

## ARTICLE

# Influence of Ammonium Polyphosphate on Thermal Decomposition of Reconstituted Tobacco and CO Evolution

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(Dated: Received on December 4, 2013; Accepted on January 10, 2014)

The thermal behaviors and burning characteristics of reconstituted tobacco (RT) are strongly related with evolved gaseous products. The effect of ammonium polyphosphate (APP) as an additive of RT on the pyrolysis behavior and CO evolution was studied, emphasizing the role of heating velocity in reducing CO delivery of the mainstream smoke by APP. Thermogravimetric analysis (TGA) was employed to investigate the influence of APP on RT thermal behavior. Slow and flash pyrolysis of RT were compared to discuss the role of heating rate in decreasing CO by APP. TGA results demonstrated that, in dependence on APP concentration, APP influenced exothermal amount and weight loss rate during RT thermal decomposition, promoted the formation of char and retarded the thermal decomposition of RT. In addition, APP had a considerable influence on the evolution of gaseous products during thermal decomposition of RT. Both CO delivery per cigarette and that per puff in the smoking process were significantly reduced in dependence on APP content in RT. Comparative analysis of CO evolution patterns in the flash and slow pyrolysis elucidated that heating rate played a key role in decreasing CO evolution by APP. The results suggest that APP is a potential burning additive for controlling CO delivery in mainstream smoke of RT.

**Key words:** Thermal decomposition, Reconstituted tobacco, Ammonium polyphosphate, CO

## I. INTRODUCTION

Reconstituted tobacco (RT) is used to improve smoke chemistry and taste quality, and serves as a utilization of tobacco dust discarded in factories for cost reduction. Introduction of RT in a cigarette leads to a reduction of benzo[*a*]pyrene, nicotine, phenols, and polyaromatic hydrocarbons in the smoke particulate matter [1–3]. Due to higher level of CO in mainstream smoke of RT [1], CO delivery in mainstream smoke of cigarette is rarely influenced by RT. There is a growing interest in reducing CO delivery of RT.

During the combustion processes of tobacco, CO is formed from the thermal decomposition, tobacco reaction with atmospheric oxygen, and the secondary reaction of primary products such as carbon dioxide and water [4]. The contributions of pyrolysis and combustion to the formation of CO are found to be approximately 1/3 and 2/3, respectively [5]. Many chemical burning additives, such as potassium organic salts [6],

nano-sized Fe<sub>2</sub>O<sub>3</sub> [7], and mesoporous MCM-41 materials [8], were added to cigarette to modify the thermal behavior, burning characteristics and reduce CO in smoke. However, to our knowledge, there is little information on the change of thermal behavior of RT by chemical burning additives and subsequent influence on evolved gas.

Ammonium-containing phosphates have commonly been used in the manufacture of RT and other processed tobaccos for flavoring, process conditioning and reduction of harshness and irritation [9]. It is noteworthy that ammonium-containing phosphate can also be used as flame retardants to modify thermal behaviors of biomass and evolution patterns of pyrolysis gaseous products [10–12]. In our previous work, it has been demonstrated that urea phosphate can modify the thermal behaviors and burning characteristics of RT, and decrease CO level in smoke [13]. Recently we found that ammonium polyphosphate (APP) modified thermal degradation and combustion behaviors of RT [14]. In this work, we pay main attention to determining whether CO delivery in mainstream smoke of RT varies in dependence on APP concentration and discussing the mechanism of CO removal by APP.

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## II. EXPERIMENTS

### A. Materials

RT was produced by a paper making process [15]. The samples were collected from a commercial RT factory in China. APP with an average degree of polymerization  $n > 1000$  was provided by Hangzhou JLS Flame Retardants Chemical Corporation, China.

### B. Sample preparation

Aqueous suspensions of APP (60 mL) were sprayed on 400 g samples of the cut RT, which was designed to provide the controlled APP contents in the samples between 2.5% and 10% (dry sample basis). The control sample was sprayed with 60 mL of water. The samples were then dried for about 20 min at 45 °C. Samples were grounded to pass through an 80 mesh screen to provide increased homogeneity for comparative purposes, prior to pyrolysis experiments. For analytical experiments of mainstream smoke, the samples were conditioned and made sample into a series of cigarette with identical design features. After conditioning at 22 °C, 60% R.H., each sample was selected by weight to keep the fractional volume of the cigarettes constant.

### C. Measurements

#### 1. Thermogravimetry and differential scanning calorimetry

RT samples were subjected to non-isothermal thermogravimetric analysis (TGA) using a Netzsch STA 449C TG/DSC. Samples of approximate 20 mg were placed in a standard aluminum pan and heated at a rate of 20 °C/min, with temperature varying from 40 °C to 1000 °C. All tests were carried out in the atmosphere of 10% oxygen in nitrogen with a gas flow rate of 100 mL/min. Procured  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> was used as the reference material.

#### 2. TG-FTIR analysis

The TG-FTIR instrument consists of a thermogravimetric analyzer (Netzsch, STA 449C) coupled with a Fourier-transform infrared (FTIR) spectrometer (Thermo Scientific, 6700 FT-IR, Nicolet Instrument Co., USA) by a thermogravimetric analysis interface (Nicolet Instrument Co., USA). The pyrolysis conditions of TG-FTIR analysis were identical with that of TG-DSC. The lines that transferred the evolved gases from the TGA to the FTIR and the IR cell were maintained at 225 and 230 °C, respectively. The FTIR was operated in the continuous scan mode covering 4000–500 cm<sup>-1</sup> at a resolution of 4 cm<sup>-1</sup> for the analysis of evolved gases.

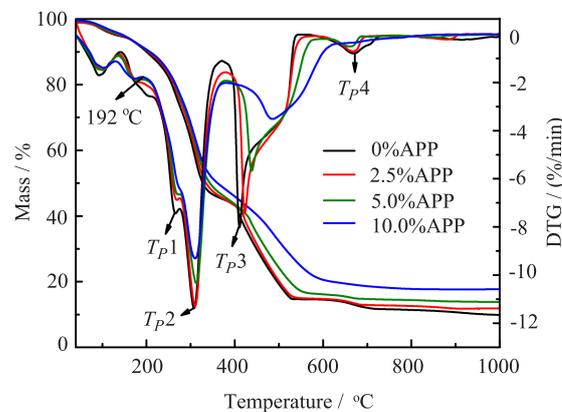


FIG. 1 Effect of APP on TG and DTG curves of RT.  $T_P$  represents temperature at the maximum decomposition rate of RT.

#### 3. Flash pyrolysis-FTIR analysis

Due to the very fast heating rate [16], flash pyrolysis (FPY) of RT was performed to simulate the heat rate during cigarette puffing. The experimental pyrolysis system and pyrolysis procedure was similar to that described previously [13]. Temperatures up to 950 °C were generated when the cigarette was puffed [4], therefore 950 °C, mimicking the temperature inside the cigarette burning zone, was set to investigate the influence on CO. When the pyrolysis conditions in the tube reached the desired value, about 60 mg sample placed in the quartz boat was rapidly pushed to the flat-temperature zone by the step-pushing pod, and the FTIR, operation parameters identical with that of TG-FTIR analysis, was immediately operated to analyze evolved gases. The residence time was 5 min.

#### 4. Cigarette smoking

A Borgwaldt RM20 machine was employed for cigarette smoking following International Standard (ISO) recommendations [17–19]. The vapor phase of mainstream smoke was channeled into a polyethylene bag connected to a non-dispersive infrared CO analyzer for the measurement of CO in the mainstream smoke [20].

## III. RESULTS AND DISCUSSION

### A. Effects of APP on TG and DTG curves of RT

TG and DTG of RT treated with varying concentrations of APP are presented in Fig.1. The temperature of the maximum weight loss rate ( $T_P$ ) of every peak was obtained from the DTG curve. The mid-point temperature of the degradation ( $T_{-50\%}$ ) and the solid residue left at 1000 °C were obtained from the

TABLE I Thermal decomposition characteristics of untreated and APR treated RT\*.

Sample	$T_{P1}/^{\circ}\text{C}$	$T_{P2}/^{\circ}\text{C}$	$T_{P3}/^{\circ}\text{C}$	$T_{P4}/^{\circ}\text{C}$	$T_{-50\%}/^{\circ}\text{C}$	Residual mass <sup>a</sup> /%
Untreated	265.9	307.8	410.8	669.6	327.7	9.9
2.5%APP	268.9	310.3	422.9	667.3	335.2	11.8
5.0%APP	*	313.0	438.4	661.5	343.8	13.8
10.0%APP	*	310.4	485.6	*	361.2	17.7

\*  $T_P$ : temperature at the maximum decomposition rate of RT,  $T_{-50\%}$ : temperature of 50% weight loss.

<sup>a</sup> Residual mass at 1000 °C.

\* Peaks were too small to be determined.

TG curve. The thermal decomposition characteristic parameters are listed in Table I.

As shown in Fig.1, the typical thermal degradation process of RT could be divided into five stages, which was consistent with our previous work [13]. The first stage took place in the temperature range of 40–145 °C with a light weight loss of 5.5%, due to the loss of absorbed water and volatile species. The other four stages occurred between 145 and 725 °C corresponding to the four peaks in the DTG curve at 265.9, 307.8, 410.8, and 669.6 °C, respectively. The four stages may be attributed to the thermal decomposition of cellulose, the combustion of the residual char, and the thermal decomposition of  $\text{CaCO}_3$  and other salts.

The thermal oxidative decomposition of RT treated with APP shows some similarities but also several differences from that of untreated RT (see Fig.1 and Table I). The illegible low peak, around 266 °C, gradually disappeared with the increase of APP addition. The temperature of the first strong peak in DTG curve ( $T_{P2}$ ) varied independently APP concentration (Table I), but corresponding maximum weight loss rate (WLR<sub>max</sub>) gradually decreased with the addition of UP (Fig.1). In dependence on APP concentration, the temperature of the second strong peak ( $T_{P3}$ ) increased rapidly and corresponding WLR<sub>max</sub> declined. Furthermore, both the value of  $T_{-50\%}$  and residual mass at 1000 °C significantly increased with APP concentration. These results imply that APP improves the thermal stability of RTS, enhances char formation and hinders the combustion of residue char. The high efficiency of phosphorus fire-retardants has been suggested to be the result of acidic degradation products which then promote the formation of non-porous insulating char [21].

## B. Effect of APP on DSC curves of the RT sheet

Differential scanning calorimetry (DSC) results with the influence of APP on the pyrolysis of RT are shown in Fig.2. APP had considerable influence on the two strong exothermic peaks of RT, especially the secondary exothermic peak. The secondary exothermic peak, attributed to the combustion of the residual char, gradu-

TABLE II Influence of APP on CO delivery in mainstream smoke of RT.

Parameter	$P^a$	Carbon monoxide	
		mg/cig.	mg/puff
Untreated	5.14 (0.04)	15.17 (0.19)	2.95
Treated	2.5%	6.17 (0.06)	11.73 (0.15)
	5.0%	8.37 (0.08)	10.29 (0.21)

Note: number in parenthesis is a standard deviation of three measurements.

<sup>a</sup> Puffs per cigarette.

ally shrunk with the increase of APP content in RT, although the peak in the DSC curve was not quantitative (Fig.2). The result fits the experimental data of TG and DTG, confirming APP inhibits the combustion of char. Moreover, the temperature at the end of combustion of residue char became progressively higher with the increase of APP addition (Fig.2). Therefore, it can be said that the addition of APP affected the oxidation of chars. The result further confirmed the fire retardant performance of APP.

## C. Influence of APP addition on CO in mainstream smoke of RT

CO in cigarette smoke is mainly formed by thermal decomposition of tobacco and reaction of tobacco with atmospheric oxygen [22]. CO delivery in mainstream smoke of RT is studied to investigate the role of APP treatment in reduction of CO. As shown in Table II, APP treatment significantly influences the CO level in mainstream smoke. 2.5% and 5.0% APP reduced 22.68% and 32.17% CO content per cigarette respectively (RT sample added by 10.0% APP self-extinguished and CO delivery could not be determined). The reduction rate of CO per cigarette in mainstream smoke was proportional to the APP content in RT. What's more important, the reduction rate of CO per puff by APP was significantly higher than that of CO per cigarette, for example 5.0% APP treatment reduced 58.30% CO content per puff. Therefore APP is a potential burning additive to reduce CO delivery in main-

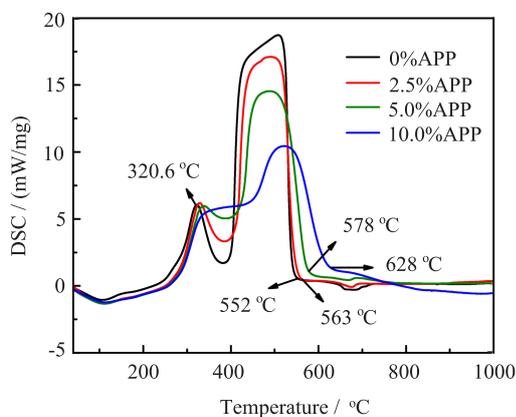


FIG. 2 Effect of APP addition on DSC curves of RT.

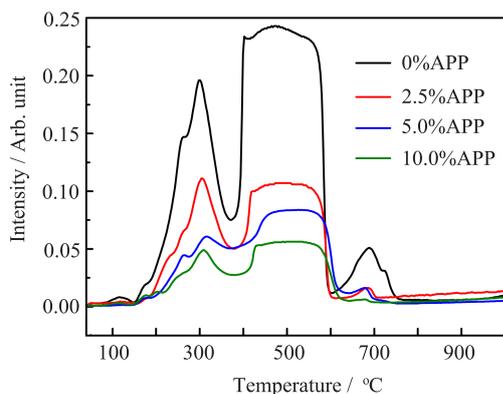


FIG. 3 The influence of APP on the Gram-Schmidt curves of the total FTIR absorbance intensity of evolved gases versus temperature gotten during the pyrolysis of RT.

stream smoke of RT.

#### D. Effects of APP on evolution patterns of pyrolysis gaseous products

Figure 3 shows the Gram-Schmidt curves of the total FTIR absorbance intensity of gaseous products during the pyrolysis of RT by TG-FTIR. Gaseous products evolution during the pyrolysis of untreated RT had three main unresolved peaks in the temperature range of 148–372, 372–602, and 602–760 °C, respectively. The absorbance intensity of the three peaks were considerably reduced with the addition of APP and the third peak faded away with the increase of APP content, especially 10.0% APP. These results indicate that APP is one of high efficient burning additives which control the gas evolution during RT thermal degradation. Comparison of Gram-Schmidt curve with TG and DTG curves indicated that the evolution patterns of gaseous products were consistent with the weight loss process of RT thermal degradation and that the profile of gases evolution coincided with that of DTG curve. These

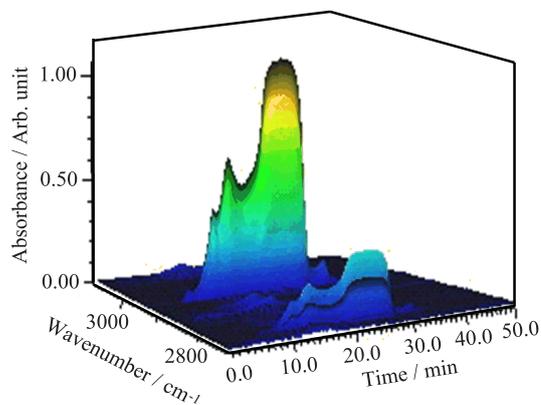


FIG. 4 The 3D surface graph for the FTIR spectra of the evolved gases produced by the pyrolysis of reconstituted tobacco.

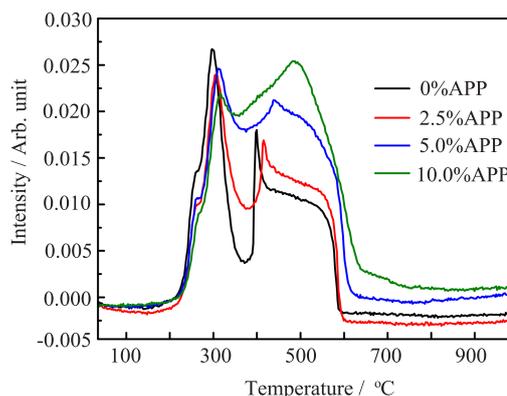


FIG. 5 The influence of APP treatments on CO evolution pattern in slow pyrolysis.

results suggest that the influence of APP on gaseous products is closely related with the change of RT thermal behavior by APP.

#### E. Effects of APP on evolution patterns of CO in slow pyrolysis

The typical 3D spectral output from the TG-FTIR analysis is shown in Fig.4, known as a waterfall spectrum. As can be observed, there are some main absorption regions (*i.e.* 3780–3485, 3100–2770, 2400–2224, 2220–2000, 1900–1600, 1600–1500, 1500–1300, 1100–930, and 760–590  $\text{cm}^{-1}$ ) in the 3D FTIR spectrum, indicating that the pyrolysis process of RT is complicated. Although it is difficult to identify every species in the mixture of gas products for the interference of their IR absorbance, the characteristic peaks of CO at 2180 and 2108  $\text{cm}^{-1}$  is undoubted [23]. CO evolution profiles, shown in Fig.5, were constructed from the waterfall spectra by selecting a key characteristic IR absorbance of CO. The profiles have been normalized to the sample weight (intensity per 60 mg of sample), so the comparisons for the influence

of APP treatment can be made on the relative amount of CO.

There are two temperature ranges of 216–376 and 376–600 °C in CO evolution (Fig.5). As shown in Fig.5, APP had a slight effect on the first peak of CO evolution regardless of the amount of APP, while the second peak of CO evolution varied systemically in dependence on the APP content in RT. From the areas of the peaks in the CO evolution curves, it is deduced that APP mainly enhances the CO evolution during the combustion of the residual char. However, it is noteworthy that the influence of APP on CO evolution in thermal gravimetric analysis is contrary with that of APP addition on CO delivery in mainstream smoke of RT. The difference in CO formation during slow pyrolysis and puffing process may be due to heating rates [24]. It is well known that heating rates as high as 500 K/s are achieved during puffing [4]. However, 20 K/min was employed in thermal gravimetric analysis. A possible explanation for the contrary effect of APP in slow pyrolysis and puffing process is that, during slow heating, the formation of non-porous particles in the presence of APP is probably limited, while during fast heating the process is extensive and the oxidation of char is inhibited.

#### F. Effects of APP on evolution patterns of CO in the flash pyrolysis

In order to investigate the role of heating rate in decreasing the CO delivery of mainstream smoke by APP, the pyrolysis conditions occurring in the flash pyrolysis experiments were performed to simulate the heating rate during cigarette puffing. As shown in Fig.6, the peak of CO evolution during the flash pyrolysis gradually shrunk with the increase of APP content in RT. From the total peak area of CO, it could be said that APP decreased CO concentration during flash pyrolysis, which was consistent with effects of APP on CO level in mainstream smoke of RT but contrary to that in slow pyrolysis. These results elucidated that the heating rate was one of the most important factors in decreasing CO amount by APP. This phenomenon is similar to the findings in the study of reducing CO evolution by urea phosphate [13].

#### IV. CONCLUSION

In this work, APP was evaluated for its potential as CO reduction additive of RT and the mechanism of CO removal by APP were discussed. Pyrolysis tests revealed that APP decreased weight loss rate of RT, enhanced the formation of char and retarded thermal behaviors of RT depending on APP concentration. Furthermore, DSC curves were influenced by APP, especially the secondary exothermic peak, which confirmed fire retardant efficacy of APP.

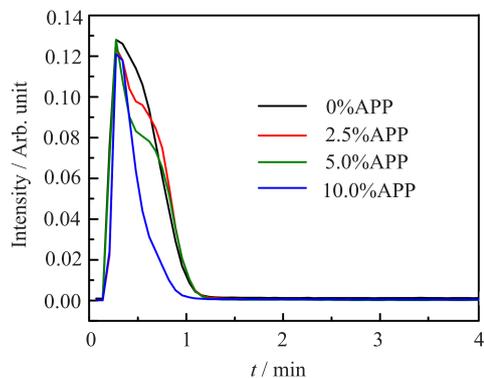


FIG. 6 The influence of APP treatments on CO evolution pattern in flash pyrolysis.

The Gram-Schmidt curves of the total FTIR absorbance intensity of gaseous products indicated that, as a highly efficient burning additive, APP significantly inhibited the evolution of pyrolysis gaseous products during RT thermal degradation. CO delivery per cigarette in mainstream smoke was gradually reduced proportionally to the APP content in RT. What's more important, comparative analysis of CO evolution patterns in the flash and slow pyrolysis elucidated that the heating rate was one of the most important factors in decreasing CO evolution by APP. APP enhanced the formation of non-porous particles in flash pyrolysis and puffing process hindering the oxidation of char and subsequently inhibited the CO evolution.

#### V. ACKNOWLEDGMENTS

This work was supported by China Tobacco Anhui Industrial Corporation (No.20121006 and No.20091002) and China National Tobacco Corporation (No.110200901002).

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