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THERMAL DEGRADATION OF WOOD TREATED WITH GUANIDINE COMPOUNDS IN AIR
Flammability study

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Abstract

Wood has been treated with guanidine phosphate, guanidine nitrate, guanidine carbonate and guanidine chloride to impart flame retardancy. The samples were subjected to differential thermal analysis (DTA) and thermogravimetry (TG) from ambient temperature to 800°C in air to study their thermal behaviors. From the resulting data, kinetic parameters for different stages of thermal degradation were obtained following the method of Broido. For the decomposition of wood and flame retardant wood, the activation energy was found to decrease from 116 to 54 kJ mol^{-1}; the char yield was found to increase from 5.6 to 34.9%, *LOI* from 18 to 41.5, which indicated that the flame retardancy of treated wood was improved. Effects of the different compounds on the degradation and flammability of wood have also been proposed.

Keywords: degradation, DTA, flame retardant, pyrolysis, TG, wood

Introduction

Cellulosic materials, which include cotton, wood, paper and hemp etc., are most frequently implicated in fire, causing injuries and fatalities [1]. When ignited, cellulosic materials undergo thermal degradation, forming combustible volatile compounds which become involved in the propagation of fire. As cellulosic materials are used for textile, furniture, decorate and building materials, it will be essential to make them flame retardant. Many flame-retardants have been developed to use for them in the last few years. Some of most successful commercial flame-retardants for cellulosic materials have been guanidine compounds which are effective and economical flame-retardants. In the recent years, the thermal degradation and kinetic parameters

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of modified cellulosic materials are studied using DTA and TG techniques. However, these investigations are mainly centered on the thermal degradation of modified cotton [2–4]. The systematic studies on the thermal degradation and the kinetic parameters of wood treated with flame retardants are relatively rare probably because of its complicated thermal degradation via its different composition containing cellulose, lignin and hemicellulose, while cotton mainly containing cellulose. Of the three components, cellulose thermally decomposes through two types of reactions. At lower temperatures (<300°C), there is gradual degradation which includes dehydration, depolymerization, oxidation, evolution of carbon monoxide, carbon dioxide, and formation of carbonyl and carboxyl groups and ultimately a carbonaceous residue. At higher temperatures (>300°C), cellulose decomposes into a tarry mixture with laevoglucose as the major constituent. Laevoglucose decomposes into volatile and flammable products. These processes are shown schematically in Fig. 1 [5].

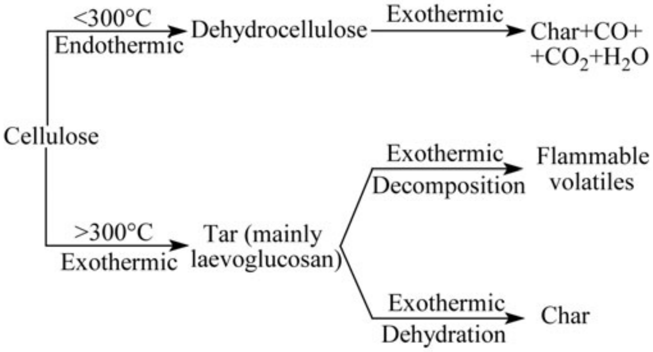

Fig. 1 Various stages in the pyrolysis of cellulose

Usually, cellulose begins mass loss at temperatures mainly above 300°C and most rapidly completes loss to yield the least char and then the greatest amount of volatiles of all wood components. On the other hand, lignin and hemicellulose decompose with lower rates to produce much more char, although the threshold temperatures of mass losses are lower than those of cellulose [6]. The pyrolytic behavior of wood is the overall behaviors of the three components, which makes it extremely complicated. However, Tang [7], Ramiah [8] and Eickner [9] propose that, of all wood components, cellulose causes and seeds flaming combustion and plays a key role in the pyrolysis because of its high pyrolysis rate. In the other words, cellulose is probably exclusively responsible for the degradation of wood [10], which is supported by the similar thermal analysis curves (DTA\DG) of cellulose and wood as shown in Figs 2 and 3. Generally, the function of flame retardant in cellulosic materials is to increase the char at the cost of flammable volatile products. Thus good flame retardant can make wood decompose at lower temperatures (<300°C) where cellulose, the critical component of wood, decomposes through the first type of reaction and products more char and correspondingly less flammable volatiles.

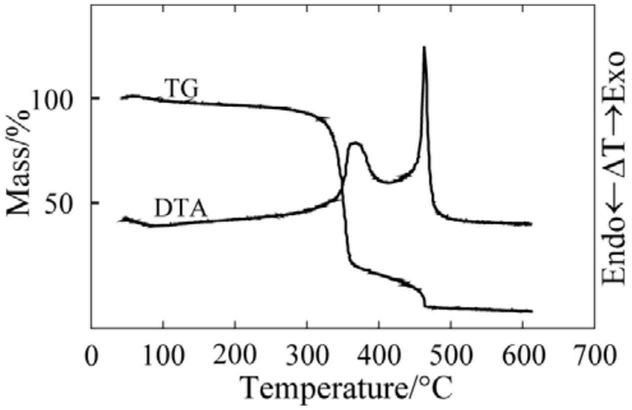

Fig. 2 Thermal analysis of cellulose in air

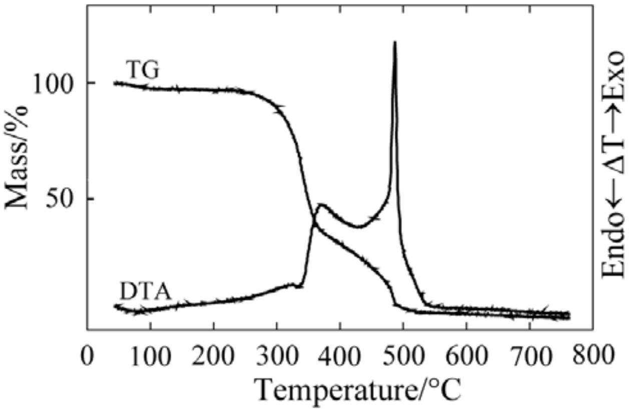

Fig. 3 Thermal analysis of wood in air

In the present study, wood was treated with five guanidine compounds. Wood and treated wood with compounds were subjected to thermal degradation using DTA and TG techniques. The values of different kinetic parameters of wood and modified wood were obtained to investigate the effects of guanidine compounds on the thermal degradation of wood. Further, the degree of flame retardancy was determined by *LOI* to get the information between degradation process and effective of flame retardant.

Experimental

Raw material

Samples of Larch (North of China) were heated for 1 h in boiling water. After this procedure, the wood was dried at 60°C. Then the wood was immersed in treating solution at 80°C for 2 h, and each sample was dried at 60°C. Samples milled passing

50 meshes were for thermal analysis. Sizes (L×W×T) were 100 mm×6 mm×3 mm for *LOI* test. The samples i–vi, pure and treated wood with the aqueous solution of guanidine dihydrogen phosphate, diguanidine hydrogen phosphate, guanidine nitrate, guanidine carbonate and guanidine chloride as flame retardants, respectively, were listed in Table 1.

Table 1 Analytical data for wood and wood treated with compounds

Sample No.	Compound	P/	N/	Cl/	*LOI*	Char yield/ mass%
		mass%				
i	Untreated wood	–	–	–	18	5.6
ii	Guanidine dihydrogen phosphate	2.03	2.09	–	41.5	34.9
iii	Diguanidine hydrogen phosphate	1.62	2.18	–	39	30.7
iv	Guanidine carbonate	–	2.35	–	24	17.2
v	Guanidine nitrate	–	3.47	–	26	18.9
vi	Guanidine chloride	–	2.27	3.89	35	27.6

Limiting-oxygen-index (LOI)

The *LOI* value is the minimum amount of oxygen in oxygen–nitrogen mixture required to support complete combustion of a vertically held sample that burns downward from the top. The higher the *LOI* value is, the more effective the flame-retardant treatment is. *LOI* values were determined in accordance with ASTM D2863-70 by means of a General Model HC-1 LOI apparatus. The results are given in Table 1.

Thermal analysis

DTA and TG were carried out on a DT-40 thermal analyzer (Shimadzu, Japan). DTA and TG were performed under a dynamic air (dried) atmosphere at a heating rate of 10°C min^{-1}. $\alpha\text{-Al}_2\text{O}_3$ was taken as the reference material.

Elemental analysis

The elemental analysis was carried out using a PE-2400 Elemental Analyzer (USA). Phosphorus was estimated by the colorimetric method. Nitrogen was determined by the Kjeldahl method, while chlorine was estimated by the Carius method. The results are given in Table 1.

Results and discussion

The associated DTA and TG curves of cellulose and samples (i–vi) were carried out in a dynamic air atmosphere from ambient temperature to 800°C and are shown in Figs 2–8. The mass losses for various stages in TG curves are given in Table 2.

It is generally observed that the amount of char formed during thermal degradation of wood treated with compounds is related to the degree of flame resistance exhibited by the treated wood. In order to understand the flame retardant properties of these samples, the char yields (in mass%) determined at 700°C from TG curves and *LOI* are given in Table 1. From Table 1, it is evident that char yield and *LOI* values for wood with flame retardant treatment (samples ii–vi) are higher than those for wood. These data suggest that the combustibility of the treated wood is decreased. With the increases of char yields, the *LOI* values increase. The relation between *LOI* and char yield is illuminated in Fig. 9. The proximate linear relation agrees with mechanism of flame retardant. Introduction of flame-retardants leads to larger amount of char formed at expense of flammable volatile products of thermal degradation, thus suppressing combustion and increasing the *LOI*.

Table 2 Activation energies for different stages of thermal degradation of wood and wood treated with compounds

Sample No.	Compound	Stage	Mass loss/ %	Temperature range/°C	E_a/ kJ mol^{-1}
i	Untreated wood	1st	4.8	240–290	81.0
		2nd	51.5	290–365	116.0
		3rd	25.3	365–480	15.8
		4th	9.6	480–515	62.4
ii	Guanidine dihydrogen phosphate	1st	5.5	165–240	36.2
		2nd	15.8	240–295	63.2
		3rd	25.7	295–570	8.3
		4th	14.8	570–660	32.4
iii	Diguanidine hydrogen phosphate	1st	3.0	184–225	57.4
		2nd	19.4	225–300	56.5
		3rd	25.0	300–505	15.0
		4th	20.4	505–700	18.3
iv	Guanidine carbonate	1st	3.8	170–204	63.2
		2nd/1st	7.0	204–224	93.1
		2nd/2nd	11.7	224–318	16.6
		2nd/3rd	21.5	318–385	43.2
		3rd	27.8	385–570	18.3
		4th	7.5	570–650	23.3
v	Guanidine nitrate	1st	2.0	180–203	74.0
		2nd/1st	11.4	203–240	54.0
		2nd/2nd	10.1	240–316	18.3
		2nd/3rd	18.5	316–366	41.6
		3rd	30.4	366–546	18.7
		4th	7.5	546–631	9.2
vi	Guanidine chloride	1st	4.0	160–232	55.7
		2nd	19.7	232–290	74.8
		3rd	22.0	290–483	13.3
		4th	23.4	483–677	8.3

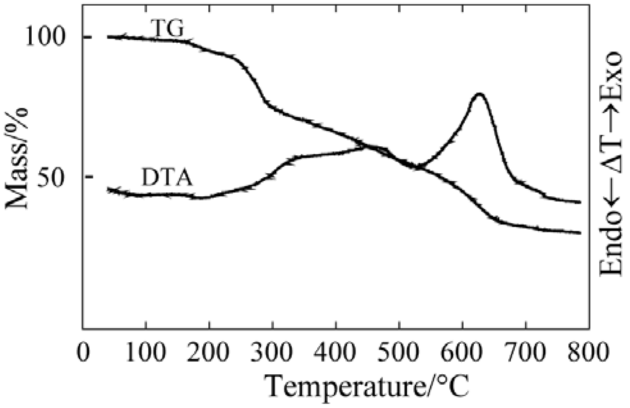

Fig. 4 Thermal analysis of sample ii in air

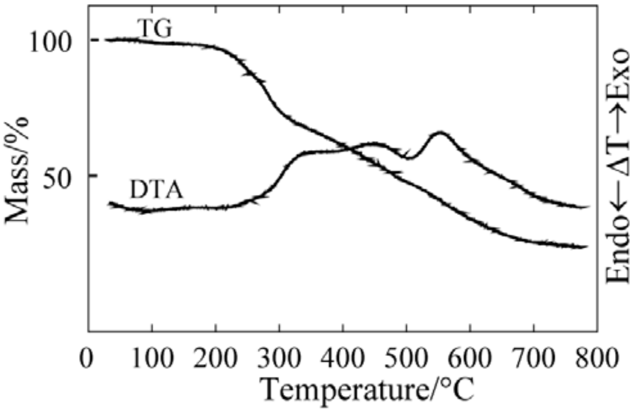

Fig. 5 Thermal analysis of sample iii in air

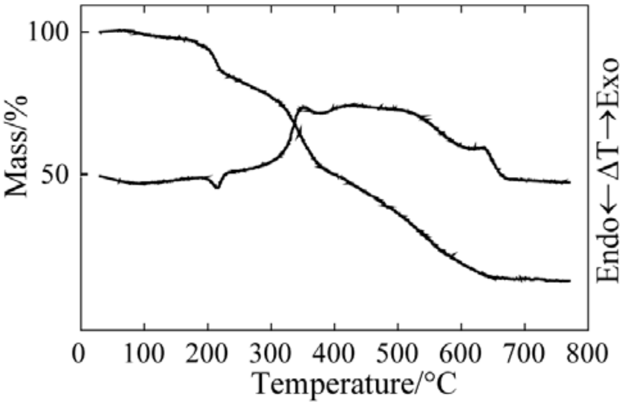

Fig. 6 Thermal analysis of sample iv in air

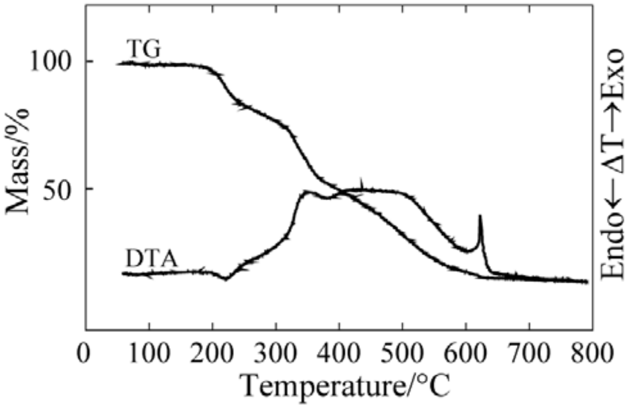

Fig. 7 Thermal analysis of sample v in air

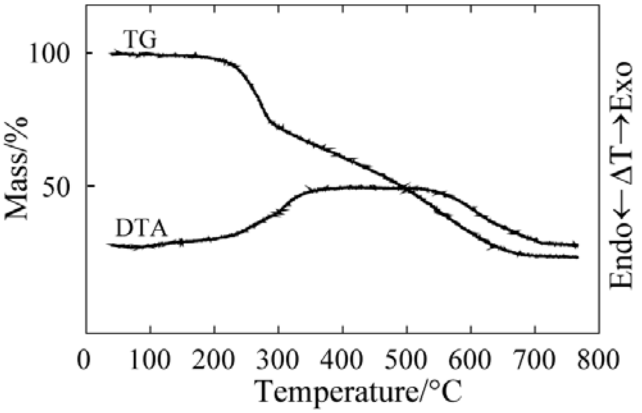

Fig. 8 Thermal analysis of sample vi in air

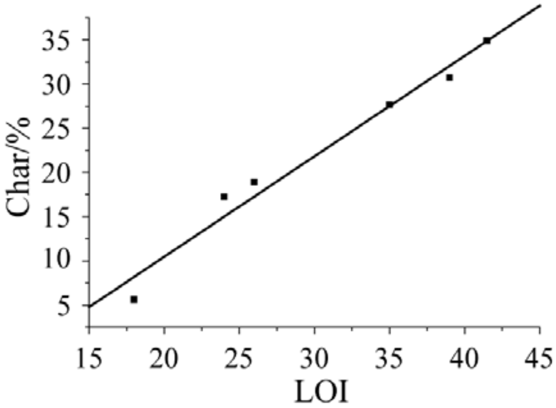

Fig. 9 Relation between *LOI* and char yield

TG curve of wood shows four stages of the thermal degradation. There is a mass loss of 4.8% in the temperature range 240–290°C in the first stage, which is due to dehydration of wood. For the second stage, a 51.5% rapid mass loss occurs in the temperature range 290–365°C, which shows the oxidative decomposition of wood occurs at higher temperatures where large amount of flammable volatile products are formed as shown in Fig. 1. The large exotherm peaking at 371°C in DTA curve is due to the oxidation of flammable volatile products [11]. After the oxidative decomposition stage, mass losses of the residual materials of wood are found to be slow in the temperature range 365–480°C. The TG curve shows a mass loss of 25.3%. There is no clear exotherm in DTA curve in this (third) stage where the less stable aliphatic groups are preferentially decomposed through hemolytic cleavage of C–C and C–H bonds, and the resultant product is a highly condensed and cross-linked carbonaceous [12]. For the fourth stage, the TG curve shows a mass loss of 9.6% in the temperature range 480–515°C. High temperature exotherm in DTA curve is due to the oxidation of the carbonaceous.

For the thermal analysis curves of wood, it is evident that the oxidative decomposition of wood occurs at higher temperatures (>300°C), and the heat release is distributed between two sharp and closely spaced exotherms, which indicates a large rate of heat release. So the heat liberated is easily transferred back to wood surfaces to continue wood pyrolysis, maintaining a continuous supply of gaseous fuel for flame propagation, which makes wood catch fire easily and burn vigorously with flame.

TG curve of treated wood with guanidine dihydrogen phosphate still shows four stages of thermal degradation. There is a mass loss of 5.5% in the temperature range 165–240°C with a slight endotherm in DTA curve. It is suggested that the initial reactions are dephosphorylation and that the released acids then catalyze the dehydration of wood [13]. For the oxidative decomposition (second) stage, 15.8% mass loss in the temperature range 240–295°C is due to acid-catalyzed decomposition of wood. The exotherm of DTA peaking at 344°C is due to the oxidation of volatile products. The third stage is prolonged in the temperature range 295–570°C. TG curve shows a mass loss of 25.7%. The exotherm in the temperature range 396–524°C is due to the oxidation of intermediate chars which may be aromatic components [14]. For the fourth stage, TG curve shows a mass loss of 14.8% in the temperature range 570–660°C. The exotherm in this stage is due to the oxidation of charred residues.

The thermal analysis curves of sample (iii) are similar to those of the sample (ii). The temperature ranges and mass losses of various stages are listed in Table 2. The first exotherm peaking at 341°C is due to the oxidation of flammable volatile products, and the next exotherm in the temperature range 393–505°C represents the oxidation of aromatic components. The exotherm in the temperature range 505–700°C is due to the oxidation of charred residues.

For the thermal degradation of wood treated with guanidine phosphate (guanidine dihydrogen phosphate and diguanidine hydrogen phosphate), compared with that of wood, it is evident that there are some differences attributed to flame retardancy in the terms of following:

a) Lowering in decomposition temperatures of the treated wood. For samples (ii, iii), the oxidative decomposition (second) stages occur at lower temperatures (<300°C), which makes pyrolytic degradation of samples (ii, iii) proceed through the first type of reaction as shown in Fig. 1. This factor will give a lower percent of flammable volatile products and correspondingly higher amount of char yield. It is also suggested that the phosphorus-containing flame retardant is effective in catalyzing the thermal decomposition.
b) Lowering in quantity and rate of heat release during the pyrolytic degradation. The exotherms of samples (ii, iii) in DTA curves become smaller, and heat release is distributed between three broad peaks covering a wide area, resulting in a major reduction in rate of heat release and flammable products which fuel the flaming combustion reaction. Though the exotherms attributed to the oxidation of charred residues are still considerable, the low amount of heat release at low temperatures makes it difficult for samples to reach high temperatures. So, the heat release in the second stage plays a key role in the propagation of fire.
c) Appearance of new exotherms in the third stage of thermal degradation. There are no exotherms due to the oxidation of aromatic components for DTA curve of wood. This may be because the oxidative decomposition of wood products large amount of flammable volatile products and leaves a low percent of carbon-poor residues which contain less aromatic components. Moreover, the two large exotherms due to the oxidation of volatile products and charred residuals may overshadow the exotherm due to the oxidation of less aromatic components.

As the decomposition temperatures and heat release of samples (ii, iii) are much lower and the char yield and *LOI* values in Table 1 are much higher than those of wood, the guanidine phosphate may be considered as good flame retardants for wood.

The thermal analysis curves of sample (iv) are quite distinct from those of samples (i–iii). For the first stage, there is a mass loss of 3.8% in the temperature range 170–204°C, which is due to the denitration and acid-catalyzed dehydration. For the second stage, it is evident that the oxidative decomposition stage is divided into three small stages (204–224, 224–318, 318–385°C). The mass loss in the low temperature range 204–224°C is due to acid-catalyzed decomposition of sample. The small endotherm in DTA curve is the result of rapid evaporation of volatile products. Then the mass loss becomes slow in the temperature range 224–318°C, which may be due to the limitation of released acids to catalyze decomposition of sample. With the temperature rising, the thermal decomposition of sample becomes fast in the temperature range 318–385°C as that of wood. The large exotherm in the temperature range 241–376°C is due to oxidation of flammable volatile products. The exotherm peaking at 418°C in the third stage is due to the oxidation of aromatic components as those of samples (ii, iii). The TG curve shows a mass loss of 27.8% in this stage. In the fourth stage, a 7.5% mass loss occurs in the temperature range 570–650°C, which corresponds to the last exotherm attributed to the oxidation of charred residuals.

The thermal analysis curves of sample (v) is similar to those of the sample (iv). The mass loss of 2.0% in the first stage (180–230°C) is due to the dehydration and decarbonation. The total mass loss of 40.0% in the oxidative decomposition (203–366°C) includes acid-catalyzed decomposition stage (203–240°C), thermal decomposition stage (240–316°C) and rapid decomposition stage at higher temperatures (316–366°C). For the next (third) stage, a 30.4% mass loss occurs in the temperature range 366–546°C with an exotherm due to the oxidation of the aromatic components. The last exotherm in the fourth stage (546–631°C) is due to the oxidation of charred residuals. The TG curve shows a mass loss of 7.5% for this stage.

For the thermal degradation of samples (iv, v), there are some differences related to flame retardancy as compared to samples (ii, iii) in the terms of following:

a) Oxidative decomposition stages are divided into three small stages, including a new thermal decomposition stage at higher temperatures (>300°C) where the thermal degradation of samples proceeds through the second type of reaction as shown in Fig. 1. This factor will give more flammable volatile products and correspondingly lower amount of char yield.
b) Increase in heat release in the beginning of pyrolytic degradation. The exotherms in the second stage become larger, which is due to the oxidation of more flammable volatiles mainly produced in the decomposition at higher temperatures above 300°C. More heat release in the initial pyrolytic degradation makes it possible for samples to continue pyrolysis and burn.

Though the decomposition temperatures of samples (iv, v) are much lower than that of wood, the introduction of rapid decomposition stage at higher temperatures (>300°C) leads to more flammable products and heat release which limit the flame retardancy of samples. The low *LOI* and char yield values in Table 1 also show that the guanidine nitrate and carbonate are not good flame-retardants for wood.

The thermal analysis curves of sample (vi) are different from any one discussed before. From the TG curve, we can see that the oxidative decomposition of sample (vi) occurs at lower temperatures and forms more char, the mass loss in second stage is decreased, and the third stage is prolonged. The exotherms due to the oxidation of volatile products and charred residuals become smaller. There is no large sharp exotherm in the whole decomposition process, which may be attributed to the different mechanism of thermal degradation of wood treated with guanidine chloride. It is suggested that chlorine radicals (Cl•) formed in the thermal decomposition as radical scavengers block the formation of volatile flammable products [15], which leads to a lower mass loss and a smaller exotherm owing to oxidation of volatile products. Further, the hydrogen chloride released exerts a further effect by catalyzing the dehydration, condensation and charring reactions, which has been shown to be acid-catalyzed. The high *LOI* and char yield values in Table 1 show that guanidine chloride is a good flame retardant for wood.

For the various stages of thermal degradation of wood, the order of reaction is between 0 and 1 [16]. So the kinetic parameters for these stages were determined using the following equation, given by Broido [17]:

$$\ln\left[\left(\ln\frac{1}{y}\right)\right]=-\frac{E_a}{R}\frac{1}{T}+\ln\left(\frac{R}{E_a}\frac{Z}{\beta}T_m^2\right)$$

where y is the fraction of initial molecules not yet decomposed. T_m is the temperature of maximum reaction rate, β is the rate of heating, Z is the frequency factor and E_a is the activation energy.

From the slopes of the TG curves in Figs 3–8, plots of $\ln(\ln 1/y)$ *vs.* $1/T$ for various stages of pyrolysis were drawn. Linear plots were obtained in each instance. The activation energies, E_a, determined from the slopes and are given in Table 2. From Table 2 it is observed that for the first stage of thermal degradation of wood, mainly due to dehydration, the activation energy is 81.0 kJ mol^{-1}; which for samples (ii–vi) reduce to 36.2, 57.4, 63.2, 74.0 and 55.7 kJ mol^{-1}, respectively. This is mainly due to deacidification and acid-catalyzed dehydration. In the case of samples (ii–vi), the lowering of the decomposition temperatures is much great. Their activation energies for the second stage of pyrolysis, in a range of 54.0–93.1 kJ mol^{-1}, decrease considerably as compared to wood. This is due to acid-catalyzed decomposition. This also shows that the flame retardants change the mechanism of thermal degradation in such a way as to reduce the decomposition temperatures of wood, which can lead to less flammable volatile products and more char.

Summary and conclusions

The thermal decomposition of wood includes four stages: first stage, dehydration at low temperatures; second stage, rapid mass loss due to oxidative decomposition; third stage, slow decomposition; fourth stage, the oxidation of charred residues. At lower temperatures (<300°C), the degradation of wood involves dehydration, rearrangement and ultimate formation of carbonaceous residue and small amount of flammable products. At higher temperatures (>300°C), the degradation of wood includes a rapid volatilization via the formation of a tarry mixture which ultimately decomposes into flammable volatiles and small amount of char.

For the decomposition of wood and flame retardant wood, the activation energy was found to decrease from 116 to 54 kJ mol^{-1}; the char yield was found to increase from 5.6 to 34.9%, *LOI* from 18 to 41.5, which indicated that the flame retardancy of treated wood was improved. For the degradation of the samples treated with guanidine phosphate and guanidine chloride, the initial reactions are dephosphorylation and dechloride and that the released acids then catalyze the dehydration and decomposition of wood, which makes the whole oxidative decomposition of wood occur at lower temperatures (<300°C), resulting in formation of less flammable products and correspondingly more char. As the decomposition temperatures and activation energies of samples (ii, iii) are much lower and the *LOI* and char yield values are much higher than those of wood, the guanidine phosphate and guanidine chloride may be considered as good flame retardants for wood. For the wood treated with guanidine nitrate and guanidine carbonate, though the decomposition temperatures and activation energies of samples (iv, v) are much lower than those of wood, the deacidification and acid-catalyzed decomposition occur partly rather than completely, which brings about a rapid decomposition at higher temperatures (>300°C) through the second type of reaction, resulting in an increase of flammable volatiles and corresponding larger heat release and less char as compared to samples (ii, iii). The low *LOI* and char yield values of samples (iv, v) show that guanidine nitrate and guanidine carbonate are not good flame-retardants for wood.

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