Organosolv-based integrated biorefinery of the (ligno) cellulosic biomass
“an evolution from pretreatment to fractionation processes”

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CO$_2$ refining processes

- Biorefinery (Biomass route)
- Electro-refinery (Non-Biomass route)

Biological and Catalytic conversion

Chemicals
Fuels
Materials
## Composition of lignified plant secondary cell walls

<table>
<thead>
<tr>
<th></th>
<th>Hardwoods</th>
<th>Softwoods</th>
<th>Grasses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose</td>
<td>40–50 %</td>
<td>33–42 %</td>
<td>25–35 %</td>
</tr>
<tr>
<td>Hemicelluloses</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Xylan</td>
<td>15–30 %</td>
<td>5–10 %</td>
<td>15–30 %</td>
</tr>
<tr>
<td>Glucomannan</td>
<td>2–5 %</td>
<td>14–20 %</td>
<td>1–2 %</td>
</tr>
<tr>
<td>Lignin</td>
<td>20–25 %</td>
<td>27–32 %</td>
<td>10–15 %</td>
</tr>
<tr>
<td>Protein</td>
<td>&lt; 1 %</td>
<td>&lt; 1 %</td>
<td>10–15 %</td>
</tr>
</tbody>
</table>
The default operation of lignocellulosic conversion processes has become almost dogmatic:

The raw material is first subjected to a pretreatment designed to improve access to the polysaccharides present in the biomass

Separation has not been a goal
Pre-treatment and fractionation, by definition
Routes for the conversion of biomass into liquid fuels

Red arrows refer to thermal routes, green arrows refer to biological routes, and blue arrows refer to catalytic routes

Serrano-Ruiz and Dumesic, 2010
Pre-treatment and fractionation

- **Pretreatment** of lignocellulosic biomass is mainly associated with biochemical enzymatic hydrolysis.
- It improves the efficiency of the following enzymatic hydrolysis step.
- Pretreatment for thermochemical processes is limited to size reduction and drying

**Pre-treatment vs Fractionation**

- Pretreatment focuses on access to carbohydrates
- Fractionation focuses on separation of lignocellulosic components
- Pre-treatment is ethanol-centric
- Fractionation is multiproduct-centric, i.e. high vol.-low value and low vol.-high value products


- Although these definitions are given, the border between fractionation and pre-treatment is sometimes unclear
The petrochemical industry gives a good example

Carbon from coal, crude oil or natural gas is used for:

- Transformation into fuel for combustion reactions, generating energy (the large majority) (high vol.-low value)
- Refinement to form the standard building blocks of the chemical industry (much smaller portion) (low vol.-high value products)

Synergistic interaction between energy from fuels and profits from chemicals has been a key component of the petrochemical industry for decades
Key characteristics of biomass fractionation technology designed for multiproduct operation will include selective separation of each component of a biomass feedstock, easy access to and isolation of the components after separation, and recovery of each component in high yield.
Well-known biomass pretreatment methods:
Dilute acid, steam explosion, hot water, AFEX

Biomass fractionation technologies:
Organosolv processes, processes based on ionic liquids, multistage acid hydrolysis
Steam explosion pretreatment

- High dry-matter content
- 160-240°C, 1-20 min.
- Rapid release of the pressure
- Works well for many materials
- in general, also softwood
- Addition of an acid, e.g., H2SO4 H3PO4, SO2, Hac, etc.
- Usually < 2%; commonly 0.2-0.5%
The explosion had a high influence on digestibility improving it by up to 90 % compared to a steam pretreatment without explosion.

A $\Delta p$ of around 20 bar is necessary to reach the maximum improvement in digestibility.

**Organosolv Pretreatment**

- **Organosolv pretreatment**: “Pretreatment of lignocellulosic biomas with an aqueous / organic solvent mixture used as the pretreatment medium
- **Typical solvents**: methanol, ethanol, acetone due to low cost, low boiling point, ease of recovery, good lignin solubility
- **Process temperatures**: T (185–210 °C)
- Achieves fractionation of the major biomass components (cellulose, lignin, and hemicellulose) into three process streams
Lignin-free carbohydrate fractions

- The enzyme cost accounts for more than 15% of the minimum bioconversion product (e.g. ethanol) selling price.

- The GHG emission associated with production of cellulases accounts for more than 40% of the GHG emissions from the bioconversion product (e.g. ethanol).

- 50-90%, of the cellulases will be adsorbed onto lignin present in the material.
Hybrid / Organosolv Solvent-Steam explosion pretreatment

Aim: “Combine component fractionation achieved by operating the reactor in organosolv mode with the defibration/physical size reduction of the biomass achieved at the final stage by the rapid decompression of the biomass.”
Hybrid / Organosolv Solvent-Steam explosion pretreatment
Spruce

No Explosion

Steam

Organosolv

Explosion
Birch

No Explosion

Explosion

Steam

Organosolv
Organosolv Biomass Pretreatment for Flexible Fuel Production (Solvefuels) (Swedish Energy Agency)

- reducing enzyme consumption by combining a novel organosolv pretreatment process with advanced fractionation of lignocellullosic biomass into lignin-free carbohydrate fractions
- implementing high gravity fermentation resulting in an increased ethanol yield

Period  2016-2018
Integrated conversion of forest residues into methane and carbonised materials

INFORMAT

FORMAS call: “Forest raw material and Biomass: Research for a transition to a bio-based economy.”

✓ Demonstration of an integrated production of methane and carbonized biomaterials (biochar, charcoal and carbon fiber) through an effective fractionation of forest biomass.

Project partners are Sveaskog, Bothnia Bioindustries Cluster Piteå Science Park, Erebia, Blatraden and Environmental Technical Center Umeå.

Period: 2017-2020
Conclusions

- The hybrid organosolv pretreatment/fractionation allows the fractionation of spruce biomass with efficient lignin and hemicellulose removal.

- High cellulose content solids, up to 72% can be obtained.

- High lignin recovery yields up to 70% are possible.

- Compatible with ethanol-centric and multiproduct-centric processes.