

Ketone-Based Organosolv Fractionation of Lignocellulosic Biomass

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Energy research Centre of the Netherlands (ECN)



- **Mission:**
 - With and for the market, we develop knowledge and technology that enable a transition to a sustainable energy system.
- **Business units:**
 - Biomass & energy efficiency
 - Solar energy
 - Wind energy
 - Policy studies
 - Environment & energy engineering



ECN

- Independent research institute
- ~550 employees
- Locations:
 - *Petten (HQ)*
 - *Amsterdam*
 - *Eindhoven*
 - *Brussels*
 - *Beijing*

Why Organosolv?

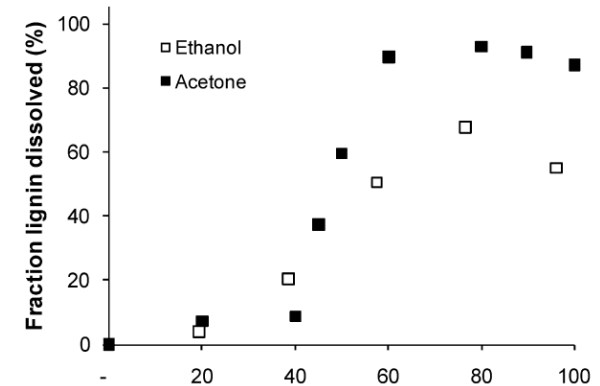
- Fractionation & valorization of all major constituents
 - Increased revenue from biorefinery
 - Financially more attractive
- Cellulose: High conversion enzymatic hydrolysis
- Lignin: High-quality for production of chemicals
- Hemicellulose: Choice for xylose or xylose derivatives (furfural)
- (Other): (Proteins, extractives, minerals, ...)

Comparison Ketone-Ethanol organosolv

- Conventional organosolv: solvent = ethanol
- Ethanol organosolv side reactions
 - Ethanol reacts with lignin and (hemicellulose) sugars
 - Market for ethyl-sugars?
 - High temperatures / severity leads to formation of furfural
 - Side-reactions change lignin structure
- Ketone (acetone) organosolv
 - No side reactions of acetone with lignin or sugars
 - Higher xylose yields
 - Lower formation of furfural
 - Mild conditions lead to a near-native lignin

‘Ketosolv’

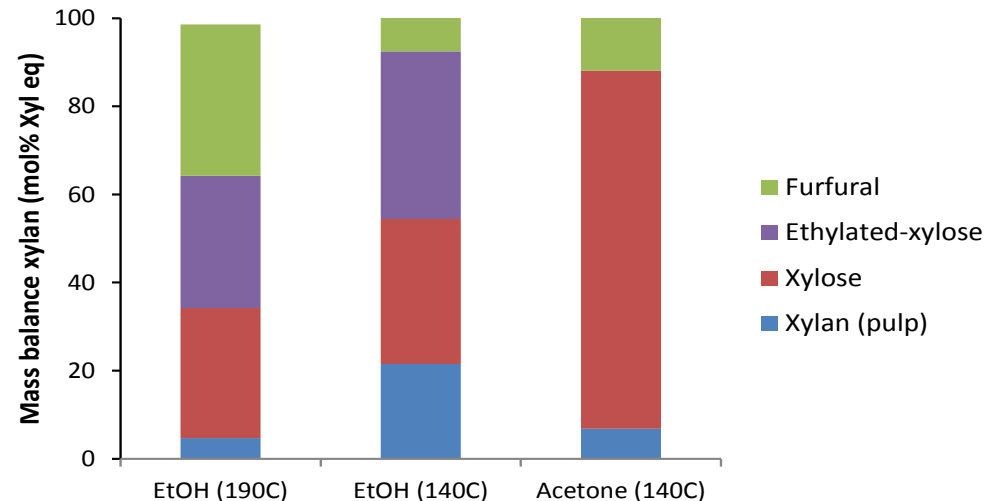
- Ketones: excellent lignin solvents
- Key features ‘Ketosolv’:
 - Typical temperature: 190°C → 140°C
 - Solvent: ethanol → acetone
 - H₂SO₄ dose used for wheat straw: 20 → 60 mM
- Effective pulping at milder conditions:
 - High cellulose pulp purity and enzymatic digestibility
 - Good lignin yield and lignin more native / less condensed lignins
 - Also feasible with longer chain ketones such as butanone
- Self-condensation of acetone at conditions applied very limited



Huijgen, W. J. J.; Reith, J. H. & Den Uil, H. (2010) Industrial & Engineering Chemistry Research, 49(20), 10132-10140

Hemicellulose products

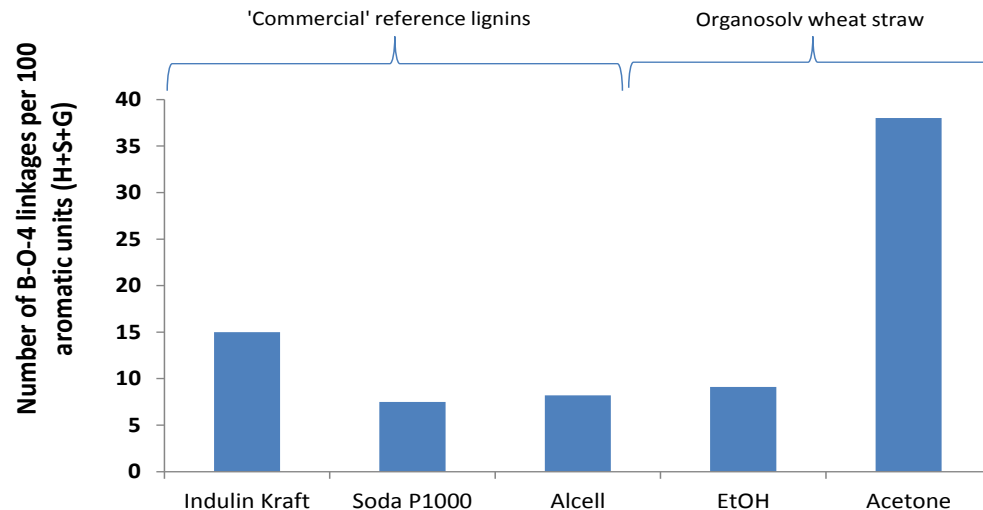
- Example: wheat straw
- High temperature ethanol:
 - Ethyl-sugars
 - Furfural
- Low temperature ethanol:
 - Ethyl-sugars
- Low temperature acetone:
 - Maximized xylose production



J. Wildschut, A.T. Smit, J.H. Reith & W.J.J. Huijgen (2013),
 Bioresource Technology, 135, 58-66

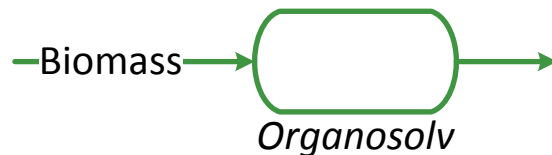
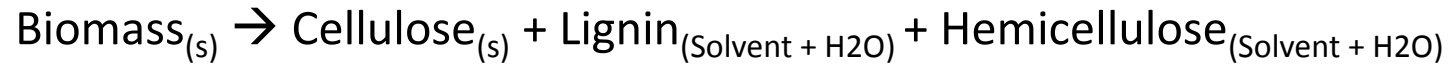
Remarkable lignin characteristics

- High number β -O-4 ether linkages
 - Suggests more native lignin (more reactive)
 - Crucial for many chemocatalytic depolymerisation routes



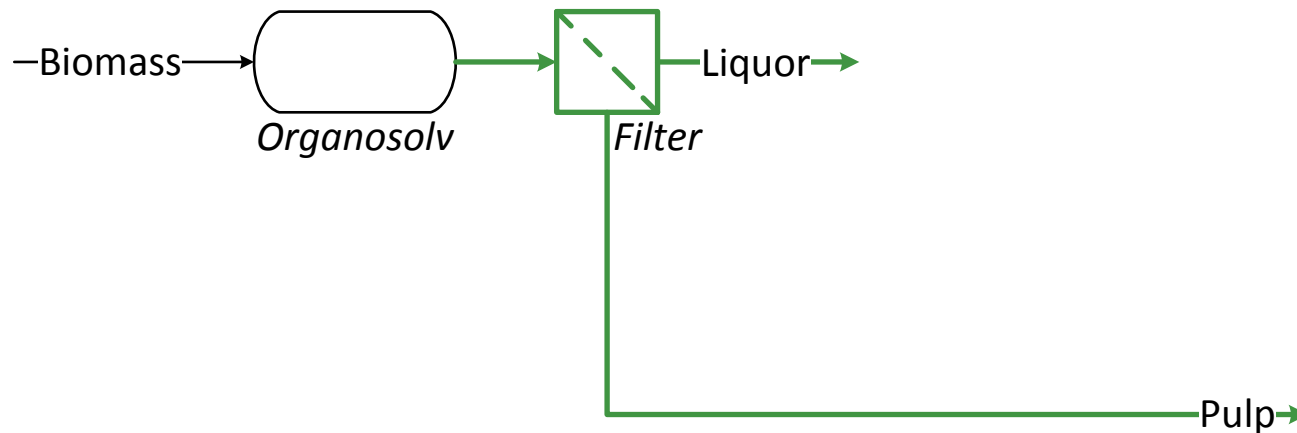
Organosolv – How?

- Specific process for lignocellulosic biomass
- Organosolv reactor:



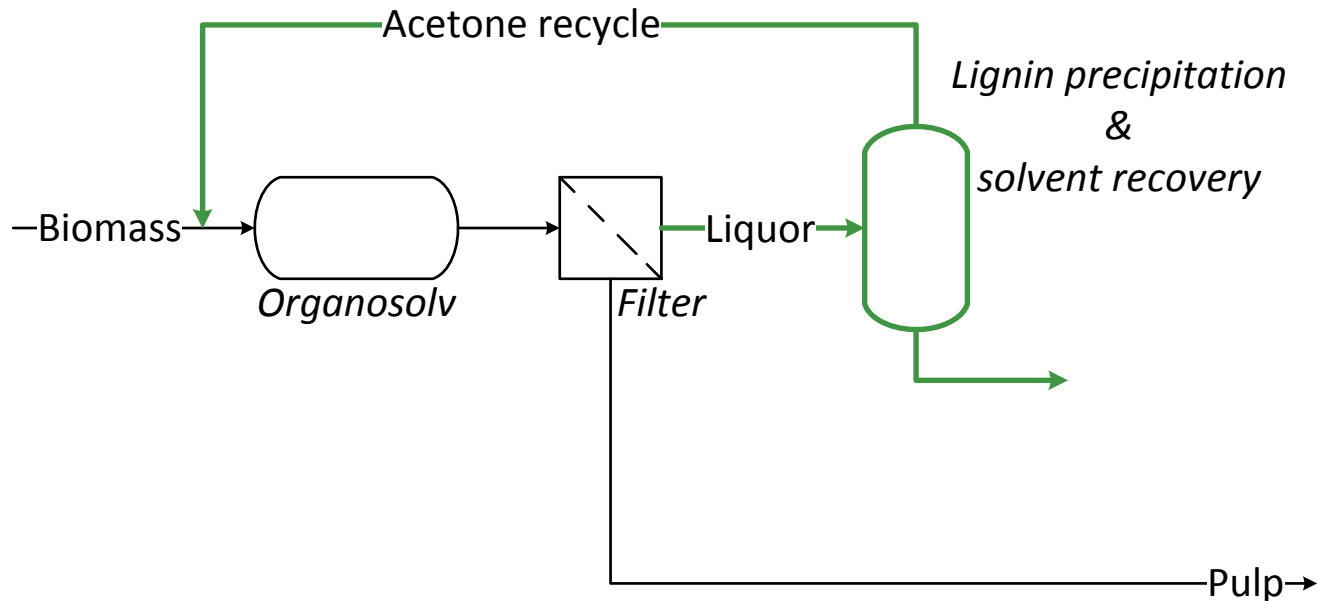
Organosolv – How?

- A filter removes cellulose from the liquor



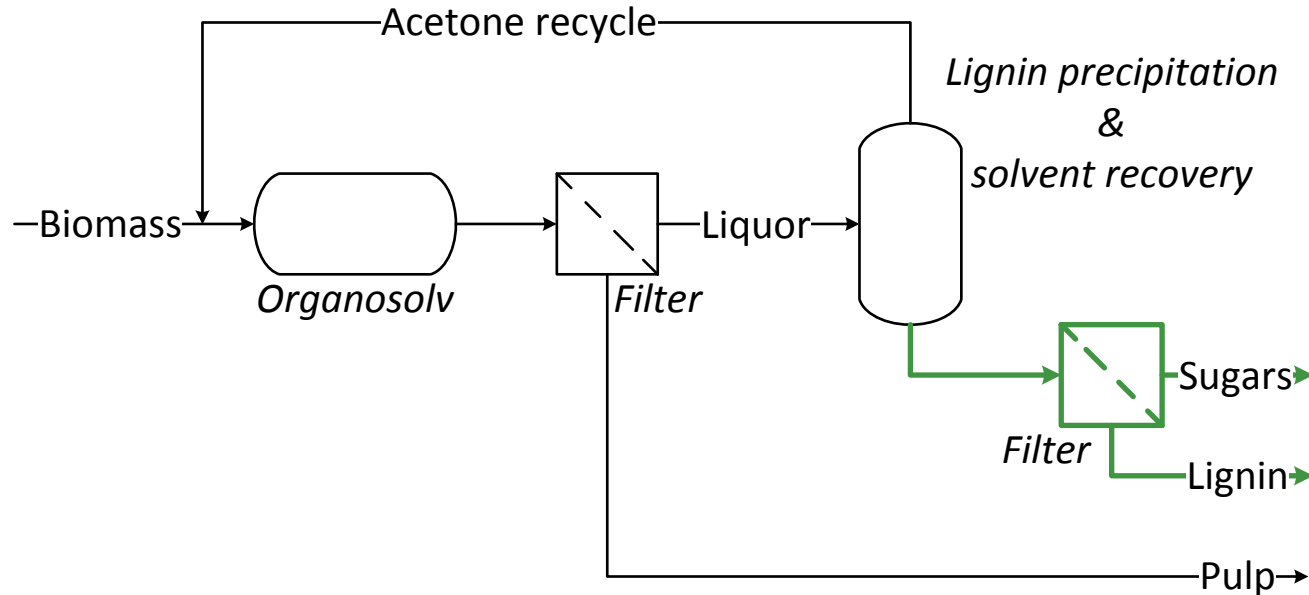
Organosolv – How?

- Lignin is precipitated by removing the acetone (lowering lignin solubility)
- Recycling is 99.9%; Crucial for economics



Organosolv – How?

- A filter separates the lignin from the C5 sugars
- Organosolv can fractionate all three main biomass components



Mass balance

- Model built in Aspen plus software

Feedstock	kt/y		Products	kt/y
Straw (dw)	1,000		Cellulose pulp	780
Straw moisture	100		(moisture)	44%
Acid (catalyst)	30		Lignin	131
Acetone	5		(moisture)	20%
Water	1,470		Sugars	1,615
Air	2,718		(water)	69%
			CO ₂	0.4
			Moist air	2,797
Total	5,323		Total	5,323

“Biomass balance”

- Water, acetone, catalyst and air excluded in “biomass balance”
- Water reacts (hydrolysis reactions)

Feedstock	kt/y		Products	kt/y
Straw (dw)	1,000		Cellulose pulp	439
Straw moisture	-		(glucan)	72%
Acid (catalyst)	-		Lignin	104
Acetone	-		(near-native lignin)	99%
Water	-		Sugars	478
Air	-		(sugars)	53%
			(xylose)	71%
			Other	1
Total	1,000		Total	1,022

Energy requirements

- Main energy consumers: all related to acetone recovery
- Reboilers acetone recovery columns:
 - Column 1: 37 MW
 - Column 3: 33 MW
- Condensers
 - Column 2, pre-cooler: 40 MW
 - Condenser / degasser column 1: 32 MW
- Heat integration very important!
 - Vapor compressed to reactor pressures before condensation
 - Increase integration potential

Energy requirements (2)

	No heat integration	After pinch analysis
Heating (MW)	126	25
Cooling (MW)	-120	-12
Electricity (MW)	19	19

	No heat integration	After pinch analysis
Heating (MJ/kg straw)	3.63	0.72
Cooling (MJ/kg straw)	-3.47	-0.35
Electricity (MJ/kg straw)	0.55	0.55

Conclusions

- New patented ketone organosolv process
- Milder conditions
 - Less degradation reactions
- High yields
 - Hemicellulose sugars not degraded as much
- A more native lignin
 - High number β -O-4 ether linkages
- Less energy consumption
 - Use of acetone positive for energy consumption
 - Process design optimized for heat integration

Cooperation

- ECN is looking for partners!
- Equipment design
- Application tests
 - Lignin applications with near-native lignin vital for acetone-organosolv
 - Cellulose for fibres or sugars
 - Hemicellulose sugar applications (and purification?)
 - Mineral cycle
- ... But we can also help you if you have other challenges for us related to biorefining!

Thank you for your attention

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