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# PULP AND BLACK LIQUOR CHARACTERIZATION OF SUBABUL WOOD AFTER KRAFT COOKING

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## Abstract

Paper manufacturing involves removal of lignin effectively from the wood by retaining cellulose. Lignin accounts for 25% of the wood and it is an integral part of cell interfaces (middlelamella) and cell walls of S2 layer. The objective of this study is to understand the impact of kraft cooking in the pulping of heartwood and sapwood separately. Subabul (*Leucaena leucocephala*) is used as raw material in paper industry that has a substantial proportion of heartwood (approx. 60% of wood cross-sectional area). In this study screened wood chips are subjected to kraft cooking (165 $^{\circ}$C, 3hours using white liquor in rotary pulp digester). The pulp separated from black liquor was characterized for various properties using FTIR data, water retention value, drying test (105 $^{\circ}$C), ash content (525$^{\circ}$C) and optical microscopy. Black liquor collected from bottom of the digester was analyzed using UV-Visible spectrophotometer prior to and after fractional distillation. The absorption bands 1660-1440 $cm^{-1}$ region from FTIR analysis attributes to the presence of aromatic rings in lignin. Also water retention value and ash content for sapwood pulp is much higher in comparison to heartwood pulp. Tests in drying and humidity chamber also revealed differences between sapwood pulp and heartwood pulps. Microscopic analysis of pulp was also carried out to know the structure of vessels and libriform fibres. The UV-visible data of black liquor revealed significant lignin peaks (Absorption 0.15-0.8 % at wavelengths 195-200 nm) indicating the removal of lignin from wood cells. Therefore it can be concluded that cooking of heartwood and sapwood requires separate process parameters.

**Key words**: Heartwood and sapwood, Kraft cooking, FTIR analysis, Water retention value, Klason lignin, Ash content, UV-Visible spectrophotometry.

# Introduction

Paper can bemade from any agricultural biomass having cellulose such as debarked wood, bagasse, and wheat straw. Wood is mainly composed of cellulose(50%), hemicellulose (25%) and lignin(25%). Cellulose is hydrophilic due to the presence of OH groups and it is a thermoplastic polymer (linear or branched). Cellulose is the most abundant organic polymer on earth with degree of polymerization values (weight average) reaching up to 3500 in case of wood and it requires a temperature of 320 °C and pressure of 25MPa to become amorphous in water (1). In general, hemicellulose is branched and non-crystalline polymer. Because of the attraction between cellulose molecules in different fiber surfaces, hemicellulose acts as a principal source of fiber to fiber bonding in paper. Lignin, which is covalently linked to hemicellulose and cellulose, confers the mechanical strength to the cellwall. Middle lamella (cell interfaces) consists of mainly lignin. But lignin is also an integral part of the secondary cell walls especially S2 layer and it serves as a binding agent or matrix to the cellulose fibrils and protects the wood from outside environment. The aim of paper manufacturing processes or viscose rayon production processes is to obtain the pulp having negligible lignin content but retaining the cellulose. For high quality paper or rayon grade pulp, lignin should be removed completely from cell walls, as it decreases the brightness and causes yellowing of the paper due to its reaction with UV light.

Softwood generally consists of 90% long tapering cells called tracheids and is used for manufacturing strong paperwhereas hardwood fibers are shorter and thinner giving a better paper formation due to less cross-linked lignin and higher density(2). Wood cross-section mainly consists of 3 parts i.e bark, sapwood and heartwood. Bark is the outer portion of wood that should be removed prior to chipping process. Sapwood initially presents as inner layer during the early growth of wood and it is the living tissue of the stem mainly consists of fibers and vessels for transportation of water&nutrients from root to the crown. With increase in age, sapwood cells become thicker and older and transform into heartwood. As shown in Fig 1, heartwood becomes the central part of tree stem, sapwood being the outer layer. Heartwood is usually much dark in color than sapwood due to deposition of resinous organic compounds in the cell walls and cavities (2). Such depositions make liquor penetration very difficult during cooking, hence pulping process becomes difficult with heartwood(1).The acetyl content is higher in sapwood compared to heart wood, but heartwood has more lignin than sapwood. Pulp and paper industries mainly focus on wood species that have less lignin content and faster growth rate such as Eucalyptus, Acacia, Subabul, and Casuarina. In this study Subabul is considered as raw materials due to its wide acceptance as plantation grown species in local region i.e Andhra Pradesh, India (3).

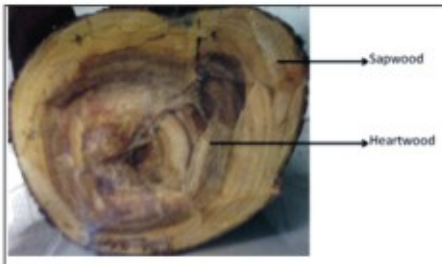


**Fig 1:** *Cross-section of Subabul wood log revealing heartwood (darker) and sapwood (lighter).*

# Experimental

## Materials and Methods

The raw material used in this study, Subabul (*Leucaena leucocephala*) wood log was taken from Kandukoor area, Ranga Reddy District, Hyderabad, India. The log is 7yrs old and it was cut from 3feet above the ground level (3). The log selected was 20 cm in diameter and 8 mt height. Around 60 % of the inner cross sectional area with diameter of 14 cms was considered as heartwood and the remaining is considered as sapwood based on the appearance as shown in Fig.1. Sapwood and heartwood were separated using a wood turning machine and were further cut down to chips of 2cm x 2cm x 1cm dimensions with the help of chisel and dried in hot air oven at 103 °C. The heartwood and sapwood chips were subjected to pretreatment process at 120°C for 1hour in an autoclave in order to reduce impregnation difficulties caused due to moisture entrapped in the chips and to remove some of the organic extractives. Pretreatment or steaming at120°C is also an effective method of softening the lignin present at the middle lamella (Fig.2). This increases the efficiency of the hydrolysis through reduction of lignin content & cellulose crystallinity due to the increase of pore size of the material.

Different methods can be used for pulping such as mechanical, chemical, thermo-mechanical. In chemical pulping,Kraft process (sulfate process) is generally preferred because of alkaline nature of chemicals which results strong pulp fibers (less damage compared to sulfite process). It also has an established chemical recovery method and can even tolerate species with bark. Kraft process uses sodium hydroxide (NaOH) and sodium sulphide ($Na_2S$), both were obtained from Sigma-Aldrich.The aqueous solution of these chemicals in required proportions is called *white liquor*. NaOH reacts with lignin and resins present in wood neutralizing organic acids. The general equation for reactions in Kraft process is shown in equation 1.

$$NaOH + Na_2S + \text{Wood chips} \longrightarrow \text{Na-org.} + \text{S-org.} + NaHS \text{ (sodium hydrosulfide)} \quad (1)$$

To minimize the damage of cellulose by NaOH, instead of using high concentrations of NaOH, $Na_2S$ is introduced which gives NaOHby reacting with water in white liquor slowly as shown in equations 2-3.

$$Na_2S + H_2O \leftrightarrow 2Na^+ + S^{2-} + H_2O \quad \ldots\ldots\ldots\ldots (2)$$

$$S^{2-} + H_2O \leftrightarrow HS^- + OH^- \quad \ldots\ldots\ldots\ldots (3)$$

$Na_2S$ produces sodium ($Na^+$), sulfide ($S^{2-}$), bisulfide ($HS^-$) ions in water. These $Na^+$ combine with $OH^-$ ions to form NaOH and these ions react with lignin molecules and lead to ether scission i.e. breakage at ether bonds. These broken molecules or fragments dissolve in white liquor ultimately leads to systematic degradation of lignin (1).

The pretreated samples along with white liquor (NaOH + $Na_2S$) as per the proportions given in literature (wood:liquor=1:4) are fed into rotary pulp digester. The volume and temperature of the digester are 15 lit and 165°C respectively (pressure of 8 $Kg/cm^2$). Continuous rotation of the digester (180°)during cooking allows better impregnation of wood especially cell walls which are 5-8 µm thick. Sapwood and heartwood samples are cooked separately for 3hours and the black liquor is retrieved from digester after 1, 2, 2.5 and 3hours. After 3hours of cooking, black liquor and pulp are separated and characterized to analyze the amount of lignin present in black liquor, the amount of lignin remaining in the pulp, and the difference in the amount of inorganics contained in the pulp. Characterization of pulp is carried out using FTIR spectroscopy, ash content, water retention value, and absorption capacity. For black liquor, characterization is done using UV-spectrophotometry and fractional distillation. The results are compared with available data and analyzed to understand the differences between heartwood and sapwood.

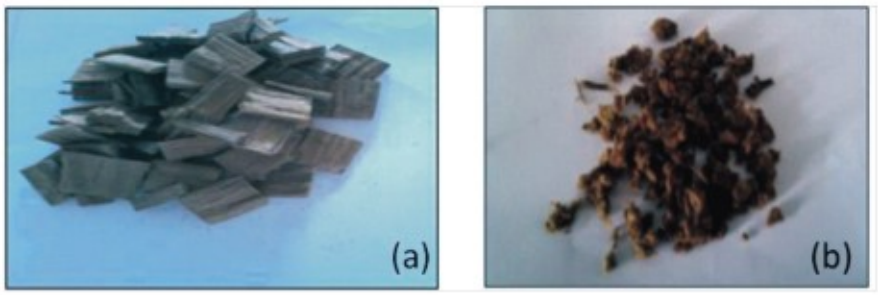


**Fig 2 :** (a) Wood chips prior to cooking (b) Wood pulp obtained after cooking and filtration. Chips shown in (a) are pretreated with steam at 120°C for 1 hour period.

# Results and Discussion

## Characterization of Delignified Pulp

### Ash Test

The ash content in the raw wood and de-lignified wood (i.e wood pulp) was measured. Fixed amounts of oven dried weights of the samples were taken in crucible. A muffle furnace was used for incineration of the samples at temperature of

525°C until sample attained a constant weight as per TAPPI T211 (4). The results obtained for the ash content value of heartwood and sapwood before and after delignification indicate that **pulp has lost only ~60 % its weight whereas wood lost almost 96 % of its weight (Table 1). This could be due to the bulk structure of wood in which combustion and pyrolysis of cellulose-lignin structure happens simultaneously because lignin remains decomposing until 900 °C where as decomposition of cellulose ends by 400 °C resulting white color reside as shown in Fig. 3** (5). **Though pulp contains more inorganics (added during cooking), its lower content of lignin causes higher rate of incineration resulting black color residue (Fig. 3).** Since heartwood contains more extractives and less inorganics than sapwood, the ash content i.e an indication of the amount of inorganic substances is expected to be higher for sapwood than for heartwood(6).

The initial mass loss of wood is generally observed at temperatures lower than 200°C, which is due to the evaporation of water. The mass loss observed at temperatures over 500°C has been found to be due to the decomposition of carbonates of both calcium and potassium resulting in white color appearance. At 500-600°C wood ash mainly consists of $CaCO_3$ and $K_2Ca(CO_3)_2$(7).Elements in the wood ash are calcium, potassium and magnesium (8). Sulfur, phosphorus and manganese are present at around 1%. With increase in temperature, the mass of sulfur, sodium, and potassium decreases. The nitrogen content in wood ash is normally insignificant due to the conversion of most of the wood nitrogen to $NH_3$, $NO_x$ and $N_2$.

**Table - 1 :** Percentage of ash content in wood (before cooking) and Wood pulp (after cooking)

| Sample type | Wood | Wood pulp |
|---|---|---|
| Heartwood | 3.23 | 29.82 |
| Sapwood | 3.41 | 36.59 |

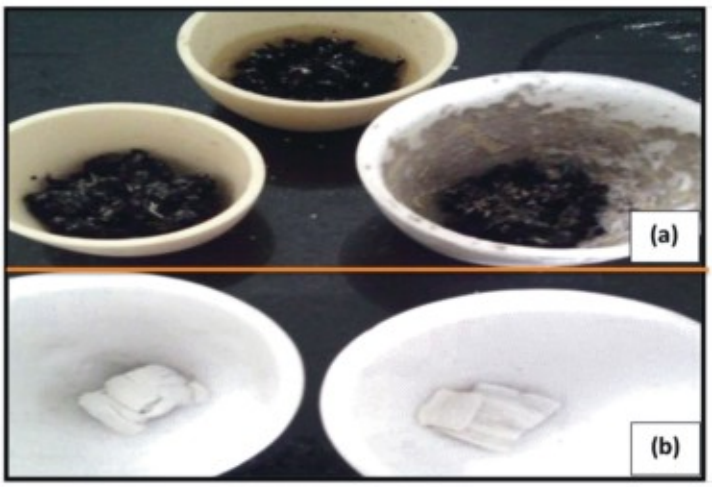


**Fig 3:** Ash obtained from wood pulp (a) and from wood chips (b). Ash test was conducted by keeping samples at 525 °C for period of 1 hour. Note the color differences between wood ash and pulp ash.

## Water Retention Value

Both the heartwood and sapwood samples of 3gms each were analyzed for their water retention value (WRV) before and after delignification as per the equation 4. A refrigerated centrifuge was used for this purpose.The wet samples were centrifuged at 2600rpm and 23°C for 15minutes followed by overnight drying in a hot air oven at 104°C (*TAPPI* UM 256).

WRV = {(weight after centrifuge/ weight after drying) – 1} .....4

**Table - 2 :** Water Retention value of wood (before cooking) and Wood pulp (after cooking)

| Sample type | Wood | Wood pulp |
|---|---|---|
| Heartwood | 0.35 | 2.32 |
| Sapwood | 0.39 | 2.77 |

Lignin is hydrophobic in nature due to the presence of aromatic groups in network structure (8-9).The WRV of the samples was measured to assess the approximate removal of the lignin during kraft cooking. The more the removal of lignin, the higher the WRV of the sample. Since the amount of lignin is similar in heartwood and sapwood, the WRV of the raw heartwood and sapwood are almost equal. However, it can also be observed that although the WRV increases for both delignified heartwood and sapwood pulps owing to the removal of lignin, the increase in the values for sapwood pulp is higher than that for heartwood pulp as shown in Table 2.

## Humidity test

The pulp should be free from moisture for ease of packing and transportation but it is difficult to attain moisture free pulp because cellulose is hydrophilic in nature (10-12). A humidity chamber is used to calculate the water absorption capacity of the pulps*(T550 om-08)* as shown in equation 5. In this study 1.5 gms of sample is taken and kept in humidity chamber at 22°C, 66% RH till constant weight is obtained (approx. 24 hrs). It is observed that the water absorption capacity of sapwood is much higher than heartwood (difference also exists in case of pulps)due to the lower percentage of lignin and void spaces in sapwood/pulp. Among the four samples considered, sapwood pulp has the highest moisture content reaching 7 % as shown in Fig.4.

*MC= (pulp weight-dry weight)/dry weight(5)*


**Fig 4 :** *Analysis of moisture content in heartwood and sapwood before and after cooking. Note the increase in moisture content of the pulp compared to wood confirming the lignin removal after 3 hours of cooking.*

## FT-IR Spectroscopy

This method helps in the identification of functional groups. About 1 mg of the samples of heartwood and sapwood, before cooking(i.e. raw wood) and after cooking (i.e.pulp) was grinded with potassium bromide to make compressed pellets and results are shown in Fig. 5 and Fig. 6.

- A broad and strong absorption band in the 3500–3100 $cm^{-1}$ region corresponds to the O–H stretching vibrations of cellulose, absorbed water, hemicellulose and lignin. This also refers to aliphatic primary and secondary alcohols found in cellulose, hemicellulose, lignin and carboxylic acids.
- The band around 1593 and 1420 $cm^{-1}$ is representative of aromatic skeletal vibrations in lignin. These bands are observed in both spectra's of the pulp.
- The band around 1160, 1114 and 1055 $cm^{-1}$, represents aromatic C-H in-plane deformation, observed in kraft cooking pulps of the both spectra's shown in Fig. 5 and Fig. 6.
- The presence of 1735 $cm^{-1}$ peak in sapwood and heartwood could be due to the carbonyl (C=O, ester) of the hemicellulose and lignin.
- Based on the percentage transmittance and the lignin peaks, it is observed that the amount of lignin extracted is lesser for heartwood than sapwood.

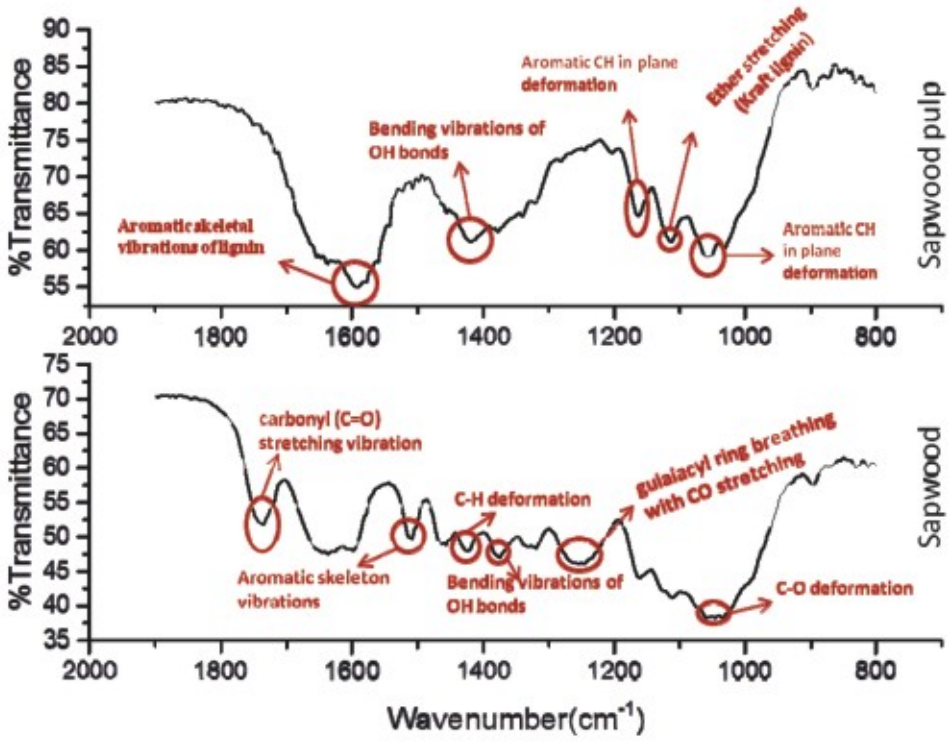


**Fig 5 :** *The absorption bands in the region of 900-1800 cm$^{-1}$ from sapwood pulp and sapwood FTIR analysis.*

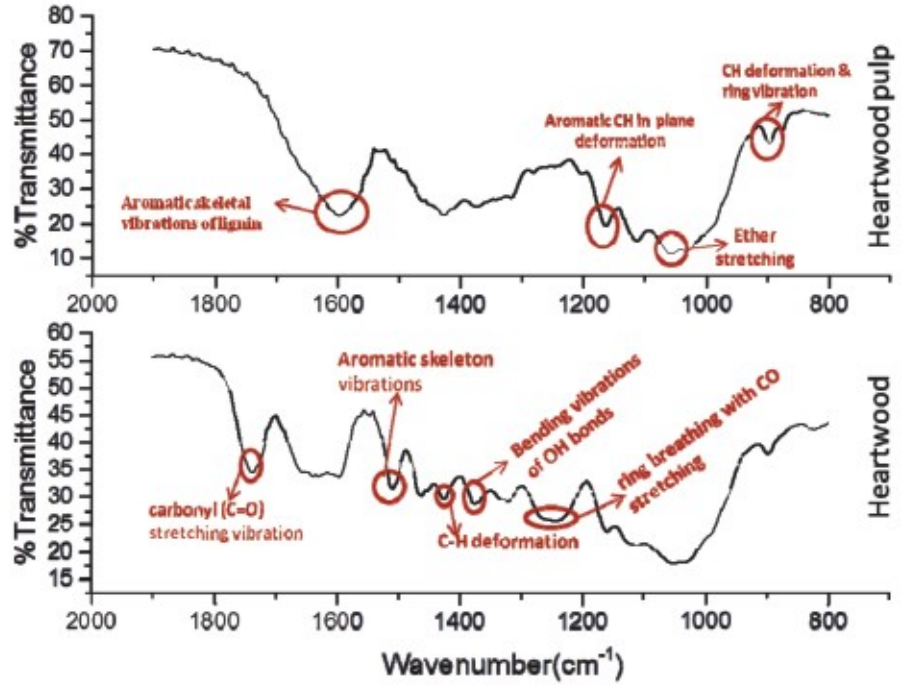


**Fig 6 :** The absorption bands in the region of 900-1800 cm$^{-1}$ from heartwood pulp and heartwood FTIR analysis.

## Klasons Lignin Estimation

The modified klason lignin method is derived from the standardized method ASTM D-1106 which is used to determine the insoluble lignin at 72 % sulphuric acid ($H_2SO_4$). 150 mg of pulp fibers were mixed with 3 ml of 72 % sulphuric acid and placed in a bath with a controlled temperature of 30$^{0}$C for one hr, later 84 ml of demineralised water was added to the sample and

placed in an autoclave at 125°C for one hour. Sample was cooled and the lignin was filtered and lignin content was calculated as per the equation 6

$$\text{Insoluble lignin content (\%)} = (W_{lignin}/W_{fiber}) * 100 \quad .....(6)$$

$W_{lignin}$ = oven-dry weight of the insoluble lignin or Klasonlignin (g); $W_{fiber}$ = oven-dry weight of pulp(g).

The filtrate obtained by the modified klason lignin was used to determine the soluble lignin content in sulphuric acid by the spectrophotometric method. In this method, 5 ml of 3 % sulphuric acid was added to 5 ml of the filtrate. A UV Visible spectrophotometer was used to measure the absorbance of the solution at a wavelength of 205 nm. Therefore the soluble lignin content was calculated as per the equation 7

$$\text{Soluble lignin content (\%)} = [CV/(1000 * W_{fiber})] * 100 \quad ..... (7)$$

C = concentration of soluble lignin in the filtrate (g/l); V= total volume of the filtrate (ml); $W_{fiber}$ = oven-dry weight of wood fibers (g). The concentration of soluble lignin in the filtrate (C) is given by equation 8

$$C = (A/110) * (V_{final}/V_{initial}) \quad ..... (8)$$

Where A = absorbance at a wavelength of 205 nm; $V_{final}$ = final volume of the solution (ml); $V_{initial}$ = initial volume of the solution (ml).

The total lignin content in percentage was obtained by the addition of insoluble lignin content and soluble lignin content obtained by both methods as shown in Table 3. Kappa number, which is a dimension less number for lignin content in biomass, is low for both pulps compared to their corresponding wood chips. Sapwood pulp can be bleachable due to its lower kappa number, whereas hardwood pulp needs extra cooking time or higher wood:liquor ratio because kappa number of 18 is not acceptable for bleaching (2).

***Table - 3:*** *Total lignin content and kappa number for sapwood and heartwood before cooking and after cooking. Note the difference in kappa number of sapwood and heartwood pulps.*

| Sample | Acid soluble | Insoluble (klason) | Total lignin | Kappa Number |
|---|---|---|---|---|
| Sapwood | 23.4% | 5.4% | 28.9% | 195 |
| Heartwood | 30.4% | 5.0% | 35.4% | 238 |
| Sapwood pulp | 0.02% | 1.2% | 1.2% | 8.4 |
| Heartwood pulp | 0.5% | 2.3% | 2.7% | 18.6 |

## Cellulose Isolation Study

This test indicates the amount of cellulose in the pulp after cooking process.The protocol involves adding 15ml acetic acid+1.5ml concentrated nitric acid to the samples and refluxing for 20 minutes as shown in Fig. 7.The samples are then washed with ethanol and filtered using a cotton cloth followed by oven drying for 12hours (material A). Further the samples are incinerated at 525°C in muffle furnace till constant weight is attained(material B).The percentage of the cellulose is calculated as per the equation 9 and results are shown in Table 4. It can be observed that the percentage of cellulose is higher in sapwood pulp than heartwood pulp.

$$\%\ Cellulose = \frac{(weight\ of\ the\ material\ A - weight\ of\ the\ material\ B)}{total\ weight\ of\ the\ sample} \quad ..... (9)$$

**Table-4:** Cellulose Content in Pulp after Kraft Cooking

| Sl. No. | Sample type | Cellulose composition (%) |
|---|---|---|
| 1. | Heartwood pulp | 48.9 ± 3.2 |
| 2. | Sapwood pulp | 52.0 ± 3.0 |

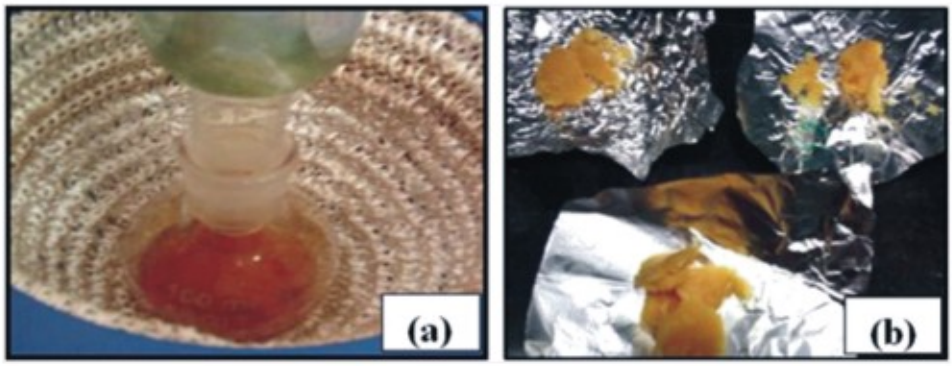


**Fig 7:** (a) Wood pulp sample during reflux (b) Wood pulp Sample after drying.

## Microscopic Analysis

Both reflectance and transmittance modes were used for microscopic analysis of pulp and results are shown in Fig.8. Both heartwood and sapwood pulp images gives the impression of middle lamella degradation resulting the network structure of loose fibres (wood cells). In the case of heartwood pulp (Fig. 8a&b), network looks denser i.e vessels and libriform fibres are not well separated compared to sapwood pulp (Fig.8 c&d). Vessels of two types (60-65 µm and other is 30-35µm width) are found in both pulps which mainly consist of guaiacyl residues of lignin. Libriform fibres of 15-18 µm width are prominent in both pulps but some kinks followed by fibre peeling can be noted from the heartwood cells. The optical images also confirm the optimized cooking parameters resulting fibers of tapered end as seen in the case of sapwood pulp. Vessel cells are filled with fragments of extractives giving a darker color in heartwood pulp.

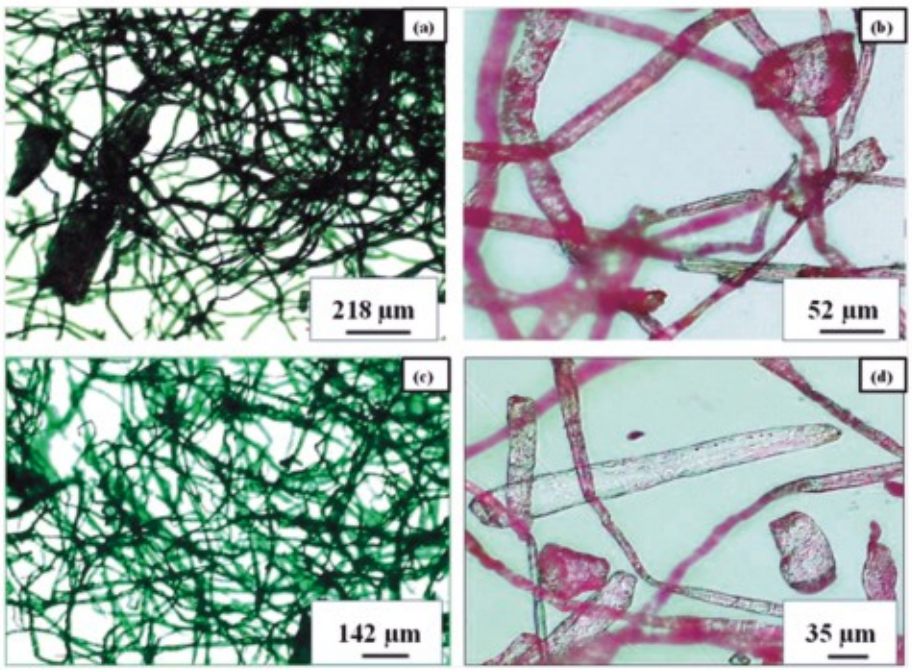


**Fig. 8:** (a&b) Heartwood pulp fibers; (c&d) Sapwood pulp fibers. Note the difference between vessel fibres and libriform fibres in both pulps obtained from kraft cooking at 165 °C.

# Characterization of Black Liquor

## UV-Vis Spectroscopic Analysis:

UV-Vis spectroscopy reveals the possible electronic transitions by measuring the absorption spectra of a sample that has been excited with ultraviolet light. The UV-Vis characterization was done for four black liquor solutions collected at different intervals. The UV analysis detects the lignin peak qualitatively as every material has its own characteristic absorption spectra.

About 0.1 ml heartwood black liquor sample was diluted with 19 ml of water for measurements and corresponding results are shown in Fig. 9. It is observed that the corresponding heartwood black liquor peak is obtained at 200 nm for all three samples whereas, absorbance is highest at 2 hours interval sample which indicates that most of the lignin is extracted from the heartwood within 2 hour of the cooking process. Similarly about 0.01 ml sapwood black liquor sample was diluted with 200 ml of water and measurements are shown in Fig. 10. It is observed that the corresponding sapwood black liquor peak is obtained at 200 nm (3 hrs sample) which is shifted from 195 nm (1 hr sample), whereas the absorbance was highest for 3 hrs sample which indicates that most of the lignin is extracted from the sapwood after three hours of cooking process. The peaks were found to be shifted about 5 nm as the time of cooking increased, probably due to the electronic transitions in phenols of sapwood during the delignification as the processes and changes in the inner sapwood are difficult to analyse (12).

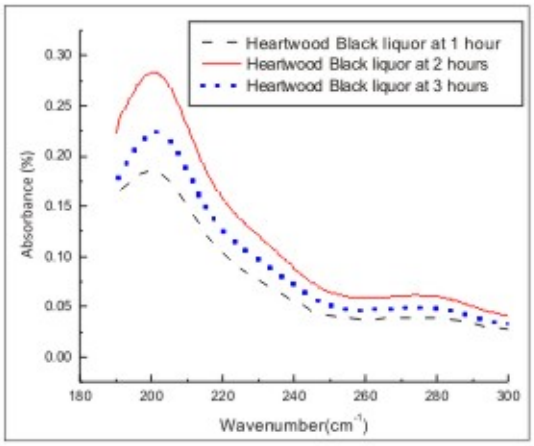


**Fig 9 :** UV analysis for heartwood black liquor collected at intervals of 1 hour, 2 hours and 3 hours.

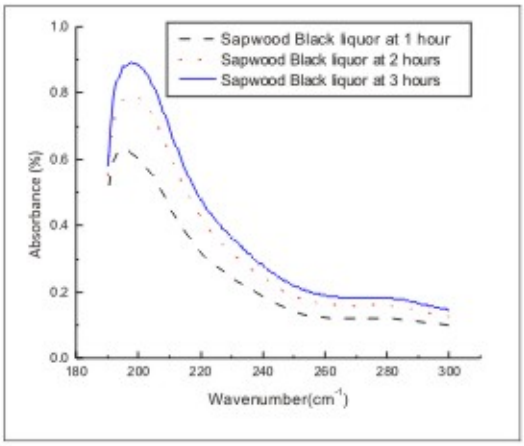


**Fig 10 :** UV analysis for sapwood black liquor collected at intervals of 1 hour, 2 hours and 3 hours.

In heartwood black liquor analysis (collected after 2.5 and 3 hours of cooking), the absorbance is same indicating no change of lignin composition between these intervals of cooking process (Fig.11). But this was not the case for sapwood black liquor analysis because the lignin degradation is gradually increasing with time as shown in Fig. 10, being highest absorbance for 3 hrs sample contrary to the 2 hrs sample showing the highest absorbance in heartwood black liquor analysis (Fig. 9-10).

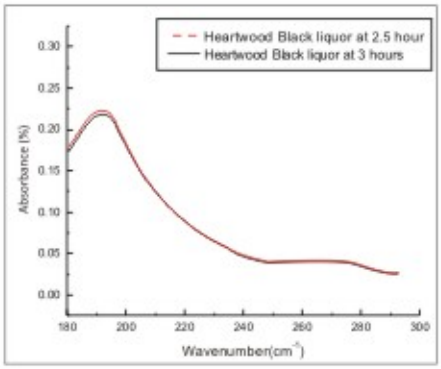


**Fig.11.** UV analysis for heartwood black liquor collected after2.5 hours and 3 hours of cooking.

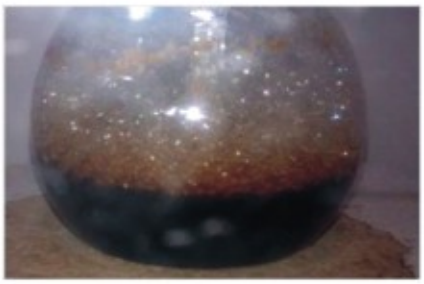

**Fig 12:** Fractional distillation of black liquor. The white bubbles on the top layer indicates organic fraction.

## Fractional Distillation

The collected black liquor samples were subjected to distillation in order to separate organics from inorganics as shown in Fig. 12. Around 25ml of black liquor sample was heated for about 85mins at 105°C and the volatile organic components were collected separately within 30 minutes condensation. The collected organic fractions are shown in Fig. 13 where (1) indicates the first fraction and (2) indicates the second fraction obtained after 10 mints.The volatile organic components were further analyzed using UV-Visible spectroscopic analysis.

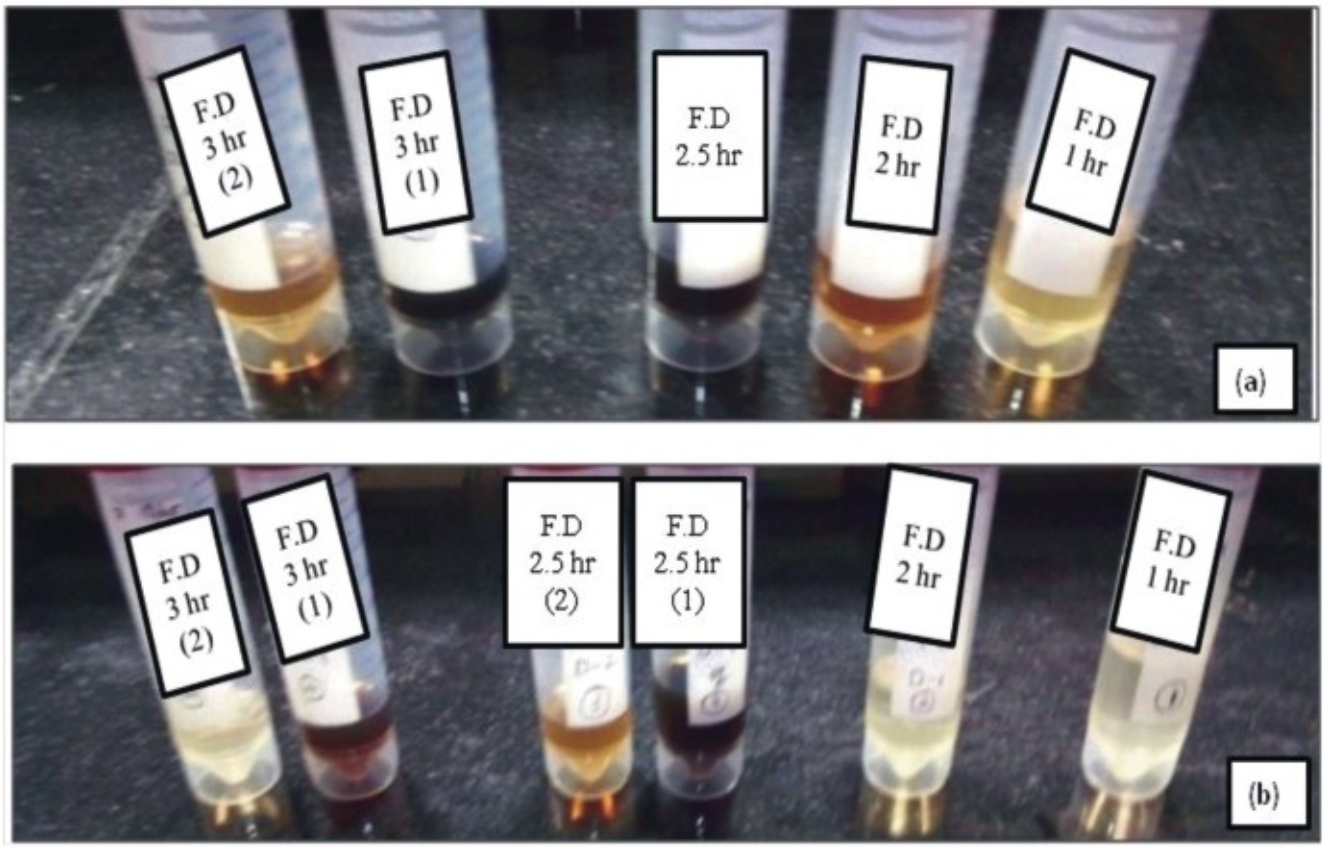


**Fig. 13 :** Black liquor was subjected to fractional distillation at 105 °C for a minimum period of 30 mints. (a)Heartwood black liquor [left to right: distillate of 3 hrs sample (3-2&3-1) followed by distillate of 2.5 hour, 2 hour and 1 hour samples] (b) Sapwood black liquor [left to right: distillate of 3 hour sample (3-2&3-1) followed by distillate of 2.5 hour (2.5-2 & 2.5-1), 2 hour and1 hour samples]

From Fig. 13 it is evident that the increasing intensity of color from light yellow to dark brown of the distillates as the cooking time increases from 1 hour to 3 hours. Similar trend was followed for both heartwood and sapwood black liquor samples as shown in Fig.13 a & b.Heartwood distillates are darker than sapwood distillates at every interval of the sample collected confirming that more number of chromophores is extracted in heartwood kraft cooking than in sapwood cooking. To confirm this UV analysis of distillates were performed and results are shown in Fig. 14 & 15.

From the analysis we can observe that there is gradual increase in the absorbance percentage for distillates of heartwood black liquor samples collected at intervals of 1 hr and 2hrs as shown in Fig.14. In the UV analysis of sapwood distillate, we can observe clearly no change in the absorbance percentage for distillates collected at intervals of 1 hr and 2 hr as shown in Fig.15. But the distillates of black liquor samples collected after cooking (3 hrs) were shown difference in absorbance percentage between first distillate (darker, 30 mints) and second distillate (lighter, 40 mints) as shown in Fig. 13-15. It can also be concluded that intensity of color of distillate (Fig. 13) is characteristic of percentage of absorbance (Fig. 14-15).

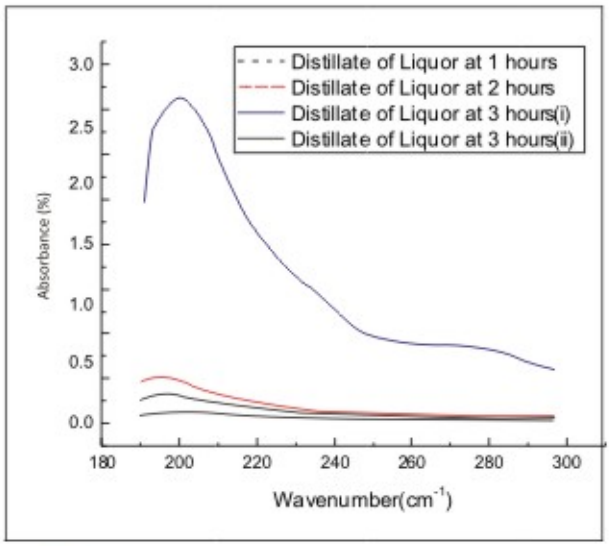


**Fig 14 :** UV analysis for heartwood black liquor distillates. Here (i) indicates first distillate (darker, collected in 30 mints) and (ii) indicates second distillate (lighter, collected in 40 mints)

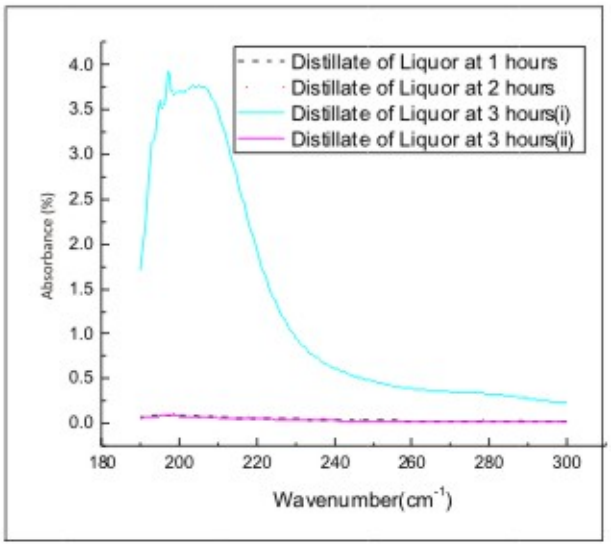


**Fig 15 :** UV analysis for Sapwood black liquor. Here (i) indicates first distillate (darker, collected in 30 mints) and (ii) indicates second distillate (lighter, collected in 40 mints)

## Conclusions

- The klasons lignin test revealed that heartwood pulp has 1.5% more lignin than sapwood pulp. Also, sapwood pulp has 2.98% higher cellulose content than heartwood pulp.
- Water retention value (WRV) for sapwood pulp is higher than that for heartwood pulp due to the differences in their residual lignin content of the pulp. WRV of the wood is lower than pulp.
- From the ash test @ 525 °C, it is found that pulp lost only 60 % its weight whereas wood lost almost 96 % of its weight. The amount of ash is higher in sapwood pulp than in heartwood pulp which could be due to the lower amount of lignin and higher amount of minerals present in sapwood pulp.
- Due to the differences in lignin and cellulose contents, sapwood pulp has (6.7%) more moisture content than heart wood pulp (4.7%).
- From absorption spectroscopy analysis, significant lignin peaks were observed in all the pulp samples considered in this study, however, the peak intensities were high in heartwood pulp than sapwood pulp. Also, the percentage of absorbance is quite less for heartwood pulp (<0.27%) in comparison with sapwood pulp (<0.9%).
- The optical images revealed individual libriform fibres of 15-20 µm width and 30-65 µm width of vessels. The heartwoodpulps consist of little denser fibre network of fibres than sapwood pulps.
- The UV-Visible spectroscopic data of black liquor (collected after 1, 2, 2.5 and 3 hrs) revealed significant lignin peaks. The peaks are obtained at 200 nm for all foursamples of heartwood black liquor, but the absorbance is highest at 2 hours interval sample which indicates that most of the lignin is removed from wood cells within 2 hour of the cooking process.
- The intensity of color of heartwood black liquor distillate (1 hr:lighter, 2hr:lighter-darker, 3hr:darker) is characteristic of percentage of absorbance in UV analysis(1 hr:<0.1%, 2hr:<0.5%, 3hr:>2.5%)
- Therefore it can be concluded that separation of heartwood and sapwood prior to chipping followed by kraft cooking with different process parameters will be economical and ecofriendly.

## Cost Analysis

In the olden days heartwood is used for timber purpose whereas sapwood for pulp production. In recent times this is not being followed in the paper and pulp industry as they are using the entire wood log (not separating heartwood and sapwood) assuming plantation grown wood logs consume less chemicals because of less lignin content. But lignin is distributed in every 100nm thick cell walls and removal of lignin from plantation grown wood cells requires same amount of chemicals unless sapwood and heartwood are cooked separately.

| **Process 1 (Existing) :** Industrial process of using directly raw wood logs. | **Process 2 (Proposed)** Process performed after separating Heartwood and Sapwood from Raw wood logs. It is easy to separate based on color and density. |
|---|---|

Chipping process to separate the heartwood and sapwood from raw wood logs

Raw wood consists of 60% heartwood and 40% sapwood. From klason's lignin analysis (Table 3), it is found that the lignin percentage in sapwood reduced from 29 % to ~1 % where as in heartwood it got reduced from 35 % to ~3 % when wood chips are subjected to kraft cooking at 165$^0$ C for 3 hours. When entire wood logs are subjected to cooking, it is possible to reduce the cooking time of heartwood by 30 mints as from UV analysis it can be confirmed that black liquor samples collected after 2.5 hour and 3 hour have shown same absorbance (Fig.11) predicting no further removal of lignin from cell walls happened between 2.5-3 hours.

| | **Raw wood** | **Heartwood** | **Sapwood** |
|---|---|---|---|
| Quantity | 1 kg | ~600 gms | ~400 gms |
| Pulp yield | 0.7609 | 0.6844 | 0.8195 |
| Time required for kraft cooking | 3 hours to attain about 2.5% lignin in pulp | 2.5 hours to attain about 2.7% lignin in pulp | 3 hours to attain about 1.2% lignin in pulp |
| Bleaching process | Chemical quantity is almost x grams | Chemical quantity is almost x grams | Chemical quantity is almost y grams(y < x), due to less lignin |

Considering the same amount of chemicals used for kraft cooking in Process 1 and Process 2, the yield obtained in both the processes are almost equal but there will be a reduction of bleaching chemicals almost to half the quantity that are used in Process 1 and also the energy is conserved to an extent as the heartwood cooking is performed in almost 2.5 hours (reduction of 30 minutes).

## Operating Parameters

Both heartwood and sapwood were cooked at 165$^\circ$ C for 3 hours maintaining 1:4 wood to liquor ratio. For the same conditions, the percentage of lignin removed from heartwood is lower than sapwood. Hence it could be concluded that different set of parameters are required for heartwood as lignin is tightly bonded to hemicellulose and cellulose fibrils as shown in schematic diagram (13). Hence it is advisable to separate heartwood from sapwood before considering the wood log for kraft cooking. Optimizing the parameters for sapwood cooking and heartwood

Sapwood Heartwood

cooking separately reduces the chemical consumption not only during pulping but also during bleaching process. This enables the process to be more economical (cooking at lower temperature) and ecofriendly (reduction of bleaching stages).

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