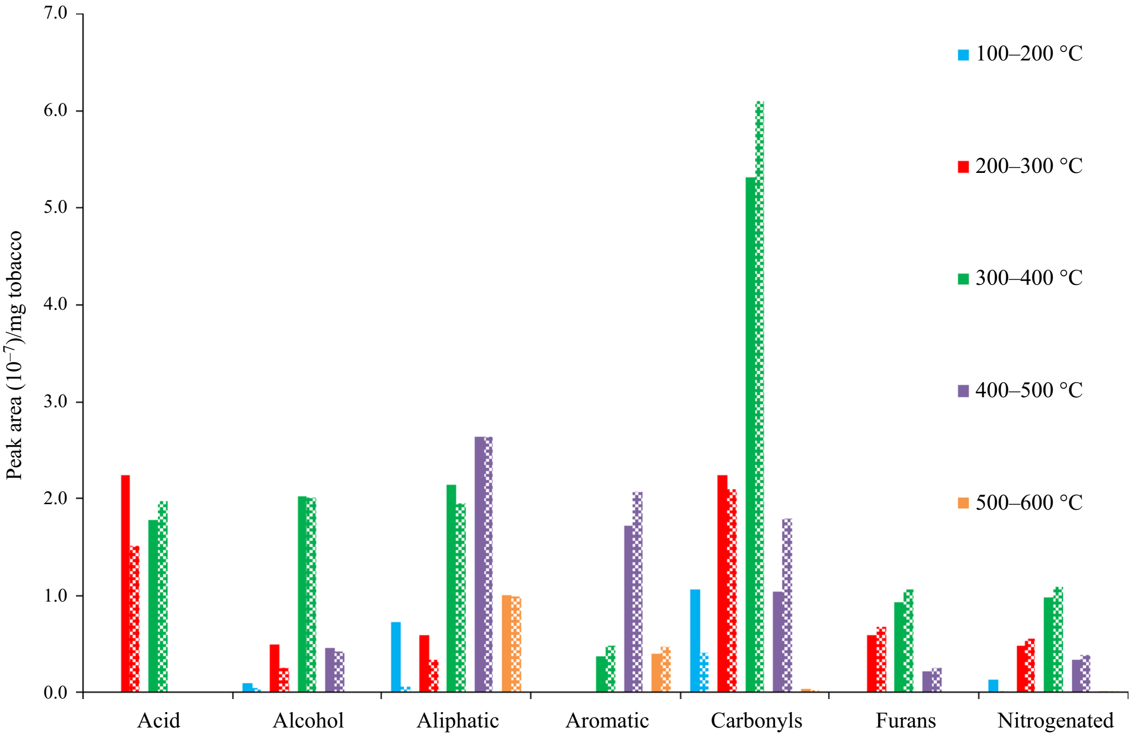


Fig. 5 Peak areas of the chemical families evolved from the pyrolysis of reference tobacco under inert atmosphere for each thermal zone

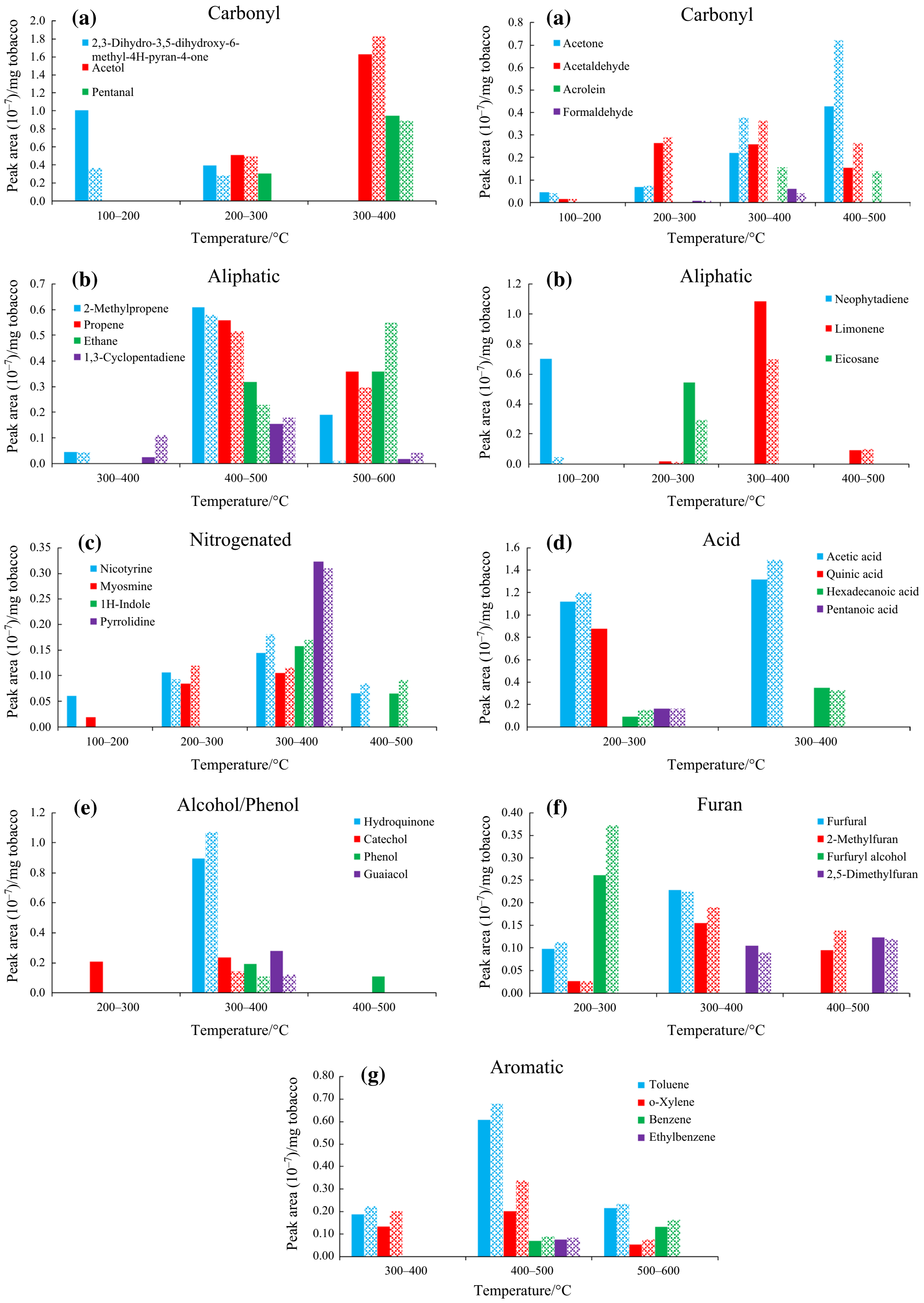


Fig. 6 Peak areas of the major chemical compounds generated for each chemical family evolved from pyrolysis of the reference tobacco an under inert atmosphere for each thermal zone

produces a decrease in the formation of carbonyl compounds at temperatures below 300 °C, although there is an increase in the generation of these compounds at higher temperatures, mainly in the generation of acetol, acetone and acetaldehyde.

The aliphatic compounds (Fig. 5) are generated in the entire temperature range studied, with two different zones. Observing Fig. 6b, the first zone is at low temperatures (100–400 °C), where heavier aliphatic compounds are formed. Neophytadine is produced in the 100–200 °C range, which would be produced by distillation from tobacco [4]. In addition, a maximum is observed in the 300–400 °C range, where mainly terpene compounds, such as limonene, evolve. In contrast, the second zone was comprised of high temperatures (400–600 °C), with lighter compounds predominating. A maximum is observed in the 400–500 °C range mainly due to the formation of alkanes (ethane and methylpropane), alkenes (propene and methylpropene) and cycloalkenes. SBA-15 effectively reduced the production of heavier aliphatic compounds at low temperatures (neophytadiene, limonene and eicosane). A slight reduction in the lighter aliphatic compounds in the range of 400–600 °C is observed. This general reduction of olefins and the increase of aromatic products indicate that at high temperatures, the catalyst is favouring the aromatisation reactions of the products evolved in tobacco pyrolysis.

The nitrogen compounds (Fig. 6c) are formed in the range between 200 and 500 °C, and most of the compounds are derived from the pyrolysis of nicotine, such as myosmine, cotinine, nicotyrine, pyrrolidine, pyridine and dipyridyl [10]. The evolution of the nitrogen compounds has a maximum in the 300–400 °C range due to the higher production of pyrrolidine. SBA-15 increases the decomposition of nicotine at temperatures above 200 °C, increasing the production of compounds such as nicotyrine and myosmine.

In the range between 200 and 400 °C, acids from the decomposition of hemicellulose appear like the acetic acid, mainly from the dissociation of O-acetyl groups linked to the xylan main chain [26], its generation being increased by the addition of SBA-15. Another organic acid that is generated between 200 and 300 °C is quinic acid, produced by the chlorogenic acid contained in the tobacco since it is thermally unstable and is readily decomposed to quinic and caffeic acid [29]. It is observed that the addition of SBA-15 eliminates the generation of quinic acid (Fig. 6d).

The generation of phenolic compounds is linked to the decomposition of lignin and chlorogenic acid. In the zone ranging from 300 to 400 °C, the depolymerisation leads to several phenols. Most of the phenolic compounds (Fig. 6e) released in this temperature range are characterised by a methyl group in the position 1 (p-cresol) or even an absence of an alkyl chain in this position (guaiacol, catechol or hydroquinone) because of the C–C bonds within and between the alkyl chains becoming unstable and reacting [28]. The greatest generation of these phenolic compounds (mainly hydroquinone) occurs in the 300–400 °C range, corresponding to the highest decomposition rate of the lignin and chlorogenic acid [30]. Observing the evolution of alcoholic compounds, it can be concluded that SBA-15 promotes the formation of hydroquinone against other phenolic compounds such as catechol, phenol or guaiacol.

The family of furans (Fig. 6f) are mainly formed by furfuryl alcohol (200–300 °C) and furfural (200–400 °C), and both are associated with the subsequent decomposition of anhydrosugars [31]. While in the temperature ranges between 300 and 500 °C, other furan compounds (2-methylfuran and 2,5-dimethylfuran) are formed due to depolymerisation of polysaccharides [28]. In this group of compounds, the SBA produces an increase in the generation of furfuryl alcohol and 2-methylfuran as shown in Fig. 6f.

The first aromatic compounds (Fig. 5) appear at 300–400 °C and their concentration becomes predominant at 400–500 °C. The aromatic compounds (Fig. 6g) (benzene, toluene and xylene), as well as the appearance of PAH (naphthalene) formed in these high-temperature regions, are believed to be the by-products of a char stabilisation reaction [32]. SBA-15 increased the production of aromatic hydrocarbons, especially the production of toluene and *o*-xylene in the range of 300–500 °C.

Oxidising atmosphere

As previously observed in TG/FTIR studies [11], at temperatures below 350 °C, the differences between the results obtained under inert and oxidising atmosphere are minimal. It is therefore expected that the results of HC-GC/MS in the oxidising atmosphere involved similar compounds to those obtained under the inert atmosphere. In contrast, at temperatures above 350 °C, combustion processes already occur and therefore the generation of gases differs between atmospheres.

As for the inert atmosphere, nicotine, carbon dioxide, water and glycerol are individually represented in Fig. 7 because they are the most evolved compounds. Most nicotine is evolved in the first temperature ranges, being predominant in the 100–200 °C range. Just as under the inert atmosphere, it is produced in these ranges due to distillation, with some degradation of the tobacco. A large amount of carbon dioxide and water was observed over the entire temperature regions, as shown in Fig. 7. The generation of CO_2 and H_2O below 400 °C is likely to be achieved by the cracking and reforming of the carboxyl, carbonyl and carboxylic acid functional groups of hemicelluloses, cellulose and lignin, like under the inert atmosphere [26].

Moreover, the release of CO_2 and H_2O at higher temperature regions (> 400 °C) is assumed to be accomplished by combustion and oxidation processes. As expected, the main CO_2 and H_2O production coincide with the combustion and oxidation processes (400–500 °C). Glycerol evaporates in the zones between 100 and 300 °C being predominant in 200–300 °C range, as it happens under inert atmosphere.

Figure 7 shows a decrease in the nicotine levels produced in the range of 100–200 °C when the catalyst is used, indicating that it may have been retained in the catalyst, observing also a small increase in the 200–300 °C range. Between 400 and 500 °C, there is a decrease in the CO_2 and H_2O produced, which indicates that the catalyst inhibits the combustion reactions of the sample; However, at higher temperatures (500–600 °C), there is an increase in the CO_2 generated. As under inert atmosphere, the glycerol is retained in the SBA-15 observing a significant reduction.

Figure 8 shows the peak areas of chemical families (acid, alcohol, aliphatic, aromatic, carbonyl, furan and nitrogenated) evolved from the combustion of reference tobacco and its mixtures with SBA-15 under an oxidising atmosphere for each temperature range and Fig. 9 shows the peak areas of the major chemical compounds generated for each chemical family. Families such as carbonyl and nitrogenated have been divided into two figures due to the higher amount of compounds generated.

Figure 8 shows the evolution of carbonyl compounds, which begin to be generated at early temperatures (100–200 °C), reaching a maximum at 200–300 °C and ending at 300–400 °C. Analysing the compounds individually, in Fig. 9a, it is observed that at the beginning (100–200 °C), mainly 2,3-dihydro-3,5-dihydroxy-6-methyl-4*H*-pyran-4-one is generated, then most of the compounds are formed, such as formaldehyde, 2-cyclopentene-1,4-dione, acetone, acetol, acetaldehyde and 2-propenal. Finally, in the range 300–400 °C, compounds are still generated that come out earlier as acetone, 2-propenal or acetaldehyde, being compounds of degradation of sugars (fructose, glucose and sucrose) contained in tobacco [33].

By analysing the effect of SBA-15, a generalised reduction can be observed in the range of 100–400 °C, with a small rise in the range of 400–500 °C. As seen in Fig. 9a, the main reduced compounds are 2,3-dihydro-3,5-dihydroxy-6-methyl-4*H*-pyran-4-one and acetone, while the other compounds, such as 2-cyclopentene or 2-propenal, are increased.

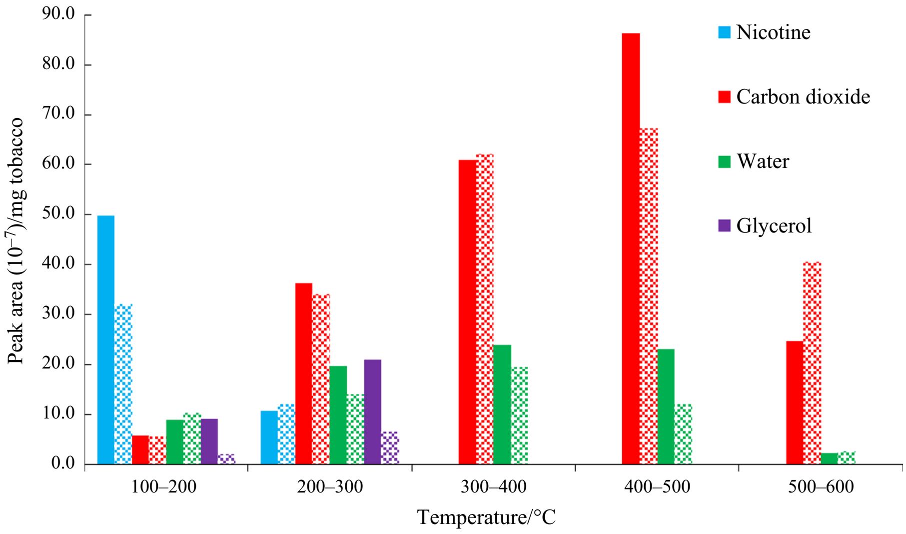
As shown in Fig. 9b, aliphatic compounds are generated at low temperatures in the range of 100–300 °C, which are attributed to neophytadiene at 100–200 °C and long-chain compounds, such as eicosane or tetratetracontane, at 200–300 °C. The SBA-15 produces a reduction of these compounds, with neophytadiene almost eliminated.

Acid compounds are produced in the range of 200–400 °C, with a maximum at 200–300 °C. Figure 9c shows that acetic acid is mainly generated, which is a derivative of the decomposition of hemicellulose. In this case, a significant reduction is observed due to the addition of SBA-15, above all in the acetic acid, eliminating it in the range of 300–400 °C.

The nitrogen compounds, like nicotyrene, myosmine and 2,3-dipyridyl, are generated at low temperatures ranges (100–300 °C), as shown in Fig. 9d. Other compounds are formed at higher temperatures, such as acetonitrile and benzonitrile, whose generation could be associated with the pyrolysis/combustion of amino acids and proteins [4]. With regard to the effect of SBA-15, an increase in the generation of all nitrogen compounds is observed, mainly in compounds, such as methaneamine and benzonitrile, having only a slight reduction in acetonitrile generation at 400–500 °C.

The alcohols and phenols are generated mainly at low temperature ranges (200–400 °C), particularly methanol and

Fig. 7 Carbon dioxide, water, glycerol and nicotine peak areas evolved from the pyrolysis of reference tobacco under oxidising atmosphere



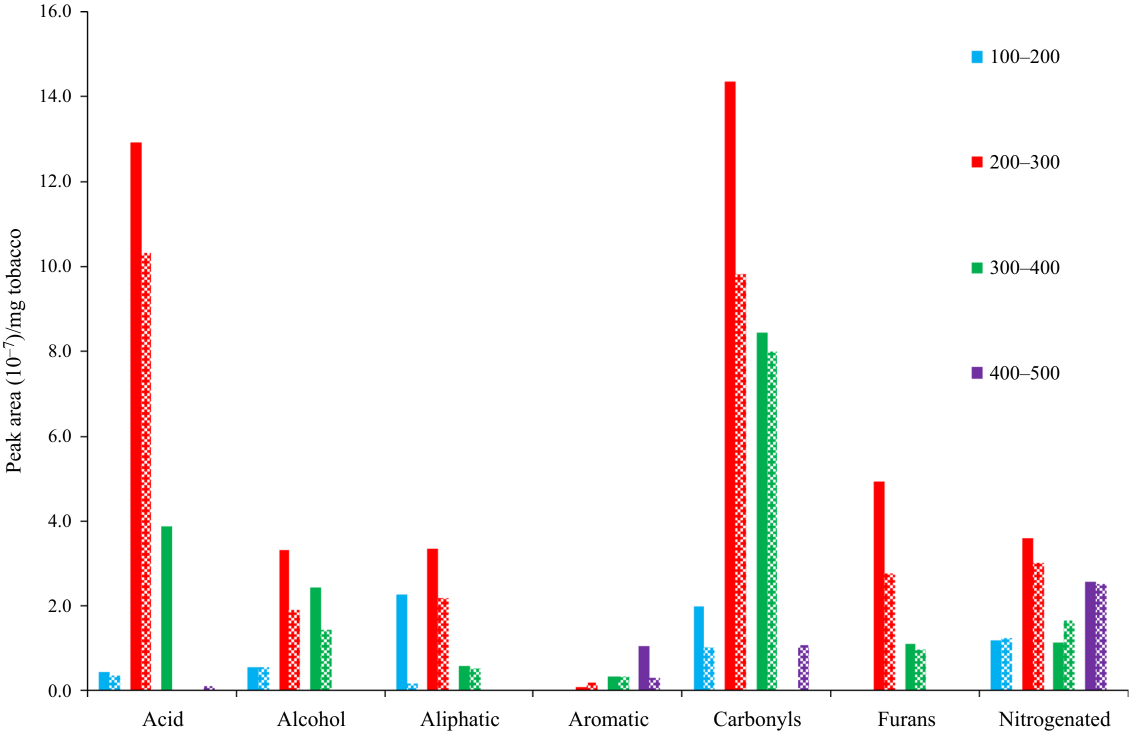


Fig. 8 Peak areas of chemical families evolved from the pyrolysis of the reference tobacco under an oxidising atmosphere for each thermal zone

phenol. In all cases, SBA-15 reduces the generation of alcohols, eliminating, for example, the cyclopentanol.

As in the inert atmosphere, furan compounds are generated between 200 and 400 °C and Fig. 9f shows that the catalyst decreases the generation of furfural, furfuryl alcohol and 2(5*H*)-furanone between 200 and 300 °C.

Aromatic compounds (Fig. 9g), such as toluene, benzene and *o*-xylene, are generated at elevated temperatures (400–500ºC), and reductions are observed due to the effect of SBA-15.

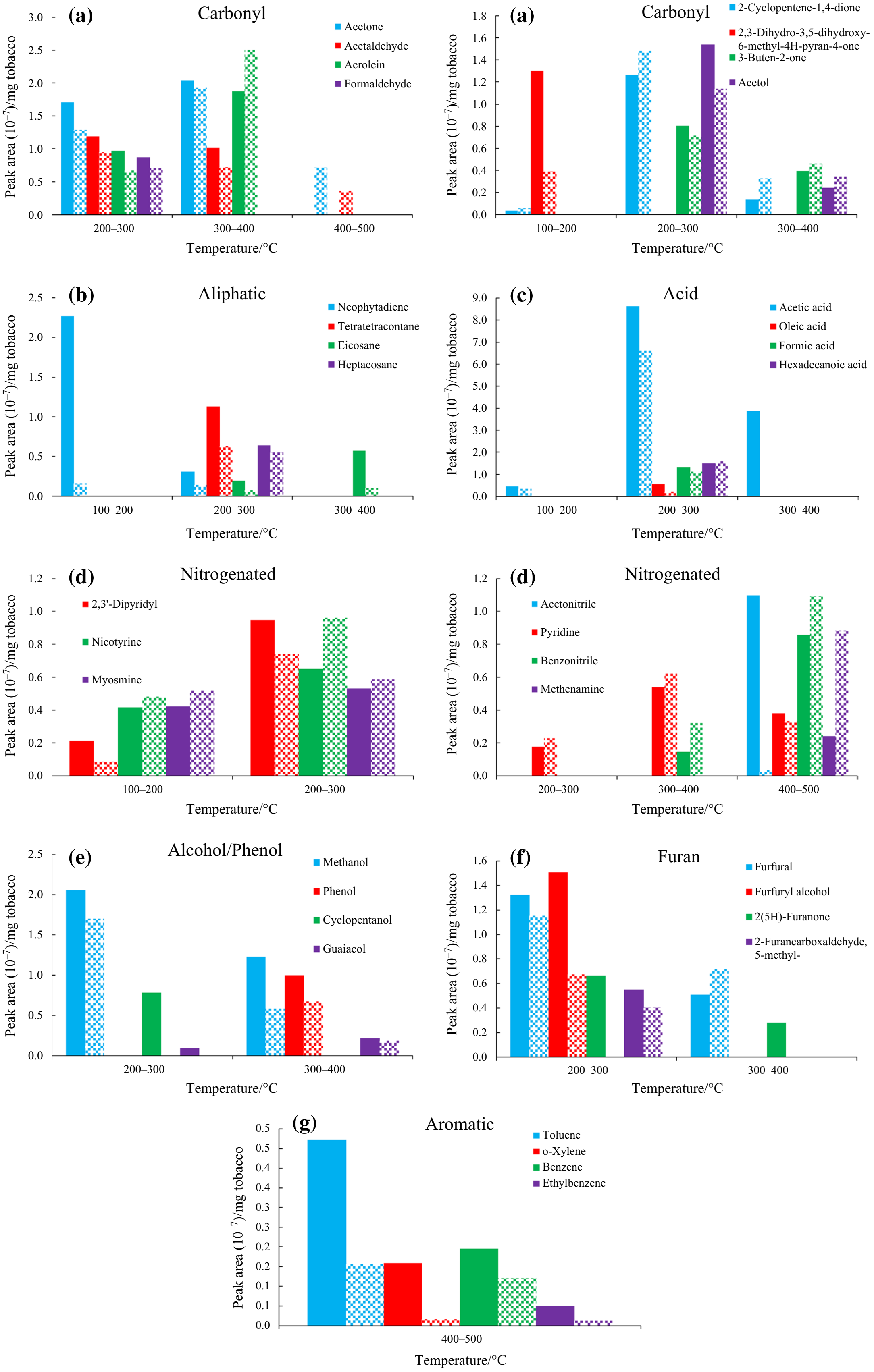
Comparing Figs. 5 and 8, the reactions are advanced under the oxidising atmosphere, with a greater generation of compounds in the range of 200–300 °C, while under an inert atmosphere the maximum is at 300–400 °C.

When comparing the compounds obtained in both atmospheres, it can be observed that the products generated at temperatures below 300 °C are quite similar in both atmospheres, as already observed in the TG–FTIR experiments [11]. The differences between generated compounds are observed above 300 °C. Under the oxidising atmosphere in the 400–600 °C range, where carbonyl compounds are no longer generated and the light aliphatic compounds (propene, ethane and so on) at 400–600 °C range or limonene that is formed under inert atmosphere are not formed either since they are consumed in the combustion processes.

Besides, there are differences between the nitrogenated, acid and alcohol compounds generated under the two atmospheres considered. Under the inert atmosphere, compounds are formed that do not appear in an oxidising atmosphere, such as pyrrolidine, quinic acid and hydroquinone, while under oxidising atmosphere compounds, such as acetonitrile, benzonitrile, methenamide and cotinine are generated, not observed under the inert atmosphere. Furan compounds present similar behaviour under both atmospheres, as well as aromatic compounds, with the only difference that these are not generated under the inert atmosphere, in the range of 500–600 °C.

The list of "harmful and potentially harmful constituents (HPHCs) in tobacco products and tobacco smoke" [34] published by the FDA, which focuses on chemicals linked to cancer, cardiovascular disease, reproductive problems, addiction and respiratory effects can be used to measure the degree of reduction in toxicity. From this list, the most toxic compounds detected are aldehydes (acetaldehyde, formaldehyde and acrolein), phenolics (phenol, catechol and hydroquinone) and volatile organic compounds (benzene, acetone, toluene and ethylbenzene), in addition to nicotine as an addictive and reproductive toxicant.

In view of the results, it is worth highlighting the reduction observed at low temperatures under oxidising atmosphere when adding SBA-15 to the mixture. So, it would be worth considering its application in HNBs since they are consumed at temperatures (200–300 °C), where interesting reductions are observed. At high temperatures, pyrolysis


(a)
Carbonyl
Acetone
Acetaldehyde
Acrolein
Formaldehyde
Peak area (10^{-7})/mg tobacco
0.0
0.5
1.0
1.5
2.0
2.5
3.0
200–300
300–400
400–500
Temperature/°C
(a)
Carbonyl
2-Cyclopentene-1,4-dione
2,3-Dihydro-3,5-dihydroxy-6-methyl-4H-pyran-4-one
3-Buten-2-one
Acetol
Peak area (10^{-7})/mg tobacco
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
100–200
200–300
300–400
Temperature/°C
(b)
Aliphatic
Neophytadiene
Tetratetracontane
Eicosane
Heptacosane
Peak area (10^{-7})/mg tobacco
0.0
0.5
1.0
1.5
2.0
2.5
100–200
200–300
300–400
Temperature/°C
(c)
Acid
Acetic acid
Oleic acid
Formic acid
Hexadecanoic acid
Peak area (10^{-7})/mg tobacco
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
100–200
200–300
300–400
Temperature/°C
(d)
Nitrogenated
2,3'-Dipyridyl
Nicotyrine
Myosmine
Peak area (10^{-7})/mg tobacco
0.0
0.2
0.4
0.6
0.8
1.0
1.2
100–200
200–300
Temperature/°C
(d)
Nitrogenated
Acetonitrile
Pyridine
Benzonitrile
Methenamine
Peak area (10^{-7})/mg tobacco
0.0
0.2
0.4
0.6
0.8
1.0
1.2
200–300
300–400
400–500
Temperature/°C
(e)
Alcohol/Phenol
Methanol
Phenol
Cyclopentanol
Guaiacol
Peak area (10^{-7})/mg tobacco
0.0
0.5
1.0
1.5
2.0
2.5
200–300
300–400
Temperature/°C
(f)
Furan
Furfural
Furfuryl alcohol
2(5H)-Furanone
2-Furancarboxaldehyde, 5-methyl-
Peak area (10^{-7})/mg tobacco
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
200–300
300–400
Temperature/°C
(g)
Aromatic
Toluene
o-Xylene
Benzene
Ethylbenzene
Peak area (10^{-7})/mg tobacco
0.0
0.1
0.1
0.2
0.2
0.3
0.3
0.4
0.4
0.5
0.5
400–500
Temperature/°C

◂**Fig. 9** Peak areas of the major chemical compounds generated for each chemical family evolved from pyrolysis of the reference tobacco under an oxidising atmosphere for each thermal zone

under inert atmosphere increases the aromatic formation, whereas oxidation conditions reduce their evolution, other compounds following different trends. Nevertheless, smoking experiments using these catalysts [15] consistently show clear reducing trends in most of the families of compounds analysed. In such smoking experiments, tars evolved every puff can be adsorbed by the catalyst upstream and the possible secondary tar cracking reactions may be responsible of the observed reductions. In this heart-cutting GC/MS experiments, tars evolved pass directly to the GC column and have no more contact with the catalysts and cannot undergo secondary reactions. Nevertheless, and as expected, there seems to be a better correlation between the smoking experiments and heart-cutting GC/MS experiments under oxidising atmosphere than under inert atmosphere.

Conclusions

The pyrolysis of a reference tobacco and a mixture with SBA-15 was investigated by heart-cutting GC/MS under inert and oxidative atmospheres. The HC-GC/MS was used to obtain the distribution of compounds generated in different ranges of temperatures for more information regarding the processes of tobacco degradation. Furthermore, the effect on the catalytic pyrolysis of tobacco by adding a mesoporous catalyst was studied. It is important to emphasise the importance and relationship of smoking processes with the products generated. This study focused on the slow heating of tobacco, a process that is more similar to HNB tobacco, unlike standard smoking processes where the sample spends less time at each temperature (flash heating). In addition, the study allows us to better understand the pyrolysis and combustion processes of tobacco and the effect of the addition of catalysts such as SBA-15, allowing us to identify more precisely the compounds generated and seeing the effect of the catalyst for each component that in previous work of TG–FTIR [11] could not be performed.

The reduction effect of SBA-15 is more significant under the oxidising atmosphere than the under inert atmosphere and at temperatures below 300 °C (both atmospheres). The addition of SBA-15 provokes a noticeable decrease of almost all compounds studied, thus confirming the utility of this material as a reducer of the toxicity of tobacco smoke, at low temperatures. In contrast, at high temperatures, an increase in the compounds generated is observed under the inert atmosphere, so it can be assumed that the compounds retained in the catalyst at low temperatures subsequently reacted.

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