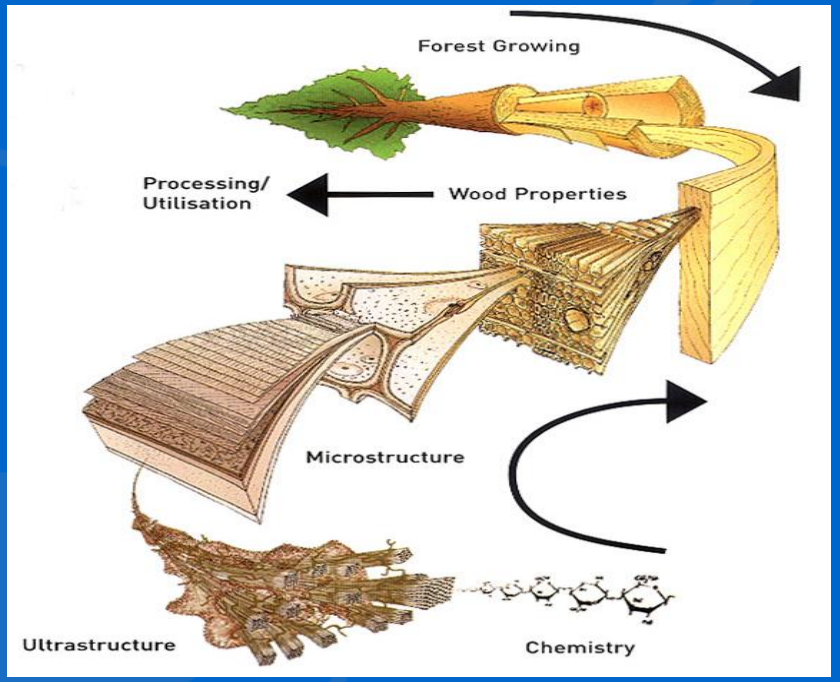
Softwood Pretreatment: Finding the Right Compromise



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University of British Columbia

Northwest Bioenergy Research Symposium, November 13th, 2012

Take home messages

- Pretreatments should be mild enabling hemicellulose recovery but also increase cellulose accessibility at low enzyme loadings.
- Lignin is the main contributor to the recalcitrance of softwoods.
- Lignin modification improves hydrolysis but lignin removal in a usable form maximizes hydrolysis and the potential for value-added products.
- Lignin removal requires conditions that can compromise the facile recovery of hemicellulose so multiple stages may be necessary.

The main goals for biomass pretreatment

- Cellulose hydrolysis at the lowest possible enzyme loadings
- Good fractionation and recovery of cellulose, hemicellulose, lignin and extractives
- Value-added products
- Feedstock “agnostic”
- Do this economically! Low CAPEX/OPEX

Organosolv and steam pretreatment

Organosolv Pretreatment

Pulping technique – Alcell process

- Solvent delignification with acid catalyst
- Softwood, hardwood and non-wood
- Wood can be treated as chips
- Solvent recyclable

Steam Pretreatment

- Limited chemicals, energy
- Maximizes cellulose and hemicellulose recovery
- Increases cellulose accessibility
- Softwood, hardwood, non-wood
- Wood can be treated as chips

Lignin

High purity, narrow polydispersity

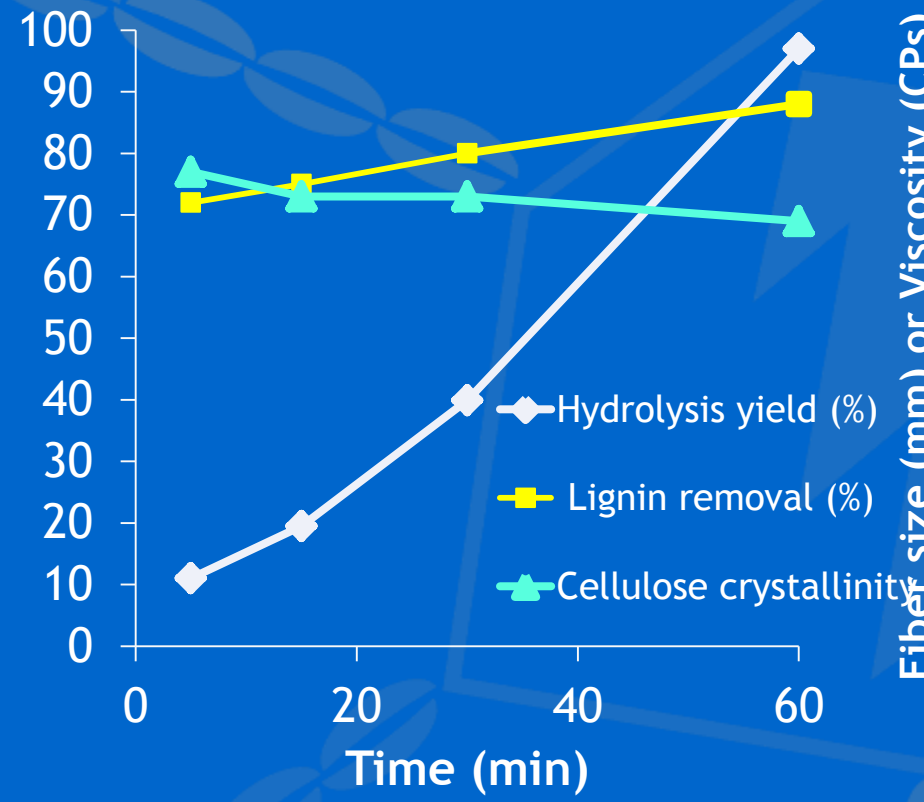
Potential for co-product applications

Hemicellulose

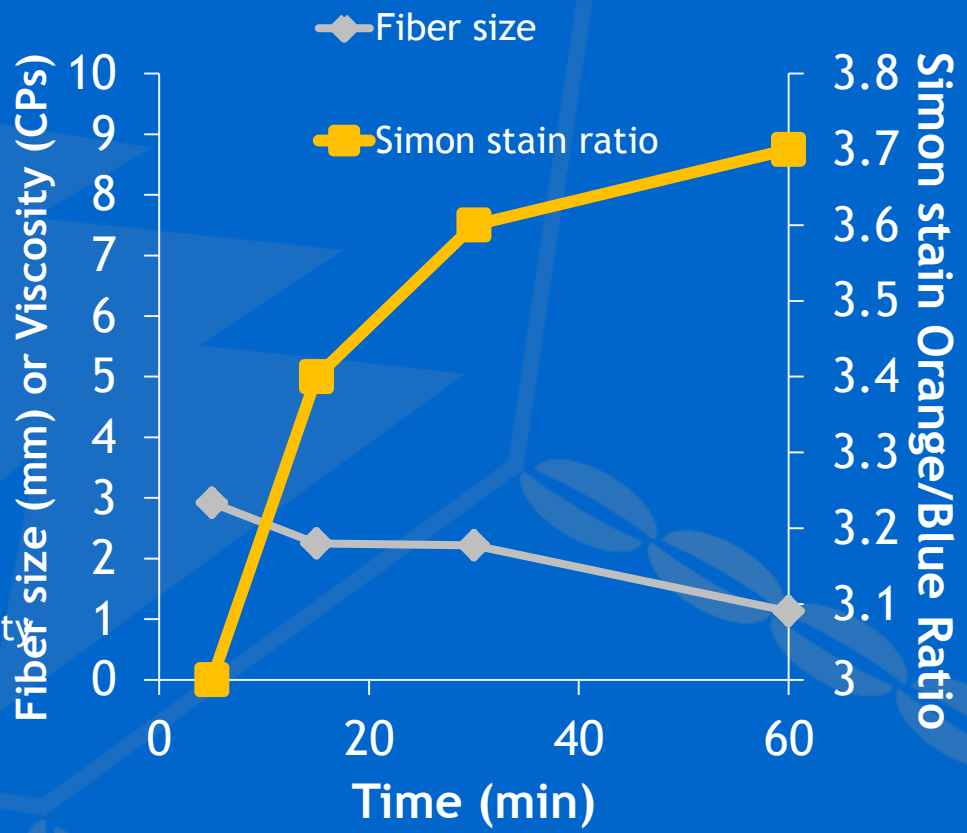
Oligomeric and monomeric in water soluble stream

Goal: Producing a readily accessible cellulosic substrate

Increasing accessibility by removing lignin



5 FPU/g Cellulose



Chandra, Chung, Saddler 2011

Goal: “Three buckets”

Lignin
Adhesives
Antioxidants
Fuels
Dispersants
Fibers
Resins etc.

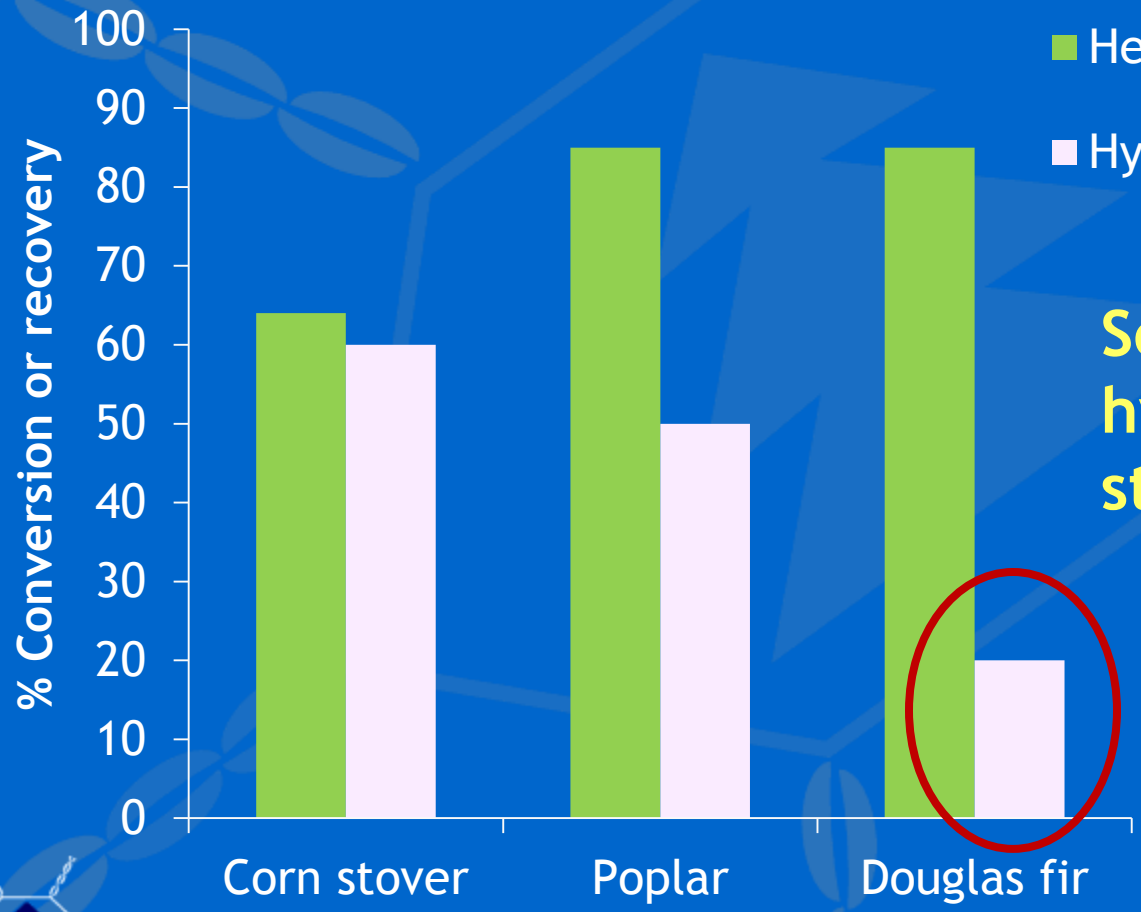
On ANY LIGNOCELLULOSIC BIOMASS!

Cellulose
Hydrolyzed at a mininum enzyme loading

Hemicellulose
Xylitol
Lactic acid
Bonding agents
Hydrogels

The recalcitrance of softwood during pretreatment and hydrolysis

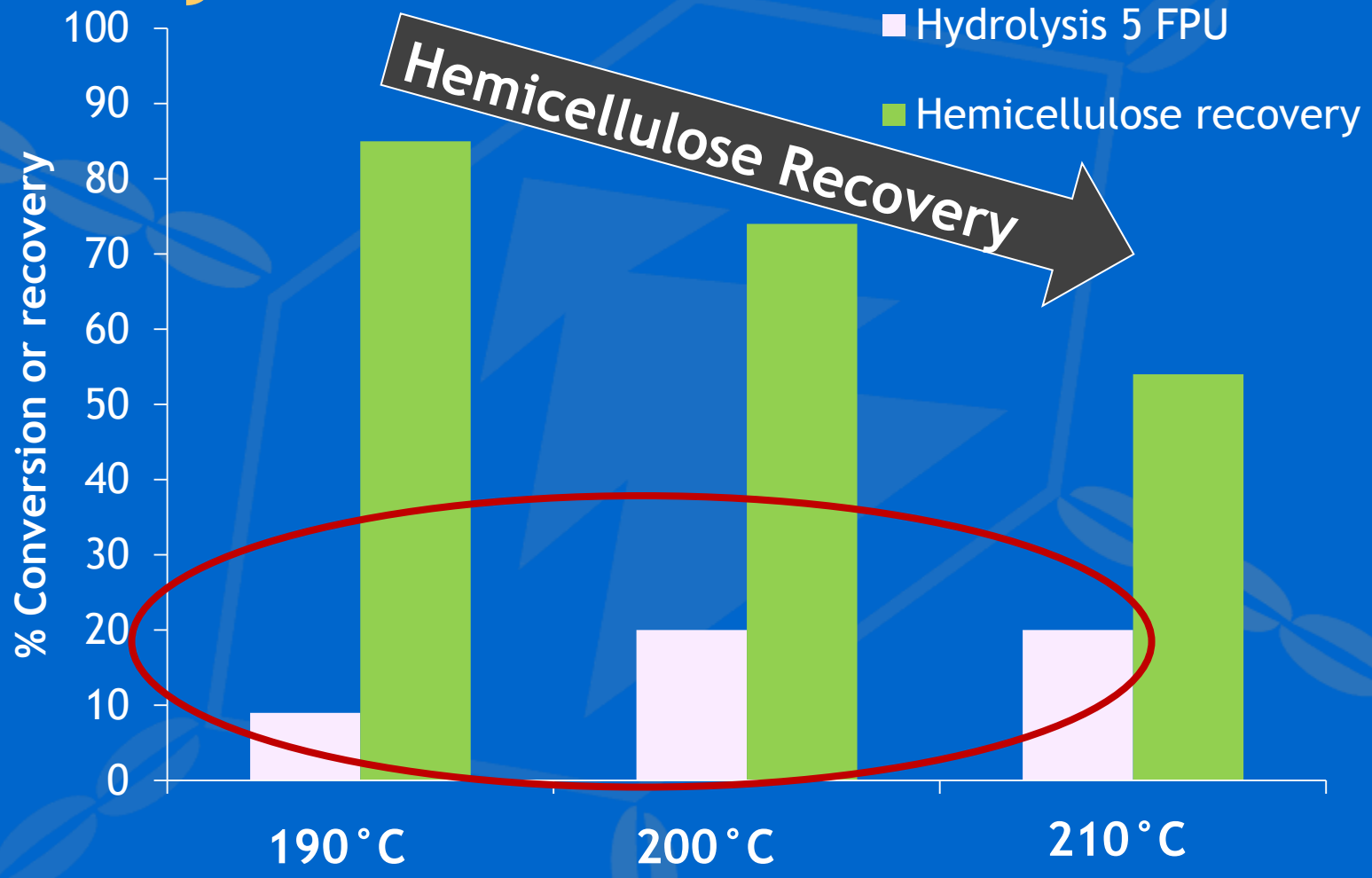
190°C 5 min in steam gun with 3 or 4% SO_2 catalyst



Softwoods have low hydrolysis yield after steam pretreatment

Bura et al 2009
Chandra 2011
Kumar et al 2010

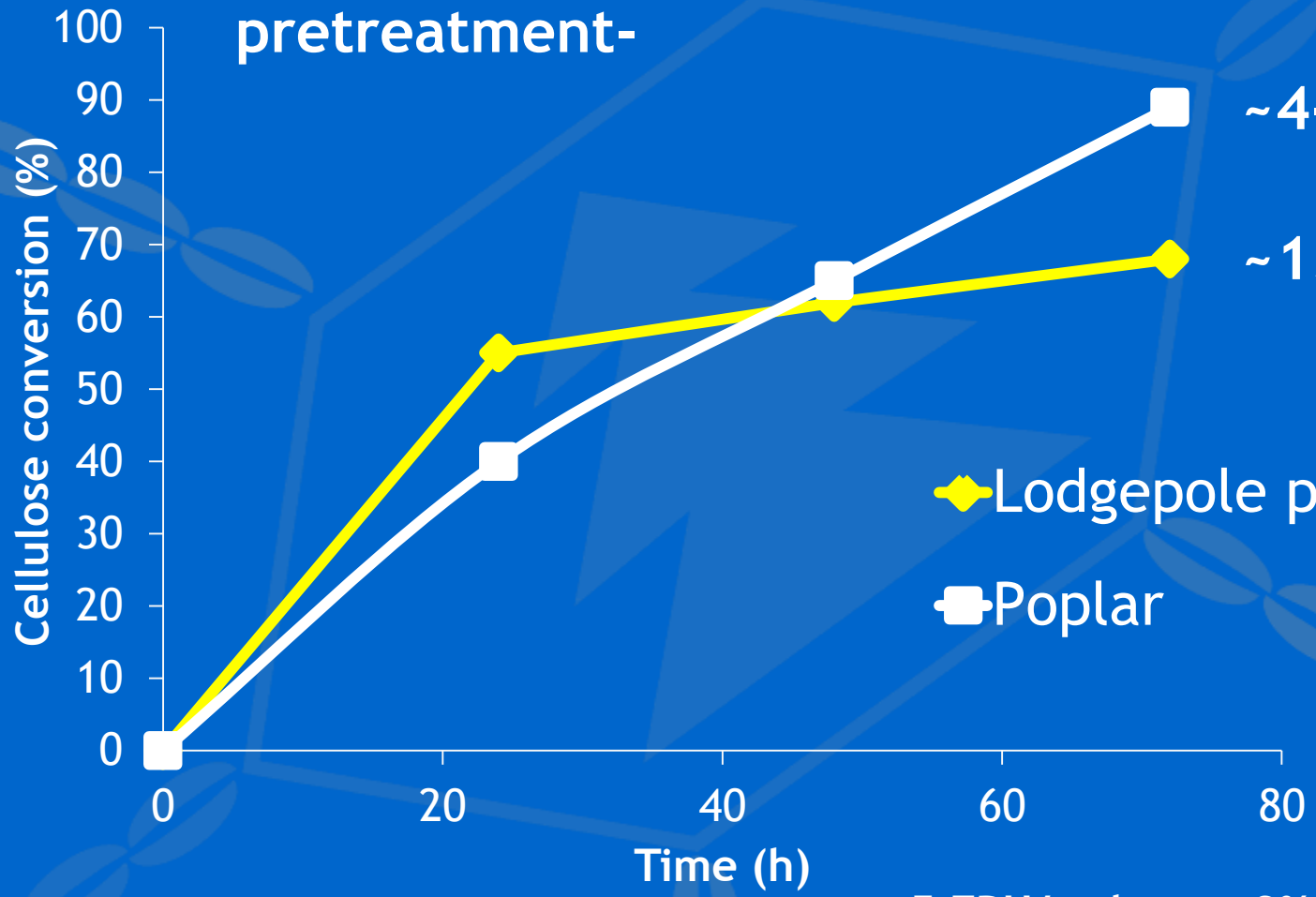
What if we increase pretreatment severity?



Kumar et al 2010
Nakagame et al 2011

Organosolv Lodgepole Pine vs Poplar

Hardwoods are more responsive to organosolv pretreatment-

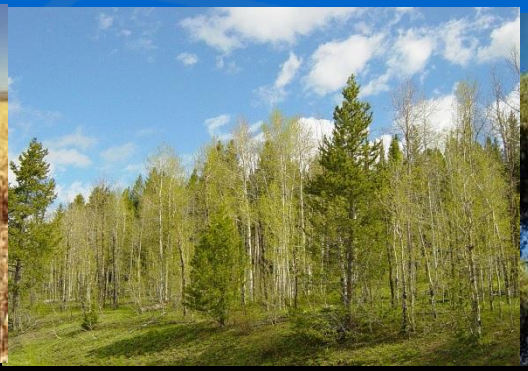


Del Rio et al 2012
Chung et al. 2011

5 FPU/g glucan, 2% solids

170°C 1h 1% H_2SO_4

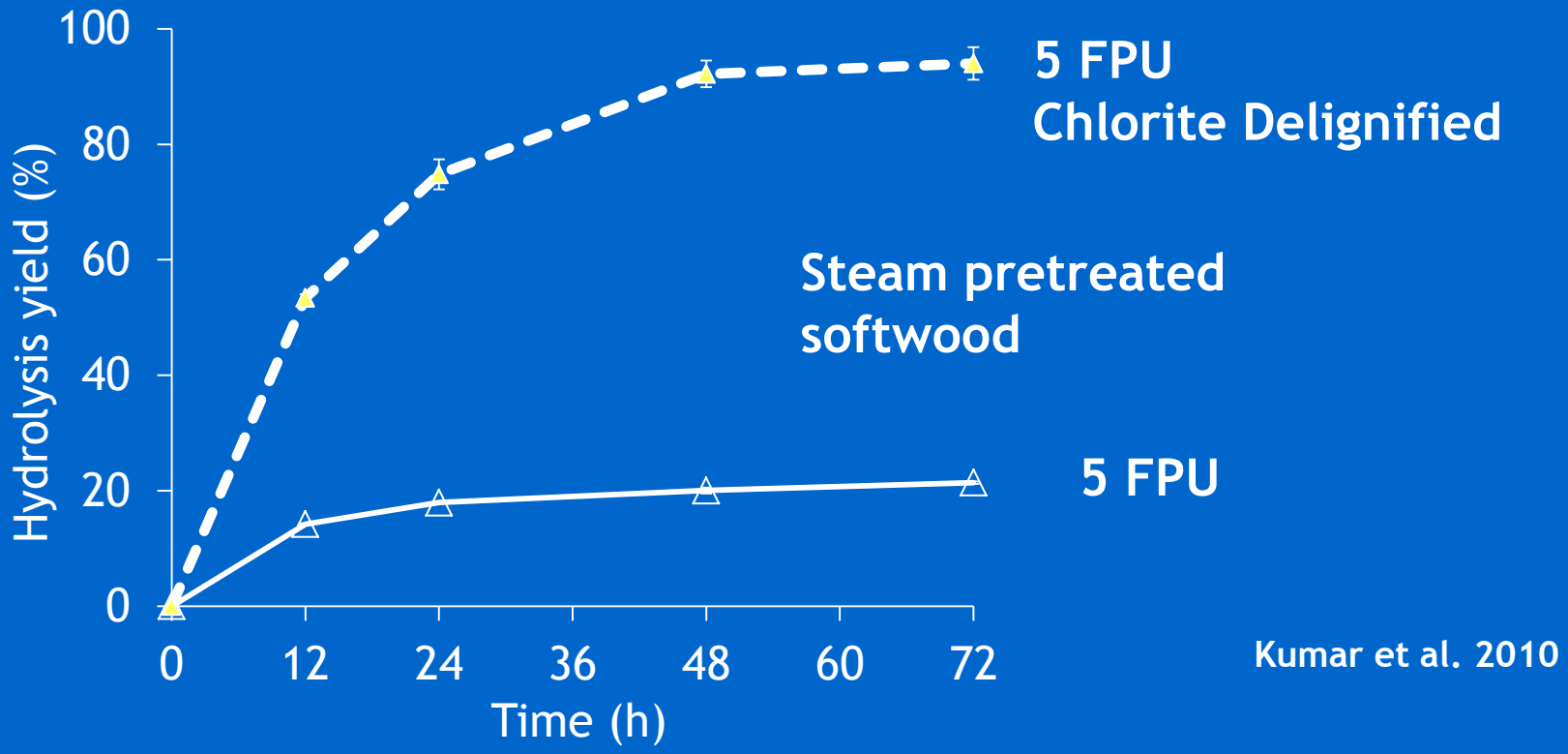
Why the challenge with softwoods?



	Agricultural	Hardwoods	Softwoods
Lignin content (%)	10-20	18-25	25-30%
Lignin type	“H” and “S”	“S”	“G”
Hemicellulose	Xylan	Xylan	Galactoglucomannan
Fiber size (mm)	0.5-1	0.5-1.2	1-3
Cell types	parenchyma, schlerenchyma, collenchyma	vessels, fibers, rays	tracheids, rays

Softwood pretreatment compromise

Lignin is the main contributor toward the recalcitrance of pretreated softwoods...so we have to alter or remove it

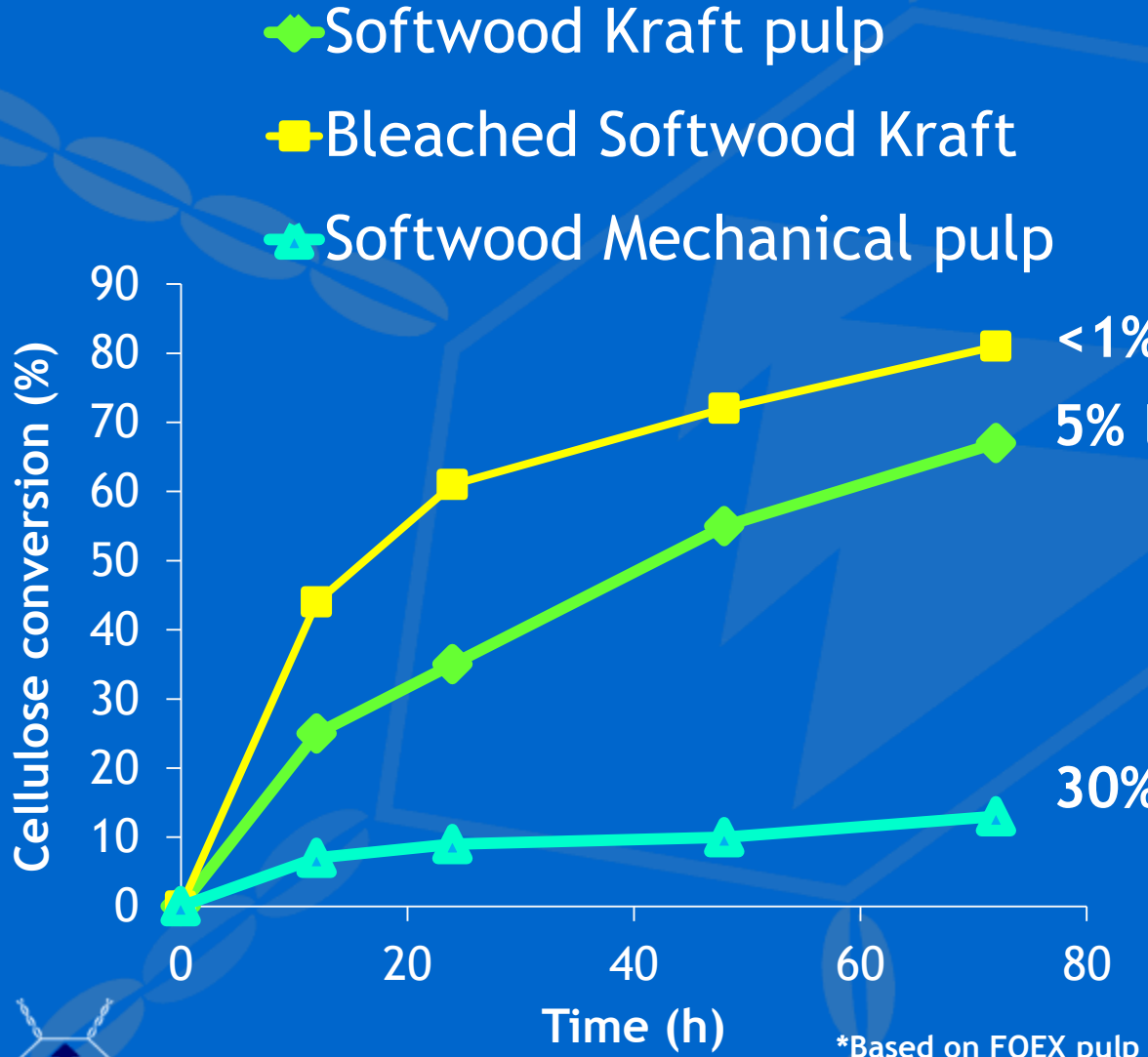


Kumar et al. 2010

BUT we need to remove lignin in a usable form to create an accessible substrate without compromising hemicellulose recovery!

Removing lignin can be expensive

Dissolving pulp
~$1000/ton*



<1% lignin,~ $850/ton*

5% lignin, ~$600/ton*

30% lignin,~$450/ton*

5 FPU/g cellulose, 2% solids

Chandra, Ewanick , Saddler, 2007

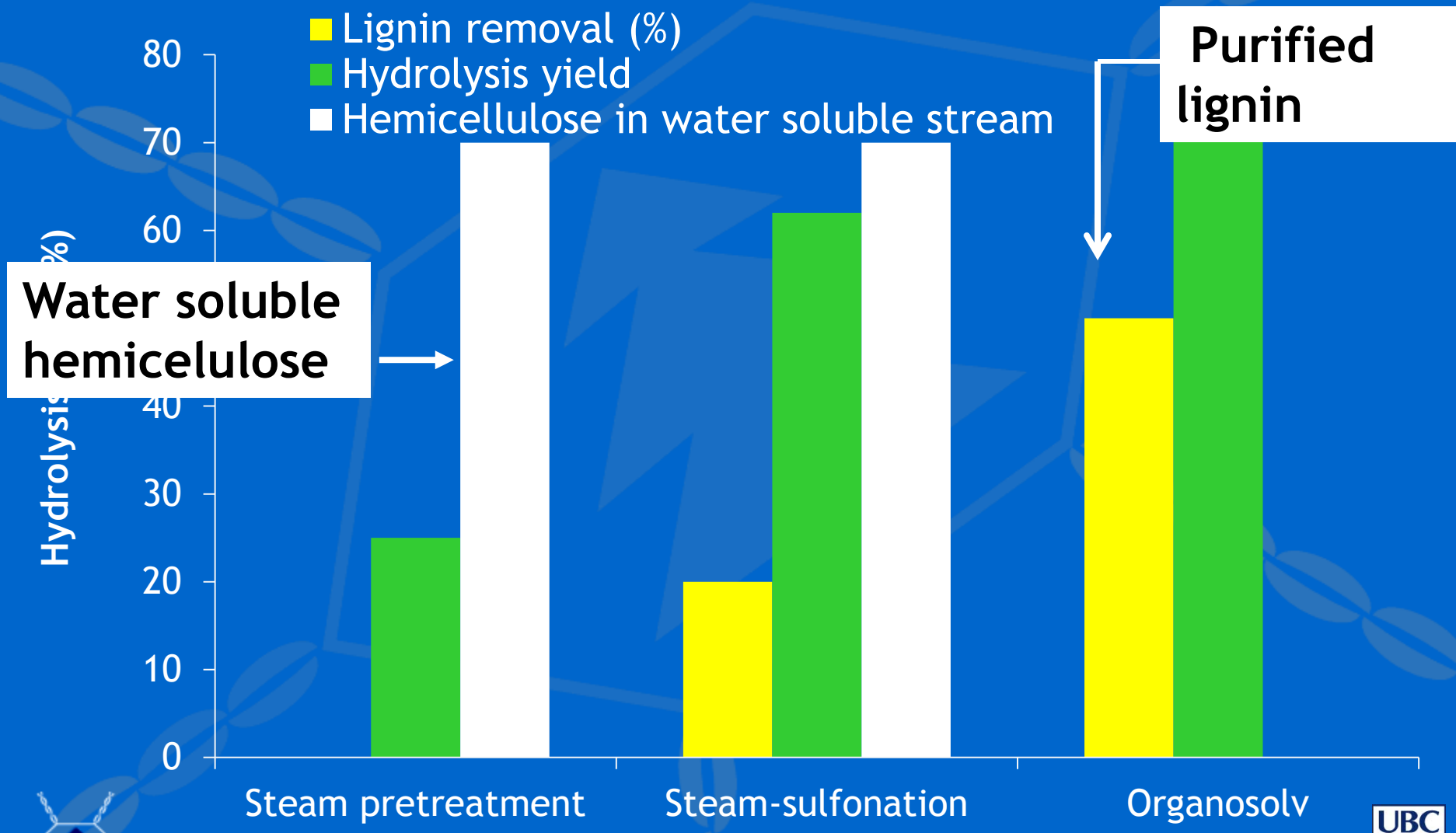
*Based on FOEX pulp pricing as of Nov 2012 for NBSK, Kraft liner and Newsprint for mechanical pulp and Stockhoue article Nov 2 2012 for dissolving pulp

Pretreatments that affect lignin can process softwoods

- SPORL
- Wet-oxidation
- Organosolv
- Steam pretreatment-post treatment

Lignin modification vs lignin removal

Steam+ Neutral Sulfonation vs Organosolv



Compromises when dealing with lignin in pretreated softwoods

- Lignin removal usually compromises hemicellulose recovery

BUT

- When lignin is only modified to preserve hemicellulose it can still hinder cellulose accessibility

Organosolv and steam pretreatment

Lignin

Hemicellulose

Organosolv Pretreatment

Lignin

Steam Pretreatment

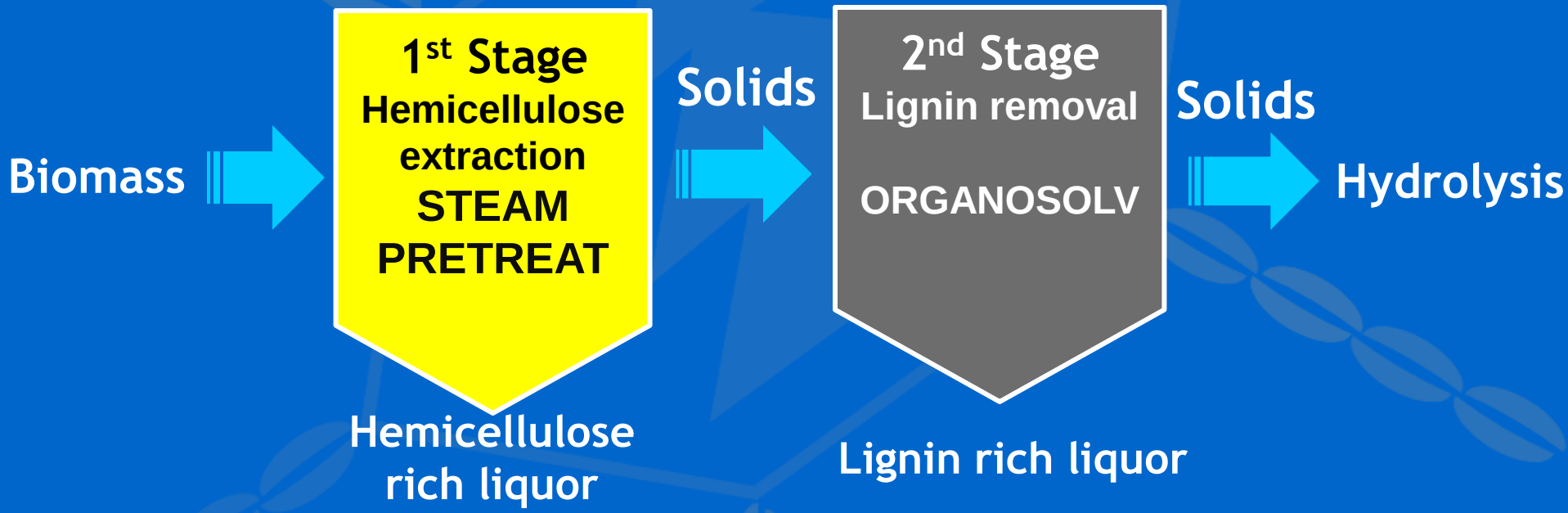
Hemicellulose

Hemicellulose in lignin rich ethanol stream

Lignin is not removed

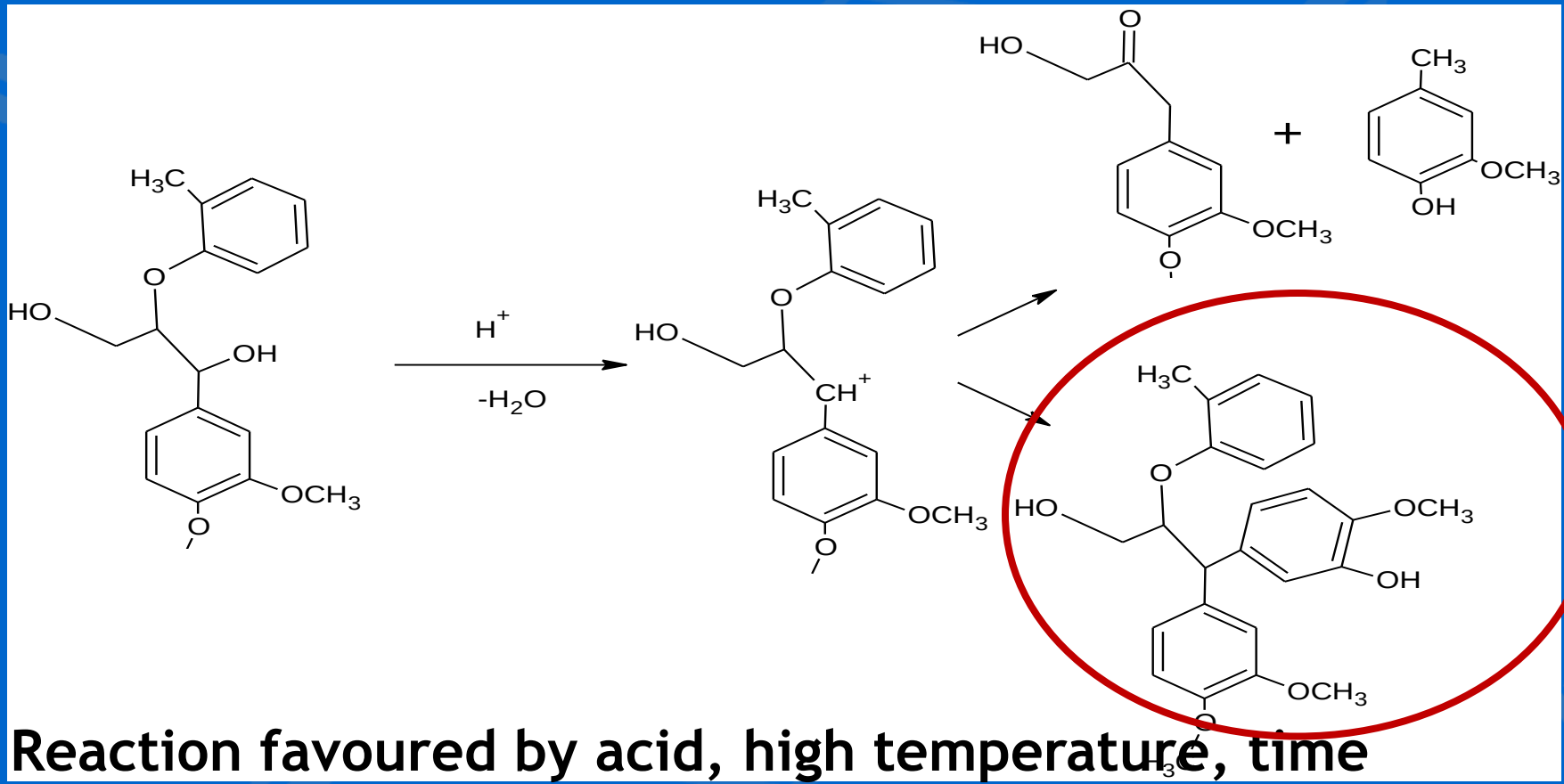
Best of both worlds?

Can we **recover solubilized hemicellulose** in a 1st stage and then remove lignin in a 2nd stage treatment to isolate a potentially **useful lignin** and **improve enzymatic hydrolysis**?



Can lignin still be extracted after steam pretreatment?

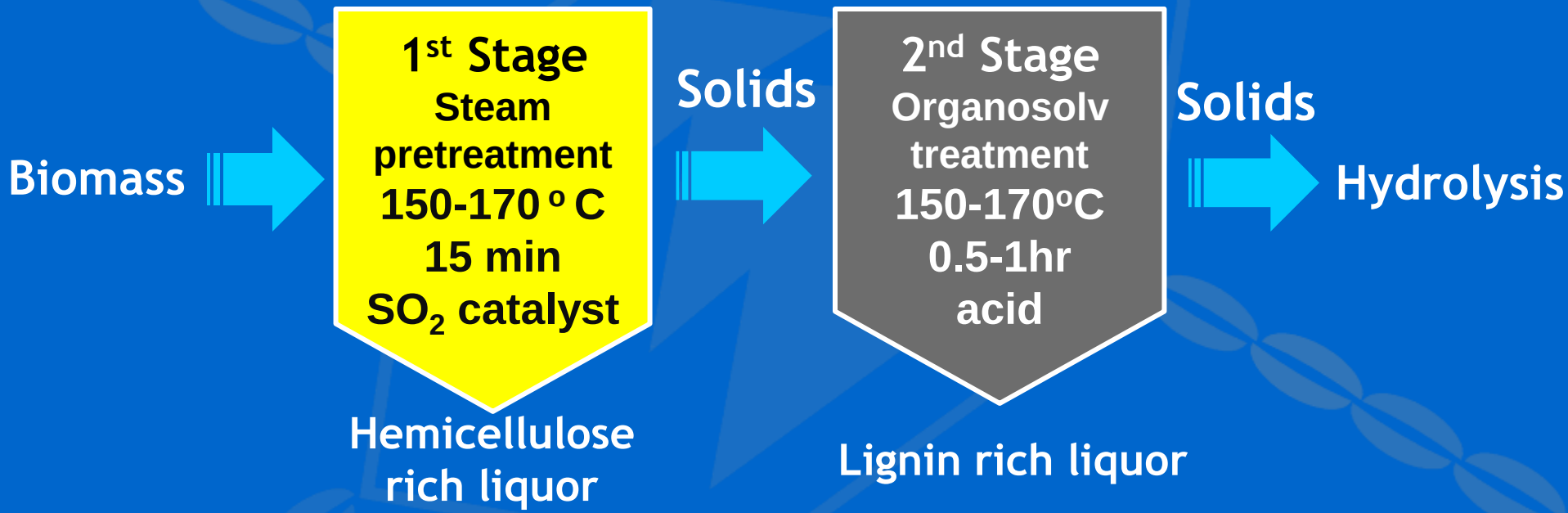
Lignin condensation during pretreatment



Reaction favoured by acid, high temperature, time

Will lignin condensation during steam pretreatment compromise lignin removal during subsequent organosolv?

Two-stage pretreatment approach



Hemicellulose and lignin recovery

Steam pretreatment isolates hemicellulose and improves lignin yields during organosolv

Organosolv pretreatment removes lignin to maximize cellulose accessibility

Panagiotopoulos et al 2012

Enzymatic hydrolysis - 5 FPU/g 72h

Softwoods still reach 70% conversion at 1/4 enzyme loading of steam pretreatment. Hemicellulose and lignin recovered!

Panagiotopoulos et al 2012

“Have your cake and eat it too”

We need a pretreatment for softwoods that enables:

- Lignin/hemicellulose removal to maximize cellulose accessibility
- Enzymatic hydrolysis of cellulose at low enzyme loadings/high solids loadings
- Hemicellulose and lignin recovery in a clean, usable form

Do this economically!

Conclusions

- Softwoods are more recalcitrant mainly due to their higher lignin content/lignin type
- For hydrolysis at low enzyme loadings (<5FPU/g glucan) lignin must be removed or modified.
- Ideally lignin can be removed/recovered for co-product value but conditions for delignification can compromise hemicellulose recovery.
- Hemicellulose and lignin recovery may require a multi-step pretreatment approach tailored to maximize yields/purity of both components.