Biorefinery of Sustainable Biomass from Land and Sea

W.J.J. Huijgen
J.W. van Hal

November 2014
ECN-L--14-068
Biorefinery of Sustainable Biomass from Land and Sea

Technology Development at ECN

W.J.J. Huijgen & J.W. van Hal

Maarssen
November 5th, 2014
Energy research Centre of the Netherlands (ECN)

• What do we do:
  – ECN develops market driven technology and know-how to enable a transition to a sustainable energy society

• Business units:
  – Biomass & energy efficiency
  – Solar energy
  – Wind energy
  – Policy studies
  – Environment & energy engineering

ECN
• Independent research institute
• ~600 employees
• Locations:
  - Petten (HQ)
  - Amsterdam
  - Eindhoven
  - Brussels
  - Beijing
Lignocellulosic Biorefinery
Lignocellulose Pretreatment

• Several physical-chemical pretreatment routes to promote enzymatic cellulose hydrolysis under development.

• Main pretreatment routes (demo/commercial-scale):
  – (Dilute) acid pre-treatment.
  – Steam explosion.

• Routes effective for cellulose, however:
  – Lignin ends up in residue (with unconverted sugars, process chemicals, ash, ...).
  – Residue generally only suitable for CHP.

• Alternative:
  – Separation of lignin prior to enzymatic hydrolysis.
  – Preserving native chemical functionalities of lignin.

Harmsen et al. (2010), Literature review of physical and chemical pretreatment processes for lignocellulosic biomass, report ECN-E--10-013.
Lignocellulose Biorefinery

• Aims:
  – Utilisation of >75wt% of biomass.
  – Fractionation of all major constituents in a sufficient quality for valorisation.
  – Including extraction of high-quality lignin for production of materials/chemicals.

Reith et al. (2011) A step towards the development of a biorefinery, NPT procestechnologie, 18(1), 26-28
Organosolv Process

- **ECN process:**
  - Solvents: aqueous ethanol, acetone, ...
  - Typical process conditions: 160-200 °C, 30-120 min, acid catalyst.

- **ECN experience:**
  - Wide range of feedstocks: softwoods, hardwoods and herbaceous biomass.
  - Know-how on optimum process parameters.
  - Multiple process (& solvent) options depending on target products.

Cellulose to Glucose

- High enzymatic digestibility of organosolv cellulose pulps.
- Spin-off organosolv development: Cellulase Saver
  - Method to reduce enzyme costs in production of sugars.
  - Herbaceous biomass.
  - Pretreatment technology independent.

More information:
- www.ecn.nl/technology-transfer.
Cellulose to Isosorbide

- One-pot conversion of (ligno)cellulose to iso-sorbide.
- Low isosorbide yields from unpretreated lignocellulosic biomass.
- Pretreatment key to efficient one-pot conversions.
- High isosorbide yields attained (63%) when using a highly delignified organosolv pulp.

Op de Beeck, B. et al., ChemSusChem 6(1) (2013) 199
Cellulose to 2G Furan Derivatives

- Direct alcoholysis of cellulose to (intermediates for) HMF-ethers.
- Main product: ethylated-glucose (glucosides).

Lignin Applications

**low volume - high value market 10000 €/t**
- specialty chemicals for food, fragrance and pharmaceuticals
- bio-plastics
- alkylphenols
- catechols
- guaiacols
- syringols

**high volume - low value market 100 €/t**
- fuel-additives
- fuel for CHP
- bio-bitumen for green asphalt
- bio-resins for wood-adhesives
- additives for flooring material
- activated carbon, carbon-fibres and carbon-black
- bio-plastics

---

P.J. de Wild et al. (2014) Lignin pyrolysis for profitable lignocellulosic biorefineries, Biofuels, Bioproducts & Biorefining (bioFPR) 8(5), 645-657
Phenol-Formaldehyde Resins

- Successful replacement of phenol by lignin in PF resins.
- Substitution up to 50% w/w (hardwood lignin).

Seaweed Biorefinery
Seaweed Biorefinery

• Development of biorefinery technologies for cultivated seaweeds to produce 3rd generation biofuels & chemicals.

• Large difference in composition between main classes of seaweed (brown, red and green).

• Need to develop specific biorefinery schemes for various types of seaweeds.

• Seaweeds still expensive feedstock → coproduction of high-value specialty chemicals and commodity carbohydrates.
Seaweed Species from the North Sea

*Saccharina lattisima*

*Laminaria digitata*

*Laminaria hyperborea*

*Ulva sp.*

*Alaria esculenta*

*Palmaria palmata*

5/11/2014

NPS 14
Why Seaweeds or Macroalgae?

- Do not compete with food
- Do not compete with any other land use
- Grow in cold seawater
- The fastest growing biomass at our latitude (Kelps)
- Composition complementary for fuel/chemicals production to lignocellulosic biomass & micro-algae.
  - Mainly composed of (specialty) carbohydrates, protein and minerals, e.g.:
    - Brown seaweeds (Kelps): mannitol (sugar alcohol) & alginic acid (thickening & gelling agent).
    - Green seaweeds: ulvans (bioactives) & rhamnose.
    - Red seaweeds: xylans & carrageenan (thickening & gelling agent).

*J.W. van Hal et al. (2014) Opportunities and challenges for seaweed in the biobased economy, Trends in Biotechnology, 32(5), 231-233*
Seaweed Biorefinery Concept

Raw Seaweed → Processing → Primary Biorefinery → Proteins → Chemical Conversion → Energy Carriers

- Sugars
- Fermentation
- Minerals
- Residues
- Energy Conversion

Bulk Chemicals
Example: Biorefinery of Kelps

- Patent filed on mannitol extraction from brown seaweed.

*J. van Hal & W.J.J. Huijgen, Process for mannitol extraction from seaweed, patent application NL 2009482*
**Saccharina tests**

- Harvest June 2013, Galway, Ireland.
  - Huge leaves → cut to ~5 cm pieces for experiments.
  - Moisture: 82-85%.

- Isolation of mannitol & laminarin by extraction with fresh water (1:1).

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>pH</th>
<th>Solids (dw%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RT</td>
<td>5.0</td>
<td>72.2</td>
</tr>
<tr>
<td>80</td>
<td>5.9</td>
<td>70.8</td>
</tr>
<tr>
<td>120</td>
<td>5.6</td>
<td>63.2</td>
</tr>
</tbody>
</table>
From Seaweed to Isomannide

Crude carbohydrates → Purification → Mannitol

Conversion into iso-mannide
Applications of Isomannide

- Isomer of isosorbide
- Interconvertable into other isomers
- Separation based on boiling point possible
- Intermediate for
  - Plasticizers
  - Fuel additives
  - PET replacements
  - Epoxy resins
  - PUR
Summary Seaweed Biorefinery

Cost analysis biorefinery of Kelps:
- Need to valorize multiple components from seaweed
- Seaweed to only biofuels not as attractive → biorefinery
- Profit driver is isomannide
- Based on pay-back time of 2 years, seaweed may cost up to €1000/ton (dry matter)

Challenges ahead:
- Increasing volumetric through-put (seaweeds ~20% dw, diluted streams).
- Early stage of development → scale-up & efficiency improvement.
- Development reliable cultivation & supply chain of seaweeds.
Question?
Further information

Jaap W. van Hal
Innovation Manager Biorefinery
Energy Research Centre of the Netherlands (ECN)
Biomass and Energy Efficiency
P.O. Box 1, 1755 ZG Petten
+31-(0)88-515-4297
vanhal@ecn.nl