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Near infrared spectroscopic investigation of the thermal degradation of wood

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ABSTRACT

In the present paper changes in the near infrared (NIR) spectra and color parameters of wood (*Dalbergia sissoo*) after thermal treatment are reported. The color change of the wood upon heating was analyzed by the CIELAB color parameters. The degradation of wood upon heating was determined by differential scanning calorimetry (DSC). Wood degradation involved from 50 °C to 80 °C changes in the amorphous region in cellulose took place, from 100 °C to 130 °C changes were observed in physically bonded water and from 150 °C to 160 °C degradation of hemicelluloses took place. The phase transition of cellulose took place at about 175 °C and changes in the crystalline region in cellulose were observed at 210 °C. The significant changes are observed in the lignin at elevated temperatures. The change in the color of the wood on increasing temperature is related to the degradation of hemicelluloses. NIR spectroscopy was found to be a powerful tool to determine the physicochemical structural changes in wood on heat treatment.

1. Introduction

Wood is a natural composite polymeric material consisting of a cellulose network bonded together by rigid fixed polyosic lingo-polysaccharide amorphous matrix chains. The mechanical and chemical properties of wood are depicted by certain parameters like, density, stiffness and strength, which are closely related to the ultra-fine cell wall structure (less than 1 Å) [1,2]. Wood is considered to be a durable material, which withstands weathering without losing its structural properties. However, there are some non-biological parameters as humidity, temperature, solar irradiation, ozone content and pollutants [3], that may be responsible for the degradation of wood. The rate of degradation depends upon the type of wood, i.e., softwood or hardwood. For architectural and industrial purposes, wood undergoes through different processes, where several chemical and mechanical changes lead to causing the degradation of the wood [4–10]. Generally the degradation of wood is caused by light irradiation or by heat treatment [5,6,11,12]. The effect of heat on color change of the different species of wood has been reported previously [13]. More recently Esteves and Pereira published a review on wood modification by heat treatment [14]. Thermal degradation of wood is highly dependent on its constituents [9,15]. The thermal stability of different wood species has been compared recently [16,17]. The complex structure of wood and the interaction between its components makes it difficult to differentiate the degradation of each component (cellulose, holocellulose, hemicelluloses and lignin) on heat treatment. The degradation of wood generally begins with decomposition of hemicelluloses followed by an early stage decomposition of lignin and then depolymerization of cellulose. Further degradation involves oxidation of wood to volatile compounds (CO_2, CO, H_2O, etc.) at higher temperatures (380–470 °C) [11,18,19]. The thermal decomposition of crystallites cellulose in wood has been reported [20,21]. Gartote et al. studied the deacetylation of hemicelluloses during the hydrothermal processing of Eucalyptus wood [22].

Variation in the color of wood is caused by changes in the chemical composition, which result from degradation or weathering [1,3,18,23,24]. Upon heat treatment the decrease in the brightness and increase in the color difference of wood arise due to the decrease in the content of hemicelluloses [15,24–28]. A change in the color of wood arising from heat treatment is closely related to the change in physicochemical structure. These kinds of changes have been characterized by infrared (IR) spectroscopy [2–8,25,26,29–33]. In addition thermal degradation of the wood is generally studied by conventional methods namely thermogravimetry, differential scanning calorimetery (DSC) and thermal volatization analysis. These conventional methods are very time consuming and expensive. Therefore, there is a need to develop a non-destructive, rapid and accurate method for analyzing the degradation of wood. This method could be used to monitor the quality of wood in industrial processes.

Though infrared spectroscopy provides a solution to the conventional methods, it introduces some limitation to sample preparation. But, near infrared (NIR) spectroscopy requires very

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little sample preparation and it is a non-destructive method for analyzing the chemical composition. Since wood species have chemical composition consisting of C–H, O–H, N–H, C–C and C–O bonds, they exhibit unique absorption in the NIR region in the form of overtones and combinations of the fundamental bands. NIR spectroscopy has shown its significant potential in analyzing the changes in mechanical, physical and chemical properties of wood upon heating [1,24,27–36]. More recently Gaspar et al. reported the application of near infrared spectroscopy for the evaluation of glue lines of timber before and after ageing [37].

In the present study we investigate the use of diffuse reflectance NIR spectroscopy for the non-destructive analysis of the degraded biomass of Shisham (*Dalbergia sissoo*) wood upon heat treatment. The wood samples were heated at different temperatures on a hot stage plate. Wood degradation was monitored by the changes in the color through measuring the CIELAB color parameters. Different steps of degradation of the heated wood sample were determined by DSC analysis. The color change and the degradation steps of wood by DSC were analyzed and correlated with NIR spectra. The change in the color of the degraded wood is easily understood by analyzing the diffuse reflectance NIR spectra.

2. Materials and methods

The wood samples of Shisham (*D. sissoo*) were taken from a timber factory in the powder form. For the NIR spectral measurement the wood powder was further ground to get almost uniform particle size using a grinder with a rotational speed of 3000 rpm. 2 mm thick circular pellets of 25 mm diameter were made by applying a pressure of 16 N/m^2 in a hydraulic pressure machine. This wood pellets was used for thermal, color coordinates and NIR spectroscopic studies. The wood pellets were heated in air on a hot stage plate (Linkam TP92, HFS 91/stage with a platinum resistor). The wood pellet was directly put on the silver block of the hot stage plate. The temperature of heating was ranges from 27 °C to 450 °C. The heating and cooling rates were maintained at 10 °C/min. During the thermal treatment, the wood pellet was held on the silver block for 1 h.

2.1. DSC measurement

The DSC experiments of the wood samples (5 mg) were carried out using Matler DSC 822 equipped with a cooling (N_2) system, at Shriram Institute for Industrial Research, New Delhi. The DSC was done in the temperature range of 50–270 °C with a temperature difference of 2 °C. Nitrogen flow rate of 40 ml/min was chosen for the analysis. The calorimeter data were obtained with the wood sample enclosed in a covered aluminum pan and an empty pan was taken as reference. This instrument monitored the differential heat flow of the sample and the reference and then the appropriate enthalpy (ΔH) was measured by integration.

2.2. Color measurement

The color coordinates of the thermally treated and non-heated wood pellets were measured by a Gonio spectrophotometer. The source used for illumination was a pulsed xenon lamp having a spectral distribution of a D_{65} illuminant. The measurements were made using a 10° standard observer in the spectral range 300–720 nm. The CIELAB color parameters L^* (lightness) a^* (redness) b^* (yellowness) and ΔE^* (overall color change) were measured.

2.3. NIR spectroscopic measurements

After heating the sample for 1 h at a fixed temperature, the spectra of the wood pellet were taken using an ELICO SL 153 NIR spectrophotometer equipped with a diffuse reflectance accessory. A ceramic block was used to collect the background spectra. The spectra were recorded with a bandwidth of 20 nm in the wavelength range of 1100–2420 nm. The wood samples were cool down to room temperature before collecting the NIR spectra, as NIR spectroscopic techniques are susceptible to temperature. The sample holder was washed with alcohol and dried before recording the next spectra to avoid any unwanted signal.

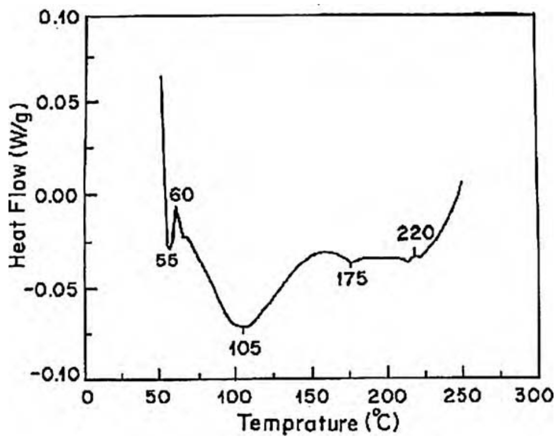

Fig. 1. Differential scanning calorimetry (DSC) thermogram of wood powder.

3. Results and discussion

3.1. DSC analysis

The degradation of wood determined by DSC analysis gives information about the interaction between the constituents of wood and the modification of their chemical structure upon heat treatment [9]. The thermal degradation of wood occurs in different ways in its crystalline and amorphous domains. These domains determine the phase and isophase transition. Transition in the amorphous domain occurs at the moderate temperature range of 50–80 °C while the transition in the crystalline domain occurs above 210 °C [11]. Exotherms in the DSC analysis of wood and its components have been assigned by Tsujiyama and Miyamori [38].

The DSC thermogram of the wood sample (Fig. 1) reveals that active pyrolysis occurs as the temperature approached about 120 °C. The changes in the amorphous region of cellulose are shown by endothermic peaks at 55 °C, 66 °C and an exothermic peak at 60 °C. Among all the wood components hemicelluloses (xylan), shows the lowest thermal stability [15,19,25,39] starting to decompose around 150 °C. In the temperature range of 80–120 °C, the weakening of the hydrogen bonds between the carbohydrates occurs with the loss of physically bonded water. This is evident by an endothermic peak observed at about 105 °C. A small endotherm observed at about 210 °C may be assigned to the condensation product of lignin as it is reported that lignin is devitrified by condensing and softening (plasticizing) process in the temperature range from 135 °C to 250 °C [11]. An endotherm observed at about 175 °C suggests the phase transition of cellulose. The glass transition is evident from an exotherm at about 220 °C. Most of these processes occur simultaneously with thermal decomposition.

3.2. Color analysis

The change in the color of wood sample caused by the thermal degradation was analyzed by determining the change in the CIELAB color parameters, i.e., lightness (L^*), redness (a^*), yellowness (b^*) and overall color change (ΔE^*) [6,40]. The results are summarized

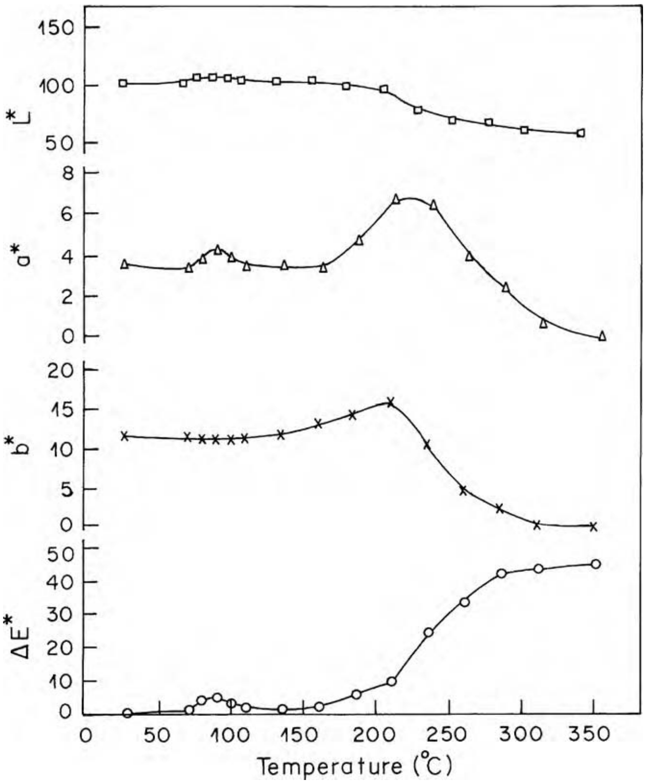

Fig. 2. Variation in CIELAB parameters (□) L^*, (△) a^*, (*) b^* and (○) ΔE* of wood at different temperatures.

in Fig. 2. The L^*, a^*, and b^* are used to calculate the ΔE^* using the Hunter–Scotfield equation:

$$\Delta E* = \{(\Delta L*)^2 + (\Delta a*)^2 + (\Delta b*)^2\}^{1/2}, \qquad (1)$$

where ΔL^*, Δa^* and Δb^* are the difference of initial and final values (before and after the heat treatment) of L^*, a^* and b^* respectively.

The overall color change (ΔE^*) determine by the Hunter–Scotfield equation is due to the combined effect of the three independent parameters i.e., ΔL^*, Δa^* and Δb^* [6,40]. It is clear from Fig. 2 that the effect of heat treatment is to decrease the L^* value and increase the b^* value. However, initially the a* value does not show a consistency in the pattern. This may be due to the resolution of the colorimeter [34]. During the color formation, the L^* value decreases (light to black) on increasing the temperature. The b^* value increases initially and attains a maximum (15.91 at 210 °C) value then starts decreasing (yellow to black) on further increasing the temperature. The a^* value attains almost a constant value in the temperature range of 27–160 °C. It starts decreasing on further increasing the temperature after attaining a maximum value of 6.68 at 210 °C. The ΔE^* value increases rapidly on increasing the temperature above 135 °C after attaining the minimum value (1.35) at temperature 135 °C.

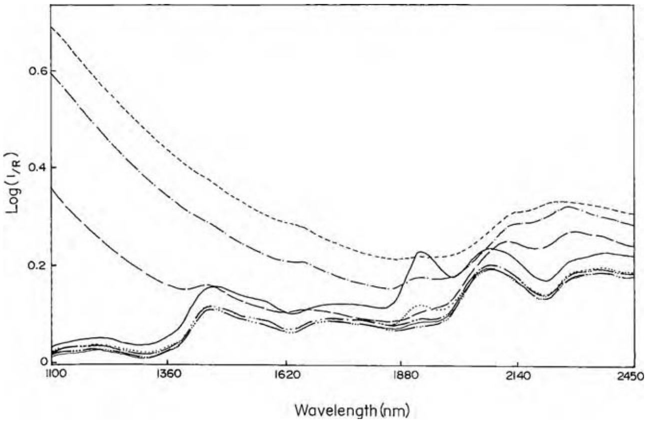

Fig. 3. NIR spectra of wood at 27 °C (—), 100 °C (. . . . . .), 160 °C (— · · —), 185 °C (–), 210 °C (— · · · —), 285 °C (– – –), 310 °C (— · —), at 350 °C (– – –), in the wavelength region of 1100 nm to 2450 nm.

The color change of the wood sample is induced by increasing temperature. Changes in the wood color reflect the chemical changes on heat treatment. For example yellowing of the wood sample indicates the modification of lignin and hemicelluloses. Degradation of wood constituents, mainly hemicelluloses and lignin, leads to the generation of chromophoric units [1,6,11,24]. Cellulose has very little effect and it is not known to discolor appreciably, lignin and hemicelluloses on the other hand are more susceptible to thermal treatment.

3.3. *NIR spectroscopic analysis*

The overlay NIR spectra of the wood sample at different temperatures (where the differences in IR band markers were highly marked) in the wavelength region from 1100 nm to 2450 nm are shown in Fig. 3. The absorption band present at 1200 nm is assigned to the second overtone of CH stretching. The band at 2272 nm is assigned to the combination of CH stretching and CH deformation vibration mode. The absorption band present at 1460 nm is attributed to the OH stretching vibration mode due to semi or—crystalline region in cellulose. The absorption band at about 1920 nm is assigned to the combination of OH stretching and OH deformation vibration mode, due to water present in the wood. The absorption band at 2080 nm may be assigned to the combination of OH stretching and CH deformation vibration modes due to OH in cellulose.

On increasing the temperature from 27 °C to 210 °C, a change in the intensity of all absorption bands is observed in the NIR spectra (Fig. 3). However, the peak position of the absorption band remains the same up to 210 °C. On further increasing the temperature up to 285 °C, a shift in the peak position takes place. It is difficult to isolate the spectral features, which are obtained from the sample

Table 1
Assignments of NIR absorption band markers of wood at different temperatures.

Peak	Wavelength (nm)	Band assignments	Remarks	Reference
1	1350	2× CH str. + CH def.	Cellulose	[39]
2	1435	OH str. first overtone	Amorphous region in cellulose	[1,29]
3	1587	OH str. first overtone	Crystalline region in cellulose	[1,29,37]
4	1668	CH str. first overtone	Aromatic skeletal due to lignin	[35]
5	1711	CH str. first overtone	Furanose/pyranose ring of hemicellulose	[37]
6	1782	CH str. first overtone	–	[46]
7	1920	OH str. + OH def.	Water	[1,29,39]
8	2066	OH str. + CH def.	Cellulose	[1,24,27,28]
9	2258	CH str. + CH def.	CH_3/Cellulose	[34,37,39]
10	2329	CH str. + CH def.	CH due to hemicellulose	[29,34,37]

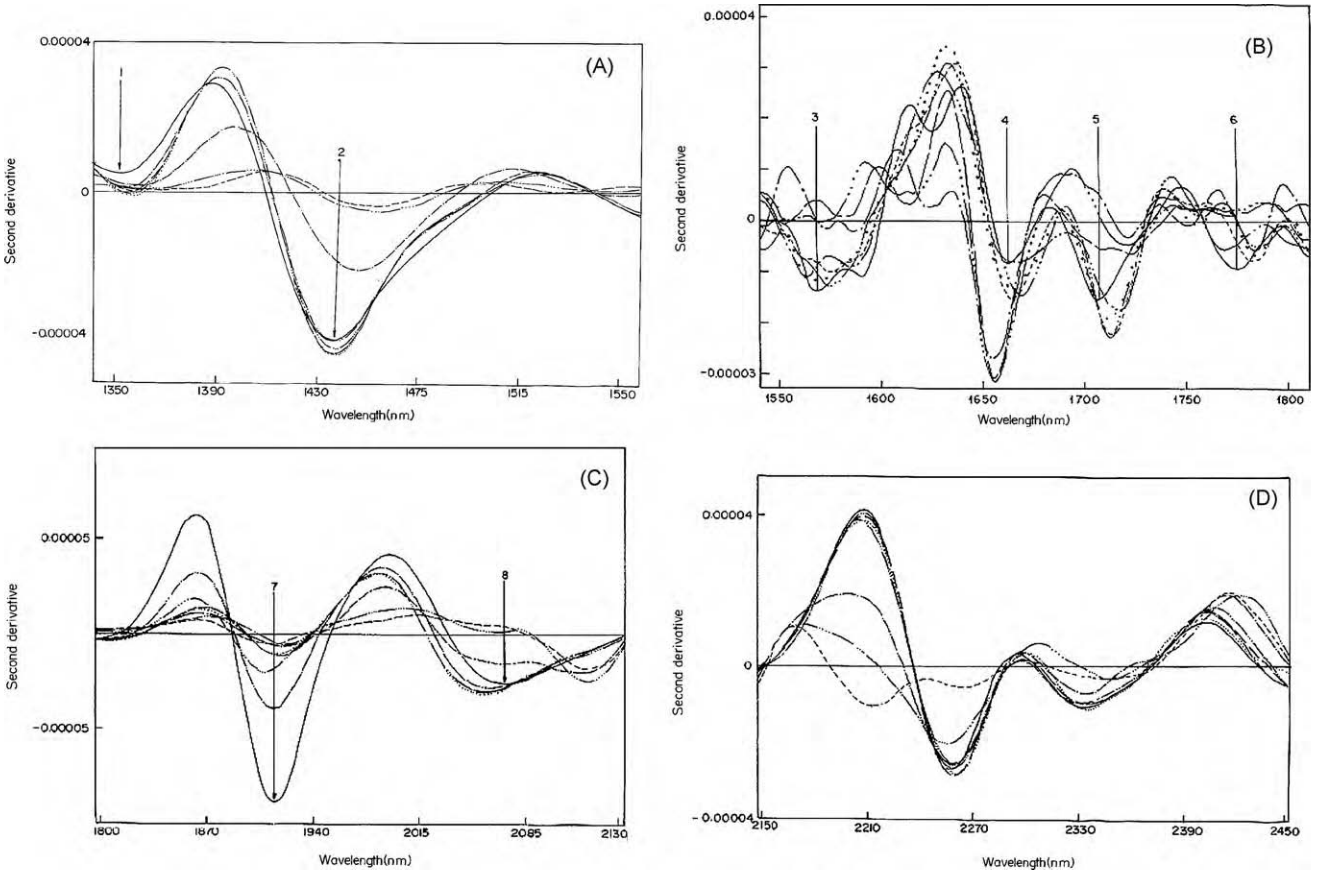

Fig. 4. Second derivative NIR spectra of wood at 27 °C (—), 100 °C (— · · —), 160 °C (– – –), 185 °C (. . . . . .), 210 °C (— · · · —), 285 °C (— · —), 310 °C (— · · · · —) and 350 °C (– – –) in the wavelength region: (A) 1350–1550 nm, (B) 1550–1800 nm, (C) 1800–2130 nm and (D) 2150–2450 nm.

heated at different temperature. This may be due to the presence of overlapping absorption bands in NIR region and also due to the baseline difference because of the change in the optical properties of the individual components present in the wood. However, the second derivative of log (1/*R*) data with respect to wavelength enhances spectral features and also compensates for baseline shifts. The Savitzky–Golay second order polynomial is used with 21 data points to obtain the second derivative spectra. Characteristic wood absorption band assignments corresponding to second derivative spectra are summarized in Table 1 and are in agreements with the literature [1,24,27–29]. Expanded view in the selected wavelength regions of the second derivative diffuse reflectance NIR spectra of the wood sample before and after thermal treatment at different temperatures are shown in Fig. 4A–D.

The absorption band at wavelength 1350 nm (Fig. 4A) is assigned to the combination of first overtone of CH stretching and CH deformation. The band at 2258 nm (Fig. 4D) is assigned to the combination of CH stretching and CH deformation vibration mode of cellulose. On increasing the temperature from 27 °C to 260 °C, the position of both the bands shift towards the higher wavelength region. But as the temperature increases to 285 °C the bands become broader and almost disappear at 310 °C and above. This shows that the C–H bonding changes due to the ring scission (depolymerization) accompanied by a rupture of C–O and C–C bonds within ring unit. This results in the evolution of carbon dioxide, carbon monoxide and water at higher temperatures [18].

In wood, cellulose has a strong interaction with water due to three hydroxyl groups attached to the glucopyranose ring [9,41]. The absorption bands assigned to the first overtone of the fundamental OH stretching mode are identified in the wavelength region of 1435–1587 nm. The absorption band present around 1435 nm (Fig. 4A) may be assigned to the amorphous regions in cellulose of the wood sample. On increasing the temperature from 27 °C to 210 °C, there is no remarkable difference in the intensity and in the peak position of the absorption bands. As temperature increases to 285 °C, a shift in the peak position towards the higher wavelength takes place. As temperature reaches to 310 °C, the absorption bands become broad and disappear on further increasing the temperature. This may be due to the decrease in the concentration of free and hydrogen bonded OH group in the cellulose due to breaking of the hydrogen bonding. The reduction in the amorphous region and an increase in the crystalline region in cellulose in the wood sample take place at higher temperatures [39–42].

The absorption band present at 1587 nm (Fig. 4B) assigned to the OH stretching vibration mode is due to the intramolecular hydrogen bonding in the crystalline regions of cellulose present in the wood sample. On increasing the temperature from 27 °C to 210 °C, the peak position of this absorption band slightly shifts towards the lower wavelength region. This may be due to changing of the random molecular arrangement to a regular molecular arrangement. A major shift in the position of the absorption peak towards the lower wavelength is observed as the temperature goes to 285 °C and at 310 °C this absorption band disappears. This may be due to the intra-ring dehydration of cellulose to the anhydrocellulose around 285 °C. On increasing the temperature above 285 °C, the thermal scission of anhydrocellulose to produce levoglucosan chain end and other anhydroglucoses, furan and furan derivative [15,39]. This shows that the crystallinity of the cellulose is affected at about 210 °C.

The absorption band at around 2066 nm (Fig. 4C) is assigned to the combination of OH stretching and CH deformation vibration modes in cellulose. As temperature increases the shift in the absorption band to lower wavelength region is observed. It may be due to the degradation of loosely bound molecular chain in the crystalline region and conversion of the random molecular arrangement to a regular molecular arrangement in crystalline region in cellulose [39–42]. At temperature around 285 °C this absorption band becomes broad and shifts towards the higher wavelength region and disappears on further increasing the temperature. This may due to the oxidation and chain degradation in cellulose [3,9,41].

Absorption band in the wavelength region at 1782 nm (Fig. 4B) may be attributed to the first overtone of the CH stretching vibrational mode (46). A shift in the absorption peak towards the higher wavelength region is observed on increasing the temperature from 27 °C to 210 °C. But as temperature increases to 285 °C, this absorption band becomes broad and disappears at 310 °C and above. This suggests the degradation of wood at higher temperature.

Hemicelluloses are polysaccharide, having the degree of polymerization lower than that of cellulose. Since their composition have several degradation pathways on thermal treatment depending upon the origin of the wood i.e., hardwood or softwood [11,18,24,26], it is difficult to assign the absorption infrared band markers in NIR region. The absorption band present at about 2329 nm (Fig. 4D) may be assigned to the combination of CH stretching and CH bending vibration modes in hemicelluloses. A shift in the peak position towards the higher wavelength region takes place on increasing the temperature. This shows that the physicochemical structure of the hemicelluloses changes rapidly and its content decreases on increasing the temperature [39].

The band present at 1711 nm (Fig. 4B) may be assigned to furanose/pyranose of hemicelluloses. On increasing the temperature from 27 °C to 210 °C a shift in the absorption band towards the higher wavelength is observed. But at temperature 285 °C and above, the absorption band become broad and almost disappears at higher temperature. This suggests that with an increase in temperature deacetylation is caused by the cleavage of acetyl groups of the hemicelluloses. Cleavage of acetyl group occurs to a high extent at higher temperature.

Lignin in wood is chemically and physically bonded to cellulose and hemicelluloses forming a three-dimensional polymer complex that contains acetal, α-phenyl-β-ether, phenyl-β-glucosidic and hydrogen bonds [11,18,25]. The band present at 1668 nm (Fig. 4B) is due to the CH stretching vibration mode of aromatic skeletal of lignin present in the wood sample. In the temperature range from 27 °C to 210 °C, a slight shifting in the absorption band towards higher wavenumber is observed. This shifting may be a consequence of the splitting of aliphatic side chain in lignin. But at temperature 285 °C and above, a major shift in the absorption band towards the lower wavelength region is observed. The band also becomes more intense at elevated temperatures. This shift may be due to the change in aromatic skeletal that involves hydrolyzing the aryl-ether linkage between lignin propane unit as well as lignin methylation and formation of hydroxyl phenolic group and α- or β-carbonyl group at higher temperature [43]. The higher intensity of the absorption band may be attributed to the existence of more condensed structure occurring at higher temperatures.

The absorption and desorption of water is an important phenomenon which causes remarkable changes in mechanical and physical properties of wood. The absorption band at about 1920 nm (Fig. 4C) is assigned to combination of OH stretching and OH bending vibration modes in water. As the temperature increases from 27 °C to 285 °C, a change in the intensity of the peak is observed. This may be due to the formation of intermolecular hydrogen bonding between hydroxyl groups and water molecules [29,41–43]. As temperature goes to 310 °C, broadness in this peak position towards lower wavelength region is observed, which may be due to cleavage of intermolecular hydrogen bonding i.e., chemical loss of water by elimination reaction and oxidation of cellulose to volatile compounds [3,9,18,43]. The broadening of peak may also be related to the water desorption at higher temperature [44,45].

At temperature 285 °C, a new absorption band at about 2122 nm is observed which may be attributed to the combination of OH stretching and CO bending vibration modes. This may be due to C–O skeletal in keto–enol tautomerism (carbonyl group) related to the dehydration of cellulose. The carbonyl group so formed might participate in a variety of thermal degradation reactions leading to carboxyl group which might fragment to give carbon monoxide and carbon dioxide. The carbonyl compound once formed undergoes transglycosilation reaction to give laevoglucosan chain end and terminal hydroxyl chain end. On further heating the latter undergoes an elimination reaction producing unsaturation in glycosidic chain end water [15,39,42].

It is evident from the above discussion that the physicochemical structure of hemicelluloses changes rapidly on increasing the temperature. Lignin and cellulose show only slight change in the temperature range of 27–210 °C. On further increasing the temperature a significant change in the lignin as well as crystallinity of the cellulose is observed.

4. Conclusions

The analysis of the CIELAB color parameters of the wood sample upon heat treatment shows that lightness (L^*) value increases up to 90 °C and then decreases on further increasing the temperature. The redness (a^*) and yellowness (b^*) increase to attains maximum value on increasing the temperature to 210 °C. Then both the parameter starts decreasing on further increases the temperature. The overall color change (ΔE^*) increases on increasing the temperature and is related with the rate of formation of carbonyl group and degradation of lignin and hemicelluloses.

Hemicelluloses, among the wood constituents degrade first on increasing the temperature. This is clear from the endothermic peak at 158 °C in the DSC analysis and also a shift in the peak position of the NIR absorption band at 1711 nm (corresponds to furanose and pyranose ring) towards the higher wavelength region on increasing the temperature.

The results obtained by the CIELAB color parameters and the DSC thermogram are correlated with the diffuse reflectance near infrared spectra of the wood sample. It is evident from the results that modification of the chemical and the physical properties of wood take place upon thermal treatment. NIR spectroscopy showed the potential to be used for the assessment of thermally treated wood. The present work may be useful for developing a non-destructive and an accurate test method to understand the degradation mechanism of wood and for monitoring the quality of wood.

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