Wood Chemistry

Wood Chemistry
PSE 406 / Chem E 470

Lecture 19
Lignin Analysis

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Important Questions

- How much lignin is in a sample?
  - » Wood
  - » Plant Material
  - » Pulp
- What is the structure of this lignin?
  - » Molecular weight
  - » Linkages
  - » Functional groups

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Quantification of Lignin

- Wood and non-woody materials
  - » Acid Insoluble lignin (along with acid soluble lig)
- Pulp
  - » Kappa number
- Other non woody materials (or I don't have a large sample to work with)
  - » Acetyl bromide

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Acid Insoluble Lignin (Klason)

- Goal is to destroy carbohydrates leaving lignin
  - » Lignin condenses (reacts with lignin) to become very water insoluble (it becomes very large)
  - » Acid cleaves glycosidic linkages in carbohydrates forming individual sugars.
  - » Sugars dissolve in water(acid) and lignin does not

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Klason Procedure

- Wood meal (or pulp) is treated with 72% H_2SO_4 for 2 hours. The material is then diluted to 3% H_2SO_4 and then boiled for 4 hours.
  - » These two steps dissolves the carbohydrates leaving chunks of lignin floating in the acid
- The lignin is filtered, washed and weighed.

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Acid Soluble Lignin

- A certain percentage of the lignin is not insoluble in the Klason lignin procedure
  - » This amount is very small with softwoods but higher >5% in hardwoods and grasses.
- The filtrate from the Klason procedure is collected and the UV absorbtivity is checked.
  - » Lignin absorbs UV light, sugars do not
  - » The amount of lignin that is soluble is determined through comparing the UV absorbance to a standard.

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Lignin Content of Pulp

- Pulps contain only small amounts of lignin so a different (and quicker) method is used: the kappa number.
- This procedure is based upon the fact that lignin reacts very quickly with $KMnO_4$ while carbohydrates (mostly) react very slowly.

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Kappa Number Procedure

- Pulp is dissolved in water and reacted with a $KMnO_4$ solution for 10 minutes under very controlled conditions.
  - » The goal is to consume 50% of the $KMnO_4$ in this time.
- Excess $KMnO_4$ is consumed with potassium iodide forming I_2 (iodine).
- The iodine is titrated with sodium thiosulfate to a starch endpoint.

Kappa Number Information

- This method is typically used with pulp containing low amounts of lignin (chemical unbleached pulp).
- It was found about 15 years ago that hexenuronic acids formed during kraft pulping from uronic acids consume $KMnO_4$ thus giving false kappa numbers (if based only on lignin).
- A typical kappa number for an unbleached kraft pulp is around 20.

Kappa to Klason

- Correction factors have been developed to convert kappa numbers to Klason lignin. These factors are different for different processes and species.
- Kraft pulps: % Klason = kappa number * 0.15
- Sulfite pulps: % Klason = kappa number * 0.167 (or 0.187 depending on who did the work).
- Kappa number 20 = ~3% lignin

Acetyl Bromide Procedure

- This procedure was developed to measure lignin content in small samples.
- Samples are dissolved by reaction with acetyl bromide (with a little perchloric acid) in acetic acid.
- The solution is analyzed by UV (remember lignin absorbs, carbohydrates do not).
- The amount of lignin in the sample is determined by comparison against standards.
  - » Every material seems to have a different standard number.

Lignin Structural Analysis

- In an earlier lecture, we discussed the fact that in order to analyze lignin, it must be removed from the plant material. Any process used to do this is going to change the lignin structure to some extent.
  - » In the procedures we have just discussed, the lignin is highly modified.
- Of course if you are analyzing lignins produced in pulping or bleaching they are already highly modified so you don't have to worry about changing their structure.

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MWL (Milled Wood Lignin)

- This preparation is typically considered to give lignin most representative of what is found in the plant.
- The plant material is ball milled under toluene for 48 hours, the toluene removed, and the sample is extracted with dioxane/water for 2 days. After removal of the solvent, the residue is extracted with various other solvents finally leaving pure MWL.
- Typical yield is about 25% of klason lignin.
  - » This brings up the question is the lignin that is being extracted from only one part (easily removed lignin) and therefore not representative of all the lignin.
- In another procedure, cellulose is cleaved with enzymes first thus increasing the yield of lignin.

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Lignin Linkages

- Although newer technologies in polymer analysis (such as C^{13} NMR, etc) over the last 20 years have improved linkage analysis, most of the original work in this area centered around unique chemical techniques.
  - » In these techniques, the lignin was broken down into fragments, the fragments were identified, and then the lignin linkages were determined.

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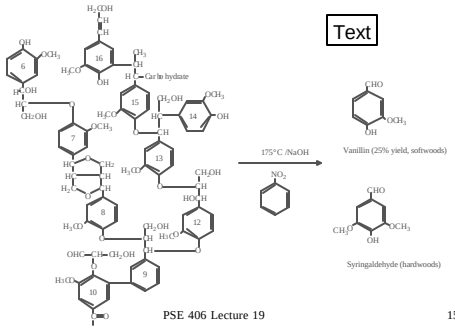
Lignin Structure Elucidation Studies
Nitrobenzene Oxidation



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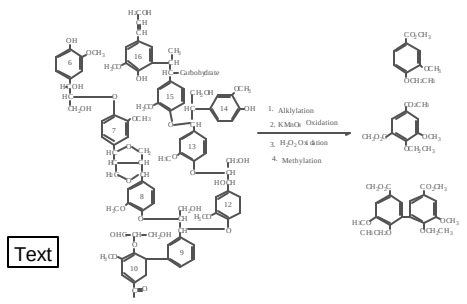
Lignin Structure Elucidation Studies
Permanganate Oxidation



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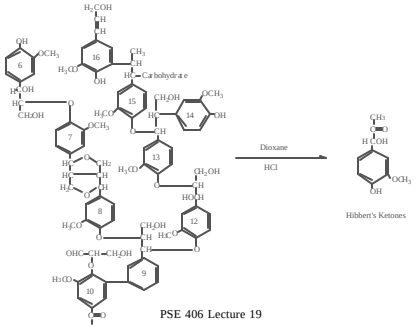
Lignin Structure Elucidation Studies
Acidolysis



Text

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Functional Groups

- I could probably teach half the quarter on the techniques used to determine functional groups…..so all I am going to do is give you a quick summary.
- These techniques are very time consuming so they are not a lot of fun.
- Many researchers perform these analysis through NMR techniques.

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Phenolic Hydroxyl

- This is probably one the of most common analysis because this group is very important in terms of lignin reactivity.
- NMR – yes it is used
- Wet chemistry techniques
  - » There are a large number of different techniques that can be used. A round robin analysis a few years ago on the same sample showed that there is some variation between all these techniques.

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Methoxyl

- NMR
- Wet Chemistry
  - » There are a couple of methods available both of which deal with the cleavage of the methoxyl group followed by quantification of the removed fragments.
  - » Nobody likes doing this.

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Carbonyl, Aliphatic Hydroxyl, etc

- I lumped these all together because there are a variety of time consuming wet chemistry techniques used.
  - » Large variations are seen between all these methods.
- Over all people are happy with the range of numbers generated over the years.

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Molecular Weight

- There has been a lot of work done over the years to determine lignin molecular weight.
- There are a lot of different techniques that have been used.
- There are lots of questions about how good these numbers really are.
- Suffice it to say it is possible to tell the difference between a large fragment and a small fragment
- If you ever want to measure lignin molecular weight, give me a call and I will push you in the right direction.