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Short communication

TGA/FTIR study of the behavior of sodium and potassium citrates in the decomposition of 3R4F tobacco. N_2 and air atmospheres

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ABSTRACT

Citrates are common burning aids added to tobacco. In this work, the effect of the cation present in the citrate, sodium and potassium, on its thermal and oxidative decomposition was studied. Citrates decompose in three stages, elimination of water, loss of CO_2, and decomposition of the remaining material. Under N_2 atmosphere, the first stage occurs at lower temperatures for sodium citrate than for potassium citrate. The second one takes place at lower temperatures for potassium citrate, whereas the last stage occurs at similar temperatures for both citrates. Moreover, under air atmosphere, sodium citrate decomposes at temperatures higher than potassium citrate. When mixed with tobacco both additives present similar behavior in inert atmosphere and produce almost no modification of the behavior of tobacco with no additive. Nevertheless, under air atmosphere, the temperature of the process associated with the combustion of tobacco is noticeably reduced and a new process appears at high temperatures.

1. Introduction

Tobacco companies add ingredients and additives to commercial tobacco products, either to improve or modify the taste or flavor of the product, or for a specific technological purpose such as preserving the moisture of the tobacco or improving its process ability. These additives decompose into other substances during the tobacco smoking process [1]. The study of the behavior of such additives under pyrolysis and oxidation conditions is the first step in its toxicological assessment. These studies are very useful for predicting whether the additives distill unchanged from the combustion zone of the cigarette, or whether they decompose into other eventually toxic or inert products. However, the experimental pyrolysis/combustion conditions must imitate as far as possible those occurring during the tobacco smoking process, within the burning tip of cigarettes; otherwise, false predictions could be obtained [2,3]. However, the TGA/FTIR technique is widely used to study this type of process [4–6].

The European Commission adopted further legislative acts to support the application procedure of Directive 2014/40/EU [7]. This legislation takes the form of implementing acts, which summarize in more detail the rules and measures regarding tobacco and related products. The principal aim is reducing tobacco consumption in young people. This includes: the design and form of the combined health warnings for tobacco products, the position of the warning and information message on roll-your-own (RYO) tobacco, the reporting format for tobacco emissions and ingredients, describe a priority list of additives which permit further examination, and create rules and mechanisms for decisive products with characterizing flavors. With respect to the additives, the new directive bans flavors that increase the attractiveness of cigarettes, due to a “characterizing flavor”. For example, in 2020 menthol in cigarettes will be prohibited [8]. The necessary additives to produce snuff, such as sugar, will be allowed. Moreover, the Commission will establish a list of authorized additives in cigarettes and roll-your-own tobacco, and generate a priority list of additives contained in tobacco subject to enhanced reporting obligations. Nowadays, the priority list of additives is formed by 15 common materials such as glycerol, cocoa, menthol and sorbitol among others [8].

It is known that the alkali metals present in other biomasses similar to tobacco have an important effect on its thermal decomposition [9–11], potassium in particular acts as a catalyst in pyrolysis reactions [12–15]. These metals increase the rate of decomposition, gases and char yields but decrease the tar products. Similarly, the presence of potassium during combustion causes increased conversions. Potassium also changes the product distribution [13,15]. Fuel pyrolysis studies of the effect of sodium have shown that the presence of this metal lowers the activation energies [16]. Biomass with high ash content tends to have high concentrations of sodium [17]. In general, the concentration of potassium in biomass is higher than that of sodium, as the number of technical studies on the influence of potassium is higher than those of sodium.

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Citrates and phosphates (sodium and/or potassium) are the most widely used materials as burning additives in cigarette papers to modify (normally increase) the rate of combustion. Sodium or potassium citrates are normally present in cigarette paper and caused the cellulose to degrade at lower temperatures [18–20]. In a previous work, the study by TGA-FTIR of the thermal decomposition of potassium citrate and the effect of SBA-15 in such reactions in N_2 and air atmospheres was described [21]. In this work, we study the different effects of the two citrates, sodium and potassium, on the decomposition of tobacco under two atmospheres, N_2 and air and the importance of the method of preparation of the samples.

2. Experimental methods

2.1. Materials

3R4F cigarettes were provided for the Reference Cigarette Program of the College of Agriculture of the University of Kentucky. 3R4F tobacco was grinded and passed through a sieve of 20 μm in order to avoid the heterogeneity associated with the different tobacco fibers. Tri-sodium citrate dihydrate from Alfa (Aesar) laboratories was supplied by VWR and Tripotassium citrate monohydrate from Alfa (Aesar) laboratories was provided by Sigma. Samples of tobacco (T) and sodium citrate (NaC) or potassium citrate (KC) were prepared in a proportion of 85% w/w tobacco/15% w/w citrate (TNaC and TKC). For the mixtures of tobacco and citrate, citrate was dissolved in the least possible amount of water and mixed with tobacco. Afterwards, the samples were dried in a stove at 50 °C for 24 h. An additional sample of tobacco (85% w/w) + potassium citrate (15% w/w) was prepared, but the sample was conditioned in a desiccator at 20 °C and 60% of humidity until the water was eliminated (1–2 weeks (i.e.: the tobacco conditioning according to the ISO 3308)). This sample was named as (TKCd). Taking into account the sensibility of the TGA/FTIR technique in this type of dynamic experiments, we have used a high amount of these additives, compared to the normal loading below 5%, in order to magnify their effect and enable a clearer observation.

2.2. TGA/FTIR analysis

Samples of tobacco (T), sodium citrate (NaC), potassium citrate (KC) and their mixtures (TNaC, TKC, TKCd), were pyrolyzed under 80 mL (STP) min^{-1} in an N_2 and air flow, using a TGA Mettler Toledo thermobalance at 35 °C/min, from 25 °C to 700 °C, with a 30 min holding time at this temperature. Initial masses were always between 6 and 7 mg, thus assuring no effect of this variable on the results. This equipment was connected to a Bruker Tensor 27 FTIR spectrometer through a heated line at 200 °C, in order to minimize the condensation of the less volatile compounds, thus allowing the FTIR analysis of the compounds.

3. Results

3.1. TGA and DTG analysis under N_2 and air atmospheres

The effect of the two different citrates on the thermal decomposition of tobacco has been studied by TGA. Table 1 shows the peak-temperatures corresponding to the DTG curves of all the samples studied. Fig. 1 shows the TGA and DTG curves under N_2 and air atmospheres for the two pure citrates and tobacco: sodium citrate (NaC), potassium citrate (KC) and tobacco (T).

Sodium and potassium citrate were analysed in previous work [21] and present three decomposition steps. The first decomposition step is related to the loss of water of crystallization [21,22], with weight losses closely corresponding to the stoichiometry of each compound. The second stage is due to the partial degradation of citrate by the elimination of CO_2. Finally, the last stage is ascribed to the decomposition of the residues from the previous step, to yield mainly the corresponding carbonate. Moreover, as can be seen in Fig. 1a, differences in the temperatures of decomposition of the different stages were observed between sodium and potassium citrate. The elimination of water occurs at higher temperatures in the presence of potassium (211 °C vs 168 °C,

Table 1
Temperatures of maximum decomposition rate in N_2 and air atmosphere for (a) NaC and KC and (b) tobacco systems.

(a)

	System	C1	C2	C3	
N_2	NaC	168	325	496	
	KC	211	291	504	
Air		C1	C2	C3	C4
	NaC	168	326	483	525
	KC	218	290	427	

(b)

	System	T1 (°C)	T2 (°C)	T3 (°C)	T4 (°C)	T5 (°C)	T6 (°C)
N_2	T	99	182	268	319	(360–550)[a]	(600–700)[b]
	TNaC	72	160	261	304	(350–550)[a]	(610–700)[b]
	TKC	72	177	255	298	(350–550)[a]	(610–700)[b]
	TKCd	68–105	164	257	311	(350–550)[a]	677
		T1 (°C)	T2 (°C)	T3 (°C)	T4 (°C)	T5 (°C)	T6 (°C)
Air	T	99	182	269	314	427	481
	TNaC	98	168	262	292	448	519
	TKC	72	181	260	296	465	542
	TKCd	75–105	177	264	298	424	

[a] Temperature range.
[b] Process is not finished at the final temperature studied.

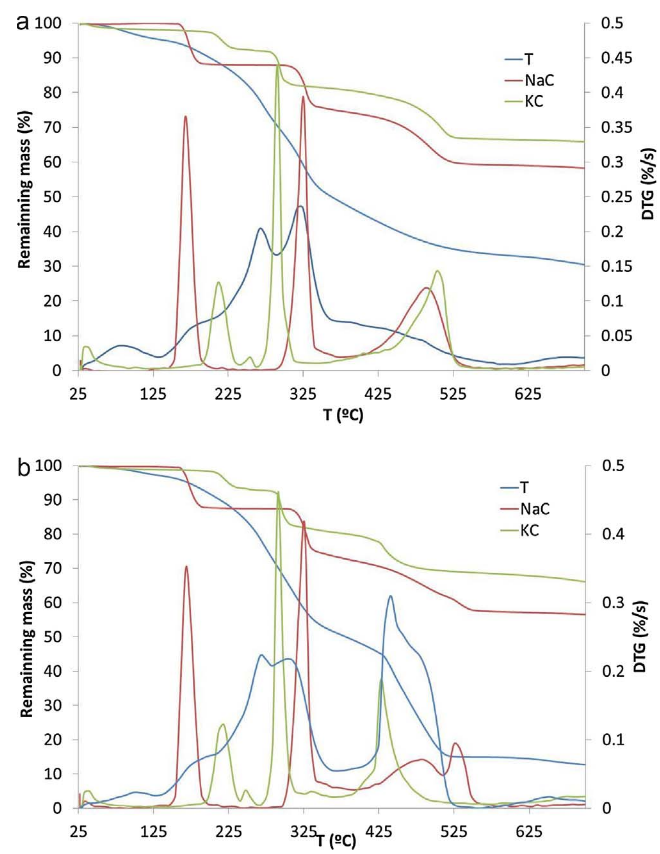

Fig. 1. TGA and DTG curves for the decomposition of T, NaC and KC under: (a) in N_2 atmosphere and (b) air atmosphere.