



Thermal behaviour of selected flavour ingredients and additives under simulated cigarette combustion and tobacco heating conditions



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ARTICLE INFO

Article history:

Received 19 April 2016

Received in revised form 8 July 2016

Accepted 21 July 2016

Available online 22 July 2016

Keywords:

Tobacco heating products

Flavour compounds

Pyrolysis

Oxidative decomposition

ABSTRACT

An experimental method of pyrolysis–gas chromatography/mass spectrometry (Py–GC/MS) is proposed to evaluate the fate of selected flavour compounds in low-temperature (300 °C) tobacco heating conditions. The thermal behaviour of five flavouring compounds (citronellol, menthol, tartaric acid, cinnamic acid, and guaiacol) was studied under conditions to simulate low-temperature tobacco heating at 300 °C, and compared with results obtained using simulated cigarette-combustion conditions with a temperature programme up to 900 °C. The impact of oxygen and nitrogen atmospheres on the thermal transfer and breakdown patterns was also investigated.

It was established that the four flavouring compounds of high volatility (citronellol, menthol, cinnamic acid, and guaiacol) evaporated to a high degree (88–100%) during the low- and high-temperature experiments, as well. Guaiacol was the most stable compound under the test conditions; only 0.3% decomposition was detected at 900 °C with the oxidative atmosphere. Thermal decomposition reactions were substantially less extensive at the low-temperature heating conditions than with the high-temperature pyrolysis and simulated cigarette combustion. Citronellol and cinnamic acid produced about 1.5% decomposition products, while menthol produced 0.8%. In general, dehydrogenation reactions were more pronounced in the oxidative atmosphere, while aromatisation was significant in the nitrogen atmosphere, and at high temperatures. More oxo-compounds and less aromatic hydrocarbons were formed in the oxidative atmosphere.

Other types of reactions took place with tartaric acid, due to its low volatility. Extensive formation of light carboxylic acids was observed at the low temperature, and cyclic compounds were also formed in addition to carbon oxides and water under both nitrogen and oxidative atmospheres. Intermolecular reactions are proposed to explain these observations. At high temperatures the pyrolysis products of tartaric acid were the same as at low temperatures, but in the oxidative atmosphere more carboxylic acids and less aldehydes were formed than in pure nitrogen.

These results demonstrate the flavour compound's thermal stability depends strongly on the exact thermal history (heating temperature, heating duration and gas atmosphere) that they are exposed to. The information obtained will be of interests in understanding the thermal behaviour of these and other flavour compounds used in tobacco heating products.

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1. Introduction

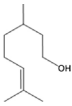
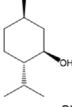
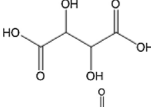
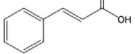

Tobacco products such as cigarettes contain a range of ingredients that are essential for physical integrity, engineering/manufacturing as well as consumer acceptability [1]. The use

of ingredients in tobacco products is regulated in most developed countries. Both “positive” and “negative” ingredient lists have been proposed to either permit or to restrict certain types of ingredients used. European Union's scientific advisory committee, SCENIHR (Scientific Committee on Emerging and Newly Identified Health Risks), has defined an “ingredient” as “tobacco, an additive, as well as any substance or element present in a finished tobacco product or related products, including paper, filter, ink, capsules and adhesives”. It classifies an “additive” as being “a substance, other

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Table 1
The main characteristics of the test materials.

Materials	CAS-Number	Chemical structure	Melting point (°C)	Boiling point (°C)
Citronellol	106-22-9		-7 (-20)	225
Menthol	89-78-1		42-45	212–216
Tartaric acid	87-69-4		168-174	decomposes
Cinnamic acid	140-10-3		132-136	350
Guaiacol	90-05-1		27-29	204-206

than tobacco, that is added to a tobacco product, a unit packet or to any outside packaging” [2]. In practice, additives can be applied during tobacco processing (e.g., cutting, expansion), or during reconstituted tobacco manufacture; by either paper-based or bandcast processes. There are further opportunities for the addition of humectants, casing and flavouring compounds during cigarette manufacturing and also during the packaging of the cigarettes.

Extensive research has been carried out to understand and to model the thermal behaviour of ingredients or additives during cigarette smoking [3–11]. Baker et al. [5,6,11] used a pyrolysis technique that simulated the thermal decomposition of tobacco inside a burning cigarette and studied the levels of thermal decomposition for 291 volatile and non-volatile ingredients. The results were then compared to mainstream smoke chemistry results obtained from cigarettes with these ingredients added at elevated levels compared to commercial usage. The only classes of ingredients with a noticeable impact on the smoke chemistry were several sugars added as tobacco casing ingredients. The chemistry changes did not cause significant differences in responsive in vitro assays targeting both genotoxicity and cytotoxicity, as well inhalation toxicity in rodents. Subsequent studies from other laboratories support these findings [12–14]. For example, a series of in vitro and in vivo studies to evaluate the potential effects of tobacco flavouring and casing ingredients have not discovered consistent differences in toxicological effects between smoke generated from cigarettes containing these ingredients against reference or control cigarettes [12]. Gen-

erally these studies show that the relationship between tobacco leaf composition and smoke components is complex. The current scientific understanding on complex chemistry does not permit a full assessment on each individual component's contribution to the final outcome [15]. Tobacco as a natural agricultural product also has variations in chemical compositions depending on crop year and agricultural practices. Additional analytical characterisations including targeted and untargeted approaches have to be taken when evaluating the effect of a single ingredient in the context of this complex matrix.

Nevertheless, tobacco regulators have called for more research on the pyrolysis behaviour of ingredients. For example, in the European Union, the Tobacco Products Directive 2014/40/EU sets out the rules and regulations on reporting the composition of tobacco products, including those used as ingredients contained in tobacco products [16]. The European Union's scientific advisory committee, SCENIHR, has recently published its “Preliminary Opinion on Additives used in Tobacco Products”, concluding that “Data on pyrolysis of most of the individual additives are scant” and calls for more pyrolysis studies on individual and complex flavour additives to be carried out [2,17]. The US Food and Drug Administration (FDA)'s Center for Tobacco Products (CTP) also considered extensive pyrolysis, smoke chemistry and biological evidence in its evaluation of menthol's role in mentholated cigarettes in US [18].

Many tobacco regulations (e.g., the Tobacco Products Directive 2014/40/EU) not only cover machine-made cigarettes, they also

Table 2
Pyrolysis and GC/MS experimental conditions for low-temperature heating and simulated cigarette combustion conditions.

Pyrolysis conditions	Low-temperature heating	High-temperature heating
Pyroprobe heating programme	300 °C (held 300 s)	300 °C (held 5 s)–30 °C/s–to 900 °C (held 5 s)
Atmospheres	100% nitrogen or 9% oxygen in nitrogen	100% nitrogen or 9% oxygen in nitrogen
Sample size	60 µg in 2 µL ethanol solution on quartz wool except tartaric acid: 600 µg as received	
Pyrolysis gas flow	276 mL/min (4.6 mL/s)	
Pyrolysis interface temperature	250 °C	
GC/MS operating conditions	Low-temperature heating	High-temperature heating
Oven programme	40 °C (held 3.5 min)–10 °C/min–to 240 °C–20 °C/min–to 280 °C (held 5 min ^a)	40 °C (held 7 min)–10 °C/min–to 240 °C– 20 °C/min– to 280 °C (held 5 min)
Solvent delay	7 min ^a	3.5 min
Column	DB 1701 (30 m length, 0.25 mm i.d., 0.25 µm)	
Injection mode	Split (split flow: 276 mL/min)	
Carrier gas	He at 1 mL/min flow	
Mass range	29–400 Da	
MS ionization mode	EI 70 eV	

^a Additional experiments were performed with tartaric acid using 75 s hold time and 3.3 min solvent delay.

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