Chemical Conversion of Hemicellulose Coproducts from Forest Biorefineries to Polymers and Chemicals

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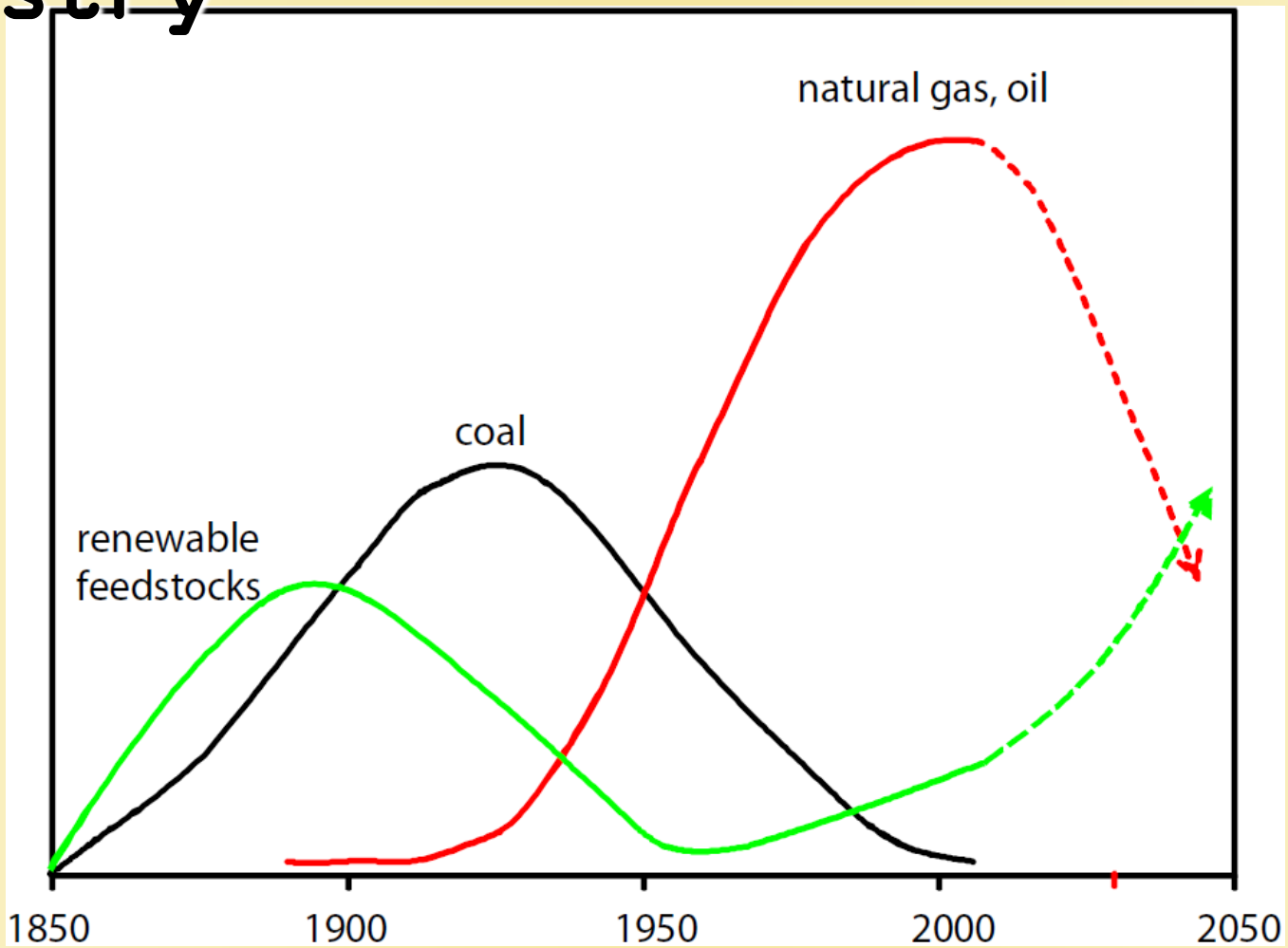
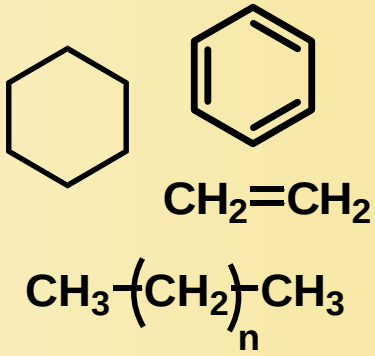
Raw Material Basis of Chemical Industry



Lichtenthaler, F. W.; Peters, S. *C. R. Chimie* **2004**, 7, 65–90

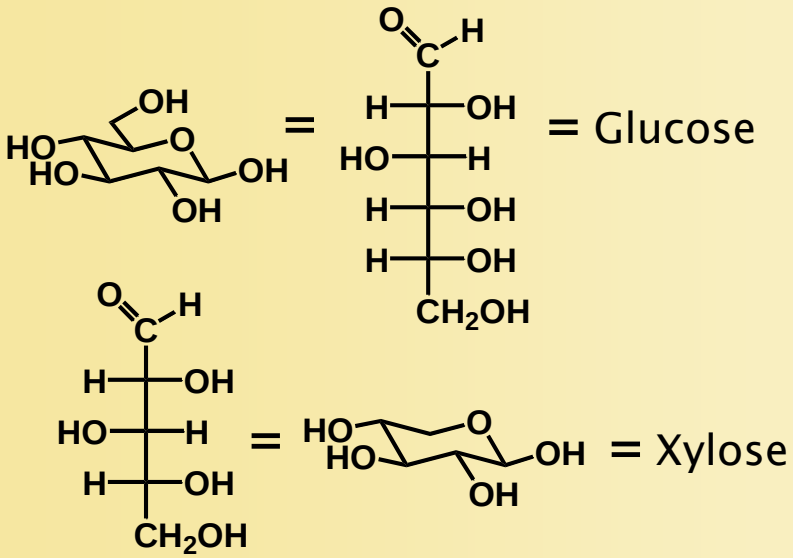
Refinery vs Biorefinery

Crude Oil → **Hydrocarbons**



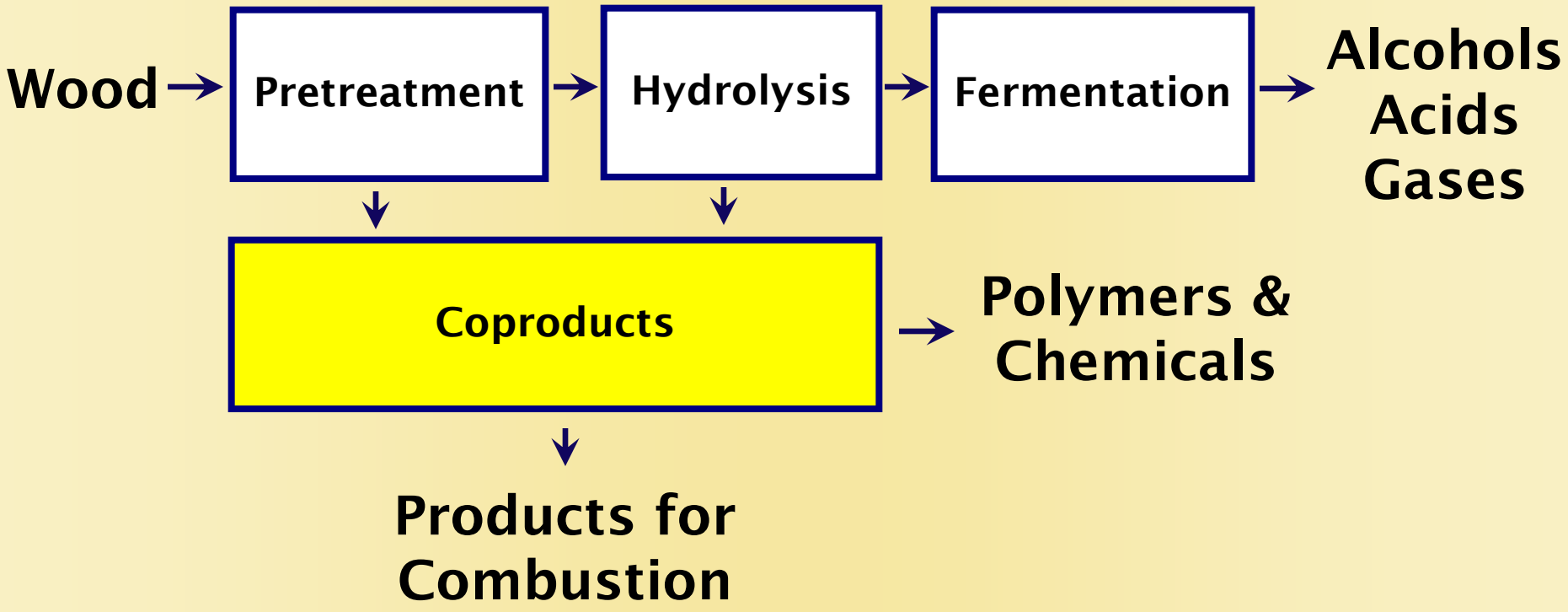
Hydrophobic
Little Oxygen

Biomass → **Carbohydrates**



Hydrophilic
Oxygen:Carbon 1:1

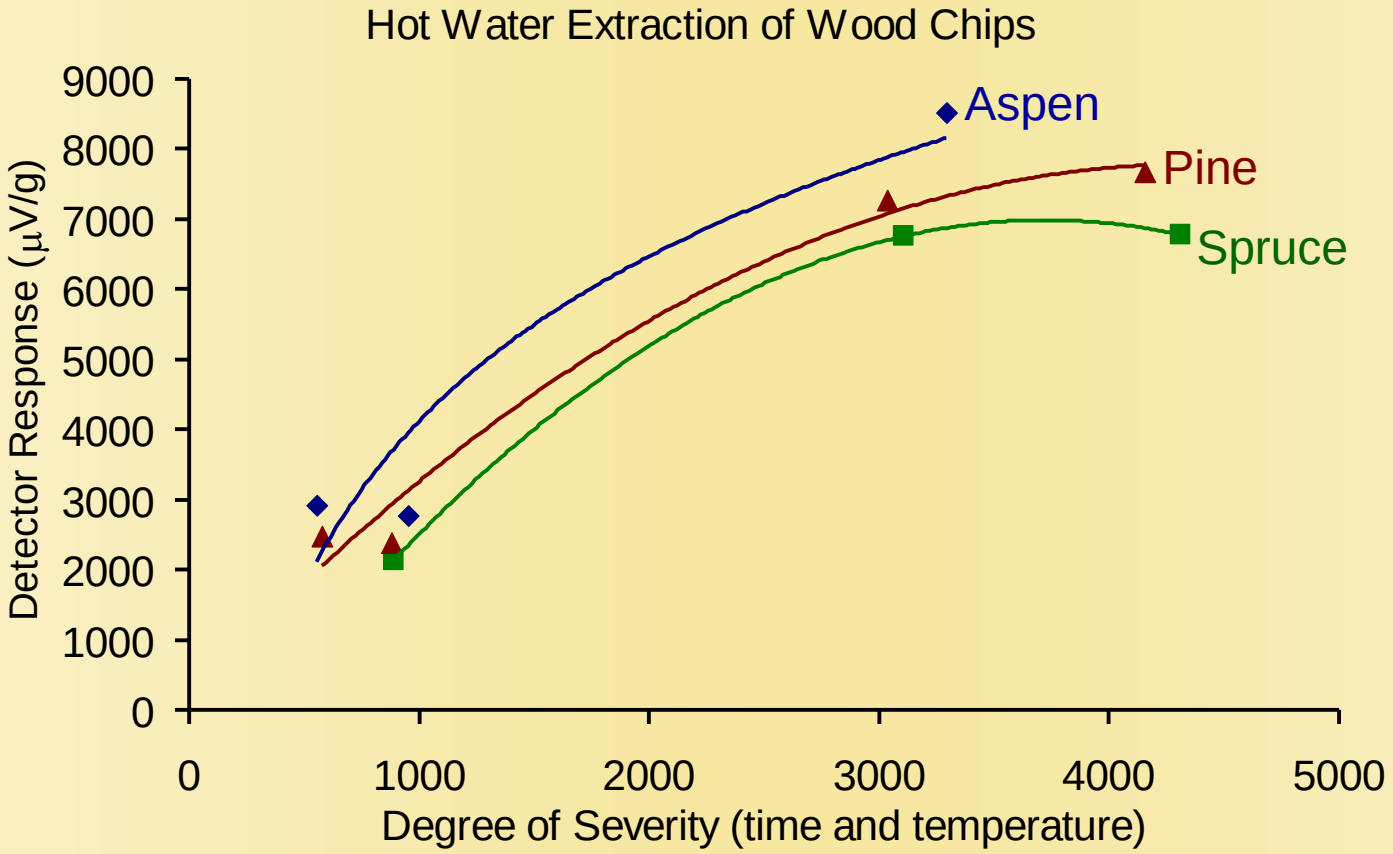
Lignocellulosic Biorefineries



Pretreatment Methods

- Physical
  - high-pressure steaming and steam explosion
  - milling and grinding
  - extrusion
  - high-energy radiation
- Chemical
  - alkali
  - acid
  - gas
  - oxidizing agents
  - solvents
- Biological
  - lignin consuming fungi
  - cellulose consuming fungi

Autohydrolysis



- Autoclave (2 L) charged with wood chips and neutral water
- Time = 2.5-10 minutes, temperature = 160 or 190°C
- HPLC used to analyze for oligosaccharides with a DP of 1−11
- RI detector peak area normalized by the sample mass

Chemical Compositions as a Percent of Feedstocks

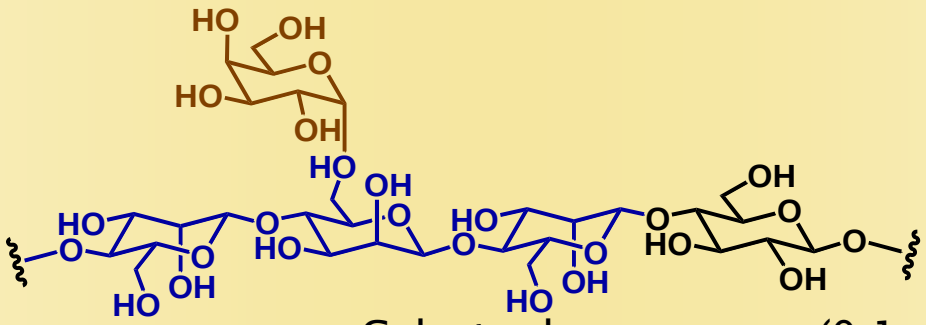
	Lignocellulosic Feedstock	Glucose	Hemicellulose			Lignin
			Xylose	Mannose	Arabinose	
Softwood	Spruce	43.4	4.9	**12.0**	1.1	28.1
	Pine	46.4	8.8	**11.7**	2.4	29.4
Hardwood	Birch	38.2	18.5	1.2	not detected	22.8
	Willow	43.0	24.9	3.2	1.2	24.2
Agricultural Fiber	Wheat straw	38.2	21.2	0.3	2.5	23.4
	Corn stover	35.6	18.9	0.3	2.9	12.3

- Softwood hemicellulose is mannan with some xylan
- Hardwood is mainly xylan

Jørgensen, H.; Kristensen, J. B.; Felby, C. *Biofuels, Bioprod. Bioref.* **2007**, 1, 119–134

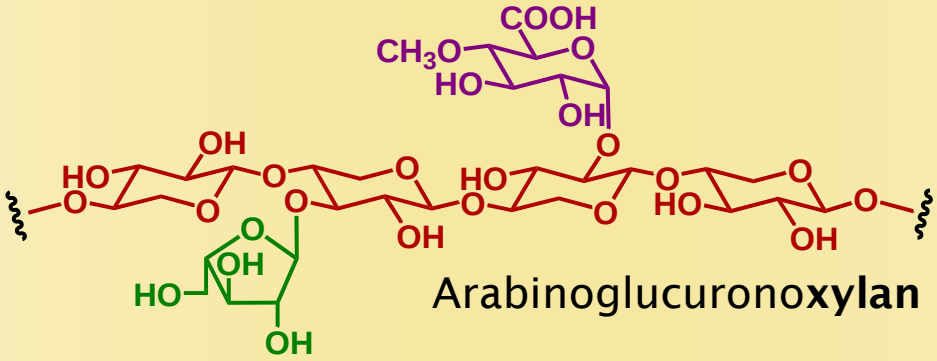
Softwood:

6-carbon backbone; hexosan



Galactoglucomannan (0.1–1:1:4) 15–23%

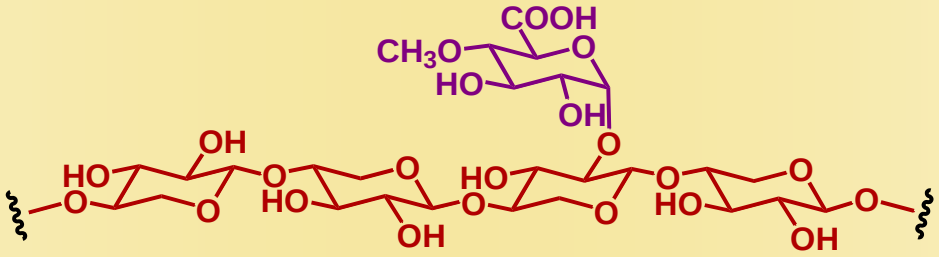
5-carbon backbone; pentosan



Arabinoglucuronoxylan (1:2:10) 5–10 %

Hardwood:

5-carbon backbone; pentosan

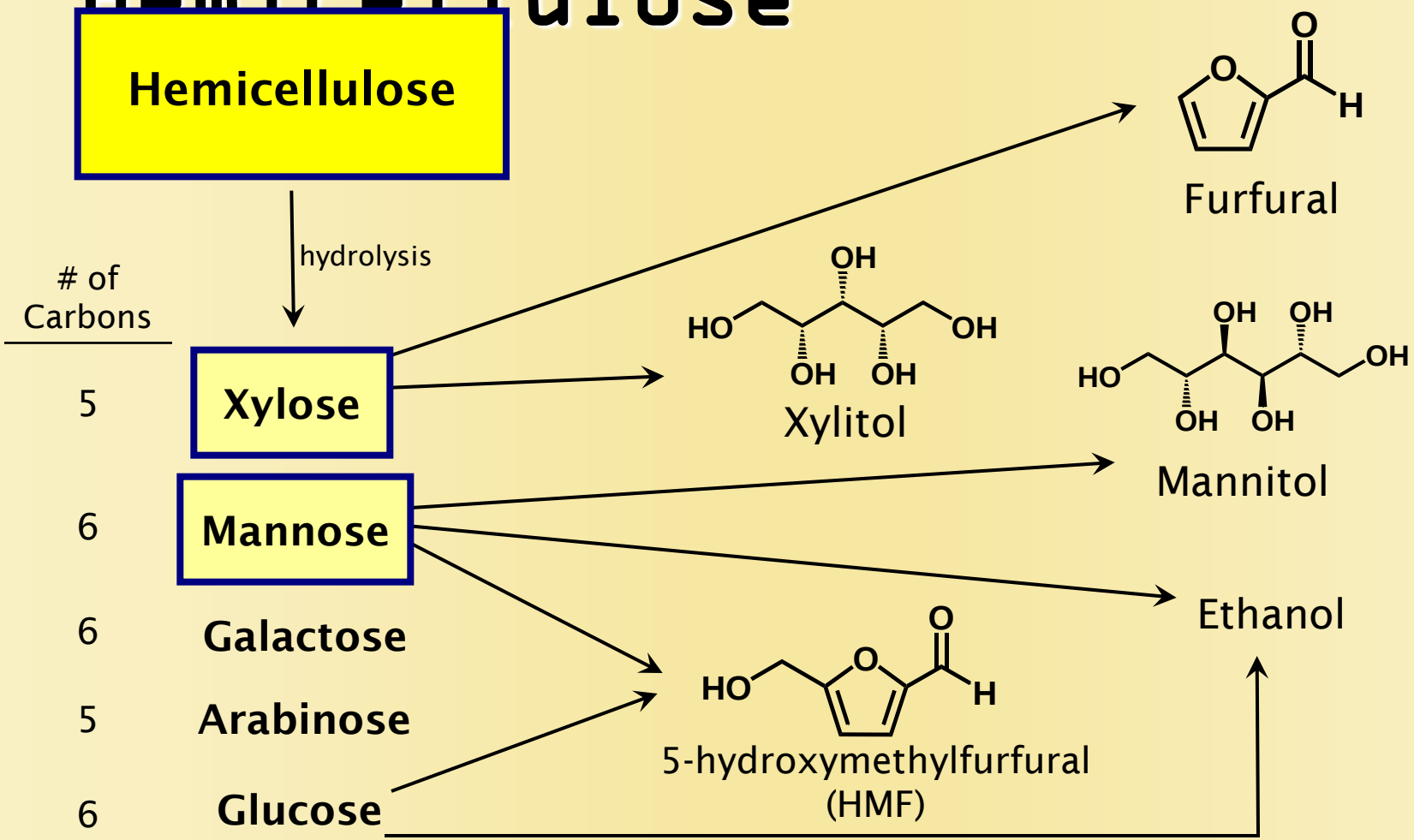


Glucuronoxylan (1:10) 15–30 %

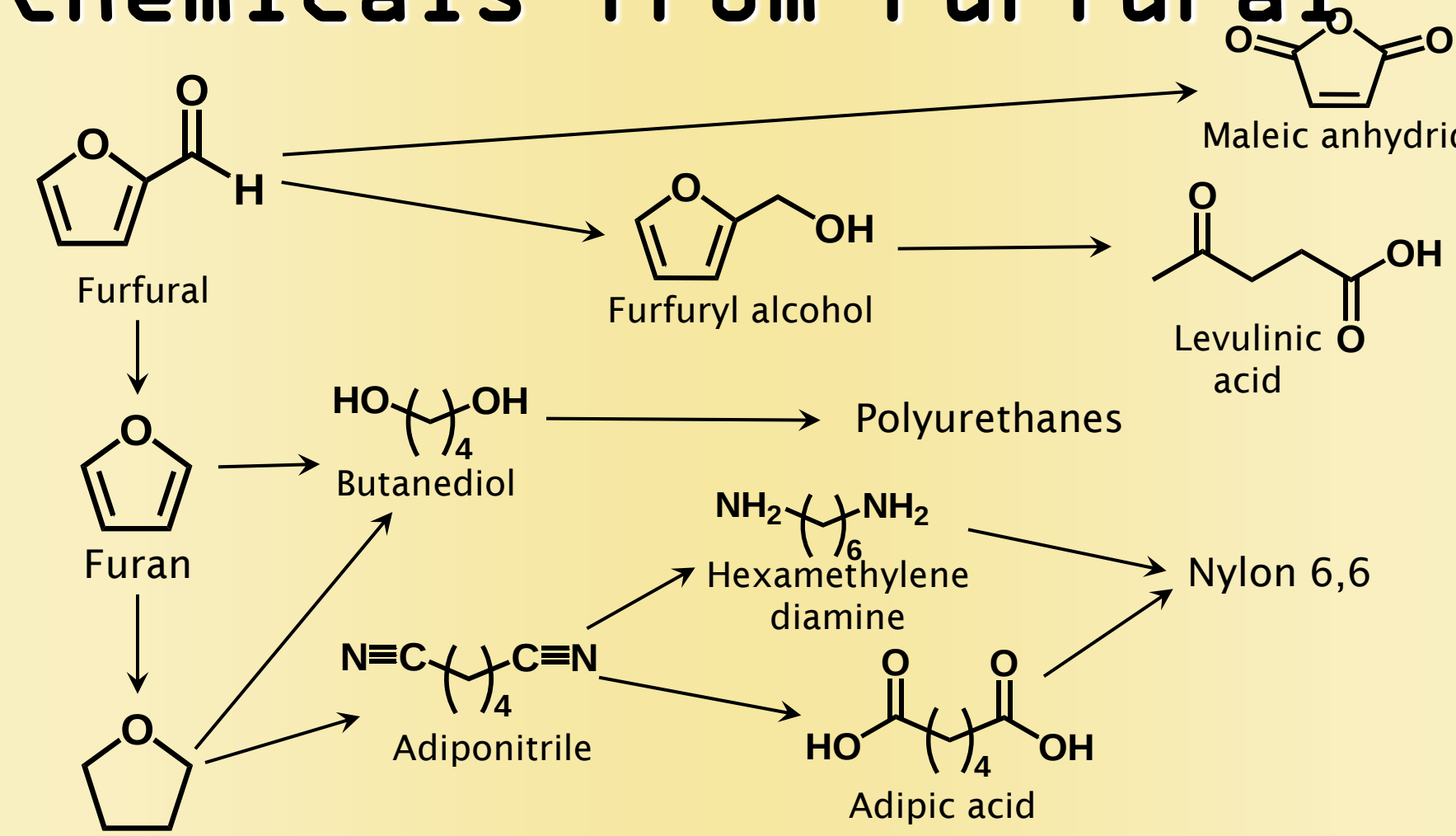
4-O-Methyl-Glucuronic Acid = Purple
Xylose = Red
Arabinose = Green
Mannose = Blue
Glucose = Black
Galactose = Brown

Sjöström, E. *Wood Chemistry Fundamentals and Applications*; Academic Press: New York, 1981; pp 60–65.

Chemicals from Hemicellulose

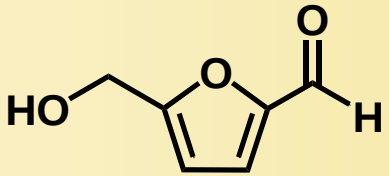


Chemicals from Furfural

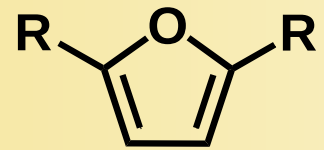


Kamm, B.; Kamm, M.; Schmidt, M.; Hirth, T.; Schulze, M. Lignocellulose-based Chemical Products and Product Family Trees. In *Biorefineries – Industrial Processs and Products Status Quo and Future Directions*; Kamm, B.; Gruber, P. R.; Kamm, M., Eds.; Wiley-VCH: Weinheim, 2006; Vol. 2, p 125.

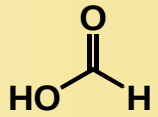
Chemicals from HMF



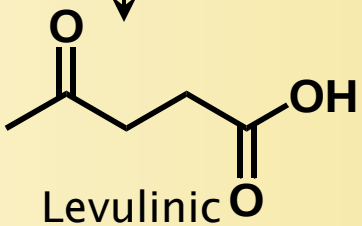
5-hydroxymethyl-furfural (HMF)



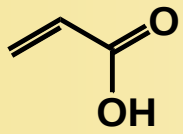
Symmetric monomers
R = COOH, CHO, CH_2NH_2, or CH_2OH



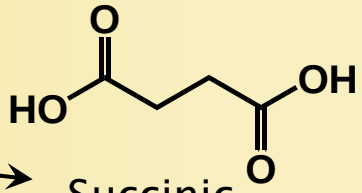
Formic acid



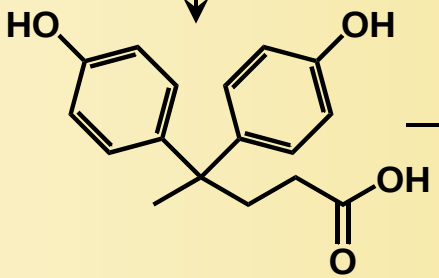
Levulinic acid



Acrylic acid

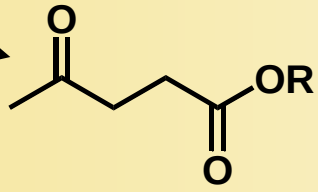


Succinic acid



4,4-Bis(4-hydroxyphenyl)-valeric acid

Polycarbonates, Epoxy



Levulinate esters

Volume and Prices of Sugars and Chemicals

Type of Material	Name	World Production (metric t/year)	Price (€/kg)
Sugars	Sucrose	140,000,000	0.20
	Glucose	30,000,000	0.30
	Fructose	60,000	1.00
	Xylose	25,000	4.50
Sugar Alcohols	Sorbitol	650,000	1.80
	Xylitol	30,000	5.00
	Mannitol	30,000	8.00
Petrochemicals	Ethylene	90,000,000	0.40
	Benzene	23,000,000	0.40
	Adipic acid	1,500,000	1.70

Lichtenthaler, F. W. The Key Sugars of Biomass: Availability, Present Non-Food Uses and Potential Future Development Lines. In *Biorefineries – Industrial Processs and Products Status Quo and Future Directions*; Kamm, B.; Gruber, P. R.; Kamm, M., Eds.; Wiley-VCH: Weinheim, 2006; Vol. 2, p 5.

Hemicellulose Films

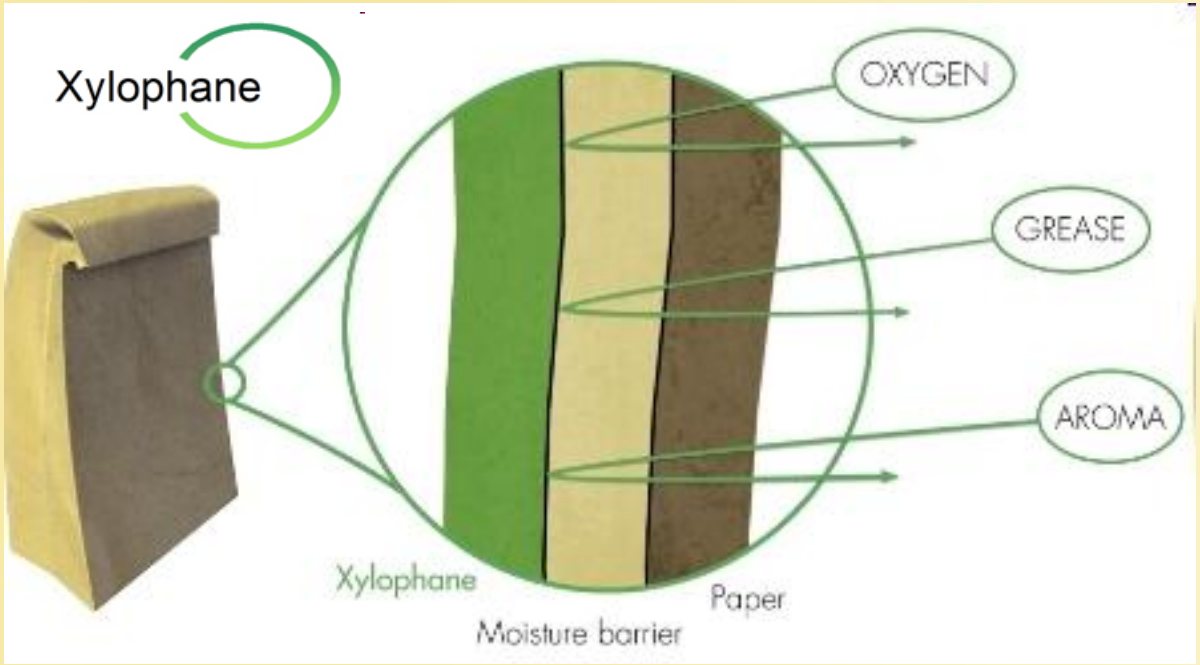
Native hemicellulose
Poor film-forming properties

Propoxylated hemicellulose
Good film-forming properties

Jain, R. K.; Sjöstedt, M.; Glasser, W. G. *Cellulose* **2001**, 7, 319-336

Xylophane

- Company founded in 2004
- Hemicellulose used as a biodegradable food packaging material
- Desirable barrier properties
- Film cast on support (paper) from water with the aid of plasticizer



www.xylophane.com

Applications of Hemicellulose Carbohydrates

- **Existing Applications**
  - food additives
  - plasticizers
  - resins
- **Potential Applications**
  - binders
  - solvents
  - monomers for polyamide, polyester, polyurethane, polycarbonate, epoxy
  - fuel additives
  - pharmaceuticals
  - specialty chemicals

Conclusions & Outlook

- Existing commercial chemical products include xylitol, mannitol, and furfural
- Furfural-based chemicals could become more attractive than their fossil-based equivalents
- Reduction in cost of 5-hydroxymethylfurfural unlocks potential for new chemicals and applications from hemicellulose
- Advances in hemicellulose films affords use as a biodegradable packaging material