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Investigation on the effects of fire retardants on the thermal decomposition of wood-derived rayon fiber in an inert atmosphere by thermogravimetry–mass spectrometry

Qingfeng Liu, Chunxiang Lv*, Yonggang Yang, Fu He, Licheng Ling

Key Laboratory of Carbon Materials, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, PR China

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Abstract

The effects of three retardants, NH_4Cl, $(NH_4)_2SO_4$ and $NH_4H_2PO_4$, on the thermal decomposition of wood-derived rayon fiber have been investigated by thermogravimetry–mass spectrometry (TG–MS) analysis. The main thermal decomposition of pure wood-derived rayon fiber, like other cellulosic materials, takes place rapidly over a narrow temperature range. When wood-derived rayon fiber is impregnated with the fire retardants, there is a shift in the temperature of maximum rate of weight loss to the values lower than 300 °C, while the amount of char residue formed is increased. The fire retardants have resulted in the increase of the intensity (peak area) of $m/z = 18$ and 28 MS signals, but the decrease of the intensity of $m/z = 44$ MS signals. Furthermore, it appears with a relative decrease of the intensity of $m/z = 60$ and 68 MS signals, which means that low levels of levoglucosan and levoglucosenone are recorded in the presence of the fire retardants. Finally, the relationship between char residue formation and the relative quantity of levoglucosan is determined.

Keywords: Wood-derived rayon fiber; Fire retardant; Decomposition; TG–MS

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1. Introduction

Although decades of research on cellulosic materials have generated a wealth of knowledge and understanding on the thermal degradation and chemical kinetics of these materials, the kinetics and mechanisms of cellulose pyrolysis reactions are not completely known, probably because of the complex nature of cellulose pyrolysis, which involves a large number of reactions [1–4]. Furthermore, there are extensive publications dealing with thermal decomposition of various cellulosic materials, but less attention is paid to the thermal decomposition of wood-derived rayon fiber untreated and treated by fire retardants.

According to the most commonly accepted Broide–Shafizadeh mechanism [1–4], at low temperatures, a reduction in the degree of polymerization of cellulose with only a small weight loss takes place, leading to the formation of the so-called "anhydrocellulose" or active cellulose. At higher temperatures, the decomposition proceeds in two competing pathways. The first pathway dominates at temperatures below 300 °C, including dehydration, rearrangement, formation of carbonyl and carboxyl groups, evolution of water, carbon dioxide, carbon monoxide, and formation of char residue. The second pathway involves a depolymerization of cellulose by end group depolymerization, which yields primarily volatile tarry products containing levoglucosan, with minor contribution of other anhydromonosacharites.

Cellulose and regenerated cellulose treated with various inorganic compounds have been reported to catalyze the dehydration reaction and thus, to enhance the first pathway [5,6]. In this way, the evolution of H_2O, CO_2 is increased at the expense of flammable volatiles and thus, the flammability is decreased. Furthermore, the increased amount of char residue formed from the first pathway acts as a thermal barrier, reducing heat transfer to the interior, and also obstructing the outward flow of combustible gases and thus, reducing the extent of cellulose decomposition.

It has be reported that $(NH_4)_2SO_4$ and $(NH_4)_2HPO_4$, as effective fire retardants can shift the decomposition temperature (temperature corresponding to the maximum weight

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* Corresponding author. Tel.: +86-351-7560941; fax: +86-351-7560941.
E-mail address: lucx@sxicc.ac.cn (C. Lv).

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loss rate) to values of lower than 300 °C in order to enhance the first decomposition pathway and consequently increase the amount of char residue formed and non-flammable volatiles such as H_2O and CO_2 [4]. In addition, in the presence of the fire retardants relative low levels of levoglucosan are recorded and relative increases of levoglucosenone are observed [4]. However, when we have investigated the effects of the fire retardants such as NH_4Cl, $(NH_4)_2SO_4$, and $NH_4H_2PO_4$ on the decomposition of wood-derived rayon fiber by TG–MS analysis, we found some interesting phenomena somewhat inconsistent with those results.

The purpose of the present work is to provide a preliminary investigation on the decomposition of wood-derived rayon fiber untreated and treated with three retardants, NH_4Cl, $(NH_4)_2SO_4$, and $NH_4H_2PO_4$, respectively, by using the TG–MS technique. The criteria on TG–MS system performance in the present work are like those described in the previous work, e.g. a high-glow stability through the TG–MS system is necessary in order to ensure reproducible results [4]. Furthermore, the intensity of the MS signal should not be affected by the temperature increase in the TG furnace and the heating rate applied in the TG analysis.

2. Experimental

2.1. Preparation of sample

It is known that cellulose has altogether five types. Rayon fiber, which is a kind of regenerated cellulose, has cellulose II structure. In this work, the cellulosic material used is pure wood-derived rayon fiber, made in Belorussia. This rayon fiber has a degree of polymerization of 350–400, and contains less than 0.15% ash. In order to remove any adsorbed impurity, this wood-derived rayon fiber has been washed with warm distilled water, and then dried overnight in a vacuum environment.

All of the $(NH_4)_2SO_4$, NH_4Cl, and $NH_4H_2PO_4$ used are of p.a. grade (>99.0%) from BJ, TJ and CHD Chemical-Reagents Corp. in PR China, respectively. Impregnation with NH_4Cl, $(NH_4)_2SO_4$, and $NH_4H_2PO_4$, respectively, is carried out by immersing the rayon fiber in 1.0 mol/l warm solution of the corresponding fire retardant for 20 min, followed by overnight vacuum drying. Finally, there are around 0.15 mol fire retardant retained on per 100 g wood-derived rayon fibers.

2.2. Thermogravimetric–mass spectrometric analysis

The experiments were carried out like those descriptions in a previous work [7]. The thermogravimetric analyzer used was a model SETARAM TGA92 of France. The atmosphere used for pyrolysis was ultra high pure argon (99.999%) at a low pressure of 150 kPa. Approximately 10 mg sample was heated at 5 °C/min from ambient temperature up to 800 °C in the dynamic experiments. In order to obtain accurate results, the TG analyzer was calibrated using Alumel and Nickel Curie point standards.

The mass spectrometer consists of an MS OmniStar 200 of Switzerland Balzers Inc. with an ion source of electron impact at 70 eV electron energy. The connection between the thermobalance and the mass spectrometer is done by means of a stainless steel capillary, maintained at 150 °C. The intensities of the several selected ions are monitored. The MS intensities were normalized on the sample mass and the intensity of ^{38}Ar isotope of the flushing gas. It should be noted that the intensity data must not be compared between the different compounds due to the different sensitivities of the mass spectrometer. However, the intensity values of a given ion are comparable between the samples because they were normalized to the carrier gas and the sample mass [7].

3. Results and discussion

3.1. TG and DTG curves of pure wood-derived rayon fiber (designed as RW)

The dynamic gravimetric (TG and DTG) curves of the pure wood-derived rayon fiber (designed as RW) are shown in Fig. 1. The TG and DTG curves of RW are similar to the typical dynamic gravimetric curves of other cellulosic materials. The rate of weight loss of this material is very high at a narrow range of temperatures. Following a plateau region to 290 °C, the wood-derived rayon fiber rapidly decomposes between 300 and 350 °C, corresponding to a weight loss of around 84% at 350 °C. After this sharp weight loss, there is a gradual but constant weight loss (additional around 7% of starting material) up to 800 °C. The first derivative plot, DTG, indicates that the maximum rate of weight loss is at 335 °C. The “smooth” dynamic gravimetric curves indicate that the transition from char dominating to tar dominating reaction is gradual. In the pyrolysis of cellulosic materials, chars formed at lower temperatures have a higher aliphatic

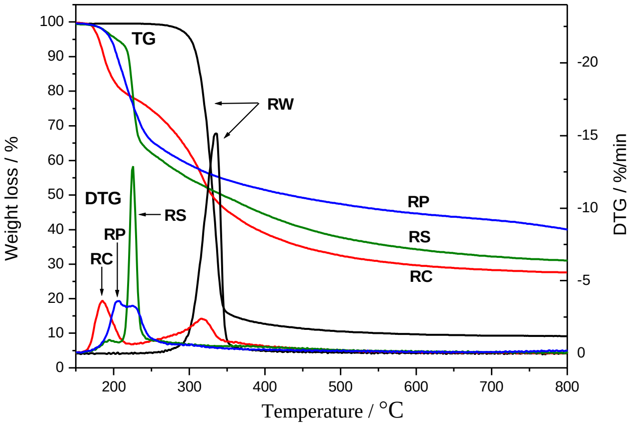

Fig. 1. TG and DTG curves of wood-derived rayon fiber untreated (RW) and treated with the fire retardants (RC, RS and RP).

content, and are more easily decomposed. This is a possible explanation of the slow but constant weight loss observed in Fig. 1 after the main decomposition step.

3.2. TG and DTG curves of wood-derived rayon fiber treated with NH_4Cl, $(NH_4)_2SO_4$ and $NH_4H_2PO_4$ (designed as RC, RS and RP, respectively)

The dynamic gravimetric curves of the wood-derived rayon fiber treated with NH_4Cl, $(NH_4)_2SO_4$ and $NH_4H_2PO_4$ (designed as RC, RS and RP, respectively) are also shown in Fig. 1. As mentioned earlier, the temperature of decomposition is shifted to lower side and the formation of char residue is increased due to the enhancement of the first decomposition pathway when the wood-derived rayon fiber is treated with the fire retardant materials. The DTG curve of RC presents two maximums, one at 186 °C and the other at 310 °C, indicating two steps in the decomposition reaction. Furthermore, the char residue is increased to 27.6% at 800 °C, while the maximum rate of the decomposition reaction is less than that of pure wood-derived rayon fiber. From the gravimetric curves of RS, it can be seen that the decomposition involves primarily one step at 230 °C, and the maximum rate of the decomposition reaction is higher than that of RC, in addition to there is a higher char residue of 31% at 800 °C. The DTG curve of RP presents one maximum around equal to that of RC, indicating one step in the decomposition reaction at around 227 °C. The weight loss continues at higher temperatures, but with a small rate, leading to a char residue of 40.0% at 800 °C.

It can be seen that NH_4Cl, $(NH_4)_2SO_4$, and $NH_4H_2PO_4$ are effective fire retardants for the decomposition of the wood-derived rayon fiber. These fire retardant materials can shift the decomposition temperature to values lower than 300 °C and decrease the maximum rate of weight loss, while increase the char residue formed. In conclusion, the four different samples have the following order of char residue formed: RW $<$ RC $<$ RS $<$ RP; order of decomposition temperature: RC $<$ RP $<$ RS $<$ RW; and order of maximum rate of weight loss: RC $\approx$ RP $<$ RS $<$ RW.

3.3. MS analysis of the decomposition of wood-derived rayon fiber untreated (designed as RW) and treated with NH_4Cl, $(NH_4)_2SO_4$ and $NH_4H_2PO_4$ (designed as RC, RS and RP, respectively)

In Figs. 2–6, the $m/z = 18$, 28, 44, 60 and 68 MS signals of wood-derived rayon fiber untreated (designed as RW) and treated with the fire retardants (designed as RC, RS and RP) are shown in arbitrary unit, respectively. The predominant ion observed is $m/z = 18$ (Fig. 2), which is attributed to water. The abundances of $m/z = 28$ (Fig. 3) and $m/z = 44$ (Fig. 4) ions have the same order magnitude, but an order of magnitude lower than that of $m/z = 18$ and two orders of magnitude higher than that of $m/z = 60$ (Fig. 5) or $m/z = 68$ (Fig. 6). It has been reported that the MS signal of $m/z = 44$

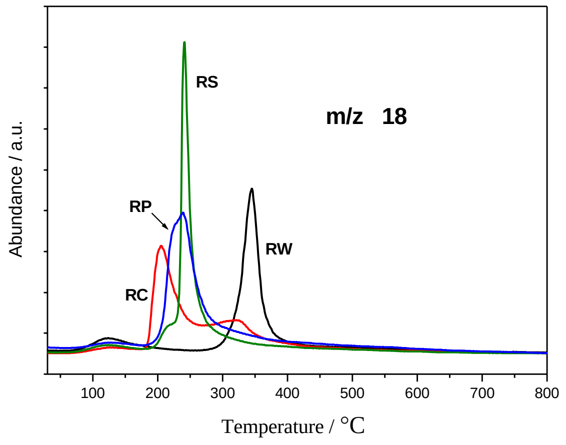

Fig. 2. MS response of $m/z = 18$ ion of TG–MS analysis of the decomposition of wood-derived rayon fiber untreated (RW) and treated with the fire retardants (RC, RS and RP).

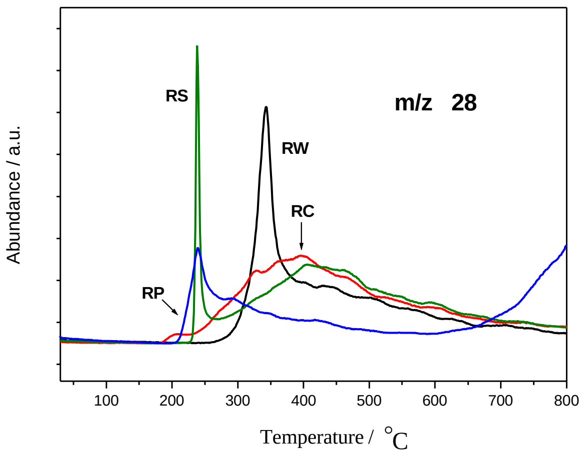

Fig. 3. MS response of $m/z = 28$ ion of TG–MS analysis of the decomposition of wood-derived rayon fiber untreated (RW) and treated with the fire retardants (RC, RS and RP).

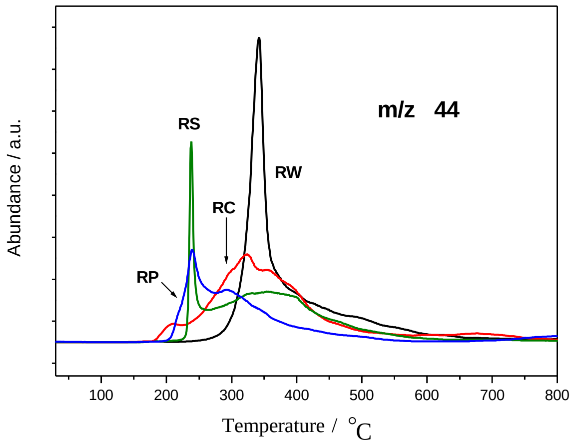

Fig. 4. MS response of $m/z = 44$ ion of TG–MS analysis of the decomposition of wood-derived rayon fiber untreated (RW) and treated with the fire retardants (RC, RS and RP).

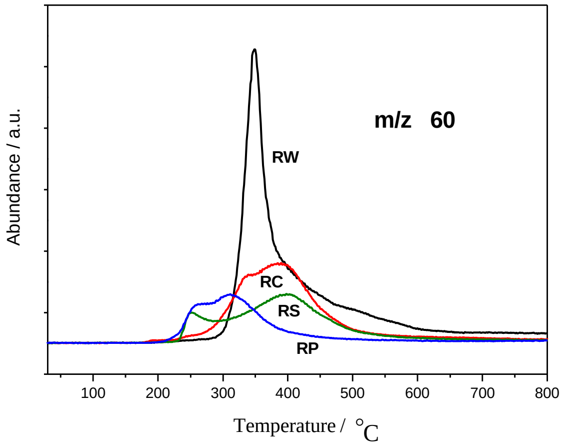

Fig. 5. MS response of $m/z = 60$ ion of TG–MS analysis of the decomposition of wood-derived rayon fiber untreated (RW) and treated with the fire retardants (RC, RS and RP).

increases again after 580 °C for pure cellulose [4]. However, we have not observed this phenomenon in the case of the wood-derived rayon fiber (RW). It is interesting that the ion of $m/z = 28$ observed increases again after around 585 °C for wood-derived rayon fiber treated by the fire retardant of $NH_4H_2PO_4$ compound (RP).

It should be noted that $m/z = 28$ is mainly due to CO and to a lesser extent aliphatic molecules in the pyrolysis of cellulosic materials. It is known that aliphatic molecules produce $m/z = 28$ and 27 ions in comparable amounts. However, the abundance of $m/z = 28$ is much higher than that of $m/z = 27$ (Fig. 7), indicating that the formation of aliphatic fragments is less significant in cellulosic materials decomposition. In the same way, $m/z = 44$ is mainly attributed to carbon dioxide, though $m/z = 44$ is, to an extent, due to the presence of acetaldehyde. Since double peaks separated by one mass unit are typical of aldehydes, and the abundance of $m/z = 43$ (Fig. 8) is much lower than that of $m/z = 44$, thus, $m/z = 44$ can be thought to mainly attribute to CO_2 in order

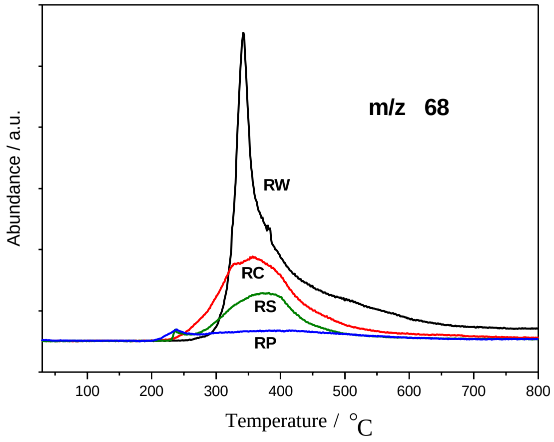

Fig. 6. MS response of $m/z = 68$ ion of TG–MS analysis of the decomposition of wood-derived rayon fiber untreated (RW) and treated with the fire retardants (RC, RS and RP).

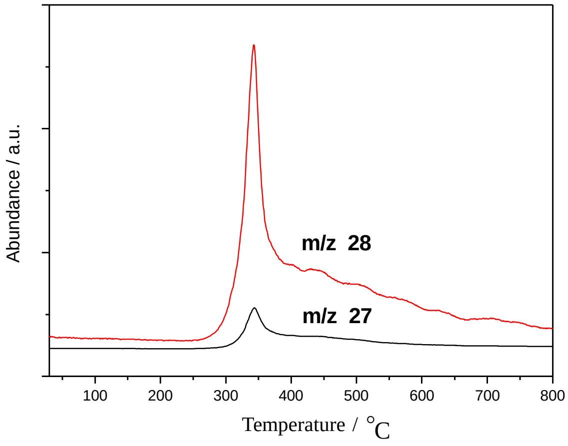

Fig. 7. MS response of $m/z = 27$ and 28 ion of TG–MS analysis of the decomposition of wood-derived rayon fiber untreated (RW).

to avoid complexity. Levoglucosan has primary ionization fragment ions of $m/z = 43$, 47, 57, 60, 70, 73, 98, and 144 [4,8,9]. Although $m/z = 60$ might also be attributed to the presence of acetic acid and to an extent, to the presence of hydroxyacetaldehyde, the ion of $m/z = 60$ is an indicator for levoglucosan [4,8]. Levoglucosenone is a major dehydration product of levoglucosan. Additionally, $m/z = 68$ is mainly attributed to levoglucosenone and can be regarded to be representative of levoglucosenone with ionization fragment ions of $m/z = 39$, 42, 52, 53, 68, 96, 98 and 126 [4,8].

In order to avoid complexity and conveniently compare relative quantities of volatiles, we have designed the relative intensity values (peak areas) of individual ions of the wood-derived rayon fiber (RW) as 100%, while the relative intensity values of individual ions of RC, RS and RP are based on those of corresponding ions of RW. As previously mentioned, although the intensity data must not be compared between the different compounds due to the different sensitivities of the mass spectrometer, the intensity values of a given ion are comparable between the samples because they were normalized to the carrier gas and the sample mass.

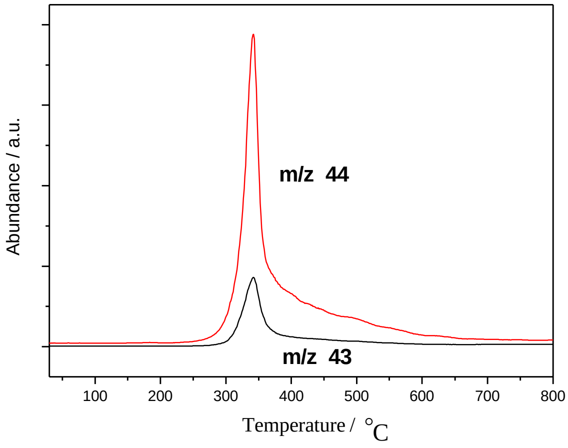

Fig. 8. MS response of $m/z = 43$ and 44 ion of TG–MS analysis of the decomposition of wood-derived rayon fiber untreated (RW).

Table 1
Relative peak areas of individual ions of the samples measured by TG–MS analysis

Ion (*m*/*z*)	RW (%)	RC (%)	RS (%)	RP (%)
18	100	106	104	138
28	100	112	114	101
44	100	88.2	69.9	56.5
60	100	58.3	42.8	31.3
68	100	56.1	30.6	14.7

Based on the intensity of corresponding individual ions of RW, which is designed as 100%.

Table 1 compiles the intensity values (peak areas) of individual ions for all the samples. It can be seen that the fire retardants of NH_4Cl, $(NH_4)_2SO_4$, and $NH_4H_2PO_4$ can result in the increases of the decomposition products such as H_2O ($m/z = 18$) and CO ($m/z = 28$). However, the intensity of $m/z = 44$ is decreased in the presence of the fire retardants, which is not consistent with those previous results [4]. In addition, it has been reported that a relative increase of $m/z = 68$ is observed, indicating that the evolution levoglucosenone is favored, while $m/z = 60$ was eliminated, meaning the decrease of levoglucosan [4]. But in this work, the intensity values of $m/z = 60$ and 68 are both observed to decrease for the decomposition of wood-derived rayon fiber in the presence of the fire retardant materials. Furthermore, the rate of intensity values of $m/z = 68$ versus $m/z = 60$ is also decreased, indicating that the decrease of $m/z = 68$ is sharper than that of $m/z = 60$. Clearly, all of the fire retardants of NH_4Cl, $(NH_4)_2SO_4$, and $NH_4H_2PO_4$ can reduce the formation of levoglucosan and levoglucosenone at the same time. Since $m/z = 60$ is an indicator for levoglucosan, thus, the peak area of $m/z = 60$ should present the relative quantity of levoglucosan. The relationship between char residue formation at 800 °C and the relative quantity of levoglucosan, which is based on that of pure wood-derived rayon fiber (designed as 100%), is shown graphically in Fig. 9. It can be seen that, if the formation of levoglucosan were equal to zero during the decomposition of wood-derived rayon fiber in the presence of the "best" effective fire retardant, the amount of char residue formation would be next to the theoretical value of 44.4%.

It is known that, in some case, MS signals arising from organic materials may be measured with lower precision than the MS signals of the inorganic materials. Nevertheless, this would only introduce a systematic error in the measurement of the amount of these volatiles evolved from the decomposition of the wood-derived rayon fiber, but it would not affect the conclusions resulting from the comparative study of these samples.

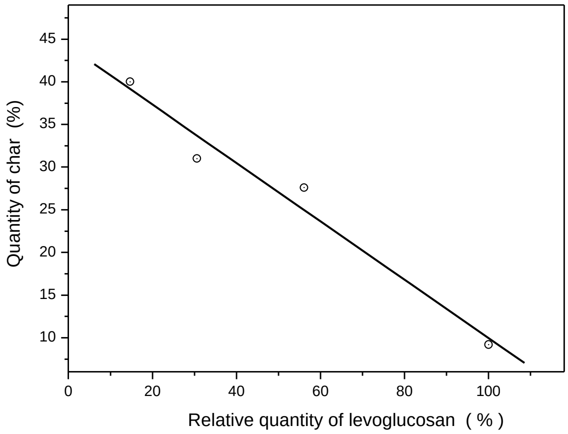

Fig. 9. Relationship of char residue formation and levoglucosan obtained by TG–MS analysis, based on the relative quantity of levoglucosan (designed as 100%) of RW.

4. Conclusions

The ammonium salts of NH_4Cl, $(NH_4)_2SO_4$, and $NH_4H_2PO_4$, as effective fire retardants, can shift the decomposition temperature of the wood-derived rayon fiber to values of lower than 300 °C, decrease the maximum rate of weight loss, and increase the amount of char residue formation. MS analysis shows that the amount of water and carbon monoxide are increased at the expense of depolymerization, which results in the formation of levoglucosan in the presence of the fire retardants. Furthermore, it appears that relative decreases of $m/z = 44$ and 68 ions are also observed in the presence of the fire retardants. The relationship between char residue formation and the relative quantity of levoglucosan approximately follows an inverse-ratio linear relation.

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