Analysis of Chemical Properties of Thermally Treated *Pinus roxburghii* Sargent Wood

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Effects of thermal modification were determined relative to chemical parameters of *Pinus roxburghii*. Thermal modification of wood was carried out at 80, 120, 160, and 200 °C for 2, 4, and 6 h. The chemical properties were different for different temperatures and different heating time. All parameters were similar except for cold water soluble extractives. Among the chemical properties studied, the maximum mean value of cold water extractives (8.20%), hot water soluble extractives (12.7%), holocellulose content (71.8%), and ash content (1.46%) were recorded at 120 °C, whereas the maximum mean values of alcohol benzene soluble extractives (13.9%) and lignin content (33.7%) were observed at 200 °C. The minimum mean value of cold water soluble extractives (5.82%), hot water soluble extractives (9.27%), holocellulose content (65.8%), and ash content (1.03%) were found to be at 200 °C, while the highest value of alcohol benzene soluble extractives 12.2% (control) and lignin content (28.0%) were found to be at 80 °C.

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INTRODUCTION

The basic idea of thermal treatment of wood is to improve its inclusive (physicochemical and mechanical) properties. Thermal treatment is an alternative for preserving wood without reliance on chemicals. Thermal modification of wood has been widely used in many areas, as it is an eco-friendly approach towards modification of wood without any adverse effect on environment at the end of the service life of the wood. Many significant chemical changes occur in the wood due to thermal processing (Piernik *et al.* 2019). Wood is composed of three primary cell wall constituents: cellulose, hemicelluloses, and lignin, which form a natural composite. Cellulose is a long-chain polymer of β -D-glucose, formed by the process of photosynthesis (Dinwoodie 2000), which constitutes 40 to 50% of the dry weight of wood. Cellulose chains within wood have an estimated length of up to 5000 nm with adjacent chains bonded to one another through a combination of hydrogen bonds and Van der Waals' Forces (Barnett and Jeronimidis 2003). Wood is susceptible to biodegradation by different agents.

Thermal treatment of wood is an attempt to improve some of its drawbacks. Bound water is lost during the process. Some of the volatile extracts evaporate, some decompose, some new ones are produced, and some may be left unchanged (Wang *et al.* 2018; Esteves and Pereira 2008). The volatile extracts are the first to be lost during treatment, and this

would likely include the volatile terpenes, 2-furon carboxyaldehyde, acetic acid v, 2propane, hydrocarbons, fatty acids, steroids, lactones, and other derivatives from the thermal degradation of the wood components (Kocaefe *et al.* 2008). Simultaneously, anhydrous and phenolic components appear in the wood mass (Esteves and Pereira 2008). Resin acids, fats, and waxes move to the surface of the wood as the temperature approaches 200 °C and almost disappears with further increase. When the volatile extracts are removed, the pH of wood decreases (Gündüz and Aydemir 2009).

Heat treatment is a method of changing the chemical structure of cell wall in wood with the influence of heat, pressure, and eventually moisture without application of chemicals (Sinkovic *et al.* 2011). However, this method can be an alternative method for improving durability and dimensional stability of wood without the use of chemical additives.

Himalayan long needle pine, also known as chir pine, belongs to the family Pinaceae. It is native of principal valley of Himalaya. Chir pine forms pure stands in the natural forest in its habitat, but in its upper and lower limits it forms mixed forest with other conifers and broad leaf species. It is an important commercial species of the Himalayan region and is valued for its timber, paper pulp, and resin (Tiwari 1994; Khare 2007).

The variation in chemical properties of thermally treated wood and non-treated wood are investigated by using TAPPI (Technical Association Pulp and Paper Industry) standard methods, aiming to improve the utilization potential of *Pinus roxburghii* wood in a wider range of applications.

EXPERIMENTAL

Sample Preparation

A wooden log from a single trunk of the species was collected from the Solan market, Himachal Pradesh, India. It was converted into small chips. Then these shade-dried wood chips were finely powdered into saw dust, with the help of a wood chipper cum grinder and placed in a desiccator.

Thermal Modification of Samples

Pine saw dust was treated according to the following procedure: (1) Oven-drying of samples at room temperature $(25 \pm 2 \ ^{\circ}C)$ in order to evaporate water from the samples; (2) oven-heating of samples at different temperatures $(80 \pm 2 \ ^{\circ}C, 120 \pm 2 \ ^{\circ}C, 160 \pm 2 \ ^{\circ}C, and 200 \pm 2 \ ^{\circ}C)$ for (2h, 4h, and 6 h) respectively.

Analysis of Samples

Proximate chemical analysis was carried out by employing TAPPI (Technical Association Pulp and Paper Industry) standard methods, as described below. The soluble content was calculated using Eq. 1.

Soluble Content (%) =
$$\frac{Initial \ weight - Oven \ Dry \ weight}{Oven \ Dry \ Weight} \times 100$$
 (1)

Cold water solubility (TAPPI T1m-59 1959)

Two grams (2 g) of oven-dried coarsely ground wood was weighed and transferred into a conical flask containing 300 mL of distilled water. The mixture was digested at room

temperature with frequent stirring for 48 h. The material was filtered through an IG-1 crucible, washed thoroughly with cold distilled water, and dried to a constant weight at 105 \pm 2 °C. The cold water solubility was determined by calculating the loss in weight of sample taken and was expressed as percentage on the basis of oven dry weight of wood.

Hot water solubility (TAPPI T1m-59 1959)

Two grams (2 g) of oven-dried coarsely ground wood was taken in a flask having 100 mL of double distilled water fitted with Reflux Condenser. It was digested in a boiling water bath for 3 h. The contents were filtered through an IG-1 crucible, and the residue was dried in an oven at 105 ± 2 °C to constant weight. The solubility was determined by calculating the loss in weight of the sample taken and expressed as percentage.

Alcohol-benzene extractives (TAPPI T6m-59 1959)

Ten grams (10 g) oven-dried coarsely ground wood was placed in a porous thimble (oven dried and weighed). The thimble was placed in a Soxhlet Apparatus and extracted with 200 mL of alcohol-benzene (1:2 v/v) mixture for six hours (6 h). The porous thimble was then taken out and allowed to dry in open air and finally in an oven at $105 \pm 2^{\circ}$ C until constant weight. The alcohol-benzene solubility was determined by calculating the loss in weight of the sample taken and expressed in percentage.

Klason-lignin content (TAPPI T12m-59 1959)

Two grams (2 g) oven-dried samples pre-extracted with alcohol-benzene (1:2v/v) was treated with 15 mL of 72% sulphuric acid for 2 h at 18 to 20 °C with constant stirring. The material was brought down to 3% by adding 545 mL of double distilled water. The solution was refluxed for 4 h and then allowed to settle. The contents were filtered and washed with hot distilled water. The material was then dried in an oven at 105 \pm 2 °C until constant weight and expressed in percentage.

Holocellulose (TAPPI T9m-59 1959)

Five grams (5 g) of oven-dried sample pre-extracted with alcohol-benzene (1:2v/v) were placed in a conical flask and 160 mL of distilled water was added to it. The contents were treated with 1.5 g of sodium chlorite and 10 drops of acetic acid at 70 to 80 °C while heated by a water bath for 1 h. The process was repeated four times until the meal became white. The contents were then filtered through an IG-2 crucible, washed with water, and finally with acetone. The sample was oven-dried at 105 ± 2 °C to a constant weight. The extracted holocellulose content was calculated on the basis of the oven-dry weight.

Ash Content (%)

Two grams (2 g) of oven-dried wood samples were placed in a silica crucible in a furnace at 575 \pm 25 °C for 3 h to burn off all carbon. The completion of ignition was indicated by the absence of black particles. The crucible was removed from the furnace and cooled to room temperature, and the ash content was weighed.

Data Analysis

The experiments were laid out in the Completely Randomized Block Design (CRBD) Factorial. In total, three replicates for each treatment were taken.

Analysis of Variance (ANOVA)

The analysis of variance table was set up as shown in Table 1:

Table 1.	Analysis	of Variance
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Source of Variation	Degree of Freedom	Mean Sum of Squares	Variance Ratio
Replication	(r-1)	Mr	
Treatment	(t-1)	Mt	Mt/Me
Error	(r-1)(t-1)	Me	
Total	(r x t)-1	Μτ	

In Table 1, r is the number of replications, t is the number of treatments, Mr is the mean sum of squares due to replication, Mt is the mean sum of squares due to treatment, and Me is the mean sum of squares due to error.

The critical difference (CD) was calculated as follows,

 $CD = SE(d) \times t_{0.05}$

(2)

where, SE (d) is the standard error of difference, which was calculated as,

$$SE (d) = \sqrt{2Me/r}$$
(3)

and to.05 is the value of t at 95 per cent level of significance.

RESULTS AND DISCUSSION

In wood, the cold water soluble content generally consists of tannins, gums, sugars, and salts. A higher heating temperature of wood typically results in a greater reduction of extractives content (Esteves *et al.* 2008). The critical examination of data revealed significant variation among different temperatures and heating times at the 5% level of significance. The maximum mean value of cold water extractives was observed at 200 °C. Among the different heating times, the maximum mean value (7.16%) was observed at 2 h. The lowest mean value of 6.91% was recorded at 6 h. The highest value of 8.32% was noticed at 120 °C (4 h), whereas the lowest value of 5.31% was recorded at 200 °C (6 h) (Table 2).

Table 2. Cold Water Soluble Extractives (%) of Thermally Treated Pinus roxburghii Wood

Temperature (°C) and Time (h)	2 h	4 h	6 h	Mean
80	6.80	7.48	7.58	7.29
120	8.02	8.32	8.26	8.20
160	7.82	7.53	6.68	7.34
200	6.47	5.67	5.31	5.82
Control	6.71	6.71	6.71	6.71
Mean	7.16	7.14	6.91	
	CD _{0.05}			
Temperature (7)			0.24	
Heating time (D)			0.19	
Temperaturex Heating time (TxD)			0.42	



Fig. 1. Variation in cold water soluble extract

This variation in cold water extractives may be due to vaporization of different extractives from wood during thermal modification. Thermally treated *Eucalyptus globulus*, at 190 and 200 °C for time duration *viz.*, 2, 4, and 6 h, the extractive content increased with increase in temperature and decrease with time duration (Esteves *et al.* 2008). Silva *et al.* (2015) conducted a study on *Corymbia citriodora* wood at 160 and 180 °C for 150 min and 200 °C for 120 min, and reported that with increase in temperature and durations, there is reduction in extractives content (17.8% to 9.6%). The maximum value of cold water extractives has been observed at 140 °C (2 h), and the minimum was observed at 200 °C (6 h) in *Fraxinus angustifolia*. Yalcin and Sahin (2015) also reported in their study that cold water extractives content decreases with increase in temperature and durations.

The hot water soluble extractives in thermally modified wood for all treatments is presented in Table 3, showing significant variation at different temperatures. The maximum value of 12.7% was recorded at 120 °C and minimum value (9.3%) was noticed at 200 °C.

Table 3. Hot Water Soluble Extractives (%) of Thermally Treated Pinusroxburghii wood

Temperature (°C) and Time (h)	2 h	4 h	6 h	Mean
80	11.64	11.73	12.05	11.81
120	12.86	12.72	12.44	12.67
160	11.53	10.90	10.06	10.83
200	9.45	9.28	9.09	9.27
Control	10.31	10.31	10.31	10.31
Mean	11.16	10.99	10.79	
CD _{0.05}				
Temperature (T)			0.45	
Heating time (D)			NS	
Temperaturex Heating time (TxD)		(T×D)	NS	

Among the heating time, the mean value of hot water extractives ranged from 10.8 to 11.2% and was found to be statistically non-significant. The interactions between temperatures and heating time were also found to be non-significant and ranged between 9.28 to 12.86%. Wood is composed of extractives in the form of organic compounds viz., fats, waxes, alkaloids and phenols, *etc.*, that are soluble in hot water. Values of hot water soluble extractives are higher than those of cold water.



Fig. 2. Variation in hot water soluble extract

The relative content of hot water soluble components increased slightly in the beginning, and then it decreased with increasing temperature and duration. Similar trends was reported by Yalcin and Sahin (2015) in narrow leaved ash wood. Yildiz (2002) concluded that the hot water soluble extractives decreases with temperature ranging from 180 to 200 °C. Sikora *et al.* (2018) in pine wood reported that at temperatures 100 to 160 °C, fats and waxes move to the surface of the wood, which leads to an increase in the extractives content and at 180 °C, decomposition starts there. Above 200 °C, resin acids are decomposed which leads to a decrease in the content of extractives.

The values obtained in Table 4 revealed significant differences in alcohol benzene extractives in wood among different temperatures at the 5% level of significance. For different temperatures, the maximum mean value of 13.87% was recorded at 200 °C, which was statistically at par with 13.6% (120 °C) and 13.8% (160 °C). The minimum mean value (12.2%) was noticed in the control. Among different heating times, the mean values were non-significant at the 5% level of significance and lay between 13.2 and 13.5%. The interactions between temperature and heating time were also found to be non-significant, and values ranged between 12.2 and 14.0%. The extractives are responsible for various functions including tree metabolism, energy reserves, defense mechanism against microbial attack, as well as in affecting the pulping quality of wood are alcohol-benzene soluble extractives, which are usually composed of oleoresins, fats, waxes and oils. Earlier work by Yalcin and Sahin (2015) has concluded that the alcohol benzene extractives were less in the control specimen of wood and that the content increases with an increase in temperature and duration. The highest alcohol benzene content was observed in samples heated at 220 °C for 6 h.

Table 4. Alcohol Benzene Soluble Extractives (%) of Thermally Treated Pinusroxburghii Wood

Temperature (°C) and Time (h)	2 h	4 h	6 h	Mean
80	12.64	13.61	13.65	13.30
120	13.75	13.40	13.65	13.60
160	13.82	13.73	13.94	13.83
200	13.70	13.92	13.98	13.87
Control	12.17	12.17	12.17	12.17
Mean	13.22	13.37	13.48	
(CD _{0.05}			
Temperature (T)			0.38	
Heating time (D)			NS	
Temperaturex Heating time (TxD)			NS	



Fig. 3. Variation in alcohol benzene soluble extract

There was significant variation (Table 5) for Klason lignin content among different temperatures at 5% level of significance. For different temperatures, the highest mean lignin content (33.7%) was recorded at 200 °C, which was at par with the control (30.9%). The lowest lignin content (28.0%) for 80 °C was at par with 28.25% (120 °C), 29.40% (160 °C), and 30.93% (control). Among the heating time, the mean values were not significant and ranged from 29.9 to 30.6%. The combinations of temperatures and heating time were not significant and ranged between 27.7 and 35.5%. When wood is exposed to high temperatures, certain extractives decompose, but new extractives are created due to decomposition of main components, and their total quantity in thermally modified wood increases.

Temperature (°C) and Time (h)	2 h	4 h	6 h	Mean	
80	28.48	27.68	27.93	28.03	
120	27.74	27.70	29.32	28.25	
160	29.59	29.27	29.33	29.40	
200	32.73	33.00	35.50	33.74	
Control	30.93	30.93	30.93	30.93	
Mean	29.90	29.72	30.60		
CD _{0.05}					
Temperature (T)			0.90		
Heating time (D)			NS		
Temperaturex Heating time (TxD)			NS		

Table 5. Klason Lignin (%) of Thermally Treated Pinus roxburghii Wood





Sikora *et al.* (2018) revealed that the quantity of thermally more stable polymers (lignin, cellulose) in modified wood increases slightly with decreasing holocellulose content. Yalcin and Sahin (2015) noticed that in narrow leaved ash wood, the lignin content increases with increased temperature; the maximum lignin content was recorded at 220 °C and minimum at 140 °C. Repellin and Guyonnet (2005) also concluded that the amount of Klason lignin increases with increase in temperatures. At 220 °C, the quantity of lignin increases significantly for treatments longer than 60 min. and at 200 °C, it decreased for

treatment time between 60 min and 180 min duration, and it increases again with a 600 min time duration. Bhoru (2015) reported the lignin content increases with temperature.

Analysis of variance showed significant differences in holocellulose content of thermally treated wood at different temperatures at 5% level of significance (Table 6). Among different temperatures, the highest mean value (71.5%) was recorded at 120 °C which was statistically at par with 80 °C (70.0%) and 160 °C (70.7%). Meanwhile, the minimum mean value (65.8%) was noticed at 200 °C, which was at par with control (68.5%). Among heating time, the mean values were not significant and ranged between 68.9 and 69.5%. The interactions between temperatures and heating time were not significant and ranged from 63.6 to 71.6%. An observed decrease in holocellulose content during thermal modification may be caused by depolymerisation of the hemicelluloses during hydrothermolysis and some degradation of the cellulose during curing (Boonstra 2008). Sikora *et al.* (2018) reported that hemicelluloses are the least stable component of wood during thermal treatment. Thus, the amount of hemicellulose decreases in modified wood, due to a relative increase in cellulose and lignin content. The latter are thermally more stable components and degrade at higher temperature.

Temperature (°C) and Time (h)	2 h	4 h	6 h	Mean
80	69.55	70.00	70.37	69.97
120	71.26	71.56	71.61	71.48
160	71.09	70.81	70.32	70.74
200	67.27	66.64	63.56	65.82
Control	68.51	68.51	68.51	68.51
Mean	69.54	69.51	68.87	
(
Temperature (T)			2.79	
Heating time (D)			NS	
Temperaturex Heating time (TxD)		(T×D)	NS	

 Table 6. Holocellulose Content (%) of thermally treated Pinus roxburghii wood



Fig. 5. Variation in holocellulose content

Hemicelluloses in spruce wood dropped by 37.4% at 210 °C and by 58.8% in oak wood, which suggests that hemicelluloses in coniferous wood are thermally more stable than hemicelluloses in deciduous wood. Bhoru (2015) reported that the holocellulose

content decreased with an increase in the temperature and with increasing duration at 200 °C. Holocellulose content decreased to 67% and was approximately 5% less than the control sample of *Pinus radiata*. Khalid *et al.* (2011), observed similar findings in *Acacia* hybrid wood and concluded that changes in wood are due to loss of polysaccharide material.

The inorganic constituents of lignocellulosic material, referred to as ash content, are the residues remaining after combustion of the organic matter at a temperature of 525 \pm 25 °C. Table 7 shows significant variations in ash content in the wood in different temperatures at 5% level of significance. Among different temperatures, the maximum mean value of 1.46% was recorded at 120 °C, while the minimum mean value of 1.03% was noticed at 200 °C compared to control (1.23%). At different heating times, the values were not significant and ranged between 1.25 to 1.27%. The combined effect of temperatures and heating time were not significant and ranged between 0.97 to 1.50%. Yalcin and Sahin (2015) found the decrease in the ash content with increase in the temperature and duration, and these results are in line with the findings of present study.

Temperature (°C) and Time (h)	2 h	4 h	6 h	Mean	
80	1.30	1.37	1.40	1.36	
120	1.40	1.47	1.50	1.46	
160	1.27	1.23	1.17	1.22	
200	1.10	1.03	0.97	1.03	
Control	1.23	1.23	1.23	1.23	
Mean	1.26	1.27	1.25		
(CD _{0.05}				
Temperature (T)			0.24		
Heating time (D)			NS		
Temperaturex Heating time (TxD)		(T×D)	NS		

 Table 7. Ash Content (%) of Thermally Treated Wood of Pinus roxburghii



Fig. 6. Variation in ash content

CONCLUSIONS

- 1. The cold and hot water soluble extractives content decreased with increase in temperature. Maximum cold and hot water soluble extractives were found at 120 °C.
- 2. The alcohol benzene soluble extractives content increased with increasing temperature.
- 3. The lignin content increased with temperature, and a comparative decrease was found in holocellulose content.

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