

Process Development for Seaweed Biorefineries

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June 2015

ECN-L--15-042



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Vienna, Austria

2nd June 2015

Contents

- ECN
- Introduction
- Examples biorefining of seaweeds:
 - Red macroalgae: *Palmaria palmata*
 - Brown macroalgae: Kelps
- Seaweed storage
- Summary and Outlook

Energy research Centre of the Netherlands (ECN)



- What do we do:
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 - Solar energy
 - Wind energy
 - Policy studies
 - Environment & energy engineering



ECN

- Independent research institute
- ~550 employees
- Locations:
 - Petten (HQ)
 - Amsterdam
 - Eindhoven
 - Brussels
 - Beijing

(Biorefining of) Seaweeds

Seaweed Biorefinery

- Development of biorefinery technologies for cultivated seaweeds to produce 3rd generation biofuels & chemicals.
- Large compositional differences between main classes of seaweed (brown, red and green).
- Need to develop specific biorefinery schemes for various types of seaweeds.
- Seaweeds still expensive feedstock → cascading biorefinery approach for coproduction of high-value specialty and commodity chemicals.



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

Seaweeds Native to the North Sea



Saccharina latissima



Laminaria digitata



Laminaria hyperborea



Ulva sp.

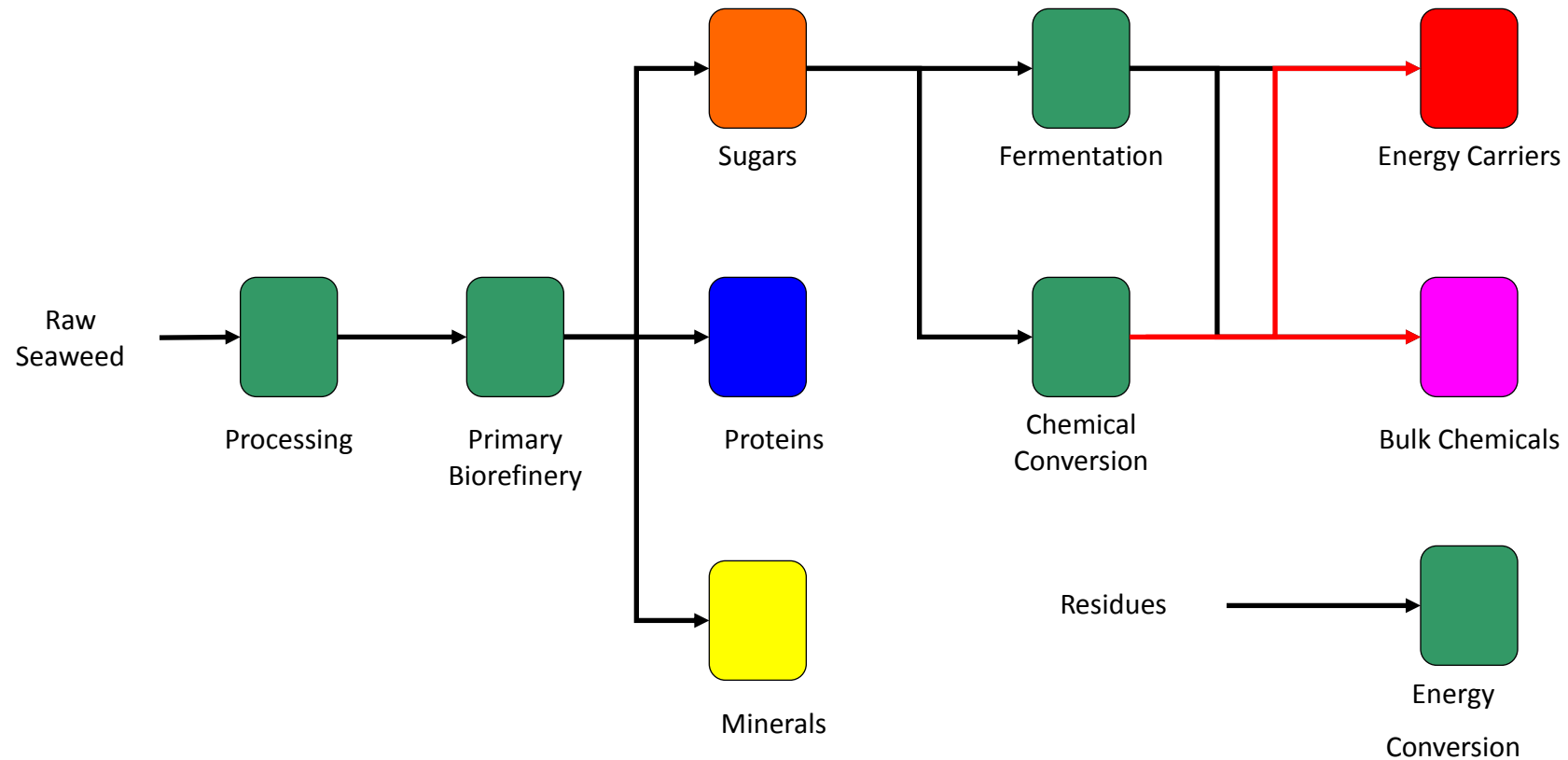


Alaria esculenta



Palmaria palmata

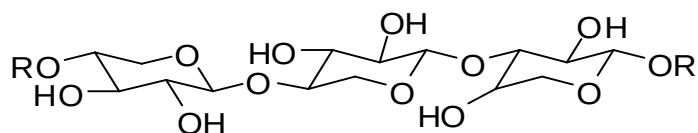
Seaweed Biorefinery Concept



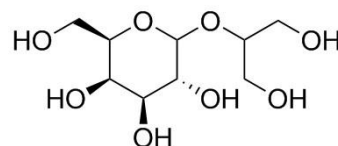
Example: *Palmaria palmata*

Palmaria palmata

- Red seaweed.
- Rich in carbohydrates xylose, galactose and glucose.



Xylan (1,3 and 1,4 linkage)

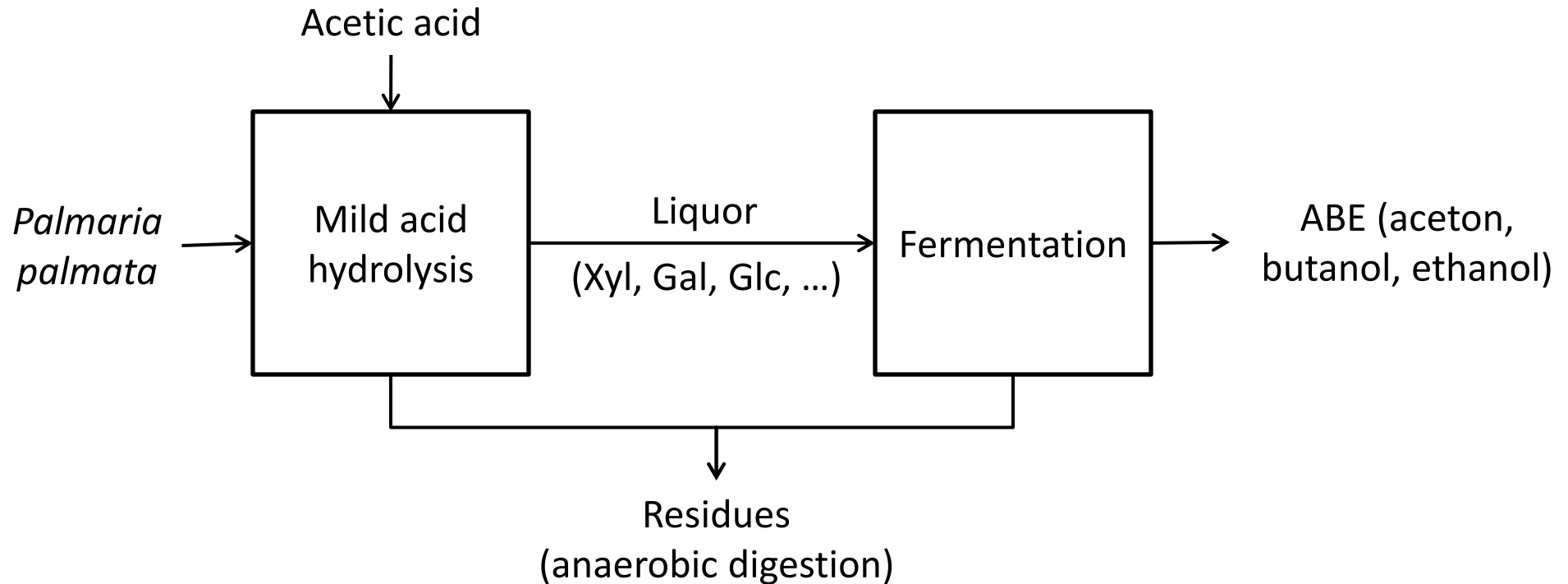


2-O-D-glycerol-α-D-galactopyranoside



	Carbohydrates				Proteins	Ash		Dw (% ar)
	Galactose	Glucose	Xylose	Glycerol				
Composition specific batch (dw%)	14.2	6.9	30.3	6.9	10.8	12.8		17.7

Palmaria Biorefinery Scheme



Hydrolysis of fresh *Palmaria*

- *Palmaria* harvested in Ireland in July and processed within one week.
- Input (20L autoclave):
 - 5 kg *Palmaria* (~1 kg d.w.)
 - 1:1 HOAc solution (0.1M acetic acid, 100 °C, 2hrs).
- Red seaweed turned into green 'soup'.
 - Solids recovery 51.6% dw.
 - Yield xylose ~45% & galactose ~60%.
 - Carbohydrates present in liquor as oligomers.



Fermentation Hydrolysates to ABE

- Microorganism: *Clostridium beijerinckii*
- Fermentation conditions:
 - Anaerobic, 37°C, 50mL serum flasks.
- Cultures:
 - *Palmaria palmata* extract (~0.1 M HOAc).
 - *Palmaria* extract pre-incubated with enzyme GC220 to hydrolyze oligomers (50°C, 24 h).

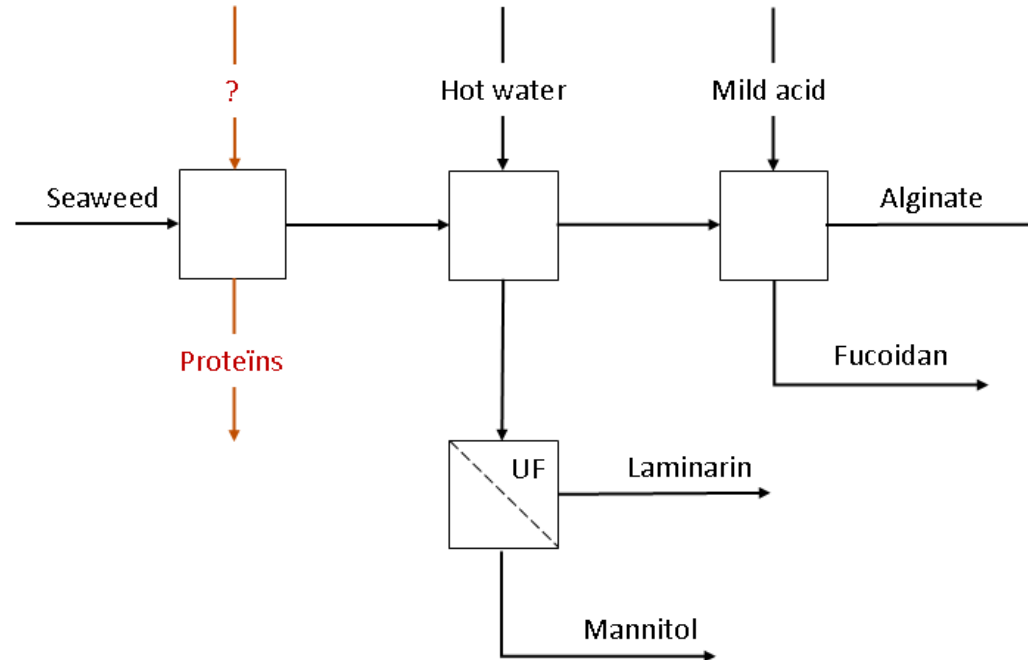


Monosugars and products concentrations (g/L)

	Extract	Extract + GC220
t=0 h		
Glucose	0	2.7
Xylose	0.8	8.3
Galactose	0.6	0.4
Acetic Acid	4.0	3.3
t=250 h		
Glucose	0.0	0.0
Xylose	12.0	1.6
Galactose	0.0	0.0
Acetic Acid	1.0	1.7
ABE	0.0	3.8
Butyric Acid	6.9	3.0

Brown Macroalgae - Kelps

Biorefinery of Kelps

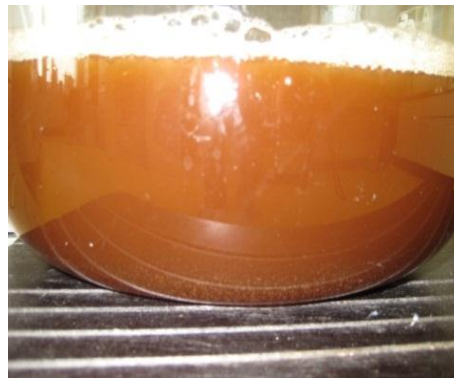


- Mannitol extraction from brown seaweed.
- UF separation mannitol and laminarin successful.
- Alginate isolation from extracted solid residue proven.

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

Saccharina tests

- Harvest June, 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).



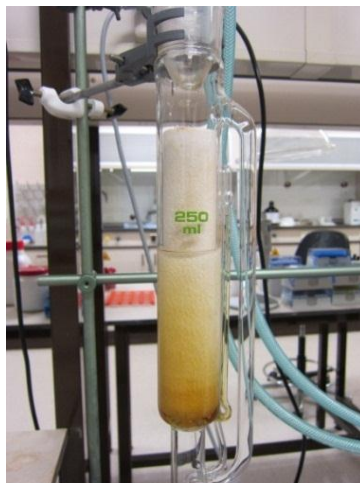
T (°C)	pH	Solids (dw%)
RT	5.0	72.2
80	5.9	70.8
120	5.6	63.2



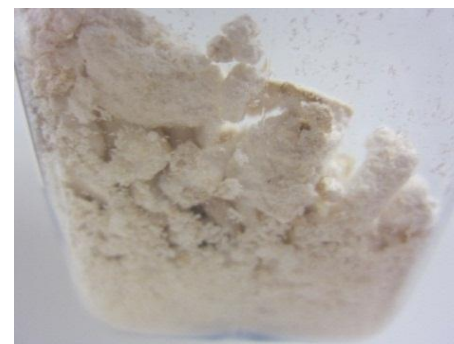
From Seaweed to Isomannide



Crude carbohydrates



Purification



Mannitol

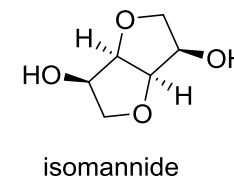
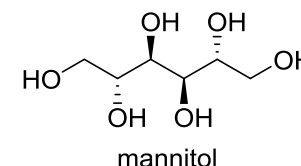


Conversion into iso-mannide



Applications of Isomannide

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



Seaweed Storage

Seaweed Storage

- Seaweed storage crucial for economy future biorefineries:
 - Seasonal growth.
 - Large seasonal variations in composition of seaweeds.
 - Fast rotting of freshly harvested seaweeds.
- Development of storage concepts at sea and on land.

Explorative Tests 2014

- First experiments led to complete seaweed decomposition.
- Tests performed in closed vessels at RT with:
 - Uncut / cut seaweed
 - Aerobic / anaerobic
- Key components:
 - 30 days: 80% loss of mannitol
15% loss of alginate
 - 75 days: Major release of H_2S gas



Fresh



After storage

Ongoing Tests

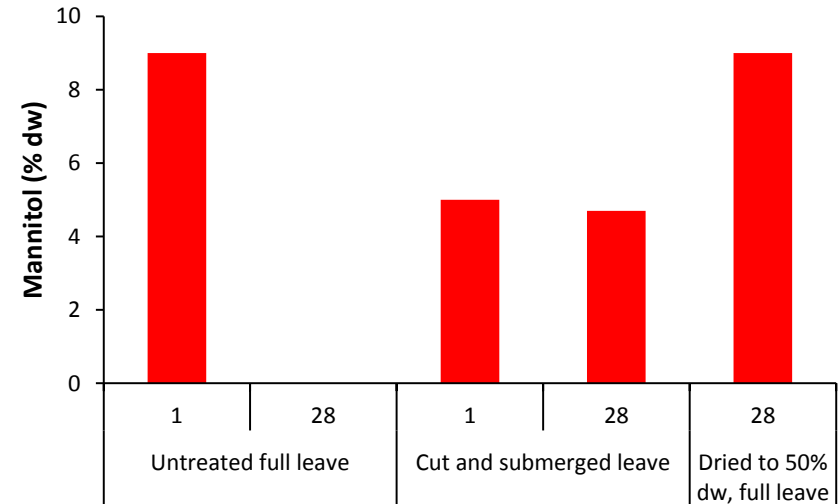
- Controlled environment:
 - 15 ± 1 °C.
 - N₂ atmosphere with gas sampling.
- Conditions compared:
 - Baseline: fresh piece of seaweed
 - Cut seaweed (optionally lactic acid and/or seawater added)
 - (Partially) dry seaweed



Experimental set-up

Preliminary Conclusions

- Whole seaweed decomposes fast if taken out of sea.
- Storing seaweed in seawater:
 - Some loss of its valuable sugars, but much smaller.
 - Fast equilibrium of mannitol between seaweed and seawater.
 - Boundary condition for storage at sea: no water exchange between tank and sea.
- Partial drying seems effective to enable storage at land.



Cut & submerged seaweed after storage

Summary and Outlook

Summary Seaweed Biorefinery

Developed seaweed biorefinery concepts:

- Palmaria → carbohydrates → ABE (biobutanol) & biogas.
- Kelps → glucose, alginate, mannitol → isomannide.
- Ulva → ABE (biobutanol) & animal feed OR → carbohydrates (rhamnose).

Cost analysis biorefinery of Kelps:

- Need to valorize multiple components from seaweed
- Seaweed to only biofuels not feasible → biorefinery

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.

Thank you for your attention

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<http://seaweed.biorefinery.nl>

This work was carried out under the Dutch program EOS-LT 08027 Seaweed biorefinery and the EU-FP7 project @Sea, FP- 280860.

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