Forest Based Biorefinery

"Chemical and Engineering Challenges and Opportunities "

Fractionation Technologies, Extraction and Utilization of Wood Components

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Åbo Akademi

2010

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European Polysaccharide
Network Of Excellence

Laboratory of Fibre and Cellulose Technology

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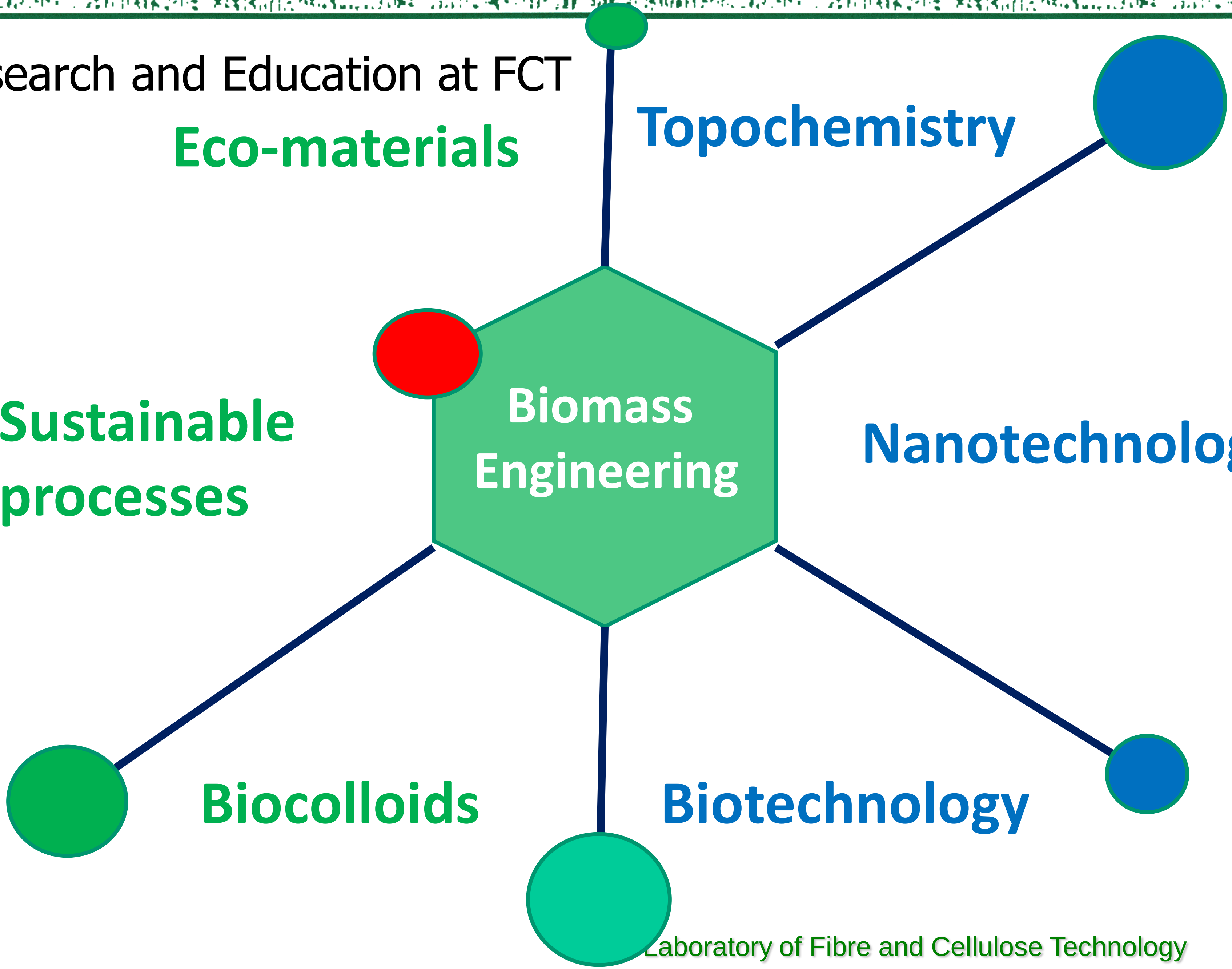
Research and Education at FCT



Eco-materials

Topochemistry

Biomass Engineering

Sustainable processes

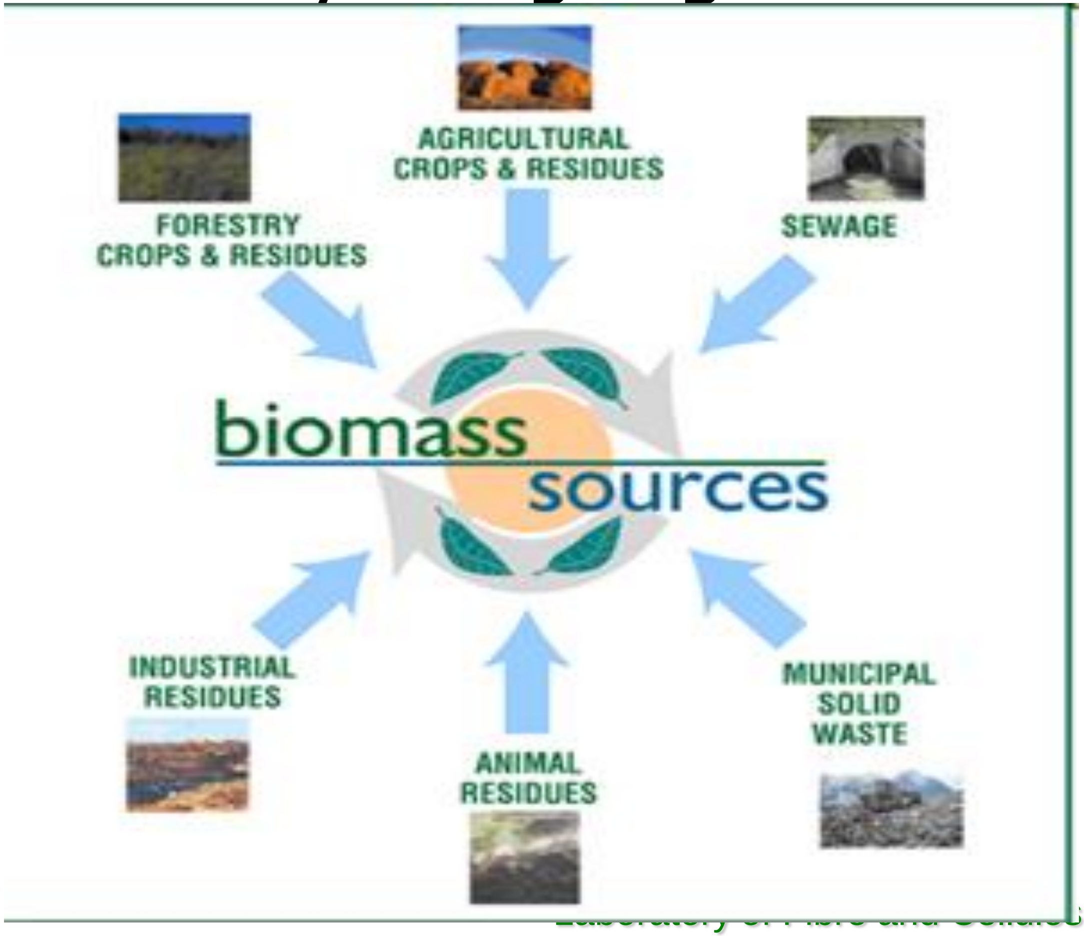
Nanotechnology

Biocolloids

Biotechnology

Biomass

- *Biomass* is biological material derived from living, or recently living organisms.



Biomass based chemicals

- 70-100 billion USD (3-4% of global market today)
- Possible increase to 17% of global market in 2025
- Oil price and type of energy to power the vehicles impact the market

Ample opportunities for bio-based materials

Biodegradability

	Fully fossil-based	*Partially Biobased*	*Fully Biobased*
Fully Biodegradable	-PBS -PBSL -PBSA	-Starch blends (with biodegradable fossil-based coplymers) -Vegetable-oil based polyesters	-Thermoplastic starch (TPS) -Starch blends (with biobased and biodegradable copolymers) -Cellulose -PLA -PHA/PHB
Partially Biodegradable			
Non-Biodegradable	-PE -PP -PET -PVC -PUR -ABS -Epoxy resin -Synthetic rubber	-Biobased PTT, PBT -Biobased PET -Biobased PVC -Biobased PUR -Biobased polyacrylates -Biobased ABS -Biobased Epoxy resin -Biobased SBR -Alkyd resin	-Biobased PE -Biobased PP -Biobased PA -Biobased PB -PO3G

Total polymer cons. Western Europe:
~50 million t p.a.

Technical potential bio-based:
~42 million t p.a. (85%)

Biobased raw material

PRO-BIP Study (2009) / EPNOE

Three sources of biomass based chemicals

1) Direct production
2) Expression in plants
3) Biorefinery

Direct production

- Biotechnology and chemical technology combined
- Propane-diol produced from corn-derived glucose (DuPont/Tate&Layle)
- Glucose converted into polylactic acid (Cargill)

Expression in Plants

- Chemicals expressed in genetically enhanced plants
- More suitable for annual crops?
- Impact of environment
- Early stage

Biorefinery

- A biorefinery is a facility that integrates biomass conversion processes and equipment to produce fuels, power, and chemicals from biomass.
- The biorefinery concept is analogous to today's petroleum refineries, which produce multiple fuels and products from petroleum.
- Industrial biorefineries have been identified as the most promising route to the creation of a new domestic biobased industry.

Biorefinery concept

- Fuel and chemicals/materials platform
- Fractionation into biopolymers and biomolecules has a key role
- Not limited to forest sector
- Chemical co-products by genetic modification of yeasts (e.g. isobutanol as co-product of ethanol)
- Pilot stage

Fractionation

- Definition of fractionation:
  - “**Fractionation** is a separation process in which a certain quantity of a mixture (solid, liquid, solute or suspension) is divided up in a number of smaller quantities (fractions) in which the composition changes according to a gradient”.

-Wikipedia

Motivation

- Why should I be interested in fractionation of biomass?
  - Separation / dissolution of components
    - Crude elimination of the components of interest from the bulk matrix
    - Avoiding a high degree of degradation of polymers components.
  - Homogenisation / isolation
    - Increase of chemical and physical uniformity of heterogenic components.
  - Purification
    - Thorough elimination of impurities

  - Obtaining a pure, homogenous raw material is a key criteria for production of new biochemicals from biomass.

Chemical components in biomass raw materials

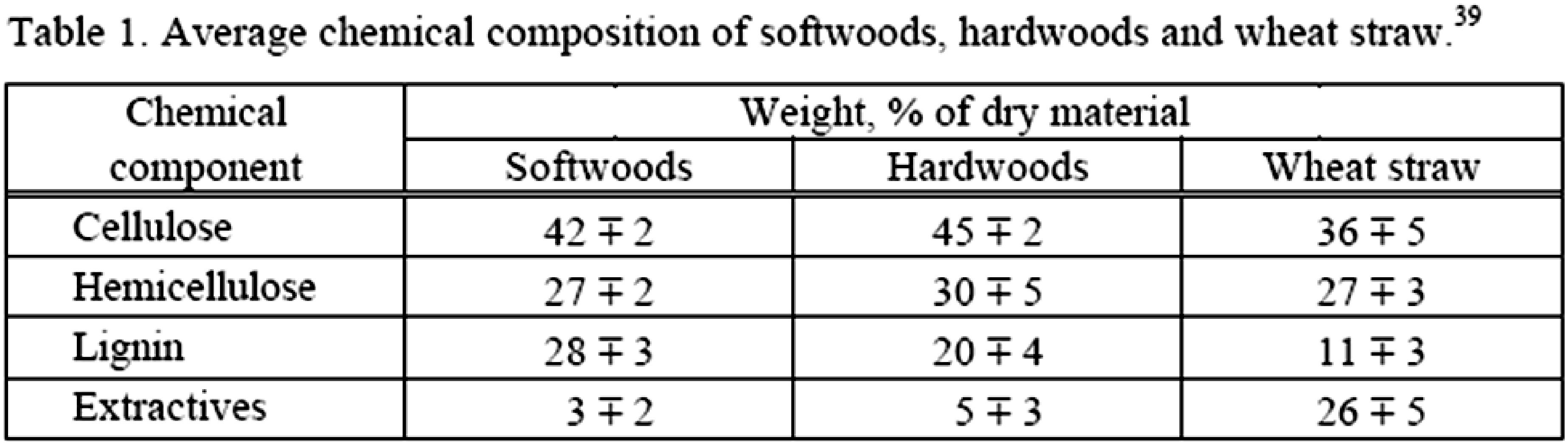


Table 1. Average chemical composition of softwoods, hardwoods and wheat straw.[39]

Chemical component	Weight, % of dry material		
	Softwoods	Hardwoods	Wheat straw
Cellulose	42 ∓ 2	45 ∓ 2	36 ∓ 5
Hemicellulose	27 ∓ 2	30 ∓ 5	27 ∓ 3
Lignin	28 ∓ 3	20 ∓ 4	11 ∓ 3
Extractives	3 ∓ 2	5 ∓ 3	26 ∓ 5

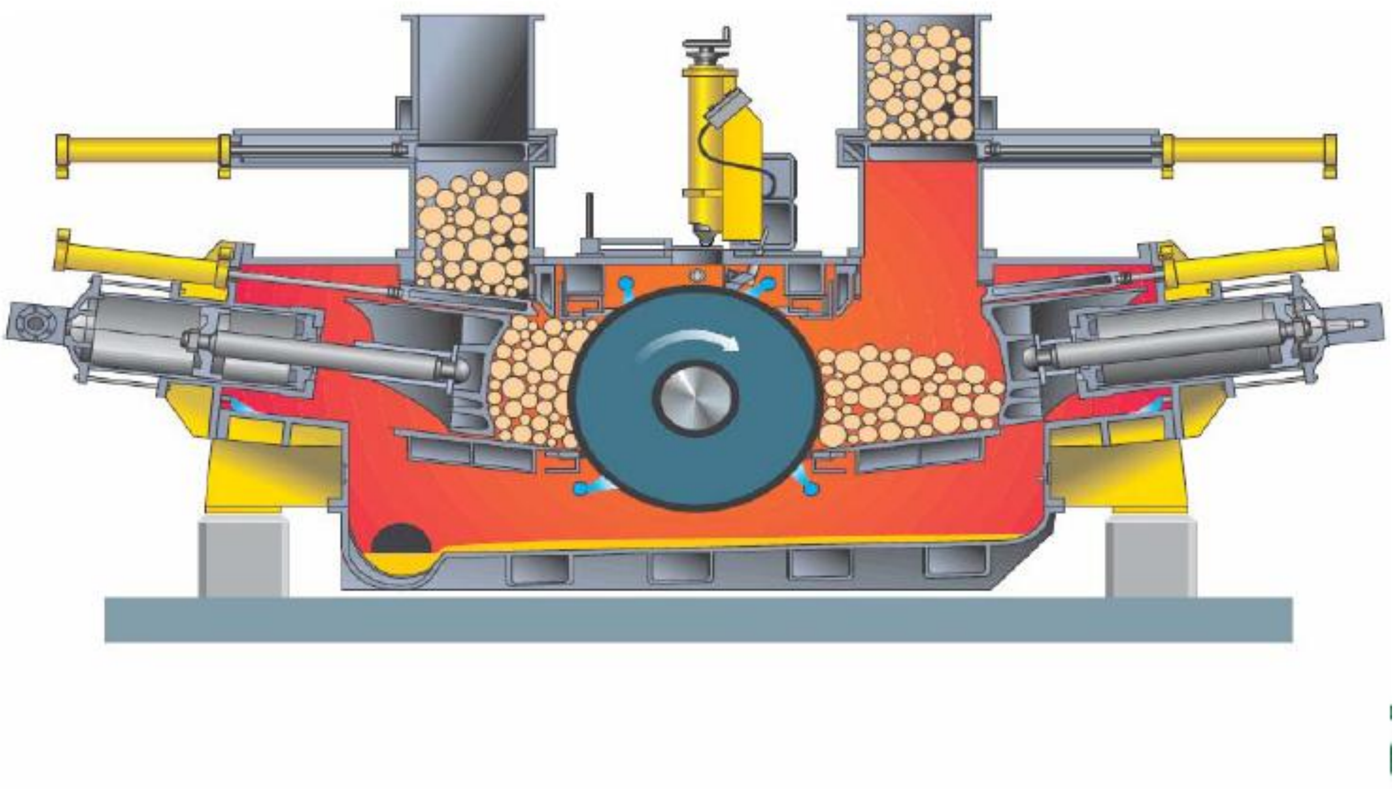
Thomas, R. J., Wood Structure and Chemical Composition, in “Wood Technology: Goldstein, Ed, ACS, 1-23, (1977).

Fractionation of solid biomass: mechanical methods for fibre separation

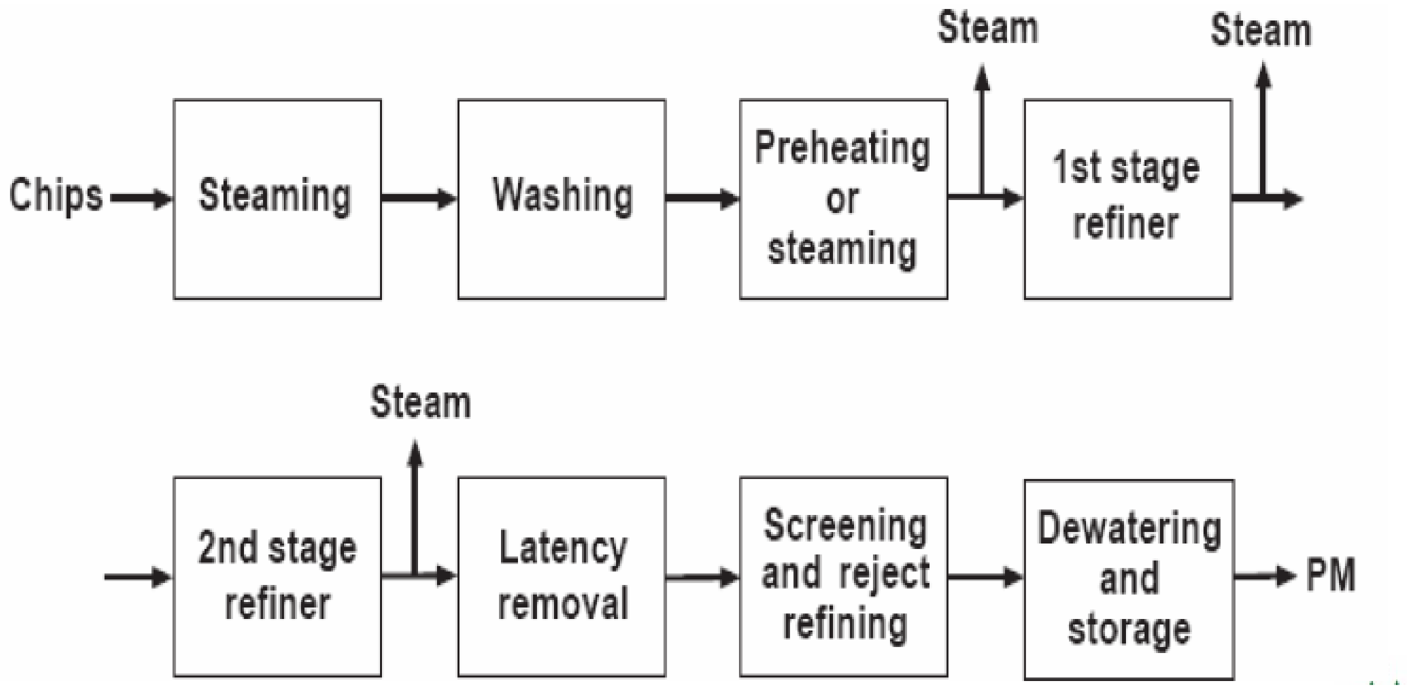
Mechanical methods for fibre separation

- Mechanical (PGW, TMP)
- Chemimechanical (CMP, CTMP)

PGW

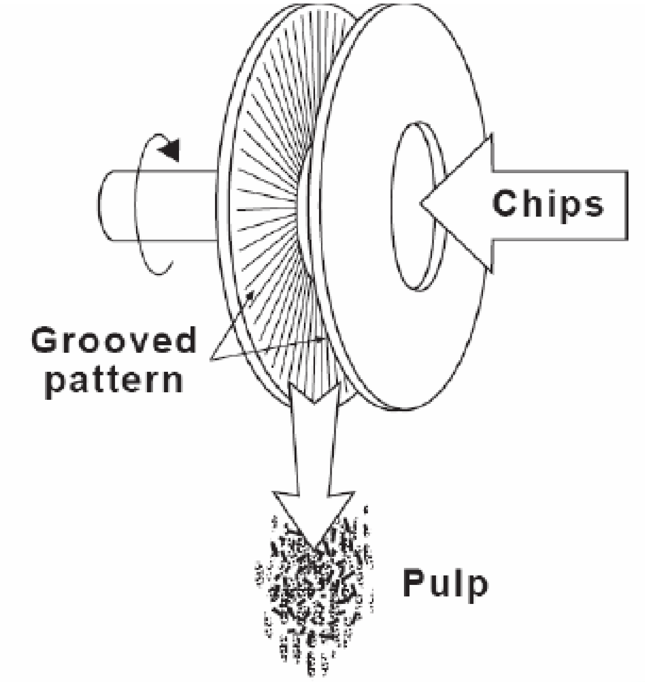


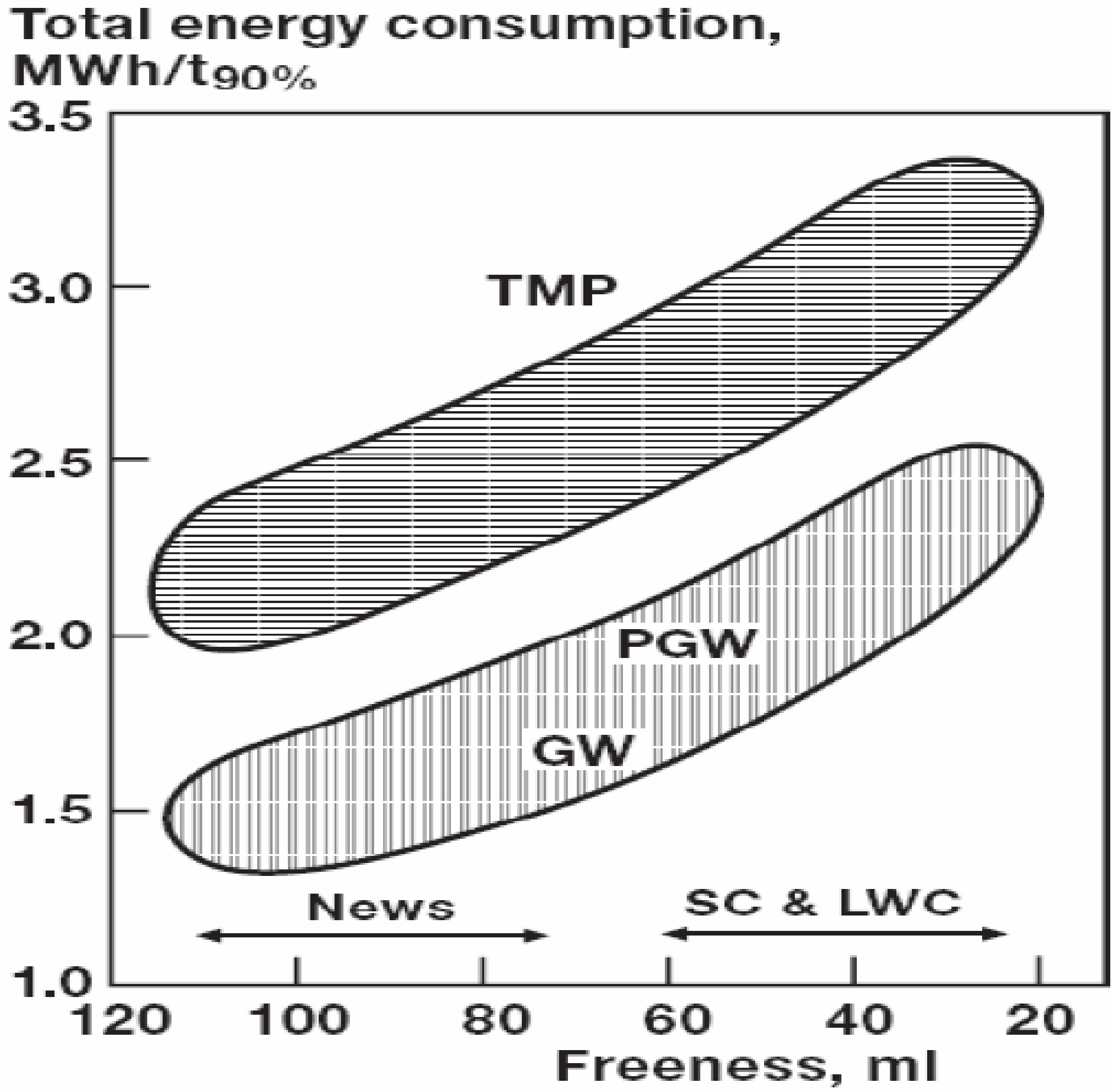
Flow sheet of a TMP plant



Refiner types

- Single disc (SD)
- Double disc (DD)
- Conical

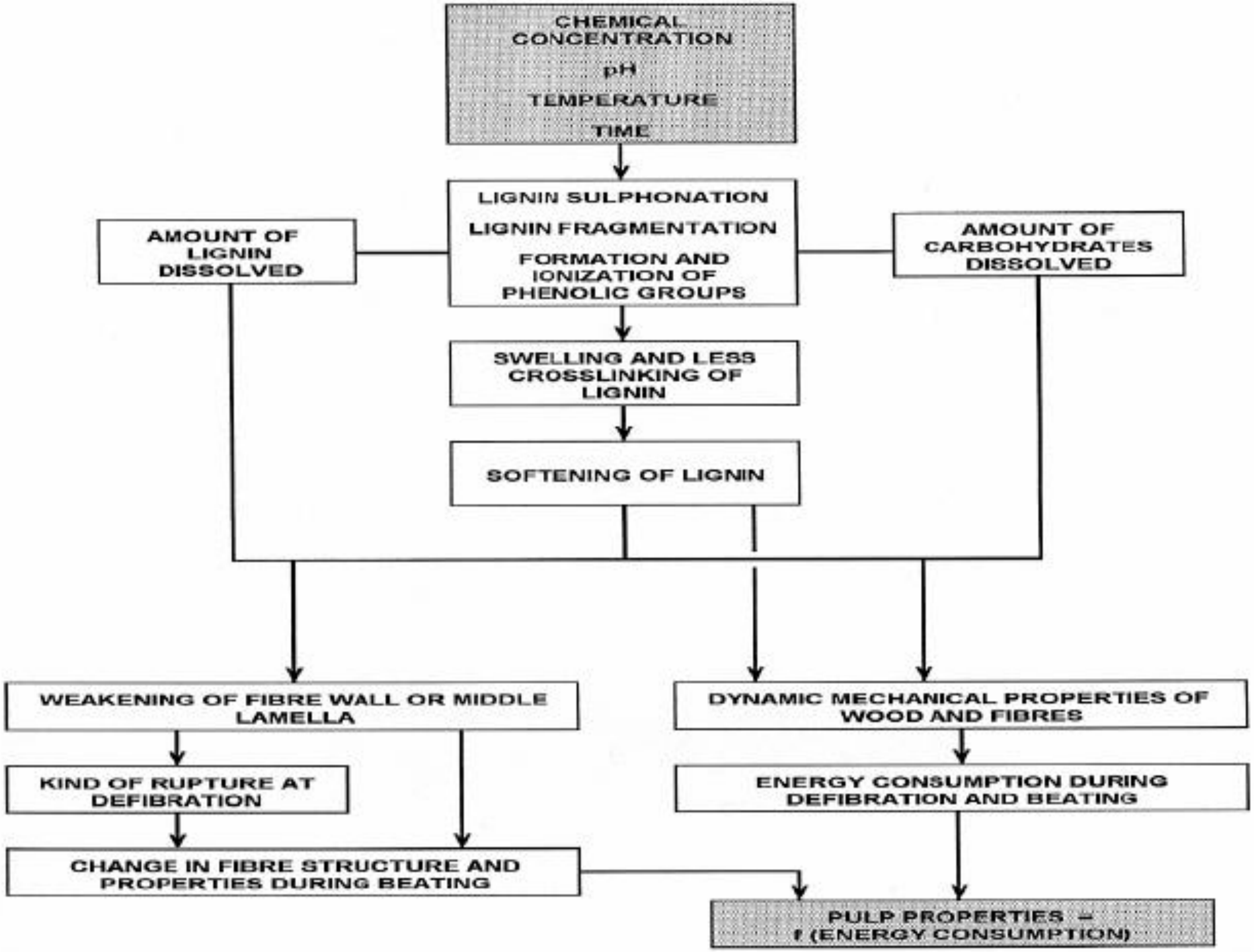



Total energy consumption, MWh/t90%
3.5
3.0
2.5
2.0
1.5
1.0
TMP
PGW
GW
News
SC & LWC
120
100
80
60
40
20
Freeness, ml

CMP and CTMP

- Operation started in 1950s
  - Printing papers from hardwoods (not suitalbe for MP)
- Breakthrough in 1970s and 1980s
  - Development of refining for TMP
- Chemimechanical pulp (CMP):
  - Refining at atmospheric pressure
  - Severe chemical treatment (yield typically below 90%)
- Chemithermomechnical pulp (CTMP):
  - Pressurized refining, low chemical doses and yield can be above 90%

Effect of pre-treatment on wood softening



CHEMICAL CONCENTRATION
pH
TEMPERATURE
TIME

AMOUNT OF LIGNIN DISSOLVED

LIGNIN SULPHONATION
LIGNIN FRAGMENTATION
FORMATION AND IONIZATION OF PHENOLIC GROUPS

AMOUNT OF CARBOHYDRATES DISSOLVED

SWELLING AND LESS CROSSLINKING OF LIGNIN

SOFTENING OF LIGNIN

WEAKENING OF FIBRE WALL OR MIDDLE LAMELLA

KIND OF RUPTURE AT DEFIBRATION

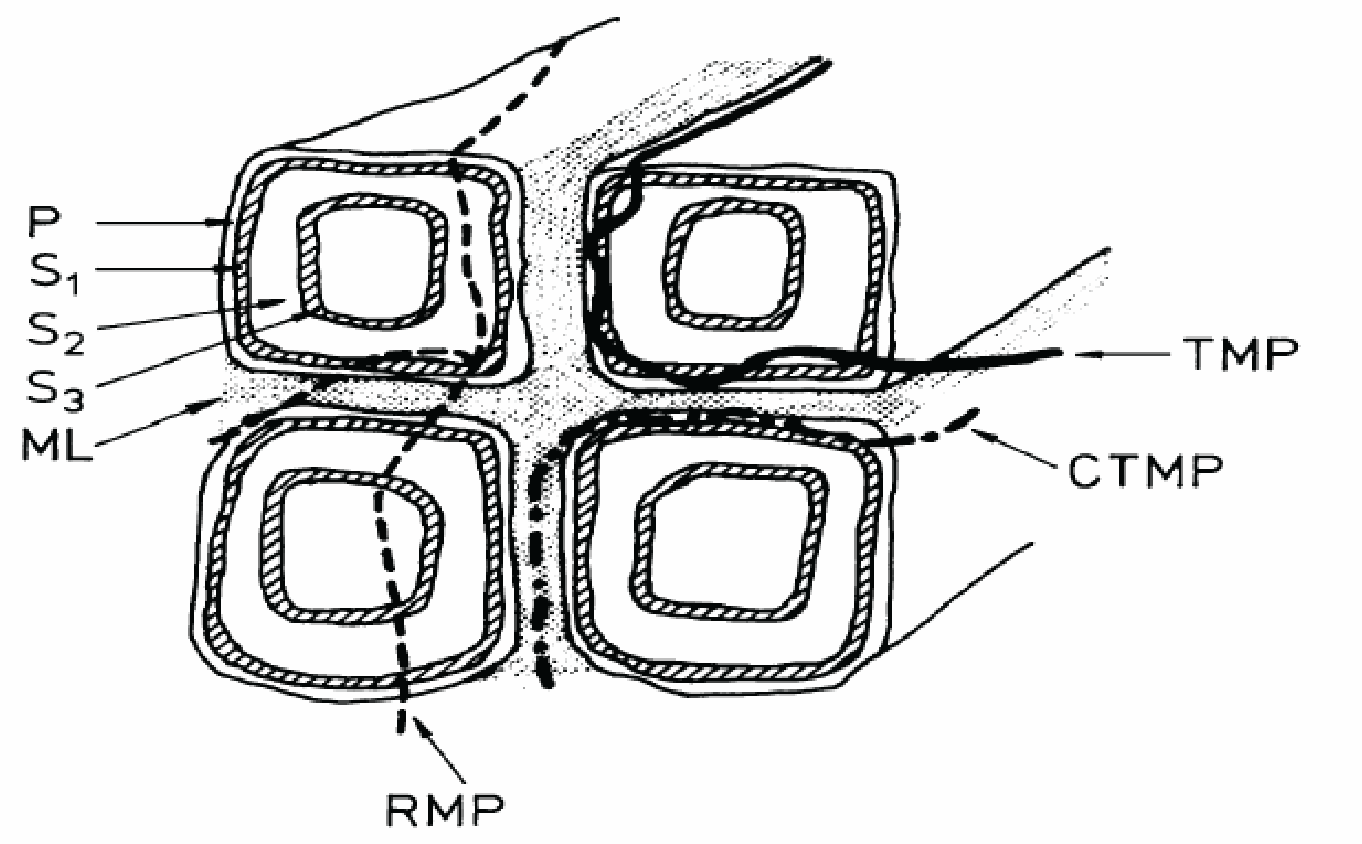
CHANGE IN FIBRE STRUCTURE AND PROPERTIES DURING BEATING

DYNAMIC MECHANICAL PROPERTIES OF WOOD AND FIBRES

ENERGY CONSUMPTION DURING DEFIBRATION AND BEATING

PULP PROPERTIES = f (ENERGY CONSUMPTION)

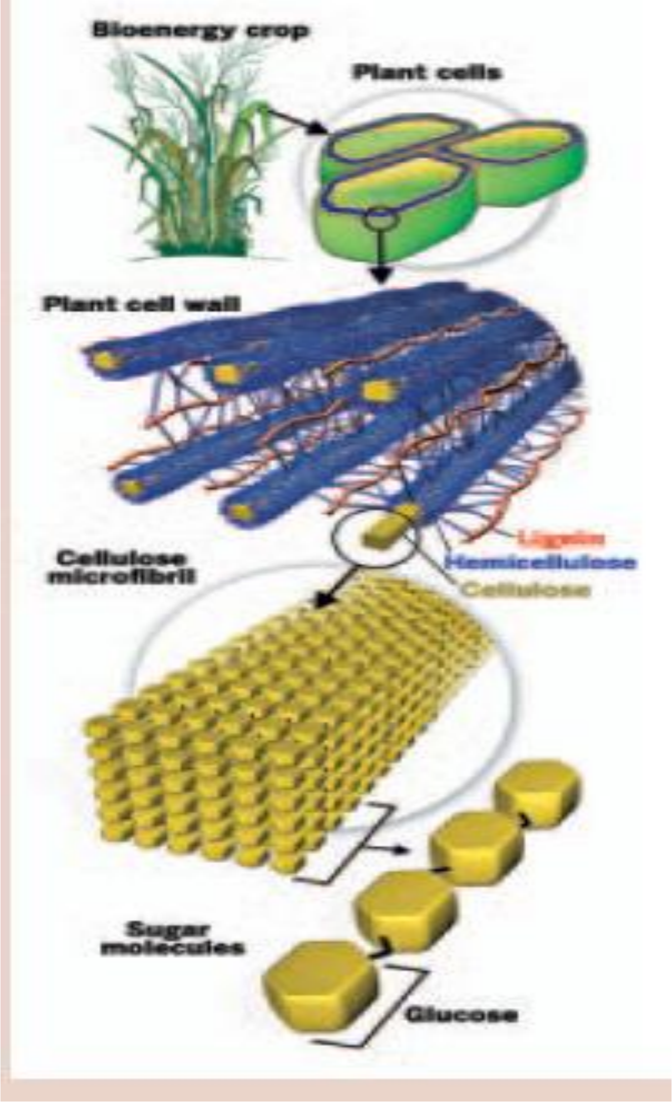
Type of rupture at defibration

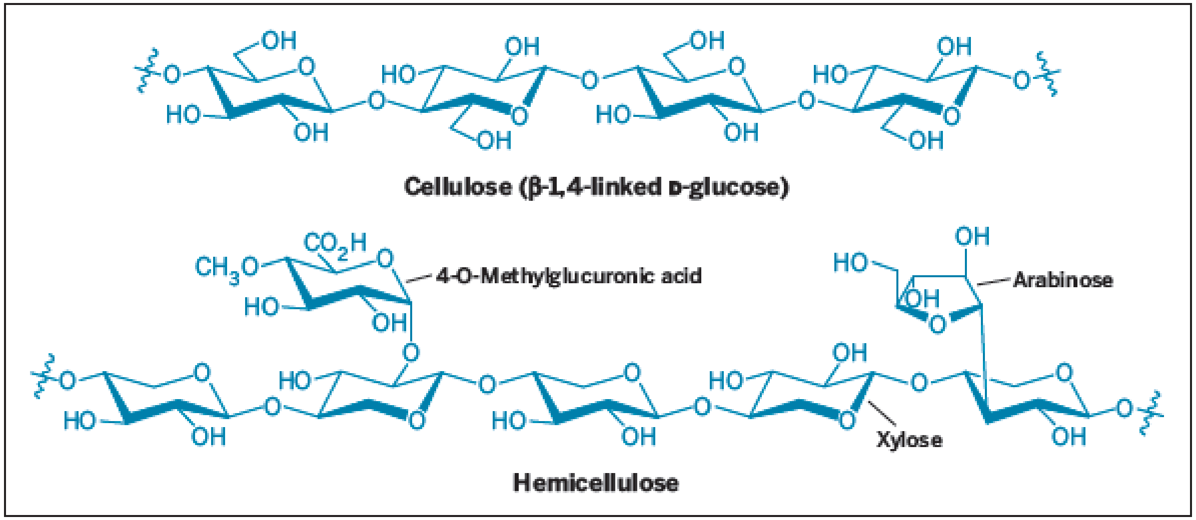


Fractionation of solid biomass:
chemical methods

Cooking and hydrolysis of wood chips or “Fractionation based on chemical reactions”

Recalcitrance in plant cell walls





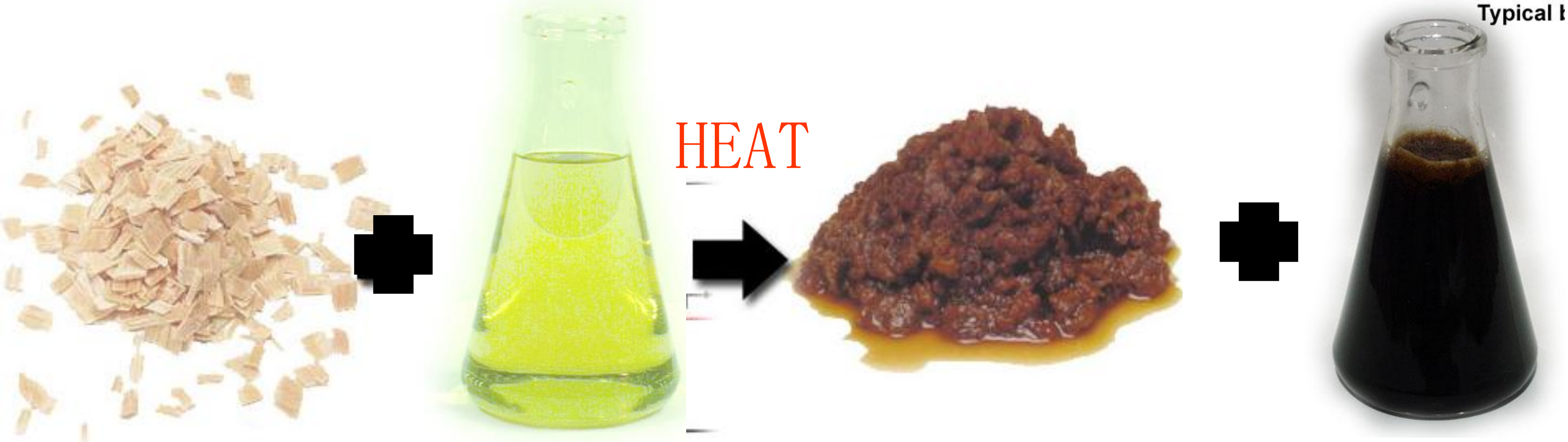
Cellulose (β-1,4-linked D-glucose)

Hemicellulose

Cooking

- Chemical cooking of wood chips
  - Kraft method (alkaline)
- Purpose: Elimination of lignin from the solid wood matrix, simultaneously maximizing the preservation of hemicelluloses and cellulose.

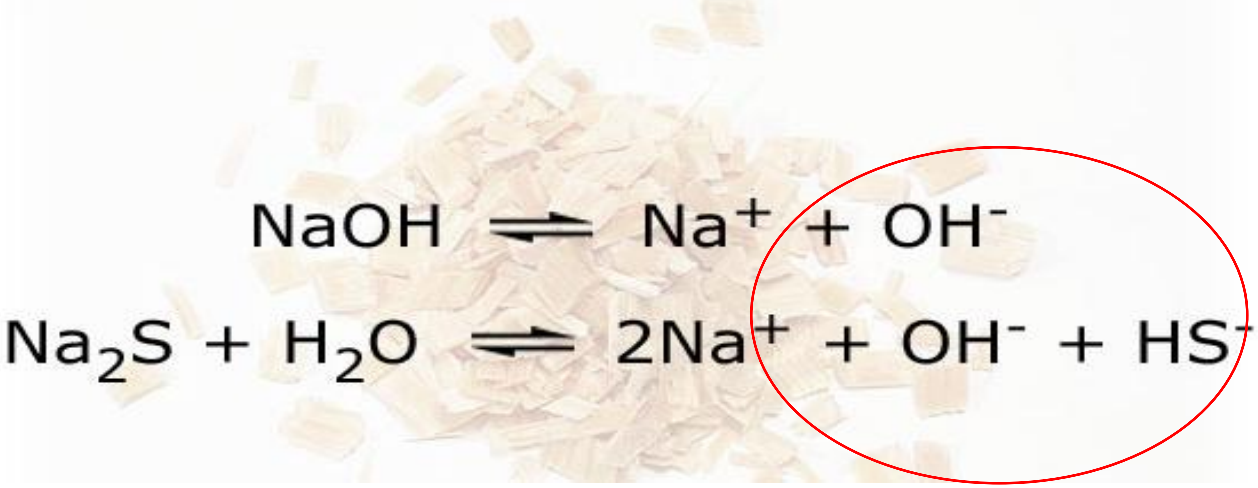
Purpose of traditional kraft cooking



HEAT

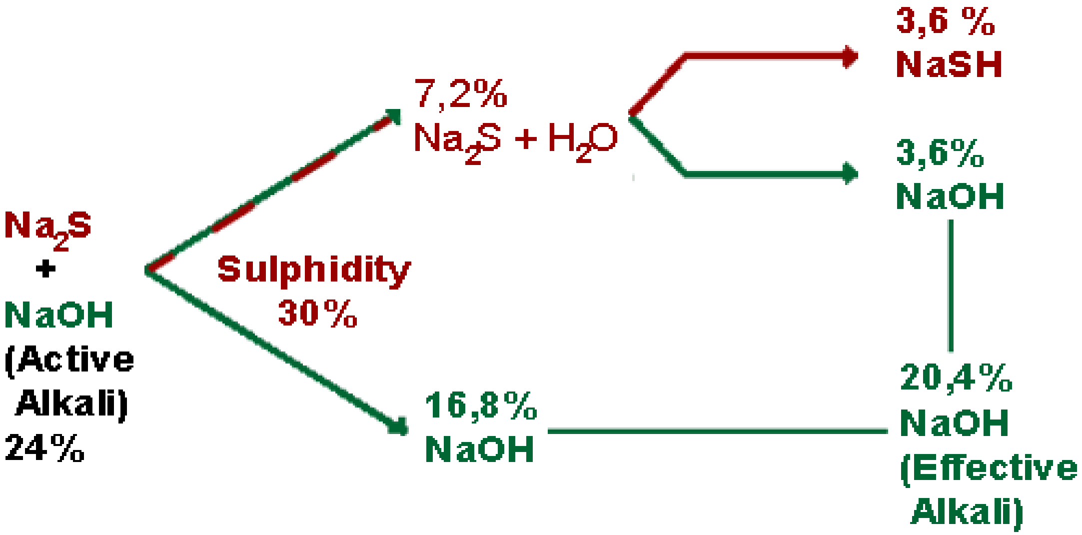
NaOH
Na_2S

Sodium hydoxide and sulfide reactions in cooking liquor



$$NaOH \rightleftharpoons Na^+ + OH^-$$

$$Na_2S + H_2O \rightleftharpoons 2Na^+ + OH^- + HS^-$$



Na_2S
+
NaOH
(Active
Alkali)
24%

Sulphidity
30%

7,2%
$Na_2S + H_2O$

3,6 %
NaSH

3,6%
NaOH

16,8%
NaOH

20,4%
NaOH
(Effective
Alkali)

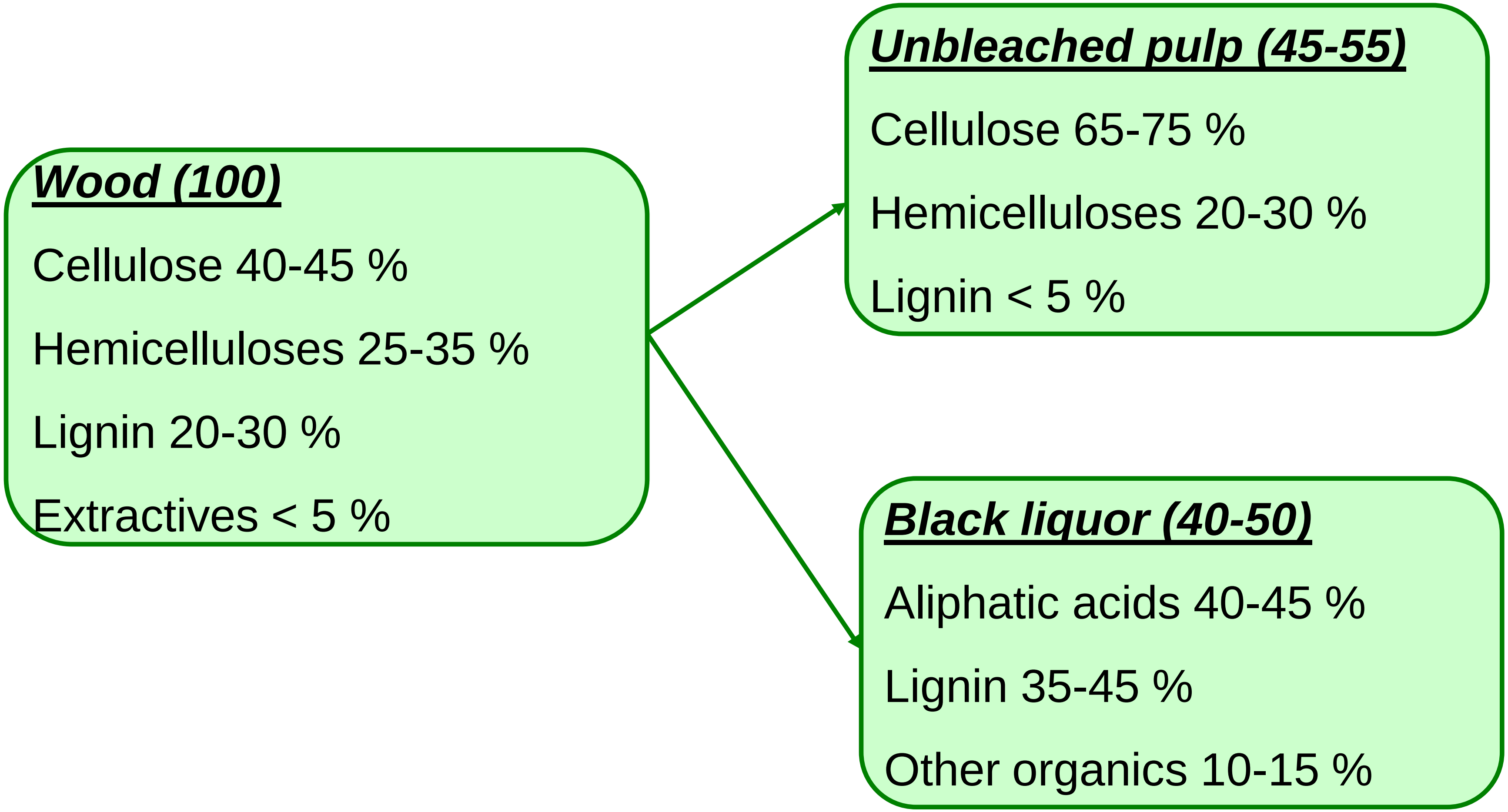
Cooking parameters

- The main cooking parameters in order to achieve the desired delignification are:
  - Temperature and temperature profiling
    - Typically 150 – 170 °C (max.)
  - Time
    - Typically 3 – 4 hours
  - Charge of cooking chemicals (alkali charge, sulphide content)
    - Typical alkali charge 160 – 240 kg effective alkali/ton of wood (16 – 24 % EA on wood)
    - EA in WL could be 120 g/l NaOH, sulphidity 28 %

Outcome

- About 90 % of lignin, 60 % of hemicelluloses and 15 % of cellulose are dissolved in kraft cooking
- Hydrogen sulfide ions (HS^-) primarily react with lignin
- About 20 % of the charged alkali is consumed to neutralize degradation products of lignin
- Carbohydrate reactions are affected by alkalinity (HO^- ions)

An example of the material balance for wood organics over the kraft process



Wood (100)

Cellulose 40-45 %

Hemicelluloses 25-35 %

Lignin 20-30 %

Extractives < 5 %

Unbleached pulp (45-55)

Cellulose 65-75 %

Hemicelluloses 20-30 %

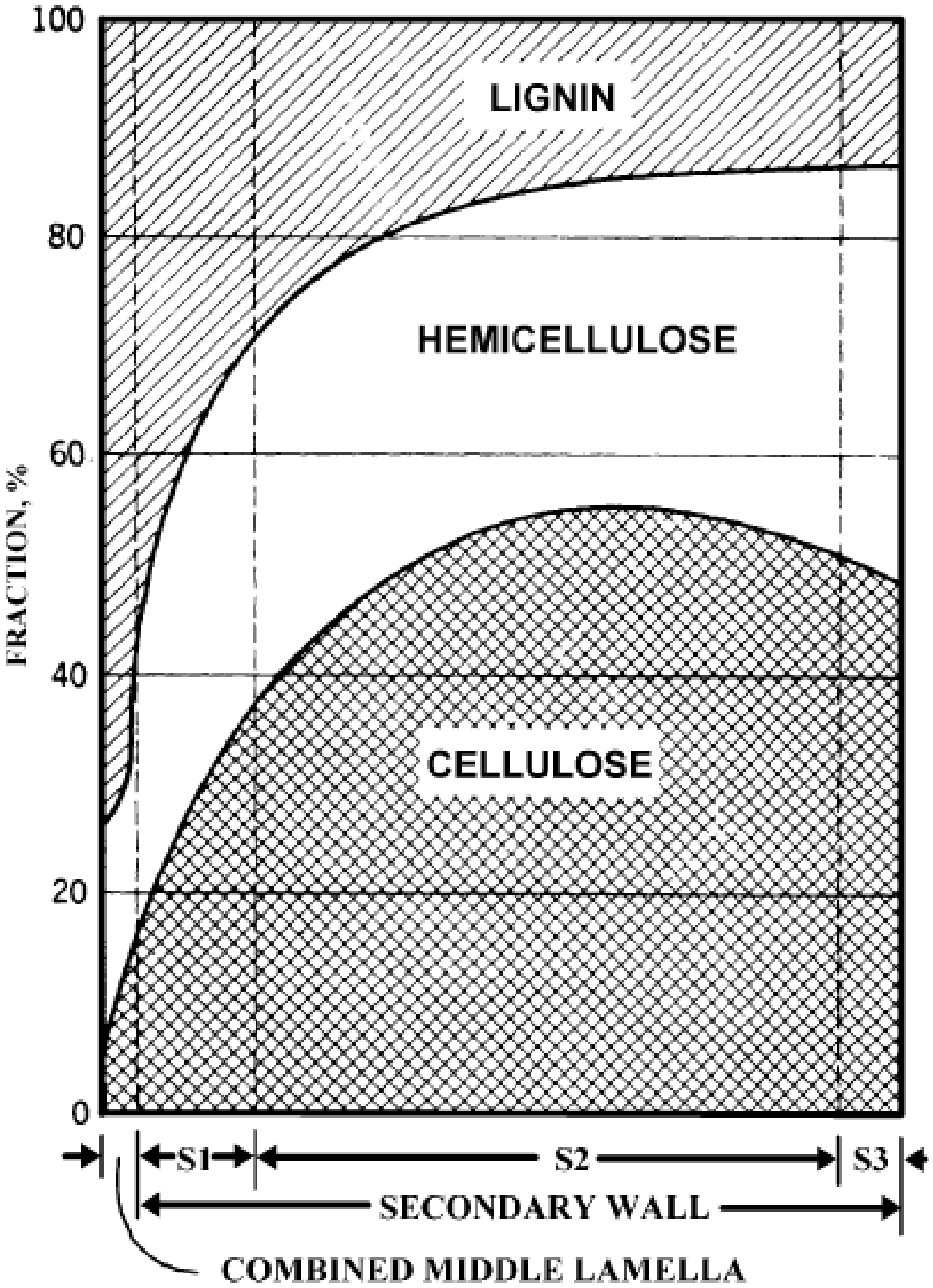
Lignin < 5 %

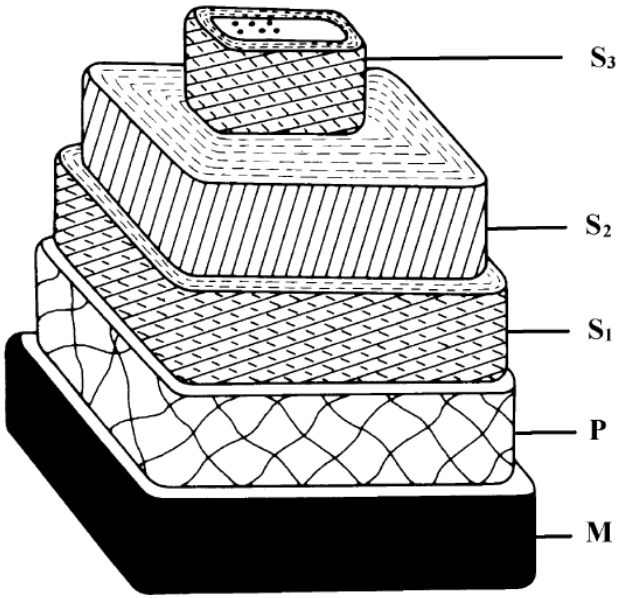
Black liquor (40-50)

Aliphatic acids 40-45 %

Lignin 35-45 %

Other organics 10-15 %

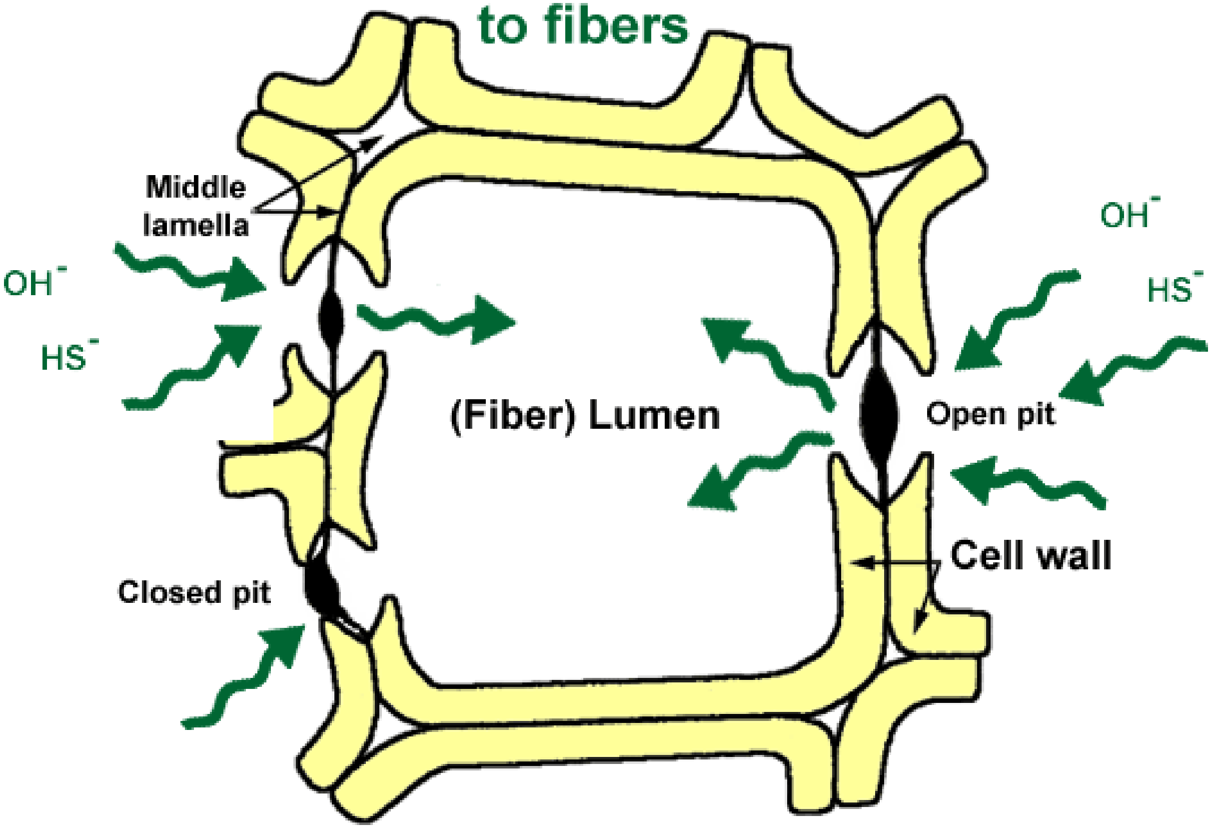




M = MIDDLE LAMELLA
P = PRIMARY WALL
S_1 = SECONDARY WALL
S_2 = SECONDARY WALL
S_3 = SECONDARY WALL

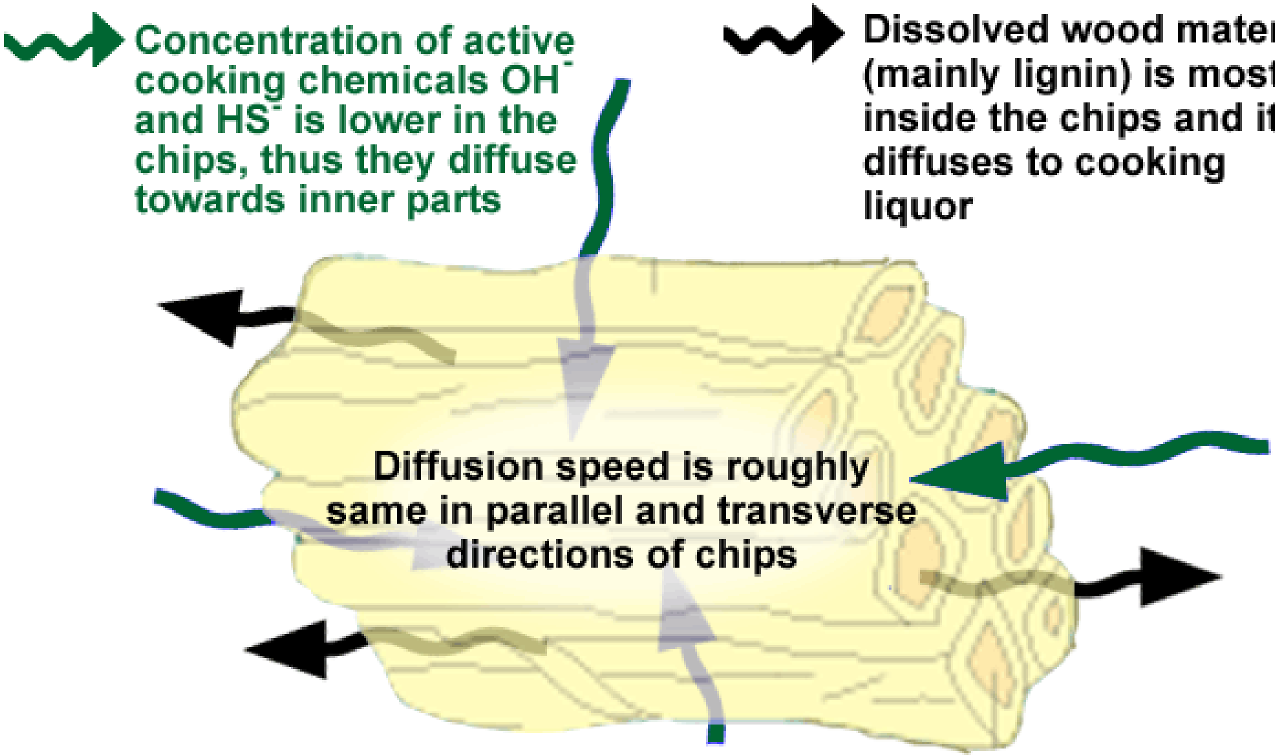
Cooking liquor penetrates into fibers through wood cell pits

However, penetration is fastest parallel to fibers



- Active chemicals probably penetrate into the middle lamella only via cell lumens and the porous cell wall
- Therefore, much of the lignin in the secondary cell wall will dissolve before the middle lamella lignin

Diffusion is caused by chemical concentration differences



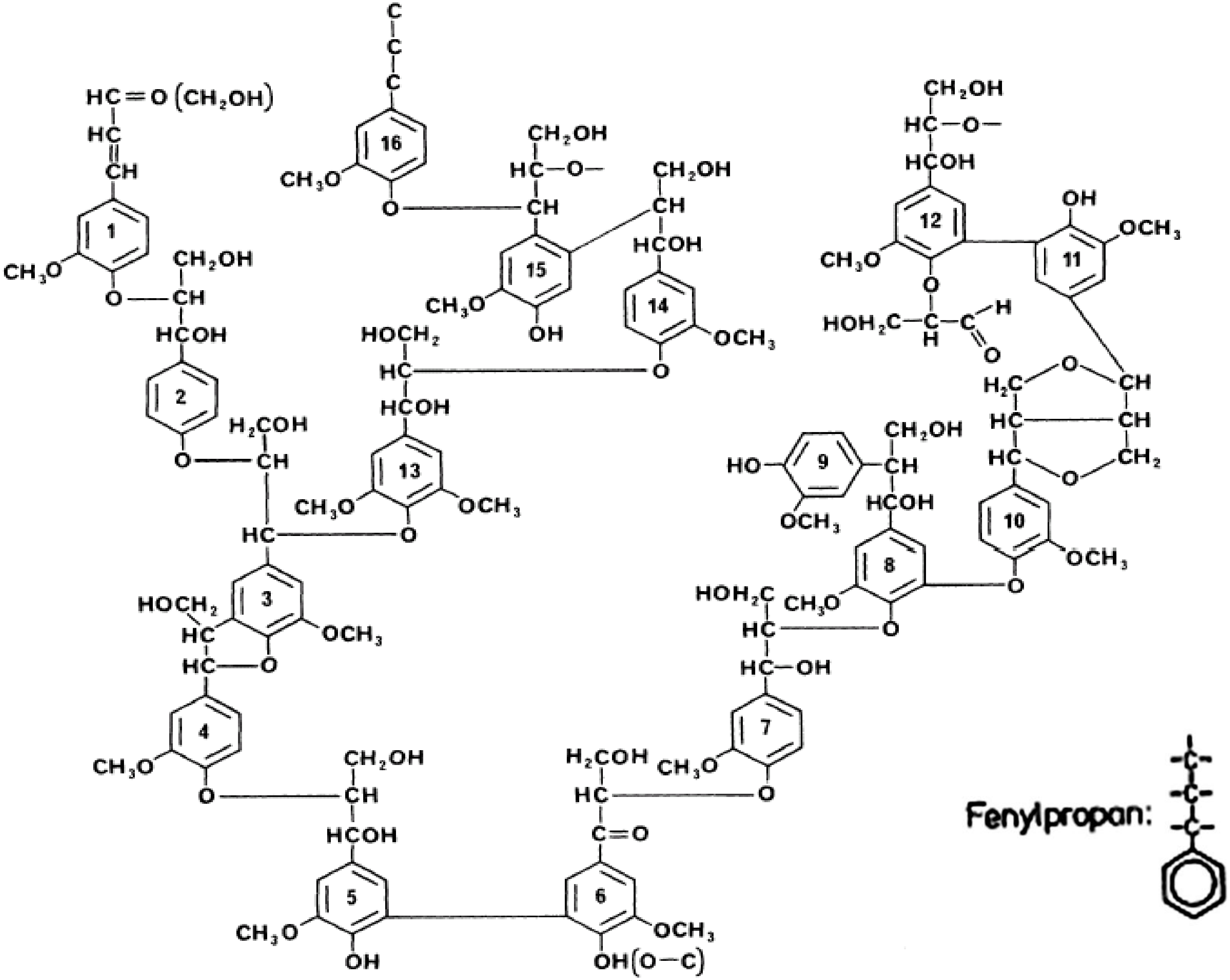
Concentration of active cooking chemicals OH^- and HS^- is lower in the chips, thus they diffuse towards inner parts

Dissolved wood material (mainly lignin) is mostly inside the chips and it diffuses to cooking liquor

Diffusion speed is roughly same in parallel and transverse directions of chips

THIS DIFFUSION SPEED HAS A SIGNIFICANT EFFECT ON COOKING SPEED

LIGNIN STRUCTURE

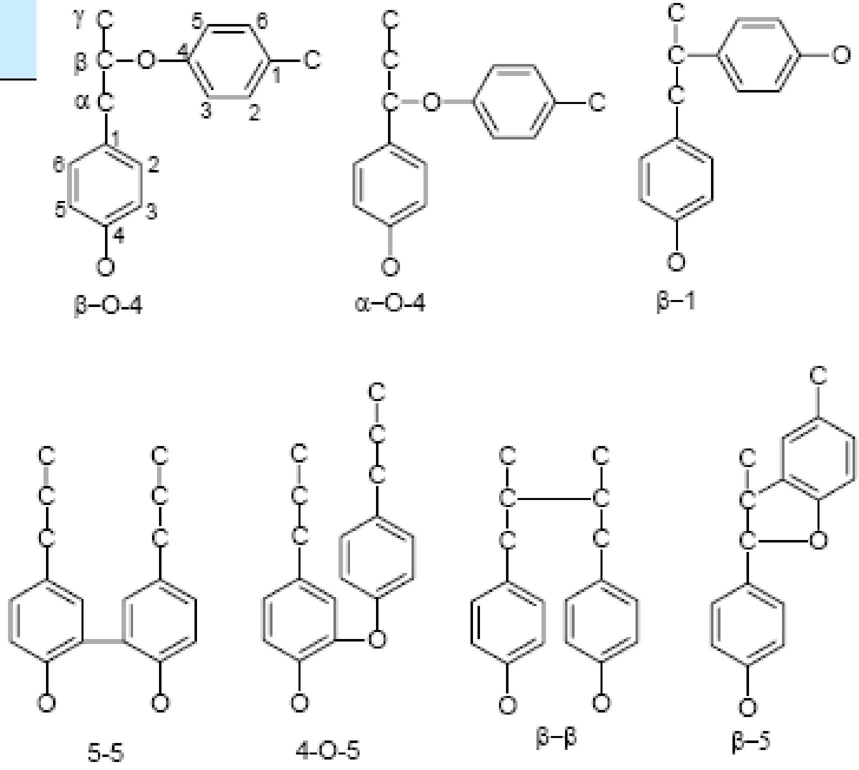


Prominent structures likely in softwood lignin

Fenylpropan:

(Sjöström, E., Wood Chemistry – Fundamentals and Applications, 2nd ed. Academic Press, 1993)

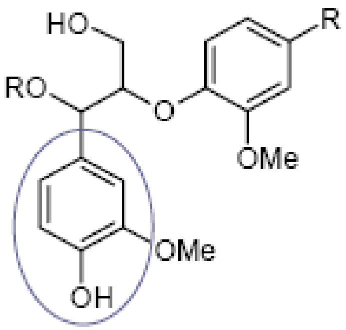
Linkage type	Softwood %	Hardwood %
β–O–4	50	60
α–O–4	6-8	6-8
β–5	9-12	6
5–5	10-11	5
4–O–5	4	7
β–1	7	7
β–β	2	3



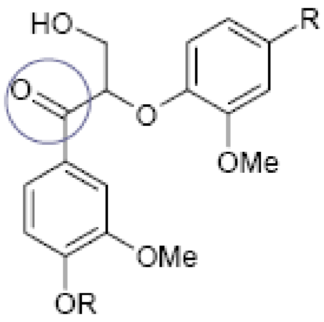
The ether bonds are more reactive than C-C bonds

I Initial delignification

- **Phenolic and carbonyl** structures react
- 20 % of lignin degrades due to these reactions in the initial stage



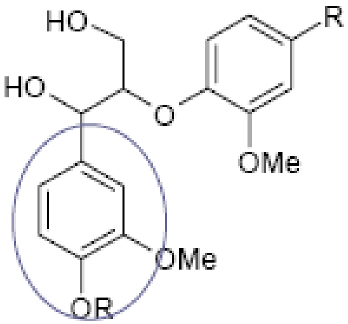
Phenolic unit



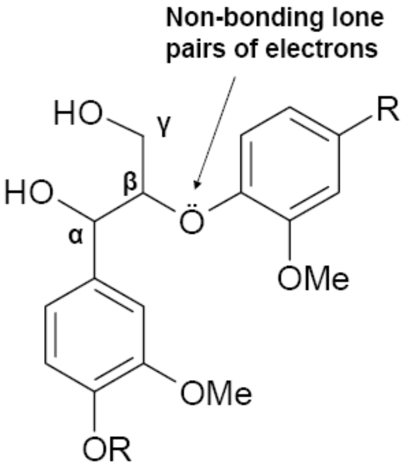
Carbonyl unit

II Bulk delignification

- Main part of lignin is removed during the bulk delignification
- **non-phenolic** structures react
- Slow reaction



Non-phenolic unit



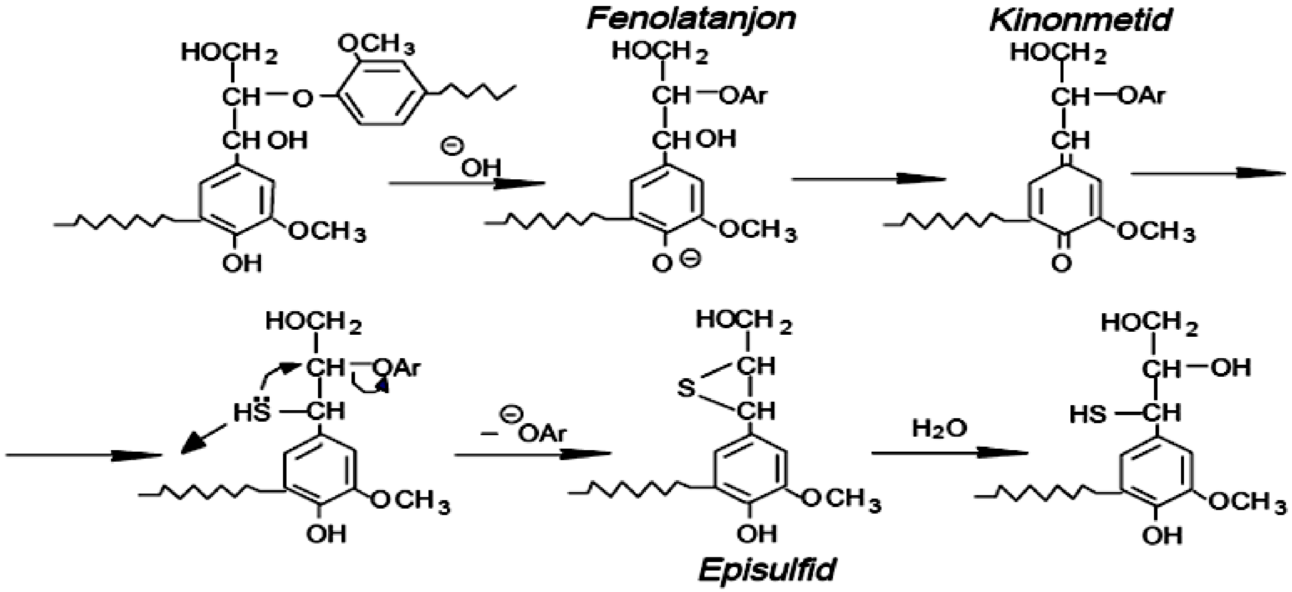
Non-bonding lone pairs of electrons

β-O-4

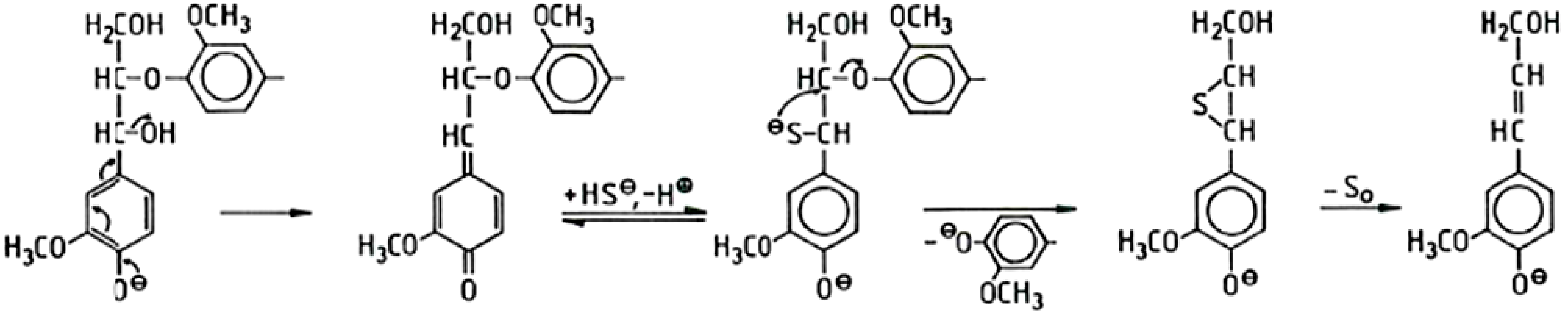
DELIGNIFICATION THROGH FRAGMENTATION OF THE LIGNIN CHAIN

Depolymerisation of lignin

Depolymerisation

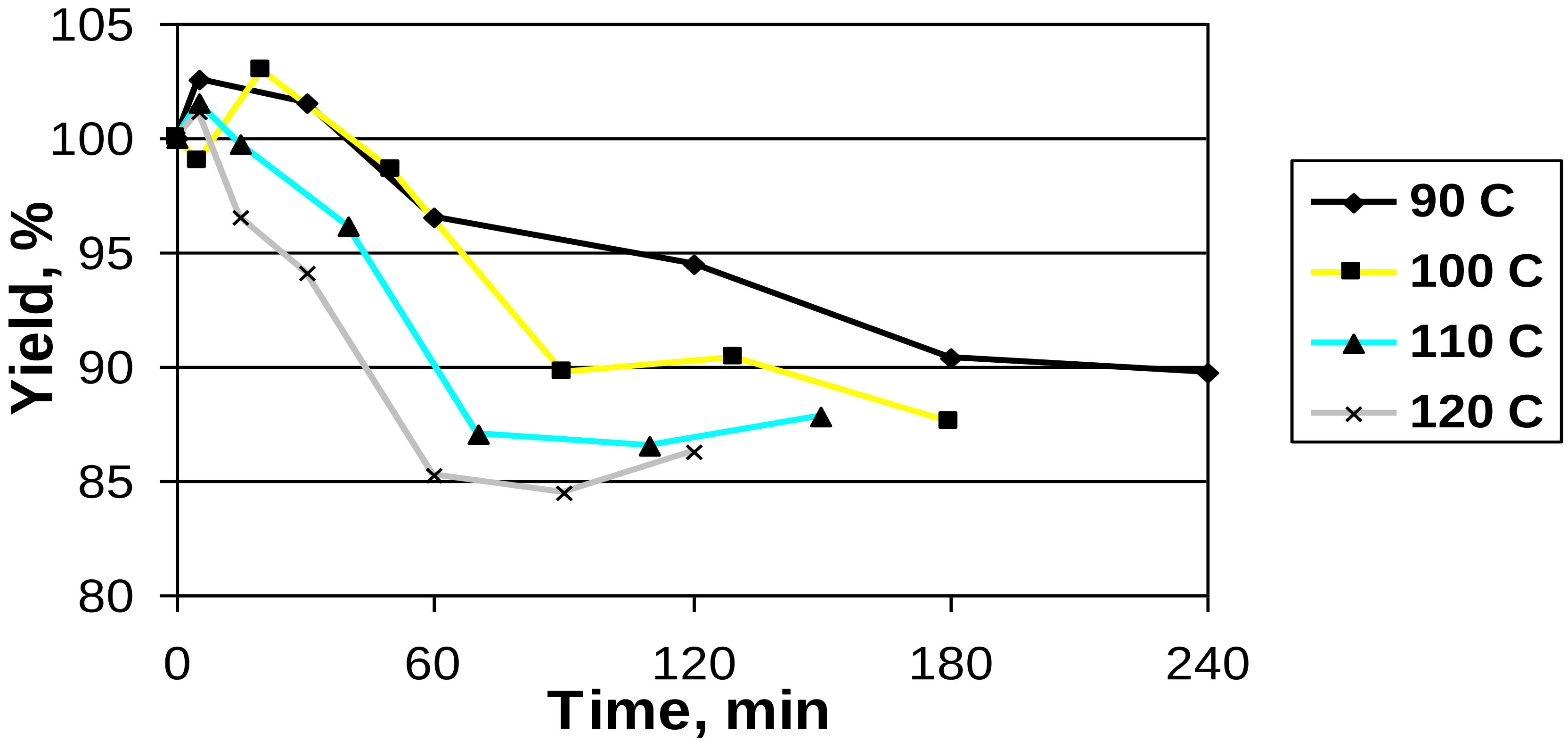


Depolymerisation of lignin

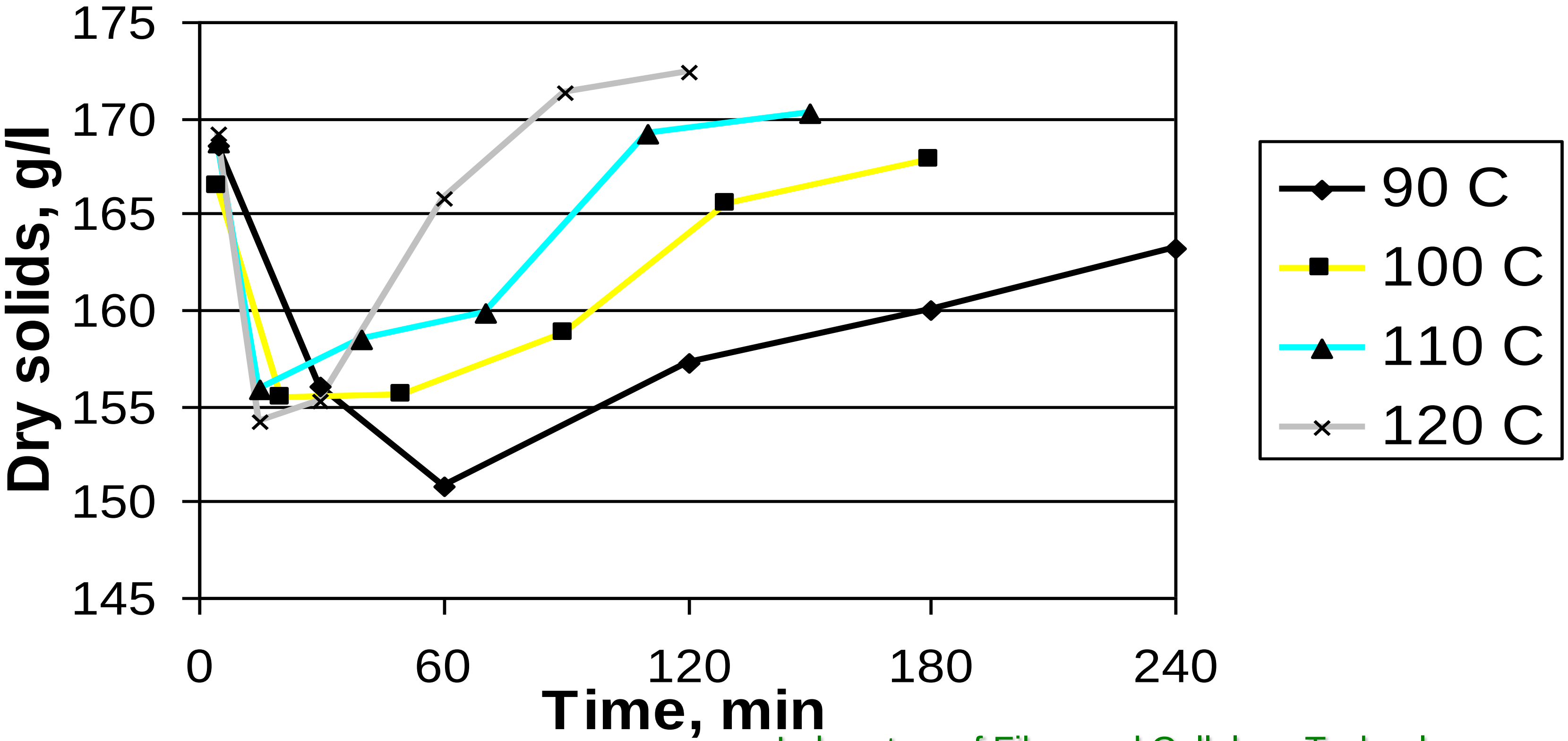


Sulfidolytic cleavage reaction of β-aryl ether bond in phenolic lignin units. (Fengel 1983).

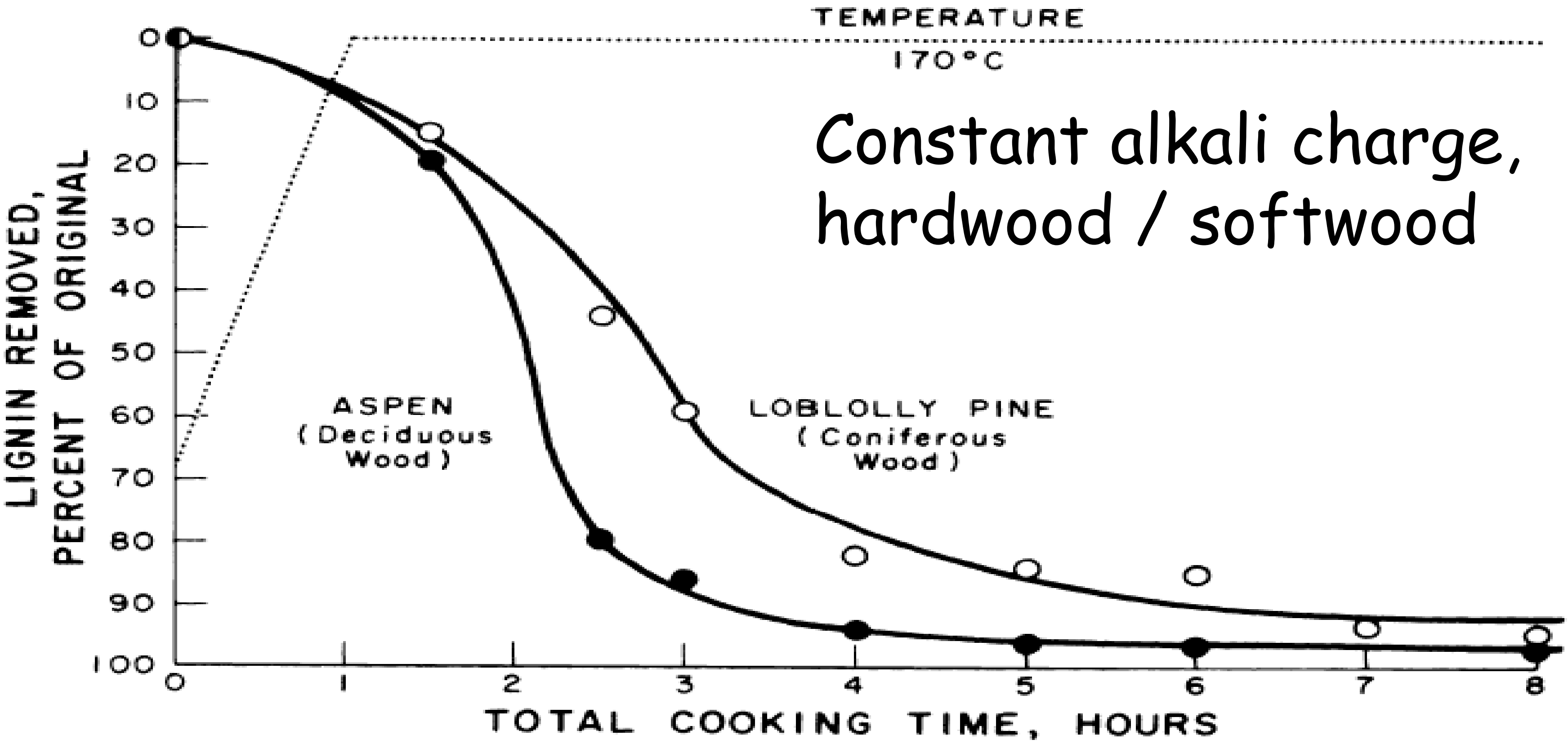
Yield during impregnation



Solids content in the impregnation liquid

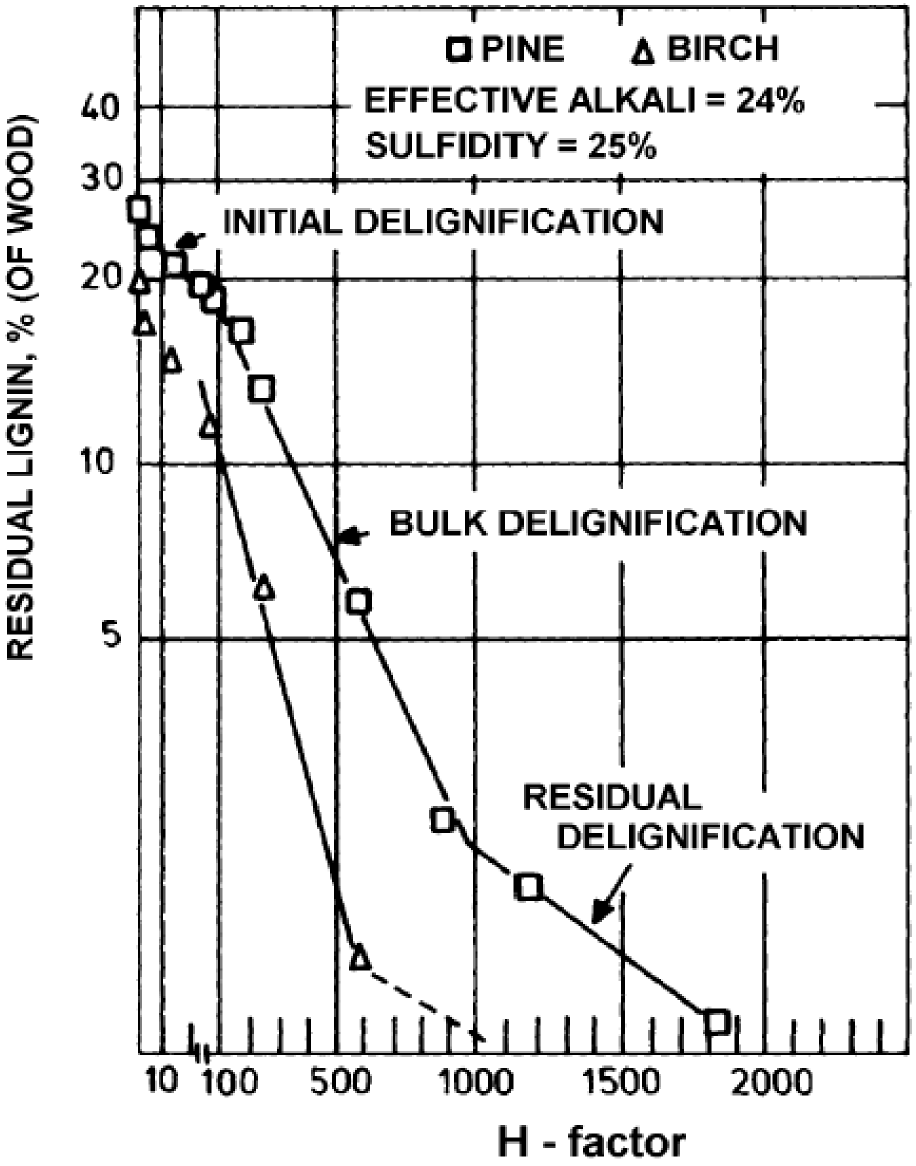


Delignification in kraft cooking



Constant alkali charge, hardwood / softwood

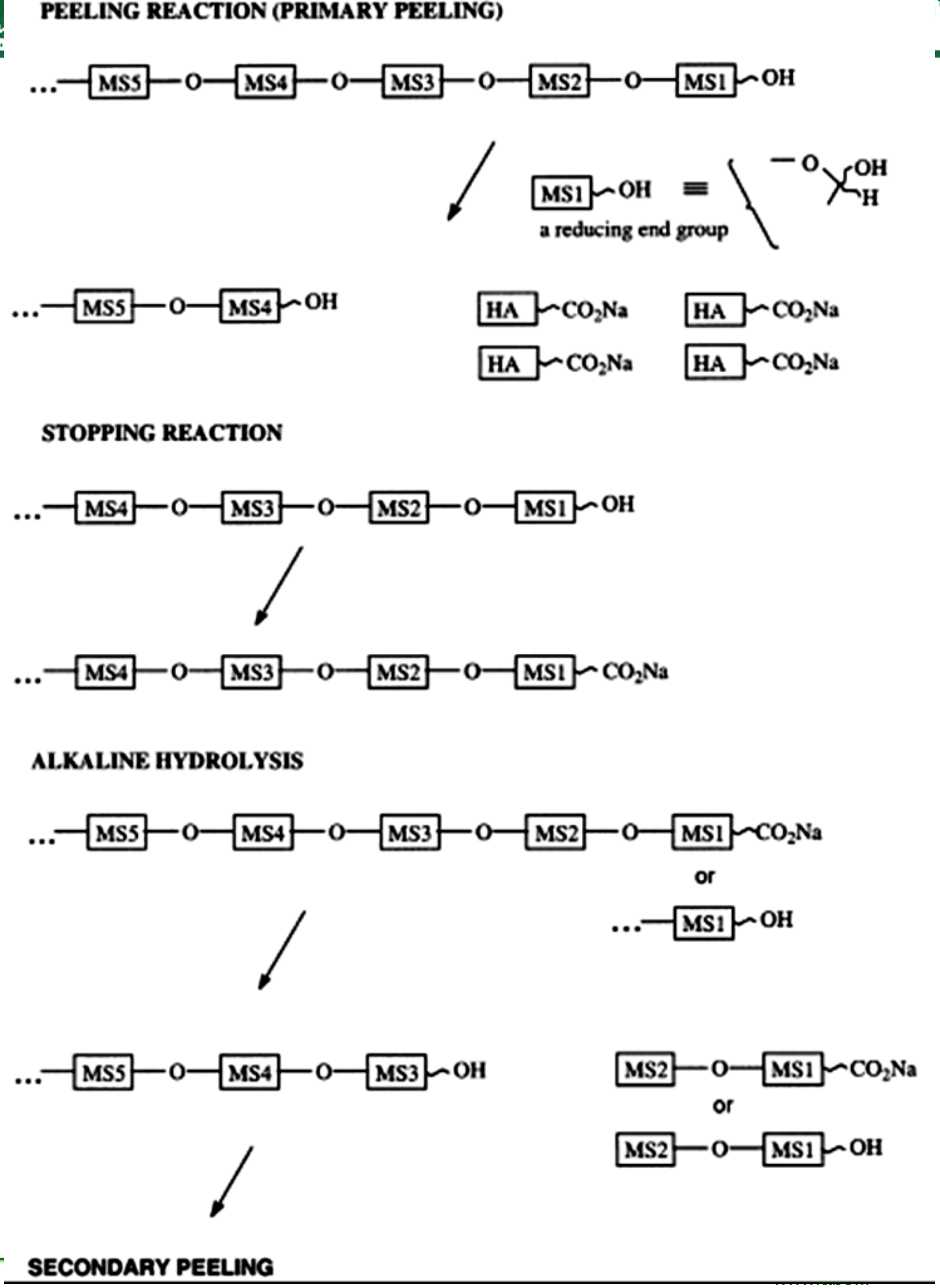
Initial, bulk and residual delignification



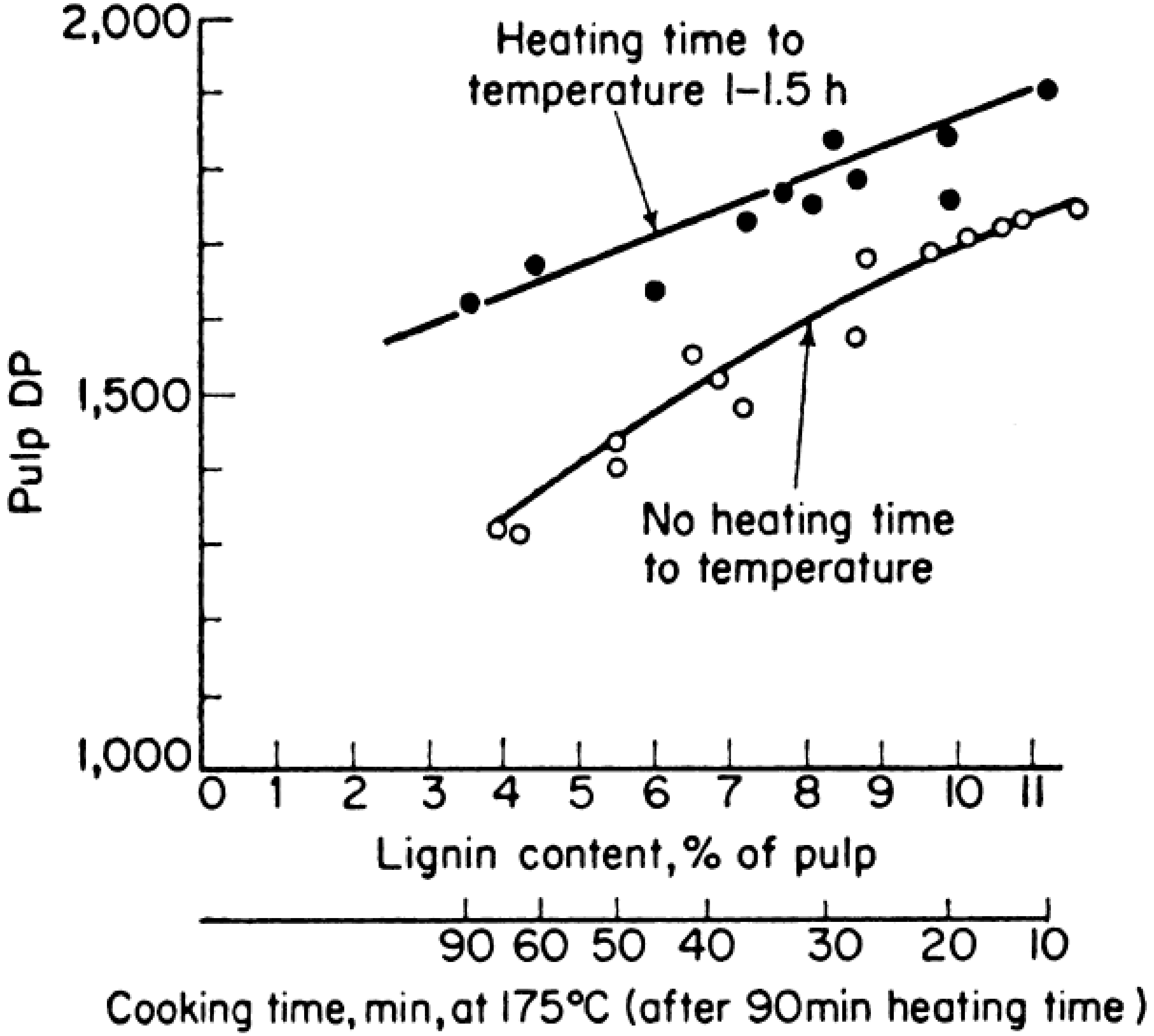
Carbohydrate reactions

- Alkaline swelling and dissolution
- Reprecipitation
- Alkaline hydrolysis of acetyl groups
- Alkaline peeling
- Stopping reactions
- Alkaline hydrolysis and depolymerization

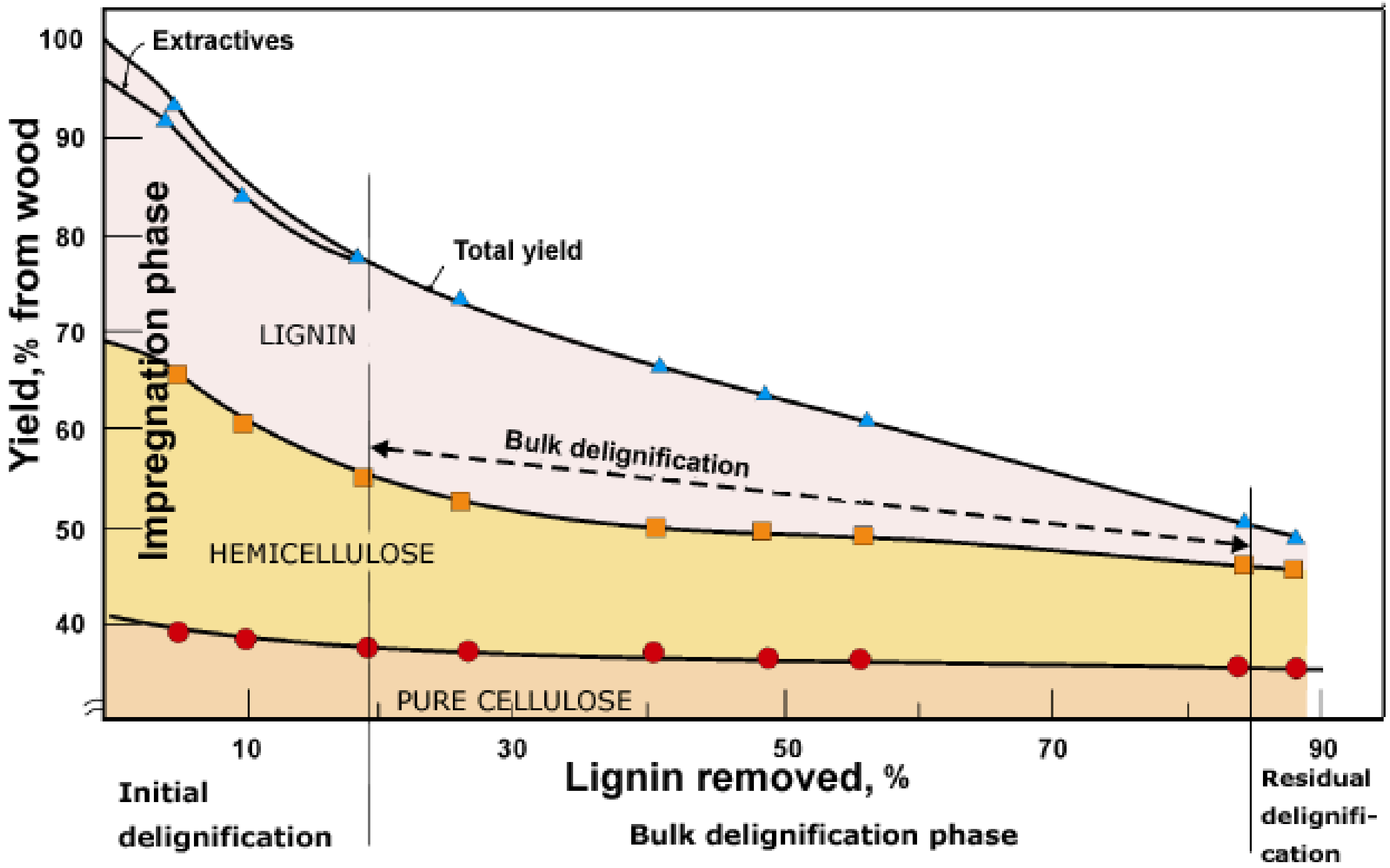
MS = monosaccharide unit
HA = hydroxy acid component



Carbohydrate degradation - cellulose



Dissolving of wood components in sulfate process



Hydrolysis

- Pre-Hydrolysis of wood chips by
  - Water (pressurised hot water extraction)
  - Acid or alkaline (dilute acid or alkaline hydrolysis)
- <u>Purpose</u>: Disassembly (dissolution) of hemicelluloses from the solid wood matrix without degradation of lignin or cellulose.

Other hydrolysis methods

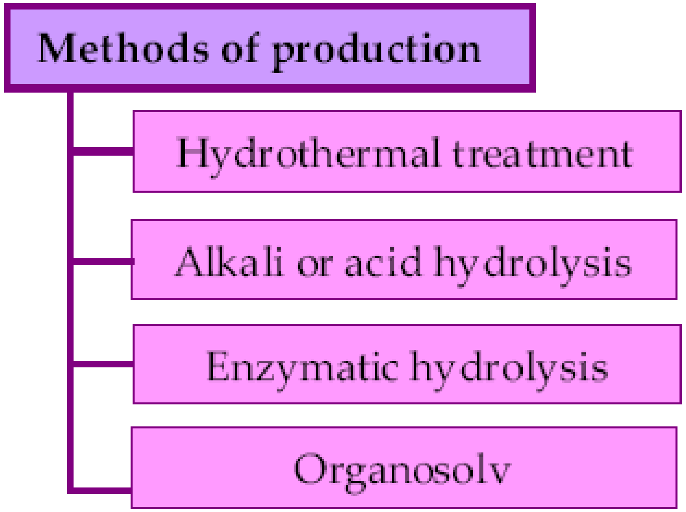
✓**Prehydrolysis**: mildly acidic by heating water at 170 °C **(Lai 1990)**.

✓**Auto hydrolysis**: steam (175-220°C) by organic solvents **(Lai 1990)**.

✓**Steam explosion**: at 200-250°C by explosive discharge **(Puls & Saake 2004)**

✓**Enzymatic hydrolysis**: by a group of enzymes **(Jeoh 1998)**.

✓**Hot water extraction**: high pressure at 140-190°C **(Yoon et al. 2006)**.



Methods of production

- Hydrothermal treatment
- Alkali or acid hydrolysis
- Enzymatic hydrolysis
- Organosolv

Figure 1.13. Main processes used in the fractionation of biomass.

Xylan

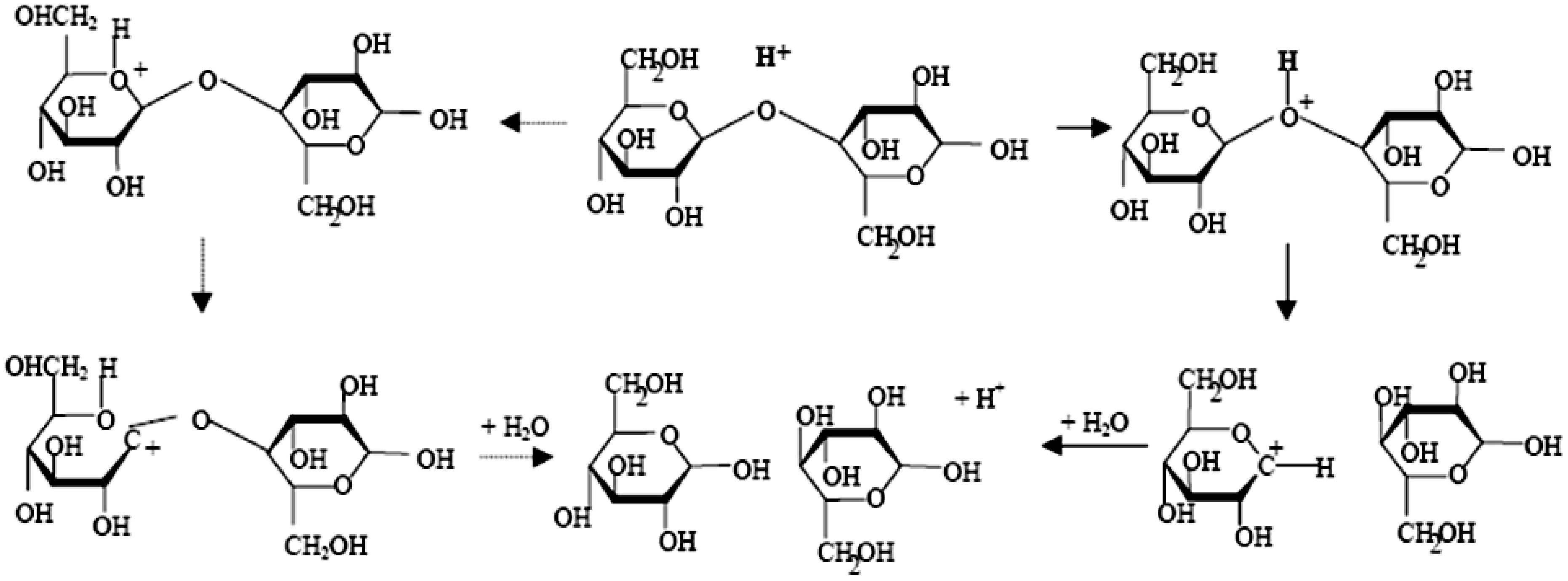


Figure 1.14. Mechanism of acid hydrolysis of glycosidic linkages [44]. ⟶ Dominant pathway.

Xylan

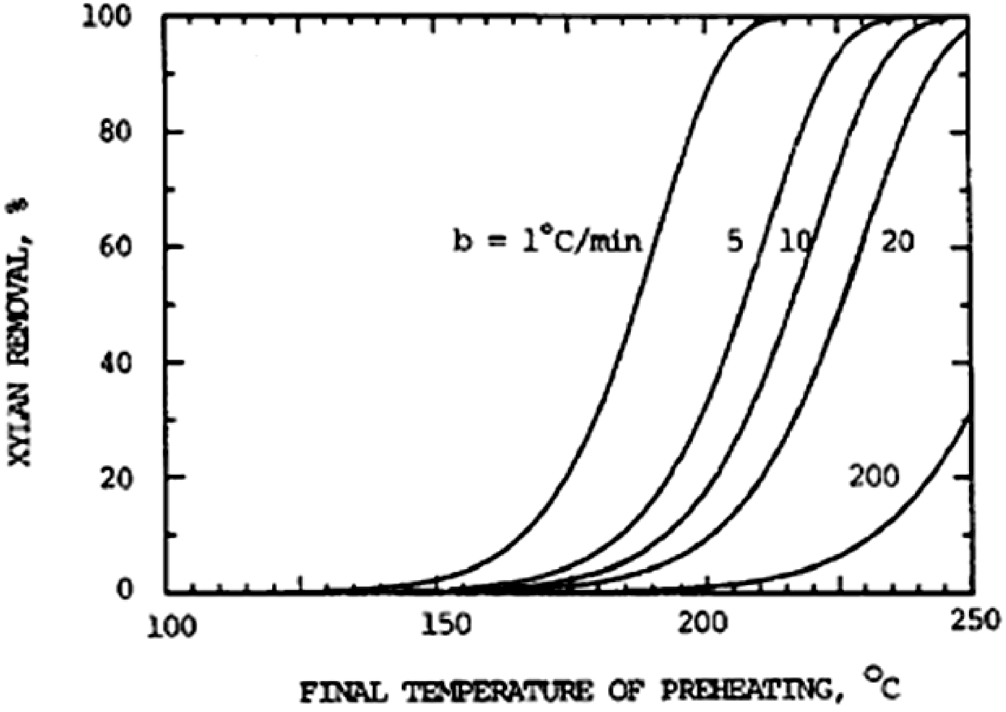


Fig. 1. Xylan removal during the preheating stage of autohydrolysis as a function of the final preheating temperature for different heating rates. Kinetic parameters are from Carrasco et al. (1987)

Hemicellulose extraction kinetics

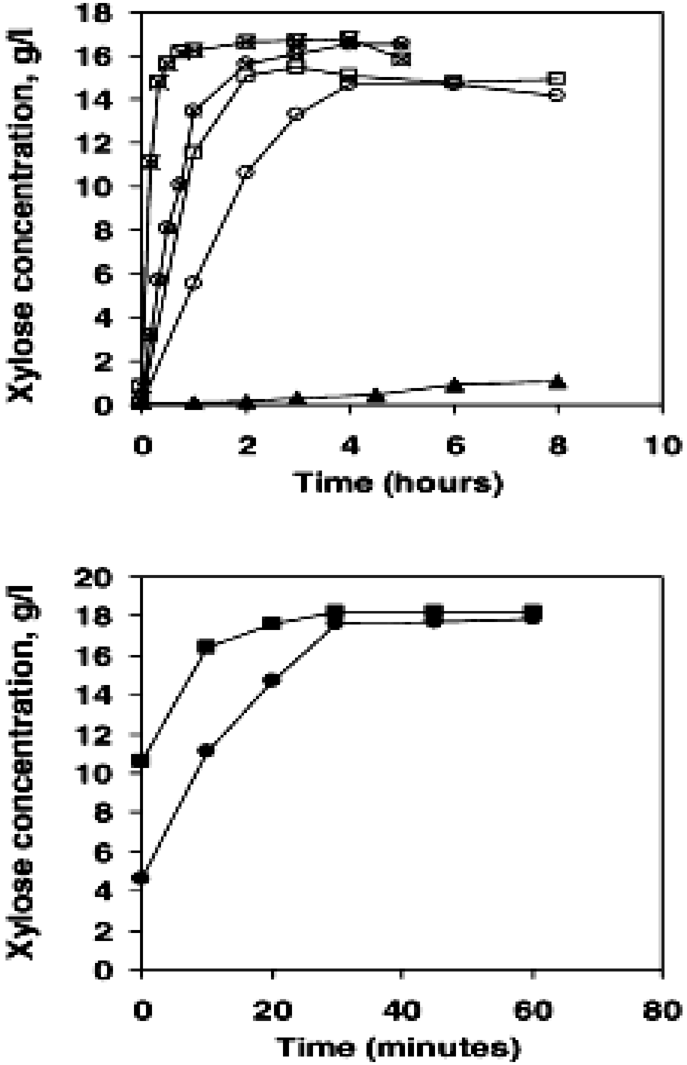


Fig. 6. Time course of xylose concentration in treatments at 100 °C—5% sulfuric acid (○), 100 °C—2.5% sulfuric acid (□), 115 °C—5% sulfuric acid (⊗), 115 °C—2.5% sulfuric acid (⊠), 130 °C—5% sulfuric acid (●), 130 °C—2.5% sulfuric acid (■) and 130 °C without externally added acid (▲).

J. González et al. / Food Chemistry 84 (2004) 243–251

Conner and Lorenz - WOOD AND FIBER SCIENCE, APRIL 1986, V. 18(2)

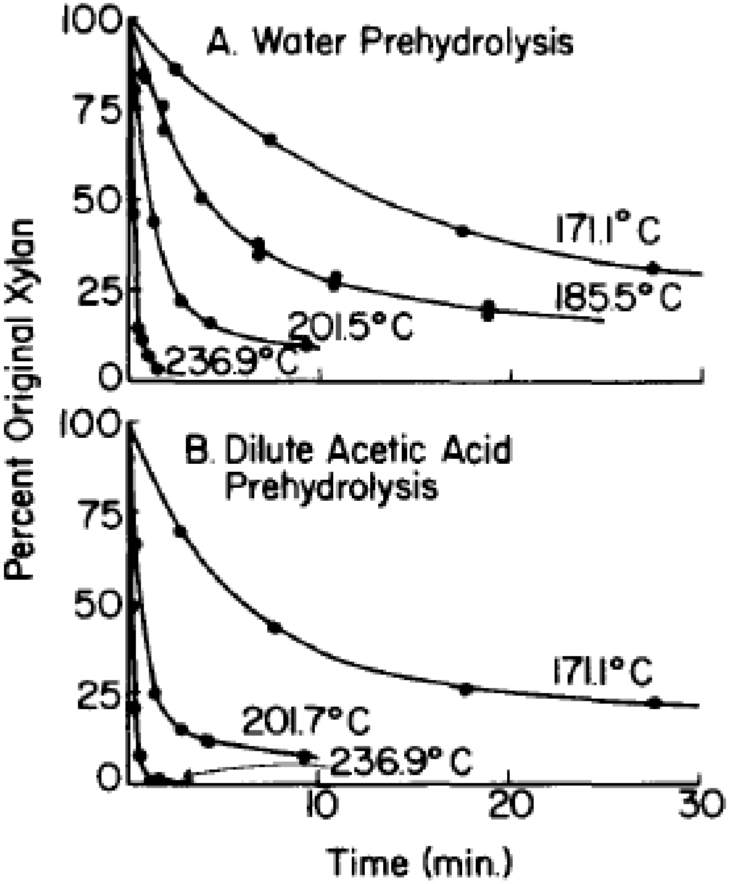
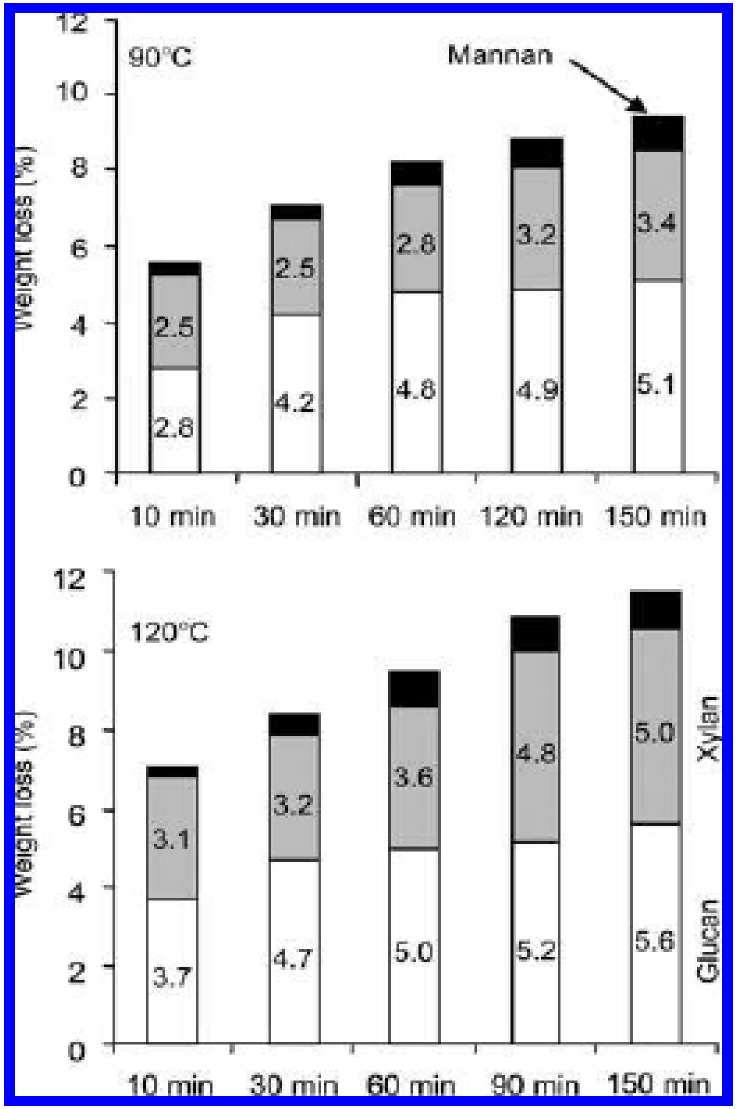


FIG. 1. Xylan removal from southern red oak wood on prehydrolysis with water or dilute (5%) acetic acid. The closed circles represent experimental data; the time for each data point is corrected by Δt (Table 1) as discussed in the text. The solid lines were calculated from numerical integration of Eqs. (5) and (6) using the parameters listed in Table 1.

Extraction of hemicelluloses



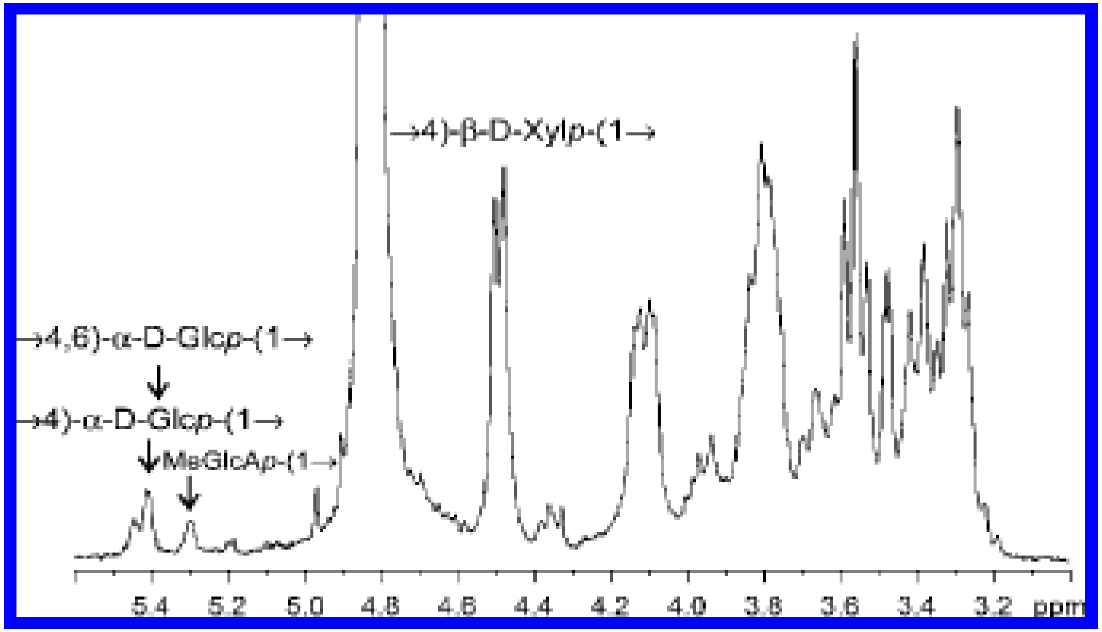


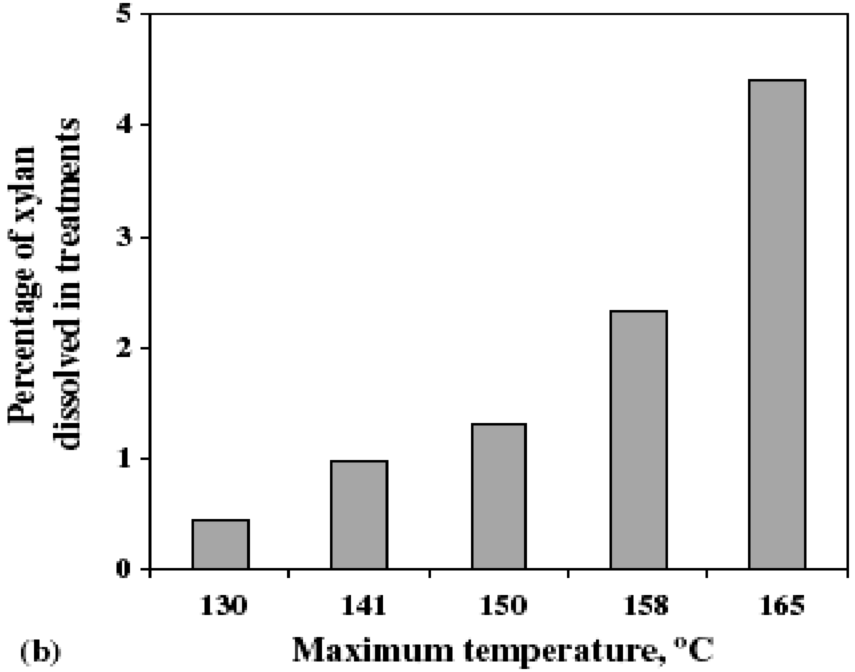
Figure 4 ¹H NMR spectrum of polysaccharides obtained by water extraction of *E. globulus* kraft pulp (WSPG) (25°C, D_2O).

. **Lisboa,**

Holzforschung, Vol. 61, pp. 476–482, 2007

Figure 2 Weight loss profiles of polysaccharides of *E. globulus* wood in the course of extraction with 0.5 M NaOH at 90°C and 120°C. Glucan, white; xylan, gray; mannan, black.

Extraction of hemicelluloses



maximum temperature. (b) Percentage of xylan dissolved in autohydrolysis experiments carried out up to reach the corresponding maximum temperature.

M.J. Vázquez et al. / Bioresource Technology 96 (2005) 889–896

Composition of an extract

Glucan	Xylan	Galactan	Arabinan	Mannan	Acetic acid
Monomeric (g/l)					
0.01	1.47	0.41	0.91	0	
Oligo- and polymeric (g/l)					
1.96	24.54	3.88	0.65	1.52	
Total (g/l)					
1.97	26.01	4.29	1.56	1.52	0.61

Table 4.2 – Composition of the extract with 10% extracted material on wood weight. (Luleå University of Technology, Christian Andersson, David Hodge)

Lidia Testova; [2006]

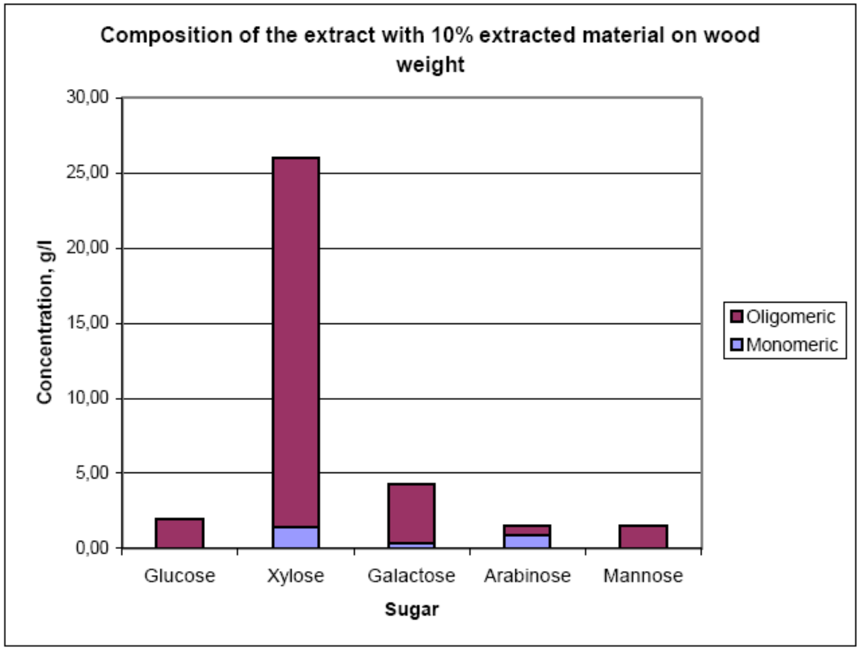


Figure 4.1.18 - Composition of the extract with 10% extracted material on wood weight. (Luleå University of Technology, Christian Andersson, David Hodge)

Lidia Testova; [2006]

Yield

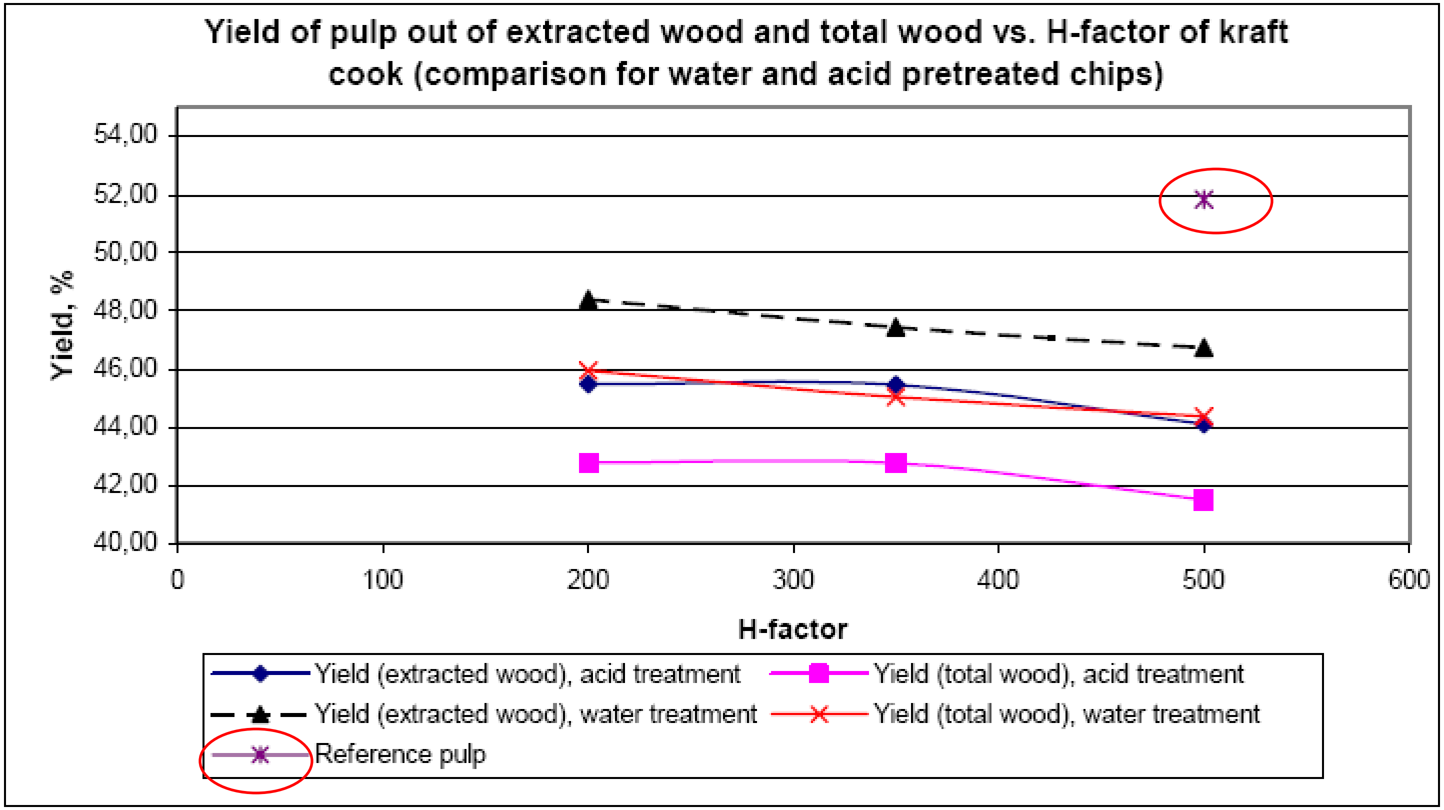
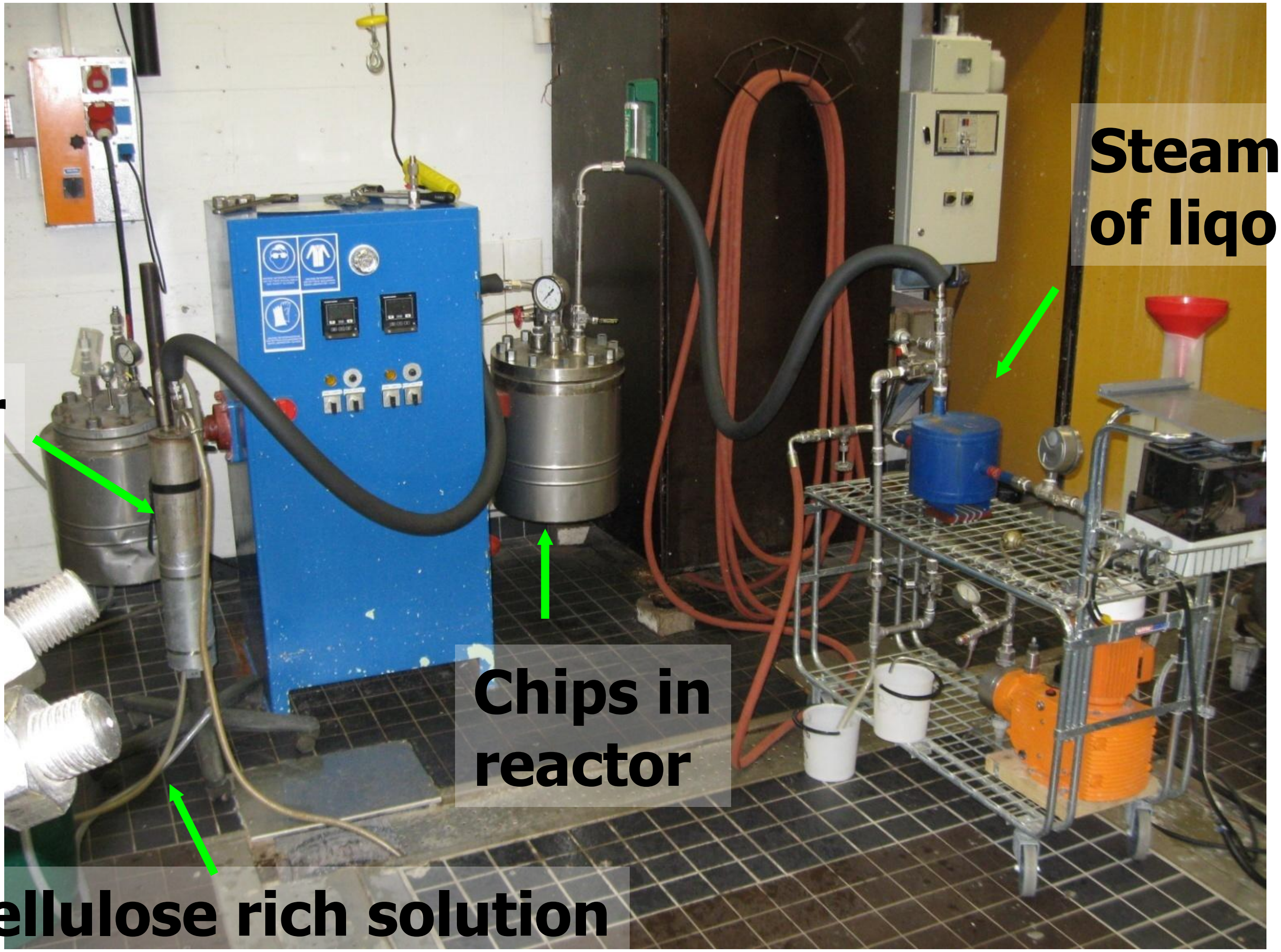


Figure 4.2.1 – The yield of pulp out of the extracted wood and total wood vs. the H-factor of kraft cook (cooking the 95% yield water extracted chips and the 94% yield acid extracted chips, 0.37 % sulphuric acid on dry wood)

Pre-Hydrolysis + Cooking @ FCT, ÅA



Steam heating of liqours

Cooler

Chips in reactor

Hemicellulose rich solution

Xylan dissolution

Experiment	Xylan Retention (mg/g)	Xylan Dissolution (mg/g)	Xylan Removal (%)	Cellulose retention (mg/g)	Lignin Removal (%)
1	188.68	106.42	36.06	560.03	**0.34**
2	178.16	116.94	39.63	493.22	**0.65**
3	150.65	144.45	48.95	632.35	13.88
4	212.42	82.68	28.02	493.12	4.59
5	106.04	189.06	64.07	362.10	9.84
6	126.18	168.92	57.24	611.20	10.68
7	119.51	175.59	59.50	493.65	14.37
8	142.35	152.75	51.76	588.80	11.45
9	88.65	206.45	69.96	422.81	17.53
10	91.12	203.98	69.12	554.20	17.70
11	41.24	253.86	86.03	383.00	0.45
12	78.68	216.42	73.34	427.76	13.42
13	18.23	276.87	**93.82**	413.19	29.84
14	16.70	278.40	**94.34**	394.61	26.64
15	16.70	278.40	**94.34**	395.56	12.73
16	15.14	279.96	**94.87**	412.51	29.37

Process for extraction of hemicelluloses

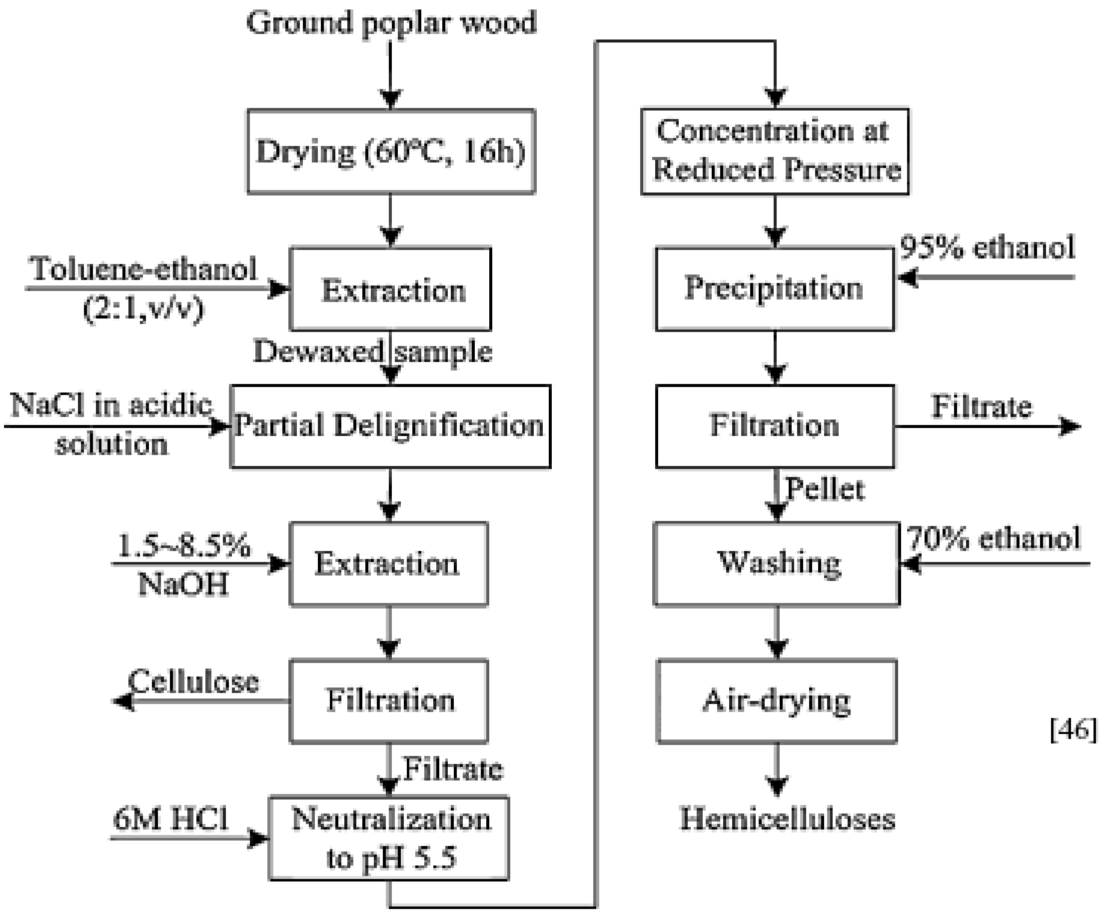
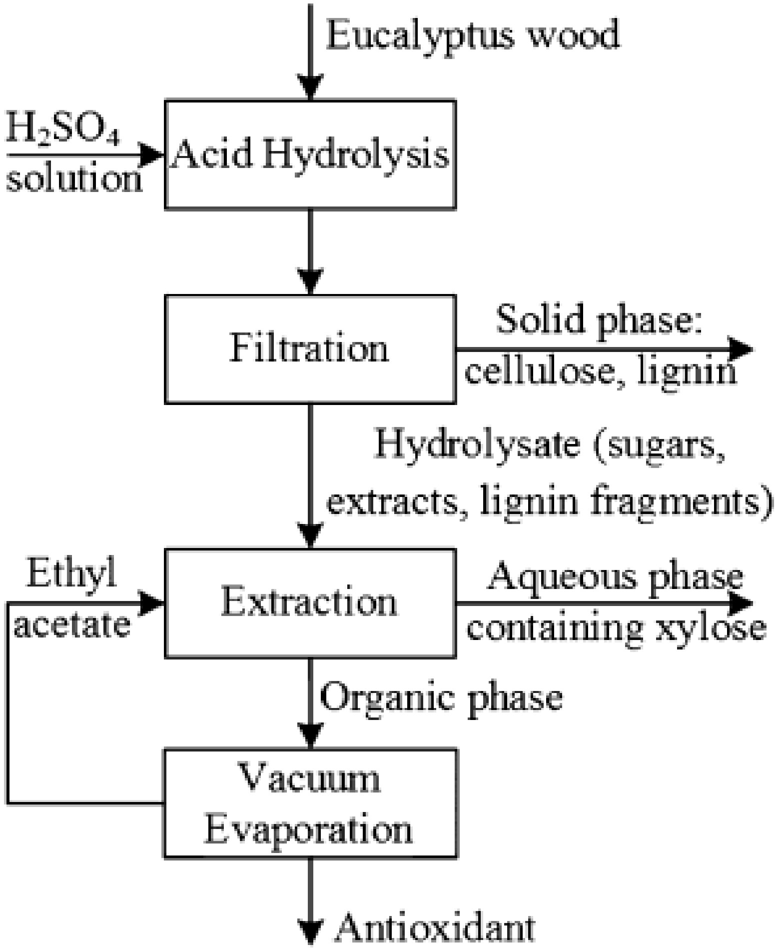


Fig. 7. Separation of hemicellulose and cellulose from fast-growing poplar wood [46].

[46] R.C. Sun, J.M. Fang, J. Tomkinson, Z.C. Geng, J.C. Liu, Fractional isolation, physico-chemical characterization and homogeneous esterification of hemicelluloses from fast-growing poplar wood, Carbohydr. Polym. 44 (2001) 29–39.

Antioxidants and hemicellulose from wood



Eucalyptus wood

H_2SO_4 solution

Acid Hydrolysis

Filtration

Solid phase: cellulose, lignin

Hydrolysate (sugars, extracts, lignin fragments)

Ethyl acetate

Extraction

Aqueous phase containing xylose

Organic phase

Vacuum Evaporation

Antioxidant

Fig. 8. Solvent extraction of hemicelluloses and antioxidant from wood [26].

- Antioxidants, e.g. phenolics and polyphenolics
- Hemicelluloses, e.g. xylose

[26] J. Gonzalez, J.M. Cruz, H. Dominguez, J.C. Parajo, Production of antioxidants from Eucalyptus globulus wood by solvent extraction of hemicellulose hydrolyzates, Food Chem. 84 (2004) 243–251.

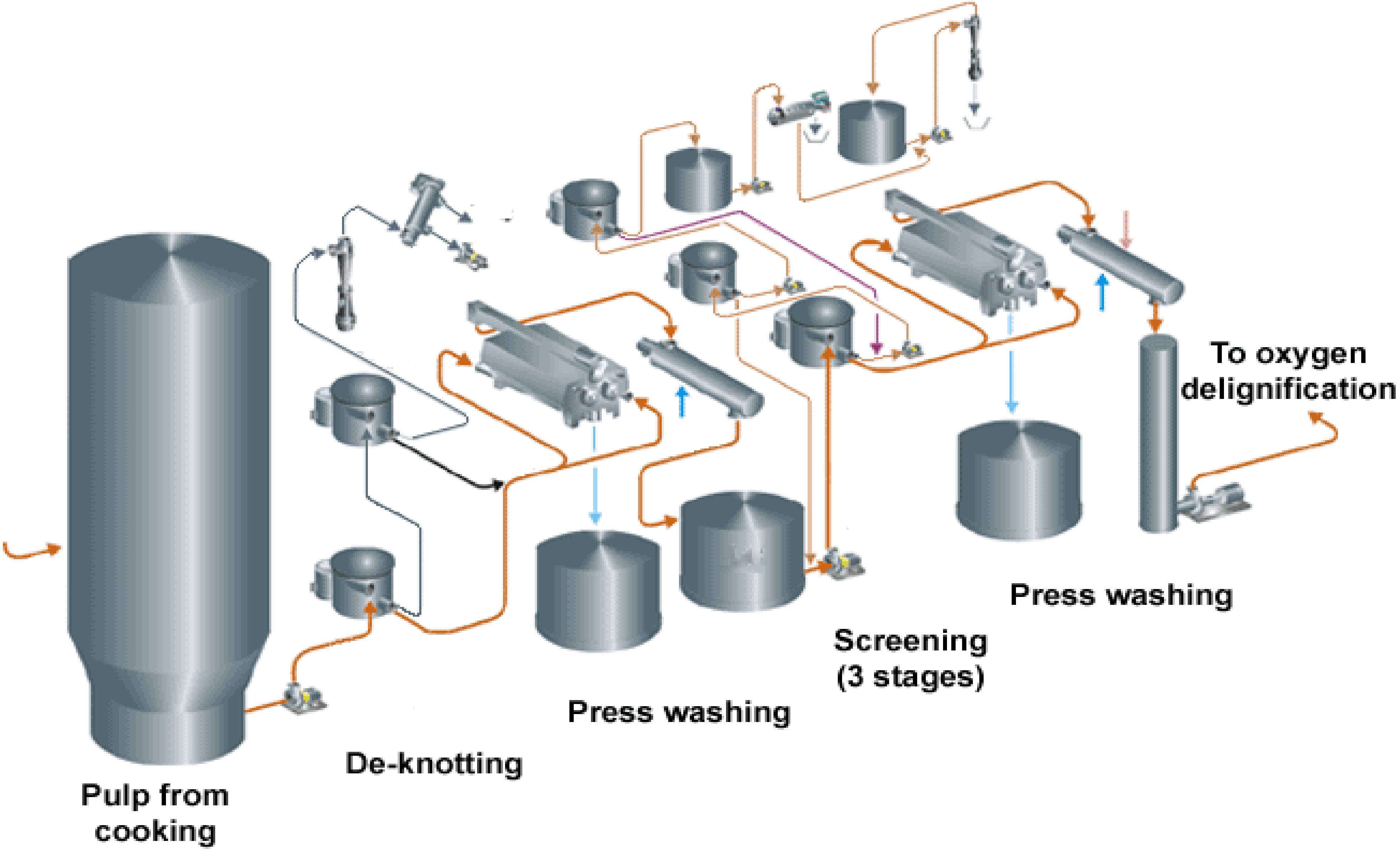
Fractionation of dispersions

- Cleaning and screening of pulp or "Fractionation based on size"

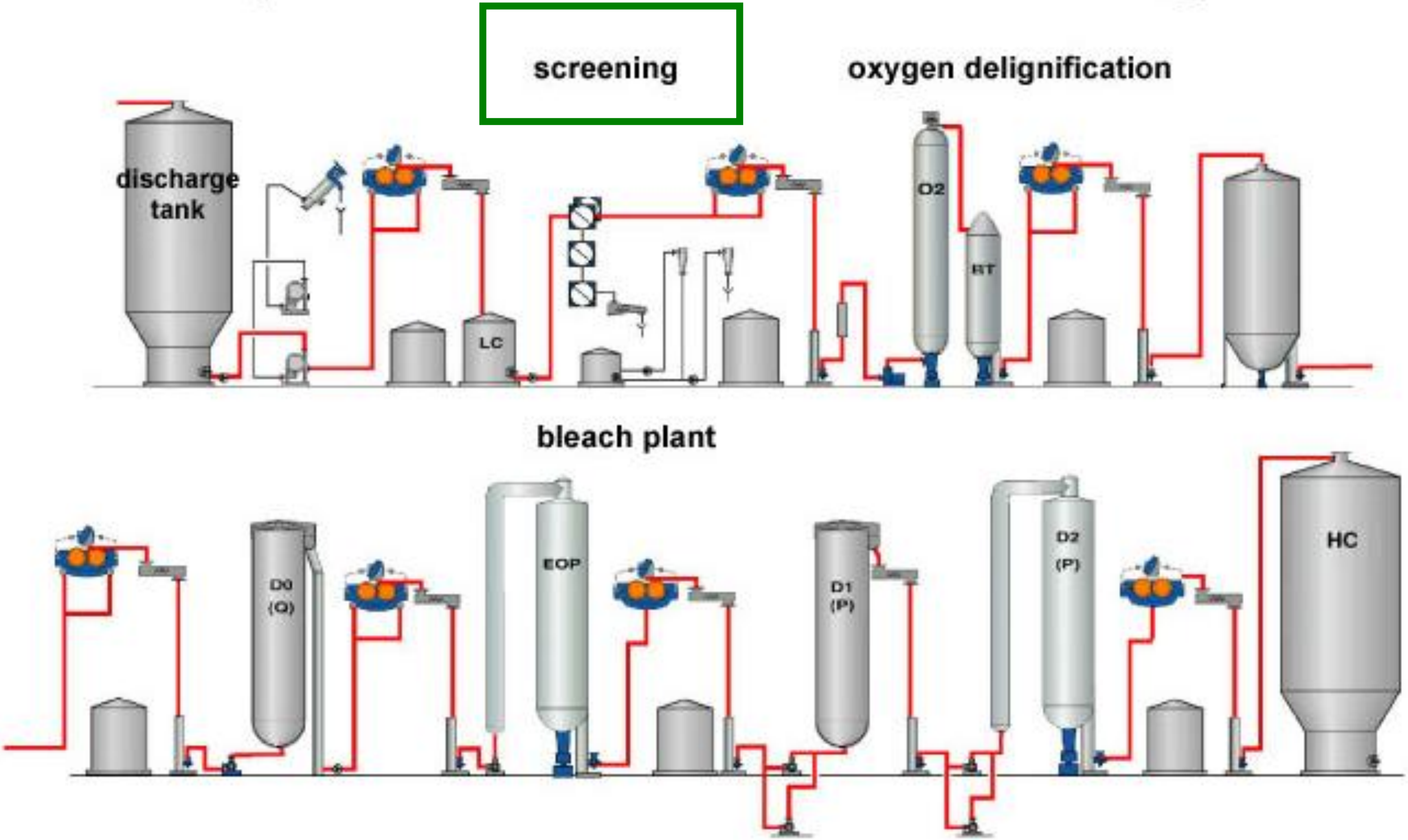
Cleaning and screening

- Purpose of cleaning: Elimination of dissolved products from the wet pulp
- Purpose for screening: Separation and elimination of “faulty” solid particles.

An example layout of brown stock washing and screening



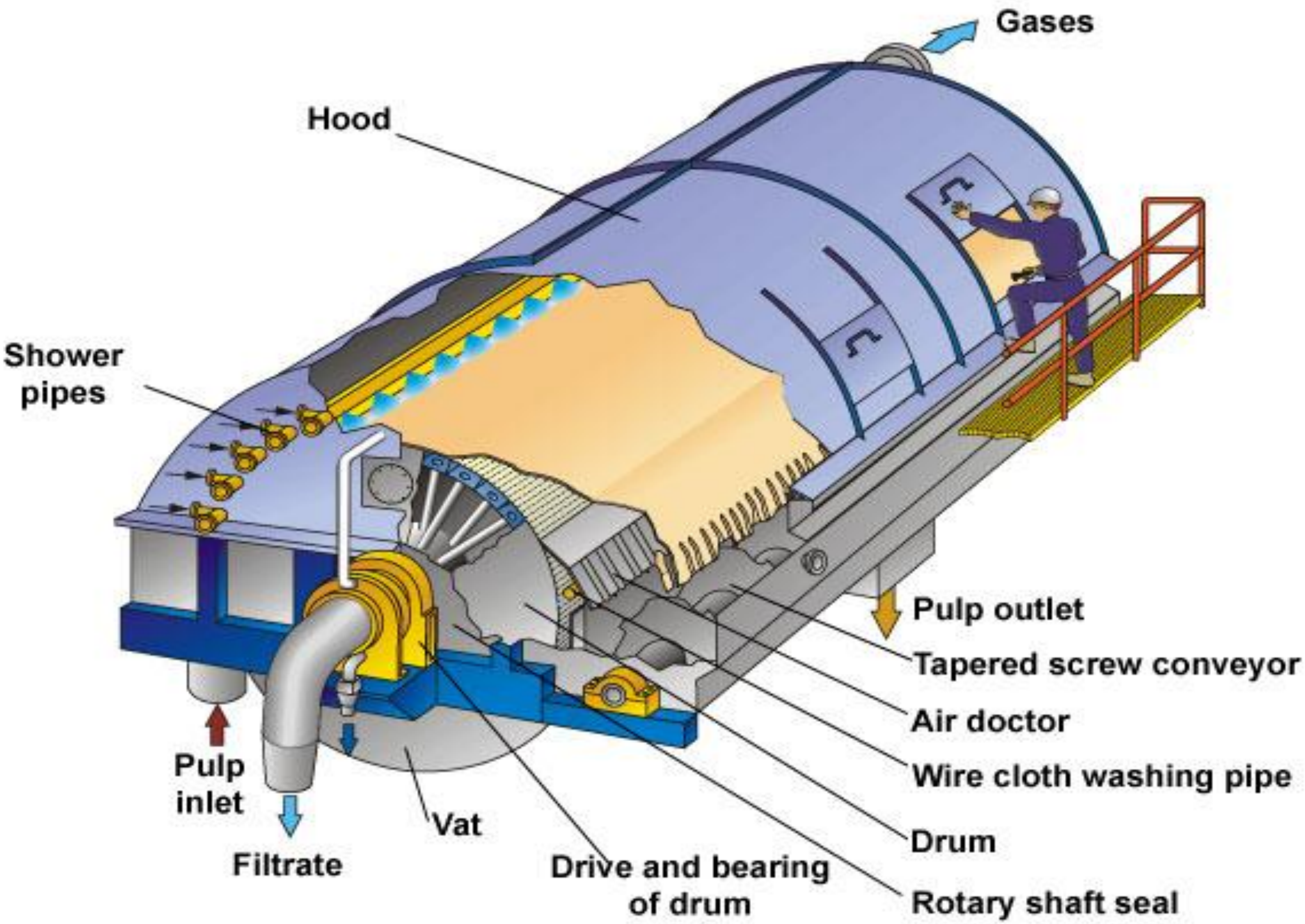
Example of a fiberline after the digester


screening

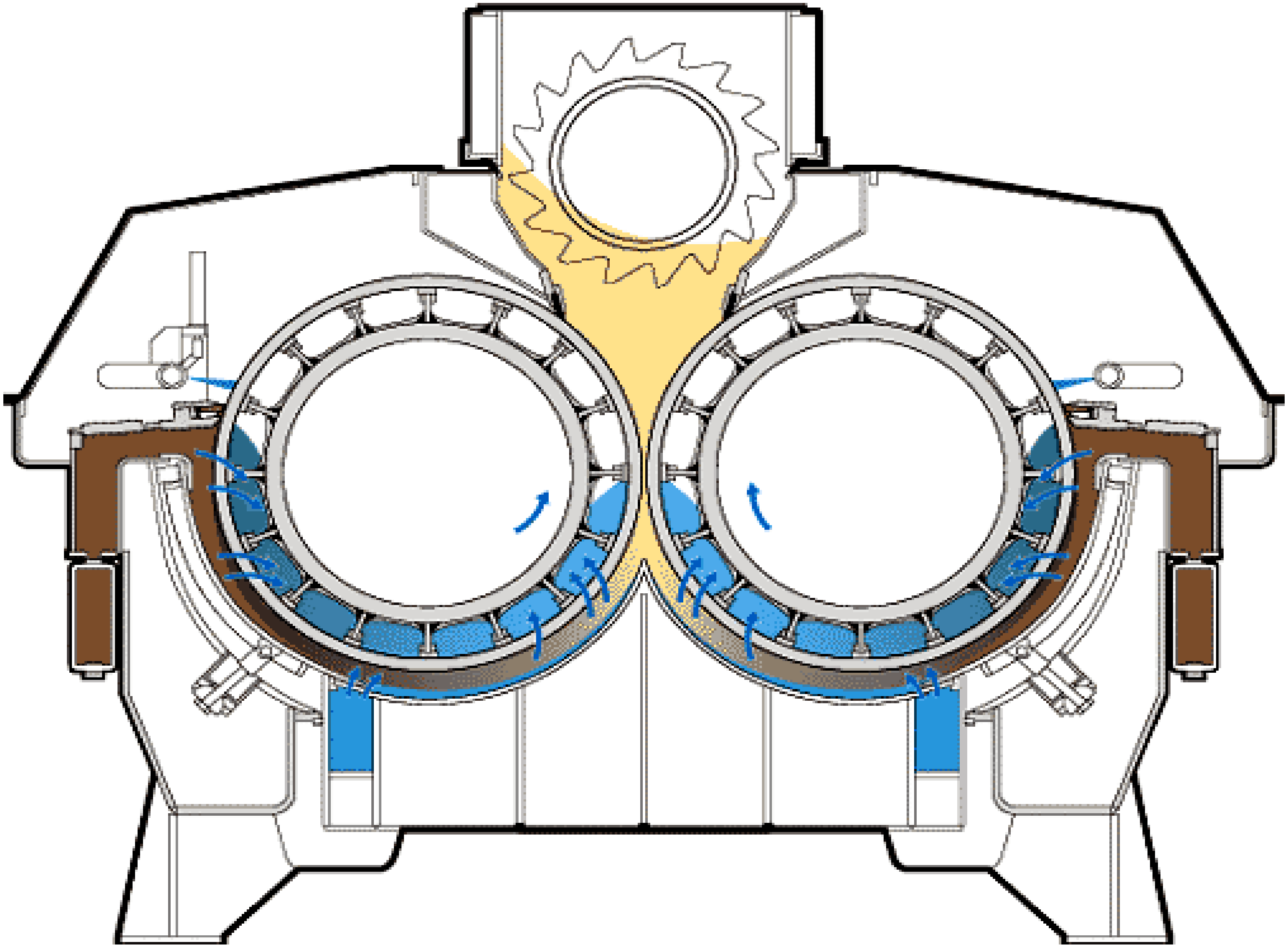
oxygen delignification

bleach plant

Suction drum filter (GasFree Filter)

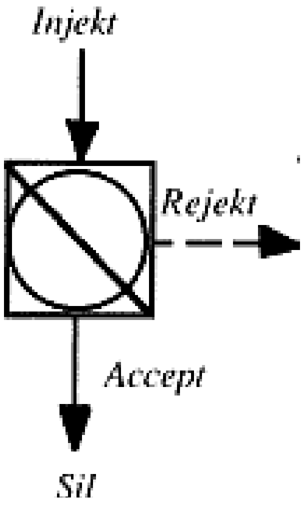


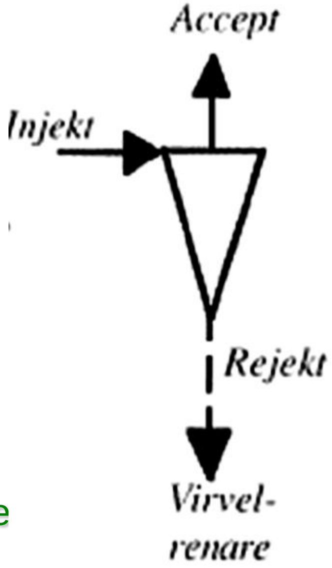
Wash press (TwinRoll-A)



Elimination of impurities in the pulp

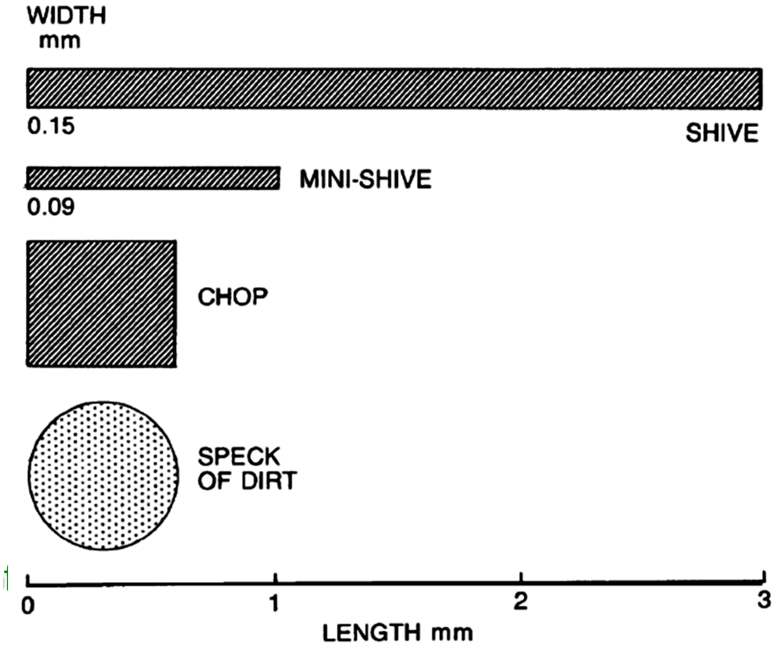
- Sedimentation
  - Heavy particles e.g. stones and metal falls rapidly to the bottom, fibres slowly
- Screening
  - The fibres are passed through a screen plate with holes or slots whereas ”big” impurities are not
- Hydrocyclone cleaning
  - Particles are separated by centrifugal and shearing forces



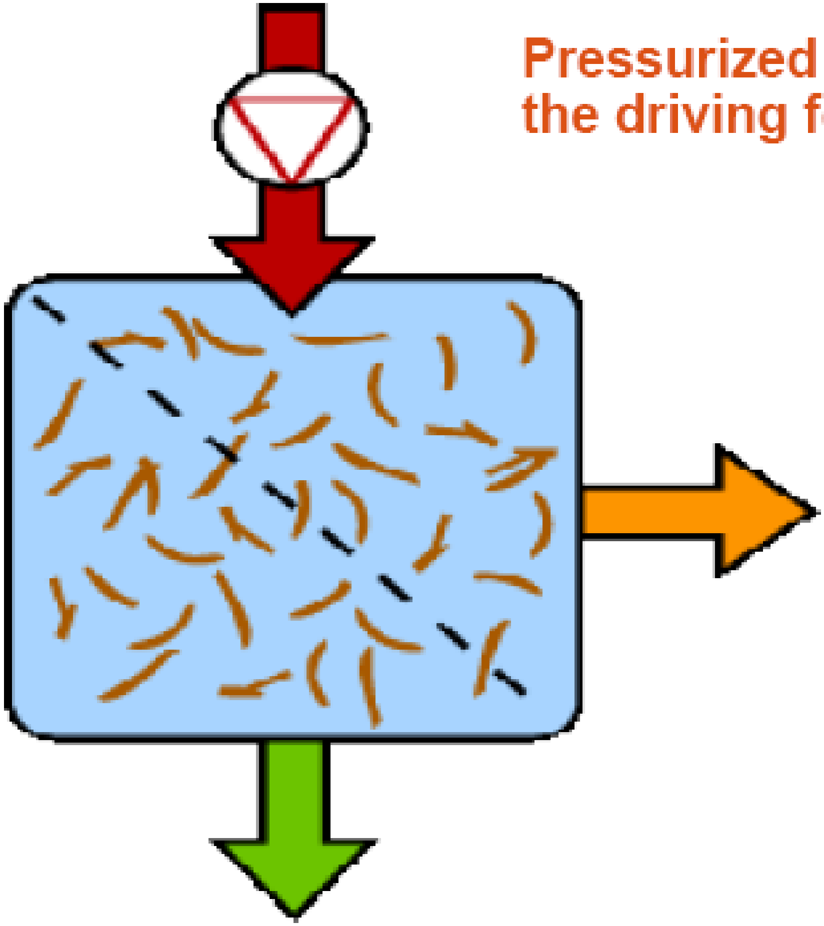


Screening

- Solid material can be separated on the basis of
  - Size
  - Density difference (sand is heavier, plastics are lighter than pulp fibre material)
- Solid contaminants which are separated from pulp consist of:
  - Uncooked pieces of chips, knots, reaction wood, heartwood (hard)
  - Shieves, fibre bundles
  - Bark
  - Sand and stones
  - Metal

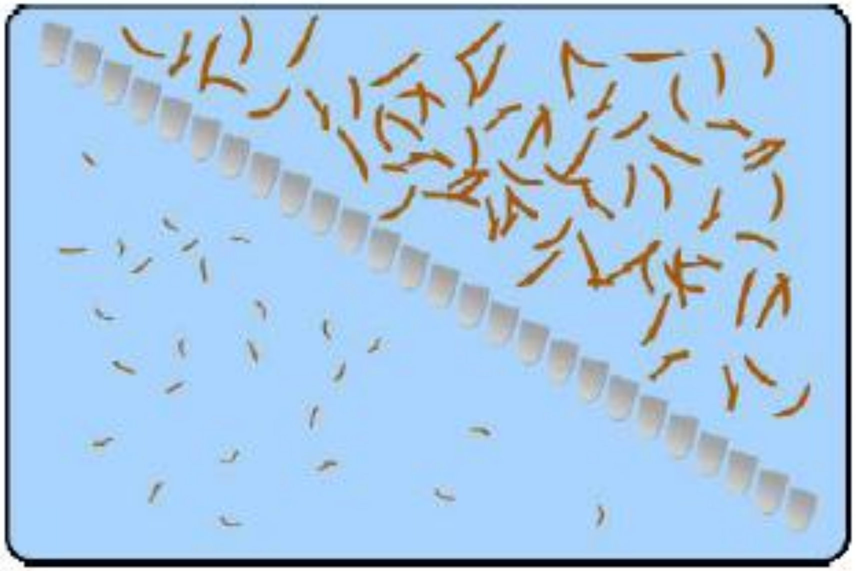


Screening process, step 1



Pressurized feeding is the driving force

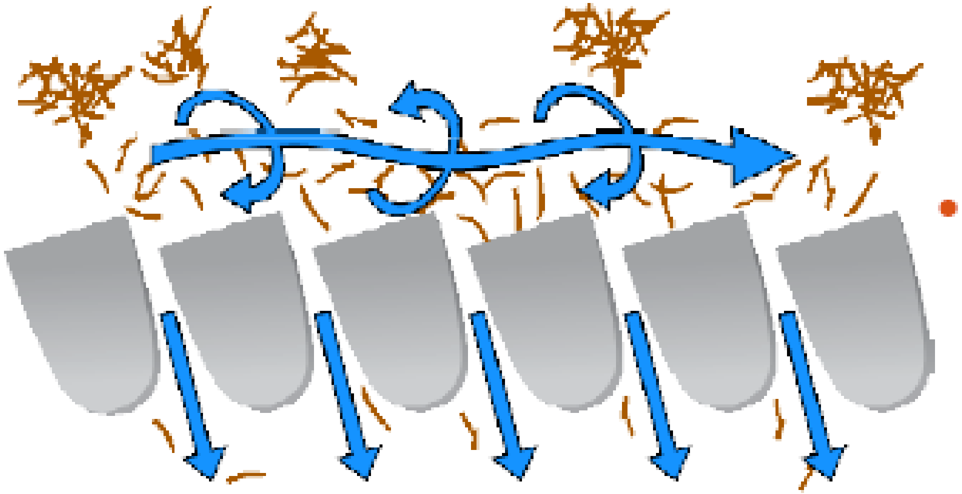
Screening process, step 2



Dewatering

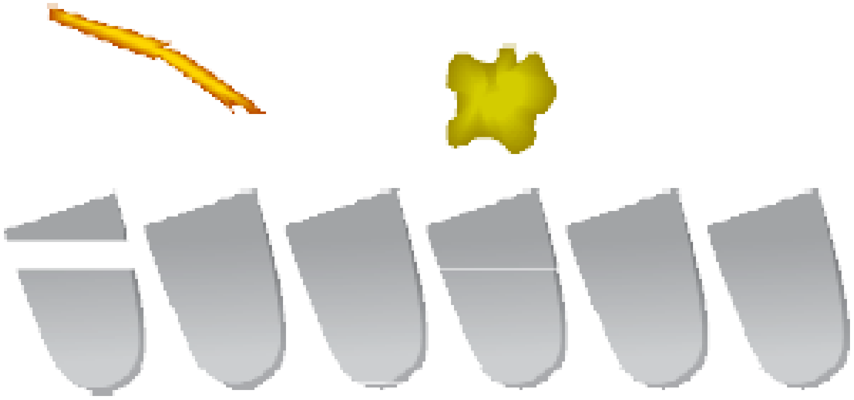
- Only filtration would happen without a rotor!

Screening process, step 3 +4



Boundary layer fluidization

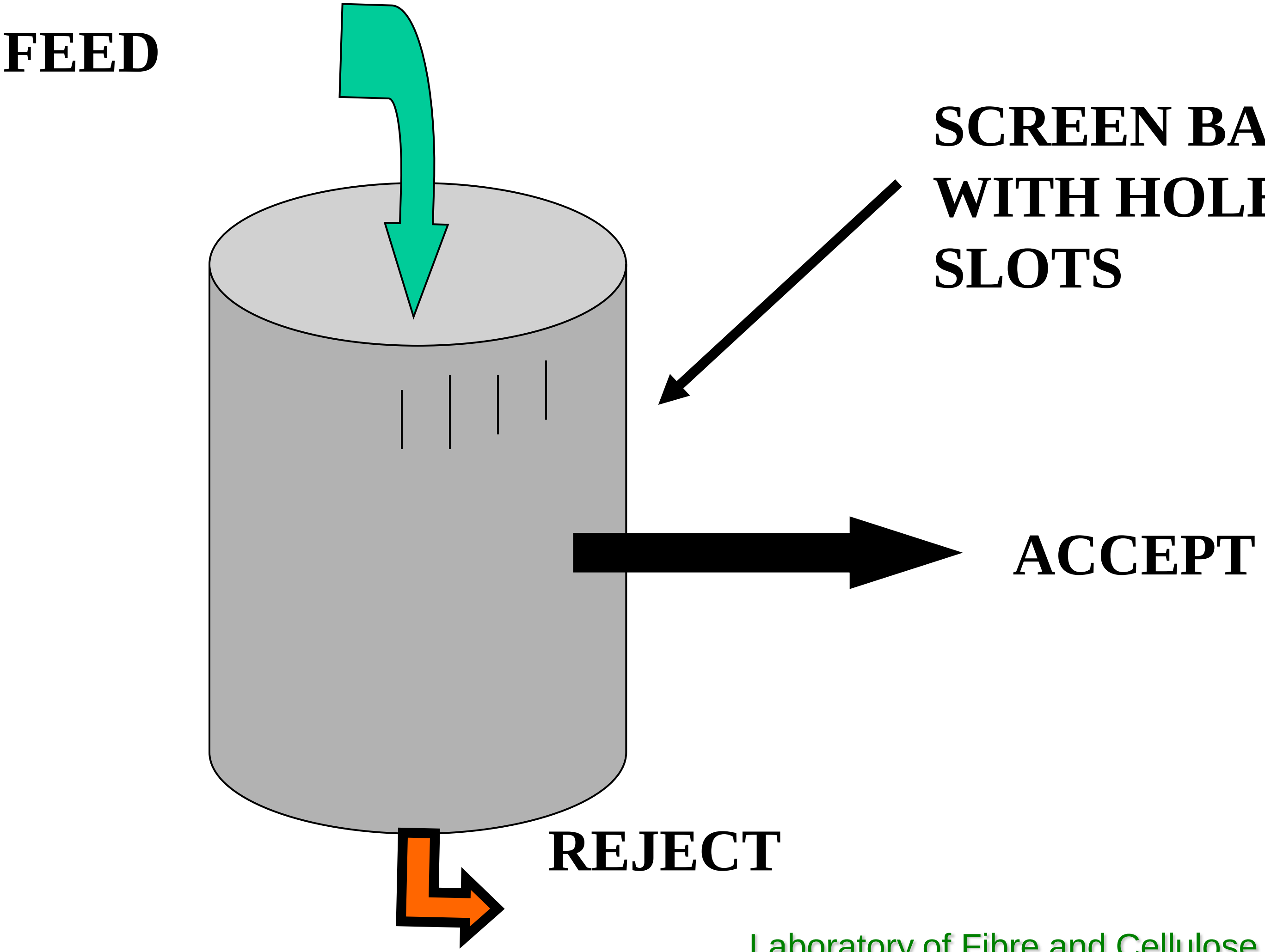
- breaks up the fiber network and allows free fibers to be accepted



Particle separation

- particle separation is accomplished by barrier effect, fiber mat and passage **probability**

Pressure screening



FEED

SCREEN BASKET WITH HOLES OR SLOTS

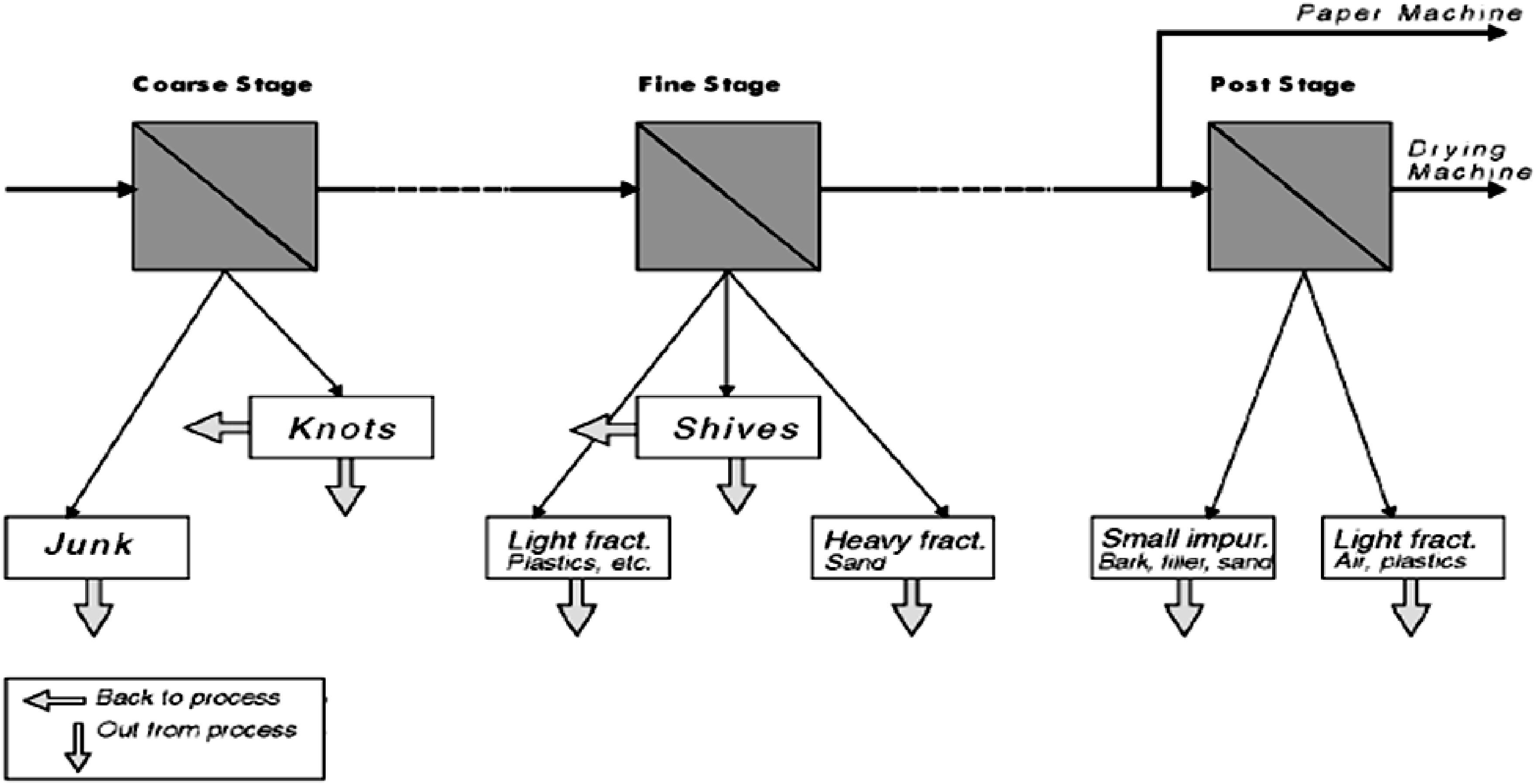
ACCEPT

REJECT

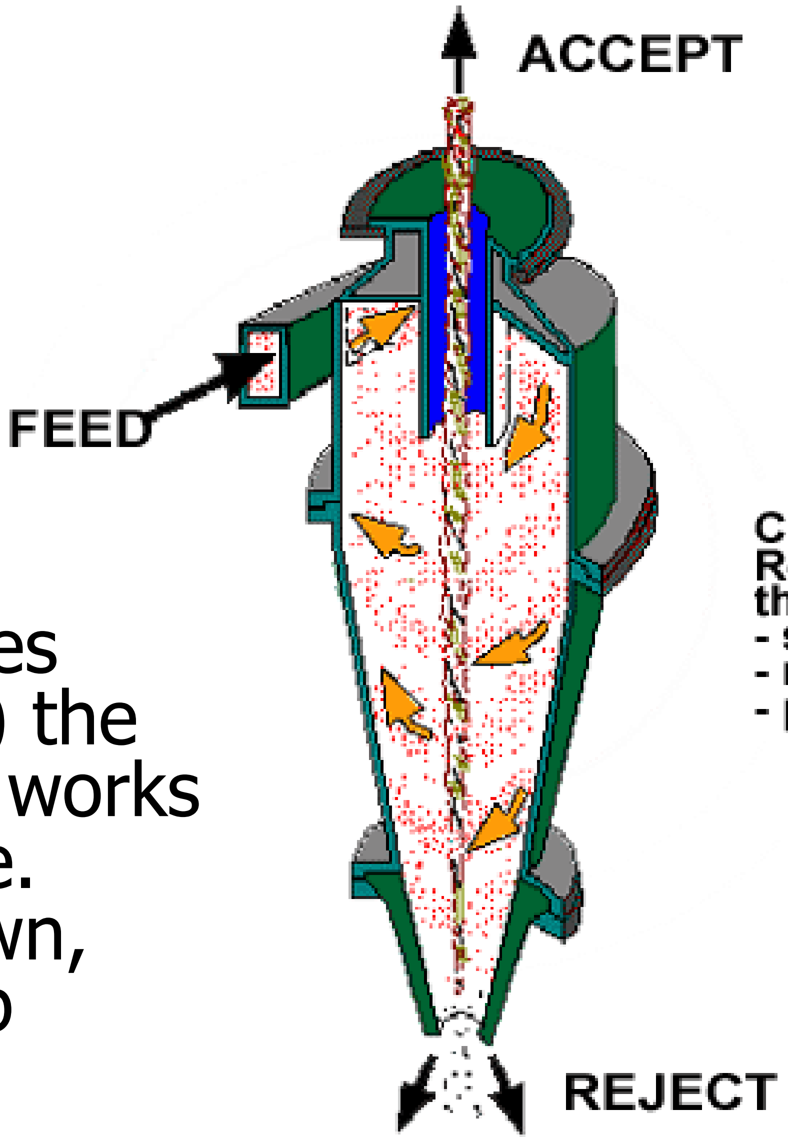
Screening basket

Slot width 0,12 or 0,15 mm

Pulp screening



The function of a centricleaner



CONSISTENCY 0.4 - 0.8 %
Removes particles heavier than fiber
- **sand**
- **metal particles**
- **pitch conglomerations**

For light particles (e.g. plastics) the centricleaner works vice versa, i.e. fibres fall down, plastics go up

Fractionation of dissolved biomass

- Purification and homogenisation by precipitation
  or
  “Fractionation based on solubility”

Solubility

- Purpose: Dissolution and selective re-precipitation of dissolved components

Solubility of polymers

- **The dissolution of polymers depends not only on their physical properties, but also on their chemical structure, such as: polarity, molecular weight, branching, crosslinking degree, and crystallinity.**
- **The general principle that states *like dissolves like* is also appropriate in the case of polymers. Thus, polar macromolecules are soluble in water.**
- **Conversely, nonpolar polymers or polymer showing a low polarity are soluble in nonpolar solvents.**

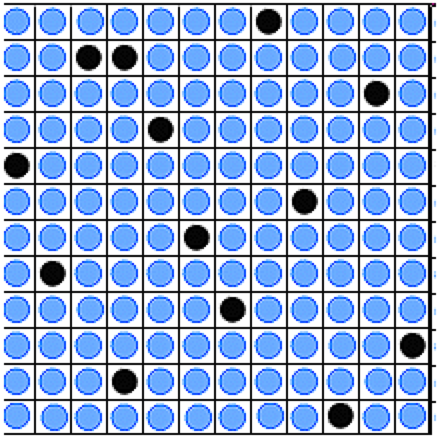
http://pslc.ws/macrog/property/solpol/ps1.htm

Solubility of polymers

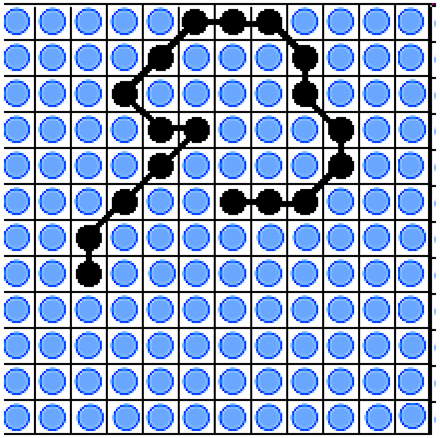
- **The molecular weight of polymers plays an important role in their solubility.**
- **In a given solvent at a particular temperature, as molecular weight increases, the solubility of a polymer decreases. This same behavior is also noticed as crosslinking degree increases, since strongly crosslinked polymers will inhibit the interaction between polymer chains and solvent molecules, preventing those polymer chains from being transported into solution.**
- **A similar situation occurs with crystalline macromolecules, although in such a case the dissolution can be forced if an appropriate solvent is available, or warming the polymer up to temperatures slightly below its crystalline melting point**

http://pslc.ws/macrog/property/solpol/ps1.htm

Solubility – DP (MW) dependence



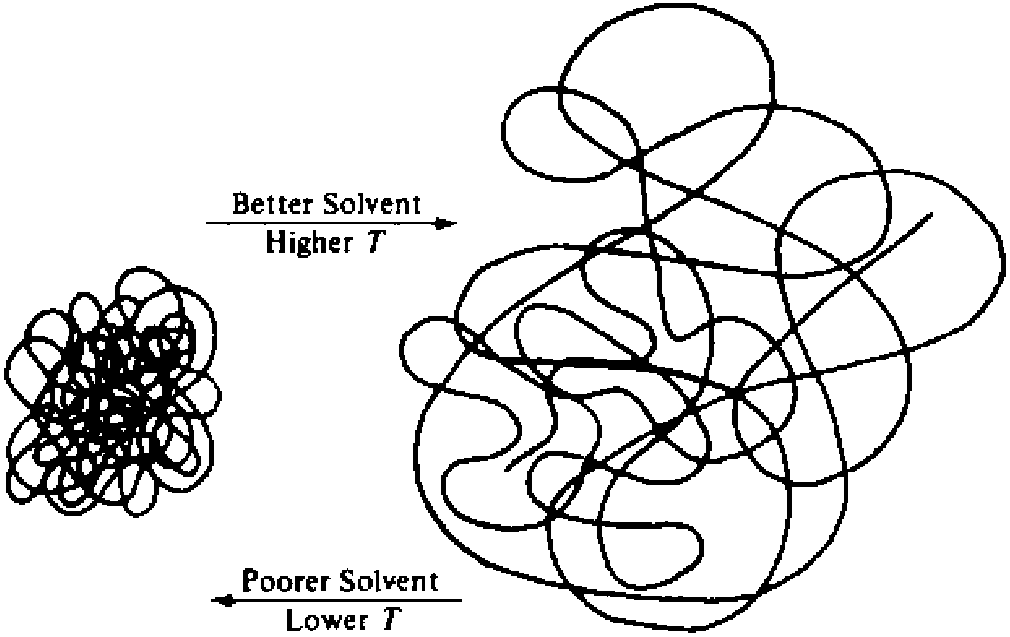
Two-dimensional lattice model of solubility for a low molecular weight solute



Two-dimensional lattice model of solubility for a polymer solute

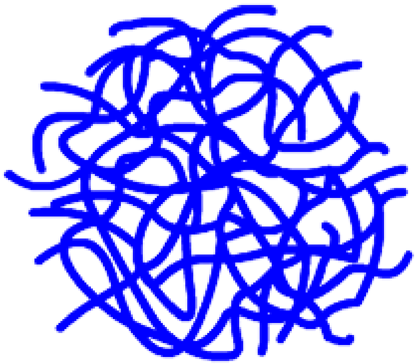
Mixing of small molecules results in a greater number of possible molecular arrangements than the mixing of a polymeric solute with a solvent.

Solubility of polymers



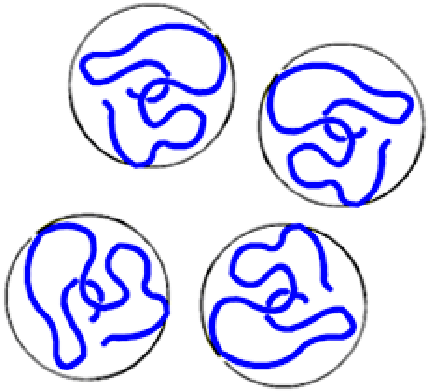
www.chemeng.queensu.ca

Dissolution of polymers



a) Polymer molecules in solid state just after being added to a solvent

b) First step: a swollen gel in solvent



c) Second step: solvated polymer molecules dispersed into a solution

http://pslc.ws/macrog/property/solpol/ps1.htm

Goal of dissolution of biomass

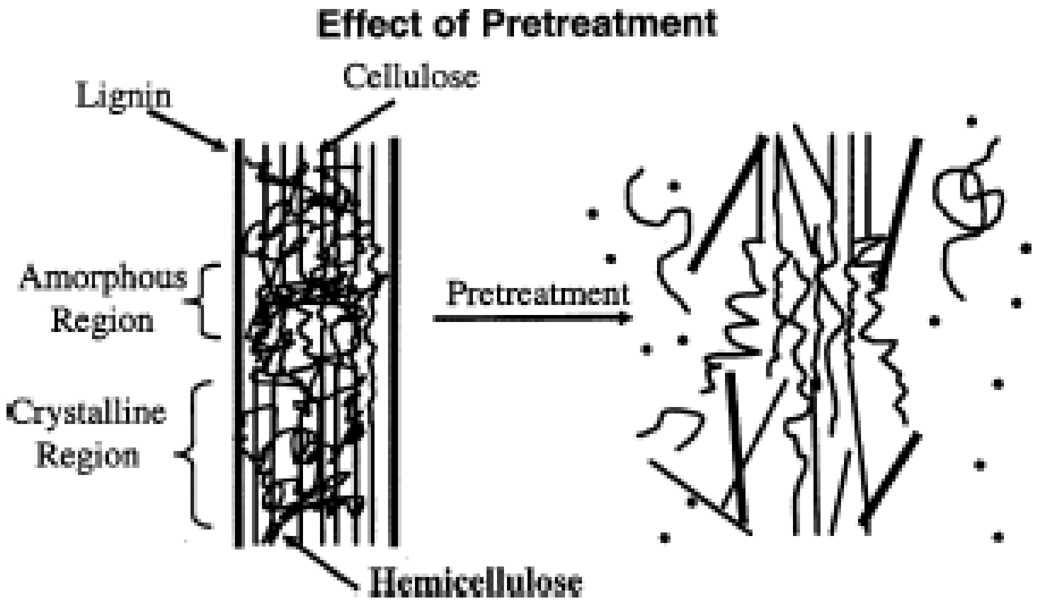


Fig. 1. Schematic of goals of pretreatment on lignocellulosic material (adapted from Hsu et al., 1980).

N. Mosier et al. / Bioresource Technology 96 (2005) 673–686

Goal of dissolution

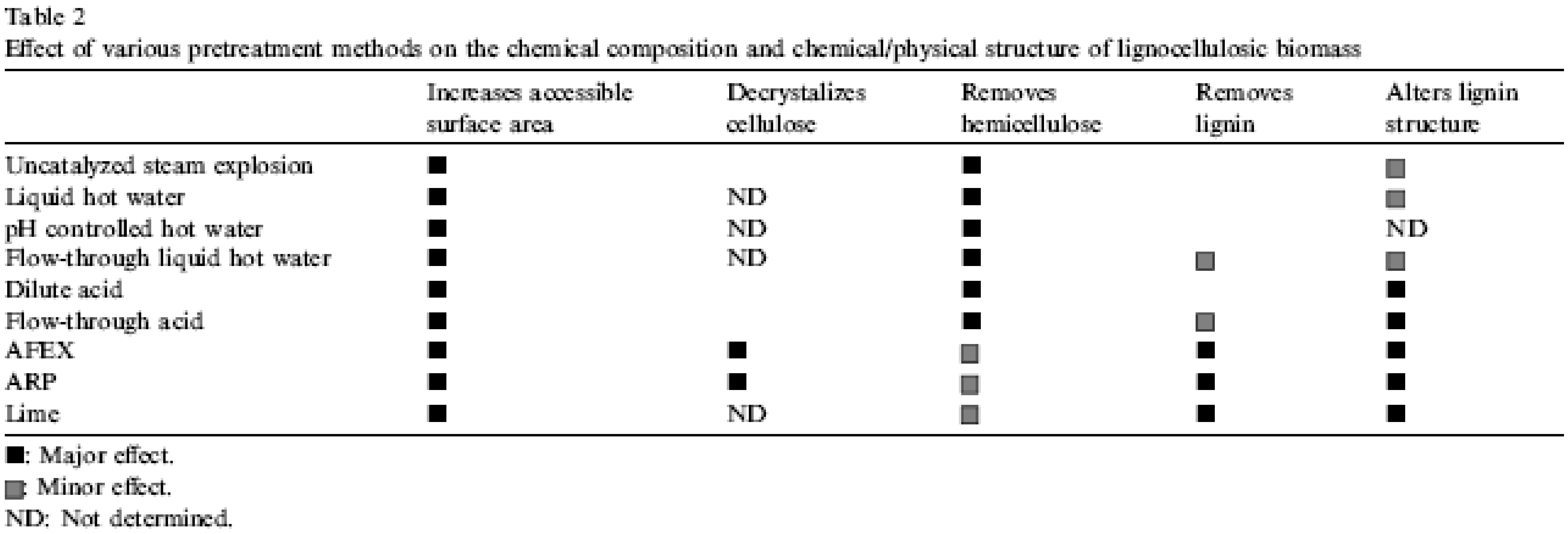


Table 2
Effect of various pretreatment methods on the chemical composition and chemical/physical structure of lignocellulosic biomass

	Increases accessible surface area	Decrystalizes cellulose	Removes hemicellulose	Removes lignin	Alters lignin structure
Uncatalyzed steam explosion	■		■		▨
Liquid hot water	■	ND	■		▨
pH controlled hot water	■	ND	■		ND
Flow-through liquid hot water	■	ND	■	▨	▨
Dilute acid	■		■		■
Flow-through acid	■		■	▨	■
AFEX	■	■	▨	■	■
ARP	■	■	▨	■	■
Lime	■	ND	▨	■	■

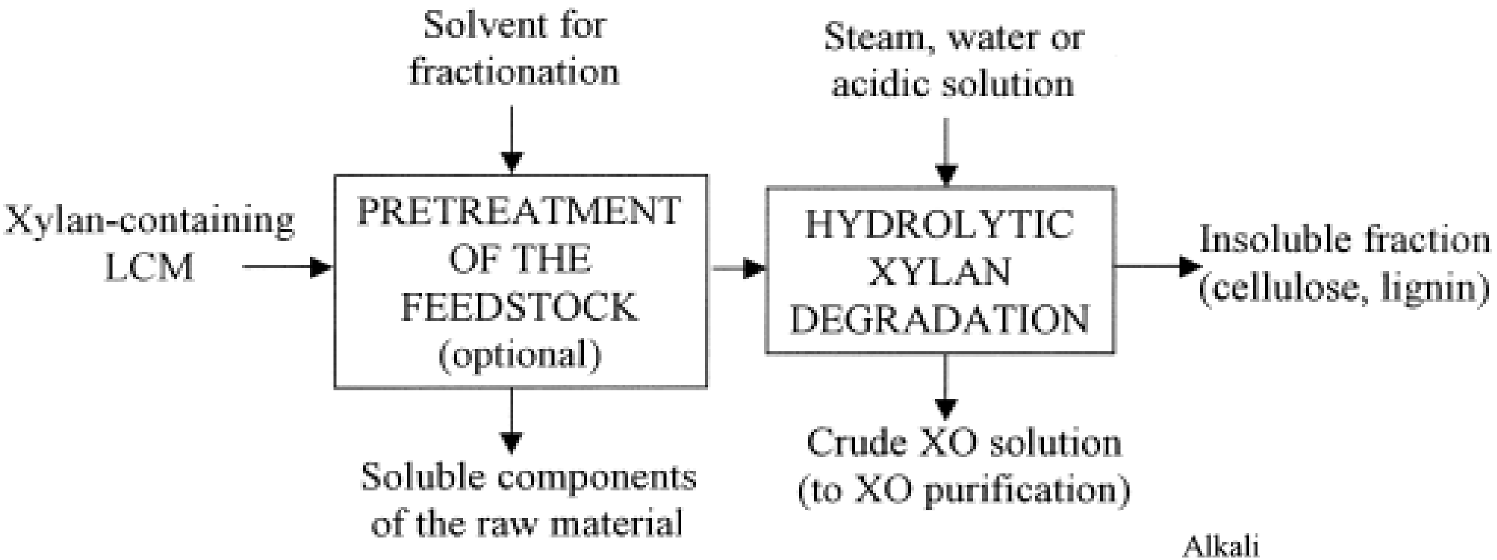
■: Major effect.
▨: Minor effect.
ND: Not determined.

N. Mosier et al. / Bioresource Technology 96 (2005) 673–686

Solubility of hemicelluloses

- In the native state the xylan is supposed to be *O*-acetylated. The content of acetyl groups of MGX isolated from hardwoods of temperate zones varies in the range 3–13%.
- The acetyl groups are split during the necessary alkaline extraction conditions resulting in partial or full water-insolubility of the xylan preparations. But the acetyl groups may be, at least in part, preserved by treating with hot water or steam.

Polysaccharides I
T. Heinze, Dieter Klemm (2006)



Solvent for fractionation

Steam, water or acidic solution

Xylan-containing LCM

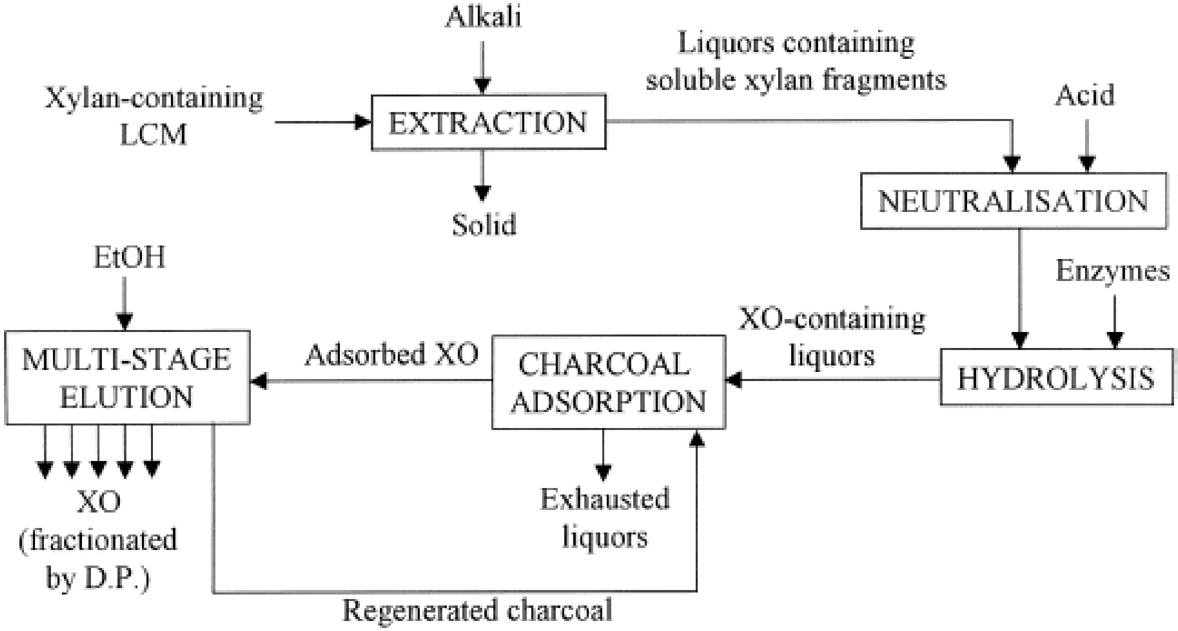
PRETREATMENT OF THE FEEDSTOCK (optional)

HYDROLYTIC XYLAN DEGRADATION

Insoluble fraction (cellulose, lignin)

Soluble components of the raw material

Crude XO solution (to XO purification)



Alkali

Liquors containing soluble xylan fragments

Acid

Xylan-containing LCM

EXTRACTION

Solid

NEUTRALISATION

Enzymes

EtOH

XO-containing liquors

MULTI-STAGE ELUTION

Adsorbed XO

CHARCOAL ADSORPTION

HYDROLYSIS

XO (fractionated by D.P.)

Exhausted liquors

Regenerated charcoal

Fig. 4. A proposed scheme for production and purification of XOs.

Vázquez

Trends in Food Science & Technology 11 (2000) 387–393

Solubility

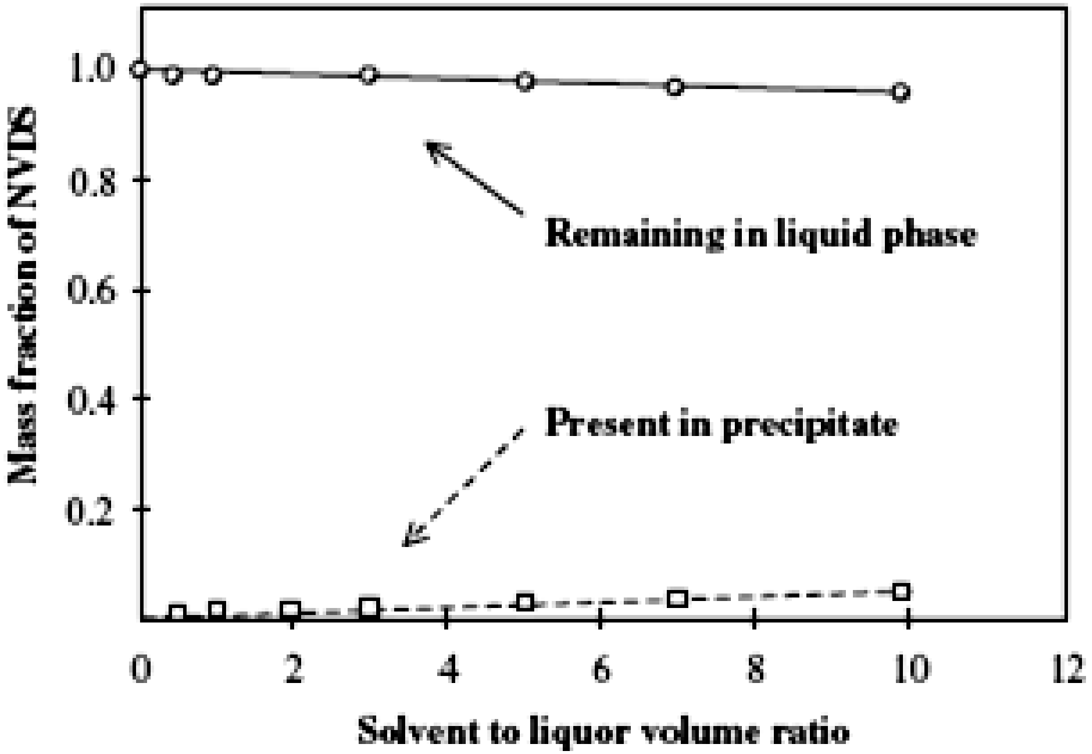


Fig. 3. Mass fraction of non-volatile dissolved solids (NVDS) remaining in solid and liquid phases in ethanol precipitation of raw autohydrolysis liquors.

Vázquez

Bioresource Technology 96 (2005) 889–896

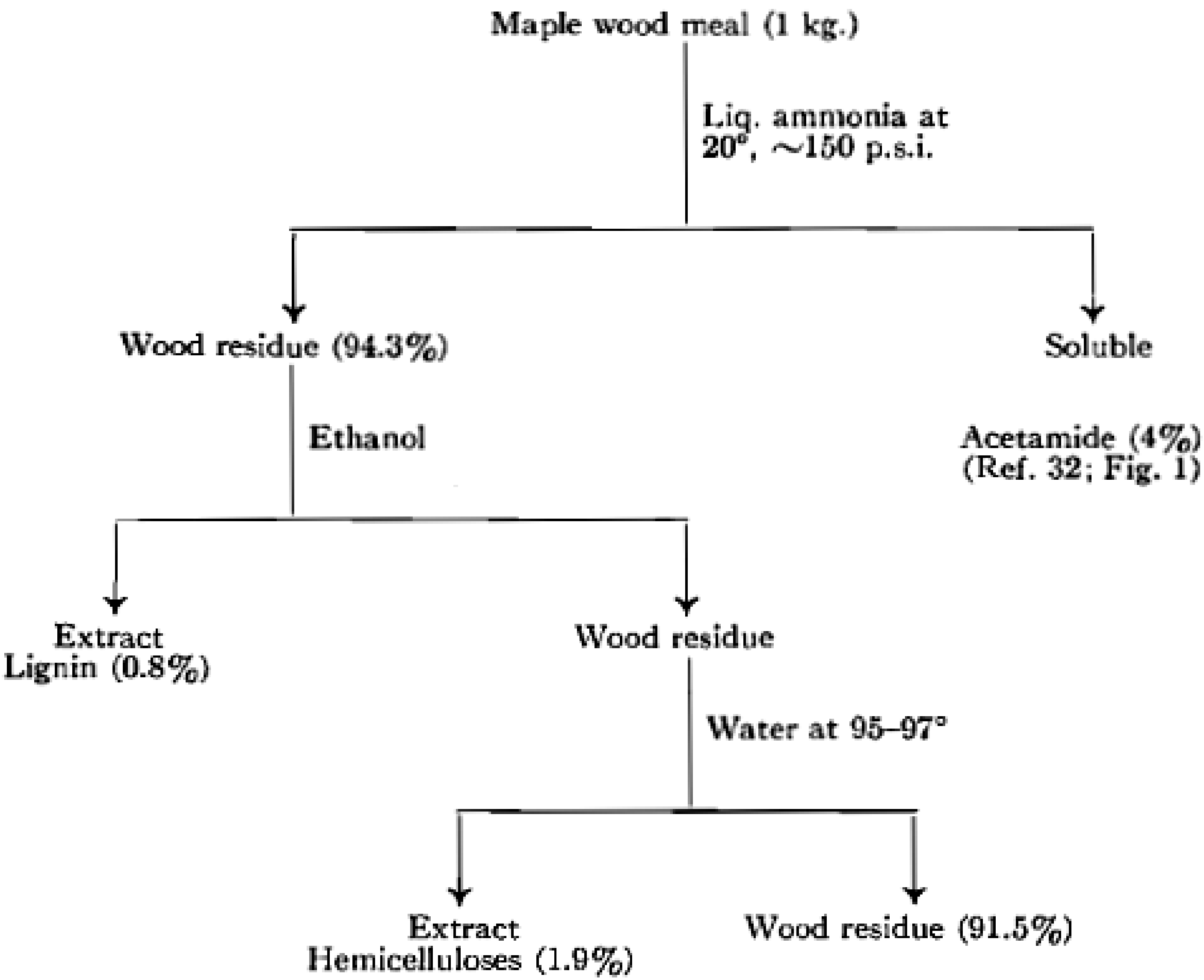


FIG. 1. Extraction of maple wood meal with liquid ammonia, ethanol, and water in succession. All percentages based on original, solvent-extracted wood meal.

Solubility of hemicelluloses

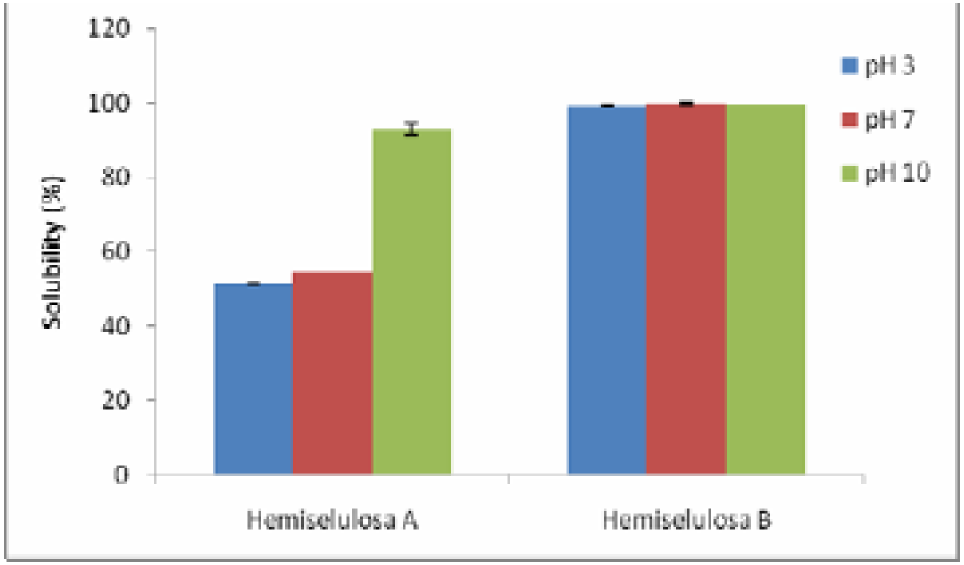
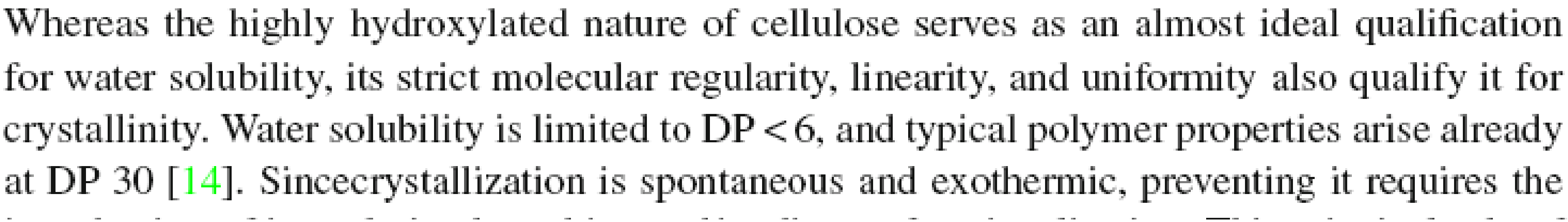


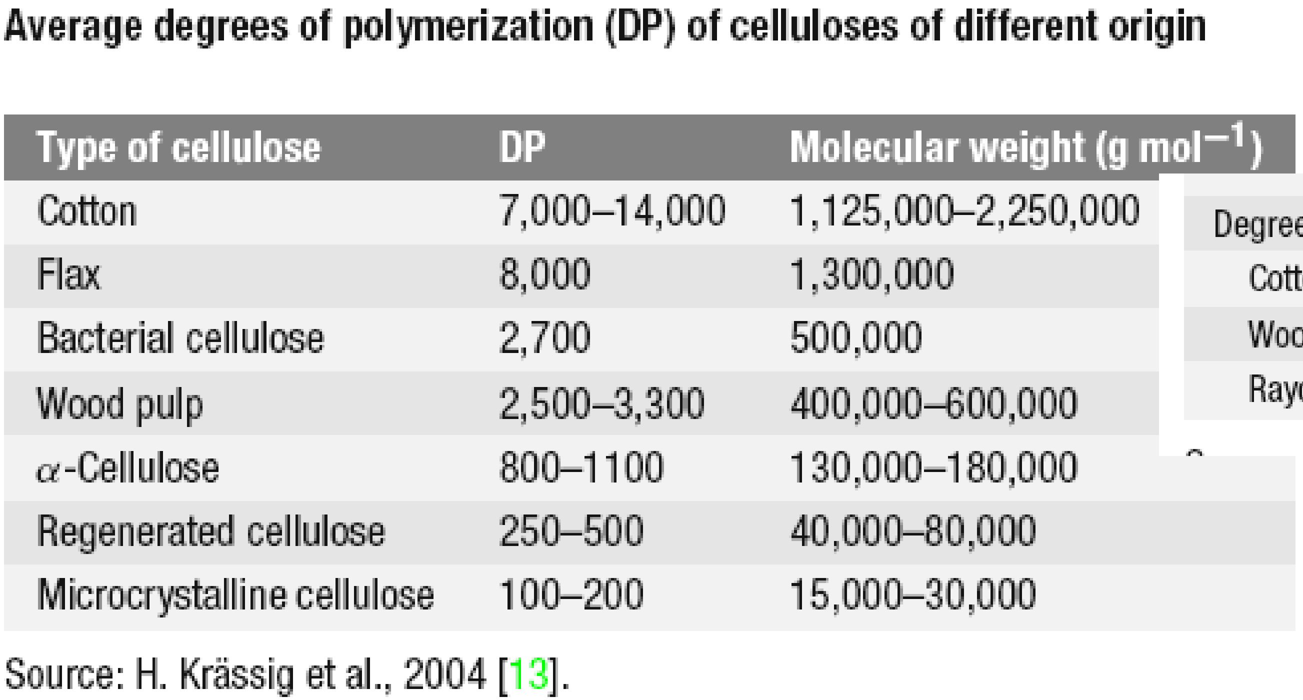
Figure 2 Effect of pH on solubility of hemicelluloses (A and B). Error bars represent standard error of means. Each value is the means of triplicates from two separate runs: $n = 3$.

Zaleha, *(ICERT 2008)*

Solubility of cellulose



Whereas the highly hydroxylated nature of cellulose serves as an almost ideal qualification for water solubility, its strict molecular regularity, linearity, and uniformity also qualify it for crystallinity. Water solubility is limited to DP < 6, and typical polymer properties arise already at DP 30 [14]. Sincecrystallization is spontaneous and exothermic, preventing it requires the



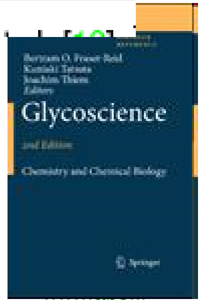
Average degrees of polymerization (DP) of celluloses of different origin

Type of cellulose	DP	Molecular weight ($g\ mol^{-1}$)
Cotton	7,000–14,000	1,125,000–2,250,000
Flax	8,000	1,300,000
Bacterial cellulose	2,700	500,000
Wood pulp	2,500–3,300	400,000–600,000
α-Cellulose	800–1100	130,000–180,000
Regenerated cellulose	250–500	40,000–80,000
Microcrystalline cellulose	100–200	15,000–30,000

Source: H. Krässig et al., 2004 [13].

Degree of crystallinity[i]	
Cotton	83
Wood pulp[j]	46–56
Rayon	67

Glasser



and Cellulose Technology

Solubility of cellulose

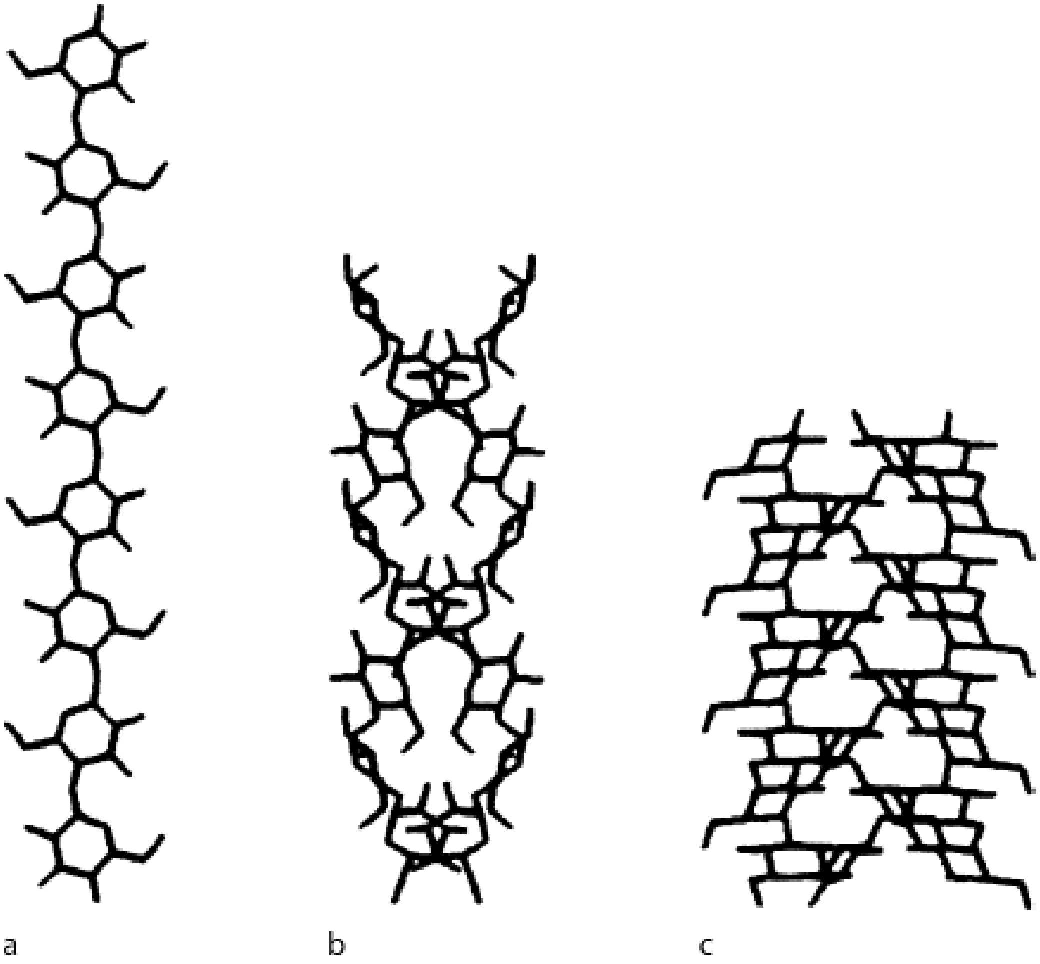


Figure 5

Three potential helical structures of polysaccharides. (a) Single helix with twofold screw axis (cellulose); (b) double helix (amylose); and (c) triple helix (β, 1–3 glucan) (according to Rees [4]). The particular structure depends largely on the constraints imposed by hydrogen-bonds and rotational freedoms around the glycosidic intermonomer bonds (i. e., ➲ *Fig. 3*, energy barriers to rotation)

Solubility of cellulose

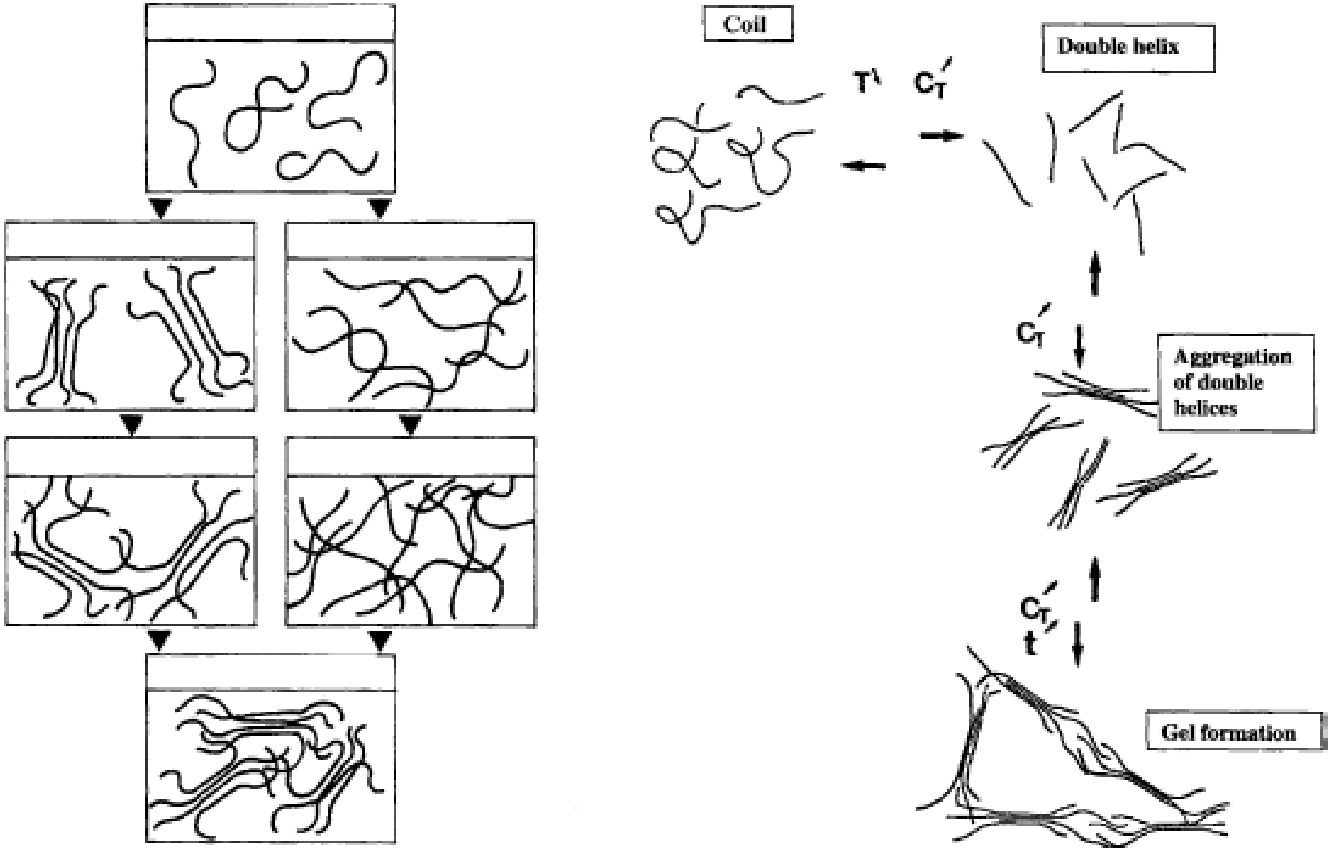


Figure 4

Organization of cellulose (left) and κ-carrageenan molecules (right) during desolvation. The figure illustrates the possible paths to the formation of solid structures: early formation of organized structures in solution (left side) leading to liquid crystalline structures of rigid-type molecules, and desolvation without organization (right) leading to a largely amorphous structure (left, according to Schurz, [35]). And gel formation by the aggregation of helices (right, according to Rinaudo, [33])

Solubility of cellulose

Degree of crystallinity[i]	
Cotton	83
Wood pulp[j]	46–56
Rayon	67

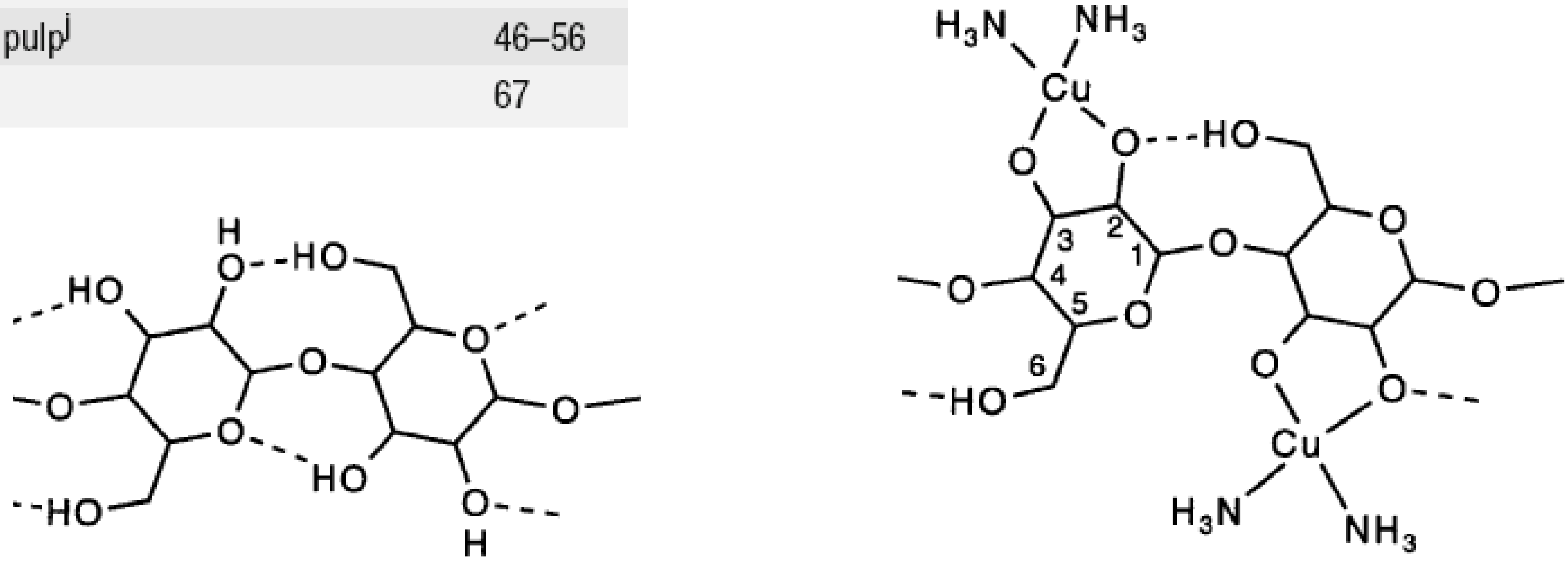


Figure 11
Complexation principle of cellulose with derivatizing solvent molecules illustrated for the case of cuprammonium hydroxide. Solvent molecules replace the existing hydrogen bonds with solvating Cu-complexes. (After Burchardt et al. [47])

Effect of molar mass on solubility

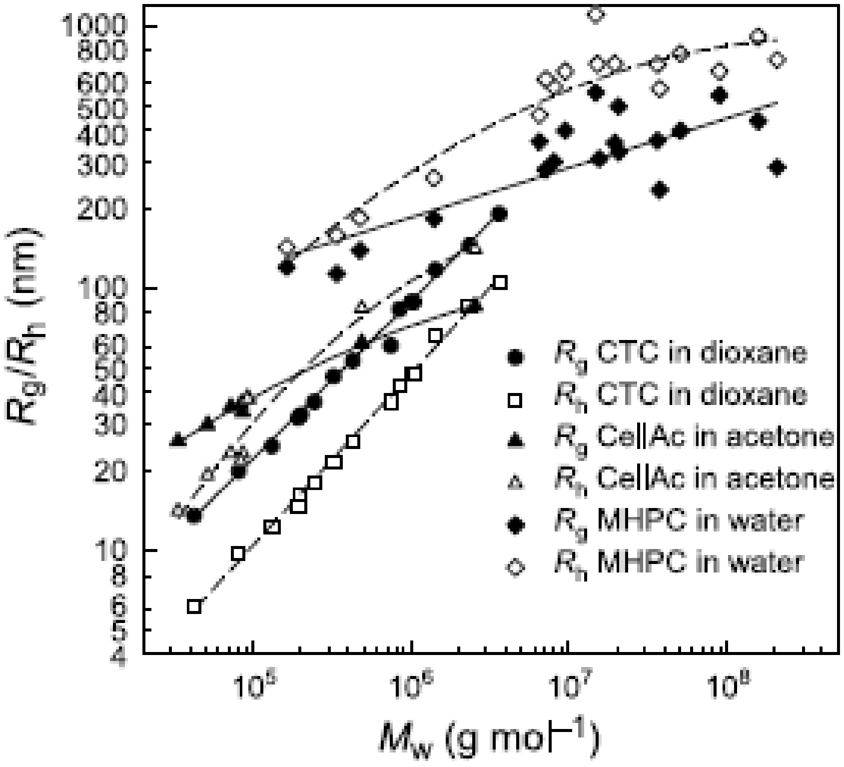


Figure 6. Molar mass dependencies of the radii of gyration (filled symbols) and the hydrodynamic radii of CTC in dioxane, Cell 2.5Ac in acetone and MHPC in water.

Burchard *Cellulose* **10:** 213–225, 2003.

Solubility of cellulose in Ionic Liquid

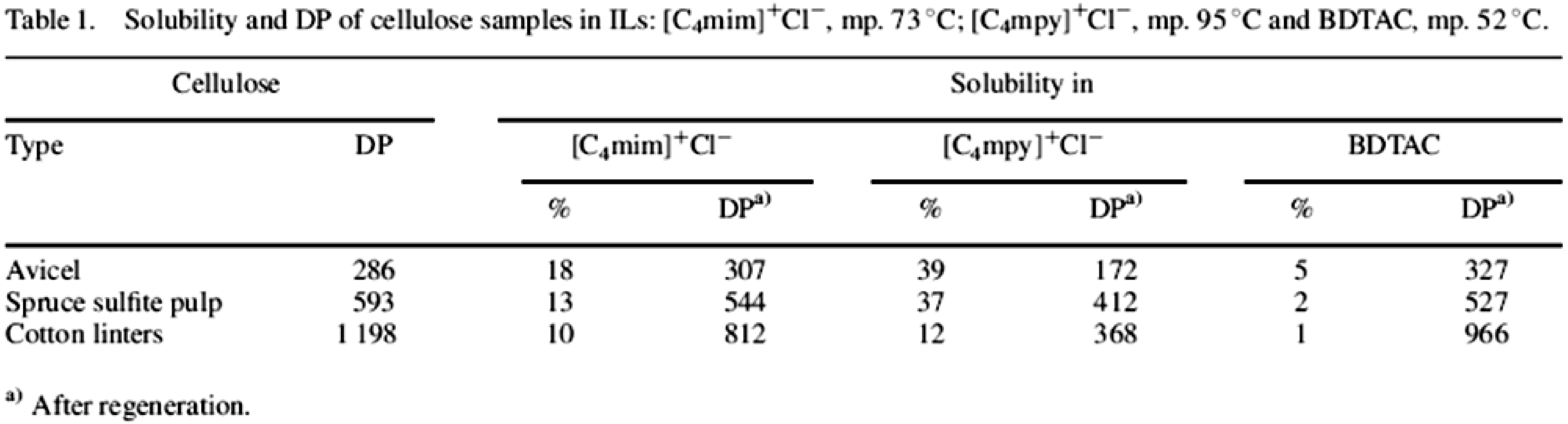
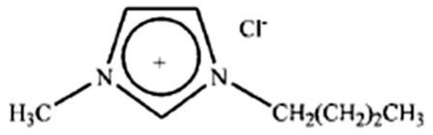


Table 1. Solubility and DP of cellulose samples in ILs: $[C_4mim]^+Cl^-$, mp. 73 °C; $[C_4mpy]^+Cl^-$, mp. 95 °C and BDTAC, mp. 52 °C.

Cellulose		Solubility in					
Type	DP	$[C_4mim]^+Cl^-$		$[C_4mpy]^+Cl^-$		BDTAC	
		%	DP[a)]	%	DP[a)]	%	DP[a)]
Avicel	286	18	307	39	172	5	327
Spruce sulfite pulp	593	13	544	37	412	2	527
Cotton linters	1 198	10	812	12	368	1	966

[a)] After regeneration.



1-N-Butyl-3-methylimidazolium chloride

Heinze, *Macromol. Biosci.* **2005**, *5*, 520–525

Solubility in Ionic Liquid

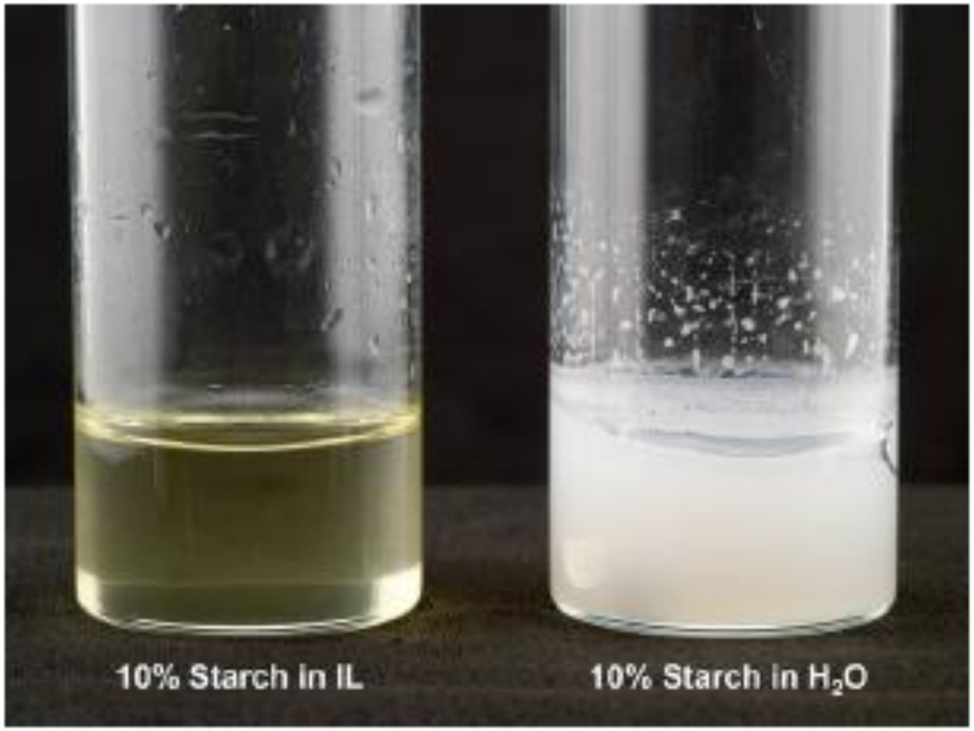
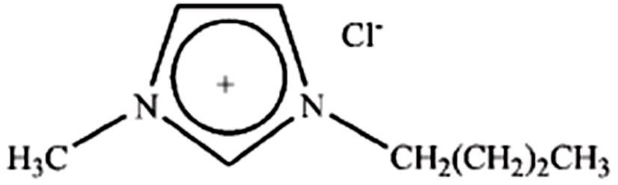


Fig. 2. Picture of 10% solutions of starch in IL and water.

Biswas

Carbohydrate Polymers 66 (2006) 546–550

Dissolving of cellulose in IL



1-*N*-Butyl-3-methylimidazolium chloride

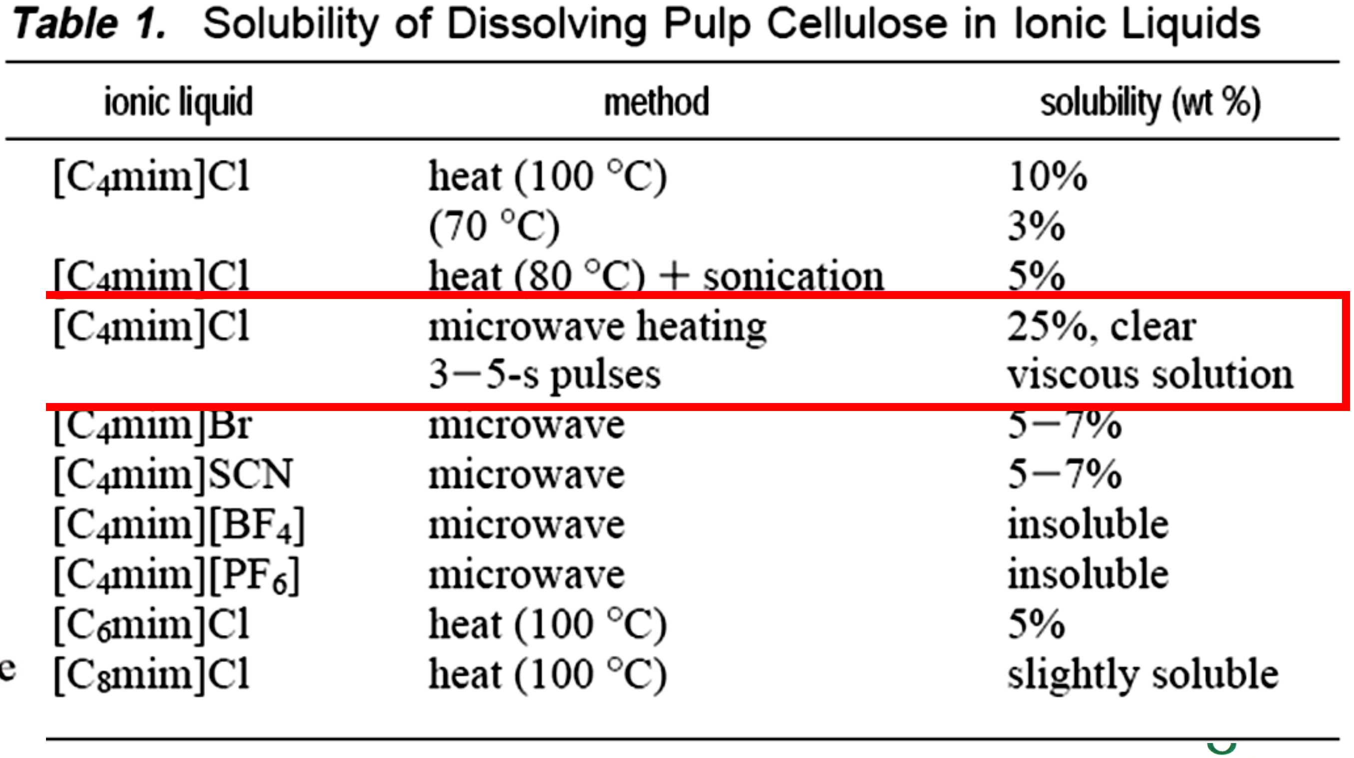


Table 1. Solubility of Dissolving Pulp Cellulose in Ionic Liquids

ionic liquid	method	solubility (wt %)
[C_4mim]Cl	heat (100 °C)	10%
	(70 °C)	3%
[C_4mim]Cl	heat (80 °C) + sonication	5%
[C_4mim]Cl	microwave heating 3−5-s pulses	25%, clear viscous solution
[C_4mim]Br	microwave	5−7%
[C_4mim]SCN	microwave	5−7%
[C_4mim][BF_4]	microwave	insoluble
[C_4mim][PF_6]	microwave	insoluble
[C_6mim]Cl	heat (100 °C)	5%
[C_8mim]Cl	heat (100 °C)	slightly soluble

Swatloski, et. al "**Dissolution of Cellulose with Ionic Liquids**" *J. Am. Chem. Soc.*, 2002, **124**, 4974.

Solubility of cellulose in IL

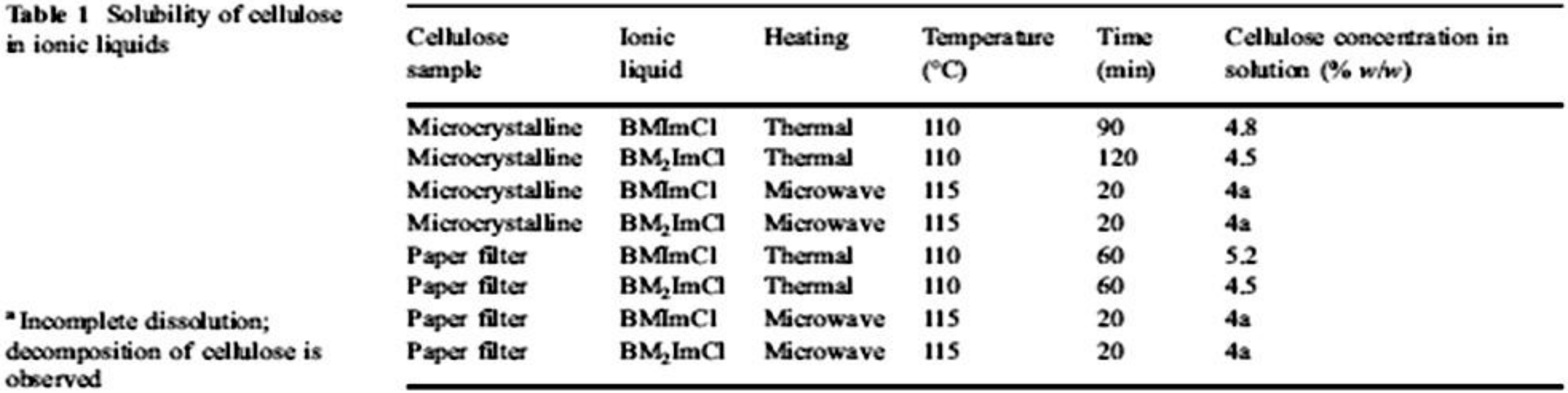


Table 1 Solubility of cellulose in ionic liquids

Cellulose sample	Ionic liquid	Heating	Temperature (°C)	Time (min)	Cellulose concentration in solution (% *w/w*)
Microcrystalline	BMImCl	Thermal	110	90	4.8
Microcrystalline	BM_2ImCl	Thermal	110	120	4.5
Microcrystalline	BMImCl	Microwave	115	20	4[a]
Microcrystalline	BM_2ImCl	Microwave	115	20	4[a]
Paper filter	BMImCl	Thermal	110	60	5.2
Paper filter	BM_2ImCl	Thermal	110	60	4.5
Paper filter	BMImCl	Microwave	115	20	4[a]
Paper filter	BM_2ImCl	Microwave	115	20	4[a]

[a] Incomplete dissolution; decomposition of cellulose is observed

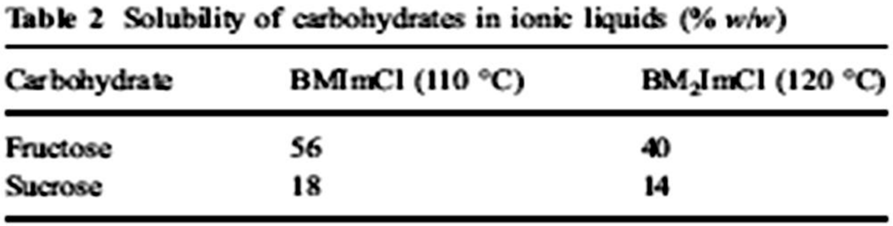


Table 2 Solubility of carbohydrates in ionic liquids (% *w/w*)

Carbohydrate	BMImCl (110 °C)	BM_2ImCl (120 °C)
Fructose	56	40
Sucrose	18	14

Egorov

Anal Bioanal Chem (2007) 387:2263–2269

Euca pulp solutions in BMIMCl - viscosity measurements

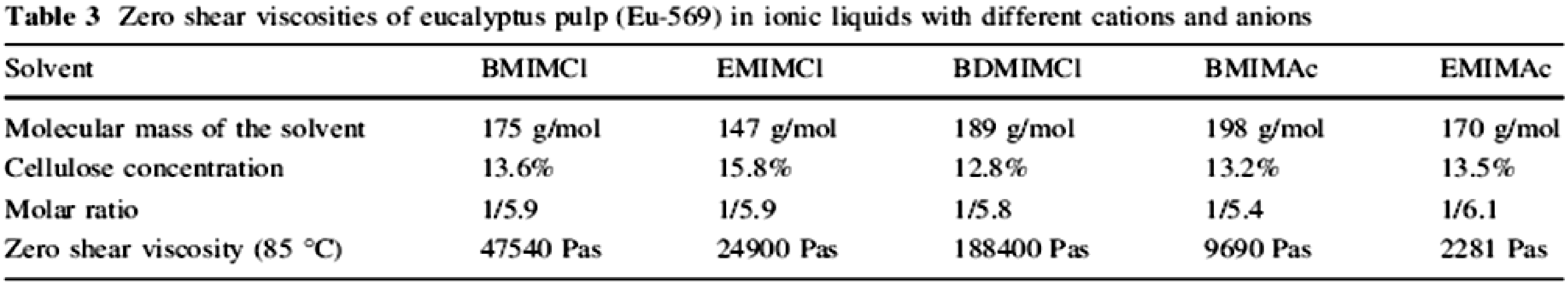


Table 3 Zero shear viscosities of eucalyptus pulp (Eu-569) in ionic liquids with different cations and anions

Solvent	BMIMCl	EMIMCl	BDMIMCl	BMIMAc	EMIMAc
Molecular mass of the solvent	175 g/mol	147 g/mol	189 g/mol	198 g/mol	170 g/mol
Cellulose concentration	13.6%	15.8%	12.8%	13.2%	13.5%
Molar ratio	1/5.9	1/5.9	1/5.8	1/5.4	1/6.1
Zero shear viscosity (85 °C)	47540 Pas	24900 Pas	188400 Pas	9690 Pas	2281 Pas

B. Kosan Cellulose (2008) 15:59–66

Partial dissolution of whole wood in IL

- Partial dissolution of wood
  - 5-8 % *)
  - 80-100 °C
  - 2-24 h
  - [bmim]Cl/15% DMSO
  - [amim]Cl *)
  - Pine, poplar, euca, oak
  - Spruce *)

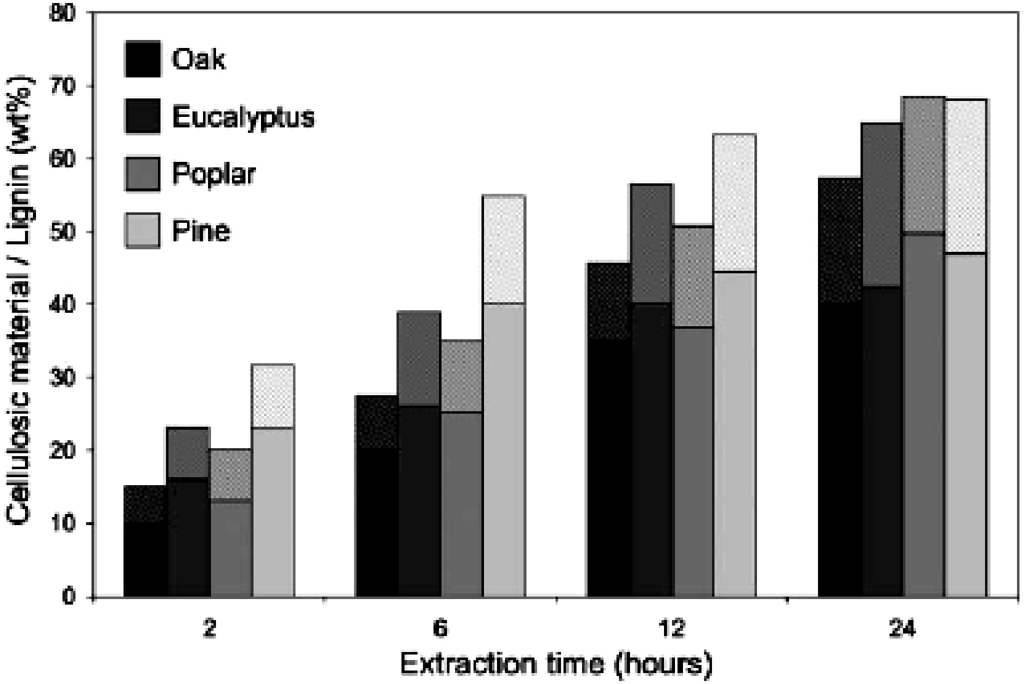


Fig. 4 Cellulosic material (solid bars) and lignin (dashed bars) extraction profiles in [C_4mim]Cl/DMSO-d_6 at 100 °C for the different wood samples considered as a function of time.

Fort et. al *Green Chem.*, 2007, 9, 63–69

*) Kilpeläinen et al.
Science and Technology of Biomasses"
(Rome, Italy, 8-10 May 2007) Italic 4

Solubility of cellulose in phosphoric acid

Table 1
Influence of type of acid on clearing temperature of solutions containing 11.4% (w/w) cellulose

Wt parts acid	P_2O_5 in solvent (%, w/w)	T_c (°C)
80.6 H_3PO_4/19.4 PPA	73	49
88.0 PPA/12.0 H_2O	74	43
92.7 $H_4P_2O_7$/7.3 H_2O	74	43
74.8 P_2O_5/25.2 H_2O	73	48

Boerstoel[2]

Polymer 42 (2001) 7371–7379

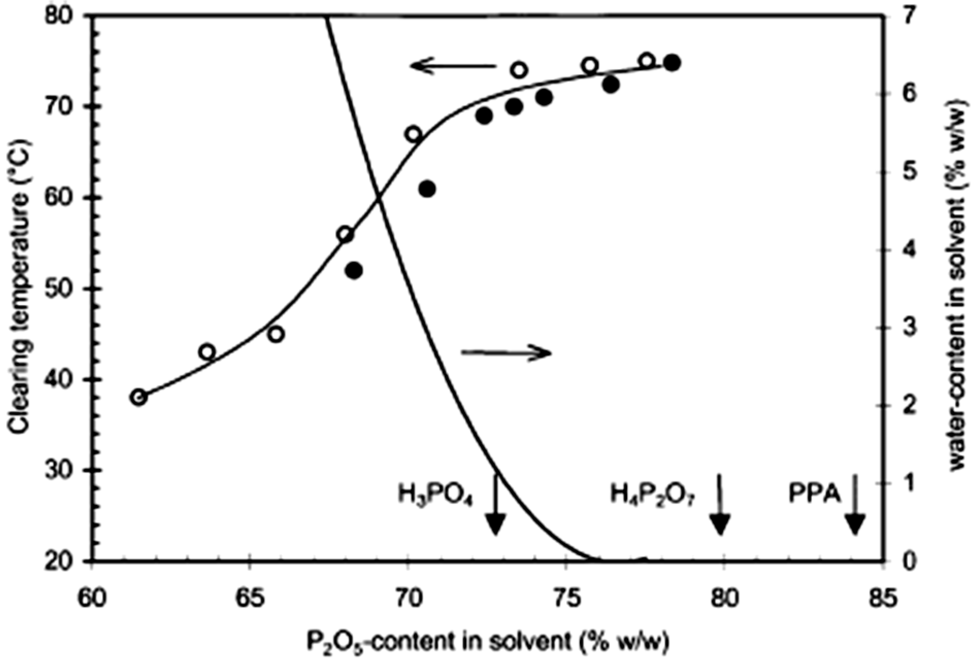


Fig. 1. Influence of P_2O_5 content in solvent on clearing temperature for solutions of cellulose (solid circles) and cellulose acetate with a DS of 2.74 (open circles). The solutions had an equivalent cellulose concentration of 17.1% (w/w). Also indicated is the amount of water in the solvent based on equilibrium data.

Solubility of viscose in DMF

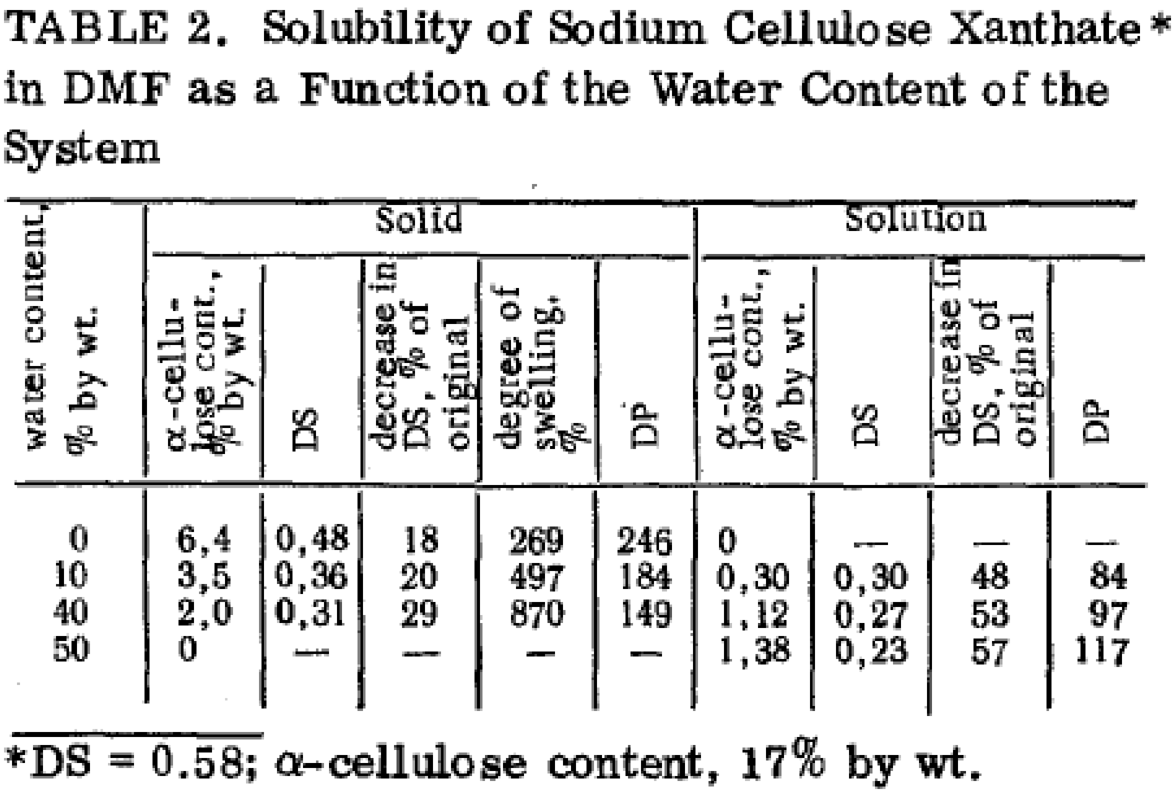


TABLE 2. Solubility of Sodium Cellulose Xanthate* in DMF as a Function of the Water Content of the System

water content, % by wt.	Solid					Solution			
	α-cellulose cont., % by wt.	DS	decrease in DS, % of original	degree of swelling, %	DP	α-cellulose cont., % by wt.	DS	decrease in DS, % of original	DP
0	6,4	0,48	18	269	246	0	—	—	—
10	3,5	0,36	20	497	184	0,30	0,30	48	84
40	2,0	0,31	29	870	149	1,12	0,27	53	97
50	0	—	—	—	—	1,38	0,23	57	117

*DS = 0.58; α-cellulose content, 17% by wt.

Malyshevskaya, Khimicheskie Volokna, No. 1, p. 27, January-February, 1984.

Solubility of cellulose in NaOH/urea

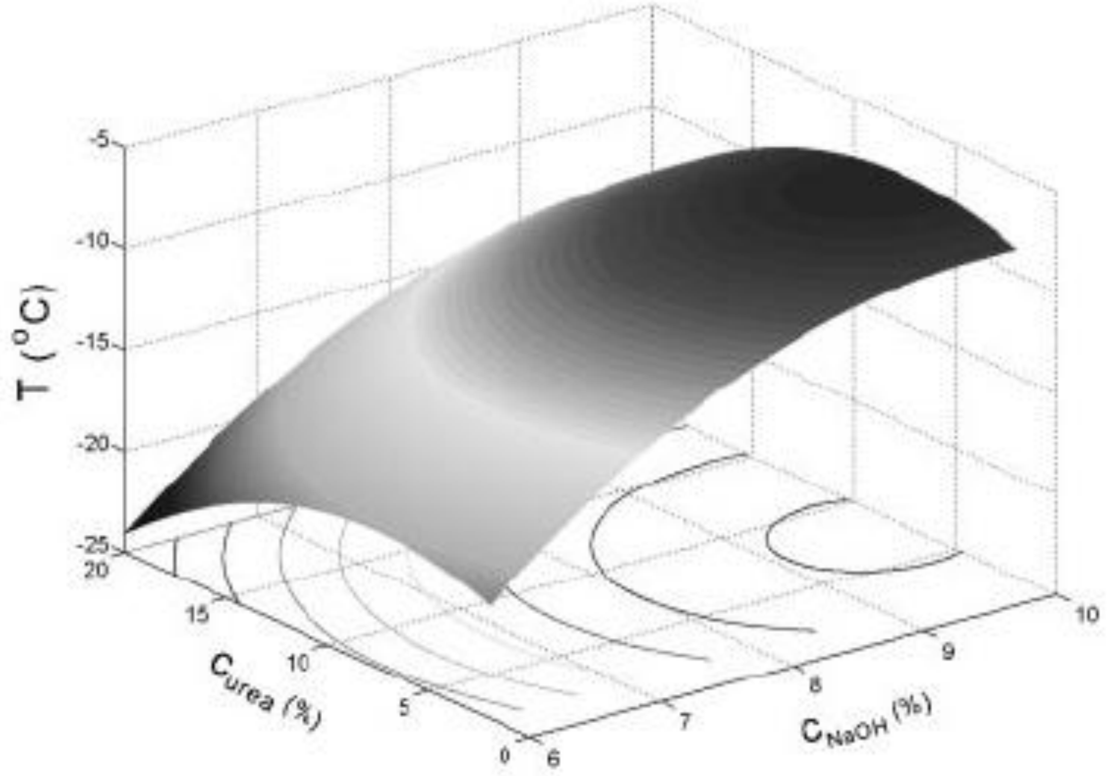


Figure 1. Three-dimensional phase diagram for solubility of cellulose in NaOH/urea aqueous solution on the pre-cooled temperature of solvent (T), the NaOH concentration (c_{NaOH}), and urea concentration (c_{urea}) relationship.

Zhang

Macromol. Biosci. **2005**, *5*, 539–548

Solubility of cellulose

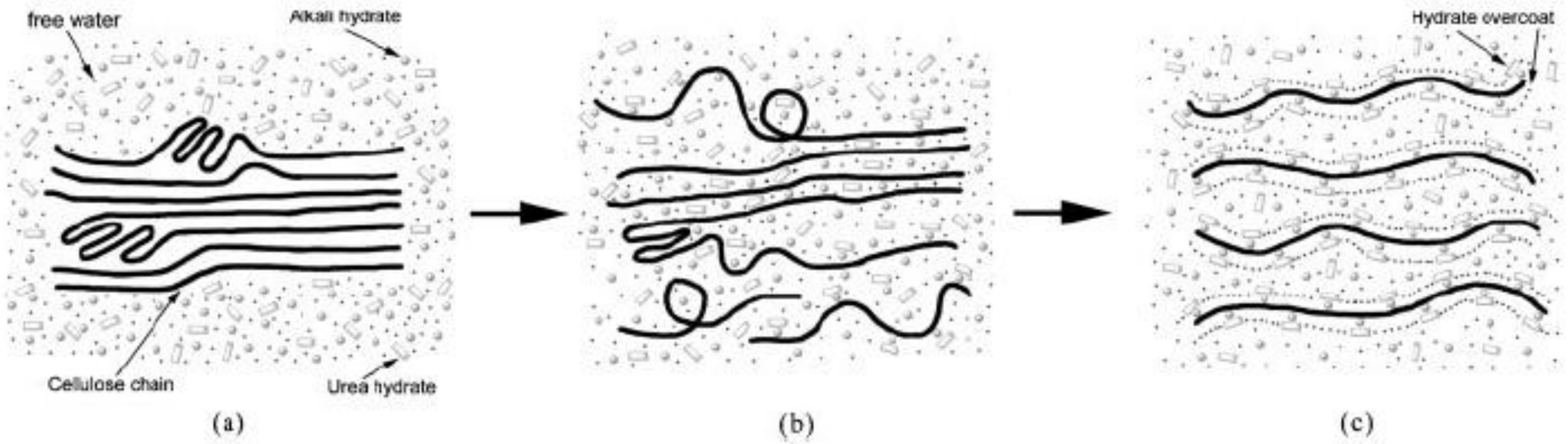


Figure 10. Schematic dissolution process of the cellulose in LiOH/urea and NaOH/urea aqueous solutions pre-cooled to −10 °C: (a) cellulose bundle in the solvent, (b) swollen cellulose in the solution, (c) transparent cellulose solution.

Zhang *Macromol. Biosci.* **2005**, *5*, 539–548

Deep Eutectic Mixtures

- A **deep eutectic solvent** is a mixture which forms a eutectic with a melting point much lower than either of the individual components.

Fig 1 *Urea–choline chloride*

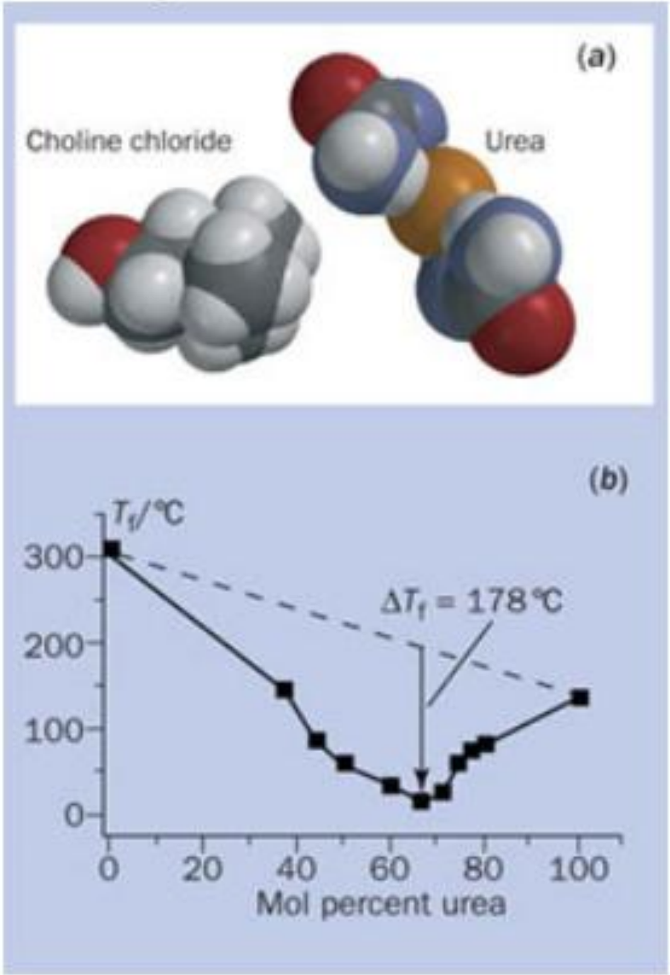


Fig 1 Urea–choline chloride

http://www.rsc.org/Education/EiC/issues/2005_Jan/salty.asp

Solubility of biomass in Deep Eutectic Mixtures

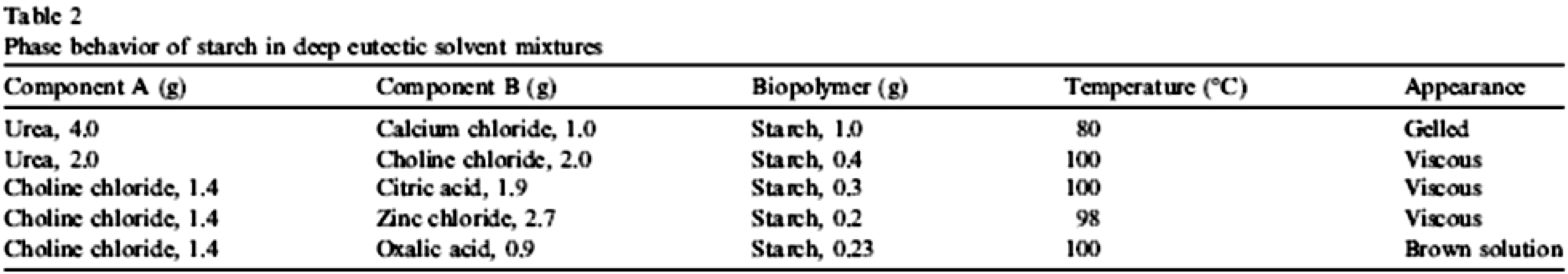


Table 2
Phase behavior of starch in deep eutectic solvent mixtures

Component A (g)	Component B (g)	Biopolymer (g)	Temperature (°C)	Appearance
Urea, 4.0	Calcium chloride, 1.0	Starch, 1.0	80	Gelled
Urea, 2.0	Choline chloride, 2.0	Starch, 0.4	100	Viscous
Choline chloride, 1.4	Citric acid, 1.9	Starch, 0.3	100	Viscous
Choline chloride, 1.4	Zinc chloride, 2.7	Starch, 0.2	98	Viscous
Choline chloride, 1.4	Oxalic acid, 0.9	Starch, 0.23	100	Brown solution

Biswas

Carbohydrate Polymers 66 (2006) 546–550

Centrifugal precipitation chromatography

Ito

JOURNAL OF LIQUID CHROMATOGRAPHY & RELATED TECHNOLOGIES
Vol. 25, Nos. 13–15, pp. 2039–2064, 2002

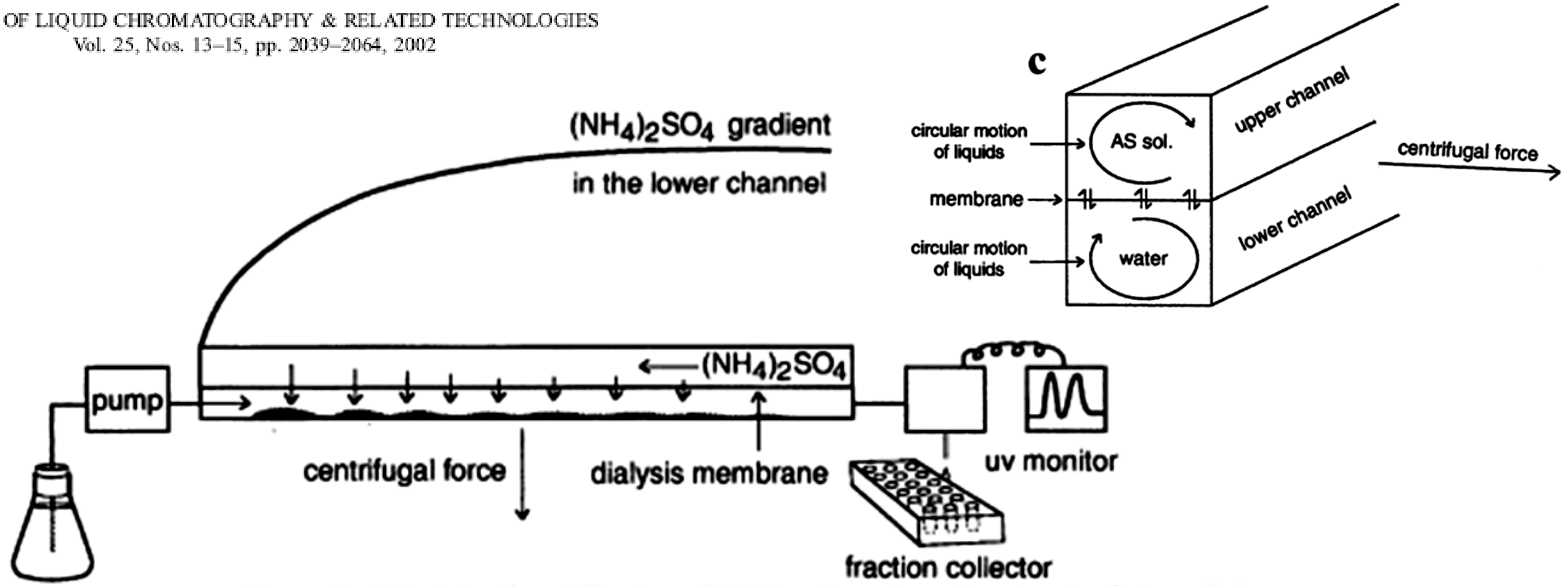


Figure 1. Principle of centrifugal precipitation chromatography. A pair of channels is partitioned with a dialysis membrane. Countercurrent of concentrated ammonium sulfate solution and water through the channel produces an exponential gradient of ammonium sulfate in the lower channel. Proteins introduced into the lower channel are precipitated and deposited at the bottom of the channel by centrifugal force. The chromatographic elution is initiated by gradually reducing the ammonium sulfate concentration in the upper channel that causes proportional reduction of ammonium sulfate concentration in the gradient in the lower channel. This in turn results in repetitive dissolution and precipitation of the proteins along the channel. Consequently, proteins are eluted from the channel according to their solubility in ammonium sulfate solution.

Centrifugal precipitation chromatography

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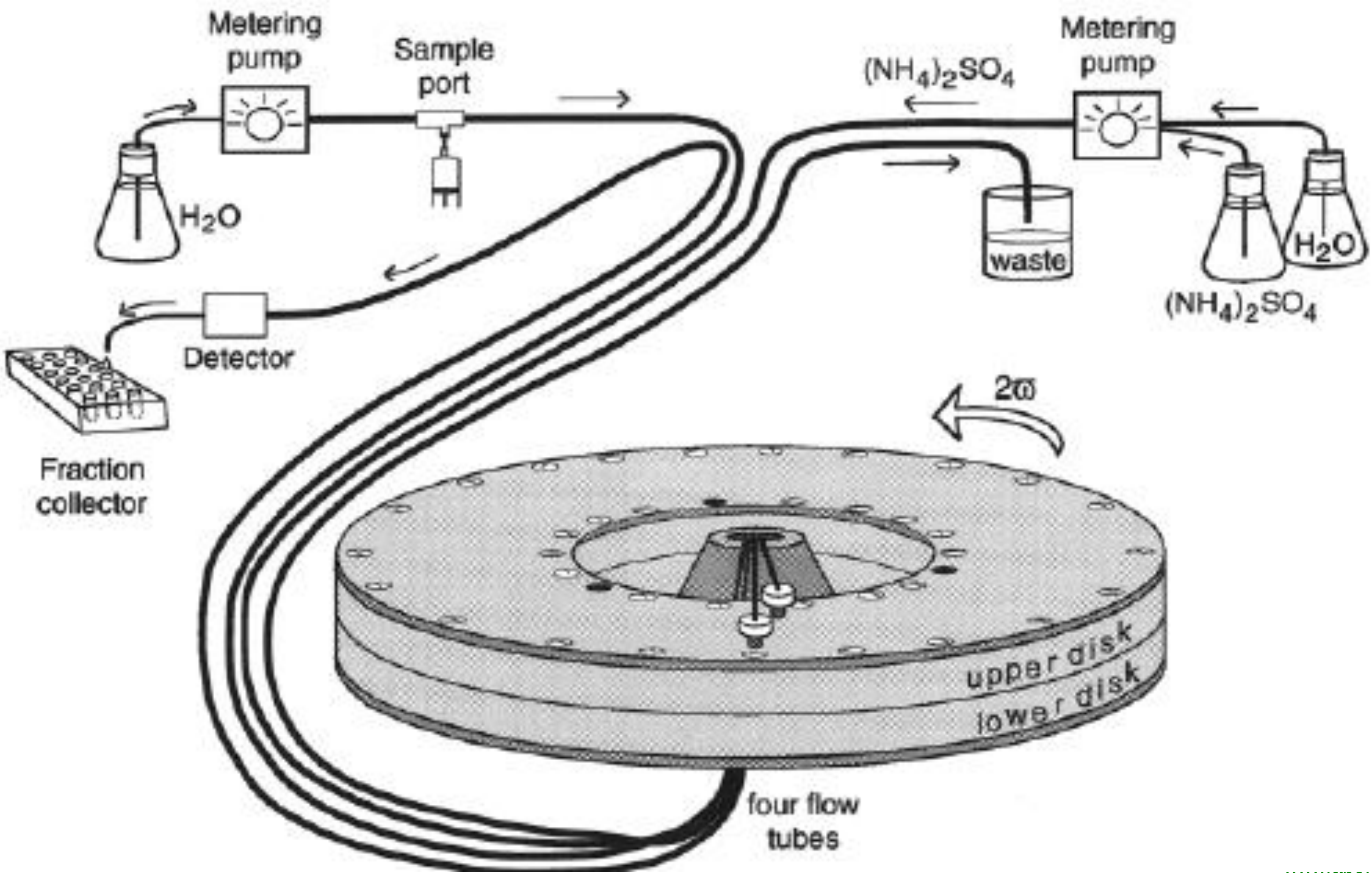

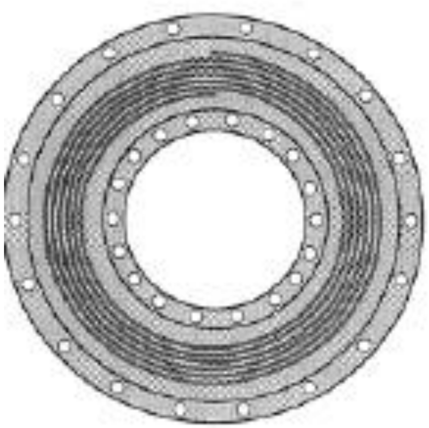

Centrifugal precipitation chromatography

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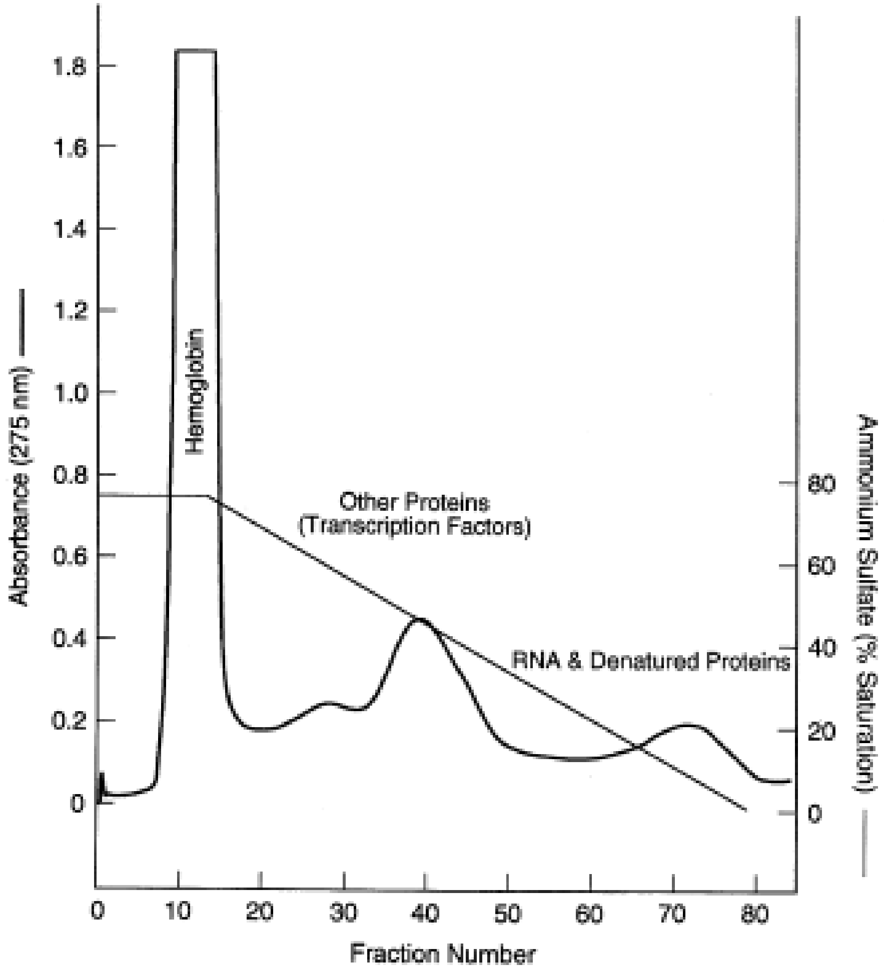

Selective precipitation

- Whole or partial dissolution of solid material
- Tuning of the solvent properties …
  - pH
  - Temperature
  - Concentration of additive (salt, polymer, adsorbent, …)
  - Dilution
  - Addition of other solvent (miscible or non-miscible)
  - ---

- … may lead to a less favorable interaction between the dissolved matter and the solvent.
- → flocculation and phase separation of the fraction(s) with least interaction with the solvent. Fractions with more favorable interaction remain dissolved.
- = DP (DS) fractionation

Summary

- Fractionation based on chemical reactions
  - Controlled by chemical charge (acid, base, additives, type of solvent) and experimental set-up (time, temp,..)
- Fractionation based on size
  - Controlled by design of the device
- Fractionation based on solubility
  - Controlled by regulating the solvent properties