New method of measuring the pH of wood chips

By B. Sitholé

Abstract: Seasoning of wood chips is commonly employed for deresination. However, excessive seasoning of chips can result in chip deterioration such as fungal stains, brittleness and high acidity. The high acidity can cause deterioration of wood, losses in yield and strength, and higher consumption of cooking chemicals in kraft pulps. Despite this, no standard procedure for measuring the pH of wood chips is available. This report describes an accurate procedure for doing this: the pH is best measured in the presence of salt.

Seasoning of wood chips, or chip storage, is a common strategy employed by pulp and paper mills to reduce the amount of wood resin present in the chips. This has the advantage of introducing less wood resin into the mill, resulting in less pitch deposition in the making of pulp and paper [2]. However, excessively long chip storage can result in chip deterioration such as fungal stains, brittleness and high acidity. When the temperature in chip piles reaches 60-70°C, a chemical reaction occurs in which the acetyl groups present in hemicellulose molecules are cleaved, forming acetic acid [8]. This reaction produces heat and raises the acidity of the chip pile. The increased heat, of course, drives this reaction even faster if it is not dissipated, releasing more acid. The acid, in large quantities, causes deterioration of wood by attacking the cellulose chain molecules. This can result in yield and strength losses when the wood is pulped [9]. The increase in acidity and heat darkens the wood, and it eventually crumbles as if burned. In extreme cases, the pH can be as low as 3.5 which will result in the chips consuming as much as 30-40 g 0.1 N sodium hydroxide per gram of wood to neutralize them. Thus an equivalent amount of alkali in kraft cooking liquor will be consumed before pulping can even begin. The use of large quantities of badly deteriorated chips requires abnormally high charges of cooking liquor, usually resulting in low pulp yields and high screen rejects. Such chips are often not worth using, even in small quantities [6].

Despite these problems, it is surprising that very few methods have been reported for measuring the pH of wood chips and no standard procedures have been developed for this purpose. Campbell and Bryant [12] measured pH values of wood by extracting one gram of wood meal with 20 mL distilled water, and then measuring the pH of the extract. A similar approach, using cold or hot water, is used in the TAPPI and PAPTAC standards for the determination of the pH of paper extracts [5]. A quick survey of several Canadian kraft mills revealed that most mills measure the pH of wood chips by the TAPPI or PAPTAC hot water extraction method. These methods are based on the premise that the pH of the liquid surrounding the solid matrix is identical to that of the solid matrix itself. However, it is conceivable that preferential dissolution of either acidic or basic extractives could affect the pH. The added water for extraction is expected to alter the measured pH values: obtained values below pH 7 would be expected to be higher than the true value; those above seven would be expected to be lower [10]. Ingruber [11] studied the chemistry of wood meal, cellulose and lignin preparations in the presence of unbuffered weak acids and bases and obtained substantial information on the ionic behaviour of these materials and how they could affect the pH of wood matrices.

Read et al. [10], in studying the impact of partial penetration of kraft cooking liquor in chips, developed a method to measure the pH of wood surfaces. The method entailed sectioning wood chips with a microtome and measuring the pH of the sections with colorimetric pH indicators. The authors compared their method with the TAPPI method (designed for paper extracts) and concluded that the colorimetric method gave more reliable results.

None of the methods described so far have considered the factors that could influence the resulting pH. We therefore conducted an investigation to determine which parameters could affect the determination of the pH of wood chips. Of particular concern were chip particle size, extraction volume, extraction time, moisture content, bark content, and ionic strength.

METHODOLOGY

Three procedures for obtaining chip extracts for pH measurement were evaluated:

1. Hot water extraction

Some mills use this method to measure the pH of wood chips. It entails the following:
   a) Place 50 g (o.d.) wood chips in a 1 L beaker.
   b) Add 200 mL distilled water.
   c) Boil for 10 minutes.
   d) Cool, decant, and measure the pH of the liquid.

2. Cold water extraction

Use the same amounts of materials as above except that the chips are left to soak overnight at room temperature.
3. Press chips to obtain pressate

We have shown that the age of wood chips can be estimated by measuring their triglyceride content [1]. The procedure involves pressing chips at high pressure to obtain a pressate that is then analyzed for triglyceride content. In this case, the pH of the pressate is measured instead as follows:

a) Place ~300 g chips in a stainless steel holder.
b) Transfer the holder to a hydraulic press and press the chips to 8000 psi for about a minute.
c) Collect the pressate and measure its pH.

The effects of the following parameters on the resultant pH were studied using the hot water extraction method: size of chips, boiling time, extraction volume, moisture content of chips, bark content, and ionic strength.

The following wood species were tested: trembling aspen (Populus tremuloides Michx.), black spruce (Picea mariana (Mill.) B.S.P.), and Douglas fir (Pseudotsuga Carr.). Grab samples of wood logs were obtained from mill wood yards. The logs were barked by hand at Paprican and chipped to produce one-inch long chips, nominally 4-10 mm thickness. Smaller sizes of the chips were achieved by screening on a Domtar chip classifier and, also, by milling on a Wiley mill (60 mesh size). The moisture content of the chips was varied by drying the one inch chips in an oven at 105°C over a time period ranging between 1 and 12 hours. The pH was measured using an Accumet 50 pH meter (Fisher Scientific) calibrated daily with buffers at pH 10.00, 7.00 and 4.00.

As mentioned earlier, the preceding methods assume that the pH measured in the medium surrounding the fibres is the same as that within the fibre walls. In reality, the pH inside the fibre wall can be five times lower, as was demonstrated by Scallan [4]. This phenomenon originates from the fact that fibres contain carboxylic acid, phenolic and hydroxyl groups bound within their polymeric matrix. The anions of these groups hold quantities of oppositely charged cations, including hydrogen ions, within the wall. The presence of fixed ionic species from such groups induces Donnan equilibrium, where the concentrations of free ionic species inside and outside the fibres are not equal, Fig. 1. The hydrogen ions can be displaced from inside the fibre walls by cations, e.g., changing the ionic strength of the surrounding medium by addition of sodium chloride. This enables sodium ions to migrate into the wood matrix and displace hydrogen ions. Consequently, we decided to extract wood chips in the presence of sodium chloride to ascertain if the Donnan equilibrium would have any effect on the resultant pH. The experiments were as mentioned previously except that the ionic strength was adjusted over a range from 0 to 0.5 M NaCl by addition of appropriate amounts of a 5 M stock solution.

RESULTS

Effects of Various Parameters on pH of Chips

Figures 2 through 5 summarize the data obtained using the hot water extraction procedure. The data show that:

a) Chip particle size has no effect on the pH of the chip extracts, Fig. 2. The same applies to time of boiling over 5 to 30 minutes. It appears that after 10 minutes of boiling, complete penetration of water into the chips occurs regardless of chip size.

b) The volume of the water used for extraction affects the final pH measured; the pH increases with increase in the volume of water, Fig. 3. This has been observed in measurement of pH of paper extracts [10] and is to be expected, since large volumes of water will result in dilution of the concentrations of the extractable (acidic) components.

c) Moisture content affects the pH of the chips; the pH rises with increasing moisture content, Fig. 4. There is a 5-fold difference in pH between wet chips (45% moisture content) and dry chips. Even more dramatic results have been reported by Read et al. [10], who determined that the pH of western red cedar increased from 4.3 to 5.3 (10-fold increase) when the moisture content of the wood was varied from 20 to 70%, and the pH of western hemlock increased from 4.0 to 4.8 as the moisture content increased from 10 to 55%. This is of major importance in chemical pulp mills that use chips from
sawmills. The sawmill chips may arrive at the mill with much lower moisture content than chips prepared at mills, implying that they will have lower pH values and thus will need more cooking chemicals than the chips prepared on site. The lower pH at lower moisture content may be due to hydrolysis of the acetyl groups to form acetic acid [2] thus decreasing the pH of the chips.

d) Increasing bark content decreases the pH of the chips, Fig. 5, probably because bark components include significant amounts of acidic phenolic moieties [3]. Thus, higher bark content in chips, in addition to raising dirt and sclereid counts in the pulp and paper produced, also results in higher consumption of cooking chemicals and lower pulp yield.

Comparison of Extraction Procedures for pH Measurement of Chips

Figure 6 shows pH results, with spruce chips, spruce bark, and a 95:5 spruce chip:bark mixture, obtained by the three extraction methods. The data show that hot water extraction gives pH values that are slightly lower than those obtained by cold water. Both hot and cold water extraction give values that are lower than those obtained via the pressing method. This seems to imply that the water extraction procedures release more acidic components present in the wood chips than can be removed by squeezing the chips. Consequently, water extraction of chips is preferable for their pH measurement. The hot water extraction method is preferable, as it is much faster (10 minutes versus overnight extraction) and yields lower pH values that may more accurately reflect the inherent pH of the wood chips.

Effect of Ionic Strength

Figure 7 shows the effect of ionic strength on the pH of cold and hot water wood chip extracts, respectively. The extent of the Donnan equilibrium is about the same in both cold and hot water extraction: pH measurements without adjustment of ionic strength give values that can be as much as 17% lower than the inherent pH. This corresponds to a significant difference in hydrogen ion concentration, since pH is measured on a logarithmic scale.

The data in Tables II and III further illustrate the effect of ionic strength on the pH of softwood and hardwood wood chip mixtures. In all cases, the pH is reduced upon addition of NaCl. Therefore, adjustment of ionic strength before pH measurement is mandatory because in a mill environment a relatively high ionic strength prevails in the chip media due to the presence of cooking chemicals.

Proposed method for measuring the pH of wood chips:

From the results of this study, the following methodology is proposed to measure the pH of wood chips:

- Dry chips in an oven at 105°C overnight;
- Place 50 g of chips in a 2 L beaker;
- Add 180 mL distilled (or deionized) water;
- Adjust ionic strength to 0.2 M by adding 20 mL of 2M NaCl solution;
- Cover beaker with a watch glass and boil for 10 minutes on a hot plate;
- Cool, decant, and measure the pH of the extract.

CONCLUSIONS AND IMPLICATIONS

This study shows that the pH of wood chips can be determined by hot or cold water extraction of wood chips and then measuring the pH of the cooled extract. Moisture and bark contents of the chips affect the pH measured. Thus, it is best to dry the chips before extraction to overcome the effects of moisture content.

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NaCl was considered a good compromise, as there are concerns that higher ionic strengths would result in inaccurate pH readings, especially in alkaline environments [7]. There may be concerns about chips from wood that has been exposed to seawater. However, we believe that the impact on this on the resultant pH should not be significant.

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LITERATURE