Carbohydrates and Furans from Seaweeds for Fuels and Chemicals

Wouter Huijgen, Guido van Hees, Arjan Smit & Jaap van Hal

Stockholm, Sweden
June 12th 2017
Take-home Messages

• Seaweeds: promising complementary feedstock for the biobased economy.

• ECN develops biorefinery processes for each main class of seaweeds with a focus on carbohydrates.

• Furan-based platform chemicals and 3rd generation biofuels can be produced from seaweed carbohydrates.
Furans

• Class of compounds with a furan-ring.
  • Reaction product of carbohydrate dehydration.

• Generally considered promising biobased building block.

• Challenge:
  • Balance between (acid-catalyzed) furan formation and degradation.

(Biorefining of) Seaweeds
Why Seaweeds?

• Large potential
  – Fastest growing biomass at the latitude of The Netherlands.
  – Earth’s surface ~70% water.

• No competition for land use
  – Opportunity for simultaneous production of food, chemicals and fuels.

• Chemical composition
  – Complementary to micro-algae and lignocellulose.
  – Comprised of (specialty) carbohydrates, proteins and ash.
  – Various potential applications of biorefinery products, including biofuels.
Seaweed Biorefinery

- ECN: Development of biorefinery processes for cultivated seaweeds to produce 3rd generation biofuels & bulk chemicals.

- Large compositional differences between main classes of seaweed (brown, red and green).

- Development of specific biorefinery schemes for each type of seaweed.

Production of isomannide from Kelp (mannitol isolation, purification, conversion).

ECN Focus: North Sea Native Seaweeds

- Saccharina latissima
- Laminaria digitata
- Ulva sp.
- Palmaria palmata

BROWN, GREEN, RED
Red Macroalgae - *Palmaria*
**Palmaria palmata**

- **Carbohydrate composition:**
  - Rich in xylose, galactose and glucose.
  - Main structural carbohydrate:
    - Xylan polymer (typically ~30wt%).
    - Floridoside (glycerol-galactose heteroside).

- **Research approach:**
Saccharification of *P. palmata*

- **Effective saccharification:**
  - Fresh *P. palmata*
  - Catalyst: HCl or commercial xylanase.
  - Residual solid: 33-36 dw%.
  - Yields monomers using HCl:
    - Xylose up to 85%
    - Galactose up to 70%.

- **Product liquors:**
  - Up to 35 g/kg monosaccharides.

---

*W.J.J. Huijgen et al. (2017) Biorefining of the red seaweed Palmaria palmata for the production of biobased chemicals and biofuels (submitted).*
Xylose to furfural

- **Single phase (H$_2$O):**
  - Optimisation of process parameters.
  - Brønsted (HCl) and Lewis (SnCl$_4$) catalysts: at optimum T similar performance.
  - Small positive effect of NaCl on furfural yield.
  - Furfural yield obtained max 60%.

- **Biphasic (H$_2$O/organic):**
  - Furfural extracted in-situ to prevent degradation.
  - Various extractants tested. Toluene selected for stability and minimal solvent losses.
  - Furfural yield increases to near theoretical (HCl).
**P. palmata** to furfural

- **Single step:**
  - Water:
    - Furfural yield 38% (0.2M HCl, 1h, 170 °C).
  - Water-toluene:
    - Furfural yield 75% (0.3M HCl / 0.9M NaCl, 1h, 170 °C, 10wt% *P. palmata*).

- **Two steps:**
  1. Hydrolysis of seaweed polysaccharides to monomers.
  2. Dehydration of xylose to furfural in hydrolysate.
    - Biphasic process hydrolysate/toluene 1:2 v/v.
    - No additional acid used.
    - Overall yield from *P. palmata* to furfural: 98%.
    - No negative matrix effects observed.
Green Macroalgae - *Ulva*
Ulva lactuca

- Why Ulva?
  - Unique carbohydrate composition, incl. rhamnose.
    - Ulvan (rhamnose, xylose, glucuronic acid, iduronic acid).
    - Cellulose (glucose).
    - Dehydration of rhamnose yields 5-methylfurfural.
    - Directly applicable as biofuel (additive).

- Research approach:
Saccharification *Ulva lactuca*

- Hydrolysis of polysaccharides to monomeric carbohydrates demonstrated with fresh seaweed.
- Monomeric yields of major carbohydrates (Glc, Rham, Xyl) of at least 85% possible.
- However, low sugar concentrations in product liquors (~5 g/kg) due to low carbohydrate content seaweed.

---

F. Groenendijk (Eds) (2016) North-Sea-Weed-Chain, Sustainable seaweed from the North Sea; an exploration of the value chain, report IMARES C055/16.

Rhamnose to 5-methylfurfural

- Not much known in literature about dehydration of rhamnose.

- Similar approach and conditions applied as for *P. palmata*.

- Direct HCl-catalyzed dehydration in water:
  - Low yield of 5-methylfurfural (max 22%).

- Biphasic approach with toluene:
  - Substantial yield increase (up to 66%).

1h, 0.3M HCl, 0.5M NaCl, water/toluene
**U lactuca to 5-methylfurfural**

- Conversion of *U lactuca* more challenging than *P palmata*:
  - Poor 5-methylfurfural yield achieved directly in water: 25%.
  - Biphasic system with toluene: 36%.
  - Two-step approach (saccharification & dehydration): 56%.

- Simultaneous conversion of other ulvan building blocks (such as xylose).
Conclusions & Future
Conclusions

• Effective saccharification of *P. palmata* and *U. lactuca* feasible.

• Effective conversion of seaweed carbohydrates to furans feasible when applying in-situ extraction.

• *P. palmata* most suited seaweed for carbohydrate or furan production.
  – Higher carbohydrate content.
  – Furfural yields higher than 5-methylfurfural yields.

<table>
<thead>
<tr>
<th>Process / yields</th>
<th><em>P. palmata</em>: Xyl → furfural</th>
<th><em>U. lactuca</em>: Rham → 5-methylfurfural</th>
</tr>
</thead>
<tbody>
<tr>
<td>One-step approach in H₂O</td>
<td>38</td>
<td>25</td>
</tr>
<tr>
<td>One-step approach in H₂O/toluene</td>
<td>75</td>
<td>36</td>
</tr>
<tr>
<td>Two-step approach with H₂O/toluene</td>
<td>98</td>
<td>56</td>
</tr>
</tbody>
</table>
Challenges Ahead

• EU-H2020 MacroFuels project:
  – Upscaling seaweed biorefinery processes for application tests.
  – Purification and concentration of process intermediates.
  – Production of furan fuels and combustion tests in engine.

• Seaweed biorefinery in general:
  – Priority: reduction of feedstock cost!
    – Early stage of development → efficiency improvement.
  – Biorefining of seaweed:
    – Development of efficient storage concepts.
    – Co-valorization of other constituents of seaweed.
      – Proteins.
      – Other carbohydrates.
Thank you for your attention!

More information:

huijgen@ecn.nl

This work was carried out under the EU-H2020 project MacroFuels (grant agreement no 654010).

Acknowledgements:

Esther Cobussen
Ben van Egmond
Lars Brunner
Adrian Macleod
Robert-Jan van Putten