DIRECT CONVERSION OF SEAWEED TO BIOFUELS.

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Acknowledgement

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The Dutch Weed Burger

The Dutch Seaweed Programme

MACROFUELS

- Seaweed cultivation area 5,000 km^2 (<10 % of the NL area of the North Sea @ 57,000 km^2)
- Integration with off-shore wind parks & (other) aquaculture operations
- Energy potential up to 350 PJ_{th} (25 Mton dry biomass per year)
- Report: ECN-C—05-008

What does ECN do?

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- 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
- Per 1/4/2018, ECN will be part of TNO.

ECN

- Independent research institute
- ~500 employees
- Locations:
  - Petten (HQ)
  - Amsterdam
  - Eindhoven

MacroFuels

The Project

www.macrofuels.eu

MacroFuels Key Facts

MACROFUELS

- Funded under the ‘Low Carbon Economy’ sub-topic in Horizon 2020
- Started in January 2016
- Duration: 48 months
- Budget: ~ 6 million Euros
- Consortium: 11 partners from six EU countries, incl. RTD, universities, SMEs, large enterprises and sole proprietors

MacroFuels Consortium

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Main Objective

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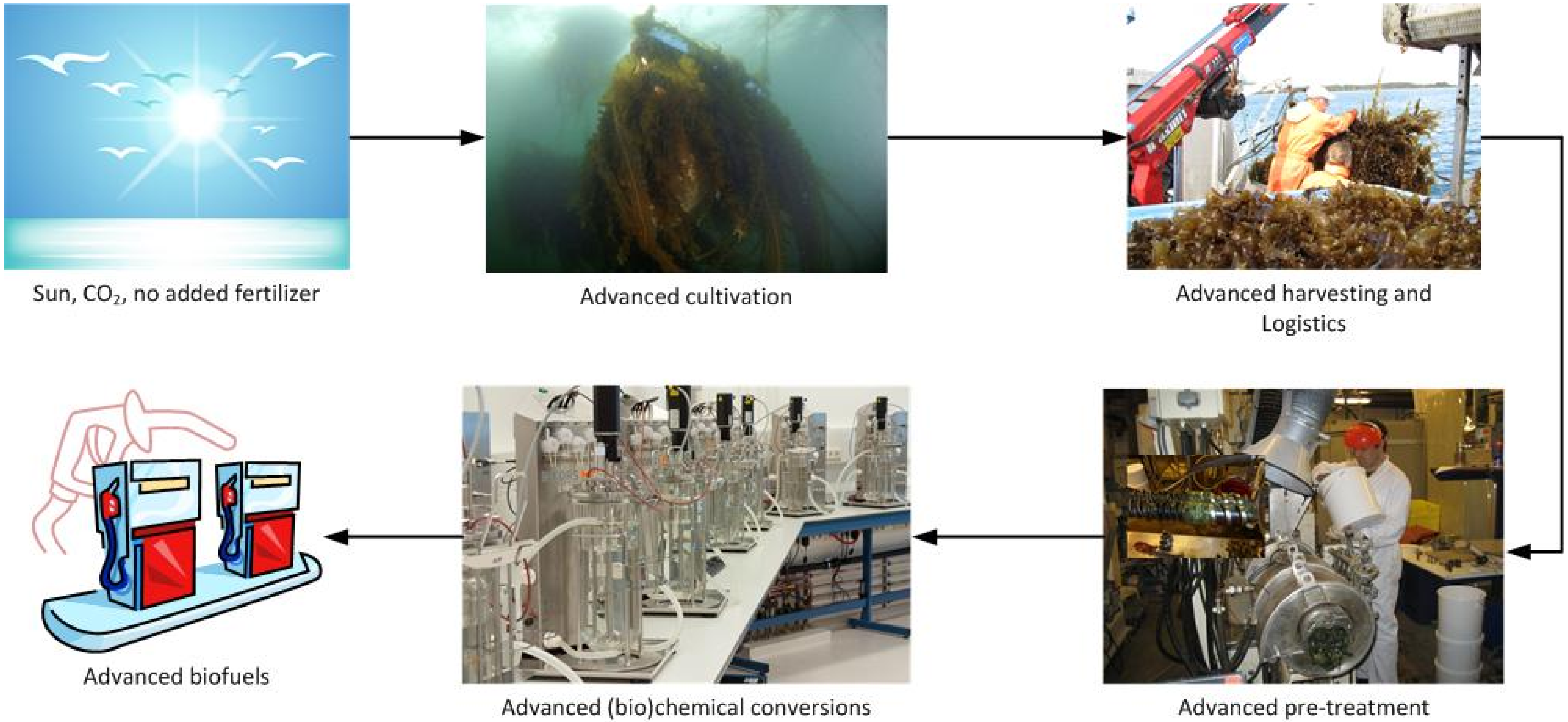
MacroFuels aims to develop technologies to produce advanced liquid biofuels from **seaweed for** transportation i.e. **aviation, cargo and**

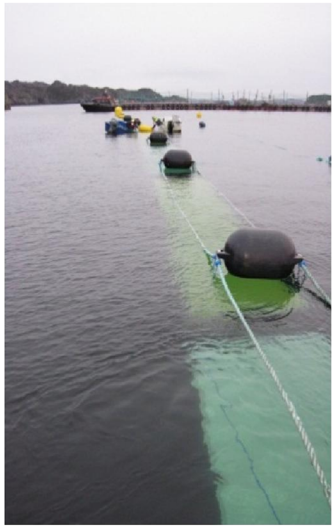
truck fuels.

The targeted biofuels are ethanol, butanol, furanics and biogas.

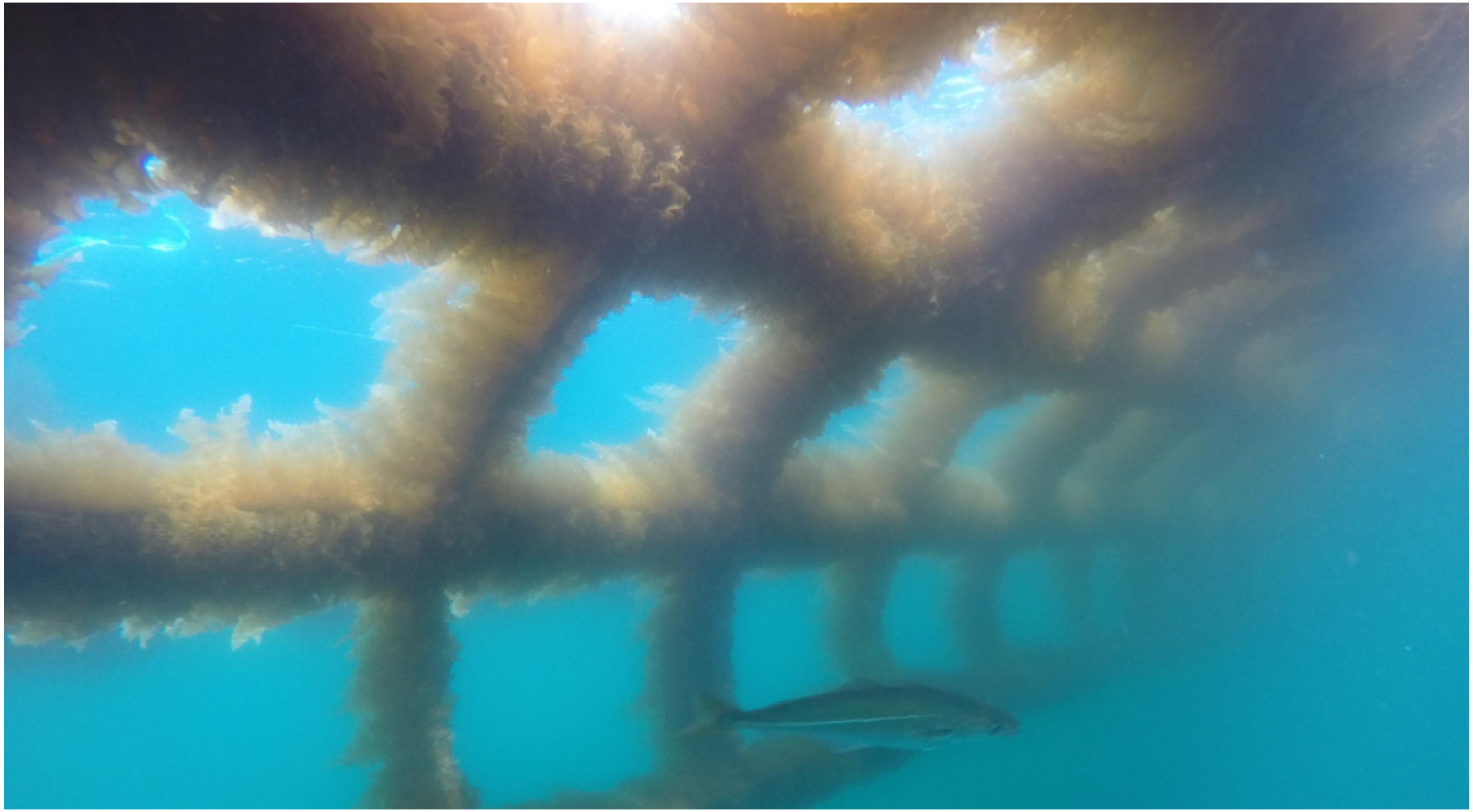
MacroFuels seaweed to biofuels chain



Building on the At~SEA project



Advanced 2D substrates



THE SYSTEM AT SEA

Drying the harvest

Our Technical Objectives

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Improved ethanol and ABE (Acetone, Butanol and Ethanol) production

- 90% conversion of hydrolysed C6 sugars to ethanol
- 90 % conversion of hydrolyse and polymeric algal sugars to ABE production
- To efficiently convert left-over carbon in residuals to methane

Thermochemical conversion of algal sugars to furan

- I.e.: Conversion of alginic acid to furans

What are Furans?

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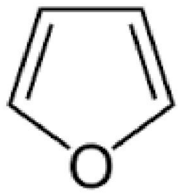
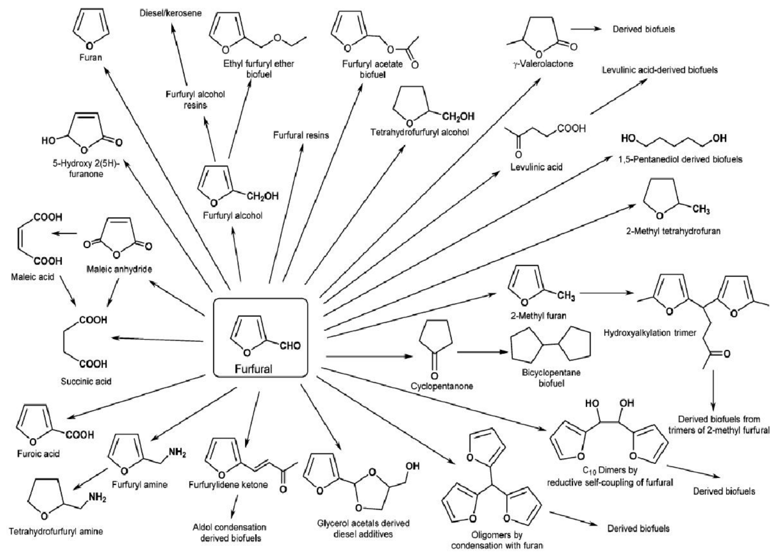
- Class of compounds with a furan-ring.
  - Reaction product of carbohydrate dehydration.
- Generally considered promising biobased building block.
- Challenge:
  - Balance between (acid-catalyzed) furan formation and degradation.

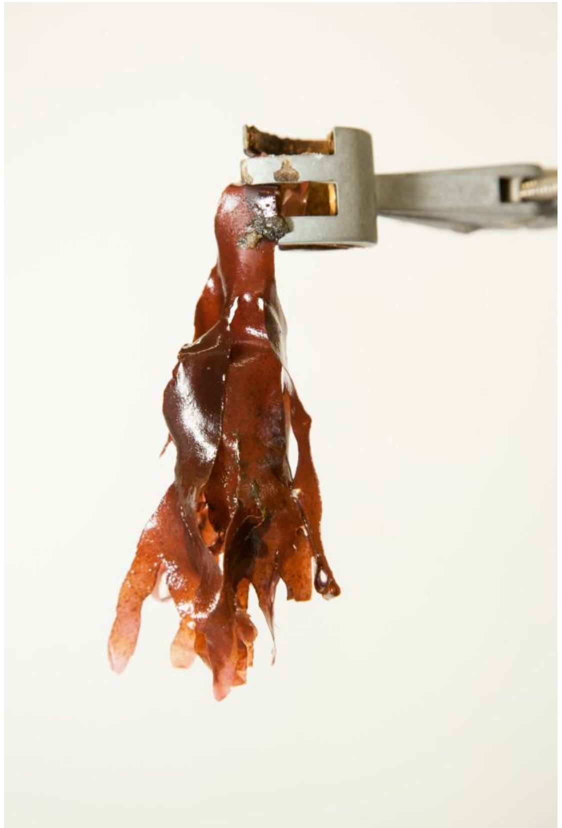




R. Mariscal *et al*. *Energy Environ. Sci.* **2016,** *9* (4), 1144-1189.

Red Macro Algae

Palmaria palmata (Dulse)



About *Palmaria palmata*

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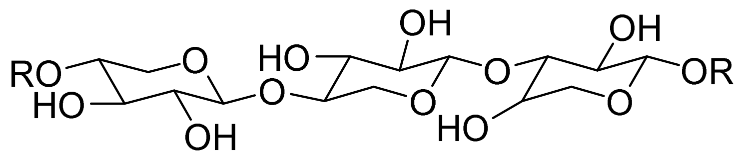
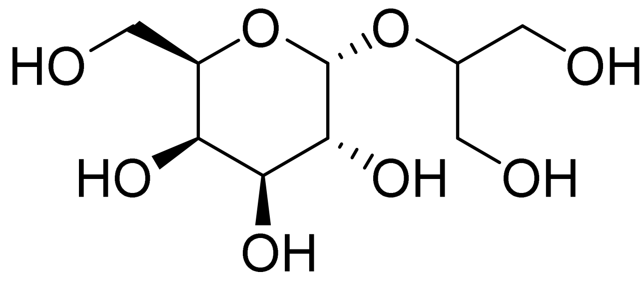
- Carbohydrate composition:
  - Rich in xylose, galactose and glucose.
  - Main structural carbohydrate:
    - Xylan polymer (typically ~30wt%).
    - Floridoside (glycerol-galactose heteroside)

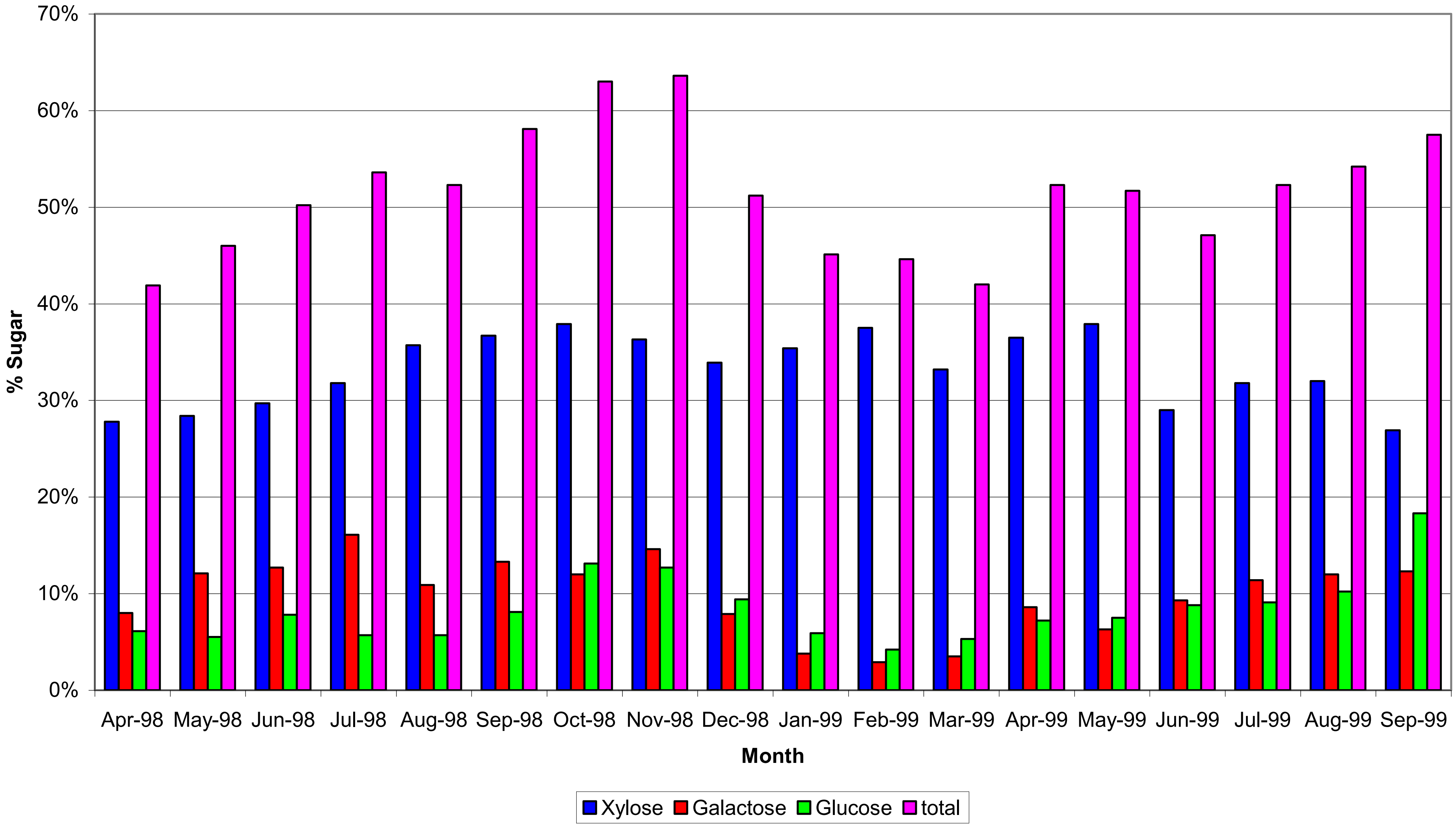


Xylan (1,3 and 1,4 linkage)

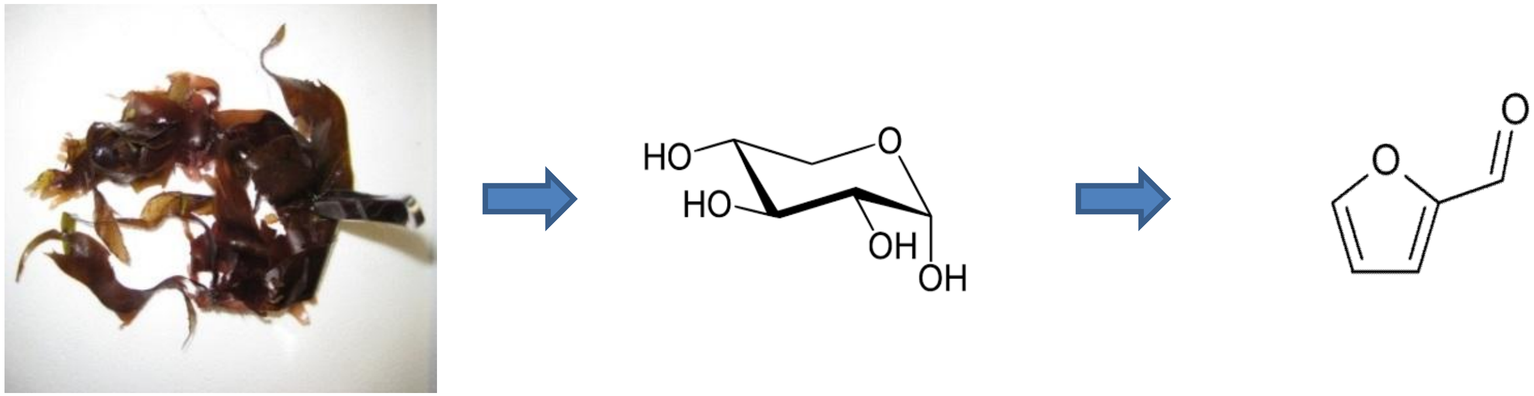


Floridoside

Total Carbohydrate compostion of Palmaria Palmata



Forming Furans



Approach

- Effect of Na/KCl on conversion
- Effect of Lewis Acid
  - No beneficial effect seen cf. HCl
- Bi-Phasic
  - N-Butanol, not effective
  - MIBK, decomposes
  - Ethyl Butyrate, decomposes
  - Toluene, CF pyrolysis gasoline

Saccharification of *P. palmata*

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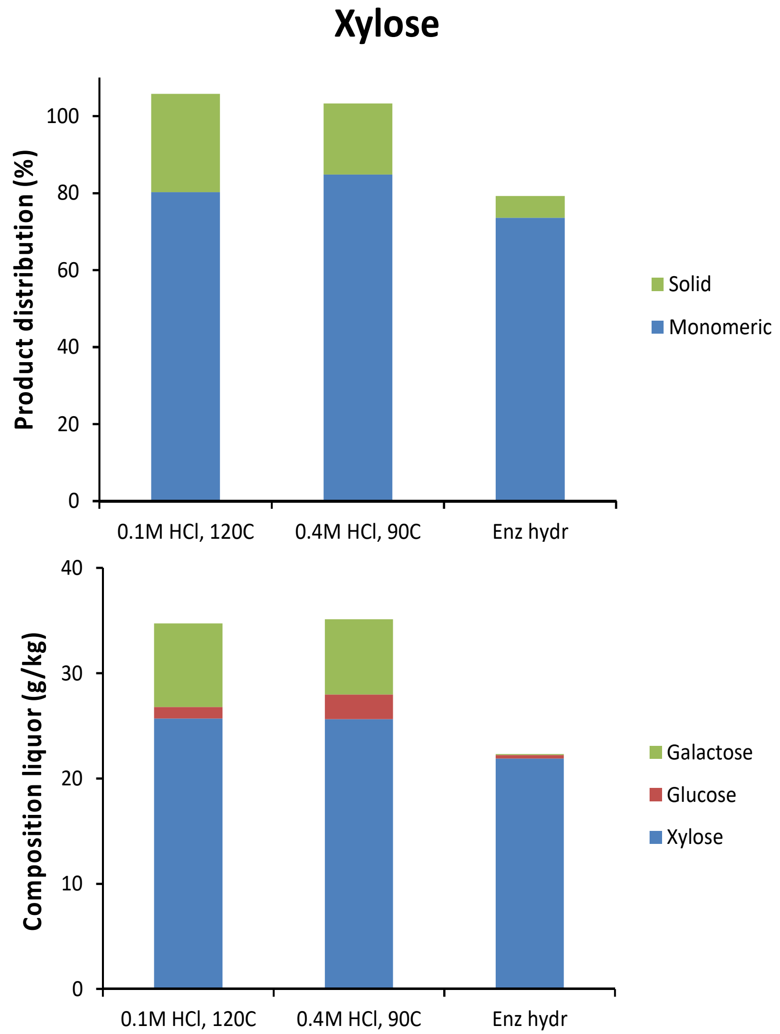
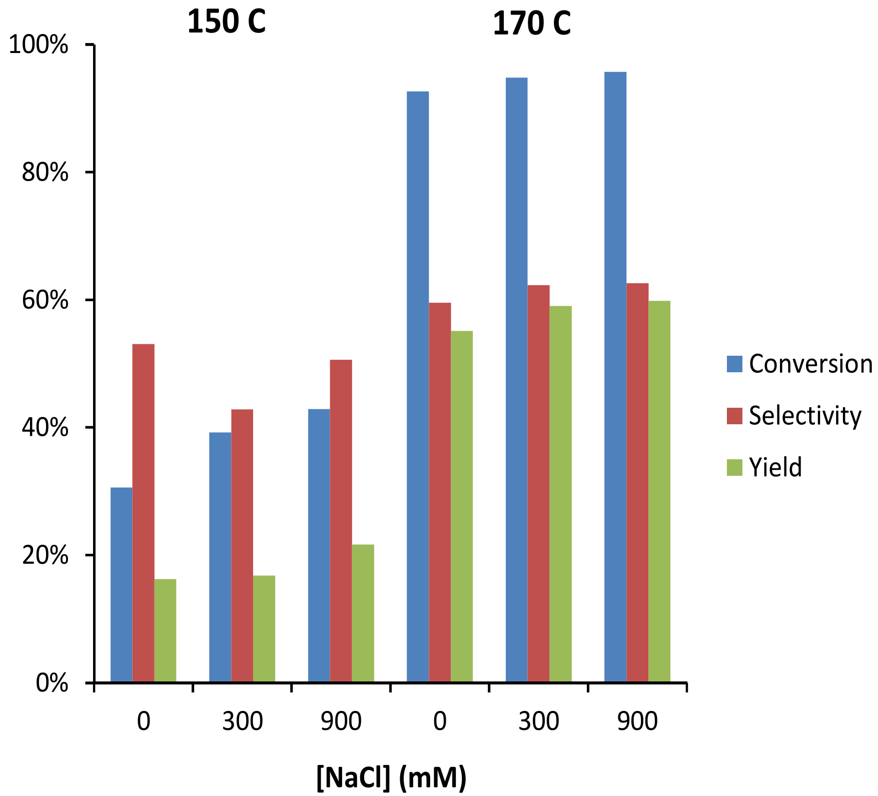
- Effective saccharification:
- Fresh *P. palmata*
- Catalyst: HCl or commercial xylanase.
- Residual solid: 33-36 dw%.
- Yields monomers using HCl:
  - Xylose up to 85%.
  - Galactose up to 70%.
- Product liquors:
  - Up to 35 g/kg monosaccharides.



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).



In one step!

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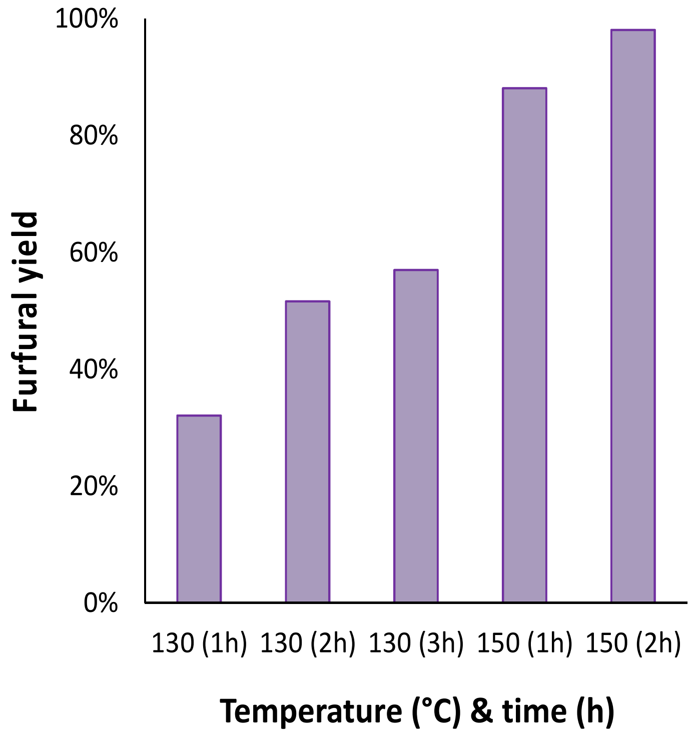
- Single step:
  - Water:
    - Furfural yield 38% (0.2M HCl, 1h, 170 °C).
  - Water-toluene:
    - Furfural yield 75% (0.3M HCl / 0.9M NaCl, 1h, 170 °C, 10wt% *P. palmata*).
- Two steps:
  - Hydrolysis of seaweed polysaccharides to monomers.
  - Dehydration of xylose to furfural in hydrolysate.
    - 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.

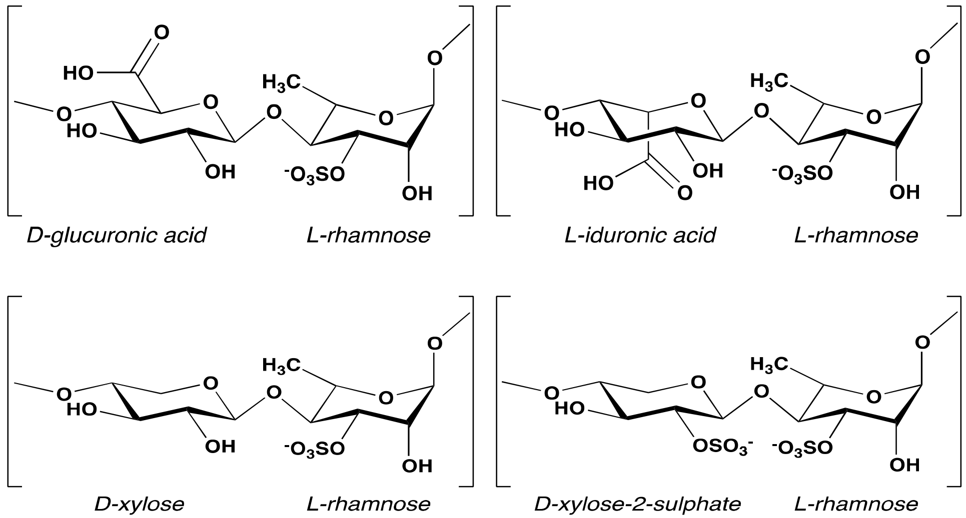


Green Macroalgae

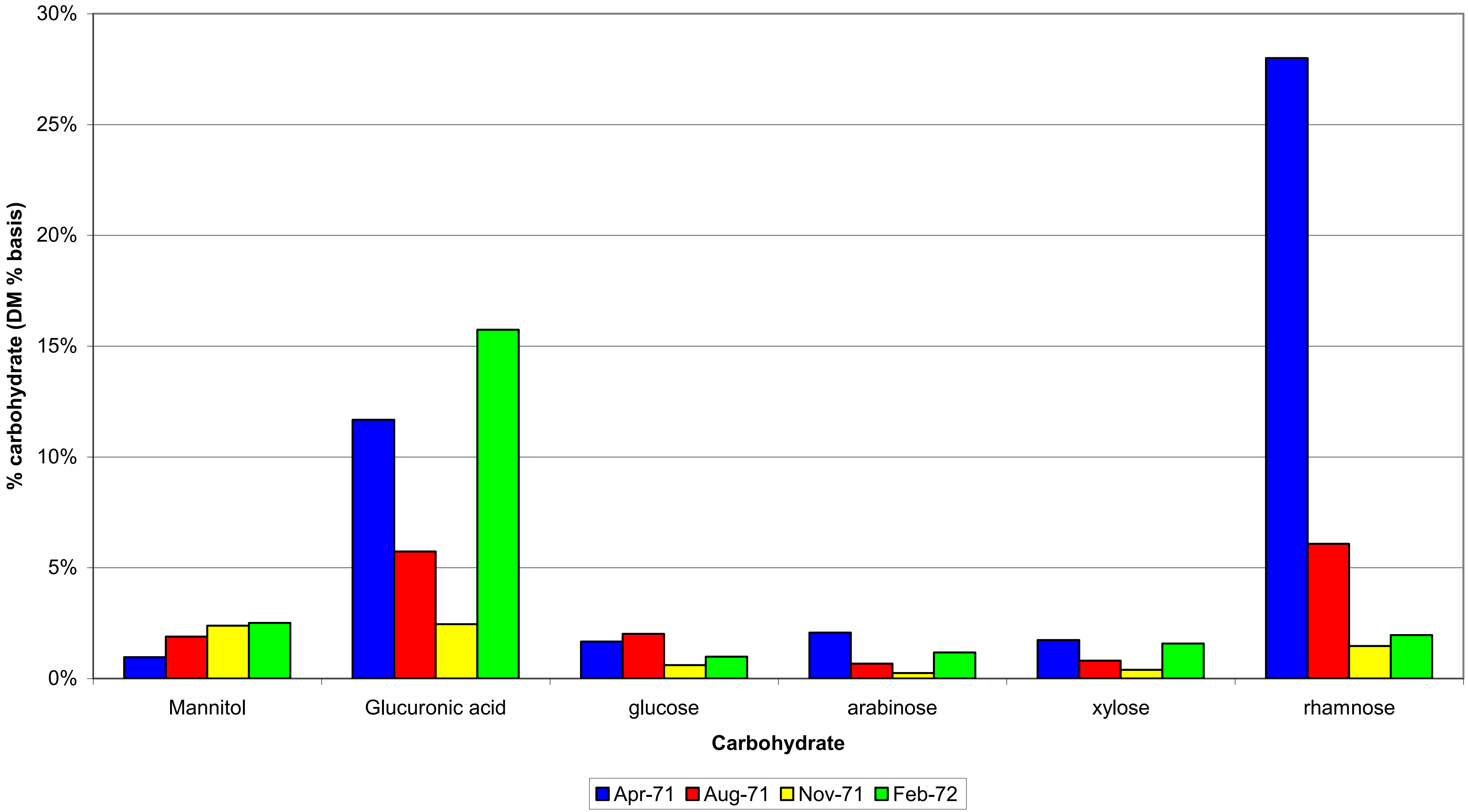
Ulva sp.

About *Ulva lactuca*

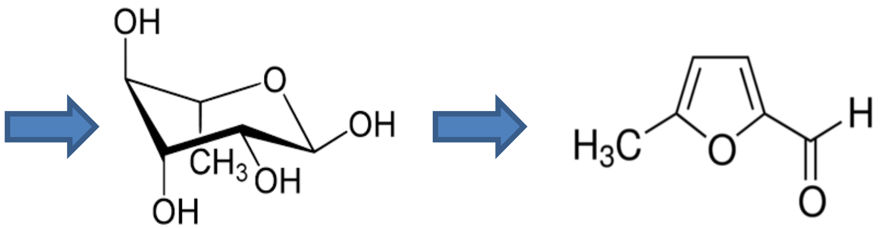
- Why *Ulva*?
  - Unique carbohydrate composition, incl. rhamnose.
  - Ulvan (rhamnose, xylose, glucuronic acid, iduronic acid).
  - Cellulose (glucose).
  - Dehydration of rhamnose yields 5-methylfurfural.
  - Directly applicable as biofuel (additive).



Ulva Lactuca carbohydrate seasonal composition changes



Forming 5-methyl furfural

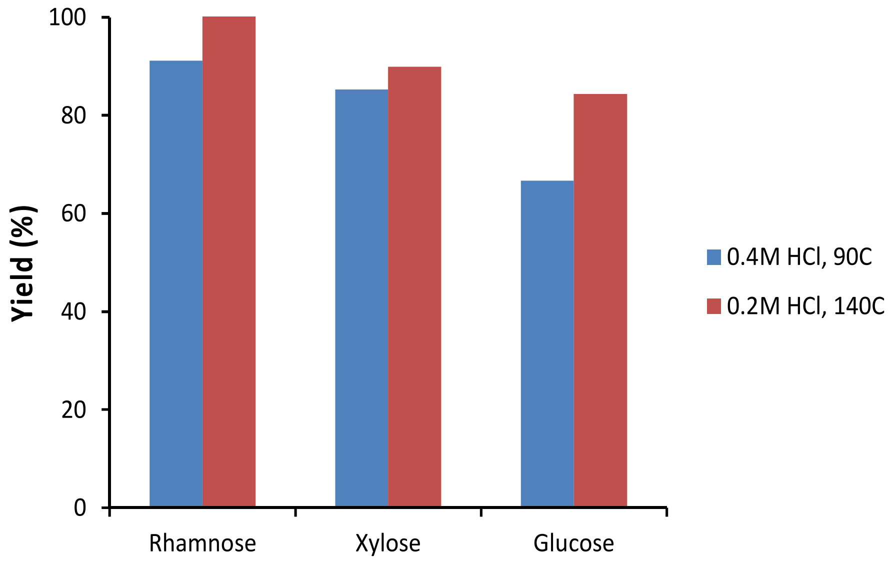


rhamnose 5-methylfurfural

Ulva lactuca

Saccharification *Ulva lactuca*

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



Rhamnose to 5-methylfurfural

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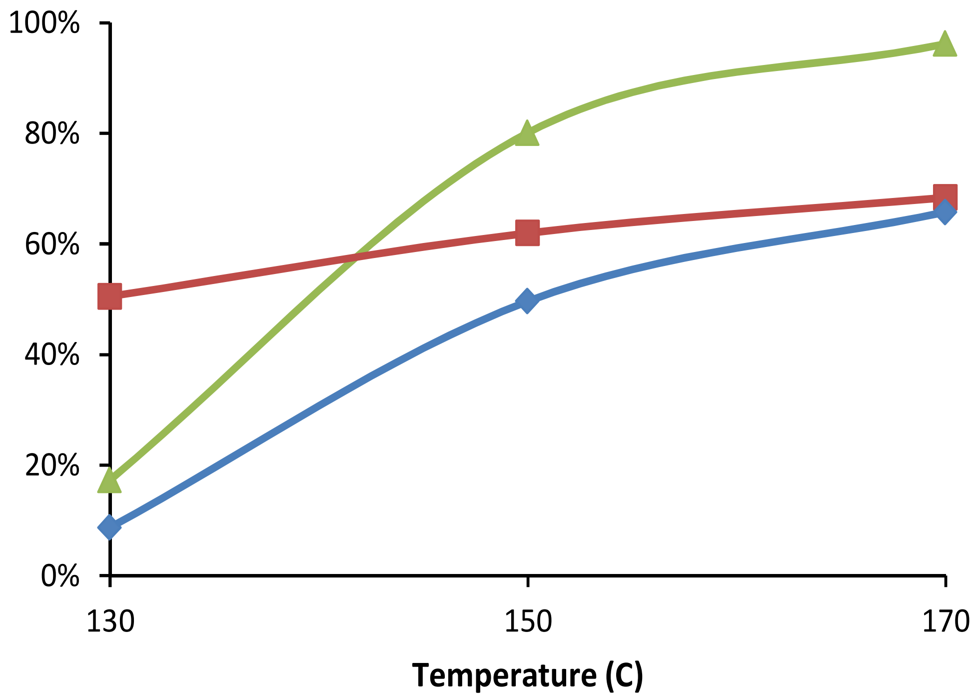
- Scant information dehydration of rhamnose in the literature.
- Similar approach and conditions applied as for *P. palmata*.
- Direct HCl-catalyzed dehydration in water:
- Low yield of 5-methylfurfural (max 22%).



1h, 0.3M HCl, 0.5M NaCl, water/toluene

U. lactuca to 5-methylfurfural

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- 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).

In pictures

Conclusions

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- 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.

In numbers

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

Thank for your attention!
Questions?

Publications:

https://www.ecn.nl/publications/

http://www.macrofuels.eu

http://www.macrocascade.eu

http://www.noordzeeboerderij.nl

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