The Forest based Biorefinery: Chemical and Engineering Challenges and Opportunities

Hemicelluloses

Stefan Willför

epnoe
European Polysaccharide
Network Of Excellence

Forest Biorefineries: not only wood and paper products

Bioenergy, Biofuels

Wood Products

Pulp and Paper → Printing, Packaging, Tissue

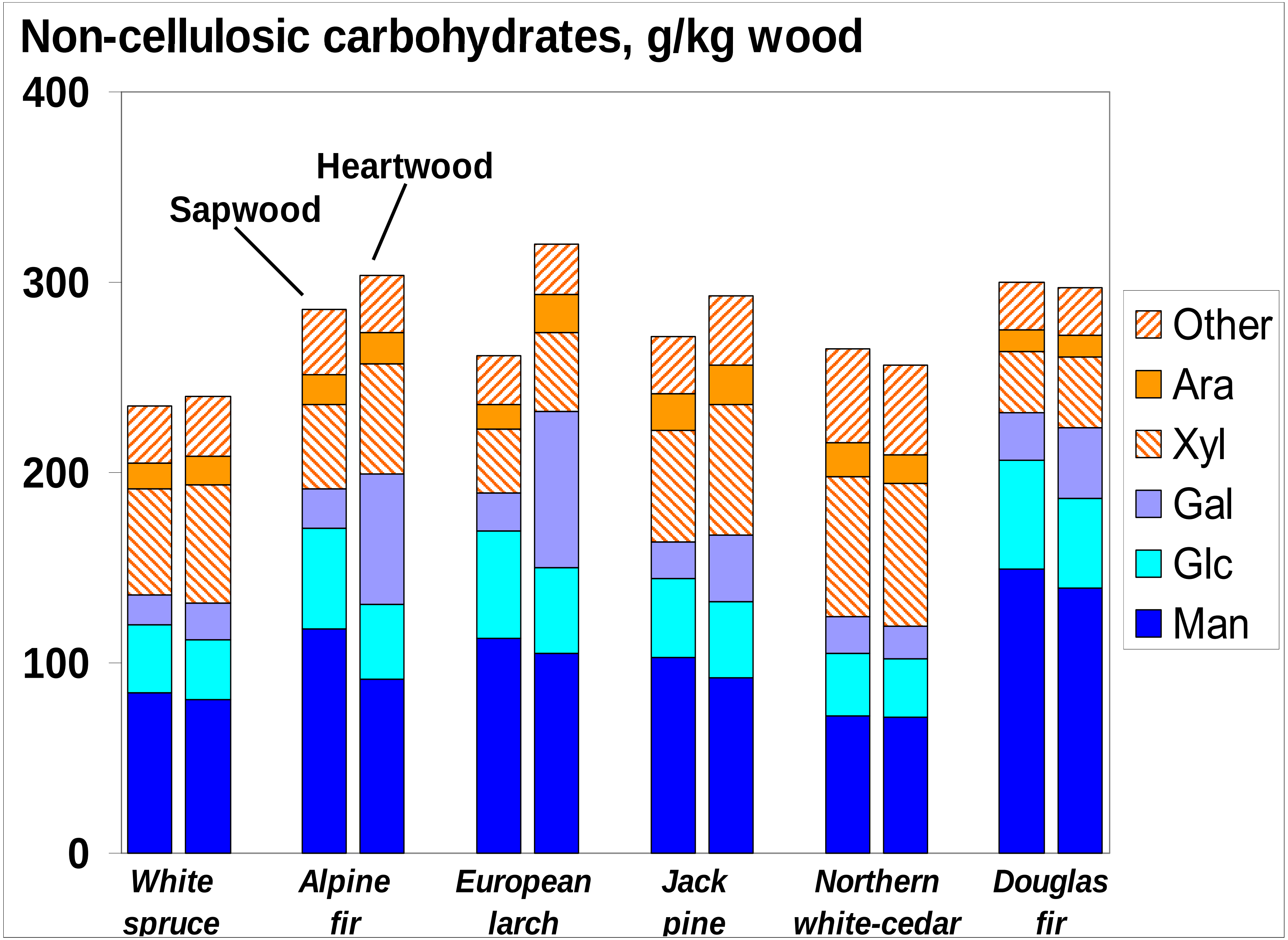
Specialty high-value biomaterials and biochemicals → Chemical markets, Food and Feed, Health

New products with essentially higher value than pulp and paper – and biofuels

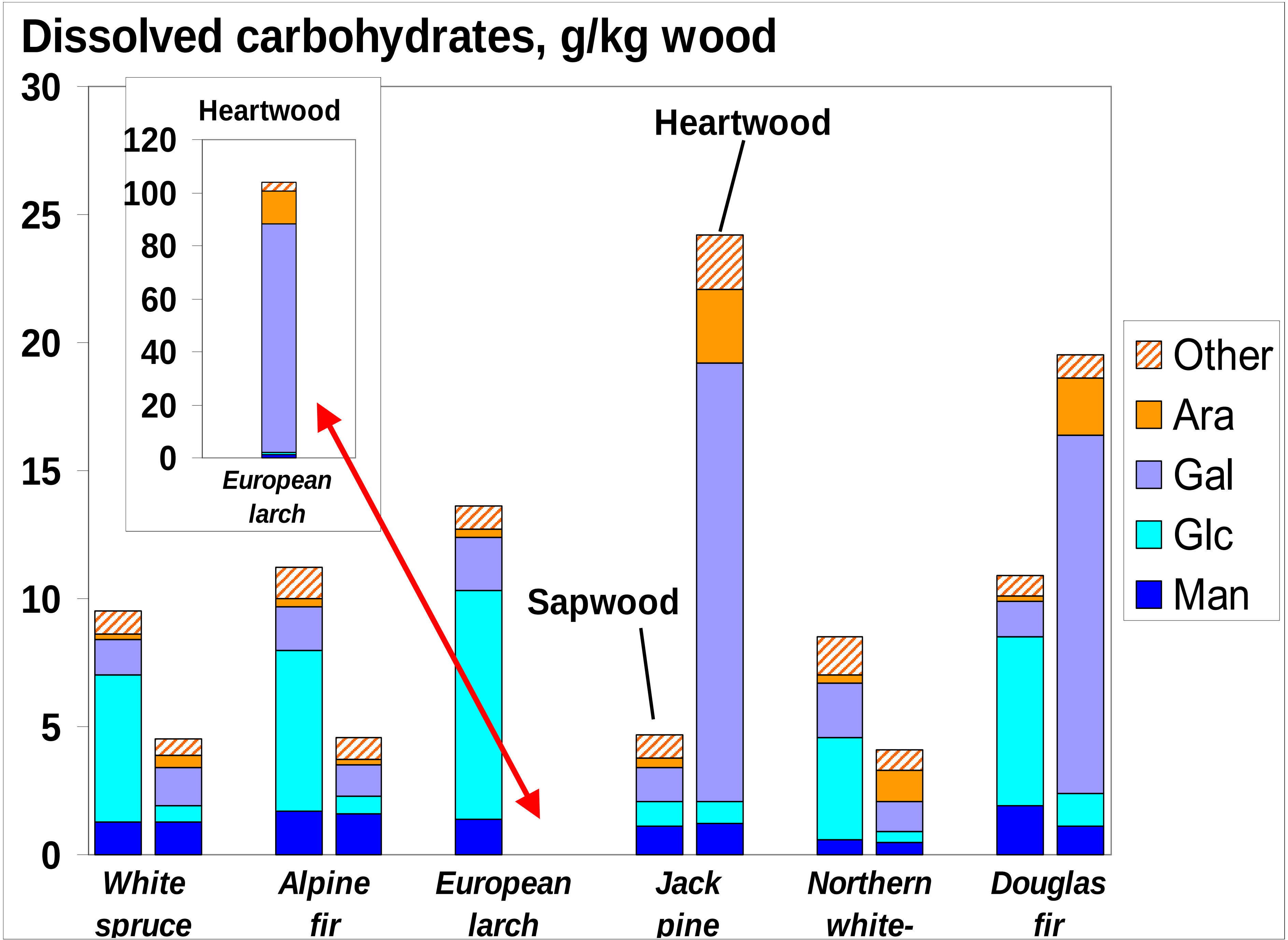
Biorefinery – getting more value (more money) from the forest resources

Challenges

- Softwoods (Coniferous woods) and hardwoods (Angiosperms)
- Globally: Softwood species about 1000, hardwood species 30 000-35 000
- Only a few are used commercially: In USA about 100, in Europe about 20
- In Finland we have 3 main species: spruce, pine and birch

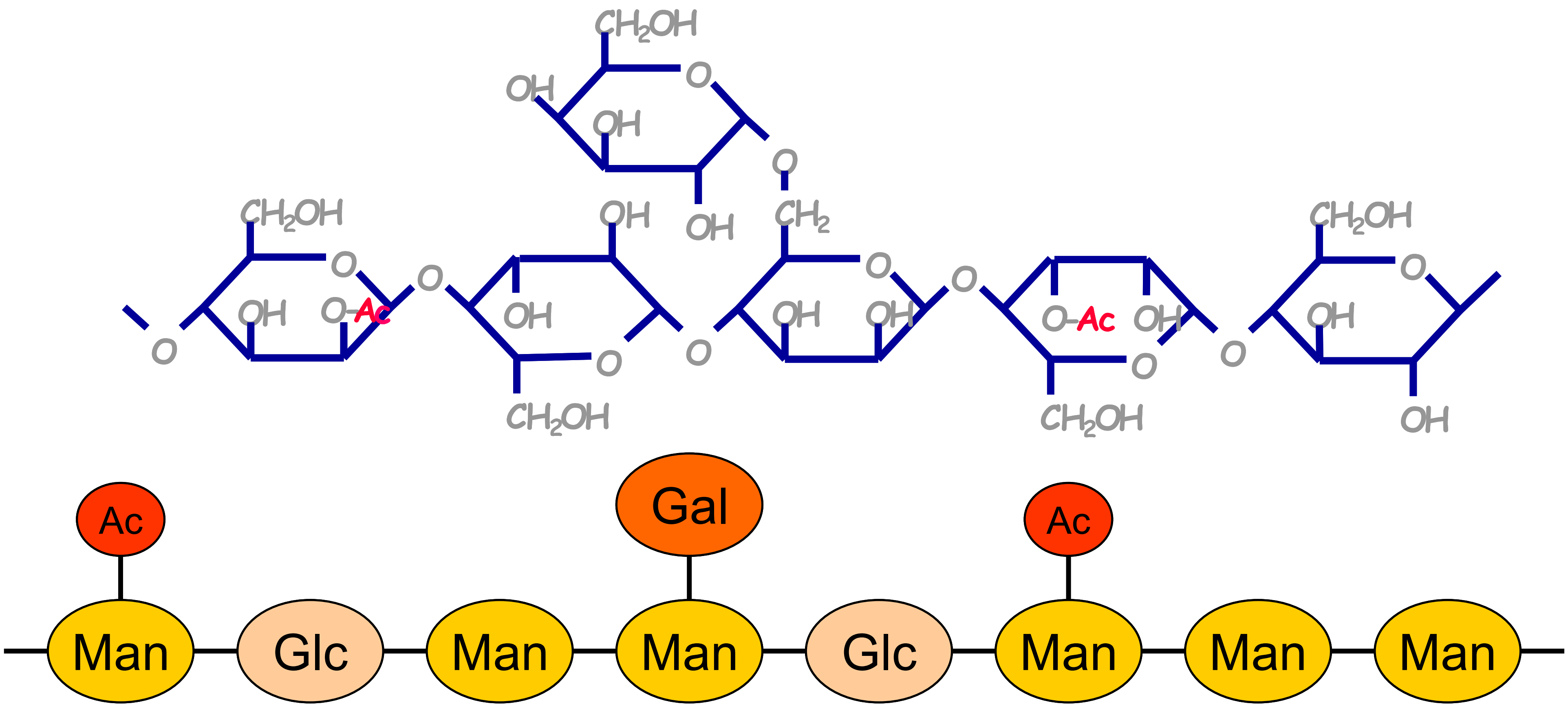


Non-cellulosic carbohydrates, g/kg wood
400
300
200
100
0
Heartwood
Sapwood
Other
Ara
Xyl
Gal
Glc
Man
White spruce
Alpine fir
European larch
Jack pine
Northern white-cedar
Douglas fir



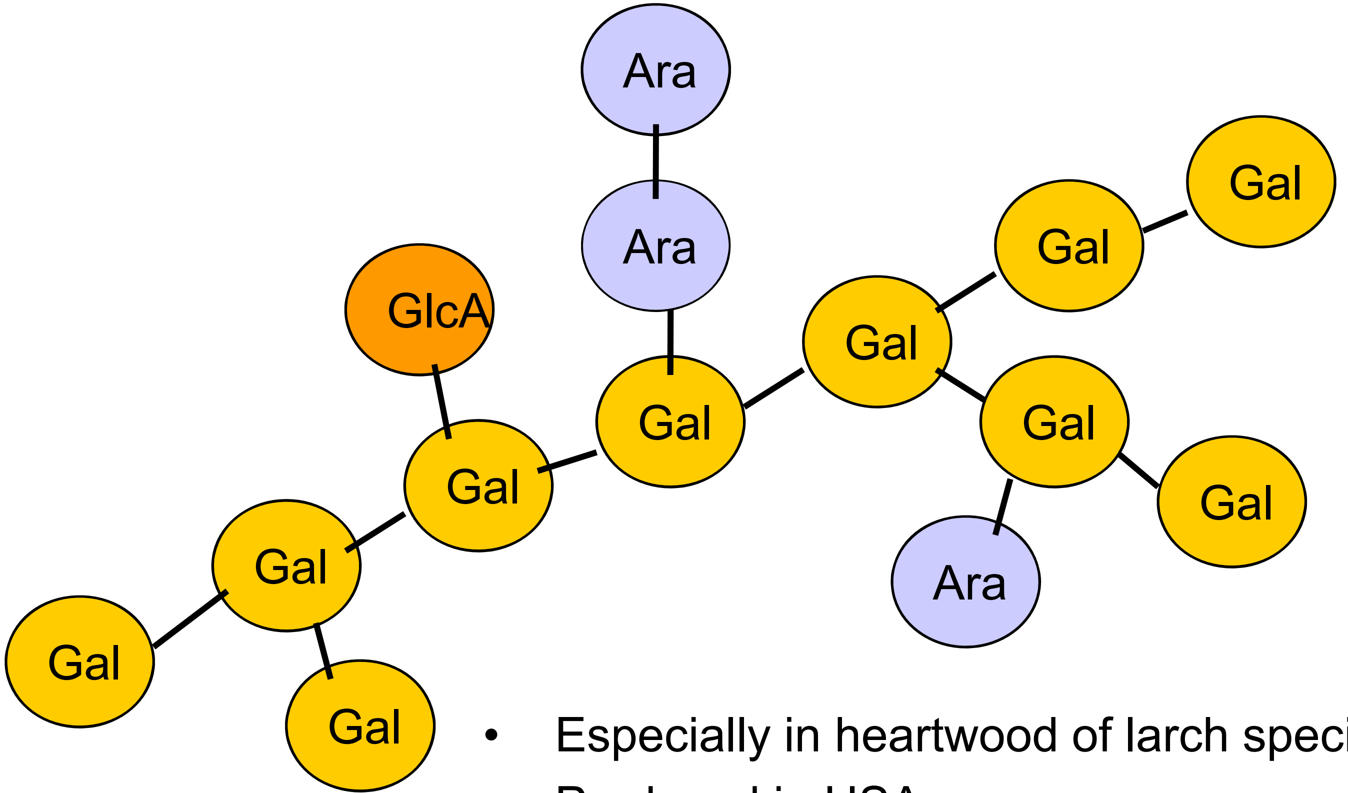
Dissolved carbohydrates, g/kg wood
30
25
20
15
10
5
0
Heartwood
120
100
80
60
40
20
0
European
larch
Heartwood
Sapwood
Other
Ara
Gal
Glc
Man
White
spruce
Alpine
fir
European
larch
Jack
pine
Northern
white-
Douglas
fir

(Softwood) spruce *O*-acetyl-galactoglucomannans (GGM)



Man : Glc : Gal : Ac ~ 4 : 1 : 0.1-0.5 : 0.2

Arabinogalactans (AG)



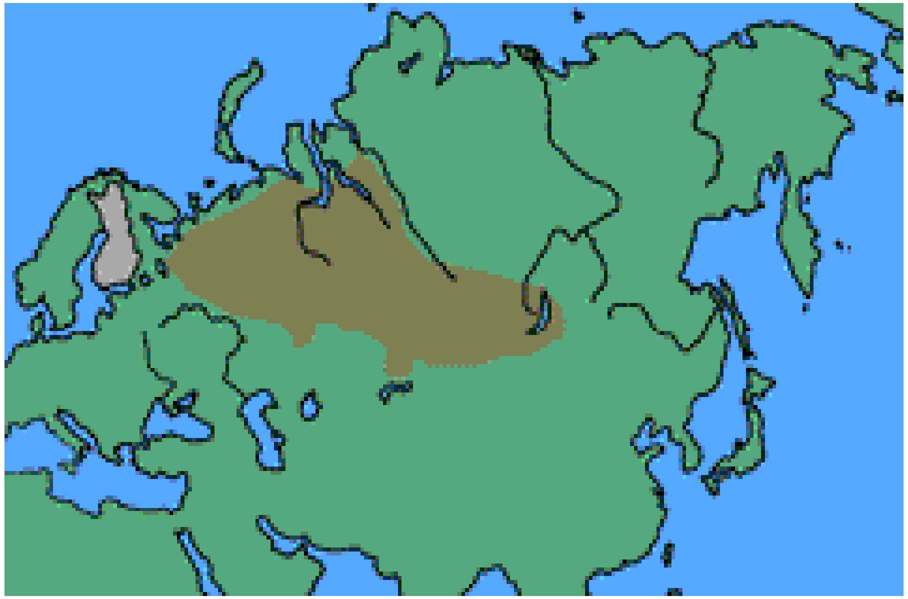
- Especially in heartwood of larch species
- Produced in USA
- Highly water-soluble

Current use of AG

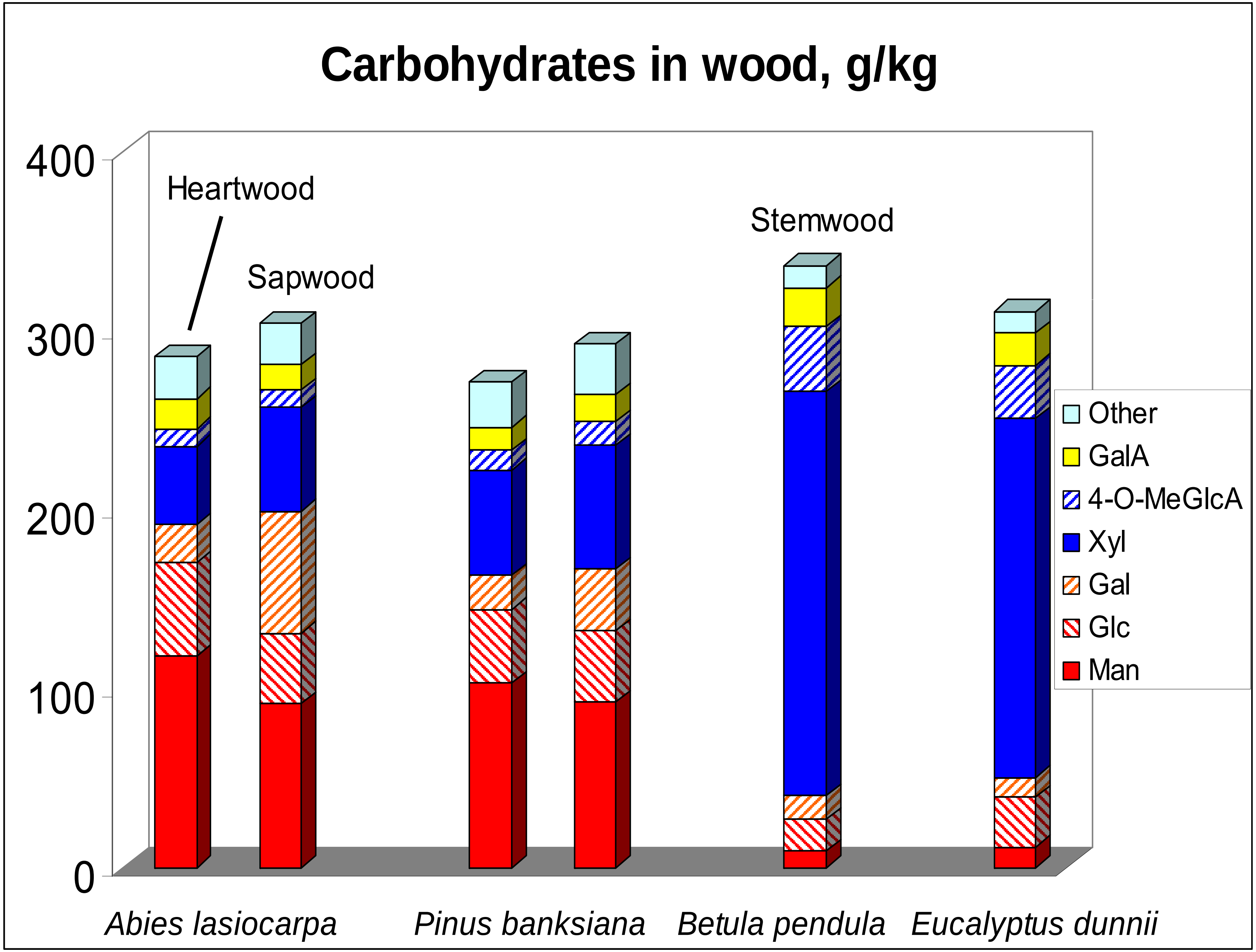
- Capacity (Lonza/Larex): 3600 ton per year (western larch)
- Current markets and products according to Lonza (Larex) web pages:
  - Prebiotic dietary fiber, supplemental ingredient for horses, pets and livestock
  - Additive for skin and hair care products
  - Rheology modification and colloidal suspensions
  - Performance additive for flexographic inks and plate solutions

Huge potential in Russia

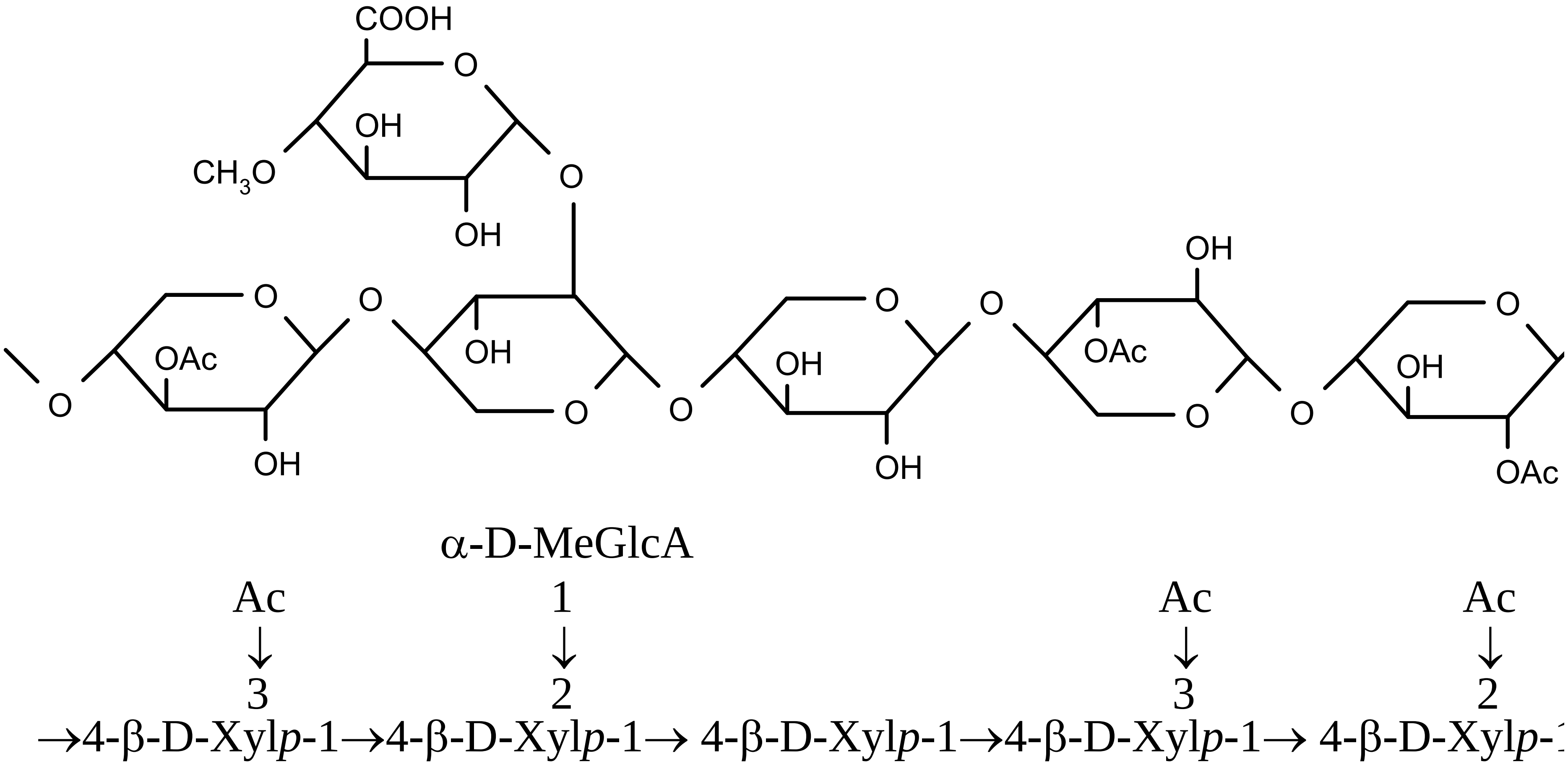
- 15-20% (w/w) of **Siberian larch** (*Larix sibirica*) heartwood consist of easily water-soluble AG
- Could be extracted prior to chemical pulping
  - Or from saw dust



http://www.metla.fi/metinfo/puulajit/lajikuvaukset/lajisivu-larix-sibirica.html


Carbohydrates in wood, g/kg
400
300
200
100
0
Heartwood
Sapwood
Stemwood
Other
GalA
4-O-MeGlcA
Xyl
Gal
Glc
Man
Abies lasiocarpa
Pinus banksiana
Betula pendula
Eucalyptus dunnii

Hardwood xylans



O-acetyl-4-*O*-methylglucuronoxylans

Polysaccharides in wood (% of d.m.)

	Softwoods	Hardwoods
Cellulose	35 - 45	35 - 50
Hemicelluloses	22 - 30	20 - 35
Glucomannans	**11 - 17**	1 - 4
Xylans	6 - 8	15 - 25
Pectins	1.5 - 2.5	2 - 3

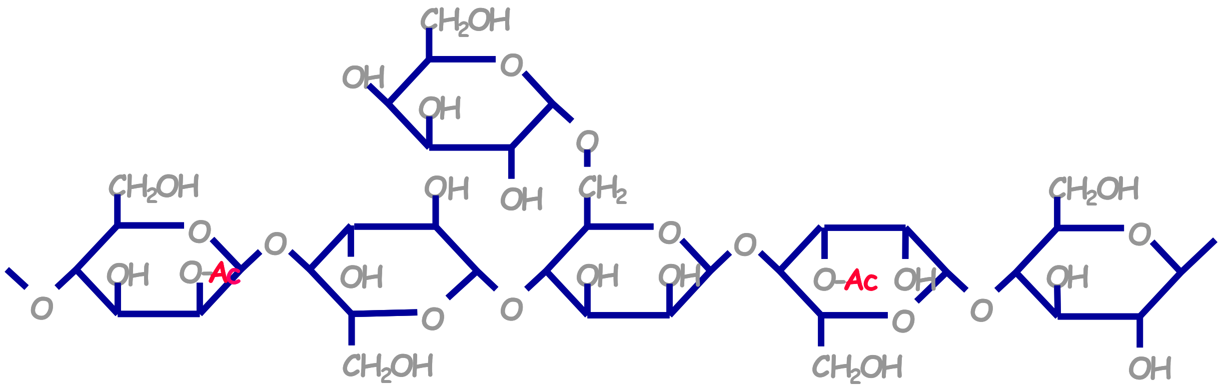
- Willför et al. (2005), Polysaccharides in some industrially important softwood species, *Wood Sci. Technol*. 39
- Willför et al. (2005), Polysaccharides in some industrially important hardwood species, *Wood Sci. Technol*. 39

Hemicelluloses from wood

- Galactoglucomannans
  - Softwoods, spruce
  - TMP waters, by UF
  - Direct extraction of wood
- Xylans
  - Hardwoods
  - Bleached Kraft pulp
- Arabinogalactans
  - Larch heartwood
  - 15 – 20% by wt.
- Other non-wood sources
  - Bark
  - Foliage
  - Peat
  - Mosses
  - Algae
  - Agroresidues

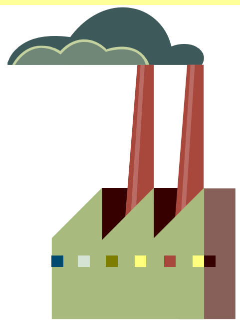
What about PS in bark?

- Research ongoing
- Potentially interesting, at least for biofuel production
- Arabinose-containing polysaccahrides
  - Structure?



How to get enough GGM for research purposes?

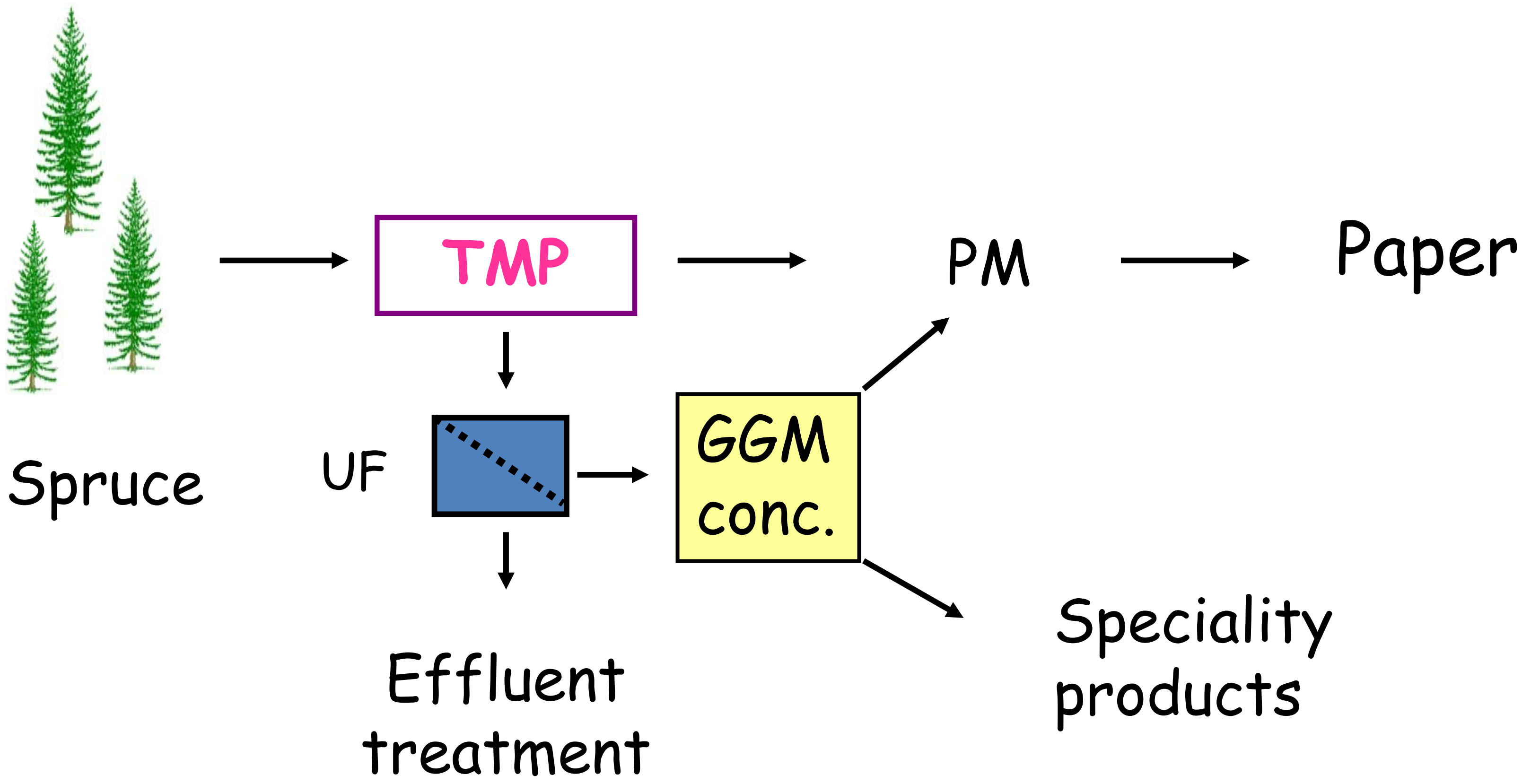
What about industrial production?



Structure-preserving methods

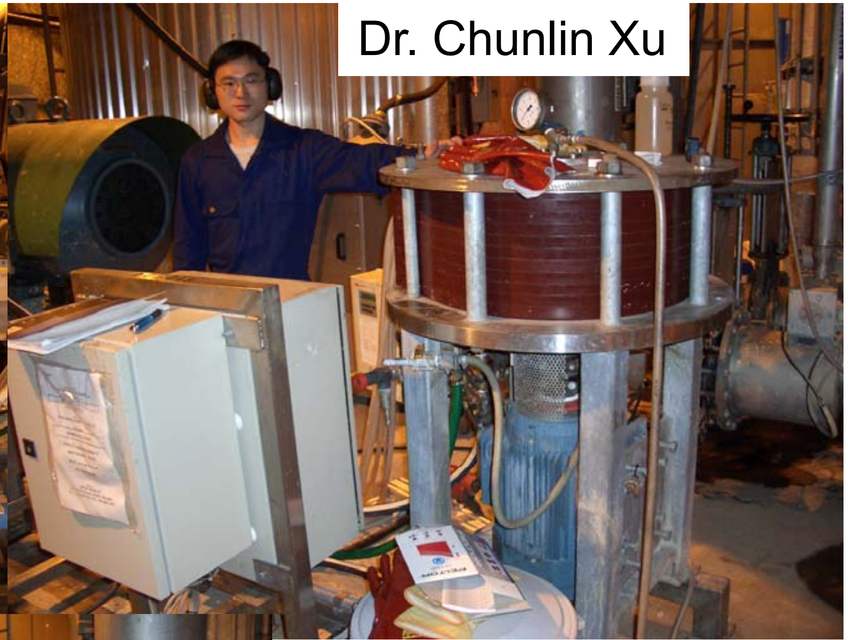
- Our interest lies within structure-preserving methods
  - Intact polymeric form
  - Acetyl groups/functionality and water-solubility still remaining

GGM can be extracted in pure form from waters in paper mills (TMP plants)



UF apparatus

Pump unit



Dr. Chunlin Xu

UF unit

Bow filter

UF apparatus
3.75 m^2 membrane area

Drying

Spray dryer at VTT in Rajamäki/Finland

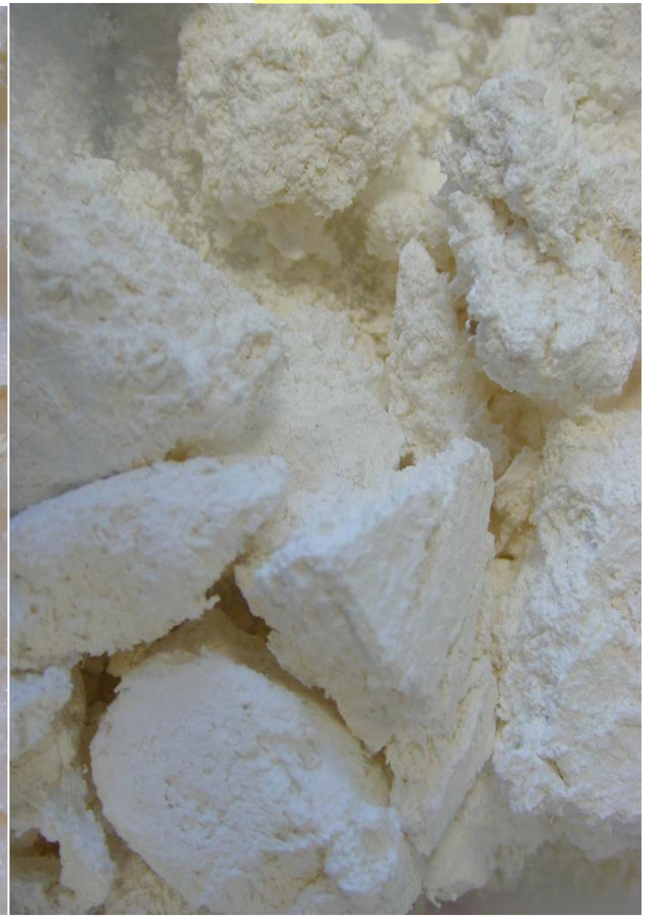
Or thin-film evaporation and precipitation in ethanol

Precipitation in ethanol

10 L vials

Close-up

Dry



GGM now available in kg-scale for research and testing

Carbohydrate mole-%	Technical GGM spray-dried
Mannose	53
Glucose	23
Galactose	13
Other	<11
Average Mw, kg/mole	20-40
Degree of acetylation	0.2 **Water-soluble**

Metals 3% (w/w)
Proteins 1% (w/w)

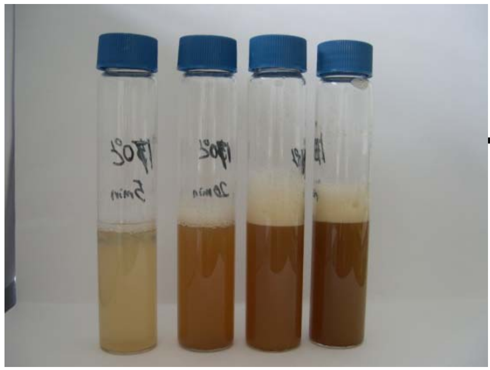
Commercial PS
100 - 1000

PHWE extraction of wood

Fresh spruce sapwood

Hand-cut chips or ground wood

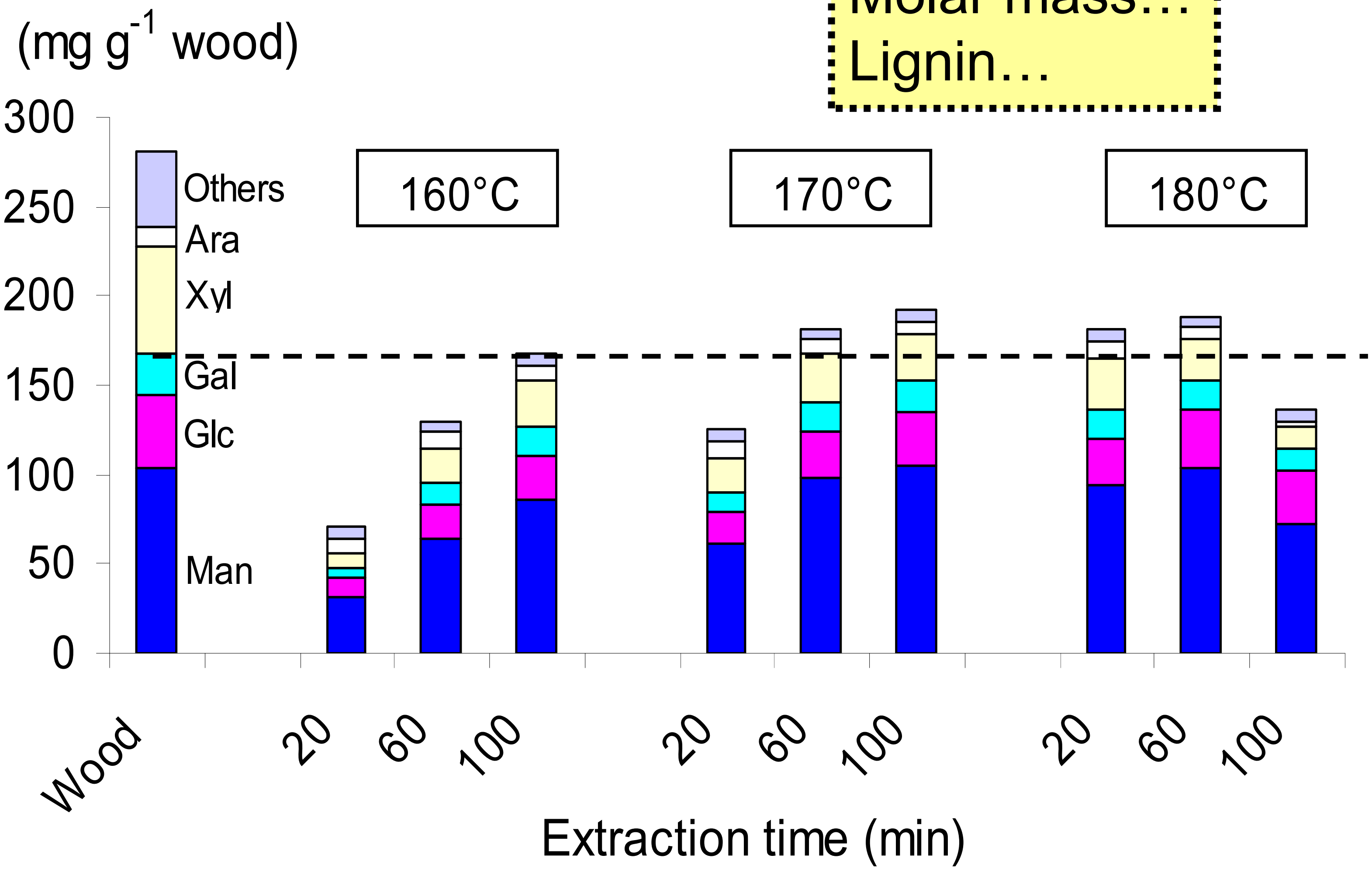
Accelerated Solvent Extractor (ASE)



Analyses

Extracted non-cellulosic carbohydrates

Molar mass…
Lignin…



Why are GGMs interesting?

Properties learned from pulping and papermaking applications
and
from recent or planned work

General challenges

- Solubility, especially during or after modifications
  - Water, organic solvents, other matrices
- Analytics
- Most methods for modifications have been developed for cellulose, starch and some other non-wood polysaccharides
  - Challenges in applying for GGM etc.

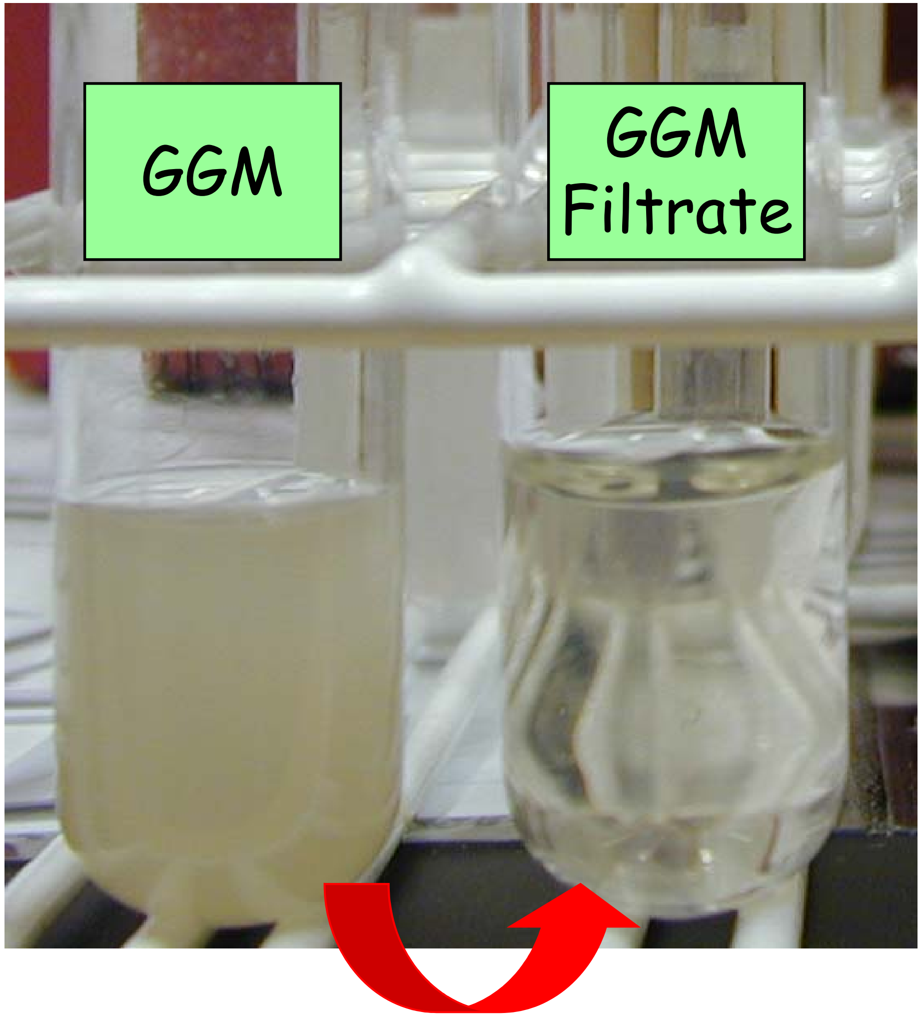
- Polysaccharides (PS) are widely used as hydrocolloids in emulsifiers, thickeners, gelling agents…

- Commercial PS are highly viscous and soluble only in low concentration

  →

  Replace by value-added, soluble, and functionalized GGM?

Solubility of spruce GGM

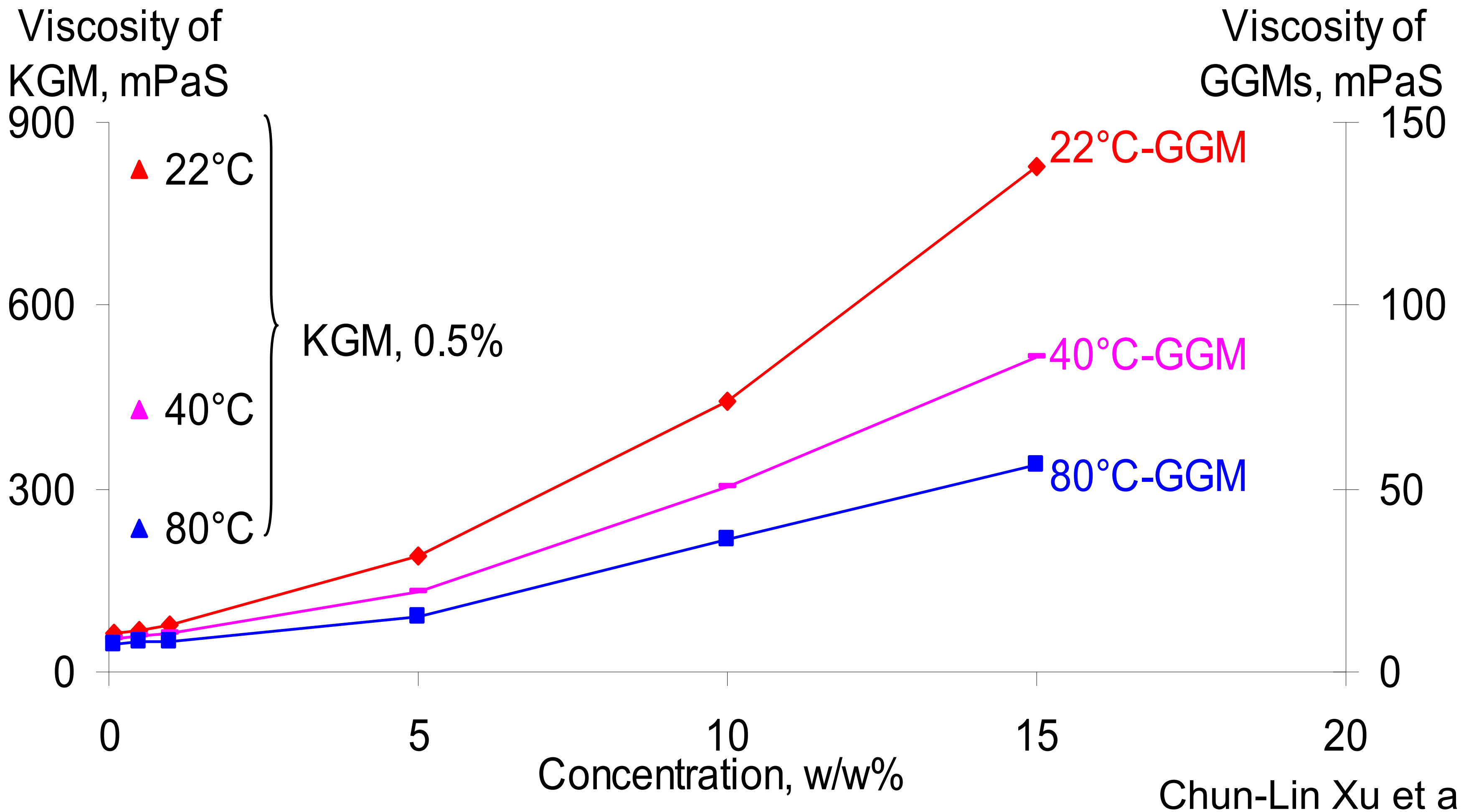


- Readily soluble in water even up to 30% concentration
- High stability for short and long term, at low and high concentrations

95% passes 0.2 micron filter

Chun-Lin Xu et al.

Viscosity of GGM at different concentrations and temperatures

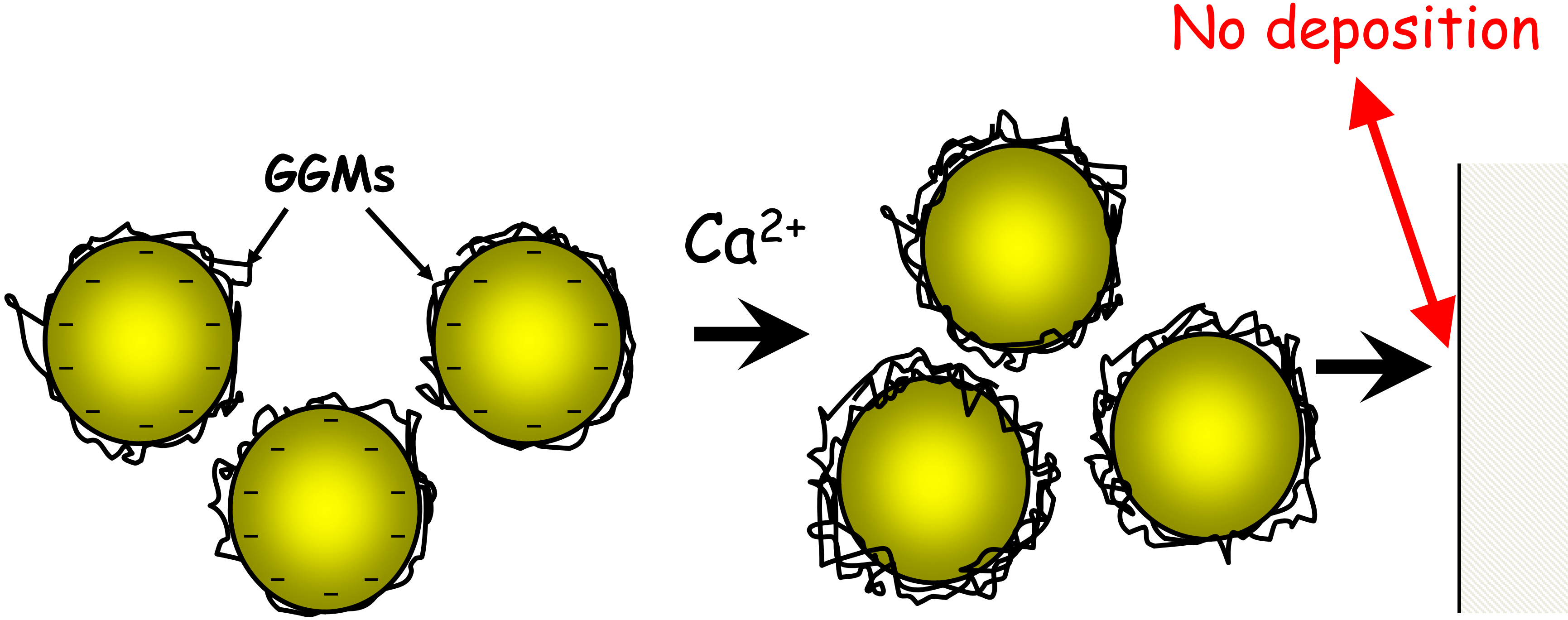


Chun-Lin Xu et al.

GGM

Accumulate around wood pitch droplets

- Steric stabilisation
- Lower deposition tendency



Mannans in oil-in-water emulsions

[1,2]Kirsi Mikkonen, [1]Maija Tenkanen, [3]Peter Cooke, [3]Kevin Hicks, [4]Stefan Willför and [3]Madhav Yadav

[1]Department of Applied Chemistry and Microbiology, [2]Department of Food Technology, University of Helsinki, Finland;

[3]Eastern Regional Research Center, ARS, United States Department of Agriculture, Wyndmoor, USA

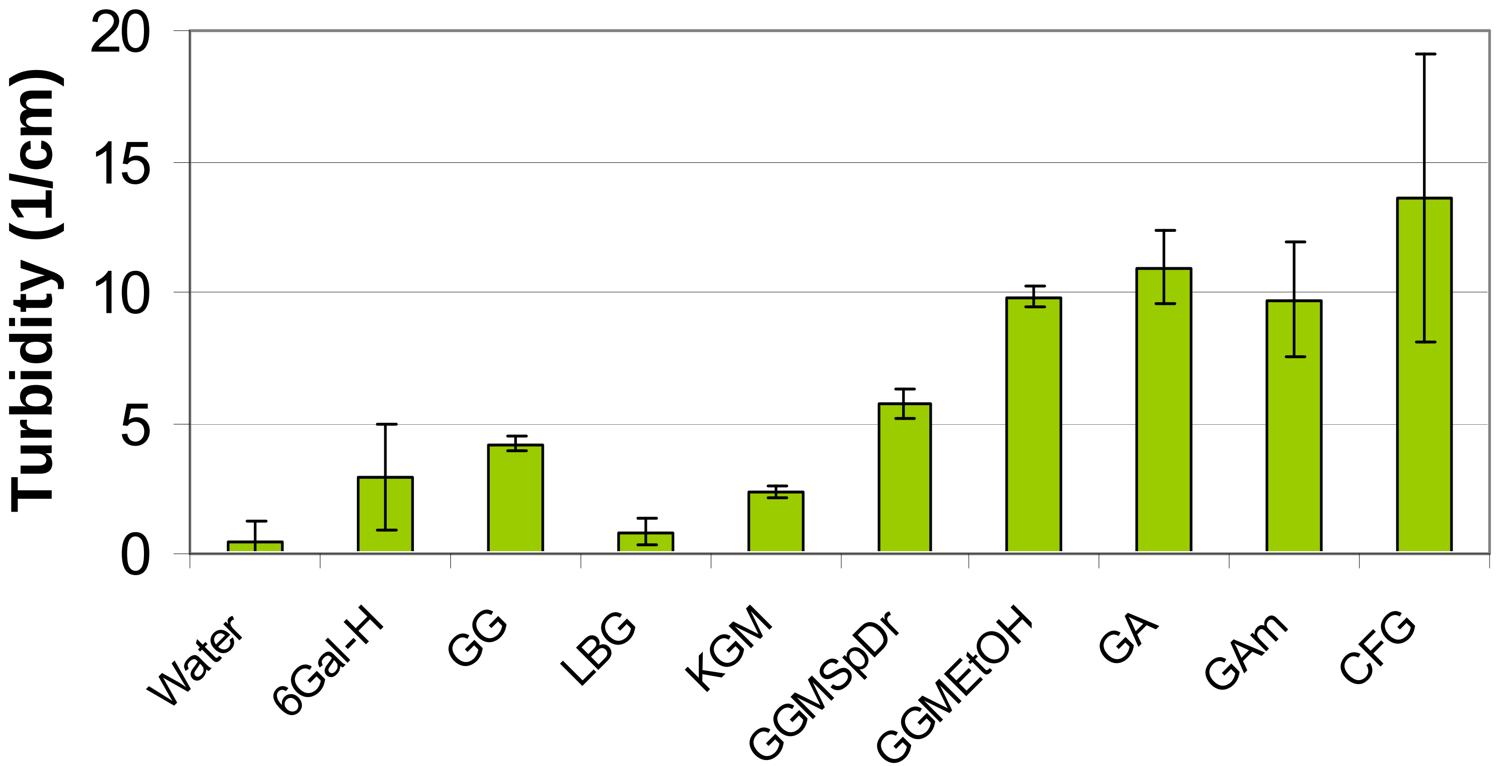
[4]Process Chemistry Centre, Åbo Akademi University, Åbo, Finland

Beverage emulsions

- Beverages contain hydrophobic aroma compounds such as citrus oils emulsified in water
- Gum arabic is widely used as emulsifier
  - Supply varies depending on climatic, political and economical conditions in Africa
    → **Could gum arabic be replaced by GGM?**

Kirsi Mikkonen et al.

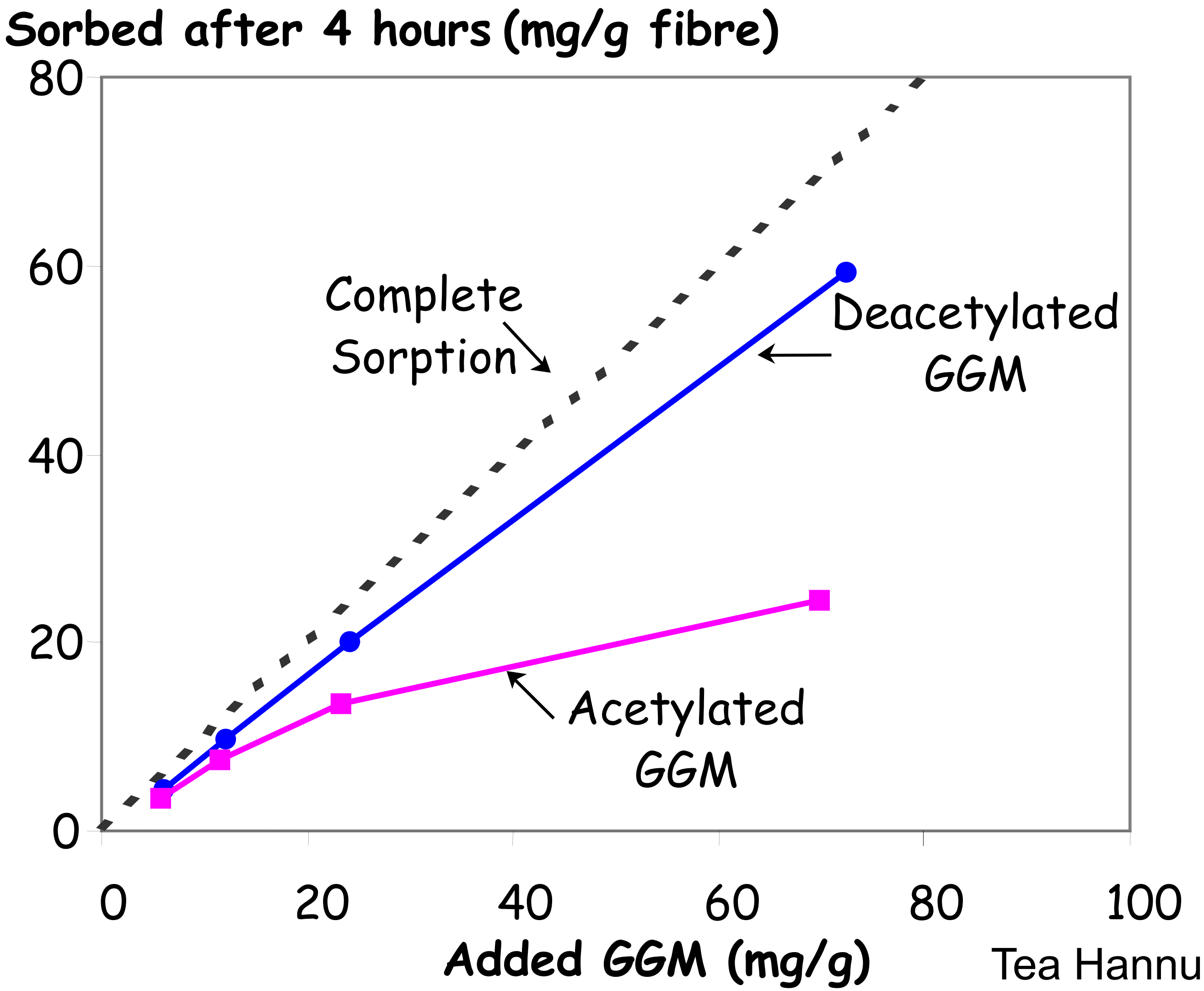
Emulsion stability of different mannans compared to gum arabic and CFG (after 14 days, 23ºC, oil to gum ratio 20:1)



6Gal-H = unmodified guar gum, **GG** = native guar gum, **LBG** = locust bean gum, **KGM** = konjac glucomannan, **GGMSpDr** = spray dried GGM, **GGMEtOH** = ethanol precipitated GGM, **GA** = native gum arabic, **GAm** = modified gum arabic, **CFG** = corn fiber gum

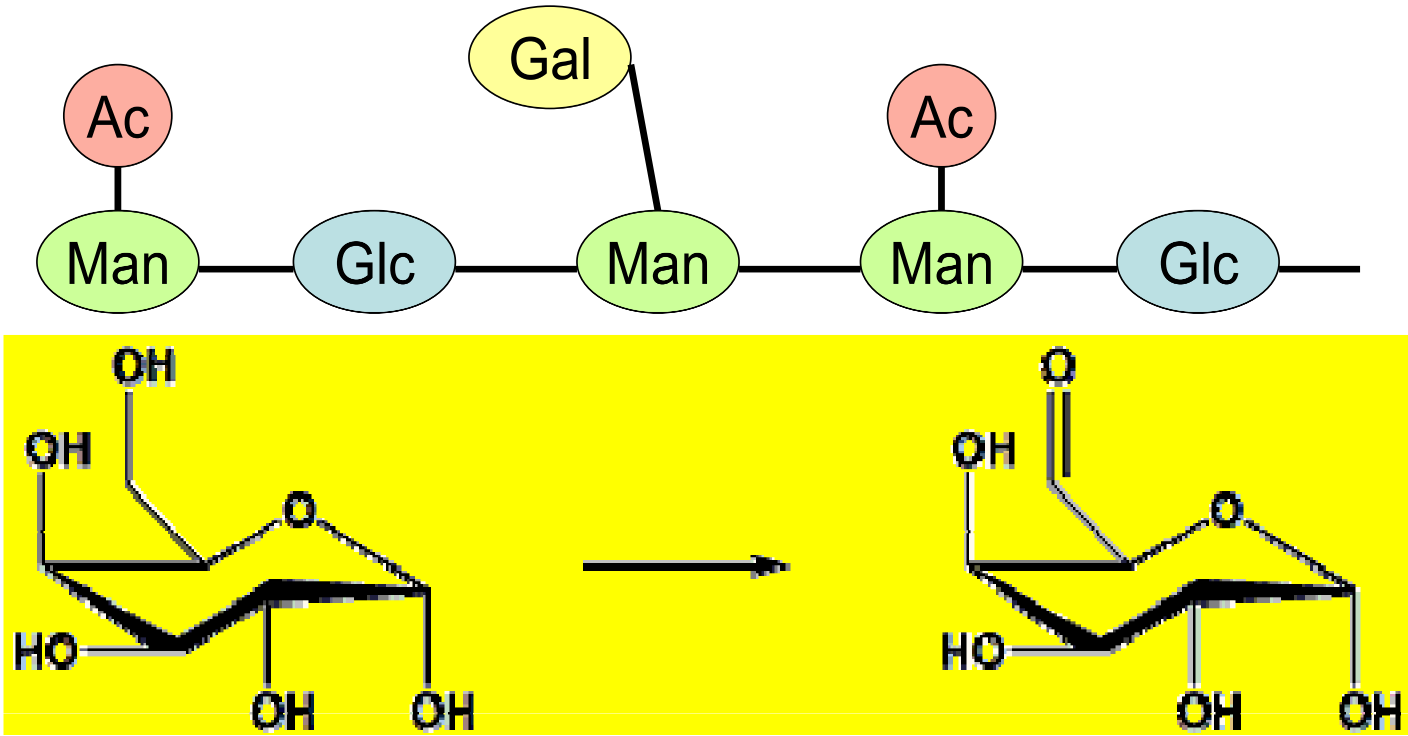
Kirsi Mikkonen et al.

Sorption of GGMs onto bleached kraft pulp



Tea Hannuksela et al.

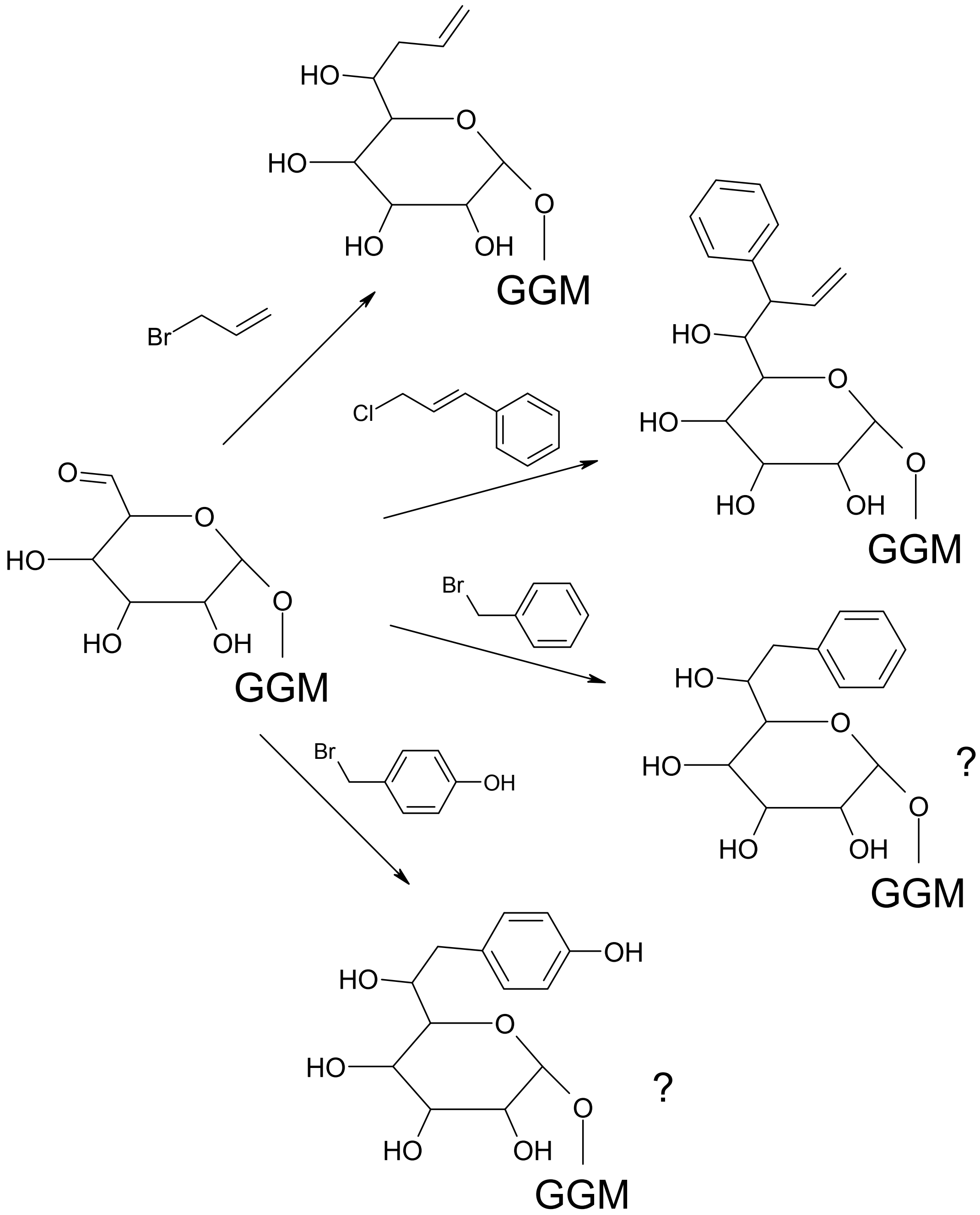
Targeted functionalization of spruce GGM with aid of galactose oxidase



Galactose oxidase acts on the primary alcohol at C-6 giving an aldehyde

Cooperation with Prof. Maija Tenkanen, Helsinki University

Chemical modification of enzymatically oxidized GGM



Metal mediated reaction in aqueous media

→ ***New properties***

Future Biorefinery - FuBio

- Five research themes:

1. Fractionation technologies – Ionic liquids, hot water treatment and separation of hydroxy acids from black liquor

2. Cellulose for material applications –New cellulose and cellulose fibre-based materials

3. Hemicelluloses for materials and hydroxy acids – New hemicellulose-based polymers

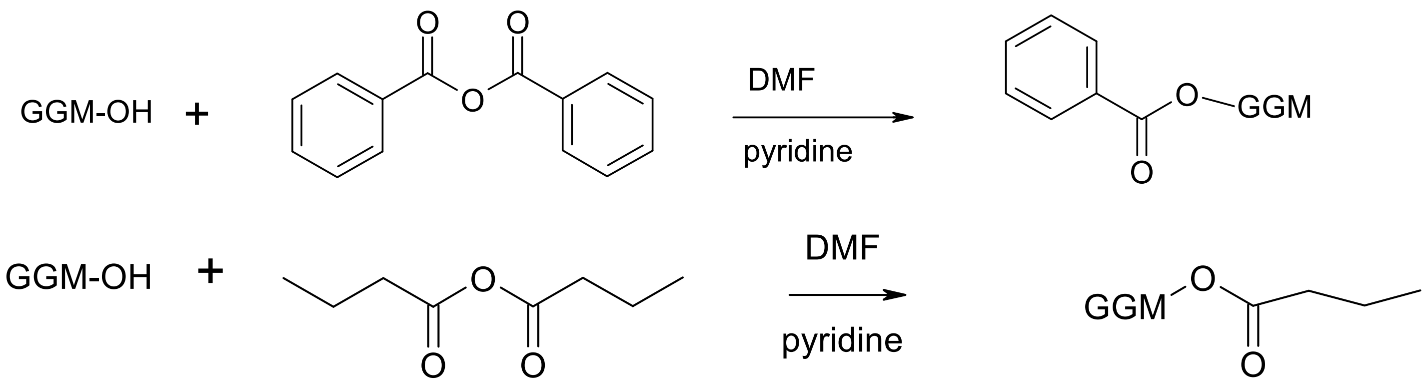
4. Lignin for energy and materials *–not active in the beginning*

5. Biochemicals for protection of products and health –High-value biomolecules for protection of products and health

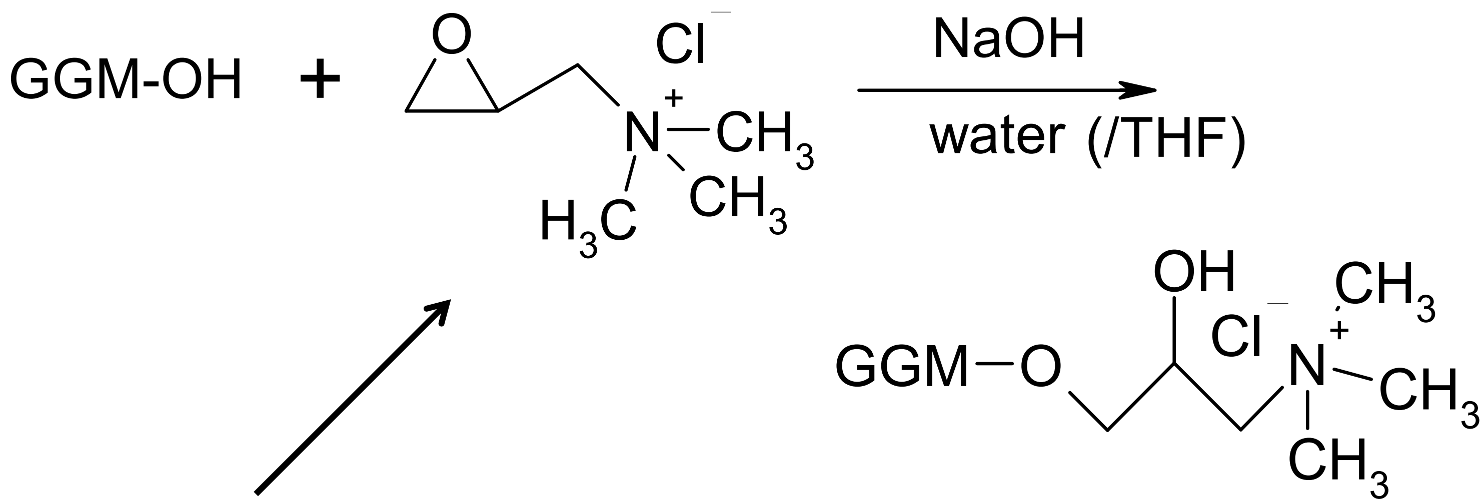
- Functional paper chemicals
  - Bifunctional GGM (e.g. amphiphilicity)
  - Cationic GGM
  - Improving runnability
  - Carboxymethylation, acetylation etc.
- Introduction of new functions to paper using GGM as a carrier of functional groups
- Improving printability
- Plasticization

Benzoyl esters of GGM (GGM-Bz) and butyric esters of GGM (GGM-But)

- Dispersion of GGM in dimethylformamide (DMF) and pyridine



Cationization of GGM



EPTMAC

(2,3-epoxypropyl trimethylammonium chloride)

Challenges

- Changes in solubility
  - Organic solvents vs water
  - Ionic liquids
- Analysis of products
- Methods established for cellulose, starch etc do not necessarily work for hemicelluloses
- Use of enzymes

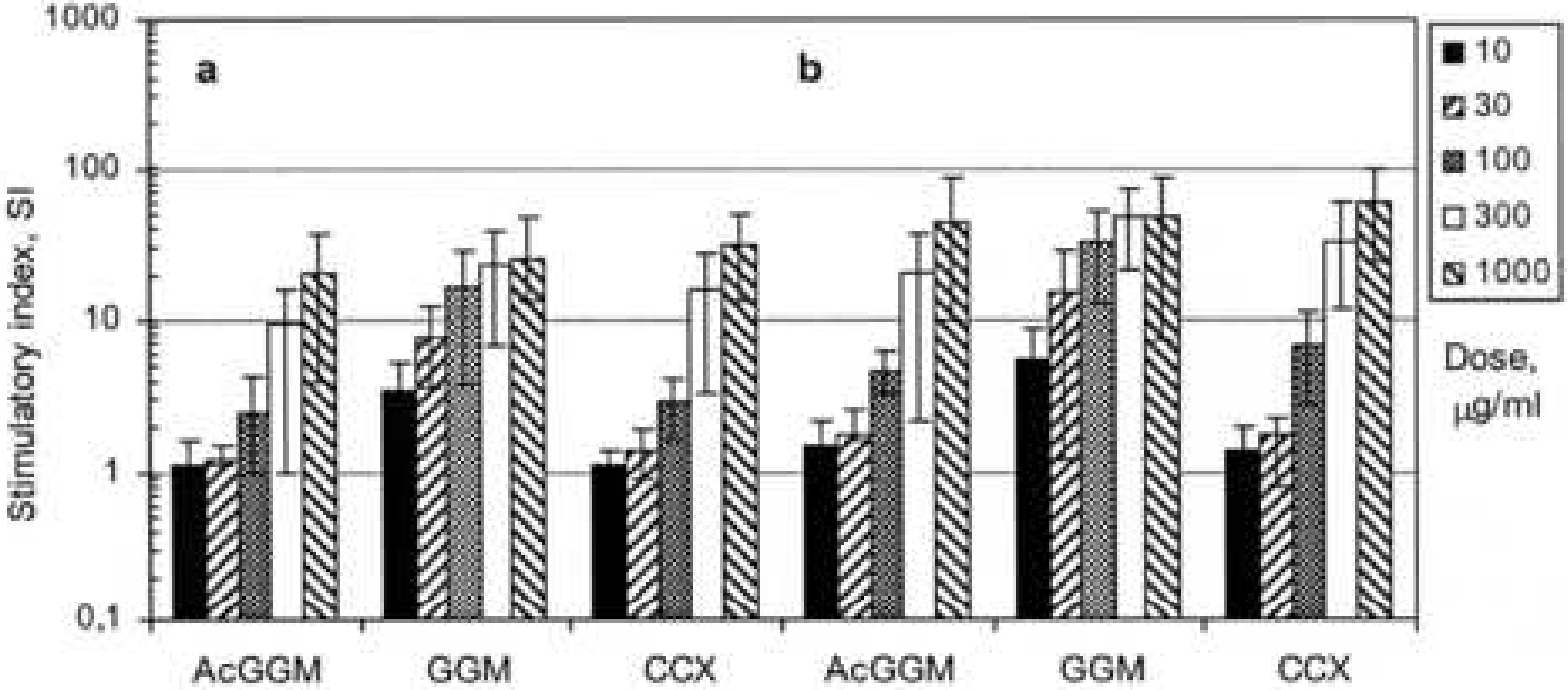
Potential in biodegradable films and for surface treatment of paper

- Films of GGM mixed with other polymers have a potential in food packaging
  - Low oxygen permeability
  - Grease barrier properties
  - Sufficient strength properties
  - Composite films with cellulose
  - Acetylation works here!

- GGM coating reduce paper porosity and provide excellent grease resistance

Kirsi Mikkonen et al.; Some work done in Sweden; M.Sc. thesis by Hong Zhai

Immunostimulatory activity



Immunostimulatory activity of AcGGM and GGM and the control CCX in the (a) mitogenic and (b) comitogenic tests (with stimulator)

Ebringerová et al. 2007

A mitogen is a chemical substance, usually some form of a protein, that encourages a cell to commence cell division, triggering mitosis

So, GGM has potential in:

- Dietary fibers
- Nutritional supplements
- Pharmaceutical applications
- Prebiotics

EPNOE conference

European Polysaccharide Network Of Excellence

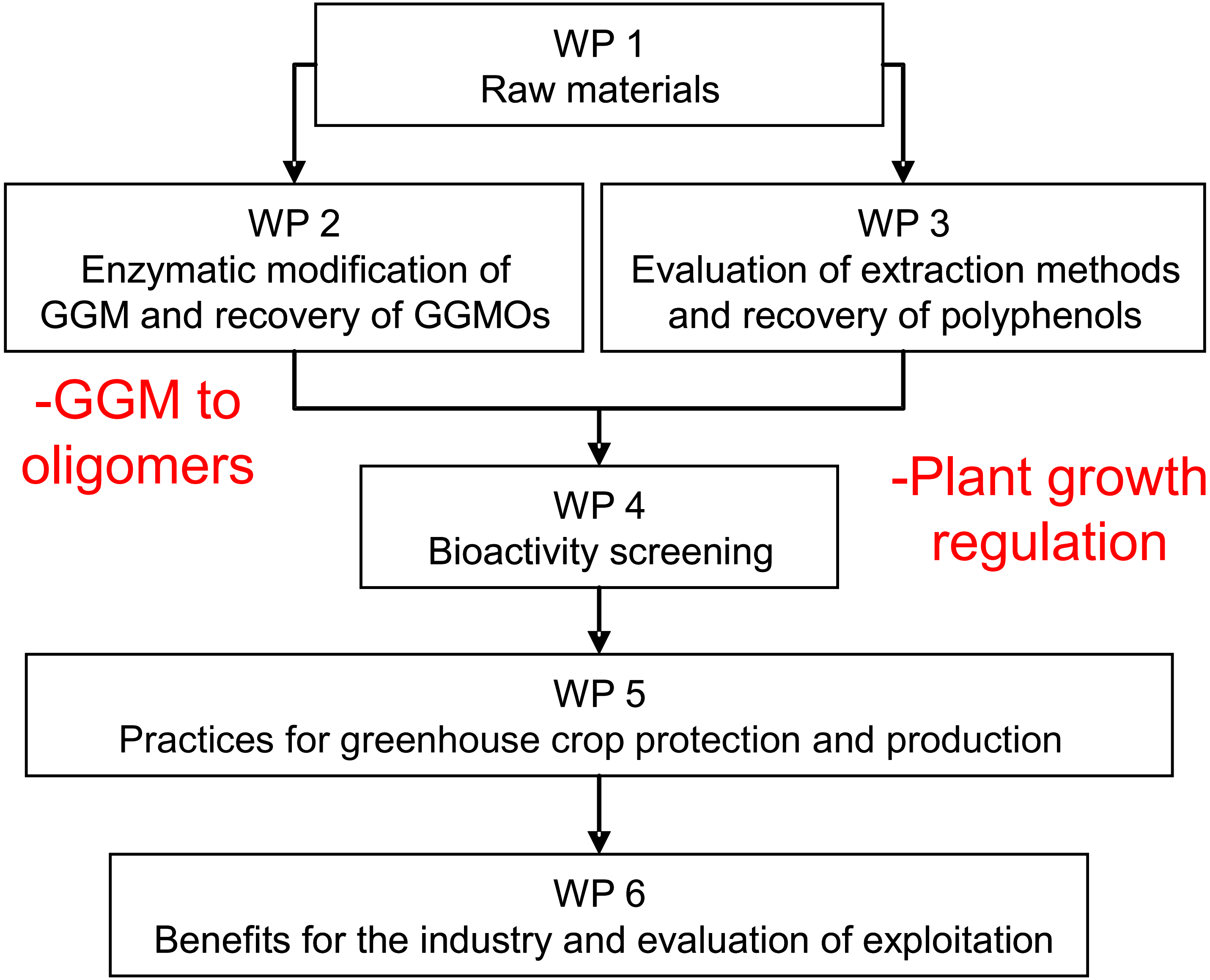
Improving the hemocompatibility of Poly(ethylene taraphtalate) surfaces by galactoglucomannan derivatives adsorption

Aleš Doliška[1], Simona Strnad[1], Volker Ribitsch[2], Stefan Willför[3], Karin Stana Kleinschek[1]

[1]*University of Maribor, Faculty of Mechanical Engineering, Institute for Engineering Materials and Design, Slovenia*
[2] *University of Graz, Institute for Chemistry, Austria*
[3] *Åbo Akademi University, Process Chemistry Centre, Laboratory of Wood and Paper Chemistry, Finland*

Sulphated spruce GGM show promising anticoagulant and antithrombotic activities

Upgrading Forest Industry Waste to Bioactive Chemicals for Crop Stimulation and BioControl



Co-operation with Slovak Academy of Science

- GGM as dietary fibres and for production of specialty sugars (Fubio T5)
- Microncapsulation of drugs or flavors (HU/ÅA)
- GGM in animal feed (MTT/ÅA/Metla)
- And so on…