Carbohydrates and furans from seaweeds for fuels and chemicals

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Take-home Messages

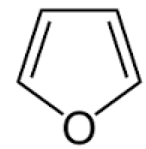
- Seaweeds: promising complementary feedstock for the biobased economy.
- ECN develops biorefinery processes for each main class of seaweeds with a focus on carbohydrates.
- Furan-based platform chemicals and 3rd generation biofuels can be produced from seaweed carbohydrates.

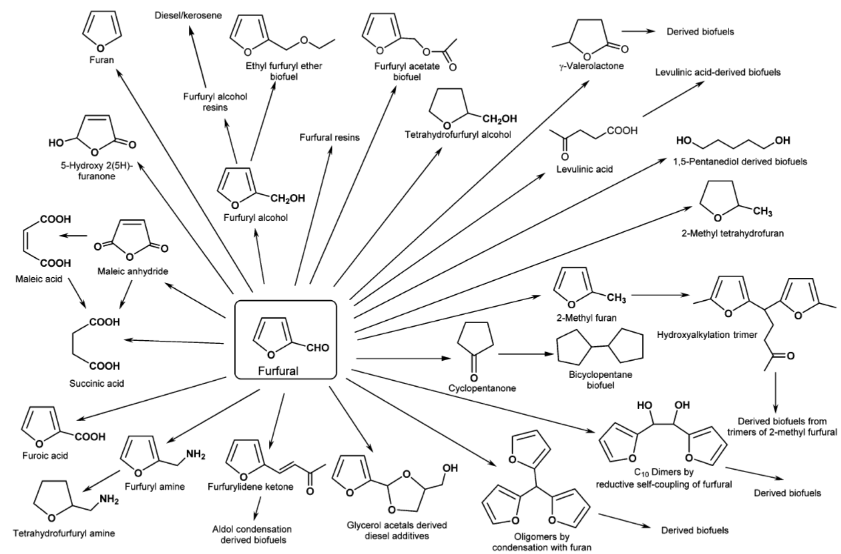
Furans

- 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.



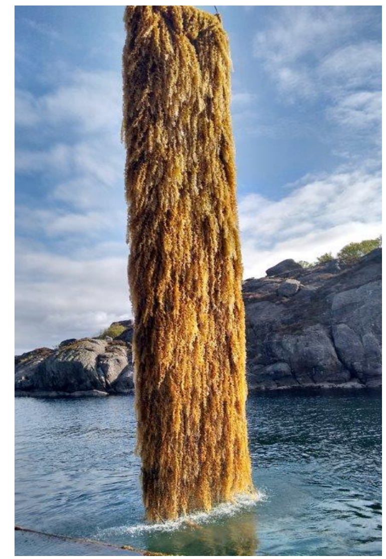


R. Mariscal *et al*. *Energy Environ. Sci.* **2016,** *9* (4), 1144-1189.

(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).

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

ECN Focus: North Sea Native Seaweeds

BROWN

Saccharina latissima

Laminaria digitata

GREEN

Ulva sp.

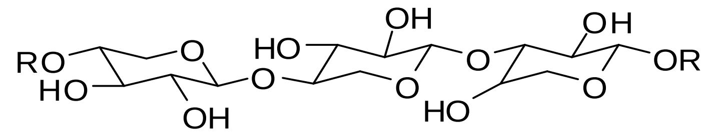
RED

Palmaria palmata

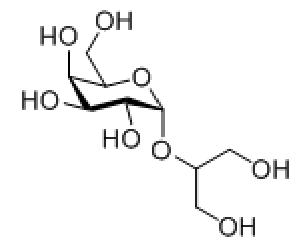
Red Macroalgae - *Palmaria*

Palmaria palmata

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

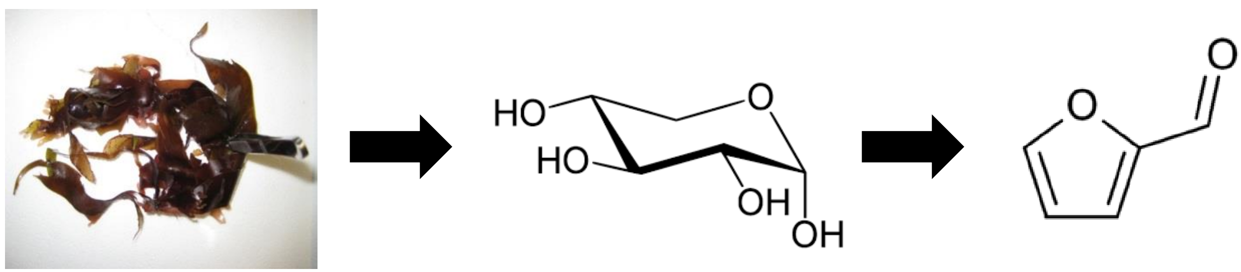


Xylan (1,3 and 1,4 linkage)



Floridoside

- Research approach:

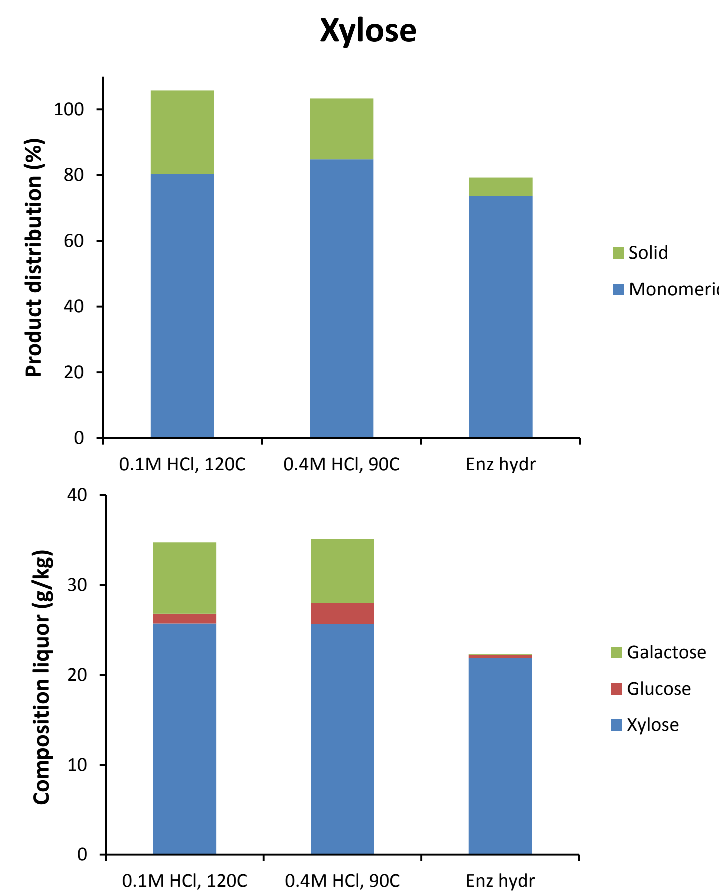


P. palmata xylose furfural

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.

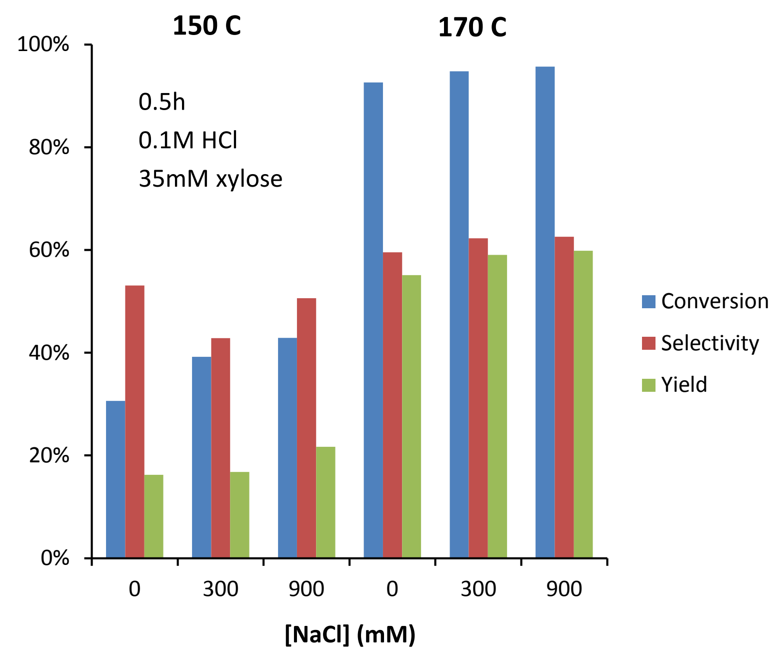


W.J.J. Huijgen et al. (2017) Biorefining of the red seaweed Palmaria palmata for the production of biobased chemicals and biofuels (submitted).

Xylose to furfural

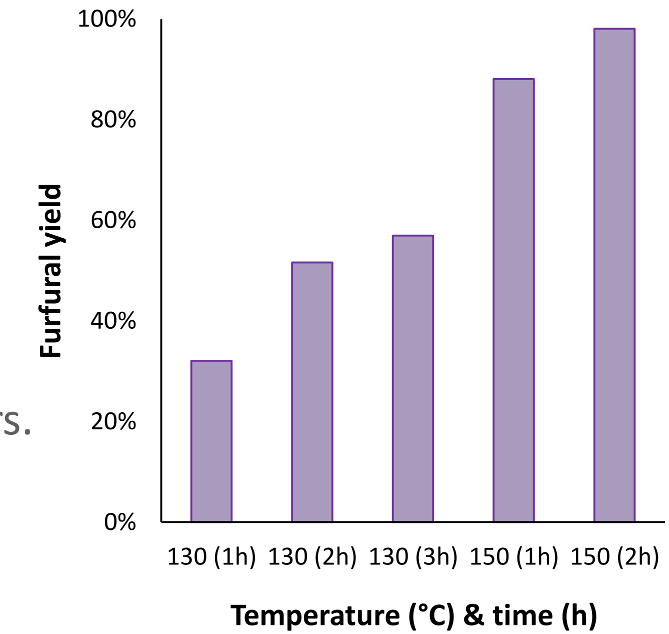
- Single phase (H_2O):
  - Optimisation of process parameters.
  - Brønsted (HCl) and Lewis ($SnCl_4$) catalysts: at optimum T similar performance.
  - Small positive effect of NaCl on furfural yield.
  - Furfural yield obtained max 60%.

- Biphasic (H_2O/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*).

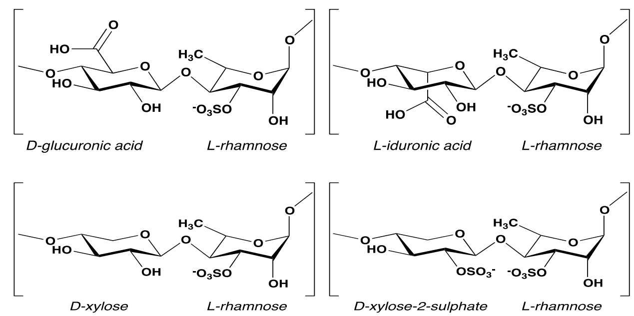


- Two steps:
  1. Hydrolysis of seaweed polysaccharides to monomers.
  2. Dehydration of xylose to furfural in hydrolysate.
     - Biphasic process hydrolysate/toluene 1:2 v/v.
     - No additional acid used.
  - Overall yield from *P. palmata* to furfural: 98%.
  - No negative matrix effects observed.

Green Macroalgae - *Ulva*

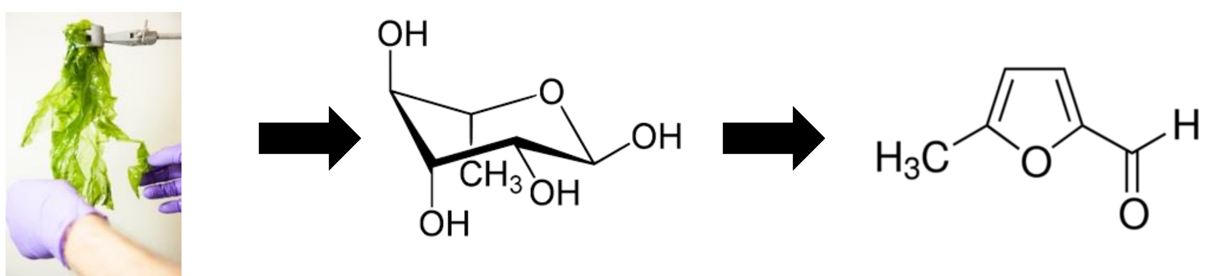
Ulva lactuca

- 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).



Ulvan

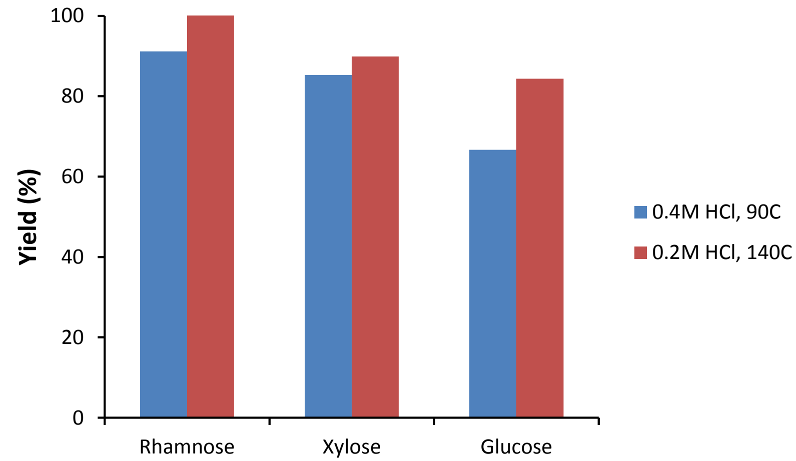
- Research approach:



Ulva lactuca rhamnose 5-methylfurfural

Saccharification *Ulva lactuca*

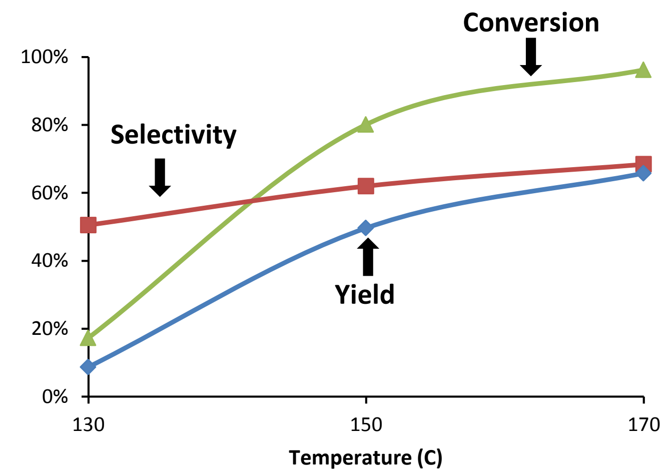
- Hydrolysis of polysaccharides to monomeric carbohydrates demonstrated with fresh seaweed.
- Monomeric yields of major carbohydrates (Glc, Rham, Xyl) of at least 85% possible.
- However, low sugar concentrations in product liquors (~5 g/kg) due to low carbohydrate content seaweed.



F. Groenendijk (Eds) (2016) North-Sea-Weed-Chain, Sustainable seaweed from the North Sea; an exploration of the value chain, report IMARES C055/16 .
W.J.J. Huijgen et al. (2016) Development of Seaweed Biorefineries for Fuels and Chemicals, 24rd EUBCE, Amsterdam, The Netherlands.

Rhamnose to 5-methylfurfural

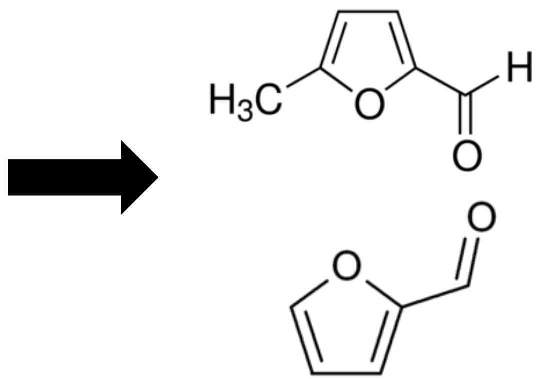
- Not much known in literature about dehydration of rhamnose.
- Similar approach and conditions applied as for *P. palmata.*
- Direct HCl-catalyzed dehydration in water:
  - Low yield of 5-methylfurfural (max 22%).
- Biphasic approach with toluene.
  - Substantial yield increase (up to 66%).



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

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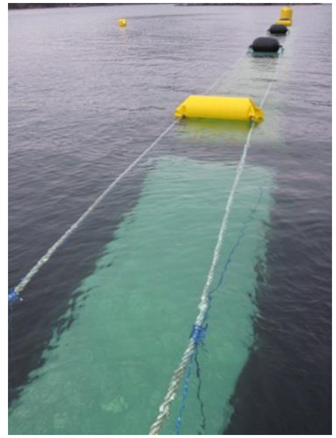
Conclusions

- 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.

Process / yields	***P. palmata:*** **Xyl → furfural**	***U. lactuca:*** **Rham → 5-methylfurfural**
One-step approach in H_2O	38	25
One-step approach in H_2O/toluene	75	36
Two-step approach with H_2O/toluene	98	56

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!

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