



May 25, 2009, Helsinki,

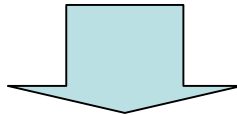
Comprehensive Utilization of Woody Biomass components

Yasumitsu Uraki, Dr. Sci.

**Professor of Forest Chemistry,
Research Faculty of Agriculture,
Hokkaido University, Japan
E-mail: uraki@for.agr.hokudai.ac.jp**

Woody biomass is

- the most abundant natural resource on the earth.
- carbon neutral.
- comprised of hydrophilic polysaccharides, **cellulose and hemicellulose** (glucomannan, glucuronoxylan, and arabinogalactan). and hydrophobic **lignin** (polyphenylpropanoid).



An alternative resource to fossil resources

Objectives: Comprehensive utilization of woody biomass

Atmospheric Acetic acid Pulping

Wood

Pretreatment

Reflux for 1h in 90-95% AcOH aq.

Pulping

Addition of 0.32% sulfuric acid
or 0.1% hydrochloric acid
Reflux for 3-4 h

Minor components
(**<10%**)

Extractives

Antibiotics,
Antioxidants,
etc.

Major components
(cell wall components)

Insolubles
(**ca. 50%**)

Acetic acid Pulp
(AP)

Cellulose

Papers,
Cellulose
derivatives,

Water-insolubles
(**20-30%**)

Lignin

Carbon fibers,
Adhesives,
Polyurethane
resins,
Ion exchangers,

Insolubles

Water-solubles
(**30-20%**)

Hemicellulose

Sugar syrups
Furfural,
Diet sweetening
materials,

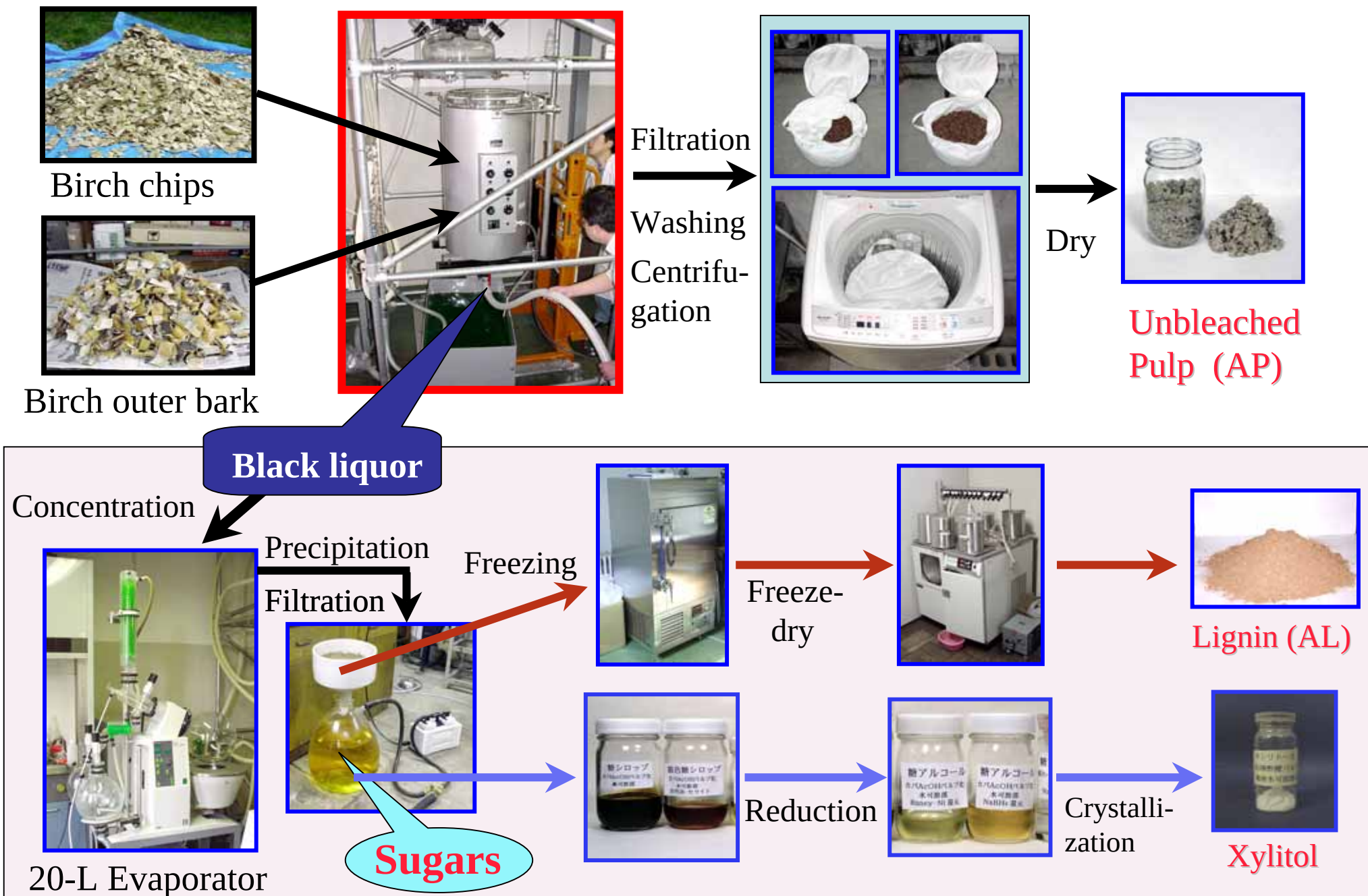


Fig. Separation scheme of woody biomass (birch) using a large reactor

Table Material balance on the atmospheric acetic acid pulping.

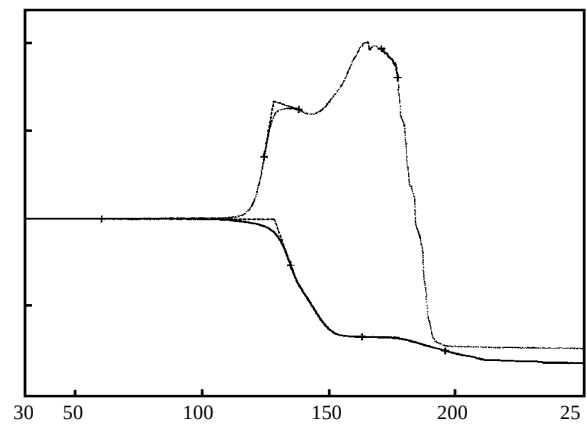
Species	Cooking conditions		Material balance (% on chips)			
	AcOH	Catalyst	Pulp (KL)	Reject	Lignin	WS
Birch	90%	0.32-SA	51.8 (5.3)	0.1	22.2	30.2
	95%	0.1-HCl	51.9 (4.7)	0.0	19.0	27.1
	90% ¹⁾	0.32-SA	46.3 (5.6)	0.8	24.9	27.7
Beech	90%	0.32-SA	47.5 (7.2)	0.4		
Poplar	90%	0.32-SA	49.9 (3.5)	0.0	22.9	22.3
Todo-fir	95%	0.1-HCl	51.7 (7.3)	0.2	24.5	25.9

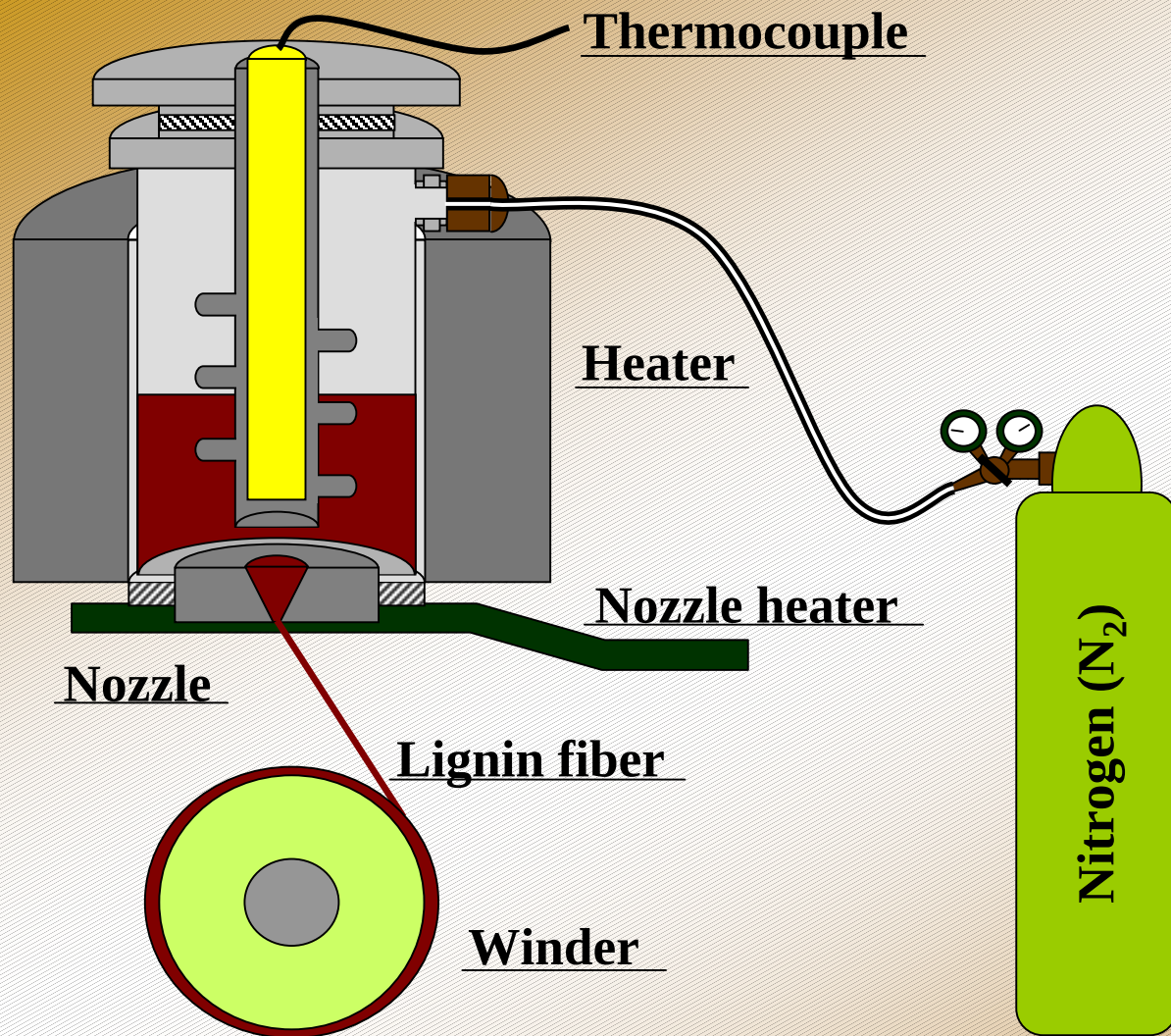
SA, sulfuric acid; Pulp, screened pulp; KL, Klason lignin (% on pulp).

¹⁾ The pulping was performed in a 100-L reactor (Chips, o.d. 9 kg; Liquor, about 60 kg)

Lignin utilization I.

**-Finding fusibility and
Preparation of carbon fibers -**





Spinning condition

Temperature:

330 - 380°C

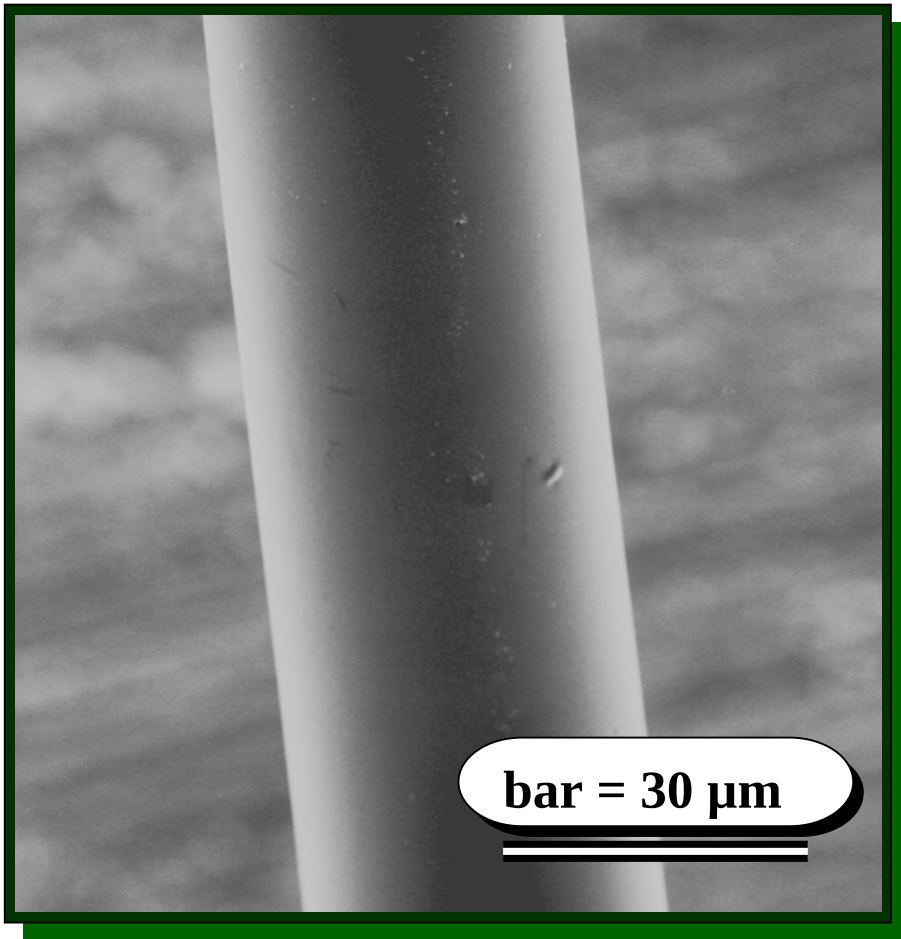
Maximum winding rate:

140 m min⁻¹

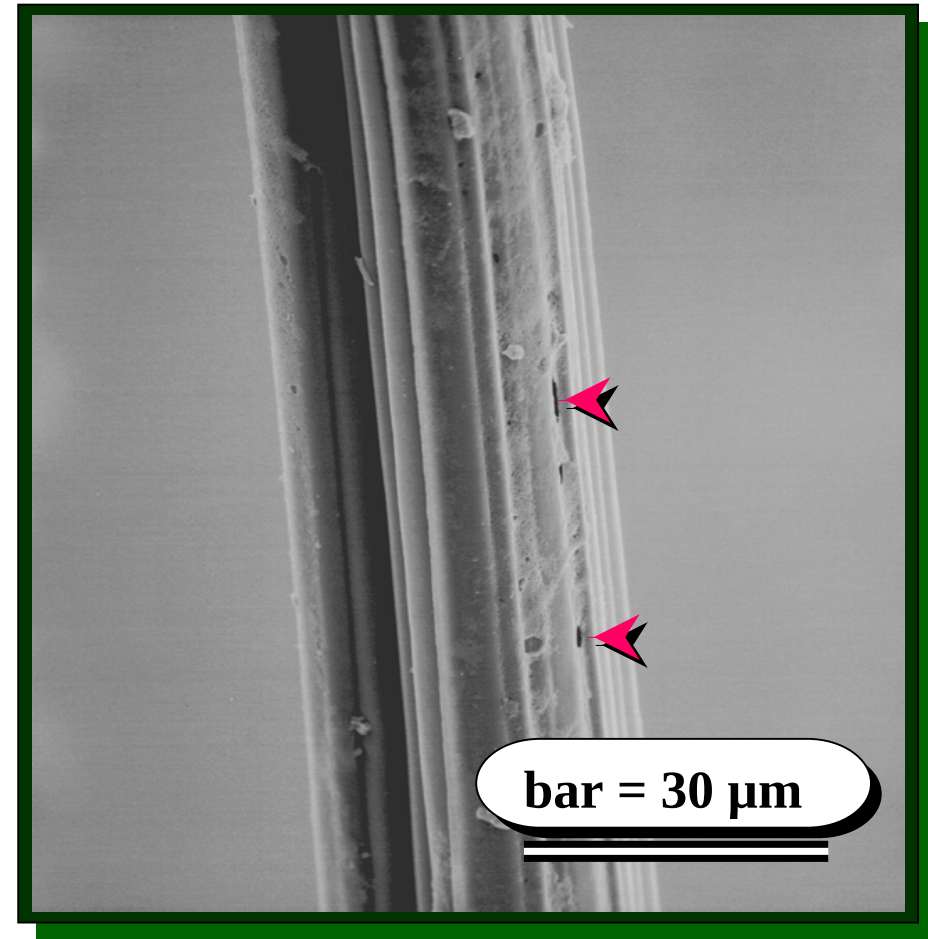
Extrusion pressure:

3 - 5 kgf cm⁻¹

Fig. Laboratory spinning apparatus for fusion spinning of lignin.



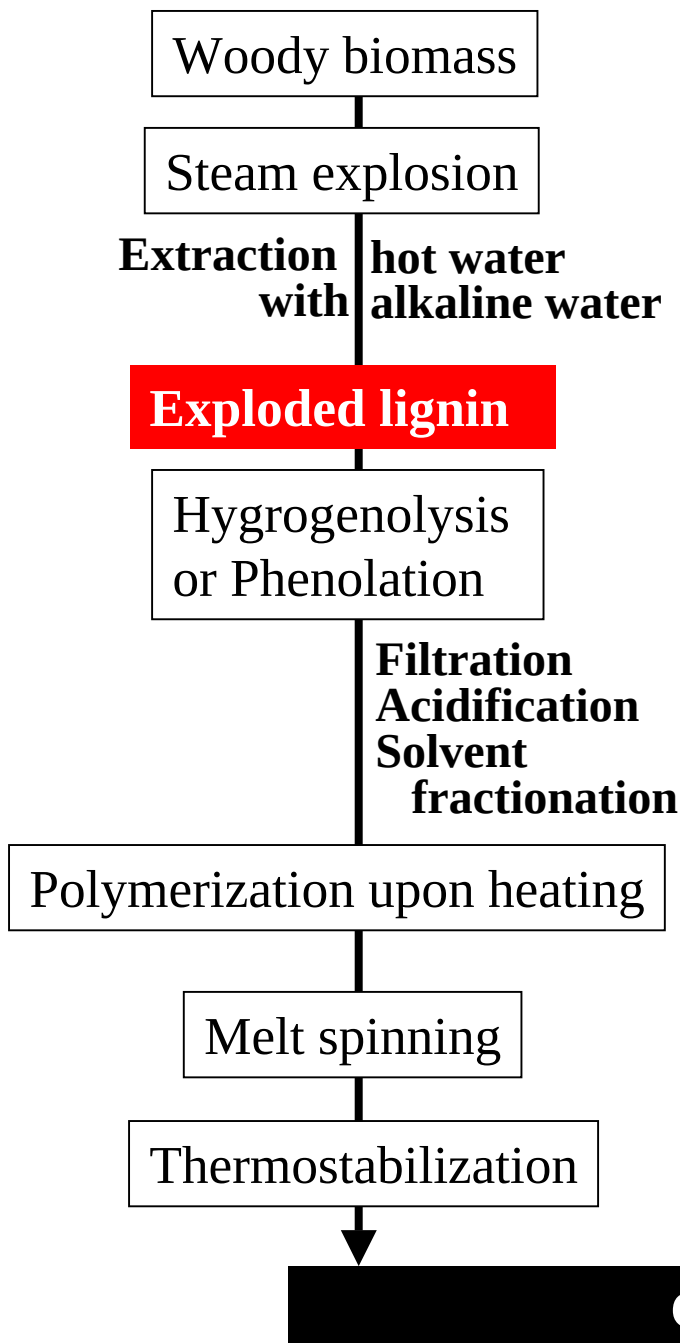
HAL carbon fiber (LAL-CF)
BET surface area of HAL-CF= 190 m² g⁻¹



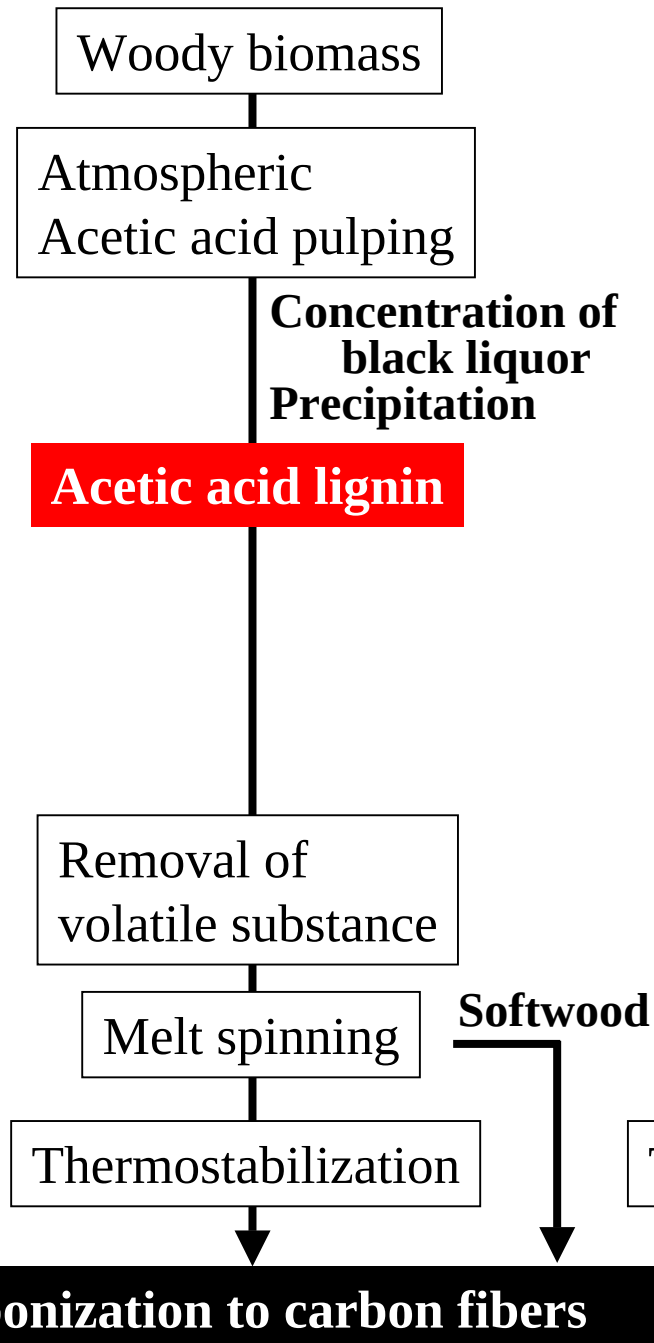
SAL carbon fiber (NAL-CF)
BET surface area of SAL-CF = 370 m² g⁻¹

Fig. Scanning electron micrographs of AL-CF.

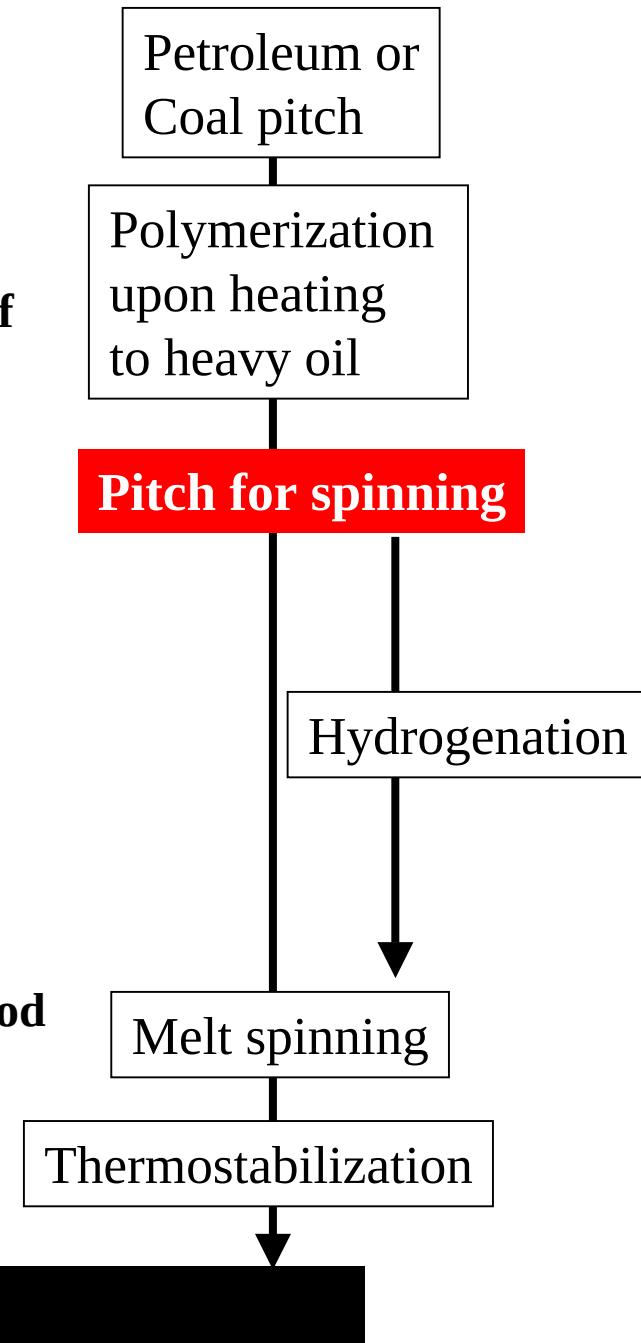
Steam exploded lignin

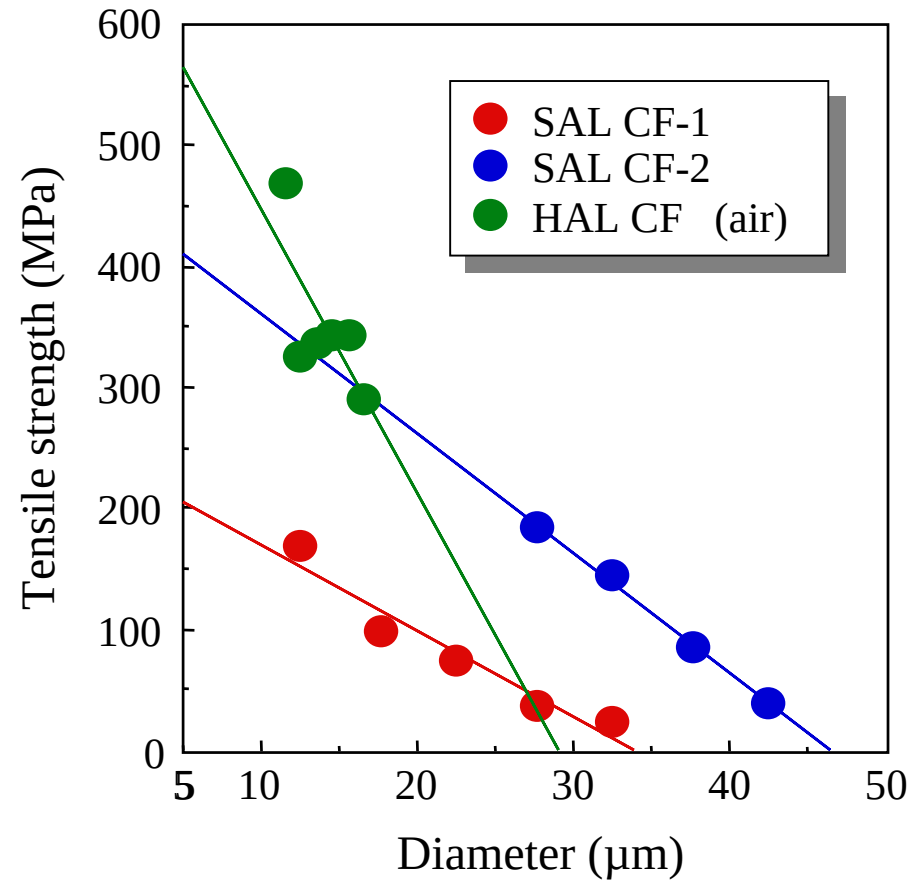


Acetic acid lignin



Pitch





Note; SAL CF-1; prepared without thermostabilized,
SAL CF-2; prepared with thermostabilization in air,
HAL CF; prepared with thermostabilization in air.

Fig. Effect of Diameter on tensile strength of AL based CFs.

Lignin utilization II.

**-Preparation of activated carbon fibers
and Hot-melt type adhesive-**

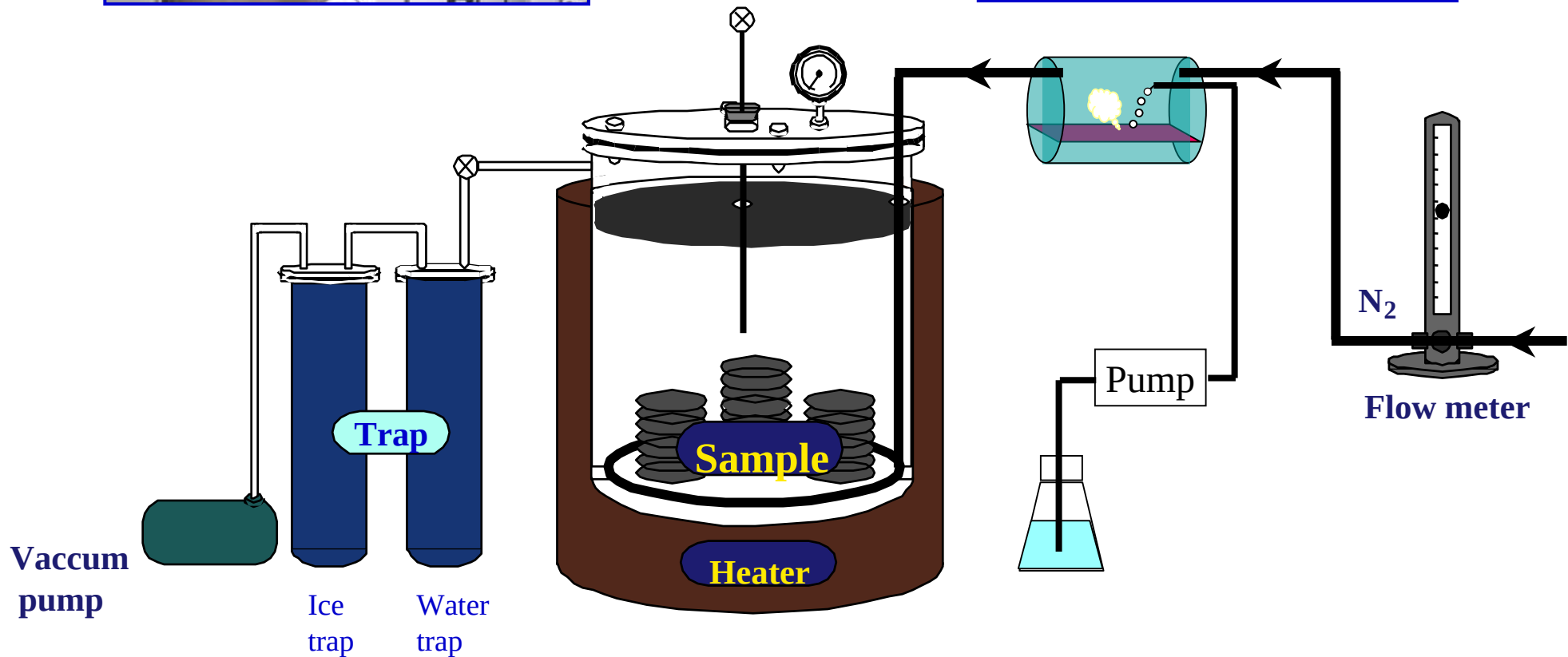


Fig. Steam activation system for producing activated carbon moldings

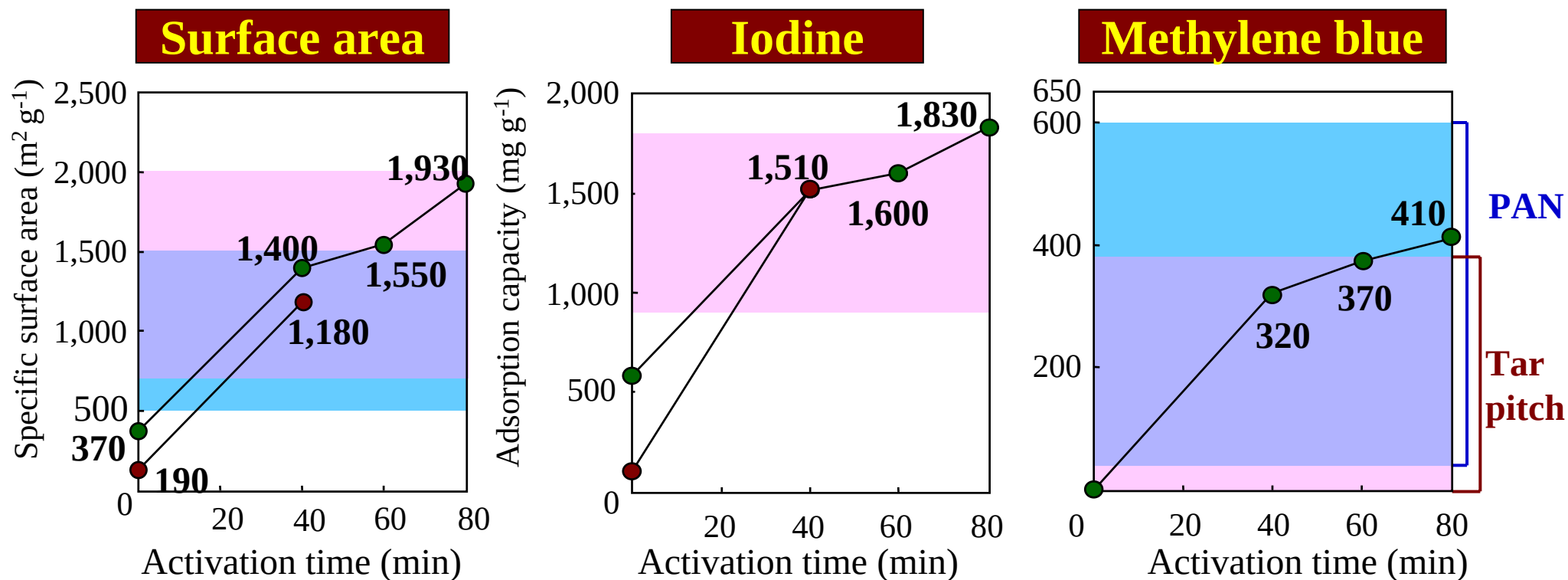


Fig. Adsorption performance of AL-based ACF

●; HAL ●; SAL

● Preparation scheme of dry-formed board



Paper

+



Lignin
(from birch)



Mixed



Dry mixture



Medium density



High density

Fiberboard



Thermal press
with a mold

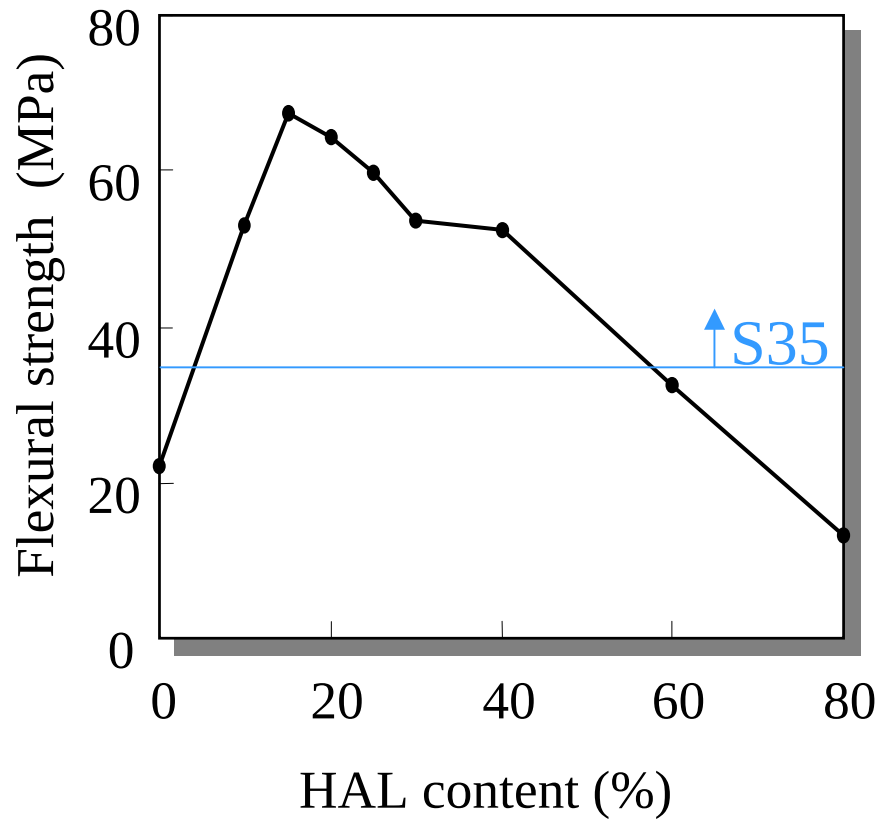


Fig. Influence of lignin content
on flexural strength

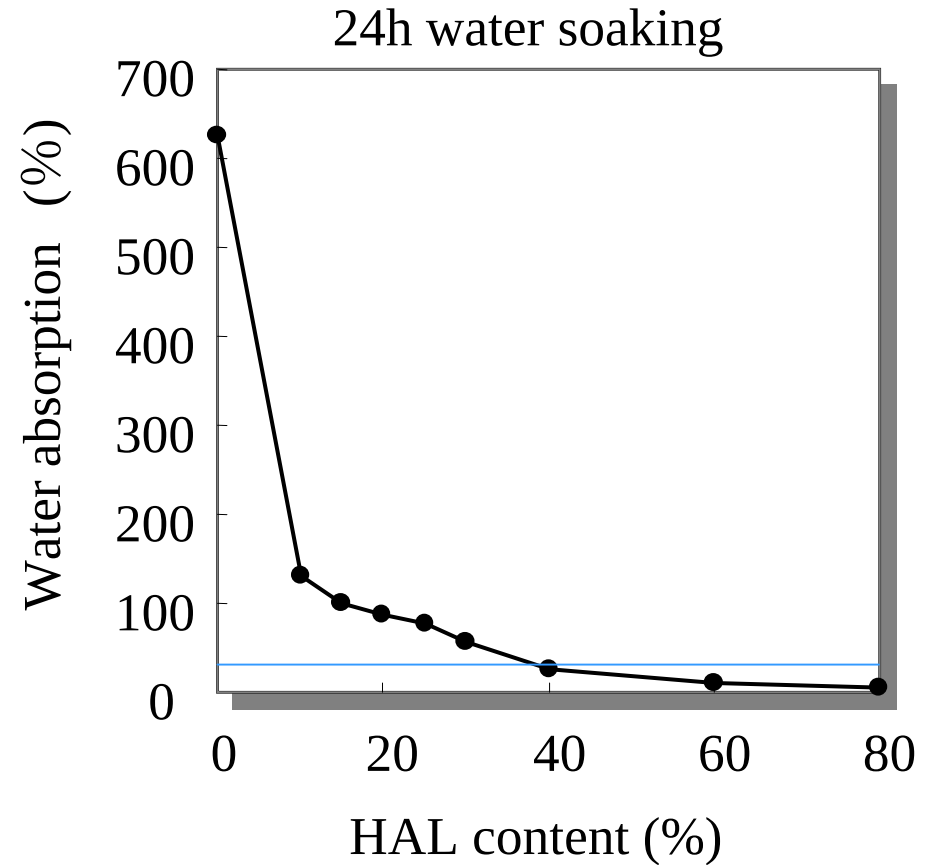


Fig. Influence of lignin content
on water absorption

Properties of lignin-wastepaper fiberboard

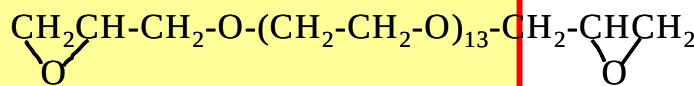
Lignin utilization III.

**-Support for Water-soluble immobilized
cellulase system
and Surfactants-**

AL 10g

← 1M NaOH 100 ml
Stirring for 24hr

Saponified
AL

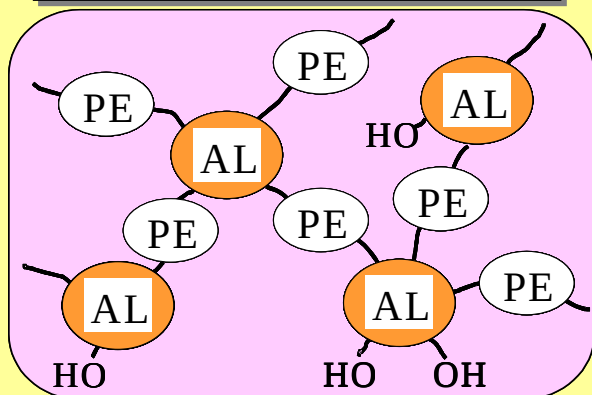


PE13

← **PE 16 g**

- 1) Stirring at 70°C for 3hr
- 2) Stirring at room temperature for 3 days
- 3) pH 4.0 with AcOH
- 4) Ultrafiltration
- 5) Lyophilization

**Amphiphilic product
(PE-AL sol)**



Branched polymer chain

AL : 25.9 wt%
PE : 74.1 wt%

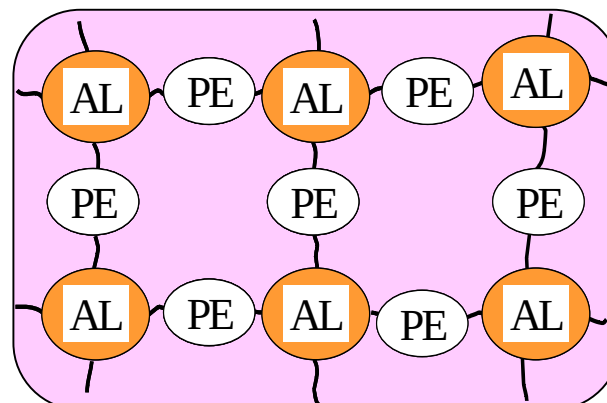
← 3.3 M NaOH 30 ml
Stirring for 24hr

Saponified
AL

← **PE 4 g**

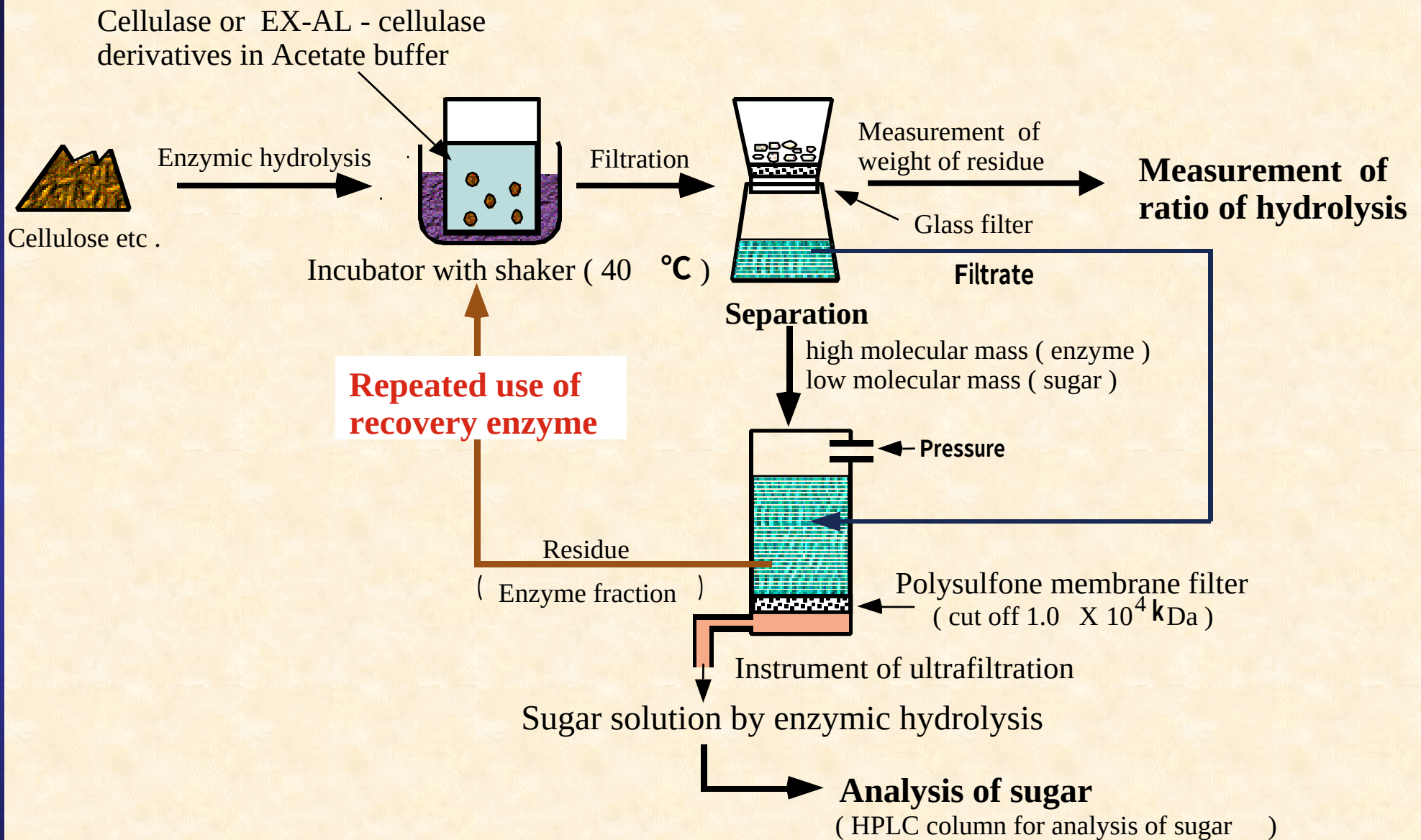
- 1) Stirring at room temperature for 5 min
- 2) Standing still at 80°C for 1hr
- 3) pH 4.0 with AcOH
- 4) Washing with hot water
- 5) Lyophilization

PE-AL gel



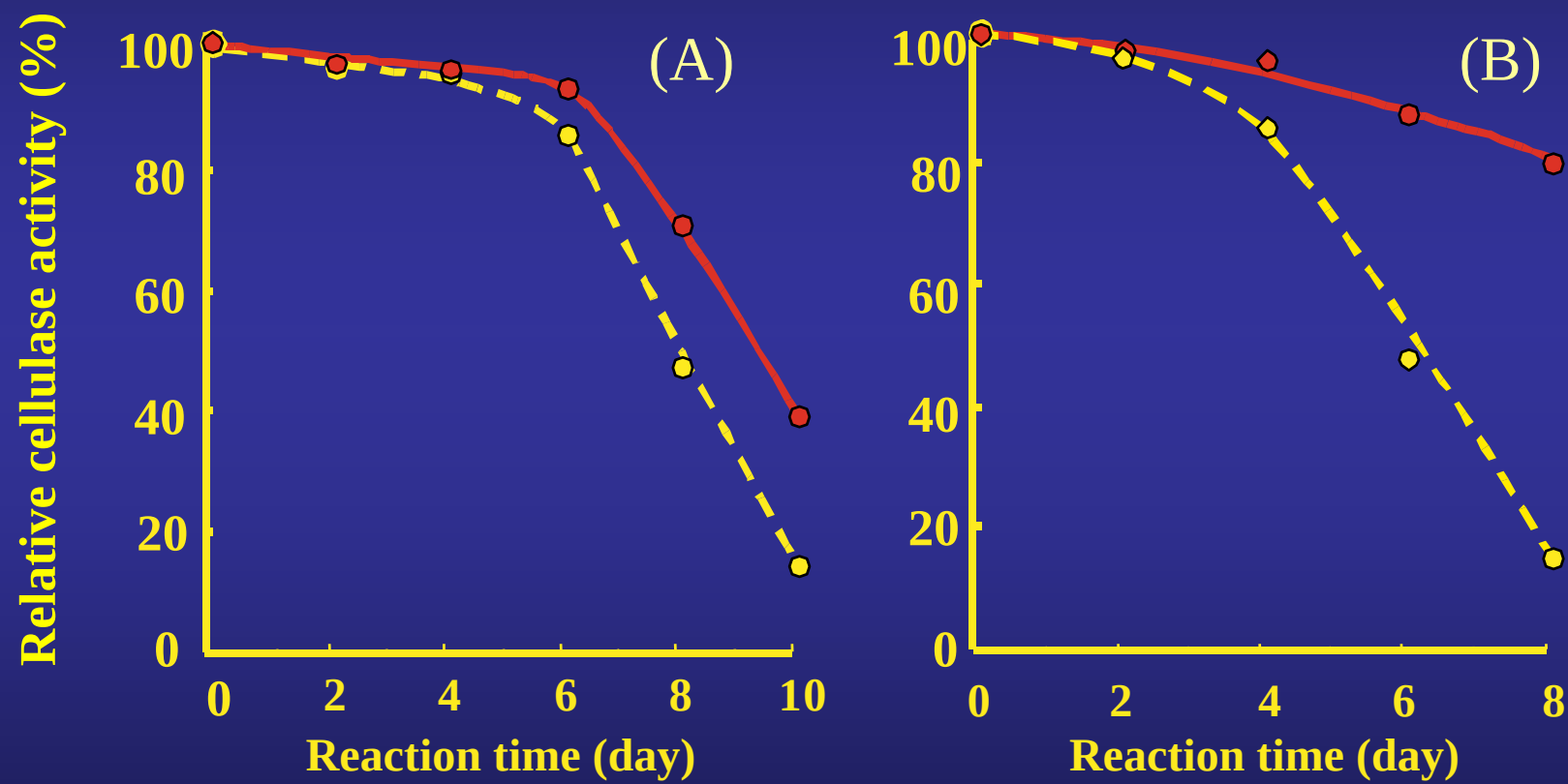
Three-dimensional network structure

AL : 40.7 wt%
PE : 59.3 wt%



Scheme. Repeating hydrolysis of cellulosic materials by cellulase or PE-AL - cellulase complex using ultrafiltration.

Repeating hydrolysis of filter paper (A) and PHA-pulp (B) by cellulase and PE-AL - cellulase complex.



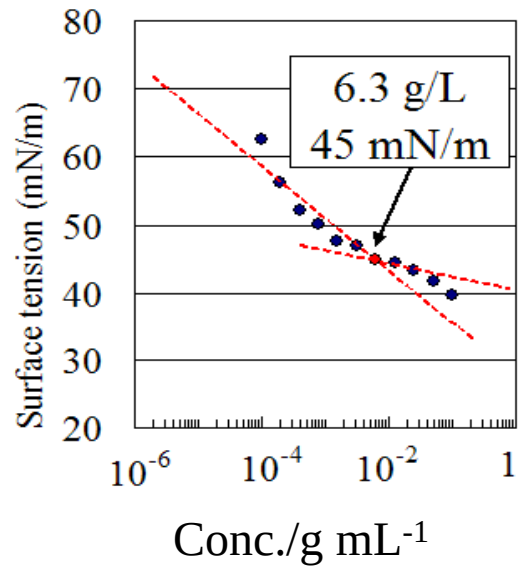
Hydrolysis conditions: Substrate, 3 g; Cellulase, 240 mg; PE-AL, 0 wt.% (●) and 0.2 wt% (●) based on 300 mL of the buffer solution

Introduction

mono-functionalized



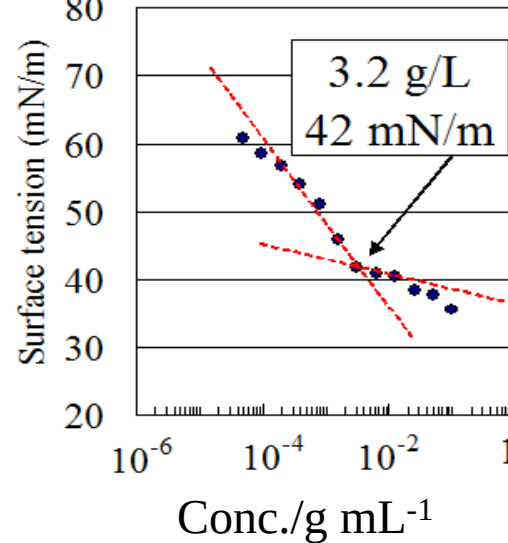
PEGDE-AL(13,1)



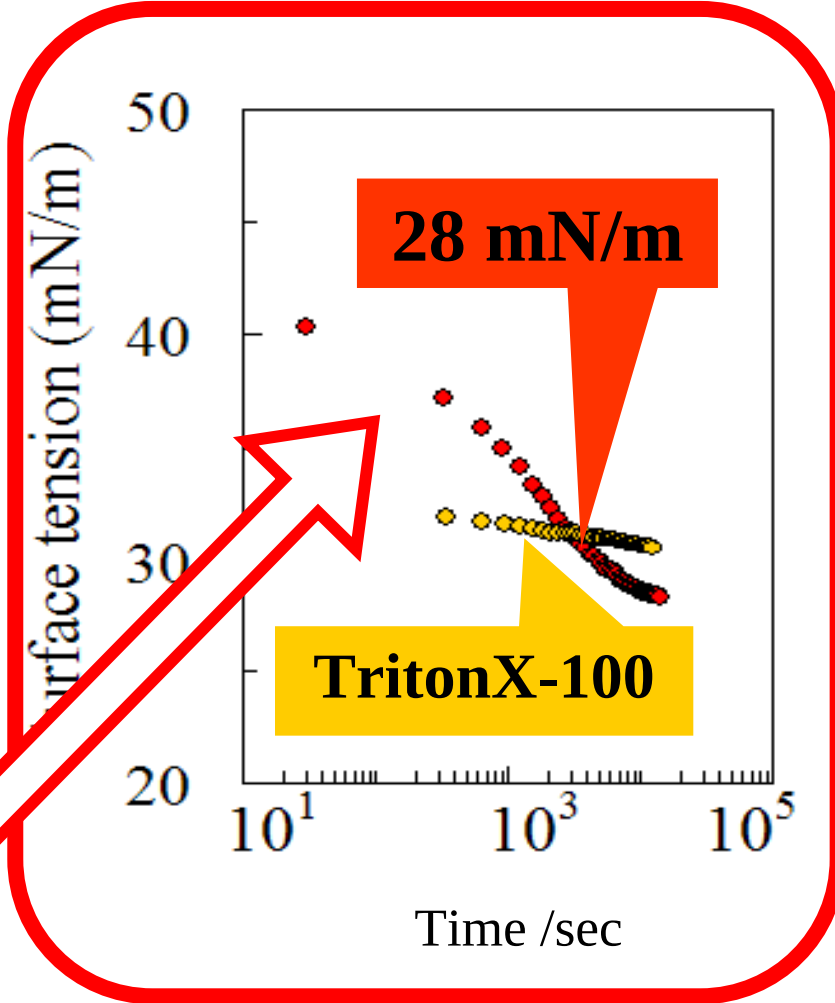
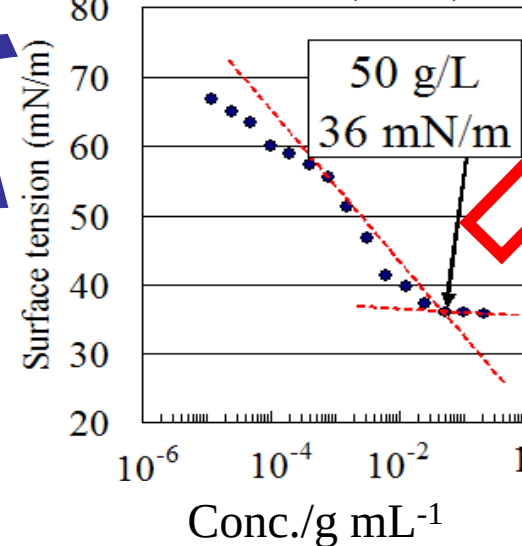
*increase in
PEG*



EPEG-AL(13,2)

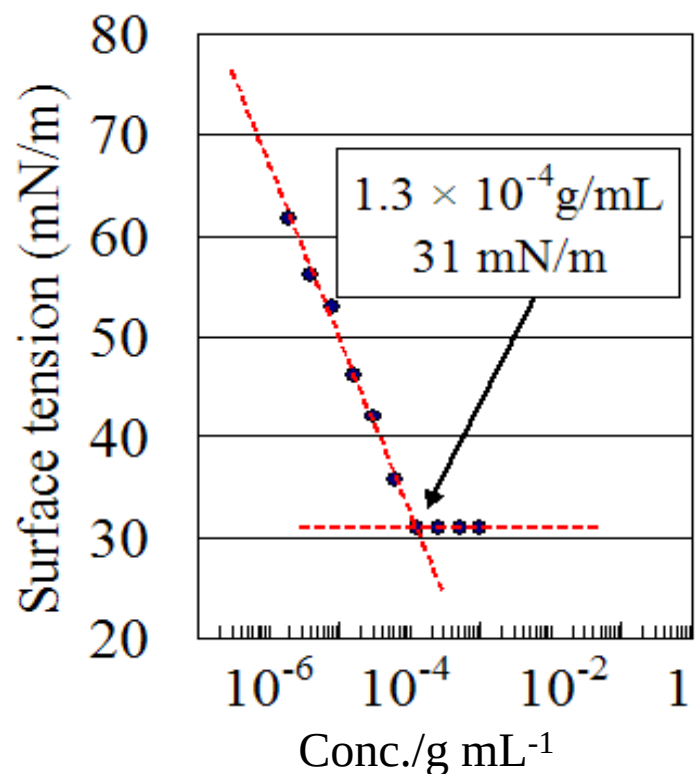
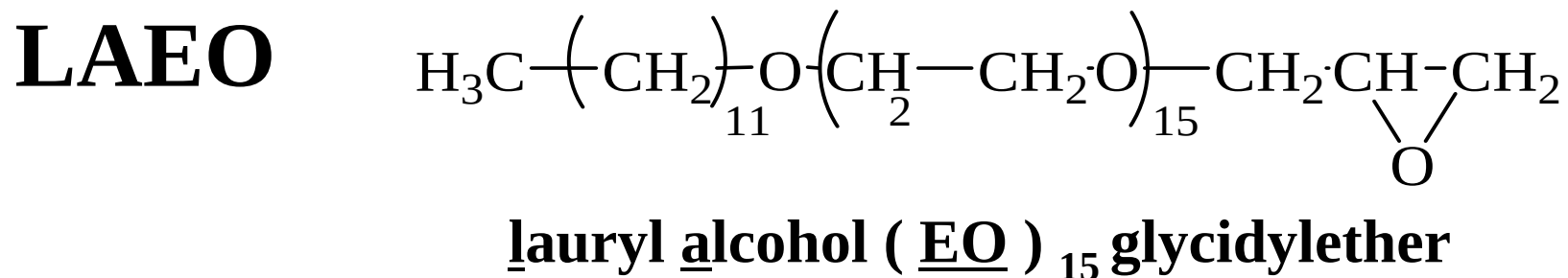


EPEG-AL(13,4)



Preparation

LAEO-AL , LAEO-KL

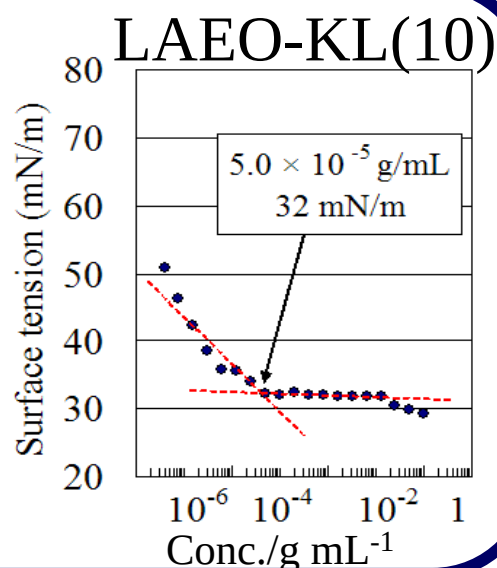
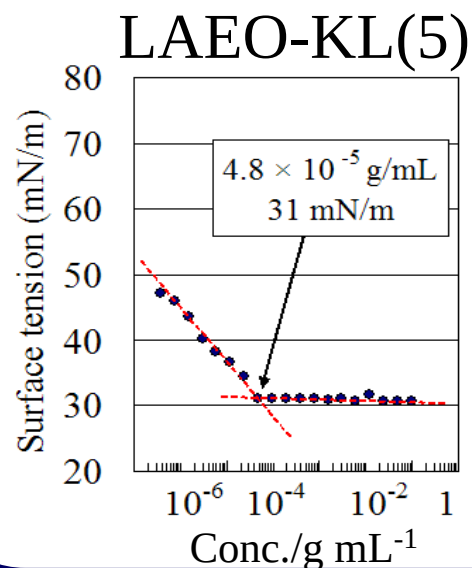
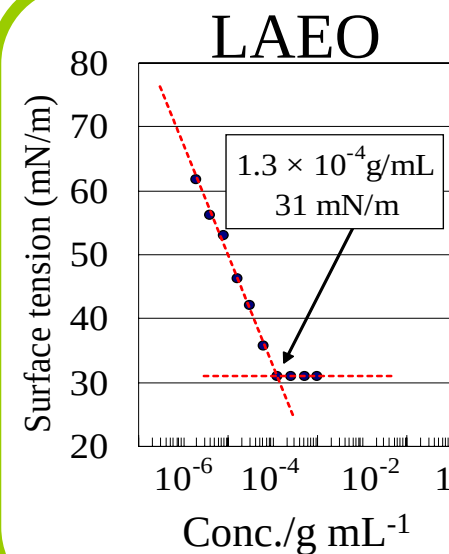
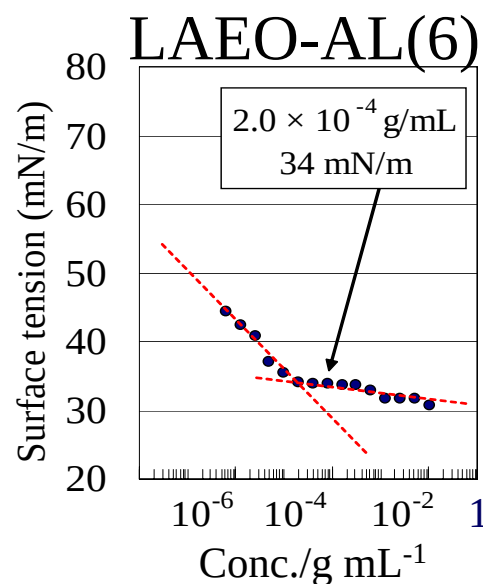
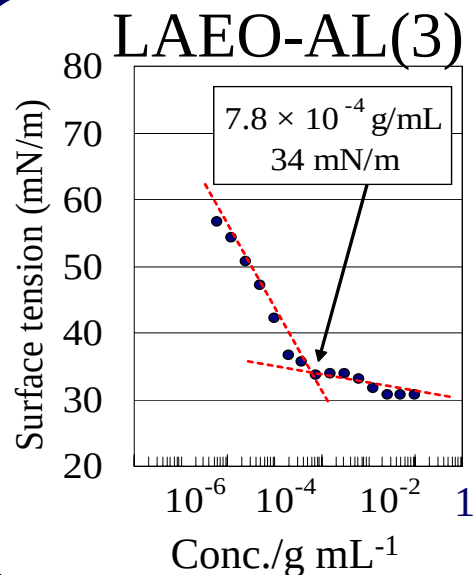


	EO (%)	HLB
<u>LAEO-AL(3)</u>	63.0	12.6
LAEO-AL(6)	68.4	13.7
<u>LAEO-KL(5)</u>	65.4	13.1
LAEO-KL(10)	70.5	14.1

* Parenthesis is a weight ratio of
LAEO/lignin

Surface Activity

LAEO-AL, LAEO-KL



Utilization of unbleached pulp.

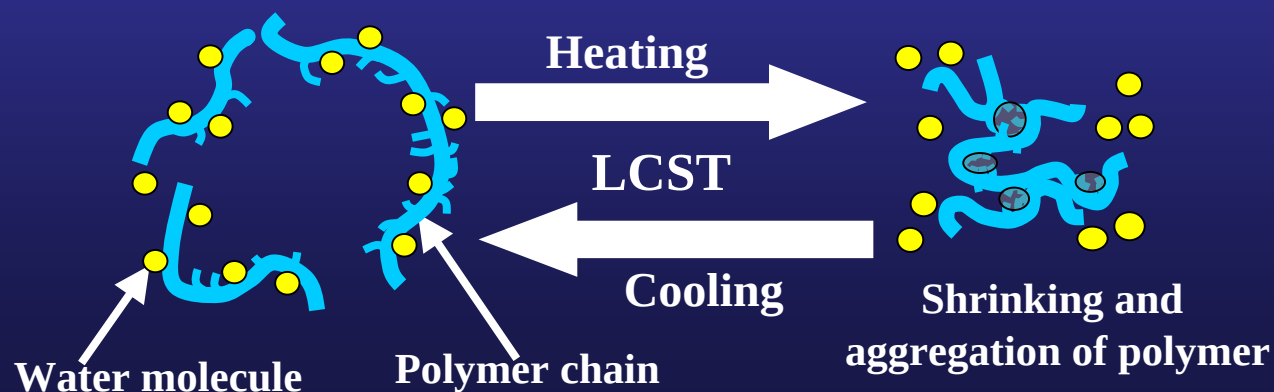
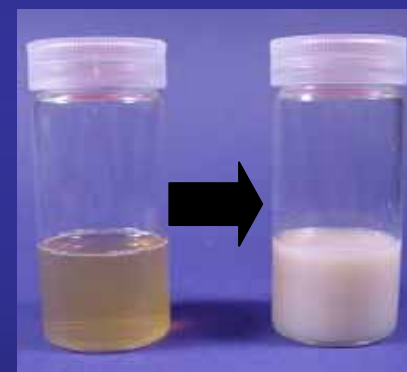
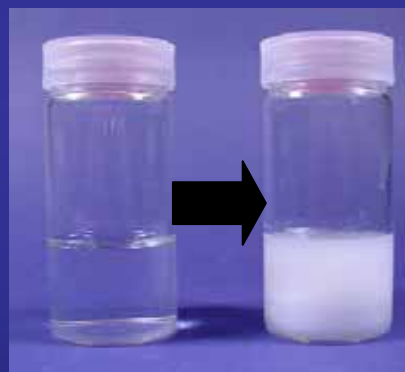
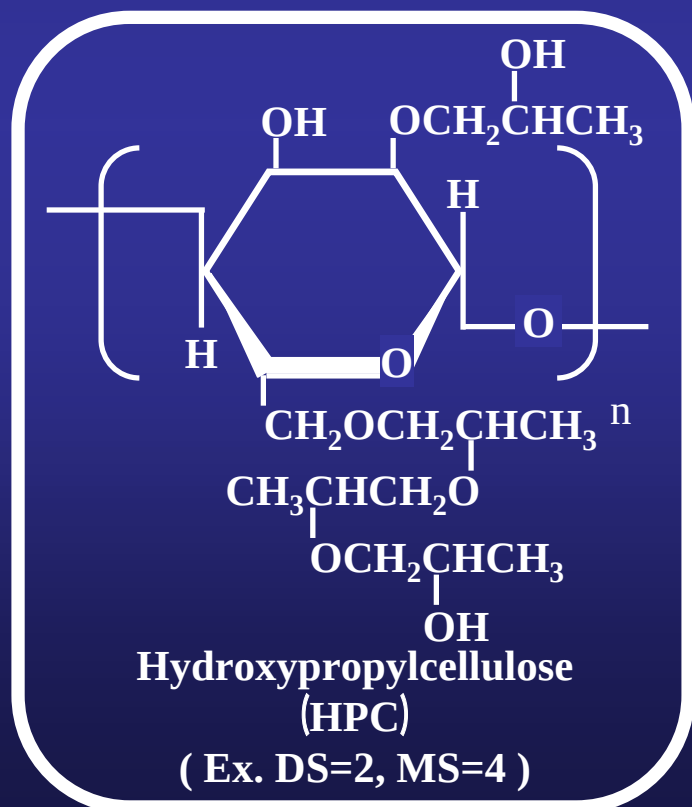
- Inclusion compounds and
Stimuli-responsive gel-**

Chemical properties of HP-samples

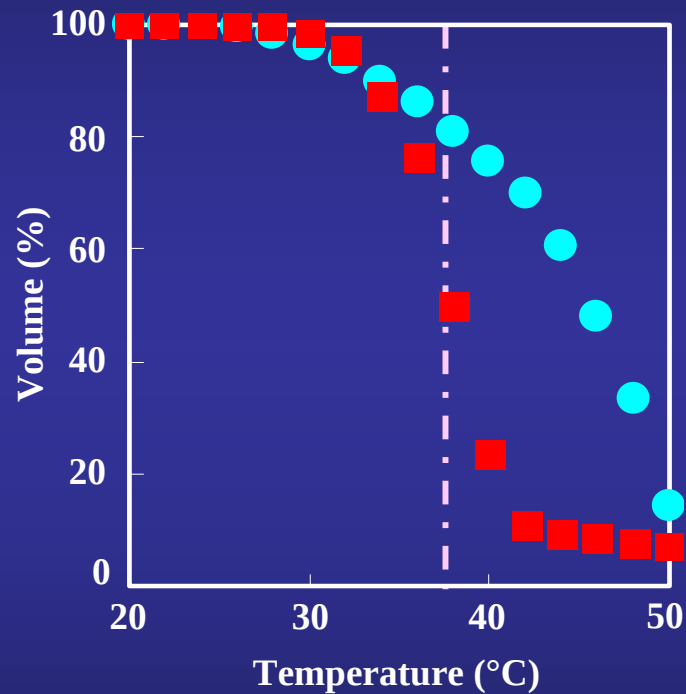
	Lignin content(%) ¹⁾	M _w ²⁾	MS ³⁾	LCST(°C) ⁴⁾
HPC	—	3.40×10^5	4.2	43
HPC · L	6.63	7.09×10^5	3.2	38

¹⁾The lignin content was estimated by UV absorption. ²⁾M_w is weight average molecular-mass determined by high performance size-exclusion chromatography.

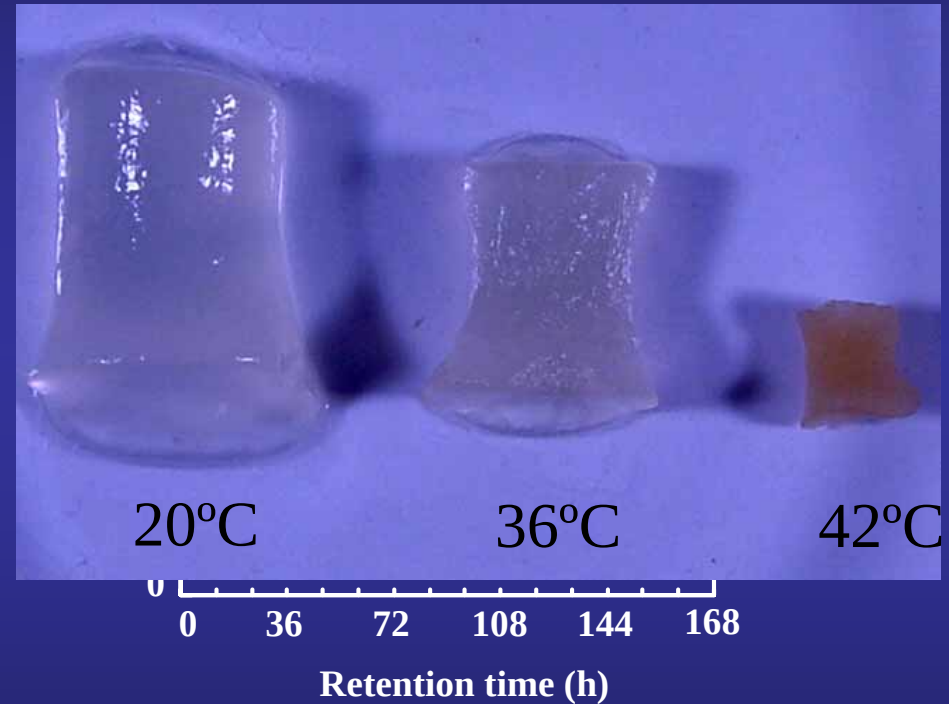
³⁾Degree of molar substitution. ⁴⁾Lower critical solution temperature.



Thermoresponse and thermoreversibility of gel ~Epoxy type~



Initial polymer concentration: 3.0% (w/v),
Addition of EGDE: 50% based on polymer.



HPC gel (●) and HPC-L gel (■)

A drastic volume transition of the HPC-L gel occurred at 38°C

**Hemicellulose utilization
and
Artificial woody cell wall using
honeycomb-patterned cellulose .**

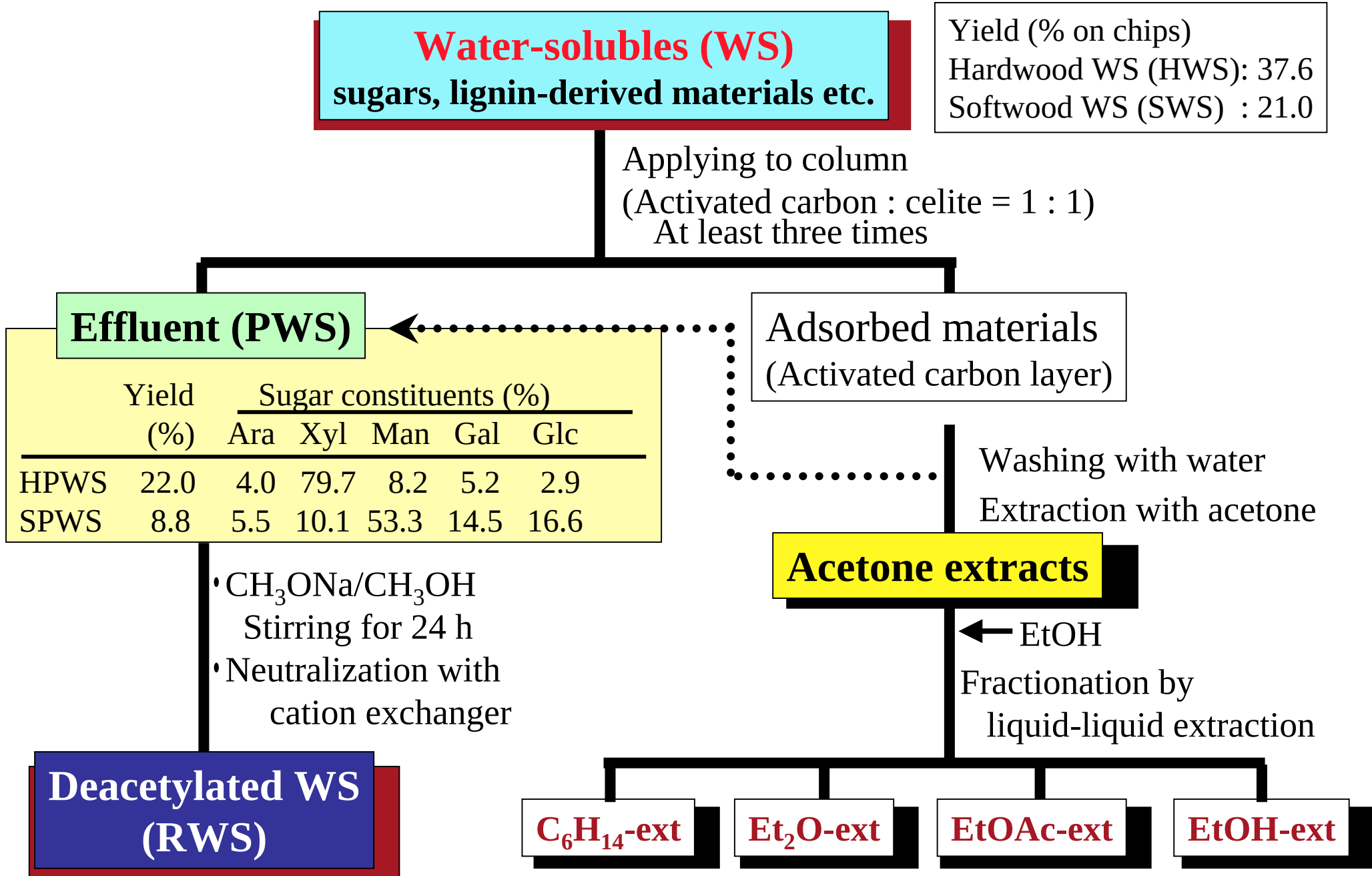


Fig. Purification sheme of water-solubles

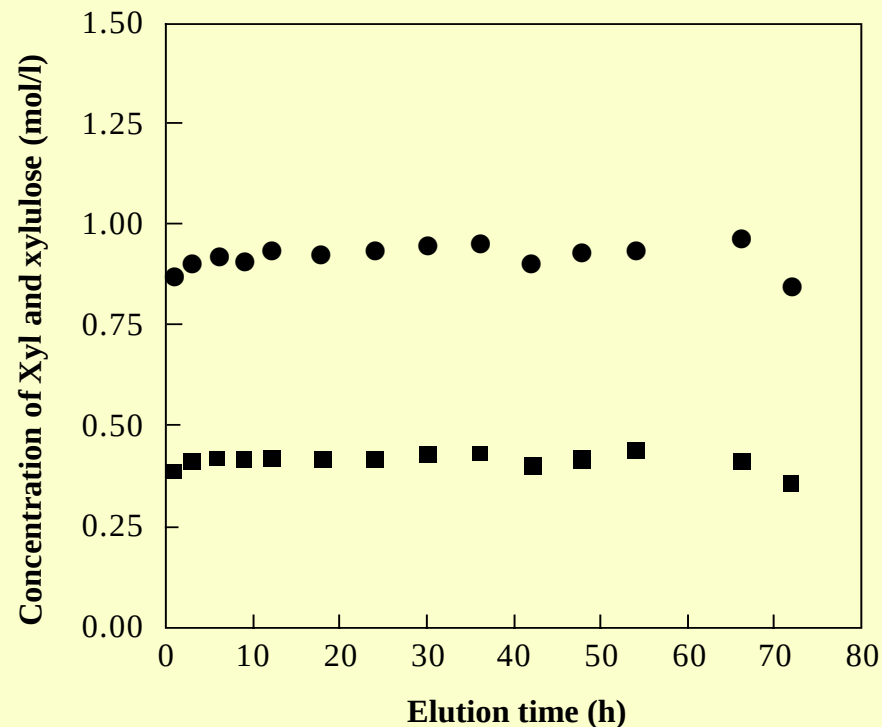
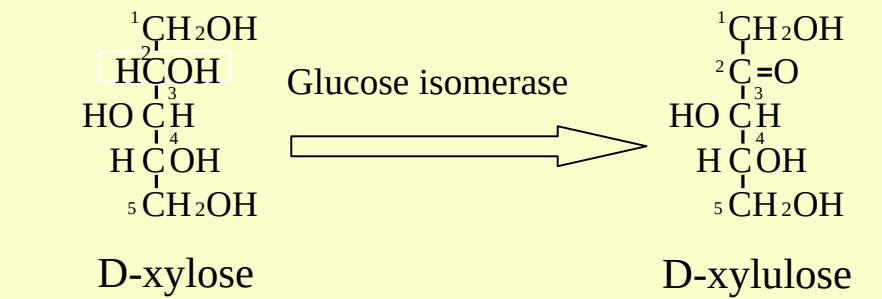
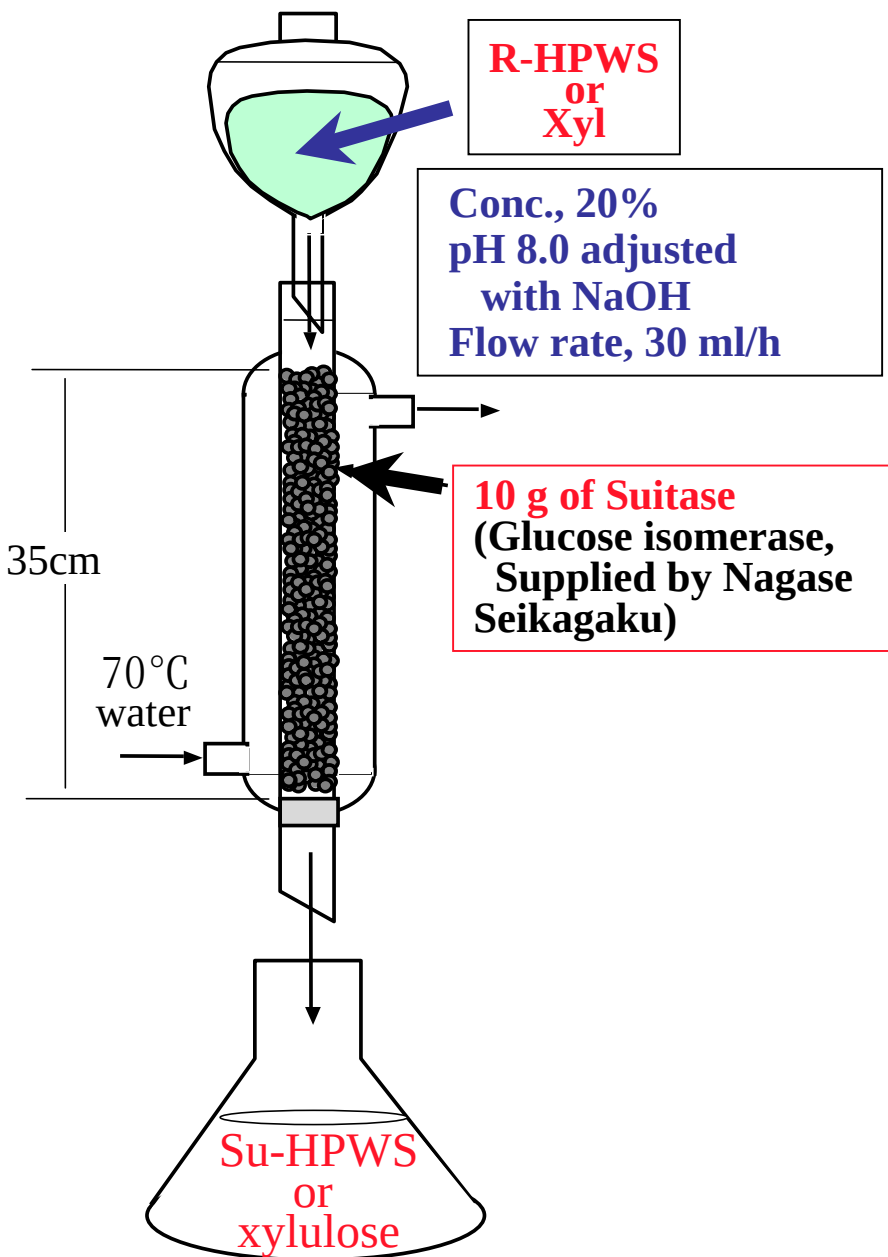


Fig. Xyl conversion to xylulose by glucose isomerase (Suitase)

Modification of Xyl and hardwood WS (HPWS)

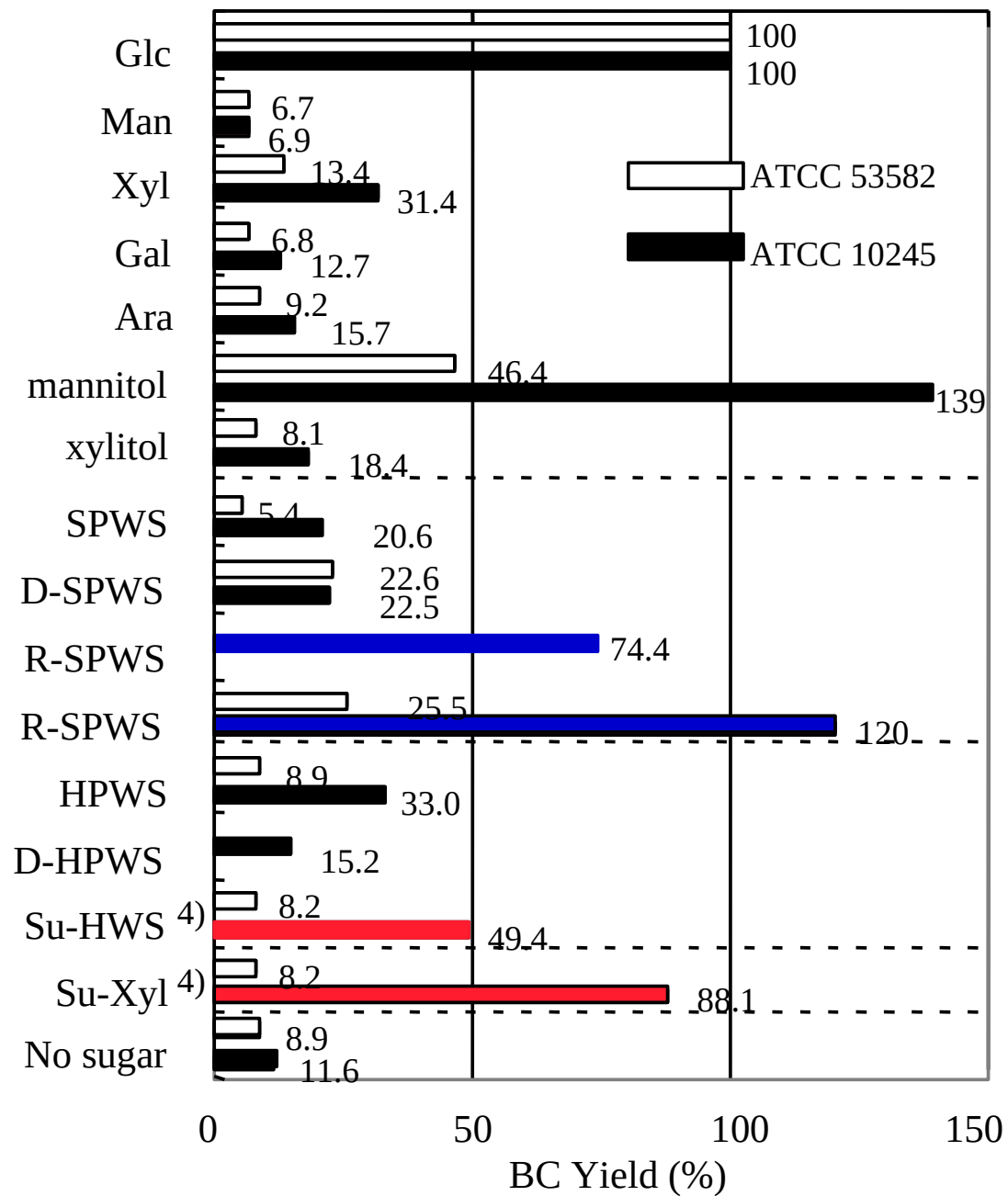
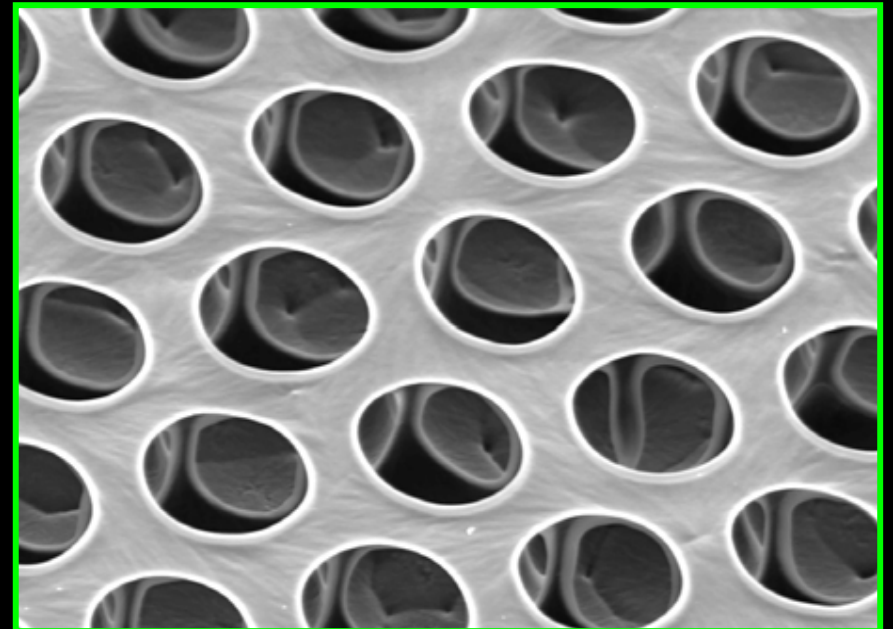
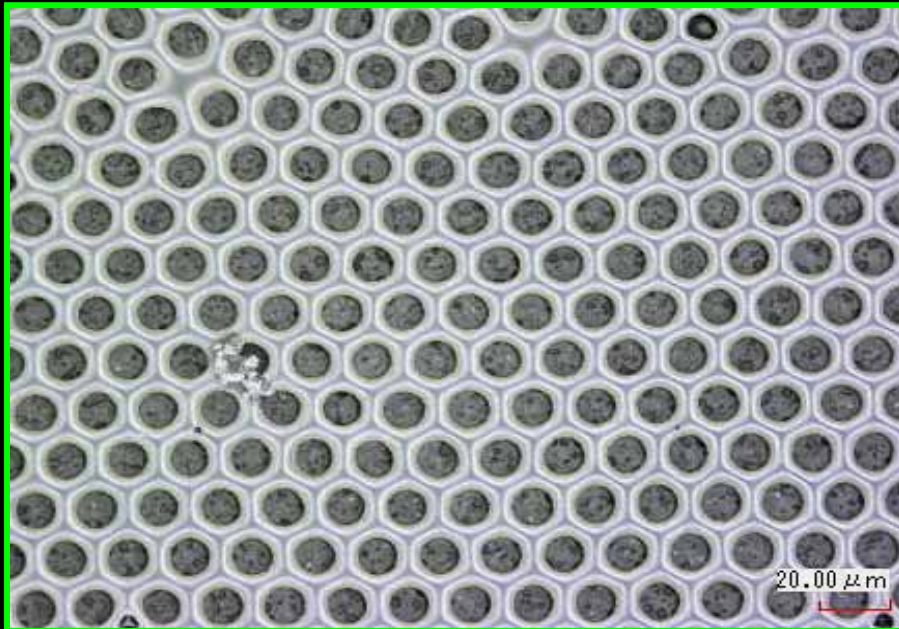
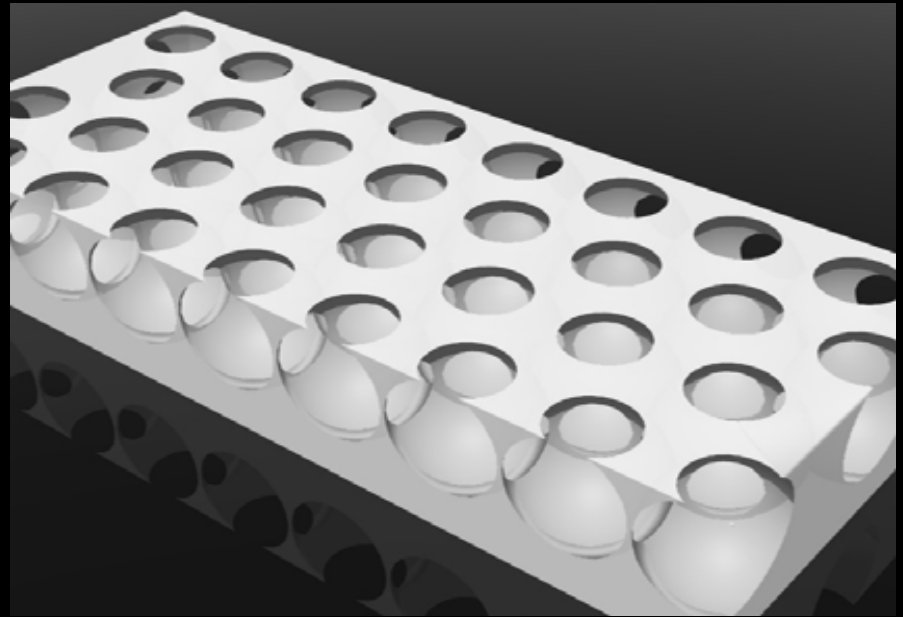
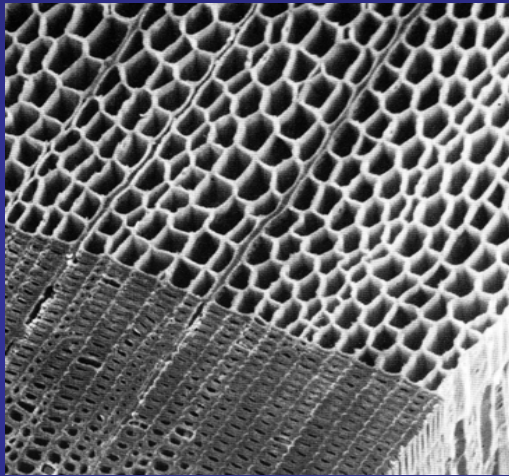


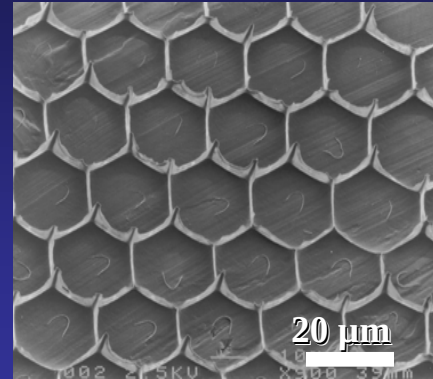
Fig. Bacterial cellulose production from various sugars.



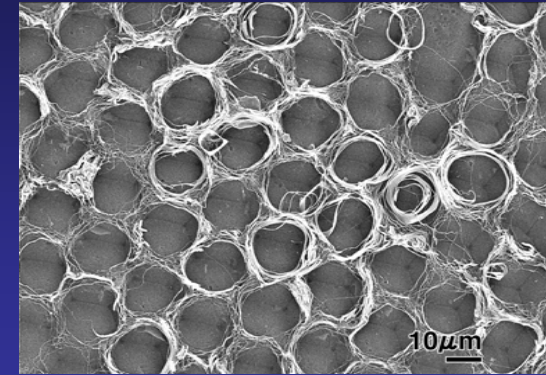
Recent study is to Create Artificial Cell Wall



Mimic

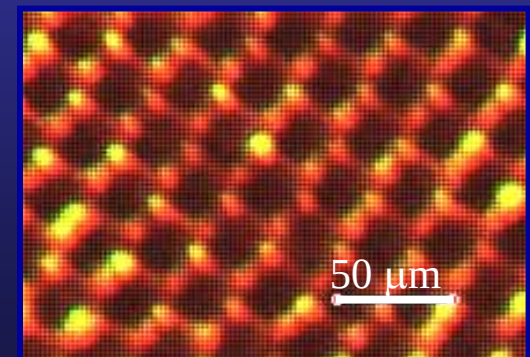
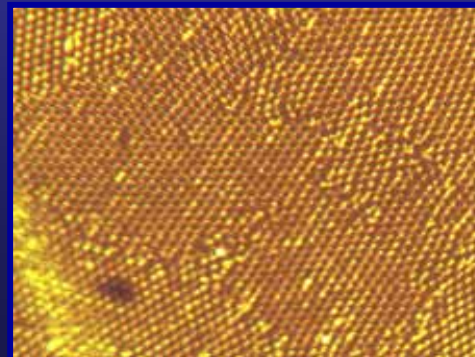


Regenerated cellulose
honeycomb

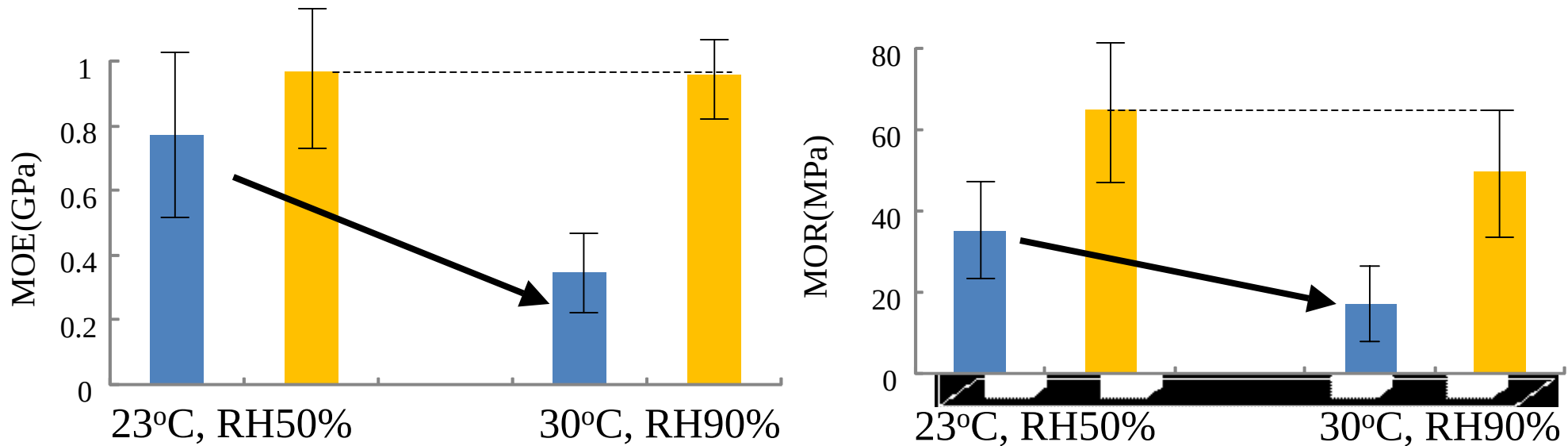


Bacterial cellulose
honeycomb

Lignin deposition



Effect of lignin adsorption on the tensile strength of honeycomb-patterned cellulose film.



- Honey-patterned BC
- Honey-patterned BC with lignin

Thank you for attention