A NEW PROCESS FOR THE CONTINUOUS ACETYLATION OF LIGNOCELLULOSIC FIBER

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ABSTRACT

A new process for the continuous acetylation of lignocellulosic fiber has been developed. 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. Composites made from acetylated fiber have been shown to have greatly improved dimensional stability and biological resistance.

Key Words: Acetylation, fiber, process, economics, properties.

INTRODUCTION

Chemical modification of wood for improved dimensional stability and decay protection has been the subject of research for many years. A wide variety of chemicals have been studied including anhydrides, acid chlorides, carboxylic acids, isocyanates, acetals, esters, alkyl chlorides, b-propiolactone, acrylonitrile, and epoxides. (Rowell, 1983). The most studied of all of the chemical modification chemistries is acetylation. The early work was done using acetic anhydride catalyzed with either zinc chloride (Ridgway and Wallington, 1946) or pyridine (Stamm and Tarkow, 1947). Through the years, many other catalysts have been tried both with liquid and vapor systems. Some of the catalyst used include urea-ammonium sulphate (Clermont and Bender, 1957), dimethylformamide (Clermont and Bender, 1957; Risi and Arseneau, 1957; Baird, 1969), sodium acetate (Tarkow, 1959), magnesium persulfate (Ami et al., 1961; Ozolina and Svalbe, 1972; Truksne and Svalbe, 1977), trifluoroacetic acid (Arni et al., 1961), boron trifluoride (Risi and Arseneau, 1957) and g-rays (Svalbe and Ozolina, 1970).

Acetylation of wood using acetic anhydride has mainly been done as a liquid phase reaction but gas phase reactions have also been reported (Tarkow, 1959; Baird, 1969; Rowell et al., 1986a). The reaction has been done without catalyst (Rowell et al., 1986b) and using an organic cosolvent (Goldstein et al, 1961). The reaction results in

$$\textbf{Wood-OH} + CH_3C(=O)\text{-}O\text{-}C(=O)\text{-}CH_3 \rightarrow \textbf{Wood-O-C(=O)-}CH_3 + CH_3C(=O)\text{-}OH$$

esterification of the accessible hydroxyl groups in the wood cell wall with the formation of byproduct acetic acid (Rowell et al. 1994).

Acetylation of wood has also been done using ketene gas (Tarkow, 1945; Rowell et al., 1986c). In this case, esterification of the cell wall hydroxyl groups takes place but

$$\textbf{Wood-OH} + CH_2{=}C{=}O \rightarrow \textbf{Wood-O-C(=O)-}CH_3$$

there is no formation of byproduct acetic acid. While this is interesting chemistry and eliminates a byproduct, it has been shown that reactions with ketene gas results in poor penetration of reactive chemical and the properties of the reacted wood are less desirable than those of wood reacted with acetic anhydride (Rowell et al., 1986c).

In spite of the vast amount of research on the acetylation of wood and other lignocellulosics, commercialization has been slow in coming. Two attempts, one in the United States (Koppers, 1961) and one in Russia (Otlesnov and Nikitina, 1977; Nikitina, 1977), came close to commercialization but were discontinued presumably because they were not cost-effective. There are reports of a commercial acetylation plant for solid wood in Japan and a pilot plant for solid wood in Holland but few details are available.

The present paper describes the acetylation method and startup of a pilot plant in Sweden with a capacity of approximately 4,000 tones of acetylated fiber a year. The process has resulted from early research at Chalmers University in Goteborg, Sweden and the USDA, Forest Products Laboratory in Madison, Wisconsin (Rowell et al. 1986b) in cooperation with British Petroleum in Hull, UK.

THE PROCESS

One of the concerns about the acetylation of solid wood, using acetic anhydride as the reagent, has been the byproduct acetic acid. Many attempts have been made for the "complete removal'' of the acid to eliminate the smell, make the process more cost effective, and to remove a potential ester hydrolysis causing chemical. While this has not been "completely" possible with solid wood, it is possible when the new acetylation process is applied to fiber. The anhydride and acid strippers in the process completely remove acetic acid and dry the fiber, after acetylation, ready for use.

Figure 1 shows the schematic of the new continuous fiber acetylation process (Nelson et al., 1999). The fiber is first dried in an optional dryer section to reduce the moisture content to as low a moisture content as is economically feasible realizing that the anhydride will react with water to form acetic acid and that a certain amount of acetic acid is needed to swell the fiber wall for chemical access.

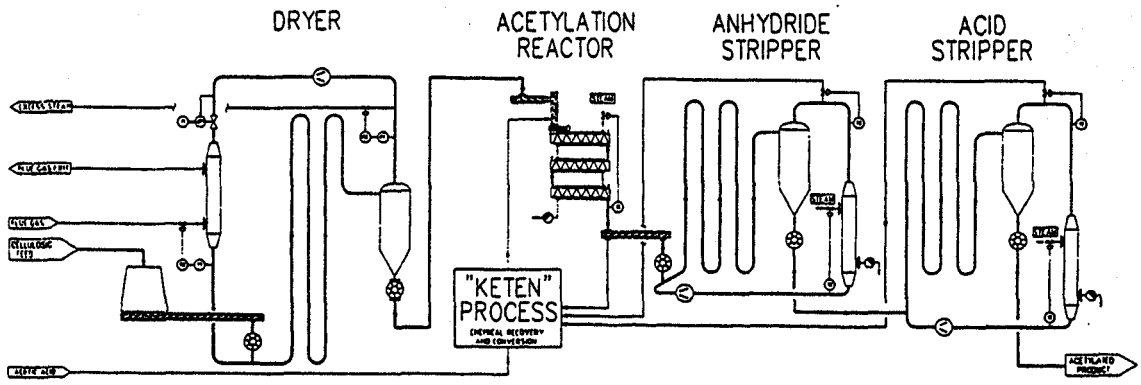

Figure 1 - Schematic of the new fiber acetylation process.

The dried fiber is then introduced, by a screw feeder, into the reactor section and the acetylating agent is added. The temperature in this section is within the range of 110 to 140 ¡ C so the acetylating agent is in the form of a vapor/liquid mixture. Back flow of the acetylating agent is prevented by a fiber plug formed in the screw feeder. A screw-conveyor or similar devise is used to move the material through the reactor and to mix the fiber-reagent mixture. During the acetylation reaction, which is exothermic, the reaction temperature can be maintained substantially constant by several conventional methods. The contact time in the reactor section is from 6 to 30 minutes. The bulk of the acetylation reaction takes place in this first reactor.

The resultant acetylated fiber from the first reactor contains excess acetylating agent and formed acetic acid as it is fed by a star feeder into the second reactor, designed as a long tube and working as an anhydride stripper. The fiber is transported through the stripper by a stream of superheated vapor of anhydride and acetic acid. The temperature in the stripper is preferably in the range of 185 to 195 ¡ C. The primary function of this second step is to reduce the content of the unreacted acetylating medium remaining in the fiber emerging from the first reactor. An additional acetylation of the fiber is, however, also achieved in this step. The residence in this step is relatively short and normally less than 1 minute. After the second reactor (stripper), superheated vapor and fiber are separated in a cyclone and part of the superheated vapor is recirculated after heating to the stripper fiber inlet and part is transferred to the system for chemical recovery.

The acetylated fiber from the second reactor may still contain some anhydride and acetic acid that is sorbed or occluded in the fiber. In order to remove remaining chemicals and the odor from them, the acetylated fiber is introduced into a second stripper step also acting as a hydrolysis step. The transporting medium in this step is superheated steam, and any remaining anhydride is rapidly hydrolyzed to acetic acid which is evaporated. The acetylated fiber emerging from the second stripper is essentially odor free and is completely dry. The acetylated fiber can, as a final treatment be resinated for fiberboard production or conditioned and baled for other uses as desired. The steam and acetic acid removed overhead from this step is processed in the chemical recovery step.

The preferred recovery of chemicals includes separation of acetic anhydride from acetic acid by distillation, and conversion of acetic acid, recovered as well as purchased, by the ketene process into anhydride. The raw materials entering the

production site is thus fiber and acetic acid to cover the acetyl groups introduced in the fiber. This minimizes the transportation costs and the chemical costs and makes the process much more cost effective.

ECONOMICS

Table 1 shows the production costs of producing acetylated fiber using the process described above. It is obvious that there is an economy of scale. These figures are based on the ketene to anhydride chemical recovery process as the cost of acetylated fiber is almost twice the cost without chemical recovery. These estimated costs do not include the cost of fiber.

Table 1 - Cost of production of acetylated fiber in Swedish crowns (SEK)

	Annual production (tonnes per year)		
	8,000	20,000	100,000
Total Investment, MSEK	78	142	365
Fixed costs, SEK/ton	1500	1100	550
Operating cost, SEK/ton	3000	2900	2450
Personnel cost (5 shift), SEK/ton	200	100	50
TOTAL COST, SEK/Kg	4.70	4.10	3.05

THE PILOT PLANT

Figure 2 shows the pilot plant being assembled. The plant was built during the spring of 2000, taken apart, and reassembled in Kvarntorp, Sweden in the summer. The designated production rate is 500 Kg per hour or 12 tones per day or about 4000 tones per year of acetylated wood fiber. The process can be applied to any lignocellulosic fiber and fiber other than wood will be used.

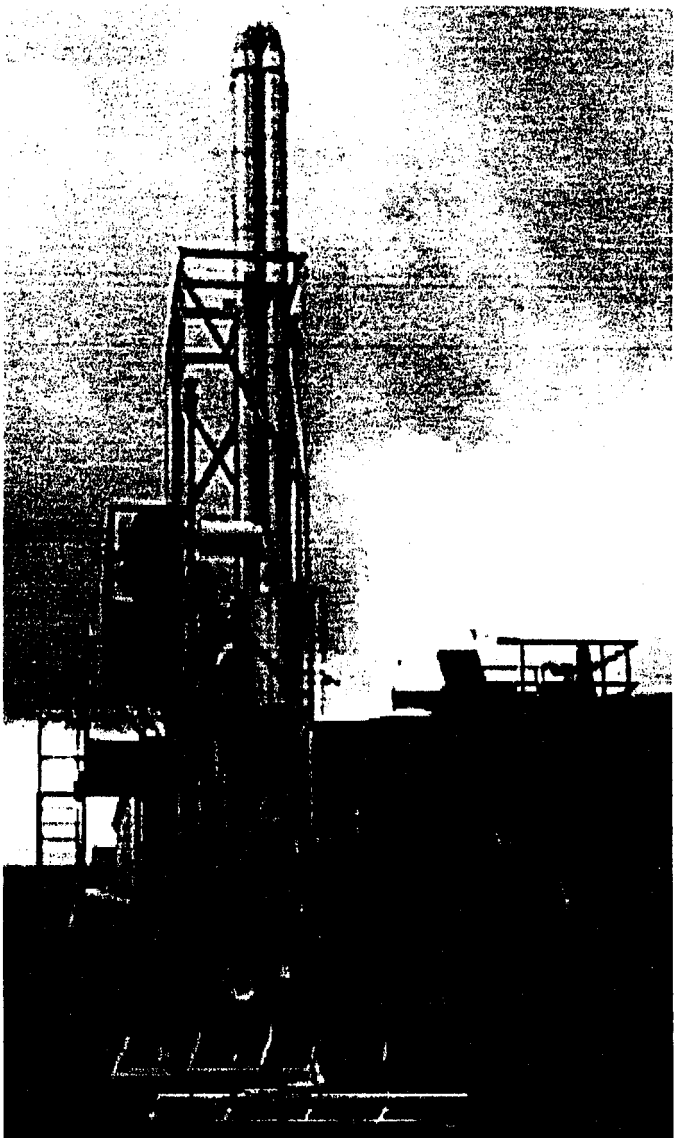

Figure 2 - Acetylation pilot plant being assembled in Kvarntorp, Sweden

PROPERTIES OF ACETYLATED FIBER AND FIBER BOARDS

Since the pilot plant is not in operation at the time of this writing, no data on properties of acetylated fiber or fiberboards can be presented at this time. However, it has been shown by many authors that the properties of acetylated fiber are the same regardless of the method of acetylation with the exception of the ketene process. It would, therefore, be expected that there will be no difference between the fiber and board produced from the new pilot plant as compared to fiber and other products produced from previous acetylation studies.

Studies on biological resistance, for example, using a fungal cellar containing unsterile soil, showed that wood acetylated by acetic anhydride vapor, refluxing acetic anhydride in xylene, and a limited amount of liquid acetic anhydride alone, were all effective in preventing attack by the microorganisms present in the soil (Rowell et al. 1986a). In general, resistance to attack by micro-organisms is achieved at acetyl add on levels above about 15 weight percent gain (WPG).

Similar studies on the reduction in moisture sorption and increases in dimensional stability using different methods of acetylation have been reported (Nilsson et al., 1988). Equilibrium moisture content (EMC) is reduced by half and a level of dimensional stability of about 90+% is achieved at WPG's of approximately 15 to 20.

Recently, extensive studies were conducted using acetylated fiber produced by British Petroleum in cooperation with the authors using a similar process to the one described in this paper (Westin, 1998). This work confirmed earlier results on moisture sorption, dimensional stability and biological resistance but also presented results on mechanical properties of fiberboards made from acetylated fiber. Table 2 shows data on bending strength (MOR), modulus of elasticity (MOE) and internal bond strength (IBS) of control and acetylated fiberboards made from a softwood fiber. Fiberboards made from

Table 2 - Mechanical properties of softwood fiberboards (900 Kg/m^3) made from control and acetylated fiber using a 10% by weight phenolic resin.

Type of fiber	Modulus Of Rupture MOR (MPa)	Modulus of Elasticity MOE (GPa)	Internal Bond Strength IBS (MPa)
Control	53	3.7	2.3
Acetylated	61	4.1	2.3

acetylated fiberboards showed slightly higher values for MOR and MOE and equal values for IBS as compared to unmodified fiberboards.

CONCLUSIONS

A new method for the acetylation of lignocellulosic fibers has been developed which is faster and less costly than all previous methods. Complete removal of acetic acid is done using high pressure steam so concern for residual acid has been eliminated. Fiber from the process is being tested for many applications. Fiberboards made using acetylated fiber are dimensionally stable and resistant to biological attack. Acetylated fiberboards are presently under long term tests, in adverse outdoor environments, in several parts of the world, as a possible alternative to preservative treated wood.

REFERENCES

Ami, P.C., J.D. Gray, and R.K. Scougall. 1961. Chemical modification of wood.II. Use of trifluoroacetic acid as catalyst for the acetylation of wood. J. Applied Chem. 11, 163-170.

Baird, B.R., 1969. Dimensional stabilization of wood by vapor phase chemical treatments. Wood and Fiber 1(1):54-63.

Clermont, L.P. and F. Bender. 1957. ffect of swelling agents and catalysts on acetylation of wood. Forest Prod. J. 7(5): 167-170.

Goldstein, I.S., E.B. Jeroski, A.E. Lund, J.F. Nielson, and J.M. Weater. 1961. Acetylation of wood in lumber thickness. Forest Prod. J. 1 1(8):363-370.

Koppers' Acetylated Wood. 196 1. Dimensionally stabilized wood. New Materials Technical Information No. (RDW-400) E-106, 23 pp.

Nilsson, T., R.M. Rowell, R. Simonson, and A.-M. Tillman. 1988. Fungal resistance

of pine particle boards made from various types of acetylated chips. Holzforschung 42(2):123-126.

Nelson, H.L., D.I. Richards and R. Simonson. 1999. Acetylation of lignocellulosic materials. European patent EP 0 650 998 B1.

Nikitina, N. Quality control of acetylated wood. 1977. Latvijas Lauksaimniecibas Akademijas Raksi, 130, 54-55.

Otlesnow, Y. and N. Nikitina. 1977. Trial operation of a commercial installation for modification of wood by acetylation. Latvijas Lauksaimniecibas Akademijas Raksi, 130, 50-53.

Ozolina, I, and K. Svalbe. 1972. Acetylation of wood by an anhydrone catalyst. Latvijas Lauksaimniecibas Akademijas Raksi, 65, 47-50.

Ridgway, W.B. and H.T. Wallington. 1946. Esterification of wood. British Patent 579255.

Risi, J. and D.F.Arseneau. 1957. Dimensional stabilization of wood. I. Acetylation. Forest Prod. J. 7(6):210-213.

Rowell, R.M. 1983. Chemical modification of wood: A review. Commonwealth Forestry Bureau, Oxford, England, Vol. 6, N0. 12, p. 363-382.

Rowell, R.M., Tillman, A.-M., and R. Simonson. (1986a). Vapor phase acetylation of southern pine, Douglas-fir, and aspen wood flakes. J. Wood Chem. and Tech., 6(2): 293-309.

Rowell, R.M., A.-M. Tillman, and R. Simonson. (1986b). A simplified procedure for the acetylation of hardwood and softwood flakes for flakeboard production. J. Wood Chem. and Tech., 6(3): 427-448.

Rowell, R.M., R.H.S. Wang, and J.A. Hyatt. 1986c. Flakeboards made from aspen and southern pine wood flakes reacted with gaseous ketene. J. Wood Chem. and Tech., 6(3): 449-471.

Rowell, R.M., R. Simonson, S. Hess, D.V. Plackett, D. Cronshaw, and E. Dunningham.
1994. Acetyl distribution in acetylated whole wood and reactivity of isolated wood cell wall components to acetic anhydride, Wood and Fiber Sci. 26(1): 11-18.

Stamm, A.J. and H. Tarkow. 1947. Acetylation of wood and boards. U.S. Patent 2417995.

Svalbe, K. and I. Ozolina. 1970. Modification of wood by acetylation. Plast. Modif. Drev. 145-146.

Tarkow, H. 1945. Acetylation of wood with ketene. Office Report, Forest Products Laboratory, USDA, Forest Service, 2 pp.

Tarkow, H. 1959. A new approach to the acetylation of wood. Office Report, Forest Products Laboratory, USDA, Forest Service, 9 pp.

Truksne, D. and K. Svalbe. 1977. Water-repellent properties and dimensional stability of acetylated pine wood in relation to the degree and method of acetylation. Latvijas Lauksaimniecibas Akademijas Raksi, 130, 26-31.

Westin, M. 1998. High-performance composites from modified wood fiber. Ph.D. Thesis. Department of Forest Products and Chemical Engineering, Chalmers University of Technology, Goteborg, Sweden.

Problem 2 **Chemical and structural modifications of wood–based materials are required to improve properties and to maximize end use performance of bio–based composite materials.**

FY2001 Research Attainments

Publications

Research Unit

Simonson, Rune; Rowell, Roger M. 2000. A new process for the continuous acetylation of lignoceilulosic fiber. In: Proceedings of the 5th Pacific Rim bio–based composites symposium; 2000 December 10–13; Canberra, Australia. Canberra, Australia: Department of Forestry, The Australian Natlonai University: 190-196.