Chemical Modification of Wood: A Journey from Analytical Technique to Commercial Reality

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Outline

- Definitions
- Introduction
- Reaction Systems
- Acetylation
  - History
  - Properties
    - Moisture
    - Biological
    - Other
- Applications
- Projected Costs
- Newest Technologies
- Conclusions

Chemical Modification

A chemical reaction between some reactive part of wood and a simple single chemical reagent, with or without catalyst, to form a covalent bond between the two.

This excludes chemical impregnations, monomer impregnation's that polymerize *in situ* but do not bond with the cell wall, polymer inclusions, coatings, heat treatments, etc.

Why Chemical Modification

Analytical technique used to isolate cell wall polymers

Change chemistry, change properties, change performance

Another way to understand wood by changing a property and studying the change

Consider

- Wood was designed by nature to perform in a wet environment
- Nature has a very efficient recycling system to degrade wood back to its original building blocks of water and carbon dioxide
  - Biological, thermal, ultraviolet, moisture: Oxidation, Hydrolysis, Reduction, Dehydration, Free radical depolymerization

Assumptions

- The properties of any resource are, for the most part, a result of the chemistry of the resource,
- If you change the chemistry to change properties,
- If you change properties, you change performance.

Change Chemistry to Improve:

- Moisture sorption
- Dimensional stability
- Decay resistance
- Ultraviolet degradation resistance
- Thermal stability
- Insect resistance
- Hardness
- Toughness
- Compatibility with other resources

Reaction Systems

Anhydrides

WOOD-OH +RC(=O)-O-C(C=O)-R → WOOD-O-C(=O)-R

Isocyanates

WOOD-OH + R-N=C=O → WOOD-O-C(=O)-NH-R

Epoxides

WOOD-OH + R-CH(-O-)CH_2 → WOOD-O-CH_2-H(OH)-R

Acetylation Chemistry

WOOD-OH + $CH_3C(=O)$-O-$C(=O)$-CH_3 →

Acetic Anhydride

WOOD-O-$C(=O)$-CH_3 + $CH_3C(=O)$-OH

Acetylated Wood **Acetic Acid**

History of Wood Acetylation

1928 – Fuchs acetylated pine to isolate lignin
1928 – Horn and Suida and Titsh acetylated beech to remove hemicelluloses
1930 – Suida Austria Patent to acetylated wood.
1945 – Tarkow acetylated balsa for decay resistance
1946 – Tarkow, Stamm and Erickson acetylated wood for dimensional stability
1961 – Goldstein et al. and Koppers' acetylated wood for commercialization
1977 – Otlesnov and Nikitina acetylated Wood for commercialization
1980's – Daiken in Japan commercialized wood acetylation for flooring
1986 – Rowell, Sinonson and Tillman limit anhydride, no catalyst

Changes in Wood Due to Acetylation

Percent Weight Gain	Change in Wood Volume	Volume of Chemical Added
17.5	3.0 cm^3	2.9 cm^3

Weight gain and acetyl analysis agree

Change in color: Light colored woods slightly darker, dark colored woods, slightly lighter

Stability of Acetyl Groups in Pine and Aspen Flakes after Cyclic Exposure Between 90% RH and 30% RH

Wood	Acetyl content (%) after cycle (number)				
	0	13	21	33	41
Pine	18.6	18.2	16.2	18.0	16.5
Aspen	17.9	18.1	17.1	17.8	17.1

Cycle time = 3 months

Distribution of Acetyl Groups in Wood

- Lignin fastest to react
- Almost complete substitution of lignin hydroxyl groups
- Approximately 25% of holocellulose hydroxyl groups substituted
- No cellulose hydroxyl substituted (some accessible surface hydroxyl on amorphous regions)

Acetylation for Dimensional Stability

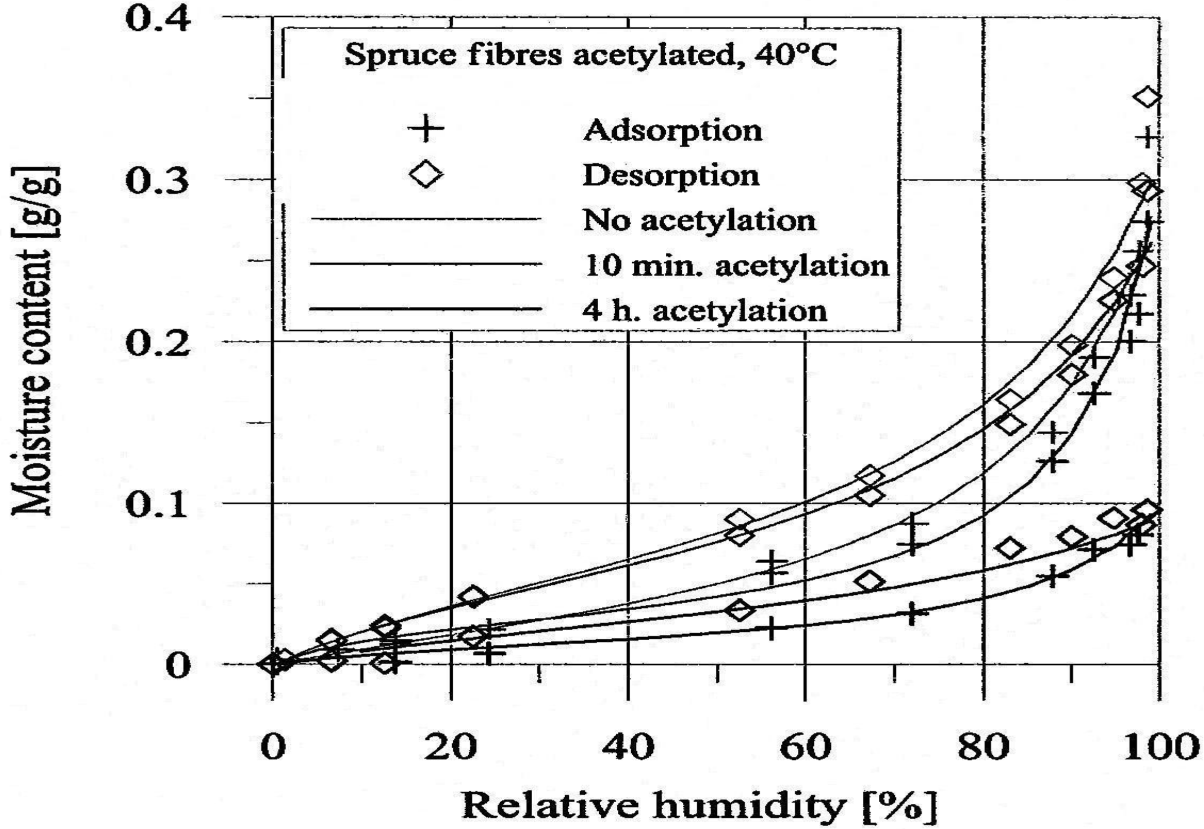
- Effects on moisture sorption
- Effects on fiber saturation point
- Effects on liquid water sorption

Swelling pressure of wood

Equilibrium Moisture Content of Acetylated Pine Particleboard

Weight Percent Gain	Equilibrium Moisture Content at 27C 30%RH	65%RH	90%RH
0	5.8	12.0	21.7
6.0	4.1	9.2	17.5
10.4	3.3	7.5	14.4
14.8	2.8	6.0	11.6
18.4	2.3	5.0	9.2
20.4	2.4	4.3	8.4

Sorption Isotherm for Acetylated Spruce



Fiber Saturation Point for Acetylated Pine and Aspen

WPG	Pine (%)	Aspen (%)
0	45	46
6	24	--
8.7	--	29
10.4	16	--
13.0	--	20
17.6	--	15
18.4	14	--
21.1	10	--

Dimensional Stability

24 hour water soak

	S	ASE
Solid Pine		
Control	13.8	----
Acetylated	4.2	69.3
Pine Fiberboard (5% phenolic resin)		
Control	21.3	----
Acetylated	2.1	90.1

Effects of Size of Spruce Specimen on Acetyl Content

Specimen	WPG	Acetyl Content
Chips Acetylated	14.2	15.6
Acetylated Chips to Fiber	14.2	15.4
Chips to Fiber and then Acetylated	22.5	19.2
Acetylated Chips to Fiber	22.5	19.4
Acetylated Chips to Fiber and again Acetylated	20.4	20.5

Mechanism of Effectiveness

- Single site reaction reacting with **accessible** cell wall polymer hydroxyl groups
- Stable cell wall bulking from dry to the green volume
- Chemical modification does not exceed the elastic limit of the cell wall

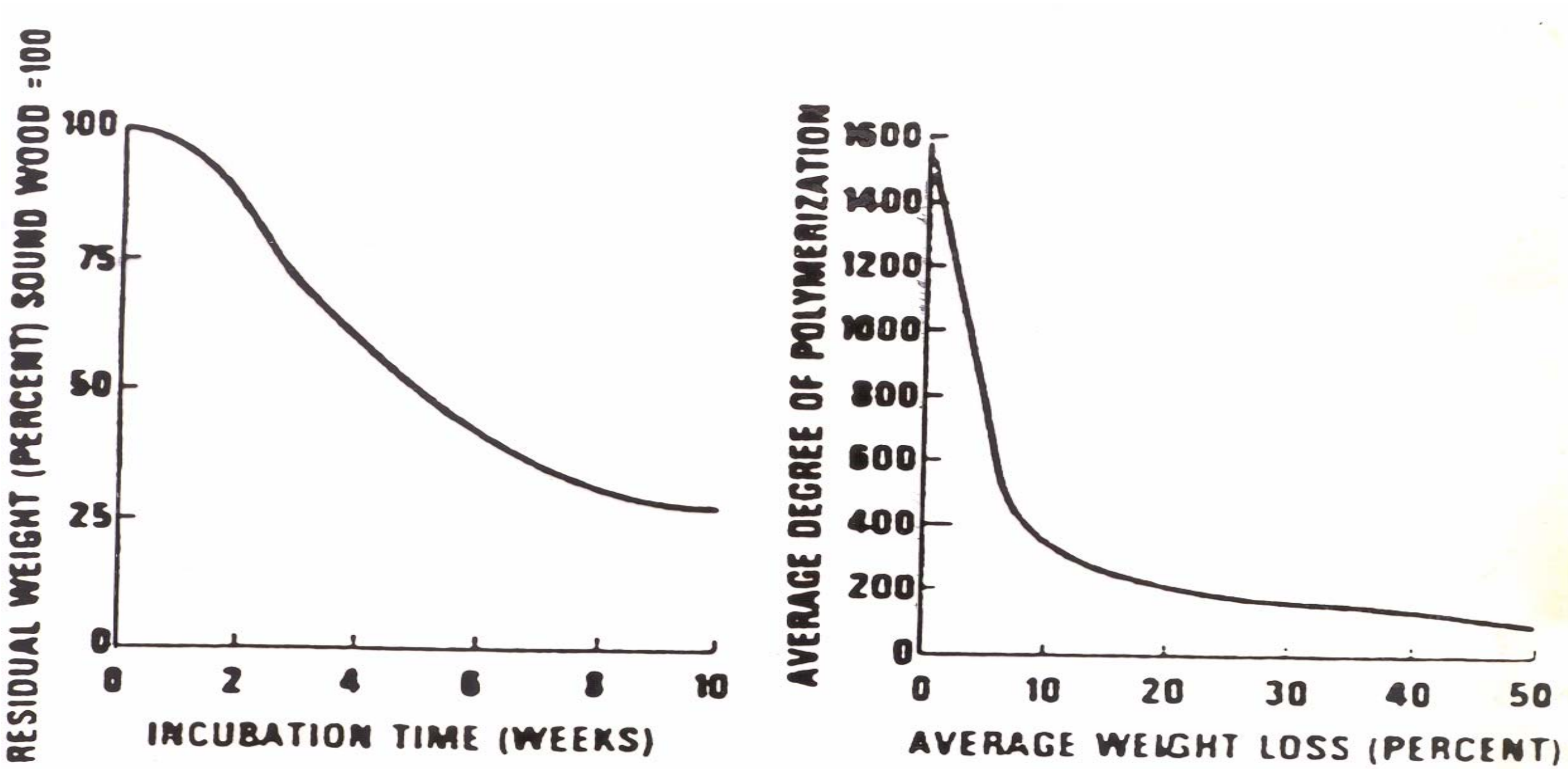
Acetylation for resistance to biological attack

- Brown-rot fungi
- White-rot fungi
- Termites
- Marine organisms

Resistance of Acetylated Pine Particleboard to Decay Fungi

Acetyl Weight Gain (%)	Weight Loss After 12 Weeks: Brown-rot Fungus (%)	Weight Loss After 12 Weeks: White-rot Fungus (%)
0	61.3	7.8
6.0	34.6	4.2
10.4	6.7	2.6
14.8	3.4	<2
17.8	<2	<2

Strength Loss vs Weight Loss for Brown-Rot Fungi



Brown-Rot Attack on Wood

ENZYMES → HEMICELLULOSES

(Energy source for generation of chemical oxidation system)

→ CELL WALL POLYMER MATRIX

(Strength losses)

(Energy source for generation of β–glucosidases)

→ WEIGHT LOSS

Acetylated Pine Particleboards in Fungal Cellar (Brown-, White-, Soft-Rot Fungi)

WPG	Rating at intervals (Months)							
	2	3	4	5	6	12	24	36
0	S/2	S/3	S/3	S/3	S/4	--	--	--
7.3	S/0	S/1	S/1	S/2	S/3	S/4	--	--
11.5	0	0	S/0	S/1	S/2	S/3	S/4	--
13.6	0	0	0	0	S/0	S/1	S/2	S/4
16.3	0	0	0	0	0	0	0	0
17.9	0	0	0	0	0	0	0	0

4 = Destroyed, 3 = Badly attacked, 2 = Some attack, 1 = Evidence of attack, 0 = No attack, S = Swollen

Resistance of acetylated pine to attack by *Reticulitermes flavipes* (2 week test)

Chemical	WPG	Weight Loss
	---------- (%) --------------	
Control	0	31
	10.4	9
	17.8	6
	21.6	5

Ratings of acetylated southern pine exposed to a marine environment[1]

WPG	Years of exposure	Mean rating due to attack by *Limnoriid and Teredinid Borers*[2]	*Shaeroma terebrans*[3]
0	1	2-4	3.4
22.0	3	8	8.8

[1] Rating system - 10 = no attack; 9 = slight attack; 7 = some attack; 4 = heavy attack; 0 = destroyed

[2] Installed in Key West, FL.

[3] Installed in Tarpon Springs, FL

Mechanism of Effectiveness

- Stabilizes the hemicelluloses against enzyme attack (no water for hydrolysis)
- Changes conformation and configuration for enzymatic reactions
- Moisture content too low for biological attack on all cell wall polymers

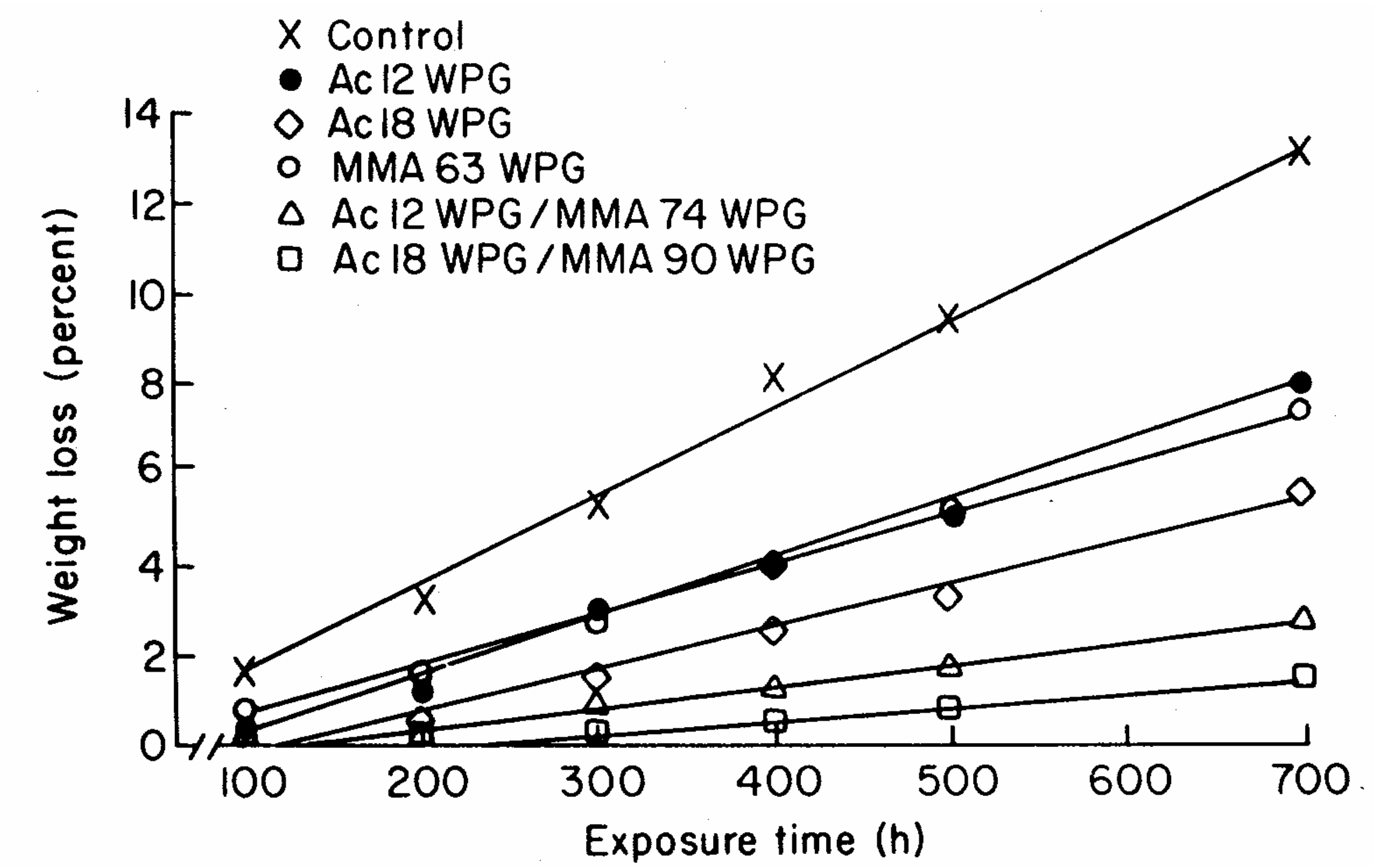
Other Properties

- Weathering (UV Protection)
- Thermal
- Strength

Weight loss and erosion of acetylated aspen after 700 hours of accelerated weathering

WPG	Weight loss (%/hr)	Erosion Rate (μm/hr)	Reduction in Erosion (%)	Depth of Penetration (μm)
0	0.019	0.121	---	199-210
21.2	0.010	0.059	51	85-105

Weathering of Acetylated and Methyl Methacrylate Treated Pine



Thermal properties of control and acetylated pine fiber

WPG	Temperature of Maximum Weight Loss (ºC)	Heat of Combustion (KCal/g)	Rate of Oxygen Consumption (MM/g sec)
0	335/375	2.9	0.06/0.13
21.1	338/375	3.1	0.08/0.14

Strength properties of control and acetylated pine fiberboards (10% phenolic resin)

WPG	MOR (MPa)	MOE (GPa)	IBS (MPa)
0	53	3.7	2.3
19.6	61	4.1	2.3
ANSI Standard	31	---	---

Shear Strength

Yellow popular, Resorcinol formaldehyde - spread rate 70 lbs of mixture to 1000 sq. ft.

Sample	Shear Strength (MPa)	Wood Failure (%)
Control		
Dry	12.2	97.2
Wet	5.6	98.6
Acetylated*		
Dry	12.9	96.4
Wet	9.4	91.4

* 21 WPG

Application of Acetylated Wood

- Decking - Pressure treated - $3.2 billion – 80% of total market
- Wood/plastic lumber
  - 2005 – 16% of market projected
- Acetylated wood
  - 20% - Limited by anhydride supply

Other Applications

- Exterior doors – both solid and molded
- Exterior windows
- Exterior structural and nonstructural
- Exterior siding
- Interior wet rooms

Industries in Acetylated Wood

Daiken – Japan (α-Wood)

A-Cell – Sweden

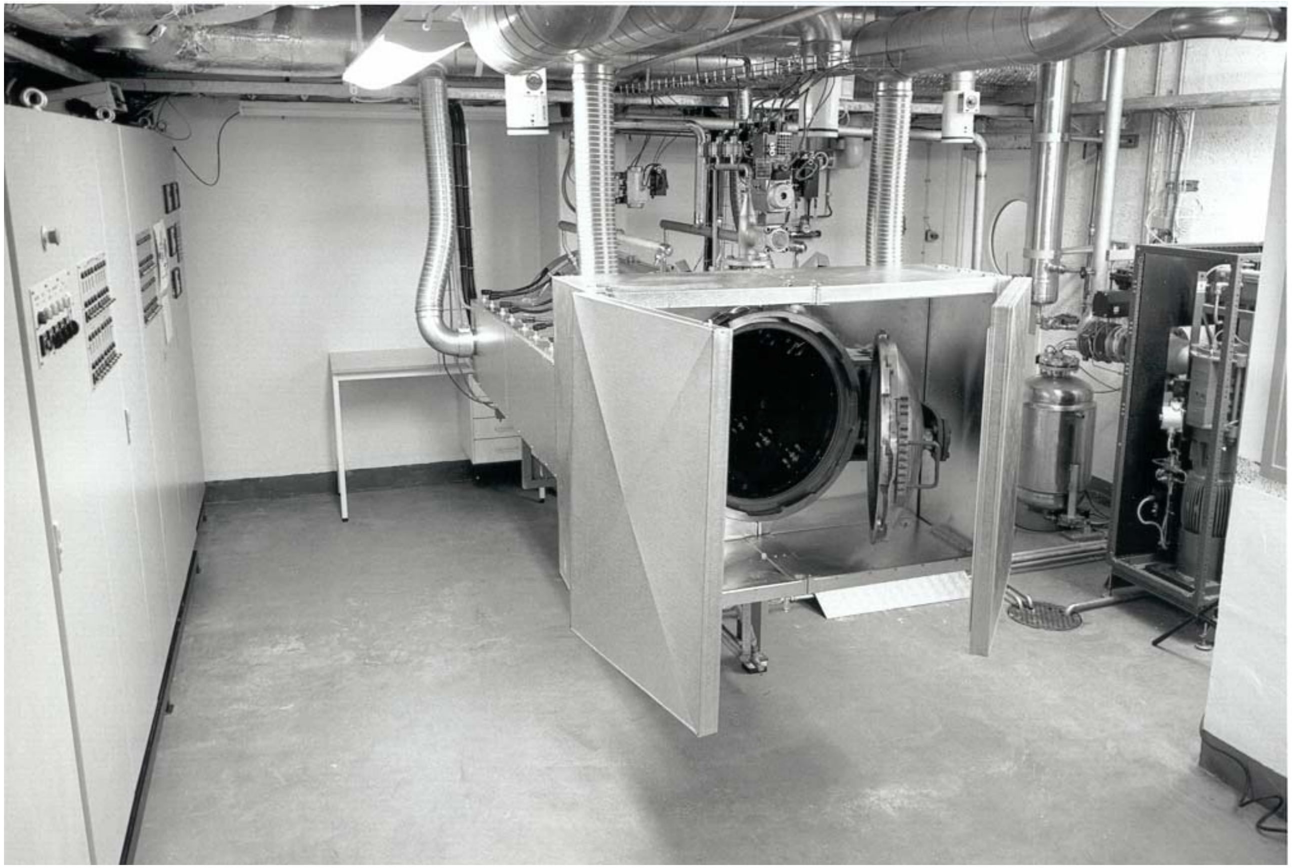
TitanWood – Netherlands and England

Weyerhaeuser – United States

Cost of Solid Wood for Decking

Unit	Unit Size	Cost/ft
Standard Treated	5/4 x 6 x 8	$ 0.50 - 65
Plastic Lumber	5/4 x 6 x 8	$ 2.75 - 5.90
Acetylated Lumber	5/4 x 6 x 8	$ 3.50 – 4.50

Microwave Reactor in Sweden for Solid Wood



Cost Projections for Acetylated Fiber

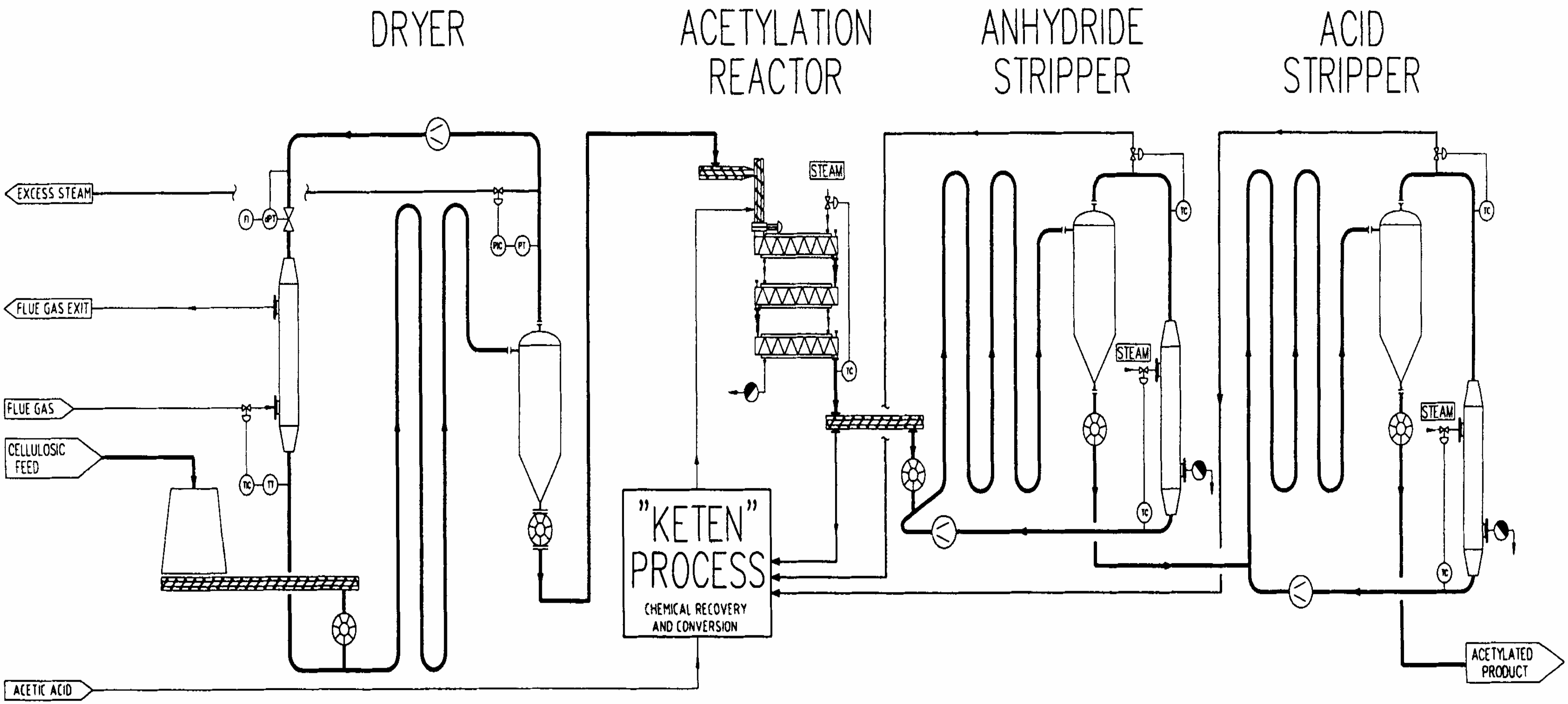
Annual production (tonnes per year)

	8,000	10,000	20,000	100,000
COST, US$/lb#		**.31**		
COST, US$/lb*	**.32**		**.27**	**.20**

 # BP Chemical 1992

*** A-Cell 2004**

Fiber Acetylation Pilot Plant in Sweden


DRYER
ACETYLATION
REACTOR
ANHYDRIDE
STRIPPER
ACID
STRIPPER
EXCESS STEAM
FLUE GAS EXIT
FLUE GAS
CELLULOSIC
FEED
ACETIC ACID
STEAM
STEAM
STEAM
"KETEN"
PROCESS
CHEMICAL RECOVERY
AND CONVERSION
ACETYLATED
PRODUCT

Conclusions

- Chemical modification provides a means of improving properties and performance of wood and wood composites
- Acetylation of wood provides a global infrastructure for improving dimensional stability, biological resistance with little change in weathering or thermal stability
- Acetylation will probably find its first application in the United States in residential decking and outdoor windows and doors.

Future Research

- Holistic approach to chemical modification (oxidation, hydrolysis, dehydration, reduction, free radical)
- More specific chemistry – only what you want and no more
- Cold plasma modification
- Enzyme modification

From the Wisdom of Pogo

WE ARE SURROUNDED BY
INSURMOUNTABLE OPPORTUNITIES