Wood Chemistry

Wood Chemistry

PSE 406 / Chem E 470

Lecture 18
Chemical Isolation and Analysis II
Hemicelluloses

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Class Agenda

- How are hemicelluloses separated from cellulose and lignin?
- How are individual hemicelluloses separated?
- How is the composition of individual hemicelluloses determined?
- How are the linkages determined?

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How are hemicelluloses separated from cellulose and lignin?

- Generate Holocelulose
- Remember….in this procedure lignin is removed through the action of sodium chlorite

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How are the hemicelluloses separated from cellulose?

- Cellulose is not soluble in almost any solvents.
- What are hemicelluloses soluble in?
- NaOH or KOH!!!!!
  - » Ok……they are mostly soluble
- Quick question…what happens to acetyl groups?
  - » Saponification

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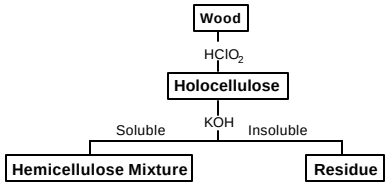
Isolation Scheme: Softwoods



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What is in the residue?

- Cellulose
  - » It is not soluble in much of anything
- Galactoglucomannan (not the water soluble one)
  - » It turns out that this hemicellulose is not all that alkali soluble at this level of KOH
  - » It takes the addition of NaOH and borate to solublize this material

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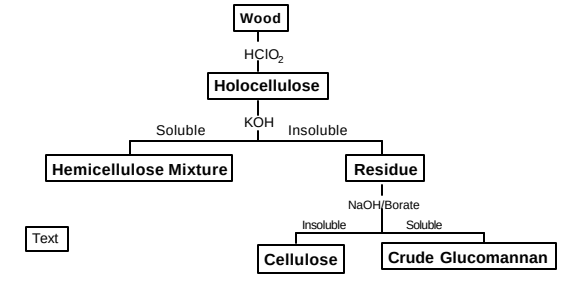
Isolation Scheme: Softwoods



Ref: Timelt TAPPI 44, 88-96 1961

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What makes up the rest of the hemicellulose mixture?

- Xylans
- Galactoglucomannans (water soluble)
- Maybe some pectins, a little glucans, and who know what else
- We are mainly concerned with the top two….
  - » How do we separate the xylans from the galactoglucomannans?

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Barium

- Because of the orientation of the C2 and C3 hydroxyl groups in mannose, it will form an insoluble complex with barium ions.
- Therefore the addition of $Ba(OH)_2$ will cause gluomannans to precipitate out of solution

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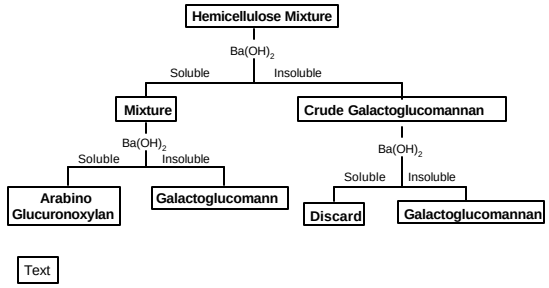
Isolation Scheme:Softwoods



Ref: TimeIt TAPPI 44, 88-96 1961

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How is the composition of individual hemicelluloses determined?

- How can hemicelluloses be broken down into individual sugars.
- Acid hydrolysis of glycosidic linkages !!!!!!!

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Hemicellulose Analysis

- The individual sugars are quantified using gas or liquid chromatography.
  - » Often the individual components require derivitization before analysis.
  - » Other analytical techniques are used to positively identify components

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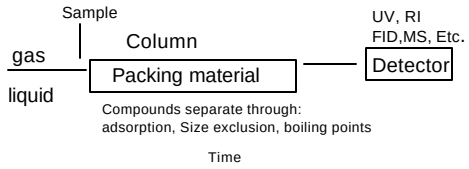
Chromatography

- Chromatography is the process in which chemicals are transported by liquid or gas past a stationary phase. The individual components are attracted bt different degrees to the stationary phase and thus travel at different speeds and are separated.



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Derivitization

- Gas Chromatography - Chemicals to be analyzed must be volatile: Sugars and uronic acids are not volatile.
- Blocking hydroxyl groups will make chemicals volatile.
- Derivitization procedures:
  - » Methylation
  - » Acetylation
  - » Silylation

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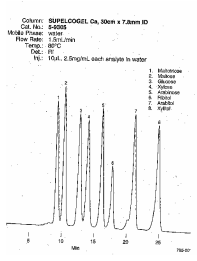
Chromatography

- Once the components are separated, they are detected by a number of different types of systems.
- A chromatograph is produced in which the components are seen as peaks.
- Quantification is accomplished by measuring the peak area



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Determination of Linkages

- How is it possible to determine how the individual sugars are linked?
- Methylation of the free hydoxyl groups
- Acid Hydrolysis
- Chromatographic determination of products
- Another method to determine linkages is the Smith degradation which involves periodate oxidation, borohydride reduction and very mild acid hydrolysis. We are not going to cover this reaction.

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Pyranose? Furanose?

- Mild hydrolysis of hemicellulose results in the presence of monomers, dimers, trimers, etc of the hemicelluloses.
  - » These materials can be separated by chromatography and compared to known dimers.