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Studies on thermal behavior of reconstituted tobacco sheet

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Abstract

Four kinds of reconstituted tobacco sheets were heated in a thermogravimetric analyzer in different atmospheres at the heating rate of 5 °C/min. The curves of thermogravimetry (TG), derivative thermogravimetry (DTG) and differential thermal analysis (DTA) of the reconstituted tobacco sheets were measured and compared. The profiles of the evolving product CO_2 were also recorded by the thermogravimetric analyzer coupled to a Fourier transform infrared (TG-FTIR) spectrometer. The results of thermal analysis and the profiles of CO_2 showed that the existence of O_2 could strongly affect the thermal decomposition of the reconstituted tobacco sheets.
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Keywords: Thermal analysis; Thermogravimetric Fourier transform infrared analysis; Reconstituted tobacco sheet; Carbon dioxide

1. Introduction

Reconstituted tobacco sheet, because of its advantageous economic impact on the manufacturing cost of cigars and cigarettes, has had increasing world-wide acceptance by the tobacco industry. Due to the technological changes, the tobacco researcher has sought to determine possible alterations in smoke composition, which may have a significant effect on physiological and biological properties of smoke. Reduced tumorigenicity in reconstituted tobacco sheet smoke particulate matter was first reported in 1965 [1], which was confirmed by subsequent studies [2,3]. Lower tar, benzo[*a*]pyrene, nicotine, phenols and polynuclear aromatic hydrocarbons (PAH) in the smoke particulate matter from sheet versus a control cigarette were reported in other studies [3,4]. With respect to the potential decrease in harm of cigarettes, reconstituted tobacco sheet may offer some opportunities.

Reconstituted tobacco sheet is combusted and pyrolyzed in a burning cigarette, which is a complex process with varying temperature and oxygen content distributions. The knowledge of the thermal decomposition pathways of reconstituted tobacco sheet is fundamental to understanding these processes [5]. On the other hand, thermal analysis is an analytical process that allows the measurement of changes in the chemical or physical properties of a substance or material as a result of temperature or time under a controlled temperature program. So thermogravimetry (TG), derivative thermogravimetry (DTG) and differential thermal analysis (DTA) have been applied in tobacco studies [6–8]. However, these thermal analysis methods were rarely used to study the reconstituted tobacco sheet [9]. In order to understand the behavior of reconstituted tobacco sheet in a burning cigarette, thermal analysis methods using conditions that simulate the conditions inside the burning zone of a cigarette should be applied to study the reconstituted tobacco sheet.

In this study, four kinds of reconstituted tobacco sheets from France (LTR, Le Mans) and China (Hanghzou, Yunnan and Guangzhou), respectively, were analyzed with TG, DTG and DTA methods. The major gas product CO_2 was also

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Table 1
The experimental conditions of TG-FTIR

Apparatus		Experiment condition
TG/DTA	Temperature range	50–1000 °C
	Heating programme	50–130 °C, 5 °C/min, hold 5 min at 130 °C; 130–1000 °C, 5 °C/min
	Reference material	α-alumina, 6.284 mg
	Atmosphere	1, N_2; 2, 5% (volume) O_2 in N_2; 3, 10% (volume) O_2 in N_2; 4, 20% (volume) O_2 in N_2
	Flow rate of carious gas	200 mL/min
Interface	Transfer line temperature	210 °C
	Cell temperature	210 °C
FTIR	No. of scans	16
	Resolution	4
	Collection start	Beginning at 150 °C of TG instrument
	Collection time	85 min

monitored with thermogravimetric Fourier transform infrared (TG-FTIR) spectroscopy.

2. Experimental

2.1. Materials

The reconstituted tobacco sheets used in this study were collected from France (LTR, Le Mans) and China (Hangzhou, Guangdong and Yunnan), respectively. The raw materials consisted essentially of fines, stems and midribs, with a much greater percentage of stems and midribs than occurs in the whole tobacco leaf. These sheets were produced by a paper making process [10], which typically resulted in loss of natural constituents of the tobacco. In this study, the additive included in the sheet is $CaCO_3$, and its obvious peak is seen in the DTG curve. Other non-tobacco components and additives are not discussed because of their unresolved peaks in the DTG curve. The percentages of $CaCO_3$ in the sheets form China were 3–5% (dry weight), and from Le Mans they are up to 9–10% (dry weight). Samples were ground to pass through an 80 mesh screen to provide increased homogeneity for comparative purposes, prior to analytical experiments.

2.2. Experiment apparatus

The TG-FTIR instrument consists of a thermogravimetric analyzer (Pyris Diamond TG/DTA, Perkin-Elmer Instrument Co. Ltd., USA) coupled to a FTIR spectrometer (Magna-IR 560, Nicolet Instrument Co., USA) by a thermogravimetric analysis interface (Nicolet Instrument Co., USA). The experimental conditions of TG-FTIR analysis are shown in Table 1. The conditions inside the burning zone of a cigarette are well defined, including temperature, heating rate, O_2 levers, gas flow conditions and so on [5]. In this study, the conditions of temperature and O_2 levers were simulated. However, the heating rate inside the cigarette (up to hundreds of degrees per second) was too fast to simulate for a TG/DTA instrument. So a normal TG/DTA heating rate (5 °C/min) was adopted in our experiments, as given in Table 1.

3. Results and discussion

3.1. Typical TG, DTG and DTA curves of reconstituted tobacco sheet

Shown in Fig. 1 are typical thermal analysis curves of the reconstituted tobacco sheet from Hangzhou in the atmosphere of 5% (v/v) O_2 in N_2. In the TG curve, there were two obvious decreases and an unobvious one at temperature <500 °C, which corresponded to the two strong peaks and a shoulder in the DTG curve, respectively. There were also two illegible declines at temperature >500 °C, which also corresponded to the two low peaks in the DTG curve, respectively. A shoulder and four peaks at 180, 292, 439, 642 and 778 °C, respectively, were observed in the DTG curve. The shoulder at 180 °C is attributed to the pyrolysis of simple sugars in reconstituted tobacco sheet [6]. The peak at 292 °C is due to the thermal decomposition of cellulose, which is a major constituent of reconstituted tobacco sheet [6,11]. The peak at 439 °C is due to the combustion of the residual char of polysaccharides (such as cellulose, hemicellulose, lignin, etc.) and other

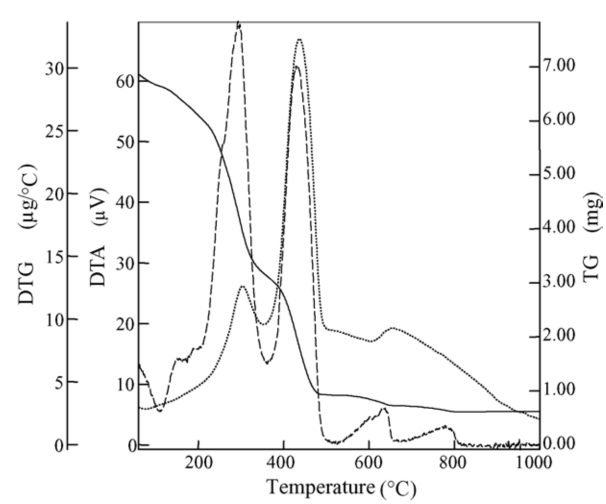

Fig. 1. Typical TG, DTG and DTA curves of the reconstituted tobacco sheet from Hangzhou in the atmospheres of 5% (volume) O_2 in N_2 at the heating rate of 5 °C /min. TG curve (——), DTG curve (– –), DTA curve (·······).

organic compounds (such as protein and amino acids) [6]. The peaks at 642 and 778 °C are attributed to the thermal decomposition of $CaCO_3$ and other salts, respectively. The DTA curve also showed two peaks at 304 and 438 °C, respectively, in the atmosphere of 5% O_2 in N_2, which are due to the exothermic oxidative reaction of the constituents in reconstituted tobacco sheet.

3.2. TG and DTG curves of reconstituted tobacco sheet in different atmospheres

TG and DTG curves of the reconstituted tobacco sheet from Hangzhou in different atmospheres are shown in Fig. 2. Data in an atmosphere of 10% O_2 in N_2 are not shown here. In the DTG curves, it is clearly seen that the thermal decomposition peaks of the reconstituted tobacco sheet shifted to lower temperature with the increase of O_2 content in the atmospheres. The reason for these phenomena is that the higher content of O_2 could accelerate the oxidation of reconstituted tobacco sheet. The magnitude of the peak at about 430 °C increased rapidly when the O_2 content in the atmosphere was increased from 0 to 20%. The reconstituted tobacco sheet burned when the atmosphere of 20% O_2 in N_2 was adopted. In addition, the DTG curve in N_2 showed more resolution, there was a shoulder at 258 °C, which was due to the thermal decomposition of hemicellulose and/or pectin [6,11]. However, it was not found in the atmosphere of 5 or 20% O_2 in N_2.

3.3. DTA curves of reconstituted tobacco sheet in different atmospheres

Shown in Fig. 3 are DTA curves of the reconstituted tobacco sheet from Hangzhou in different atmospheres. In the atmosphere of N_2, the DTA curve showed no peaks. However, the curvature of the curve may indicate that there was some heat transfer, most likely due to the thermal decomposition

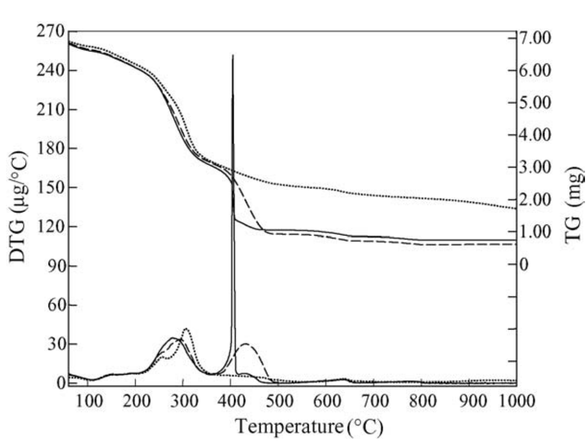

Fig. 2. TG and DTG curves of the reconstituted tobacco sheet from Hangzhou in different atmospheres at the heating rate of 5 °C/min. Atmosphere: N_2 (·······), 5% (volume) O_2 in N_2 (– –), 20% (volume) O_2 in N_2 (——).

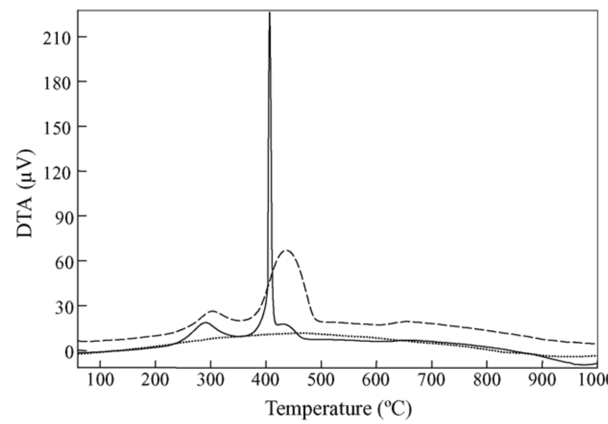

Fig. 3. DTA curves of the reconstituted tobacco sheet from Hangzhou in different atmospheres at the heating rate of 5 °C/min. Atmosphere: N_2 (·······), 5% (volume) O_2 in N_2 (– –), 20% (volume) O_2 in N_2 (——).

process seen in the TG and DTA curves in Fig. 2. In the atmosphere of 5% O_2 in N_2, two peaks appeared at 304 and 438 °C, respectively, indicating exothermic combustion with O_2. Along with the increase of O_2 content in the atmospheres, the peaks indicate exothermic combustion shifted to lower temperature. These tendencies were similar for the DTG curves in Fig. 2. In the atmosphere of 20% O_2 in N_2, there was a sharp peat at 407 °C, indicating the combustion of the residual char of polysaccharides (such as cellulose, hemicellulose, lignin, etc.) and other organic compounds (such as protein and amino acids). From the areas of the peaks in the DTA curves, it may be deduced that heat was mainly produced by the combustion of the residual char and other organic compounds, although the peaks in the DTA curve are not quantitative.

3.4. Comparison of the thermal decomposition of different reconstituted tobacco sheets

The peak temperatures of different reconstituted tobacco sheets in the DTG curves in different atmospheres are listed in Table 2. In the atmosphere of N_2, the temperature of thermal decomposition of cellulose (peak 1) in the reconstituted tobacco sheet from Yunnan was higher than the others. In the atmospheres of 5 and 20% O_2 in N_2, the temperatures of peak 1 of different reconstituted tobacco sheets were similar. The temperatures of the combustion of the residual char and other organic compounds (peak 2) in the reconstituted tobacco sheets from Hangzhou and Le Mans were lower, and those from Guangdong and Yunnan were higher. With some exceptions, in the atmospheres used the thermal decomposition temperatures of the reconstituted tobacco sheet from Yunnan were higher, and those from Le Mans were lower. Salts will typically lower the decomposition temperature for cellulosic materials and possibly alter the product distribution [6]. The percentages of $CaCO_3$ in sheets form China were 3–5% (dry weight), and from Le Mans is up to 9–10% (dry weight). The lower thermal decomposition temperatures

Table 2
The peak temperatures of different reconstituted tobacco sheets in DTG curves in different atmospheres

	N_2	5% (volume) O_2 in N_2		20% (volume) O_2 in N_2	
	Peak 1[a] (°C)	Peak 1[a] (°C)	Peak 2[b] (°C)	Peak 1[a] (°C)	Peak 2[b] (°C)
Hangzhou	306	292	439	280	406
Guangdong	306	296	453	280	439
Yunnan	312	295	457	282	434
Le Mans	308	291	433	280	421

[a] The thermal decomposition of cellulose in the reconstituted tobacco sheet.
[b] The combustion of the residual char of polysaccharides (such as cellulose, hemicellulose, lignin, etc.) and other organic compounds (such as protein and amino acids) in the reconstituted tobacco sheet.

of the reconstituted tobacco sheet from Le Mans may be due to the higher contents of salts in it. The specific reasons for the above differences were not clear, however, they could be attributed to the materials and the methods used in the production of the sheets [10].

3.5. *Carbon dioxide profiles of reconstituted tobacco sheet during heating*

Carbon dioxide is a major thermal decomposition product of reconstituted tobacco sheet. Shown in Fig. 4 are carbon dioxide profiles of the reconstituted tobacco sheet from Hangzhou generated during heating. In the atmosphere of N_2, there were two CO_2 peaks at about 265 and 315 °C in the profile, respectively. These two peaks should be due to the thermal decomposition of hemicellulose (and/or pectin) at 258 °C and cellulose at 306 °C, respectively (Fig. 2) [11]. In the atmosphere of 5% O_2 in N_2, two CO_2 peaks at about 310 and 445 °C, respectively, were found in the profile. The peak at about 310 °C was due to the pyrolysis of polysaccharides (cellulose, hemicellulose, etc.) in the reconstituted tobacco sheet, and the peak at about 445 °C should be attributed to the thermal decomposition of the residual char of polysaccharides (such as cellulose, hemicellulose, lignin, etc.) and other organic compounds (such as protein and amino acids) in the reconstituted tobacco sheet (Fig. 2) [11]. In the atmosphere of 20% O_2 in N_2, the thermal decompositions of the main constituents in the reconstituted tobacco sheet were similar

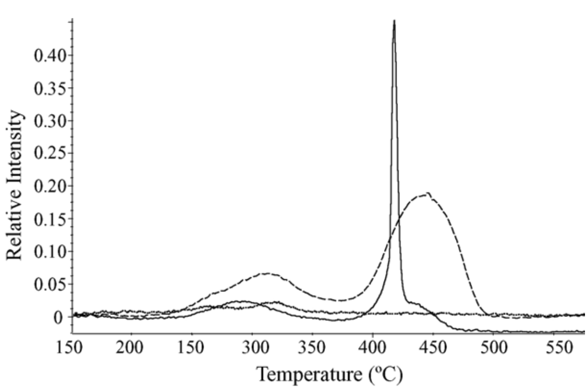

Fig. 4. The CO_2 profiles of the reconstituted tobacco sheet from Hangzhou in different atmospheres. Atmosphere: N_2 (·······), 5% (volume) O_2 in N_2 (– –), 20% (volume) O_2 in N_2 (——).

to those in the atmosphere of 5% O_2 in N_2. The profile of CO_2 in the atmosphere of 20% O_2 in N_2 was also similar to that in the atmosphere of 5% O_2 in N_2. However, the positions and intensity of the CO_2 peaks in the two atmospheres were different. In the atmosphere of 20% O_2 in N_2, the CO_2 peaks appeared earlier, and the CO_2 peak at about 415 °C was sharp. By the areas of peaks (although they were not quantitative), it may be deduced that CO_2 was mainly produced by the oxidation of the residual char of polysaccharides and other organic compounds (peak at 406 °C in Fig. 2).

The CO_2 profiles of the reconstituted tobacco sheets from Guangdong, Yunnan and Le Mans were similar to those from Hangzhou. A little CO_2 was released in the atmosphere of N_2, most CO_2 was observed during the combustion of reconstituted tobacco sheet in the oxidative atmospheres. The process of CO_2 production was strongly affected by the atmosphere.

4. Conclusions

Based on the above study, the following conclusions can be drawn:

1. The thermal decomposition pathways and the CO_2 profiles of different reconstituted tobacco sheets were similar.
2. The existence of O_2 could strongly affect the thermal decomposition of reconstituted tobacco sheet. Oxygen can accelerate the thermal decomposition of reconstituted tobacco sheet, and can oxidize the residual char of polysaccharides.
3. In an oxidative atmosphere, carbon dioxide was mainly produced by the oxidation of the residual char of polysaccharides and other organic compounds in reconstituted tobacco sheet.
4. Simulation of smoking conditions (atmosphere, heating rate, etc.), under which cigarette burns and smolders, should be the direction of a future study of primary tobacco constituents.

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