The potential of wood acetylation

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ABSTRACT

Wood, having the lowest embodied energy of any mainstream building material, is carbon neutral. As such, wood, our only naturally renewable construction resource, helps combat global warming by absorbing carbon from the atmosphere and storing it away for the life of the wood product. Not only is wood renewable, but it is also biodegradable and sustainable. Nature is programmed to recycle wood back into its basic building blocks of carbon dioxide and water through biological, thermal, aqueous, photochemical, chemical, and mechanical degradations. Once broken down, these elements contribute to the circle of life by providing nutrients or biomass energy for the growth of new plant life which will grow and, in turn, absorb atmospheric carbon. The rate of recycling depends on the natural durability of the wood species. Many tropical hardwoods are known for their durability characteristics. However, a large number of higher yield sustainable softwood and hard wood species do not possess inherent durability, dimensional stability and other valued characteristics. By altering the wood cell wall polymers at the molecular level, the properties of wood species with low durability could be enhanced. Acetylation is well known to increase the resistance of wood against wood decaying fungi and destructive insects as well as improving the dimensional stability in moist circumstances. Acetylation of wood creates opportunities to improve the utilization of low value soft and hardwood species and to extend the balance of carbon sequestration capabilities of otherwise non-durable species. For the first commercial production of acetylated wood, Accsys Group has utilised the acetylation technology on radiata pine (Pinus radiata D. Don). For world-wide production of acetylated wood using a wider range of species and use in new application areas with varying material property requirements, other wood species will be considered. This paper gives an overview of research done on acetylation of soft and hardwood species and their performance in a series of applications.

1. INTRODUCTION

Since the early-days mankind has utilized trees for its timber for building material, paper, fuel, art and other craftwork, and has been important for development of the human society. Wood is a renewable and biodegradable. Nature is programmed to recycle it, in a timely way, back into its basic building blocks of carbon dioxide and water through biological, thermal, aqueous, photochemical, chemical, and mechanical degradation processes. Most problems with timber in service are associated with wood destroying fungi under high humidity conditions and dimensional changes in changing climates. Furthermore, wood exposed outdoors undergoes photochemical degradation caused by ultraviolet radiation, and is subjected to discoloration due to mould and blue stain fungi.

The rate of recycling depends on the natural durability of the wood species. Many tropical hardwoods are known for their durability characteristics. However, a vast majority of the world's wood species do not posses inherent durability, dimensional stability and other valued characteristics such as highly attractive surfaces (aesthetics), defect free qualities and easiness of processing . The world's supply of durable wood suitable for long term performance in outdoor applications is becoming more and more scarce. Furthermore, environmental regulations on the use of toxins to enhance the durability of wood species are increasing. An environmentally friendly alternative is the chemical modification of wood which results in improved wood performance. By altering the wood matrix on a molecular level, the properties of wood species with low durability can be enhanced. Acetylation is well known to increase the resistance of wood against wood decaying fungi and destructive insects as well as improving the dimensional stability in humid circumstances (Rowell and Dickerson 2014).

2. ACETYLATION OF WOOD

2.1. ACETYLATION PROCESS

Acetylation of wood has been studied extensively and has shown to be one of the most suitable methods for improvement of technical properties of low durable wood species (Hill 2006, Rowell and Dickerson 2014). In the last decade most work has been done with uncatalyzed acetic anhydride and without solvent as described by Rowell *et al*. (1986). The reaction of acetic anhydride with wood results in esterification of the accessible hydroxyl groups in the cell wall to acetyl groups with the formation of by-product acetic acid (Figure 1). It is a single-addition process and all weight gain is accounted by the acetyl groups added. The wood also swells during the acetylation process. When the wood is acetylated to high extent (20 weight percent gain and more) the volume is almost similar to that of 'green'(undried untreated) wood (Rowell and Dickerson 2014).

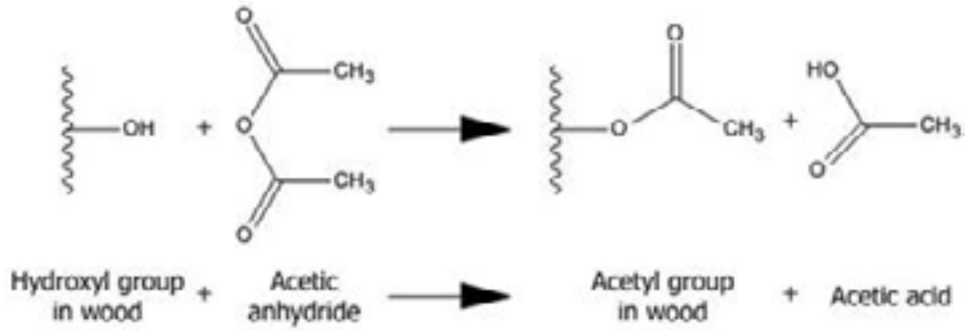

Figure 1: Schematic reaction of acetic anhydride with wood.

2.2. SUITABLE WOOD SPECIES

Solid wood

Over the last century, acetylation of different wood species has been tried, both on laboratory as well as (semi)commercial scale. When a sufficient degree of acetylation is achieved the resistance against fungal decay and the dimensional stability in changing climates can be improved considerably. Generally all wood species which are easily dried, have a good liquid impregnatable and have a low to intermediate density (300 to 700 kg/m^3) have high potential for the acetylation process. Also important is the dimension of the boards for the feasibility of acetylation. In general, the higher surface area to volume ratio, the easier acetylation becomes. Other factors for commercial production are purchasing characteristics (available volume, dimensions, quality, price and properties), acetylation economics and potential markets (Bongers *et al*. 2008).

With refractory wood species of large dimensions, such as spruce and Douglas fir, non-uniform acetylation results in wood quality issues such as distortions and cracking, and low performance. The presence of different qualities within a board of good permeable wood species (sapwood, heartwood, reaction wood, knots, resins) can also lead to uneven acetylation and associated wood quality issues. To improve permeability of wood species different methods have been tried over the years. Common methods for preservative treatments are pre-steaming and incising, but do not result in full penetration of the cross section. Other methods to improve acetylation with refractory wood species such as fungal pre-treatment (Messner *et al*. 2003), super-critical CO2 impregnation, and microwave acetylation are not exploited commercially.

Currently Accsys Group is commercially acetylating Radiata pine (*Pinus radiata* D. Don), but has been researching acetylation of other wood species such as southern yellow pine (USA), scots pine (EU), beech (EU) and masson pine from China. Also work was done on various tropical wood species of which tauari vermelho (*Cariniana micrantha*) was most promising (Bongers *et al*. 2008). Bollmus *et al*. (2015) acetylated boards of beech (*Fagus sylvatica*), alder (*Alnus glutinosa*) lime (*Tilia* spp.) and maple (*Acer* spp.) and the resistance to fungal decay and cyclic dimensional stability tests gave very promising results. Other species that have shown high prospects for acetylation are hornbeam (*Carpinus betulus*) (Fodor *et al.* 2017), scots pine (*Pinus sylvestris*) (Larsson and Tillmann 1989), Corsican pine (*Pinus nigra*) (Hill and Jones 1996), aspen / poplar (*Populus* spp.) (Beckers and Militz 1994) and Southern pines (*Pinus* spp.) (Goldstein *et al*. 1961).

Chips and flakes

Whereas the permeability of wood is important for solid wood to obtain uniform acetylation throughout the board, this plays less a role in acetylation of smaller dimensions. Even less permeable wood species can be acetylated in the forms of chips, flakes or fibres. Over the years many research groups have studied acetylation of smaller elements to produce wood-based materials. Rowell *et al*. (1986) acetylated southern pine, aspen and Douglas-fir flakes. Hadi *et al*. (1995) made high dimensional stable composite boards from acetylated rubber wood (*Heavea brasillensis*) fibres, and

Rowell and Plackett (1988) produced flakeboards from acetylated radiata pine. Acetylated fibres also show improved resistance against fungal decay and dimensional stability when used in wood plastic composites (Segerholm 2012).

2.3. CONSISTENCE OF TREATMENT

To gain and maintain market acceptance, it is important that acetylated wood is manufactured in a uniform manner such that it will provide consistent, reliable and acceptable performance (Bongers and Van Zetten 2017). This is important since, the mechanism of protection of acetylated wood is not based on toxicity, unlike preservative treatment and highly durable wood species, and thus lower acetylated sections can be attacked by fungi (Emmerich *et al.* 2019). Therefore a board should be acetylated throughout the cross section, and be acetylated to a uniform sufficient level throughout the board's length. Furthermore the acetylation treatment should be sufficient for all boards within a batch (uniformity) and also the treatment process should be reproducible. Important for quality control is that the degree of acetylation can be quantitative determined reliably by a number of chemical analysis methods such as High Performance Liquid Chromatography (HPLC) and Gas Chromatography (GC) and spectroscopic methods like FTIR and NIR (Beckers *et al*. 2003, Schwanninger *et al*. 2011).

Accsys Group has developed a management system to warrant consistent day-to-day production. This is extended to National Level accreditations through several (private label) certification schemes which incorporate regularly independent third party audits, such as the KOMO® certification scheme of modified wood (Homan and Tjeerdsma 2005).

2.4. COMMERCIAL PRODUCTION

Over the last century several attempts to commercially produce acetylated wood were initiated on different locations worldwide (Rowell 2006, 2014). During the 1940's to 1960's the USDA Forest Product Laboratory developed an acetylation process by use of acetic acid anhydride where pyridine was used as catalyst (Tarkow 1946). In the 1960's Koppers (USA) made first attempt to introduce acetylated wood to the market by acetylation with a mixture of acetic anhydride and xylene without catalyst (Koppers 1961). Daiken started commercial production of acetylated wood for flooring called alpha-wood in the late 1980s in Japan. In the early 1990s a commercial attempt to acetylate fibres was made by a collaboration of British Petroleum (BP), A-Cell acetyl cellulosics AB ("A-Cell"), and the BioComposites Centre (Sheen 1992). Due to technical and economic reasons these attempts were commercially unsuccessful.

Accsys Group introduced acetylated wood, named Accoya® wood (www.accoya.com), into the market in 2007. Accoya® wood is based on the acetylation of radiata pine (*Pinus radiata* D. Don) and is mainly used for applications such as joinery, cladding, decking and (light) civil works in the Netherlands, UK and Germany (Alexander 2007, Bongers *et al*. 2009, Kattenbroek 2007). In addition to solid wood acetylation, Accsys Technologies also developed a process for the acetylation of wood elements (under the brand name Tricoya®) for use within medium density fiberboard (MDF), particle board and wood plastic composites (Rowell 2014, Suttie *et al*. 2015).

3. PROPERTIES OF ACETYLATED WOOD

3.1. PHYSICAL PROPERTIES

Due to the acetylation the hydroxyl groups are replaced with acetyl groups which reduce directly the amount of moisture that can be bound to the cell wall (Hill 2008, Rowell 2015). The Equilibrium Moisture Content (EMC) and the Fibre Saturation Point (FSP) is reduced with increasing acetylation level. Water absorption within the cell wall is also accompanied by swelling of the wood. When the wood dries then the wood shrinks. Since the acetylation reduces the cell wall sorption behavior the swelling and shrinkage behavior in changing humidities is reduced. The higher the degree of acetylation the more dimensional stable the wood (Engelund 2013).

An Anti-Swelling-Efficiency (ASE) of circa 70-80% can be obtained by highly acetylating radiata pine (Bongers *et al*. 2008). Unmodified and acetylated radiata pine samples were conditioned at the following climates: oven dry, 25, 35, 50, 65, 80, 95% relative humidity and water saturated (all at a temperature of 20 °C). In this order (adsorption sequence), as well as in the reverse order (desorption sequence). The weight and dimensions (radial and tangential) of the samples were determined for each of the conditions. Based on the weight measurements, the relation between the relative humidity (of the air) and the corresponding equilibrium moisture content (EMC) of the wood was determined for both the adsorption and desorption sequence. The corresponding shrinking and swelling was measured in the radial and tangential orientations of the wood structure. The results are expressed in Figure 2. The results illustrate that the equilibrium moisture content of acetylated radiata pine has been significantly be reduced. Further the dimensional stability is improved considerably.

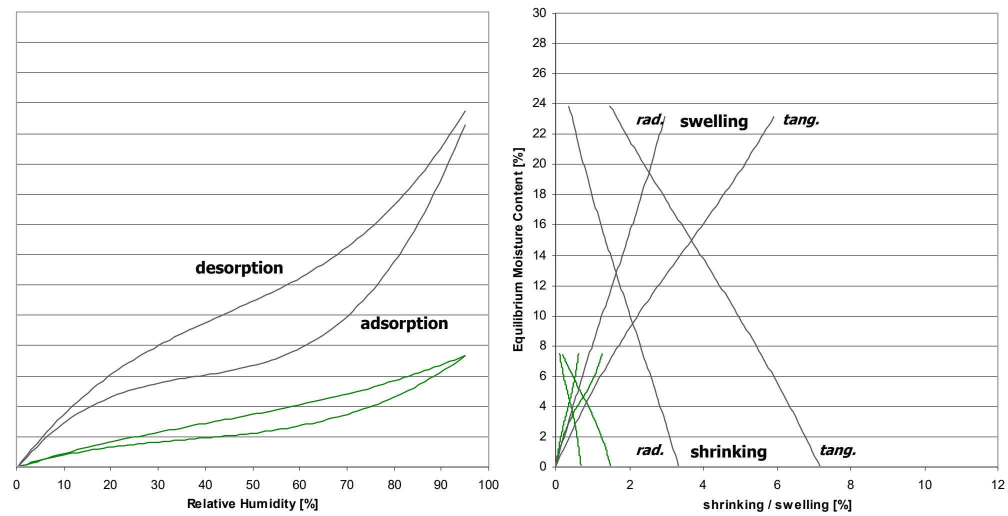

Figure 2: Hygroscopic behavior (left) of acetylated radiata pine (green line) and (unmodified) radiata pine (black line) under different moisture conditions and the corresponding swelling and shrinking behavior (Bongers *et al*. 2008).

3.2. DURABILITY

Fungi

Considerable research has been conducted to determine the effect of wood acetylation on the resistance to fungal degradation (Alexander *et al*. 2014, Alfredsen *et al*. 2013, Beckers *et al*. 1994, Militz 1991, Papadopoulos and Hill 2002, Peterson and Thomas 1978, Rowell and Dickerson 2014, Suttie *et al*. 1999, Takahashi *et al*. 1989). Bongers *et al*. (2008) studied the resistance of acetylated radiata pine, treated to different degrees, to brown-, white-, and soft rot fungi according to EN 113 and ENV 807. The higher degree of acetylation the better the resistance against fungal decay (see Figure 3). There is generally good agreement amongst researchers that, at least above weight percent gains (WPG) of 15-20%, acetylated wood shows marked resistance to attack by most wood destroying fungi. Long term in-ground stake testing (18 years) have confirmed that long term durability against fungal decay is achieved around 22% WPG (Larsson-Brelid and Westin 2010).

The 'mode of action' of acetylated wood to resistance of fungal decay is not fully understood. Recently Emmerich *et al*. (2019) confirmed that fungal hyphen can grow through acetylated wood and attack unmodified sections. Various hypotheses are linked with reduction of the moisture content of the cell wall (Alfredsen *et al*. 2013, Engelund *et al*. 2013, Hill 2009, Rowell 2015, Thygesen *et al*. 2010). The amount of bound water in the cell wall and Fiber saturation point (FSP) is significantly reduced by increasing degree of acetylation (Beck et al. 2018a, 2018b, Hill 2008). By extending the duration of laboratory testing up to 36 weeks under optimum condition with the highly aggressive brown rot fungus *Rhodonia* (*Poria*) *placenta,* Pilgård *et al*. (2012) found for the highly acetylated SYP no mass loss. Alfredsen *et al*. (2016) found that acetylated wood has a higher resistance against the first step in the decay process of this brown rot fungus (oxidative degradation of the cell wall).

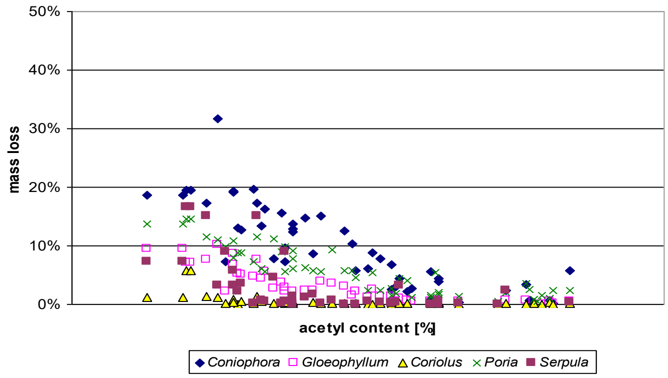

Figure 3: Mass loss of acetylated radiata pine caused by basidiomycetes (EN 113 test) in relation to the acetyl content (Bongers *et al*. 2008).

Marine organisms

A variety of studies on different locations have demonstrated that the resistance to marine borer attack of wood increases with increasing level of acetylation (Bongers *et al*. 2018, Johnson and Rowell 1988, Klüppel *et al*. 2010, Papadopoulos *et al*. 2008a), although the 'mode-of-action' is not fully understood as well as whether highly acetylated wood will be able to prevent marine-borer attack completely in all locations (Westin *et al*. 2016). With respect to the latter, running tests with highly acetylated radiata pine in Denmark, are showing no attack of marine borers after nine years of exposure (Bongers *et al*. 2018).

Termites and insects

Over the years a number of assessments have been made of the termite resistance of acetylated solid wood (Alexander *et al*. 2014, Bongers *et al*. 2015, Imamura and Nishimoto 1986, 1987, Militz *et al*. 2009, Papadopoulos *et al*. 2008b, Rowell and Dickerson 2014). The various studies showed that in most forced feeding tests with acetylated wood the mortality of soldiers was far higher than that of workers, and that the acetylated wood is subjected to exploratory attack. Imamura and Nishimoto (1986) demonstrated that acetylated wood cannot be decomposed by the symbiotic protozoa in *Coptotermes formosanus* and *Reticulitermes speratus*, resulting in a kind of starvation effect. However, other factors that may affect the termite resistance for acetylated wood are suggested such as smell, hardness, reduced equilibrium moisture content, level and uniformity of acetylation (Bongers *et al*. 2015).

3.3. MECHANICAL PROPERTIES

Acetylation changes the cell wall chemistry that impacts the physical and mechanical properties of the wood (Rowell 1996). The overall mechanical properties of acetylated wood relate on varying increasing and decreasing effects resulting from the acetylation process (Bongers and Beckers 2013, Dreher *et al*. 1964, Larsson and Simonson 1994). Several mechanical properties such as compression strength and hardness are increased by acetylation due to 1) the lower equilibrium moisture content of acetylated wood, and 2) increase of density. On the other-hand, some mechanical properties such as tensile strength can be (slightly) reduced due to 1) the amount of fibres per volume being reduced compared to untreated wood, as acetylated wood is permanently in its 'swollen' dimension, and 2) the acetylation process being performed at elevated temperature that can create thermal degradation of cellulose, hemi-cellulose and lignin.

Many research has focussed on small clear samples, and mostly on bending stiffness and strength ((Bongers and Beckers 2003, Dreher *et al*. 1964, Larsson and Simonson 1994). Epmeier *et al*. (2007) investigated creep behaviour and found a significant reduction for acetylated wood. More recent large amount of research is done on large commercial sections of acetylated Radiata pine, and could a strength class of C22 as described in EN 338 be allocated for a defect free quality (Bongers and Alexander 2018). Furthermore Marcroft *et al*. (2013) found that the impact of high wood moisture content on reduction of the mechanical properties is less for acetylated radiata pine compared to untreated wood species. This has enabled to use acetylated radiata pine in load-bearing exterior applications (see paragraph 4.2).

3.4. *BONDING AND FINISHING*

Due to the acetylation process various material properties are altered that may influence bonding quality (Bongers *et al*. 2013, Brandon et al. 2006, Frihart et al. 2017, Hunt *et al*. 2007, Ormstad 2007, Treu *et al.* 2018, Vick & Rowell 1990):

- Acetylation replaces the hydrophobic hydroxyl groups with acetyl groups (see Figure 1). This has directly impact for adhesives on chemical bonding to hydroxyl groups.
- Increased hydrophobicity of the surface decreases the ability of water-based adhesive to wet, flow, and penetrate a bonding surface (Bryne and Wålinder 2010).
- Reduced equilibrium moisture content, improved dimensional stability and water uptake behaviour.
- Presence of small amount of acetic acid (by-product of the acetylation reaction) can impact the (surface) pH of the wood and its buffering capacity which play an important role for reaction and curing rates of several types of adhesives.
- Increased surface hardness and changed mechanical properties, especially increased wet strength resulting in different failure mechanisms in strength tests of laminated acetylated wood.

Lamination, finger-jointing and edge-glueing of acetylated wood is possible with various types of adhesives. Tjeerdsma and Bongers 2009) found good performance of acetylated Radiata pine with a PRF and PUR adhesive for structural applications. Vick and Rowell (1990) had good results with bonding acetylated Yellow poplar (Liriodendron tulipifera L.) with a water-borne non-polar high molecular weight and high solid content EPI adhesive, and with high viscosity PUR adhesives. The tested PVAc adhesive had difficulties to wet and penetrate acetylated wood and showed less performance in wet conditions. Bongers *et al*. (2016) tested several commercial available PUR adhesives and all showed good bonding with acetylated Radiata pine. In wet conditions Melamine Urea Formaldehyde (MUF) adhesive show a bad performance, but improvement is seen when a primer is used (Treu *et al*. 2018).

The increased dimensional stability of acetylated wood, and subsequent reduction in swelling and shrinkage of the wood in exterior applications, has a positive effect on reducing stresses in film-forming coating systems. This improves coating lifetime and thereby significantly extends maintenance intervals (Rowell and Bongers 2015, 2017, Uphill *et al*. 2018). Furthermore due to increased hardness, Uphill *et al*. (2018) found for acetylated radiate pine no negative impact on coating adhesion due to hail damage whereas other softwood species such as thermal modified pine, Scots pine, and Nordic Spruce were susceptible to coatings failure due to hail impact.

3.5. *ENVIRONMENTAL ASPECTS*

A series of methods are available to assess the environmental impact of a product such as Life Cycle Analysis (LCA following ISO 14040/44) and Environmental Product Declarations (EPD following ISO 14025 and EN 15804). Furthermore different Ecolabels exists worldwide.

Van der Lugt *et al*. (2014) performed a Cradle-to-Grave carbon footprint evaluated for acetylated radiata pine windows frames. The results of a similar evaluation for a pedestrian bridge was presented by Van der Lugt *et al*. (2016). In a carbon footprint assessment, the greenhouse gas emissions during the life cycle of a material can be measured, and compared to alternative products in terms of kg CO2 equivalent. The results show that if lifespan considerations are included, acetylated wood has a considerably lower carbon footprint than non-renewable materials (such as concrete, PVC, steel, and aluminium) and unsustainably sourced hardwood, and is competitive in terms of carbon footprint with sustainably sourced hardwood. Because of the limited emissions during production and carbon credits related to temporary carbon storage and bio-energy production during End of Life, all sustainably sourced wood alternatives, including acetylated wood, are even CO2 negative over the full life cycle. Van der Lugt *et al*. (2014, 2016) also indicate that several environmental issues cannot be caught by a carbon footprint, such as the high growing speed of species suitable for acetylation, compared to slow growing tropical hardwood species.

4. APPLICATIONS OF ACETYLATED WOOD

4.1. *NON-LOAD BEARING APPLICATIONS*

The material properties of acetylated wood; high dimensionally stability, extended coating performance and increased durability, make it very suitable for many applications such as joinery, cladding, decking, and non-structural civil works (such as canal lining). Applications and design, however, are not limited anymore to the traditional concept but acetylated wood gives opportunity for new kind of designs and applications (Lankveld *et al*. 2014, 2015). It should be noted, that although more opportunities are available, standard design and building practise for wood structures still apply.

4.2. STRUCTURAL APPLICATIONS

Based on extensive research, the mechanical properties of acetylated radiata pine have been determined (see paragraph 3.3). Together with information on safety factors and the effect of service class, load-bearing constructions are possible (Bongers and Alexander 2018). Properties of glulam from acetylated radiata pine was investigated by Blaß *et al*. 2013. Already in 2008 and 2010 two heavy load-bearing traffic bridges were constructed in Sneek the Netherlands (Jorissen and Lüning 2010, Tjeerdsma and Bongers 2009). Encouraged by this success, several pedestrian bridges and various other column type structures situated in wet (Service Class 3) conditions have been completed over the last decade. Recent work by the University of Kaiserslautern, Germany on the mechanical properties of acetylated beech, indicated the potential for use in bridges and towers (Graf 2019).

4.3. MUSICAL INSTRUMENTS

For high quality music instruments superior quality wood is required that is dimensional stable, homogeneity of grain, hardness, flexibility and plasticity. The available wood for these instruments is getting more difficult to obtain, and modified wood could be an alternative (Ahmed and Adamopoulos 2018).

Acetylation of wood reduces the variability in the wood moisture content of the cell-wall throughout a board, and moisture contents are minor changing with different conditions (Yano *et al*. 1993). Thereby the physical and acoustic properties are stabilised and making acetylated wood suitable for music instruments such as violin, piano soundboard, guitar, recorder, bagpipe chanter, trumpet and trombone mouthpieces (Rowell 2013).

5. SUMMARY AND OUTLOOK

By acetylation, the resistance against fungal decay and insects as well as the dimensional stability of wood can be improved, thereby enabling the opportunity to upgrade and utilization of lower quality soft and hardwood species. Currently more than 10 years of experience with commercial acetylation of radiata pine, selling over 250.000 m^3 of acetylated material world-wide (with the largest market being the UK and the USA), Accsys has confirmed the high potential of acetylated wood in many different applications across the globe. Independent inspection of 17 projects with acetylated wooden doors, windows, cladding, and decking built between 2007 and 2016 in the Netherlands showed that the use of acetylated wood increases the lifetime of timber products and decreases the intensity of maintenance (Klaassen *et al*. 2018), but special attention is needed to avoid fast water uptake in outdoor as well as in indoor (condensation) conditions by using appropriate design and application practises.

With expansion to other regions, local wood species will be explored . However, to be able to warrant uniform and reproducible products that meets the required performance, takes several years of development. Other opportunities are engineered acetylated wood products such as CLT and marine use.

Another field of opportunity is the acetylation of particles (such as acetylated MDF that is f.i. produced under the brand name Medite Tricoya®), and other engineered wood products such as lamella. Due to higher surface/volume ratio's, the acetylation process is much less dependent on the permeability of the wood species, thereby opening up the opportunity for many other wood species.

What is important with all these future opportunities is that the species and application are fully investigated and assessed such that the high quality of commercially available acetylated material continues.

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