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# BioResources

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Cover image: Endgrain of freshly cut Douglas Fir, *Pseudotsuga menziesii*; Photo credit: Allen Hubbe.

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# *B i o R e s o u r c e s*

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# THE "LOVE-HATE" RELATIONSHIP PRESENT IN LIGNOCELLULOSIC MATERIALS

Martin A. Hubbe and Lucian A. Lucia

The three main types of chemical components in wood are cellulose, hemicellulose, and lignin. These three components have rather different physical and chemical characteristics. In some respects, the three types of materials can be described as "incompatible." However, most of the biomass existing on the planet depends on their successful interactions. It can be useful to think of wood as being a natural composite structure. Concepts related to composites also are useful as we envision possible new and improved uses of wood-derived materials.

*Keywords: Cellulose, Hemicellulose, Lignin, Hydrophilic, Hydrophobic, Compatibility*

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## A RELATIONSHIP MEANT TO LAST?

Most of the world's biomass consists primarily of three somewhat incompatible types of biopolymers – cellulose, hemicellulose, and lignin. Together, these are the most abundant natural organic polymers. Our very existence depends on the successful interactions and structures involving an intimate relationship among these three.

Let us examine each of these biopolymers piecemeal. Cellulose is a regular, linear polymer, having a high tendency to form crystalline regions. Though it has a very strong hydrogen bonding tendency, many of the hydrogen bonding sites of cellulose become tied up in the intra-chain and inter-chain associations inherent in the crystalline nature of this macromolecule. From a materials standpoint, cellulose is quite rigid, having a high dimensional stability in the direction of the macromolecular chains. It also has a tendency to swell – especially in the amorphous regions – in dimensions perpendicular to the primary orientation of the macromolecules and fibrils.

Despite their similar name, hemicelluloses are quite different from cellulose. The macromolecules are irregular, having side groups or substituent groups, as well as different sugar units along the chains. Hemicellulose materials, by themselves, do not have sufficient moduli of elasticity to hold promise as a structural material. Rather, hemicellulose acts like a semi-soluble polyelectrolyte and bonding agent.

Finally, lignin's characteristics from a constructionist's point of view can cause even greater doubts regarding whether the relationship among these three types of chemicals is destined to last. Lignin is a highly randomized condensed polymer, full of aromatic groups, as well as chemically resistant cross-links of various types. Lignin is much more hydrophobic than cellulose, let alone hemicellulose. Based on solubility principles alone, the three components would be classed as "incompatible"

## A NATURAL COMPOSITE

As in any composite, the physical properties of wood seldom equal what would be predicted from a linear sum of properties of its main constituents. Manufacturers of counter-top laminates take advantage of this principle when they impregnate highly porous "saturating kraft" paper with phenolic or melamine resins. The combination of the cellulosic fiber matrix, together with solidified resin filling the void spaces, achieves a dimensional stability far in excess of what can be achieved by either component.

The success of a final paper product often depends on the relative abundance of hemicelluloses. Paper's tear strength is directly related to the levels of hemicelluloses, but pulping operations tend to remove it easily by virtue of its relatively labile nature. Clever scientists are pursuing the concept of VPP (Value Prior to Pulping) to take advantage of this materials loss. The idea is to collect the hemicelluloses and then use them in standard fermentation reactions to make bioethanol.

To further extend the idea of a "natural composite" (perhaps dangerously so), one can regard hemicellulose as an adhesive between the rigid semi-crystalline cellulose and the tough "inclusions" of lignin within the wood structure. A need to explain the coupling between the cellulosic and lignin-rich phases lends credibility to some recent results supporting the existence of covalent bonds between hemicelluloses and lignin.

Hemicellulose and lignin also help wood resist microbial attack. Whereas it can take as few as three enzymes to efficiently degrade cellulose, it takes a wide assortment of enzymes, working together, to degrade all of the different types of chemical structures present in hemicellulose and lignin. These same factors help to explain why it has been such a challenge to bring lignocellulosic ethanol into widespread commercial success.

## NEW USES AND NEW OPPORTUNITIES

Manufacturers of kraft pulp for papermaking work hard to remove lignin, retaining just the polysaccharide materials to make paper structures having high strength or high brightness. The lignin portion is mainly incinerated to recover its heat value, providing power and steam for the pulping and papermaking processes, as well as recovering the pulping chemicals. Opportunities to make fuller use of byproducts from pulping will be featured in future review articles and editorials in this journal.

Considering how long cellulose, hemicellulose, and lignin have coexisted in woody systems, it may be surprising to see how easily the material can be manipulated. For example, by genetic engineering it is possible to vary the ratio of lignin to cellulose, and also to control whether the lignin is rich in syringyl vs. guaiacyl groups. Though *a priori* it is doubtful whether seriously lignin-deficient trees would thrive in the wild, some of them appear to grow satisfactorily under controlled conditions.

Another way that lignocellulosic materials can be transformed is by dissolving the wood material and then reconstituting it. Such transformations have become possible to contemplate recently due to advances in ionic liquids. The reconstituted wood material can take on a wide range of properties and be chemically manipulated according to the type of solvent in which it is dissolved.

# RECYCLING OF CHEMICAL PULP FROM WHEAT STRAW AND CORN STOVER

Ulrike Tschirner,[a*] James Barsness,[b] and Tamara Keeler [c]

Handsheets produced from corn stalks and wheat straw soda AQ pulps were recycled in the lab. Pulping of corn stalks resulted in a low pulp yield, low bonding strength, and low recyclability. Conversely, wheat straw fiber had a better yield, very good tensile properties, and showed a considerably better response to recycling. The tensile index of wheat straw fibers retained 67% of its original value after four cycles. It could be shown that recycling caused only small changes in chemical composition, but that the crystallinity index increased considerably. To be able to understand the behavior of wheat straw fiber as part of a commercial papermaking furnish, a paper containing 20% wheat straw fiber was produced on a 24 inch pilot paper machine and was recycled using a handsheet mold with white water return. Chemical analysis of the control (no wheat fiber) and the wheat-containing paper demonstrated slightly higher xylan content for the wheat-containing material. Recyclability increased slightly with addition of wheat fibers to a commercial furnish.

*Keywords: Wheat, Corn, Recycling strength loss, Crystallinity index, Chemical composition*

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## INTRODUCTION

In recent years, non-wood fibers have been increasingly considered as a potential source of papermaking raw material (Paavilainen 1997, Kramer 1998). While there is a large body of information available regarding different pulping conditions and characteristics of these fibers, there is limited information on the behavior of non-wood fibers during paper recycling. In this paper we are focusing on recycling properties of fully bleached chemical fibers produced from corn stalks and wheat straw. It is well known that all chemical fibers show a significant loss in strength properties upon recycling (Szwarcsztajn 1996; Phillips 1994; McKee, 1991; Nazhad and Paszner 1994). It is generally accepted that the loss of strength in low yield pulps during recycling is caused by "hornification," a loss of wet fiber flexibility and bonding ability caused by self association of cellulose microfibrills during drying (Jayme 1958). While this effect was originally thought to be caused by the removal of lignin (Scallan 1992), several researchers have found that the xylans present in the pulp fiber have a distinct impact on recycling behavior of wood fiber (Cao et. al 1998; Aravamuthar 1998). In pulps with high levels of xylans, loss of pulp strength during recycling was reduced (Cao et. al 1998). Since non-wood plant material tends to have high xylan content, it was expected that these fibers might show a good potential for recycling.

There have been limited studies on recyclability of non-wood chemical fibers. In addition, these studies have used lab handsheets. For example, Garg and Singh (2004) studied recyclability of bleached chemical pulps from wheat straw and bagasse. While wheat straw pulps showed relatively less strength loss during recycling, bagasse fiber had a low recycling potential. Aravamuthan and Greaves (1998) studied recycling behavior of handsheets containing up to 30% of wheat straw fibers, the remaining materials being softwood kraft fibers. They found that the presence of wheat straw did not significantly alter the recycling potential but did not offer an explanation. Interestingly, in several cases the handsheets made with the mixed fibers showed higher strength than the 100% softwood fiber. It also was observed (Aravamuthar and Greaves 1998) that unbeaten wheat pulp had a better recycle potential than beaten wheat pulp.

As mentioned before, the few recycle studies available all have been based on handsheets. It is known that there is a significant discrepancy between machine-made paper and handsheets with regard to recycling behavior (Eastwood and Clarke 1978; van Wyk et al. 1982). To address some of these issues, we produced a commercial type paper, containing typical amounts of fillers and wet end chemicals, on a pilot paper machine. A control paper sample contained a mixture of hardwood and softwood fiber (70% HW, 30% SW), while in the trial runs 20% of the wood fiber was replaced with bleached wheat straw fiber (56% HW, 24% SW). Both the control and the wheat trial paper were not coated, but did contain 14% PCC (Precipitated Calcium Carbonate) as filler.

## EXPERIMENTAL

### Lab Experiments

For the handsheet experiments both corn stover and wheat straw were processed in an M/K digester with 12% NaOH and 0.1 % anthraquinone (AQ). The liquor to wood ratio was 10:1 and the maximum temperature was 160 $^{o}$C. Cooking time was 90 minutes. The pulps were screened and bleached to 87.5% ISO brightness (wheat pulp) and 88.9 % ISO (corn stalks) using a DED sequence. All paper was recycled using a sheet mold with white water recirculation, discarding the first 10 sheets while building up fines concentration in the white water system. For each cycle a portion of the pulp was used to produce standard handsheets according to TAPPI Method T205, including pressing and restrained drying on drying rings under controlled humidity. These sheets were used for testing purposes only (not recycled). The remaining sheets were dried on a hot plate under restraint and were reslushed in a British disintegrator to be used for the next cycle. Tensile index, tear index, ash content, burst index, opacity and brightness were determined using standard TAPPI test methods T 220, T 211, and T 453. Data presented in this paper are average numbers of at least two repeats.

### Pilot Plant Runs

Pulping of wheat straw for the pilot paper machine run was done in a rotary globe digester. The total fiber charge for each cook was 36 kg (based on dry fiber weight) at a liquor-to-wood ratio of 8:1. The chemical addition rate was 14% NaOH and 0.1 % AQ (based on o.d fibers). Time to temperature was 60 minutes and time at temperature was

35 minutes. A maximum cooking temperature of 160 °C was used. Pulp was bleached using a DED sequence. The pilot paper machine runs were conducted using a Fourdrinier machine with a wire width of 24 inches and a speed up to 200 ft/min. The selected control furnish contained a mixture of fully bleached softwood and hardwood chemical pulps at the ratio of 3:7. In addition, the furnish contained 14 % of precipitated calcium carbonate (PCC) and a typical mixture of wet end chemicals (internal size, starch, retention aid). For the trials with wheat fiber, 20 % of the fibers were replaced, retaining the ratio of softwood: hardwood. All other conditions were kept constant.

### Analytical Procedures

Solid-state $^{13}C$ NMR was used to determine cellulose crystallinity. Cellulose shows separate signals for the C4 carbon of the glucose in crystalline regions of cellulose (88 ppm) and amorphous regions (84 ppm) (Liitiae et al. 2003, Witter et al. 2006), which makes it possible to calculate the crystallinity index based on the intensity of these two peaks. The NMR experiments were carried out on a Varian VNMR spectrometer (Palo Alto, CA) operating at a resonance frequency of 150.8 MHz for $^{13}C$. The temperature was maintained at 25 °C and the spinning speed was regulated at 5 kHz ±3 Hz. Carbohydrate and Klason lignin analyses were performed using the HPLC procedure proposed by Sluiter et al. (2006). Fiber length was determined using an Optest™ fiber analyzer. Fines content was determined using a Britt Jar and TAPPI Method T261.

## RESULTS AND DISCUSSION

### Recycling of Lab Handsheets

There was a distinct difference noticeable between corn stalk and wheat straw Soda AQ pulps. As seen before, the use of corn stalks in the pulping process results in a lower fiber yield (30%), as well as a shorter fiber length. The average length weighted fiber length for corn stalk pulp was determined to be only 0.43 mm. Wheat fiber showed an average length weighted fiber length of 0.9 mm, very similar to the fiber length of hardwood. As expected, this resulted in superior strength properties for wheat pulps (higher tear, tensile and burst index) (Table 1, Fig. 1). In addition, as the pulp was formed into handsheets and recycled, corn stock fibers showed a larger strength loss than wheat straw fibers (Fig. 2). The difference in recyclability increased with continued recycling. After the first cycle, paper produced from corn fiber retained 69% of its tensile strength and wheat fiber 73%. While the strength loss leveled off fairly quickly for wheat straw paper (at around 67% of the original tensile strength), corn fiber paper continued to lose strength in subsequent cycles and reached a total strength loss of around 50% after three cycles.

Due to the loss in bonding properties, tear index increased slightly during recycling for both corn and wheat straw fibers. While both pulp types started at a similar tear index of 4.8 and 4.9 $mNm^2/g$ respectively, wheat pulp tear index increased up to 6.5 $mNm^2/g$, maintaining this value through cycle four. Corn pulp, on the other hand, reached a maximum at 5.5 $mNm^2/g$ tear index and started to decrease at cycle three.

TAPPI Opacity increased for both pulps during recycling, most likely due to increased generation of fines.

**Table 1:** Properties of Bleached Corn and Wheat Straw Fiber during Recycling

| | Tensile Index [kN/m] | | Tear index [mNm$^2$/g] | | Burst Index [kPa m$^2$/g] | |
|---|---|---|---|---|---|---|
| | Corn | Wheat | Corn | Wheat | Corn | Wheat |
| Starting | 45.3 | 84.4 | 4.8 | 4.9 | 3.8 | 5.0 |
| Cycle 1 | 31.4 | 61.4 | 5.0 | 6.2 | 2.5 | 5.0 |
| Cycle 2 | 26.3 | 53.0 | 5.5 | 6.3 | 2.2 | 4.6 |
| Cycle 3 | 23.2 | 57.4 | 4.5 | 6.5 | 2.0 | 4.8 |
| Cycle 4 | | 57.1 | | 6.5 | | 4.5 |

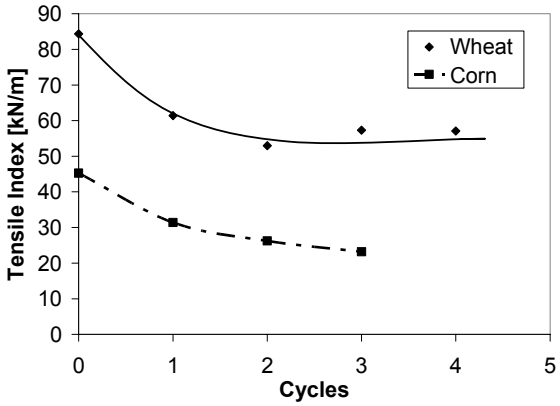


**Figure 1.** Tensile index changes during recycling of corn and wheat straw fiber

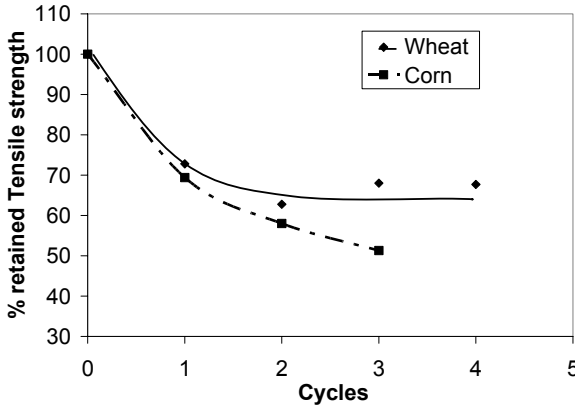


**Figure 2.** Loss of tensile strength properties during recycling of corn and wheat fiber

There have been discussions in the past regarding the significance of carbohydrate losses, specifically the loss of xylan during recycling (Sjöström et al. 1963; Eastwood et al. 1978; Bouchard et al. 1994; Cao 1997). Table 2 shows the chemical composition of bleached wheat straw fiber during recycling. All of these tests were run in duplicate.

No mannose could be detected during the analysis, and the Klason lignin content of the fully bleached pulp was below 0.5%. Examination of the bleached wheat straw fiber during recycling indicated a slight change in chemical composition, specifically during the first cycle. The glucan level increased from 68.1 % to 69.1% in the first cycle and reached 70.7 % during cycle four. While these differences are very small, they are statistically significant. Standard deviation for this test was determined to be +/- 0.25%. Xylan levels also increased slightly. This resulted in the fact that glucan/xylan ratio remained constant through all cycles.

It is generally accepted that the main reason for bonding strength loss during recycling is the effect called "hornification", a decrease in fiber flexibility caused by increased crystallinity. The crystallinity index of our wheat straw pulp was determined using $^{13}$C NMR according to Liitiae and Witter. There was a significant increase in crystallinity index noticeable during recycling of wheat straw fiber. The crystallinity

index increased from 38 % to 40.4% during the first cycle and showed a continuous increase to up to 49.7 % (Table 2). Clearly, changes in pulp fiber crystallinity index have a strong impact on the fibers during recycling.

**Table 2:** Chemical Composition and Crystallinity Index of Wheat Straw Pulp during Recycling

| | Glucan [%] | Xylan [%] | Galactan [%] | Arabinan [%] | Crystallinity Index [%] |
|---|---|---|---|---|---|
| Starting | 68.1 | 22.4 | 0.8 | 1.9 | 38.1 |
| Cycle 1 | 69.1 | 23.7 | 1.1 | 2.1 | 40.4 |
| Cycle 2 | 70.0 | 23.5 | 0.9 | 2.0 | 42.8 |
| Cycle 3 | 70.0 | 23.1 | 0.8 | 1.0 | 48.3 |
| Cycle 4 | 70.7 | 23.1 | 0.9 | 1.9 | 48.3 |
| Cycle 5 | 69.9 | 22.9 | 1.0 | 2.1 | 49.7 |

## Recycling of Pilot Plant Paper

The commercial type paper recycled for this part of our study was produced on a 24 inch pilot paper machine, using a softwood/hardwood furnish, filler, and wet end chemical levels typical for a commercial printing and writing grade paper. A control run used a fully bleached softwood and hardwood furnish (3:7 SW:HW ratio). For the wheat fiber trial, 20% of the wood fiber was replaced by fully bleached wheat pulp (replacement of equal amounts of softwood and hardwood). Since wheat straw produced with the above mentioned pulping and bleaching conditions continuously shows a very high tensile strength (Tschirner et al 2003), it was not surprising that the sample containing 20% wheat straw had a higher starting tensile index than the control.

As expected, we could observe a strength reduction for both the control and wheat-fiber-containing papers during recycling. As demonstrated in most other recycling studies, the drop was most dramatic during the first cycles (Figs. 4 and 5). The first cycle was especially important in our study, since only the first cycle used a paper formed on a paper machine. The following cycles were again using handsheets. Interestingly, the wheat-containing material not only started out at a higher strength property, but it also showed a lower percent reduction in strength (Fig. 5). Wheat-containing paper retained 86% of its original tensile strength and was able to maintain this level through the subsequent stages. The control paper retained only 82% of its tensile strength after stage one and continued to show strength reductions to levels as low as 75% of the original. As before, the recycling experiments were run in duplicate, and the tests showed a very good repeatability. For tensile strength, the difference between two independent runs was only 1-4%.

There was no significant difference in tear index or change in tear index between the two papers. Fines content for the control sample was determined to be 7%, while fines content for the wheat containing paper was slightly higher (9.4%). Neither fines content nor average fiber length of the samples changed significantly during recycling. Table 3 shows the chemical composition of both types of paper used for this study. It is well known that wheat straw fibers have high xylan and silica content, so it was not surprising to find that the wheat containing paper machine paper had a slightly higher xylan and ash content than the control. The slightly improved recyclability of material

with wheat straw fiber content agrees well with Cao's conclusion that higher levels of xylan promote resistance to bonding strength loss during recycling. Clearly, wheat pulp fiber, if added to commercial papermaking furnish, has the potential to retain comparable or slightly better strength properties than wood-derived fiber.

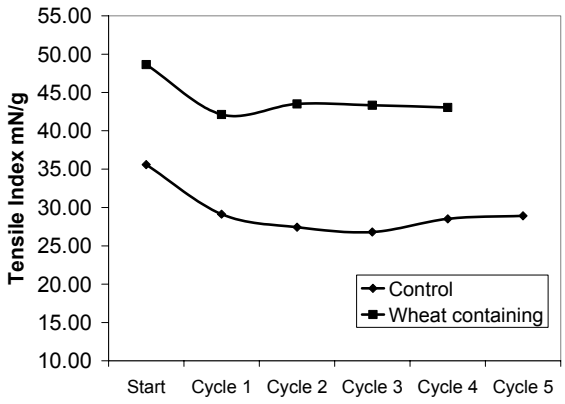


**Figure 4.** Changes in tensile strength during recycling of pilot plant paper

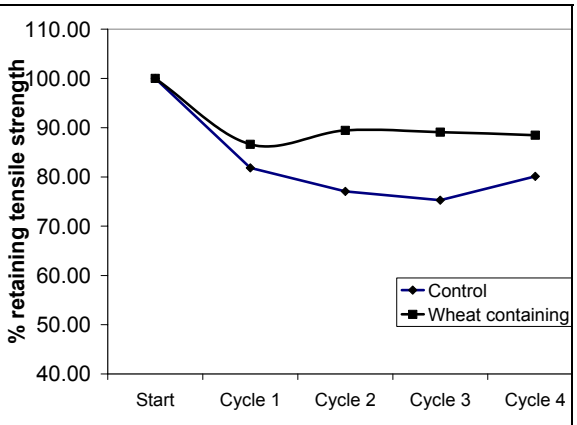


**Figure 5.** Percent tensile loss during recycling of pilot plant paper with/ without wheat fiber

**Table 3.** Chemical Composition of Control and Wheat-Containing Paper

| | Control % | Wheat containing % |
|---|---|---|
| **Glucan** | **71.2** | **70.1** |
| **Xylan** | **13.7** | **15.4** |
| **Galactan** | **0.0** | **0.0** |
| **Arabinan** | **0.4** | **0.7** |
| **Mannan** | **2.3** | **2.2** |
| **Lignin** | **0.4** | **0.4** |
| **Ash** | **7.7** | **8.5** |

## CONCLUSIONS

1. Corn stover pulping resulted in unacceptably low pulp yield and up to 50% loss in bonding potential during recycling.
2. Wheat straw pulping produced pulp with high initial strength properties and greater resistance to strength loss during recycling.
3. The change in chemical composition of wheat straw during recycling was minor. The change in crystallinity index during recycling, on the other hand, was significant and clearly is the main contributor to loss in strength properties.
4. Commercial type paper produced on a pilot paper machine showed better resistance to strength loss during recycling than a control sample containing only hardwood and softwood fiber.

5. The improvement in strength retention during recycling of wheat-straw-containing fiber was most likely due to increased levels of xylan.

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# MILL DEMONSTRATION OF TMP PRODUCTION FROM FOREST THINNINGS: PULP QUALITY, REFINING ENERGY, AND HANDSHEET PROPERTIES

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High-value, large-volume utilization of forest thinning materials from U.S. National Forests is a potentially important contributor to sustainable forest health. This study demonstrated the utilization of wood chips produced from thinnings for the production of thermomechanical pulp (TMP). Both whole-log chips (primarily from small-diameter logs, tops, and reject logs) and sawmill "residue" chips from a Hewsaw™ system (Mäntyharju, Finland) were evaluated. The residue chips produced in this study were substituted for a TMP mill's standard residue chips up to about 50%. The whole-log chips were substituted for the mill's whole-log chips up to about 30%. The results show that substitution of chips produced from forest thinnings reduced refining energy in all trials. Pulp quality was maintained throughout all trials.

*Keywords: Forest thinning, Small diameter trees, Suppressed growth trees, Thermomechanical pulp (TMP), Forest fire, Whole log, Saw mill residues, Pulp quality measurement, Sheet properties*

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## INTRODUCTION

Decades of forest fire suppression practices in U.S. National Forests have created fuel overloading as a result of an overpopulation of small-diameter, suppressed-growth trees. To reduce the incidence and extent of catastrophic wildfires in these forests, various remediation strategies are being implemented. One such strategy is selective thinning, targeting the removal of small-diameter trees (Mason et al. 2006). This practice is desirable because it can restore the forest to a more natural state, providing an environment that is far less fire prone and more recreationally attractive. But selective thinning operations are very expensive. Finding high-value, large-volume uses for small-diameter timber is critical to leveraging the costs associated with selective removal strategies. The production of solid wood products such as dimension lumber, poles, or posts is a preferred use in terms of best value. But many of these small-diameter trees are too small to be converted in a conventional sawmill operation. Several sawmill operators in the Pacific Northwest region of the United States have recognized this opportunity and have installed equipment to process logs as small as 10 cm (4 in.) in diameter. Although these new installations can process ever-smaller logs, a substantial volume of unused material remains in our forests. Fortunately, quality wood chips are needed for paper production in this region. Integrating the production of lumber and paper using chips

from small-diameter trees would be highly desirable and could add considerable value to the resource. However, chip quality and consistency is a paramount concern in paper production. Research must demonstrate that residues from these new equipment installations, chips produced from the smallest diameter trees, and other removals such as tree tops are suitable for paper production. Only then would thinned materials be considered a viable resource for paper production.

Our goal in this study was to investigate the suitability of sawmill residues and whole-log chips from selective removals for production of thermomechanical pulp (TMP). Our study demonstrated the viability of using forest thinnings in the integrated production of lumber and paper. By adding value to the resource, this strategy could also alleviate the high costs associated with selective thinning operations and enhance their implementation as important tools for sustainable forest management.

Forest thinning materials from the National Forests are very different from traditional small-diameter trees from commercial thinning in plantation forests. High juvenile wood content is the major characteristic of small-diameter trees produced from plantations. This is a concern for wood-fiber production by the pulp and paper industry because juvenile wood fibers have lower mechanical strength (Zobel and van Buijtenen 1989). Much research on evaluating the papermaking potential of commercial thinnings has been conducted. Of those studies that reported mechanical pulping of thinning materials, Hatton and Johal (1993, 1996) and Hatton (1997) indicated that more energy may be required to refine commercial thinnings. Also, they found that chips from commercial thinning produced different pulp properties than chips from final harvests. Conversely, forest thinning materials from the National Forests include many older trees that have small diameters as a result of several decades of growth suppression, primarily from overcrowding. For example, the tree diameter at breast height (DBH) of a 100-year-old tree can be as small as 12.5 cm (5 in.) or less. Juvenile wood content in such trees is low, but the industry perception has been that forest thinning materials are inferior for fiber production. As a result, this resource has not been well accepted nor fully utilized by the pulp and paper industry as a viable fiber source. Scientific evaluation through laboratory and pulp mill trials is required to elucidate the value of these materials and make the case for broad industry acceptance for incorporating forest thinnings in the commercial production of pulp and paper.

Several laboratory studies on the production of TMP from small-diameter trees have been conducted at the USDA Forest Service Forest Products Laboratory (FPL), Madison, Wisconsin (Meyers et al. 1999, Myers 2004). These studies indicated that mechanical properties (tensile, tear, burst) of handsheets made from thinning materials are consistently lower (10%–30%) than those of paper made from sawmill residues. However, the laboratory refining protocol employed in these studies involved multi-pass refining (up to 5 passes) to achieve a target freeness of 100 Canadian Standard Freeness CSF (Myers et al. 1999). This process can cause significant fiber damage, resulting in about half the weighted average fiber length of commercial pulp. Consequently, the quality of pulp produced under this protocol could not be compared to commercial production with high confidence.

Recently, we studied the effect of growth rate on wood properties, including trees harvested from National Forests that have experienced severe growth suppression (Zhu et

al. 2007). We found that suppressed growth resulted in less distinction between earlywood and latewood fibers in terms of wood density and tracheid geometry. Normally, this distinction is dramatic, particularly for the variation in tracheid wall thickness. This makes it very difficult to optimize TMP process conditions (Rudie et al. 1994). Either the earlywood fibers are severely damaged (shortened) when refining conditions are optimized for latewood, or the latewood is not well refined when refining is optimized for earlywood. Therefore, we hypothesize that small-diameter suppressed-growth trees with a more uniform tracheid wall thickness distribution should refine more easily (giving higher consistency and requiring less energy), which could improve pulp properties in the production of TMP.

To evaluate our hypothesis that thinnings should be suitable for TMP production, we decided to conduct pulping trials at an industry pilot-scale, refining facility (Andritz, Inc., Springfield, Ohio) (Klungness et al. 2006). The objectives of this pilot demonstration were to (1) dispel the notion through rigorous laboratory testing that thinning residues are inferior to conventional wood sources and (2) encourage collaboration between industry and the Forest Service by attempting a commercial demonstration. The control run used sawmill residue chips from "normal" growth trees supplied by a pulp mill, Ponderay Newsprint Company (PNC), Usk, Washington, containing about 50% lodgepole pine (*Pinus contorta*) and 50% mixed hemlock and grand fir (*Tsuga heterophylla* and *Abies grandis*). In the trial with materials from thinnings, about 25% of the chips were from small-diameter logs supplied by a nearby sawmill, Ponderay Valley Fiber, Inc. (PVF), Usk, Washington. These chips were 50% Douglas-fir (*Pseudotsuga menziesii*) residue chips and 50% lodgepole pine whole-log chips. Residue chips are from the outside of the log and do not normally include heartwood, whereas whole-log chips do, of course, include heartwood. Comparisons of the tear strengths of the handsheets made from refined pulp samples at various freeness levels for both the control and small-diameter mixed blends were equivalent. Furthermore, the small-diameter blends produced paper with slightly higher tensile energy absorption than from control chips (Klungness et al. 2006). These results confirmed our initial expectations about the viability of producing TMP from forest thinnings and warranted the full-scale TMP mill evaluation described below.

## EXPERIMENTAL

### Raw Materials

A 70-acre site in the Colville National Forest at East LeClerc Creek near Usk, Washington, was selectively harvested by PVF according to Forest Service specifications (FS 1999). The logs were collected, inspected, and sorted at a nearby landing site and were later hauled to PVF for processing. All logs with severe defects (heart rot, checks, and distortion) and minimum diameters less than 10.41 cm (4.1 in.) (small logs and tree tops) were segregated from the saw logs and chipped as "whole logs." Visual inspection suggested that of the whole logs chipped, about one-third on a volume basis were small-diameter logs, one-third were tree tops, and one-third were large logs with defects that made them unsuitable for lumber production. Figure 1 shows a load of whole logs on the

infeed deck at PVF. Logs to be sawn were processed through an automated Hewsaw™ system (made by the Veisto Group, Mäntyharju, Finland; http://www.hewsaw.com/) to produce dimension lumber. The Hewsaw™ system was developed to maximize the recovery of lumber while converting sawing residues from the outside of the logs directly into chips. Both the LeClerc whole-log (LWL) chips and the LeClerc residue chips (LRC) were shipped to PNC for separate pulping trials.

**Fig. 1.** Whole-log samples being transported to debarking machine.

## TMP Production

The TMP mill at PNC has two production lines. Both lines have primary and secondary refining stages, after which the pulp is diluted and screened. The pressure-screen accepts (about 40%) move forward to the paper machine stock tanks, and the rejects (about 60%) from both production lines are thickened through a reject refiner and screened again. Each refiner is rated at 25,000 hp. Two separate mill demonstration studies were conducted over a 3-week period. The first study was conducted over a two-day period in late February 2006. It involved substituting normal PNC whole-log (PWL) chips with LeClerc-thinning whole-log chips (LWL). The second study was conducted over a two-day period in early March 2006, and involved substituting PNC mill residue chips (PRC) with LeClerc-thinning residue chips (LRC). Only partial substitution was carried out in both studies. Two trial runs were conducted in each demonstration study with different chip substitution ratios.

In the whole-log chip study, 20% substitution of PWL and PRC chips with LWL chips was carried out in the first run, and this was increased to 30% in the second run (Fig. 2). The first run lasted 5 h but the second run lasted only 3.75 h when the LWL chips ran out. The ratio of LWL to PWL chips was approximately 2:1 in both runs for a total chip blend of 30% whole-log chips with 70% residue chips in the first trial (LWL:PWL:PRC = 20:10:70) and 44% whole-log chips with 56% residue chips in the second trial (LWL:PWL:PRC = 30:14:56). The pulp mill technical staff was uncomfortable with increasing the whole-log chip content to 44% (two thirds from thinnings of

small diameter and tree tops) because they feared inferior chip quality. The mill was, however, willing to attempt this level for a short time. The whole-log chip study was of particular interest to the mill because a large quantity of this material is available; however, its quality for papermaking was unknown.

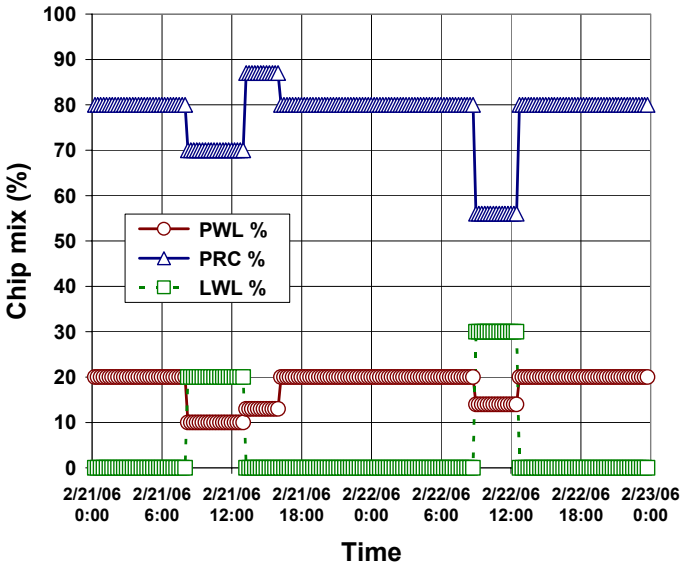


**Fig. 2.** Time series showing the chip-mix ratios during the whole-log chip study.

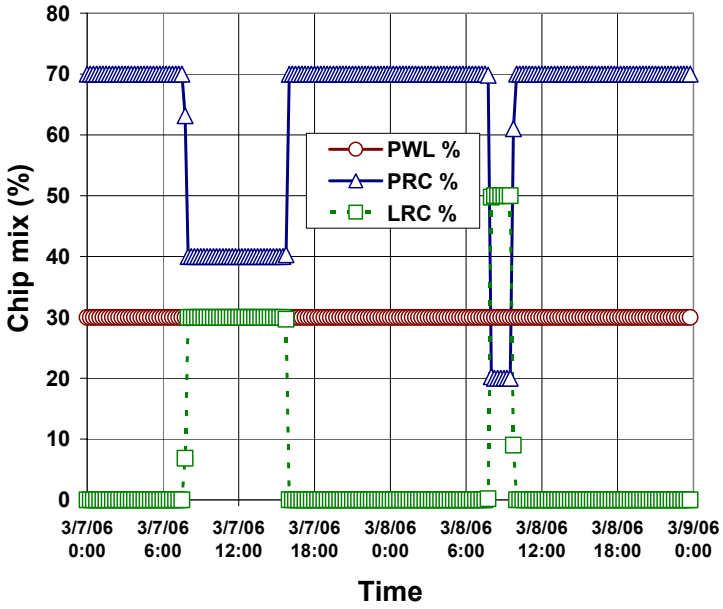


**Fig. 3.** Time series showing the chip-mix ratios during the residue chip study.

In the residue chip study, 30% of the PNC mill residue chips (PRC) were substituted with LeClerc thinning residue chips (LRC) in the first trial run (trial 3), and the substitution was increased to 50% in the second run (trial 4) (Fig. 3). The first run lasted 8 h, and the second run lasted 1.75 h, when the LRC ran out. No changes in pulp quality were expected from these trials.

### Pulp Sampling and Control System Data Recording

Pulp sampling was conducted at several locations along the production line; i.e., primary and secondary refiner transfer lines (diluted), pressure screen accepts and rejects, and reject refiner discharge. Samples were taken hourly, starting 1 h before each trial run and continuing until up to 2 h after. The samples were then shipped to the Forest Products Laboratory in Madison, Wisconsin, to test for pulp freeness and fiber length after latency removal. Pulp freeness was measured according to TAPPI standard method T 227 (1996b), while fiber length was measured by the Fiber Quality Analyzer (FQA, OpTest Equipment Inc., Ontario, Canada). The pulp mill control system records production data such as refining power for each refiner every 5 min. It also records pulp quality data such as pulp freeness as measured by the Pulp Quality Measurement (PQM) system about every 30 min.

### Handsheets Preparation and Testing

The pulp samples were tested for freeness and then made into handsheets for testing. To reduce the number of samples tested, two to three pulp samples collected in the same trial run with similar freeness levels were combined into one pulp sample. Handsheets were prepared using a semiautomatic handsheet mold (Messmer Instrument Limited, Model 255/SA, UK) according to TAPPI standard T205 (1996a). All handsheets were made using recycled white water that had passed through the sheet mold. The white water accumulated in a small holding tank during handsheet making. The tank would fill after making about three handsheets. Overflow of white water was not collected. The accumulated white water was recycled to retain fines that would normally pass through the handsheet screen. The effectiveness of fines retention was demonstrated by measuring changes in handsheet properties as fines accumulated in the white water tank. The properties of the handsheets stabilized as soon as system equilibrium was reached (about three sheets). Paper testing was carried out by the Paper Test Laboratory at the Forest Products Laboratory according to TAPPI standard methods. A set of 10 handsheets was used in paper physical property measurements.

## RESULTS AND DISCUSSION

### Wood Chip Analysis

Wood chip analysis was conducted by Integrated Paper Service, Inc. (Appleton, Wisconsin) according to TAPPI Standard 401 (1996c) (Table 1). Most notable is the low amount of Douglas-fir in the trial chips in spite of the fact that Douglas-fir makes up more than one-quarter of the volume of logs processed at the sawmill. The PNC specifically requested that whole-log Douglas-fir chips be excluded from the trials

because of the dark coloration common in Douglas-fir heartwood, so the logs were segregated at the sawmill and processed separately. In spite of this, Table 1 shows that the PNC chips contained about 15% Douglas-fir; the exclusion was more effective for the chips from the LeClerc site. Table 2 shows the species composition of the chip blends that were used during the four trial runs based on the substitution levels shown in Figs. 2 and 3.

**Table 1.** Chip Species Analysis (columns add to 100%)

| Species | LWL[a] | LRC[b] | PWL[c] | PRC[d] |
|---|---|---|---|---|
| Douglas-fir | 3.6 | 0.8 | 14.1 | 15.5 |
| Grand fir | 38.0 | 18.3 | 33.8 | 18.3 |
| Hemlock | 2.5 | 8.2 | 17.5 | 0.0 |
| Hard pine | 28.1 | 57.5 | 23.0 | 53.2 |
| White pine | 26.8 | 1.4 | 1.4 | 0.0 |
| Spruce | 0.9 | 13.8 | 10.1 | 13.1 |

[a] LeClerc-thinning whole-log chips.
[b] LeClerc thinning residue chips.
[c] Ponderay Newsprint Company whole-log chips.
[d] Ponderay Newsprint Company mill residue chips.

For the whole-log trials, the main difference in species composition between the control chips and trial chips was that the trial chips contained a little less Douglas-fir, hard pine (lodgepole), and spruce and a little more white pine and grand fir. For the residue chip trials, both trial blends contained substantially less Douglas-fir and slightly more hemlock than the control chips. We also observed that the residue chips (PRC and LRC) produced by the Hewsaw™ system were smaller than the whole-log chips (PWL and LWL).

**Table 2.** Species Composition of Chips Used in the Mill Demonstration Runs (columns add to 100%)

| Species | Whole-log trial 1 | | Whole-log trial 2 | | Residue chip trial 3 | | Residue chip trial 4 | |
|---|---|---|---|---|---|---|---|---|
| | Control | Trial | Control | Trial | Control | Trial | Control | Trial |
| Douglas-fir | 15.2 | 13.0 | 15.2 | 11.7 | 15.1 | 10.7 | 15.1 | 7.7 |
| Grand fir | 21.4 | 23.8 | 21.4 | 26.4 | 23.0 | 23.0 | 23.0 | 23.0 |
| Hemlock | 3.5 | 2.3 | 3.5 | 3.2 | 5.3 | 7.7 | 5.3 | 9.4 |
| Hard pine | 47.2 | 45.2 | 47.2 | 41.4 | 44.1 | 45.4 | 44.1 | 46.3 |
| White pine | 0.3 | 5.5 | 0.3 | 8.2 | 0.4 | 0.8 | 0.4 | 1.1 |
| Spruce | 12.5 | 10.4 | 12.5 | 9.0 | 12.2 | 12.4 | 12.2 | 12.6 |

To further examine the differences among the different wood chips, we measured the fiber lengths and widths of the Kraft pulps derived from these wood chips. The final pulp kappa number was around 25. The measured fiber length and width of a Kraft pulp are a reliable measure of the natural wood fiber dimension. As shown in Table 3, the differences in length-weighted mean fiber lengths and arithmetic mean widths were very small between LeClerc-thinning chips and PNC mill chips when comparing whole-log with whole-log chips and residue with residue chips. The differences in fiber dimension between the control and trial 2 chips used in the whole log trial were also insignificant.

**Table 3.** Comparison of Fiber Length of Kraft Pulps from Wood Chips Used in the Mill Demonstration

| Wood Chips | Length Weighted Pulp Mean Fiber Length (mm) | Arithmetic fiber width (μm) | Pulp Kappa Number |
|---|---|---|---|
| LWL | 2.59 | 37.2 | 25.5 |
| PWL | 2.59 | 34.1 | 28.7 |
| LRC | 2.49 | 34.5 | 25.4 |
| PRC | 2.52 | 35.5 | 23.3 |
| Whole-log Trial Chips | | | |
| Control | 2.69 | 34.7 | 25.2 |
| Trial 2 | 2.54 | 33.8 | 25.2 |

## Pulp Quality

The data collected from the mill's PQM system and laboratory testing of the pulp samples were used to assess pulp quality. For the whole-log study, no significant differences in pulp freeness (Fig. 4) and weighted-average fiber length (WAFL) (Fig. 5) were observed for pulps produced from control chips or pulps produced from trial chips. The PQM data were not available for the freeness of pulps obtained from pressure screen accepts. However, these freeness values were later determined from laboratory tests at FPL. For all pulps tested, the FPL lab data showed slightly higher freeness and WAFL than the corresponding PQM data did. However, the lab data showed the same trends as the PQM data, indicating that the PQM data were quite reliable. To determine the extent of refining in the whole-log trials, the pulp long-fraction data from PQM were plotted against pulp freeness (Fig. 6) and the pulp shive content was plotted against WAFL (Fig. 7). No substantial differences were observed in either of these relations between the pulp from the control and trial runs.

A simple statistical analysis was conducted to confirm conclusions from the visual comparisons. The limited amount of chips available for the trails restricted the trail runs to only a few hours and thus produced much less data than were available for the control runs. Therefore, the data do not conform to strict statistical standards and a full analysis of variance could not be justified. For pulp from transfer line A, a *t* test ($\alpha = 0.05$) of the mean freeness between the control run and the combined trial 1 and 2 runs suggests a significant difference in the means of about 10 mL. It is expected that different blends of wood chips would produce different results. In practice, a difference of 10 mL in pulp freeness at a mean of about 200 mL can be ignored even if it is statistically significant. This is because the measurement error in Canadian Standard Freeness at a freeness level of about 200 mL can easily be 10 mL. The measured standard

deviation of pulp freeness for the control run was 11 mL. For pulps from the reject refiner, a *t* test found no significant difference in mean freeness between the control and trial runs. Table 4 summarizes the results from the statistical analysis and shows that few of the tests found statistically significant differences. In the cases where statistically significant differences were indicated, the magnitudes of the differences fell within normal measurement error. Overall, we therefore conclude that the quality of pulp produced from the chip blends incorporating whole-log chips from forest thinnings was essentially equivalent to the quality of pulp produced from standard mill chips. This same result was obtained for the residue chip trials.

## Refining Energy

Analysis of total specific refining energy (primary + secondary + reject) was an integral part of this study. As the trials proceeded, we observed a drop in total specific refining energy (Fig. 8) and a substantial drop in refining energy for both chip substitution levels for the whole-log trial. The data presented in Fig. 8 were calculated by multiplying the PQM-specific refining energy and the corresponding PQM production tonnage of each production line A and B (sum of the primary and secondary) and the reject refiner (the rejects from both A and B were fed into one reject refiner; the rejection ratios were about 50% to 65%).

**Table 4.** Statistical Analysis of Key Parameters for Pulp Produced during the Control and Trial Runs (null hypothesis = same, $\alpha$ = 0.05; STD = standard deviation)

| | **Pulp Freeness (mL)** | | **Long Fraction (%)** | | **Length Weighted Mean Fiber Length (mm)** | |
|---|---|---|---|---|---|---|
| **Transfer Line A** | **Control** | **Trial 1+2** | **Control** | **Trial 1+2** | **Control** | **Trial 1+2** |
| Mean | 213 | 204 | 31.6 | 31.2 | 1.24 | 1.23 |
| STD | 11.3 | 15.3 | 1.17 | 1.36 | 0.037 | 0.043 |
| *t* test (Mean) | Different | | Same | | Same | |
| Levene's test (Variance) | Different | | Same | | Same | |
| **Reject Refiner** | **Control** | **Trial 1+2** | **Control** | **Trial 1+2** | **Control** | **Trial 1+2** |
| Mean | 172 | 170 | 38.5 | 37.9 | 1.47 | 1.45 |
| STD | 5.7 | 6.0 | 0.73 | 0.68 | 0.023 | 0.023 |
| *t* test (Mean) | Same | | Different | | Different | |
| Levene's test (Variance) | Same | | Same | | Same | |

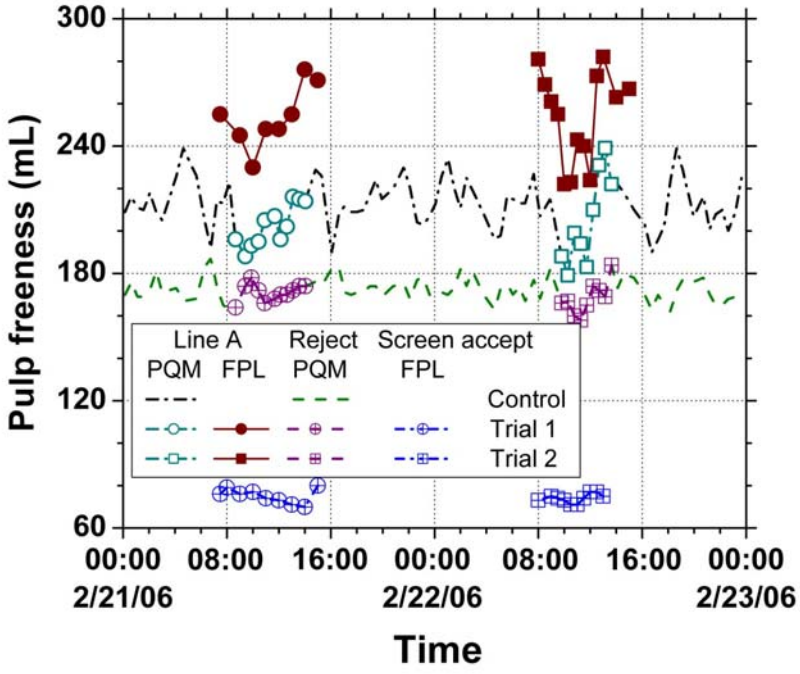


**Fig. 4.** Time series of pulp freeness measured by Pulp Quality Measurement (PQM) and Lab (FPL) analysis during the whole-log chip study (see Fig. 2).

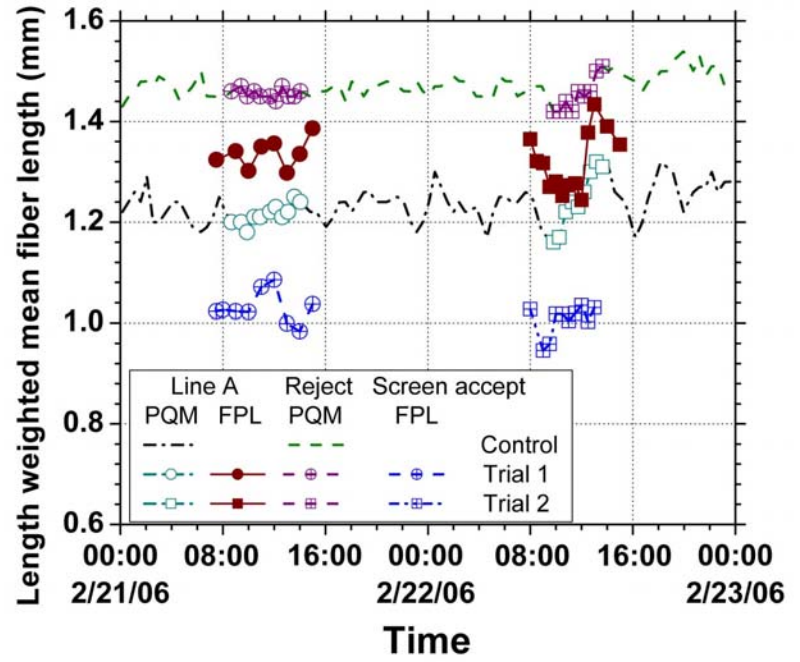


**Fig. 5.** Time-dependent pulp length weighted mean fiber length measured by Pulp Quality Measurement (PQM) and Lab analysis during whole-log chip study (see Fig. 2).

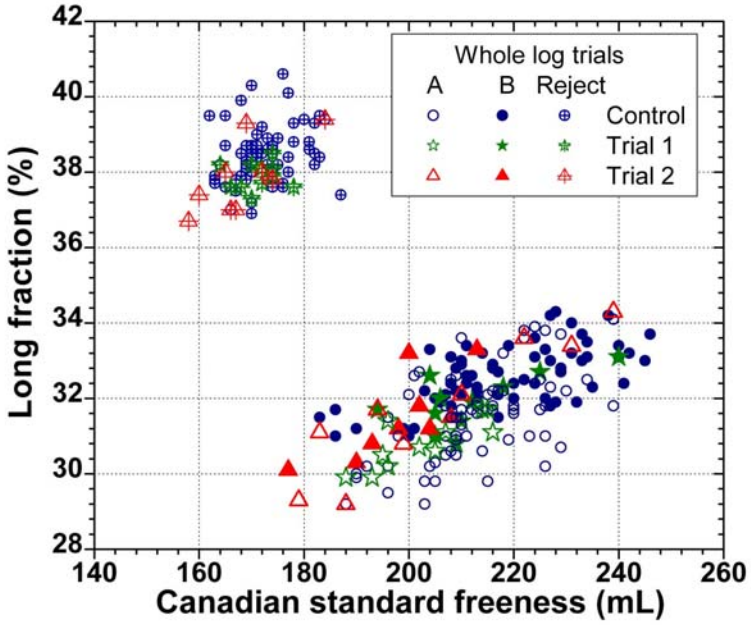


**Fig. 6.** Long fraction plotted against freeness for pulp produced during the whole-log chip study.

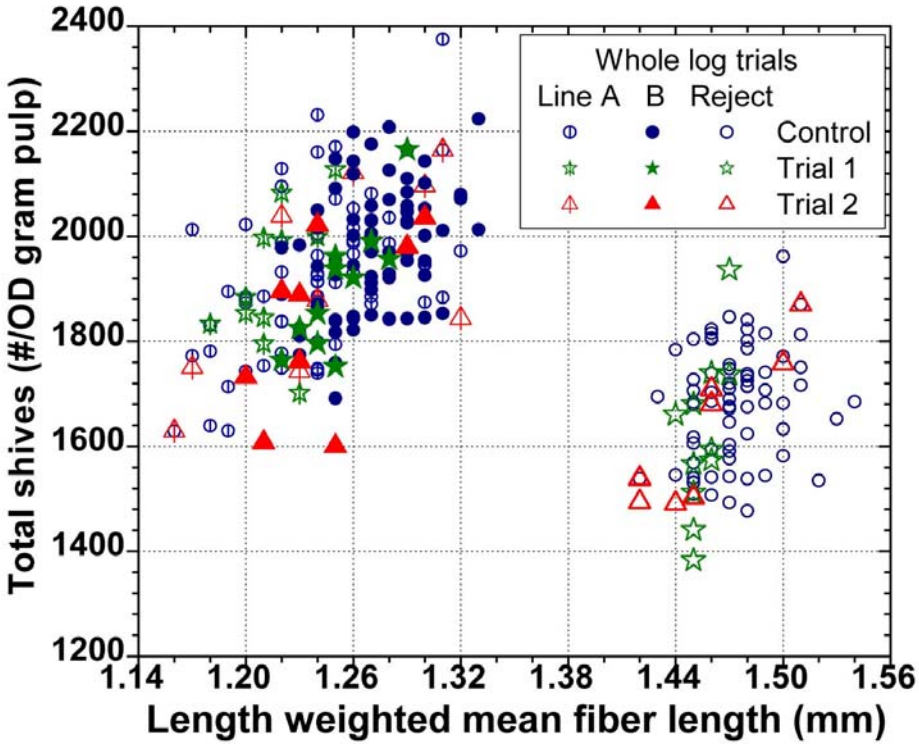


**Fig. 7.** Shive content plotted against length-weighted mean fiber length for pulp produced during the whole-log chip study.

Further analysis revealed that the energy reduction occurred in the secondary and reject refiners, not in the primary refiner (Fig. 9). We observed a similar trend for production line B (not shown). No abnormal adjustments to refiner CD or flat-plate gaps were observed during either the whole-log or residue chip trial runs. Nor were any abnormal changes in pulp freeness observed during the trial runs. These observations suggest that a reduction in refining energy could be obtained under normal operating conditions without sacrificing pulp quality, a conclusion that supports our hypothesis that TMP production from suppressed-growth trees with a narrower distribution of tracheid wall thicknesses (Zhu et al. 2007) may require less refining energy (Klungness et al. 2006). The observed reduction in energy required to refine mixed wood chips from forest thinnings in a U.S. National Forest is opposite to that reported in the literature using commercial thinnings (Hatton and Johal 1996, Hatton 1997). In the cited publications, more refining energy was required to produce pulp of a given freeness from commercial thinnings than from the wood of mature trees.

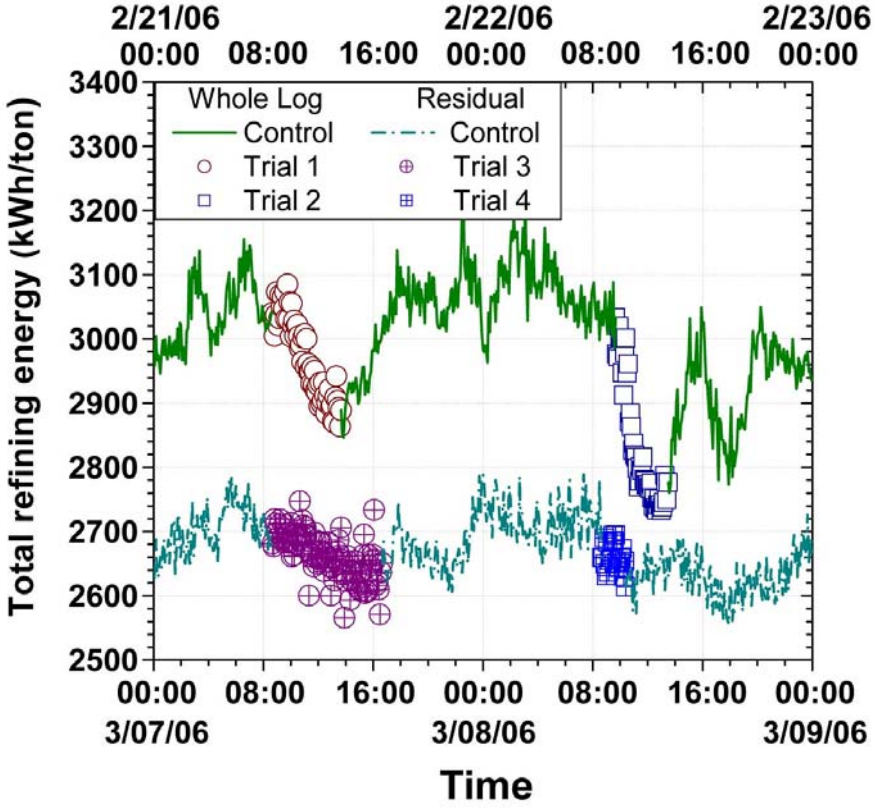


**Fig. 8.** Time series of specific energy consumption during refining for the whole log and residue chips studies.

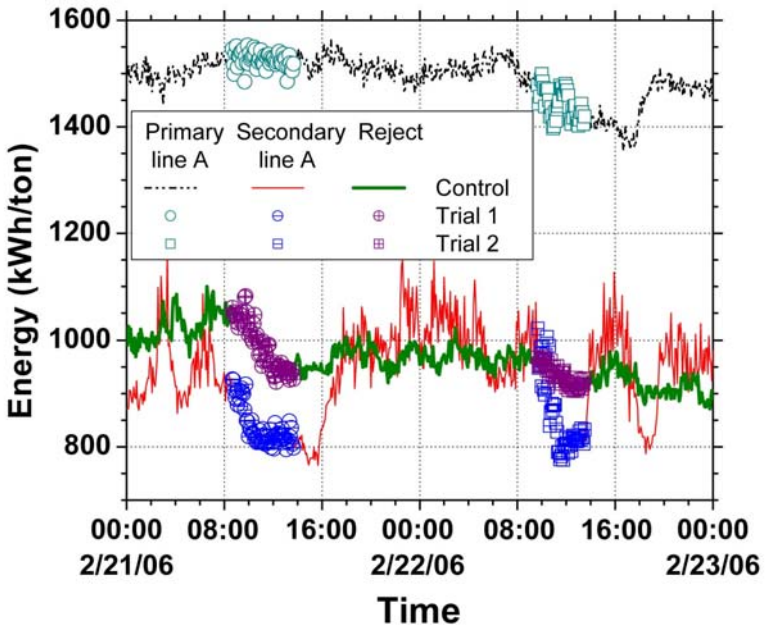


**Fig. 9.** Time series of specific energy consumption for the primary and secondary refiners for production line A plus the reject refiner during the whole-log chips study.

## Handsheet Properties

The properties of handsheets made of pulp samples collected during mill trials reinforced our hypothesis that pulp quality would not be diminished by the addition of whole-log or residue chips from forest thinnings. For each control run, only two pulp samples were collected, one before the trial run and one after the trial run. Therefore, only two sets of handsheets were made for each control run. Many pulp samples were collected during each trial run. The trial pulp samples were combined based on the freeness level (see Experimental section) to reduce the number of sets of handsheets for testing. Figure 10 shows the relationship between handsheet tensile energy absorption and apparent density for all pulp samples collected in trial 2 (44% whole-log chips with 30% whole-log substitution) and trial 3 (30% residue chips substitution). From this figure, no obvious difference can be attributed to either chip blend used (mill or trial). Figure 10 also shows that the quality of pulp from the reject refiner was generally better than the quality of pulp from the pressure screen accepts. The two outliers around a density of 390 kg/m$^3$ and a TEA of 21 J/m$^2$ were due to the low stretch measured from those two sets of handsheets. The measured average stretches of those two handsheets were about 12% below the expected value of sheets with similar density. However, the standard deviations in stretch measurements of all the handsheet sets were between 5% and 13%. Apparently, the measured stretches of these two sets of sheets were at the low end of measurement accuracy, which caused the outliers in TEA data. The tensile and burst indices of all handsheets (for control and trial blends) were also indistinguishable (Fig. 11). Comparing the tear and tensile indices reveals that pulps from the reject refiner produced stronger handsheets (Fig. 12). Again, no obvious difference can be attributed to either chip blend used (mill or trial).

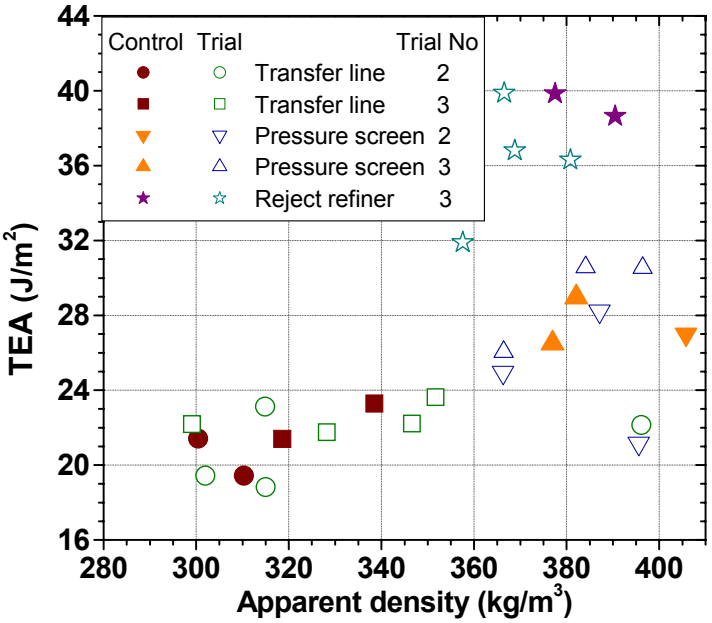


**Fig. 10.** Tensile energy absorption (TEA) comparisons of handsheets made of pulps produced from control chips and trial chips.

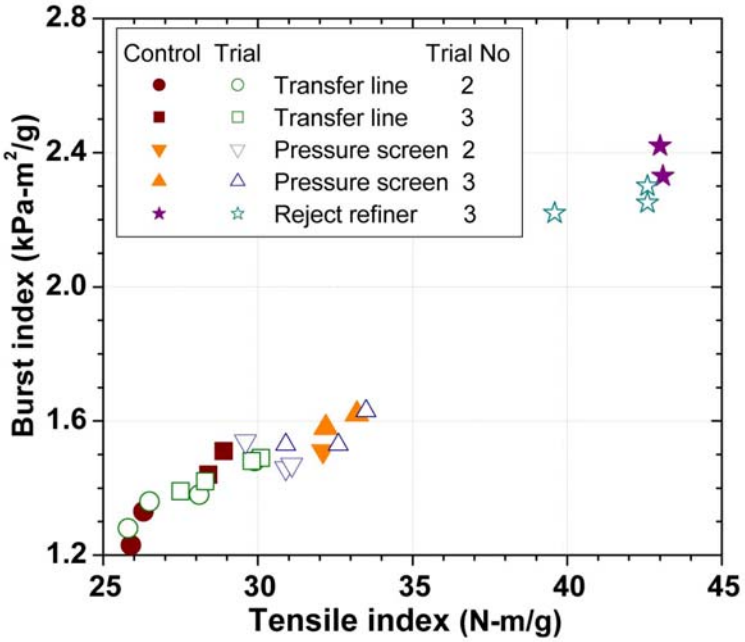


**Fig. 11.** A comparison of handsheet tensile–burst correlation between control and trial runs.

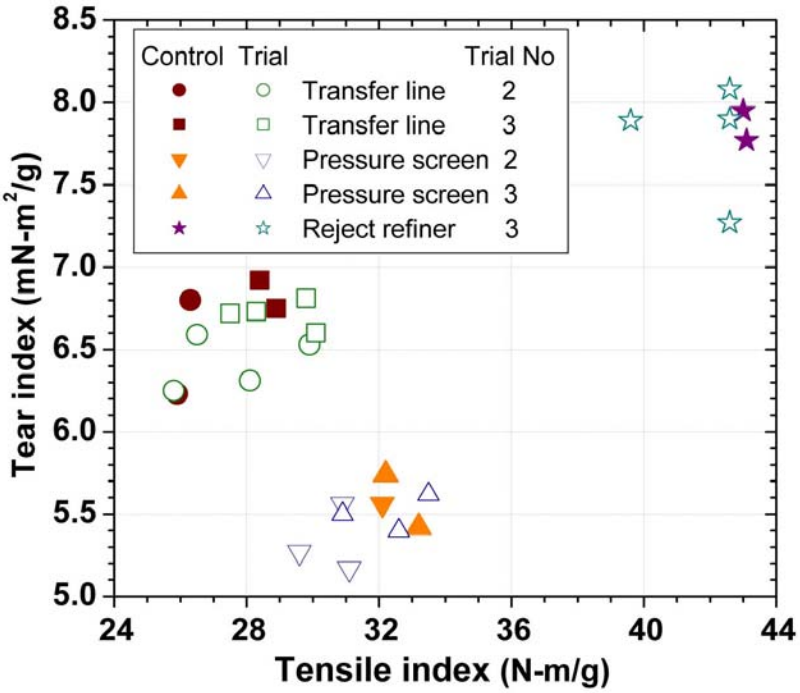


**Fig. 12.** Comparisons of handsheet tear and tensile relation between control and trial runs.

## CONCLUSIONS

Finding high-value, large-volume uses for small-diameter trees removed in thinnings is of critical importance if the strategy to reduce forest fuels is to be achieved in the U.S. National Forests. The integrated production of lumber and paper from small-diameter trees is an important utilization strategy that could add significant value to a resource that is currently considered inferior. We have demonstrated that forest-thinning materials from older, small-diameter trees can serve as a viable wood fiber source for paper production in a full-scale TMP production facility. Our results suggest that less refining energy is consumed when wood chips are mixed with chips from forest thinnings, including those from whole logs as well as those from sawmill residues. In this study, pulp quality obtained from trial runs using chips from forest thinnings was equivalent to that obtained from control runs using normal mill chip blends. Quality was measured in terms of pulp freeness, WAFL, shive content, and handsheet properties. Of particular interest is the fact that whole-log chips could be substituted up to about 44% without an obvious decrease in pulp quality. It would be of great interest to conduct longer trials (days not hours) with various species blends to more fully assess the value of chips obtained from thinning materials for the production of paper.

## ACKNOWLEDGMENTS

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# FIBER LOADING OF HARDWOOD PULP BY IN-SITU PRECIPITATION OF ALUMINOSILICATE

Vipul S. Chauhan,[a] Surendra P. Singh,[a] and Pramod K. Bajpai[b]*

Sodium aluminosilicate has been precipitated in-situ as filler on hard-wood bleached kraft pulp fibers using papermaker's alum and sodium silicate. The filler was produced in two ways, first in the absence of the fibers and second in the presence of fibers, i.e. in-situ precipitation of filler. The filler produced in absence of fiber was then added to the pulp slurry. Various pulp and paper properties were compared for direct loading of market filler, fresh filler loading, and filler prepared in-situ with fibers. In-situ precipitation technology provided paper with significant improvements in various properties of paper as compared to fillers directly added to the stock. Bulk and stiffness of the handsheets prepared with in-situ precipitation were much higher as compared to those of sheets prepared with fillers directly added to the pulp. There was no appreciable increase in brightness and whiteness of paper with in-situ precipitation, as an appreciable proportion of filler was precipitated inside the fibers. In-situ filler loaded pulps showed a higher filler retention value as compared to directly filler loaded pulps, as a high dose of retention aid was needed with the fillers directly added to the stock.

*Keywords: Lumen loading, Aluminosilicate, Eucalyptus pulp, Stiffness, Bulk*

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## INTRODUCTION

For some applications of paper, its strength, stiffness, and bulk become the critical properties. Using more filler in paper can increase opacity, but this usually decreases paper strength and stiffness (Bown, 1985). Thus, paper structure should be altered in such a way that desirable paper properties are maintained. Both pigments and cellulosic materials need to be used effectively in order to achieve the desired properties at increased levels of filler. New developments such as precipitated fillers and pigments are known to offer new opportunities to improve paper properties. Improved information on synergism and interaction of precipitated pigments with fibers and fines may provide papermakers with new ways to improve paper properties. It has also been assumed that inorganic salts precipitated within fiber walls may increase fiber stiffness, with some impact also on light scattering and paper stiffness (Silenius, 1996).

The tradition method of adding mineral content to paper can be described as direct filler loading. In comparison to the traditional approach, fiber-loading technology may offer a new route to improve strength of paper, formation, and retention (Klungness *et al.*, 1996) simultaneously, since filler retention may be less dependent upon chemical

retention, flocculation, and agglomeration. The studies on filler-loading show that the filler can be incorporated onto or within fibers by three different ways: i) the direct loading of filler with fibers - presently used in most of the pulp and paper industries, ii) lumen loading of softwood fibers by mechanical diffusion of filler into fiber lumens through pit apertures (Middleton *et al.*, 2003), and iii) lumen and/or cell wall loading by in-situ precipitation of filler (Siven and Manner, 2003).

Incorporating fillers inside fibers has been extensively studied, not only as a means of achieving better filler retention but also for better paper properties (Green *et al*., 1982; Middleton *et al.,* 2003; Miller and Paliwal, 1985; Petlicki and van de Ven, 1994). The in-situ precipitation in the fiber can either be within the cell wall or within the lumen. Many investigators have reported that fiber wall filled paper exhibits greater tensile, burst, and tear strength than corresponding conventional paper. The better strength that is observed is assumed to be due to increased hydrogen bonding of fibers, because the filler is located inside the fibers (Green *et al*., 1982; Miller and Paliwal, 1985; Allan *et al*., 1992). In summary, methods of incorporating fillers inside fibers can be based on precipitation, or filler can be mechanically stirred with pulp slurry, transferring filler into the fiber lumen. In precipitation, the approach has usually been to saturate pulp fibers with a soluble salt and to precipitate filler by another soluble salt. Fiber loading using an aluminum compound for improving the physical strength properties has been reported by Siven and Manner (Siven and Manner, 2003). However, published information related to the effects of in-situ precipitation of filler inside hardwood fibers is limited, and issues related to bulk and bending stiffness have not received sufficient attention.

The present study deals with the effects of in-situ precipitation of aluminosilicate within bleached hardwood kraft pulp on handsheet properties including bulk, bending stiffness, and other strength and optical properties.

## EXPERIMENTAL

### Materials

A never dried bleached kraft pulp obtained from an integrated pulp and paper mill in north India using hardwoods (mainly 50% eucalyptus and 50% poplar) was used in this study. The beating of pulp was done in a PFI mill (Hamjern Maskin A/S, Hamar, Norway; PFI mill no. 616) to achieve 420 mL CSF value. Fresh sodium alumino-silicate was prepared in two different ways, i) precipitation in absence of fibers, and ii) in-situ precipitation (in presence of fibers). Commercial grade sodium silicate and papermaker's alum were collected from indigenous sources.

### In-situ Precipitation of SAS

In-situ precipitation of sodium aluminosilicate (SAS, i.e. precipitation in presence of fibers, SAS-ISP) was done as per the following procedure. A fixed amount of 44% aluminum sulfate-14 hydrate (alum) solution was impregnated into the never dried beaten pulp of 5% consistency. The mixing of this slurry was done for about 10 minutes in a high-speed disintegrator at room temperature (around 26 $^{o}$C) so that the fiber lumen and cell wall are saturated with the ionic solution. Thereafter, sodium silicate of 35%

concentration was added gradually, over about 15 minutes, to the impregnated pulp slurry while stirring. The optimum end pH was 7.5-7.8. The slurry was further agitated for 10 minutes to allow the surface to become saturated with mineral. To determine the actual amount of filler precipitated within the fiber, the pulp was washed in a Bauer McNett classifier to remove the excess filler that either was not attached or attached loosely to the outer surfaces of the fibers. The general process steps involved in this process are depicted in Fig. 1. Sodium alumino-silicate in absence of fibers was also prepared in a similar manner as described above.

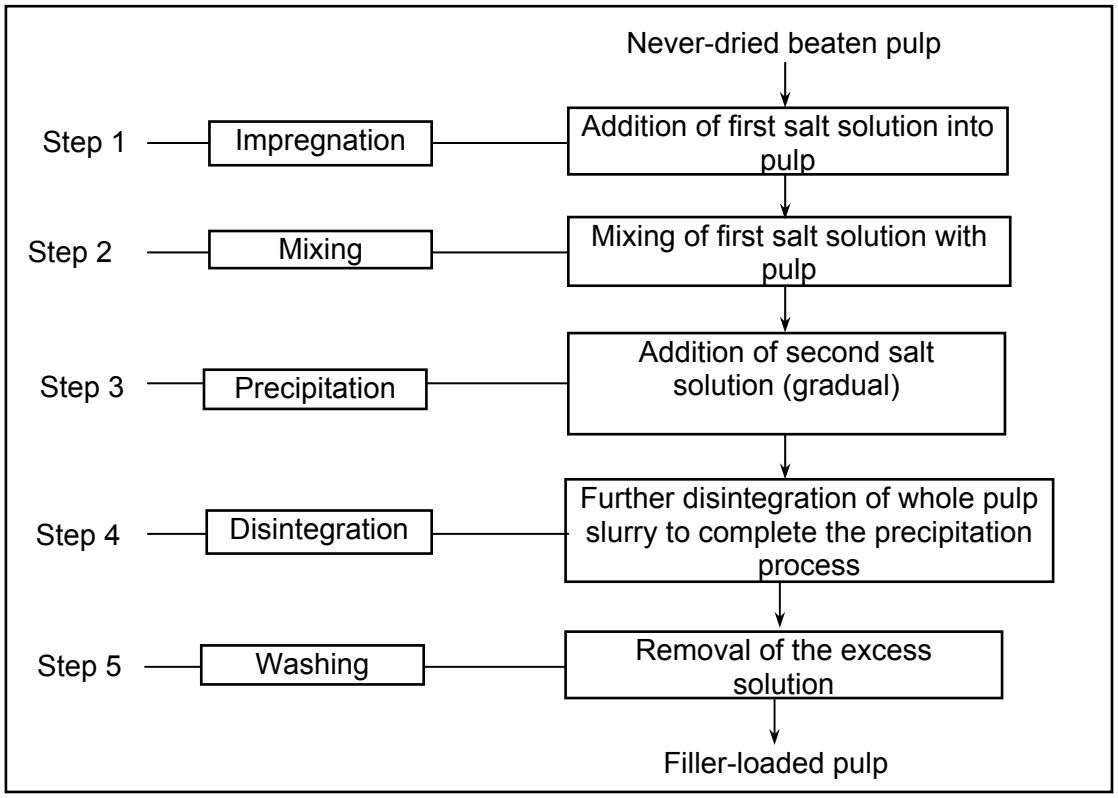


**Fig. 1:** General process steps for SAS-ISP

## Direct Filler Loading

The fillers added directly to the pulp slurry were Hydrex-P® (Na-Mg alumino-silicate from Huber Corporation) and Finex (talc - magnesium silicate from a local supplier) in the form of slurry having 20% solids. The freshly prepared sodium alumino-silicate (SAS) was also added directly in the pulp. The retention aid (Percol-47® of CIBA Specialty Chemicals) was used with Na-Mg aluminosilicate and freshly prepared SAS to achieve good first pass ash retention. Paper hand sheets were prepared at 2.5, 5.0, and 7.5% ash levels with all fillers.

## Preparation of Handsheets

Paper handsheets having a basis weight of 70 g/m$^2$ were prepared for all of the experiments. In the case of SAS-ISP, sheets were prepared without washing of pulp in

Baur McNett classifier (as such precipitated filler and fibers). This slurry consisted of both fiber loaded filler as well as filler outside fibers. The properties of handsheets formed by in-situ precipitated sodium alumino-silicate (SAS-ISP) were compared to those of directly added fillers i.e., SAS, Na-Mg aluminosilicate and talc.

### Analytical Techniques

The physical properties of the handsheets were determined according to relevant standard methods. The optical properties were tested on a Datacolor brightness tester (Datacolor, USA; model: Spectraflash 300 UV) brightness tester. Ash in the paper was estimated according to TAPPI Test Method T-211 om-93 by the incineration of paper at 575±25 $^{o}$C in a muffle furnace. First pass ash retention was calculated from the ash content in the stock and that in the white water. Particle size of filler was determined using 10% slurry in a Particle Size Analyzer (Microscan II from Quantachrome Corporation, USA).

All of the experiments were performed in duplicate and repeated once more to confirm the results and observations of the earlier set. The average values of all of the parameters for 95% confidence limits, from up to four replicates, were calculated and reported herewith.

## RESULTS AND DISCUSSION

The physical properties of different fillers used in this study are presented in Table 1. The brightness and whiteness of Na-Mg aluminosilicate were the highest. SAS was the finest filler, having around 87.3% of the particles less than 2-µm.

**Table 1.** Physical Properties of Different Fillers

| Parameter | Talc | Na-Mg aluminosilicate | SAS |
|---|---|---|---|
| Brightness (%ISO) | 93.5 | 99.2 | 96.3 |
| CIE Whiteness | 94.2 | 101.7 | 94.9 |
| Particles < 2 µm (%) | 20.0 | 78.0 | 87.3 |
| pH | 9.21 | 9.70 | 7.22 |

The actual amount of SAS precipitated within the fiber was determined by thoroughly washing the pulp in the Bauer McNett classifier after the complete process of in-situ precipitation of aluminosilicate. During the process of washing (in the Bauer McNett device), the fines were removed, which also carried away the SAS precipitates outside the fiber. Unwashed and washed pulps were also examined under the microscope to see the location of the precipitated alumino-silicate. The unwashed pulp showed precipitated material at the outer surface of the fiber, whereas the washed pulp was totally free from outside precipitate. The ash in the pulp was found to decrease as a consequence of washing. This trend was seen at all the ash levels (Table 2). The ash content of the pulp after washing corresponds to the filler (ash) inside the fiber.

**Table 2.** Ash Contents in Pulp

| Sr. No. | Ash in pulp (%) | |
|---|---|---|
| | Before Washing (in Bauer McNett) | After Washing (in Bauer McNett) |
| 1 | 4.0 | 1.8 |
| 2 | 5.5 | 2.1 |
| 3 | 7.1 | 2.6 |
| 4 | 10.1 | 3.0 |

First pass ash retention (FPAR) of SAS-ISP was the highest, as expected based on the information from the literature. This was attributed to the precipitation of some amount of the filler inside the fibers. The same trend could be seen at all the ash levels (Fig. 2). The FPAR of talc was also relatively high, which is attributed to its larger particle size. The higher FPAR value provides a cleaner white water system. Therefore, in the case of SAS-ISP, the white water system would be expected to be cleaner in comparison to the white water system of directly filler-loaded pulps.

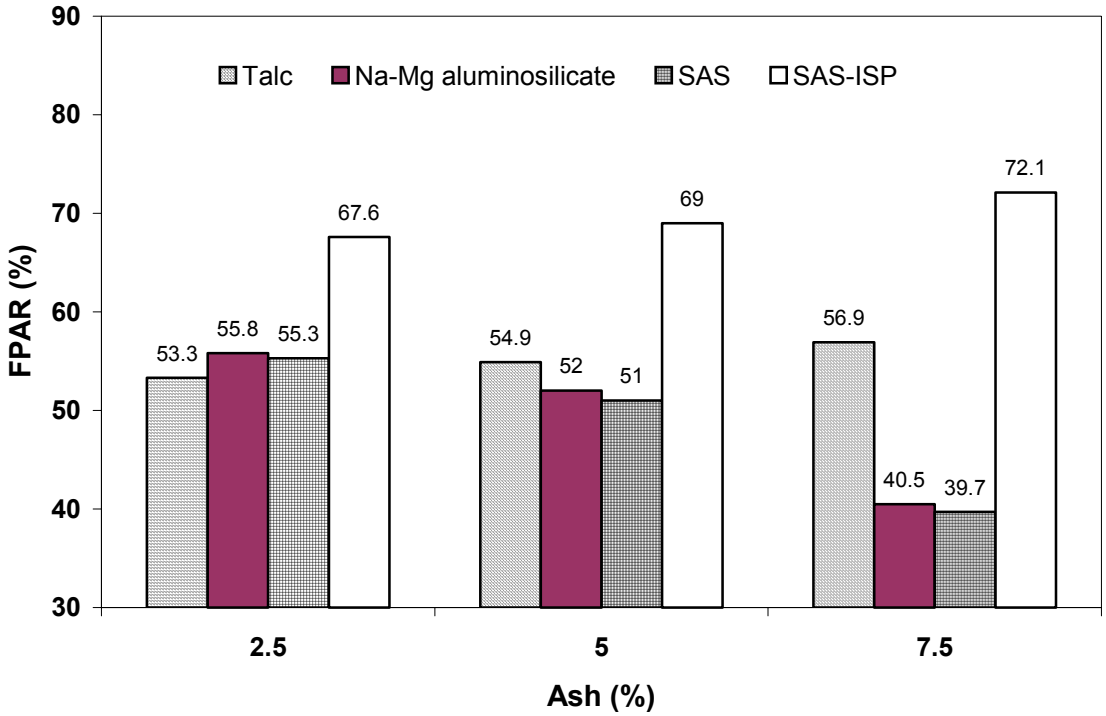


**Fig. 2.** Effect of filler on first pass ash retention (FPAR) at different ash levels

Normally, paper's bulk decreases with increasing ash content. From Fig. 3, it can be seen that the bulk also depended on the type of filler used. In some cases it decreased, whereas in others it increased. The bulk of paper decreased in case of talc, whereas in case of Na-Mg aluminosilicate and SAS it increased as compared with the blank. This difference in behavior may be due to the bulk density of the fillers. The bulk in case of SAS-ISP increased appreciably, probably due to some precipitation of filler inside the

fibers, which decreased the collapsibility of fibers, resulting in increased thickness of the paper. From these results, it is confirmed that some of the filler had been precipitated within the fiber in the case of SAS-ISP. The SAS filler precipitated inside the fiber could be either in the fiber lumen or in the fiber wall or in both. However, no such differentiation could be made in this study.

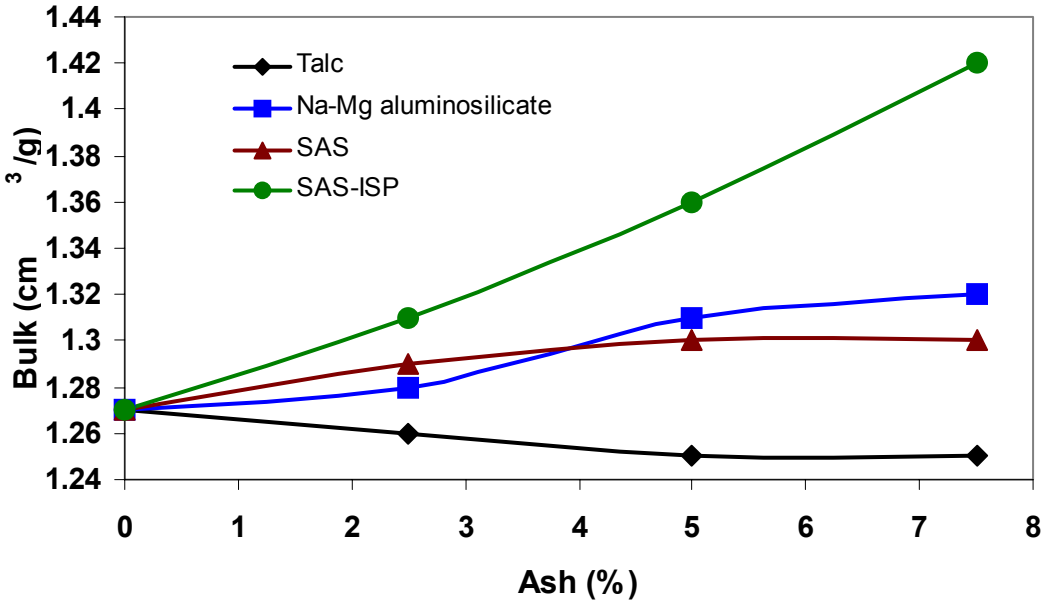


**Fig. 3.** Effect of ash content on bulk with different fillers

The bending stiffness normally decreases with increase in filler loading. In fact, bending stiffness of paper depends upon the elastic modulus of the fibers and the thickness of the paper. With increase in thickness, stiffness increases. It can be seen from Fig. 4 that the bending stiffness (L&W stiffness) of paper handsheets was highest in case of SAS-ISP, as compared to that of direct filler-loaded sheets. The elastic modulus of the fiber is expected to increase with the fiber loading due to gluing effect of the mineral precipitate and the thickness of the fiber will increase due to non-collapsibility of the fiber on getting filled with the precipitate. Thus, the bending of individual fiber is affected by the same, resulting in high values of bending stiffness of the paper. Initially, the stiffness increased and afterwards decreased slightly with increasing ash level (Fig. 4) due to precipitation of aluminosilcate on the outer surface after certain ash levels.

All of the physical strength properties decreased to a large extent with direct loading of fillers, whereas in the case of SAS-ISP, all of the strength properties were on the higher side as compared with direct filler loading. The breaking length decreased with the addition of filler in all the cases (Fig. 5). The extent of drop in breaking length was much lower in the case of SAS-ISP as compared with direct filler loading.

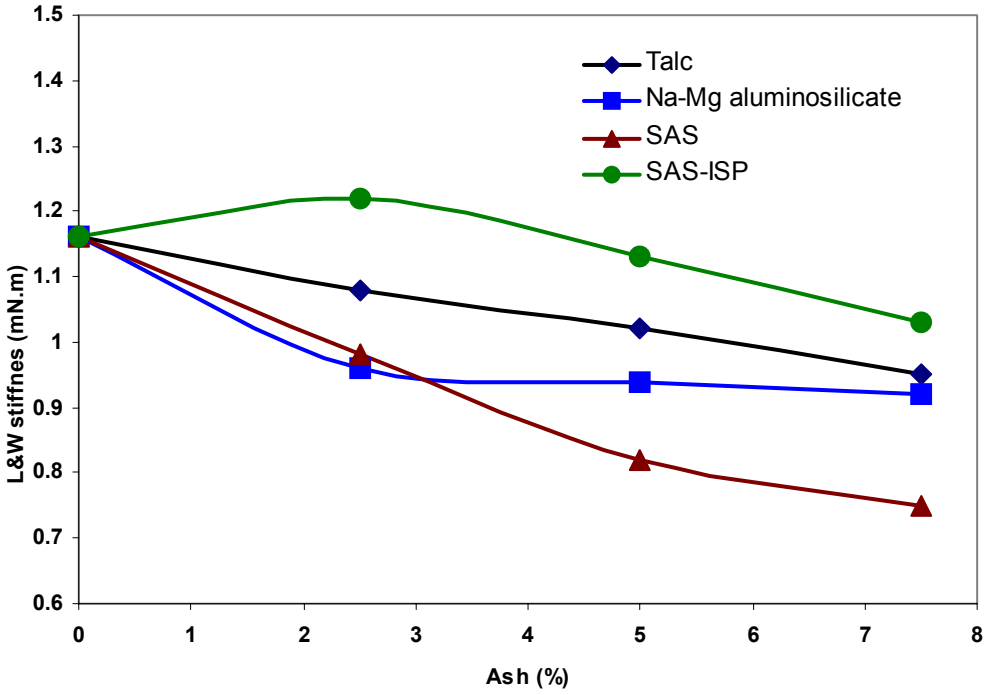


**Fig. 4.** Effect of ash content on stiffness with different fillers

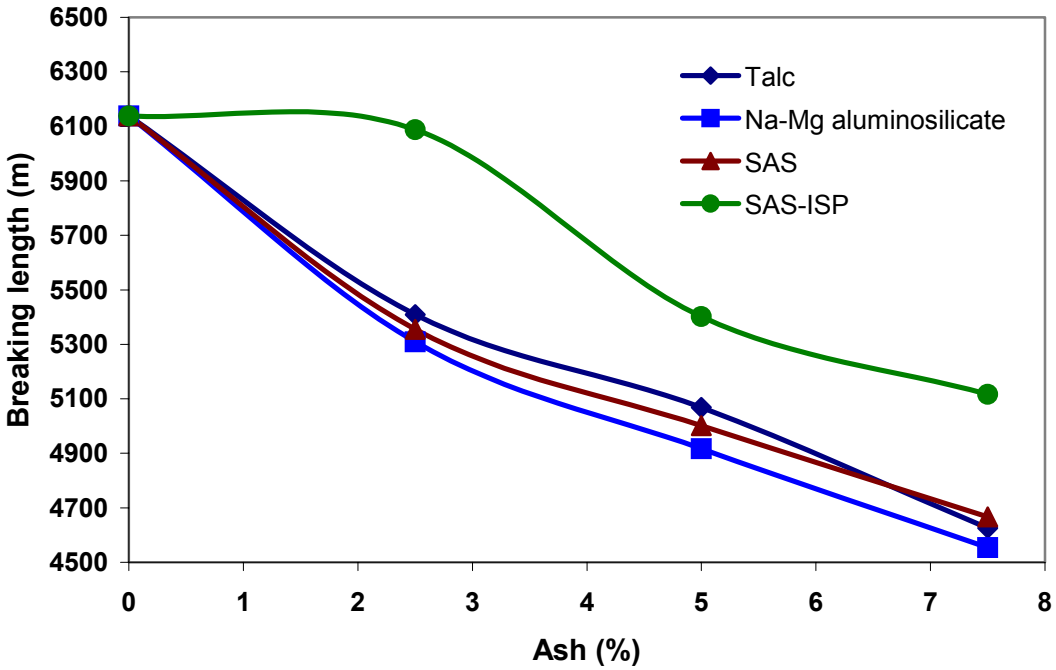


**Fig. 5.** Effect of ash content on breaking length with different fillers

The smallest size filler had the most detrimental effect on paper strength. A good indication of the role of particle size is that the loss of burst index increases with the total surface area of fillers (Li *et al.,* 2002). From Fig. 6, it can be seen that the burst index of paper handsheets decreased with increase in ash level in all the cases. However, the loss in burst index was much lower in the case of SAS-ISP as compared with direct filler loading. The highest loss was seen in case of Na-Mg aluminosilicate, followed by SAS and talc, in order of increasing particle size (refer Table 1).

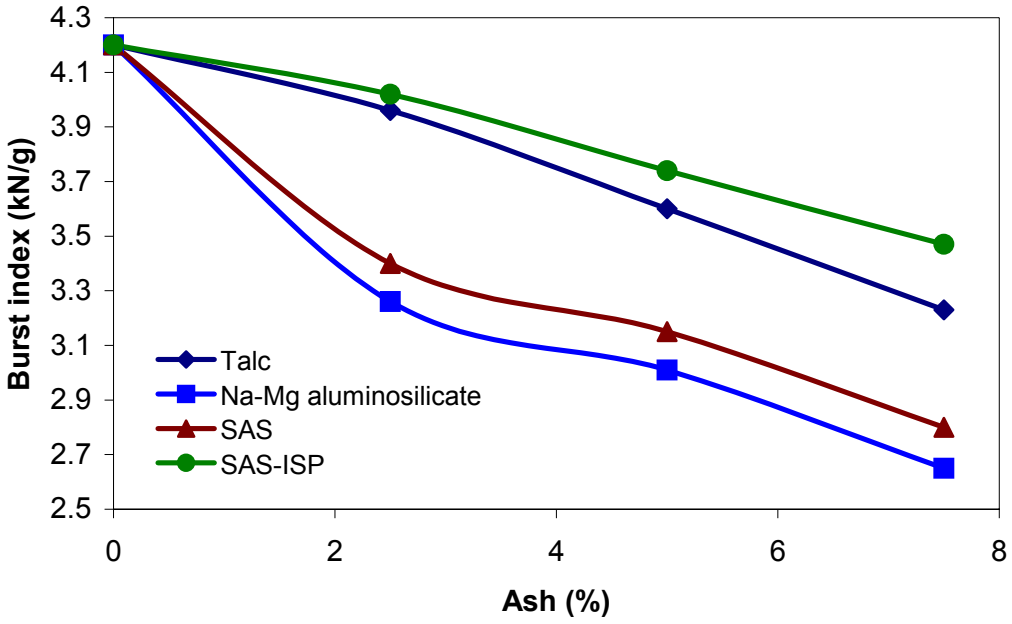


**Fig. 6.** Effect of ash content on burst index with different fillers

In case of direct filler loading, the tear index of paper handsheets decreased with addition of filler (Fig.7). The trend of decrease in tear index was different for different fillers. It was highest in case of Na-Mg aluminosilicate, followed by SAS and talc, whereas in case of SAS-ISP, this trend was the opposite. There was an increase in tear index with increase in ash content. This increase may be because of an increase in the fiber thickness on filling of fiber with SAS precipitate, so that the force required to tear the sheet increased.

The internal bond strength (Scott bond) of paper hand sheets prepared with direct filler-loaded pulp in comparison to the blank decreased with increase in ash level, whereas it slightly increased in the case of SAS-ISP (Fig. 8). Often, the Scott bond value for a paper has a strong positive correlation with the tensile strength, however this unusual behavior for SAS-ISP sheets supports the assumption that an appreciable portion of the filler precipitated inside the fiber lumen.

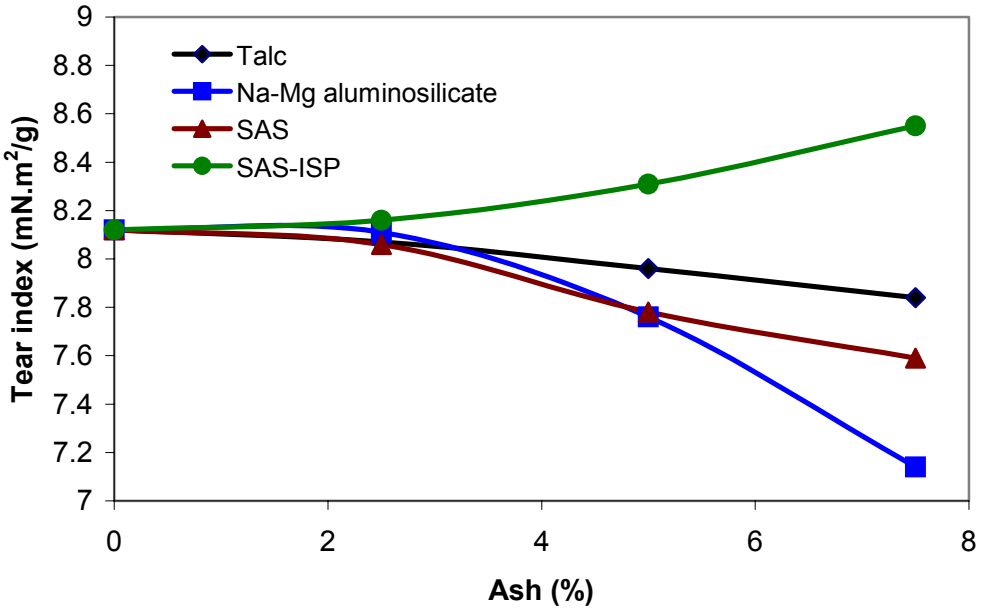


**Fig. 7.** Effect of filler on tear index at different ash levels

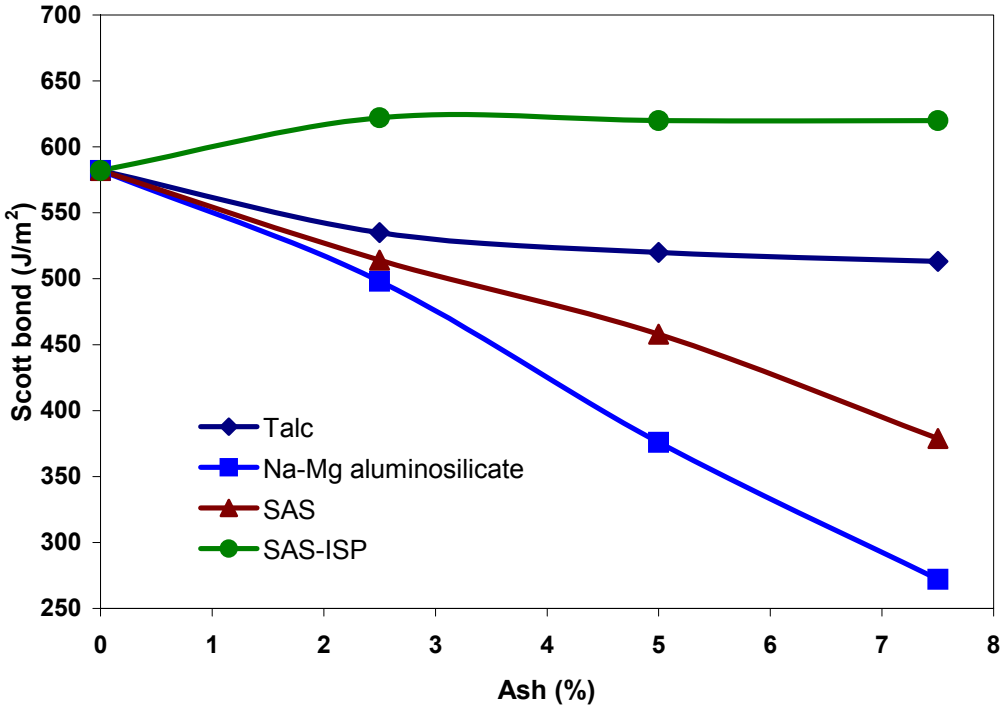


**Fig. 8.** Effect of filler on Scot bond value at different ash levels

While a tensile tester measures the tensile force required to rupture a sheet, the Scott bond tester measures the energy required to rupture the sheet in the thickness-direction. The increased precipitation of filler inside the fiber should decrease the intra-fiber bonding and it is likely that an increased number of partial breakages within fibers take place before delamination of the sheet occurs, adding to the increased Scott bond test value for SAS-ISP sheets. In addition, the internal bond strength is sensitive to any non-uniformity or layering in the thickness direction since delamination will occur at the weakest plane. The weakest location depends on the z-directional distribution of fines and fillers, and the bonding degree. It seems that the filler precipitated outside the fiber in case of SAS-ISP at higher ash content, reduces the no-uniformity across the thickness direction of the paper sheet though it might reduce the inter-fiber bonding area, resulting in no drop in internal bond strength. Whereas for direct filler-loaded sheets, the filler tends to reduce the inter-fiber bonding area; the finer the filler the greater is the interference with the fiber bonding and probably non-uniformity across the thickness.

Values of all the optical properties were lowest in the case of SAS-ISP as compared with direct filler loading (Fig. 9, 10). In fact, a major portion of the SAS-ISP was precipitated inside the fibers, and it was not affecting the reflectance or scattering of light to the same extent as direct SAS addition. In case of direct filler loading, the filler seemed to have more direct interaction with the light, hence there was more reflection of light. The highest brightness was achieved in the case of sheets prepared with Na-Mg aluminosilicate (Fig. 9) because of the small particle size and high brightness of this filler as shown in Table 1.

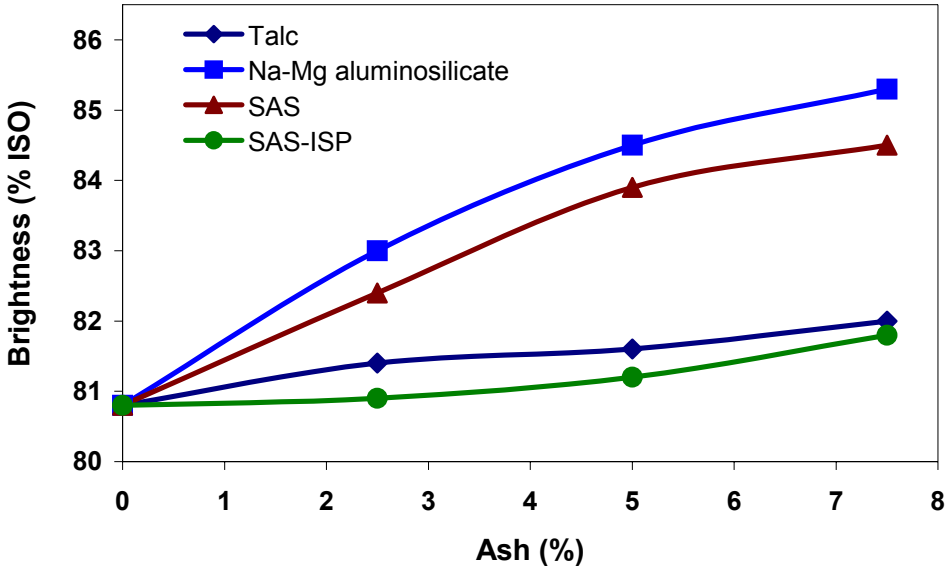


**Fig. 9.** Effect of filler on brightness as a function of ash content

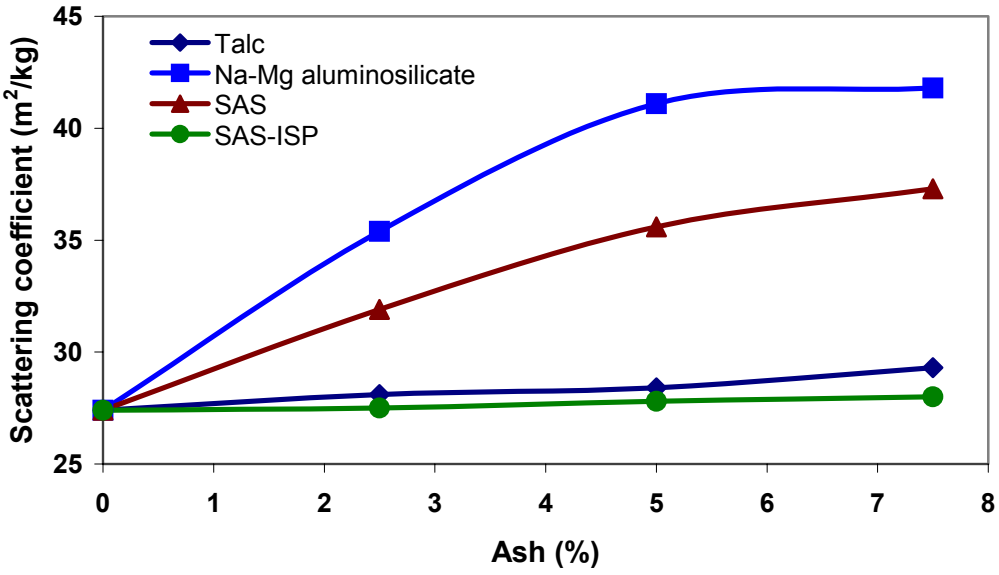


**Fig. 10.** Effect of filler on scattering coefficient as a function of ash content

The freshly prepared SAS was also providing good brightness, as compared with other fillers. When the comparison was made between SAS and SAS-ISP (i.e. as such filler preparation in absence of fibers and in-situ precipitation of filler in presence of fibers respectively), it was seen that the brightness of paper in case of SAS-ISP was quite low. The scattering coefficient was also quite low in case of SAS-ISP as compared with direct filler loading (Fig. 10) since appreciable portion of the filler got precipitated inside the fiber, which was not affecting the light scattering. The highest scattering was observed with Na-Mg aluminosilicate, presumably due to its having the smallest particle size.

## CONCLUSIONS

Sodium aluminosilicate (SAS) has been precipitated in-situ as a filler inside the fibers. From this study, the following conclusions can be drawn. The amount of SAS precipitate inside the fiber did not increase in the same proportion as of total SAS precipitate (ash content); after a certain level, precipitation took place mainly at the outer surface of the fiber. In the case of freshly prepared SAS added directly to the pulp, strength properties of paper were slightly on the higher side as compared to those of Na-Mg aluminosilicate. Bulk and bending stiffness of handsheets prepared with SAS-ISP were much higher as compared to that of sheets prepared with fillers added directly to the pulp. All the strength properties were higher in case of SAS-ISP as compared to those of direct filler loading. There was no appreciable increase in brightness and scattering coefficient of paper with SAS-ISP, as the filler appeared to be retained in the fiber (within the lumen or within the fiber wall).

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# EFFECT OF THE MODIFICATION OF LIGNOCELLULOSIC MATERIALS WITH A LIGNIN-POLYMER COMPLEX ON THEIR MULCHING PROPERTIES

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The lignosulphonate/polymer complex, in which the macromolecules of both components are linked together by physico-chemical bonds, has been applied as a new effective lignin-based soil conditioner (LSC). It has an adhesive affinity both for mineral soil particles and the organic surface of lignocellulosic mulch. The modification of the mulch particles with aqueous solutions of the developed conditioner by means of impregnation makes it possible not only to anchor mulch to sandy soil and, thereby, to diminish significantly the evaporation from the soil surface, but also, due to mulch biodegradation, to enrich soil with the main nutrient elements and to create favourable conditions for plant growth. The effect of the mulch modification is determined by the complex composition and depends on its content in the aqueous solution and the application rate.

*Keywords: Lignocellulosic mulch, Lignin-polymer complex, Soil conditioner, Modification, Impregnation, Hydrolysis lignin, Sawdust, C/N ratio*

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## INTRODUCTION

Biomass in the form of lignocellulosic waste represents an abundant renewable feedstock for the production of both energy and new organic materials for mankind's needs. The purposeful application of lignocellulosic waste in agriculture and forestry may be regarded as an innovative avenue for its utilization.

A known management practice for controlling soil erosion combines the application of grass seedings and mulch as a soil surface covering. Possibilities of different types of lignocellulosic mulch for protection of the soil surface have been demonstrated (Barkley et al. 1965; Bristow 1988). For the Baltic countries, having well-developed wood processing, the application of lignocellulosic waste such as sawdust, bark, and hydrolysis lignin as a soil mulch is economically grounded and promising. Hydrolysis lignin is formed during the treatment of wood with sulphuric acid at high temperature and pressure. In the hydrolysis industry, this treatment of wood is carried out mainly within Eastern Europe for manufacture of poly- and monosaccharides, followed by further processing to ethanol and fodder yeast (Sarkanen 1971). However, the use of unanchored dispersed mulch leads to its washout, blowing off, and, as a result, to the destruction of the mulch layer under the action of unfavourable weather conditions. One

of the attractive solutions to this problem may be the simultaneous application of organic mulch, grass seeds, and a soil polymer conditioner, which acts as an adhesive. A polymer conditioner attaches the mulch and grass seeds to the sandy surface, thus preventing their washout, leaching and blowing off, as well as reinforcing the sandy surface, forming an upper stabilised layer that resists the water runoff and soil loss (Kay 1978; Shulga et al. 1998).

The application of commercial technical lignins, a low-cost polymeric feedstock for the production of lignin-based soil stabilisation agents, is well-known. Commercial products include the following: Sandstop, Dustex, Lima, Lia, Copolima, Copoliba, RoadBond, RP Ultra Plus$^{TM}$, etc.

Environmentally friendly, inexpensive, lignin-based soil conditioners (LSCs) with a pro-nounced adhesive and gluing ability have been developed by the Latvian State Institute of Wood Chemistry (Shulga et al. 1998; Shulga et al. 2001). They were synthesised by modification of both sodium- and ammonium lignosulphonate with various complementary eco-friendly water-soluble polymers or oligomers (Shulga et al. 2000, 2002). Chemically, LSCs represent interpolyelectrolyte complexes, in which the macromolecules of both components are linked together *via* physico-chemical bonds. The developed interpolymer complexes may be used as an effective conditioner and amendment for improving hydrophysical properties of sandy and clay soils. Some of them have been already applied as ameliorants under field conditions in Latvia (Smilga et al. 1982, Shulga et al. 1984).

A new effective lignin-based soil conditioner (LSC) has been specially developed for protecttion of erodable sandy soil in the sea coastal zone, with the application of mulch and plant seeds. It differs by having a higher aggregation stability in aqueous solutions and the ability to change viscosity within a wide range, depending on its composition.

The objective of this work is to study the effect of the modification of lignocellulosic waste materials with the developed LSC on the mechanical properties of the composite coverings formed from mulch and soil particles, as well as the moisture evaporation and chemical transformations in sandy soil.

## EXPERIMENTAL

### Materials

Commercial sodium lignosulphonate (LS) by-products of softwood delignification, were used for obtaining the new soil conditioner. The LS elementary and functional analysis performed according to (Zakis 1994) gave the following formula:

$$C_9\ H_{8.35}O_{4.54}(OCH3)_{0.82}\ S_{0.41}$$

Its average molecular weight was 30 kg mol$^{-1}$. The new lignin-based soil conditioner (LSC), representing a lignin-polymer complex, has been obtained as a result of the interpolyelectrolyte interaction of LS with an environmentally friendly acrylic polyelectrolyte by mixing their concentrated solutions under well-defined synthesis conditions. The LSC composition of Z = polymer/lignin in the solutions was varied from 0.02 to 0.2. For the obtained polycomplex solutions, the dynamic viscosity in the

indicated range of Z varied from 30 mPa·s to 1.25 $10^4$ mPa·s, and their pH values did not exceed 5.0.

The air-dried fractionated sawdust of different wood species such as aspen, birch, spruce, and pine, representing a heavy-tonnage waste of Latvia's woodworking enterprises, and fractionated hydrolysis lignin after the manufacture of fodder yeast, representing the remaining wide-scale waste of the former Lithuanian hydrolysis industry, were used as mulches. The fractions of particles with the size between 1.0 and 2.0 mm and less than 0.5 mm dominated the mechanical composition in both mulch types after grinding.

The chemical composition of the applied sawdust (content of cellulose, lignin and extractives) is represented in Table 1. The chemical composition of hydrolysis lignin is listed in Table 2. Besides lignin substances, this organic waste also contained non-hydrolysed polysaccharides, sugars, organic acids, as well as small quantities of cations of polyvalent metals.

**Table 1.** Chemical Composition of Sawdust

| *Wood species* | *Moisture, %* | *Ash, %* | *$OCH_3$, %* | *Cellulose, %* | *Lignin, %* | *Extractives, %, soluble in* | |
|---|---|---|---|---|---|---|---|
| | | | | | | *hot water* | *organic mixture** |
| Pine | 4.8 | 0.21 | 5.1 | 58.2 | 28.4 | 1.8 | 3.2 |
| Spruce | 5.1 | 0.18 | 4.9 | 57.6 | 28.1 | 1.5 | 2.1 |
| Birch | 4.9 | 0.23 | 5.6 | 51.7 | 20.2 | 1.4 | 1.6 |
| Aspen | 5.0 | 0.33 | 5.2 | 52.1 | 21.4 | 1.1 | 1.5 |
| * ethyl alcohol : benzene is close to 1:2 | | | | | | | |

**Table 2.** Chemical Composition of Hydrolysis Lignin

| *pH* | *Moisture, %* | *$P_2O_5$, mg $kg^{-1}$* | *$K_2O_5$, mg $kg^{-1}$* | *Organic carbon, wt %* | *Total nitrogen, wt %* |
|---|---|---|---|---|---|
| 5.1 | 7.1 | 404 | 831 | 30.91 | 0.34 |

The soil under study was a sandy dune soil (humus content 0.08 wt% and pH 5.9). It contained 3.1% of particles ranging from 1.0 to 0.25 mm, 93.9% of particles ranging from 0.25 to 0.05 mm, and 3.0% of particles less than 0.01 mm in size.

## Methods

The modification of the 2-cm sawdust and hydrolysis lignin mulched soil surface was carried out by spraying of 5-20 wt % water solutions of LSC at the rate 1.5-6.0 l $m^{-2}$. After applying an aqueous solution of the developed LSC onto the mulched soil, the impregnation of the mulch and soil with the solution occurred, and a two-layer sandwich-type composite covering was formed upon drying. It consisted of an upper glued thicker layer of mulch and a lower reinforced thinner layer of sandy soil.

To study the ability of the soil conditioner to bind sandy soil particles, the soil was treated by spraying aqueous solutions of LSC on its surface at different application rates, and then the soil was dried at room temperature. The penetration resistance and

thickness of the reinforced upper sandy layers was measured, using a manual laboratory coner penetrometer (angle 30) and a calliper square. The number of replicates was equal to three, and the presented results were average arithmetic values.

To study the ability of the soil conditioner to bind mulch particles, raw composite blends were made by mixing the mulch with LSC at different weight ratios with their subsequent compacting in the form of cylinders at the pressure 0.1 MPa and duration 3 min. The ability of the air-dried cylinders to withstand the crushing force was determined in 7 days after their preparation and was characterised by the value of compressive strength according to ASTM D695 using a universal testing machine. Three replicates tests were carried out, and average arithmetic values are presented.

The water evaporation from the mulched soil was evaluated from the weight loss upon its standing in the open air. For this purpose, at first, the 2-cm mulch surface was treated with an aqueous solution of LSC with a concentration of 50-200 g $l^{-1}$ at an application rate of 1.5-6.0 l $m^{-2}$. The obtained soil samples were brought to an air-dry state. Then equal amounts of water were applied to the surface of each sample so that the total content of moisture in all samples was equal and made up 12.5-12.8 wt %. The water evaporation from the soil surface was evaluated from the weight loss of the bath using an electron balance upon its standing in the open air at the temperature 293 ± 2K and an air humidity of 60 ± 2% in every 24 hours. The soil sample was considered air-dry, if the weight of the bath stopped varying with increasing storage time in the given experimental conditions. Again, the number of replicates was three, and the presented results were average arithmetic values.

The biochemical transformation process in the upper soil layers was investigated, using 10 litre buckets. A mulch layer of different thickness was placed on the soil top and treated with LSC water solutions. The effect of LSC alone and with mulch on the chemical composition of soil was estimated based on the alteration in the content of carbon and nitrogen in one and three months, and a year after the beginning of the experiments. The mulched soil samples were taken with a special soil perforator at the full depth of the buckets (height 32 ± 1cm including the mulch layer). Taking into account the density of sandy soil and wood sawdust, as well as the relative heights of the mulch layer and soil one in the bucket, the obtained results reflected mainly the changes on the content of C and N in soil. Phosphorus in the form of $P_2O_5$ was determined by the photoelectric colorimeter method with molybdate; $K_2O$ using a flame photometer by the A-L method; carbon by the burning method (ISO 10694, 1995) using a "Heraeus" devise; and total N by the Kjeldahl method (ISO 11261, 1995). The presented results are average arithmetic values, as the number of replicates of each experiment was equal to three.

## RESULTS AND DISCUSSION

### Properties of Sand- and Mulch Composite Materials

The reinforced upper soil layers, representing soil-based composite coverings, were obtained by spraying the water solutions of LSC on the soil surface. The penetration resistance and thickness of the reinforced sandy layers depend both on the concentration of the applied water solutions at the specified application rate, as well as on the lignin/polymer complex composition (Fig. 1). The observed increase in the strength of

the reinforced soil layers can be governed by the enhancement of the soil conditioner's adhesion to the soil particles as a result of an increase in the molecular weight of the interpolymer complex with increasing Z. The latter was demonstrated by the growth in the dynamic viscosity of the LSC solutions with the growth of Z. At the same time, the thickness of the reinforced layers decreased with the growth in the composition of the soil conditioner. In this case, the higher was the concentration of the applied conditioner solution, the lower was the thickness of the reinforced soil layers. Evidently, the high viscosity of the LSC solutions limited the depth of their infiltration into the soil. The higher values of thickness for the reinforced layers were typical for the sandy soil of the solutions of LSC with the composition Z = 0.02-0.05, having lower values of dynamic viscosity.

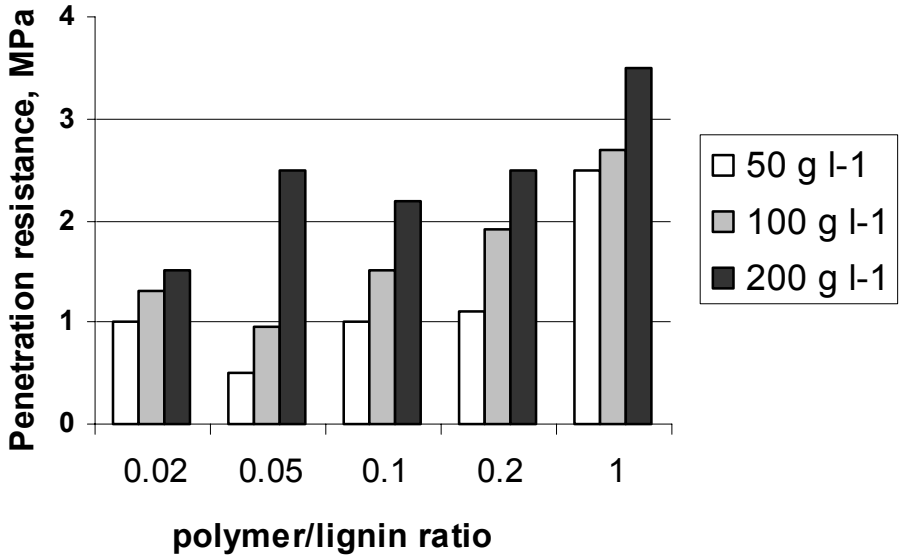


**Fig. 1**. Penetration resistance of reinforced soil layers *versus* LSC composition at different concentrations of the applied solutions; application rate - 1.5 l $m^{-2}$.

The application of LSC water solutions to the top of the mulch led to the formation of mulch-based composite coverings. To investigate the binding properties of the soil conditioner with respect to the mulch, several series of composition materials in the form of cylinders were prepared, in which sawdust and hydrolysis lignin were used as a filler and LSC as a binder. With increasing LSC content from 5 wt % to 25 wt % in the values range of the composition Z = 0.02-0.2, the compressive strength of the composites from the mulch increased 2.1- 4.5 times, which was determined by the adhesion affinity of the soil conditioner to the mulch particles. The effect of the LSC composition on the compressive strength of the composites from sawdust of different tree species and hydrolysis lignin at a mulch content of 75 wt % is demonstrated in Fig. 2. The compressive strength of the obtained composites increased with increasing the lignin/polymer complex composition and was characterised by maximum values at Z = 0.2.

The composites filled with the sawdust of deciduous wood species had higher values of compressive strength than the composites filled with the sawdust of coniferous wood species. The different binding ability of the soil conditioner relative to the sawdust of different wood species is obviously governed by the peculiar features of their chemical composition and different content of resinous substances in them.

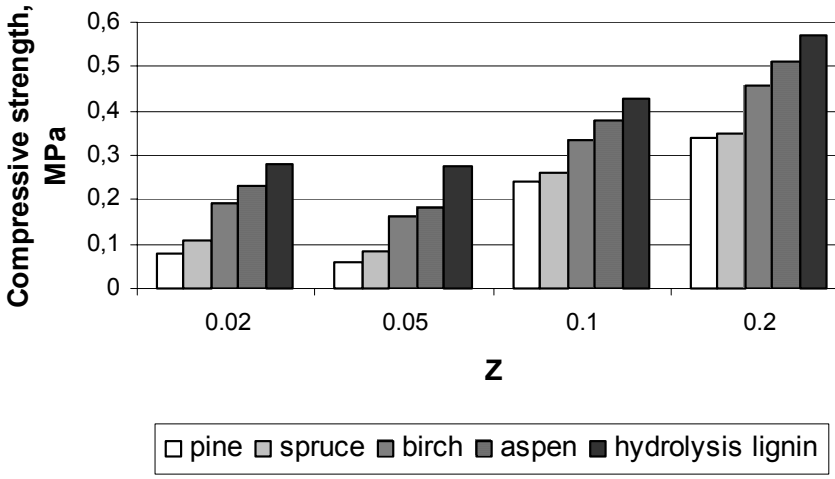


**Fig. 2.** Compressive strength for the composites made from different mulch *versus* the composition of LSC; content of LCS – 25 wt % (on the dry matter).

This is clearly demonstrated by the data of extraction with the organic solvents of the sawdust of deciduous and coniferous wood species (Table 1). It is known that the presence of a great amount of the resin in conifers weakens the adhesion interaction between glues and the wood filler (Hse et al. 1988). At the same time, the composites from hydrolysis lignin were characterised by the highest values of mechanical strength at the given composition.

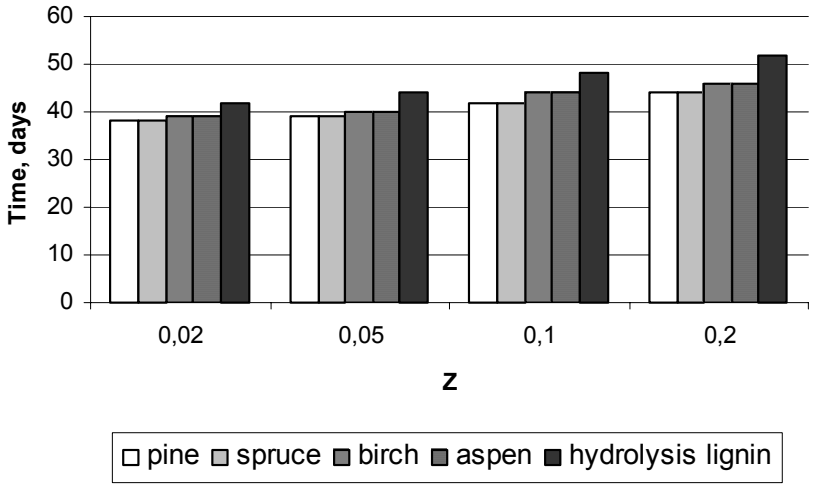


**Fig. 3.** Time of the achievement of moisture evaporation from the soil surface covered with the composite formed from different mulch *versus* the composition of LSC; concentration – 100 g $l^{-1}$, application rate – 4.0 l $m^{-2}$.

Formation of composites having relatively high strength may be favoured by the presence of the active reaction centres on the surface of hydrolysis lignin particles in the form of hydroxyl and carboxyl groups as well as ions of polyvalent metals, enhancing the adhesion interaction at the LSC/filler interface, which is in accordance with literature data (Matte et al. 1988).

### Effect of Mulch Modification on Soil Evaporation

The time required for moisture evaporation from the samples covered with the soil conditioner-modified mulch was up 38-52 days and depended on the composition of LSC, the concentration of its solution and the application rate, as well as the type of the mulch. These parameters exceeded the values of the time of moisture evaporation from the non-mulched soil and that covered with untreated mulch. With increasing composition Z, at the same concentration and application rate of the soil conditioner solution, the mulching effect tended to grow. Figure 3 shows the values of the time of moisture evaporation (in days) from the soil samples covered with treated mulch, depending on the composition of the soil conditioner. The increase of the composition of LSC resulted in the increase of the time of moisture evaporation from the soil. In this case, this tendency manifested itself most distinctly with increasing Z in the range 0.05-0.2. The greatest suppression of moisture evaporation from the soil was reached in the case of treating the sawdust of deciduous wood species and hydrolysis lignin with the soil conditioner of the composition Z = 0.1-0.2. In the average, the time of moisture evaporation from the soil samples covered with the LSC-treated mulch exceeded by 16-57% the time of moisture evaporation from the samples covered with untreated mulch.

### Effect of Mulch Modification on Soil Chemical Transformations

Hydrolysis lignin, characterised by the most attractive mulching properties, was used for the further study of the influence of the mulch particles modified with the lignin/polymer complex solutions on the chemical composition of sandy soil and its microbiological activity. The concentration of the LSC solutions and their application rate were chosen based on the results of the investigation of the effect of the treated mulch on the duration of the soil moisture evaporation. The changes in the chemical composition of sandy soil without and covered with mulch were defined in one and three months, and one year after the beginning of our experiment.

The quantity of mobile $P_2O_5$ and $K_2O$ forms in the mulched soil was enhanced, depending on its thickness and the composition of LSC. With increasing thickness of the mulch to 5 cm, the content of mobile forms of phosphorus in the mulched soil increased by 13.6% relative to the uncovered soil and practically did not differ from the content of $P_2O_5$ in the soil treated only with solutions of the soil conditioner. The impregnation of a 5-cm layer of hydrolysis lignin with the LSC solution with Z = 0.2 increased the content of the potassium form in the soil almost 1.7 times relative to the unmodified mulched soil and 4.2 times relative to the uncovered sandy soil.

It is known that, during biotransformation, organic molecules of wood are able to decompose, mineralise, or be applied as building units for humic substances (Kogel-Knabner 2002). The direction of these transformations is fully determined by the

chemical substances participating in the process and the process conditions. The C/N ratio may serve as a "key" indicator showing a dominant process direction. In the uncovered soil, the initial value of the C/N ratio was equal to 6/1, which indicates that the mineralisation process in soil proceeds passively.

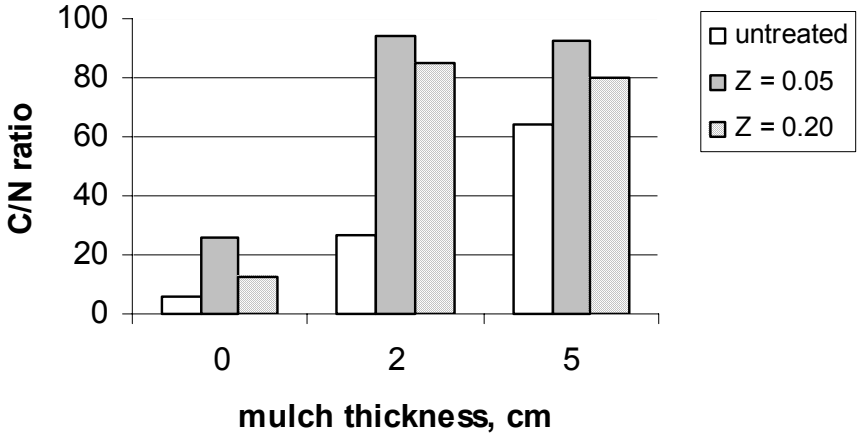


**Fig. 4.** Effect of the mulch thickness on the C/N ratio at the beginning of the experiment.

In one month after starting the test, the treatment of the soil surface with LSC solutions only led to increasing the C/N ratio from 2.1 to 4.3 times (Fig. 4), depending on the composition Z, in comparison with the case of the unmulched soil. Mulching led to a 4.4- and 10.5-fold increase in the C/N ratio for the soil covered with 2 cm and 5 cm of untreated mulch, respectively. When the mulch was modified with LSC solutions, the C/N ratio in the soil increased 11.4-15.5 times relative to the unmulched soil, and 1.5-3.5 times relative to the soil covered with the untreated mulch. This indicates more favourable conditions for immobilisation of nitrogen in the sandy soil covered with the modified mulch in comparison with the application of LCC solutions and the mulch alone.

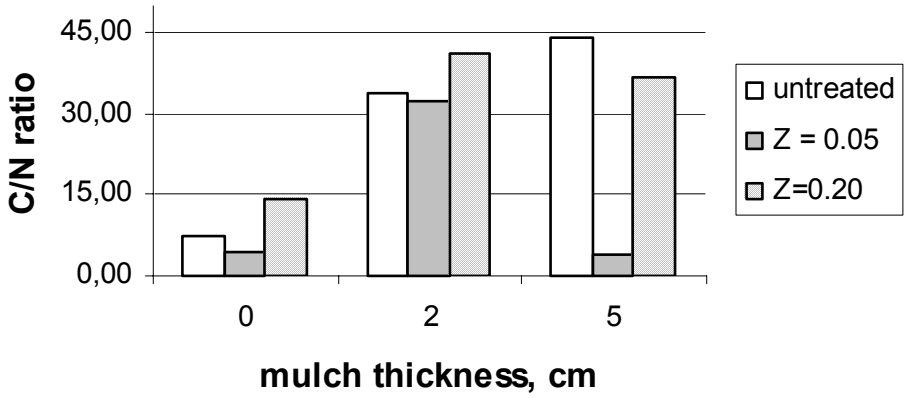


**Fig. 5.** Effect of the mulch thickness on the C/N ratio in a year after the biginning of the experiment.

In one year after starting the test, according to Fig. 5, the C/N ratio in the unmulched and 5-cm mulched soil samples treated with LSC solutions having Z = 0.05 remarkably decreased, equalling 4.2/1 and 3.6/1, respectively. This indicates an intensive biodegradation and mineralisation of organic matter, with the formation of nutrients in these variants. On the other hand, it may be assumed that the modification of hydrolysis lignin particles within the solutions of LSC, having a lower value of the composition, is more efficient for the acceleration of mineralisation processes in sandy soil. For other mulched soil samples, the C/N ratio also essentially decreased, however, its values changed in the range 30/1 – 40/1. This may testify that the biochemical transformations in hydrolysis lignin mulch modified with the lignin/polymer complex in these variants were still going on (Tuomela et al. 2000, Sjöberg 2003). This suggestion has been confirmed with the analysis of the drainage water determined after 2 years from the beginning of the study. The content of nitrate ions in the drainage water determined for these variants with the modified mulched soil was very high and sometimes exceeded their permissible available concentration.

Our experiments have revealed that the observed compositional transformations of the mulch modified with the lignin/polymer complex during the immobilisation and mineralisation of nitrogen were accompanied by an essential enhancement in the biocenosis activity of bacteria and micromycetes in the soil samples (Ambrazaitiene et al. 2006). Earlier, our vegetation test has also shown that the developed LSC has a beneficial action on the germination and development of seeds of plants typical for the Baltic coastal dune zone (Belous et al. 2006).

## CONCLUSIONS

1. The modification of sawdust and hydrolysis lignin used as mulch by impregnation with water solutions of the developed lignosulphonate/polymer complex leads to the formation of a layered composite covering consisting of an upper modified layer of mulch and a lower reinforced layer of sandy soil.
2. With increasing composition of the lignosulphonate/polymer complex, at the same concentration and application rate of its water solutions, the mechanical properties of the composite layers and the time of moisture evaporation from the mulched soil increase, which indicates the enhancement of the adhesion affinity of the polycomplex structure for the mulch and soil surface particles as a result of its molecular weight growth with increasing Z.
3. The modified mulch-based composites, containing the bark of deciduous wood species, have higher values of compressive strength than composites containing the bark of coniferous wood species. However, the modification of hydrolysis lignin mulch gives the highest values of this indicator at the same composition and application rate of the polycomplex.
4. The changes in the soil chemical composition (P, K, C, N) have shown their dependence on the thickness of the modified mulch layer and the lignosulphonate/polymer complex's composition at the same application rate.
5. The increase in the C/N ratio for the soil covered with modified hydrolysis lignin relative to the soil covered with the unmodified one at the beginning of the experiment

indicates more favourable conditions for immobilisation of nitrogen. The remarkable decrease in C/N ratio values in one year indicates an intensive biodegradation and mineralisation of hydrolysis lignin for soil, where the solution of the polycomplex having a lower value of the composition was applied.

## ACKNOWLEDGMENTS

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# OBTAINING MICROCRYSTALLINE CELLULOSE FROM SOFTWOOD AND HARDWOOD PULP

Marianna Laka,* and Svetlana Chernyavskaya

Conditions for obtaining microcrystalline cellulose (MCC) by the thermocatalytic method from hardwood (birch, aspen) and softwood (pine) bleached sulphate pulp have been developed. After thermocatalytic treatment, cellulose polymerization degree has decreased to the so-called levelling-off degree of polymerization (LODP), which, in the case of birch, aspen and pine wood pulp, made up 450, 370 and 250 units, respectively. After grinding the destructed pulp in a ball mill, MCC powder samples were obtained with particles, the major part of which had sizes of 2-20 μm. In terms of physico-chemical indices investigated in this work, the obtained samples conform to the pharmacopoeia requirements. Dispersing the destructed pulp in water medium, at a sufficiently high cellulose concentration (≥ 8%), MCC gel samples were prepared, with rheological properties typical for liquid crystalline polymers. The indices of the obtained hardwood and softwood MCC were compared.

*Keywords: Microcrystalline cellulose, Thermocatalytic destruction, Viscosity, Shear rate, Hardwood, Softwood*

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## INTRODUCTION

At present, microcrystalline cellulose (MCC) is used in various fields such as pharmacy, cosmetics, the food industry, the plastics processing industry, etc. (see, for example, Ioelovich and Leykin 2004 ).

In the powder form, it is used, for example, as a filler and binder in medical tablets and food tablets for dietary purposes. In the gel form, MCC is used as a viscosity regulator, a suspending agent, emulsifier in different pastes, creams, etc.

In our earlier work, a thermocatalytic method for obtaining MCC has been developed (Laka and Chernyavskaya 1996).

In the present work, optimal thermocatalytic treatment conditions were developed for obtaining MCC from softwood and hardwood pulp, and the properties of the obtained MCC samples were investigated.

## EXPERIMENTAL

### Development of Thermocatalytic Treatment Conditions

Hardwood (birch and aspen) and softwood (pine) bleached sulphate pulp samples were used for the thermocatalytic treatment (Laka et al. 2000). Pulp samples were impregnated with acid catalyst (e.g., hydrochloric acid) solutions of different concentrations and dried during 5-6 hours until the moisture content in the sample

reached 3%. The dependence of the degree of polymerization of cellulose samples, which was determined from the intrinsic viscosity of cellulose cadoxen solution (Obolenskaya et al. 1991), on the hydrochloric acid concentration and thermal treatment temperature was determined. Optimal thermocatalytic treatment conditions, at which the degree of polymerization reaches its constant value, were established.

### Obtaining of MCC Powders and Gels

To obtain MCC powders, the degraded pulp samples were ground in a ball mill. After grinding, they were washed-off from the remaining acid, dried at 80°C and additionally ground to get rid of agglomerates.

To prepare MCC gels, the degraded cellulose pulp samples were dispersed in an aqueous medium in a ball mill. At sufficiently high cellulose concentrations (≥ 8%), MCC gel samples were obtained.

### Investigation of the Properties of the Prepared MCC Powder and Gel Samples

The structural and physico-chemical properties of the obtained MCC and the rheological properties of the gels were investigated.

For studies of the form and sizes of powder particles, an optical microscope BIOLAM and a scanning electron microscope Tescan 5136 were used.

The sizes of the particles present in the gels were investigated by the photon correlation spectroscopy method on a Zetamaster S 500 ZEM. For measurements, the fine fraction of MCC gels was used, which was obtained by way of precipitation of very diluted gels and removal of precipitated particles. This was necessary to avoid sedimentation during the measurements, undesirable when using the given method.

Water retention value (WRV) was determined by the Jayme method (Jayme and Hahn 1960).

Physico-chemical properties, for example, solubility, pH value, mass losses when drying etc. were determined by the methods specified in the European Pharmacopoeia, 5th Ed. (2005).

The rheological properties of the gels were determined using a viscosimeter Rheotest-2 with coaxial cylinders in the shear rate range from 0.50 to 437 $s^{-1}$ at 20°C.

## RESULTS AND DISCUSSION

### Change in Degree of Polymerization of Cellulose after Thermocatalytic Treatment

Figure 1 shows the dependence of the change in the degree of polymerization of hardwood and softwood cellulose on the hydrochloric acid solution concentration at the thermal treatment temperature 110°C. As can be seen, with increasing hydrochloric solution concentration, the degree of polymerization first decreases dramatically, while, at a 0.025% concentration, in the case of hardwood and at a 0.04% concentration in the case of softwood, reaches a constant value – levelling-off degree of polymerization (LODP), when the amorphous part is destructed, while the crystalline one remains almost intact.

Figure 2 shows the dependence of the degree of polymerization of hardwood and softwood cellulose on the thermal treatment temperature at a constant hydrochloric acid

solution concentration (0.04%). With increasing thermal treatment temperature, LODP is reached at 90°C and 110°C for hardwood and softwood cellulose, respectively.

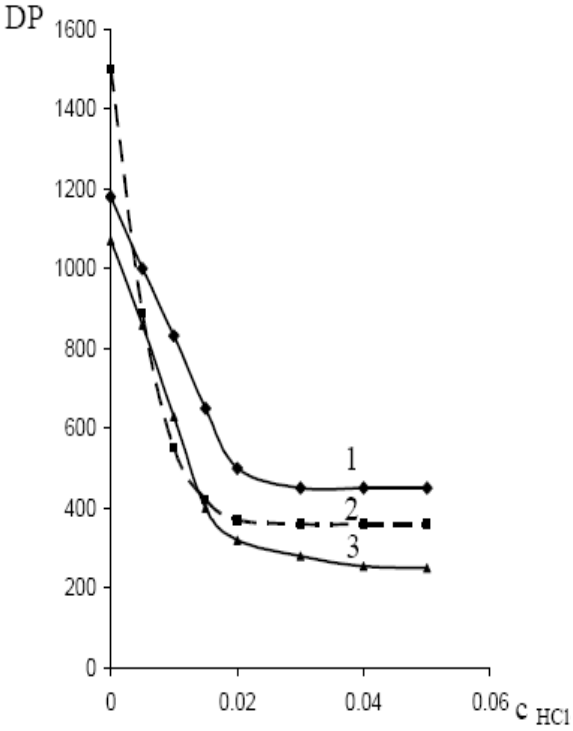


**Fig. 1.** Cellulose polymerization degree *versus* hydrochloric acid solution concentration at the treatment temperature 110°C for birch (1), aspen (2) and pine (3) pulp samples

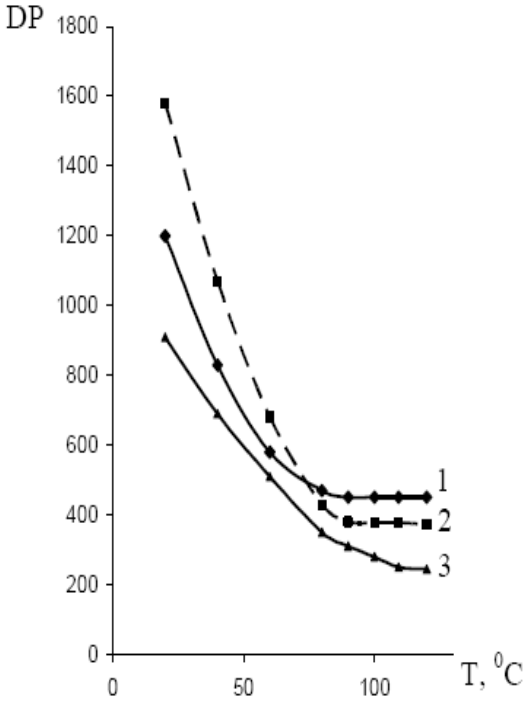


**Fig. 2.** Cellulose polymerization degree *versus* thermal treatment temperature at the hydrochloric acid solution concentration 0.04% for birch (1), aspen (2) and pine (3) pulp samples

From the obtained results, the following thermocatalytic treatment conditions for reaching LODP were established: hydrochloric acid solution concentration 0.025-0.05% and 0.04-0.10%; thermal treatment temperature 90-120°C and 110-130°C for hardwood and softwood, respectively.

## Properties of Hardwood and Softwood MCC Powders

After grinding in a ball mill the pulp sample destructed to LODP, MCC powder samples were obtained, whose particles' longitudinal and transversal sizes differed little. The longitudinal size of 60% of particles and the transversal size of 80% of particles are in the range 2-20 μm. The maximum particle size for hardwood and softwood MCC powder does not exceed 60 and 100 μm, respectively.

Figures 3a and 3b shows micrographs of aspen and pine powder particles obtained using a scanning microscope at two different magnifications.

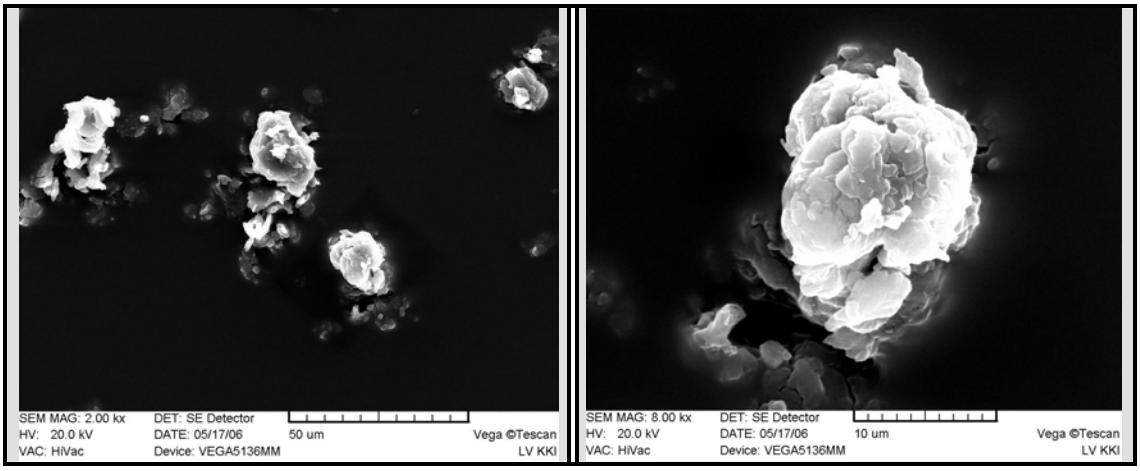


**Fig. 3a.** Electron micrographs of aspen MCC powder particles

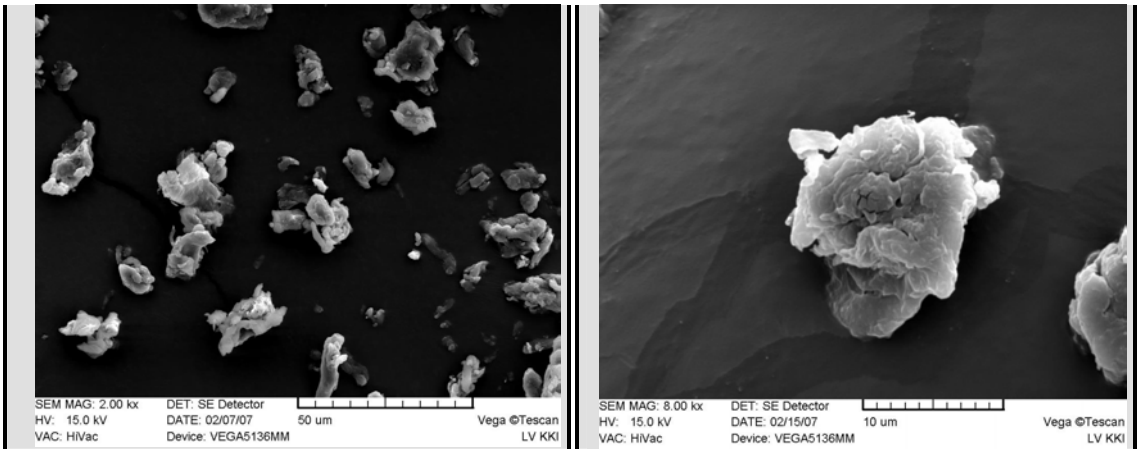


**Fig. 3b.** Electron micrographs of pine MCC powder particles

**Table 1.** Physico-chemical and Quality Indices of Hardwood and Softwood MCC and Pharmacopoeia Requirements

| No. | Index | Hardwood MCC | Softwood MCC | Requirements of the Pharmacopoeia |
|---|---|---|---|---|
| 1 | Solubility | Corresponds | Corresponds | Practically insoluble in water, 96% ethanol, diluted acids, acetone, toluene |
| 2 | pH | 6.1-6.5 | 6.2-6-8 | 5.5-7.0 |
| 3 | Weight losses upon drying | 5.1-5.9 | 3.7-5.8 | No more than 6 |
| 4 | Water-soluble substances, % | 0.28-0.31 | 0.12-0.16 | No more than 0.2 |
| 5 | Starch and dextrins | Corresponds | Corresponds | 0.1 of the preparation in 5 ml of water. 0.2 ml of 0.05 *M* iodine solution is added. Blue and red-brown colours must not appear |
| 6 | WRV, % | 72-85 | 50-55 | - |

Table 1 shows quality indices for hardwood and softwood MCC samples. In terms of physico-chemical indices, they conform to pharmacopoeia requirements, although the chemical purity of the obtained hardwood MCC samples is somewhat lower, which can be explained by the fact that they are not additionally bleached. WRV for hardwood MCC powders is by 30% higher than for softwood.

## Properties of Hardwood and Softwood MCC Gels

Figure 4 shows flow curves for the obtained hardwood and softwood MCC gel samples. As can be seen, at the same cellulose concentration (10%), viscosity in the whole shear rate range in the case of hardwood MCC gel is higher. The flow curves for both hardwood and softwood MCC gels have three pronounced regions, which, as has been shown in our earlier works (for example, Laka et al. 2003), is connected with their liquid crystalline structure. Region I corresponds to the gel flow with microcrystallite domains aligned in different directions, region II corresponds to the domains' break-up and the microcrystallites' alignment in the flow direction, and region III corresponds to the gel flow with microcrystallites aligned in the flow direction.

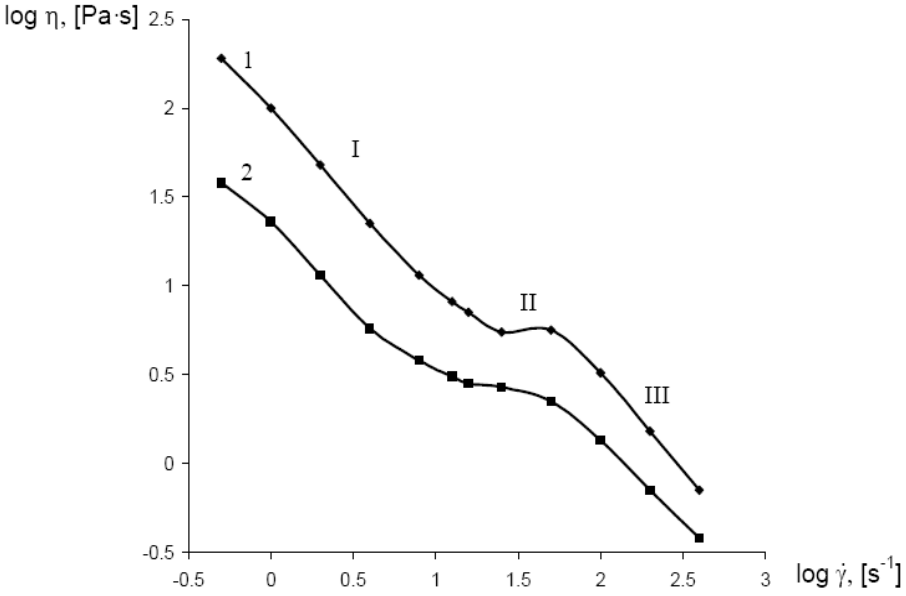


**Fig. 4.** Viscosity *versus* shear rate for birch (1) and pine (2) MCC gels

The liquid crystalline structure formed by microcrystallites is validated also by the distribution graphs of the gel fine fraction particle number and their occupied volume in their longitudinal size, determined by the photon correlation spectroscopy method (Fig. 5).

It can be seen that the maximum of the distribution graphs is located at 500 nm, which is close to the microcrystallite longitudinal sizes. The transversal sizes are 30-100 times smaller. Thus, by dispersing the destructed pulp in water medium, attrition of the microcrystallites occurs. The presence of microcrystallite whiskers in dispersions at their sufficiently high concentration provides an MCC gel formation with liquid crystalline rheological properties.

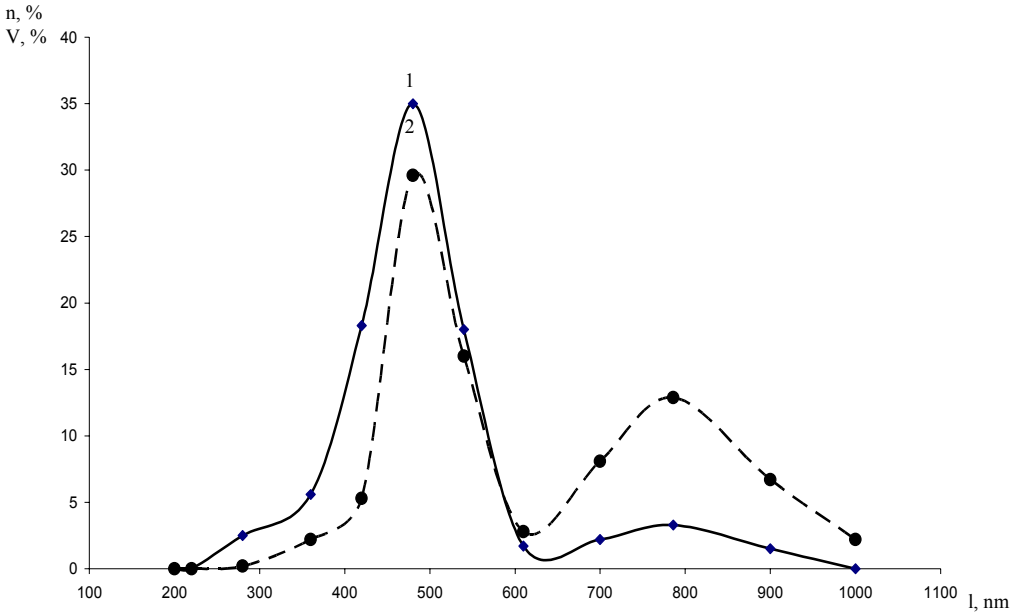


**Fig. 5.** Percentage distribution graphs of the number of particles n (1) and the particle-occupied volume V (2) for the fine fraction of the MCC gel with respect to the longitudinal size of particles

## CONCLUSIONS

1. In this work, the thermocatalytic treatment conditions were established for degradation the hardwood and softwood pulp till the levelling-off degree of polymerization, which, in the case of birch, aspen and pine, were 450, 370 and 250 units, respectively.
2. After grinding in a ball mill the degraded pulp, MCC powder samples were obtained. The major part of the powder particles had the sizes 2-20 μm. The investigated physico-chemical indices of the obtained MCC powder samples conform to the European Pharmacopoeia requirements.
3. After dispersing the degraded pulp in aqueous medium, MCC gel samples were obtained, with rheological properties typical for liquid crystalline polymers.

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# THE STEREOCHEMISTRY AND CONFORMATION OF LIGNIN AS JUDGED BY X-RAY CRYSTALLOGRAPHIC INVESTIGATIONS OF LIGNIN MODEL COMPOUNDS: ARYLGLYCEROL β-GUAIACYL ETHERS

Vratislav Langer,[a] Knut Lundquist,[b*] and Jim Parkås [b†]

The conformations of a variety of crystalline lignin models representing different diastereomeric forms of structural elements in lignin of the arylglycerol β-guaiacyl ether type have been studied using X-ray crystallography. Based on X-ray crystallographic data, sequences of units attached to each other by β-guaiacyl ether linkages were constructed. The appearance of the resulting oligomers shows that stereoisomerism can be expected to influence the shape of the lignin molecules to a great extent. The constructed oligomers provide an idea about the contribution to the complexity of lignins by stereochemistry alone. It is proposed that structural differences, together with conformational variations, are the main reasons for the broadness of the signals in NMR spectra of lignins.

*Keywords: Arylglycerol β-guaiacyl ethers, Conformation, Crystallography, Lignin*

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## INTRODUCTION

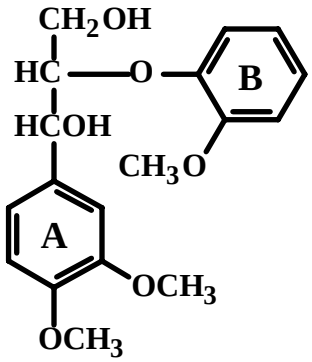
In spite of the polymeric nature of lignins, the peak positions in $^{13}C$ NMR spectra (Robert 1992) and $^{1}H$ NMR spectra (Lundquist 1992) of lignins agree very well with those expected from examinations of appropriate low molecular weight model compounds. However, due to superimposition of signals the resolution of the lignin spectra is rather limited. This is related to the irregular and complex structure of lignins. Even signals separated from other signals in the lignin spectra are typically broad, in particular in $^{1}H$ NMR spectra. The broadness of lignin NMR signals is also reflected in the appearance of 2D NMR spectra (see, e.g., Ralph et al. 2004). We think that not only structural variation but also differences in conformation contribute to the broadness of the signals. The appearance of lignin spectra reflects a regular lignin structure in the sense that lignins consist of phenylpropane units attached to each other by different types of linkages (Adler 1977). Substances completely lacking in structural order, e.g. "humic substances", give rise to almost featureless NMR spectra (Lundquist et al. 1985). It is evident that the stereochemistry and conformation of the lignin molecules are of interest in connection with the interpretation of NMR spectra of lignins. Aiming at an elucidation

of the stereochemistry and conformation of the lignin molecules, the conformation of a variety of lignin models, representative of different types of lignin structures, was examined by X-ray crystallography (Lundquist et al. 2003). It was found that the bulky aromatic groups in many cases tend to be far apart from each other in the conformations adopted. This suggests that π-π electron repulsion (Hunter and Sanders 1990) between aromatic groups plays a role. However, it is evident that other factors (e.g. hydrogen bonding) also influence the conformations of the model compounds examined. Chen and Sarkanen (2003) have speculated that charge-transfer complexes cause attraction between aromatic nuclei in lignins. However, the geometrical requirements for such complexes are very precise (Hunter and Sanders 1990). In our opinion they are normally not fulfilled in lignins.

We have paid special attention to model compounds representative of arylglycerol β-aryl ethers, since such structures represent a major type of structural elements in lignins. Here we have focused on sequences of arylglycerol β-guaiacyl ethers (Fig. 1). Sequences of such structural elements can be expected to occur rather frequently in lignins, since the number of this type of β-aryl ethers is large, in particular in softwood lignins (Adler 1977). Lignin degradation products partly consisting of sequences of β-ethers are known (Nimz 1974). It is noteworthy that Erdtman and Leopold (1949) as early as 1949 speculated about the existence of β-ether sequences of the topical type within lignin.

## MATERIAL AND METHODS

The *threo* form of **1** was lately obtained in crystalline form, and its crystal structure was determined (Langer and Lundquist, 2002). The crystal structure of the *erythro* form of **1** has been reported by Stomberg and Lundquist (1994).




**1**

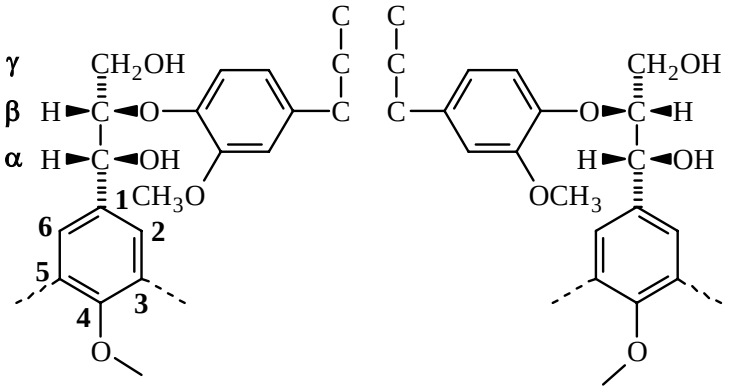
Based on the molecules in the crystal structures, oligomers consisting of structural elements of arylglycerol β-guaiacyl ether type were constructed digitally. This was accomplished by replacing the guaiacyl groups (e.g. ring B in **1**) in the molecules by ring

A ("demethylated" in the 4-position) in attached molecules of **1**. The computer work required was carried out using the program MERCURY (Macrae et al. 2006).

MERCURY is a program for visualization and analysis of crystal structures. In its full version, provided to users of the Cambridge Structural Database system, display and overlay of multiple structures as well as editing of molecules is possible. By applying this program to molecules of **1** taken from the crystal structures it was possible to construct the oligomers by superimposing the B ring (in **1** or in constructed oligomers) with the A ring in **1**, whereupon the B ring and the *p*-methoxy group in A was removed. The geometries of the two rings (A and B) are almost identical, implying that all the geometrical details of the constructed oligomers are identical or practically identical with those found in the crystal structures. Constructed oligomers are shown in Results and Discussion.

## RESULTS AND DISCUSSION

It is in general assumed that lignins are optically inactive and that the structural elements within lignins are "racemic." The correctness of this assumption has been confirmed in recent studies (Ralph et al. 1999; Akiyama et al. 2000). It is important to recognize that the occurrence of "racemic" structural elements in lignins by no means excludes an uneven distribution of different diastereomeric forms. However, investigations have shown that about equal amounts of the *erythro* and *threo* forms of arylglycerol β-guaiacyl ethers (Fig. 1) are present in lignins (Hauteville et al. 1986; Akiyama et al. 2005).




***erythro*** ***threo***

**Fig. 1.** The *erythro* (α*R**, β*S**) and *threo* (α*R**, β*R**) forms of arylglycerol β-guaiacyl ethers.

We have studied the conformational options of such structural elements based on X-ray crystallography of lignin model compounds (Stomberg et al. 1988; Stomberg and Lundquist 1994; Lundquist et al. 1996; Langer and Lundquist 2002). Computational studies constitute an alternative approach to study the conformation of this type of structural elements (Simon and Eriksson 1998; Besombes et al. 2003). The results obtained by the two approaches concur in general (Lundquist et al. 2003). The

conformation of compounds of the arylglycerol β-guaiacyl ether type is largely determined by two torsion angles: $C_{aryl}$-$C_\alpha$-$C_\beta$-O and $C_{aryl}$-O-$C_\beta$-$C_\alpha$ (Fig. 2).

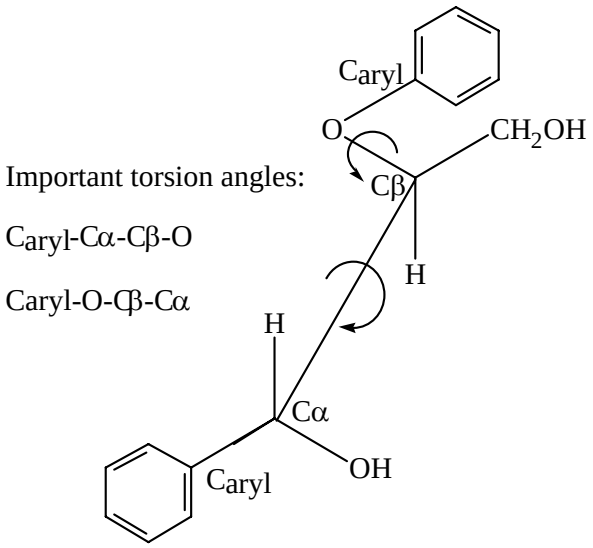



**Fig. 2.** Torsion angles of importance for the conformation of arylglycerol β-aryl ethers: $C_{aryl}$-$C_\alpha$-$C_\beta$-O and $C_{aryl}$-O-$C_\beta$-$C_\alpha$.

In the following discussion of torsion angles we have considered the isomer with *R*-configuration at $C_\alpha$. In all the *erythro* forms of dimeric lignin models so far examined the $C_{aryl}$-$C_\alpha$-$C_\beta$-O angle is about 60° and the $C_{aryl}$-O-$C_\beta$-$C_\alpha$ angle is about -140°. A more complex model of *erythro* β-guaiacyl ether type adopts a similar conformation (Roblin et al. 2000). In contrast, the $C_{aryl}$-$C_\alpha$-$C_\beta$-O angle is about 180° in the *threo* forms examined, while the $C_{aryl}$-O-$C_\beta$-$C_\alpha$ angles range from 105° to 165°. The angle between the aromatic ring planes is also of interest in this context. This angle is fairly large in the compounds examined; the smallest ring plane angle (38°) is found in the rather complex model examined by Roblin et al. (2000). Evidently the examined lignin models adopt similar conformations regardless of structural variation. Therefore we think that the conformational results obtained in model compound studies are applicable to lignin too.

We have constructed sequences of arylglycerol β-guaiacyl ethers based on different enantiomeric forms of the crystal structures of the *erythro* and *threo* forms of 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)-1,3-propanediol (**1**) (Stomberg and Lundquist 1994; Langer and Lundquist 2002). The conformations of these compounds are fairly representative for all the other arylglycerol β-guaiacyl ethers examined, although the $C_{aryl}$-O-$C_\beta$-$C_\alpha$ angle in the *threo* form (165°) is somewhat larger than the corresponding angle in the other *threo* forms. The constructed oligomers illustrate the influence of stereochemistry on the shape of the lignin molecules. The constructed "lignin models" are representative of segments of lignin molecules, and they should not be viewed as models for individual lignin molecules. Figure 3 shows a series of oligomers constructed by combining X-ray crystallographic data for pairs of the stereoisomeric forms of **1**. The configuration (*R*,*S*) of the chiral carbon atoms in the oligomers is shown. The total number of stereoisomers is 16 (8 racemates).

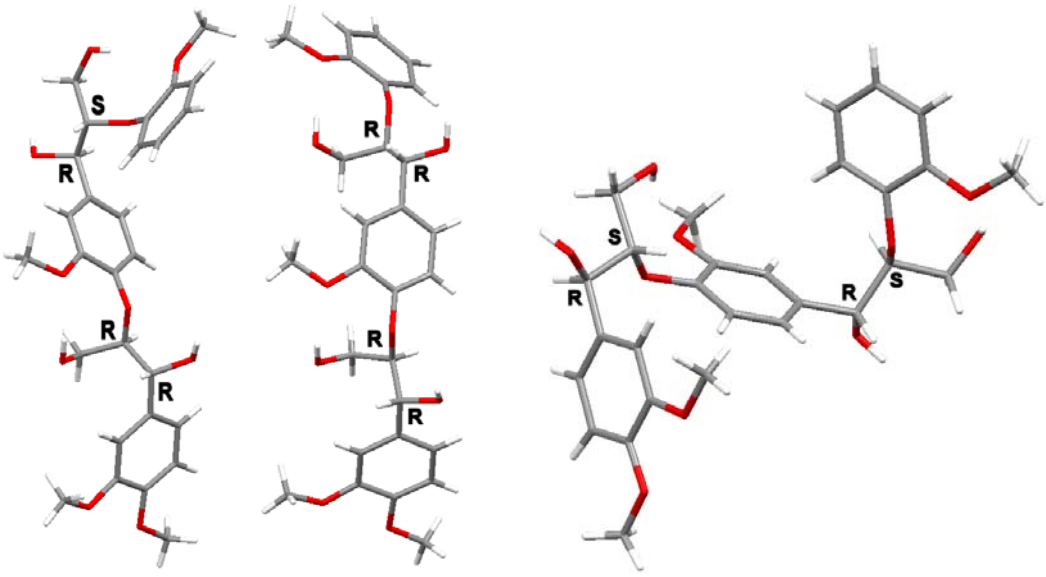



**Fig. 3.** Examples of stereoisomers of lignin models consisting of sequences of 3 units attached to each other by β-guaiacyl ether linkages. The mirror images of the compounds constitute additional examples of stereoisomers of the topical lignin models.

The examples in Fig. 3 illustrate the influence of stereochemistry on the shape of the molecules. To further study the influence of stereochemistry on the shape of this type of molecules we have constructed oligomers consisting of five units. In this case there are 256 isomers. Two of the isomers are shown in Fig. 4. The shapes of the two molecules are very different.

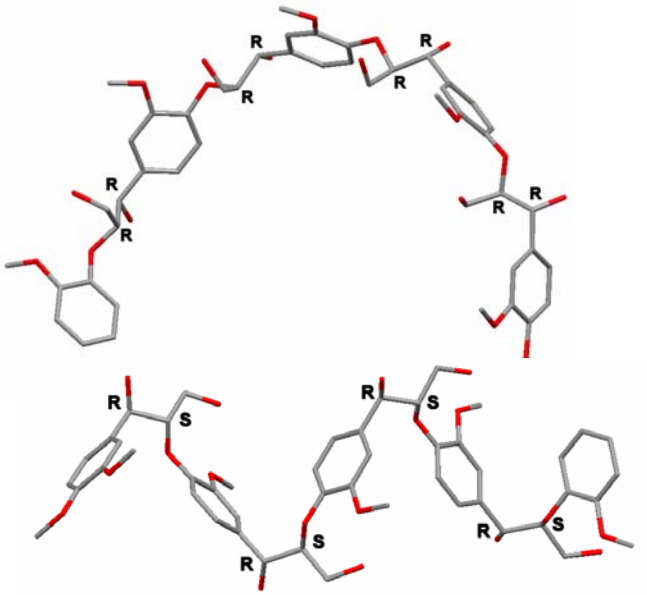



**Fig. 4.** Examples of stereoisomers of lignin models consisting of sequences of 5 units attached to each other by β-guaiacyl ether linkages. The mirror images of the compounds constitute additional examples of stereoisomers of the topical lignin models.

As pointed out above, it is known that lignin is "racemic" and that about equal amounts of *erythro* and *threo* forms of arylglycerol β-guaiacyl ethers are present in lignins. These facts have been considered in the construction of one of the stereoisomers of an oligomer consisting of nine units (Fig. 5). The constructed stereoisomer consists of both enantiomers of two *erythro* forms and two *threo* forms of arylglycerol β-guaiacyl ethers. The total number of isomers is 65536. The discussion of the complexity of the lignin structure in more general terms by Ralph et al. (2004) is of interest in this context.

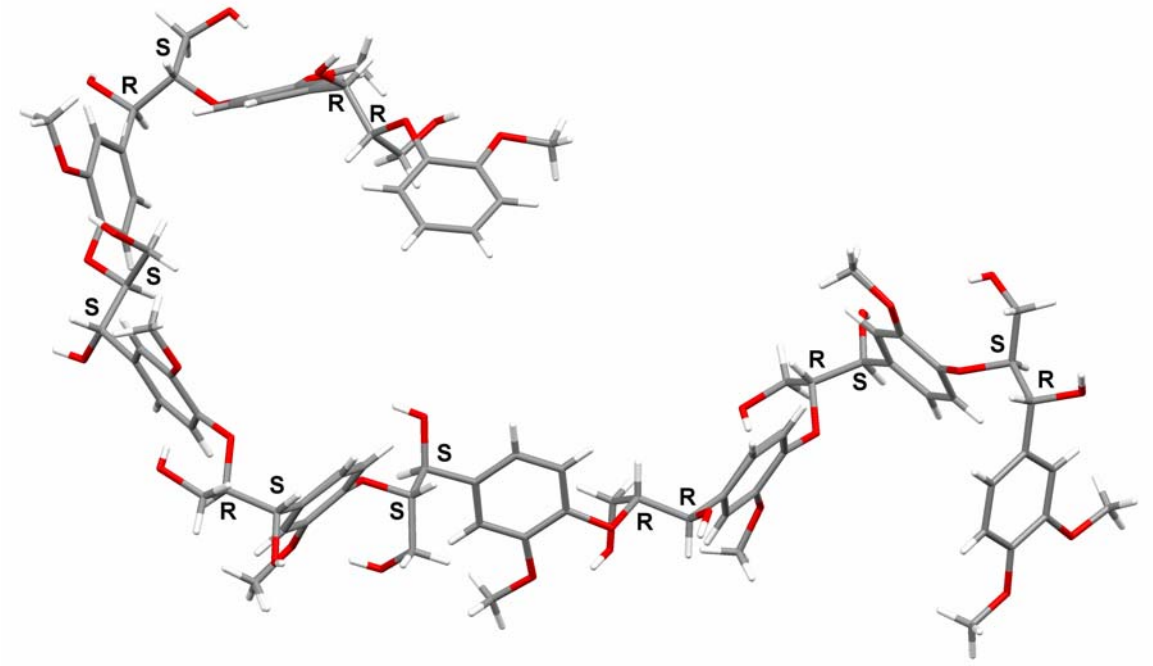



**Fig. 5.** Stereoisomer of a lignin model consisting of a sequence of 9 units attached to each other by β-guaiacyl ether linkages. The distribution of enantiomers and diastereomers is representative of what on an average is prevailing in lignins.

It is well known that stereochemistry and conformation influence the positions of NMR signals. Stereochemical and conformational differences result in small changes of chemical shifts (upfield or downfield) of the signals in NMR spectra. The constructed sequences of lignin units discussed in this paper exemplify that there is a considerable diversity with respect to stereochemistry and conformation in lignins. This is consistent with the fact that in spite of the broadness of the lignin NMR signals, the signal positions fit very well with what is expected from examinations of appropriate model compounds.

## CONCLUSIONS

1. Stereochemistry and conformation have a decisive influence on the shape of the lignin molecules.

2. The sequences of arylglycerol β-guaiacyl ethers studied exist in a very large number of stereoisomeric forms. This provides an idea about the considerable contribution of stereoisomerism alone to the complexity of the lignin structure.
3. Lignin stereochemistry is of importance in connection with analytical lignin work.

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# STUDIES ON THE FUSION OF LIGNINOLYTIC ENZYME cDNAS AND THEIR EXPRESSION

Jun Xie,[a*] Lei Feng,[a] Ning Xu,[a] Guohui Zhu,[a] Jun Yang,[a] Xiaoli Xu,[a] and Shiyu Fu[b*]

Manganese peroxidase (MnP) and lignin peroxidase (LiP) are two major peroxidases involved in lignin biodegradation. The cDNA *mnp1* encoding a kind of MnPs, and cDNA *clg5* encoding a kind of LiPs were fused to one cDNA *mnp1- clg5* (rmc15) by over-lap PCR technology in this research. Then the recombinant cDNA rmc15 was cloned into a vector pTrcHisB to construct its efficient expression plasmid pTHmc15 in *Escherichia coli*. The *E. coli* transformed by pTHmc15 was induced by isopropyl-β-D-thiogalactoside. The expressed protein was analyzed by SDS-PAGE, and a new one was observed with a molecular weight of about 77KD. Enzyme activities of MnP and LiP could not be observed in the unfolded fused protein. However, the enzyme activity of MnP was detected in the recombinant protein after it was refolded and activated by $Ca^{2+}$ and heme, while the activity of LiP was not detected. These results show that the enzyme activity of the protein at N-terminal was not affected, but at C-terminal it was affected in the fusion protein of ligninolytic enzymes. Therefore, it is unfeasible to construct the gene of bifunctional ligninolytic enzyme with the fusion of the cDNA *mnp1* encoding MnP and cDNA *clg5* encoding LiP.

***Keywords:*** *Ligninolytic Enzymes; Over-lap PCR technology; Gene Expression; Folding and Activating of proteins*

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## INTRODUCTION

*Phanerochaete chrysosporium* is a model microorganism to investigate the degradation of lignin, which can secrete peroxidases in nitrogen-limited growth medium, i.e., manganese peroxidase (MnP) and lignin peroxidase (LiP). The protein sequences (Mayfield et al. 1994; Tien and Kirk 1984; Timofeevski et al. 1999; Zhang 1987) of MnP and LiP indicate that the third amino acid of their mature protein is Cys, and it can interact with other Cys moieties to form a double-sulfur bond, essential in enzyme construction. So it can be deduced that if MnP or LiP is fused with another peroxidase, the activity of one protein may be influenced, while another would not be.

In order to verify the above-mentioned hypotheses, over-lap PCR technology was used to fuse the encoding area of two kinds of peroxidases, i.e., cDNA *mnp1* and cDNA *clg5*, then the fused gene *mnp1-clg5* was expressed in *Escherichia coli* (*E. coli*). After folding and activating the protein, the enzyme activities of these two kinds of enzymes were monitored to determine their different activities.

## MATERIALS AND METHODS

### Bacteria, Vector and Plasmid

*E.coli* DH5α, clone vector pUC18 and expression vector pTrcHisB were provided by the molecular biology laboratory of Sichuan University. Plasmid pATTMnP1 and pBSCLG5 was constructed by Xie (Xie 2001)

### Reagents

The enzymes and PCR purification kits were bought from Japan TaKaRa Bioengineering Company (Dalian), Germany Boehringer Mannheim Company and U.S.A. BRL Company, separately. Isopropyl -β-D-thiogalactoside (IPTG) and bovine chlorohemin, oxidized glutathione (GSSG ), dithiothreitol (DTT), and Triton X-100 were bought from Sigma. All other reagents were of analytical grade.

Primers and DNA fragments were synthesized and purified by Japan TaKaRa Bioengineering Company (Dalian).

### Gene Operation

Plasmid extraction, the enzyme cut reaction, the recovery of DNA fragments, joint reaction, the transform and culture of bacterium, SDS-polyacrylamide gel electrophoresis, Bradford protein detection, and the PCR overlap extension technique were all performed with little modification (Sambroo et al. 1989).

The expression of fusion protein was carried out according to the expression of H2 gene of LiP in *E. coli* by Nie et al. (1998) and H8 gene by Doyle et al. (1996).

The folding and activating of mutated protein were previously reported (Nie et al. 1998; Timofeevski et al. 1999; Doyle et al.1996).

The enzyme activity of MnP was similar to what has been previously reported (Gold and Glenn 1988), while the detection of the enzyme activity of LiP was detected by veratryl alcohol (Tien and Kirk 1984).

## RESULTS

### The Fusion of rmc15 cDNA and the Construction of Its Plasmid

According to the total sequences of cDNA *mnp1* of MnP and cDNA *clg5* of LiP, primers were designed by DNASIS software. There are no *Nco*I, *BamH*I sites in *mnp1* and *clg5* (Mayfield 1994; Tien and Kirk 1984; Timofeevski 1999; Zhang 1987). To clone the amplified fragments into the vector pTrcHisB, *Nco*I and *BamH*I sites were designed at the 5'-end of P1 and P4, respectively.

- *mnp1* forward primer (P1 ): 5'ATT CCA TGG CAG TCT GTC CAG ACG G3'
- *mnp1* backward primer (P2 ) backward: 5'CTT GCC GTT CGA GCA GGT CGC AGC AGG GCC ATC GAA CTG3'
- *clg5* forward primer (P3 ): 5'GTT CAG TTC GAT GGC CCT GCC GCG ACC TGC TCG AAC GG3'
- *clg5* backward primer (P4 ): 5'ATT GGA TCC TTA AGC ACC AGG AGG AGG 3'

A 1.07 Kb DNA fragment, *mnp1*, was obtained by using the plasmid pATTMnP1 DNA as the template and PCR amplification of P1 and P2 primers, while a 1.03 Kb DNA fragment, *clg5*, was obtained by using the plasmid pBSCLG5 DNA as the template and PCR amplification of P3 and P4 primers.

Then, *mnp1* and *clg5* were purified by PCR purification kits and used as the template; thus a 2.1 Kb DNA fragment could be obtained by the second PCR amplification of P1 and P4 primers. This DNA fragment was *mnp1-clg5* cDNA (1.07+1.03 Kb) and named as *rmc15* (Lane 3 and 4 in Fig.1). If *rmc15* was directionally inserted into the corresponding sites of expression vector pTrcHisB in *E. coli*, the expression plasmid of fusion cDNA was constructed and named as pTHmc15.

By using *Nco*I and *Bam H*I to restrict pTHmc15, two DNA fragments were detected by gel electrophoresis. Among them, the DNA lane with 4.3 Kb was the same with pTrcHisB restricted by *Nco*I/*Bam H*I. Another DNA lane with 2.1Kb (Lane 2 in Fig. 2) was similar to the fusion cDNA fragment as expected a priori.

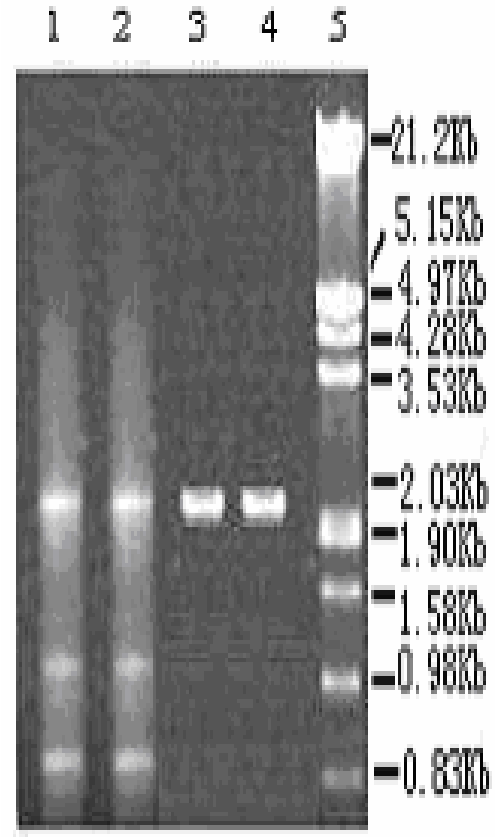


**Fig. 1.** Overlap-PCR amplification of fused cDNA *rmc15.* Lanes 1-2: the amplification product of fused cDNA *rmc15*; Lanes 3-4: the purified product of fused cDNA *rmc15*; Lane 5: λ/ *Hind* III-*Eco*R I DNA standard.

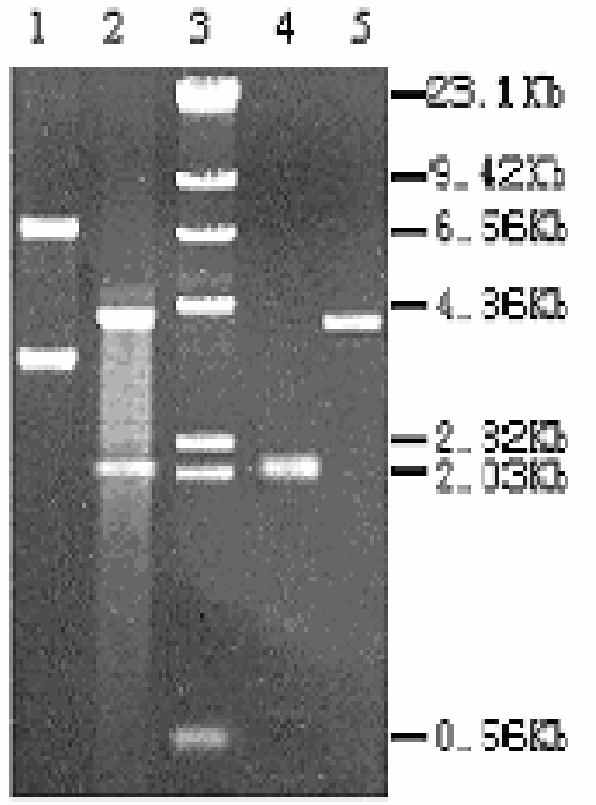


**Fig. 2.** Restriction analysis of recombinant plasmid pTHmc15. Lane 1: unrestricted pTHmc15; Lane 2:The restriction product of pTHmc15 by *Nco* I/*Bam* HI; Lane 3: λ/ *Hind* III-*Eco*R I DNA standard; Lane 4: The PCR product of pTHmc15; Lane 5: The restriction product of pTrcHisB by *Nco* I/*Bam* HI.

### The Expression of Fused cDNA *rmc15* in *E. coli*

There are 358 amino acid residues (108-1181) in the *mnp1* encoded area of natural MnP, while there are 344 amino acid residues (115-1146) in the *clg5* encoded area of the natural LiP; therefore, a fusion protein will contain 702 amino acid residues, and its molecular weight will be approximately 77.2 kD. In Fig. 3, when *E. coli* with recombinant plasmid was induced by IPTG with a different time, and analyzed with SDS-PAGE, a protein of approximately 77 kD, termed rMnP1-LiP5 (abbreviated as rML15), could be observed after a one-hour inducement, while this protein could not be observed if it was not induced by IPTG.

*E.coli* DH5 α, which contained expression plasmid pTHMC15, was cultured and induced for 4 h by 0.5 mmol/L IPTG. The cultured bacteria were then suspended in lysate. After being broken by ultrasonic waves, a small fraction of the protein solution was removed, and the enzyme activities of MnP and LiP were detected, respectively. The remaining protein solution was centrifuged, and the precipitate was stored at -20°C. The experimental results indicate that the protein expressed by *E. coli* that was transformed by either pTrcHisB and pTHmc15 had no enzymatic activity for MnP and LiP.

After thawing, the protein was folded and activated according to the literature (Nie et al. 1998; Timofeevski et al. 1999; Doyle et al. 1996), and then its enzyme activity was determined. In Fig. 4 the curve (MnP) is the absorbance at 240 nm of the solution with 0.06 mg/mL of total protein, 0.1 mmol/L $Mn^{2+}$, 0.1 mmol/L $H_2O_2$, and 0.1 mol/L lactic acid buffer (pH 4.5). The solution without recombinant protein was used as a reference. The curve (LiP) is the absorbance at 310 nm of the solution with 0.22 mg/mL of total protein, 2.0 mmol/L veratryl alcohol, 0.4 mmol/L $H_2O_2$, 0.1% Tween 80, and 0.1 mol/L tartaric acid buffer (pH3.0).

The results showed that the protein concentration of *E.coli* transformed by pTrcHisB was 1.50 mg/mL, with no enzyme activity of LiP and MnP. The protein concentration of *E.coli* transformed by PTHmc15 is 1.53 mg/mL, and the concentration of the recombinant protein (rML15) was about 0.1 mg/mL by SDS-PAGE. It can be seen from Fig. 4, after folding and activating, if the recombinant protein was treated with veratryl alcohol, the value at $A_{310}$ value did not change with time, while the value at $A_{240}$ increased with increase in reaction time if it was treated with $Mn^{2+}$. Therefore, after folding and activating, this fusion protein showed the enzyme activity of MnP, but no activity of LiP. The enzyme activity of MnP was calculated as 26.96 U/L, with specific activity as 0.3 U/mg, while the specific activity from natural MnP can be up to 100 U/mg (Gold and Glenn 1988).

## DISCUSSION

### The Folding Conditions of the Expression Result of Fusion Gene and Its Enzyme Activity

The above results show that after folding and activating of rML15, the specific activity of MnP was approximately 0.3 U/mg, just 0.3% of natural MnP. This indicates only approximately 0.3% of rML15 was correctly folded, so it is necessary to optimize the folding conditions.

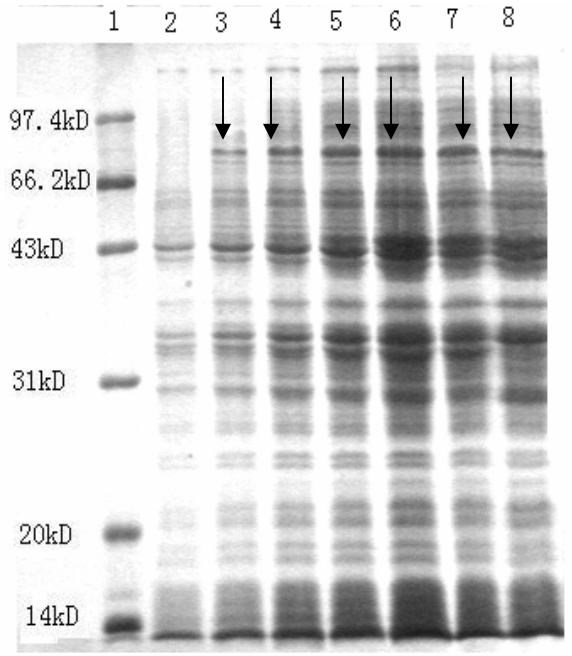


**Fig. 3.** SDS-PAGE analysis of the total proteins of *E.coli* containing expression plasmid pTHmc15.

Lane 1: molecular weight of standard protein;Lane 2: the recombinant *E.coli* without IPTG inducement;Lanes 3-8: the recombinant *E.coli* with IPTG inducement for different times: 1, 2, 3, 4, 5, 6h.

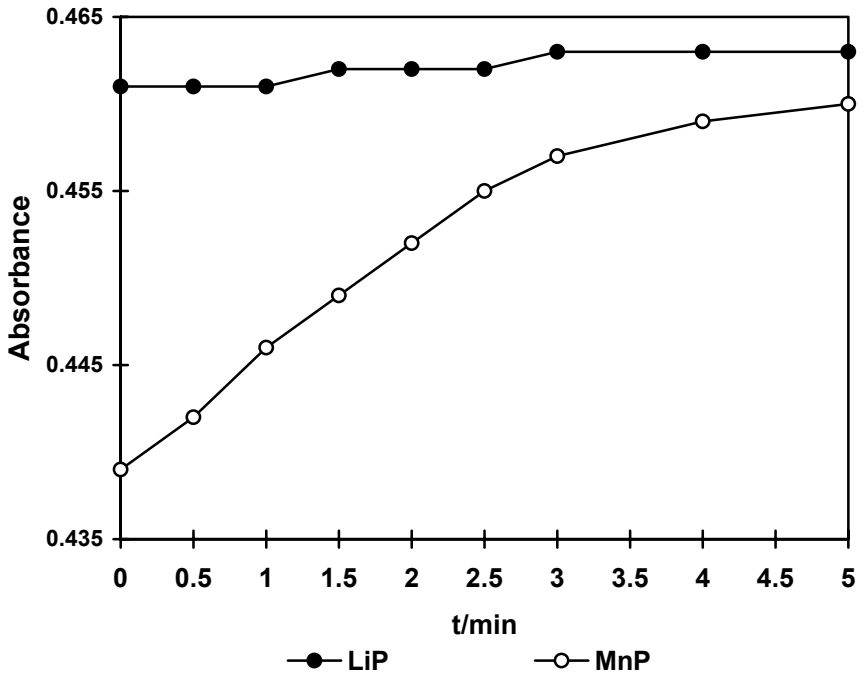


**Fig. 4.** Absorbance changes of the oxidation of veratryl alcohol and $Mn^{2+}$ by rML15.

The folding conditions of MnP and LiP in *E.coli* were performed according to earlier literature reports and on the basis of their protein structure. Nie et al. (1998), Timofeevski et al. (1999) and Doyle et al. (1996) have also discovered that the folding conditions used were all suitable for MnP and LiP. Therefore, it can be concluded that enzyme inactivity of the last kind of protein of rML15 was not due to the folding conditions. Since rML15 had been correctly translated, the main influence factor for enzyme activity of LiP is the structure of fusion protein.

### The Influence of Gene Fusion of MnP and LiP on Enzyme Activity

If the 3'-end of cDNA *mnp1* encoded MnP was directly fused with the 5'-end of cDNA *clg5* encoded LiP, the protein encoded by this fusion cDNA should be the fusion protein by direct association of the carboxyl end of MnP with the amino end of LiP. So, the third amino acid of the expressed protein should still be Cys of MnP, but the Cys of the corresponding LiP is the 361st. If this fusion protein is folded and activated by ferroheme and $Ca^{2+}$, the enzyme activity of MnP can be detected, while LiP cannot.

This result has proven that if another peroxidase gene was fused into MnP or LiP gene, the enzyme activity of the first protein will not been influenced, while that of the second protein will be affected. The essential reason may be that the existence of the first protein has influenced the correct folding of the second protein, so it is difficult for the second protein to form a three-dimensional conformation, electron shift channel and substrate binding sites, so there is no enzyme activity for the second protein.

Therefore, it is unfeasible to construct a bifunctional enzyme gene by fusing the cDNA in the encoding area of MnP and LiP.

## CONCLUSION

The mature protein coding regions of MnP cDNA mnp1 and LiP cDNA CLG5 were fused to form one cDNA called rMC15 in which the mnp1 is upstream of CLG5 by employing extend-overlap PCR.

The *E.coli* transformants containing recombinant plasmid pTHMC15 were induced with IPTG, and the total proteins were analyzed by SDS-PAGE. A new protein was observed, in which the molecular weight was approximately 77 kD, as expected.

After folding and activation by $Ca^{2+}$ and heme, the fused protein rMC15 showed only the activity of MnP but not LiP, indicating that the MnP activity was not affected, but the LiP activity was lost.

## ACKNOWLEDGEMENTS

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# $T_g$ AS AN INDEX OF CONVERSION IN PMDI-IMPREGNATED WOOD

Darren A. Riedlinger,[a] Nanjian Sun,[b] and Charles E. Frazier[c*]

It is well established that the glass transition temperature ($T_g$) is a sensitive measure of cure in neat thermosets. As cure advances, network mobility declines and the $T_g$ rises in a systematic fashion. This study sought to determine if such a relationship exists for polymeric isocyanate adhesives (pMDI) cured in the presence of wood. Yellow-poplar (*Liriodendron tulipifera*) specimens were impregnated with neat pMDI and then isothermally cured for various periods in two different differential scanning calorimeters (DSCs). After this isothermal cure period, the $T_g$ and residual heat of cure were determined. These thermal scans were performed using either constant (conventional) or modulated (MDSC) heating rates. For both methods, the degree of resin cure varied significantly under identical isothermal curing conditions; nevertheless a strong relationship was found between the degree of resin cure and the associated $T_g$. While the conventional DSC method yielded slightly improved sensitivity and reproducibility, results from both methods compared favorably.

*Keywords: Wood adhesion, Isocyanate, Cure, Glass transition temperature*

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## INTRODUCTION

The classic work by Gillham and coworkers (Wisanrakkit and Gillham 1990) established that the glass transition temperature ($T_g$) is a sensitive measure of cure in thermosets. As cure advances, network mobility declines and the $T_g$ rises in a systematic fashion. For the neat epoxy system studied by Gillham, the relation between $T_g$ and percent conversion was found to be independent of the isothermal cure temperature. This fundamental relationship has since been demonstrated for a variety of other thermosets (Cook et al. 2004; Cook et al. 1997; Harismendy et al. 2000; Li et al. 2000; Malkin et al. 2005; Park et al. 2002; Scott et al. 2002; Teil et al. 2004; Toffey and Glasser 1997).

Modeling of polymeric methylenebis(phenylisocyanate), pMDI, wood adhesive cure has significant importance for optimizing industrial hot-pressing (Harper et al. 2001). Unfortunately, reliable modeling is complicated by the fact that pMDI requires moisture to undergo cure, yet pMDI is itself water immiscible. Although pMDI will cure in the presence of water or water vapor, in such a scenario pMDI's access to water is markedly different from that of pMDI impregnated in a wood substrate. In the latter scenario the water sorbed on wood promotes reaction, but wood's complicated surface is expected to influence the cure state. For instance, it has been demonstrated that the

precise moisture content of wood and, in some instances, the wood species itself affect the reaction kinetics (He and Yan 2005; He and Yan 2007). Furthermore, competing reaction pathways exist for the isocyanate conversion and the exact nature of the pMDI-wood bond is not fully understood. The relative proportion of polyurea, biuret/polyuret, allophanate, and polyurethane bonds are strongly influenced by wood moisture, cure temperature and wood species (Das et al. 2007; Harper et al. 2001; Owen et al. 1988; Weaver and Owen 1995; Wendler and Frazier 1996). As such, the cure of neat pMDI and of pMDI impregnated wood will likely differ, and this necessitates the development of *in situ* cure monitoring. The method developed by Gillham appears to lend itself to the study of pMDI-impregnated wood specimens and may be useful for developing kinetic based hot-pressing models for wood-pMDI systems. However, the fundamental relationship between $T_g$ and isothermal cure time has only been demonstrated for neat adhesives and it is unknown if this relationship is valid for pMDI-impregnated wood. Therefore, this study was intended to determine if the wood/pMDI system will conform to the classic relationship between $T_g$ and the degree of cure.

Yellow-poplar (*Liriodendron tulipifera)* specimens were treated with neat pMDI and then isothermally cured for various times and temperatures inside a differential scanning calorimeter, DSC. After this isothermal cure period the samples were cooled and thermally scanned to detect both the $T_g$ and the residual heat of cure of the partially cured resin.

## EXPERIMENTAL

Separate DSC experiments were conducted using modulated (MDSC) and constant (conventional DSC) heating rates. In each case a commercial pMDI (Rubinate® 1840 from Huntsman Polyurethanes) was used: viscosity 166 mPa•s (25°C), NCO content 31%. Yellow-poplar flakes 0.3-0.5mm (conventional DSC) or 1.5 mm (MDSC) in thickness were sliced from the tangential wood surface using a disk flaker. The flakes were equilibrated to 7-8% moisture content over saturated aqueous $K_2CO_3$. Disks 3 mm in diameter were punched from the equilibrated wood specimen and soaked in pMDI for 5 min (conventional DSC) or 1 min (MDSC). For the MDSC specimen the excess resin was simply wiped off with tissue paper. For the conventional DSC specimen the excess resin was removed by placing the impregnated disks between tissue papers and pressed under a 10kg mass for 1 minute. The average weight increase from resination (based on the moisture equilibrated wood mass) was 52 +/-2% for the MDSC specimens and 32 +/-11% for the conventional DSC specimens. While these resin loadings were far in excess of those used in commercial applications, they approached the minimum necessary to obtain adequate heat flow responses for all DSC experiments. All specimens were analyzed immediately following impregnation.

MDSC experiments were conducted on a TA Instruments 2920 DSC equipped with a nitrogen purge (50 $cm^3$/min) and a refrigerated cooling system. Sapphire was used for the heat capacity calibration; indium was used for the temperature and cell constant calibrations. The resin impregnated disks were sealed in hermetic aluminum DSC pans and isothermally cured within the DSC at 80, 60 or 50°C for prespecified times between 0

and 16 hours. The partially cured specimens were then quench cooled to -90°C and thermally scanned at 2°C/min with a modulation amplitude of 0.4°C and a period of 60s.

Conventional DSC experiments were conducted on a TA Instruments Q100 DSC equipped with a nitrogen purge (50 $cm^3$/min) and a refrigerated cooling system. Indium was used for the temperature and cell constant calibrations. The resin impregnated disks were sealed in stainless steel high volume sample pans and isothermally cured at 80, 60 or 40°C for prespecified times between 0 and 24 hours. The partially cured specimens were then quench cooled to -90°C and thermally scanned at a constant heating rate of 20°C/min to 200°C. After this initial scan the sample was again quench cooled and rescanned over the above temperature range. This latter scan served as a fully-cured baseline and was subtracted from the initial scan, providing more reproducible measurements of the $T_g$ and the heat of reaction. For both methods, heat of reaction calculations were made with TA Instruments Universal Analysis 2000 software using the sigmoidal baseline fit model. Reported $T_g$'s are for the transition's midpoint.

## RESULTS AND DISCUSSION

### Detection of $T_g$ and Residual Cure Using MDSC

Typical MDSC thermograms for specimens precured for 0, 4 and 6 hrs (60°C) are shown in Figure 1. The non-reversible heat flow exhibits the respective cure exotherms.

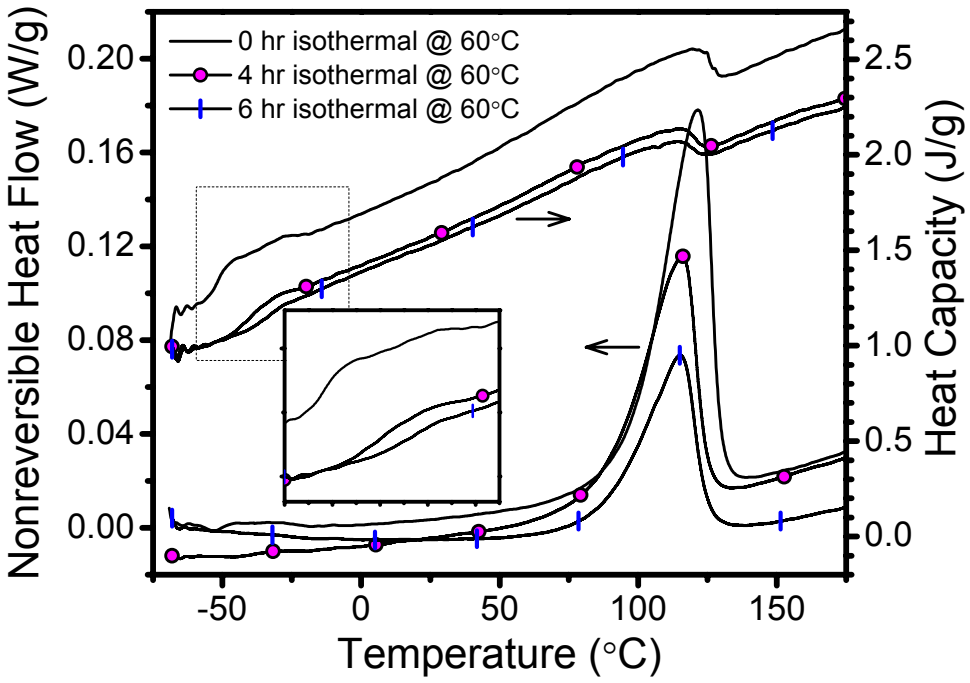


**Figure 1.** MDSC thermograms of pMDI impregnated yellow-poplar previously cured for various times at 60°C (Heating Rate = 2°C/min; amplitude = 0.4°C; period = 60s). Inset shows an expanded view of heat capacity (Tg traces).

The residual heat of reaction ($\Delta H_R$) decreased with increasing isothermal cure time, relative to the total heat of reaction ($\Delta H_T$) measured for the uncured specimen. The heat flow trace does not clearly show the resin glass transition. The heat capacity curve does reveal the $T_g$ (near -50°C), and vitrification is also seen in the high temperature region corresponding with the heat flow exotherm. As expected, the Tg rose following isothermal pre-curing. However, as the $T_g$ rose its magnitude was proportionately reduced, making accurate detection more difficult.

The fractional conversion, *x*, defined as

$$x = 1 - \frac{\Delta H_R}{\Delta H_T} \quad (1)$$

is plotted versus isothermal cure time at various temperatures in Fig. 2. Using the MDSC method, $T_g$s were unambiguously detected for factional conversion only below approximately 0.6. Figure 2 shows significant variation between fractional conversion and isothermal cure time. For example the 60°C, 4 hr cure data varied about the mean value by as much as +/- 50%. Similarly, the 50°C fractional conversions were somewhat uniform, but the corresponding cure times ranged from 6 to 15 hours. The reason for this great variation was unknown, nor was it investigated. With a 52% resin content, the MDSC specimens likely contained both adsorbed and free liquid pMDI. Perhaps the data scatter reflects differential degrees of resin adsorption and penetration. However, the corresponding plot of $T_g$ versus fractional conversion (Fig. 3) displays a clear trend that is not discerned in Fig. 2. While some scatter remains, the $T_g$ rises in a systematic fashion with increasing fractional conversion. Furthermore, this relation between $T_g$ and fractional conversion was independent of the isothermal cure temperature. While Fig. 2 exhibits a complex relationship between fractional conversion and isothermal cure time, Fig. 3 demonstrates that $T_g$ is an accurate indicator of resin cure. Furthermore, Fig. 3 validates the accuracy of the fractional conversions that varied so drastically with isothermal cure time.

## Detection of Tg and Residual Cure Using Conventional DSC

Using conventional rather than modulated heating it was possible to use a significantly greater heating rate (20°C/min vs. 2°C/min). This larger heating rate and, to a lesser extent, the greater sensitivity of the Q100 DSC increased the intensity of the observed Tg's. As such, using the conventional DSC method the Tg's were unambiguously detected in the heat flow signal even at fractional conversions greater than 0.9.

Typical conventional DSC 1st and 2nd heating scans are shown in Figure 4 along with the difference (subtraction) of these two scans. The subtraction trace exhibits an improved baseline relative to the 1st heating scan, and this made the definition of the Tg and the heat of reaction more reproducible.

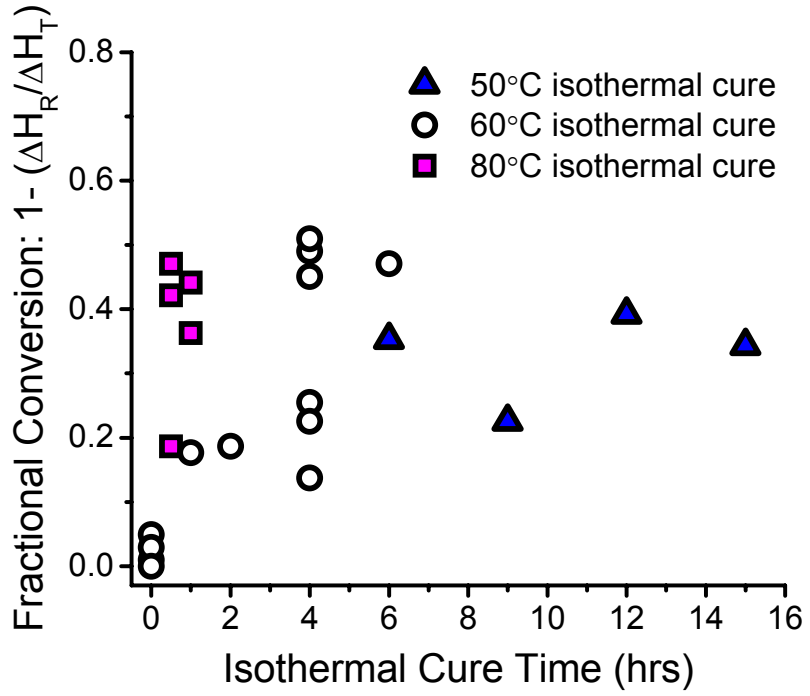


**Figure 2.** Comparison of fractional conversion versus isothermal cure time at different temperatures analyzed using MDSC.

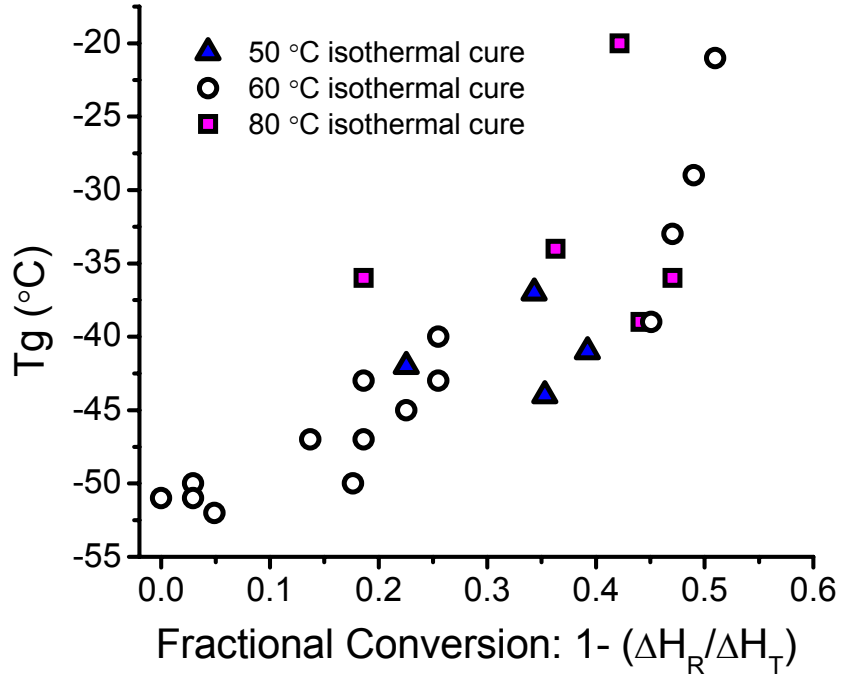


**Figure 3.** Comparison of Tg versus fractional conversion for MDSC specimens.

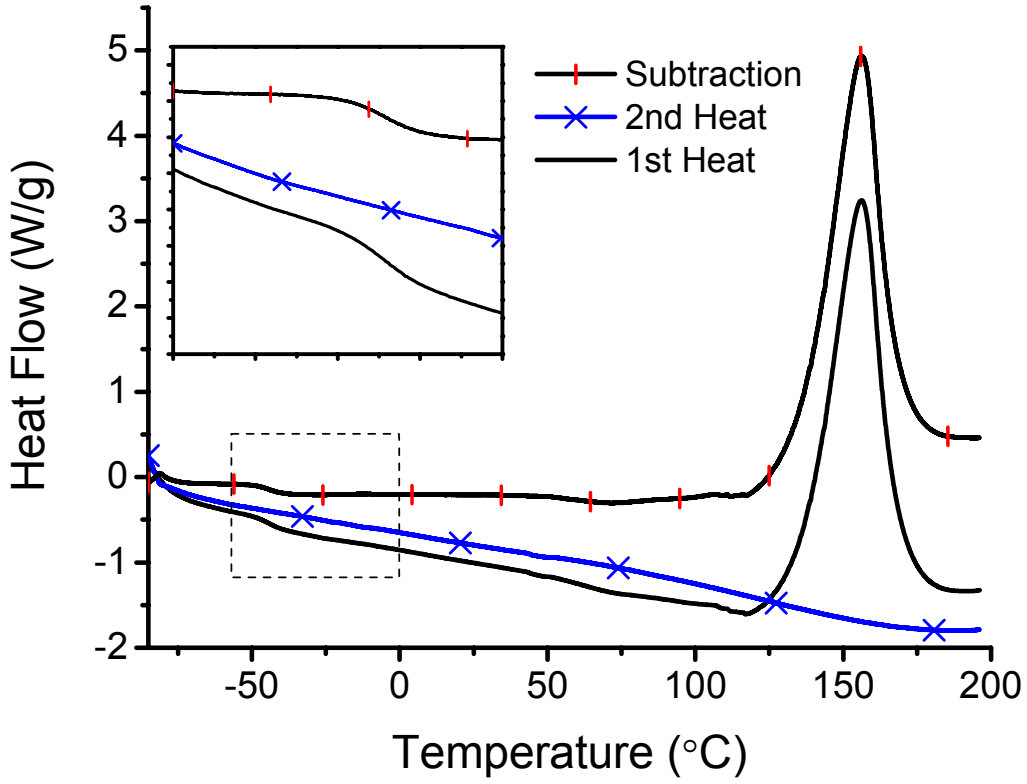


**Figure 4.** Typical conventional DSC 1st and 2nd heats and the difference thereof (subtraction) for pMDI impregnated yellow-poplar (heating rate = 20°C/min)

Analogous to Fig. 2, the plot of fractional conversion versus isothermal cure time for the conventional DSC specimens is presented in Fig. 5. Despite some improvement relative to the data in Fig. 2, Fig. 5 still shows significant variation (e.g. the 80° data at 0.66 hours and the 60°C data at 3 hrs isothermal cure). With a 32% resin content, the conventional DSC specimens should contain mostly adsorbed pMDI, in comparison to the MDSC specimens that had 52% resin. Again, it is unknown why the relationship between fractional conversion and isothermal cure time was so varied. As previously mentioned, perhaps the micro- and nanoscale penetration varied and influenced the cure rate. While the wood specimens were very small, yellow-poplar has a very uniform grain. Perhaps during wood preparation (punching from a flake) the specimens experienced different degrees of compression and damage that could influence resin penetration.

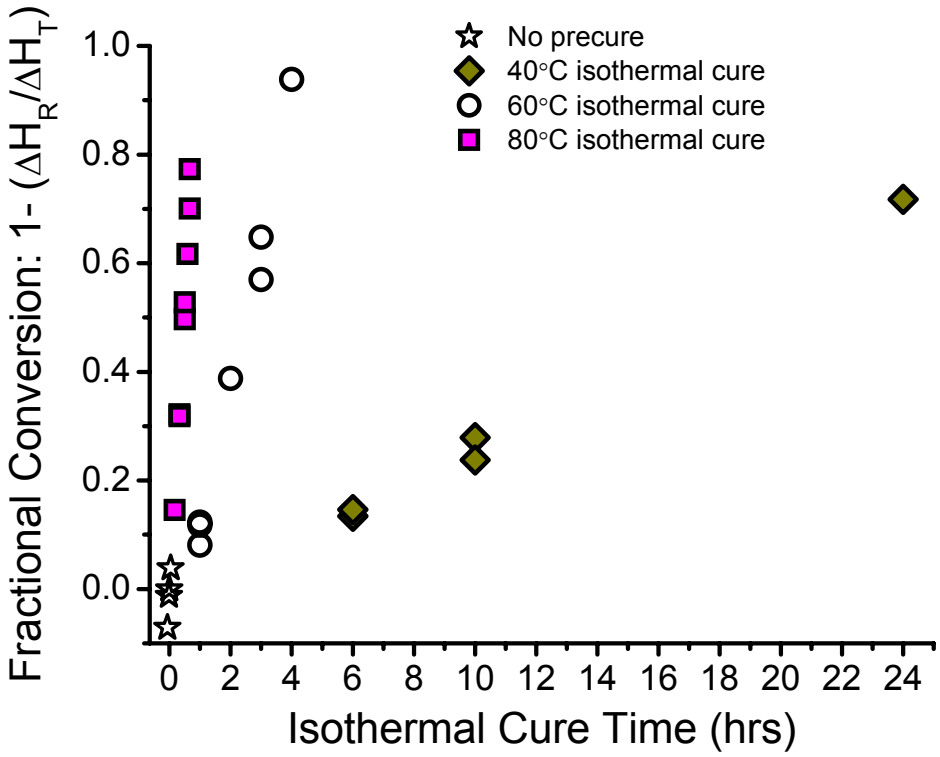


**Figure 5.** Comparison of fractional conversion versus isothermal cure time at different temperatures for samples analyzed using conventional DSC.

The corresponding plot of $T_g$ versus fractional conversion is presented in Fig. 6. The overall trend was similar to that observed in Fig. 3 using the MDSC method. Again, the $T_g$ serves as an accurate indicator of fractional conversion despite the noted variation between fractional conversion and isothermal cure time. However, the techniques employed in the conventional DSC method result in less scatter with discernable Tg's even at very high fractional conversions. This greater sensitivity and lower variability of the conventional DSC method is especially significant, considering that the conventional specimen contained approximately 60% less pMDI than the MDSC specimen.

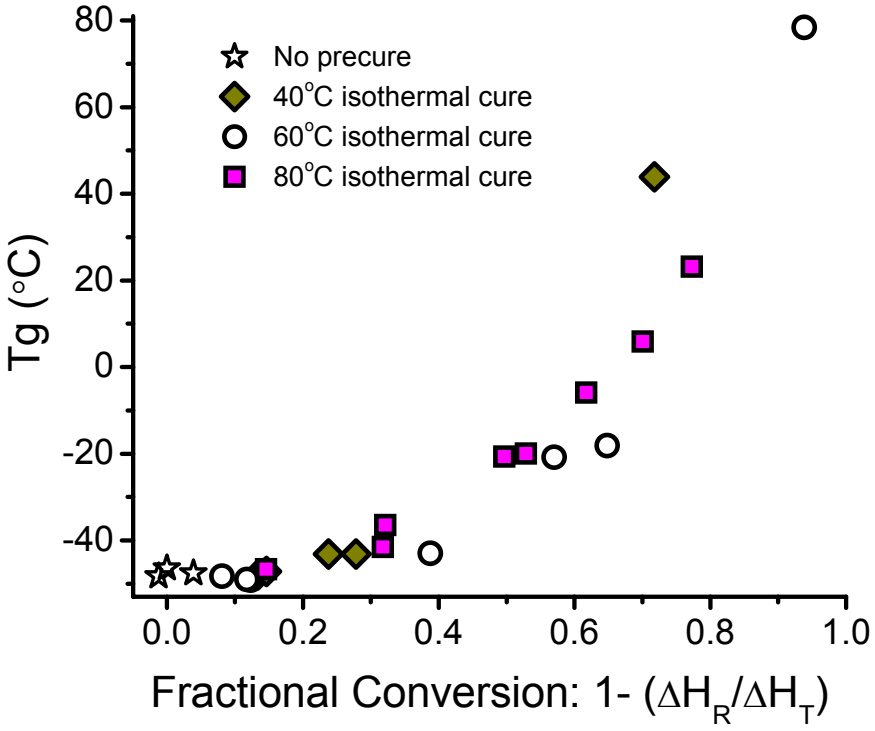


**Figure 6**. Comparison of $T_g$ versus fractional conversion for conventional DSC specimens.

Finally, $T_g$ versus fractional conversion data for the two different DSC techniques (Figs. 3 and 6) is overlaid in Fig. 7. Despite the differences in sample preparation, DSC operation, and data analysis techniques, the two methods compared favorably. As such, using DSC to measure the $T_g$ of pMDI impregnated wood appears to be a robust and reproducible method for determining the degree of conversion.

Curing of pMDI impregnated wood significantly differs from that of most neat thermosets; wood provides a complex and catalytic surface. Perhaps arising from this complexity, both the conventional and MDSC methods exhibited significant variability between $T_g$ and isothermal cure time. Despite these complexities the fundamental relationship indeed still exists between the $T_g$ and the fractional conversion of the wood-pMDI system. However, it remains questionable whether this method can actually be extended to the study of commercial OSB. Certainly the resin loadings used in this study were significantly greater than those of commercial OSB. Furthermore, actually adopting this method to a pilot-scale press system seems rather challenging. Perhaps this method's greater utility will be in investigating the species dependence of pMDI performance or as a general method for analyzing various wood/adhesive systems.

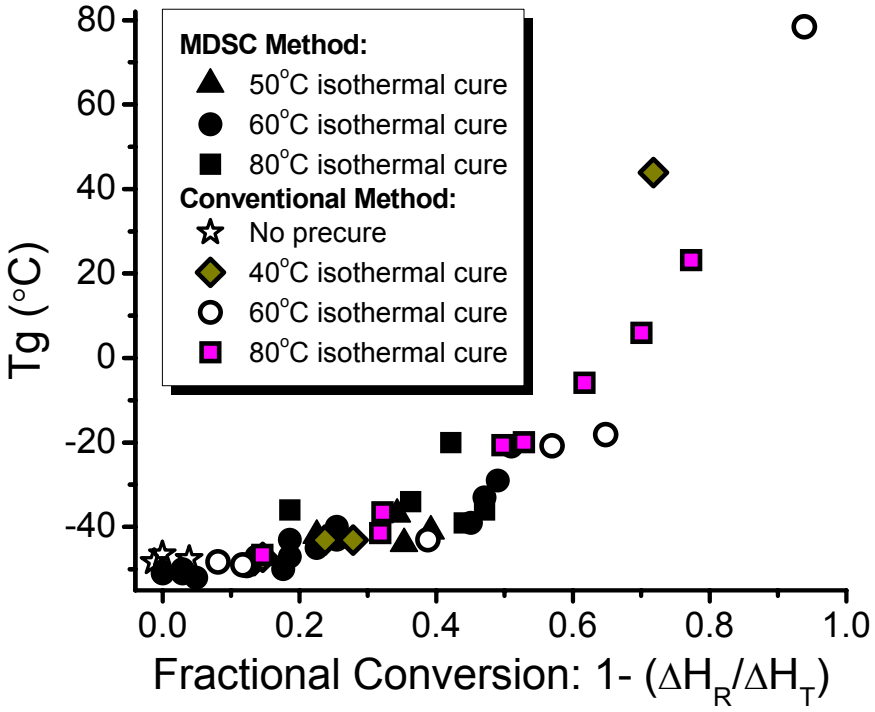


**Figure 7.** Overlay of Tg versus fractional conversion for both the MDSC and conventional DSC specimens.

## CONCLUSIONS

1. This study demonstrated a fundamental relationship between the $T_g$ and the fractional conversion of pMDI impregnated wood. Whereas this relation has previously been demonstrated for neat thermosets, the pMDI impregnated wood introduces an added layer of cure complexity involving catalytic interactions between the water, wood, and resin.
2. For both the MDSC and conventional DSC techniques significant variability was noted in the $T_g$s of specimens cured under identical conditions. However, despite the inability to accurately predict $T_g$ from the isothermal curing conditions, both methods demonstrated that the $T_g$ remains a good indicator of the system's fractional conversion.
3. The MDSC method was limited to fractional conversions below approximately 0.6, beyond which the $T_g$ could not be accurately detected. The conventional DSC techniques provided greater sensitivity with accurate $T_g$ detection possible at fractional conversion greater than 0.9. The conventional DSC results also exhibited less variability than those of the MDSC method.

## ACKNOWLEDGMENTS

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# CHEMICAL CHARACTERIZATION OF PULP COMPONENTS IN UNBLEACHED SOFTWOOD KRAFT FIBERS RECYCLED WITH THE ASSISTANCE OF A LACCASE/HBT SYSTEM

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Oxidative treatments, without and with assistance of a Laccase-Mediator System (LMS), were characterized in relation to their effects on the chemical composition and strength properties of the fibrous fraction of an unbleached recycled softwood kraft pulp. The LMS, composed of a *Trametes hirsuta* laccase extract and 1-hydroxybenzotriazole (HBT), was applied on the fibrous fraction of a recycled pulp at low consistency under continuous stirring and oxygen bubbling. Control treatments adding neither the enzyme nor the mediator were also considered. The LMS treatment caused a partial reversion of the detrimental effects of hornification. A considerable increase in the amount of carbonyl groups on the lignin structure was observed as a result of the enzyme treatment. The amount of extractives in ethanol:toluene also increased after the enzymatic treatment, and the dioxane-soluble kraft lignin underwent a noticeable decrease in its apparent molecular mass. This latter effect was readily attributed to the hydrolysis of aryl-ether bonds that survived the severity employed in the pulping process. These observations were useful to explain why LMS-recycled fibers produce handsheets with 9.4% better tensile strength than the control pulps.

*Keywords: Unbleached recycled kraft pulps, Laccase/mediator system, HBT, Trametes hirsuta, Chemical properties, Tensile index*

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## INTRODUCTION

The production and usage of paper have increased considerably over the past several years. The forecasted demand annual growth of paper and board until the year 2010 is 2.7% (Diesen 1998a). Therefore, it can be expected that environmental concerns regarding paper consumption will continue to grow. The increase in the use of wood resources as raw material, the environmental impact of industrial production, the need of more suitable landfill sites and the amount of waste to be disposed of by incineration are some of them.

The use of recycled fibers is growing rapidly. The global shares of recycled fibers in the furnish composition is expected to grow to 48% by 2010 (Diesen 1998b). For paper grades like corrugating material and cartoon board, the shares are expected be as high as 61% for the year 2010.

Recycled fibers have inferior papermaking properties in relation to the corresponding virgin fibers. The fiber detriment is ascribed to the hornification process (Nazhad and Paszner 1994; Nazhad *et al.* 1995) but other reasons have also been indicated: (a) the inactivation or decrease in hydrophilicity of the fibrous surface during drying, particularly due to the redistribution or migration of resinic and/or fatty acids to the surface (Nazhad and Paszner, 1994) and (b) changes in fiber morphology such as curling and microcompression (Page and Tydeman 1962).

Several authors have studied the effects of recycling on bleached pulps (Howard and Bichard, 1992; Bhat *et al*. 1991). However, recycling of unbleached pulps has been scarcely studied.

Oxidative treatments have been used for improving papermaking properties. Zanuttini *et al.* (2007) found that the ozone treatment of recycled liner pulps improved the interfibrillar bonding, probably due to the reversion of the inactive external surface. Nevertheless, the pulps freeness was also negatively affected.

One alternative for improving the papermaking properties of unbleached pulps could be the modification or partial removing of lignin by enzymatic treatment. Previous reports have shown the efficiency of the Laccase-Mediator System (LMS) for the wet-strength improvement of unbleached kraft pulp (Lund and Felby 2001), as well as kraft pulp delignification when followed by alkaline extraction (Chakar and Ragauskas 2000), and lignin demethylation in kraft pulp bleaching (Paice *et al*. 1995; Sealey and Ragauskas 1998). Wong *et al.* (1999) applied the laccase-HBT system on a virgin softwood kraft pulp of *kappa* 70 prior to refining. They found that, at the same density, the tensile index was increased by 6-7 units when compared to the pulp treated with the mediator alone.

Mocchiutti *et al.* (2005) found that the LMS, in combination with alkali treatment, could be useful to improve the bonding capacity of recycled softwood kraft pulps. The tensile index of the LMS-treated pulp was 11% higher than that of pulps treated exclusively with alkali. However, these authors did not characterize the effects of the LMS treatment on the chemical composition of the recycled kraft pulps.

In this paper, oxidative treatments, without and with the assistance of a laccase/ HBT system, were characterized in relation to their effects on the chemical composition and strength properties of the fibrous fraction of an unbleached recycled softwood kraft pulp. We hoped to identify whether changes in strength properties could be correlated with changes in the pulp chemistry, including data on residual lignin, carbohydrates and extractable materials.

## EXPERIMENTAL

### Materials and Methods

A softwood kraft liner paper (*kappa* 91.6) supplied by "Papel Misionero S.A." (Argentina) was soaked for 20 h, disintegrated in a standard laboratory disintegrator (freeness: 715 mL CSF), and refined in a PFI mill (TAPPI T248 cm-85) at 4000 revolutions using a 1.8 $N.mm^{-1}$ load (final freeness: 625 mL CSF). The pulp obtained was classified using a Bauer-McNett classifier (SCAN-M6:69) and only the R30 fraction was collected. This pulp fraction was separated in two parts. One part was washed with

sodium azide 0.02% ($m.v^{-1}$) and stored until use (one cycle pulp, identified as K pulp). Handsheets were formed from the other part (SCAN-C 26:76) with a grammage of 470 $g.m^{-2}$. These handsheets were dried under tension and under standard conditions (23ºC, 50% relative humidity) and subsequently oven dried at 105 ± 2ºC for 1.5 h for further storage in polyethylene bags until use.

Recycled pulps were prepared by soaking the handsheets overnight with water, followed by disintegration for 5 minutes. Metallic ions were removed by treating the fibers twice with HCl (pH 2.0) during 45 minutes. The pulp was then washed with distilled water until the pH was between 4.0 and 5.0 and stored at 4ºC until use (two cycles pulp, identified as R pulp).

*Treatment with the Laccase/Mediator System*

Laccases from *Trametes hirsuta* were produced and partially purified at the VTT Biotechnology laboratories (Espoo, Finland) as described by Poppius-Levlin *et al.* (1999). The laccase activity of 124.7 $U.mL^{-1}$ (specific activity: 11.6 U/mg protein) was determined at 40ºC and pH 5.0 (acetic acid-sodium acetate buffer, 38 mM) using guaiacol as substrate (Guillén *et al.* 1992). One unit of laccase activity was defined as the amount of guaiacol oxidized by 1 mL of enzyme per minute.

The enzymatic treatment was carried out for 4 h at 2% pulp consistency, 40 ± 1ºC and pH 5 (sodium-acetate buffer, 38 $mmol.L^{-1}$) under stirring and oxygen bubbling. The laccase extract (15.6 $U.g^{-1}$ dried pulp) was added to a solution of the HBT mediator (1-hydroxybenzotryazole, monohydrate from ICN Biomedicals) and immediately mixed with the pulp suspension. The charge of the HBT was 3% on dried pulp. After the reaction, the pulp was filtered, washed several times with distilled water and stored at 4ºC until use (identified as LMR pulp). As a control treatment, the pulp was treated as described above adding neither the enzyme nor the mediator. This pulp was identified as OR pulp.

*Evaluation of the tensile index of pulp handsheets*

Handsheets with a grammage of 60 $g.m^{-2}$ were prepared from the K, R, OR, and LMR fibrous fractions (SCAN-C 26:76). After drying at standard conditions (SCAN-P 2:75), the tensile strength was evaluated according to the TAPPI T494 om-88 Standard Method.

*Pulp chemical composition*

Moisture and ash contents were determined according to TAPPI Standards T550 and T244, respectively.

Extractives were determined by treating a fraction of the dried pulp with the following solvent sequence: ether, dichloromethane, 95% ethanol (remainder water):toluene (1:2 $v.v^{-1}$) and 95% ethanol (remainder water) according to TAPPI Standard T204. The resulting pulp was extracted with boiling distilled water according to TAPPI Standard T264.

Holocelluloses were determined following the method proposed by Guerra (2002). The pulp samples were delignified by a series four treatments with an aqueous solution of sodium chlorite in acid medium at 75°C, filtered, dried and weighed.

Hemicelluloses were isolated from the holocellulose employing 5% of KOH (wt% in water) and then 24% of KOH at 25°C for 2 h under inert (nitrogen) atmosphere. The residual material corresponded to α-cellulose. The filtrate obtained from each alkaline extraction was precipitated with a solution of ethanol:acetic acid (1:1), generating the hemicelluloses A and B, respectively. These fractions were then filtered, dried and weighed.

The pulp Klason lignin content was determined according to Gomide and Demuner (1986). Extractive-free pulps were pre-hydrolyzed with 72% (m/m) sulfuric acid at 20°C, followed by dilution to a 3% (m/m) acid strength and autoclaving for 1h at 118°C. Acid-soluble lignin was determined according to the TAPPI Useful Method 250.

The Klason lignin hydrolysates were centrifuged, filtered through a 0.45 μm nylon membrane and examined by ion exchange chromatography using a Shimadzu System model LC10AD (Kyoto, Japan) equipped with a SIL10A autosampler, a RID10A refraction index detector, and an SPD-M10A-VP photodiode array detector. The analyses were made with an Aminex HPX-87H (Bio-Rad) column at 65°C, in the presence of a precolumn Cation–H (Bio-Rad). The mobile phase used was $H_2SO_4$ 8 mM at a flow rate of 0.6 $mL.min^{-1}$. Calibration curves were obtained for each of the following components: cellobiose, glucose, xylose, arabinose, acetic acid, 2-furoic acid, hydroxymethylfurfural (HMF) and furfural. Since both 2-furoic acid and HMF displayed similar retention times, their quantification was made at different UV wavelengths because the latter has a $\lambda_{max}$ at 280 nm ($\varepsilon_{max}$ of 20156 $L.cm^{-1}.mol^{-1}$) and an ε of 3650 $L.cm^{-1}.mol^{-1}$ at 252 nm, whereas the former has a $\lambda_{max}$ at 252 nm ($\varepsilon_{max}$ of 13014 $L.cm^{-1}.mol^{-1}$) and an ε of 398 $L.cm^{-1}.mol^{-1}$ at 280 nm (or only 2% of the HMF absorptivity at 280 nm). Hence, in order to account for the interference of HMF at 252 nm, the area integration of 2-furoic acid at this wavelength was adjusted by the following equation:

$$A_{2-Fur}^{252} = A_{Total}^{252} - \left( A_{HMF}^{280} x \frac{\varepsilon_{HMF}^{252}}{\varepsilon_{HMF}^{280}} \right) \quad (1)$$

The amount of 2-furoic acid was used to quantify the occurrence of hexenuronic acids (HexA) in the kraft pulp samples. After the 2-furoic acid concentration was expressed in relation to the dry pulp mass (%, m/m), the HexA content was generated by multiplying these values by a factor of 1.5624, which corresponds to the stoichiometric conversion of 2-furoic acid to HexA.

The amounts of HMF and furfural in pulp hydrolysates were also converted back to pulp polysaccharides (glucans and pentosans, respectively) to account for the dehydration of pulp carbohydrates during hydrolysis. The conversion factors employed for this purposed were 1.4286 and 1.5625 for HMF and furfural, respectively. Likewise for HexA, these calculations were useful to obtain the mass balance of the entire acid hydrolysis procedure.

Determination of the monosaccharide constituents of extractives-free kraft pulps was based on Blakeney et al. (1982). The samples (10 mg) were treated with sulfuric acid 72% (0.125 mL) at 25°C for 45 min. After that, the acid was diluted with 1.35 mL of water and heated for 1 h at 105°C. After cooling, the samples were neutralized with

ammonia and the internal standard (*myo*-inositol) was added. The reduction of monosaccharides was made with a solution of sodium borohydride in DMSO for 90 min at 40°C. Methyl imidazole followed by acetic anhydride were added to the reduced mixture and kept for 10 min at 25°C. Cold water was then added to the mixture and the acetylated monosaccharides were extracted with dichloromethane. The resulting alditol acetates (1 μL in a 1:25 split ratio) were analyzed in a Shimadzu GC-14B gas chromatograph with detection by flame ionization (FID). Analysis were carried out in three replicates using a Supelco SP2380 capillary column (30 m × 0.25 mm), programmed from 190°C (0.5 min) at 25°C/min to 260 °C (then hold) with helium as the carrier gas. FID response factors were calculated for arabinitol (1.379), xylitol (1.076), mannitol (1.044), galactitol (1.004) and glucitol (1.003) acetates in relation to the internal standard. These components were individually expressed as anhydrous sugars before the monosaccharide composition of the kraft pulps was determined.

The molecular mass (MM) distribution of pulp holocelluloses was obtained by gel permeation chromatography (GPC) of their tricarbanyl derivatives. The procedure used for carbanylation (Ramos, 2001) was an adaptation of the method previously described by Schroeder and Haigh (1979). The GPC analysis of the tricarbanyl derivatives was carried out using a Shimadzu LC10AD liquid chromatograph. The tricarbanylated samples were solubilized in tetrahydrofuran (THF, 2.0 $mg.mL^{-1}$) and filtered through a Teflon membrane with a pore size of 0.45 μm. Analyses were carried out using a series of one TSK-L guard column and four TSK-GEL (G6000 HXL, G4000 HXL, G3000 HXL and G1000 HXL) columns at 45°C, with exclusion limits ranging from $4x10^7$ to $1x10^3$ MM units. THF was the elution solvent at a flow rate of 1 $mL.min^{-1}$ and the column eluent were monitored by UV/vis spectroscopy (Shimadzu SPD-M10A-VP) at 240 and 254 nm.

The calibration curve was generated from the elution profile of twenty polystyrene standards. A typical dispersion of 2-3% was observed in the bimodal calibration curve as a result of quadratic fitting. Universal calibration was performed using the Mark-Houwink coefficients reported by Valtasaari and Saarela (1975). The degree of polymerisation (DP) of cellulose was obtained by dividing the MM of the tricarbanyl derivatives by the corresponding MM of the per-carbamylated anhydroglucose (MM of 519 Da). Both the number average ($MM_N$) and the mass average ($MM_M$) molecular mass, from which the $DP_N$ and $DP_M$ of cellulose were derived, were determined as described previously (Yau *et al*. 1979).

*Lignin extraction and characterization*

Lignin extractions were performed in extractive-free pulp fibrous fraction. Pulp samples were Soxhlet extracted for 6 h with a 9:1 solution of dioxane:HCl 2 $mol.L^{-1}$. After removing the solvent, the lignin component was recovered in water and the pH was neutralized with sodium bicarbonate. The isolated lignins were filtered, suspended in water and freeze-dried for storage until use.

The phenolic hydroxyl groups ($OH_{phe}$) were determined by UV differential spectrophotometry according to Guerra (2002), with the lignin spectra being obtained under alkaline and acid conditions. The percentage of $OH_{phe}$ was determined by measuring the absorbance at 250 nm after the subtraction of the relative absorbance of the

baseline spectrum (acidic condition). The aliphatic hydroxyl groups ($OH_{ali}$) were estimated based on their reaction with phthalic anhydride in pyridine in the presence of benzene (Zakis, 1994). The percentage of $OH_{ali}$ was obtained by titrating the excess of phthalic anhydride using KOH.

The occurrence of acid groups in lignin was determined by neutralization with an excess of lithium hydroxide in ethanol (Zakis 1994), whereas the carbonyl groups were determined by lignin oximation with a mixture of hydroxylamine hydrochloride ($NH_2OH{\cdot}HCl$) and triethanolamine in dimethylsulfoxide (Zakis,1994).

Lignin acetylation was carried out according to Dence and Lin (1992). Lignin samples were treated with a mixture of acetic anhydride:pyridine, extracted in chloroform and dried over $P_2O_5$ and KOH after solvent elimination. Complete acetylation was ensured through the disappearance of the O-H stretching band in the FTIR spectra of the lignin derivative (data not shown).

The apparent MM distribution of each acetylated lignin derivative was obtained by GPC. Samples were dissolved in THF, filtered through a Teflon membrane with a pore size of 0.45 μm and analysed in duplicates at 40°C using a series of two TSK-GEL columns (2000HXL and 1000HXL). THF was used as the eluting solvent at a flow rate of 1 $mL.min^{-1}$ and the column eluate was monitored by UV spectroscopy at 280 nm.

## RESULTS AND DISCUSSION

The fibrous fraction (R30) of a recycled unbleached softwood kraft pulp was selected for this study because, when compared to the whole pulp, it allowed a better observation of changes in the interfibrilar bonding. Under this lower sheet consolidation, the rupture of the paper under tensile stress could be ascribed to the failure in the interfibrilar bonding, having the fiber strength a lower and/or secondary significance. According to the theory developed by Page (1969), the paper tensile strength can be used to estimate the ratio between the number of broken fibers and the number of intact fibers crossing the rupture zone of the paper sheet. For the fibers used in this work (zero span tensile index of 133 $kNm.kg^{-1}$ and tensile index lower than 40 $kNm.kg^{-1}$), this linear relationship indicates that more than 65% of the fibers would be pulled out during the rupture.

The tensile strength of the handsheets made from pulps dried at 105ºC for 1.5 h (R pulp: fibrous fraction that had two cycles) was nearly 50% lower than that made with the K pulp (fibrous fraction that had one cycle). A decrease from 44.5 to 21.9 $Nm.g^{-1}$ was observed as a result of drying under drastic conditions (Nazhad *et al.* 1995). In a direct attempt to minimize this problem, the recycled fibers (R pulp) were oxidized in the absence (OR = Oxygen Recycled pulp) and presence (LMR pulp) of a LMS (laccase-HBT) to evaluate the effect of the enzyme treatment on the pulp tensile strength. The tensile strength of OR pulp was increased to 30.8 $Nm.g^{-1}$, whereas the corresponding value for the LMR pulp reached 33.7 $Nm.g^{-1}$. This means that oxygen bubbling under continuous stirring increased the papermaking properties of the recycled kraft fibers and this favorable effect was further improved by 9.4% when the treatment was assisted by a laccase-HBT system. In both situations, it was not possible to regenerate the value

originally observed in the original pulp (K pulp) but the favorable effects of oxidation were clearly demonstrated. The chemical reasons that justify this considerable improvement in pulp properties are discussed below.

## Effect on Pulp Chemical Composition

Table 1 demonstrates that the treated fibers had lower *kappa* numbers (65-73) than the original liner paper (91.6), which includes fibers and fines. In general, the recycling procedure, without (R pulp) or with the assistance of oxygen (OR pulp) and/or the laccase/HBT system (LMR pulp), did not significantly modify the amount of holocellulose in the kraft pulp. The slightly higher holocellulose content of the K pulp was probably attributed to the experimental error usually attached to these measurements.

**Table 1.** Chemical Composition of the Untreated (K), Recycled (R) and Partially Oxidized Kraft Pulps that were Treated with Oxygen (OR) or with the Laccase:HBT System (LMR).

| Component (% on o.d. pulp) | Kraft pulp | | | |
|---|---|---|---|---|
| | One cycle | | Two cycles | |
| | K | R | OR | LMR |
| Holocellulose | 84.09 ± 0.41 | 82.78 ± 0.11 | 83.08 ± 0.23 | 83.61 ± 0.14 |
| Hemicellulose A | 5.49 ± 0.30 | 4.46 ± 0.06 | 6.94 ± 1.62 | 7.14 ± 1.79 |
| Hemicellulose B | 4.80 ± 1.40 | 8.52 ± 0.74 | 6.21 ± 2.82 | 6.40 ± 2.98 |
| Hemicelluloses A + B | 10.29 | 12.98 | 13.15 | 13.54 |
| α-Cellulose | 73.84 ± 2.56 | 73.31 ± 0.28 | 70.82 ± 0.59 | 73.23 ± 0.51 |
| Ash | 0.90 | 1.00 | 0.66 | 0.64 |
| Kappa no. | nd | 72.7 ± 0.1 | 70.9 ± 0.1 | 65.3 ± 0.3 |
| Klason lignin | 11.20 ± 0.15 | 11.14 ± 0.22 | 11.41 ± 0.92 | 11.18 ± 0.55 |
| Acid-soluble lignin | 1.74 ± 0.05 | 1.76 ± 0.21 | 2.74 ± 0.46 | 2.23 ± 0.05 |
| Total lignin | 12.94 ± 0.09 | 12.90 ± 0.39 | 14.15 ± 0.67 | 13.41 ± 0.57 |
| Extractives in ether | 0.13 ± 0.03 | 0.27 ± 0.15 | 0.13 ± 0.02 | 0.20 ± 0.03 |
| Extractives in DCM | 0.35 ± 0.05 | 0.31 ± 0.08 | 0.42 ± 0.05 | 0.32 ± 0.09 |
| Extractives in ET | 0.18 ± 0.05 | 0.91 ± 0.06 | 0.72 ± 0.01 | 1.84 ± 0.08 |
| Extractives in ethanol 95% | 0.45 ± 0.17 | 0.29 ± 0.15 | 0.71 ± 0.18 | 0.56 ± 0.02 |
| Total extractives* | 1.11 ± 0.33 | 1.78 ± 0.45 | 1.98 ± 0.29 | 4.15 ± 0.18 |
| Extractables in hot water | 0.53 ± 0.05 | 0.58 ± 0.04 | 0.36 ± 0.04 | 1.23 ± 0.02 |
| Mass balance** | 99.04 ± 0.27 | 98.46 ± 0.32 | 100.13 ± 0.87 | 101.31 ± 0.29 |
| *DCM, dichloromethane; ET, ethanol:toluene, 2:1 (v/v) | | | | |
| **Summation of the pulp content in holocellulose, total lignin, total extractives and ash | | | | |

Compared to the K pulp, the *kappa* number of the OR pulp was reduced by 1.8 units, whereas the laccase/HBT system (LMR pulp) imparted an even greater reduction of 7.3 units in this pulp property (Table 1). However, no effect was observed in the amount of acid-insoluble lignin (Klason lignin), and changes in total lignin content were solely attributed to a slight increment in acid-soluble lignin. Hence, it seems that the lower *kappa* number of both OR and LMR pulps was associated to the higher state of oxidation of their non-carbohydrate components.

Chakar and Ragauskas (2000) found that the LMS treatment caused delignification of a high kappa number pulp when the pulp was subsequently washed thoroughly with alkali. Since alkali extraction was not performed in this work, it is possible that the oxidized lignin fragments were still retained in the pulp fibers with an average MM high enough to compromise their extractability in the aqueous media.

Regardless of the presence or absence of laccases, the oxidative treatments (OR and LMR pulps) increased the total extractives content of the kraft fibers (K and R pulps) (Table 1). It seems that more extractable lignin fragments of low MM were generated by oxidation. The ethanol:toluene (1:2) mixture extracted more material from the LMR pulp than from any of the other pulps involved in this study (K, R, and OR pulps), suggesting that the LMS released a greater amount of oxidized phenolic compounds that were readily solubilized in the solvent mixture. The amount of extractable materials in ethanol 95% was also greater after both oxidative treatments but the LMS system (LMR pulp) produced less of these polar compounds than the oxidation with molecular oxygen acting alone (OR pulp). This was a preliminary indication that the laccase-assisted oxidative treatment was more specific than molecular oxygen, because compounds that are insoluble in ethanol:toluene, but extractable with ethanol 95%, are likely to be residues derived from the carbohydrate moiety of the kraft pulp. This assumption was also confirmed by the amount of extractable materials in hot water. While undetectable in the unoxidized kraft pulps, 1.23% of the LMR pulp was water extractable, a nearly four-times greater value than that of the OR pulp.

## Carbohydrates Composition and Characterization

Comparing the data of Table 1 for both K and R pulp samples, the recycling process produced a significant increase in the amount of hemicellulose B in relation to the amount of hemicellulose A. This behavior could be due to the hornification of pulp fibers, whereby the chemical accessibility of hemicelluloses is considerably decreased, together with their susceptibility to alkaline extraction. However, the oxidative treatment, without (OR pulp) and with (LMR pulp) the assistance of laccases, seemed to cause a partial reversion of this hornification effect because the ratio between their hemicelluloses A and B was closer to that of the K pulp (fibrous fraction that had one cycle) used as a reference.

The pulps derived from both oxidation procedures (OR and LMR pulps) displayed a greater hemicellulose contents than those detected in both original (K) and recycled (R) kraft pulps (Table 1). Since oxidation was not expected to result in an increase in pulp hemicellulose content, it is possible that this observation is a consequence of changes in their chemical accessibility. By contrast, the α-cellulose content remained relatively constant in all kraft pulps except the one recycled with molecular oxygen (OR), which had slightly lower values compared to that of the other pulps.

Table 2 reveals the effect of recycling on the carbohydrate composition of the unbleached kraft pulp as determined by HPLC of Klason lignin hydrolysates. These results have shown that the oxidative treatments caused no significant change in the amount of pulp glucans (mostly cellulose). This same analytical procedure also revealed that both OR and LMR pulp hydrolysates had furfural contents higher than those of the unoxidized kraft pulps (K and R pulps), suggesting that the oxidative treatments

increased the chemical accessibility of hemicelluloses. However, the proper accounting for these side reactions confirmed that none of the treatments had any significant effect on the original pulp carbohydrate composition.

For a better carbohydrate analysis, each of the kraft pulps involved in this study was hydrolysed and converted to alditol acetates for GC analysis (Table 3). In general, pulp polysaccharides were always composed of the same five monosaccharide residues, arabinose, xylose, mannose, galactose, and glucose, but the ratio among them varied a little from one sample to another. Heteroxylans were readily identified as the most predominant pulp hemicellulose. On the other hand, the carbohydrate profile of the unoxidized R30 fibrous fraction (pulp K) was similar to that of the LMR pulp, whereas the molecular oxygen-treated had a relatively lower hemicellulose content. This seemed to be consistent with the hypothesis that the LMS increased the selectivity of the process, leading to lower losses of pulp carbohydrates as a result of recycling.

**Table 2.** Chemical Composition of the Various Kraft Pulps (K, R, OR and LMR) Acid Hydrolysates in Relation to their Original Dry Mass, as Determined by HPLC

| Component (% on o.d. pulp) | Kraft pulp | | | |
|---|---|---|---|---|
| | K | R | OR | LMR |
| Glucose[a] | 70.60 ± 2.48 | 68.92 ± 2.35 | 68.75 ± 2.75 | 68.16 ± 2.13 |
| Other hemicellulose sugars[b] | 14.26 ± 1.02 | 14.04 ± 0.87 | 13.05 ± 0.46 | 12.80 ± 1.10 |
| Arabinose[a] | 1.61 ± 0.36 | 1.57 ± 0.29 | 1.51 ± 0.18 | 1.56 ± 0.22 |
| Hexuronic Acid[a] | 0.015 ± 0.002 | 0.014 ± 0.002 | 0.041 ± 0.023 | 0.041 ± 0.009 |
| Furfural[c] | 0.542 ± 0.034 | 0.522 ± 0.066 | 1.356 ± 0.350 | 1.358 ± 0.179 |
| Hydroxymethylfurfural[d] | 0.129 ± 0.011 | 0.126 ± 0.008 | 0.123 ± 0.016 | 0.131 ± 0.014 |
| Total[a] | 86.54 | 84.09 | 82.98 | 81.35 |

[a]Expressed as anhydrous sugars to represent the corresponding contribution to pulp polysaccharides (cellulose and hemicellulose)
[b]Includes sugars that are not resolved by the HPLC system: xylose, mannose and galactose
[c]Expressed as pentosan (anhydropentose) equivalents
[d]Expressed as hexosan (anhydrohexose) equivalents

**Table 3.** Chemical Composition of Pulp Polysaccharides, as Determined by GC of their Alditol Acetates

| Component (%) | Kraft pulp | | |
|---|---|---|---|
| | K | OR | LMR |
| Arabinose | 3.00 ± 0,20 | 2.34 ± 0.21 | 2.83 ± 0.43 |
| Xylose | 16.50 ± 1.75 | 14.80 ± 0.47 | 17.80 ± 1.10 |
| Mannose | 9.21 ± 0.49 | 8.21 ± 0.25 | 9.30 ± 0.39 |
| Galactose | 2.20 ± 0.43 | 1.40 ± 0.29 | 1.33 ± 0.13 |
| Glucose | 69.09 ± 1.32 | 73.25 ± 0.64 | 68.74 ± 0.84 |

There was a noticeable disagreement between the percentages of total pulp hemicelluloses displayed in Tables 1 and 2. Hence, it seemed that the gravimetric procedure based on alkali extraction (hemicelluloses A and B) did not ensure the complete isolation of pulp hemicelluloses. The subsequent analysis of the isolated α-cellulose by HPLC revealed that it still contained c.a. 7-8% of the hemicellulose content originally present within the pulp fibers (data not shown). Therefore, the total hemicellulose content (summation of hemicelluloses A and B) derived from the gravimetric procedure was partially underestimated.

The average degree of polymerization (DP) of pulp holocelluloses was similar for the original fibrous fraction (K pulp, one cycle) and the recycled fibrous fractions (OR and LMR, two cycles). The K pulp holocellulose had a $DP_W$ of 1083 anhydroglucose (AnGlc) units for a polydispersity ($DP_W/DP_N$) of 10.61, whereas the holocellulose extracted from OR and LMR had $DP_W$ figures of 979 ($DP_W/DP_N$ of 6.94) and 1028 ($DP_W/DP_N$ of 10.89) AnGlc units, respectively. Oxidation with molecular oxygen (OR) decreased the polydispersity of pulp holocellulose and this is clearly shown in Figure 1, where there is a decrease in the width of the elution profile, particularly at the region attributed to low MM oligosaccharides. By contrast, treatment of the recycled fibers with LMS prevented part of the hornification effect, with the LMR-derived holocellulose displaying a GPC elution profile very similar to that of the untreated kraft pulp.

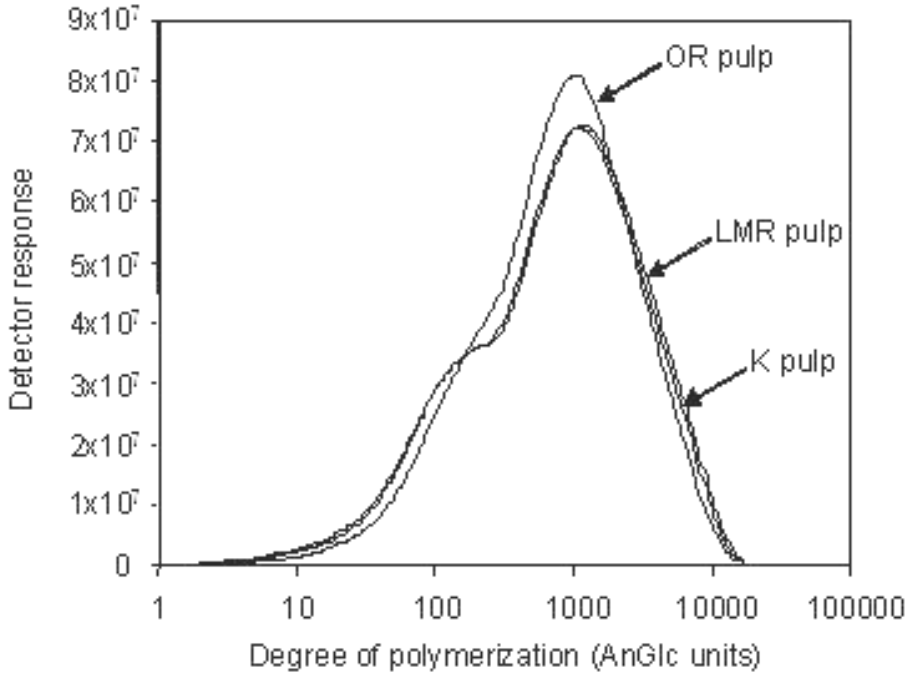


**Fig. 1.** Weight-average degree of polymerisation of holocellulose fractions derived from unrecycled (K) and recycled (OR and LMR) kraft pulps

The hexenuronic acids (HexA) were determined indirectly by the HPLC quantitation of 2-furoic acid at the retention time of 29.8 min and UV detection at 252 nm. For this purpose, the residual HMF absorptivity at this wavelength was subtracted from the detector readings as already described in the methods section. Both oxidative treatments had a measurable effect on the amount of HexA, but the detected levels were very low in relation to other pulp components.

## Lignin Analysis

Lignin isolation was carried out by extracting untreated and partially oxidized kraft pulps with dioxane:HCl 2 $mol.L^{-1}$, 9:1 ($v.v^{-1}$). The average extraction yield varied between 6-7% of the original dry pulp mass.

GPC analyses were carried out after lignin acetylation. Figure 2 shows that the pulp drying followed by an oxygen treatment (OR pulp) produced an increment in the lignin apparent MM. It seems that lignin condensation reactions and/or an increase in associative intermolecular forces produced this slight displacement of the elution band. By contrast, the enzymatic treatment on the recycled fibrous fraction (LMR pulp) reduced this effect on the lignin structure, generating lower MM lignin fragments that were detected at higher elution volumes (around 26 min in Figure 2). Compared to the K pulp, pulp drying followed by the enzymatic treatment also decreased the amount of intermediate MM lignin fragments, leading to the accumulation of oligomers that seemed to correspond to a typical homologous series because their respective elution volumes suggested the loss of lignin fragments with almost equivalent average MM.

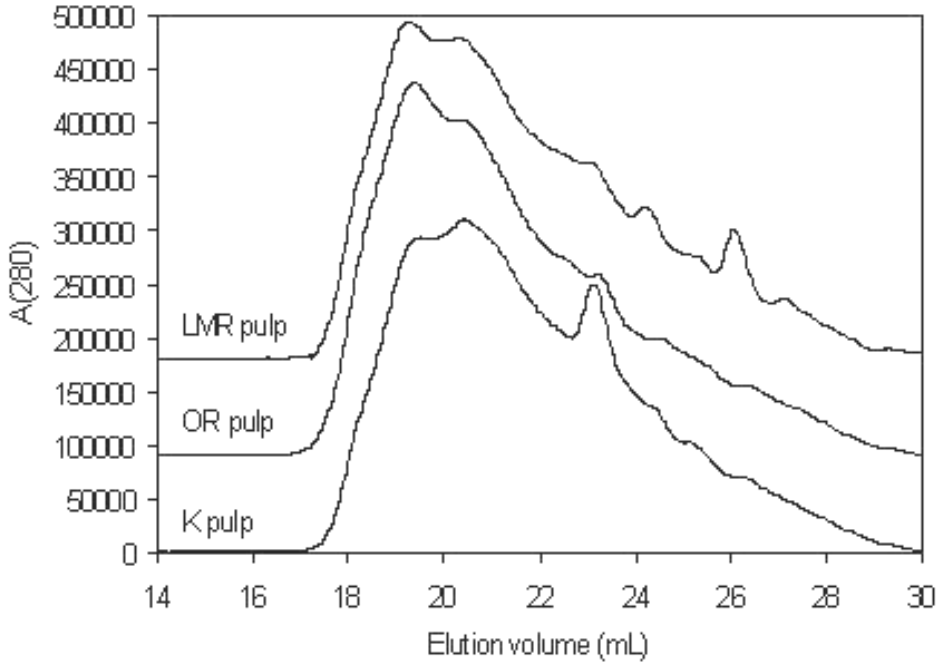


**Fig. 2.** Gel permeation chromatography of per-acetylated dioxane lignins isolated from unrecycled (K) and recycled (OR and LMR) kraft pulps

The oxygen treatment (OR pulp) also changed the amount of oxygenated functional groups in lignin (Table 4). Compared to the control (K pulp), there was an increase in $OH_{phe}$ groups and a decrease in $OH_{ali}$ groups, suggesting that oxidation was probably associated with the cleavage of arylether bonds and the modification of aliphatic side chains. The assistance of a laccase-HBT system changed this pattern considerably: a small, but noticeable increase on $OH_{phe}$ was observed and there was a lower decrease in $OH_{ali}$ groups.

Both oxidation procedures increased the amount of carbonyl and carboxyl (acid) groups in lignin. The LMS treatment increased the occurrence of these two functional groups by a factor of 8, whereas a much lower effect was observed as a result of oxidation with molecular oxygen (factors of 4.23 and 2.78 times, respectively). These modifications in the lignin structure, which are potentially beneficial for the bonding capacity of the fibers, revealed the selectivity of the laccase-HBT system for the phenolic structures found in lignin. This was also apparent from the FTIR analysis of the isolated lignins (data not shown). The C=O stretching vibration in LMR lignin was much broader and slightly displaced towards lower wavenumbers, revealing that the use of laccases increased the occurrence of conjugated carbonyl groups in the laccase-HBT recycled kraft fibers.

**Table 4.** Determination of Functional Groups in Dioxane Lignins Isolated from Kraft Pulp Samples (K, OR, and LMR)

| Component (% of lignin mass) | Kraft pulp dioxane lignin | | |
|---|---|---|---|
| | K | OR | LMR |
| $OH_{phe}$ | 0.305 ± 0.011 | 0.490 ± 0.099 | 0.315 ± 0.056 |
| $OH_{ali}$ | 0.825 ± 0.014 | 0.526 ± 0.164 | 0.623 ± 0.033 |
| Acid Groups | 0.090 ± 0.013 | 0.250 ± 0.004 | 0.720 ± 0.014 |
| Carbonyl Groups | 0.220 ± 0.058 | 0.930 ± 0.179 | 1.790 ± 0.180 |

## CONCLUSIONS

The Laccase/Mediator System (LMS), composed of laccases from *Trametes hirsuta* and HBT, produces changes in the chemical composition of unbleached recycled kraft pulps that contribute to the improvement of their bonding capacity. Compared to the control pulp, the results obtained from the LMS treated pulp led to the following conclusions: (a) the LMS treatment caused a partial reversion of the detrimental effects of fiber hornification; (b) pulp oxidation increased the amount of extractable materials in polar extraction solvents, and the assistance of the laccase/HBT system (LMS) increased this effect even more; (c) the apparent molecular mass of the kraft lignin decreased and the lignin acid groups and carbonyl groups increased as a result of the oxidative action of the LMS treatment.

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# LACTOSE TO NATURALIZE TEXTILE DYES

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Many natural dyes, for example carminic acid, are soluble in water. We present a simple strategy to naturalize synthetic azadyes through their linkage with lactose to induce their water solubility. The dyeing process of textile fibres then becomes possible in water without additives such as surfactants and mordants, which result in products that are difficult to eliminate. Glyco-azadyes (GADs) we are presenting here are obtained through a diether linker to bond the azadye and the sugar. Tinctorial tests were carried out with fabrics containing wool, polyester, cotton, nylon, and acetate. GADs were found to be multipurpose and capable of dyeing many fabrics efficiently under mild conditions.

*Keywords: Lactose, Conjugation, Dyeing , Azadyes, Ethers*

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## INTRODUCTION

Dyeing chemistry started from an early time, during a period when the majority of dyes were extracted from natural compounds, i.e. from vegetable and animal sources. Currently the global production of textile dyes is estimated to be $7x10^5$ tons per year (Neamtu et al. 2002), and a significant part of this quantity is eliminated in the effluents of dyeing plants, polluting salt and fresh waters throughout the world.

Dyes are generally applied in an aqueous solution and they require auxiliary chemicals to improve the dyeing process. For instance, surfactants are used to increase solubility, mordants to enhance the fastness of the dye on the fibers, and salts to adjust the pH. Effluent from textile industries therefore can contain a broad spectrum of contaminants, such as highly hydrophobic dyes, suspended solids, chlorinated organic solvents, surfactants in huge concentrations, mordents, metals, etc. (Poon et al. 1999). Reactive dyes are another class of environmentally dangerous textile dyes; as the name suggests, these are very reactive molecules that form covalent bonds with fibers, but they also react with water, leading to inherent losses. Moreover, it's well known that the azo molecules can degrade to aromatic amines, which can further damage the environment if they are released (Neamtu et al. 2000). Selective treatment of effluent is not possible, because the type and extent of contamination varies, depending on the fabric dyed or the class of dye used. Because most pollutants present in the water have different physical and chemical properties, normally the chromophores are attacked using oxidative treatments of the contaminated waters (ozone, $H_2O_2$, UV), removing only the visible pollution (Rott and Minke 1999; Bianchini et al. 2002; Selcuk 2005). These treatments are efficient for the depletion of the colour, but the yields of these are variable and the final oxidation products (Mascolo et al. 2002) are often unknown; most importantly, the colorless oxidation products are possibly even more dangerous than the starting dyes (Pierce et al. 2003).

Because of the large variety of species present, a biological approach is also difficult. Therefore, increasing attention has been devoted to natural dyes, with the aim of finding environmentally friendly materials. Natural dyes extracted from plants or animals do not cover all the market requirements, and their isolation from natural sources is difficult.

Furthermore, the impact on the environment is far from negligible when high quantities of dye are required. These factors, together with the cost of these processes, have slowed the development of dyes based on natural products. In order to devise a new strategy to solve these problems, we initiated a naturalization of synthetic dyes, by means of their glycosylation (Bianchini et al. 2004). The aims of this attempt are multiple: a) use of carbohydrates, which are widely and cheaply available, such as lactose, or D-glucose and D-galactose; these compounds often are discarded in huge quantities to the environment, and the environmental impact should not be neglected; b) achievement of hydrophilicity of dyes through their glycoconjugation, so that dyeing processes with dispersed dyes could be carried out without surfactants, which can be very difficult to treat; c) attainment of easier dyeing processes, avoiding high temperatures and high pressures; d) increased affinity towards the textiles, improving efficacy, and reducing waste; e) possibility of efficient and more selective waste treatments using, for instance, live micro-organisms to attack the sugar moiety and consequently the covalently bonded chromophoric part, or the use of enzymes able to destroy dyes; and f) preparation of multipurpose dyes able to dye different fabrics (synthetic, natural, artificial).

On the other hand, also some natural dyes are endowed with saccharidic moieties. For instance, the well known carminic acid is such a dye, but the characteristic is more general, since the hydrosolubility is often a requirement of this class of dyes. Therefore, we devised a completely new approach, consisting on the preparation of glyco azadyes, we will call 'naturalized dyes'. The word naturalize refers to the use of a natural glycide, lactose, that in our process glycoconjugates the dye. As in carmicic acid or other similar natural compounds, a chromophore is transformed into a hydrosoluble species through glycoconjugation with a sugar.

## EXPERIMENTAL

### General Methods

The synthetic details of our approach are given in two recent papers (Bartalucci et al. 2007, Bianchini et al. 2007). Red azadye **1a** (Disperse Red 1) is commercially available (Sigma-Aldrich), yellow dye **1b** was prepared according to literature (Podsiadly 2003). Literature methods were used to prepare 6'-O-(1-methoxy-1-methylethyl)-2,3:5,6:3',4'-tri-*O*-isopropylidenelactose dimethyl acetal **2** (Barili et al. 1997).

To measure reflectance a spectrophotometer Varian Cary 4000 was used, endowed with reflectance apparatus. Fastness was measured according to ISO 105 (X-12) C06 standard pattern.

### General Procedure for the Preparation of Protected GADs:

A mixture of the appropriate etherified sugar (1.0 mmol), KOH (4.0 equivalents) and 18-crown-6 ether (0.01 equivalent) in THF (10 ml) was stirred at room temperature for 1 hr, then the dye was added and the mixture left stirring under the same conditions for several hours. The mixture was then neutralized with a saturated aqueous solution of $NH_4Cl$ and extracted with $CH_2Cl_2$. The organic phase was dried over $Na_2SO_4$, concentrated, and the resulting residue purified by flash chromatography.

## RESULTS AND DISCUSSION

GADs are a new class of naturalized, multipurpose, glycoconjugated dyes, consisting of a synthetic, commercially available dye linked to a saccharide from natural and renewable sources (lactose, D-glucose, D-galactose). The linkage is made using a bifunctional linker.

The modification of the azadyes is carried out on their side chain in order to avoid changes on the chromophoric group and maintain their original colour. The choice of difunctional linkers to be used for the linkage of glycide and dye has been devised on the basis of their ease availability and the simplicity of the practical procedure, with the final aim of an industrial development of the new glycoazadyes. Figure 1 shows two complementary approaches to synthesis these GADs: Path "a" begins by attaching the linker to a protected glycide, while path "b" starts in the reverse order. The resulting structures are diethers, with the formation of two etheric bonds, one between the sugar and the bridge, and a second between the bridge and the hydroxyl group on the side chain of the azadye. Furthermore, the ethers have proven to be stable even under the stressful conditions of dyeing.

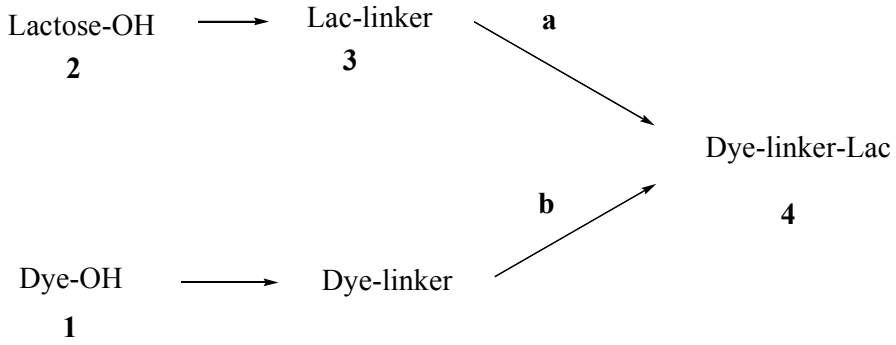



**Figure 1.** Schematic approach to glycoazadyes (GADs)

The study of the influence of GADs glycosidic moiety on the tinctorial properties is the aim of this research. For this purpose, protected lactose (**2**, Fig. 2), together with other protected and linked monosaccharides here not reported for brevity, have been selected in order to prepare a collection of building blocks that can be used to prepare final different GADs.

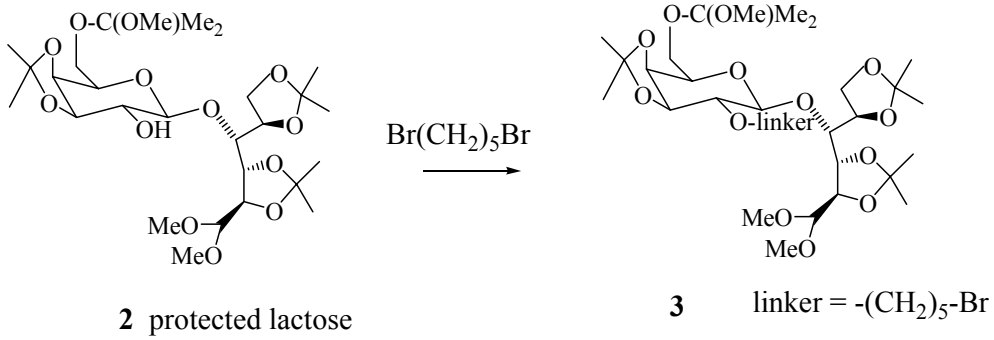
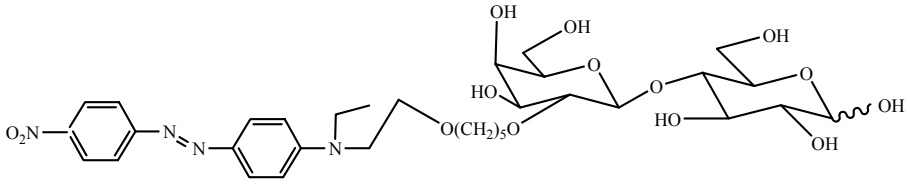
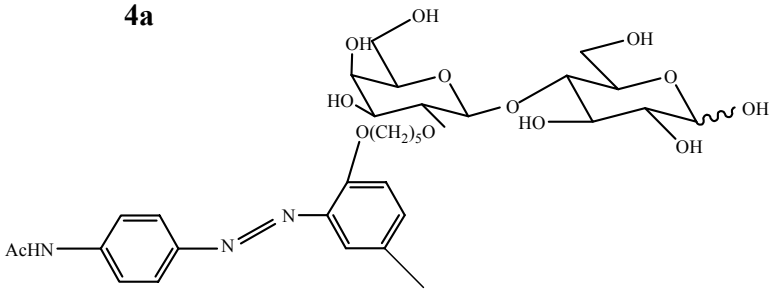



**Figure 2.** Protected lactose, and linked lactose

These modified glycides were used to react with a number of azadyes: Here are shown 2 of them, corresponding to the GADs of red disperse **1** (**1a** and yellow disperse 3 (**1b,** Fig. 3). Of course, products **4a** and **4b** are obtained upon final, single-step, deprotection following the coupling between the linked lactose and the dye, or the linked dye with the protected lactose but bearing a free hydroxyl in position 2'.




**4a**




**4b**

**Figure 3.** list of modified dyes

## Tinctorial Tests

Preliminary tinctorial studies were carried out on these GADs, and some of the results are reported in the following tables, thanks to a collaboration with "Italvelluti" SpA Company (Montemurlo, Italy). Later these tests were confirmed and extended by the Lanartex cnc company (Montemurlo, Italy). In Table 1 are shown the conditions of dyeing with this new class of dyes, based on the conjugation with lactose.

Table 1. Dyeing with GADs

| *fabric* | *polyester* | *cotton* step 1 | *cotton* step 2 | *acetate* | *wool* | *acrylic* |
|---|---|---|---|---|---|---|
| Temperature bath (°C) | 98 | 80 | 98 | 84 | 98 | 98 |
| Time (min) | 30 | 35 | 15 | 30 | 20 | 30 |
| Bath Ratio[1] | 50/1 | 50/1 | 50/1 | 50/1 | 50/1 | 50/1 |
| Dye conc. (g/l) | 1,0 | 1,0 | 1,0 | 1,0 | 1,0 | 1,0 |
| Acetic acid added | 1% | -- | --- | 1% | 1% | 2% |
| other | --- | $Na_2SO_4$ (10gr/l) | $Na_2CO_3$ (0,5g/l) | -- | $(NH_4)_2SO_4$ | |
| Fastness[2] | 4 | | 4/5 | 4 | 3 | 3/4[2] |

[1]mL of water/fabric(g)
[2]washing and scraping fastness

The first evidence consists in the 'multipurposity' that characterizes now the initial aza-dye, that is a disperse dye in origin. But, as a matter of fact, when the naturalization process is carried out, through the glycoconjugation with lactose, the original dye becomes able to dye extremely different fabrics, extending from natural to artificial and synthetic ones. Moreover, the conditions applied for the dyeing processes are extremely mild and easy, especially, for example, upon considering the conditions for polyester. Polyester can be dyed with these GADs in basic conditions, not only using an acidic medium, as usual, and at a temperature near the water boiling point, but far from the 130 °C used for this fabric. Finally, no surface-active agent is added, as reported in the table, which is an evident environmental advantage. Let's consider the last row. The fastness obtained for each fabric can be considered as the evidence that the dyeing is not a lacquering, but it is in fact a proper dyeing, with good results. Also, here we are reporting on the tristimulus values for each dye and fabrics, so that the colours are well defined in the coordinates of luminosity, chromaticity, and tone, as we can see from Table 2. These tabulated values can be considered as a clear-cut demonstration that dyeing works with natutalized dyes, and that this is now an open research space for textile innovation.

Table 2- Tristimulus values for tissues dyed with GADs

| *Champion* | *material* | *luminosity* | *Chromaticity* | *Tune* |
|---|---|---|---|---|
| **4a** | Wool | 53,936 | 39,920 | 32,778 |
| **4a** | Nylon[1] | 42,816 | 61,373 | 43,612 |
| **4a** | Acetate[1] | 43,921 | 65,709 | 41,513 |
| **4a** | Cotton | 66,850 | 26,393 | 27,380 |
| **4a** | Polyester[2] | 62,126 | 46,993 | 29,776 |
| **4a** | Polyester[3] | 71,917 | 32,502 | 32,430 |
| **4b** | Wool | 74,075 | 47,630 | 85,632 |
| **4b** | Nylon[1] | 76,454 | 65,012 | 85,532 |
| **4b** | Acetate | 73,584 | 76,054 | 89,939 |
| **4b** | Polyester[1] | 78,994 | 60,524 | 82,505 |

[1]values read on a multi-fabric witness. [2]Dyed in a basic way (see Table 1)
[3] Dyed in a acid way.

Also we are confident that Table 3 will add important information on the quality of dyeing using these new generations of dyes. And in fact we can see that using ethereal glycoconjugated derivatives of Red (**4a**) or yellow (**4b**) dyes, we gave reflectance values at the two more significant wavelengths, and also K/S values, where K stands for the Kubelka-Munk absorption coefficient and S represents the scattering coefficient at the respective wavelength. Of course where we have high values of reflectance the absorption is low, and scattering is high, and viceversa.

Table 3- Reflectance and K/S Values of Fabrics Dyed with GADs **4a** and **4b**

| **4a** | | | | | **4b** | | | |
|---|---|---|---|---|---|---|---|---|
| febric | R% (500 nm) | R% (700 nm) | K/S (500 nm) | K/S (700 nm) | R% (450nm) | R% (700nm) | K/S (450 nm) | K/S (700 nm) |
| wool | 8 | 63 | 7,5 | 0,2 | 12 | 60 | 2,5 | 0,1 |
| Nylon | 5 | 65 | 9,5 | 0,1 | 10 | 63 | 5,5 | 0 |
| Acetate | 12 | 75 | 3,7 | 0,0 | 2 | 55 | 15 | 0 |
| Cotton | 20 | 72 | 1,7 | 0,1 | | | | |
| Polyester[1] | 20 | 1,6 | 1,6 | 0,2 | 10 | 72 | 3,9 | 0 |

[1]Dyed in basic conditions (see Table 1)

We think that these data can be considered as a demonstration that environmentally compatible naturalized dyes can work appreciably well in the dyeing processes. The tests showed that these generations of GADs are soluble in water, as expected, and also that these dyes are multipurpose, since they dyed all of the fabrics so far tested. The results of some of these tests are reported in Fig 1. In this case the polyester has been dyed according to the basic procedure reported in Table 1. As far as we know this is the first time that a dye, which is in principle a disperse dye, at the end of story is able to directly dye wool and polyester under mild conditions. These tests, and many others not reported here, since they are covered by a deposited patent, or others on the way, have been carried out under standard conditions and were performed in water without the addition of surfactants, under mild conditions of temperature and pressure. Dispersed dyes, such as the starting azadyes, do not effectively dye wool, and they dye polyester only under drastic conditions (such as high temperature or pressure).

**Figure 1.** Polyester (upper row) and wool (lower row) dyed with **4a** (left) and **4b** (right).

## CONCLUSIONS

A naturalization of industrial commercial dyes has been proposed, in order to maintain their good properties and improve their applications to various textiles. The synthetic modifications applied have brought:

- a higher hydrophilicity of dyes through their glycoconjugation, so that the trial dyeing processes have been carried out without the use of surfactants, or other potential pollutants;
- easier dyeing processes, avoiding high temperatures and high pressures;
- better affinity towards textiles, improving efficacy and reducing waste;
- multipurpose dyes able to dye different fabrics (synthetic, natural, artificial);

- the utilization of carbohydrates largely and cheaply available such as D-glucose, D galactose and lactose; normally discarded in huge quantities in the environment, with not negligible impact;
- new possibilities for efficient and more selective waste treatment by using, for instance, live micro-organisms to attack the sugar moiety and consequently the covalently bonded chromophore, or the use of enzymes able to destroy dyes.

## ACKNOWLEDGMENTS

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# ISOLATION OF PECTIC ACIDS FROM BLEACHED TMP WATER AND AGGREGATION OF MODEL AND TMP PECTIC ACIDS BY CALCIUM

Ville J. Saarimaa,* Andrey V. Pranovich, Anna C. Sundberg, and Bjarne R. Holmbom

Pectins are important structural elements in spruce fibres. Alkaline peroxide bleaching of spruce thermomechanical pulp (TMP) causes degradation and demethylation of pectins, yielding high-charge-density pectic acids. The pectic acids in fibres contribute strongly to the negative fibre charge, and the dissolved pectic acids increase the cationic demand of bleached TMP water. In this study, a method to isolate pectic acids from peroxide-bleached TMP pulp water is presented. The pectic acids were isolated and purified in good yield using a polyacrylate resin to remove lignin, a cellulose filter to remove galactoglucomannans (GGM), and an anion exchange resin to separate pectic acids from neutral carbohydrates. Salts and residual low-molar-mass carbohydrates were further removed from the isolated pectic acids by dialysis. The isolated pectic acids (>80% purity) had a low molar mass and a wide polydispersity (5.9 kDa, $M_W/M_N$ 3.3). The aggregation and precipitation of the isolated pectic acids, as well as citrus fruit pectic acids with well-defined molar masses, by $Ca^{2+}$-ions were studied. The molar mass of pectic acids was a key factor determining the precipitation of $Ca^{2+}$-pectates. Pectic acids below 6 kDa were not precipitated by $Ca^{2+}$, while higher molar masses led first to partial and then to complete precipitation. The precipitated $Ca^{2+}$-pectates may impair paper machine runnability and paper quality.

*Keywords: Spruce pectic acids, Calcium, Aggregation, TMP, Peroxide bleaching*

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## INTRODUCTION

Pectins are traditional gelling agents, thickeners, and water binders. Pectin-containing fruits, such as apple and currant, have been well known for centuries for their unique properties, which give gels and jellies their specific consistency (International pectin producers association 2007). Today, pectins are widely used as additives in many foods, such as yoghurt and ketchup, and also in pharmaceutical applications (Schols and Voragen 2002). The presence of pectins as fibre wall constituents in wood was demonstrated for the first time in the beginning of the 20th century (Hägglund 1928). Pectins in wood are largely composed of a backbone of methylated D-galacturonic acid units occasionally interrupted by L-rhamnose units. Later on, clarification of the morphological distribution of pectins in pine and spruce fibres led to increased attention to potential effects of pectins in papermaking from softwoods (Sjöström 1989; Rättö et al.

1993; Thornton et al. 1993; Westermark and Vennigerholz 1995; Sundberg K. et al. 1998). Pectins are concentrated in the primary wall and middle lamella (Westermark et al. 1986). Norway spruce (*Picea abies*) is a commonly used softwood species in production of mechanical pulp and paper in northern Europe. Although the concentration of pectins in spruce is relatively low (1-2%), pectins, together with xylans, are generally accepted to be the main contributors to anionic fibre charge of spruce pulp (Sjöström 1989; Sundberg A. et al. 2000). The anionic fibre charge is essential for adsorption of cationic papermaking polymers, such as retention aids, on fibres, and for fibre swelling. Fibre swelling in turn positively influences fibre bonding area, higher bonding area being beneficial for pulp and paper strength properties (Engstrand et al. 1991). Mechanical pulping introduces new fibre surfaces, exposing pectin-rich fibre middle lamellas and primary walls. Also cellulosic fine material, which is particularly rich in those fibre regions, is released during mechanical defibration (Hardell et al. 1980). Mechanical pulps are commonly bleached using hydrogen peroxide under alkaline conditions. Mainly due to high pH, during peroxide bleaching pectins are degraded to low-molar-mass fractions and demethylated, which causes 1/3 of the original pectins in fibres to dissolve into process water as high-charge-density pectic acids (Thornton et al. 1993; Pranovich et al. 2003). The residual pectic acids in fibres and fines contribute strongly to increased charge properties of TMP after peroxide bleaching, and the dissolved pectic acids constitute the major part of anionic charge (cationic demand) of bleached TMP water (Thornton et al. 1993). Due to their capacity to consume cationic retention chemicals, pectic acids are commonly regarded as detrimental substances, or so-called anionic trash, in papermaking (Thornton et al. 1993; Kekkonen et al. 2002; Ricard et al. 2005a,b). Degradation of the polymeric pectic acids into monomeric galacturonic acid by enzymatic pectinase treatment has been suggested and actually already used in some paper mills in order to eliminate their detrimental effects (Thornton 1994; Thornton et al. 1996; Reid and Ricard 2000; Peng et al. 2003; Ricard et al. 2005a,b).

Apart from forming complexes with cationic polymers, pectins are known to interact with cations such as $Na^{+}$, $Mg^{2+}$, $Ca^{2+}$, $Cu^{2+}$, $Cd^{2+}$, $Ni^{2+}$, $Zn^{2+}$, $Pb^{2+}$, and $Sr^{2+}$ (Kohn 1987; Dronnet et al. 1994). Complexes with $Na^{+}$ and $Mg^{2+}$ are water soluble, while aggregation with other cations brings about precipitation of corresponding pectates (Rolin 1993; Wellner et al. 1998). In mechanical pulping, especially in peroxide-bleached TMP, $Na^{+}$, $Ca^{2+}$, and $Mg^{2+}$ are some of the most abundant metal ions (Sundberg A. et al. 2000). Calcium concentrations in mechanical pulping and bleaching can be really high, especially if calcium carbonate or gypsum are used to fill or coat papers and the circulation waters from paper machine are run in countercurrent flow to pulp and paper production (Bräuer et al. 2001). The aggregation of pectins and pectic acids by $Ca^{2+}$-ions has been well established in literature (Grant et al. 1973; Dronnet et al. 1994; Garnier et al. 1994; Bracchini and Pérez 2001; Capel et al. 2006). $Ca^{2+}$-complexation is a two-stage process with an initial, strong dimerization of pectins by cross-linking, followed by formation of weak inter-chain associations governed by electrostatic interactions (Fig. 1). Recently, we have investigated how the formation of $Ca^{2+}$-pectates affects the release and retention of pectic acids during peroxide bleaching of TMP, drainage of mechanical pulp, deposition tendency of colloidal pitch, and the removal of pectic acids by dissolved air flotation (Saarimaa et al. 2006a-c 2007).

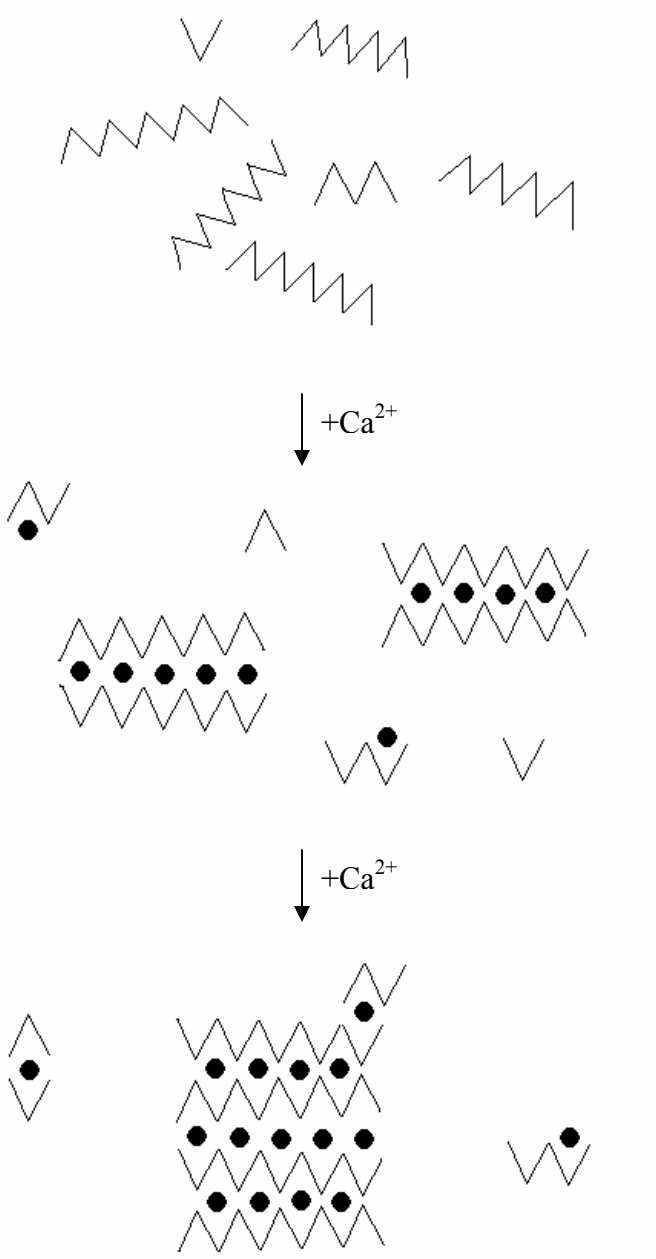


**Fig. 1.** Schematic picture of two-stage aggregation of pectins (/\/\/\) by calcium (•) (modified from Jarvis 2002).

However, although the effects of pectic acids in mechanical pulping and papermaking have received wide interest among paper researchers during the past 20 years, there is still limited information available of the structure and characteristics of the pectic acids released during mechanical pulping and bleaching. Therefore, in this study we introduce a novel method to isolate pectic acids from mechanical pulping process waters. The aggregation of the isolated pectic acids, as well as the aggregation of model pectic acids with well defined molar masses, by $Ca^{2+}$-ions were investigated.

## EXPERIMENTAL

### Materials

A typical press filtrate from peroxide-bleached thermomechanical pulp (TMP) was obtained from a mill in southern Finland using Norway spruce. The water was stored at -17°C and centrifuged prior to use in order to remove suspended solids. $CaCl_2$ of analytical grade was used. An Amberlite XAD-8 macroporous polyacrylate resin and an IRA-93 styrene divinylbenzene resin were from Fluka Chemie (AG, Switzerland). A dialysis membrane with a cut-off of 12-14 kDa was obtained from Medicell International LTD, UK. Tesorb cotton linters were used (Tervakoski Oy, Finland). The polyvinylidene difluoride (PVDF) membranes with pore size of 0.2 μm and cut-off of 180 000 g/mol were from Microdyn-Nadir Gmbh (Wiesbaden, Germany).

### Measurements and Analyses

Carbohydrates were determined using acid methanolysis to obtain methyl glycosides of neutral sugar units and methyl ester methyl glycosides of uronic acids, followed by gas chromatography to determine monomer concentrations (Sundberg A. et al. 1996). Calcium in the water samples was measured using inductively coupled plasma optical emission spectroscopy (Optima 5300 DV, PerkinElmer, USA). Total organic carbon (TOC) was measured on a TOC-5050 Analyzer (Shimatzu Corp., Japan).

### Preparation of Model Pectic Acids

Pectic acids with a narrow molar mass distribution (Table 1) were prepared from commercial citrus fruit pectin (Sigma-Aldrich Chemie GmbH, Germany) by alkaline hydrolysis with carefully controlled reaction time, pH and temperature (Patent pending). The reaction mixtures were cooled to room temperature, acidified to pH 4.0, concentrated in a vacuum rotor-evaporator, and then freeze-dried. The molar mass of the prepared pectic acids was determined by SEC-HPLC on an Agilent 1100 Series chromatograph equipped with Linear Ultrahydrogel column (Waters Corp., MA, USA). A miniDAWN Tristar MALLS detector by Wyatt Technologies (CA, USA) and a Shimadzu RID-10A refractive index detector (Japan) were used. The eluent was 100 mM NaCl, and the flow rate 0.5 mL/min. Previously published values of specific refractive index increments (dn/dc) were used for $M_W$ determinations (Michielsen 1999; Fishman et al. 2000).

**Table 1.** Pectic Acids Used in Experiments.

| Molar mass, $M_w$ | Degree of Polymerization | Polydispersity |
|---|---|---|
| kDa | DP | $M_W/M_n$ |
| 3.7 | 21 | 1.7 |
| 4.3 | 24 | 1.6 |
| 6.0 | 34 | 1.8 |
| 6.6 | 38 | 1.6 |
| 7.8 | 44 | 1.5 |
| 11.6 | 66 | 1.5 |

The prepared pectic acids contained less than 20% of neutral sugars. The dominating neutral sugars were arabinose (about 5%) and galactose (about 10%), which is typical for citrus fruit pectin (Renard and Thibault 1996). The model pectic acids contained about 20 w-% ash, mostly $Na^+$.

## Isolation of Pectic Acids From Bleached TMP Water

The isolation of pectic acids was carried out on a typical press filtrate from peroxide-bleached thermomechanical pulp from a mill in southern Finland using Norway spruce. Extractives and other colloidal material were removed by polyvinylidene difluoride (PVDF) membranes with pore size of 0.2 μm and cut-off of 180 000 g/mol. A schematic overview of the isolation procedure is shown in Figure 2.

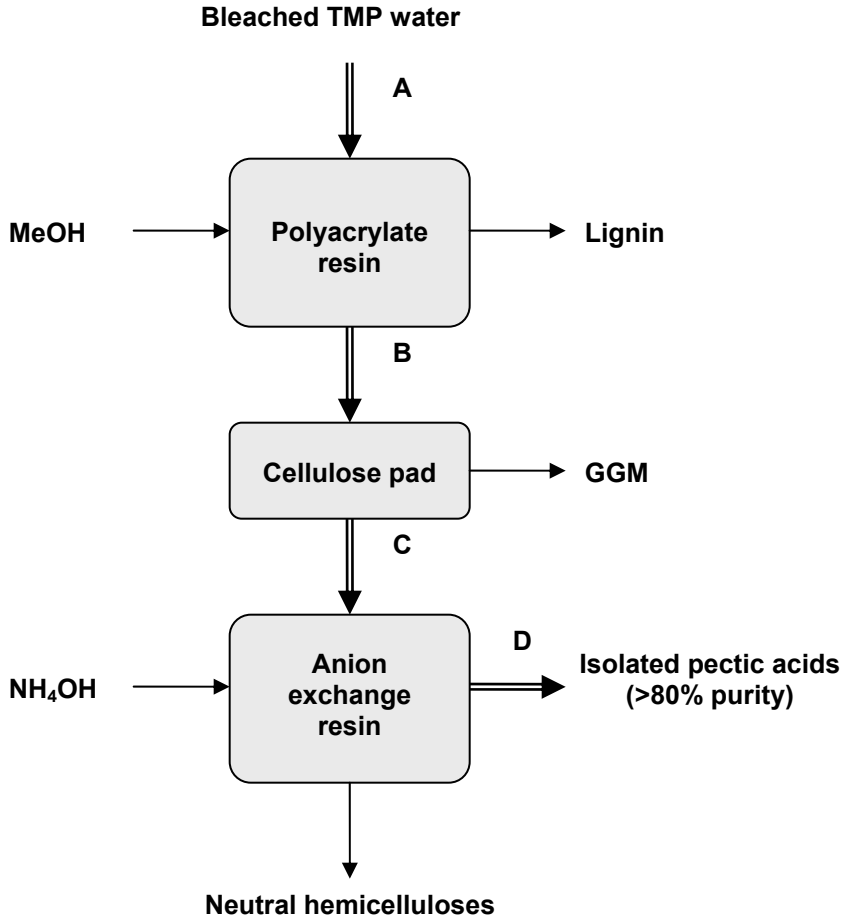


**Fig. 2.** Isolation of pectic acids from peroxide-bleached TMP water. Different steps in the isolation procedure are referred to as "A"-"D" in the text and in Figure 3.

The removal of lignin and other aromatic substances from the filtrate was carried out with a macroporous polyacrylate resin (Sjöström 1990, Sundberg, K. and Holmbom 1997, Pranovich et al. 2005). The resin was first cleaned by washing with 0.1 M NaOH, with distilled $H_2O$ and with 0.01 M HCl. The XAD-8 resin was packed in a column (3 cm in diameter, 35 cm in height) and the column was rinsed with 0.01 M HCl until the total

organic carbon (TOC) of the effluent was <2 mg/L. About 0.9 L of the bleached TMP filtrate was acidified to pH 2.0 with 0.1 M HCl and passed through the column. The last void volume of influent was displaced with 0.01 M HCl. The hydrophilic effluent was collected, the pH was adjusted to 5.0 with 0.1 and 0.01 M HCl and the effluent was concentrated to approximately 1 L with a vacuum rotor-evaporator. The aromatic substances were desorbed from the resin with methanol.

After the lignin removal, the next step was to remove galactoglucomannans, filtering the sample through a pad of disintegrated cotton linters. The cotton linters (10x10 cm) were first cut into small pieces, put into hot water (70°C), and disintegrated with a household mixer. A uniform layer (1-2 cm) of cellulose was packed in a filter funnel with a diameter of 10 cm, and the lignin-free TMP filtrate was passed through the filter three times under suction in order to retain the GGM.

The final step of the isolation procedure was carried out with an anion exchange resin, a weak base of styrene divinylbenzene having an exchange capacity of 1.2-1.4 meq/mL (Sjöström 1990, Sundberg, K. and Holmbom 1997). The resin was first stirred for 1 h in 0.1 M NaOH, followed by decanting the solution. After that, the resin was washed with distilled water and with 0.1 M HCl. A glass column (3 cm in diameter, 35 cm in height) was packed with resin and rinsed with 0.5 M NaOH. The column was then rinsed with distilled water until the pH was stable, followed by rinsing with 1 M HCl and again with distilled water. The filtrate was passed through the column, followed by rinsing with distilled water. The resin was regenerated with 100 mL of 3 M $NH_4OH$, and the anionic hemicellulose fraction was collected.

### Precipitation of Pectic Acids by $Ca^{2+}$

Solutions of pectic acids (about 30 mg/L) were prepared in distilled water, and the pH was carefully adjusted to 5.0, 6.5 or 8.0 with 0.01-0.1 M HCl and 0.01-0.1 M NaOH. The prepared solutions were pipetted into test tubes, 10 mL in each, and $Ca^{2+}$ was added to obtain concentrations between 0 and 10 mmol/L. The test tubes were vigorously shaken and left to stand overnight. The next morning they were centrifuged (500 g, 30 min), and the concentration of pectic acids in the supernatant was determined by GC (Sundberg A. et al. 1996).

## RESULTS AND DISCUSSION

### Isolation of Pectic Acids from Bleached TMP Filtrate

The bleached TMP filtrate contained 0.47 mmol/L (19 mg/L) of $Ca^{2+}$ and only traces of lipophilic extractives (<30 mg/L). The carbohydrate composition of the filtrate was: galactoglucomannans, 40.5%, arabinogalactans, 8.8%, arabinoglucuronoxylans, 5.6%, pectic acids, 35.5% and starch and glucans, 9.6%. The total polysaccharide concentration was 930 mg/L ("A" in Fig. 3). Monomer concentrations are presented instead of polysaccharide concentrations, since some of the sugars were most probably present in very low-molar-mass carbohydrates, especially in the last steps of the isolation procedure, which made the conversion to polysaccharides difficult. For polygalacturonic acids, for instance, it has been shown that a decrease in molar mass by acid de-

esterification yields a lower amount of rhamnose in the polymer backbone (Garnier et al. 1993).

The removal of lignin and other aromatic substances from the filtrate with a polyacrylate resin resulted in a slight decrease in total yield, but no specific removal of galacturonic acids or hemicelluloses was detected. The composition of the effluent is shown as column "B" in Fig. 3. The aromatic substances were desorbed from the resin with methanol. This fraction (about 1.1 g) contained only traces of hemicelluloses (15 mg/g) with no change in the original hemicellulose composition.

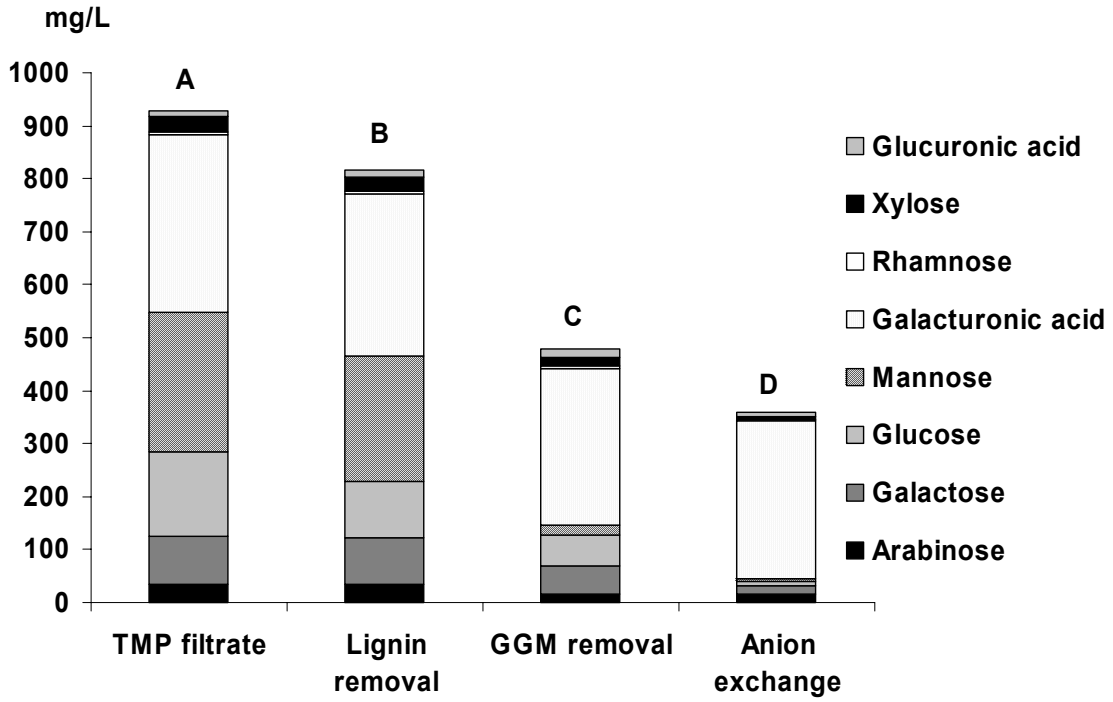


**Fig. 3.** Hemicelluloses in the TMP filtrate in the different steps of the pectic acid isolation procedure. Different steps in the isolation procedure (Fig. 2) are referred to as "A"-"D" in the text.

The sorption of galactoglucomannans (GGMs) onto different pulp fibres, especially onto chemical pulps, has been well demonstrated by Hannuksela (2004). The degree of glucomannan sorption increases after the glucomannans are deacetylated during peroxide bleaching of TMP. Galactoglucomannans were indeed efficiently removed by filtration through a cellulose pad ("C" in Fig. 3). Further purification of the filtrate with an anion exchange resin caused selective retention of acidic components. Neutral hemicelluloses passed through the column. The resin was regenerated with $NH_4OH$, revealing that galacturonic acids (>80%) were the main carbohydrates in the isolated product. Minor, but significant amounts of arabinose and galactose were also detected. Arabinose and galactose are known to exist as side chains of pectins, also in wood (Simson and Timell 1978; Schols and Voragen 2002). Traces of arabinose and galactose could also indicate the presence of acidic arabinogalactans (Willför et al. 2002). The anionic, pectic acid-rich fraction was finally purified by dialysis in order to remove salts and low molar-mass hemicelluloses. No galacturonic acids were removed by dialysis.

Some (about 10%) of the other carbohydrates were removed. The TMP pectic acids had a molar mass of about 5.9 kDa (DP 34) with a polydispersity of 3.3. Pectic acids in bleached TMP waters generally contain much more galacturonic acid (GalA) units and significantly less rhamnose (Rha) than pectins in fibres (Pranovich et al. 2003, Sundberg A et al. 2002). In the studied TMP water only a small amount of rhamnose was detected, and thus the pectic acids were practically completely composed of galacturonic acid units.

## Aggregation of Pectic Acids with Different Molar Masses by $Ca^{2+}$

The aggregation and precipitation of pectic acids by $Ca^{2+}$ was studied with model pectic acids from citrus fruit pectin and pectic acids isolated from the bleached TMP filtrate. The molar mass of pectic acids largely determined the degree to which they were precipitated and also influenced the required $Ca^{2+}$-concentration for complete precipitation (Figs. 4 and 5). The model pectic acids having molar mass less than 6 kDa (DP 34) were not precipitated, neither at pH 5 nor 6.5, while the pectic acids of higher molar mass were strongly precipitated. Precipitation of pectic acids occurred drastically at a certain $Ca^{2+}$-concentration, provided that the molar mass of pectic acids was high enough. Depending on the molar mass, there were still some pectic acids left after complete precipitation. The concentration of the residual pectic acids is most probably an indication of the molar mass distribution of the pectic acids: the lower the molar mass, the larger the low-molar-mass fraction that was not aggregated by $Ca^{2}$. Generally, some fluctuation in the percentage of residual GalA was seen before precipitation. The fluctuation can be attributed to inaccuracy in sampling and analysis.

It has been shown that the $Ca^{2+}$-binding of oligomeric pectic acid fragments is dependent on the degree of polymerization of pectic acids (Kohn and Larsen 1972; Kohn 1987). Aggregation of pectic acids by calcium is a two-stage process with initial dimerization followed by aggregation of the formed dimers (Grant et al. 1973). $Ca^{2+}$-pectates with DP lower than 7 (1.2 kDa) have been shown to be water-soluble, while higher DP (>10) leads to partial precipitation (Kohn 1987). It is also known that oligomeric pectic acids below DP 5 do not form complexes with cationic polymers (Thornton et al. 1993). A threshold of DP ~ 20 (3.5 kDa) has been proposed for strong cooperative effect in calcium binding (Kohn 1974). This was explained by presence of an array of specific binding sites regularly distributed along the pectic acid chain that present an ordered conformation (Bracchini and Pérez 2001). The difference between the molar masses required for precipitation in this study (6 kDa) and in the literature (3.5 kDa) could be explained by centrifugation forces. Kohn and Larsen (1972), Kohn (1974) and Kohn (1987) used centrifugation at 13.000-20.000 g to separate the pectates from the solution, while in this study the centrifugation was carried out at 500 g. The milder centrifugation force is justified by the relatively mild shear forces in papermaking wet-end, and the results in this study probably correlate well with the behaviour of pectic acids in real papermaking processes.

The rate of precipitation of the isolated pectic acids was in good accordance with the precipitation of the model pectic acids (Fig. 4), taking into account that the polydispersity of the isolated pectic acids was much wider than the polydispersity of

model pectic acids. Based on earlier studies and on our preparation procedure, both the model and the TMP pectic acids are assumed to be practically completely demethylated with a theoretical charge density of about 5-6 meq/g.

The MALLS detector used for determination of molar masses of pectic acids in this work is highly selective for high-molar-mass polymers. Since the prepared model citrus fruit pectic acids had extremely narrow molar mass distributions, the chromatogram peaks were clear and narrow. However, the isolated TMP pectic acid fraction resulted in a flat "peak" due to high polydispersity. Since the concentration of the polymer to be analyzed by MALLS has to be high in order to get a peak that does not disappear in the background noise, determination of the molar mass of the residual pectic acids left in the supernatant after precipitation was not carried out. Furthermore, those fractions probably also would have had extremely low molar mass, which causes difficulties in determination.

Increasing the pH from 5.0 to 6.5 did not affect the aggregation of pectic acids by $Ca^{2+}$ (Figs. 4 and 5). Some experiments were also carried out at pH 8.0, giving similar results as at lower pH. The pKa-value of pectic acids is about 3.7. It has been reported that pectic acids are totally dissociated at pH 4.5 (Capel et al. 2006), and that pH does not influence pectin gels formed by $Ca^{2+}$-ions at a pH > 3.5 (Lootens et al. 2003). Therefore, it can be concluded that pectic acids behave in a similar manner in practically the whole papermaking pH range, from pH 5 to 8.

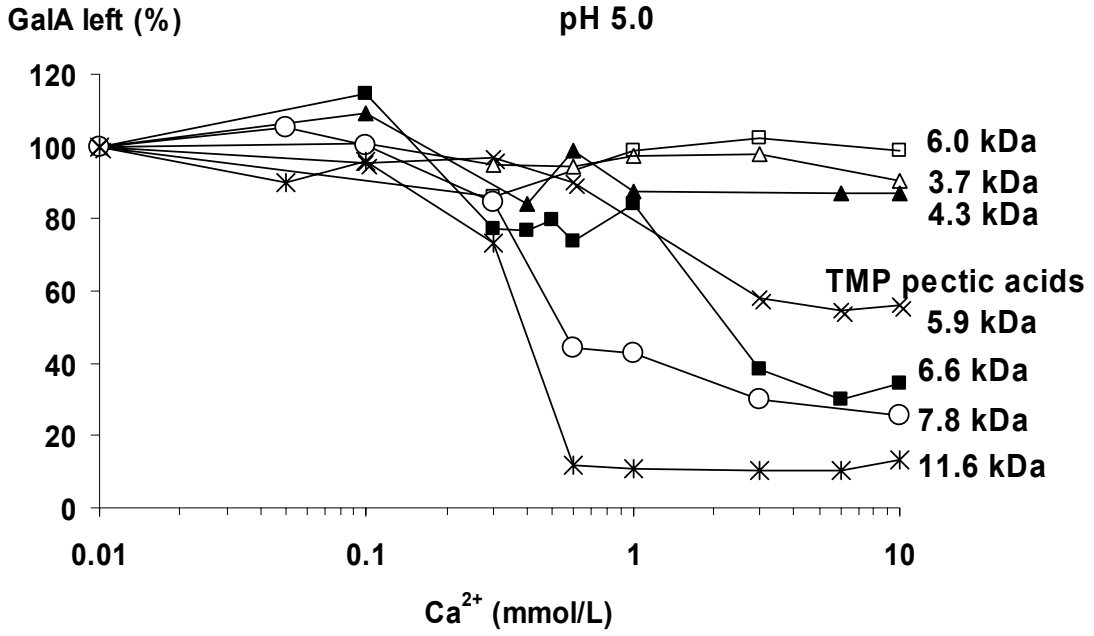


**Fig. 4.** Precipitation of pectic acids (about 30 mg/L) was determined by $Ca^{2+}$-concentration and molar mass at pH 5.0.

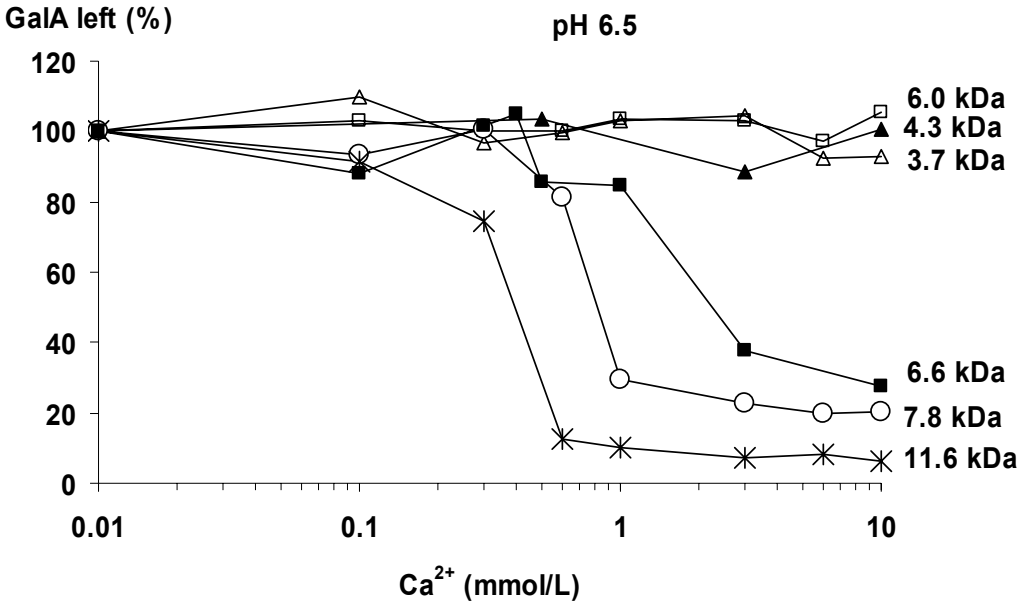


**Fig. 5.** Precipitation of pectic acids by $Ca^{2+}$ at pH 6.5 was similar to pH 5.0.

A clear molar mass threshold for precipitation of pectic acids by $Ca^{2+}$ was thus observed. Pectic acids below 6 kDa formed water-soluble complexes and are therefore probably not precipitated onto fibres in papermaking processes. However, at least some of the TMP process water pectic acids exceeded the critical molar mass for precipitation. Since the higher-molar-mass pectic acids were to a large extent aggregated and precipitated already at quite low $Ca^{2+}$-concentrations, it can be assumed that some of the pectic acids released during peroxide bleaching of TMP were instantly precipitated onto fibres and were not present in the bleached TMP filtrate that was used as a starting point in the isolation procedure.

Precipitated pectic acids can give manifold effects in mechanical papermaking. Detrimental dissolved and colloidal material has been claimed to interfere with wet-end additives such as retention polymers and wet/dry strength additives, and retard press dewatering and reduce dryer efficiency (Chung et al. 1993). Recently it has been shown that $Ca^{2+}$-pectates can impair dewatering during sheet formation, probably due to blocking of the voids and cavities in the porous fibre matrix (Saarimaa et al. 2007). The retained pectic acid aggregates also slightly decreased brightness of the formed paper sheets. Brightness is determined by light scattering (s) and absorption (k) coefficients. A decrease in light scattering coefficient was attributed to less scattering sites due to blocking of the porous sheet structure by $Ca^{2+}$-pectates. An increased adsorption coefficient in turn reflected higher retention of slightly coloured pectic acids in the pulp. Pectic acids are also precursors to various furan derivatives that are formed via hydrolysis, dehydration and condensation reactions under heat and humidity (Theander and Nelson 1988; Fischer and Beyer 2000; Jääskeläinen et al. 2007). Furan compounds are one of the key substances causing yellowing in pulps.

An enzymatic pectinase treatment could be used to depolymerize pectic acids to low-molar-mass fractions that are not retained in the pulp and thus do not show detrimental effects in papermaking (Thornton et al. 1996). In the literature, a 2% higher ISO brightness of TMP after pretreatment of wood chips with pectinase was obtained (Peng et al. 2003). After peroxide bleaching, a major part (2/3) of pectic acids is still associated with fibres. Based on the results of this study, the pectic acids remaining within the fibres might play greater role in brightness stability and pulp dewatering properties than the dissolved fraction, since the largest part (50-60%) of the dissolved pectic acids were low-molar-mass, non-detrimental pectic acid fragments.

## CONCLUSIONS

1. Pectic acids can be selectively isolated from bleached mechanical pulping waters using a polyacrylate resin column to remove lignin, a cellulose pad to remove galactoglucomannans, an anion exchange resin to separate neutral and acidic carbohydrates, and finally a dialysis membrane to remove salts and residual low molar-mass carbohydrates. In this study, pectic acids with >80% purity were obtained.
2. The dissolved pectic acid fraction after peroxide bleaching of TMP is a polydisperse mixture of low-molar-mass galacturonic acids fragments.
3. The molar mass of pectic acids is the key factor, besides calcium concentration, determining the precipitation of dissolved pectic acids by $Ca^{2+}$. Pectic acids of molar masses <6 kDa are not precipitated by $Ca^{2+}$, but higher-molar-mass pectic acids are efficiently precipitated.

## ACKNOWLEDGMENTS

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# AKD AND ASA MODEL SURFACES: PREPARATION AND CHARACTERIZATION

Juha Lindfors,* Jani Salmi, Janne Laine, and Per Stenius

Model surfaces of alkyl ketene dimer (AKD) and alkenyl succinic anhydride (ASA) were prepared by casting and spin-coating methods. The surface chemical composition and surface topography were investigated by XPS, ellipsometry, AFM and contact angle studies. Spin-coating resulted in layered structure of AKD and ASA surfaces; the molecular layer thickness of both AKD and ASA was found to be ca. 2.5 nm. To achieve a covering surface layer, an average thickness of ca. 35 nm was required. The rms roughness of the created surfaces was 1 - 6 nm. Colloidal probe adhesion measurements were performed to verify that the roughness was in a range suitable for these measurements. The high reactivity of ASA with water generated stability problems with the ASA layers and it has to be recognized that surface force measurements with ASA in aqueous environment are very difficult, if not impossible. However, surfaces created in this way were found to be useful in providing explanations of earlier ASA adhesion studies. The contact angle measurements on ASA layers also indicated that it might be possible to asses the hydrolysis rate issues through a set of similar measurements.

*Keywords: Alkyl ketene dimer, Alkenyl succinic anhydride, Model surface, Adhesion, XPS, Ellipsometry, AFM, Contact angle*

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## INTRODUCTION

Alkyl ketene dimers (AKD) and alkenyl succinic anhydrides (ASA) are amphiphilic molecules having a hydrophobic olefin chain backbone and a hydrophilic functional group. Structurally, alkyl ketene dimers are unsaturated lactones, frequently synthesised through the preparation of the acid chloride of a carboxylic acid, followed by intermolecular lactone ring condensation (Neimo 1999). ASA is produced by an ene-reaction (Alder et al. 1943) from an unsaturated alkenic hydrocarbon backbone and a succinic anhydride. General synthesis routes and basic structures of AKD and ASA are shown in Figs. 1 and 2.

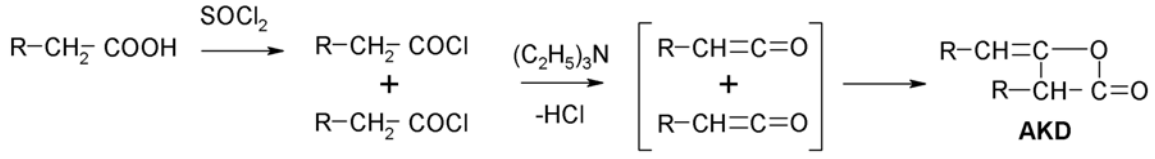


**Fig. 1.** General synthesis route and structure of AKD. R = alkyl chain.

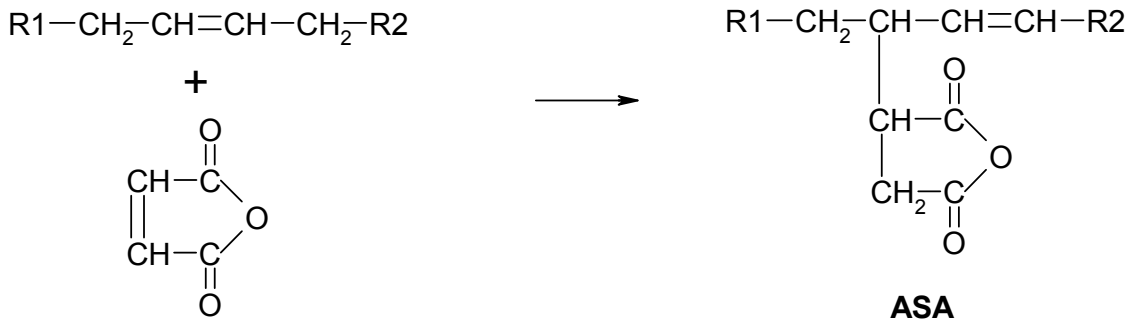


**Fig. 2.** General synthesis route and structure of ASA. R1 and R2 are alkyl chains.

With reference to Figs. 1 and 2, it should be noted that the detailed structures of commercial AKD and ASA vary according to the used olefin chain compositions (e.g. length, typically $C_{14}$-$C_{20}$, and branching).

AKD and ASA are extensively used in papermaking as sizing agents (Gess 1992; Neimo 1999). These so-called reactive sizes were first introduced already in the 1950s (Davis et al. 1956) and 1960s (Wurzburg and Mazzarella 1963). Yet, they were not very widely applied before the increased use of calcium carbonate and trend towards alkaline papermaking during the last two decades. Currently they are used to confer hydrophobicity to cellulose fibres in neutral and alkaline papermaking. Various features, related to their use in papermaking process, have been studied. These include e.g. adhesion forces between AKD and cellulose (Bogdanovic et al. 2001), adhesion properties of ASA sized paper surfaces (Dickson and Berg 2001), wetting dynamics of AKD on cellulosic surfaces (Garnier et al. 1999), spreading and adhesion of ASA on different surfaces (Lindfors et al. 2005a; Lindfors et al. 2005b), and many aspects of emulsion stability and sizing efficiency (Asakura et al. 2006; Hodgson 1994; Isogai et al. 1992a; Isogai et al. 1992b; Isogai et al. 1994; Isogai et al. 2004; Taniguchi et al. 1993). Nonetheless, more detailed knowledge of chemical interactions, and phenomena such as adhesion and adsorption, is still needed to be able to better master the use of AKD and ASA, to formulate more stable emulsions, to optimize the sizing result, and to avoid contamination. In the study of basic chemical interactions, model surfaces are essential. It is noteworthy that in spite of numerous studies, there is still a lack of controlled model surfaces prepared from AKD and ASA. Such model surfaces can contribute to further investigation of e.g. formation of stabilizing polyelectrolyte layers in size emulsification, interactions of sizing agents with cellulose and other materials present in papermaking stock, and adhesion forces leading to contamination of paper machines.

The aim of this study was to establish simple methods for preparing well-defined AKD and ASA model surfaces for fundamental studies of adhesion interactions. Surfaces prepared here are not intended to simulate paper sizing as such. In addition, adhesion force measurements with atomic force microscopy (AFM) and through contact angle measurements were performed in order to demonstrate the applicability of the created surfaces to these measurements.

## EXPERIMENTAL

### Materials

A commercial Alkyl Ketene Dimer (AKD) with a melting point above 60°C, from Kemira Oyj, Vaasa, Finland, was used for all AKD model surfaces. The AKD was purified by recrystallizing it twice from acetone. Recrystallized AKD was used in all experiments. Alkenyl Succinic Anhydride (ASA) surfaces were prepared from a wax, which was solid at room temperature. The ASA was supplied by Kemira Chemie GmbH, Krems, Austria. The original purity, before recrystallization, of both AKD and ASA was > 95 % (according to the supplier). Impurities were mainly residual olefin chains from the synthesis. Untreated smooth silicon wafers (Okmetik Oy, Helsinki, Finland) and QCM-D gold crystals (Q-Sense AB, Gothenburg, Sweden) were used as substrates for the AKD and ASA films. Glass spheres (Whitehouse Scientific Ltd., UK) were used for colloidal probe measurements. All other chemicals used were of analytical grade and Milli-Q water was used throughout the investigation.

### Surface Preparation

*Casting*

Sodium chloride IR crystal windows from Sigma-Aldrich were used for casting AKD and ASA surfaces from molten wax (method earlier described by Zbik et al. (2006)).

*Spin-coating*

A Laurel Technologies Corporation WS-400B-6NPP/LITE spin-coater (Laurell Technologies Corp., USA) was used. Spin-coating time was 60 s, AKD and ASA solution concentration and spin-coating speed were varied to prepare films of different thicknesses.

### Surface Characterization and Adhesion Measurements

*Ellipsometry*

Angle resolved laser (632.8 nm) ellipsometry (Picoellipsometer, Beaglehole Instruments) was used to determine the thickness of the AKD and ASA films on $SiO_2$ substrates. The data were collected in 0.5 degree intervals from 68 to 80 degrees. The angles were chosen around the Brewster angle since the sensitivity for changes in the layer thickness is the highest close to this angle. The thicknesses of the AKD and ASA films were determined by fitting the measured data to a two-layer model. The optical properties of the silicon substrate were taken from the data bank of the fitting software (TFCompanion, Semiconsoft). AKD and ASA were considered as dielectric materials having a real index of refraction equal to 1.46 (Mischki et al. 2006).

*X-ray photoelectron spectroscopy, XPS*

An AXIS 165 electron spectrometer and monochromatic Al Kα irradiation was used for acquisition of XPS spectra. Before analysis, all samples were pre-evacuated overnight in order to stabilize vacuum conditions. By parallel measurements on a reference sample (TKK reference sample (Johansson and Campbell 2004)), included with

each sample batch, it was verified that UHV conditions remained satisfactory and non-contaminating. No sample deterioration was detected during the experiment. All samples were analysed at three locations (analysis area ca. 1 $mm^2$). Elemental surface compositions were determined from low-resolution scans recorded with 80 eV analyser pass energy and 1 eV step. Carbon and oxygen high resolution spectra were recorded from O 1s and C 1s regions using 20 eV analyser pass energy and 0.1 eV step.

*Atomic Force Microscopy, AFM*

AFM imaging was performed using a NanoScope IIIa Multimode scanning probe microscope (Digital Instruments, Inc. Santa Barbara, CA, USA). The surfaces were scanned in tapping mode in air using commercial Si cantilevers (Digital Instruments) with a resonance frequency of about 300 kHz. Four images were recorded for each surface and representative micrographs were chosen for presentation. Atomic force microscopy (Nanoscope IIIa) was also used to measure surface forces using the colloidal probe technique (Butt 1991; Ducker et al. 1991). Briefly, a glass sphere with diameter 31.3 μm was glued to the tipless end of a cantilever with a reported spring constant of 0.38 and 0.58 N/m (Veeco Instruments, Santa Barbara, CA, USA). Surface forces were measured against AKD and ASA surfaces in air and in 1 mM $NaHCO_3$. The surface force was calculated from the deflection of the cantilever using Hooke's law in the conventional way and normalized by the radius of the glass spheres (Derjaguin 1934). The spring constants were determined by the reference spring method (Torii et al. 1996; Tortonese and Kirk 1997). For the sake of clarity, only one representative curve per system is shown in the figures. However, the actual values of the pull-off forces and the pressing loads may contain an error due to the nonlinearity of the AFM piezo scanner and the sliding of the colloidal probe (Stiernstedt et al. 2005).

*Contact angle measurements*

A CAM 200 contact angle goniometer (KSV Instruments Ltd, Helsinki, Finland) was used for determination of contact angles of water and diodomethane on the AKD and ASA model films in ambient air The size of the water drops was ca. 10 μl and that of diodomethane drops ca. 3 μl. Contact angles were calculated by Axisymmetric Drop Shape Analysis (ADSA) using software delivered with the instrument. This analysis is based on fitting experimentally determined drop profiles to the full equations for drop profiles of sessile drops under the influence of gravity derived from the Young-Laplace equation. The fitting method is based on the principle described by Jennings and Pallas (1988).

## RESULTS AND DISCUSSION

### Surface Preparation

Casting is an easy and fast method for creating fully covering surfaces from both AKD and ASA. However, melting the hydrophobic wax and letting it cool down in air results in a noticeably rough surface. To overcome this roughness, surfaces were cast against freshly cleaved sodium chloride crystals and the salt crystal was removed by

dissolution in water after letting the wax to cool down slowly at room temperature. Mirror-like surfaces of both AKD and ASA were achieved in this way. Zbik et al. have earlier used similar casting method in preparing paraffin wax surfaces (Zbik et al. 2006). Using a NaCl crystal resulted in significantly smoother surfaces than casting in air or against any smooth surface that had to be cleaved from the wax after casting.

Cast surfaces can be used e.g. for adhesion measurements using the colloidal probe technique and for contact angle measurements. These surfaces are also ideal for recording reference spectra using surface sensitive techniques such as XPS, because rather thick and fully covering layers are formed. However, many surface interaction measurement techniques do require thin or ultra-thin surfaces, which can be fast and feasibly created e.g. by spin-coating.

Model films of AKD and ASA were also prepared by spin-coating from different organic solvents on $SiO_2$ and gold substrates. AKD and ASA concentrations from 0.5 g/l to 50 g/l were applied, and toluene, n-hexane, ethanol, and acetone were used as solvents. Spin-coating speed was varied between 1000 rpm and 6000 rpm. Spin-coated layers from both toluene and n-hexane solutions were reasonably uniform in macroscopic scale. Films from toluene solutions were selected to be further investigated here, because of the good solubility of AKD and ASA in toluene and the low evaporation rate of this solvent. Microscopy images (magnifications of 5x, 20x, and 100x) of AKD and ASA layers on $SiO_2$ substrates spin-coated from 2.5 g/l toluene solution at a spin rate of 2700 rpm are shown in Figs. 3 and 4. The AKD surface (Fig. 3) appeared so smooth through the microscope that some scratches were made to the surface in order to introduce contrast to the image and to verify that there was an AKD layer on the $SiO_2$ substrate. On the ASA surface (Fig. 4) circles of 50 – 300 μm in diameter can be seen. The surface is not as smooth in macroscopic scale as that of AKD.

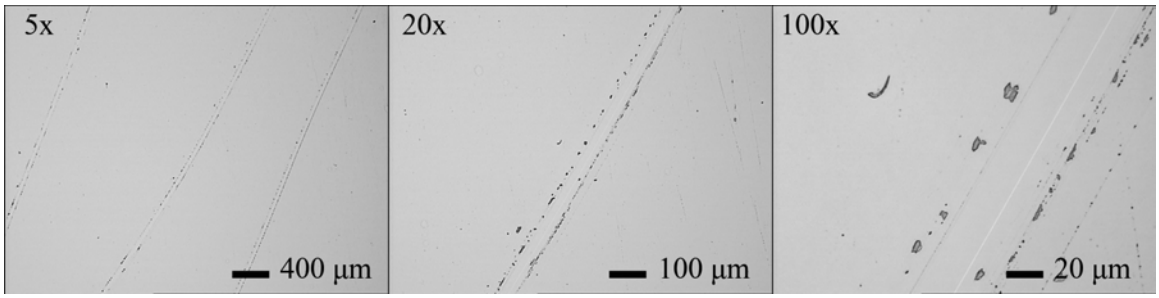


**Fig. 3.** Microscopy images of spin-coated AKD (2.5g/l in toluene, 2700 rpm) of different magnifications (5x, 20x, and 100X). Scratches on the surfaces are made to introduce some contrast to the image.

Patterning of ASA surfaces was observable regardless of the solvent used, spin-coating parameters, or ASA concentration. An example of clear patterning is shown in Fig. 5, where microscope images of ASA layer spin-coated on $SiO_2$ from 50 g/l toluene solution at a spin rate of 5000 rpm are shown. Based on thinner surface layers of ASA (Fig. 4) one might consider that incomplete wetting could cause the patterns. However, the thick surface (Fig. 5) indicates that, at least here, this is not the case. The patterns could rather be because of ASA molecule orientation.

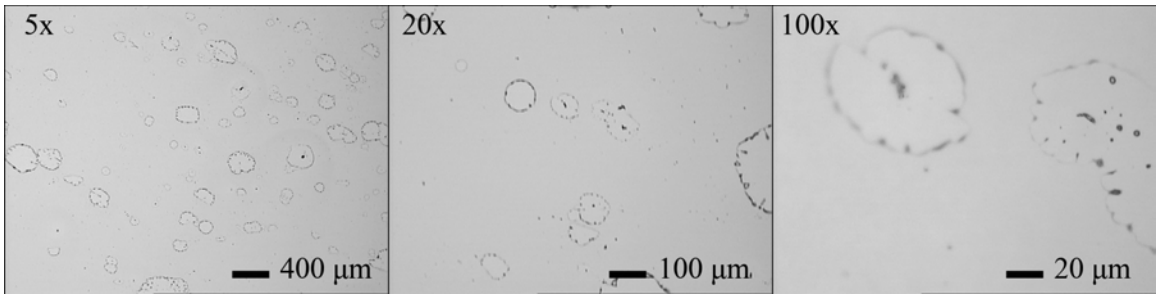


**Fig. 4.** Microscopic images of spin-coated ASA (2.5g/l in toluene, 2700 rpm) of different magnifications (5x, 20x, and 100X).

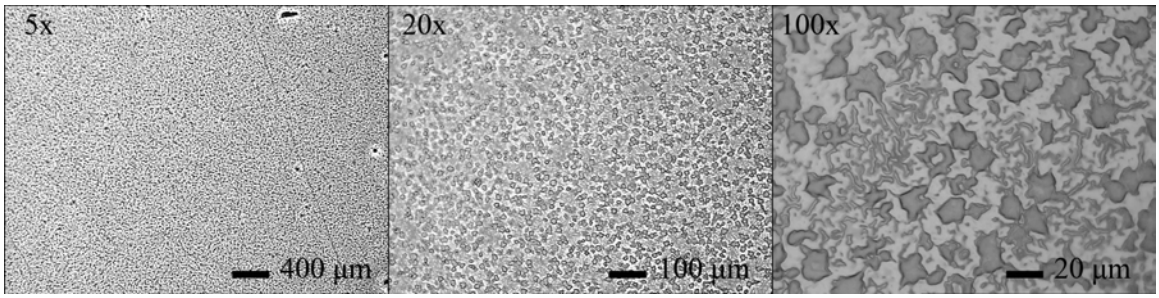


**Fig. 5.** Microscopic images of spin-coated ASA (50g/l in toluene, 5000 rpm) of different magnifications (5x, 20x, and 100X).

## Determination of AKD and ASA Film Thickness

The thickness of spin-coated AKD and ASA films was determined using ellipsometry. AKD layer thickness as a function of the AKD concentration of the spun toluene solution is shown in Fig. 6 (spin rate 5000 rpm).

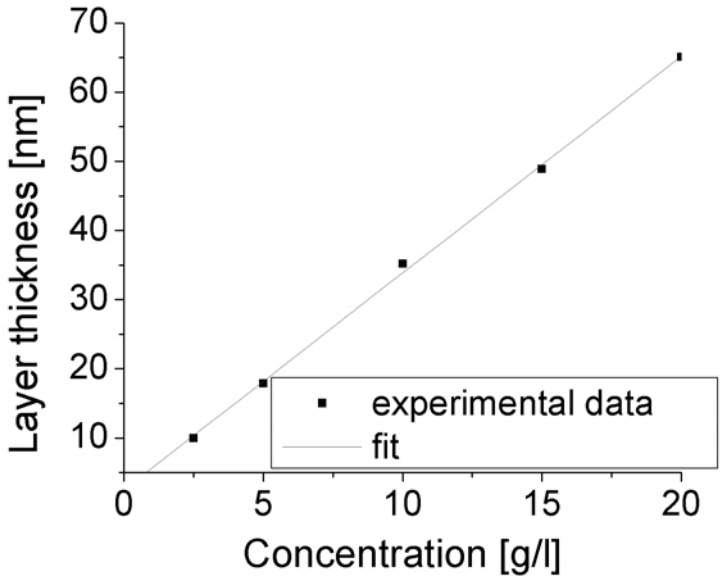


**Fig. 6.** Thickness of AKD model film vs. spin-coating solution conc. (spinning rate: 5000 rpm).

Similar data for ASA is presented in Fig. 7. The results show that films of varying thickness could be easily prepared by simply changing the concentration of the spin-coating solution. The same effect could also be reached by variations of spin rate; at constant concentration the layer is the thicker, the lower the speed of spinning. It is also obvious that layers created from AKD and ASA had very similar thicknesses when identical concentrations were used.

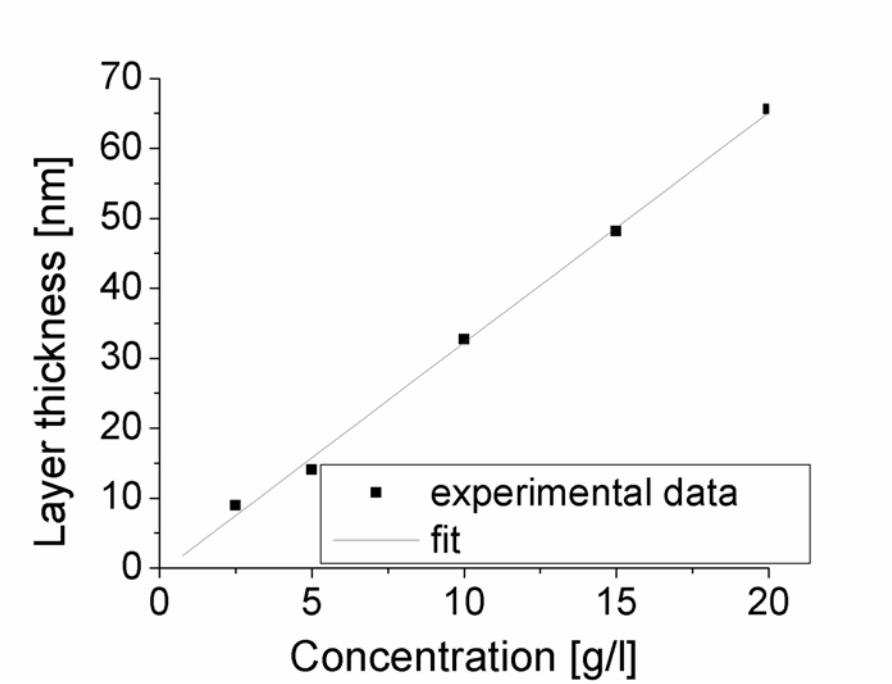


**Fig. 7.** Thickness of ASA model film vs. spin-coating solution conc. (spinning rate: 5000 rpm).

## Chemical Composition of the Model Surfaces

The elementary composition of the model surfaces of AKD and ASA was determined using XPS. The atomic ratios between oxygen and carbon, between silicon and carbon, and the relative amounts of different carbon peaks for AKD and ASA films spin-coated from 2.5 g/l, 10 g/l, and 20 g/l toluene solutions (at spin rate 5000 rpm), in addition to those of cast surfaces, are shown in Table 1. The thinnest surface layers (prepared from 2.5 g/l solution), which were found to be ca. 10 nm thick by ellipsometry, showed significant amounts of silicon and oxygen on the surface. Thus, these surface layers of AKD and ASA were obviously not fully covering, because the $SiO_2$ substrate was clearly detectable by XPS. Layers prepared from higher concentrations (10 g/l and 20 g/l) of AKD and ASA provided almost similar atomic ratios as the cast surfaces, and one can conclude that these concentrations were high enough to create a covering model surface from AKD and ASA. XPS spectra of different AKD layers are presented in Fig. 8 to visually demonstrate the effect of the layer thickness to the recorded spectrum. The most significant changes can be seen in the Si peaks at ca. 150 eV and 100 eV.

**Table 1.** O/C Atomic Ratio, Si/C Atomic Ratio and Relative Amounts of Different Carbons for the Model Surfaces

| Material | O/C | Si/C | C1 | C2 | C3 | C4 |
|---|---|---|---|---|---|---|
| AKD, 2.5 g/l | 0.32 | 0.45 | 37 | 47 | 3 | 1 |
| AKD, 10 g/l | 0.076 | 0.065 | 63 | 8 | 1 | 1 |
| AKD, 20 g/l | 0.045 | 0.015 | 76 | 5 | 2 | 1 |
| AKD, cast | 0.044 | 0.003 | 89 | 1 | 2 | 1 |
| ASA, 2.5 g/l | 0.32 | 0.29 | 75 | 17 | - | 7 |
| ASA, 10 g/l | 0.18 | 0.041 | 80 | 12 | - | 8 |
| ASA, 20 g/l | 0.17 | 0.034 | 80 | 13 | - | 7 |
| ASA, cast | 0.19 | 0.025 | 84 | 9 | - | 7 |

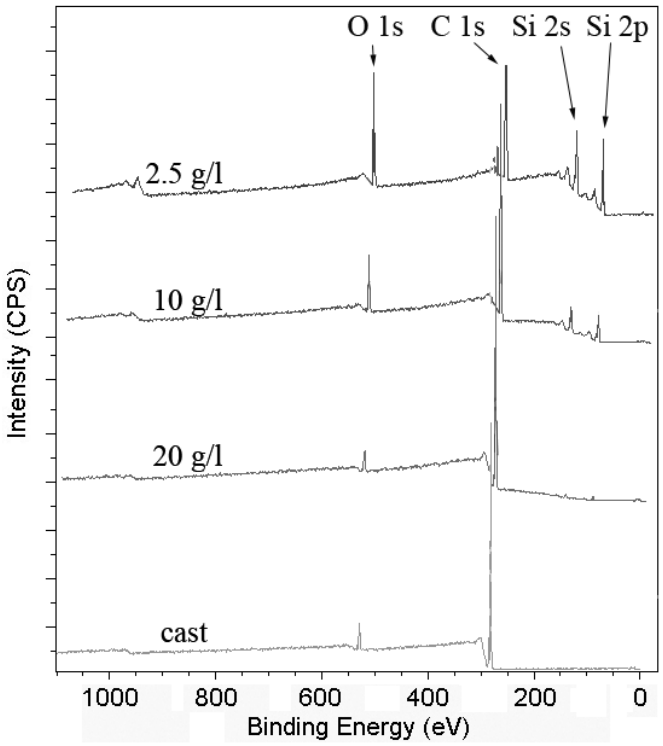


**Fig. 8.** XPS wide scan spectra of AKD. 2.5 g/l, 10 g/l, 20 g/l, and cast surface. The spectra are shift vertically for clarity.

## Surface Topography of AKD and ASA Films

An AFM topographic image of the AKD film cast against NaCl crystal is shown in Fig. 9. The rms value of the 1 $\mu m^2$ image area is 5.95 nm. However, there is a higher peak to the right on the image, which contributes substantially to the roughness, and the rms of the rather flat area to the left was determined to be 1.34 nm. Cast ASA surfaces showed a generally similar topography to the one shown here for AKD. Although cast surfaces were not completely flat, i.e. there occurred some larger roughness features (as that shown in Fig. 9), which were most likely due to uneven cleavage of NaCl crystals,

their rms values was well within the range that is appropriate for adhesion measurements by colloidal probe technique and contact angle measurements (e.g. Notley et al. have recently used cellulose spheres with similar surface roughness in colloidal probe microscopy measurements (Notley et al. 2006)).

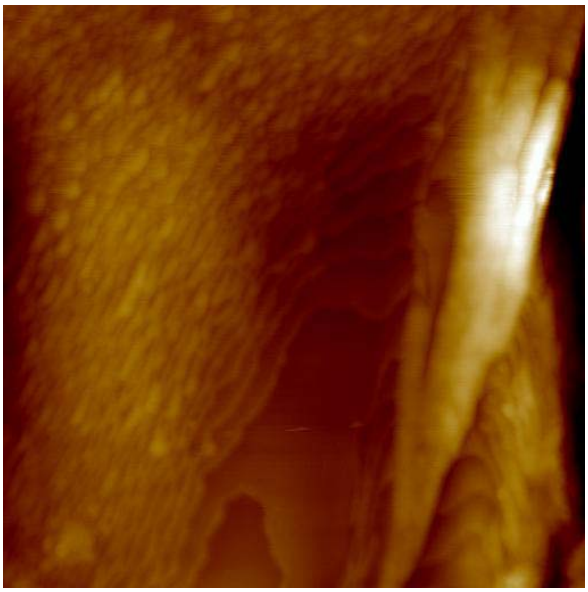

**Fig. 9.** AKD NaCl (1 µm, z = 45 nm, rms = 5.95 nm/upper left corner 1.34nm).

Both macroscopic inspection and ellipsometry indicated that even the AKD and ASA layers spin-coated from the lower concentrations would be relatively smooth and covering. However, XPS analysis showed that full coverage was not reached. AFM imaging was used to further study these surfaces. A 25 $\mu m^2$ topography image of a spin-coated AKD film is presented in Fig. 10a and a 1 $\mu m^2$ image within the former image is shown in Fig. 10b. The surface was spin-coated on $SiO_2$ from 2.5 g/l toluene solution. From the larger image it is clear that no uniform coating was reached, but a layered structure was formed. Individual layer steps can be more clearly seen in the 1 $\mu m^2$ image. The structure of spin-coated ASA films was very similar to that of AKD (see Fig. 11a,b). In Fig. 11b shows a step profile of the surface, indicating clearly the ca. 2.5 nm layers of ASA. Ren et al. (2004; 2003) have recently studied stearic acid, which has a C-18 carbon chain, and can thus be used as a reference for the ASA used here. The ASA monolayer thickness of ≈ 2.5 nm corresponds fairly well with the value of ca. 2 nm found for stearic acid. Apparently the deepest spots on the surfaces presented in Fig. 10a and 11a are not covered by AKD or ASA at all, so that the $SiO_2$ substrate can still be seen. As the ellipsometry data showed, the surface thickness was ≈ 10 nm, while the AFM images indicate that the thickness of one molecular layer was ≈ 2.5 nm. Thus, it is obvious that an average four layers of AKD/ASA was deposited on the surface. The rms values of spin-coated AKD and ASA layers are generally acceptable for model surface purposes.

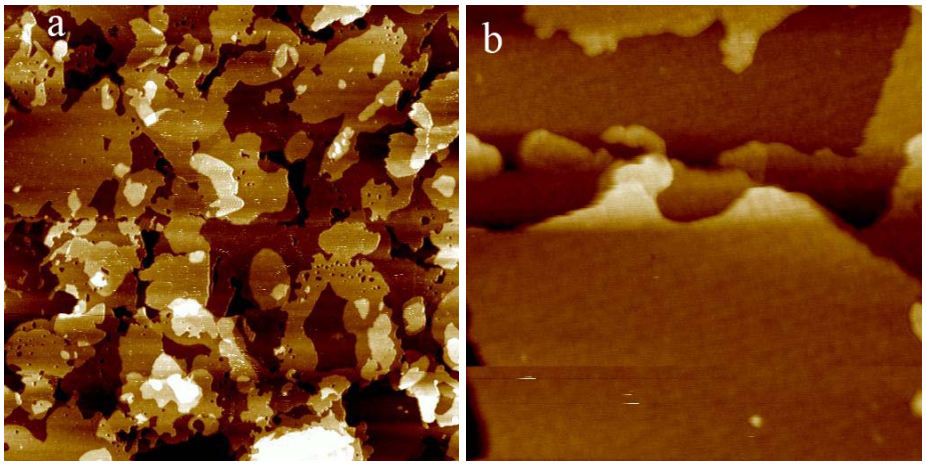


**Fig. 10.** Spin-coated (2.5 g/l, 2700 rpm) AKD on $SiO_2$ a) 5 µm, z = 14 nm, rms = 3.14 nm b) 1 µm, z = 14 nm, rms = 1.36 nm.

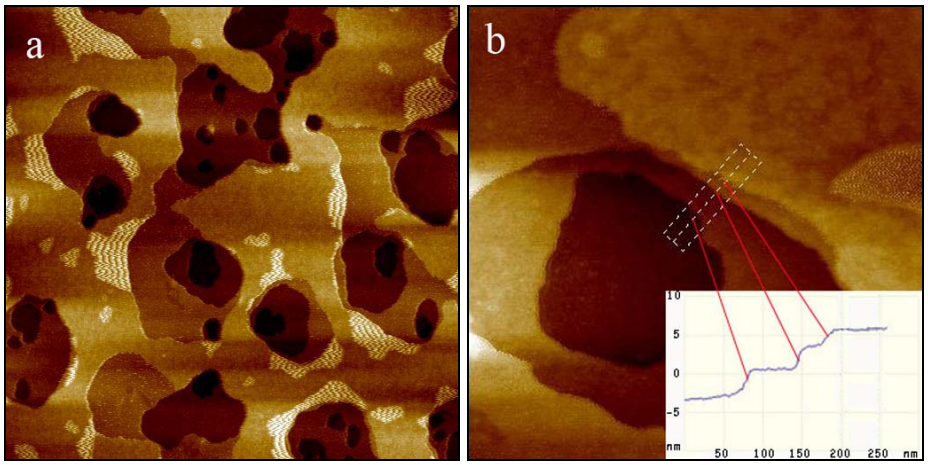


**Fig. 11.** Spin-coated (2.5 g/l, 2700 rpm) ASA on $SiO_2$ a) 5 µm, z = 18 nm, rms = 2.88 nm b) 1 µm, z = 15 nm, rms = 1.38 nm.

To check how the spin-coated layer followed the topography of the used substrate, a layer of AKD was spin-coated on gold. Fig. 12a shows an AFM image of the gold substrate and Fig. 12b an AKD film spin-coated on top of it. It can be seen that the topography of the substrate with spherical texture is well reproduced on the AKD surface. Also, the layered structure observed on AKD coated on $SiO_2$ can be seen and the rms roughness is of the same order of magnitude as on $SiO_2$.

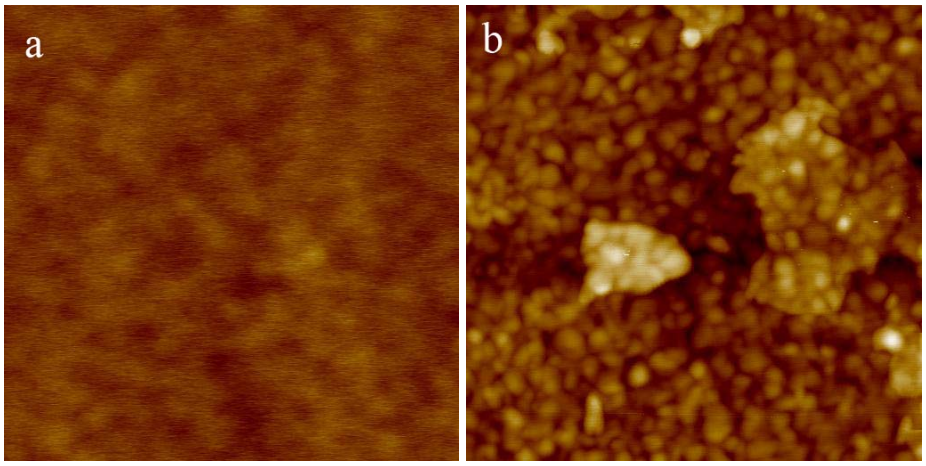


**Fig. 12.** a) Au b) AKD on Au (1 µm, z = 15 nm, rms = 1.46 nm).

## Water Contact Angles on AKD and ASA Surfaces and the Surface Stability

Contact angles of water on AKD surfaces prepared by casting and spin-coating are presented in Fig. 13. It can be seen that even the thinner (not fully covering) AKD film was clearly more hydrophobic than the $SiO_2$ substrate. The contact angles of water on the cast and the thicker spin-coated surface were nearly equal. This supports the finding that a concentration of 10 g/l was roughly sufficient to spin-coat a covering AKD layer. The contact angle on the thinner AKD surface was not as high as on the thicker surfaces, which must be due the contribution of the more hydrophilic $SiO_2$ spots to the overall contact angle. The contact angle data recorded on each of the AKD surfaces showed good stability of the surfaces (the contact angle remained stable after a very short equilibration period).

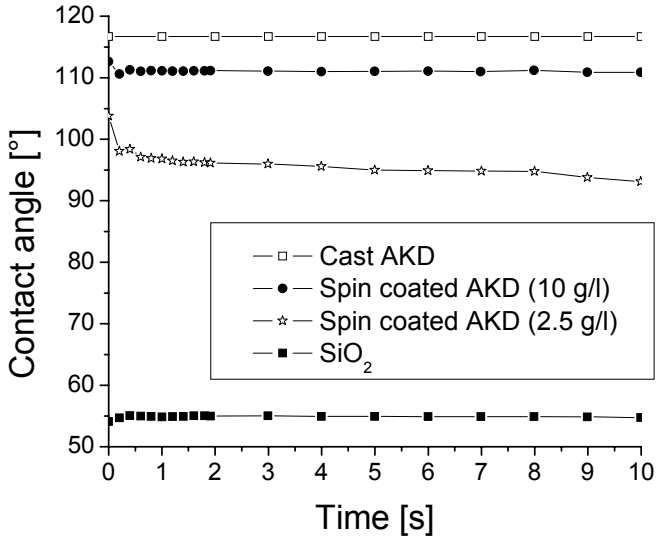


**Fig. 13.** Contact angle of water on AKD surfaces prepared by casting and spin-coating, and on the $SiO_2$ substrate.

Contact angles of water on ASA surfaces are presented in Fig. 14. These follow a rather different trend from the one observed with AKD; water spreads fairly fast on thin ASA layers, and a thick cast film was needed to create a hydrophobic surface. In fact, a smaller contact angle was obtained on these spin-coated ASA layers than on the $SiO_2$ substrate. We believe that this is associated with the reactivity of ASA (hydrolysis reactions of spin-coated ASA layer with water droplet on it). The reaction products of hydrolysed ASA are probably highly surface active and reduce the water contact angle to an even lower level than that of pure water on $SiO_2$. Figure 15 shows water contact angles recorded on a thicker spin-coated ASA surface. This surface was prepared from a 50 g/l concentration and the layer thickness was determined to be ca. 200 nm. A clear drop in contact angle was observed after ca. 90 s. This indicates that even a rather thick spin-coated layer of ASA on $SiO_2$ is unstable in presence of water. These measurements performed on ASA layers of different thickness indicate that it might be possible to e.g. assess the hydrolysis rate issues through a set of similar measurements with several different ASA layer thicknesses.

Contact angles of diiodomethane (which is not reactive towards ASA like water) on ASA surfaces were recorded to verify that the observations of water spreading on the ASA films was really due to the hydrolysis reactions. Diiodomethane contact angles are presented in Fig. 16. Relatively similar spreading kinetics was observed both on the ultrathin (ca. 10 nm) ASA film and on the thick cast ASA layer. This indicates that when there is no reactivity between the probing liquid and the model surface the layer thickness does not affect the spreading of the liquid. This result further supports the conclusion that ASA reactivity caused the instability of the ASA layers in contact with water.

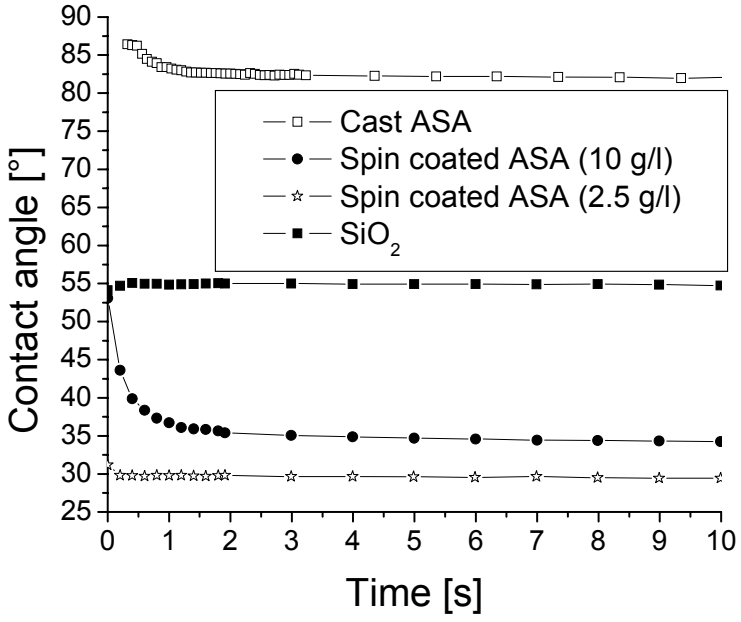


**Fig. 14.** Contact angle of water on ASA surfaces prepared by casting and spin-coating, and on the $SiO_2$ substrate.

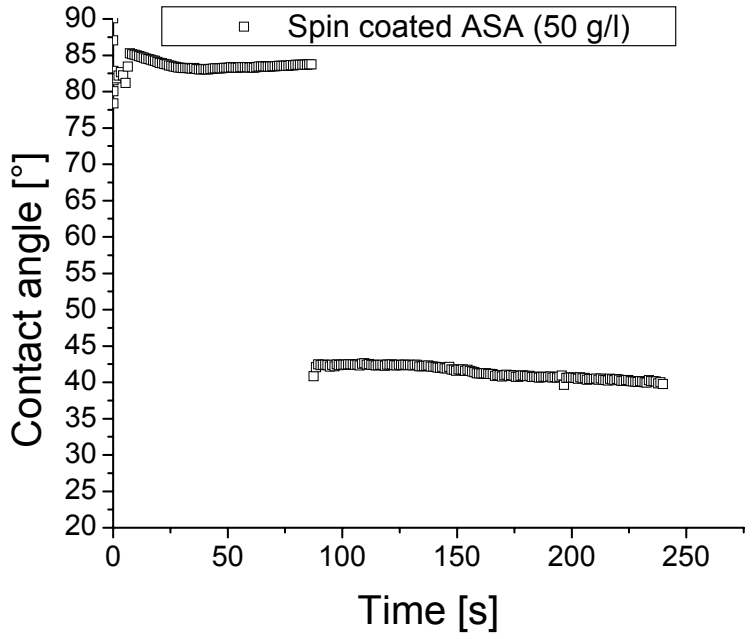


**Fig. 15.** Contact angle of water on a ca. 200 nm ASA surface prepared by spin-coating.

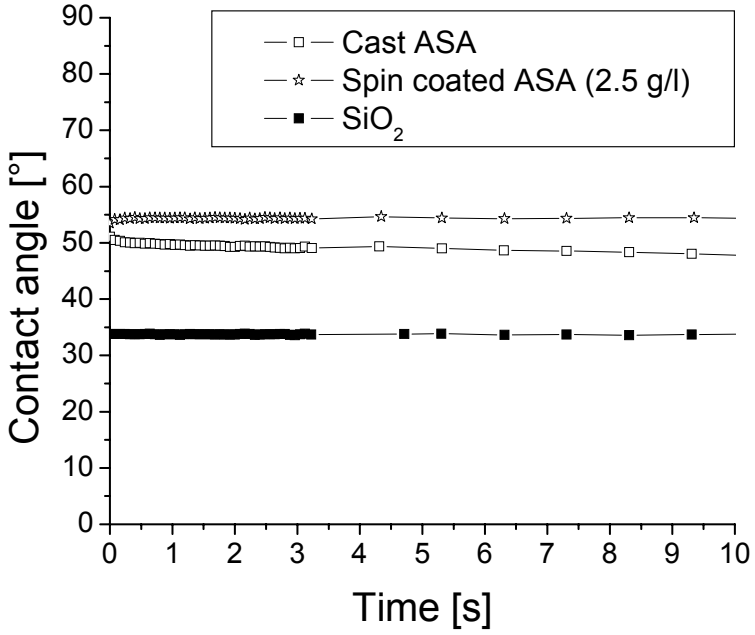


**Fig. 16.** Contact angle of diodomethane on ASA surfaces prepared by casting and spin-coating, and on the $SiO_2$ substrate.

## Adhesion of AKD and ASA

The suitability of the created model surfaces for adhesion studies was demonstrated by contact angle and colloidal probe experiments. Measurements of adhesion, utilizing spin-coated AKD and ASA surfaces, have also been done using a contact mechanics measurement technique, and are presented elsewhere (Lindfors et al. 2007).

Adhesion of ASA on hydrophilic and hydrophobic surfaces was evaluated earlier, using contact angle measurements (Lindfors et al. 2005b). These showed a discrepancy in the calculation of ASA contact angles on aqueous solutions, which we deemed to originate from the fact that the fast hydrolysis reactions occurring on the ASA/aqueous solution interface resulted in incorrect interfacial tension values. We have used the contact angles recorded here on a cast ASA surface to calculate ASA/water interfacial tension, $\gamma_{ASA\text{-}water}$ from Young's equation:

$$\cos\theta = \frac{\gamma_{ASA-air} - \gamma_{ASA-water}}{\gamma_{air-water}} \quad (1)$$

where $\theta$ denotes the contact angle of water on ASA and $\gamma_{ASA\text{-}air}$, $\gamma_{ASA\text{-}water}$ and $\gamma_{air\text{-}water}$ are interfacial tensions. Assuming that earlier measured value of ASA surface tension in air (33.2 mJ/m$^2$) is correct and using water surface tension 72.8 mJ/m$^2$, $\gamma_{ASA\text{-}water}$ can be calculated. The contact angle data recorded here show that even on the cast surface some spreading occurred in the beginning of the measurement (≈ 82° is not the initial value). Using a contact angle of 95° $\gamma_{ASA\text{-}water} \approx 39$ mJ/m$^2$ is received. If one uses this value to predict interfacial contact angles of ASA in water instead of the interfacial tension value recorded earlier (Lindfors et al. 2005b), estimates of 170° for hydrophilic and 25° for hydrophobic surfaces are obtained. These match exactly with the true interfacial contact angle values that we have reported earlier (Lindfors et al. 2005b).

We also used the cast surfaces, because of their better stability, for adhesion measurements by AFM colloidal probe technique. Surface forces between glass and AKD were measured in air and in 1.0 mM $NaHCO_3$. In air, surface force on approach was unchanged before snap-in at short separations (Fig. 17). A jump off the contact was observed, when surfaces were pulled apart. The pull-off force depended on the measuring location on the AKD surface and on the load by which the surfaces were pressed together in the contact (Fig. 18). The pull-off force increased with the load. The average of the pull-off force in all measurements was 5.3 mN/m with an average load of 5.2 mN/m.

Surface forces between glass and AKD surfaces were also measured in 1.0 mM $NaHCO_3$, Fig. 19. The surfaces forces between approaching surfaces were repulsive. This could be most likely due to the elasticity of the surfaces. The major proportion of the repulsion is due to deformation of AKD surface (Rutland et al. 2004), and thus the range of repulsion seems to be large. An attractive pull-off force between separating surfaces was observed in some locations, but it was clearly smaller than in air.

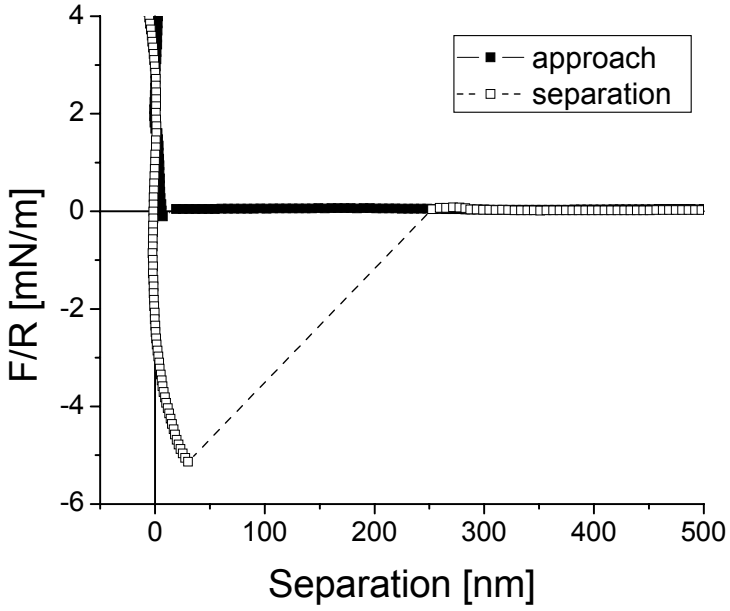


**Fig. 17.** Surface forces between glass and AKD measured in air. Filled symbols are for approaching force curve and open symbols are for separating force curve. The dotted line indicates a jump to a larger distance on separation.

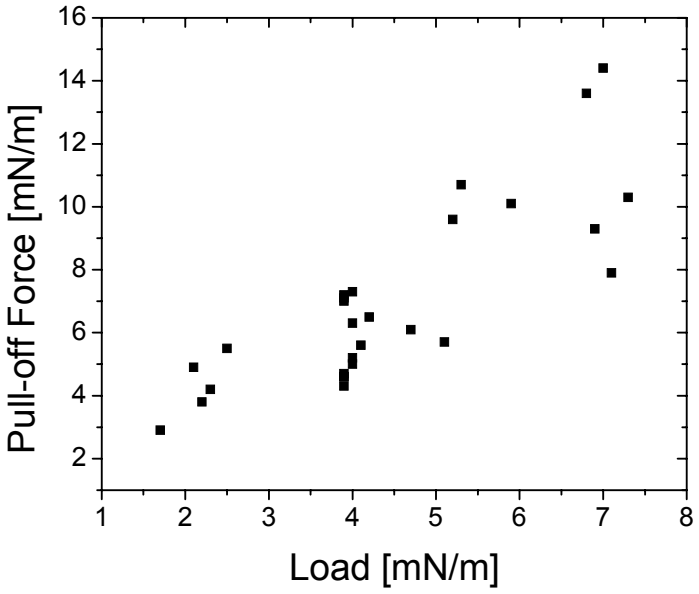


**Fig. 18.** Pull-off force of glass sphere and AKD surface as a function of load between these two. The Force is measured in air, and in one location.

A clear jump off, like the one in air, was not observed, but the surfaces remained connected at larger separations. This indicates that the surfaces were soft, and thus they stuck together. In addition, the minimum in the separation curve was not close to contact. This supported the conclusion about the deformable surface (Stiernstedt et al. 2006). The pull-off force was not systematically dependent on the load. The average of the pull-off force was 0.6 mN/m with the loads varying from 2.5 to 5.5 mN/m. The pull-off force was again dependent on the location.

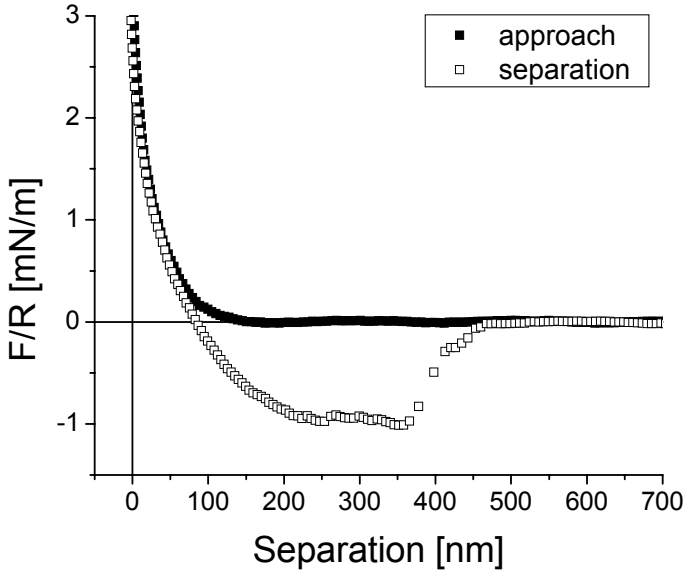


**Fig. 19.** Surface forces between glass and AKD measured in 1.0 mM $NaHCO_3$. Filled symbols are for approaching force curve and open symbols are for separating force curve.

The surface interactions between glass and ASA in air exceeded the measuring range of the AFM, i.e. the AFM cantilever was deflected beyond the range of the detector. However, the estimated pull-off force was between 25 mN/m and 55 mN/m in air when loads were varied between -4 and 6 mN/m. An attraction was observed between approaching surfaces. Force measurements with ASA in 1.0 mM $NaHCO_3$ showed that ASA swelled and softened in solution. It was impossible to get appropriate force curves under these conditions. However, it was clear that the pull-off force was lower in solution.

## CONCLUSIONS

1. Model surfaces of AKD and ASA, suitable for variety of surface interaction measurements, were created and their feasibility for adhesion studies was demonstrated.
2. By using the created surfaces, we were also able to explain the inconsistency observed earlier in the spreading of ASA. The results obtained using the created

model surfaces verified the assumption that the hydrolysis of ASA molecules at the liquid-liquid interface is very fast and leads to erroneous interfacial tension results.
3. The molecular layer thicknesses of both AKD and ASA were found out to be ca. 2.5 nm. This knowledge can be utilized in further studies using these chemicals.
4. Force measurements with AKD and ASA with suitable corrections in experimental conditions proved that both surfaces can be used in this purpose. However, it must be recognized that surface force measurements with ASA in aqueous environment are very difficult, if not impossible. This is due to the high hydrolysis rate of ASA.

## ACKNOWLEDGMENTS

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# CUTTING FORCES BY PERIPHERAL CUTTING OF LOW DENSITY WOOD SPECIES

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In this paper multifactor non-linear dependencies of cutting forces from several machining parameters for low density wood of *Liriodendron tulipifera Linn*., known as Yellow Poplar, and *Cordia alliodora Ruiz. & Pav*., known as laurel blanco wood or capa prieto, were evaluated from experimental matrices. In the analyzed relations there was evidence for several strong interactions, which have been graphically illustrated and discussed.

*Keywords: Cutting Forces, Routing, Milling, Wood,* Liriodendron tulipifera, Cordia alliodora

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## INTRODUCTION

The problem of cutting forces, especially for routing and milling of low density wood of *Liriodendron tulipifera,* and *Cordia alliodora*, have not been worked out yet. In the literature from the field of wood machining there exists a method for evaluation of the main (tangential) $F_c$ and normal $F_n$ cutting forces, in the form of formulas (1) and (2), for the ten most common European wood species. These formulas employ the relative cutting resistance $K$ and correction coefficients (Afanasev 1961; Amalitskij and Lyubchenko 1977; Bershadskij 1967; Deshevoy 1939; Orlicz 1982). However, large differences, as high as 40% and more between values predicted from equations (1) and (2), relative to the observed forces, suggest that the problem of cutting forces, namely the wood cutting theory, has not yet been worked out completely.

$$F_c = a_p \cdot w_s \cdot K \cdot C_r \cdot C_\delta \cdot C_\rho \cdot C_{ap} \cdot C_{vc} \cdot C_{mc} \cdot C_T \quad (1)$$

$$F_n = C_n \cdot F_c \quad (2)$$

In Eqs. (1) and (2) the terms are defined as follows:

| | |
|---|---|
| $a_p$ | - Thickness of cutting layer (also known as chip thickness). |
| $w_s$ | - Cutting width. |
| $K = f(\varphi_r)$ | - Specific cutting resistance [N/mm$^2$, MPa]. |
| $C_r$ | - Coefficient of wood species, *Pinus silvestris* wood $C_r = 1$. |
| $C_\delta = f(\delta_f)$ | - Coefficient of cutting angle $\delta_f$. |
| $C_\rho = f(\rho$ or $VB)$ | - Coefficient of cutting edge dullness $\rho$, $VB$. |
| $\rho$ | - Radius of cutting edge round up. |

| | |
|---|---|
| $VB$ | - Recession of cutting edge. |
| $C_{ap} = f(a_p)$ | - Coeff. of a thickness of a cutting layer (chip thickness) $a_p$. |
| $C_{vc} = f(v_c)$ | - Coefficient of a cutting speed $v_c$. |
| $C_{mc} = f(mc)$ | - Coefficient of a moisture content $mc$. |
| $C_T = f(T)$ | - Coefficient of a temperature $T$. |
| $C_n = f(\rho$ or $VB)$ | - Coefficient of normal force $F_n$. |

In the authors' opinion there are several reasons for the lack of fit. The most important cause is not taking physical and mechanical properties into account in formula (1), instead of an arbitrarily assumed value or range of the correction coefficient $C_r$. The wood, even of the same wood species, may differ considerably in physical and mechanical properties, resulting in a large dispersion of predicted cutting forces in comparison to observed ones. Another reason is, in the authors' opinion, a general assumption that there is a lack of dependence of the value of one correction coefficient from other cutting parameters, including wood species properties. The average specific cutting resistance $K$, evaluated without taking into account early and late wood of growth rings, cannot be used to calculate real maximum and minimum cutting resistances. It is already known from the literature that the normal force $F_n$ does not follow the tangential force $F_c$ proportionally to the change in cutting edge wear. An important disadvantage of the method based on equations (1) and (2) in most published works is also a tabular form of the correction coefficients. All assumptions above seem not to be supported by any multifactor experiment, making the method of evaluation of cutting forces based on formula (1) and (2) a rather rough approximation of the problem (Axelsson et al. 1993; Kivimaa 1950; Amalitskij and Lyubchenko 1977).

There are older and newer published works, describing the dependence of main $F_c$ and normal $F_n$ cutting forces on several cutting parameters for different kinds of machining in the form of multinomial or power type functions. However, the limited number of independent variables involved, as well as not having exactly the same and limited range of their variation, makes models difficult to compare (Axelsson et al. 1993). The models available in the literature for most machining methods, including routing and milling, were worked out and collected in the program Wood_Cutting (Porankiewicz 2007).

The present study attempts to evaluate the dependence of main (tangential) $F_c$ and normal (radial) $F_n$ cutting forces from cutting edge dullness $VB$, average angle $\varphi_r$ between wood grains and cutting plane, the cutting speed $v_c$, feed per edge $f_z$, and moisture content $mc$ during peripheral cutting of low density wood of *Liriodendron tulipifera* and *Cordia alliodora*.

## MATERIALS AND METHODS

In the first experiment (Cyra 1997), the cutting forces were measured with use of a measuring system equipped with Hasegawa Tekko Type 4321 load cells, amplifier, and multi-pen recorder, as shown in Fig. 1.

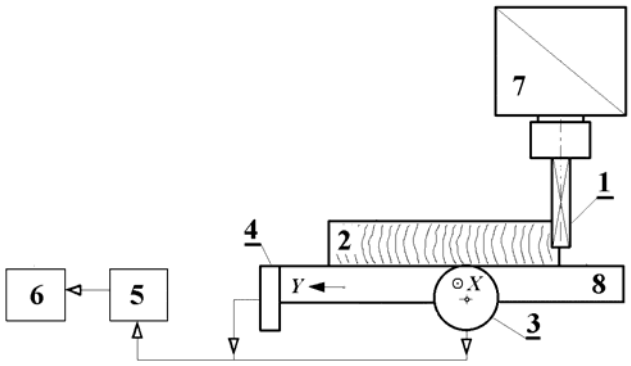


**Fig. 1.** General scheme of measuring system used in first experiment; 1 - Router bit, 2 – Work-piece, 3,4 – Load cells, 5 – Amplifier, 6 – Multi-pen recorder, 7 – Motor, 8 – Workpiece feed table

In the second experiment (Bermudez 2005; Bermudez et al. 2005) cutting forces were measured with the use of a measuring system equipped with a Hasegawa Tekko Type 4321 load cell, an NEC Type AS1202 amplifier, and a National Instruments Type NI PCI-6034E A/D converter integrated with LabVIEW program software, as shown in Fig. 2. The sampling rate was 100 Hz.

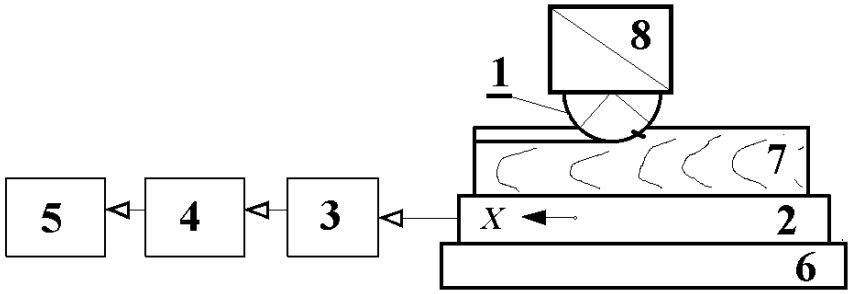


**Fig. 2.** General scheme of measuring system used in second experiment; 1 – Cutting tool, 2 – Load cell, 3 – Amplifier, 4 – A/D converter, 5 – Computer, 6 – Workpiece feed table, 7 – Workpiece, 8 – Motor

Experiments were performed on a CNC Shoda Fanuc NC-3 vertical router at Shimane University, Matsue, Japan. The $X$ and $Y$ cutting force components for the first experiment and the $X$ component for the second experiment, measured in workpiece feed table coordinates were recalculated to average tangential $F_c$ and normal $F_n$ forces, according to minimum and maximum contact angle, defined by cutting radius $r_c$ and cutting depth $g_s$. Parameters for the first experiment (Cyra 1997) performed by peripheral up routing (Fig. 3 a) were as follows:

Mechanical and physical properties of wood of *Liriodendron tulipifera*:

Wood density $D = 400$ kg/m$^3$.
Modulus of rupture by bending $R_b = 69.6$ MPa.
Modulus of rupture by compression parallel to grains $R_c = 38.2$ MPa.
Moisture content $mc = 11$ %.

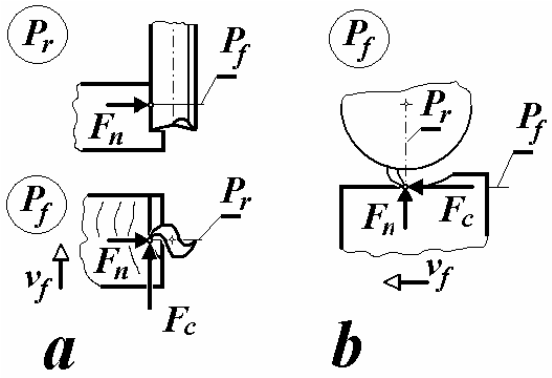


**Fig. 3.** Scheme of: a – up routing, and, b – up milling, with tangential $F_c$ and normal $F_n$ cutting forces

Machining parameters:

Cutting edge recession measured in bisector of a wedge angle $VB_w$< 4; 27; 52; 65; 82 μm >.
Contour wedge angle $\beta_f = 37^o$.
By $\beta_f = 37^o$, the range of variation of the $\rho$ is $\rho$<2; 38 μm >.
Contour rake angle $\gamma_f = 33^o$.
Contour clearance angle $\alpha_f = 20^o$.
Cutting edge inclination angle $\lambda_p = 0^o$.
Cutting radius $r_c$ = 5 mm.
Spindle rotational speed $RPM$ = 5000 $min^{-1}$.
Cutting speed $v_c$ = 30 m/s.
Feed speed $v_f$ = 2 m/min.
Feed per edge $f_z$ = 0.2 mm.
Cutting depth $g_s$ = 2 mm.
Width of cut $w_s$ = 10 mm.
Number of cutting edges z = 2.
Average angle between cutting speed and cutting plain direction and wood grains $\varphi_r$ and $\varphi_s$ <23.4; 38.4; 53.4; 68.4; 83.4; 98.4; 113.4; 120.4; 143.4; 158.4; 173.4; 188.4 $^o$ >.
The angle between cutting edge direction and wood grains $\varphi_k = 90^o$.
Growth rings grains orientation towards cutting edge $\varphi_{rt} = 0^o$ .
Material of the cutting edge was the cemented carbide K05.

Parameters for the second experiment by peripheral up milling (grooving) with a one side contact (Bermudez 2005; Bermudez et al. 2005; Fig. 3 b) were as follows:

Mechanical and physical properties of wood of *Cordia alliodora* in air dried state:

Wood density $D$ = 456 kg/$m^3$.
Modulus of rupture in bending $R_b$ = 729.8 MPa.
Modulus of rupture in compression parallel to grains $R_c$ = 324.8 MPa.

Moisture content $mc$<11.5; 100 %>.

Machining parameters:

Contour wedge angle $\beta_f = 45^o$.
Contour rake angle $\gamma_f = 25^{o,}$
Contour clearance angle $\alpha = 20^o$.
Cutting edge inclination angle $\lambda_p = 0^o$.
Side angle in main plane $\kappa'_r = 1.8^o$.
Side angle in back plane $\tau_p = 4.3^o$.
Cutting radius $r_c$ = 100 mm.
Cutting speed $v_c$<10; 20; 30; 40 m/s>.
Spindle rotational speed $RPM$<955; 1910; 2865; 3820 $min^{-1}$>.
Feed speed $v_f$< 0.5; 1; 1.5; 2 m/min>.
Cutting depth $g_s$< 0.5; 1; 2; 3 mm>.
Average angle between cutting speed and wood grain direction $\varphi_r$<2; 7$^o$>.
Width of cut $w_s$ = 1 mm.
Number of cutting edges z = 1.
The angle between cutting edge direction and wood grains $\varphi_k = 90^o$.
The angle between cutting plain direction and wood grains $\varphi_s = 0^o$.
Radial and tangential orientation of growth rings grains towards the cutting edge were not taken into account.
Material of the cutting edge was the high speed steel SKH 51.
Cutting force was analyzed for sharp cutting edge.

In the second experiment, during cutting *Cordia alliodora* wood, the feed velocity $v_f$ was varied in the range of $v_f$<0.5; 2 m/min>, instead of varying the feed per edge $f_z$ for different cutting speeds $v_C$. This was achieved by increasing the spindle rotational speed $RPM$, without any increment in the feed velocity. As a result, the feed per edge $f_Z$ did not have the same set of values for the different cutting speeds $v_C$ that were considered.

In order to evaluate the relations $F_c = f(\varphi_r, VB_w)$, $F_n = f(\varphi_r, VB_w)$, and $F_c = f(\varphi_r, f_z, v_c, mc)$, linear models and second order multinomial models, as well as power type functions without and with interactions were analyzed in preliminary calculations. The model should fit experimental matrix by the lowest summation of residuals square $SK$, by the lowest standard deviation $SD$, and by the highest correlation coefficient of predicted and observed values $R$. The experimental matrix can be fitted with more simple models, but this will result in decreasing approximation quality, which means that the $SK$ and $SD$ values will increase, and $R$ will decrease. In this case all predicted values of dependent variable will have higher expected error. Many years of experience by the first author lead us to believe that efforts to fit such data with overly simple models can be expected to hurt the quality of the approximation of the influence of independent variables, especially in the case of variables with small importance, making such a model nonsensical. The proper influence of low importance variables can be only extracted from an experimental matrix when using a more complicating model. The most adequate formulas appeared to be the non-linear, multivariable equations with interactions (3) through (7).

$$F_C = a_1 \cdot e^{a_2 \cdot \sin(\varphi_r + a_3) + a_4 \cdot \sqrt{VB_w} + a_5 \cdot \varphi_r^2 \cdot VB_w + a_6} + a_7 \quad [\mathrm{N}] \tag{3}$$

$$F_n = b_1 \cdot e^{b_2 \cdot \sin(\varphi_r + b_3) + b_4 \cdot \sqrt{VB_w} + b_5 \cdot \varphi_r^2 \cdot VB_w + b_6} + b_7 \quad [\mathrm{N}] \tag{4}$$

$$W_1 = c_2 \cdot \varphi_r + c_3 \cdot f_z + c_4 \cdot v_c + c_5 \cdot \varphi_r / mc + c_6 \cdot \varphi_r / f_z \tag{5}$$

$$W_2 = c_7 \cdot f_z \cdot v_c + c_8 \cdot \varphi_r \cdot v_c + c_9 \cdot v_c \cdot mc + c_{10} \tag{6}$$

$$F_c = c_1 \cdot e^{W_1 + W_2} + c_{11} \quad [\mathrm{N}] \tag{7}$$

For evaluation of estimators from experimental matrixes (containing 60 and 128 measuring points, in case of the first and second experiments, respectively), a special optimization program was applied, based on a least squares method combined with gradient and Monte Carlo methods (Porankiewicz 1988) with further changes. Elimination of the unimportant or low-importance estimators was carried out by use of the coefficient of relative importance, *CRI*, during evaluation of process models (3) through (7). *CRI* was defined by formula (8). It was assumed that $CRI > 0.1$.

$$CRI = (SK - SK_{OK}) / SK \cdot 100\ [\%] \tag{8}$$

In Eq. (8) the new terms are:

$SK_{OK}$ = the summation of residuals square by $c_K = 0$
$c_K = k$ estimator evaluated in statistical model

Calculations were performed at Poznań Networking and Supercomputing Center PCSS on an SGI Origin 3800 computer. For characterization of approximation quality, a summation of residuals square *SK*, standard deviation *SD*, and a square of correlation coefficient of the predicted and observed values $R^2$ was used.

For comparison of results obtained in the present work with similar data from the literature, the main cutting force $F_c$ was calculated for up routing and up milling, with application of the Wood_Cutting program (Porankiewicz 2007) for *Tilia cordata* low density wood, was used.

## RESULTS AND DISCUSSION

For formula (3), describing the relation between the main force $F_c$ and the average angle $\varphi_r$ between cutting speed direction, wood grains, and cutting edge dullness $VB_w$ for wood of *Liriodendron tulipifera*, the following estimators were evaluated: $a_1 = 0.091$; $a_2 = 0.9662$; $a_3 = -0.7276$; $a_4 = 0.2769$; $a_5 = -0.0007$; $a_6 = 2.7357$; $a_7 = 9.0847$, by range of

variation of independent variables: $\varphi_r$ <23.4; 188.4°>; $VB_w$<4; 82 μm>. The quality of the fit to the model (4) is shown by Fig. 4a and the values of the quantifiers: $SK$ = 770.2; $R^2$ = 0.86; $SD$ = 3.6 N.

The following estimators were evaluated for formula (4), describing the relation between the normal force $F_n$ and the average angle between cutting speed direction and wood grains $\varphi_r$, as well as cutting edge dullness $VB_w$ for the wood of *Liriodendron tulipifera*: $b_1$ = 0.0006; $b_2$ = 2.8537; $b_3$ = 0.3148; $b_4$ = 0.5061; $b_5$ = 0.0029; $b_6$ = 3.5853; $b_7$ = 8.5167, by variation of independent variables: $\varphi_s$<23.4; 188.4°>; $VB_w$<4; 82 μm>. The quality of the model (4) fit is characterized by the quantifiers: $SK$ = 853.8; $R^2$ = 0.94; $SD$ = 3.8 N, and is also illustrated in Fig. 4b.

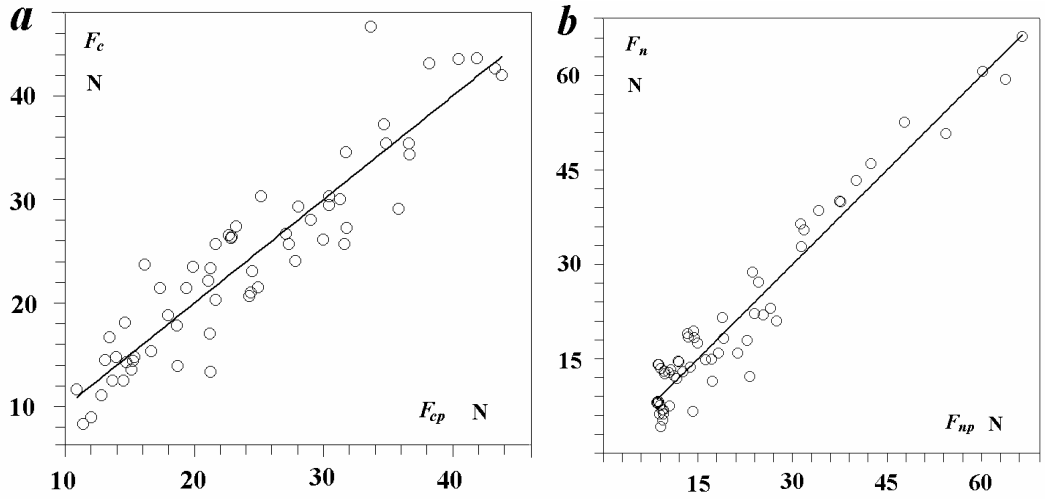


**Fig. 4.** Plots of main $F_c$ and normal $F_n$ cutting forces observed by routing Liriodendron tulipifera routing against predicted main $F_{cp}$ and normal $F_{np}$ forces according to models: a - (3) and b - (4)

From Fig. 5a it can be seen that for maximum cutting edge dullness $VB_w$, the $F_c$ and the $F_n$ increased with increasing average angle $\varphi_R$, and reached their maximum at average angles $\varphi_r$ = 117.7° and $\varphi_r$ = 87.3°, respectively. Such a relation was not evidenced for the sharp cutting edge. In the dependences $F_c$ and $F_n = f(VB_w, \varphi_r)$, a strong interaction $VB_w \cdot \varphi_r$ was evidenced. The $F_n$ reaches it's larger maximum by the $\varphi_r$ angle as much as 30.4° lower than in case of the $F_c$. Different shapes of relations $F_c = f(VB_w, \varphi_r)$ and $F_n = f(VB_w, \varphi_r)$, as well as a presence of their maximum beside $\varphi_r$ = 90° for sharp and dull cutting edge is a phenomenon that is in contradiction with equations (1) and (2).

For almost parallel cutting, by $\varphi_r$ <30° and $\varphi_r$ > 160°, enlargement of the cutting edge recession $VB_w$ caused rather small increases of the $F_c$ and $F_n$ values, slightly more for the $F_c$. This finding also contradicts information from the literature. In the analyzed range of the cutting edge recession $VB_w$<4; 82 μm>, the ratio between the largest and the lowest value of the $F_c$ was as high as 4.2 in this paper, while only 1.3 according to the literature (Amalitskij and Lyubchenko 1977, Orlicz 1982).

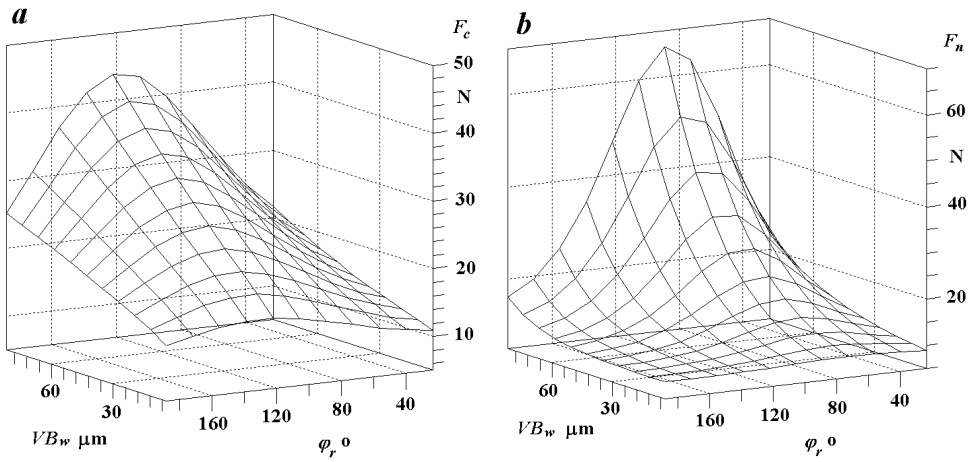


***Fig. 5.*** Dependence between main force $F_c$ and normal force $F_n$, the grain angle $\varphi_S$, and the cutting edge dullness $VB_w$, according to models: a - (3) and b - (4)

For formulas (5) through (7) describing the relationship between the main force $F_c$ and $\varphi_r$, $f_z$, $v_c$, and $mc$, for wood of *Cordia alliodora*, peripheral up-milling, the following estimators were evaluated: $c_1$ = 1.1364; $c_2$ = 1.3095; $c_3$ = 1.2049; $c_4$ = 1.2561; $c_5$ = -0.2581; $c_6$ = $-7.36 \cdot 10^{-2}$; $c_7$ = 0.3623; $c_8$ = 1.2681; $c_9$ = 0.2485; $c_{10}$ = 0.9209; $c_{11}$ = 1.1441; $c_{12}$ = 2.1219; $c_{13}$ = 0.1764; $c_{14}$ = 0.603; $c_{15}$ = 1.6861, by a range of variation of independent variables: $\varphi_r$<1.99 ; 6.96° >; $f_z$<0.13; 2.09 mm>; $v_c$<10; 40 m/s>; $mc$<11.5; 30> %. The quality of the models (5) through (7) fit is characterized by the quantifiers: $SK$ = 47.7; $R^2$ = 0.93; $SD$ = 0.61 N, and is also illustrated in Fig. 6.

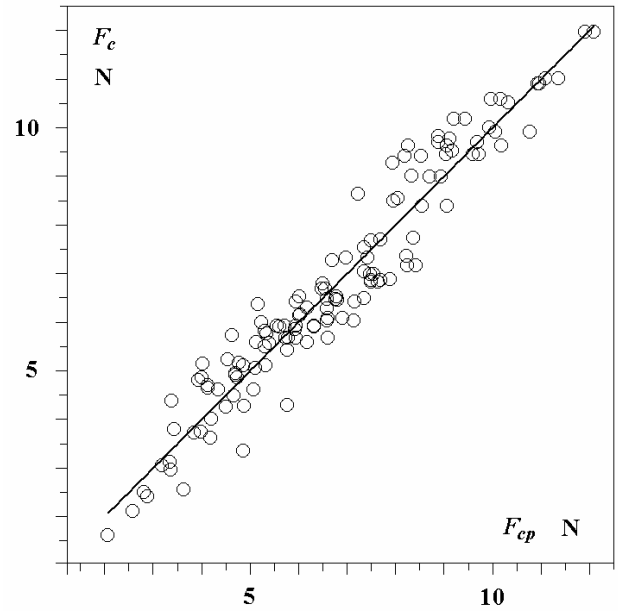


**Fig. 6.** Plot of main $F_c$ cutting force observed by milling Cordia alliodora against predicted main $F_{cp}$ force according to models (5) through (7)

Graphical illustrations of the relations (5) through (7) are shown in Figs. 7 and 8. From Fig. 7 an increase in the main force $F_c$ was observed with increasing feed per edge $f_z$ and the average angle $\varphi_r$ between cutting speed direction $v_c$ and wood grain. This relation dropped down for the lowest values of analyzed independent variables. In the range of the feed per edge $f_z$<0.13; 2,09 mm>, a ratio between the largest and the lowest value of the $F_c$ was in similar range with values given in literature for lime tree wood. Fig. 8 shows that the $F_c$ slightly declined with an increase in *mc* by the highest value of $v_c$. This is in agreement with the literature. The interactions $\varphi_r / f_z$, $f_z \cdot v_c$, and $\varphi_r \cdot v_c$, and the much weaker interactions $\varphi_r / mc$ and $v_c \cdot mc$ are new findings.

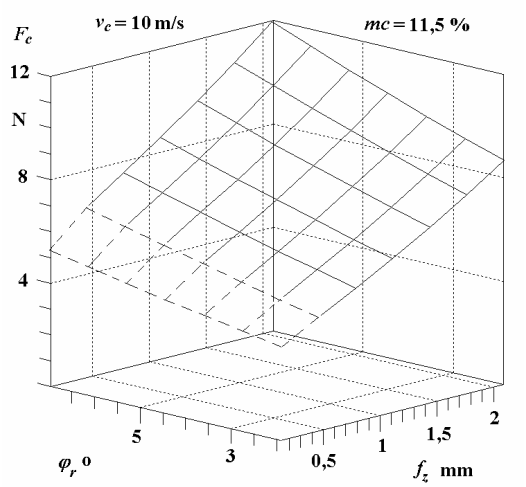


**Fig. 7.** Dependence of the main force $F_c$ from the average grain angle $\varphi_r$ and the feed per edge $f_z$, according to models (5) through (7) by the lowest value of $v_c$ and *mc*; region marked by broken line lay outside experimental matrix

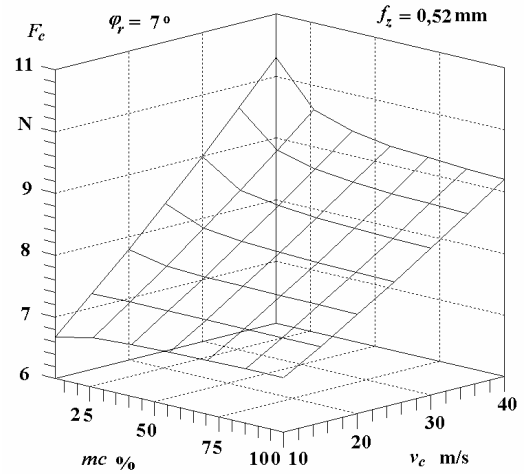


**Fig. 8.** Dependence of the main force $F_c$ from the cutting speed $v_c$ and the moisture content *mc* according to models (5) through (7)

From Fig. 8 it can be seen that the main force $F_c$ increased with an increase of the $v_c$ over the whole analyzed range, slightly more for the lowest moisture content *mc*, which contradicts information from the literature. Figure 8 also shows that the moisture content *mc* had limited influence on the main force $F_c$, to the lowest analyzed value. Within the analyzed range of the moisture content *mc*<11.5; 100 %>, the ratio between the largest and the lowest values of the $F_c$ was as high as 1.13 in the present paper, in comparison with 1.25 according to the literature (Kivimaa 1950; Amalitskij and Lyubchenko 1977; Orlicz 1982).

Analysis performed in the present study indicates that for an adequate description of wood cutting forces, including the dependence on machining parameters, more precise formulas have to be applied in place of the relations (1) and (2).

## CONCLUSIONS

1. By peripheral up-routing of *Liriodendron tulipifera* wood, for the highest cutting edge dullness $VB_w$ = 82 μm, the main cutting force $F_c$, strongly increases with increasing average grain angle $\varphi_r$ towards cutting speed $v_c$ up to $\varphi_r = 117.7^o$. This is followed, for yet higher $\varphi_r$ values, by rapid decreases in $F_c$.
2. For the lowest cutting edge dullness $VB_w$ = 4 μm, the main cutting force $F_c$ slightly increases with increasing $\varphi_r$, up to $\varphi_r = 117.7^o$ and afterwards for higher $\varphi_r$ the $F_c$ slowly decreases.
3. The differentiated influence of the cutting edge dullness represented by the $VB_w$ on the main cutting force $F_c$ has it's source in very strong interaction $VB_w \cdot \varphi_r$.
4. By peripheral up-routing of *Liriodendron tulipifera* wood, for the highest cutting edge dullness $VB_w$ = 82 μm, the normal cutting force $F_n$, strongly increases with increasing average grains angle $\varphi_r$ towards cutting speed $v_c$ up to $\varphi_r = 87.3^o$ and afterwards for higher $\varphi_r$ the $F_n$ rapidly decreases.
5. The normal force $F_n$ does not follow the main cutting force $F_c$. Rather, the $F_n$ reaches it's maximum by the $\varphi_r$ angle $30.7^o$ lower than the $F_c$. force.
6. For the lowest cutting edge dullness $VB_w$ = 4 μm, the normal cutting force $F_n$ slightly increases with an increase of $\varphi_r$ up to $\varphi_r = 87.3^o$ and afterwards for higher $\varphi_r$ the $F_n$ slowly decreases.
8. A lack of the maximum cutting forces near average angle $\varphi_r = 90^o$ for a sharp tool by routing of *Liriodendron tulipifera* wood was evidenced.
9. By up-milling of wood of *Cordia alliodora*, the main force $F_c$ strongly increases with increasing rate per edge $f_z$ within the range $f_z$<0.13; 2.09 mm>.
10. The main force $F_c$ increases with increasing average grain angle $\varphi_r$ towards cutting speed $v_c$ within the range $\varphi_r$<1.99; $6.88^o$>, during up-milling of *Cordia alliodora*.
11. During up-milling of *Cordia alliodora*, the main force $F_c$ increases with an increase of cutting speed $v_c$ over the whole analyzed range $v_c$<10; 40 m/s>.
12. An increase of the moisture content *mc* reduces the main force $F_c$. This relation is important only at the lowest value of mc and the largest cutting speed *vc*.

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# BIO-MODIFICATION OF EUCALYPTUS CHEMITHERMO-MECHANICAL PULP WITH DIFFERENT WHITE-ROT FUNGI

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Modification of chemithermomechanical pulp (CTMP) by fungal treatment was investigated. Eucalyptus CTMP was treated with three different types of white-rot fungi, namely, *Phanerochaete chrysosporium* (*P.c*-1767), *Trametes hirsute* 19-6 (*T.h*-19-6), and *Trametes hirsute19-6w (T.h-19-6w),* under a stationary culture condition. Pulp total weight loss, lignin loss, and cellulose loss were determined to compare the different enzymes secreted by the three fungal strains. Pulp physical strengths, optical properties, and bleachability after the fungal treatment were investigated to compare the effect of fungal treatment on the pulp quality improvement. The results show that lignin reduction by both *T.h*-19-6 and *T.h*-19-6 (w) was about twice as much as that by *P.c*-1767. However, the selectivity of *T.h*-19-6 (w) towards lignin over cellulose was only 0.82, while that of *T.h*-19-6 was as high as 4.43. After *T.h*-19-6 treatment, pulp tensile, tear, and internal bonding strength increased by about 27%, 38%, and 40%, respectively.

*Keywords: Eucalyptus CTMP pulp, White-rot fungi, Trametes hirsute 19-6, Bio-modification*

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## INTRODUCTION

Chemithermomechanical pulp (CTMP) has been used increasingly in traditionally wood-free paper grades due to its relatively low costs and some specific qualities such as high bulk, high opacity, and good printability (Zhou 2004; Cannel and Cockram 2000; Zhou and Zou 2003). However, the bonding ability of CTMP fibers is not as high as kraft pulp fibers, since most of the lignin is kept in the CTMP fibers. This sets a limit on the maximum addition rate of CTMP fibers in wood-free paper. It has been found that a large portion of the CTMP fiber surface is covered by lignin-rich middle lamella material (Cisneros et al. 1995; Börås et al. 1999; Li et al. 2006), and lignin on the fiber surface is particularly detrimental to inter-fiber bonding (Shao and Li 2006; Li and Reeve 2002).

Fiber modification refers to any processes that can alter the papermaking property of the fibers (Gruber 2000). Traditional fiber modification includes chemical modify-ation and mechanical modification. For CTMP fibers, the bleaching process is not only for increasing the brightness of the pulp fiber, but also for adjusting the bonding ability and the flexibility of the fibers (Zhou and Zou 2003). Mechanical modification, i.e. low-consistency (LC), refining is becoming a more popular means for papermakers to fine-

tune the pulp property (Zhou and Zou 2003; Franzén 1986).

Use of lignin-degrading fungi prior to mechanical pulping, so-called bio-pulping, has been studied extensively by several research groups. Most studies were targeted on reducing the energy consumption of the refining process by fungal treatment of wood chips. It has also been found (Abuhasa et al. 1988; Bar-Lev et al. 1982; Pere et al. 1996; Leatham et al. 1990b) that by treating the CTMP fibers with fungi after the first-stage refiner, not only the energy consumption of the second-stage refiner is reduced, but also the physical strength of the resultant pulp is improved. Some studies (Hunt et al. 2004; Ferraz et al. 2002) proposed that the benefits of biopulping, including energy savings and increased handsheet strength, are due to the structure changes of the residual wood components and the increase of acid group content of wood. However, some studies (Akhtar et al. 1992; Leatham et al. 1990a) found that with fungal treatment, pulp strength was deteriorated. It was suggested (Setlife et al. 1990) that the contradictory results might be due to the difference in the types of fungi and in the treatment conditions used in different studies.

Fungal treatment of wood chips is environmentally friendly and saves energy consumption in the refining process, but the treatment time is quite long, and the process itself is complicated in comparison with the chemical pretreatment process (Scott et al. 1998; Scott et al. 1998). The present study attempts to explore the possibility of using lignin-degrading fungi to modify the CTMP fiber for improved strength properties. The rationale behind is that when pulp fibers, rather than wood chips, are treated, only a minor or a relatively short period of fungal treatment may remove most of the lignin-rich material from the fiber surface. It is expected that sole removal of the fiber surface lignin will improve the inter-fiber bonding strength significantly, and at the same time retain the other properties of the CTMP fibers. This paper reports the first step in this study, which is to compare the overall effect of different stains of white-rot fungi on eucalyptus CTMP fibers. The effect of fungal treatment on lignin removal, yield loss, pulp strength properties, optical properties, and bleachability are compared.

## EXPERIMENTAL

### Pulp Samples

*Eucalyptus urophylla* chemi-thermomechanical pulp was provided by the Chinese Academy of Forestry, Nanjing, China. The brightness of the pulp was 49.6% ISO, and the CSF freeness was 700 ml. The pulp was air-dried to a moisture content of 15% and stored at 4 $^{o}$C until use.

### Fungi

The white-rot fungus *Phanerochaete chrysosporium* (*P.c*-1767) used was the same as that described by Pease and Tien (1992). *Trametes hirsute* 19-6 (*T.h*-19-6) and *Trametes hirsute*19-6w (*T.h*-19-6w) were isolated from bamboo in the wild field by the State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou, China. The *P.c*-1767 produces lignin peroxidase (Lip), manganese peroxidase (Mnp), cellulase, and hemicellulase. *T.h*-19-6 and *T.h*-19-6 (w) produce

manganese peroxidase (Mnp), laccase, hemicellulase, and cellulase. *T.h*-19-6 produces only a minor portion of cellulase. All the fungal strains were cultured on PDA bevel culture medium, and a spore suspension of 9-day-old culture was used as the inoculum. Seeding of the pulp was carried out as 0.5 ml/g of pulp (o. d.).

## Fungi Culture Conditions

The incubation was performed in 1000 ml flasks with 30 g of CTMP pulps (o. d.), 15 ml of spore suspension, and some of the culture medium, without using a buffer. Sterilized water was added to give a final pulp consistency of 25% (w/v). The solution, flask, and pulp samples were sterilized in an autoclave (30min, 121 °C). The control samples contained sterile water instead of the spore suspension. The flask was incubated under a stationary culture condition as shown as in Table 1.

**Table 1.** The Culture Conditions for White-Rot Fungi

| | Temperature (°C) | Time (days) | Initial pH |
|---|---|---|---|
| *P.c*-1767 | 35 | 7 | 4.8 |
| *T.h*-19-6 | 28 | 7 | 4.5 |
| *T.h*-19-6w | 28 | 7 | 4.5 |

The flasks were flushed with oxygen for 10 min every day. After incubation, all pulp samples were filtered with a 400-mesh nylon screen and washed with water to remove the superficial mycelium and then dried in air. The residual lignin content was determined as Klason lignin (TAPPI Standard T222), and cellulose content was determined according to TAPPI Standard T249. Three replicate experiments were performed for each test, and the average values are reported.

## Handsheet Properties

Handsheet properties, including tensile, tear, and internal bonding strength, were determined according to TAPPI standard methods T 205, T220, T248 respectively. Optical properties (brightness, opacity, scattering coefficient) were determined with a Technidyne TechniBrite™ Micro TB-1C Photospectrometer according to the ISO standard.

## Electron Microscopy

Scanning Electron Microscope (SEM) images of pulp fibres were obtained using a JEOL JSM-6400 scanning electron microscope, operated in secondary electron mode at an accelerating voltage of 10kv. CTMP fibres were dehydrated with an ethanol dehydration series and then dried with critical point drying method. The fibres were coated with gold for 120s using a S150 sputter coater prior to scanning.

Transmission Electron Microscope (TEM) images of pulp fibres were obtained using a JEOL 2011 Transmission Electron Microscope, operated at 120 kV. Images were taken with a Gatan digital camera. Prior to analysis, the fibre samples were embedded in Spurr-resin after dehydration with an ethanol dehydration series. Ultra-thin sections (70 nm) were cut with a diamond knife onto distilled water. Sections were collected onto

uncoated, copper grids. Some grids with sections were post-stained with uranyl acetate and lead citrate to enhance contrast.

### Bleaching

A two-stage bleach sequence ($Na_2S_2O_4$ + $H_2O_2$) was used. The dosages of $Na_2S_2O_4$ and $H_2O_2$ were 1.5% and 3.0% (w/w), respectively. Detailed bleaching conditions are listed in Table 2. Before $H_2O_2$ bleaching, the pulp was treated with an EDTA solution (0.3%) at 3% consistency to remove metal ions. $MgSO_4$ (0.5g/L) was used to stabilize the peroxide and to prevent degradation of carbohydrates.

**Table 2.** Two-Stage Bleaching Conditions

| | Initial pH | Pulp consistency (%) | Temperature ($^oC$) | Time (min) |
|---|---|---|---|---|
| $Na_2S_2O_4$ | 8.0 | 1.5 | 60 | 60 |
| $H_2O_2$ | 11.0 | 3 | 70 | 90 |

## RESULTS AND DISCUSSION

### Pulp Chemical Composition Change after Fungal Treatment

White-rot fungi can degrade all the major components of wood, i.e., cellulose, hemicellulose, and lignin, since they can secrete lignin-degrading enzymes, cellulase, and hemicellulase at the same time (Eriksson 1990). However, different fungal strains may secret these enzymes in different proportions. Table 3 lists the changes of the chemical composition of the CTMP after fungal treatment. It can be seen that all three strains had significant effects on the CTMP fibers. The total weight loss by the *T.h*-19-6 (w) was the highest, about 7%, and the total weight losses by *P.c*-1767 and *T.h*-19-6 were only about 3%. The cellulose loss by *T.h*-19-6 (w) was even greater than the lignin loss, with a selectivity factor of 0.82. In contrast, lignin loss by *T.h*-19-6 was much larger than cellulose loss, more than four times. This indicates that the *T.h*-19-6 secreted a higher level of lignin-degrading enzymes than cellulase and hemicellulase. *P.c*-1767 removed much less lignin, but the total weight loss was almost the same as that by *T.h*.-19-6, which means that *P.c*-1767 also hydrolyzed a significant amount of hemicellulose. For the purpose of CTMP fiber modification, it is desirable that only lignin is removed. Removal of cellulose and hemicellulose not only reduces pulp yield, but may also decrease the physical strengths and interfibre bonding ability of the fibers, since cellulose constitutes the framework of the fiber structure, and hydrophilic hemicellulose promotes fibre swelling, and inter-fiber hydrogen bonding. Therefore, of the three fungal strains, the *T.h*-19-6 was the most suitable one for the fiber modification.

**Table 3.** Changes of Pulp Chemical Composition after Fungal Treatment

| Fungi strains | Total weight loss (%) | Lignin loss (%) | Cellulose loss (%) | Lignin selectivity (lignin loss/cellulose loss) |
|---|---|---|---|---|
| Control | 0.35 | 0.12 | 0.49 | 0.24 |
| *P.c*-1767 | 3.28 | 3.95 | 1.02 | 3.78 |
| *T.h*-19-6 | 3.46 | 7.70 | 1.74 | 4.43 |
| *T.h*-19-6w | 7.24 | 6.23 | 7.62 | 0.82 |

## Pulp Physical Strength Properties

In the present study, the freeness of CTMP used was CSF 700 ml, which is toward the high end of the freeness range of commercial CTMP pulps. If handsheets are made by the CTMP fibers only, the physical strength will be very low, and it will not be easy to compare the effect of fungal treatment. Therefore, the control pulp and fungal-treated pulps were further refined in a PFI mill to a target freeness level of CSF 300 mL. As shown in Table 4, treatment with white-rot fungi *P.c*-1767 and *T.h*-19-6 improved the strength properties of handsheets produced from the CTMP pulps. In particular, tensile index and internal bonding were increased significantly after white-rot fungus 19-6 treatment.

**Table 4.** Pulp Physical Strength Properties after Fungal Treatment

| Fungi Strains | Control | *P.c*-1767 | *T.h*-19-6 | *T.h*-19-6w |
|---|---|---|---|---|
| Freeness (ml) | 325 | 320 | 320 | 325 |
| Tensile index (N.m/g) | 24.20 | 26.68 | 30.76 | 22.54 |
| Tear index ($mN.m^2/g$) | 3.28 | 3.98 | 4.52 | 3.12 |
| Internal bonding ($J/m^2$) | 59.18 | 77.23 | 82.79 | 60.92 |

As discussed previously, both *P.c*-1767 and *T.h*-19-6 removed relatively small amounts of lignin, being about 4% and 8%, respectively. It is expected that if a small portion of lignin on the fiber surface can be removal, then the increase in inter-fiber bonding will be significant. *T.h*-19-6 (w), although it removed about 6% of lignin, it also removed about the same amount of cellulose. Therefore, the effect on the physical strength may be balanced by these two counteracting factors.

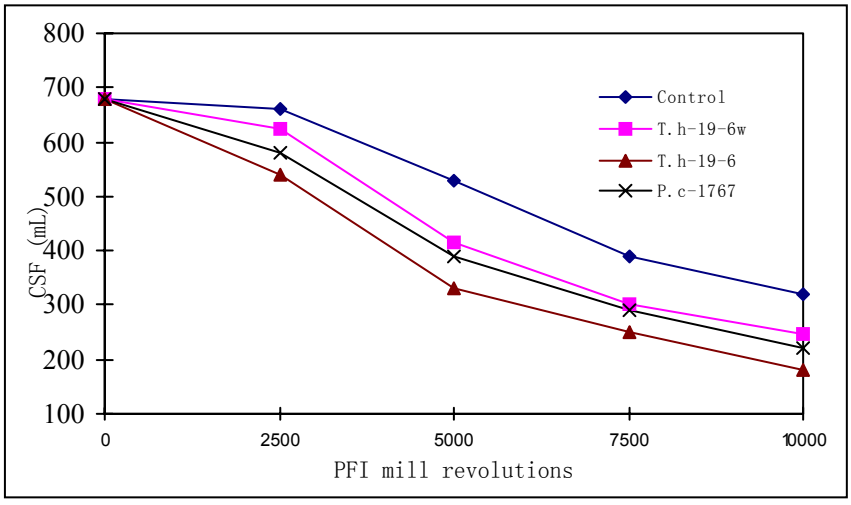



**Fig. 1.** Freeness change PFI mill revolutions of the control and fungal-treated eucalyptus CTMP pulps.

Figure 1 shows the freeness change as a function of PFI revolutions for the control pulp and fungal-treated pulps. It can be seen that in comparison with the control pulp, all three fungal treated pulps were easier to be refined to lower freeness levels, and *T.h*-19-6 treated pulp was the easiest. This implies that, for a targeted freeness level, *T.h*-19-6 treatment will reduce the energy consumption in the LC refining process. In commercial practice, LC refining becomes necessary for fine-tuning the pulp properties for most paper grades. Therefore, the fungal treatment will benefit the LC refining.

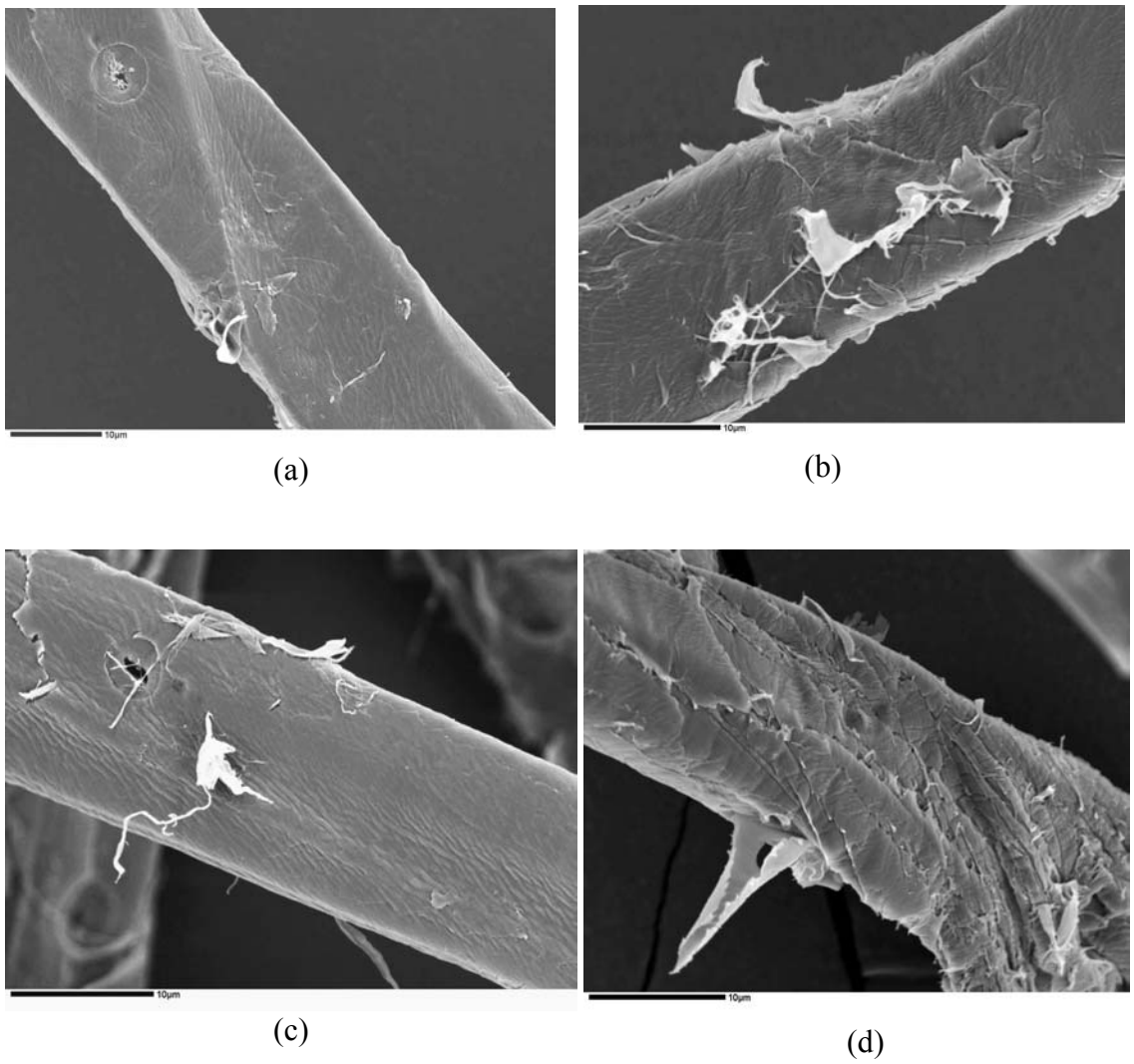
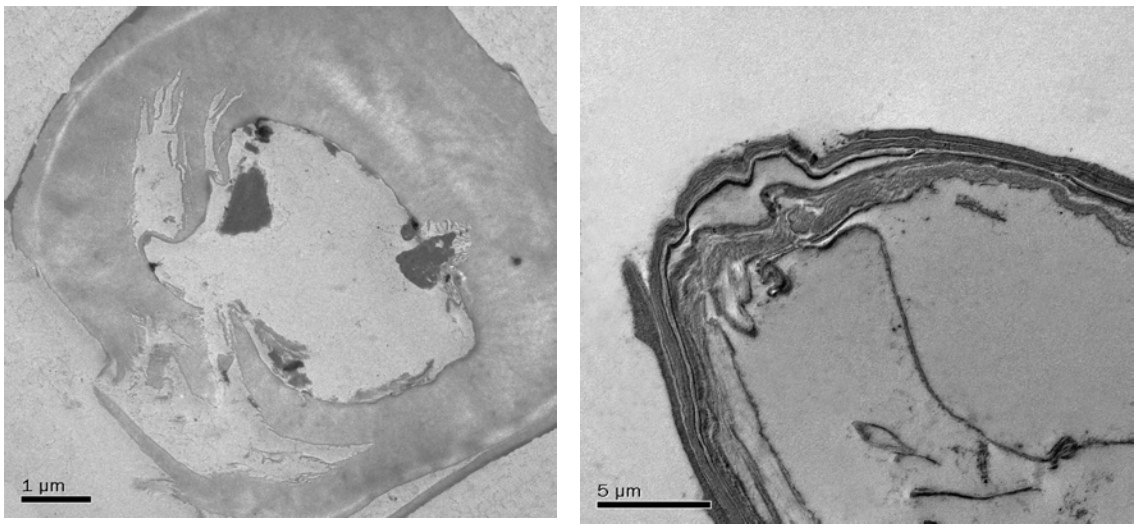



**Fig. 2.** SEM images of eucalyptus CTMP fibers before and after *T.h*-19-6 fungal treatment. (a) image of a control CTMP fiber; (b) a control CTMP fiber after PFI treatment; (c) a fungal-treated CTMP fiber; and (d) a fungal-treated CTMP fiber after PFI treatment.

In fact, the beneficial effect of the fungal treatment was better realized by the subsequent LC refining process. As shown in Figure 2, without PFI treatment, the CTMP fibers of control pulp and fungal-treated pulp looked almost the same. After PFI treatment, a slight increase in external fibrillation could be observed on the control fibers.

In contrast, a substantial change could be observed on the fungal-treated fibers. The entire structure of the fiber had been loosened, and cracks between microfibrils could be seen. The fiber also appeared twisted and more flexible due to the overall structural change. The difference in the structural change after PFI refining is not surprising. It is understood that the fungal treatment dissolves some of the fiber wall components, but the total weight loss was relatively small, being about only 3.46% in case of *T.h*-19-6 treatment. Such a small amount of material loss may not be seen from the structural change, as shown in Fig. 2. However, even a small degree of lignin and/or cellulose degradation in the fiber wall will loosen the bonding between microfibrils. When a subsequent mechanical treatment such as PFI refining is used, the weak points in the fibre structure due to fungal treatment will be broken, leading to a significant structure change. This can be better seen from the cross-sectional images of fiber wall as shown in Fig. 3. Before PFI treatment only some damage such as cracks or voids due to fungal treatment could be seen of the fiber walls. After PFI treatment the entire fiber wall was delaminated, resulting in extensive internal fibrillation of the fiber wall. This also, on the other hand, explains the increased pulp physical strength after the fungal treatment




(a) (b)

**Fig. 3.** TEM images of eucalyptus CTMP fibers after T.h-19-6 fungal treatment.
(a) without PFI refiner treatment; and (b) after PFI treatment.

## Pulp Optical Properties

One of the major concerns for bio-mechanical pulping is the pulp brightness. While most studies on Kraft pulp have reported that fungal treatment increases pulp brightness (Reid and Paice1994; Fujita and Kondoi 1991), the results from fungal treatment of mechanical pulp show a decrease in pulp brightness (Abuhasan et al. 1988; Sykes 2003; Pellinen et al. 1989). It was suggested that the brightness loss is caused by melanin synthesized during the secondary stage of growth and lignin modification by enzymes (Fukui et al. 1991). It was also suggested that the discoloration of mechanical pulp seems to be connected to the presence of sulfonate groups, since Kraft pulp did not

turn dark (Pellinen et al. 1989). It has also been shown by some recent studies (Scott et al. 2002; Guerra et al. 2005; Guerra et al. 2006) that although the brightness of fungal treated Eucalyptus mechanical pulp was reduced, high brightness levels of bio-mechanical pulp could be attained after bleaching.

Brightness and opacity were determined to evaluate the effect of fungal treatment on optical properties of CTMP pulp (Table 5). The data shows that fungal treatment has a slight effect on opacity but causes a sizable decrease in the pulp brightness. Compared with other studies in the literature, the brightness reduction by fungal treatment can be as high as by 140% (Abuhasan et al. 1988). The difference may be attributed to the different fungal strains, wood species, and the CTMP processing conditions.

**Table 5.** Pulp Optical Properties after Fungal Treatment

| Fungi strains | Opacity % | Brightness (prior to bleaching) %ISO | Brightness (after bleaching) %ISO |
|---|---|---|---|
| Control | 99.3 | 49.6 | 72.6 |
| *P.c*-1767 | 99.5 | 36.9 | 58.6 |
| *T.h*-19-6 | 99.5 | 37.8 | 70.8 |
| *T.h*-19-6w | 99.6 | 35.4 | 54.8 |

The bleachability of fungal treated pulps was evaluated by using a two-stage bleaching sequence. Sodium hydrosulfite was used in the first stage, and alkaline hydrogen peroxide was used in the second stage. As shown in Table 5, the brightness of the pulp treated by *T.h*-19-6 increased by 33 brightness units to 71% ISO, which was almost the same as the final brightness of the control pulp (73% ISO). However, brightness of the pulps treated by *P.c*-1767 and *T.h*-19-6 (w) was only 58.6% ISO and 54.8% ISO, respectively. The results indicate that different fungi have different effects on the pulp bleachability. Treatment of CTMP by *T.h*-19-6, although it reduced the initial pulp brightness, the pulp could be further bleached to a high brightness level by a conventional bleaching process. The result is encouraging since in many cases, the brightness of mechanical pulps is reduced by fungal treatment and it is difficult to bleach the pulps to a higher bright brightness level.

## SUMMARY

1. The properties of CTMP fibers can be improved by a fungal treatment process. Removal of a small amount of lignin from the CTMP fibers can improve the pulp strengths significantly; however, removal or degradation of cellulose will deteriorate pulp strengths.

2. For the three types of white-rot fungi, namely, *Phanerochaete chrysosporium* (*P.c*-1767), *Trametes hirsute* 19-6 (*T.h*-19-6) and *Trametes hirsute19-6W (T.h-19-6w)*, *T.h*-19-6 has the highest selectivity towards the degradation of lignin over cellulose. The amount of lignin removed by *T.h*-19-6 is more than four times the amount of cellulose. After *T.h*-19-6 treatment, pulp tensile, tear and internal bonding increased by 27%, 38% and 40% respectively. With *T.h*-19-6 (w)

treatment, cellulose loss is greater than lignin loss. Therefore, pulp physical strengths decreased after the fungal treatment.

3. Electron micrographs of fibers revealed that fungal treatment loosened the fiber wall structure due to the removal and/or degradation of the fiber wall components. A subsequent PFI refining treatment further promoted the fungal treatment effects, resulting in both external and internal fibrillation, which is the reason behind the increased bonding strength.

## ACKNOWLEDGMENTS

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# ABRASIVE WEAR BEHAVIOUR OF BAMBOO (*DENDROCALAMUS STRICTUS*) POWDER FILLED POLYESTER COMPOSITES

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An experimental study was conducted to determine the abrasive wear behaviour of different weight percentage bamboo powder filled polyester composites under the multipass mode. The effect of bamboo powder concentration and sliding distance on the weight loss of composites has been analyzed. Worn surface have been analyzed to observe the mechanism of wear. The weight loss depends on bamboo powder concentration. The weight loss decreases with the increase of sliding distance. Samples having 20 weight percentage (wt%) of bamboo powder show the maximum weight loss during abrasion.

*Keywords: Abrasive wear, Bamboo powder, Polyester composite*

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## INTRODUCTION

Bamboo is a natural composite material. Presently it is used in making baskets and housing structures (Rohatgi et al. 1991; Chand et al. 1985; Chand et al. 2007; Hashmi et al. 2006). Bamboo is available in large quantities. Being lightweight, cheap, and biodegradable, it is a useful filler material to develop polymer composites (Rohatgi et al. 1991). Bamboo powder filled polymer composites have found application in developing structural components. A lot of literature is available on bamboo and bamboo/ polymer composites that deal with mechanical behaviour. Bamboo powder filled unsaturated polyester composites are used for making panels for low stress applications. During use these items are subjected to abrasion, and hence the multipass abrasive wear tests was done to characterize the wear performance of bamboo powder filled polyester composites.

Abrasive wear of composites is strongly influenced by the filler loading and operating parameters (Hashmi et al. 2006; Chand and Dwivedi 2006). The interaction of both parameters influences the abrasive wear behaviour (Chand et al. 1995; Venkateswarlu 2006). Wear studies on pure bamboo (*Dendrocalamus strictus*) stems were reported in the literature in which the effect of fibre's direction was analyzed (Chand et al. 2007). Jain et al. (1992) have studied the mechanical behaviour of bamboo and bamboo composite. They found that bamboo has excellent mechanical properties with specific strength and modulus. Chand and Hashmi (1995) have predicted the tensile behaviour of red mud filled polymers in the past as a function of different experimental conditions such as red mud loading, by using the factorial design approach. In this paper, bamboo powder filled polyester composites having different weight percentage of

bamboo powder are developed and their wear behaviour is determined under the multipass mode.

## EXPERIMENTAL

### Sample Preparation

Bamboo (*Dendrocalamus strictus*) powder, having size less than 355 μm was dried in an air oven at 80°C for 2 h. to remove moisture. Commercially available unsaturated polyester resin, which cures at room temperature, was used as matrix. In the mix of polyester resin, 2% accelerator and 2% hardener were added and stirred for one min., and then different amounts of bamboo powder (10, 20 and 30) wt% were added separately. The final mix was poured into the cylindrical moulds to make composite pins of length 30 mm and diameter 10mm. The mix was kept in the mould for curing at room temperature 30°C for 24 hours. Cured samples were then removed from the moulds and used for multipass abrasive wear measurements.

### Tensile Tests

Tensile testing of different bamboo powder filled polyester resin composites was done by using a Tensile tester (Scientific Testing India make). Samples were prepared as per ASTM D638.

### Abrasive Wear Tests

Abrasive wear studies were carried out under multipass condition on a pin-on-disc type wear machine model TR-201, Ducom make. Abrasive paper of 400 grade (grit-23 μm) was fixed by double sided adhesive tape on a disc rotating at 200 rpm in a track diameter of 6 cm. Emery paper had irregularly shape embedded SiC particles. The sample pin was fixed in a holder and was abraded at 10 N applied load for varying sliding distance on the same track. The samples were cleaned by using a soft brush to remove particles etc. before and after each run. This work took half an hour, which cooled the samples to room temperature. The wear loss (weight loss) was determined after each run, using a Mettler Toledo higher precession balance of $10^{-5}$ gm accuracy.

### SEM Observation

Worn surfaces of samples were observed by using a scanning electron microscope (model 35 CF JEOL, Japan). The sample surfaces were gold coated before observation. Worn microstructure for the composites having maximum bamboo particles, 30wt%, has been taken to show the maximum effect of bamboo particles under the multi pass wear condition.

### Factorial Design

A two-level full factorial design of the experiment has been used in this study. Two parameters were varied on two levels i.e. upper level and lower level. The upper level and lower level of the two parameters i.e. bamboo particles concentration and sliding distance, are given in Table 1. This table also gives the coded values of upper and lower levels of each of the parameters in parenthesis.

**Table 1.** Bamboo Filler Concentration and Sliding Distance Values along with Coded Values.

| Sl. No. | Bamboo Filler conc. (wt%) (upper and lower level) | Sliding Distance (m) (upper and lower level) |
|---|---|---|
| 1 | 30(+1) | 62.8(+1) |
| 2 | 30(+1) | 15.7(−1) |
| 3 | 10(−1) | 62.8(+1) |
| 4 | 10(−1) | 15.7(−1) |

The following regression equations were obtained from full factorial design method.

$$W = 0.0121 + 0.0051\ C - 0.00803\ S - 0.00371CS \quad (1)$$

A positive value of the coefficients signifies an increase in wear loss due to an increase in associated parameters and their interactions. Similarly, a negative coefficient signifies a decrease in the weight loss due to an increase in the associated parameters. The magnitude of the coefficient gives an idea about the extent of influence of the individual parameters or their interactions on the wear rate.

## RESULTS AND DISCUSSION

Average tensile strength values determined for 10, 20, and 30wt% bamboo powder filled polyester composites were 10.8, 10.6, and 5.36 MPa respectively. The decrease in strength on adding bamboo powder is because bamboo powder acted as filler, not as reinforcement. The average tensile strain values of 10, 20, and 30wt% bamboo powder filled polyester composites were 0.091, 0.078, and 0.072, respectively. Figure 1 shows the plot for weight loss as a function of sliding distance for different bamboo composites. Initially the wear loss decreased with increase of sliding distance for all the samples. Also initially high wear loss was observed because the abrasive paper was fresh. With consecutive runs, wear loss decreased gradually, because the abrasive grits became less effective. The wear debris filled the space between the abrasives (SiC grits), which reduced the depth of penetration in the sample. In other words, contact stress was reduced when debris came between the surfaces. The composite with 10wt% bamboo powder showed the minimum wear loss. Increase of bamboo content to 20wt% showed the maximum wear loss. Further increase of bamboo powder content reduced the wear loss. This is because at higher bamboo powder loading, wear mechanism was dominated by bamboo powder, which is less brittle than the polyester matrix. Samples having 20wt% bamboo content showed the critical weight percentage for lower wear resistance.

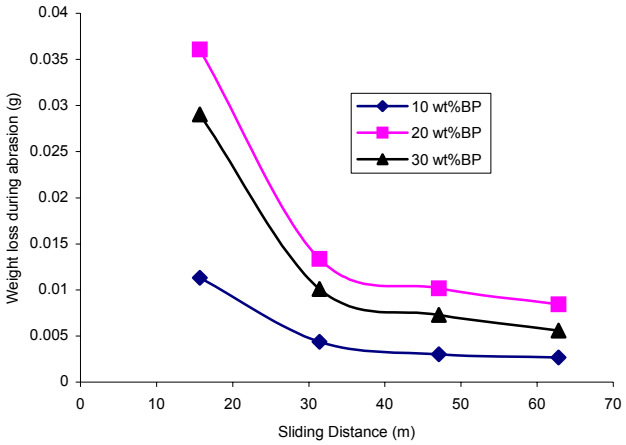


**Fig. 1.** Variation of wear loss with sliding distance for bamboo polyester composites having different wt% of bamboo.

Figures 2a and 2b show the worn microstructure of 30wt% bamboo powder composite after 62.8 m sliding distance under multipass abrasive wear at different magnification. Wear tracks are formed during multi pass wear due to micro-cutting.

In the magnified worn microstructure, initially micro-cracks are formed around the bamboo particles, and particles were removed under compression and shear. Increase of the bamboo content to 30wt% increased the resistance to shear force due to its fibrous and cellular structure.

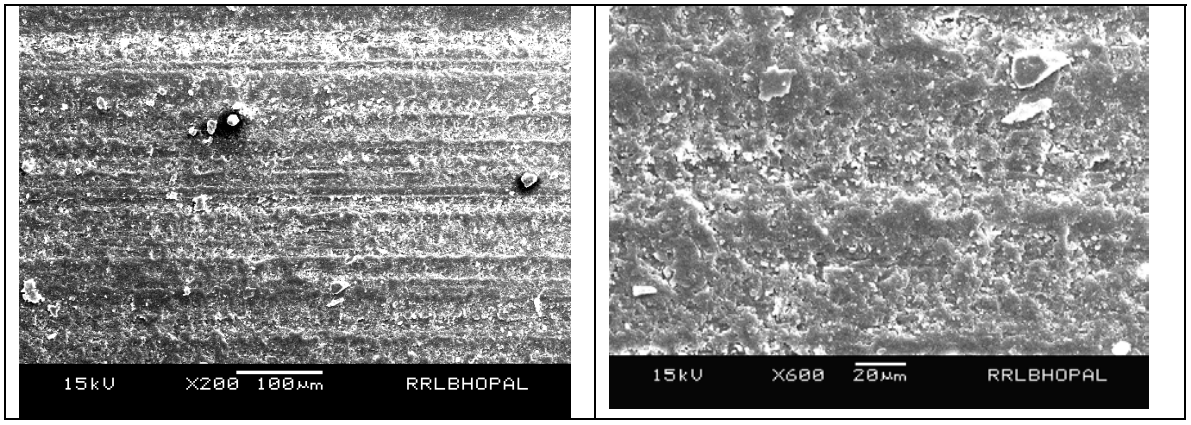


**Fig. 2 a (x200) and b (x600).** Worn microstructure of 30wt% bamboo powder unsaturated polyester composite after 62.8 m sliding distance.

## Validity of the Weight Loss Data

The validity of the equation was tested by conducting a series of tests at randomly selected experimental parameters such as filler concentration ($C$), and sliding distance (S). The calculated values under such selected experimental parameters were compared

with the experimental values. During the calculation of the wear loss under selected experimental conditions, the coded values of the experimental parameters were considered. The calculated value (CV) is defined as follows (**Venkateswarlu** et al. 2006):

$$CV = \frac{(SL-BL)}{Abs(BL-UL)} \quad \text{or} \quad \frac{(SL-BL)}{Abs(BL-LL)} \qquad (2)$$

where SL is the selected value, BL, UL, and LL are values of the selected parameters in the base level, the upper level and the lower level, respectively. The experimental values of wear loss at randomly selected experimental parameters (Table 2) were in agreement with the wear loss calculated using the coded values of the experimental parameters in equation (1). In most cases, the variations between the experimental and the calculated values were of the order of 8-18% The factorial design approach could be used for developing a regression equation to predict the wear behaviour that depends upon the composition, and experimental parameters.

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**Table 2.** Experimental and Calculated Values of Wear Loss

| S.N | Experimental value of weight loss in g | Predicted value of weight loss in g |
|---|---|---|
| 1 | 0.00438 | 0.008426 |
| 2 | 0.00303 | 0.005574 |
| 3 | 0.03608 | 0.02013 |
| 4 | 0.01334 | 0.01475 |
| 5 | 0.01015 | 0.00945 |
| 6 | 0.00843 | 0.00407 |
| 7 | 0.01011 | 0.021074 |
| 8 | 0.0073 | 0.016813 |

## CONCLUSIONS

Based on the wear studies carried out on bamboo powder filled polyester composites in abrasive wear mode, it was found that bamboo powder loading influenced the wear behaviour. Composite containing above 20wt% bamboo powder exhibited the lowest wear resistance. However, increase in sliding distance decreased the wear loss.

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# FAST PYROLYSIS – EFFECT OF WOOD DRYING ON THE YIELD AND PROPERTIES OF BIO-OIL

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The composition and properties of the products of fast pyrolysis of hardwood, obtained in a two-chamber (drying and pyrolytic) ablation type reactor in the temperature range 450-600ºC, were investigated. It has been found that, upon the additional drying of wood at 200ºC and subsequent pyrolysis, the quality of bio-oil is improved owing to the decrease in the amount of water and acids. It has been shown that the increase of the drying temperature to 240ºC decreases the yield of the main product. Optimum parameters of the drying conditions and the temperature of the pyrolysis of wood, at which the bio-oil yield exceeds 60% and its calorific value makes up 17-20 MJ/kg, have been determined.

*Keywords: Pyrolytic oil, Wood, Fast pyrolysis, Drying, Ablation type reactor*

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## INTRODUCTION

The annual world's stock of plant biomass increases by 117 billion tons (in terms of the weight of oven dry material), including by 80 billion tons in forests, which is equivalent to 40 billion tons of petroleum (Zaykov 2002).

The application of renewable plant biomass resources for energy production is becoming increasingly urgent worldwide, because it becomes evident that the sources of fossil fuel energy can be exhausted dramatically with increasing industrial, transport, and agricultural outputs. As resources, low-grade wood and other forms of biomes, for example, peat, straw and bark may be used. One of the methods for utilizing waste wood for energy purposes is thermal processing.

Along this line, technologies for fast pyrolysis of wood are progressing rapidly, which enables the conversion of solid wood biomass into a liquid product – bio-oil, which can be used as a fuel or as a raw material for producing valuable chemicals. As a fuel, bio-oil is neutral with respect to the release of carbon dioxide. Upon its burning, a low amount of nitrogen oxide is released, and no sulphur dioxides are formed. Bio-oil can be stored, pumped over, and transported in the same manner as petroleum products. However, its corrosive activity (pH 2.0-2.5), high viscosity, and possible stratification, which depend strongly on temperature, should be taken into account (Bridgwater 1999). Bio-oil can be burned directly in boilers, gas turbines, and diesel engines for heat and power supply (Bridgwater et al. 2001; Czernik and Bridgwater 2005).

The composition of pyrolysis oil is similar to the biomass composition. In comparison with wood, it has a somewhat higher heat capacity, namely, 15-20 MJ/kg. The products' composition depends on the pyrolysis conditions and the wood type. Pyrolytic oils, in comparison with other fuel oils, have a similar density and a low content of ash elements (Oasmaa and Meier 2002).

In realizing the fast pyrolysis of wood, a raw material with the water content 8-10% is commonly used (Oasmaa and Meier 2002). However, the water content in pyrolytic oil is equal to 25% on average, as it includes pyroligneous water, which is formed mainly upon the dehydration of carbohydrates. The high content of water in bio-oil has an adverse effect on the calorific value of the end product. To decrease the amount of water in bio-oil, wood with a low moisture content should be used for pyrolysis. However, the temperature range of wood drying is limited by the possibility of the development of thermal-oxidative reactions, which lead to a more cross-linked condensed system of components and a higher thermal stability of the wood complex (Domburg et al. 1980).

The objective of the present work was to investigate the effect of the drying process parameters and subsequent fast pyrolysis of hardwood on the properties, chemical composition and yield of bio-oil.

## EXPERIMENTAL

### Raw Materials

Mixed hardwood chips (fraction 0.1-1.0 mm, moisture 8.5-9%) were used.

### Pyrolysis

Fast pyrolysis was carried out using a two-chamber pyrolytic laboratory device that allows changing of the pyrolysis and drying temperatures and the duration of drying. The program "Maple10" was used for plotting the dependencies, based on multiple regression analysis.

The equipment's capacity was 150 g of the raw material in one cycle. The main constituent parts of the reactor (Fig. 1) are as follows:

- A drying chamber with a mixer and an autonomous heating and temperature control system (1).
- A pyrolysis chamber with a mixer, and an autonomous heating and temperature control system (2). The main constituent part of the pyrolysis chamber is a pan, which is heated to a definite temperature (450-700ºC). When opening a hatch, which connects chambers 1 and 2, the wood particles get onto the heated surface of the pan, where pyrolysis proceeds within 30 sec in an atmosphere of the gases formed.
- The volatile products' cooling and condensation systems (3). Condensation proceeds using a water cooling system, which consists of 2 coolers and a collector.
- Char collector.

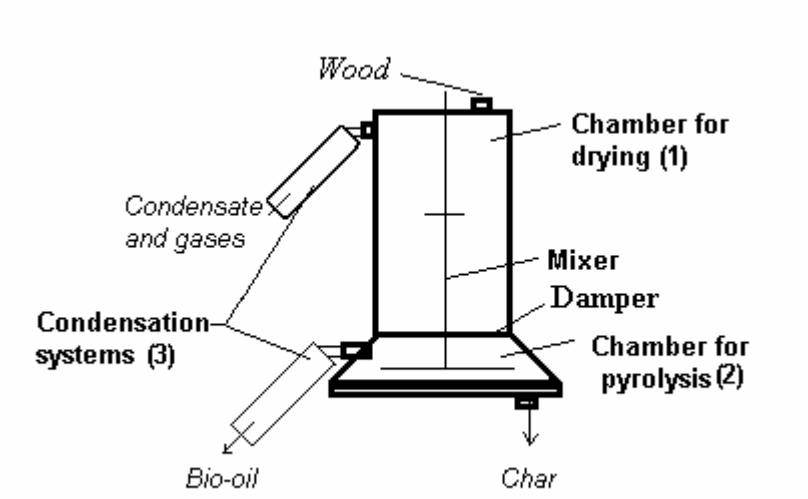


**Figure 1.** Schematic diagram of the laboratory pyrolytic device.

## Gas Chromatography – Mass Spectrometry (GC-MS)

The pyrolytic oil was characterized with a Shimadzu GC/MS – QP 2010, capillary column RTX-1701, 60 m x 0.25 mm x 0.25 μm film. The injector temperature was 250°C, and the ion source was 250ºC with EI of 70 eV. The MS scan range was m/z 15-350. The carrier gas was helium at a flow rate of 1 ml $min^{-1}$, and the split ratio was 1:30. The oven program was 1 min isothermal at 60ºC, then 6ºC/min to 270ºC, and finally 10 min at 270ºC. The mass spectral database Library MS NIST 147.LI13 was used, and authentic reference compounds were found for substance identification.

## Water Content in Bio-oil

A titrator Karl Fischer-270, and solution HYDRONAL-Conlomat AG were used.

## Heat Capacity

Heat capacity was determined in compliance with ISO 1928-76, using an Oxygen Bomb Calorimeter-1341.

## RESULTS AND DISCUSSION

To investigate the influence of drying conditions of wood, the sample was heated in the upper chamber of the reactor (1) at the temperature 200°C during 90 min, and the volatile products were cooled and condensed (Fig. 1). The results of the analysis have shown that the main component of the condensate is water, whose relative content

according to GCMS data is 80% (Table 1). Acids, ketones, and furans were present in the condensate. Among monomeric compounds, acetic acid, hydroxipropanone, and furfural were found in major amounts. The formation of these compounds is typical for low-temperature degradation of wood hemicelluloses (Kislitsin 1990).

To study the effect of wood drying on the composition of bio-oil, pyrolysis was carried out at 550°C, using wood samples with the moisture content 8.5-9% and with drying at 200°C during 90 min. The bio-oils obtained as a result of pyrolysis were analysed by GCMS. The results show that the relative content of water in the composition of the bio-oil obtained upon pyrolysis of dried wood decreased by 7.6% (Table 1). Besides, the content of acids decreased mainly at the expense of acetic acid, and the content of compounds with carbonyl groups and anhydrosaccharides increased.

**Table 1.** Chemical Composition of Volatile Products, Obtained upon Drying and Pyrolysis of Wood (relative content from GCMS, %)

| Compounds | Content in volatile products, relative % | | |
|---|---|---|---|
| | Drying (200°C, 90 min) | Pyrolysis (550°C) | Drying (200°C, 90 min) and pyrolysis (550°C) |
| $H_2O$ | 80.1 | 22.0 | 14.4 |
| Acids, Esters | 11.6 | 20.2 | 17.8 |
| Alcohols, Aldehydes | 0.9 | 9.3 | 11.9 |
| Ketones, Lactones | 3.1 | 15.0 | 16.0 |
| Pyrans | 0.0 | 1.5 | 1.5 |
| Furans | 1.7 | 6.6 | 7.4 |
| Levoglucosan | 0.0 | 1.6 | 3.7 |
| Phenols, lignin derivatives | 0.8 | 23.5 | 24.2 |

The amount of water in bio-oil, determined by titration according to the Fischer method, decreased to 19-20% upon pyrolysis of dried wood in comparison with the 25-28% in bio-oil, obtained upon pyrolysis of a moist wood sample (Table 2).

The results of the analysis of the heat capacity of pyrolytic oils showed an increase in this parameter from 14 MJ/kg (without drying) to 17-20 MJ/kg, when the wood was dried and then pyrolysed (Table 2). Obviously, the main factor that influences this parameter is the decrease in the amount of water in the bio-oil.

An increase in pH (Table 2) during the two-stage process has been observed. It can be explained by the release of acetic acid in the first stage of the process. This factor is very important, taking into account the high corrosive activity of pyrolytic oils, which also determines the required construction material of the reactor.

**Table 2.** Properties of pyrolytic oil*

| Characteristics | Pyrolysis at 550°C | |
|---|---|---|
| | Without drying | Drying at 200°C, 90 min |
| Heat capacity, MJ/kg | 14 | 17-20 |
| Water amount, % | 25-28 | 19-20 |
| pH | 2.3 –2.5 | 3.0-3.2 |
| Bio-oil yield, % | 62-64 | 63 |

* 4 replicates of experiments were made

To elucidate the effect of the temperature and duration of drying on the yield of liquid, solid, and gaseous products, pyrolysis of wood dried at different temperatures was carried out (Figs. 2, 3).

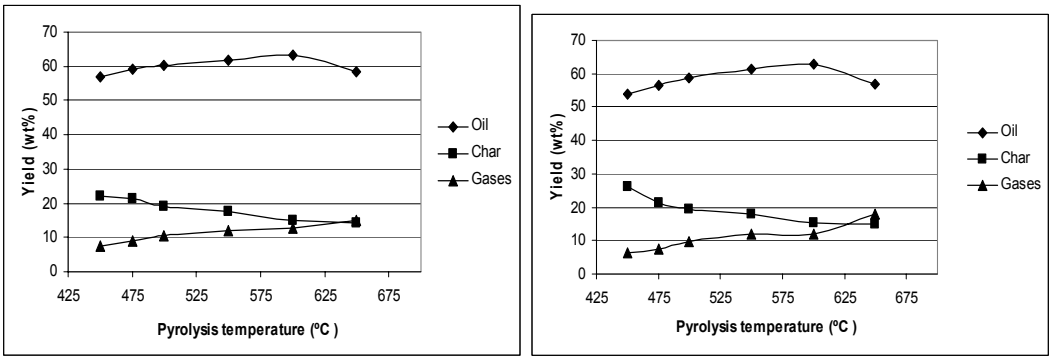


**Figure 2.** Change in the yield of oil, char and gases *versus* the temperature of pyrolysis of wood (drying temperature 200ºC (a) 45 min, (b) 90 min).

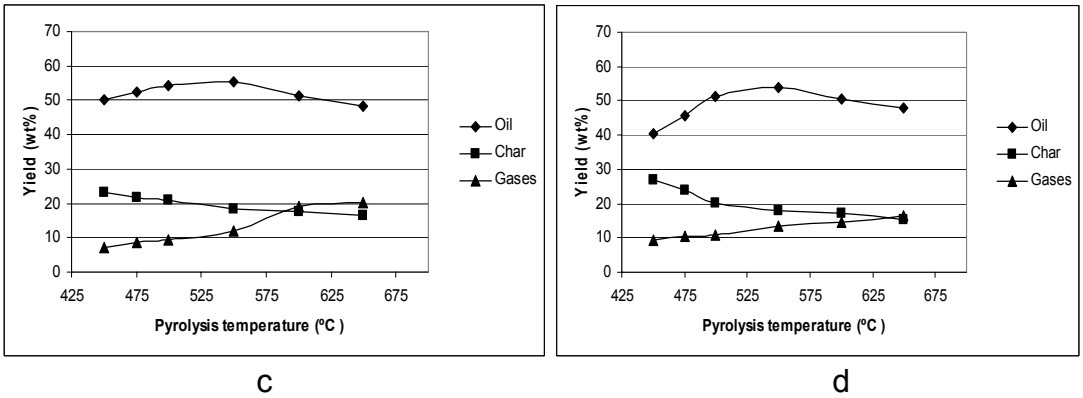


**Figure 3**. Change in the yield of oil, char and gases *versus* the temperature of pyrolysis of wood (drying temperature 240ºC (c) 45 min and (d) 90 min).

The results of the pyrolysis of wood samples, dried at temperatures of 200 and 240ºC, have shown that the increase in the drying temperature influenced the yield of pyrolysis products, while the increase in the drying time from 45 to 90 min did not affect it (Figs. 2 (a, b), 3 (c, d)). Upon pyrolysis of the wood dried at 200ºC, the bio-oil yield grew with increasing temperature from 450ºC to 600ºC, reaching 63% (Fig. 2 (a, b)). Further rise in temperature led to a decrease in the bio-oil yield and an increase in the amount of non-condensing gases.

Upon pyrolysis in the temperature range 450-650ºC of wood samples, whose drying was performed at 240ºC (Fig. 3 (c, d)), the bio-oil yield was lower. Its maximum value was reached at a lower temperature, in comparison with the case of the samples dried at 200ºC. At increasing pyrolysis temperature above 550ºC, no additional amount of liquid products was formed. Obviously, upon drying of wood at 240ºC, the formation of new, thermally more stable bonds occurs (Chirkova et al. 2006), which results also in

a higher yield of the char residue and an increase in the amount of non-condensing gases upon pyrolysis of these samples.

The results of modelling of the pyrolysis process show that the yield of pyrolytic oil changed upon varying both drying temperature and pyrolysis temperature (Fig. 4). The optimum conditions for the formation of bio-oil were a drying temperature of 200°C and a pyrolysis temperature of 550°C. The maximum yield of bio-oil was 63% of the dry raw material. The decrease in the drying temperature below the optimum level influenced the bio-oil yield only insignificantly.

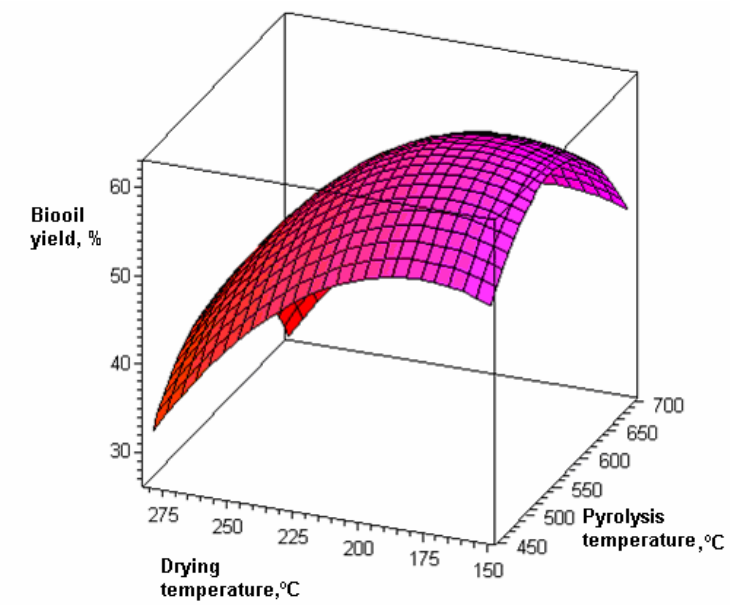


**Figure 4.** Change in the yield of bio-oil upon pyrolysis of wood *versus* the temperature of drying and pyrolysis (drying time 90 min).

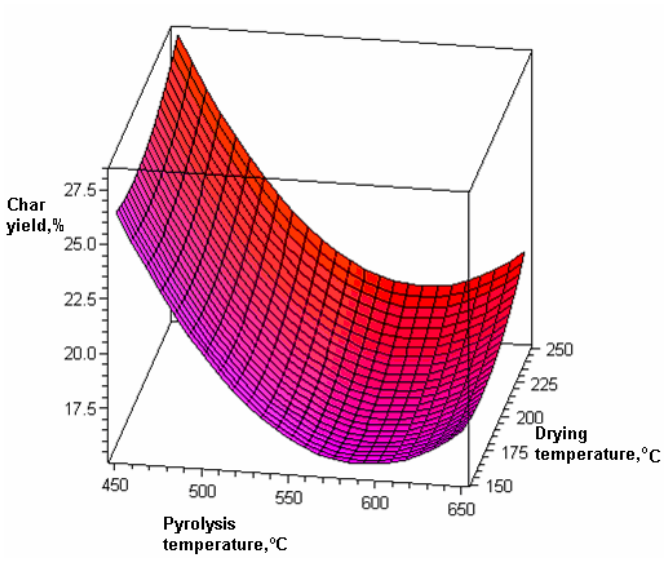


**Figure 5.** Change in the yield of char upon pyrolysis of wood *versus* the temperature of drying and pyrolysis (drying time 90 min).

At the same time, the increase in the drying temperature and the changes in the pyrolysis temperature below and above the optimum levels had an equal adverse action on the bio-oil yield. The latter decreased and reached about 40% at the drying temperature 275°C.

The drying temperature practically did not influence the formation of char (Fig. 5).

The lowest quantity of char was formed under pyrolysis conditions that were optimum for obtaining bio-oil. At a temperature of 450°C, the char yield was the highest, namely, 27%.

## CONCLUSIONS

1. The process of fast pyrolysis of hardwood using a two-chamber ablation type reactor has been investigated, depending on the drying conditions and pyrolysis temperature.
2. It has been found that the drying of the raw material at 200ºC and pyrolysis at 550ºC resulted in improving of the quality of bio-oil. The improvements included a decrease in the water content to 19-20%, increased pH, and a calorific value of 17-20 MJ/kg.
3. It has been found that the drying of wood at the temperature 240ºC obviously led to condensation reactions and cross-linking of wood components, as well as a decrease in the yield of bio-oil.
4. The maximum yield of bio-oil (above 60%) was obtained under the conditions of drying at 200ºC and pyrolysis at 550ºC. The lowest quantity of char was formed under pyrolysis conditions that were the optimum for obtaining bio-oil.
5. Drying of wood at a higher temperature (above 200°C) decreased the yield of liquid products of pyrolysis.

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# ENZYME-BASED HYDROLYSIS PROCESSES FOR ETHANOL FROM LIGNOCELLULOSIC MATERIALS: A REVIEW

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This article reviews developments in the technology for ethanol production from lignocellulosic materials by "enzymatic" processes. Several methods of pretreatment of lignocelluloses are discussed, where the crystalline structure of lignocelluloses is opened up, making them more accessible to the cellulase enzymes. The characteristics of these enzymes and important factors in enzymatic hydrolysis of the cellulose and hemicellulose to cellobiose, glucose, and other sugars are discussed. Different strategies are then described for enzymatic hydrolysis and fermentation, including separate enzymatic hydrolysis and fermentation (SHF), simultaneous saccharification and fermentation (SSF), non-isothermal simultaneous saccharification and fermentation (NSSF), simultaneous saccharification and co-fermentation (SSCF), and consolidated bioprocessing (CBP). Furthermore, the by-products in ethanol from lignocellulosic materials, wastewater treatment, commercial status, and energy production and integration are reviewed.

*Keywords: Lignocellulosic materials, Enzymatic hydrolysis, Ethanol, Fermentation*

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## INTRODUCTION

Ethanol is the most important product of biotechnology in terms of volume and market values. The current raw materials are sugar substances, such as sugarcane juice and molasses, as well as starch-based materials such as wheat and corn. However, intensive research and developments in the last decades on lignocelluloses will most likely make them important raw material for ethanol production in the future.

Lignocelluloses are composed of cellulose, hemicellulose, lignin, extractives, and several inorganic materials (Sjöström 1993). Cellulose or β-1-4-glucan is a polymer of glucose made of cellobiose units with about 2,000 to 27,000 glucose residues (Delmer and Amor 1995; Morohoshi 1991). These chains are packed by hydrogen bonds in so-called 'elementary fibrils' originally considered to be 3 to 4 nm wide and contain about 36 chains, although larger crystalline fibrils up to 16 nm were also discovered (Ha et al. 1998). These elementary fibrils are then packed in so-called microfibrils, where the elementary fibrils are attached to each other by hemicelluloses, amorphous polymers of different sugars as well as other polymers such as pectin and covered by lignin. The microfibrils are often associated in the form of bundles or macrofibrils (Delmer and Amor 1995).

In order to produce ethanol from lignocellulosic materials, we should (a) open the bundles of lignocelluloses in order to access the polymer chains of cellulose and hemicellulose by a process of so-called pretreatment, (b) hydrolyze the polymers in order to achieve monomer sugar solutions, (c) ferment the sugars to ethanol solution (mash) by microorganisms, and (d) purify ethanol from mash by e.g. distillation and dehydration (Fig. 1). By-product recovery, utilities (steam and electricity generation and cooling water), wastewater treatment, and eventually enzyme production are the other units which are demanded in ethanol production from lignocellulosic materials.

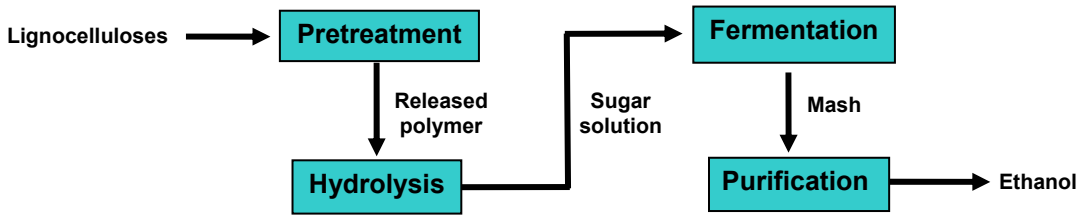


**Fig. 1.** Different units in the main line of ethanol production from lignocellulosic materials

The hydrolysis of cellulose and hemicellulose in this process can be carried out chemically by e.g. dilute sulfuric acid or enzymatically. We have recently reviewed the acid-based processes (Taherzadeh and Karimi 2007), and the present work is dedicated to enzymatic processes of ethanol production from lignocellulosic materials. The enzymatic hydrolysis is catalyzed by cellulolytic enzymes. Without any pretreatment, the conversion of native cellulose to sugar is extremely slow, since cellulose is well protected by the matrix of lignin and hemicellulose in macrofibrils. Therefore, pretreatment of these materials is necessary to increase the rate of hydrolysis of cellulose to fermentable sugars (Galbe and Zacchi 2002).

There are several advantages and disadvantages of dilute-acid and enzymatic hydrolyses, which are listed in Table 1. Enzymatic hydrolysis is carried out under mild conditions, whereas acid hydrolysis requires high temperature and low pH, which results in corrosive conditions. While it is possible to obtain cellulose hydrolysis of close to 100% by enzymatic hydrolysis (Ogier et al. 1999), it is difficult to achieve such high yield with the acid hydrolyses. Furthermore, several inhibitory compounds are formed during acid hydrolysis, whereas this problem is not so severe for enzymatic hydrolysis (Lee et al. 1999; Taherzadeh 1999; Wyman 1996).

Table 1. Comparison between Dilute-acid and Enzymatic Hydrolyses

| Comparing variable | *Dilute-acid hydrolysis* | *Enzymatic hydrolysis* |
|---|---|---|
| Mild hydrolysis conditions | No | Yes |
| High yields of hydrolysis | No | Yes |
| Product inhibition during hydrolysis | No | Yes |
| Formation of inhibitory by-products | Yes | No |
| Low cost of catalyst | Yes | No |
| Short time of hydrolysis | Yes | No |

On the other hand, enzymatic hydrolysis has its own problems compared to dilute-acid hydrolysis. A hydrolysis time of several days is necessary for enzymatic hydrolysis (Tengborg et al. 2001), whereas a few minutes is enough for the acid hydrolysis (Taherzadeh et al. 1997). The prices of the enzymes are much higher than e.g. sulfuric acid that is used in acid hydrolysis (Sheehan and Himmel 2001), although some breakthrough in cutting the prices by e.g. the Danish Novozyme company has recently been reported. In acid hydrolysis, the final products, e.g. released sugars, do not inhibit the hydrolysis. However, in enzymatic hydrolysis, the sugars released inhibit the hydrolysis reaction (Eklund and Zacchi 1995; Hari Krishna and Chowdary 2000; Kádár et al. 2004; Linde et al. 2007). In order to overcome this problem, simultaneous saccharification and fermentation (SSF) was developed, in which the sugars released from the hydrolysis are directly consumed by the present microorganisms (Wyman 1996). However, since fermentation and hydrolysis usually have different optimum temperatures, separate enzymatic hydrolysis and fermentation (SHF) is still considered as a choice.

## PRETREATMENT OF LIGNOCELLULOSIC MATERIALS

Pretreatment of lignocelluloses is intended to disorganize the crystalline structure of macro- and microfibrils, in order to release the polymer chains of cellulose and hemicellulose, and/or modify the pores in the material to allow the enzymes to penetrate into the fibers to render them amenable to enzymatic hydrolysis (Galbe and Zacchi 2002). Pretreatment should be effective to achieve this goal, avoid degradation or loss of carbohydrate, and avoid formation of inhibitory by-products for the subsequent hydrolysis and fermentation; obviously, it must be cost-effective (Sun and Cheng 2002). There are several methods introduced for pretreatment of lignocellulosic materials, which are summarized in Table 2.

The pretreatment methods may be classified into "Physical pretreatment" such as mechanical comminution, pyrolysis, and irradiation (McMillan 1994; Wyman 1996), "Physico-chemical pretreatment" such as steam explosion or autohydrolysis, ammonia fiber explosion (AFEX), $CO_2$ explosion and $SO_2$ explosion (Alizadeh et al. 2005; Ballesteros et al. 2000; Boussaid et al. 1999; Dale et al. 1996; Eklund et al. 1995; Holtzapple et al. 1991; Ogier et al. 1999; Ohgren et al. 2005; Sassner et al. 2005; Stenberg et al. 1998a; Tengborg et al. 1998; Vlasenko et al. 1997), "Chemical pretreatment" including ozonolysis, dilute-acid hydrolysis, alkaline hydrolysis, oxidative delignification, and organosolv processes (Arato et al. 2005; Barl et al. 1991; Berlin et al. 2006; Karimi et al. 2006a; Karimi et al. 2006b; Lee et al. 1999; Nguyen et al. 2000; Sanchez et al. 2004; Schell et al. 2003; Sidiras and Koukios 2004; Tucker et al. 2003), and "Biological pretreatment" (Fan et al. 1982; Wyman 1996). However, not all of these methods have yet developed enough to be feasible technically or economically for large-scale processes. In some cases, a method is used to increase the efficiency of another method. For instance, milling could be applied to create a better steam explosion by reducing the chip size. Furthermore, it should be noticed that the selection of pretreatment method should be compatible with the selection of hydrolysis. For example,

if acid hydrolysis is to be applied, a pretreatment with alkali may not be beneficial (Taherzadeh and Niklasson 2004). The pretreatment methods were reviewed by McMillan (1994) , Wyman (1996), Sun and Cheng (2002), and Mosier et al. (2005b).

Table 2. Pretreatment Methods of Lignocellulosic for Enzymatic Hydrolysis

| Method | Processes | Mechanism of changes on biomass |
|---|---|---|
| **Physical pretreatments** | - *Ball-milling*<br>- *Two-roll milling*<br>- *Hammer milling*<br>- *Colloid milling*<br>- *Vibro energy milling*<br>- *Hydrothermal*<br>- *High pressure steaming*<br>- *Extrusion*<br>- *Expansion*<br>- *Pyrolysis*<br>- *Gamma-ray irradiation*<br>- *Electron-beam irradiation*<br>- *Microwave irradiation* | - Increase in accessible surface area and size of pores<br>- Decrease of the cellulose crystallinity and its degrees of polymerization<br>- Partial hydrolysis of hemicelluloses<br>- Partial depolymerization of lignin |
| **Physicochemical & chemical pretreatments** | Explosion:<br>- *Steam explosion*<br>- *Ammonia fiber explosion (AFEX)*<br>- *$CO_2$ explosion*<br>- *$SO_2$ explosion*<br>Alkali:<br>- *Sodium hydroxide*<br>- *Ammonia*<br>- *Ammonium Sulfite*<br>Gas:<br>- *Chlorine dioxide*<br>- *Nitrogen dioxide*<br>Acid:<br>- *Sulfuric acid*<br>- *Hydrochloric acid*<br>- *Phosphoric acid*<br>- *Sulfur dioxide*<br>Oxidizing agents:<br>- *Hydrogen peroxide*<br>- *Wet oxidation*<br>- *Ozone*<br>Cellulose solvents:<br>- *Cadoxen*<br>- *CMCS*<br>Solvent extraction of lignin:<br>- *Ethanol-water extraction*<br>- *Benzene-water extraction*<br>- *Ethylene glycol extraction*<br>- *Butanol-water extraction*<br>- *Swelling agents* | - Delignification<br>- Decrease of the cellulose crystallinity and its degrees of polymerization<br>- Partial or complete hydrolysis of hemicelluloses |
| **Biological pretreatments** | - *Actinomycetes*<br>- *Fungi* | - Delignification<br>- Reduction in degree of polymerization of hemicellulose and cellulose |

Dilute-acid hydrolysis is probably the most commonly applied method among the chemical hydrolysis methods. It is a method that can be used either as a pretreatment preceding enzymatic hydrolysis, or as the actual method of hydrolyzing lignocellulose to the sugars. Different types of reactors such as batch, plug flow, percolation, countercurrent, and shrinking-bed reactors for either pretreatment or hydrolysis of lignocellulosic materials by the dilute acid processes have been applied so far. Most of the commercial programs underway are using dilute acid pretreatment (Taherzadeh and Karimi 2007). The dilute-acid pretreatment can achieve high reaction rates and significantly improve cellulose hydrolysis. Different aspects of dilute-acid hydrolysis have recently been reviewed (Taherzadeh and Karimi 2007). One of the main advantages of dilute acid hydrolysis is achieving high xylan to xylose conversion yields, which is necessary to achieve favorable overall process economics in ethanol production from lignocellulose (Sun and Cheng 2002). On the other hand, a main disadvantage of this pretreatment method is the necessity of neutralization of pH for the downstream enzymatic hydrolysis. Furthermore, different chemical inhibitors might be produced during the acid pretreatment which reduce cellulase activity, and therefore, water wash is necessary for the pretreated biomass before enzymatic hydrolysis (Mes-Hartree and Saddler 1983; Sun and Cheng 2002). The main advantage of this method is the possibility to recover a high portion (e.g. 90%) of the hemicellulose sugars. The hemicellulose, mainly xylan or mannan, accounts for up to a third of the total carbohydrate in many lignocellulosic materials. Thus, hemicellulose recovery can have a highly positive effect on the overall process economics of ethanol production from lignocellulosic material.

Steaming with or without explosion (autohydrolysis) is one of the popular pretreatment methods of lignocellulosic materials. Steam pretreatment removes the major part of the hemicellulose from the solid material and makes the cellulose more susceptible to enzymatic digestion. In this method the biomass is treated with high-pressure steam. The pressure is then swiftly reduced, in steam explosion, which makes the materials undergo an explosive decompression. Steam explosion is typically initiated at a temperature of 160 to 260°C for several seconds to a few minutes before the material is exposed to atmospheric pressure (Cullis et al. 2004; Kurabi et al. 2005; Ruiz et al. 2006; Sun and Cheng 2002; Varga et al. 2004b; Wyman 1996). Negro et al. (2003) evaluated steam explosion to enhance ethanol production from poplar (*Populus nigra*) biomass and compared the results with hydrothermal pretreatment. The best results were obtained in steam explosion pretreatment at 210 °C and 4 min, taking into account cellulose recovery above 95%, enzymatic hydrolysis yield of about 60%, SSF yield of 60% of theoretical, and 41% xylose recovery in the liquid fraction. The results also showed that large particles can be used for poplar biomass in both pretreatments, since no significant effect of particle size on enzymatic hydrolysis and SSF was obtained. Ballesteros et al. (2004) used steam explosion for ethanol production from several lignocellulosic materials with *Kluyveromyces marxianus*. They treated poplar and eucalyptus biomass at 210 °C for 4 min; wheat straw at 190 °C for 8 min; sweet sorghum bagasse at 210 °C for 2 min, and *Brassica carinata* residue at 210 °C at 8 min. These conditions were selected with regard to the maximum glucose recovery after 72 h of enzymatic hydrolysis. Hemicellulose sugars were extensively solubilized during steam explosion and xylose content decreased by about 75–90%, depending on the substrate.

Steaming and mechanical treatment might be combined to effectively disrupt the cellulosic structure. Several technologies for this combination have been developed (Mason 1926; Katzen et al. 1995; Chum et al. 1985). Generally, steam explosion is the basic pretreatment of lignocellulosic substrates because the process is so well documented, was tested at several levels and at various institutions, and satisfies all the requirements of the pretreatment process. Its energy costs are relatively moderate, and the general process has been demonstrated on a commercial scale at the Masonite plants (Chum et al. 1985).

AFEX, or ammonia fiber explosion, is one of the physicochemical pretreatment methods in which lignocellulosic materials are exposed to liquid ammonia at high temperature (e.g. 90-100°C) for a period of time (such as 30 min), and then the pressure is swiftly reduced. There are many adjustable parameters in the AFEX process: ammonia loading, water loading, temperature, time, blowdown pressure, and number of treatments (Holtzapple et al. 1991). AFEX, with a concept similar to steam explosion, can significantly improve the enzymatic hydrolysis. The optimal conditions for pretreatment of switchgrass with AFEX were reported to be about 100°C, ammonia loading of 1:1 kg of ammonia per kg of dry matter, and 5 min retention time (Alizadeh et al. 2005). Enzymatic hydrolysis of AFEX-treated and untreated samples showed 93% vs. 16% glucan conversion, respectively. An advantage of AFEX pretreatment is no formation of some types of inhibitory by-products, which are produced during the other pretreatment methods, such as furans in dilute-acid pretreatment. However, cleaved lignin phenolic fragments and other cell wall extractives may remain on the biomass surface, which can easily be removed by washing with water (Chundawat et al. 2007). Although AFEX enhances hydrolysis of (hemi)cellulose from grass, the effect on biomass that contains more lignin (soft and hardwood) is meager. Furthermore, the AFEX pretreatment does not significantly solubilize hemicellulose, compared to dilute-acid pretreatment. On the other hand, to reduce the cost and protect the environment, ammonia must be recycled after the pretreatment (Eggeman and Elander 2005; Sun and Cheng 2002; Wyman 1996). SunOpta BioProcess Group claimed to have developed the first continuous process in the world to pretreat cellulosic materials with the AFEX process (www.sunopta.com/).

Hydrothermal pretreatment or cooking of lignocellulosic materials in liquid hot water (LHW) is one of the old methods applied for pretreatment of cellulosic materials. Autohydrolysis plays an important role in this process, where no chemical is added. It results in dissolution of hemicelluloses mostly as liquid-soluble oligosaccharides and separates them from insoluble cellulosic fractions. The pH, processing temperature, and time should be controlled in LHW pretreatment in order to optimize the enzymatic digestibility of lignocellulosic materials (Mosier et al. 2005a; Mosier et al. 2005c; Wyman 1996). LHW pretreatment of corn fiber at 160 °C and a pH above 4.0 dissolved 50% of the fiber in 20 min (Mosier et al. 2005c). The results showed that the pretreatment enabled the subsequent complete enzymatic hydrolysis of the remaining polysaccharides to the corresponding monomers. The carbohydrates dissolved by the LHW pretreatment were 80% soluble oligosaccharides and 20% monosaccharides with less than 1% of the carbohydrates lost to degradation products. LHW causes ultrastructural changes and formation of micron-sized pores that enlarge accessible and susceptible surface area and make the cellulose more accessible to hydrolytic enzymes (Zeng et al. 2007). Without

any pretreatment, corn stover with sizes of 53-75 μm was 1.5 times more susceptible to enzymatic hydrolysis than the larger stover particles of 425-710 μm. However, this difference was eliminated when the stover was pretreated with liquid hot water at 190 °C for 15 min, at a pH between 4.3 and 6.2 (Zeng et al. 2007). Laser et al. (2002) compared the performance of LHW and steam pretreatments of sugarcane bagasse in production of ethanol by SSF. They used a 25-l reactor, temperature 170-230 °C, residence time 1-46 min and 1% to 8% solids concentration. Both of the methods generated reactive fibers, but LHW resulted in much better xylan recovery than steam pretreatment. It was concluded that LHW pretreatment produces results comparable with dilute-acid pretreatment processes.

Organosolv may be used to provide treated cellulose suitable for enzyme hydrolysis, using solvents to remove lignin (Itoh et al. 2003; Pan et al. 2006). The process involves mixing of an organic liquid and water together in various portions and adding them to the lignocellulose. This mixture is heated to dissolve the lignin and some of the hemicellulose and leave a reactive cellulose cake. In addition, a catalyst is sometimes added either to reduce the operating temperature or to enhance the delignification process. Most of these processes produce similar results and for that reason are grouped here as a single class (Chum et al. 1985). Delignification of lignocellulosic materials has been known to occur in a large number of organic or aqueous-organic solvent systems with or without added catalysts at temperatures of 150-200°C. Among the solvents tested, those with low boiling points (ethanol and methanol) have been used as well as a variety of alcohols with higher boiling points (ethylene glycol, tetrahydro furfuryl alcohol) and other classes of organic compounds such as dimethylsulfoxide, phenols, and ethers (Chum et al. 1985). In these methods, the solvent action is accompanied with e.g. acetic acid released from acetyl groups developed by hydrolysis of hemicelluloses. The main advantage of the use of solvents over chemical pretreatment is that relatively pure, low-molecular-weight lignin can be recovered as a by-product (Katzen et al. 1995; Sun and Cheng 2002). Organic acids such as oxalic, salicylic, and acetylsalicylic acid can be used as catalysts in the organosolv process. Usually, a high yield of xylose can be obtained with the addition of the acids. However, addition of the catalysts is unnecessary for satisfactory delignification at high temperatures (above 185 °C). Solvents used in the process need to be drained from the reactor, evaporated, condensed, and recycled to reduce the operational costs. Removal of solvents from the system is usually necessary because the solvents may be inhibitory to the growth of organisms, enzymatic hydrolysis, and fermentation (Sun and Cheng 2002). The delignification is accompanied by solvolysis and dissolution of lignin and hemicellulosic fractions, depending on the process conditions (solvent system, type of lignocellulose, temperature, reactor design [batch versus continuous processes]), as well as by solvolysis of the cellulosic fraction to a smaller extent (Chum et al. 1985).

Wet oxidation is the process of treating lignocellulosic materials with water and air or oxygen at temperatures above 120 °C (e.g. 148-200 °C) for a period of time of e.g. 30 min (Garrote et al. 1999; Palonen et al. 2004; Varga et al. 2004a). Oxygen participates in the degradation reactions, enhancing the generation of organic acids and allowing operation at comparatively reduced temperatures. The fast reaction rates and heat generation by reaction make the control of reactor temperature critical. Wet oxidation is

among the simplest process in terms of equipment, energy, and chemicals required for operation (Chum et al. 1985). Bjerre et al. (1996) combined wet oxidation and alkaline hydrolysis for pretreatment of wheat straw. The process resulted in convertible cellulose (85% conversion yield of cellulose to glucose) and hemicellulose. However, this method is suitable for materials with low lignin content, since the yield decreases with increased lignin content, and also a large fraction of the lignin is oxidized and solubilized. As with many other delignification methods, the lignin produced by wet oxidation cannot be used as a fuel, which considerably reduces the income from by-products in industrial-scale ethanol production from lignocellulose (Galbe and Zacchi 2002).

## ENZYMATIC HYDROLYSIS

Enzymatic hydrolysis of cellulose to glucose is carried out by cellulase enzymes that are highly specific catalysts. The hydrolysis is performed under mild conditions (e.g. pH 4.5-5.0 and temperature 40–50°C). Therefore, one may expect low corrosion problems, low utility consumption, and low toxicity of the hydrolyzates as the main advantages of this process.

### Cellulolytic Enzymes

Enzymatic hydrolysis of cellulose and hemicellulose can be carried out by highly specific cellulase and hemicellulase enzymes (glycosylhydrolases). This group includes at least 15 protein families and some subfamilies (Rabinovich et al. 2002). Enzymatic hydrolysis of cellulose consists of the cellulase adsorption onto the surface of the cellulose, the biodegradation of cellulose to fermentable sugars, and desorption of the cellulase. Enzymatic degradation of cellulose to glucose is generally accomplished by synergistic action of at least three major classes of enzymes: endo-glucanases, exo-glucanases, and ß-glucosidases. These enzymes are usually called together cellulase or cellulolytic enzymes (Wyman 1996).

The endoglucanases attack the low-crystallinity regions of the cellulose fiber and create free chain-ends. The exoglucanases further degrade the sugar chain by removing cellobiose units (dimers of glucose) from the free chain-ends. The produced cellobiose is then cleaved to glucose by β-glucosidase (Fig. 2). This enzyme is not a cellulase, but its action is very important to complete depolymerization of cellulose to glucose. Since hemicellulose contains different sugar units, the hemicellulytic enzymes are more complex and involve at least endo-1,4-β-D-xylanases, exo-1,4-β-D-xylosidases, endo-1,4-β-D-mannanases, β-mannosidases, acetyl xylan esterases, α-glucuronidases, α-L-arabinofuranosidases, and α-galactosidases (Jorgensen et al. 2003). Several species of bacteria such as *Clostridium, Cellumonas, Thermomonospora, Bacillus, Bacteriodes, Ruminococcus, Erwinia, Acetovibrio, Microbispora,* and *Streptomyces*, and fungi such as *Tricoderma, Penicillium, Fusarium, Phanerochaete, Humicola,* and *Schizophillum spp.*, are able to produce cellulases and hemicellulases (Rabinovich et al. 2002; Sun and Cheng 2002). Among the cellulases produced by different microorganisms, cellulases of *Trichoderma reesei* or *T. viride* have been the most broadly studied and best characterized. A full complement production of cellulase, stability under the enzymatic

hydrolysis conditions, and resistance of the enzyme to chemical inhibitors are the advantages of the cellulase produced by *Trichoderma.* The main disadvantages of *Trichoderma* cellulase are the suboptimal levels and low activity of ß-glucosidases. On the other hand, *Aspergilli* are very efficient ß-glucosidase producers. In several studies, *Trichoderma* cellulase was supplemented with extra ß-glucosidases and showed good improvement (Hari Krishna et al. 2001; Itoh et al. 2003; Ortega et al. 2001; Tengborg et al. 2001; Wyman 1996).

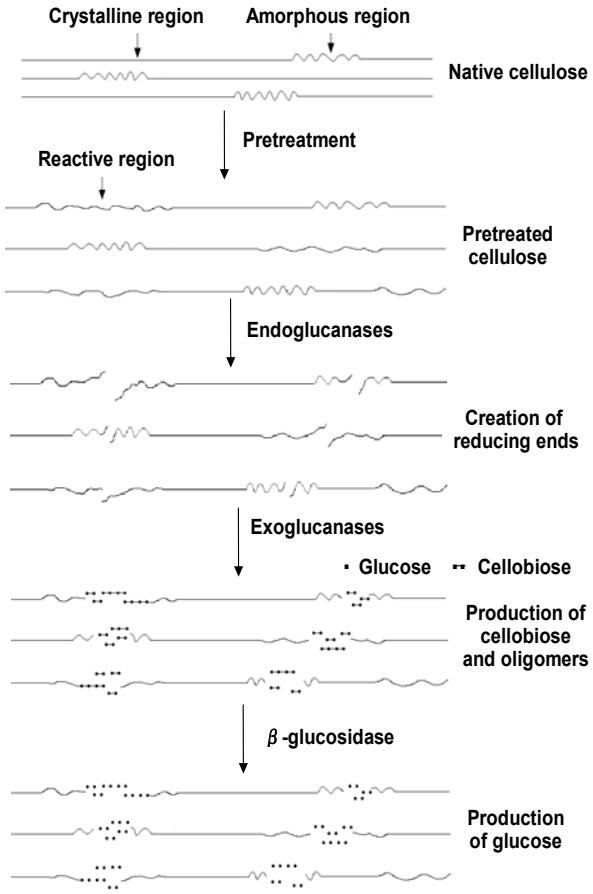


**Fig. 2**. Schematic presentation of hydrolysis of cellulose to glucose by cellulolytic enzymes.

Production and application of cellulase by *Trichoderma* has some difficulties. The enzyme is produced in the late stage of fermentation and needs a well-controlled pH, and its activity is reduced by adsorption to cellulose and lignin. Furthermore, it has problems in scaling-up of the enzyme production process due to oxygen transfer into mycelial broth; lower cell-bound enzyme activity; and poor mixing due to shear sensitivity of the fungus (Lee 1997; Wyman 1996). However, in spite of these deficiencies, the soft-rot fungus *T. reesei* is currently among the best vehicles for cellulase production (Xia and Shen 2004; Wyman 1996). Most commercial cellulases are produced from *Trichoderma spp.*, with a few also produced by *Aspergillus niger.*

## IMPORTANT FACTORS IN ENZYMATIC HYDROLYSIS

Substrate concentration and quality, applied pretreatment method, cellulase activity, and hydrolysis conditions such as temperature, pH, and mixing are the main factors in enzymatic hydrolysis of lignocellulosic materials. The optimum temperature and pH are functions of the raw material, the enzyme source, and hydrolysis duration. The optimum temperatures and pH of different cellulases are usually reported to be in the range of 40 to 50 °C and pH 4 to 5 (Olsson and Hahn-Hägerdal 1996). However, the optimum residence time and pH might affect each other. Tengborg et al. (2001) showed an optimal temperature of 38 °C and pH 4.9 within 144 h residence time for cellulase (Commercial enzyme solutions, Celluclast 2 L, Novo Nordisk A/S, Bagsværd, Denmark).

One of the main factors that affect the yield and initial rate of enzymatic hydrolysis is substrate (cellulose and/or hemicellulose) concentration in the slurry solution. High substrate concentration can cause substrate inhibition, which substantially lowers the hydrolysis rate. The extent of the inhibition depends on the ratio of total enzyme to total substrate (Sun and Cheng 2002). Problems in mixing and mass transfer also arise in working with high substrate concentration. The ratio of enzyme to substrate used is another factor in enzymatic hydrolysis. Obviously application of more cellulase, up to a certain level, increases the rate and yield of hydrolysis. However, increase in cellulase level would significantly increase the cost of the process. Cellulase loading is usually in the range of 5 to 35 FPU per gram of substrate.

Addition of surfactants during hydrolysis can modify the cellulose surface properties. An important effect of surfactant addition in a process for lignocellulose conversion is the possibility to lower the enzyme loading. A number of surfactants have been examined for their ability to improve enzymatic hydrolysis. Non-ionic surfactants were found to be the most effective. Fatty acid esters of sorbitan polyethoxylates (Tween® 20 and 80), and polyethylene glycol, are among the most effective surfactants reported for enzymatic hydrolysis (Alkasrawi et al. 2003; Börjesson et al. 2007; Kim et al. 2006a). Addition of polyethylene glycol to lignocellulose substrates increased the enzymatic conversion from 42% to 78% in 16 h (Börjesson et al. 2007). One reason for this effect might be adsorption of surfactants to lignin, which prevents unproductive binding of enzymes to lignin and results in higher productivity of the enzymes (Eriksson et al. 2002). However, the surfactant should be selected carefully, since it may have negative impact on the fermentation of the hydrolyzate. For instance, addition of 2.5 g/l Tween 20 helped to reduce enzyme loading by 50%, while retaining cellulose conversion (Eriksson et al. 2002). However, this surfactant is an inhibitor to *D. clausenii* even at low concentration of 1.0 g/l (Wu and Ju 1998).

The recycling of cellulase enzymes is one potential strategy for reducing the cost of the enzymatic hydrolysis during the bioconversion of lignocelluloses to ethanol (Tu et al. 2007). However, presence of solid residuals (mainly lignin) and dissolution of the enzymes in the hydrolyzates make the enzymes difficult to separate. Immobilization is an alternative to retain the enzymes in the reactor, but steric hindrance, freedom of movement and gradual reduction of the cellulases' activity must be considered. In this regard, it should be kept in mind that endoglucanase and exoglucanase should diffuse into lignocelluloses and be adsorbed to the surface of the particles in order to initiate

hydrolysis and convert the cellulose to cellobiose. However, cellobiose is in the aqueous phase, where it is converted to glucose by ß-glucosidase. Therefore, immobilization of ß-glucosidase might theoretically be possible and effective (Tu et al. 2006). It is also possible to co-immobilize ß-glucosidase and a fermenting microorganism in order to improve the overall conversion of cellulose to ethanol (Lee and Woodward 1983). One of the major problems in immobilization is to separate the immobilized support from the residual solid of the reactor. One possible solution could be immobilization of the enzymes in magnetic particles, such as magnetic agarose composite microspheres (Qiu and Li 2000; Qiu and Li 2001), or magnetic chitosan microspheres (Feng et al. 2006).

## HYDROLYSIS & FERMENTATION STRATEGIES

### Separate Enzymatic Hydrolysis and Fermentation (SHF)

In this process, pretreated lignocelluloses are hydrolyzed to glucose and subsequently fermented to ethanol in separate units (Fig. 3). The major advantage of this method is that it is possible to carry out the cellulose hydrolysis and fermentation at their own optimum conditions. The optimum temperature for cellulase is usually between 45 and 50 °C, depending on the cellulose-producing microorganism (Olsson et al. 2006; Saha et al. 2005; Söderström et al. 2003; Wingren et al. 2003). However, the optimum temperature for most of the ethanol-producing microorganisms is between 30 and 37°C.

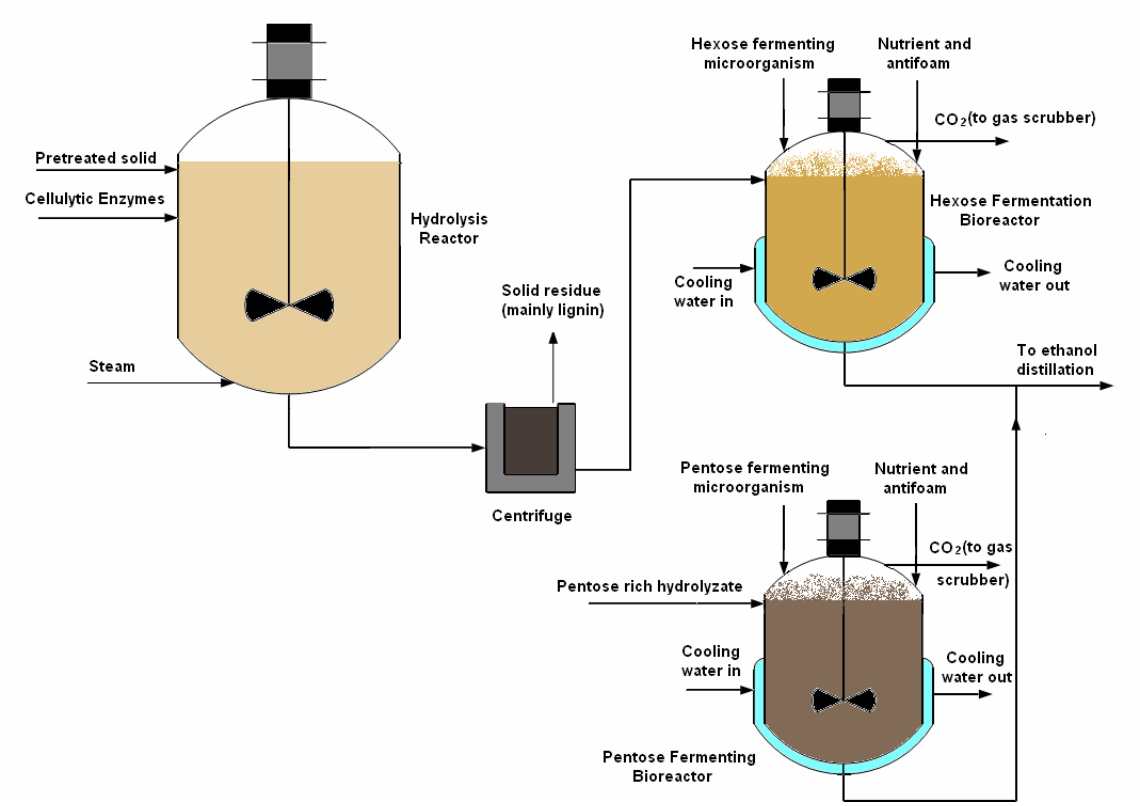


**Fig. 3.** Simplified process flow diagram for separate enzymatic hydrolysis and fermentation (SHF)

Inhibition of cellulase activity by the released sugars, mainly cellobiose and glucose, is the main drawback of SHF. At a cellobiose concentration as low as 6 g/l, the activity of cellulase is reduced by 60%. Although glucose decreases the cellulase activity as well, the inhibitory effect of this sugar is lower than that of cellobiose. On the other hand, glucose is a strong inhibitor for ß-glucosidase. At a level of 3 g/l of glucose, the activity of ß-glucosidase is reduced by 75% (Philippidis and Smith 1995; Philippidis et al. 1993). Another possible problem in SHF is that of contaminations. The hydrolysis process is rather long, e.g. one to four days, and a dilute solution of sugar always has a risk of microbial contaminations, even at rather high temperature such as 45-50 °C. A possible source of contamination could be the enzymes. In practice, it is difficult to sterilize the cellulase in large scale, since it should be filtered because of its deactivation in an autoclave.

Softwood hemicellulose is mainly composed of mannose, which can be separated during the pretreatment by e.g. dilute-acid pretreatment and fermented in a separate bioreactor (as indicated in Fig. 3) or possibly fermented together with the pretreated cellulose in the SHF bioreactor. However, the dominant sugar in hemicellulose derived from hardwood and crop residues is usually pentose, which can be converted to ethanol in a separate pentose-fermenting bioreactor (Fig. 3).

## Simultaneous Saccharification and Fermentation (SSF)

One of the most successful methods for ethanol production from lignocellulosic materials is combination of the enzymatic hydrolysis of pretreated lignocelluloses and fermentation in one step, termed SSF (Fig. 4).

In this process, the glucose produced by the hydrolyzing enzymes is consumed immediately by the fermenting microorganism present in the culture. This is a great advantage for SSF compared to SHF, since the inhibition effects of cellobiose and glucose to the enzymes are minimized by keeping a low concentration of these sugars in the media. SSF gives higher reported ethanol yields from cellulose than SHF and requires lower amounts of enzyme (Eklund and Zacchi 1995; Karimi et al. 2006a; McMillan et al. 1999; Sun and Cheng 2002). The risk of contamination in SSF is lower than in the SHF process, since the presence of ethanol reduces the possibility of contamination. Furthermore, the number of vessels required for SSF is reduced in comparison to SHF, resulting in lower capital cost of the process.

An important strategy in SSF is to have the optimum conditions for the enzymatic hydrolysis and fermentation as close as possible, particularly with respect to pH and temperature. However, the difference between optimum temperatures of the hydrolyzing enzymes and fermenting microorganisms is still a drawback of SSF. The optimum temperature for cellulases is usually between 45 and 50 °C, whereas *S. cerevisiae* has an optimum temperature between 30 and 35 °C and is practically inactive at more than 40 °C. The optimum temperature for SSF by using *T. reesei* cellulase and *S. cerevisiae* was reported to be around 38 °C, which is a compromise between the optimal temperatures for hydrolysis and fermentation (Tengborg 2000). Hydrolysis is usually the rate-limiting step in SSF (Philippidis and Smith 1995). Several thermotolerant bacteria and yeasts, e.g. *Candida acidothermophilum* and *Kluyveromyces marxianus* have been proposed for use in SSF to raise the temperature close to the optimal temperature of hydrolysis

(Ballesteros et al. 2004; Golias et al. 2002; Hari Krishna et al. 2001; Hong et al. 2007; Kadam and Schmidt 1997).

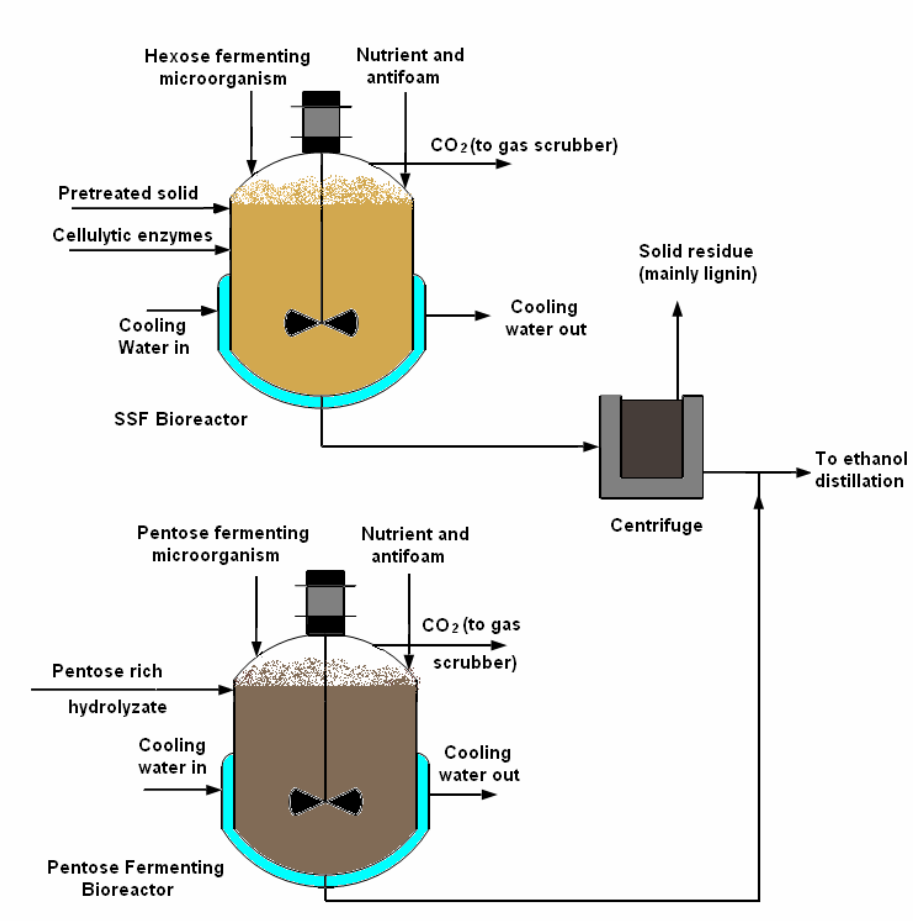


**Fig. 4.** Simplified process flow diagram for simultaneous saccharification and fermentation

Inhibition of cellulase by produced ethanol might be also a problem in SSF. It was reported that 30 g/l ethanol reduces the enzyme activity by 25% (Wyman 1996). Ethanol inhibition may be a limiting factor in producing high ethanol concentration. However, there has been less attention to ethanol inhibition of cellulase, since practically it is not possible to work with very high substrate concentration in SSF because of the problem with mechanical mixing and insufficient mass transfer. Despite the mentioned problems, SSF is the preferred method in many laboratory studies and pilot scale studies for ethanol production.

In the case of ethanol production from hardwood and agriculture residues, the hemicellulose mainly contains pentoses. If the pentose is separated during the pretreatment, the pentose-rich hydrolyzate (hemicellulosic hydrolyzate) can be converted to ethanol in a separate pentose-fermenting bioreactor (Fig. 4).

## Nonisothermal Simultaneous Saccharification and Fermentation (NSSF)

The enzymatic hydrolysis reaction in the SSF process is operated at a temperature lower than the optimum level of enzymatic hydrolysis. This forces the enzyme activity to be far below its potential, which results in raising the enzyme requirement. In order to overcome this problem, a nonisothermal simultaneous saccharification and fermentation process (NSSF) was suggested (Wu and Lee 1998). In this process, saccharification and fermentation occur simultaneously but in two separate reactors at different temperatures (Fig. 5). The lignocellulose is retained inside a hydrolysis reactor and hydrolyzed at the optimum temperature for the enzymatic reactions (e.g. 50 °C). The effluent from the reactor is recirculated through a fermentor, which runs at its optimum temperature (e.g. 30 °C). The cellulase activity is increased 2-3 times when the hydrolysis temperature is raised from 30 to 50 °C.

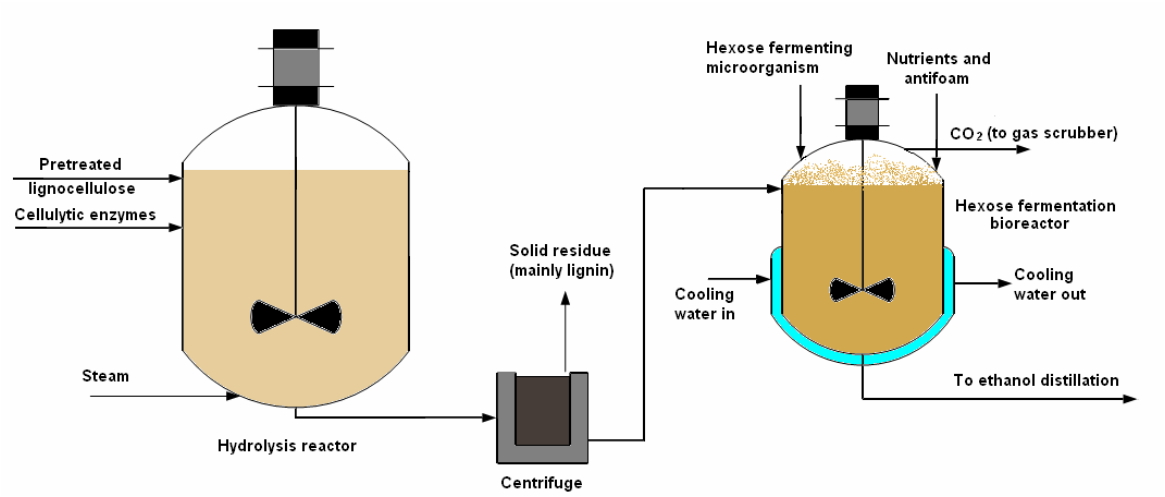


**Fig. 5.** Simplified process flow diagram for nonisothermal simultaneous saccharification and fermentation process (NSSF)

The NSSF process has improved the kinetic enzymatic reaction compared to SSF, resulting in reduction of the overall enzyme requirement by 30-40%. It is suggested that the effect of temperature on ß-glucosidase activity is the most significant among the individual cellulase enzymes. Higher ethanol yield and productivity have been observed in the NSSF compared to SSF at an enzyme loading as low as 5 IFPU/g glucan. With 10 IFPU/g glucan, improvement in productivity was clearly observed for the NSSF. Besides, the overall time in NSSF was significantly lower than SSF. The terminal yield, which has been obtained in 4 days with the SSF, was obtained in 40 h with the NSSF (Wu and Lee 1998).

Varga et al. (2004a) suggested another form of NSSF for production of ethanol from pretreated corn stover. In the first step, small amounts of cellulases were added at 50 °C, the optimal temperature of enzymes, in order to obtain better mixing conditions due to some liquefaction. To maximize the solid concentration, the prehydrolysis step was carried out in fed-batch manner to obtain better mixing conditions by some liquefaction of the cellulase containing substrate. In the second step, more cellulases were added in combination with the fermenting organism, *S. cerevisiae*, at 30 °C. This method

made it possible to carry out the SSF at a higher dry matter content, and is referred to as nonisothermal SSF. This process can be compared with a similar suggestion made by Kádár et al. (2004). They proposed 24 h prehydrolysis at 50 °C prior to inoculation with *S. cerevisiae* or *Kluyveromyces marxianus*. After the prehydrolysis, the media was inoculated with yeast cells and incubated at 30 °C. They compared the results of the NSSF method with traditional SSF at 40 °C for both microorganisms. Their results showed that the NSSF operation did not increase the ethanol yield at all, and slightly lower values were obtained compared to SSF with both microorganisms. However, they did not check the NSSF at higher temperature in the latter stage. Although 30 °C is suitable for fermentation, the activity of cellulase is very low at this temperature, which could result in incomplete hydrolysis of cellulose.

## Simultaneous Saccharification and Cofermentation (SSCF)

Another mode of operation is simultaneous saccharification and cofermentation (SSCF), in which cofermentation refers to the fermentation of both five-carbon and six-carbon sugars to ethanol. The hydrolyzed hemicellulose during pretreatment and the solid cellulose are not separated after pretreatment, allowing the hemicellulose sugars to be converted to ethanol together with SSF of the cellulose (Teixeira et al. 2000).

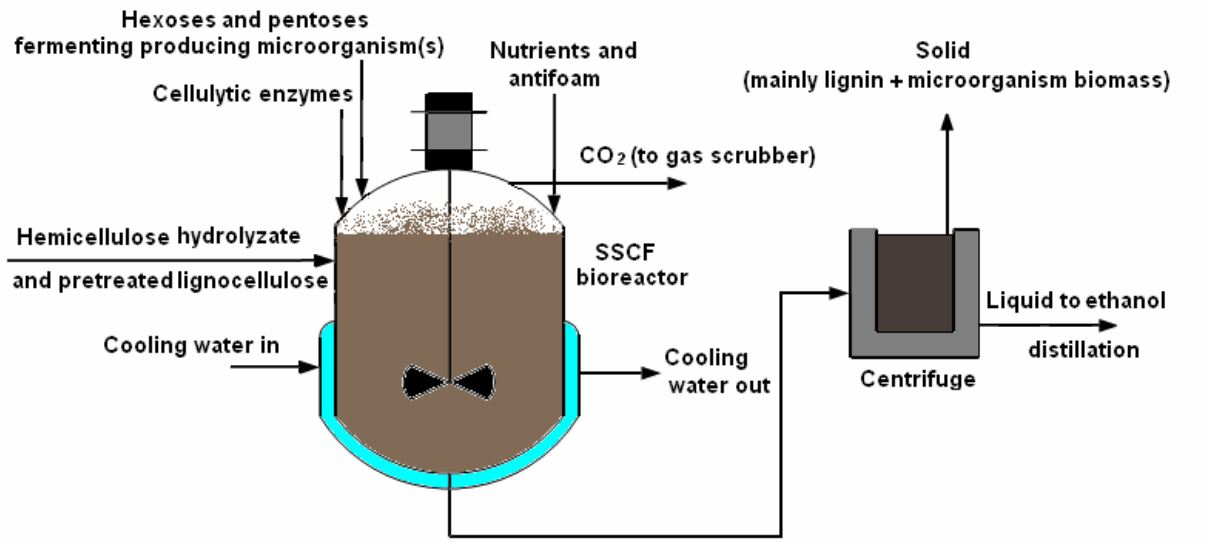


**Fig. 6.** Simplified process flow diagram for simultaneous saccharification and cofermentation (SSCF)

The SSCF process is considered to be an improvement to SSF (Hamelinck et al. 2005) and is meanwhile being tested at pilot scale by the U.S. Department of Energy. In SSF bioreactor, only hexoses are converted to ethanol, and pentoses can be fermented in another bioreactor with different microorganism. Therefore, two bioreactors and two biomass production setup is required in SSF. In SSCF process, it is suggested to ferment both hexoses and pentoses in a single bioreactor with a single microorganism. Therefore, only a single fermentation step is required to process hydrolyzed and solid fractions of the pretreated lignocellulose (McMillan 1997).

Lawford and Rousseau (1998) used a metabolically engineered strain of *Zymomonas mobilis* that can coferment glucose and xylose, developed in the National Renewable Energy Laboratory (NREL) for ethanol production by SSCF from a synthetic hardwood prehydrolyzate and glucose. McMillan et al. (1999) used an adapted variant of the NREL xylose-fermenting *Z. mobilis* for ethanol production from dilute-acid-pretreated yellow poplar by SSCF. The integrated system produced more than 30 g/l ethanol and achieved 54% conversion of all potentially available sugars in the biomass (total sugars) entering SSCF. Kim et al. (2006b) used a recombinant *E. coli* in the SSCF of corn stover, which was pretreated by ammonia. Both the xylan and glucan in the solid were effectively utilized, giving an overall ethanol yield of 109% of the theoretical maximum based on glucan, a clear indication that at least some of the xylan content was being converted into ethanol. Teixeira et al. (2000) used a recombinant strain of *Z. mobilis* for ethanol production from hybrid poplar wood and sugarcane bagasse. The biomasses were pretreated by peracetic acid combined with an alkaline pre-pretreatment. The SSCF with the recombinant strain resulted in ethanol yields of 92.8 and 91.9% of theoretical from pretreated hybrid poplar wood and sugarcane bagasse, respectively.

A complete process design and its economic evaluation for production of ethanol from corn stover is being analyzed by Aden et al. (2002) in the National Renewable Energy Laboratory (NREL). The process applies dilute acid process for pretreatment and SSCF process for conversion of glucose and xylose to ethanol. The process design also includes feedstock handling and storage, product purification, wastewater treatment, lignin combustion, product storage, and all other required utilities.

## Consolidated Bioprocessing (CBP)

In all of the processes considered up to this point, a separate enzyme production unit operation is required, or the enzymes should be provided externally. In consolidated bioprocessing (CBP), ethanol together with all of the required enzymes is produced in a single bioreactor by a single microorganism's community (Fig. 7). The process is also known as direct microbial conversion (DMC). It is based on utilization of mono- or co-cultures of microorganisms which ferment cellulose to ethanol. CBP seems to be an alternative approach with outstanding potential and the logical endpoint in the evolution of ethanol production from lignocellulosic materials. Application of CBP entails no operating costs or capital investment for purchasing enzyme or its production (Hamelinck et al. 2005; Lynd et al. 2005).

Two potential paths have been identified for obtaining organisms for use in CBP. The first path involves modification of excellent ethanol producers, so that they also become efficient cellulase producers, while the second path involves modification of excellent cellulase producers, so that they also become efficient ethanol producers (Lynd et al. 2005). Cellulase production, ethanol tolerance, and ethanol selectivity are considered for both Path 1 and Path 2 organisms (Hogsett et al. 1992). In the past, several cellulolytic anaerobes have been isolated and characterized for potential technology development for fuel or chemical production by CBP of lignocellulosic materials (Lee 1997). This type of activity is shown by various anaerobic thermophilic bacteria, such as *Clostridium thermocellum*, as well as by some filamentous fungi, including *Neurospora*

*crassa*, *Monilia SP.*, and *Paecilomyces SP.* However, the fermentation process utilizing these microorganisms was very slow (e.g. 3-12 days), and resulted in poor yield of ethanol (Szczodrak and Fiedurek 1996). Furthermore, several by-products, primarily lactic and acetic acids, are produced.

In order to obtain high ethanol yield from the lignocellulosic materials by CBP, intensive research for new thermophilic strains has been carried out. Microorganisms have been sought that do not produce organic acids and are more resistant to higher ethanol concentrations (Szczodrak and Fiedurek 1996; Wyman 1996). South et al. (1993) compared the conversion efficiencies of pretreated hardwood to ethanol in SSF process by *T. reesei* cellulase and *S. cerevisiae* and in a CBP process by *C. thermocellum* through continuous experiments. The SSF system achieved substrate conversions varying from 31% in 9 h retention time to 86% at 48 h retention time. At comparable substrate concentrations (4-5 g/l) and residence times (12-14 h), substrate conversion in the CBP system (77%) was significantly higher than that in the SSF system (31%).

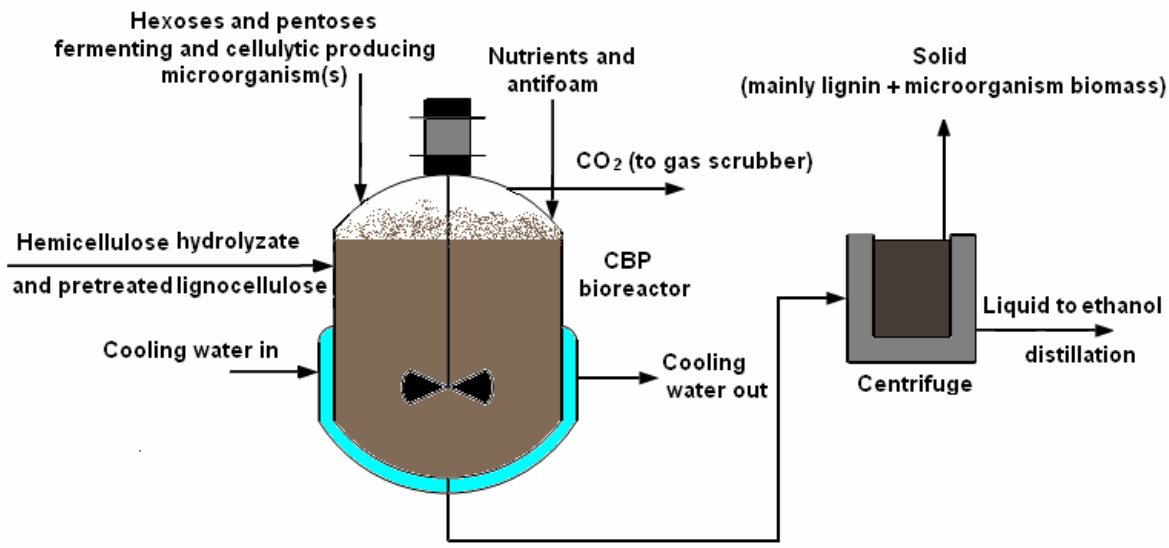


Fig. 7. Simplified process flow diagram for consolidated bioprocessing (CBP)

There are as yet no organisms or compatible combinations of microorganisms available that produce cellulase and other enzymes at the required high levels and also produce ethanol at the required high yields and concentrations, although various organisms already combine multiple functions (Hamelinck et al. 2005). Fujita et al. (2004) constructed a whole-cell biocatalyst with the ability to induce synergistic and sequential cellulose hydrolysis reaction through codisplay of three types of the cellulolytic enzyme on the cell surface of *S. cerevisiae*. Efficient direct fermentation of cellulose to ethanol was achieved by developing the yeast strain. A yield (in grams of ethanol produced per gram of carbohydrate consumed) as high as 0.45 g/g was obtained, which corresponds to 88.5% of the theoretical yield. This indicates that simultaneous and synergistic saccharification and fermentation of the cellulose to ethanol can be efficiently accomplished by using an ethanol-producing yeast strain codisplaying the three cellulolytic enzymes.

Den Haan et al. (2007) developed a recombinant strain of *S. cerevisiae* which can be used for CBP. Two cellulose-encoding genes, an endoglucanase of *T. reesei*, and the β-glucosidase of *Saccharomycopsis fibuligera*, in combination, were expressed in *S. cerevisiae*. The resulting strain was able to grow on cellulose by simultaneous production of sufficient extracellular endoglucanase and β-glucosidase. They demonstrated the construction of a yeast strain capable of growing and of converting cellulose to ethanol in one step, representing significant progress towards realization of one-step processing of lignocellulose in a CBP configuration.

## BY-PRODUCTS IN ETHANOL FROM LIGNOCELLULOSIC MATERIALS

The fermented broth or "mash" should be further processed toward pure ethanol. Downstream processing of the produced ethanol depends on the method of ethanol production and the fermentation broth composition. In addition to water and ethanol, the mash contains a number of other materials that we can classify into microbial biomass, fusel oil, volatile components, and stillage. In the SSF, NSSF, SSCF, and CBP processes, residual lignin is also available in the mash.

The main by-product of the process of ethanol production from lignocellulosic materials is lignin. Lignocelluloses contain typically 10-30% lignin; however, its amount and quality in the solid residue differ with feedstock and the applied processes. Part of the lignin might be solubilized during the pretreatment process (e.g. during dilute-acid hydrolysis) or possibly degraded by lignin-degrading enzymes, which are usually present in commercial cellulases. Lignin-degrading enzymes have been found in the extracellular filtrates of many white-rot fungi (Sun and Cheng 2002).

Production of co-products from lignin is important in order to reduce the environmental effects of the ethanol process and increase its competitiveness. Lignin can be gasified into several chemicals and fuels (Osada et al. 2004; Yoshida and Matsumura 2001). NREL has developed a conceptual design for a process that converts lignin into a hydrocarbon that can be used as a high-octane automobile fuel additive. In the first stage of the NREL process, alkali catalyzes depolymerization and breaks the lignin polymers into phenolic intermediates that can be hydroprocessed into the final product. The depolymerized lignin is a mixture of alkoxyphenols, alkylated phenols, and other hydrocarbons. In the second stage, the depolymerized lignin is subjected to a two-step hydroprocessing reaction to produce a reformulated hydrocarbon gasoline product (Montague 2003). Lignin also can replace phenol in the widely used phenol-formaldehyde resins (Pérez et al. 2007). However, both costs of production and market value of these products are complex (Hamelinck et al. 2005). The residual solids of the process (lignin, residual cellulose and hemicellulose) can be efficiently used for heating, cooling, and electricity generation, which can be partly used within the process and partly as final products to the market.

Fusel oil is another by-product of the process. This oil needs to be separated only in order to produce a potable and pharmaceutical grade of ethanol, but not for production of fuel ethanol. The dominant components in fusel oil are found to be a mixture of primary methyl propanol and methyl butanol, formed from α-ketoacids, derived from or

leading to amino acids. Depending on the resources used, the important components of fusel oil might be isoamyl alcohol, n-propyl alcohol, n-butyl alcohol, isobutyl alcohol, sec-butyl alcohol, active amyl alcohol, isoamyl alcohol, and n-amyl alcohol. The amount of fusel oil in the fermented broth depends strongly on the pH of the fermentation. Furthermore, acetaldehyde and trace amounts of other aldehydes and volatile esters are usually produced during fermentation (Kosaric et al. 1983; Maiorella 1983).

The biomass of the fermenting microorganisms is a by-product of the ethanol production processes. It is not possible to avoid formation of the biomass during fermentation. In the ethanol production process, it is desirable to recirculate the produced cell mass to various degrees depending on the conditions in the fermentation (Brandberg 2005; Brandberg et al. 2007). Filtration, immobilization, encapsulation, and sedimentation are possible methods for separation of cells from the media and its recirculation (Purwadi 2006; Talebnia and Taherzadeh 2006). However, in the SSF, NSSF, SSCF, and CBP processes it is not easy to separate the cells from the solid residue. The possibility of cell recirculation is one of the advantages of the SHF process.

## WASTEWATER TREATMENT

The remaining liquid after distillation of alcohol is the major part of the plant's wastewater, which contains non- or low-volatile fractions of materials. Its composition depends greatly on the type of feedstock. It generally contains residual sugars (e.g. non-fermentable sugars), traces of ethanol, other metabolites produced during fermentation such as glycerol, inhibitors produced during hydrolysis, waxes, fats, and mineral salts (Kosaric et al. 1983). In the actual process, the liquid streams must be partly recirculated to minimize the requirement for fresh water and the production of wastewater. However, the consequence of recirculation is an accumulation of inert materials and of compounds inhibitory to the cellulase enzymes and/or fermenting microorganisms in the process. The degree of recirculation depends on the process conditions. As a rule of thumb, 40-75% of the streams might be safe to recirculate to the process (Alkasrawi et al. 2002; Stenberg et al. 1998b).

Since there is no large-scale process based on the enzymatic hydrolysis for ethanol from lignocellulosic materials, we should still rely on the results from labs and pilot plants while discussing the wastewater. Generally speaking, the characteristics of stillage from cellulosic materials might be comparable with those of conventional feedstocks and, therefore, methods of stillage treatment and utilization applied to conventional feedstocks might also be applicable to cellulosic feedstocks. Two possible exceptions to the similarity of cellulosic and conventional stillage characteristics deserve attention: (a) the potential for higher levels of heavy metals from the acid pretreatment equipment, and (b) the presence of inhibitors, such as hardwood extractives, associated with phenolic compounds present in the feedstock (Wilkie et al. 2000). The non-circulated stillage and other wastewater in the plant, such as condensed pretreatment flash vapor, cooling tower blowdown, boiler blowdown, and CIP wastewater, could be concentrated by evaporation. The concentrated wastewater could be incinerated or neutralized with alkali, followed by incorporation into some special application such as

road-building materials (Davies 1946). Similar to other substrate stillage, the stillage of lignocellulosic materials may be used for production of potentially viable biological products including enzymes (Morimura et al. 1994; Morimura et al. 1991), chitosan (Yokoi et al. 1998), astaxanthin (Fontana et al. 1997), and single cell protein (Cabib et al. 1983; Kujala et al. 1976). Anaerobic digestion can be used as an effective process for removing COD from stillage and converting it to biogas, which is a readily usable fuel for the ethanol facilities (Wilkie et al. 2000).

## COMMERCIAL STATUS

Several companies and government-funded laboratories have already engineered enzymes and microorganisms to optimize lignocellulose hydrolysis and help turn it into fuel (Service 2007). Pilot plant and commercial-scale facilities for converting lignocellulosic biomass to ethanol have existed since the mid-1900s. However, all these early plants used acids for hydrolysis of cellulose to ethanol, while enzymatic conversion technologies are on the agenda of the new plants (Nguyen et al. 1996).

Several cellulosic-based ethanol production companies are to be built in the near future. The U.S. Department of Energy (DOE) announced awards of $385 million for six commercial-scale cellulosic-ethanol biorefineries that are expected to produce more than 500 million liters of ethanol per year. Poet Company (formerly Broin) is probably the largest U.S. dry-mill ethanol producer, with 18 ethanol plants and more than 3.8 billion liters of ethanol annually. The company will expand one of the existing corn-grain ethanol plants in Emmetsburg, Iowa, to produce approximately 100 million liters of ethanol per year from corncobs and other cellulosic feedstock. The facility in Emmetsburg is expected to be operational by 2009. Recently, DOE awarded Poet an $80 million grant to fund its new cellulosic ethanol facility. Named Project LIBERTY, the biorefinery is part of a $200-million expansion of Poet's two-year-old Voyager ethanol plant in Emmetsburg. Furthermore, "BlueFire Ethanol" from waste wood, "Alico" from wood and agriculture wastes, "Abengoa Bioenergy" from corn stover, wheat straw, etc., "Iogen Biorefinery" from agricultural wastes, and "Range Fuels" from waste wood and energy crops are among the companies which have expected to start cellulosic-based ethanol plants in the next 2-5 years and received the awards from DOE (Service 2007).

A large pilot plant is run by Iogen (Ottawa, ON, Canada), which is one of the enzyme manufacturers. Iogen's cellulose ethanol process is designed to prove the feasibility of the ethanol process by validating equipment performance and identifying and overcoming production problems prior to the construction of larger plants. The plant is claimed to be able to handle all functions involved in the production of ethanol from lignocellulose, including receipt and pretreatment of up to 40 tonnes per day of wheat, barley and oat straw; cellulose conversion to glucose; fermentation; and distillation. The plant is designed to produce up to 3 million liters of ethanol per year. The yield of cellulose ethanol is claimed to be more than 340 l/ton of the feedstocks.

Another pilot plant for ethanol production from lignocellulosic materials is the NREL bioethanol pilot plant in Golden, Colorado, USA, at a scale of about 900 kilograms per day of dry biomass. This Mini-Pilot Plant is ideal for preliminary testing of

the process at small scale. The pilot equipment includes four 9000-liter, two 1450-liter, and two 160-liter fermentors for enzymatic hydrolysis and fermentation (Nguyen et al. 1996). Since opening in 1994, the bioethanol pilot plant has already been used for a number of cooperative projects to help developing bioprocessing technologies for bioethanol production, and several of them are now going into commercial ethanol production from biomass.

Another pilot plant is SEKAB in Sweden, which has a capacity of 500 liters of ethanol per day. In order to manufacture this quantity, approximately 2 tonnes (dry weight) of wood chips are used. The technology is based on both dilute-acid and enzymatic hydrolysis of cellulose and hemicellulose, whereupon the sugar is fermented to ethanol and purified by distillation. In dilute-acid hydrolysis or pretreatment, sulfuric acid or sulfur dioxide is used as a catalyst at temperatures of around 200 ºC within a two-stage continuous hydrolysis unit. In enzymatic hydrolysis, the material is first treated with dilute acid at mild conditions, after which enzymes hydrolyze the remaining cellulose in a third stage. Both the dilute-acid and enzymatic processes are being evaluated at the plant. In the four fermentors, it is possible to perform the fermentation with fed-batch or continuous technology (www.sekab.com).

SunOpta built the first cellulosic ethanol plant 20 years ago in France. There are four cellulosic ethanol projects that are or will be operational using SunOpta's technology and equipment to produce ethanol from lignocellulose. The company has provided the technology to (a) China Resources Alcohol Corporation in September 2006, and the plant began production of ethanol from local corn stover in October 2006, (b) Spain for the start-up of the Abengoa wheat straw to an ethanol facility located in Salamanca in the summer of 2007, (c) the Celunol facility being built in Jennings, Louisiana, to produce ethanol from wood and sugarcane bagasse, and (d) GreenField Ethanol Inc., Canada's largest producer of ethanol (www.sunopta.com)

Xethanol recently announced aggressive plans for its new BlueRidge facility. The Xethanol company was to begin producing lignocellulosic ethanol in Spring Hope, NC, by February 2007 using acid hydrolysis. It announced plans to construct a 190-million liters per year lignocellulosic ethanol plant in Augusta, GA, which was supposed to begin producing ethanol by mid-2007 (www.xethanol.com). In Soustons, France, there is a pilot plant for steam-explosion pretreatment of lignocellulose with large fermentors (e.g. 30-50 $m^3$). A pilot plant at the Voest-Alpine Biomass Technology center used a 3000-liter steam digester either for pretreatment and produced cellulase or for performing saccharification in 15 $m^3$ fermentors (Nguyen et al. 1996).

Researchers are also looking for improvements in different parts of the process, e.g. development of biocatalysts and process design. A final target for many researchers lies inside plants themselves, whereas some companies and academic groups are working to re-engineer resources such as poplar trees, corn, and switchgrass to boost their yields and make them easier to turn into fuel. Development of engineered poplar trees with 50% less lignin and more cellulose content than conventional varieties is among the efforts in this area (Service 2007).

Cellulase prices have a high impact on ethanol production from lignocellulosic materials. Iogen uses its own proprietary cellulases and is laying plans for a 30-million-gallon-per-year facility with partners such as Royal Dutch / Shell Oil (London and The

Hague) and PetroCanada (Calgary, AB, Canada). Two other enzyme-producing companies, supported by large grants from the DOE, have brought down the costs of the enzymes (Aden et al. 2002). Genencor International (Palo Alto, CA, USA) and the Danish company Novozymes (Bagsvaerd, Denmark) have significantly reduced the cost of cellulases, about 20-fold, to about 4-5 cents per liter. However, the price of cellulase is still high compared to amylases, the enzymes that break down corn starch for fermentation (Schubert 2006).

## ENERGY PRODUCTION AND INTEGRATION

Running processes for ethanol production from lignocellulosic source material requires electricity and heat, mainly used for steam generation and for cooling water. It would be ideal if a process can produce the necessary required energy. In ethanol production from lignocelluloses, this can be achieved by using the solid residue, which mainly contains lignin, and the concentrated stillage residue from the evaporation plant. Combustor, boiler, and turbogenerator subsystems can be used to burn various by-product streams for electricity and steam generation (Aden et al. 2002). However, the lignin is a valuable by-product, which could be essential for the process economics. Therefore, it is necessary to minimize the energy demand in the process and thereby increase the fraction of lignin that can be sold as a by-product (Galbe et al. 2007; Galbe and Zacchi 2002). This can be achieved by energy integration. A technology for design of heat exchanger networks, such as pinch technology, can be used for heat integration (Cardona and Sanchez 2007). Grisales et al. (2005) studied heat integration of fermentation and recovery steps for fuel ethanol production from lignocellulosic materials by using the software ASPEN PLUS for the preliminary balances of mass and energy. Pinch technology was employed for optimal design of heat exchanger networks. Application of a proper heat exchange between cold and hot streams can reduce the use of utilities (cooling water and steam). There are diverse possibilities in distillation of the produced ethanol. Heat exchange between the stripping and rectifying distillation columns can be used to reduce the utility consumption in distillation. However, in order to provide a temperature difference that favors heat exchange, the rectifying section should operate at higher pressures than the stripping section (Batista et al. 1998; Cardona and Sanchez 2007). Various process configurations to reduce the energy demand, such as running the distillation integrated with a multiple-effect evaporation unit, were suggested by Larsson et al. (1997). Running the process at higher solids consistency or to recirculated process streams, in order to maintain a high concentration of ethanol and dissolved solids, are other ways to reduce the energy consumption. Higher ethanol concentration would reduce the energy requirements in the distillation, especially in azeotropic distillation, and also in evaporation units (Cardona and Sanchez 2006; Galbe et al. 2007; Galbe and Zacchi 2002).

The remaining wastewater can be considered as another source of energy. Anaerobic digestion of the wastewater results in biogas, which contain 50-70% methane. The biogas can be sold as a by-product or be burned to generate steam and electricity, allowing the plant to be self sufficient in energy. This approach results also in reduction

of disposal costs of the wastes and generates additional revenue through sales of excess electricity.

## CONCLUDING REMARKS

During recent years much valuable work has been performed on different aspects of ethanol production from lignocelluloses based on enzymatic hydrolysis, and great achievements have been attained. Starting with a simple SHF process, there are now several advanced alternatives for the process. Numerous commercial plants are in the commissioning stage. With the start of these plants, abundant real data will be obtained and also many questions and problems will arise. Struggling with the problems will open some new areas in ethanol production from lignocelluloses. Process integration and optimization will also improve the energy consumption of the process. Scientists' efforts in reduction of prices of cellulase, as well as progress in optimization of the enzymatic hydrolysis process, will help to improve the economy of the process. Generally, these strivings in basic and applied sciences are essential to lead the world toward clean and reliable sources of energy.

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# WHAT HAPPENS TO CELLULOSIC FIBERS DURING PAPERMAKING AND RECYCLING? A REVIEW

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Both reversible and irreversible changes take place as cellulosic fibers are manufactured into paper products one or more times. This review considers both physical and chemical changes. It is proposed that by understanding these changes one can make better use of cellulosic fibers at various stages of their life cycles, achieving a broad range of paper performance characteristics. Some of the changes that occur as a result of recycling are inherent to the fibers themselves. Other changes may result from the presence of various contaminants associated with the fibers as a result of manufacturing processes and uses. The former category includes an expected loss of swelling ability and decreased wet-flexibility, especially after kraft fibers are dried. The latter category includes effects of inks, de-inking agents, stickies, and additives used during previous cycles of papermaking.

*Keywords: Paper recycling, Drying, Deinking, Hornification, Inter-fiber bonding, Refining, Fines, Fiber length, Conformability*

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## INTRODUCTION

Cellulosic fibers can change significantly when formed into a wet web of paper and subsequently subjected to such processes as pressing, drying, printing, storage, repulping, and deinking. Some of the changes can be subtle. Often it is possible to substitute recovered fibers in place of virgin fibers used for the production of paper or paperboard. On the other hand, characteristic differences between recycled fibers and virgin fibers (fresh from pulping wood, not recycled) can be expected; many of these can be attributed to drying. Drying is a process that is accompanied by partially irreversible closure of small pores in the fiber wall, as well as increased resistance to swelling during rewetting. Further differences between virgin and recycled fibers can be attributed to the effects of a wide range of contaminating substances. Important progress in understanding the changes that occur when fibers are made into paper, and then recycled, has been reviewed (Howard 1990, 1995; Laivins and Scallan 1993; Nazhad and Paszner 1994; Howarth 1994; Phipps 1994; Ackermann et al. 2000; Shao and Hu 2002; Hubbe et al. 2003b; Hubbe and Zhang 2005; Nazhad 2005). To provide context, this review will begin by describing some characteristics of papermaking fibers just before the forming process and then will discuss issues relevant to the recycling process and its effect on fiber properties.

## THE "ACTIVATED" NATURE OF FRESHLY PREPARED FIBERS

Several processes must take place before the cellulosic fibers in wood are in a form suitable for the production of paper. The net effect of the processes to be outlined below has been described by the word "activation" (see Stürmer and Göttsching 1979). "Activation" implies that the material is converted into a form that is, in some respects, more susceptible to changes, including those associated with formation of bonds between adjacent fibers when a wet web of paper is dried. The concept of an activated state of the cellulosic material also can be helpful when discussing various effects associated with papermaking and conversion, storage, use and recycling (including repulping, and deinking operations) of paper and paperboard. As will be discussed, the net effect of these latter processes, especially recycling, can be understood in terms of a "deactivation" of the fiber material (Nazhad and Paszner 1994). As some researchers have remarked, many factors that improve bonding between cellulosic fibers during a given cycle of papermaking unfortunately tend to reduce the capability of the fibers to form strong inter-fiber bonds again when the recovered paper is made into recycled paper (Pycraft and Howarth 1980b; Weise 1998). Increased refining and increased wet-press pressure are key examples.

Paper can be defined as a sheet-like material that is formed from individualized fibers by the removal of water. Wood is the most important source, at present, of such fibers. Thus, the separation of wood into its component fibers, i.e. "pulping," might be considered to be the first step in their "activation." Billosta et al. (2006) compared the ultrastructural details of papermaking pulps that were prepared in different ways, i.e. chemical, mechanical, thermomechanical or a combination thereof (Gullichsen and Fogelholm 1999; Sundholm 1999). It was found that fibers experience extensive delamination, as well as the formation of fibrils at their surfaces. These effects occur to different degrees, depending on the type of pulping process used. Microscopic observations provide clear evidence that fibers are present in pulp in the form of layered structures with domains of hemicellulose and lignin, which are present to different extents, depending on the type of pulp (Xu 2006; Li 2004a, 2004b, 2005, 2006; Shao, 2006).

In terms of physical attributes, one of the most important ways in which the individualized fibers in pulp are different in comparison to the wood from which they originated is the great increase in surface area per unit of dry mass, i.e. specific surface area. Studies have shown that the specific surface area of never-dried pulp fibers can be more than 100 square meters per gram (Stone and Scallan 1966). Mechanical pulping processes tend to separate the fiber material into a wide range of sizes, due to partial breakage of many of the individual tracheids and libriform fibers. By contrast, chemical pulping operations tend to leave the fibers relatively intact.

### Chemical Pulping as a Means of Rendering Fibers More Active

One of the ways in which pulping operations can render fibers more susceptible to forming bonds with each other is by increasing the free energy of their surfaces. As reviewed by others, the free energy of a surface can be evaluated by testing the contact angles of those surfaces with selected liquids (Chatterjee et al. 1991; Jacob and Berg 1993; Whang and Gupta 2000; Shen et al. 2000; Tze and Gardner 2001b), as well as by

inverse gas chromatography techniques (Felix and Gatenholm 1993; Tze and Gardner 2001b; Santos et al. 2001) in which one evaluates the interactions of the solid phase (fibers) with a series of chemicals in the gas phase. Such studies have shown that the removal of relatively hydrophobic lignin and natural resins from wood can greatly increase the free energy of cellulosic surfaces. Cellulosic fibers that are derived from mechanical vs. chemical pulping can contrast sharply with respect to surface chemical composition and structure. The surfaces of fibers formed by chemical (e.g., kraft or sulfite) processes will tend to have higher free energy in comparison to fibers that were separated from each other mainly by mechanical means (Backström et al. 1999). Because mechanical pulping methods, such as thermomechanical pulping (TMP), typically separate fibers from each other at the lignin-rich middle lamella (Kibblewhite 1983; Gregersen et al. 1995), the resulting external surfaces of TMP fibers tend to be rich in lignin, relatively non-compliant, and somewhat hydrophobic. By contrast, removal of lignin and extractives during kraft pulping, and also by any subsequent bleaching and associated washing stages, yields fiber surfaces that are rich in carbohydrates.

Another way in which kraft or sulfite pulping tends to activate never-dried cellulosic fibers is by increasing the size and net volume of submicroscopic pore spaces within the cell walls. Such changes have been quantified by means of solute exclusion experiments (Stone and Scallan 1968; Berthold and Salmén 1997), by determination of the water retention (Jayme and Büttel 1964), and by various other methods (Li et al. 1993; Alince and van de Ven 1997; Andreasson et al. 2003).

Solute exclusion tests are carried out by exposing known amounts of fibers to known amounts of solutions containing given levels of sugar-like polymers. The polymers have different, narrowly-distributed molecular sizes. Experimental results are obtained by measuring the concentrations of sugar in the bulk phase. In cases where the sugar-like molecules are too big to enter the pores in the fiber material, the measured concentrations in the bulk solution will exceed the values that would be expected if the polymers were able to enter the small pores. Such tests have shown that many of the slit-like pores within mechanical pulp fibers tend to be somewhat larger than 1 nm in thickness, whereas such pores in chemically pulped, but never-dried fibers can be at least 2 nm to 50 nm (Stone and Scallan 1968; Berthold and Salmén 1997). The difference is attributed to the selective removal of lignin-rich domains from the fiber material during pulping. Recently this nanoporous nature of fibers was confirmed indirectly by electro-kinetic methods (Hubbe 2006a).

Chemical pulping also tends to increase the flexibility and conformability of never-dried fibers (Tam Doo and Kerekes 1982; Paavilainen 1993). One of the most dramatic consequences of such changes is that kraft fibers more readily flatten into a ribbon-like form under compression and shear forces in the wet state. Flexible, ribbon-like fibers tend to form stronger inter-fiber bonding, compared to relatively stiff fibers, in which the open lumen structure may persist during papermaking.

## Bond-Activation by Refining

To further prepare fibers for their role in papermaking, often they are subjected to compression and shearing forces, i.e. they are "refined" (Paulapuro 2000). The goal is to optimize the conditions of refining so that the fibers' wet-conformability, capability of

bonding together, and tendency to form a bulky or a compact structure is sufficient to meet the requirements of a typical grade of paper.

Kraft fibers usually are refined by one or more passes between a rotor and a stator of a typical refiner. Bunches of fibers within the suspension become squeezed and sheared between the working surfaces of the refiner. As a consequence of this action, parts of the outer layers of fibers unravel, resulting in fibrillated fiber surfaces, as well as detached fines. In addition, delamination within the cell wall tends to render the fibers more flexible when they are still in the wet condition. Though it is well known that the strength of paper can be substantially improved by refining, subsequent loss in inter-fiber bonding potential also can be much larger when (kraft) fibers are refined before they are dried and recycled (Stürmer and Göttsching 1979; Peng et al. 1994).

Fascinating new insights on the effects of kraft pulp refining have been provided by a study that used highly contrasting methods of refining (Kang and Paulapuro 2006). One set of pulp samples was refined under specialized conditions that mainly delaminated the interior structure of the cell walls (internal fibrillation), making the fibers very flexible. The other set was refined under conditions that favored external fibrillation, leaving the bulk of the cell walls relatively unchanged. In both cases the resulting pulps were able to form substantially stronger paper in comparison to unrefined fibers of the same type.

## OVERVIEW OF CONDITIONS TO WHICH FIBERS ARE EXPOSED

As has been shown by many studies, the recycling of cellulosic fibers, especially in the case of chemically pulped fibers, usually is associated with a loss of physical strength properties (Brecht 1947; McKee 1971; Cildir and Howarth 1972; Horn 1975; Koning and Godshall 1975; Cardwell and Alexander 1977; Göttsching and Stürmer 1978a; Yamagishi and Oye 1981; Van Wyk and Gerischer 1982; Ferguson 1992a; Howard and Bichard 1992; Mansito 1992; Klofta and Miller 1993; Laivins and Scallan 1996; Law 1996; Wistara and Young 1999; Jahan 2003; Hubbe and Zhang 2005; Garg and Singh 2006). Significant losses in the bonding potential of recycled fibers has been observed even in cases where the dried and redispersed fiber were refined again to the same level of freeness before they were first dried (Brecht 1947; McKee 1971; Koning and Godshall 1975; Göttsching and Stürmer 1978a; Van Wyk and Gerischer 1982). To discuss the evidence to explain these changes, this section gives a quick overview of the conditions to which papermaking fibers are exposed, not only during the manufacture of paper, but also during its subsequent printing and converting operations, storage, use, repulping, de-inking, and re-refining.

### Papermaking

The moment just before fibers are first formed into paper can be considered as a useful point of reference. As should become increasingly clear from subsequent discussions, kraft and sulfite fibers that have been freshly prepared for the first generation of papermaking are often at the highest state of readiness that they ever will be, in terms of forming strong paper. Though, as will be described, such a statement is not always true

in the case of mechanical pulp fibers, the reference point is still useful in describing changes in mechanical pulps, as well.

*Wet End Additives*

To a large extent, the addition of chemical additives to the wet end of a paper machine can be considered to be a reversible process, with respect to recycling. Many such chemicals, such as cationic starches (Marton 1976; Roberts et al. 1986; Malton et al. 1998), are prepared in such a way that they will tend to remain attached to the cellulosic materials. A substantial proportion of such chemical additives can remain associated with the fibers when they are recycled. It has been shown that highly charged wet-end additives will continue to influence the charge characteristics of papermaking fibers, even after they have been dried and repulped (Grau et al. 1996; Sjöström and Ödberg 1997). Likewise, the effects of hydrophobic sizing treatments may be passed down to subsequent generations of recycled paper (Sjöström and Ödberg 1997). Overviews describing the effects of various papermaking additives have been published elsewhere (Scott 1996; Neimo 1999).

*Pressing*

The next event in the papermaking process that affects the quality of cellulosic fibers (including fibers after they are recycled) is passage through a wet-press nip. Various authors observed decreases in the water-holding capacities of fibers that have been subjected to wet-pressing conditions (Robertson 1964; Carlsson and Lindström 1984). Scallan (1998) attributed such changes to somewhat irreversible formation of hydrogen bonds between cellulosic surfaces within void spaces of the cell wall that become pressed together due to the applied force. The theory is that semi-crystalline regions of hydrogen bonds form on the contacting pressed surfaces. Scallan (1998) also proposed that the process involves swollen hemicellulosic material as a kind of natural dry-strength agent. Weise and Paulapuro 1996 used laser confocal microscopy and swelling measurements and reported that irreversible hornification (meaning a loss of swelling when the fibers are rewetted) began above solids contents of 30-35%.

*Drying*

Much of the subsequent discussion in this article will deal with effects of drying, so only a brief description needs to be given here. As will be shown later, it can be useful to distinguish between two aspects of what happens when paper is dried. On the one hand, the wet paper already becomes hot when the web still contains substantial moisture (heat-transfer dominated stage). On the other hand, water evaporation makes the paper web dryer (mass-transfer-dominated stage).

Temperatures and durations of time associated with the drying of paper can be expected to vary widely, depending on the basis weight of the product, the speed of the paper machine, and other paper machine design and operation parameters. Conventional drying on paper machines takes place under atmospheric pressure. For this reason, the temperature of the paper will tend to remain at the boiling point or lower, as long as liquid water remains within the pore spaces adjacent to the sheet's surface (Garvin and Pantaleo 1976). However, due to the dynamic nature of the drying process, and also due

to above-boiling surface temperatures of dryer can surfaces, it may be possible to measure temperatures at paper surfaces that are above the boiling point of water, especially when the web is approaching a dry condition.

*Calendering*

The calendering of paper can be defined as a process whereby the sheet passes through one or more nips between smooth rolls under high pressure, resulting in a smoother surface. Göttsching and Stürmer (1978c) observed significant effects of calendering on the quality of the fibers after they had been repulped and formed into new sheets of paper. The calendered fibers had a reduced tendency to swell with water during repulping. Soft-nip calendering, in which a steel roll is pressed against a cellulose-covered or polymer-covered roll, was found to be less damaging to strength characteristics after recycling of the fibers relative to hard calendering under conditions that provided comparable smoothness.

Sohn and Paik (2006) observed surprisingly large differences in the way hardwood vs. softwood kraft pulps responded to calendering. The calendered softwood fibers yielded a reduced strength of the recycled paper, whereas calendering actually had a positive effect in the case of hardwood fibers. These effects were over and above effects due to the drying and recycling; those processes tended to degrade the bonding ability of all of the fibers tested, including chemithermomechanical pulp (CTMP) fibers.

*Printing*

Effects of printing on the visible appearance of recycled paper, even after deinking, are so noticeable that it is easy to overlook the effect of the ink or toner on other attributes of the paper. Not all recycling of paper involves deinking. Many ink materials are quite hydrophobic, so they tend to decrease the surface energy of fibers to which they remain attached (Etzler et al. 1995). Kuys and Zhu (2004) observed that the presence of toner significantly increased the cationic demand of redispersed xerographic paper. Likewise, coatings used to enhance printing quality have an important effect on the cationic demand. Recycled stock from old magazine paper can be expected to have a much higher cationic demand than uncoated newsprint. Because the fiber compositions of the base sheet of the magazine paper was similar to that of newsprint, such results can be attributed to the negatively charged latex, phosphate dispersants, and clays found in the respective aqueous coating formulations.

*Converting*

The word "converting" can include a very wide range of procedures that are used to increase the value of a paper product in the eyes of a specific user. Converting processes can include cutting, laminating, folding, gluing, and creping, etc. In terms of the quality of recycled fiber furnish, many of these converting processes have the potential to increase the level of contaminants in recycled streams of cellulosic fiber. In some cases the difficulty of removing glue or laminated layers may render converted paper or paperboard products unattractive as a potential source of recycled fibers, even in cases where the fibers themselves may have relatively high potential value for use in paper. High levels of wax, wet-strength agents, release agents, adhesives, and exotic inks

generally decrease the "recyclability" of waste paper (Webb 1992; Venditti et al. 2000; Watanabe and Mitsuhiro 2005). Another parallel issue of importance relates to the increased popularity of shredding documents and the extensive cutting of fibers that occurs during shredding.

## Storage and Use

*Aging*

During the time that paper is stored, shipped, and used for various purposes there are opportunities for the fibers to undergo chemical as well as physical changes. As noted by Kato and Cameron (1999), it is reasonable to expect some embrittlement of high-temperature-aged paper due to increased cross-linking, which is usually attributed to hydrogen bond formation and increased crystallinity. But the high temperature conditions also are likely to accelerate chemical breakdown of cellulosic chains, an issue that will be considered in more detail later in this review. As noted by McComb and Williams (1981), the hydrolysis of cellulosic material is accelerated in the presence of acidity; for this reason, paper that has been produced under weakly alkaline conditions tends to "age" less compared with "acidic" papers (Hubbe 2005a).

Effects of acidic vapors were demonstrated persuasively in an unplanned experiment that occurred in one of the authors' laboratories. A stack of pressure-sensitive labels had been left in a top shelf of a cabinet that also contained bottles of reagent-grade acid solutions. After two years of such storage, the labels themselves, as well as the release paper backings, had become very brittle. Similar labels, kept in another cabinet, were not brittle.

*Age distribution*

While on the subject of aging, it has been noted that a piece of recycled paper is likely to contain fibers having a wide range of age. The different fibers making up a paper sample are likely to have been subject to different number of (recycling) cycles. Cullinan (1992) and Gerspach et al. (1993) developed models to estimate the likely distributions in age of fiber in recycled paper products. To be useful, such models require sound data concerning wastepaper collection. Related work led Phipps (1994) to conclude that large amounts of recycled fiber can be incorporated into newsprint furnish without major loss in physical properties.

Cildir and Howarth (1972) carried out a study in which the fraction of recycled fibers that were incorporated into each successive generation of handsheets was carefully varied, up to a maximum proportion of three-quarters. They defined a parameter called the "recycle factor." Its value was found to be critical; paper quality was not greatly affected by recycling until the value of "recycle factor" approached the upper end of the range studied.

As a caution against overestimating effects of multiple recycling sequences on fiber strength characteristics, Nazhad (2005) noted that, in many cases, kraft fibers tend to reach a plateau of physical characteristics after about five cycles of drying and repulping. Such effects even can be viewed as beneficial, to the extent that repeatedly-recycled fibers might be expected to have a more consistent quality. Issues related to

increased dimensional stability and ease of drying of kraft fibers that have been dried at least once will be considered at the end of this article.

## Recycling

After various types of wastepaper are collected and sent to a paper recycling mill, there are many possible unit operations. Many of them are optional. The most basic is to redisperse the fibers in water, i.e. "repulping." Despite the large shear and energy used in repulping equipment, most researchers agree that there is little damage to individual fibers as a result of the initial repulping. The forming of damp fibers into sheets, in the absence of drying, has relatively little effect on fibers' characteristics. By contrast, as will be described in the next two subsections, significant changes in the suitability of recovered fibers for making recycled paper can be expected when the pulp is subjected to further refining. In some respects, neither de-inking nor further refining is absolutely required in order to make recycled paper. On the other hand, product requirements in terms of appearance and strength are likely to render both de-inking and further refining absolutely essential in many cases.

*Deinking*

The subject of deinking is complex and multifaceted (Ferguson 1992b; Göttsching and Pakarinen 2000; Rojas 2004). In terms of fiber quality, deinking operations mainly affect the degree to which the fibers are contaminated with non-cellulosic materials. The types of contaminants that are often encountered in the paper machine systems of paper recycling mills recently have been reviewed (Hubbe et al. 2006). On the one hand, an effective de-inking program is expected to reduce the levels of inks, stickies, and dirt, etc. But on the other hand, it can be expected that some of the chemicals used in the deinking process will remain with the recovered fiber. The latter chemicals may include fatty acids (and especially, the calcium salts of fatty acids), nonionic surfactants, dispersants, and, in the case of mechanical pulps, often the byproducts of bleaching with hydrogen peroxide (Haynes and Röring 1998). Peroxide bleaching is known to increase the cationic demand of the bleached mechanical pulp to relatively high levels due to release of carboxylated hemicellulose species and breakdown products. On the other hand, de-inking operations do not appear to significantly damage the fibers themselves, and deinked fibers tend to be rather "clean" with respect to the presence of wood resins (Webb 1992; Klungness 1993; Alanko et al. 1995).

*Re-refining*

As will become clear from later discussion, recycled kraft or sulfite fibers, when dispersed in water, and even when subjected to deinking, can have a reduced bonding tendency in comparison to their condition just before they were originally made into paper. Papermakers often strive to make up for this deficiency by judicious application of compression and shearing forces in a refiner. The word "judicious" should be stressed for two reasons. First, it can be expected that most of the recovered fibers already have been refined. Second, harsh refining of recovered fibers can be expected to produce a lot of fines. Though it is reasonable to expect that drying of kraft fibers would render the

pulp more susceptible to creation of fines when redispersed in water and subjected to additional refining, this expectation does not appear to have been definitively proven.

A high level of fines tends to slow down the dewatering of the wet web of paper (Hubbe and Heitmann 2007) and the associated loss of fiber length is likely to decrease other strength attributes of the paper product, such as tear strength and folding endurance. Strategies for optimal refining of recycled fibers will be discussed later, when considering ways to overcome various adverse effects of recycling on fiber attributes.

## PHYSICAL EFFECTS OF DRYING, STORAGE, AND USE

The conditions to which fibers are exposed during paper production, converting, storage, use, and recycling can induce various different changes in fiber morphology, surface characteristics, and suitability for use in the formation of recycled paper. Such changes can be described in various ways, using terms such as hornification (i.e. loss of ability of the fibers to swell with water), semi-irreversible closure of nano-sized pore spaces, decrease of the external surface area, decreases in flexibility and conformability, breakage or other damage to the fibers, and a number of other such changes. A note of warning is appropriate, though. As mentioned by Garg and Singh (2006), even if one is successful in describing all of the significant changes that occur when a given set of fibers is made into paper, used, and recycled, it may remain unclear which of the factors have the major influence on the product attributes.

### Hornification

Although all researchers don't agree concerning a definition of "hornification," most users of the word imply both a reduction in the amount of water that fibers hold within their cell walls, and also a tendency for rewetted fibers to be stiffer and less conformable than before being subjected to drying or other kinds of stresses (Jayme 1944; Stone and Scallan 1966; Szwarcsztajn and Przybysz 1976, 1978; De Ruvo and Htun 1983; Mansito et al. 1992; Laivins and Scallan 1993; Minor 1994; Nazhad and Paszner 1994; Scallan 1998; Weise 1998; Weise and Paulapuro 1999; Diniz et al. 2004; Welf et al. 2005; Billosta et al. 2006). "Hornification" also can be used when cellulosic fibers are subjected to other kinds of stresses, including heating without drying (Lyne and Gallay 1950; Roffael and Schaller 1971; Welf et al. 2005), as long as there is a simultaneous loss of water-holding ability and strength potential.

Figure 1 illustrates a general concept that can be used to explain changes in the water-holding ability of kraft fiber cell walls. According to this concept the process of refining tends to open up submicroscopic spaces within the lamellar structure of the fiber cell walls. Evidence of internal fibrillation during refining includes swelling in the thickness direction of fibers (Jayme 1944; Jayme and Büttel 1968), and also an increase in wet fiber flexibility (Paavilainen 1993). As will be described, spaces created in the fiber cell wall tend to close in a semi-irreversible manner when the fibers are dried.

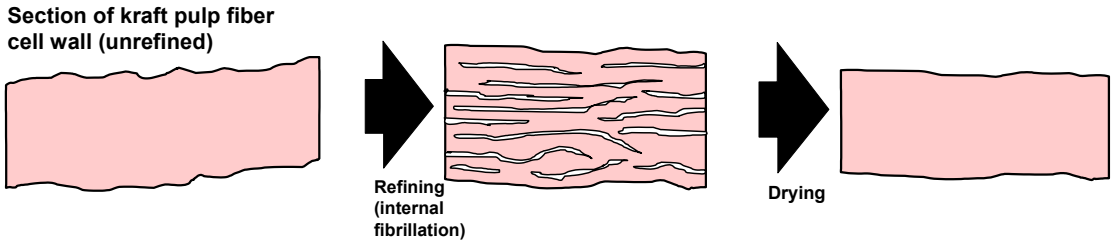


**Figure 1.** Schematic illustration of the swelling of kraft fiber cell walls during refining, followed by semi-permanent closure of inter-lamellar pore spaces when the fibers are dried

*Water retention value tests*

The most commonly used method to assess the swelling ability of cellulosic fibers has been the so-called water retention value (WRV) test (Jayme 1944; Anon. 1981, 2000). It even has been proposed that WRV results be used as the defining criterion of whether or not hornification has occurred in a given case (Weise 1998). To carry out a WRV test, a wet sample of fibers is inserted into a specially prepared centrifuge tube. The wet fibers rest on a filter surface, and there is space below to accommodate any water that is removed from the fibers. Most researchers, starting with Jayme (1944), who developed the method, have assumed that centrifugation mainly removes water from the spaces between adjacent fibers, as well as from fiber lumens, and that the water remaining after fibers is located within the cell walls. Recently, however, it has become clear that a substantial portion of the water remaining after centrifugation may be associated with fibrils at the outer surfaces of fibers. The importance of externally held water to the results of WRV tests is supported by the fact that high-mass cationic polymers, which are far too large to affect water held within the cell walls of fibers, can significantly decrease WRV results (Ström and Kunnas 1991). Thus, it can be said that WRV tests give a measure of "overall" water retention, including both water in the cell wall and also water associated with fiber surfaces.

Results of WRV tests have shown that the most dramatic losses in water-holding ability of relatively low-yield fibers take place in the case of well refined fibers (De Ruvo and Htun 1983). These authors reported that most of the gain in WRV that had been achieved upon refining of the fibers was lost even under very gentle drying conditions. More recently, it has been shown that losses in WRV tend to occur in two stages, an initial loss due to drying itself, regardless of temperature, and then a further loss when the temperature of drying exceeds about 150 $^{o}$C (Hubbe et al. 2003b; Welf et al. 2005). A remarkable parallel was found between such WRV results and the results of strength tests. The reason that both sets of results showed losses due to drying itself, regardless of temperature, was attributed to pore closure. Pore closure can be expected to cause fibers to be stiffer for the same reason that a stick is much stiffer than a rope of equal size and density; stiffness depends on the degree to which the fibrous components of a structure are bonded together, preventing them from sliding past each other. The fact that both WRV and paper strength experienced further losses when kraft fibers were exposed to relatively high temperatures during drying was attributed to further shrinkage, possibly due to plastic flow. Related work by Weise et al. (1996) showed that most of the loss in WRV occurred as the solids content of unbeaten bleached kraft fibers was increased in

the range 20 to 75%, which corresponds to the removal of free water. Further loss of water due to evaporative drying caused further shrinkage, but only a relatively small additional loss of WRV when the fibers were subsequently placed back in water.

*Fiber saturation point tests*

The term "fiber saturation point" (FSP) has become associated with a reputedly more reliable, but also more painstaking method of evaluating the amount of water held within fiber cell walls. An FSP test involves mixing a relatively high consistency fiber slurry with a solution of high molecular mass dextran (Scallan and Carles 1972; Scallan 1977). The dry mass of fibers, the total amount of water, and the total amount of dextran need to be precisely known. After a period of mixing, a filtrate sample is obtained, and the dextran concentration is determined e.g. by interferometry (Stone and Scallan 1968). The validity of this test relies upon the assumptions that the dextran has no affinity for the fiber surfaces and that its molecular size does not allow it to pass into the spaces within a cell wall.

Recently, fiber hornification was evaluated by a parameter termed 'hard-to-remove (HR) water content,' which was defined as the ratio of water mass to fiber mass at the transition between the constant rate zone and the falling rate zone from the isothermal thermogravimetric analysis (TGA) experiments (Park, et al. 2006b). The results indicated that the HR water content could be used as a measurement technique for fiber hornification, showing a close correlation with the WRV over repeated drying and wetting cycles. As expected, fully bleached kraft pulped fibers demonstrated a much larger decrease in the HR water content upon experiencing multiple drying and wetting cycles than did mechanically pulped fibers. Further, refined fibers experienced increased hornification over multiple drying and wetting cycles relative to unrefined fibers.

*Factors that influence the extent of hornification*

An important clue about the nature of hornification is provided by the fact that high-yield pulps, such as thermomechanical pulp (TMP), appear to be much less susceptible to changes when they are dried (Bovin et al. 1973; Ferguson 1992a, 1994; Houen et al. 1993; Rossi et al. 1994; Phipps 1994; Alanko et al. 1995; Chakravarthi et al. 1995; Gavazzo et al. 1995; Law et al. 1995; Göttsching 1995; Putz 1996; Ackermann et al. 2000; Qian et al. 2005; Law et al. 2006; Park et al 2006b). Göttsching and Stürmer (1978b) observed contrasting results in the case of stone groundwood pulps, which appeared to lose a significant amount of swelling ability upon drying. Lyne and Gallay (1950) found that bleached sulfite pulps were more susceptible to losses of swelling ability upon drying, in comparison to unbleached sulfite. In addition, relatively low-yield pulps do not appear nearly as prone to hornification effects until they have been refined (Stürmer and Göttsching 1979). Bayer (1996) compared a variety of different mechanical and chemi-mechanical pulps, both hardwood and softwood, with kraft fibers, and found a wide range of hornification behaviors. Billosta et al. (2006) proposed that such differences between different types of pulps can be explained in terms of their differing morphology on a sub-microscopic scale. The opening up of inter-lamellar spaces within fiber cell walls by either removal of lignin or by refining appears to make them more susceptible to subsequent changes when the fibers are dried. Jang et al. (1995) noted that

mechanical pulp fibers appear to flatten as a net result of papermaking, use, and recycling, an effect that can yield denser, stronger recycled paper in comparison to the first time that the fibers were used. Law (1996) observed significant decreases in water retention when mechanical pulp fibers were dried and recycled, but, unlike kraft pulps, such loss of swelling ability was accompanied by increases, rather than decreases in the strength of the recycled paper.

## Pore Closure and Failure to Re-open

Many researchers have concluded that the loss of swelling ability of low-yield cellulosic fiber upon drying is due to the closure of pore spaces in the cell walls, plus the inability of many of the pores to reopen if the fibers are rewetted (Stone and Scallan 1966; De Ruvo and Htun 1983). To support such a hypothesis, it is necessary to quantify not only the total volume of pores within fibers, but also the distribution of pore sizes.

*Solute exclusion with probe molecules of different sizes*

Aggrebrant and Samuelson (1964) were apparently the first to use the solute exclusion method for the study of cellulose fibers, mixing fibers with a known concentration of non-adsorbing polymer solution, and then measuring the concentration of free solution in the bulk. In cases where the polymer has a very high molecular mass, this is basically the same as the FSP test, as just described. Stone and Scallan (1966) were able to obtain considerably more information by carrying out such tests by using a series of dextrans molecules having widely different, but narrowly defined molecular mass. The ability of the polymers to penetrate into the fibers was found to be a strong function of molecular mass, consistent with the idea that the effective size of the molecule in solution corresponds to the minimum size of pore spaces that it can enter. By use of these tests Stone and Scallan (1966) were able to show substantial irreversible pore closure, due to drying. The pores that failed to reopen after rewetting corresponded to those that were just large enough to accommodate probe molecules having solution dimensions in the range of about 2 to 20 nm. Because of an effect called "excluded volume," it can be expected that the physical dimensions of the pore spaces measured in this way may be about two times larger than the physical diameters of the probe molecules (Alince and van de Ven 1997). Related work, in agreement with the main conclusions, has been reported by others (Yamagishi and Oye 1981).

*NMR studies of pore size distribution changes*

Because NMR tests can distinguish between water molecules adjacent to surfaces vs. those in the bulk, researchers have used NMR analysis to obtain information about pore size distributions in cellulosic materials (Maloney et al. 1997; Haggkvist et al 1998). Based on results of such research Haggkvist et al. (1998) concluded that shrinkage of pores as a result of drying was similar to what happens when wet fibers are pressed to remove water. Due to differing spin-lattice relaxation profiles of the protons, depending on the method of water removal, it could be concluded that the sizes of typical pores decreased gradually as more and more water was removed. Maloney et al. (1997) concluded, based on NMR results, that pressing had a disproportionate effect in closure of the larger pores that were present in fibers.

*Microcalorimetry for analysis of pores within fibers*

Yet further information about pores within cellulosic fibers has been revealed by differential scanning calorimetry (DSC) studies (Maloney et al. 1998a,b; Park et al. 2006a,b,c). Such studies are based on the principle that the freezing characteristics of water can depend on how close the water molecules are to various surfaces. Maloney et al. (1998) identified three types of water associated with cellulosic fibers, bulk water, freezing bound water, and nonfreezing bound water. The freezing temperature of the freezing bound water was depressed, relative to that of bulk water, and the authors used the freezing point depression as evidence that such molecules are in a region of reduced structure, compared to bulk water, and that the more disorganized layer of water always extends to the same distance out from a wetted surface. It is reasonable to assume that the non-freezing water identified in such experiments consists of "water of hydration," i.e. molecules of water that are directly interacting with the cellulose. Park et al. (2006a), using similar methods, concluded that the larger pores within kraft fiber cell walls were the earliest to close during drying, followed by smaller pores.

One way in which to simplify interpretation of the DSC data from experiments of this type is to replace water, as the suspending medium, with a non-aqueous liquid. Wang et al. (2003) used this approach with cyclohexane. After making some allowance for a de-swelling effect of the liquid, results were in general agreement with water-based DSC tests of the pore size distribution.

While questions remain about the fundamental reasons behind the three types of water, it has been possible to conclude from such studies that bulk water ceases to exist within fibers if they are pressed and dried to solids levels between 47% and 67% (Maloney et al. 1998). At this point the capillaries in the fiber have collapsed, and the hemicellulose begins to dehydrate. After further drying to 78-81% solids, the fine pores are completely collapsed, and only non-freezing bound water remains.

## Surface Area

Another approach to characterizing changes that occur upon drying, using, and recycling paper involves various measurements of surface area. Results of such measurements are likely to be affected by the extent of fibrillation at fiber surfaces, whether or not the fibrils have become matted down to the surface as a result of their history of treatment (Ackermann et al. 2000), and whether the method employed is able to detect internal "surfaces" associated with sufficiently large pores in the cell walls. Using a nitrogen adsorption technique, following a solvent-replacement-drying method, Stone and Scallan (1966) observed significant decreases in the surface areas of sulfite pulp in cases where the water content was reduced to 42% or below. Once the fibers had been completely dried, the surface area had decreased to about 1% of its initial value.

*Polyelectrolyte adsorption as a surface area assay*

The reason that cationic polyelectrolytes can be used to evaluate the surface areas of cellulosic materials is that they tend to adsorb with high affinity onto negatively charged substrates. The cationic polyelectrolytes' charged nature also guarantees that no more than a single layer of molecules will be formed. One can safely assume that

positively charged polyelectrolytes of suitably high molecular mass will continue to adsorb onto the surfaces of interest from an aqueous solution until no uncovered areas remain. Although many different factors can affect the molecular conformations, and therefore the density of adsorbed polyelectrolyte molecules (Wågberg and Ödberg 1989), it is reasonable to assume that adsorption is proportional to the area of accessible surfaces.

Gruber et al. (1996) used polyelectrolyte adsorption to study the effects of drying and recycling sulfite fibers. In the case of poly-DADMAC molecules larger than about 50,000 g/mole there was only a moderate decrease in the adsorbed amount when the fibers were dried and recycled, compared to their initial condition. However, there was a marked decrease in the adsorbed amount of a lower-mass poly-DADMAC, having a mean molecular mass of 14,000 g/mole. These observations were taken as evidence that pores roughly within the size range between that of the 14,000 g/mole molecules and the 50,000 g/mole molecules existed in the never-dried sulfite samples, but at least some such pores closed irreversibly during drying and recycling. Similar effects were reported by Hubbe et al. (2003), for unbleached kraft fibers, and by Lee and Joo (2000) in the case of bleached kraft fibers. Thode et al. (1955) used similar principles, but with a strongly adsorbing dye, to show reductions of surface area of sulfite pulps due to drying.

*Enzyme reactivity as a measure of surface area*

Because enzymes consist of large, multiply-folded protein molecules, it is reasonable to expect them to be excluded from pores in the cell walls of cellulosic fibers, depending on the pore size. Though it would make sense that rates of hydrolysis by cellulases can depend on many different factors, such as the extent of crystallization of the cellulosic material, it is still possible to use the overall rate of hydrolysis as a rough measure of surface area. This approach requires the use of an excess addition of the enzyme, such that surface area becomes a limiting factor. As described by Pycraft and Howarth (1980a), the extent of hydrolysis can be followed by sugar analysis. Further work by the same authors (1980b) revealed a strong correlation between the initial rates of enzyme hydrolysis and the strength of paper that had been subjected to a range of conditions during drying or pressing. Drying decreased the hydrolysis rates significantly, and the effects became increasingly larger with increasing severity of drying conditions on a pilot paper machine.

Related work was carried out by Fan et al (1980), but they interpreted their results not in terms of surface area, but in terms of degree of crystallinity. In fact, one could argue that either a decrease in accessible surface area or the presence of more difficult-to-hydrolyze crystalline material at the surfaces both might be able to explain the same observations.

## Flexibility, Relative Bonded Area (RBA), and Sheet Density

*Flexibility of Fibers in the Wet State*

Various researchers have reported strong correlations between the flexibility of wet fibers and the strength of paper formed by such fibers (Tam Doo and Kerekes 1982; Steadman and Luner 1985; Pavilainen 1993). It is reasonable to expect that more flexible fibers should better conform to the shape of adjacent fibers, developing a higher

proportion of bonded area. Scallan and Tigerström (1991) and Dulemba et al. (1999) found that the elastic modulus of wet kraft fibers was sometimes doubled due to the effects of drying and recycling. The effect is illustrated in Fig. 2. In the case of sparingly refined, moderately high-yield unbleached kraft pulp the method of Steadman and Luner (1985) was used to show significant decreases in fiber flexibility due to drying (Zhang et al. 2004; Hubbe and Zhang 2005). After a moderate degree of refining of the redispersed fibers it was still possible to detect a deficit in flexibility. However, the additional refining increased the water retention value back near to its original value, and the strength of the paper also could be recovered by subsequently refining the once-dried fibers to the same degree as a control sample (e.g. 6000 revs. of a PFI refiner).

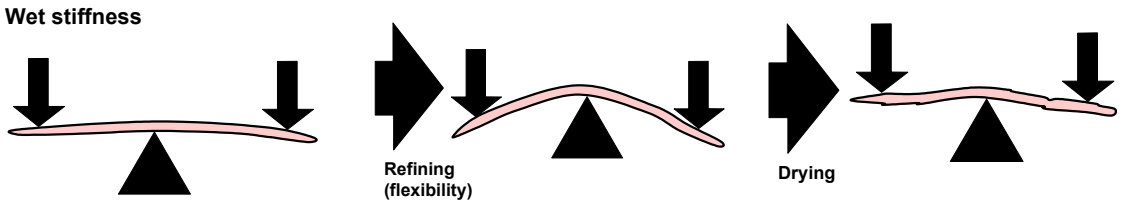


**Figure 2.** Kraft fiber wet-flexibility typically increases due to refining, but the fibers become stiff when they are dried and rewetted, as in the case of papermaking, followed by recycling.

Cao et al. (1999) concluded that wet-flexibility was a major factor in determining the bonding potential of fibers from red cedar. Their study compared thermomechanical pulps (TMP) to fibers having various degrees of hemicellulose removal. Based on the apparent densities, these authors concluded that the once-dried fibers were less conformable, and that this factor was responsible for the reduced strength of paper that was made from them. Somwang et al. (2001) reached similar conclusions regarding bleached kraft pulps, comparing never-dried and dried samples; bonded areas were compared by confocal laser scanning microscopy.

*Relative Bonded Area*

One of the most elegant ways to quantify the ability of fibers to conform to the surface morphology of adjacent fibers is based on the ability of a resulting sheet of paper to scatter light. To a first approximation it has been found that the tendency of paper material to scatter light, i.e. the "*s*" coefficient of Kubelka-Munk analysis (Page 1969; Scott et al. 1995), is directly proportional to the exposed surface area of the fibers. The analysis effectively ignores any features, including pores that are smaller than about 100 nm in size, since such features are too small to be effective in scattering visible light. A quantity called the relative bonded area (*RBA*) is defined as follows,

$$RBA = 100\ \% \times ( s_{\text{unbonded}} - s_{\text{test}}) / s_{\text{unbonded}} \quad (1)$$

where $s_{\text{test}}$ is the light scattering coefficient of the paper sheet under consideration, and $s_{\text{unbonded}}$ is the light scattering coefficient of a sheet having the same composition, but which has been prepared from a non-swelling solvent, such as butanol. The latter kind of

"paper," tends to be very bulky, very opaque, and extremely weak. The $s_{unbonded}$ parameter also can be determined by extrapolating to zero strength from the plot of scattering coefficient versus tension strength (Page 1969).

Gurnagul and Page (2001) carried out an analysis, using the *RBA* criteria, to determine the cause of loss in bond strength of kraft sheets due to recycling. The results showed little change in *RBA*, leading the authors to conclude that the main effects of drying and recycling involved a loss in the shear bond strength per unit of bonded area. In other words, there was a lower strength at near-equal optical properties of the paper. These findings were in reasonable agreement with those of McKee (1971) and Nazhad (2005), but contrary to those of Ellis and Sedlachek (1993) as well as those of Cao et al. (1999).

*Bulk and apparent density of the paper*

A less quantitative, but highly practical means of judging the wet-conformability of papermaking fibers is to compare the apparent density values of uncalendered sheets prepared under constant conditions of wet-pressing. Various authors have cited evidence of this type to support their conclusions that dried and recycled fibers were less conformable than they had been just before the formation of the initial paper (Göttsching and Stürmer 1978b; Guest and Weston 1990; Somwang et al. 2001; Hubbe et al. 2003). Fahmy and Mobarak (1971) showed that the drying of biological cellulose increased its density to the point that the calculated amount of extra space in the material became essentially zero.

## Re-Adhesion of Fibrils and Fines to Fiber Surfaces

The next subject to consider is an effect due to air-water interfaces, i.e. capillary forces. The enormous strength of such forces was described by Campbell (1947, 1959), who was among the first to suggest that capillary forces played a key roll in the development of paper's dry strength. The process of drawing the cellulosic surfaces close together, just as water is being evaporated from between the fibers, appears to facilitate the formation of hydrogen bonds (Hubbe 2006b).

Evidence suggests that capillary forces also play a role in the matting down of fibrils, as well as fiber fines, on fiber surfaces during evaporation of water from paper. The effect is illustrated in Fig. 3. Klofta and Miller (1993) described such effects with bleached kraft fibers.

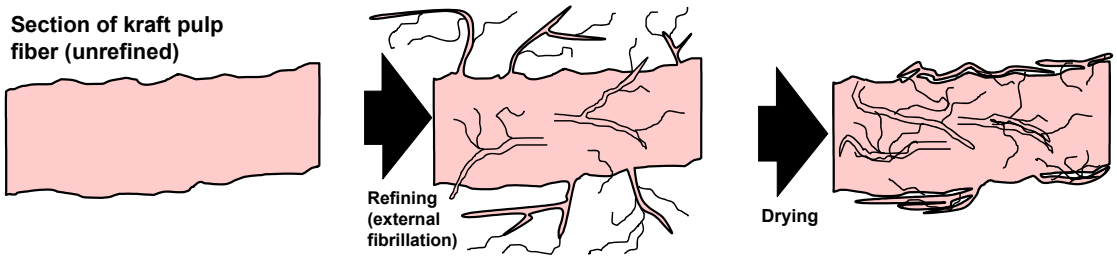


**Figure 3.** Schematic illustration of external fibrillation of a kraft fiber due to refining and the tendency of fibrils to become tightly matted down on fiber surfaces as a result of drying

## Fiber Length

If you ask a stranger what causes recycled paper often to be weaker than paper made from freshly prepared fibers, one often gets the answer that, "probably it's because the fibers are shorter due to breakage." This conventional wisdom, though often true, is often overstated. Ellis and Sedlachek (1993) listed "fiber length" among four key factors that possibly can account for changes in the strength of paper made from recycled fibers. They identified the quantity of C/PL (C is coarseness, P is fiber perimeter and L is fiber length, weight average) in a model of the tensile strength of paper. This quantity did not change much during repeated drying and wetting cycles (no repeated refining) in a laboratory setting. According to Ackermann et al. (2000), the effects of changes in fiber length usually are negligible relative to other factors.

The fuller truth about "fiber length" requires that one consider at least three key effects. The first is the extent to which fine matter may be lost when fibers are recycled. Especially in cases where recovered fibers are subjected to deinking treatments, substantial amounts of fiber fines and fillers can be expected to end up as part of the sludge obtained from coagulation of wastewater coming from the process (Göttsching and Pakarinen 2000). Second, additional fine matter can be generated when the fibers are refined, for an additional time, in an attempt to achieve the needed inter-fiber bonding, depending on the specifications of the paper product. And third, it is reasonable to expect that refining of recycled kraft fibers, depending on its intensity (Paulapuro 2000), may exert forces within occasional fibers that exceed their tensile strength. A higher proportion of fine matter automatically lowers the *average* fiber length. Moreover, it has been suggested that the brittle nature of recycled fibers renders them more susceptible to breakage during refining (de Ruvo and Htun 1983).

## Fiber Cross-Sectional Shape

Recycled fibers also tend to differ in shape, in comparison to the first time that they were prepared for papermaking.

*Kraft fiber effects*

Weise and Paulapuro (1996) observed changes in kraft fibers by means of confocal laser microscopy. The relatively early stages of drying, up to about 70% solids, caused uneven shrinkage, and the fibers became visibly wrinkled. The effect is illustrated in Fig. 4. The authors pointed out that such change occurred within the same range of moisture loss associated with hornification, i.e. the irreversible losses of water retention and inter-fiber bonding ability. Further drying to higher solids levels, merely caused isotropic shrinkage, without causing additional changes in the cross-sectional shape of the fibers.

*Flattening of mechanical fibers*

In the case of mechanical fibers, various authors have reported a tendency for flattening, associated with a more collapsed lumen, after recycling (Ackermann et al. 2000; Houen et al. 2003; Jang et al. 1995). It has been suggested that such flattening is why recycled mechanical fibers sometimes yield denser and stronger paper than they did during the first cycle of papermaking (Ferguson 1992a, 1994; Houen et al. 2003; Jang et

al. 1995; Ackermann et al. 2000). However, compared to the effects of recycling on chemical pulps, the effects for mechanical pulps tend to be rather subtle (Bovin et al. 1973; Ferguson 1992a, 1994; Howard and Bichard 1992).

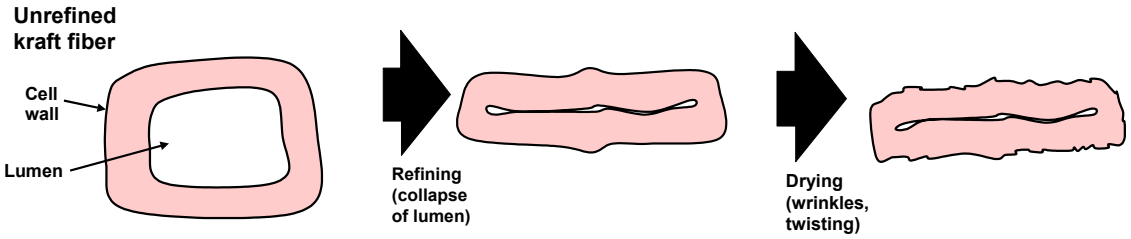


**Fig. 4.** Expected changes in cross-sectional shape of kraft fibers due to refining followed by drying

## Microcompressions

Because of the mostly lengthwise orientation of cellulose polymer chains, as well as fibrillar elements within the predominant S2 layer of fibers in most woody plants, it follows that individual fibers will be quite dimensionally stable in their length-wise dimension, even when subjected to large changes in moisture content. The fact that kraft fibers can shrink by up to 20-30% in the transverse and radial thickness dimensions (Page and Tydeman 1962), when dried, can be attributed to such factors as amorphous (non-crystalline) regions in the cellulosic polymer structure, the existence of inter-lamellar pore spaces (Stone and Scallan 1968), and the further internal delamination of fibers when they are refined. But something interesting happens when two fibers, at right angles to each other, are dried while in contact with each other. The two surfaces can appear to hold onto each other with such tenacity that shrinkage of one fiber in its radial or transverse direction causes the adjacent fiber to undergo microcompressions, becoming wrinkled and shorter than it was before (Page et al. 1986). The effects of microcompression can be so prominent that a "skirt" is visible at the edges of the contact region even after the fibers have been separated from each other (Page and Tydeman 1962; Clark 1985; Nanko and Ohsawa 1989).

*Restrained drying*

In what appears to be a closely related phenomenon, substantial differences in the strength potential of dried and redispersed fibers have been found, depending on whether the fibers were dried under restraint, as part of a sheet of paper formed under tension (Gurnagul 1995). For example, Mocchiutti et al. (2006) found that the strength of paper formed from unbleached kraft fibers fell to a greater extent if they were dried without restraint, compared to when the sheets were held at a constant dimension during drying.

## Delamination, Fragmentation, and other Damage

In addition to the other physical changes mentioned above, recycled fibers show effects that might be called "damage." For instance, recycled fibers tend to show a higher frequency of micro-indentations (Nazhad and Paszner 1994). The term micro-indentation refers to features that, though small, can adversely affect properties such as

compression strength and dimensional stability of paper (Hartler 1995). Kraft fibers subjected to repeated papermaking, drying, and relatively gentle repulping in water were found to become increasingly delaminated (Okayama 2002). Cracks were observed, and physical strength attributes of the recycled sheets were reduced.

## CHEMICAL EFFECTS OF DRYING, STORAGE, AND USE

Physical changes, as summarized in the previous section, account for only part of what happens to fibers when they are made into paper, dried, subjected to various conditions of use, and then recycled. Chemical changes can be equally important.

### Chemical Aspects of Pore Closure and Bonding

From a chemical standpoint, one of the most interesting questions to consider is why the closed pores in the cell walls of fibers don't simply imbibe water and re-open when dried kraft fibers are placed back into water. The facile answer is that hydrogen bonds form between adjacent cellulosic surfaces (including all components, such as hemicellulose and lignin) when they are dried in contact with each other. Many scientists have mentioned "hydrogen bonding" as being mainly responsible for preventing re-opening of pores when dried chemically pulped fibers are rewetted (Higgins and McKenzie 1963; Laivins and Scallan 1993; Scallan 1998; Kato and Cameron 1999). But hydrogen bonds ordinarily would be expected to be highly reversible. For instance, the bonding between two fibers in paper is easily disturbed upon slushing paper in water, and the fibers are readily released from one another. Thus, one needs to ask why hydrogen bonds joining cellulosic surfaces within fiber walls don't just become replaced by hydrogen bonds involving water molecules.

It can be speculated that the hydrogen bonding between fibers is reversible because the original two surfaces have independent surface topography with random imperfections; hence they do not "fit together" effectively when dried. Thus, the bonds are less permanent with respect to re-wetting. In contrast, for a pore in the cell wall that is created by separating two adjoining lamella, the two sides of the formed "pore" would have perfectly meshing topologies as they were formed from the same rupture area. Thus, when these two surfaces are re-joined by drying, the topologies will mesh almost perfectly, providing a more intimate, permanent bond. Although this argument is plausible, no evidence of this is known. Chemical changes of surfaces that are exposed by refining, e.g. depolymerization or oxidation, would be expected to render such healing more difficult.

*Crystallization as a "locking" mechanism*

Lundberg and de Ruvo (1978a) proposed that there must be some kind of locking mechanism when pores within cellulosic fibers close due to drying. These authors proposed that such closure "erases the memory" that a pore existed. In effect, the solid phase becomes continuous across where there used to be a gap in the cellulosic structure. It is well known that cellulose owes its insoluble nature to the existence of crystalline domains (Attala 1977). Within these domains the hydrogen bonds are arranged in a

regular pattern, including both intra- and inter-molecular chain hydrogen bonding. It has been proposed that the local formation of semi-crystalline domains at the facing surfaces of closed pores within fibers can account for the inability of such pores to re-open (Kulshreshtha et al. 1977; Weise 1998; Ackermann et al. 2000). The mechanism is illustrated in Fig. 5. Newman and Hemmingson (1997) proposed, in addition, that when adjacent crystalline regions of cellulose are dried in contact, they essentially can be healed together and become one.

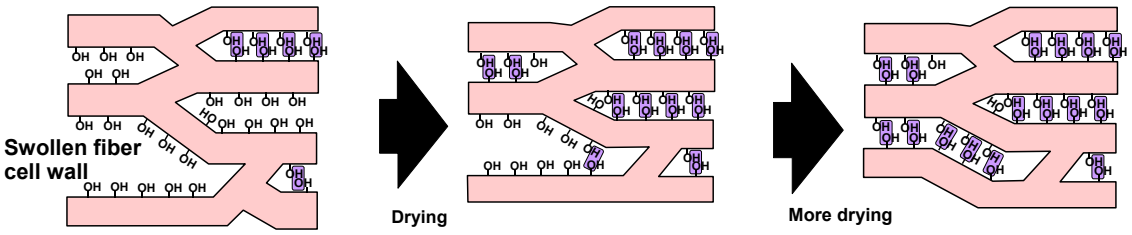


**Figure 5.** Schematic diagram of mechanism by which the "zipping" shut of pores is mediated by highly orderly hydrogen bonds, resulting in crystalline micro-domains that resist separation. Inter-fibril hydrogen bonds are shown with shading.

Support for the idea that localized crystallite formation may prevent re-opening of pores makes sense in terms of cellulose's very high tendency to crystallize, especially in the presence of heat and moisture. Amorphous cellulose can be produced only by special treatments, such as extensive ball-milling in the absence of moisture (Hatakeyama and Hatakeyama 1981). The same authors showed, by means of differential scanning calorimetry (DSC), X-ray diffraction, and density gradient tests, that amorphous cellulose was rapidly converted back to a partly crystalline state when it was exposed to moisture (see also Wadehra and Manley 1965). Atalla (1977) showed that the level of crystallization within cellulosic material can be increased by such conditions as heating the aqueous suspensions under pressures corresponding to a typical kraft pulping operation. Likewise Kimura et al. (1974) concluded, based on DSC tests, that heating in the wet state can increase the proportion of crystalline regions within amorphous cellulose. Water appears to plasticize cellulose, facilitating easier transformation to a crystalline phase; this assertion is further supported by work showing that steam-drying tends to hurt bonding properties of fibers to a greater degree, in comparison to oven drying (Guest and Voss 1983). Heating to yet higher temperatures can have different effects, however. Hattula (1986) found that heating under pressure in distilled water increased the crystallization of cellulose in TMP fibers over the range 130 to 170 $^{o}$C, but crystallinity decreased with further heating in the range 175 to 200 $^{o}$C.

It has been difficult to obtain direct evidence of changes in crystallization that might explain various effects associated with drying for fibers. Somwang et al. (2002) used X-ray diffraction methods and detected slight increases in crystallinity as a result of recycling of handsheets. The increased crystallinity was attributed to decreases in the proportion of amorphous (non-crystalline) cellulose. The relative changes were too small, however, to be detectable by Raman spectroscopy. More distinct evidence of increased crystallinity has been obtained based on changes in the displacement density of

bacterial cellulose, comparing dried vs. undried samples (Fahmy and Mobarak 1971). Further evidence of persistent, crystal-like hydrogen bonding has been obtained by deuterium exchange rate studies (Sumi et al. 1963). Drying reduced the proportion of deuterium-exchangeable groups, as would be expected if the relative amount of crystalline cellulose increases. In the case of cotton, Iyer et al. (1991) observed a much greater increase in crystallinity resulting from slow drying in humid environments, in comparison with dry heating. The most favorable conditions of moist drying increased the level of crystallinity by ten to fifteen percentage points. Yamagishi and Oye (1981) likewise found increases in crystallinity due to recycling. Back et al. (1967) observed a sharp drop in dry tensile strength when samples of paper were heated above 200 $^{o}$C; they concluded that his effect was due to thermal softening, leading to a hardening of the fiber surfaces.

To make matters even more complicated, work by Atalla et al. (1984) showed that high temperature treatment of cellulose in the presence of moisture is able to convert cellulose into various different crystalline forms. These forms, which have been given titles such as "cellulose II" and "cellulose IV," can be distinguished from each other based on Raman spectroscopy. It was found that the transformations in crystal form tended to occur in early stages of heating, and that they became more rapid with increasing moisture. However, no evidence has been collected regarding the type of cellulose crystals existing within practical samples of recycled paper, or whether or not such distinctions can explain differences in paper properties.

*Auto-crosslinking*

Some researchers still have trouble believing that the hydrogen bonding mechanism, given the inherent reversibility of hydrogen bonds, truly can explain why closed pores fail to open up again. If one thinks of the hydrogen bonding occurring in zipper-like fashion, these researchers are, in effect, seeking to find an explanation as to why bonded regions between previously separated elements of cellulosic material don't gradually "unzip" during protracted exposure to aqueous solution.

Back and Klinga (1963) were perhaps the first to consider the nature of covalent bonds that can form within cellulosic materials that are strongly heated. These authors observed that heating of papermaking fibers at 190 $^{o}$C in dry air caused permanent shrinkage, from which the fibers did not recover when rewetted. The heated fibers also had reduced bonding potential for the formation of recycled paper. Though no detailed mechanism was proposed, the term "auto-crosslinking" was coined to describe the phenomenon (Nazhad and Paszner 1994). Back (1967) later suggested that the effect was due to formation of ester bonds between carboxyl groups and hydroxyl groups within the fibers (see also Ruffini 1967).

In support of the idea of ester bond mechanism, it is well known that ester bonds form when cellulose is heated above about 150 $^{o}$C in the presence of poly-acids, such as polyacrylic acid or citric acid (Caulfield 1994; Mao and Yang 2001). Strong heating in the presence of monomeric, multifunctional acids, such as citric acid, yields relatively brittle cellulosic materials, whereas heating in the presence of long-chain polyacids can yield tough paper, having a high degree of wet-strength (Caulfield 1994, Xu et al. 1999). It has not been shown, however, that such a mechanism can be important under the usual

conditions of paper drying, or at the much lower levels of carboxylic groups ordinarily present in, say, the hemicellulose component of papermaking fibers.

*Lactone formation*

Possibly the most radical chemical-based explanation that has been offered to account for the irreversibility of pore closure when kraft fibers are dried is that of Diniz et al. (2004). Based on the observation that sugar-like molecules have a high propensity for formation of lactones, these authors proposed that lactones also can play an important role in cross-linking of cellulosic material. In principle, according to these authors, lactone cross-links can be expected to form between carboxyl groups, in their associated form, and nearby hydroxyl groups, forming a cyclic ester, i.e. a lactone.

Perhaps the reason that the proposal of Diniz et al. (2004) has not received wider attention is that it does not offer an explanation as to why irreversible hornification readily occurs in the case of very low yield chemical pulps. To a first approximation, the carboxyl group content of papermaking fibers tends to decrease with decreasing yield (Herrington and Petzold 1992; Lloyd and Horne 1993). In other words, pulping and bleaching processes, as a general rule, tend to remove acidic groups, leaving behind a higher purity cellulose residual, which is lower in carboxyl content. Lindström and Carlsson (1982) demonstrated strong hornification in the case of highly carboxylated fibers when they were dried in their protonated form. However, such hornification was no more severe in comparison to the case of fibers having much lower levels of acidic groups. Also, there has been no evidence of wet-strength development when paper is dried under acidic papermaking conditions (e.g. pH 4 to 6) at ordinary temperatures that a paper web reaches during papermaking (e.g. not much above the boiling point of water).

*Colloidal forces and pore closure*

Allan and Ko (1995) carried out an interesting analysis in an attempt to find out whether short-range forces of interaction between facing surfaces might account for the closure of tiny pores, as well as for their inability to re-open when dried fibers are placed back into water. In principle, short-range van der Waals forces of attraction can be expected to work in concert with hydrogen bonding and other forces that may act to hold facing surfaces of cellulose in contact with each other (Bergström et al. 1999; Claesson et al., 2003; Rojas et al. 2005).

## Depolymerization, Hydrolytic Scission

As described by Page (1969), paper's strength may be limited either by the strengths of individual fibers or by the number of bonds that form between them. So far our discussion has been focused on the latter quantity. Howard and Bichard (1992) showed that the zero-span dry and wet tensile strength (considered to be measures of the individual fiber strength) remained constant for both high and low yield pulps over 5 recycling cycles. This laboratory experiment involved relatively mild conditions but utilized recirculation of white water fines during the preparation of handsheets. However, the same authors cited several other studies that disagreed with their results (see Howard and Bichard, 1992). The differences were attributed to different recycling

procedures used. In some of these studies, the decrease in fiber strength was about 15-20% after multiple recycles.

When fibers are exposed to acidic conditions, especially in the presence of high humidity or moisture, the fibers themselves can be severely weakened (Back 1978). As shown by various authors, such effects often can be correlated to reductions in molecular mass (Kato and Cameron 1999; Ackermann et al. 2000). The effect is illustrated schematically in Fig. 6.

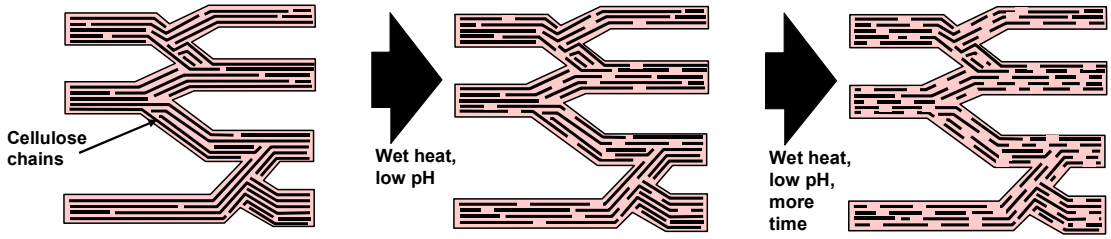


**Figure 6.** Schematic illustration of hydrolytic cleavage of cellulose chains within a "fringed micelle" structure of cellulose in a kraft fiber cell wall. A small amount of hydrolysis may go un-noticed, but eventually the fibers become brittle and susceptible to mechanical damage (Kato and Cameron 1999).

Because the time that paper is exposed to intense heat during drying is short, no more than a couple of minutes on a conventional paper machine, it is reasonable to question whether this is sufficient time for significant hydrolysis of cellulosic chains to take place. It has been shown that the loss of degree of polymerization (DP) in cellulosic wet fibers exposed to high temperature without drying tends to be much greater in comparison to the loss of DP if the same fibers are permitted to dry (Klungness and Caulfield 1982; Welf et al. 2005). However, as shown by both of these studies, there still can be substantial loss of molecular mass even if the fibers are dried in air at temperatures within the range of conventional papermaking. Klungness and Caulfield (1982) observed significant loss of DP during drying only in the case of bleached pulp. By contrast, Hubbe et al. (2003) observed significant losses in DP during drying of both bleached and unbleached kraft pulps. Due to a much greater initial chain length of cellulose molecules in the case of the unbleached kraft fibers, the relative change in DP appeared to be greater. Example calculations were provided, showing that the greater relative loss of DP in the case of a higher chain length is consistent with what would be expected based on random cleavage at a fixed rate in both cases.

Unfortunately, the problem of acid hydrolysis of paper does not end after the paper has been dried. Rather, paper can continue to suffer from hydrolysis during storage and use, especially if it has an acidic pH, based on aqueous extraction or surface-pH tests (McComb and Williams (1981). Williams (1980) attributed the affect to acid hydrolysis of amorphous regions of the cellulose within the fibers. The good news is that this kind of degradation of cellulose chains easily can be minimized by producing the paper under neutral or weakly alkaline pH conditions (McComb and Williams 1981; Hubbe 2005a).

## Redistribution of Wood Components

Along with hornification and hydrolysis, the third major change that can distinguish recycled fibers from freshly prepared fibers, according to Back (1978), is redistribution of wood-derived materials. Such redistribution can be expected to be especially significant in the case of mechanically pulped fibers, which retain a substantial portion of the wood resins that were originally present. However, as papermakers know well, substantial amounts of triglyceride fats, fatty acids, resin acids, and unsaponifiable materials are also found in kraft and sulfite pulps, especially in the case of unbleached pulps.

*Rehydrophobization*

A potentially problematic consequence of redistribution, and further chemical reactions involving wood-resins in paper is called "self-sizing" (Swanson and Cordingly 1959; Aspler et al. 1985). This phenomenon manifests itself as an increased resistance to wetting. Though, for some types of paper products, self-sizing even can be considered to be an advantage, other types of products require rapid spreading and penetration of aqueous glues or of spilled aqueous materials. For instance, corrugating medium, as used in the production of shipping containers, needs to be able to rapidly absorb aqueous starch-based glue. Poor glue reception of the paper surface has generally been attributed the presence of fatty and resin acids on fiber surfaces in the paper. Such materials may have migrated to the fiber surfaces during paper formation, drying, or storage. If aluminum species also are present at the paper surface, then it is reasonable to expect that such aluminum can act as a mordant, holding onto the carboxylate groups of the wood resins and orienting the hydrophobic groups outward from the fiber surfaces. The mechanism is illustrated in Fig. 7. One of the ways that papermakers can overcome the effects of self-sizing, when the effect is undesirable, is by adding surfactants. It also has been noted that self-sizing problems usually are not significant after recovered fibers have been de-inked, a process that tends to remove hydrophobic wood-derived materials (Webb 1992).

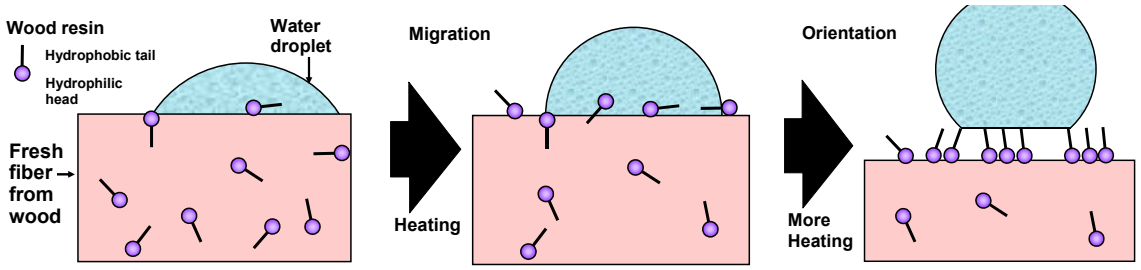


**Figure 7.** Schematic illustration of how surface-active agents, generally hydrophobic resins present in the wood-derived material, can be expected to migrate to fiber surfaces, gradually rendering them hydrophobic. The hydrophobic character can be made apparent by observing the initial contact angles of water droplets. (wood resin molecular size not to scale)

In support of the ideas given above, Swanson and Cordingly (1959) demonstrated that paper became much more hydrophobic after exposure to vapors of stearic acid. It was shown that radioactively tagged stearic acid molecules were able to diffuse through several layers of paper, rendering all of them hydrophobic, though to an extent that decreased with distance. Brandal and Lindheim (1966) showed, on the other hand, that

the strength potential of mechanical fibers could be increased substantially by extracting the wood resins from mechanical pulp fibers. Tze and Gardner (2001b) quantified changes in wettability of cellulose fibers by means of dynamic contact angle (DCA) measurements and inverse gas chromatography (IGC). The DCA measurements were judged to be more useful in terms of quantifying changes in hydrophobicity, in addition to changes in the degree of expression of acidic and basic groups at fiber surfaces.

A hopeful aspect related to the effects just described is that sometimes they become less important when paper is recycled. Thus Singh and Roy (1996) found lower and lower levels of extractives in mechanical pulp furnish during successive generations of recycling in the lab. Even if one makes allowance for the fact that lab tests often involve very clean water, it makes sense that the importance of wood-derived pitch-like materials should decrease relative to other matters during repeated recycling. Also significant is the extraction of the hydrophobic materials into the recycling process water system, a very likely source of deposits on papermaking equipment (Hubbe et al. 2006.)

*Fines and surface composition*

Papermakers have long understood that both the quality and the level of cellulosic fine materials can affect paper's strength characteristics (Laivins and Scallan 1996; Retulainen et al. 2002; Pruden 2005). The effects of fines on paper recycling has remained less certain (Laivins and Scallan 1996). For instance, Rundlöf el al. (2000) showed that the fines fraction present in mechanical pulp can contain such a high level of extractives that the paper strength is impaired, especially when the white water had been subjected to hydrogen peroxide bleaching. Nazhad (2004) carried out further research aimed at answering the question of whether the increased dry-strength of recycled TMP sheets might be attributable to fines generation. Unlike traditional experiments of this type, the fines fraction was removed before papermaking. Tests were carried out with pulp that had been delignified to different degrees, resulting also in different levels of extractives content. The results could be explained based on the extractives content of the sheets. It was concluded that reported increases in physical strength due to recycling of high-yield furnishes may be partly due the "surface condition," which would be affected by losses of extractives-rich, and lignin-rich fines during various unit operations.

## EFFECTS OF NON-CELLULOSIC SUBSTANCES

Recycled fiber supplies can contain substantial quantities of materials that are unrelated to wood (Göttsching and Stürmer 1978a; Webb 1992; Ackermann et al. 2000; Venditti et al. 2000; Venditti et al. 2001; Stauffer et al. 2001; Putz et al. 2003). Many such components can be called "contaminants" relative to the intended use of the fibers (Scott 1989; Klungness 1993; Brink 1997; Watanabe and Mitsuhiro 2005; Venditti et al. 2005). Deposits that occur on the wetted surfaces of papermaking equipment often can be blamed on non-cellulosic components, though the problems often involve a combination of both wood-derived and other substances (Douek et al. 2003; Hubbe et al. 2006).

## Papermaking Additives

The effects of various chemical additives used during the production of paper are well known (Eklund and Lindström 1991; Scott 1996; Roberts 1996; Neimo 1999). However, two questions are worth asking: First, to what extent do such chemicals remain in or on fibers when they are recycled? Second, and perhaps more importantly, do chemicals that are recycled along with the fibers still exhibit significant effects on the resulting recycled paper?

*Hydrophobic sizing agents*

In the case of alkyl ketene dimer (AKD) sizing Sjöström and Ödberg (1997) found that hydrophobic effects partly survived laboratory processing conditions designed to simulate ordinary deinking. Depending on the level of treatment in the initial cycle, the amount of freshly added AKD could be reduced by 30-70%, while achieving a given level of water holdout in recycled sheets.

The sizing properties of recycled fibers also can be affected by extraneous materials (Boone 1996). For example, residual surface-active agents that are used in deinking operations can be expected to make the recycled fibers more difficult to hydrophobize. If substantial quantities of recycled filler particles are present, then there may be a higher total surface area that needs to be covered by sizing molecules. Recycled paper sometimes contains high levels of anionic materials (Kuys and Zhu 1994), which have the potential to hurt the efficiency of retention of sizing agents and other finely dispersed components in the papermaking furnish.

Not all effects of recycled sizing agents are beneficial. Guest and Voss (1983) found that sizing with rosin and alum tended to decrease the bonding potential of the fibers when recycled. Though no debonding effect was observed when they instead used AKD for sizing, the relative advantage of using the reactive size was no longer detectable after another cycle of re-use of the fibers.

*Dry-strength agents*

Recent studies have shown that dry-strength chemicals, when they are recycled along with kraft fibers, still can contribute substantially to the strength of the resulting paper (Zhang et al. 2001, 2002; Hubbe et al. 2003a; Hubbe and Zhang 2005; Mocchiutti 2006). Such benefits can be found when the paper strength is compared to that of paper produced in parallel tests in which no dry-strength polymer was used during the initial papermaking. The recycled dry-strength chemicals do not prevent losses in water retention. However, when dried papers are reslurried, the residual effects of chemicals added during the first cycle can be relatively large, even in comparison to their contributions during the first cycle of papermaking with never-dried unbleached kraft pulp (Zhang et al. 2002). These results are attributed to a more critical importance of inter-fiber bonding ability in the case of dried and reslurried kraft fibers, which can be expected to develop a lower relative bonded area (RBA).

Especially promising results with respect to the strength of recycled sheets were obtained in cases where the chemicals either had a cationic charge, e.g. cationic starch, or there was combined treatment with a high-charge cationic polymer and an anionic dry-strength chemical such as carboxymethylcellulose or a copolymer of acrylic acid and

acrylamide (Zhang et al. 2002; Hubbe et al. 2003a). It is worth noting that a similar two-component treatment also can be applied directly to the wet end furnish when making paper from recycled furnish (Kimura and Hamada 1992). Grau et al. (1996) found that benefits due to treatment of the never-dried fiber with dry-strength additives was significant in the first and second cycles of fiber recovery, but the residual effect of strength agents added initially were not significant any more after three cycles of sheetforming, disintegration, and formation into the next generation of handsheets.

## Deinking Materials

Efforts to improve the cleanliness, brightness, and other characteristics of recycled fibers, in preparation for their use in papermaking, usually result in substantial quantities of waste. Materials that can end up in sludge from such operations include fiber fines and mineral fillers, along with inks, stickies, and waxes. D'Souza et al. (1998) found that most of the metal content in recycling systems was introduced with various kinds of wastepaper, and almost all of the metals ended up in the sludge. As long as one is willing to sacrifice some yield, a higher reject rate during deinking generally results in a higher quality of recycled fibers (Cardwell and Alexander 1977).

As mentioned briefly at the start of this article, fibers obtained from printed papers, even after deinking, are never completely clean. In addition to ink, dirt, etc., one can expect that such fibers will contain traces of chemicals that were used during the recycling process. Hunold and Göttsching (1996) found that when deinking was carried out as part of multiple recycling steps, in which the paper also was printed during each cycle, the physical properties were not significantly degraded. On the other hand, the appearance of the multiply-recycled paper got worse and worse as a result of repeated printing and deinking cycles. Likewise Bouchard and Douek (1993) found that a typical deinking treatment did not cause significant changes to the physical properties of various different types of fibers. Alanko et al. (1995) found that de-inking chemicals actually could have a beneficial effect on inter-fiber bonding, which was attributed to the fact that they helped remove oleophilic materials from the fiber surfaces. Kofta and Miller (1993), testing another type of bleached kraft pulp found that fiber strength properties fell significantly as a result of repeated cycles of papermaking, deinking, and formation of new paper sheets.

The types of additives that are commonly used during the recycling of paper have been reviewed (Shrinath et al. 1991; Ferguson 1992b; Haynes and Röring 1998; Göttsching and Pakarinen 2000). In cases where substantial amounts of deinking surfactants fail to get washed from the pulp before it passes to the paper mill, the resulting pulp may be very difficult to size. In particular, certain nonionic surfactants often used for deinking tend to act as wetting agents, covering up and reversing the effects of hydrophobic sizing agents (Moyers 1991). Another commonly used set of deinking chemicals is based on combinations of fatty acids and calcium salt addition. Korpela (1999) showed that the release of significant amounts of such chemicals into a paper machine system can be expected to decrease paper strength and the operating efficiency of paper machines.

Another noteworthy effect of recycling operations is observed when high-yield waste fibers are bleached with hydrogen peroxide. The oxidative treatment tends to

release large quantities of polygalacturonic acids (pectic acids), which can greatly increase the cationic demand of the furnish (Sundberg et al. 1998; Jiang et al. 2000). Another incremental contribution to cationic demand may come from phosphates, which are often used to chelate transition metal ions that otherwise would interfere with peroxide bleaching. Though, in principle, papermakers can use highly charged cationic additives to compensate for a high cationic demand of the process, in practice the addition of large amounts of charge-control additives is expensive and can result in pitch-like deposits. It makes sense to avoid sending large amounts of negatively charged colloidal and polymeric materials to the paper machine, where they can hurt retention efficiency and raise costs. By washing the pulp after peroxide bleaching, such problems can be greatly reduced.

## EFFORTS TO BLOCK THE EFFECTS OF DRYING

Higgins and McKenzie (1963) carried out the first detailed evaluation of possible ways to inhibit the effects associated with drying of kraft or sulfite fibers. Four main approaches were explored, (1) blocking formation of new hydrogen bonds, (2) formation of hydrogen bonds of a type that can be reversed, (3) reduction of the surface tension forces present during drying, and (4) inhibition of the collapse of fibers.

One of the most effective, but not necessarily practical methods of preventing hornification involved drying chemical pulp fibers in the presence of high concentrations of low-mass sugars (Higgins and McKenzie 1963). It appears that the sugar molecules inhibit hornification by getting in the way of hydroxyl groups at the surfaces and within pores of fibers. In this way the sugar molecules block the development of extensive intra-fiber hydrogen bonds (see previous discussion in *Crystallization as a "locking" mechanism*). Higgins' and McKenzie's main findings, with respect to sugar treatments, have been confirmed more recently (Laivins and Scallan 1993; Zhang et al. 2001, 2004).

Klungness et al. (2000) followed similar logic when they precipitated calcium carbonate particles within the cell walls of fibers. By placing the mineral within the interior of the fibers, rather than on the surface, it was possible to achieve greater strength at any given level of filler. The "loaded" fibers retained higher WRV after they were dried, in comparison to ordinary fibers and conventional calcium carbonate filler.

A more aggressive, but generally more expensive way to minimize hornification effects involves chemical derivatization of the fiber surfaces before they are first made into paper (Laivins and Scallan 1993). Thus, Ehrnrooth et al. (1977) observed that fibers that had been partially acetylated did not lose their swelling ability to as great an extent when they were dried. Though acetylation normally would be expected to increase the hydrophobic character of cellulose, it can be expected that low levels of acetylation can have a greater incremental effect in terms of interrupting the regular structure of cellulose chains, thus inhibiting local formation of crystal-like domains. Gruber and Weigert (1998) showed likewise that hornification effects could be suppressed by pretreating the fibers with alpha, beta- unsaturated substances and amino derivatives.

Scallan (1998) reviewed a number of additional derivatization schemes including carboxymethylation. Carboxymethyl groups appear to be effective in blocking horni-

fication, as long as the pH is high enough to dissociate the carboxyl groups (Lindström and Carlsson 1982; Laivins and Scallan 1993). It is reasonable to expect, in these cases, that the water-loving nature of carboxylate groups, in their sodium form, ought to promote rewetting and reswelling. Carboxylic acid groups are much less water-loving when in their associated form. This difference helps to explain why Lindström and Carlsson (1982) observed significant decreases in WRV when fibers were dried in their acidic, associated form, regardless of the density of acidic groups on the fiber surfaces.

*Hemicellulose content effects*

A practical approach to try to take advantage of the effects of pH and carboxylic groups at fiber surfaces, as just mentioned, involves selection of fibers having a naturally high level of negatively charged hemicellulose components. Thus, Oksanen et al. (1997) varied the amounts of xylan and glucomannan in a series of pulp samples. Though removal of the hemicellulose components did not hurt the properties of the original paper, the recycled sheets formed from fibers having low hemicellulose levels were much reduced in strength. Likewise, Cao et al. (1998) observed that pulps having higher pentosan content were inherently more recyclable. Those findings help to explain the relatively good retention of strength properties when wheat straw pulp is recycled (Aravamuthan and Greaves 1998; Garg and Singh 2004; Tschirner et al. 2007); wheat straw is known to have relatively high pentosan content. Related studies have shown that hemicellulose contents of pulps can decrease with repeated recycling (Eastwood and Clark 1978; Wistara and Young 1999; Qian et al. 2005), leading to concerns that the benefits of having a high hemicellulose content in the virgin pulp may be lost during repeated recycling.

## RESTORATIVE TREATMENTS

Strategies based on preventing deterioration of fiber quality are seldom under the direct control of those who want to use the recovered fibers. Rather, paper recyclers usually are at the mercy of what becomes available in terms of wastepaper cost and quality. Thus, there is a critical need to enhance the properties of used fibers after they have been collected (Minor et al. 1993; Howarth 1994).

### Blending

When dealing with recycled fibers, a practical approach is to blend them with other materials, including freshly pulped fibers. The blending of different fibers types, depending on product requirements, can be considered to be "business as usual" for papermakers. Almost every machine utilizes broke. The broke often contains fully dried paper that has not been made into saleable product, and this is a simple form of paper recycling. Because recycled kraft fibers tend to be stiff and deficient in bonding ability, it is reasonable to blend them with a proportion of well-fibrillated kraft fibers. For instance, it has been suggested to blend a portion of fresh wheat straw pulp with recycled fibers (Aravamuthan and Greaves 1998).

As observed by Hawes and Doshi (1993) and Fjerdingen and Houen (1997), cellulosic fines that are freshly prepared as a result of refining tend to be especially effective for promoting bonding within paper. By contrast, it has been proposed to remove hornified fines before the recovered kraft stock is subjected to further refining (Szwarcsztajn and Przybysz 1976). Microscopic observations by Somwang et al. (2001) suggest that virgin fines can help fill in the spaces within and adjacent to fiber crossings, thus increasing the effective area of bonding between fibers. Peterson and Zhang (2000) observed that recycled fiber quality tended to go through an optimum in strength properties with increasing amounts of fines. Also, one should bear in mind that fines of the type produced by refining of kraft fibers tend to be especially deleterious to rates of dewatering (Laivins and Scallan 1996).

## Fractionation

Fractionation is often mentioned as a promising strategy when dealing with papermaking pulp of low quality (Pekkarinen 1985; Minor et al. 1993; Youn et al. 2007). Proponents of fractionation seem never to have any difficulty in describing possible uses for the long-fiber fraction. The difficulty generally lies in figuring out a profitable use for the fraction that becomes enriched in fines or stickies. In some grades it may be possible to "hide" inks and stickies within a center ply, thus minimizing effects on paper machine runnability, as well as in product appearance. There have been some efforts to develop a technology in which fiber fractionation is performed using a combination of screens and cleaners to produce a long fiber fraction and a short fiber fraction that is useful in developing softness in tissue (Vinson et al. 2001; Byrd et al. 2002). However this technology has not been implemented.

## Re-swelling

Given the tendency for recycled kraft fibers to have reduced water retention, reduced flexibility, and reduced bonding potential, a number of researchers have evaluated possible ways to restore such fibers to something approximating their former conditions. In a sense, such approaches aim to "re-swell" the hornified fibers.

*Re-refining*

As papermakers well know, often the most practical way to restore swelling, flexibility, and bonding potential to recycled cellulosic fibers consists of repeated compression and shearing action on the slurry, i.e. "refining" (Szwarcsztajn and Przybysz 1976; Minor et al. 1993; Nahzad 2004; Zhang et al. 2004). However, two points should be kept in mind. First, the fibers already may have been refined, earlier in their history. Second, recycled kraft fibers can be more prone to fragmentation than they were the first time around. If refining is carried out to a sufficient degree to meet the original strength characteristics, then one can expect that the drainage characteristics of the furnish will suffer greatly (Bovin et al. 1973; Ehrnrooth et al. 1977; Laivins and Scallan 1996). In some cases it may be beneficial to employ high-consistency refining strategies. Such conditions of refining can minimize damage to fibers and help to defibrillate the fiber surfaces (de Ruvo and Htun 1983).

As was already demonstrated by Brecht (1947), additional refining can make up for only part of the strength potential that is lost when fibers are dried. A possible explanation is that refining of recovered kraft fibers induces morphological changes that are distinct from those that occur as a result of refining freshly produced kraft fibers. Different behavior can be expected based on morphological differences between recycled vs. never-dried kraft pulps (Billosta et al. 2006). Rather than re-open the submicroscopic pores that closed as a result of drying, it is likely that re-refining delaminates the fibers in new areas. Such an effect may explain why some investigators have found little or no re-swelling when recycled fibers are refined. Thus, Bawden and Kibblewhite (1997) did not detect physical change in the dimensions of recycled kraft fiber cell walls in the course of refining. Klungness and Caulfield (1982) found that refining of such fibers restored the original surface area of the fibers, before they were dried, but not their specific volume.

Recent research findings suggest that it is possible to optimize refining conditions such that one can achieve high quality in the first cycle of papermaking, but also preserve the value of the fibers for later use. Thus, Kang and Paulapuro (2006) observed that re-refining of kraft fibers recycled under laboratory conditions was especially effective if, in the first cycle, those fibers had been refined in such a way as to fibrillate just the external surfaces. By contrast, if the fibers had been "internally fibrillated," using repeated compression of the wet fibers, the strength potential was substantially used up during the first cycle of papermaking.

Researchers have disagreed regarding whether the swelling ability of fines can be restored by refining (Szwarcsztajn and Przybysz 1976, 1978; Howard 1990; Laivins and Scallan 1996). It is difficult to imagine how a conventional refiner system would impart enough compression or shearing action on extremely small entities in order to alter their properties. Rather, it would seem more likely that most of the stresses within a refiner would be carried by the fibers that are present, since they are larger and thicker. Laivins and Scallan (1996) observed, however, that re-refining restored the swelling ability of both fibers and fines, even when the proportion of newly created fines was relatively small. The same study showed that cellulosic fines tend to hold onto about twice as much water, per unit mass, in comparison to fibers.

*Caustic treatment*

Besides refining, the second most reliable way to restore swelling and flexibility to cellulosic fibers has been to expose them to high pH conditions. For example, Weise et al. (1998) found that "cooking" of recycled kraft fibers under strongly alkaline conditions was more effective in restoring their properties, in comparison with refining or hot disintegration. These authors observed, however, that the restoration of the fiber characteristics lasted only for the next cycle of papermaking. Anything that was done to increase the swelling of the recycled fibers resulted in greater hornification the next time the fibers were dried. Ogden (1999) patented the combined use of pressure, high temperature, and refining. Bhat et al. (1991) found that a combination of alkaline conditions and high shear yielded optimal effect with a minimum of fines creation. Minor et al. (1993) obtained the most promising results under conditions of alkaline treatment that were sufficiently concentrated, causing significant delignification. Such strategies were judged to be more successful, in terms of enhancing the strength

properties of recycled fibers, in comparison with the use of bonding agents added at the wet end.

By use of certain organic solvents it is possible to achieve even higher levels of fiber swelling, in comparison to alkaline aqueous solutions. Tze and Gardner (2001a) found that such an approach was quite effective in restoring not only the swollen nature of fibers, but also the free energy of their surfaces. Of the various solvents tests, formamide offered the best prospects as a possibly cost-effective treatment.

## Enzymatic Treatments to Restore Fiber Quality

When papermakers treat recycled fibers with cellulase, their main goal usually is to allow water to drain more quickly during paper forming. Such an effect can increase the rate of production on drainage-limited paper machines. More importantly, faster drainage often makes it possible to apply higher levels of refining, while still running the paper machine at top speed. Studies have shown that a judicious choice of the enzyme dosage and the duration of treatment can make it possible to achieve significant freeness increases, while still not causing unacceptable levels of degradation to the fibers (Bhat et al. 1991; Eriksson et al. 1998; Choi and Wan 2001).

Mechanistic questions can be raised about the findings just cited, since some of the same effects sometimes have been achieved by inactive enzyme materials. Pala et al. (2001) obtained superior results when non-hydrolytic binding domains of cellulase were used instead of the active enzyme. Such an approach was able to produce fast drainage in combination with preservation of the fibers' inherent strength.

Other ways to promote faster dewatering of papermaking furnish were reviewed in the previous issue of this journal (Hubbe and Heitmann 2007). Though not usually regarded as ways to "restore fiber properties," drainage benefits not unlike those resulting from enzyme treatment can be obtained.

## Fiber Modification

The words "fiber modification" have been used in various different senses, including covalent derivatization of fiber surfaces. In principle it should be possible to increase the bonding potential of recycled kraft furnish by carboxymethylation (Walecka 1956; Lindström and Carlsson 1982; Fors 2000) or by high-temperature treatment of the pulp with carboxymethyl-cellulose (CMC) (Laine et al. 2000, 2002, 2003; Ekevåg et al. 2004). Either of these approaches will tend to increase the negative charge character of the fiber surfaces, making the surfaces more swellable and more bondable. Several alternative ways to the same basic goals were cited in an earlier review (Hubbe 2006b). A practical question facing users of such strategies is whether such treatments are cost-effective, considering the initially low value of some recycled fibers.

Potentially lower-cost approaches can be considered that do not require chemical reactions or high-temperature treatments. For instance, Torgnysdotter and Wågberg (2006) formed polyelectrolyte multilayers on the surfaces of hornified fibers. Higher dry-strength in the resulting paper was attributed to a combination of increased contact area and an increased surface free energy of the surfaces to be contacted (Wågberg et al. 2002; Eriksson et al. 2006). Although studies involving polyelectrolyte multilayers have

helped to promote progress in understanding dry-strength treatments, it is not clear how such a treatment would be achieved in a paper mill.

An alternate approach has been demonstrated recently that has the potential to achieve the same objectives as just mentioned. The dry strength of paper handsheets could be increased greatly by successive treatment of the furnish with balanced amounts of cationic and anionic polyelectrolytes (Lofton et al. 2005; Lvov et al. 2006). The first additive was in excess of the adsorption capacity of the fibers. Follow-up tests showed that the effect was due to the in-situ formation of polyelectrolyte complexes in the pulp suspension, followed by deposition of those complexes onto fiber surfaces, where they functioned as bonding agents (Hubbe et al. 2005; Hubbe 2005b). If the polyelectrolytes were allowed to mix with each other even for a few seconds before their addition to the fiber suspension, then the resulting contribution to strength was only half of what could be achieved if the mixing took place in the presence of an agitated fiber suspension.

## CONCLUSIONS

### Taking Advantage of Different Fiber Characteristics

After considering the research findings covered in this article, it becomes apparent that recycled fibers – especially in the case of kraft pulps – tend to be somewhat different than they were just before the first cycle of papermaking. However, many of these effects are quite subtle. Also, there are many ways to overcome such differences. In short, as long as one takes adequate measures to remove unwanted materials, e.g. inks, stickies, and even filler and cellulosic fines, then it is often possible to substitute recycled fibers in place of freshly prepared fibers.

Recycled fiber's difference relative to virgin fiber sometimes can be counted as an advantage. The recycled fibers may be stiffer, have a reduced tendency to swell with water, and tend to be more dimensionally stable (Ackermann et al. 2000). The relatively non-conformable nature of many recycled kraft pulps explains why the resulting paper often has a low apparent density (Wahren and Berg 1972); this often can be considered as an advantage when making printing grades, file folder, boxboard, and other grades of paper. Finally, a lower degree of swelling of many recycled kraft pulps can translate into lower energy expenditure in the dryer section of a paper machine (Cameron and Zwick 2003). As has been discussed in this article, deficiencies with respect to inter-fiber bonding actually can be overcome in numerous ways, including the use of wet-end additives or blending with refined, never-dried fibers. It is appropriate to understand that different fiber types, such as hardwood, softwood, mechanically pulped, chemically pulped, bleached, and non-bleached and of course, recycled forms of these, all will have different properties and will be suited for different applications. The judicious use of recycled fibers in applications in which they perform well and are economical is an essential task for the papermaker.

### Recyclability and Responsible Use

Something else that becomes clear from considering the wide variety of research cited in this article is that the recycling of paper involves many compromises. As was

noted in an editorial piece in this journal (Hubbe 2007), it can be quite complicated to determine the most appropriate, and even the most ethical way to deal with the recycling of paper. Success of any recycling program depends, to a large extent, on the responsible actions taken by the original producer of the paper, the printer, the user, and even the care taken in collection of wastepaper. The activities of a paper recycler can be made unnecessarily ineffective by the introduction of hard-to-remove stickies, inks, waxes, and other even more problematic materials (Watanabe and Mitsuhiro 2005).

But recycling is not the only possible choice. Another way to capture the potential value of waste fibers is to use them as a source of energy. Yet another approach is to avoid over-production of items that aren't actually used, as in the case of certain newspaper segments that remain unread in a given household. This review article has demonstrated that a great deal of progress has been achieved within the paper recycling industry in meeting the needs of customers in a cost-effective way, using renewable resources, and taking steps to minimize environmental impacts by using the resource multiple times.

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# INFLUENCE OF TEMPERATURE ON CRACKING AND MECHANICAL PROPERTIES OF WOOD DURING WOOD DRYING – A REVIEW

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The occurrence of cracks and loss of mechanical properties are major problems in wood drying, and careful control of drying conditions is necessary in order to avoid this form of defects. Wood drying at different temperatures, especially high temperatures, has gained much interest in the last several decades. Some solutions for minimizing drying defects, such as cracks and decrease of mechanical properties due to the increase of drying rates, decrease of drying time and thus cost, must be acknowledged and understood. The present review tries to summarize the influence of temperature during kiln drying on the mechanical properties of wood and on the occurrence of cracks.

*Keywords: Wood, Drying temperatures, Kiln drying, Cracks, Mechanical properties*

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## INTRODUCTION

Kiln drying of wood within different ranges of temperatures, especially at high temperatures, has gained much interest over the last several decades. Drying at elevated temperature is one way to reduce drying time, and this reduction may in turn reduce manufacturing costs and improve kiln throughput. According to Thiam et al. (2002), drying affects the mechanical properties of wood in three ways: the direct effect of moisture loss, the internal drying strain and stresses, and the direct influence of temperature on wood components. Milota (2000) suggested that by increasing the temperature (from 82°C to a range of 116°C-132°C) during drying of western hemlock and fir timber, the time required decreases by almost 50 %. Similar results were found for western hemlock by Kozlik and Ward (1981) and Thiam et al. (2002). Kozlik and Ward (1981) found that high temperature (HT) drying intensified internal cracking and collapse in wood. However, it was suggested that not all of these defects degrade the timber in industrial practice. Similar work was performed by Thiam et al. (2002), who found that western hemlock and fir timber showed a decrease of warp, particularly bow and crook, by applying a high temperature drying schedule (116°C), compared to a conventional drying schedule (82°C). A decrease in mechanical properties was in this case recorded.

Strength is not permanently affected by short exposures to temperatures below 100°C, but may be reduced permanently by extended exposures to temperatures greater than 65°C. The magnitude of this permanent strength reduction depends on the heating medium, temperature (Kudela and Laurová 2006; Lagana et al. 2006; Popović et al.

2006), the moisture content (MC) (Bastendorff and Polensek 1984; McCollum 1986; Popović et al. 2006), the exposure period (Kudela and Laurová 2006; Lagana et al. 2006), species, and specimen size (Tsoumis 1991; Junkkonen and Heräjärvi 2006). The effect is greater when the MC is high (Bastendorff and Polensek 1984; McCollum 1986). Detailed information concerning the direct influence of moisture and temperature on some mechanical properties of beech wood is given by Popović et al. (2006). In the study performed, they stated that each increase of hygroscopic moisture, depending on wood temperature, causes a decrease of modulus of elasticity (MOE) and modulus of rupture (MOR) by 1.3-3.3% and by 2.1-7.1%, respectively. It was also found that, depending on the moisture and anatomic directions, an increase of temperature by 1 °C causes a decrease of MOE and MOR by 0.17-0.59% and by 0.40-0.59%, respectively.

According to Brunner (1987) there are three ranges of temperature that are nowadays used in the industry for wood drying, namely low temperature (LT) drying (15-45°C), normal temperature drying (40-90°C), and high temperature drying (90-130°C). Also combinations of the LT/HT drying schedules are used, while higher ranges of temperature (160-260°C) are considered as thermal treatments (Hill 2006). The drying schedule is chosen according to several parameters, wood species dried, initial MC, mechanical properties desired, and final application of the product.

Thermal treated wood is used in indoor or outdoor applications such as furniture, paneling, or flooring. Recent work on heat treatment processes of timber (known as Thermowood® in Finland, "Thermoholz"® in Austria, "Plato wood" in the Netherlands, "Retification" and "Perdure process" in France, and "Oil heat treatment", "Lignostone" and "Lignofol" in Germany, and "Staypak" and "Staybwood" in the United States) has shown that such types of processes can improve the performance of timber considerably in several respects (Patzelt et al. 2002; Hill 2006). The main effects gained by heat treatment of wood are distinct improvements in hygroscopicity, dimensional stability, and biological durability, and in some cases control of color changes.

Dimensional stability is strongly connected to the hygroscopicity of wood (e.g., Wang and Cooper 2005). When wood is exposed to elevated temperatures, the hemicelluloses are partially decomposed, resulting in reduced hygroscopicity (Stamm 1956; Espenas 1971; Sehlstedt-Persson 1995), and thus influencing the wettability of wood (Hakkou et al. 2005a,b; Johansson et al. 2006; Sehlstedt-Persson et al. 2006; Esteves et al. 2007). Yet, undesirable side effects have been observed, in particular the loss of strength and increased brittleness of the treated wood (e.g. Tjeerdsma et al. 1998).

The decomposition of cellulose, hemicellulose, and lignin, which are the principal organic components of wood, is the main cause of degradation during elevated temperature drying. Within hemicellulose, the reaction of acetyl groups is one possible cause of permanent strength reduction by high-temperature drying. After the acetyl groups form acetic acid, cellulose is depolymerised. After the depolymerisation of cellulose, the tensile strength of Douglas fir is more sensitive to changes in moisture content in comparison to wood having cellulose of long-chain structures (Ifju 1964). The acid hydrolyzes the bonds that connect the glucose monomers. The rate of strength losses increases as the production of acid is accelerated by high temperature and high MC (Mitchell and Barnes 1986; Tjeerdsma et al. 1998).

Another negative outcome of elevated temperature drying schedules which affects the loss of mechanical properties of wood is the occurrence of cracks, i.e. "checking." There are several types of wood cracking due to drying, as presented by Simpson (1991), such as surface cracks, end cracks and splits, collapse and honeycomb.

It is generally considered (Schniewind 1963) that cracks occur during the initial stages of drying because moisture gradients lead to high tensile stresses on the face of the drying board. These are generally named surface cracks and they can be removed by machining if the final application requests it and/or allows for it. The width limit for the visibility of cracks by the naked eye is stated by Hanhijärvi et al. (2003) as being 0.1 mm.

A honeycomb is described as an internal crack caused by a tensile failure across the grain of the wood that usually occurs in the wood rays (e.g. Simpson 1991). This defect occurs when the core is still at relatively high moisture content above fiber saturation point (FSP), while the surface is starting to dry and the drying treatment is being carried out at excessively high temperatures for too long periods of time. Severely honeycombed timber frequently has a wavy appearance on the surface, and the defect is often associated with severe collapse (Simpson 1991). Collapse is a deformation caused by flattening or crushing of wood cells. It may be caused by compressive drying stresses in the inner part of the boards that exceed the compressive strength of the wood or liquid tension in cell cavities that are completely filled with water. Collapse is usually associated with excessively high dry-bulb temperatures (DBT) early in kiln drying, but this type of defect is not usually visible on the wood surface until later in the process (Simpson 1991). It is usually seen to occur in the sapwood part of the boards (Innes 1996). Therefore, low initial dry-bulb temperatures in species which are susceptible to collapse are recommended by Simpson (1991).

Hart (1984) stated that the relationships between the relative humidity (RH), moisture content, and shrinkage in the early stages of drying are of particular importance, because of the collapse-type shrinkage that may occur with some species of wood, in particular, species such as oak in which the honeycomb appears to be one of the most serious drying defects. Regular high humidity treatments at low temperatures have a significant influence in reducing cracks (Neumann and Saavedra 1992); a possible explanation might be that they can avoid or continuously recover from the collapse, especially with respect to the surface cells, and thus prevent the formation of micro-cracks, which might extend to visible surface cracks. This would also increase the surface permeability and thus reduce the moisture gradients. Another possible reason is that there might be a hysteresis effect that retards the contraction of the surface layers at lower MCs after the high humidity treatments. A reduction of cracking might be obtained if the boards are pre-steamed (Neumann and Saavedra 1992) or if a reconditioning step follows the HT drying process (Innes 1996).

## THE OCCURRENCE AND DEVELOPMENT OF CRACKS DURING DRYING

### General Considerations

The concept of fracture mechanics was used for a long time in order to characterize the failure of wood under load. Research has been performed by several

scientists to determine the fracture mechanics parameters for a variety of wood species and for different grain orientations (Johnson 1973; Schniewind and Lyon 1973; Mindess and Bentur 1986). Wood drying has also consequences at the micro-scale, e.g., at the cell wall level. The wood cell is a natural composite made up of middle lamella, primary wall, and three secondary cell wall layers with different orientations of microfibrils in relation to the fiber direction (Kifetew et al. 1998). According to Côté and Hanna (1983), three types of cell fracture are recognized: intercell failure, which is the separation of cells at the middle lamella; intrawall failure, which occurs within the secondary cell wall; and transwall failure, which is the fracture across the cell walls. These terms are shown in a schematic diagram in Fig. 1.

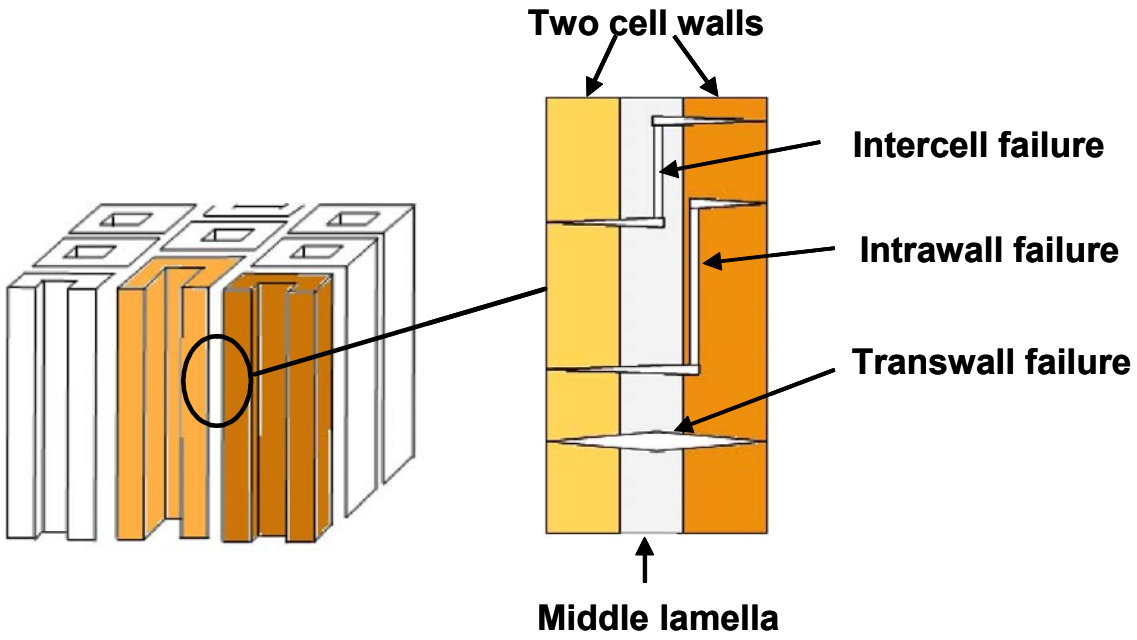



**Fig. 1.** Schematic diagram showing the different types of failures at the cell wall level (according to Kifetew et al. 1998)

The effect of drying on wood fracture surfaces of thin specimens of Scots pine subjected to uni-axial tensile tests in wet conditions was studied by Kifetew et al. (1998). One set was in a green state, while the other one was dried and then re-soaked to wet conditions to test the material at the same MC. The dried/resoaked specimens showed a flatter and more brittle appearance, which leads to the hypothesis that drying is responsible for cell wall damage.

Subsequent studies (Triboulot et al. 1984) employing finite element calculations, showed that at least some of the assumptions underlying the use of the linear elastic fracture mechanics (LEFM) for wood, namely, the assumption of plane strain, and orthotropic and linear elastic behavior, may be considered valid. Specific attention was given by Mindess and Bentur (1986) to the microscopic details of the physical process that takes place during crack propagation in Douglas fir by compact tension loading. In general, the pattern of crack propagation was found to be a straight path, parallel to the

direction of the grain. At the microscopic level, the crack could not be described as an ideal straight, parallel-sided crack. Its path was characterized by various irregularities, such as branching, bridging, and discontinuities, and in some regions of the crack its walls were inclined. When the crack became stable and had to be induced to propagate beyond it, this implied that the stable crack tip had been arrested at a zone of high toughness; in order to propagate further, the crack preferred the path of the least resistance, which bypasses the tough zone.

Several studies have been performed concerning the occurrence and development of cracks during drying (Schniewind 1963; Mackay 1972; Kozlik and Ward 1981; Kozlik and Boone 1987; Hanhijärvi et al. 2003), but not many studies were found in the literature on the development of cracking during the variation of drying temperatures and their effects on mechanical properties (Schneider 1973; Terziev and Daniel 2002; Poncsák et al. 2006). The latter topic will be discussed in the last section of this review, "Influence of occurring and developing cracks on the mechanical properties of wood during kiln drying."

Crack formation in wood during drying might differ due to different parameters, such as the kiln drying schedule, the moisture gradient within the wood, but also due to the micro-structure of different wood species and dimension of specimens.

The work done by Schniewind (1963) on the mechanism of crack formation in wood confirmed the theory that for Californian black oak, rays are the sites of maximum tensile stresses in the early stages of drying, and therefore, cracks would be expected to first develop in the rays. In the case of Tasmanian Eucalyptus oblique, Mackay (1972) found that after initiating at vessel sites, cracks spread in a radial direction not necessarily along a ray but frequently between them. In addition, one common pattern of crack development was through nearby vessels aligned radially. After breaking through a vessel element wall, the zone of failure was in the middle lamella, causing a separation of adjacent cells rather than a fracture of cell walls. Furthermore, it was found that the occurrence of end cracks started and spread in and along a ray.

Increased internal cracking and collapse in sapwood of young-growth western hemlock dimension timber occurred during drying at HT (110°C) compared to LT drying (82°C) (Kozlik and Ward 1981). During HT drying at a DBT of 110°C of red alder timber, Kozlik and Boone (1987) observed that excessive cracking of board ends, areas surrounding knots, and cracks in large rays decreased as the wet-bulb temperature (WBT) decreased. A detailed investigation of 12 wood species dried at 110°C HT drying or a combination of conventional drying, below 82.2°C, from green to 20% MC and then dried at 110°C to final MC of 6-8%, was performed by Boone (1984). The results of HT drying are summarized in Table 1, indicating the location of drying defects in relation to sapwood, heartwood, natural defects, and severity of defects in unacceptable boards. The combination of the conventional with HT drying decreased the drying degradation, but increased kiln residence time over the HT drying schedule alone.

In the case of Scots pine sapwood boards dried at HT in the range of 110-180°C, Schneider (1973) found no surface cracking on the longitudinal surfaces without collapse and without warping, but internal cracking occurred in many cases. In the case of beech wood, the occurrence of internal cracking was much higher, compared to pine wood.

**Table 1.** Location of Drying Defects in Relation to Sapwood, Heartwood, and Natural Defects; Response to High-Temperature (ht) Drying from Green and Severity of Defects in Unacceptable Boards by Percentage (Boone 1984)

| Wood species | Ratio sapwood and heartwood in boards | Primary defect and location | Response to HT Drying from green | Severity in un-acceptable boards % rated as slight (1) |
|---|---|---|---|---|
| *Fraxinus americana* | Mostly heartwood | Honeycomb (HC) around knots in sapwood and heartwood | Suitable | 75 |
| *Tilia americana* | Mostly sapwood | HC around knots | Suitable | 75 |
| *Fagus grandifolia* | Mostly heartwood | HC all surfaces | Unsuitable | 76 |
| *Prunus serotina* | Mostly heartwood | HC all surfaces especially around knots | Unsuitable | 51 |
| *Nyssa sylvatica* | 40:60 | HC; more in sapwood; around knots | Intermediate | 85 |
| *Populus deltoides* | 80:20 | HC and collapse | Intermediate | 74 |
| *Ulmus americana* | Mostly heartwood | HC in heartwood, around knots; warp in heartwood | Intermediate | 51 |
| *Acer saccharum* | 50:50 | HC in sapwood and heartwood, slightly more in sapwood | Unsuitable | 64 |
| *Acer rubrum* | 50:50 | HC in sapwood and heartwood, slightly more in sapwood | Suitable | 75 |
| *Carya sp.* | Mostly heartwood | HC all surfaces | Unsuitable | 81 |
| *Liquidambar styraciflua* | Mostly sapwood | HC more in sapwood than in heartwood, around knots | Suitable | 96 |
| *Liriodendron tulipifera* | 50:50 | HC in heartwood around knots, pin knots and pith | Suitable | 74 |
| (1) Slight equals 1% severity of defects related to 25 % area of board | | | | |

Collapse and internal cracking are important defects often found after drying in the timber of several wood species. Using a stress and drying model it has been demonstrated by Innes (1996) that in order to avoid collapse cracking, the timber of *Eucalyptus regnans* should be dried at temperatures below the critical temperatures for collapse of both the earlywood (26°C) and the latewood (could not be determined, but it collapsed at an ambient temperature of 20°C) until all parts of the wood were below the fiber saturation point (FSP). This comes in accordance with the study performed by Neumann and Saavedra (1992), who found that cracking inside the boards of *Eucalyptus globulus* wood dried from a green state will be reduced significantly if the initial drying temperature is as low as possible, preferably below 30°C. A study performed by Ilic

(1999) contradicts the concept of critical collapse temperature (Innes 1996), while for drying *Eucalyptus regnans* below temperatures of 24-30°C, the collapse and cracking were not eliminated.

A one dimensional stress model incorporating the various strain components was developed by Chen et al. (1997) based on a physically realistic model of HT drying behavior of *Pinus radiata*. The drying of sapwood is assumed to be characterized by two principal stages, first dominated by an evaporative front receding into the board, and the second dominated by bound water and vapor diffusion. As the drying proceeds, a progressive fall in the relative liquid permeability of wood is observed. The sapwood consistently loses liquid continuity at about 60% of the local MC, which is significantly higher than the FSP. The moisture in the evaporative zone is driven by a small, but adequate vapor pressure difference between irreducible saturation and the FSP, which corresponds to an equilibrium moisture content (EMC) of 99%. The wood is assumed to be a viscoelastic material with its mechanical properties varying with both temperature and MC. Also under HT conditions the wood may be capable of sustaining some extent of the plastic strain after passing through the yield point, without cracking. Cracking is assumed to occur only after the ultimate stress is exceeded.

Hanhijärvi et al. (2003) found a way to detect the development and growth of micro-cracks on the wood surface during early stages of drying by applying focused laser beam reflected intensity measurements on Scots pine (*Pinus sylvestris L.*). The results showed that by increasing the temperature from 30°C (for 24 h) to 50°C (for 6h) and 80°C (for 6h), the development of cracks increased compared to air drying at room temperature (20°C, for 26h). Furthermore, results showed that drying under dry conditions produces more cracks than drying under humid conditions. The development of internal cracking of spruce wood (*Picea abies*) heat treated at 212°C with several steps applied at different temperatures and time durations was also studied (Johansson 2006). Boards pre-dried to initial 18% MC, and dried in the secondary step at 212°C for 12h showed severe internal cracking, compared to 18 or 24h duration or pre-dried to lower initial MC (6%). Problems in terms of internal cracking can be encountered in the case that pith is present in the cross section of the board.

## Possible Pre-treatments to Reduce Cracking

The steaming or pre-heating of wood prior to drying has generally been considered to reduce drying time and increase drying rate (Mackay 1971; Alexiou et al. 1990; Ananias et al. 1995; Chafe and Ananias 1996). It was suggested that after high temperature drying, collapse might be recovered by steam reconditioning (Chafe 1995; Innes 1996). Mackay (1971) stated that these treatments have a double effect. First, chemical changes take place due to acid hydrolysis, which causes re-crystallization of cellulose and relocation of extractives. Second, the physical collapse and recovery of individual cell walls would respectively decrease and then increase porosity through closing by a crumpling action and re-opening by an expansion of the cell cavities through which the diffusion occurs. The duration of steaming is also important. A longer steaming period was found to lead to a decreased equilibrium moisture content (EMC) of red oak (Kubinsky and Ifju 1974) and European beech wood (Schmidt 1982a, b), because

the degradation processes of hemicelluloses already had occurred due to the influence of elevated temperatures.

Esteves et al. (2007) tested pine (*Pinus pinaster*) and eucalyptus (*Eucalyptus globulus*) wood by steaming it for 2 to 12 hours at 190-210°C and found the MOE to be very little affected by steaming, but the bending resistance was reduced. Chafe and Ananias (1996) found that the steaming of green boards of *Eucalyptus regnans* at 100°C for 1, 2, 4, and 8 hours caused an increase in the drying rate during HT drying. For *Eucalyptus globulus* no significant increase was evident. For *Eucalyptus regnans* wood species boards of radial/intermediate grain orientation, a positive relationship between average evaporable moisture available during drying and basic density showed density to be a negative influence on the drying rate. In the case of tangentially oriented material, both the size and number of internal cracks declined after the first preheating step (50°C), whereas in radial/intermediate material the size and number of internal cracks increased at 50°C before subsequently decreasing. These patterns were evident for a pre-steaming period up to 2 to 4 hours.

A high external shrinkage is associated with higher internal cracking, which is reversed in the study performed by Chafe (1995), where increased shrinkage was accompanied by a decrease in internal cracking. The difference might be due to the severity of drying conditions in the study performed by Chafe and Ananias (1996), while in Chafe (1995) the drying was done more gradually (30°C and 67% RH), and preheating was carried out at various temperatures in water rather than by pre-steaming.

In the case of *Eucalyptus pilularis* heartwood boards steamed in saturated conditions at 100 C for 3 hours after a one hour heating-up period, the drying rate was increased by 7-16%. A partial removal of extractives during pre-steaming was found, which allowed greater access of water molecules to cell walls resulting in rapid radial and tangential diffusion during drying. Longitudinal permeability was not found to be influenced significantly by the pre-steaming treatment, as tyloses appeared unaltered and also volumetric shrinkage was unchanged by pre-steaming (Alexiou et al. 1990).

For the Chilean eucalyptus species (*Eucalyptus globulus*), preheating in a water-saturated atmosphere at 80°C can have a beneficial effect in collapse recovery and relief of drying stresses. The drying rate is also increased by about 7% in the preheated material. Initial MC and/or the MC at the moment of reconditioning also appear to be of importance (Ananias et al. 1995).

Ward and Groom (1983) studied bacterial infected heartwood of red oak (*Quercus rubra L.*) and concluded that, compared to the normal wood, it is more prone to develop surface defects, honeycombing, and ring failure when kiln dried (at 52-82.2$^{o}$C) or under mild heating conditions (40.5-82.2$^{o}$C) to 8% MC from green state. In order to minimize the weight losses, pre-drying should be applied down to 25% MC with mild conditions of drying at 32.2°C and 60% RH.

Barnes and Taylor (1985) found no correlation between cracking patterns of southern pine veneer cores and drying schedules such as conventional schedule (82.2°C), HT drying (DBT=118.3°C, WBT=74°C), or HT drying in superheated steam (118.3$^{o}$C) at atmospheric pressure. The number of cracks, length and width were weakly correlated with specific gravity, and their magnitude was reduced after three month's storage.

Wood species density might influence the occurrence of internal cracking and collapse. In the case of *Eucalyptus regnans F.Muell.*, Ilic (1999) found that material with high mean basic density above 530 kg/m³ was associated with low levels of internal cracking and collapse. However, the highest expected density (640 kg/m³) corresponding to the complete elimination of collapse and hence of internal cracking in *Eucalyptus regnans*, is greater than the highest naturally occurring density of species (580 kg/m³). This provides support for the proposition that other eucalypt species of similar structure, but of higher density are less collapse prone.

In the case of small diameter wood, Chestnut (*Castanea sativa Mill.*) presents good mechanical properties, but shows cracking during drying. Even though previous studies showed that lower temperatures of hot oil bath treatments of 110°C increased the shrinkage values and above 140°C lead to critical collapse, the study performed by Berard et al. (2006) showed different results. Green logs of chestnut wood (with 55-75% MC) with a diameter of 70 and 160 mm were subjected to hot oil bath treatments for 1 hour at 130°C temperature in rapeseed and linseed oil (boiling points near 400°C). A 75% reduction of cracks with a better efficiency for small diameter logs was observed. In the case of treated logs with a greater diameter very narrow end cracks located at the heart were observed. Moreover, this heart cracking occurs during oil treatment due to hydrothermal recovery phenomena, thus the surfaces generated by this cracking process will also be protected against tannin leaching by a thin oil impregnation (Berard et al. 2006).

## INFLUENCE OF TEMPERATURE ON THE MECHANICAL PROPERTIES OF WOOD DURING DRYING

Kiln drying of wood is one of the most important drying methods used in commercial applications throughout the world. The behavior of wood during the drying process depends on the drying conditions in the kiln (e.g. ambient temperature, relative humidity, and air velocity) and on the properties of the wood itself (e.g. density, chemical composition) (Möttönen 2006). Some problems related to air drying methods, such as long drying times, costs, and drying defects, can be overcome by alternative methods, such as low-temperature (LT) drying and high-temperature (HT) drying (Bekhta and Niemz 2003).

The influence of the drying temperature during conventional and high temperature drying on mechanical properties has been investigated for a long time. A summary of these results is presented in Table 2.

Thompson (1969) found that the clear size specimens of Southern pine wood kiln dried at temperatures of 66.7°C and 83.3°C showed a reduction of MOE and compression strength up to 1.6% and up to 6.1%, respectively, for an 83.3°C kiln drying schedule compared to a 66.7 C kiln drying schedule.

Drying at high temperatures may result in hydrolysis of the cellulose and other chemical compounds in wood, and subsequently in a permanent reduction of mechanical properties. A summary of the work done until 1969 is presented by Salamon (1969) concerning the effect of temperature on the strength properties of wood. It is shown that

the effect of elevated drying temperature on wood strength varied among species and strength properties, namely some species did not lose strength when dried at high temperatures, while others lost 7 to 20% compared to conventionally dried samples. Several findings were apparent, namely decrease in shear or tensile strength perpendicular to the grain, unchanged static bending strength, or influence of high temperature drying on toughness, which can be higher or lower compared to conventional drying.

Early research studies (Ladell 1953; Combem 1955; Petri and Ananyin 1960; Schneider 1973; Yao and Taylor 1979; Gerhards 1983) showed that an increase of temperature will not affect the mechanical properties of wood (hardwoods and softwoods) significantly; but later intensive studies (Hillis 1984; Zhou and Smith 1991; Sehlstedt-Persson 1995; Kubojima et al. 2000; Terziev and Daniel 2002; Thiam et al. 2002; Bekhta and Niemz 2003; Müller et al. 2003; Junkkonen and Heräjärvi 2006; Poncsák et al. 2006; Frühwald 2007) proved the influence of temperature on the mechanical properties of wood.

Schneider (1973) found a slight reduction in the compression strength parallel to the grain of Scots pine sapwood samples dried at HT in the range of 130-180°C, but an increase was detected in the case of beech wood samples. In the case of modulus of rupture (MOR), a reduction was observed for both species with increasing temperature (Table 2). Teischinger (1992) found that MOE and MOR of spruce wood (*Picea abies*) show a less significant influence of the drying temperature during drying. However, conventional drying schedules at 50°C and HT drying (100-110°C) showed a significant influence on the EMC and shrinkage behavior of wood. No effect of HT drying (115°C) on the strength properties (MOE, MOR) of red alder (*Alnus rubra Bong*.) compared to conventional drying (54.4-71.1°C) was found by Layton et al. (1986).

A survey of papers is presented by Teischinger (1992) concerning the temperature influence during drying on mechanical properties of wood, which includes the work performed by several scientists: Salamon (1969); Gerhards (1979); Yao and Taylor (1979); Gerhards (1983) and Zhou and Smith (1991). In Table 2 an up-to-date summary is presented according to the softwood and hardwood species tested.

Gerhards (1979) dried Douglas fir by using three different kiln schedules. It was found that average tensile strength was 10% lower with progressive LT-HT schedules (up to 110°C) and 18% lower with constant HT (110°C) than with conventional schedules (not exceeding 85°C). The study shows that tensile strength is significantly affected by the type of kiln schedule, while MOE is not. This agrees closely with the results from other studies reviewed by Gerhards (1979) or some having somehow different experimental design and longer kiln schedules (Kozlik 1976). Kifetew et al. (1998) and Thuvander et al. (2001) reported a higher loss in tensile strength of about 50% due to drying. Millett and Gerhards (1972) observed that long exposure (60 days) at high temperature drying (110°C) leads to strength and mass loss of about 15% and 2%, respectively, represented by a clear reduction of MOR.

Kubojima et al. (2000) performed bending strength tests on Sitka spruce wood (*Picea sitchensis Carr.)* to determine the influence of heat treatment at 160°C for 0.5 hours up to 16 hours in nitrogen gas and air on the mechanical properties of wood. The results showed that MOE, the bending strength, and the energy absorbed in impact bending increased at the onset of the heat treatment and decreased later. The MOR

decreased steadily as the heat treatment time increased, which was thought to be the cause of the plastic and not the elastic behavior of wood.

**Table 2.** Strength Properties Reduction (%) of Different Wood Species Influenced by Temperature during Drying (according to Teischinger 1992 and updated) #

| Botanical Name | T(°C) | MOR | MOE | CS | SS | Reference |
|---|---|---|---|---|---|---|
| **Softwoods** | | | | | | |
| *Abies balsamea* | 116 | 16 | | | | Cech, Huffman (1974) |
| *Larix decidua* | 120 | 0 | 0 | | | Frühwald (2007) |
| *Larix decidua* | 170 | 0 | 0 | | | Frühwald (2007) |
| *Larix decidua* | 190 | 0 | 0 | | | Frühwald (2007) |
| *Picea abies* | 103 | 9.1 | 7.1 | 6.7 | | Müller et al. (2003) * |
| *Picea abies* | 110 | 0 | 0 | | | Teischinger (1992) |
| *Picea abies* | 115 | 9.5 | 0 | | | Bengtsson, Betzold (2000) |
| *Picea abies* | 116 | s.r. | | s.r. | | Egner (1952) |
| *Picea abies* | 120 | 11.5 | 0 | | | Bengtsson, Betzold (2000) |
| *Picea abies* | 120 | 5.5 | 0 | | | Frühwald (2007) |
| *Picea abies* | 170 | 7.4 | 0 | | | Frühwald (2007) |
| *Picea abies* | 190 | 2.3 | 0 | | | Frühwald (2007) |
| *Picea abies* | 200 | 44 - 50 | 0 | | | Bekhta, Niemz (2003) ** |
| *Picea abies* | 210 | 16 | d.r. | | | Frühwald (2007) |
| *Picea glauca* | 116 | 4 | 3 | | | Cech, Huffman (1971) |
| *Picea glauca* | 116 | 10 | | | | Cech, Huffman (1974) |
| *Picea glauca* | 160-180 | 13.7 | 15 | | | Zhou, Smith (1991) ** |
| *Picea sitchensis* | 138 | d.r. | | 0 | | Köhler (1933) |
| *Picea sitchensis* | 160 | s.r. | s.r. | | | Kubojima et al. (2000) |
| *Pinus banksiana* | 116 | 16 | | | | Cech, Huffman (1974) |
| *Pinus contorta* | 104 | 5 | i. 2 | | 2.5 | Troxell, Luza (1972) |
| *Pinus contorta* | 104 | 10 | 3 | | 9.6 | Troxell, Luza (1972) |
| *Pinus palustris* | 100 | 8 | i.6 | | | Thompson Stevens (1972) |
| *Pinus palustris* | 107 | 14 | i.13 | | | Thompson Stevens (1972) |
| *Pinus palustris* | 110 | 0 | | | | Comstock (1963) |
| *Pinus palustris* | 116 | 4 | | | | Koch (1971) |
| *Pinus palustris* | 116 | 0 | 0 | | | Yao, Taylor (1979) |
| *Pinus palustris* | 83.3 | | 1.6 | 6.1 | | Thompson (1969) |
| *Pinus sylvestris* | 60 | 17.2 | 12.8 | | | Terziev, Daniel (2002) |
| *Pinus sylvestris* | 100 | | | | 3 | Sehlstedt-Persson (1995) |
| *Pinus sylvestris* | 110 | | | →9 | →12 | Leont'ev et al. (1957) |
| *Pinus sylvestris* | 110 | 3 | | 0 | | Schneider (1973) |
| *Pinus sylvestris* | 115 | | | | 17 | Sehlstedt-Persson (1995) |
| *Pinus sylvestris* | 115 | 7.8 | 5.4 | | | Terziev, Daniel (2002) |
| *Pinus sylvestris* | 116 | 0 | 0 | | | Comben (1955) |
| *Pinus sylvestris* | 121 | | 0 | | | Petri, Ananyin (1960) |
| *Pinus sylvestris* | 130 | 0 | | i. 1 | | Schneider (1973) |

| | | | | | | |
|---|---|---|---|---|---|---|
| *Pinus sylvestris* | 130 | 8 | | 6 | | Schneider (1973) |
| *Pinus sylvestris* | 150 | 7 | | i. 2 | | Schneider (1973) |
| *Pinus sylvestris* | 150 | 30 | | 7 | | Schneider (1973) |
| *Pinus sylvestris* | 180 | 19 | | 2 | | Schneider (1973) |
| *Pinus sylvestris* | 180 | 32 | | 2 | | Schneider (1973) |
| *Pseudotsuga menziesii* | 94 | 3 | 1 | | | Graham (1957) |
| *Pseudotsuga menziesii* | 104 | 7 | 8 | | | Graham (1957) |
| *Pseudotsuga menziesii* | 107 | 10 | 5 | i.6 | | Eddy Graham (1955) |
| *Pseudotsuga menziesii* | 110 | →15 | | | | Comstock (1963) |
| *Pseudotsuga menziesii* | 110 | →20 | 0 | | | Kozlik (1968) |
| *Pseudotsuga menziesii* | 110 | 5 | 12 | | 15-20 | Kozlik(1967) |
| *Pseudotsuga menziesii* | 110 | 17 | | →14 | | Salamon (1963) |
| *Pseudotsuga menziesii* | 121 | 13 | 2 | 12 | | Eddy Graham (1955) |
| *Tsuga canadensis* | 71-113 | 0-s.i. | | 0-s.i. | | Salamon (1965) |
| *Tsuga canadensis* | 107 | 0 | | 0 | | Salamon (1965) |
| *Tsuga canadensis* | >100 | 0 | | | | Ladell (1953) |
| *Tsuga heterophylla* | 110 | 0 | 0 | | | Kozlik (1968) |
| *Tsuga heterophylla* | 110 | 12 | 4 | | 8 | Kozlik(1967) |
| *Tsuga heterophylla* | 116 | 8.1 | 0 | | 14 | Thiam et al. (2002) |
| **Hardwoods** | | | | | | |
| *Alnus rubra* | 115 | 0 | 0 | | | Layton et al. (1986) |
| *Betula alleghaniensis* | 102-104 | | s.r. | | | Ladell (1956) |
| *Betula papyrifera* | 200-230 | d.r. | 0 | | | Poncsák et al. (2006) |
| *Fagus sylvatica* | 110 | 4 | | i.3 | | Schneider (1973) |
| *Fagus sylvatica* | 116 | s.i. | s.i. | s.i. | | Keylwerth (1952) |
| *Fagus sylvatica* | 130 | 7 | | i.3 | | Schneider (1973) |
| *Fagus sylvatica* | 150 | 9 | | i.16 | | Schneider (1973) |
| *Fagus sylvatica* | 180 | 23 | | i.4 | | Schneider (1973) |
| *Liriodendron tulipifera* | 113 | 0 | i.4 | | | Gerhards (1983) |
| *P. tremula x tremuloides.* | 180 | 13.7 | i. 2.5 | i. 13 | | Junkkonen, Heräjärvi (2006) |
| *Populus tremula* | 180 | 8.5 | i. 12.7 | i. 12.5 | | Junkkonen, Heräjärvi (2006) |

Legend: SS-shear strength; CS-compression strength; MOR-modulus of rupture; MOE-modulus of elasticity; d.r.-definite reduction; d.i.- definite increase; s.r.-slightly reduced; s.i.-slightly increased; i. -increased; → up to

# Values given are compared to low or normal temperature drying (exceptions: *-compared with DIN 68364 (1979); **-compared with HT-drying). Due to incomplete information, strength adjustments for moisture content differences were not made.

The influence of high temperature drying on the mechanical properties of Norway spruce was also studied by Bengtsson and Betzold (2000), who used three drying schemes, high temperature (HT-115°C), low/high temperature (L/HT-70 C/120°C), and low temperature (LT-75°C). Four-point bending tests were performed in order to observe the influence of temperature during drying on the bending strength and stiffness of wood. The results showed that, on the average, the bending strength decreased by 11.5% and 9.5% for the specimens dried by a combined L/HT drying scheme and a HT drying scheme, respectively, compared to a LT drying scheme. No effects of HT drying on the bending stiffness were found.

Western hemlock was dried using conventional (82°C) and accelerated (116°C) kiln schedules to determine the influence of temperature on the mechanical properties of wood. The accelerated drying schedule reduced the base design bending stress by 8.1 % and shear stress by 14.0 %, while the allowable stiffness was not affected (Thiam et al. 2002).

The effect of HT drying on mechanical properties, dimensional stability, and color of spruce wood were investigated by Bekhta and Niemz (2003). The wood specimens conditioned at different RH (50, 65, 80 and 95%) were subjected to heat treatment at 100, 150, and 200°C for different time periods. The results showed that heat treatment mainly resulted in a darkening of wood tissues (the greatest darkening occurred in the first 4h of exposure), improvement of dimensional stability of wood, and reduction of its mechanical properties. The average decrease in bending strength of samples dried at 200°C compared to samples dried at 110°C was about 44-50%, while MOE was not affected in this case. It was found that the treatment time and temperature were more important than the relative humidity regarding the color responses. Strong correlations between total color differences and both MOE and bending strength were found.

Müller et al. (2003) tested macroscopic spruce samples (*Picea abies L.*) in bending and compression parallel to the grain in green state and oven dried (103°C)/re-moistened by three vacuum cycles (25 mbar, with a MC higher than 160%). In bending, a highly significant reduction of 10% for MOE and 16.5% for MOR was found for dried/re-moistened samples, compared to fresh ones. Compression tests showed 15% lower compression strength for spruce samples, compared to fresh ones, while the MOE was not altered. In the case of microscopic spruce samples, tensile and compression tests were performed with samples oven dried (103°C) and air dried (for 3 days at 20°C)/re-moistened by two cycles of water vacuum impregnation (10 min, 25 mbar, resulting in an MC=210-220%). The oven dried/re-moistening procedure leads to a 9.8% and 14.9% lower tensile and compression strength respectively compared to the air dried/re-moistening procedure. For air dried/re-moistened samples, compared to fresh ones, no difference in tensile strength was found, but for the compression strength a 10% reduction was observed. The results of this study compared to the ones of DIN 68364 (1979) shows strength losses of 9.1% for bending, 6.7% for compression, and 7.1% for tensile strength testing.

Frühwald (2007) kiln dried spruce and different larch species to 6% MC at 80, 120 and 170°C. The experiment was complemented by heat-treated spruce (Thermowood®), which had been treated at 190 and 210°C in an industrial process. The results (Table 2) showed that the temperature affects some properties; however, the results were not equal for all species; e.g., with larch MOE and MOR were not influenced by the drying temperature, which was probably due to the small sample size, resulting in high variation.

## INFLUENCE OF OCCURRING AND DEVELOPING CRACKS ON THE MECHANICAL PROPERTIES OF WOOD DURING KILN DRYING

Generally speaking, the mechanical properties of wood are influenced by the occurrence of internal cracks during drying at different levels of temperature. There are few research papers which deal with the correlation between these two issues (Graham and Womack 1972; Schneider 1973; Kozlik 1982; Terziev and Daniel 2002; Hanhijärvi et al. 2003; Poncsák et al. 2006).

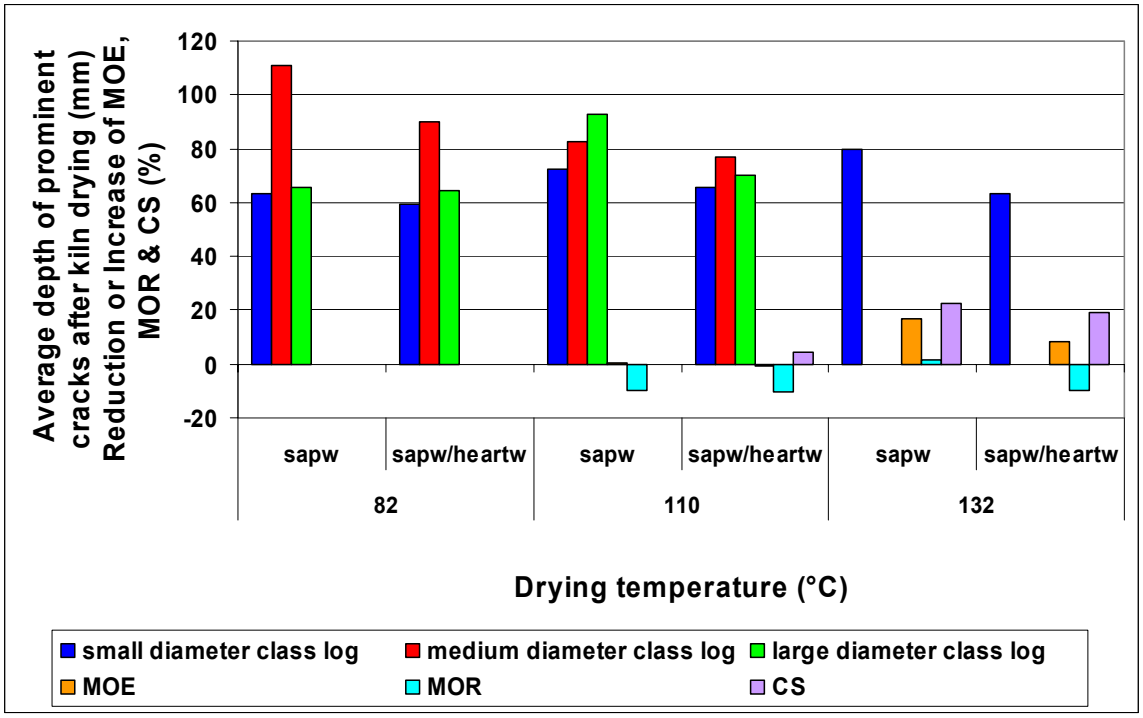
Douglas fir was dried using different drying schedules in order to establish the effect of the drying temperature on the mechanical strengths and cracking (Graham and Womack 1972, Kozlik 1982).

Graham and Womack (1972) dried 2.4 m length Douglas fir timber at high temperatures (104°C, 124°C, 143°C) and the width of the cracks that occurred after drying were 2.5 mm, 7.2 mm and 5.5 mm, respectively. The size of surface cracks was believed to be caused by the stress relieving effect of internal cracks formed just beneath the wooden surface. A strength reduction of at least 10% was assumed to be expected (real value not given). Similar results were recorded by Kozlik (1982), who studied the effects of three drying schedules on the occurrence of cracks in Douglas fir logs and the changes in mechanical properties of clear wood specimens. The results of his work are summarized in Fig. 2.

Recent studies of Terziev and Daniel (2002) showed that conventional kiln drying had only minor effects on the microstructure of Scots pine wood (*Pinus sylvestris*). The HT drying (115°C) partly damaged the apertures of some bordered pits, provoking nano- (10-20 nm) and micro-cracks (1-2 μm) in the warty and S3 layers of cell walls, and probably modified the structure of the polymer structure in order to facilitate the penetration of liquids. Impact bending strength, hardness, MOE, and MOR tended to decrease regardless of the drying method, while only the MOR was significantly reduced in the case of conventional drying.

Poncsák et al. (2006) studied the effect of high temperature with humid (100 g water vapor/m³) and dry gases on the mechanical properties of birch wood (*Betula papyrifera*). Birch wood dried at HT (220°C) in water vapor showed no failure, such as crack formation during drying. In the absence of humidity in the heating gas, one to three cracks per samples were observed and also an increase in the weight loss rate. The reason might be that if the humidity of gas is low, then the difference between the moisture content of the gas and the initially humid wood (moisture concentration gradient) is high.

This increases the moisture removal rate and might cause crack formation in wood, especially around the knots. The influence of drying temperature and the occurrence of cracks on the MOE and MOR of several wood species is shown in Table 4.




Legend: MOE-modulus of elasticity; MOR-modulus of rupture; CS-compression strength; sapw, sapw/heartw – sapwood, sapwood in combination with heartwood

**Figure 2.** Effect of temperature drying schedules on the occurrence of cracks in different log diameter classes of Douglas fir, on sapwood or combination of sapwood and heartwood and the increase or decrease in mechanical properties after drying compared to conventional drying (82 °C) (Kozlik 1982)

As was shown by Hanhijärvi et al. (2003), an increase in temperature of 30°C up to 50°C and 80°C for different time periods increases the development and occurrence of cracks, compared to air drying at room temperature (20°C). Furthermore, results showed that drying under dry conditions produces more cracks than drying under humid conditions.

**Table 4.** Research Work Concerning the Occurrence and Development of Cracks and Changes in Mechanical Properties of Wood during Drying at Different Temperatures

| Author | Wood species | Drying Temperature | Cracking | Mechanical properties |
|---|---|---|---|---|
| Schneider (1973) | *Pinus sylvestris* (20 mm sapwood) | 110-180°C | no surface cracking on the longitudinal direction, no warping or collapse, but internal cracking occurred in many cases | no reduction in compression strength |
| | *Fagus sylvatica* (20 mm sapwood) | 110-180°C | no surface cracking on the longitudinal direction, no warping or collapse, but internal cracking occurred in many cases | small increase in compression strength compared to control samples |
| | *Pinus sylvestris* and *Fagus sylvatica* (40 mm) | 110-180°C | for beech wood a higher number of internal cracks occurred compared to Scots pine | 5% decrease in compression strength |
| Terziev and Daniel (2002) | *Pinus sylvestris* | 60°C | no micro-cracks are observed, or damage of pit apertures | reduces MOR significantly |
| | | 115°C | provoke nano (10-20 nm) and micro-cracks (1-2 μm) in the warty and S3 layer of cell walls | no critical reduction of impact bending, strength, hardness, MOE and MOR |
| | | <100°C | | reduces MOR significantly |
| Poncsák et al. (2006) | *Betula papyrifera* | 200-230°C (in humid inert gas) | no cracks were detected | MOR decreases with an increase in temperature |
| | | 220°C (in dry gas) | one to three cracks/sample occurred | MOE is not affected significantly |

## CONCLUSIONS

This review attempted to summarize the work done on the influence of temperature and the occurrence of cracks during drying on the mechanical properties of wood. Due to large differences in the conditions under which temperature levels were compared and the variety of wood species tested in the different studies, it was possible to show a general trend, but not a universally valid picture to what extent the properties will change at a certain temperature level and what the impact is on the occurrence and development of cracks in timber during drying.

Negative outcomes during elevated temperature drying processes are the depolymerization of hemicellulose resulting in reduced hygroscopicity and further loss of

strength and increase in brittleness of treated wood. By increasing the drying temperature, the moisture gradients increase, which leads to high internal stresses that are released as cracks. The crack formation in wood during drying might differ due to different parameters such as the drying schedule, moisture content of wood, the microstructure of different wood species, and dimension of samples tested.

In general, it could be concluded that drying temperature has a greater effect on the reduction of the modulus of rupture compared to the modulus of elasticity, which is only slightly reduced. A different behavior of hardwood and softwood species in general could not be noticed, but it should be elaborated more widely due to the fact that most of the papers mainly focused on high temperature drying of softwoods.

A critical general temperature when the mechanical properties start to decrease could not be stated, due to the time dependence behavior during wood drying, but also due to wood species behavior. It is generally known that mechanical properties depend on the time duration of the high temperature drying process, but information of the influence of time at lower temperature ranges could hardly be found in the literature concerning mechanical properties or cracking behavior. In general, conservative drying schedules (e.g., low temperatures and low drying rates) would affect the mechanical properties to a lesser extent compared to severe drying schedules, but the longer drying durations used would not lead to economical processing. An optimum compromise has to be found for each specific wood species and product.

Surprisingly, only few papers dealt with the influence of temperature during drying on both the mechanical properties of wood and on the occurrence of cracks. Usually research was conducted either on one issue or the other, but the important correlation between the influence of temperature and the occurrence of (micro-) cracks and their influence on the mechanical properties was seldom found as the main focus of the research. It is evident that both degradation of wood components by temperature and cracking could have a distinct influence on the mechanical properties of wood. As both factors can occur together or separately, it would be important to know to which extent both of them are responsible for any change in mechanical properties. Of course it is known that the problems of degradation and cracking increase with increasing temperature, but the majority of studies which examine that problem deal with high temperature drying or even thermal treatment. In the lower or normal temperature region for wood drying these effects have not been analyzed in a very detailed way up to now, which would be especially important for the upper region of normal temperature drying. This would be an interesting direction for further work.

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