

# Characterisation of black liquor constituents

Klaus Niemelä, Tarja Tamminen, Taina Ohra-aho

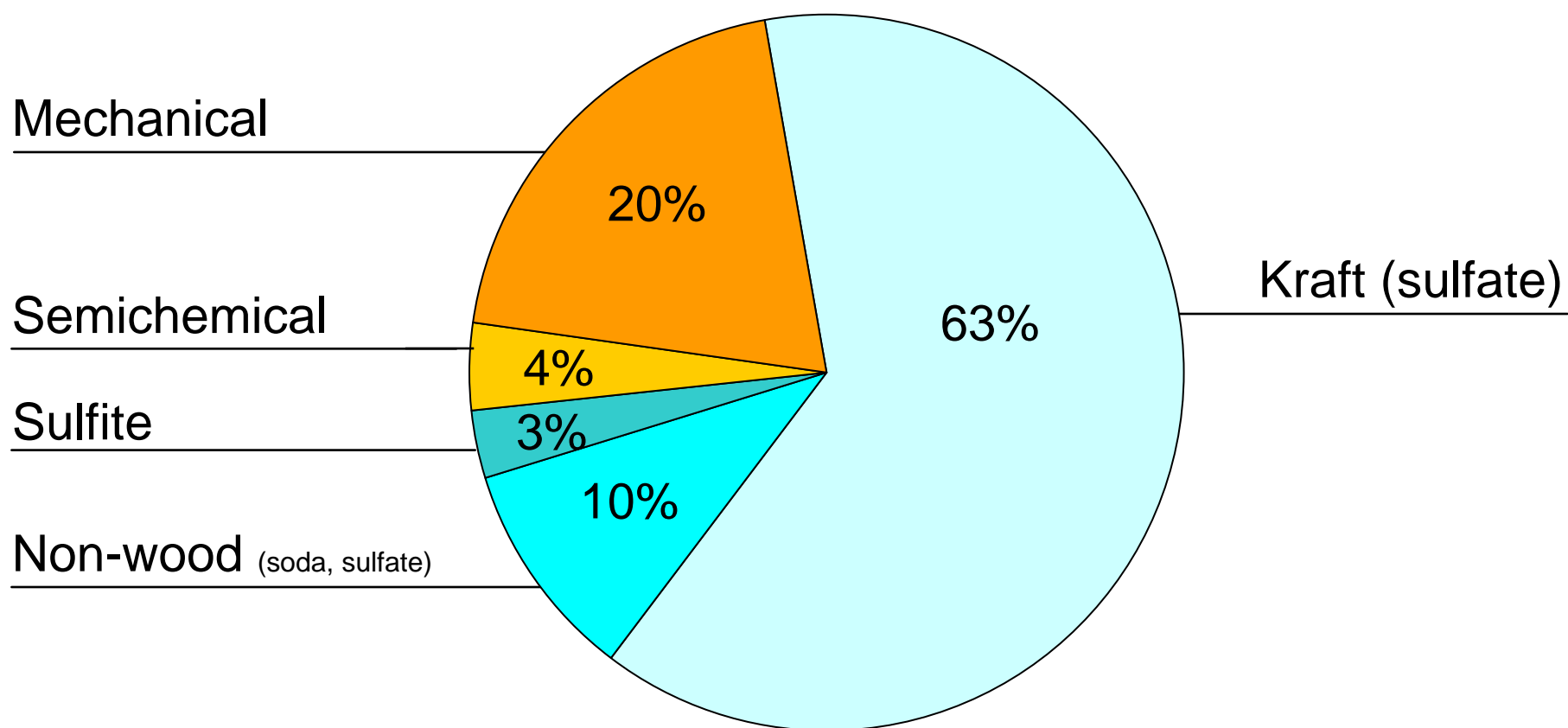
FP0901 Workshop, Wien, Austria

February 4-5, 2010

# Main topics

- Current pulp production and by-products
- Where is potential for new by-products?
- Characterisation of the fractions; analytical methods

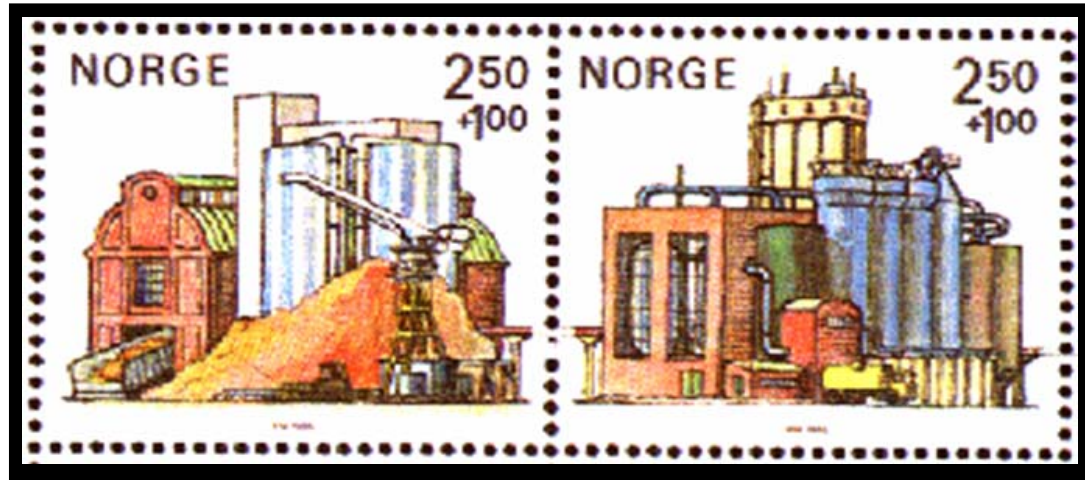
# Global pulp production – 190 million tons



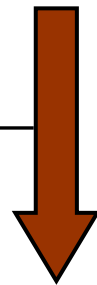
# By-product potential from kraft pulping



Chips  
240 million tons



*Current by-products*  
*<2 million tons*



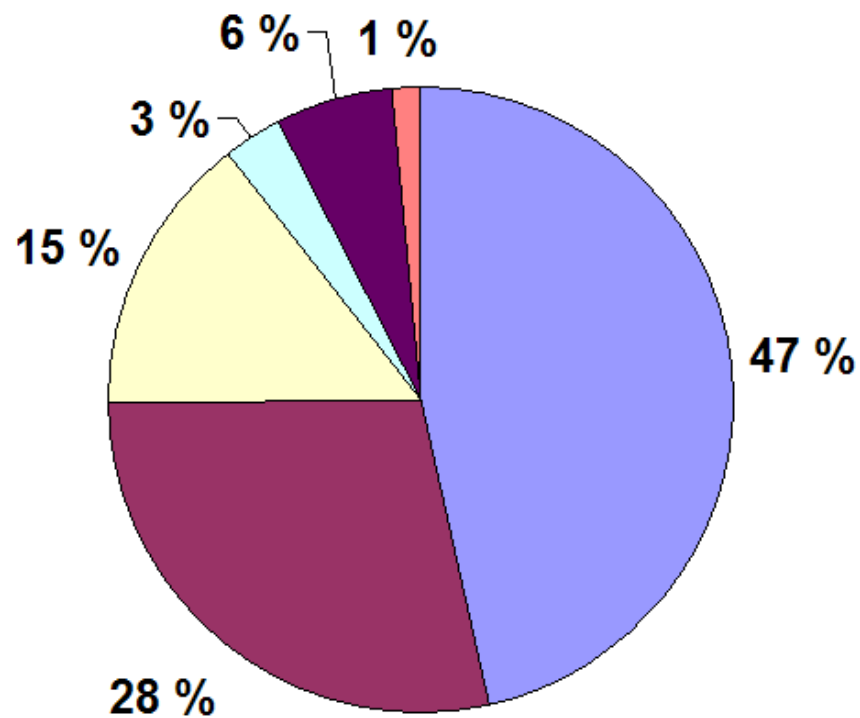
Black liquor organics  
120 million tons



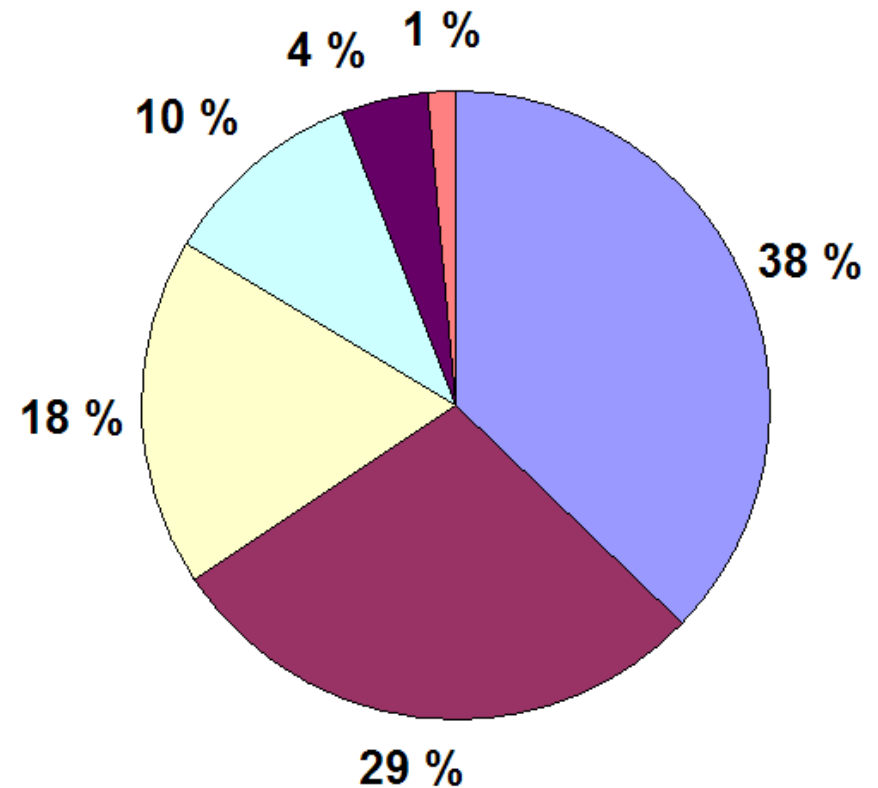
Kraft pulp (wood)  
120 million tons

# Distribution of black liquor organics

## Softwood



## Hardwood



# Tall oil and turpentine

- Production by kraft cooking
  - Tall oil: 1.5 million tons
  - Turpentine: 200,000 tons
- Production by pine tapping
  - Rosin: 700,000 tons
  - Turpentine: 100,000 tons



# Kraft and soda lignin

- "Production" >60-70 million tons
- <100,000 tons isolated for chemical applications



# Other products

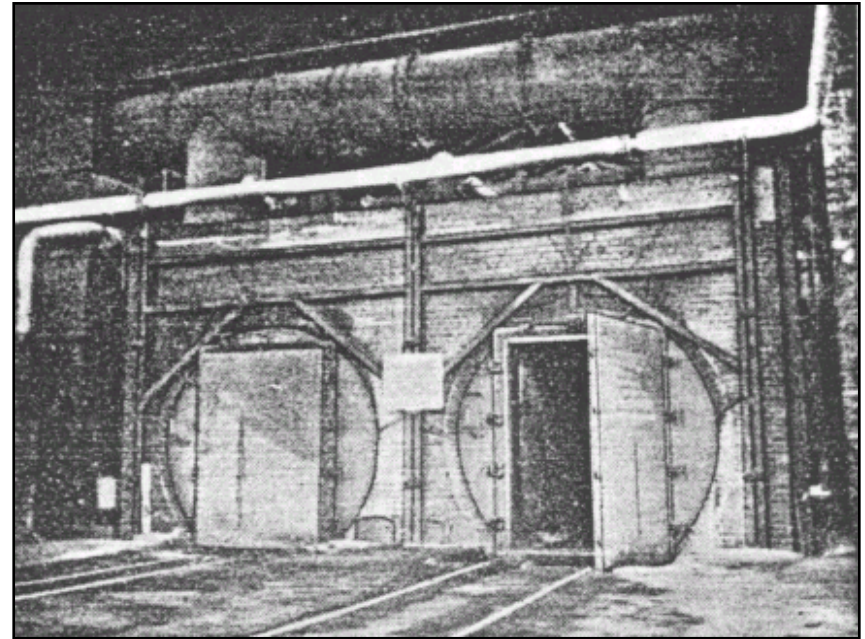
## **Past:**

Methanol, acetone, butanone

Oils (incl. diesel oil)

Ammonia

Prehydrolysis products



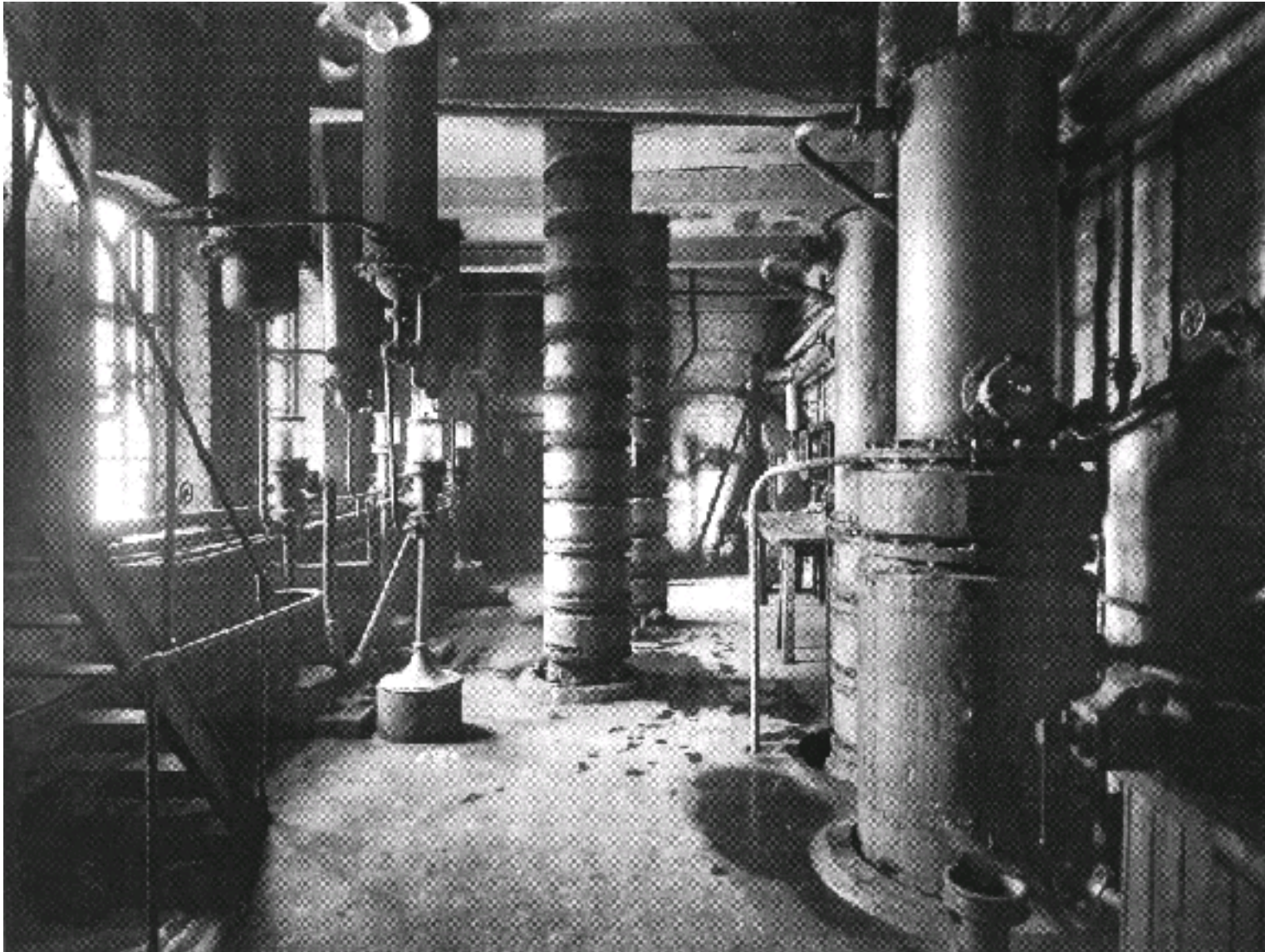
## **Present:**

DMS, DMSO, DMSO<sub>2</sub>



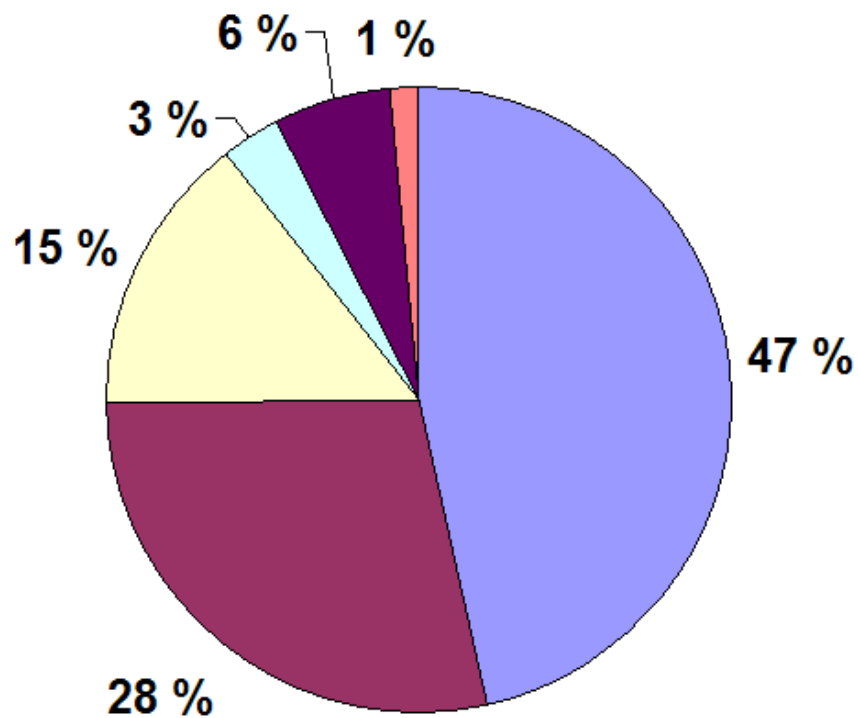


# Pulp mill methanol distillation column, Finland, 1910s

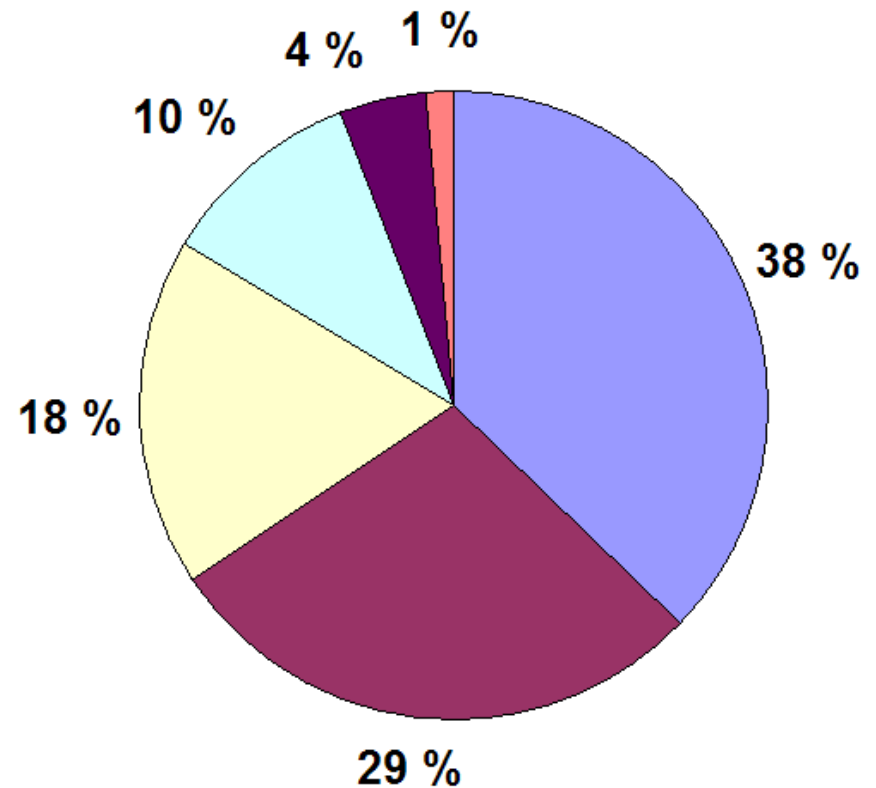


# Distribution of black liquor organics

## Softwood



## Hardwood



# Polysaccharide-derived products

- Hydroxy monocarboxylic acids
- Dicarboxylic acids
- Acetic and formic acids
- Polysaccharides
- Oligosaccharides
- Miscellaneous (minor) products

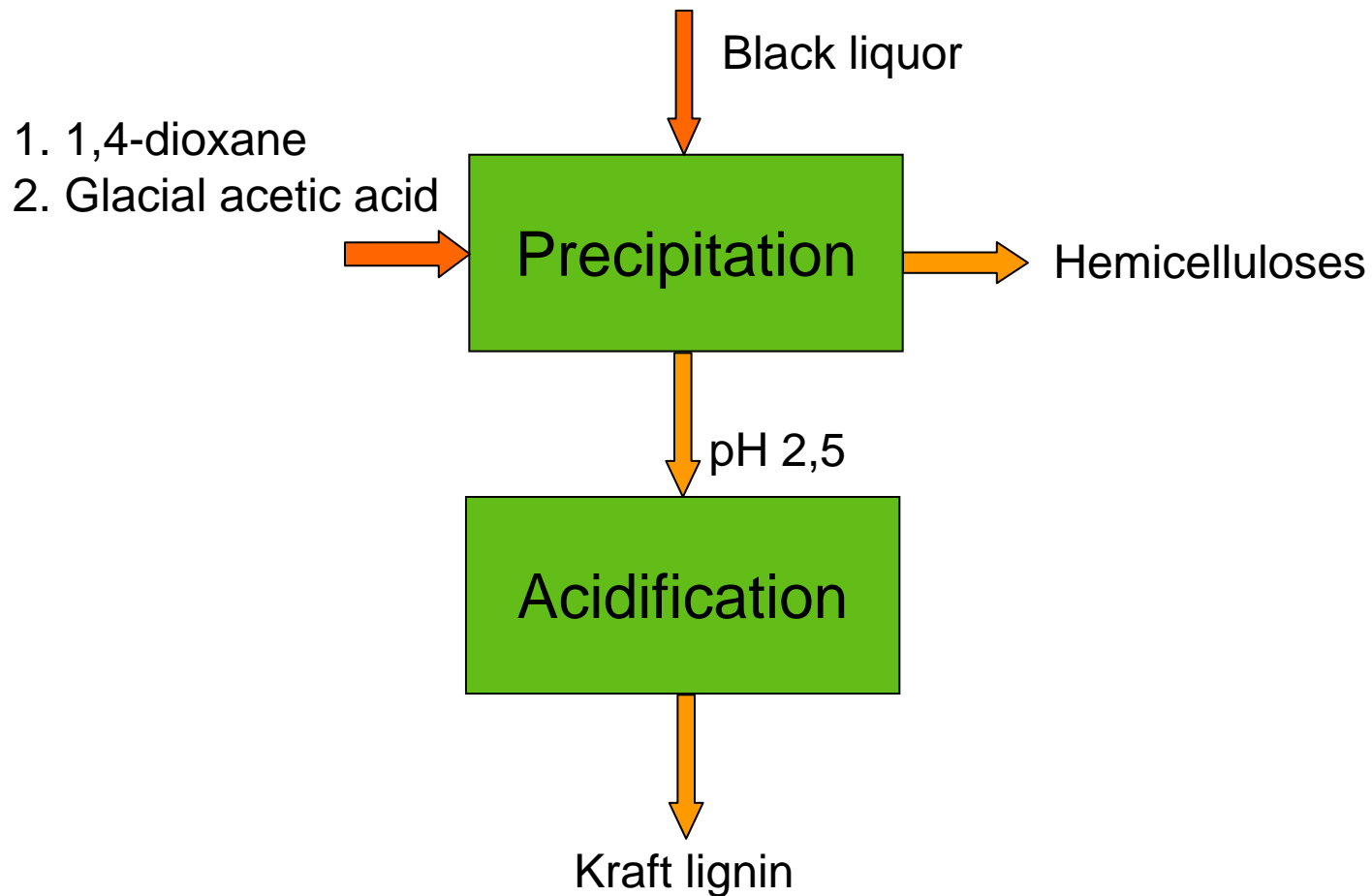
Kraft lignin

# Isolation and characterization of lignin and hemicelluloses from pine kraft black liquor

Three series of kraft cooks conducted:  
normal (reference, R), slow (low-sulfidity, LS), and fast (high-alkalinity, HA)

<b>Cook</b>	<b>H factor</b>	<b>Yield, %</b>	<b>Kappa</b>
R	30	74.0	-
R	1000	50.9	50.6
R	2500	45.0	21.8
LS	3000	49.0	49.8
HA	350	45.4	45.2

# Applied fractionation of black liquor



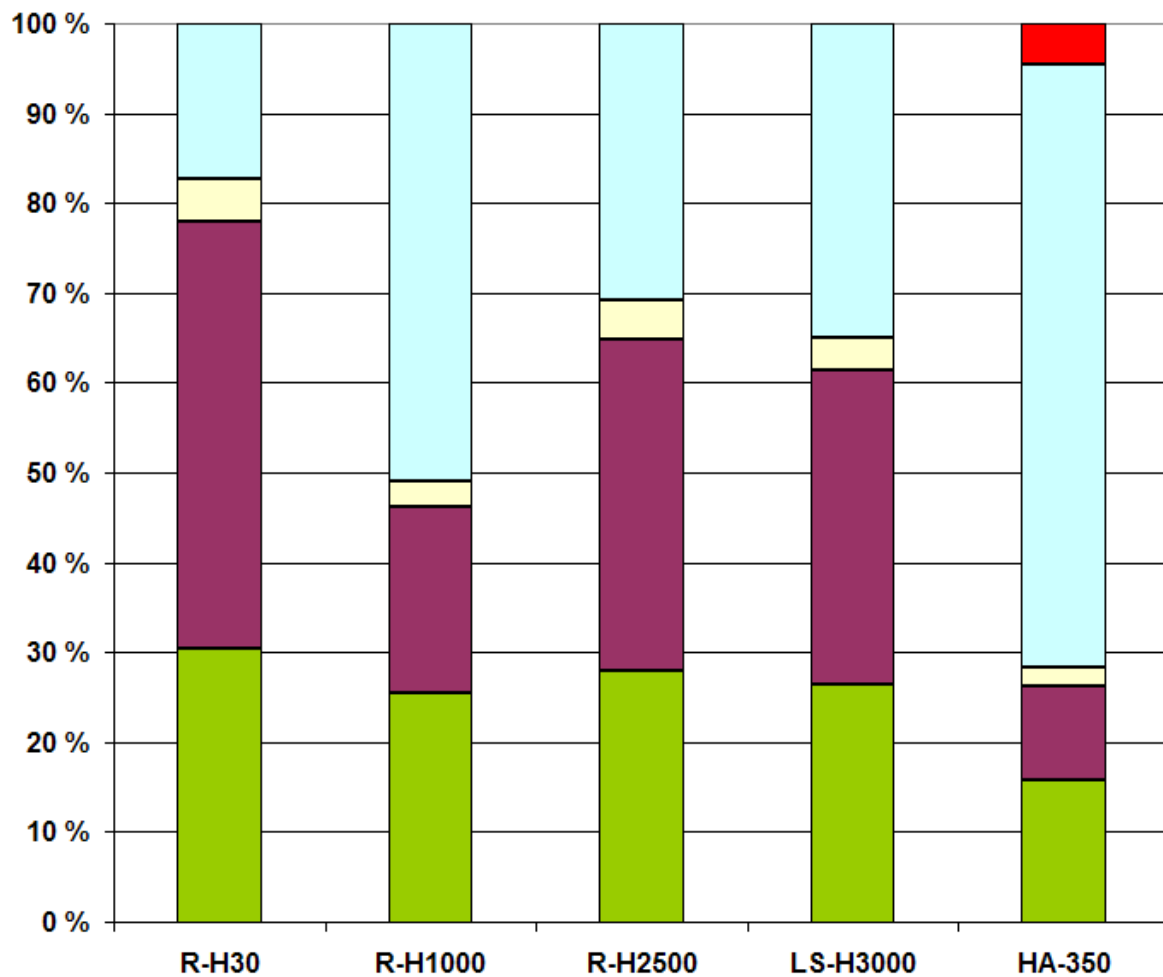
N. Engström et al.,  
ISWPC 1995, Vol. III, p. 195.

# Total carbohydrates in black liquors

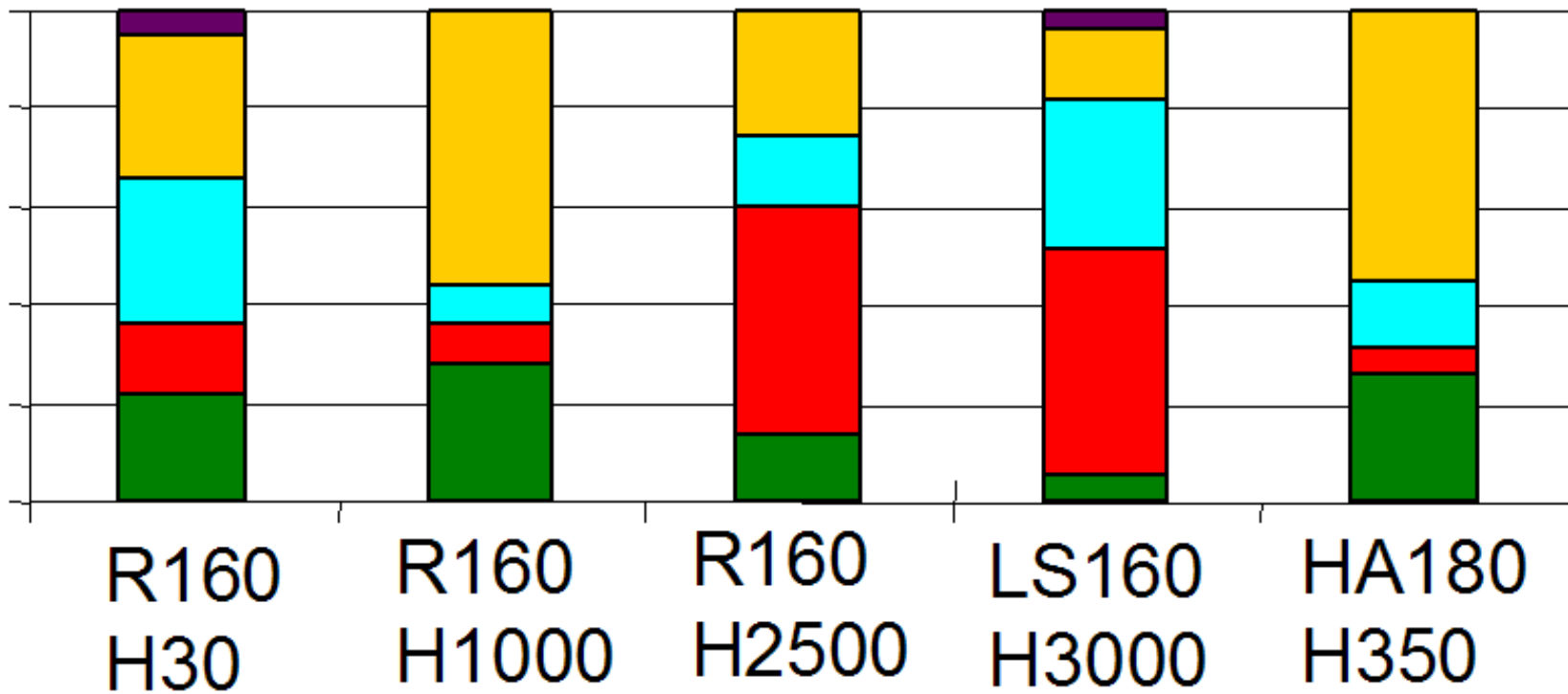
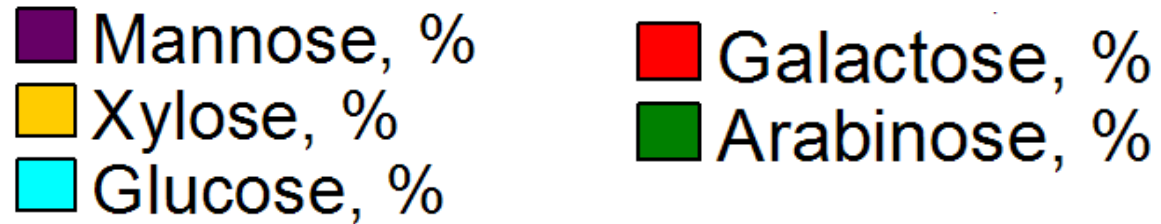
Concentration, g/l  
Isolation yield, %

1.7	4.3	3.2	3.1	9.6
59	93	34	10	93

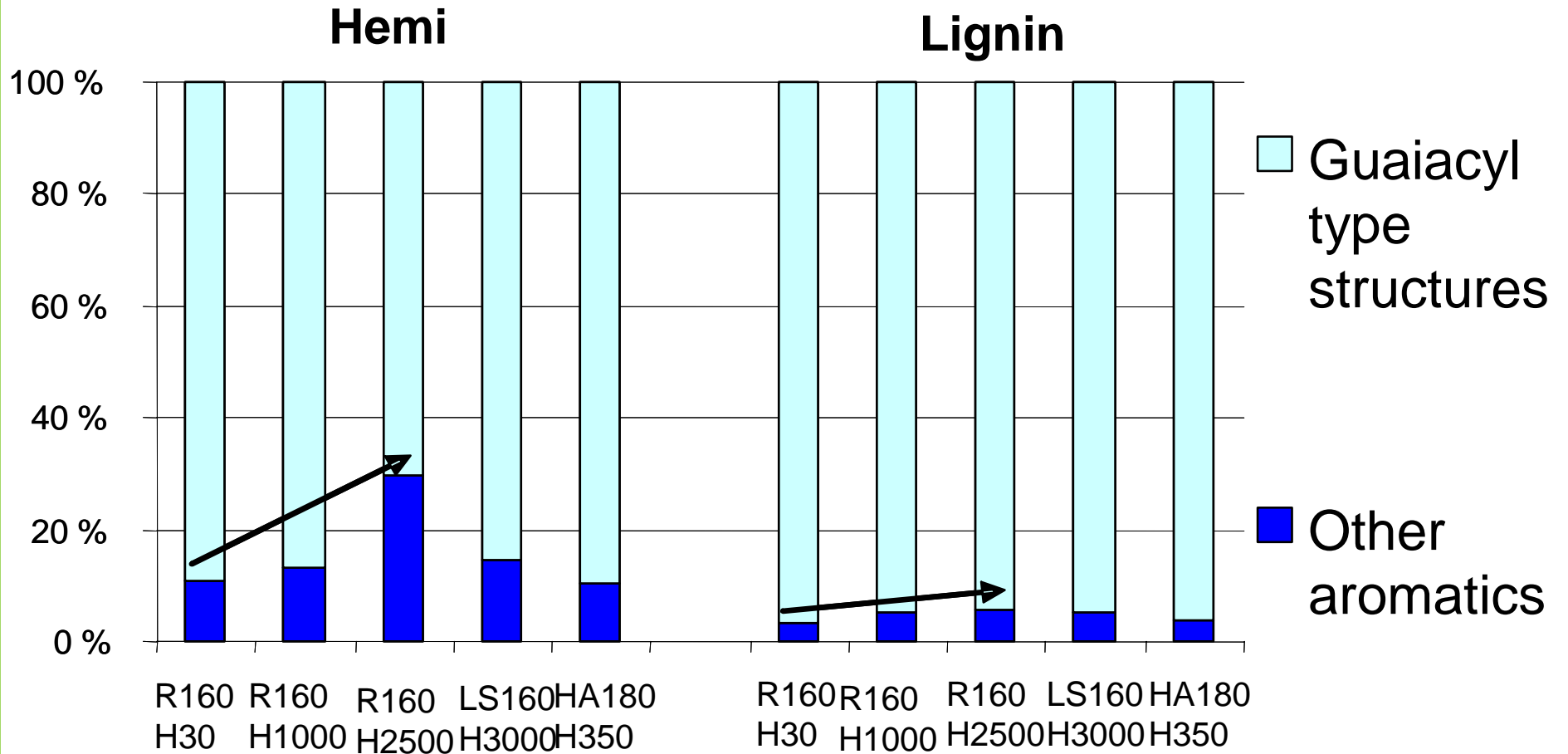
- Mannose
- Xylose
- Glucose
- Galactose
- Arabinose



# Isolated hemicelluloses

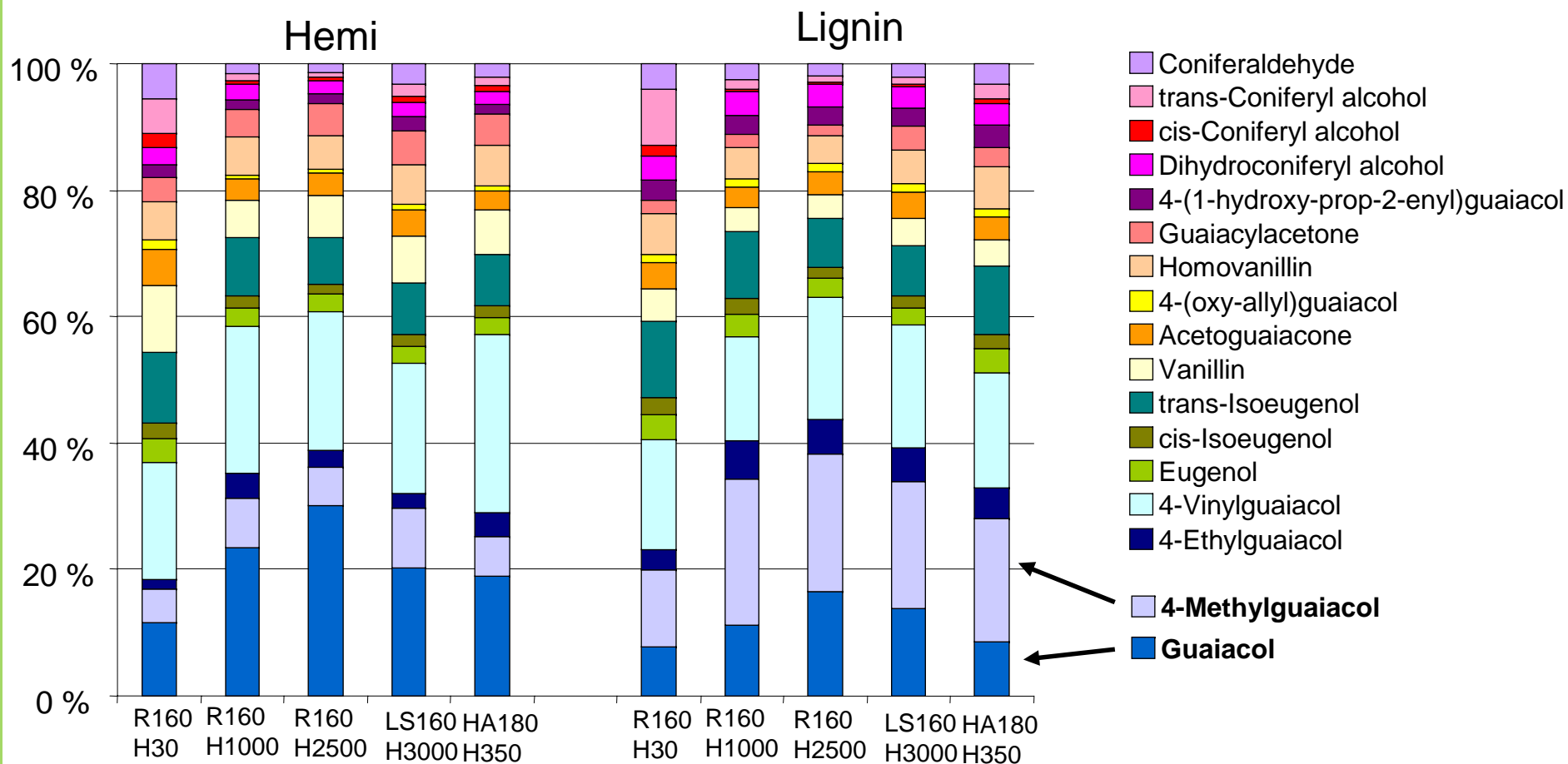


# Distribution of aromatic pyrolysis products

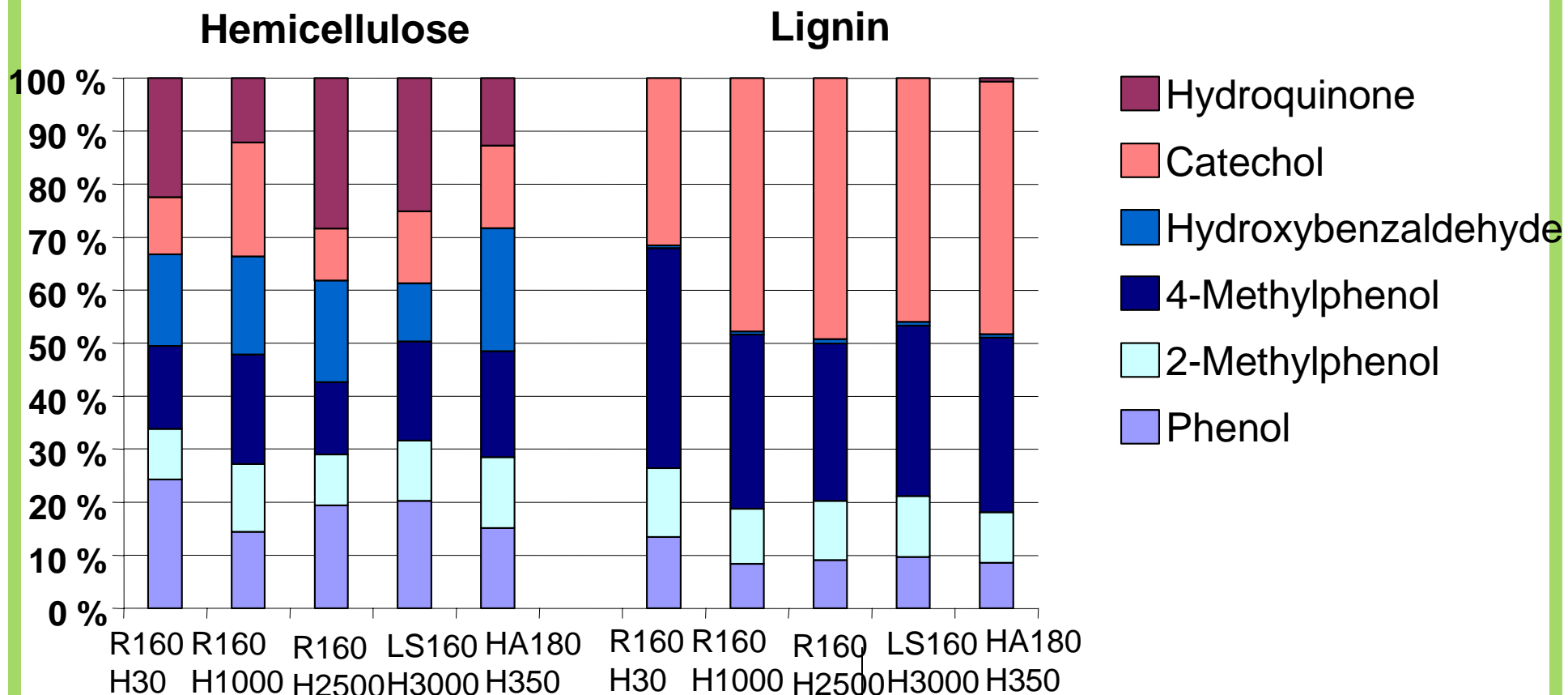




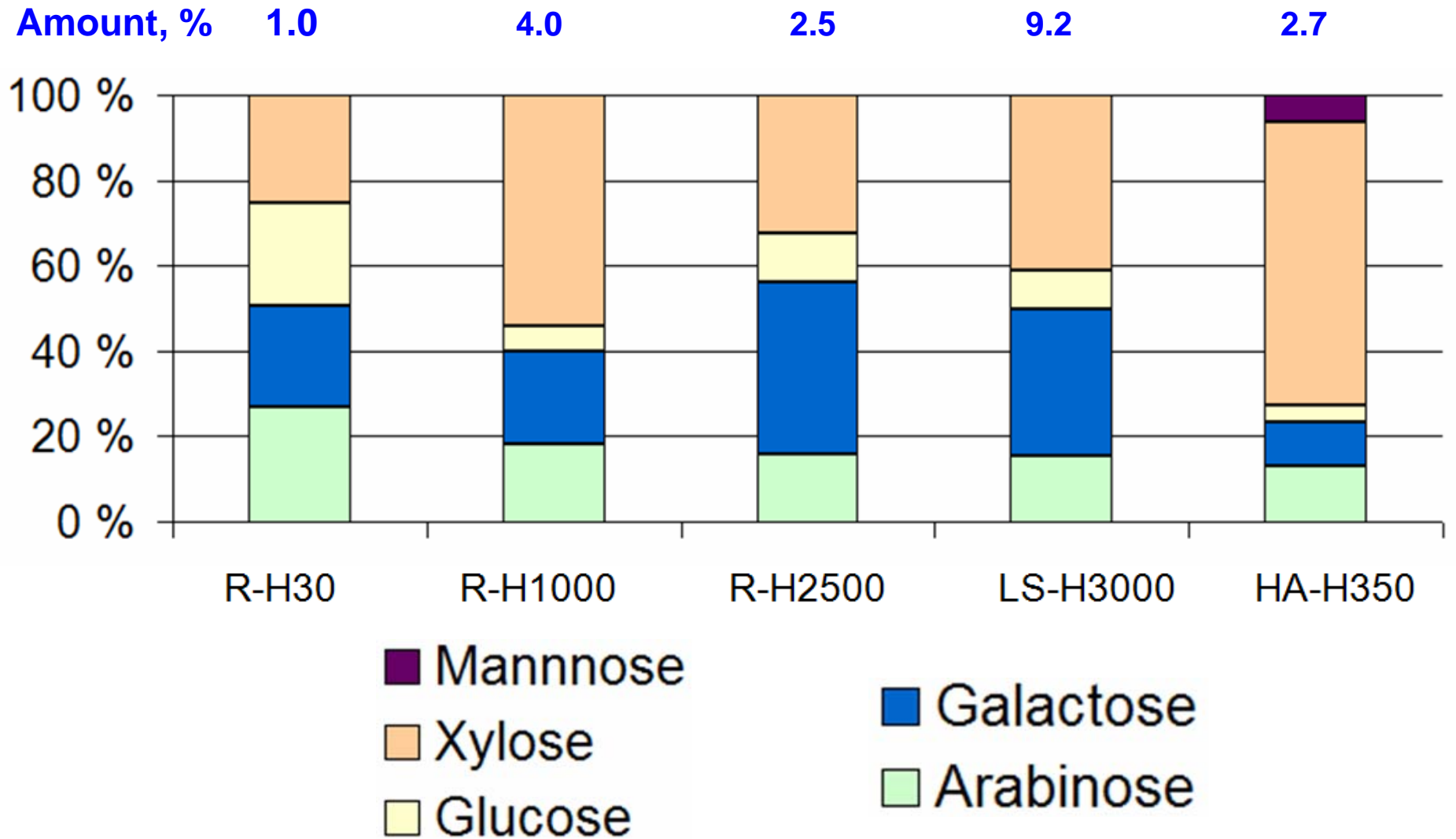
# Guaiacyl-type pyrolysis products



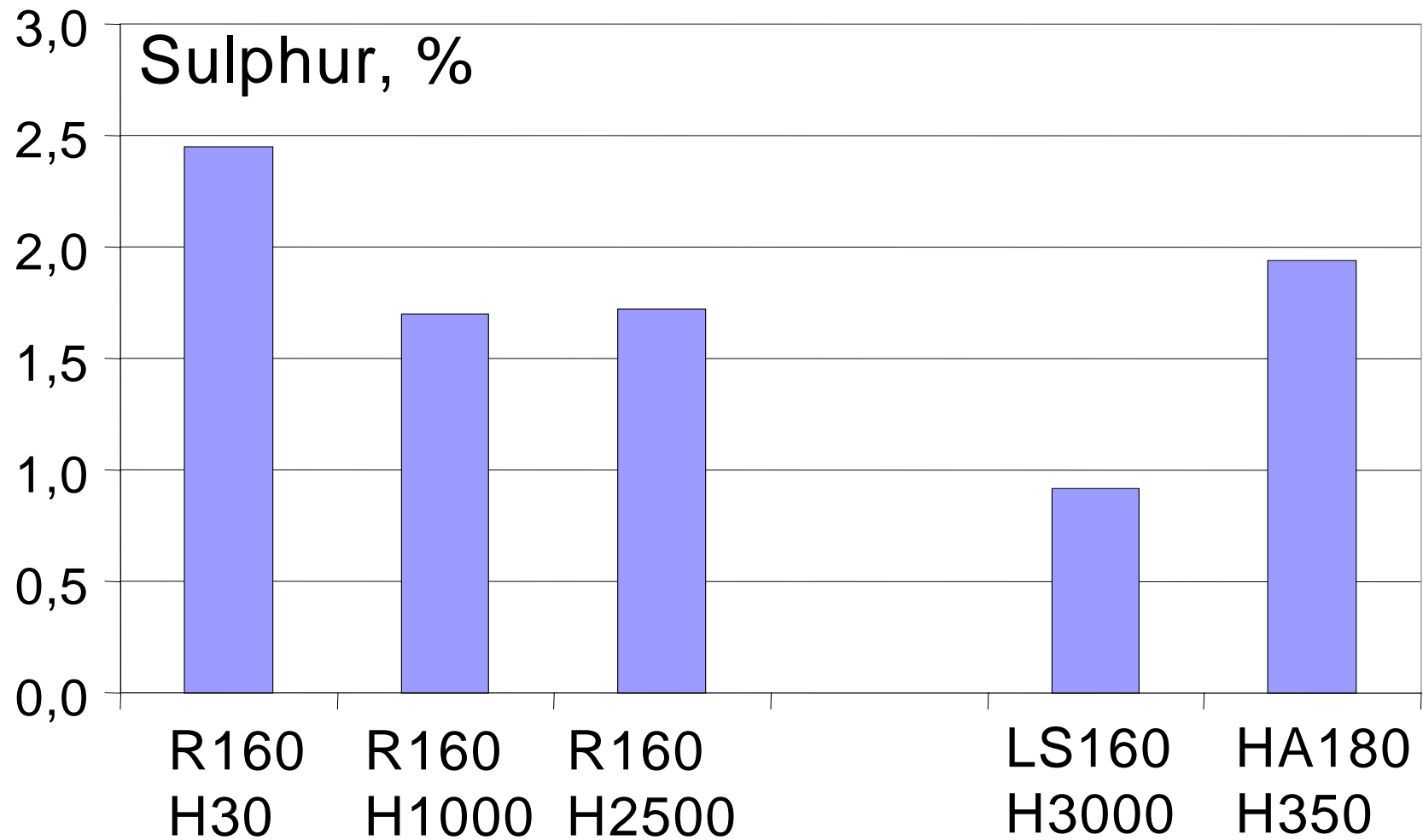
# Non-guaiacyl type pyrolysis products



# Carbohydrates in the isolated kraft lignins



# Sulfur in the isolated kraft lignins



# Is the nature of black liquor sulfur known?

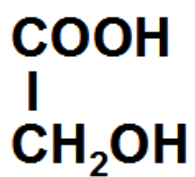
- Some evidence for the presence of methylthio groups
- S-bearing lignin monomers identified by GC/MS from black liquors

**Ar-S-Me type compounds**

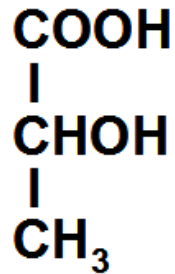
# Analysis of hydroxy carboxylic acids

- GC and GC/MS
  - TMS derivatives after converting the acids into their **ammonium salts**
  - TMS derivatives of free acids + **lactones**
- Capillary electrophoresis
  - limited availability of standards
  - not suitable for polyhydroxy acids

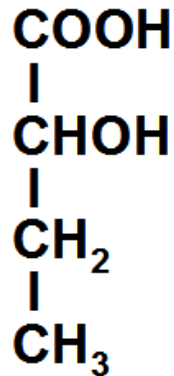
# Main hydroxy monocarboxylic acids



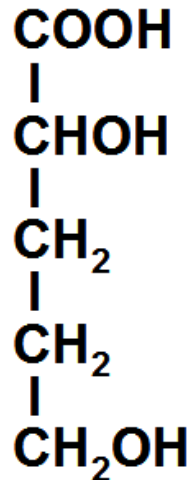
1



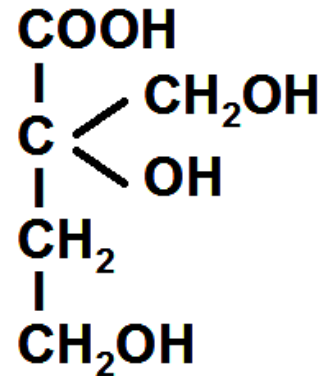
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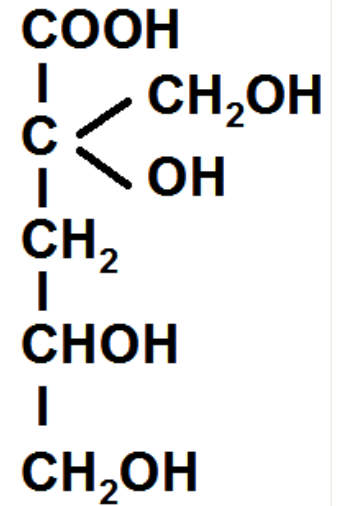
3



4



5



6

1, glycolic acid

2, lactic acid

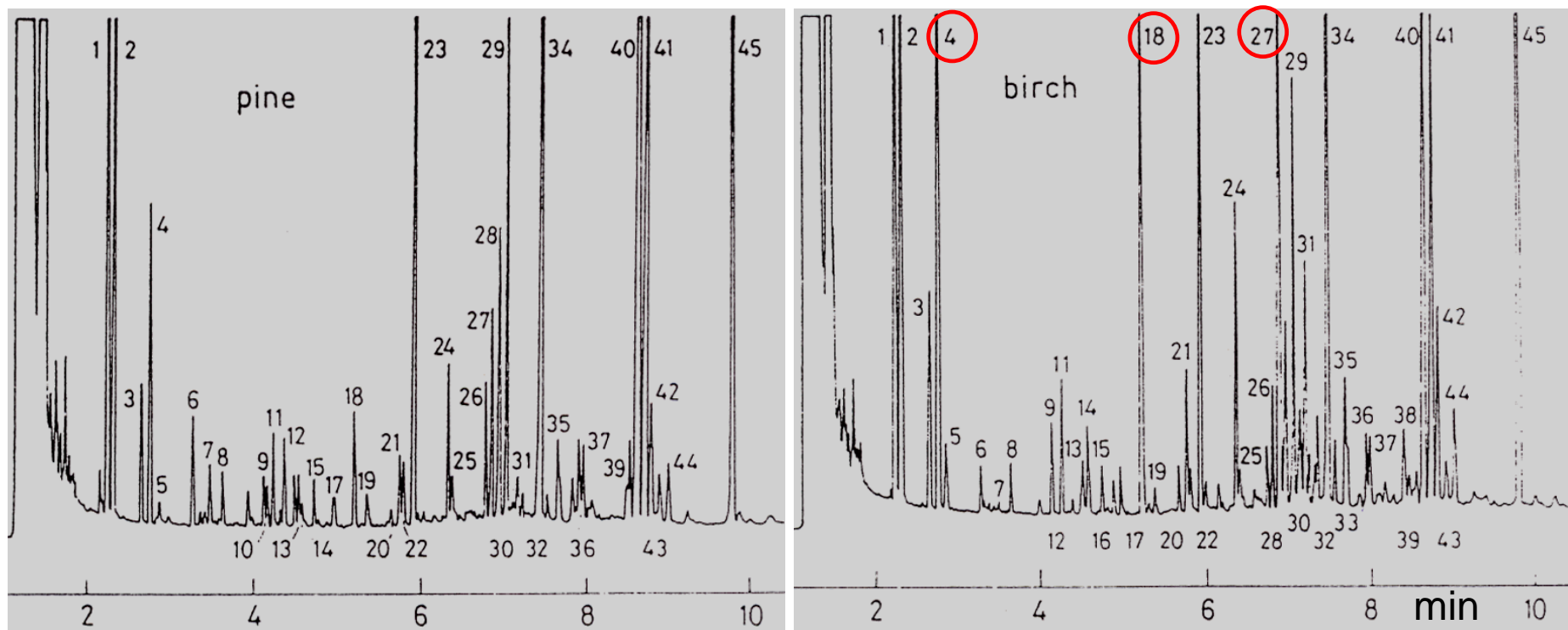
3, 2-hydroxybutanoic acid

4, 2,5-dihydroxypentanoic acid

5, xyloisosaccharinic acid

6, glucoisosaccharinic acids  
(2 stereoisomers)

# GC analysis of the main hydroxy acids



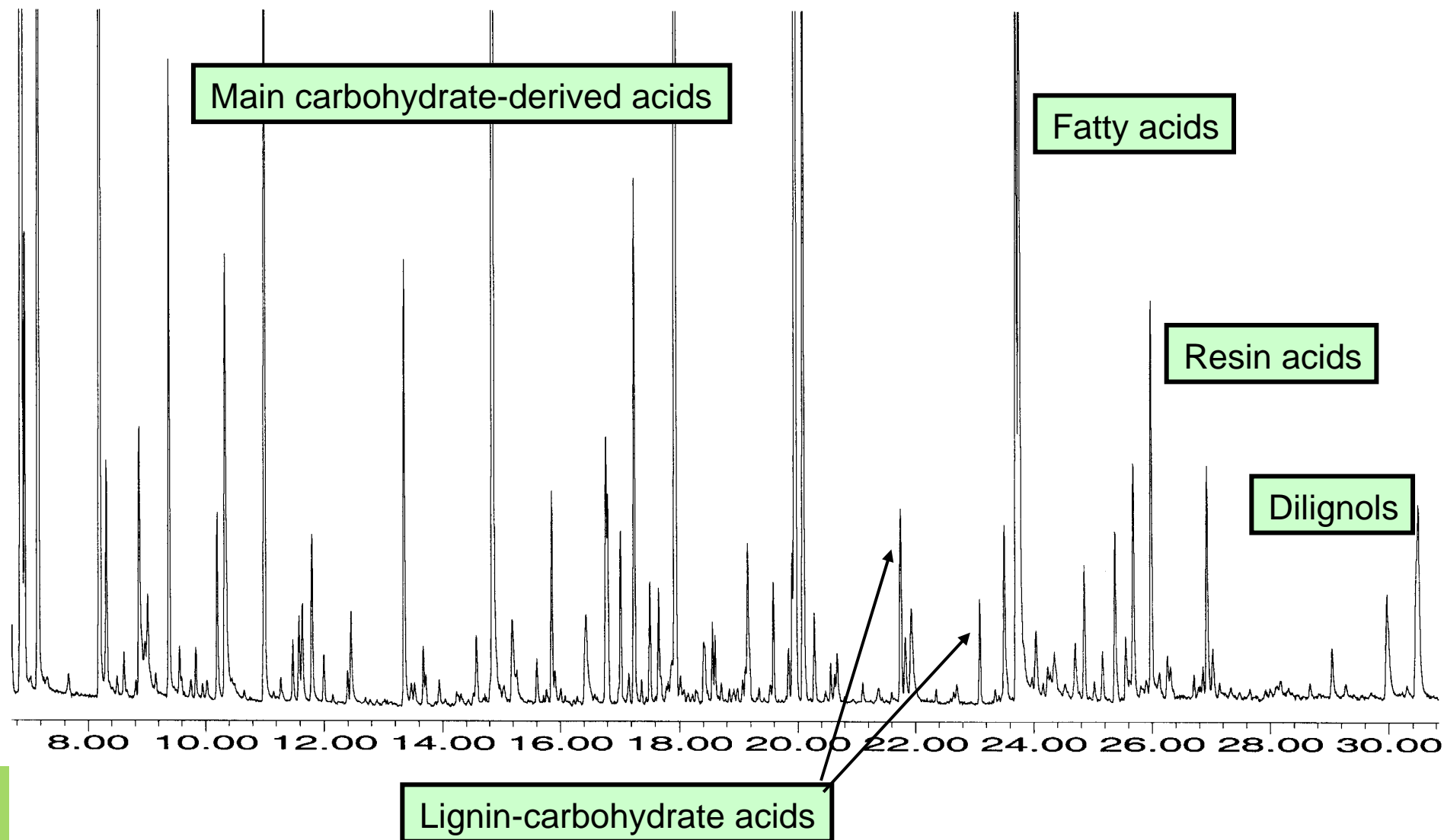
4 = 2-hydroxybutanoic acid

18 = 2,4-dihydroxybutanoic acid

27 = xyloisosaccharinic acid

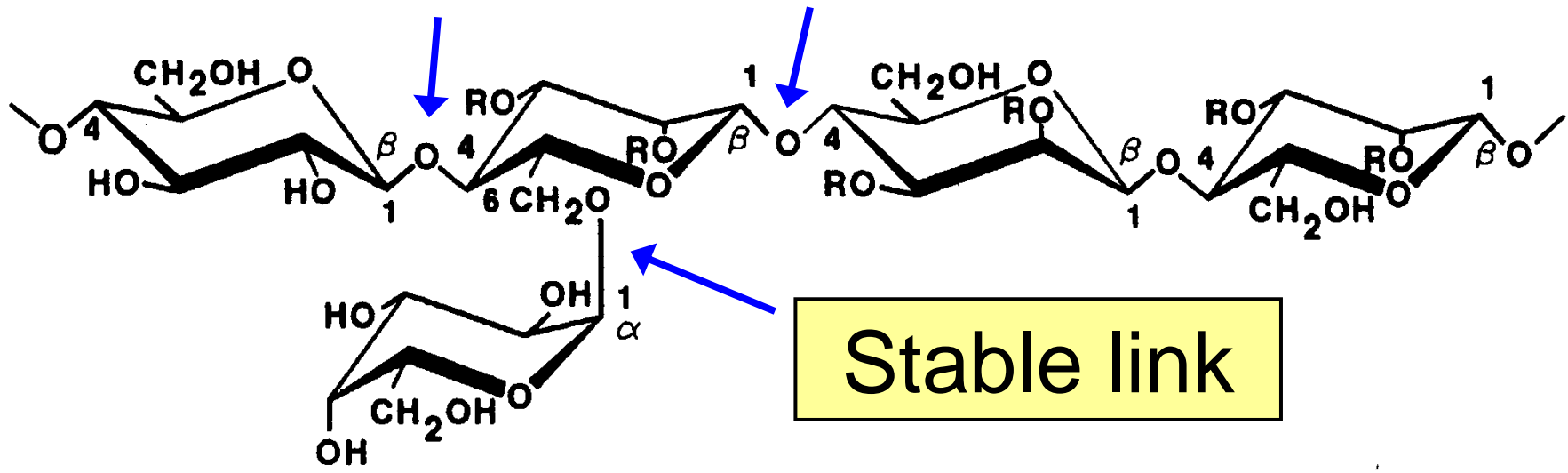


# GC/MS analysis of black liquors



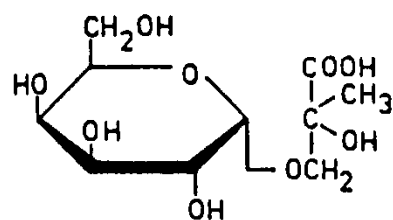
# Dimeric acids from galactoglucomannans

Labile links

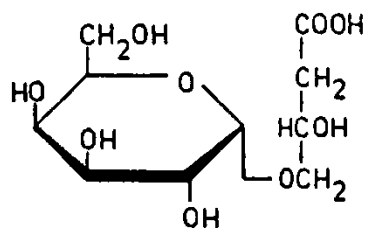


Stable link

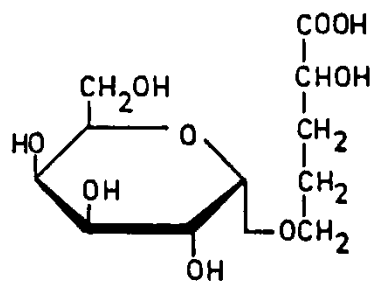
# Dimeric acids from galactoglucomannans



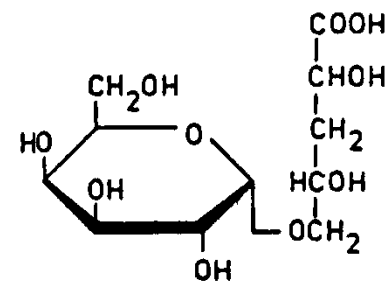
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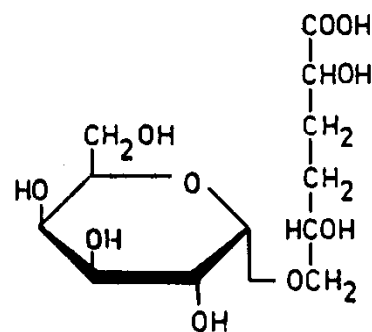
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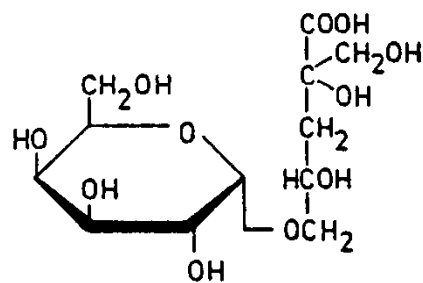
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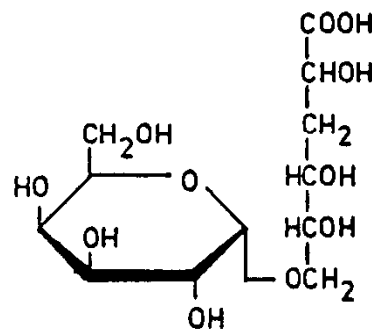
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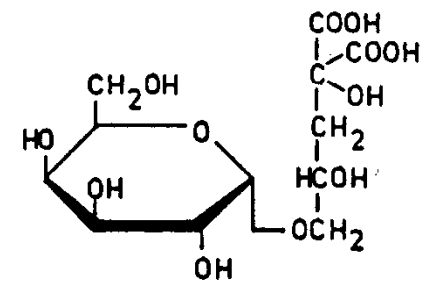
6, 7



8, 9



10, 11



12

# Condensed conclusions

There is still a lot of by-product potential in black liquors

