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## Short Communication

# Investigation of Pine Needles for Pulp/Paper Industry

**Asadullah Jan*, Amin Ur Rahman, Farid Ullah Khan and Jehangir Shah**
Materials Science Centre, PCSIR Laboratories Complex, Peshawar-25120, Pakistan

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**Abstract.** Pine needles (pine leaves) were analyzed for their chemical constituents, and the dimensions of the extracted fibres were determined to assess their utilization for pulp making. Cellulose content of pine needles (41%) was comparable to softwood (42%), whereas the lignin content (35.1%) was high as compared to both softwood (28%) and hardwood (20%). Ash content of pine needles (3.2%) was less than wheat straw (4-9%) and comparable to bagasse (1.5-5 %). The average length of the pine needle fibre (13mm) was greater than fibres of sugarcane (1.7 mm), wheat straw (1.4 mm) and esparto (1.2mm), but less than cotton (30 mm). The average diameter of pine needle fibre (32 ìm) was greater than all the common fibres used for papermaking.

**Keywords:** pine needles, pulp making, paper industry, pine needle fibre

Paper is made from cellulose derived from a limited number of plants. Agro-based or non-wood fibres are the potential sources for pulp and paper making (Ilvessalo-Pfäffli, 1995). The non-wood fibre is usually obtained from the high-cellulose containing materials like cotton, cotton linter, bagasse, flax, abaca and grasses of various types. The use of non-wood fibres in combination with wood fibres is also useful for paper making, as it can reduce the amount of chemicals used and can also shorten the pulping time, thus saving energy. Besides this, the non-wood fibres have some other disadvantages also, because microorganisms can easily attack them and thus deteriorate during storage. Pine needles are among the non-wood materials and are abundantly available in Pakistan.

Pine needles are the long leaves of the evergreen pine trees. Five species of pine trees are available in Pakistan (Nasir and Nasir, 1987). Generally, *Pinus longifolia* (‘chir pine’) is found in the forests of 1200-1850 m altitudes, while *Pinus wallichiana* (blue pine) is found in the forests between 1850-2750 m altitudes. These species of the genus *Pinus* are abundantly available in the Northwestern areas of Pakistan, i.e., Hazara, Murree, Dir, Swat, Chitral, and Azad Jammu and Kashmir. In Pakistan, the total area of these coniferous forests is 1928 thousand hectare spread over the range lands of the North West Frontier, the Punjab and Baluchistan provinces of Pakistan (Siddiqui, 1991).

The length of pine needles of various species varies from 14 to 16 cm. These are bluish to grey-green and turn dark brown when mature. The mature dried needles fall throughout the year and are spread in the entire bed of the forests. The present study deals with the chemical composition of pine needles, their fibre extraction, physical characteristics of the extracted fibre, and suitability for pulp and papermaking.

The mature and dry leaves of the two pine species, namely, *Pinus longifolia* and *P. wallichiana* were collected from Hazara forests. The needles were washed, air-dried and milled. The moisture content was determined by heating the sample to a constant weight at 110 °C. The ash content was determined by muffling the samples at 580-600 °C in a Muffle furnace (ASTM, 2002), and the silica content was determined by heating the sample at 900 °C. The cellulose content was determined by Cross and Bevan chlorination method (Doree, 1950). Oven-dried pine needle sample (5 g) was boiled for 30 min in 200 ml sodium hydroxide (1%) solution. The sample was drained on a cloth filter. After squeezing, the sample was subjected to chlorine gas exposure, until the colour changed to golden-yellow. The chlorine treated sample was thoroughly washed with distilled water, then 100 ml of 2% sodium sulphate solution was added and the temperature was gradually raised to boiling. Sodium hydroxide (0.2 g) was added and boiling was continued for further 5 min. The sample was bleached with 200 ml potassium permanganate (0.15 M) solution. The bleached sample was treated with 200 ml sulphurous acid (10%), washed and digested for 30 min. The percentage of cellulose was then determined. Lignin was determined by the AOAC method (AOAC, 2002). Calcium and magnesium were determined volumetrically (Furman, 1963), while sodium and potassium were determined by using flame photometer (Corning-4000). Atomic absorption spectrophotometer (Hitachi Z-8000) was used for the determination of Fe and Mn.

Chemical procedure was used for the extraction of fibres. NaOH was used for the chemical treatment of pine needles. 10 g of the oven-dried sample of pine needle was boiled with

*Author for correspondence

4% NaOH for 60 min. The samples to solution ratio was 1 : 50. After boiling, the sample was thoroughly washed with water and was oven-dried at 105 °C to constant weight. The yield of pine fibre was 61%. Diameter of the extracted fibre was measured by Lanameter/projection microscope (Reichert, Austria).

The moisture content of pine needles was noted to be 6%, while the ash content was 3.2% (Table 1). The cell cavities in the pine needles contain large amounts of air and moisture. The amount of moisture varied with the type of fibre and season. Ash content of pine needles was less than rice straw (15-20%), wheat straw (4-5%), esparto (6-8%), bagasse (1.5-5%), but was higher than cotton linters (1-2%). Ash content is a measure of $SiO_2$ and mineral salts, which usually contain salts of Ca, K and Mg and sometimes Mn. $SiO_2$ content of pine needles (0.63%) was less than rice straw (9-14%), wheat straw (3-7%), esparto (2-3%), bagasse (0.7-3%), but higher than cotton linters (<1 %) (Hunter, 1988). Silicon is the most unwanted element in the raw materials for pulping because it complicates the recovery of chemicals, wears out the installations of pulp mills and paper factories, and can lower the quality of paper (Jeyasingam, 1985). K, Na, Ca, Mg, Fe and Mn are also harmful elements for the pulping process (Keitaanniemi, 1982). Percentage of various important elements in pine needle is given in Table 1. The metal ion concentration has a direct effect on brightness, for example, iron lowers the brightness of paper. Metal ion concentration also affects the bleaching efficiency of the bleaching agents for example, the presence of iron, copper, and manganese causes decomposition of hydrogen peroxide. Sometimes the harmful radical species of iron and copper are formed, which degrade cellulose. Iron and manganese are also important because these react with extractives and thus cause discolouration to the pulp (Suleman and Kausar, 1990).

The cellulose content of pine needle was noted to be 41%, which is compatible to softwood (Table 2). Cotton contains 91% cellulose, while straw contains 35% cellulose. Cellulose is a complex carbohydrate substance and is the major component of plant tissues. Its percentage varies from plant to plant. The percentage of lignin in pine needles was observed to be 35%, which is high compared to both hardwood and softwood. Lignin is an aromatic organic polymer and is the major component of cell wall, which is unwanted for papermaking. It is composed of coniferyl, *p*-coumaryl and sinapyl alcohols and contains mainly anisyl, vanillyl and syringyl nuclei (Simoneit *et al.*, 2000). Poor colour and bleachability are the problems associated with lignin contents. Various cooking chemicals are used for the removal of lignin, which dissolve and degrade lignin and separate it in the form of black liquor. About 95% lignin is removed during the pulping process. Strong oxidizing agents, like elemental chlorine, chlorine dioxide, sodium hypochlorite, ozone and hydrogen peroxide are used for bleaching. For obtaining good quality of pulp and paper, complete removal of lignin is necessary (Reeve, 1996).

The pine needles are hard and it is difficult to extract fibres with the common retting process. Chemical method is suitable for the extraction of fibres from pine needles. The percent yield of pine fibre with 4% NaOH solution ranged between 60 to 65%. This yield can be further optimized by varying the treatment time and concentration of NaOH solution. The mean length of pine needle fibre was 13 mm (Table 3). The length of pine needle fibre (13 mm) was higher than cotton linters (3.5 mm), sugarcane (1.7 mm), wheat straw (1.4 mm), rice straw (1.4 mm) and esparto (1.1 mm), but was less than cotton (30 mm). The average diameter of pine needle fibre was 32 μm, which was greater than cotton linters (21 μm), cotton (20 ìm), sugarcane (20 μm), wheat straw (13 μm), rice straw (8 μm) and esparto (9 μm). The fibre properties of the raw material affect the quality and use of the papers. The long fibres from softwoods or from non-woody species form a strong matrix in the paper sheet (Hunter, 1988).

Cellulose, lignin, extractives and ash forming minerals are the main constituents of all types of woods and agro-based materials. The amounts of these components and cellular structures determine the quality of wood fibre. For good quality of

**Table 1.** Chemical constituents of pine needles (%)

| Chemical constituents | percentage |
|---|---|
| Cellulose | 41.04 |
| Lignin | 35.10 |
| Moisture | 6.0 |
| Ash | 3.2 |
| Silica | 0.63 |
| Ca | 0.64 |
| Mg | 0.26 |
| Na | 0.1 |
| K | 0.51 |
| Fe | 0.05 |
| Mn | 0.04 |

**Table 2.** Comparison of softwood, hardwood and pine needles in terms of cellulose, lignin constituents and fibre length

| Material | Cellulose (%) | Lignin (%) | Fibre length (mm) |
|---|---|---|---|
| Softwoods | 42 | 28 | 2.6 |
| Hardwoods | 45 | 20 | 0.6-1.5 |
| Pine needles | 41 | 35.10 | 13 |

**Table 3.** Comparison of length and width of fibres extracted from pine needles with some common non-wood fibres

| Source of fiber | Fibre length (mm) (average) | Fibre width (μm) (average) |
|---|---|---|
| Pine needles | 13 | 32 |
| Cotton lint | 18 | 20 |
| Cotton | 30 | 20 |
| Sugarcane | 1.7 | 20 |
| Wheat straw | 1.4 | 15 |
| Rice straw | 1.4 | 8 |
| Esparto | 1.2 | 13 |

pulp and paper, high cellulose content, low lignin, and low ash content is preferred. Fibre morphology also plays an important role (Hunter, 1988).

The results show that cellulose content of pine needle is comparable to that of softwood. The lignin content was high compared to both softwood and hardwood and required harsh pulping conditions. The ash content was not high, while the percent yield, average diameter and length of the pine needles fibre were suitable for pulp and papermaking.

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