

Catalytic effect of bases in impregnation of guanidine nitrate on Poplar (*Populus*) wood

Flammability and multiple heating rate kinetic study

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Abstract Wood, one of the flammable material, was treated with aqueous solution of guanidine nitrate (GUN) and also with small amount of bases like *N,N*-dimethylformamide, 4-dimethylaminopyridine, pyridine, and triethylamine in the treating solution. These bases catalyze the impregnation of GUN as indicated by increase in mass gain percentage, elemental analysis, and scanning electron microscopy. To study their thermal behavior, dynamic thermogravimetry (TG) and derivative thermogravimetry (DTG) analysis under nitrogen atmosphere have been applied from ambient temperature to 973 K on all samples, at multiple linear heating rates 2.5, 5, 10, and 20 K min⁻¹. Non-isothermal, “model free” iso-conversional multiple heating rate methods, Ozawa–Flynn–Wall (O–F–W) and modified Coats–Redfern are used to calculate activation energy of samples. The activation energy of samples is found in the range 109–208 kJ mol⁻¹. Thermal parameters like overall pyrolysis duration, maximum mass loss rate, corresponding to DTG peak maximum and percentage char yield calculated at 873 K from TG curves are used to appraise the flammability of samples. Also, flammability of samples is determined by reliable methods namely limiting oxygen index and underwriters laboratories 94 (UL 94) test. The aforesaid study indicates that base catalyzed impregnated samples are less flammable than those impregnated with only GUN and untreated ones.

Keywords Wood veneer · TG kinetics · SEM · CHN · LOI · UL 94

Introduction

Wood is a mixture of 40–50% cellulose, 20–35% hemicellulose, and 15–30% lignin together with some extractives [1]. Cellulose, a major component of wood, thermally decomposes below 573 K under dehydration, depolymerisation and oxidation with release of CO, CO₂ and carbonaceous residue [2]. Cellulose undergoes degradation on ignition, forming combustible volatile compounds mainly laevoglucosan which result in propagation of fire causing injuries and even fatalities [3]. As wood is used as a building material, so it is necessary to make it flame retardant. It is well known that materials made up of wood can be treated with compounds containing nitrogen, phosphorus, halogens, and boron to improve fire retardancy and to accelerate the formation of a carbonized layer on the materials. On this subject, Gao et al. [4] reported the thermal degradation behavior of treated wood with various flame retardant compounds containing nitrogen, phosphorus, halogens, and boron. Blasi et al. [5] worked on the thermal and catalytic decomposition of impregnated wood with sulfur and phosphorus compounds containing ammonium salts. Further, Luneva and Petrovskaya [6] have clarified the thermal decomposition and stability of nitrogen–phosphorus containing compounds in fire retardant treated wood samples and discussed about the theoretical aspects on the action of fire retardants in preventing and minimizing degradation process. Fire retardants can act chemically and physically in solid or in gaseous phase depending upon nature of material [7]. Some of the most successful commercial flame retardants for cellulosic materials have been guanidine compounds which are effective and economical flame retardants. Kulakov et al. [8] explained that GUN did not form any chemical bond with cellulose. Gao et al. [9, 10] also studied the thermal

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degradation of wood treated with guanidine compounds in air and calculated their kinetic parameters by TG technique. TG study [4, 9, 10] on wood shows that initial decomposition temperature of flame retardant treated wood decreases and char yield increases. And also higher the char yield; the better will be the flame retardant character.

Earlier research has contributed to understand flammability, thermal decomposition kinetics of wood and treated wood. Ellis et al. [11] had reported about the catalytic effect of pyridine in the impregnation of phosphorus containing flame retardants on wood when pyridine is used as solvent. While in this study, wood was impregnated with guanidine nitrate (GUN) and along with small amount of bases/catalysts such as *N,N*-dimethylformamide (DMF), 4-dimethylaminopyridine (DMAP), pyridine (Py), and triethylamine (TEA). Thus, the objective of this study is to investigate the improvement in flame retardancy imparted by GUN in presence of different bases, with a view to study thermal decomposition parameters and to calculate degradation activation energy (E_a) values using model free methods. Besides this, the degree of flame retardancy was determined by limiting oxygen index (LOI), underwriters laboratories 94 (UL 94), maximum mass loss rate (MMLR), overall pyrolysis duration (OPD), and percentage char yield in order to get the information regarding degradation process and effectiveness of flame retardancy.

Materials and methods

Materials

Wood veneers were collected from Galaxy Plywood Industry, Yamuna Nagar, India. These veneers were prepared from the sapwood portion of Poplar (*Populus*) using lathe machine. GUN and DMAP were purchased from Himedia Laboratories Pvt. Ltd., Mumbai (India). DMF was purchased from RFCL Limited, Delhi; the Py was supplied by Qualigens Fine Chemicals, Bombay; and trimethylamine was purchased from Acros Organics, New Jersey, USA. The microcrystalline cellulose was supplied by Acros Organics, USA. All chemical used were of analytical grade.

Impregnation

The samples sizes ($L \times W \times T$), $150 \times 100 \times 2.5 \text{ mm}^3$, were immersed into hot water for 1 h. Then samples were dried at 343 K for 24 h under vacuum. Minimum three wood specimens were used for each impregnation condition. Sample (i) was untreated poplar wood and samples (iii)–(vi) were obtained by impregnation of 20% hot aqueous GUN solution on wood for 30 min in presence of catalytic amount of bases such as DMF, DMAP, Py, and TEA, respectively whereas no base/catalyst added to sample (ii). The samples formulation is listed in Table 1.

Mass gain percentage (MGP) due to chemical load was calculated using following equation:

$$\text{MGP} = [M_{\text{odf}} - M_{\text{odi}}/M_{\text{odi}}] \times 100$$

where M_{odi} and M_{odf} are oven dried mass (g) of specimens before and after treatment, respectively.

Elemental analysis

The elemental analysis (CHN) was performed on a Thermo Finnigan Flash EA TM1112 analyzer to investigate mass percentage of carbon (C), hydrogen (H), and nitrogen (N) elements in all samples.

Scanning electron microscopy (SEM)

The surface morphology of samples was characterized by SEM technique. The scanning electron micrographs of silver coated selected samples were analyzed by SEM model EVO 50 with an accelerating voltage of 20 kV. The SEM photographs of selected samples were taken at a magnification of 5,000 times.

Limiting oxygen index (LOI)

The LOI 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, more effective is the flame retardant. The LOI values were determined in accordance

Table 1 Carbon, hydrogen, and nitrogen mass percentage composition and mass gain percentage of all samples

Samples	Compounds formulation	C/%	H/%	N/%	MGP/%
(i)	Untreated wood	42.2	6.1	–	–
(ii)	Wood-GUN	41.2	6.2	3.4	33.3
(iii)	Wood-GUN-DMF	39.9	6.0	8.8	36.6
(iv)	Wood-GUN-DMAP	41.5	6.4	11.0	52.5
(v)	Wood-GUN-Py	39.4	6.1	10.1	40.0
(vi)	Wood-GUN-TEA	40.0	6.2	10.5	46.6

with ASTM D 2863 standard with Platon S. A. Associates oxygen index apparatus. Samples sizes were $(L \times W \times T)$ $100 \times 6 \times 2.5 \text{ mm}^3$ for LOI tests.

UL 94 (horizontal burning test)

A set of three samples sizes $125 \times 13 \times 2.5 \text{ mm}^3$ were used to investigate the rate of flame spread between two bench marks at 25 and 100 mm position. The specimen was mounted on a stand oriented in the horizontal direction with its thickness vertically. The flame is applied to the free end of the specimen for 30 s. The time for the flame front to move between the benchmarks is measured. Sample will be classified as HB (horizontal burning) rating if the burning rate does not exceed 75 mm min^{-1} or sample self extinguish (SE) before 100 mm benchmark. If a sample is completely combustible (CB) or horizontal burning rate exceeds 75 mm min^{-1} , then it will fail to pass HB rating.

Thermal analysis

Thermogravimetric (TG) analysis was carried out using Perkin Elmer Diamond TG/DTA thermogravimetric analyzer. The resolution of this instrument is $0.02 \mu\text{g}$ as a function of temperature. Samples milled passing 75 meshes were used for thermal analysis. Thermograms of treated and untreated samples were recorded at linear multiple heating rates (β) 2.5, 5, 10, and 20 K min^{-1} from ambient temperature to 973 K under high purity nitrogen (99.999%) at a flow rate of 20 ml min^{-1} . In addition, a TG run of cellulose at a heating rate of 10 K min^{-1} was recorded under same conditions. Before starting each run, nitrogen was used to flush the furnace for 30 min to create an inert atmosphere so as to avoid unwanted oxidation. The TG/DTA analyzer was calibrated before recording thermograms. Dried alumina powder was used as a reference material and ceramic sample holder was employed for taking thermograms. In order to insure the uniformity of temperature of the sample and good reproducibility, small amounts (3–6 mg) were taken. Three runs of same sample were conducted under same set of experimental conditions.

Data processing and activation energy calculation

TG curves were analyzed by using Pyris software from TG Analyzer and data was used in MS Excel and origin software to calculate activation energy (E_a) and correlation coefficient (r). The E_a values of samples were calculated by “model free” iso-conversional methods. The methods used in calculating activation energy at different conversions (α) were Ozawa–Flynn–Wall (O–F–W) [12, 13] and Coats–Redfern (modified) [14]. The final equations used for calculation of E_a by O–F–W and modified Coats–Redfern

methods are given in Eqs. 1 and 2, respectively. In these equations, β is the heating rate, R is the universal gas constant, A is the pre-exponential factor, α is the degree of conversion and $g(\alpha)$ is a function of α .

$$\log(g(\alpha)) = \log\left(\frac{AE_a}{R}\right) - \log(\beta) - 2.315 - 0.4567\left(\frac{E_a}{RT}\right) \quad (1)$$

$$\ln\left[\frac{\beta}{T^2\left(1 - \frac{2RT}{E_a}\right)}\right] = \ln\left[-\frac{AR}{E_a \ln(1 - \alpha)}\right] - \frac{E_a}{RT} \quad (2)$$

In iso-conversional O–F–W method, $\log \beta$ was plotted against $1/T$ which leads to slope $-0.4567E_a/R$ of a line at a particular conversion value. The modified Coats–Redfern method is a multiple heating rate application of the Coats–Redfern equation. In this method, $\ln(\beta/T^2)$ is plotted against $1/T$ which gives slope $-E_a/R$ of line at any degree of conversion. Using the value of slope of each line, E_a was calculated by both methods at different conversions.

Results and discussion

Confirmation of catalytic effect of bases in impregnation of GUN

The bases act as catalyst in the impregnation process was confirmed by MGP, CHN, and SEM analysis, which are discussed as below

Mass gain percentage by samples

The MGP values for treated samples are given in Table 1. When wood is treated with GUN in absence of a base “sample (ii),” the mass gain is 33.3%. The gain in mass confirms the impregnation. The addition of small amount of bases in treating solution, i.e., samples (iii)–(vi) results the mass gain increase from 33.3% to a maximum value of 52.5%. It means bases are catalyzing the impregnation of GUN [11]. Perhaps bases acting as catalyst provide the free sites on surface for incoming molecule of GUN from the solution and resulting in mass gain. The highest value of MGP is for sample (iv) and lowest in case of sample (iii) among the base catalyzed samples. Evidently DMAP is catalyzing the impregnation the most and DMF the least.

Elemental analysis

The mass percentage of C, H, and N are reported in the Table 1. The C and H% is almost the same in all samples but N% changes are adequate. Wood treated with GUN, i.e., sample (ii) has 3.4 N% while the N% in samples

treated with GUN in presence of base “(samples (iii)–(vi))” lie in the range 8.8–11.0%. It can be concluded that small amount of nitrogenous bases themselves can not increase N% in samples (iii)–(vi) but this may be due to the catalyzing effect of bases which helps in increasing the concentration of GUN in samples supporting to the above inference [11].

SEM analysis

The scanning electron micrographs of samples (i)–(iv) are reported in Fig. 1. The pores (empty cells) of sample (i) are clearly visible and in sample (ii) GUN had impregnated into the pores. From micrographs, it is clearly visible that the concentration of GUN is more in sample (iv) than (iii). The pores of sample (iv) are almost completely covered. From SEM, study it can also be inferred that bases catalyzes the impregnation process as shown in micrographs. DMAP is catalyzing the impregnation of GUN in a better way than DMF.

Thermal, flammability, and kinetic study

Overall decomposition of samples

Figure 2 exhibits the thermal profile for samples (i)–(vi), at a heating rate of 10 K min^{-1} and the thermal profile of sample (iii) at multiple heating rates in nitrogen atmosphere is shown in Fig. 3, for illustration. TG curves of all samples at multiple heating rates shifts toward a higher temperature with increase in heating rates. The decomposition of untreated

sample (i) starts at around 513 K and gets completed by 923 K while the decomposition of treated samples (ii)–(vi) starts around 475 K and is completed by 873 K. The initial onset decomposition temperature of treated wood samples (ii)–(vi) are found to be lower than untreated wood sample (i) and residue mass percentage at 873 K of treated samples is higher (~ 19 – 26.7%) than untreated sample ($\sim 9.8\%$) (Table 2). The degradation of untreated wood sample (i) occurs in single step while degradation of treated samples (ii)–(vi) arises in two steps which are also confirmed by DTG. For comparative purpose, DTG thermograms of sample (i) and (v) at a heating rate of 10 K min^{-1} in nitrogen atmosphere are shown in Fig. 4.

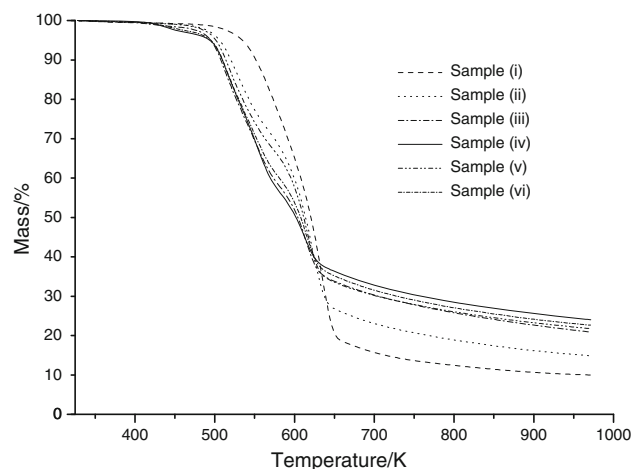
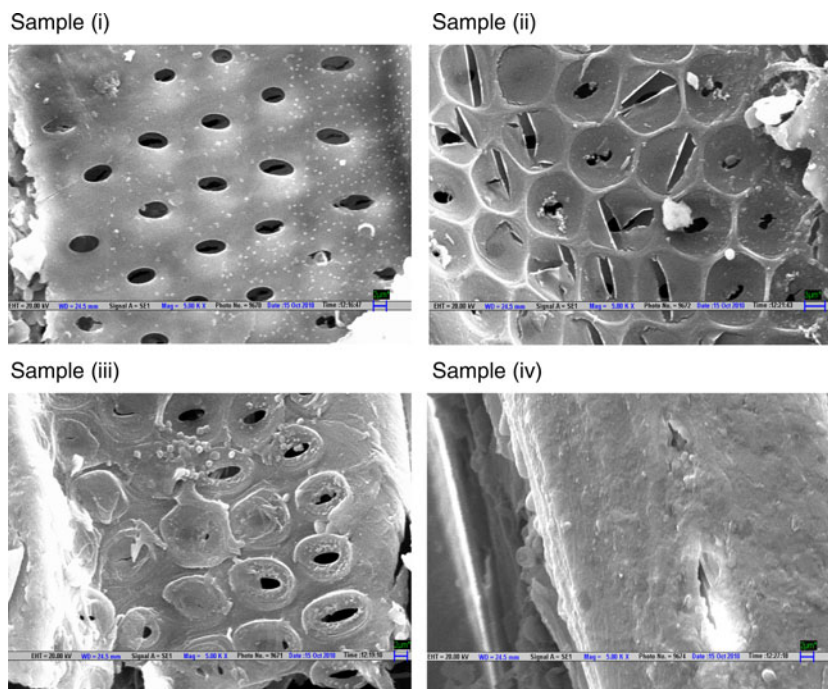


Fig. 2 TG analysis of samples (i)–(vi) at a heating rate of 10 K min^{-1} in nitrogen atmosphere

Fig. 1 Scanning electron micrographs of samples (i)–(iv)



Thermal decomposition characteristics and their correlation with flammability of samples

The onset temperature (T_o), shift temperature (T_s) from TG curves and peak temperature (T_p) from DTG, for which maximum mass loss was observed, were calculated for individual samples at different heating rates. The temperature parameters T_o , T_s , T_p and corresponding percentage mass loss ML_o , ML_s , ML_p , respectively, for each sample at all heating rates were calculated using Pyris software manager. The residue mass percentage was calculated at 873 K. It is well known that characteristic temperature would move to higher value with increase in heating rates. To avoid the influence of linear heating rates in determining parameters T_o , T_s , and T_p , four values from four heating rates of individual samples were extrapolated to a value where $\beta = 0$ [15]. In addition, mass loss parameters ML_o , ML_s , ML_p , and residue percentage at 873 K were obtained by averaging four values from four heating rates. The thermal decomposition

parameters and residue percentage at 873 K are summarized in Table 2.

The parameter, T_o , represents that onset decomposition temperature of treated sample (ii)–(vi) was found in the range 476–483 K and is lower than untreated wood sample (i) which is ~ 514 K (Table 2). The corresponding percentage mass loss, ML_o , for treated samples (ii)–(vi) were observed in the range 3–5 and 3.7% for sample (i) (Table 2). This mass loss is corresponding to dehydration and decomposition of samples [9, 10]. When wood is treated with GUN, the onset degradation temperature, T_o , decreases up to ~ 483 K. This is due to release of acid which catalyzes the decomposition and dehydration process [16]. For the wood samples which were treated with GUN solution along with bases (samples (iii)–(vi)), the onset degradation temperature further decreases (range 476–481 K). This is due to the presence of comparatively larger amount of GUN resulting in production of more nitric acid which in turn catalyzes the dehydration and decomposition process more effectively.

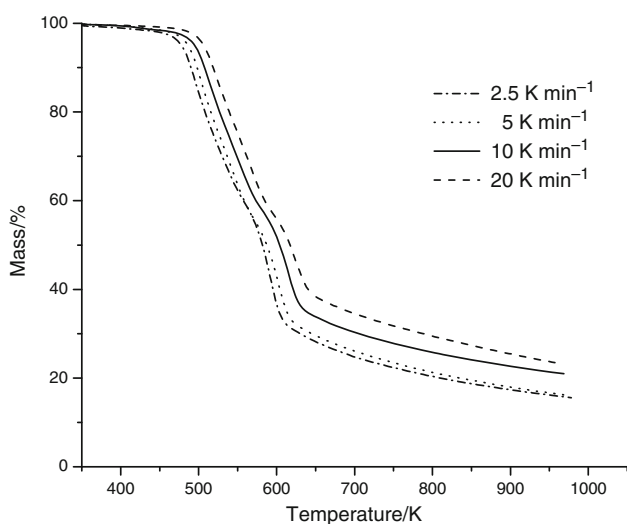


Fig. 3 TG analysis of sample (iii) at heating rates of 2.5, 5, 10, and 20 K min⁻¹ in nitrogen atmosphere

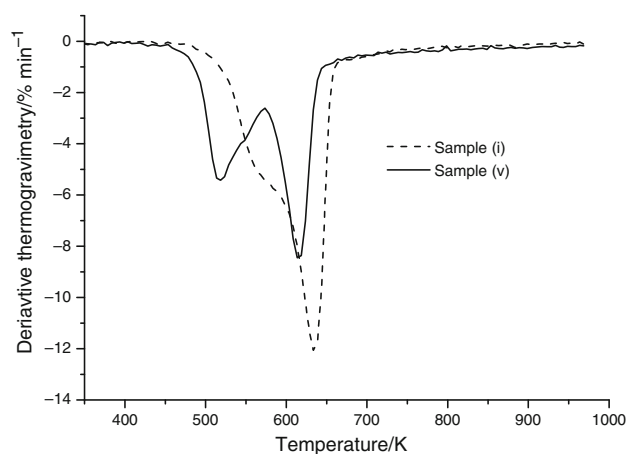


Fig. 4 DTG curves of samples (i) and (v) at a heating rate of 10 K min⁻¹ in nitrogen atmosphere

Table 2 Thermal decomposition parameters of untreated and treated woods

Samples no.	$T_{O\beta \rightarrow 0}/K$	$ML_o/\%$	$T_{S\beta \rightarrow 0}/K$	$ML_s/\%$	$T_{P\beta \rightarrow 0}/K$		$ML_p/\%$		Temperature range/K		Char yield/%	LOI/%
					I	II	I	II	I	II		
(i)	513.7	3.7	623.0	81.7	607.5	–	65.1	–	473–673	–	9.8	21
(ii)	483.3	3.3	603.0	69.1	501.5	592.8	12.4	61.5	468–573	573–668	19.2	27
(iii)	476.1	3.1	606.3	66.2	493.7	591.2	12.1	56.7	448–583	583–668	21.6	28.5
(iv)	478.5	4.9	601.7	60.6	483	591.2	17.8	54.3	466–578	578–673	26.7	30
(v)	480.7	2.9	601.0	64.2	498.4	591.4	11.7	56.0	453–573	573–683	23.0	28
(vi)	479.6	4.0	609.3	63.5	500	596.7	12.2	55.5	466–578	578–673	24.2	29

A coupled decomposition of hemicellulose and cellulose is observed in DTG of sample (i) (Fig. 4). A “shoulder” in DTG peak is as a result of thermal decomposition of hemicelluloses and main peak corresponds to decomposition of cellulose mainly in inert atmosphere [17]. The pyrolytic behavior of wood is overall behaviors of the three components, i.e., hemicellulose, cellulose, and lignin, which make it extremely complicated; however, the thermal decomposition of wood is largely affected by cellulose [9]. The parameter, T_p , for sample (i) is 607.5 K and corresponding mass loss, ML_p , is 65% (Table 2). Similarly, T_p , for first peak of samples (ii)–(vi) is found to occur in the range 483–502 K (temperature range 448–583 K) and the corresponding ML_p falls in the range 11–18%. This first peak in DTG curves in treated samples is due to acid catalyzed dehydration and decomposition of samples. The parameter, T_p , for second DTG peak is observed in the range 591–596 K (temperature range 573–683 K) for a sample (ii)–(vi) and the corresponding mass loss ranges in ~54–62% (Table 2). As the pyrolysis range of cellulose (553–673 K) in nitrogen atmosphere overlaps with second DTG pyrolysis peak range (573–683 K) of treated samples (ii)–(vi). So it is concluded that second degradation peak in samples (ii)–(vi) is corresponding to degradation of cellulose mainly. For illustration, DTG of cellulose and sample (vi) at a heating rate of 10 K min⁻¹ is shown in Fig. 5. However, rate of pyrolysis of sample (vi) is slower than cellulose which is due to formation of non-combustible products and hence attributing toward better flame retardancy.

The parameter, T_s , for the sample (i) is 623 K and corresponding ML_s is about 82%. Whereas for treated samples, T_s , values lies in the range 601–610 K and the maximum value of ML_s is 69% (Table 2). Also, the ML_s values of compounds containing base (samples (iii)–(vi))

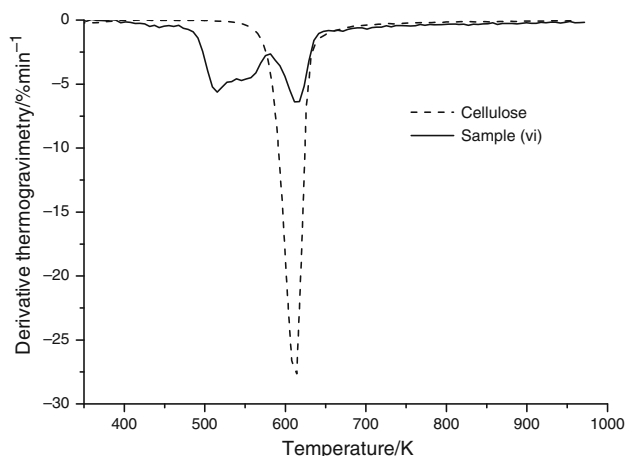


Fig. 5 DTG of cellulose and sample (vi) at a heating rate of 10 K min⁻¹ in nitrogen atmosphere

are lower than sample (ii), which clearly displays the improvement in the flame retardancy. After the shift temperature, char formation from cellulose and lignin take place [9].

Also, DTG data have great importance to evaluate the flame retardancy of samples [18]. The two parameters, i.e., maximum mass loss rate (MMLR) and overall pyrolysis duration (OPD), were calculated from DTG curves for all samples at a heating rate of 10 K min⁻¹, as given in Table 3.

The parameter MMLR was calculated corresponding to peak maxima of DTG curves for all samples. The untreated sample (i) shows single DTG peak having MMLR of 12.1% min⁻¹. On the other hand treated wood samples, exhibits two DTG peaks comparatively with lower MMLR values. It can be noticed that MMLR₁ values corresponding to first DTG peak are relatively higher for samples (iii)–(vi) as compared to (ii) (Table 3). This might be due to the reason that base catalyzed impregnated samples contain high mass percentage of GUN, which in turn produce more nitric acid and accelerate the degradation process. Opposite to first peak, MMLR₂ values corresponding to second DTG peak show a reverse trend, i.e., samples containing bases have lower MMLR values as compared to sample (ii) (Table 3). This might be due to the higher concentration of flame retardant in base catalyzed impregnated samples results in production of comparatively larger amount of non flammable products which in turn inhibits the degradation process.

The OPD was calculated by subtracting the onset and shift values of DTG curve in minutes and are reported in Table 3. The OPD for untreated wood sample (i) is 16.2 min which increase to 19.2 min for sample (ii). The OPD values further increases up to 20.7 min for compounds in which the impregnation was carried out in presence of bases (samples (iii)–(vi)) (Table 3). This is because the degradation of samples (iii)–(vi) starts earlier (shown by T_o , Table 2) as compared to samples (i) and (ii). The flame retardant increases the OPD value according to their effectiveness [19]. Thus, the presence of a base is attributing toward the increase in flame retardancy.

Table 3 Maximum mass loss rate and overall pyrolysis duration data of samples

Samples	MMLR ₁ /% min ⁻¹	MMLR ₂ /% min ⁻¹	OPD/min
(i)	12.1	–	16.2
(ii)	4.8	10.0	19.2
(iii)	5.7	6.4	19.5
(iv)	5.6	5.0	20.7
(v)	5.4	8.5	20.4
(vi)	5.5	6.4	20.5

Activation energy

The iso-conversional plot of O–F–W for samples (i) and (iv) and modified Coats–Redfern for samples (ii) and (v) are shown in Figs. 6, 7, 8, and 9, for illustration. The iso-conversional plot of O–F–W and modified Coats–Redfern showed a general trend of activation energy. The average E_a and r values for all samples are given in Table 4. The $r > 0.97$ were used to calculate E_a at a particular α value. The average E_a of sample (i) for single pyrolytic stage calculated by O–F–W and modified Coats–Redfern methods are 137.0 and 134.7 kJ mol⁻¹, respectively. The average E_a values were calculated in the conversional range 0.03–0.8. The average E_a values for sample (i) are in agreement with those reported in the literature for sound wood (~ 150 kJ mol⁻¹) [20]. Yao et al. [15] reported the E_a for maple wood ~ 155 kJ mol⁻¹ calculated by model free methods under nitrogen atmosphere. These activation energy values for sample (i) corresponds to the degradation of cellulose mainly as it is main component of wood. Also, the average E_a values for sample (i) are close which are reported in literature for cellulose [21–23]. However, average E_a of sample (i) is different by a small value from values reported in literature [15, 20–23] for wood and cellulose. This deviation is due to difference in holocellulose/lignin ratio of wood [20] and also due to sample origin, processing and experimental condition and method used to calculate activation energy [24, 25]. Since DTG of treated wood samples show two peaks so E_a was calculated separately for each degradation stage. The E_a for treated samples (ii)–(vi) have been calculated in a common α range, i.e., 0.04–0.3 and 0.3–0.8 corresponding to first and second pyrolytic stages, respectively, except for sample (iv). The E_a for samples (ii)–(vi) calculated using O–F–W and modified Coats–Redfern methods for the first stage are 109.3, 130.6, 184.8, 161.2, 176.5 kJ mol⁻¹ and 106.9, 128.9, 183.6, 160.9, 174.5 kJ mol⁻¹, respectively. This is corresponding to

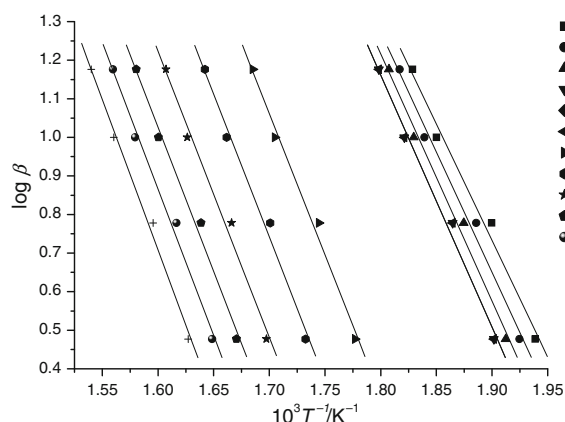


Fig. 6 Iso-conversional plot of O–F–W method for sample (i)

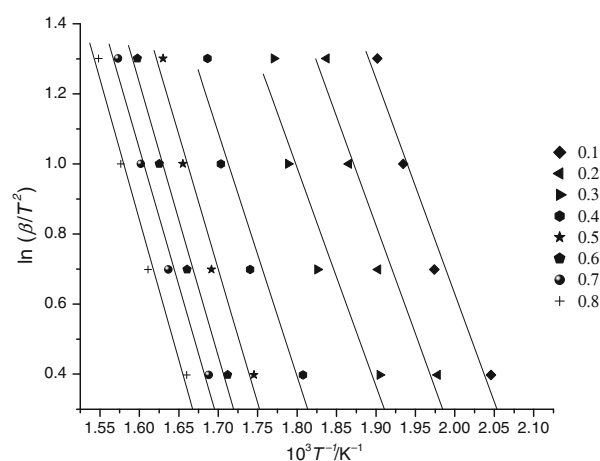


Fig. 7 Iso-conversional plot of modified Coats–Redfern method for sample (ii)

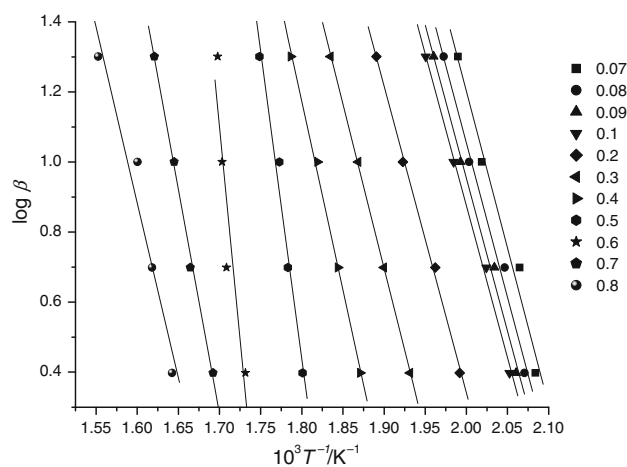


Fig. 8 Iso-conversional plot of O–F–W method for sample (iv)

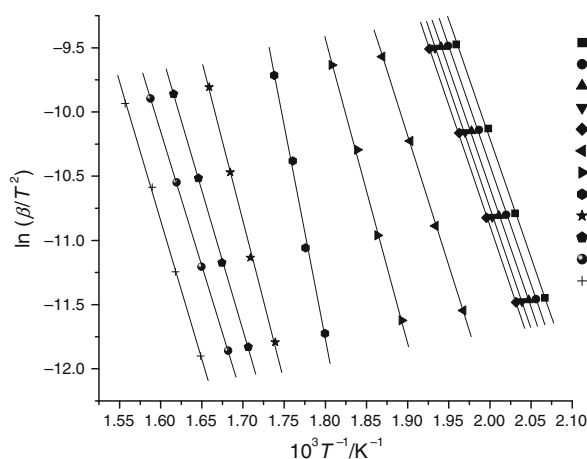


Fig. 9 Iso-conversional plot of modified Coats–Redfern method for sample (v)

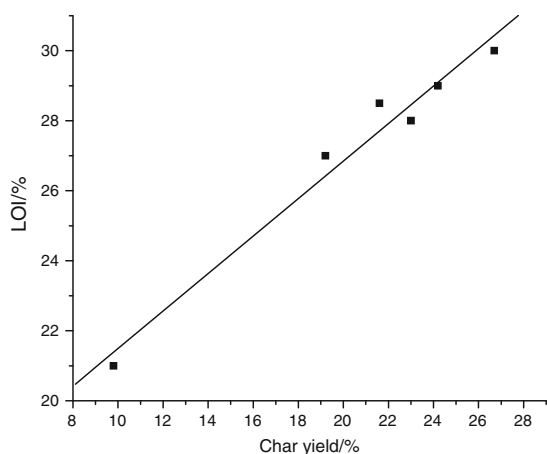
Table 4 Average activation energy and correlation coefficient of samples

Samples	$E_a/\text{kJ mol}^{-1}$								α value	
	O-F-W				Coats-Redfern (modified)				Stage I	Stage II
	Stage I	r	Stage II	r	Stage I	r	Stage II	r		
(i)	137.0	0.9951	–	–	134.7	0.9942	–	–	0.03–0.8	–
(ii)	109.3	0.9962	142.2	0.9965	106.9	0.9954	138.4	0.9960	0.04–0.3	0.3–0.8
(iii)	130.6	0.9975	176.0	0.9980	128.9	0.9971	174.2	0.9975	0.04–0.3	0.3–0.8
(iv)	184.8	0.9991	207.6	0.9992	183.6	0.9989	206.4	0.9986	0.06–0.5	0.5–0.8
(v)	161.2	0.9981	204.6	0.9985	160.9	0.9980	203.6	0.9978	0.04–0.3	0.3–0.8
(vi)	176.5	0.9979	205.7	0.9990	174.5	0.9975	204.3	0.9984	0.04–0.3	0.3–0.8

Table 5 Horizontal burning rate in accordance with UL 94 test

Sample	Horizontal burning test				Burning character
	Burning length/mm	Burning time/min	Rate of burning/mm min ⁻¹	Status	
(i)	95	0.9	105.5	Fail	CB, No charring
(ii)	–	–	SE within 0.3 min	Pass, HB	Charring
(iii)	–	–	SE within 0.2 min	Pass, HB	Charring
(iv)	–	–	SE within 0.13 min	Pass, HB	Charring
(v)	–	–	SE within 0.2 min	Pass, HB	Charring
(vi)	–	–	SE within 0.16 min	Pass, HB	Charring

SE self extinguish, CB completely combustible

**Fig. 10** Relationship between LOI and char yield

dehydration and deacidification process [9]. The E_a calculated by O-F-W and modified Coats-Redfern methods for second pyrolysis stage for samples (ii)–(vi) are 142.2, 176.0, 207.6, 204.6, 205.7 kJ mol⁻¹ and 138.4, 174.2, 206.4, 203.6, 204.3, kJ mol⁻¹, respectively. The second stage E_a values correspond to decomposition of samples left after first stage. The E_a for second pyrolytic stage of treated samples is higher than of untreated sample (i). This

suggests the increased stability of treated samples and this might be due to formation of the non-combustible products which inhibits the degradation process. The E_a values calculated by Coats-Redfern (modified) method are in good agreement with those of calculated by O-F-W [26].

UL 94 test

Horizontal burning rate calculated in accordance with UL 94 test is reported in Table 5. Sample (i) burnt completely without charring while all other treated samples get self extinguish after the flame application and charring take place. Horizontal burning rate of untreated sample (i) is 105.5 mm min⁻¹ and it fails to pass HB rating. But all treated samples (ii)–(vi) self extinguish and pass HB rating. The self extinguish time for samples (iii)–(vi) lie in the range 0.1–0.2 min which is less than the SE time for sample (i) (0.3 min). Self extinguish time is the least for sample (iv) and is maximum for sample (ii). Here, it is clear that with addition of small amount of bases self extinguish time decreases and can be arrived at that the flame retardancy imparted by GUN on wood is improving in presence of bases. Thus, wood treated with GUN-DMAP is imparting best flame retardancy among all treated samples.

LOI and char yield

Studies [4, 7, 12] show that application of flame retardant increases LOI and char yield according to their efficiency. Higher the value of LOI and char yield better is the flame retardancy. The percentage char yield at 873 K and LOI values of untreated and treated samples were reported in Table 2. The relationship between LOI and char yields is shown Fig. 10. Char yield of untreated sample (i) is 9.8% and the corresponding LOI value is 21%. When wood is treated with GUN in absence of a base (sample (ii)), char yield increases from 9.8 to 19.2% and LOI values increase from 21 to 27%. When wood is treated with GUN in presence of bases (samples (iii)–(vi)), char yield increases from 19.2 to 26.7% and LOI values increase from 27 to 30%. Hence, with addition of small amount of bases in GUN, both char yield and LOI value increases, thereby indicating in improvement of flame retardancy.

Conclusions

The SEM, CHN, and MGP analysis of samples reveal that the bases are catalyzing the impregnation of GUN. The DTG study indicates that degradation of treated samples occurs in two stages while there is single stage degradation of untreated samples. The activation energy of all samples is calculated by O–F–W and modified Coats–Redfern corresponding to each degradation stage. The E_a for second pyrolytic stage of treated samples is higher than those E_a values which are corresponding to single pyrolytic stage of samples (i). This is due to formation of the non-combustible products which inhibits the degradation process. Further, percentage char yield and LOI of samples (iii)–(vi) are greater than untreated sample (i) and sample (ii). All treated samples self extinguish in horizontal burning test (UL 94) and pass HB rating but untreated samples fail to pass the HB rating. The self extinguish times for samples treated in presence of the bases are lower than sample treated in absence of bases. This is due to production of more non-combustible inert gases which dilute the fuel supply.

It is concluded that the flame retardancy imparted by GUN on wood can be improved by the addition of small amount of bases in the flame retardant GUN solution. In this study, sample impregnated with GUN with DMAP is imparting best flame retardancy than others.

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