Acetylated Wood Fibres - Next Stop: Commercialisation

Dennis Jones[1], Mark Lawther[2], Ronny Torgilson[3] and Rune Simonson[4]

[1]Woodknowledge Wales, BRE Wales, Engineering Centre for Manufacturing and Materials (ECM2), Heol Cefn Gwrgan, Margam, Neath Port Talbot SA13 2EZ, UK
[email:jonesd@bre.co.uk]

[2]DanAcell Denmark A/S, Goldschmidtsvej 10,2 DK-4670 Vordingborg, Denmark
[email:ml@tla-development.com]

[3] TLA Development I/S, Gevninge Bygade 55, DK-4000 Roskilde, Denmark
[email: rt@tla-development.com]

[4] A-Cell Acetyl Cellulosics AB, Saavedalen, Sweden
[email: rsimon@a-cell.se]

Keywords: Acetylation, commercialisation, fibres

ABSTRACT

Whilst the acetylation of solid wood has made significant steps towards commercial success, the acetylation of wood fibres has to date remained, of laboratory-scale and small pilot plant interest. Plans have been conceived at several sites over the past 3 decades to develop a suitable treatment method and market a product, but without final commercialisation. The ever-increasing need for materials suited to specific performance profiles has once again opened up an opportunity for the acetylation of wood fibres. This paper will outline the past, present and hopefully commercial future of the process. The past will consider the methods used, the intended markets, the commercial environment at the time, lack of the present day "green driving force" and conclude why the process was not commercialised at that time. The present will look at how needs have changed, and where acetylated fibres can realistically play a role in today's society. The future will look at ongoing developments to re-establish acetylation of fibres as a commercial reality, as well as exploring possible market expansions.

INTRODUCTION

The concept of acetylation of solid wood and fibres is well understood, and has been reported several times at the previous three ECWMs. The most interesting aspect has been the commercial development of acetylated solid timber during this period, through the inception and growth of Titanwood. Indeed, its marketed product, Accoya, has made significant inroads into several markets. The properties generated through acetylation, as a result of the chemical bonding at the microscopic level, are present at the fibre level as well as on solid timber products. Thus benefits on water repellency, product stability and increased durability, may be imparted on products made using acetylated fibres. Indeed, wood fibres prepared using the Asplund type process employed in "MDF" refining have high available surface area, have lignin rich surfaces and in some ways offer an ideal "substrate" for acetylation. Likewise the oleophilic nature of the modified fibres possessing very high effective surface areas, may offer further business opportunities. When considering the anticipated products and their performance, against the relative ease of treatment of fibres compared to solid wood, it is necessary to ask the question "why has the acetylation of wood fibres not been commercially developed?" This paper will attempt to answer this through the description of ongoing activities in Sweden and Denmark.

A HISTORICAL PERSPECTIVE OF COMMERCIAL ACETYLATION

In order to assess the acetylation of wood fibres, it is necessary to look at previous developments, and those currently being considered, whether these are for solid wood or wood fibres.

Early attempts

Attempts have been made to commercialise acetylation of timber using four varying methods:

- The use of acetic anhydride
- The use of ketene
- The use of vinyl acetate
- The use of mixed anhydrides.

The first two methods represent the majority of methods used (since these were the methods conceived at the onset of acetylation), whilst the last two represent recent attempts to find alternative chemical pathways to acetylated timbers (and will be considered in the following section). The acetylation of wood through the use of acetic anhydride has been regarded as scientifically plausible at the laboratory level since the late 1920's (Suida and Titsch 1928). However, it was the systematic studies undertaken by Stamm and Tarkow (1947) that led to the methodologies that are still more or less practiced in the wood modification sector. Within 25 years, there were two early attempts at commercialisation, one in the US (Koppers 1961), the other in USSR (Burkalov *et al.* 1972), though these ceased activities soon afterwards due to mainly financial issues. The next commercial activity came about in the early 1990s, from collaborative work between British Petroleum, A-Cell acetyl cellulosics AB ("A-Cell"), and the BioComposites Centre (Sheen 1992). A detailed review of this collaboration has been recently published (Hill 2006), through which several key factors were identified:

- Feed fibres needed to have a moisture content around 5%
- Residual acetic acid inhibited the reaction at elevated levels (above 30%)
- Fibre damage occurred at temperatures above 130 ^{o}C
- Removal of residual acetic acid could be carried out by drying at around 50 ^{o}C

Despite the production of several batches of acetylated fibres, and their subsequent assessment, British Petroleum withdrew their interest in acetylation in the mid-1990s, leading to a temporary halt in the commercial development by the group as a whole, though A-Cell continued their activities, in association with Chalmers University (Sweden) and Forest Products Laboratory, Madison (USA). At around the same time as the European developments led by British Petroleum, commercial activities were being developed in Japan by Daiken Wood Industry, leading to the sale of a product called alpha wood. It is uncertain whether this process continues, as many chemical modification activities in Japan ceased during the 1990s due to economic uncertainties. However it was recently reported (Rowell 2006) that alpha wood was still commercially available. The use of ketene was also considered as an option for commercial production of acetylated timber (Morozovs *et al.* 2003). Ketene, resulting from the pyrolysis of liquid diketene, is a toxic, explosive gas. It is capable of acetylating dry wood and fibre at low temperatures, with optimum conditions found to be 47 °C. However the health and safety factors associated with its use have restricted its use as a commercial acetylation process.

Current methods

The successful implementation of commercial acetylation was achieved in 2006 by Titan Wood, in The Netherlands. This batch process was based on some of the early developments at SHR, which led to the creation of AKBV, an industrial pilot scale process capability based in Arnhem, The Netherlands. This process was bought out by Titan Wood, and was combined with some of the acetylation capability and expertise from the acetylation of cellulose. Capacity began at 0.9 cubic metres pre batch, though the premises allows for expansion in processing capacity, as the demand for acetylated timber increases. Whilst there may be scope to expand into the acetylation of fibres in the future, the focus of Titan Wood presently appears to be solely with solid wood. A-Cell has in recent years also further developed a process for acetylation of solid wood, which utilises microwave technology to aid efficient acetylation and clean-up. This has been successfully demonstrated at pilot scale by the company and a group at Chalmers University in Sweden, and the technology is deemed ready for the next scale-up step towards commercialisation. A license arrangement is in place outside of Europe, and the technology is available for license within the EU region, but as yet no full-scale production has been achieved. Whilst A-Cell are still active in their pursuit of commercially acetylated fibres (as will be described in the next section), another fibre acetylation process seemingly co-exists. This process (Murray 1998) has some similarity with other existing patents, with documentation on the internet outlining business development for commercial set-up and operation within the UK. However, this actually appears to be most focused on applications such as pipe linings on more detailed examination of the patent. The concept of esterification with vinyl esters was explored by researchers at Bordeaux (Jebrane and Sèbe 2007), in an attempt to avoid secondary processing for the removal of odorous components (as is the case with the removal of acetic acid with conventional acetylation). Experiments using vinyl acetate (Figure 1, where R=CH_3) showed moderate yields of acetylated material could be achieved at a temperature of 90 °C.

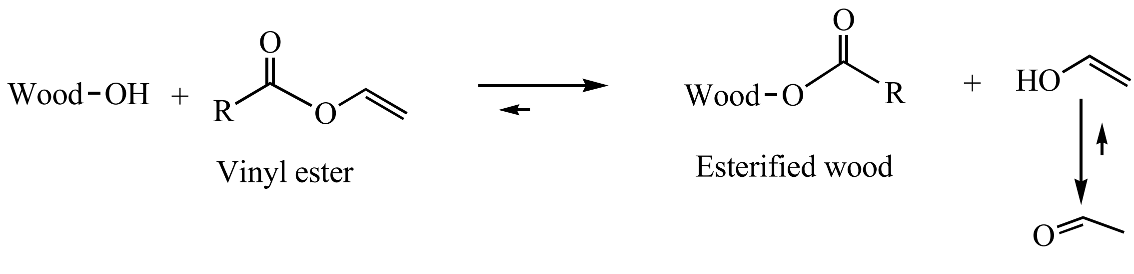

Figure 1: Example of esterification of wood with vinyl esters

Whilst this work offers scope for future development, two potential obstacles exist in the use of solvent (N,N-dimethylformamide) and a catalyst (potassium carbonate). One of the advantages of conventional acetylation is its ability to proceed without the need of solvent or catalyst. Another development in France has resulted in the launch of Wood Protect®, an example of the use of a mixed anhydride. Researchers at the INRA-INPT-ENSIACET Joint Research Unit in Toulouse combined their R&D capabilities with Lapeyre, resulting in the launch of the process in 2004. The treatment comprises the reaction of acetic anhydride with the fatty acid constituents of rapeseed oil or sunflower seed oil, with the subsequent mixed anhydride reacting with wood at temperatures around 140 ^{o}C. Further commercial developments are likely to be marketed through the Lapeyre group.

THE POSITION OF COMMERCIAL ACETYLATION OF FIBRES TODAY

A-cell have teamed up with a Danish SME: Danish Plant Fibre technologies A/S (“DanFibre”) and have formed a new joint venture known as DanAcell Denmark A/S (“DanAcell”). DanFibre have a need for modified fibres to be used for production of filtration systems for treatment of contaminated water. Within this venture, A-Cell has followed on from experiences gained at the Kvarntorp acetylation pilot plant and continued with the improved design of a plant for wood fibre acetylation. A-Cell strongly recognise the need for a truly continuous process for fibre modification, rather than a batch process, particularly with a view to full scale production at many thousands of tonnes per annum. In the design, planning and construction of such a plant, the following critical factors must be borne in mind:

- Wood fibres are low bulk density and are difficult to handle if not part of a dynamic process (*e.g.* blow-line blending of resins into refined fibres for MDF). Fibre feed must be addressed
- Effective stripping of anhydride and acid by-product from the reacted fibres must be achieved on the plant (impacts on product quality and process economics)
- Fast, clean reaction, minimising fibre damage and increasing throughput
- Preferred use of anhydride to fibre ratios of maximum 2:1 within the reactor
- Flexibility in plant to operate at pressures (and concomitant temperatures) ranging from ambient up to moderately high pressure
- Sealing of pressures due to anhydride and acetic acid vapour and all feeding and discharge issues around this
- Breaking of any fibre conglomerates formed in the system
- Capability to also handle wood flours / meals giving rise to acetylated materials suitable for use in Wood filled plastic composites: “WPCs”

If all these factors can be satisfactorily addressed, fibres of adequate acetyl content and free of residuals, can be delivered at a cost that enables utilisation in a range of “sizeable niche product” sectors. A-Cell, within DanAcell, is now working towards the commissioning and installation of a pilot / demo plant, at a site in southern Denmark, which is basically the smallest version of the perceived full commercial, continuous plant. Crucially, this is fully scaleable to the necessary large plants that will be constructed to achieve economy of scale. Based on past experiences from the 1990’s and from A-Cell experiences in operating the semi-continuous pilot plant in Kvarntorp, the plant incorporates design features that address all of the issues listed above. This plant constructed in Kvarntorp was basically set up as described by Simonson and Rowell (2000):

“The fiber enters a pre-heated reactor and a specified concentration of acetic anhydride is applied. The fiber moves through the reactor at a rate needed for the acetylation to take place to the desired weight gain. The fiber then goes into a first stripper loop unit where the loop atmosphere consists of superheated vapors of acetic anhydride and acetic acid. Excess chemicals are evaporated from the fiber material and the chemicals recovered. In a second stripper, any remaining acetic anhydride is hydrolyzed to acetic acid by treatment with water vapor and the acetic acid is stripped off in a stream of superheated steam. The acetylated fiber can be conditioned and resinated in a final step before processing into composites."

This plant functioned reasonably well in terms of achieving acetylated fibres of the required acetyl contents. However, considerable problems were encountered with sealing of the system at both ends with escape of anhydride vapour being a persistent and dangerous problem. The new plant design takes all these lessons and issues on board. The sealing issues are considered solved after careful trials at two very different facilities. The new plant consists of a continuous feed system for fibre into a pre-conditioner, wherein anhydride is introduced, and then a reactor capable of withstanding moderately high pressure, and finally a unit for stripping off excess anhydride and generated acid. The fibre is continuously moving throughout its transit through the plant. The pilot/demo plant is designed to produce around 45 kg acetylated fibre per hour. More precise details cannot be disclosed at this point, the proof of concept will be the successful running of the pilot plant. However, it can be stated that the demo plant has maximum flexibility built in to allow variation of key parameters such as temperature, pressure and residence time in the reactor, and will yield comprehensive information and facilitate process optimisation, along with precise final design parameters for the next, upscaled plant. It is therefore the stated aim of A-cell / DanAcell to iron out final processing issues on the pilot / demo plant in Denmark, and create the "best practice design Blueprint" for up-scaled plants for continuous wood fibre acetylation. The technology will be licensed to strategic end-users.

Plant implementation

All activities during the first 4 – 6 months from commissioning will focus on the optimization of the wood-fibre acetylation reaction to produce fibres suitable for exterior grade MDF type board production: *i.e.* with acetyl group contents between 18-22%. This will be achieved through a series of carefully planned trials. The plant itself will be pushed to its limits and thoroughly tested during this trial sequence. Optimally produced fibres will be used to select a suitable resin system and method of resin application. MDF test boards will be produced and evaluated. Results will be used to finalise the design of the first up-scaled commercial plant. This will be costed and presented to preferred licensees. Full process economics and forecasting will be included in the reporting. This is a major project **milestone**. The plant will then be used to produce test quantities of acetylated wood flour / meal for initial trials in WPC products. By mid 2010 it is hoped that all optimisation data will be collected and processed and the first full-scale plant design in place and perhaps under construction.

Further issues

Any scaled up plant (11,000 tonnes per annum minimum product fibre) must be located at, or very close to, a source of wood fibre and / or wood meal. It is not economically viable to "buy" fibres on the market or even to encounter prohibitive transportation costs moving low bulk density wood fibres large distances. This of course implies location at an existing MDF production site, wherein pressurised refiners are producing fibres ready for modification, or in the case of wood flours, at a large saw mill complex. A less attractive, but possible, option is to install a dedicated pressurised refiner for the upscaled modification plant. The first listed option, to locate at an existing MDF plant, is the most interesting. This gives at least two important advantages: a ready source of "low-cost" wood fibre and immediate access for the modified fibres back into an MDF production process. Indeed, a licensee can considerably leverage on existing on-site infrastructure, with positive impact on investment costs and ultimately, profit. Adhesives commonly used in the MDF industry, such as liquid UFs, do not glue acetylated fibres very effectively. This is thought to be due to a combination of factors including increased hydrophobicity of the fibre surface leading to a varied wetting effect and perhaps the lower pH causing some pre-cure of acid hardened glues of this type. In addition, such gues have relatively poor water resistance, so should not be considered for use in an exterior grade product. It is known that more alkaline Novolac type resins and some MUFs work well with these fibres (Gomez-Bueso *et al*. 1999). However, effort must be expended in reformulating and adapting common resin types to perform in acetylated board products. A future key issue is centred around the efficient use of the acetic anhydride component of the equation: the costly part. Given that the anhydride costs around 10 times that of wood fibre, and a large part added to the wood needs to be recovered and recycled, there is much merit in considering and aiming for the "Integrated acetylation plant" scenario. In this, production lines for the acetylation of solid wood, wood fibres and wood flours / meals are installed and run at the same production site. This crucially optimises economy in anhydride issues: bulk storage, bulk purchase, recycling efficiency and regeneration. This must be a target for the future of the industry.

Cost of Acetylated Fibres?

Until the plant is running optimally, it is difficult to estimate a real cost of the acetylated fibre end product. However, in basic terms of raw material consumption, and assuming a reasonable recovery of anhydride and acetic acid, and a nominal price for re-sale of recovered acid, along with an assumed process cost, the composite fibre cost can be estimated at around €600 - 800 per tonne. This is based on anhydride bulk prices between €1000 – 1100 per tonne and an operation at full scale (around 11,000 tonnes per annum or more). Further more, it assumes access to low-cost fibres at an MDF plant or similar production facility. The real price of course depends on a combination of complex factors, one of which is the **actual** verified process cost and this will not be known with any real accuracy until the demo plant has been run, tested and optimal operation is achieved.

IS THE MARKET READY FOR ACETYLATED FIBRES?

Whilst it is certainly possible to create a range of excellent materials based on acetylated wood fibres, it is only through the understanding of market needs that a great product is established. It has been shown that the acetylation of wood fibres should be feasible on a commercial scale, but will these fibres be put to use in an effective way? It would appear that the market place is now much more ready for acetylated wood fibres than it was even ten years ago. The study of Mats Westin (Table 1) referenced at the last European Conference on Wood Modification (Jones 2007) suggested that several years ago, companies were prepared to consider products made from acetylated fibres.

There are several product ranges where acetylated wood fibres could compete favourably with existing materials.

Table 1: Overview of possible product ranges for modified wood (Jones 2007)

Type of product range	Most belief in
Garden wood (furniture)	Thermally modified wood
Window frames	Acetylated wood
Exterior doors and frames	Acetylated wood and MDF
Flooring	Several types of modified wood / fibres
Wet room & façade panels	Acetylated fibres
Building products etc.	Acetylated / Heat modified wood
Automotive / nautical applications	Furfurylated wood
Use by architects /govt. organizations	Acetylated /Heat modified wood

Exterior/marine grade composites

There has been resurgence in the use of quality wood products in recent years over modern materials such as glass fibre. This could be developed further to offer opportunities for acetylated wood fibres. In several cases the use of exterior or marine grade plywood has resulted in high value products. It is feasible that the use of acetylated wood fibres for the manufacture of a dimensionally stable MDF could lead to an even more uniform product (in effect acetylated MDF, hereafter referred to as aMDF). MDF surfaces are typically easy to coat, resulting in high quality finishes, the same should be true for aMDF. The stability of the product would reduce stresses on any applied coating, leading to increased periods between maintenance cycles or even the end of service life. Alternatively, it may prove beneficial to use an aMDF core with high quality veneer adhered to external surfaces. Such benefits in stability could prove useful in the manufacture of, for example, exterior doors. A portion of the exterior cladding market is also another target for the product.

Interior products for use in high humidity

Providing dimensional stability is essential in products used in areas where humidity can vary considerably, such as in bathrooms and kitchens. Wet-room panels and even flooring components can conceivably be fabricated with some content of acetylated wood fibres. The hydrophobic properties of acetylated wood fibres promote their use in cabinet manufacture and for interior doors or as door skins pressed from non-woven, resinated mats of acetylated wood fibres. The ease of profiling aMDF into decorative features would suggest strong market opportunities. One particular product range suited to profiled aMDF is in the manufacture of architraves. The thinly profiled regions of architraves are prone to excessive dimensional movement, warping and twisting with varying moisture levels. aMDF would not suffer form such problems.

High strength equipment

Sports equipment has benefited greatly from advances in synthetic fibre composites, through reduction of equipment weight and increase in product strength. Much of this has been accompanied with a loss of aesthetical look. Certain product ranges are considered as having to look like wood (*e.g.* hockey sticks, lacrosse sticks, cricket bats). Opportunities may exist for incorporation of acetylated wood fibres into sports equipment, so maintaining the look of wood, but allowing the benefits associated with synthetic composites. The level of acetylation may also have an effect on the compatibility of wood fibres into synthetic mixes, which could then be extruded or moulded into the form desired. It is not impossible to envisage a low density product with a high percentage of acetylated wood fibres being used in future generations of sports equipment. Other equipment may also benefit from the look imparted by acetylated wood fibres. Examples here may be the resurgence of wooden dashboards in cars (only this time with the strength of currently used products), or where wood was previously the finish of convenience.

Environmental uses

A common use of wood fibres, or any finely ground material, has been in cleaning up oil spills, due to the absorptive properties of the fibres. Difficulties arise when oil is mixed with water, as in cases of crude oil spills from ships. The absorption of water would compromise that of the oil. However the use of acetylated wood fibres could offer benefits through the hydrophobicity of the fibres themselves (in that they would not absorb water), which also makes the fibres oleophilic (more likely to absorb the oil). Maintaining a stock of acetylated fibres for such uses would guarantee demands for a large percentage of initial production. Such fibres can also be formed into non-woven mats for application to contaminated water, or for the further fabrication of designed filter elements. The performance of acetylated and other modified wood fibres produced at lab and very small batch pilot scale in this arena is impressive: the fibres can absorb between 25 – 50 times there mass in oil if utilised correctly. In these markets, competing materials with such performance are relatively costly, so this sector offers a very good margin for the wood fibre products, especially during initial years of sale. This will help support the overall acetylation scenario.

CONCLUSIONS

Whilst the commercialisation of solid wood has taken off, that of wood fibres has yet to do so. However, developments in Scandinavia mean that we are well placed to make this a commercial reality. The market appears ready for a material capable of meeting a wide range of applications, and it will be necessary to ensure acetylated wood fibres have the right market entry price. The key barrier to break is to achieve a consistent, continuous production plant that can be run at scales concomitant with fibre production rates in the MDF industry. The planned pilot / demo facility will lead to the establishment of such plants. The sale of acetylated fibres into an environmental sector, wherein pricing of the fibre products can be higher, will help in the overall economic equation. Provided fibres can be provided at reasonable cost “per performance”, the market will utilise the material. Indeed the production and reflected effective retail cost of the acetylated fibres in the wood-based panels sector could well largely govern market penetration. A range of possible product ranges has already been identified, with more being explored. This should ensure high levels of take-up of fibres produced. Meeting the criteria stipulated by manufacturers will allow the commercial development of acetylated wood fibres to become a reality.

REFERENCES

Burlakov, V. D.; Duduns, M.; Nikitina, N. F.; Ozolina, I.; Otlesnov, Yu. P.; Svalbe, K. (1972). Modification of wood. *Russian Patent* SU 400473.

Gomez-Bueso J, Westin M, Torgilsson R, Olesen PO and Simonson R (1999): Composites made from acetylated lignocellulosic fibers of different origin : Part II. The effect of nonwoven fiber mat composition upon molding ability. *Holz als Roh- und Werkstoff,* **57**, 178-184.

Hill, C.A.S. (2006). *Wood modification: Chemical, thermal and other processes*. John Wiley and Sons, Chichester, England.

Jebrane, M. and Sèbe, G. (2007). A novel route to wood modification by transesterification with vinyl esters. In *Proceedings of the Third European Conference on Wood Modification*. Cardiff, UK. pp. 65-70.

Jones, D. (2007). The commercialisation of wood modification – past, present and future. In *Proceedings of the Third European Conference on Wood Modification*. Cardiff, UK. pp 477-484.

Koppers Inc. (1961). Dimensionally stabilized wood. *New Materials Technical Information No. (RDW-400)*, **E-106**. Koppers Inc., Pittsburgh, PA. 23 pp.

Morozovs, A., Aboltins, A., Zoldners, J. and Akerfelds, I. (2003). Wood modification in Latvia. In: *Proceeding of the First European Conference on Wood Modification*, Gent, Belgium. pp. 351-362.

Murray, J.E. (1998). Acetylation of lignocellulosic materials and applications thereof. World patent WO98/01497

Rowell, R.J. (2006). Acetylation of wood: journey from analytical technique to commercial reality. *Forest Products Journal,* **56**, 4-12.

Sheen, A.D. (1992). The preparation of acetylated wood fibre on a commercial scale. In: *Pacific Rim Bio-Based Composites Symposium: Chemical Modification of Lignocellulosics.* FRI Bulletin **176**, Plackett, D.V. and Dunningham, E.A. (Eds.), pp. 1-8.

Suida, H. and Titsch, H. (1928). Chemistry of beech wood: Acetylation of beech wood and cleavage of the acetyl-beech wood. *Berichte* **61B**,1599-1604.

Stamm, A.J. and Tarkow, H. (1947). Dimensional stabilization of wood. *Journal of Physical and Colloid Chemistry*, **51**, 493-505.

Simonson, R; Rowell, R.M. (2000). A new process for the continuous acetylation of lignoceilulosic fiber. In: *Proceedings of the 5th Pacific Rim bio-basedcomposites symposium; 2000 December 10-13; Canberra, Australia. Canberra, Australia: Department of Forestry, The Australian Natlonal University*: 190-196.