

Cascading valorisation in seaweed biorefineries

A.N.G. Wortel
W.J.J. Huijgen
J.W. van Hal

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Cascading valorisation in seaweed biorefineries

André Wortel, Wouter.J.J. Huijgen & Jaap.W. van Hal

Germany, Hamburg
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Energy research Centre of the Netherlands (ECN)



- What do we do:
 - ECN develops market driven technology and know-how to enable a transition to 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

Biomass – a diverse energy source

- Biomass = all organic material of non-fossil origin meant for energy or chemicals/materials production



waste



wood



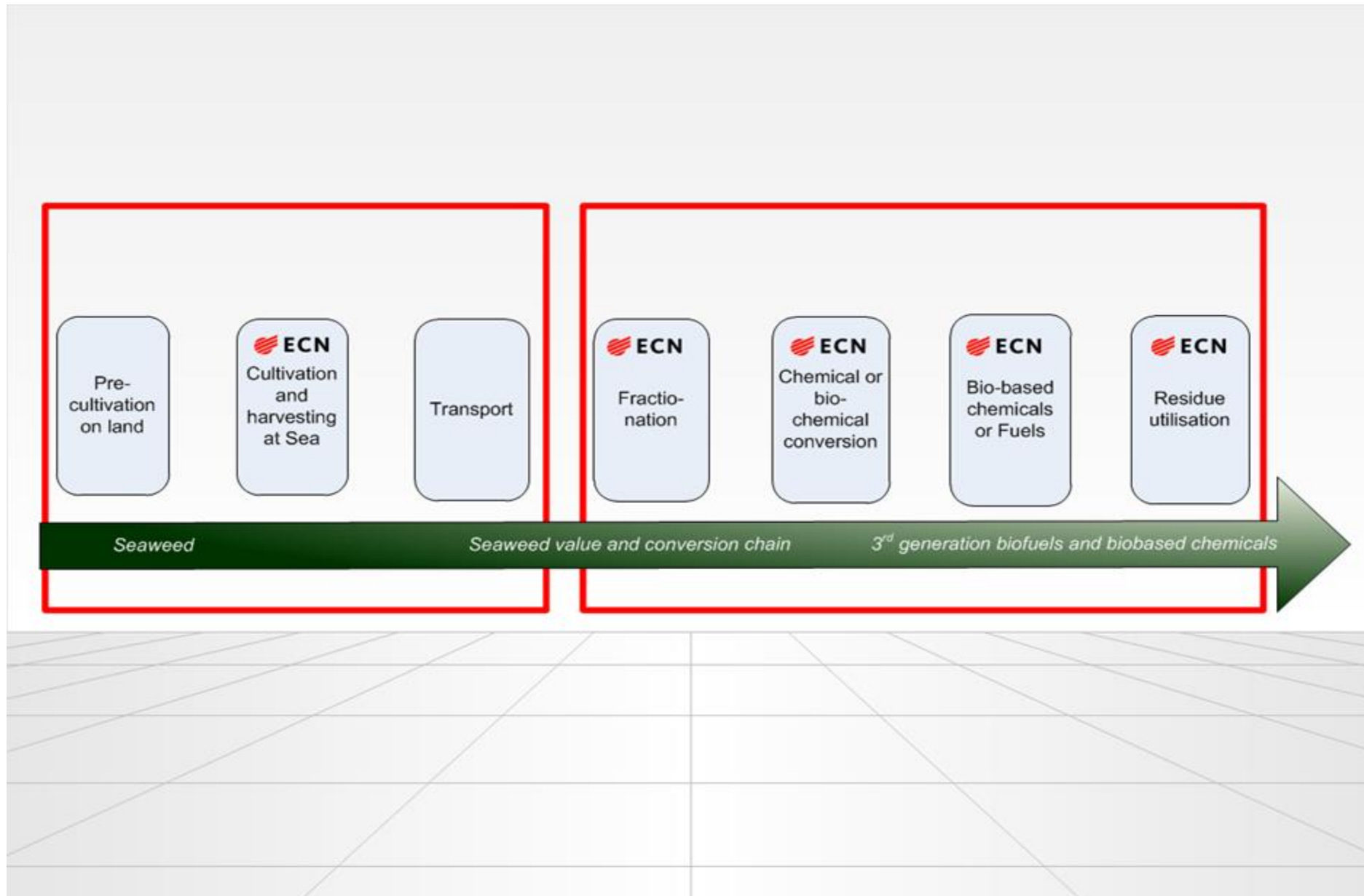
(agricultural) residues



energy crops

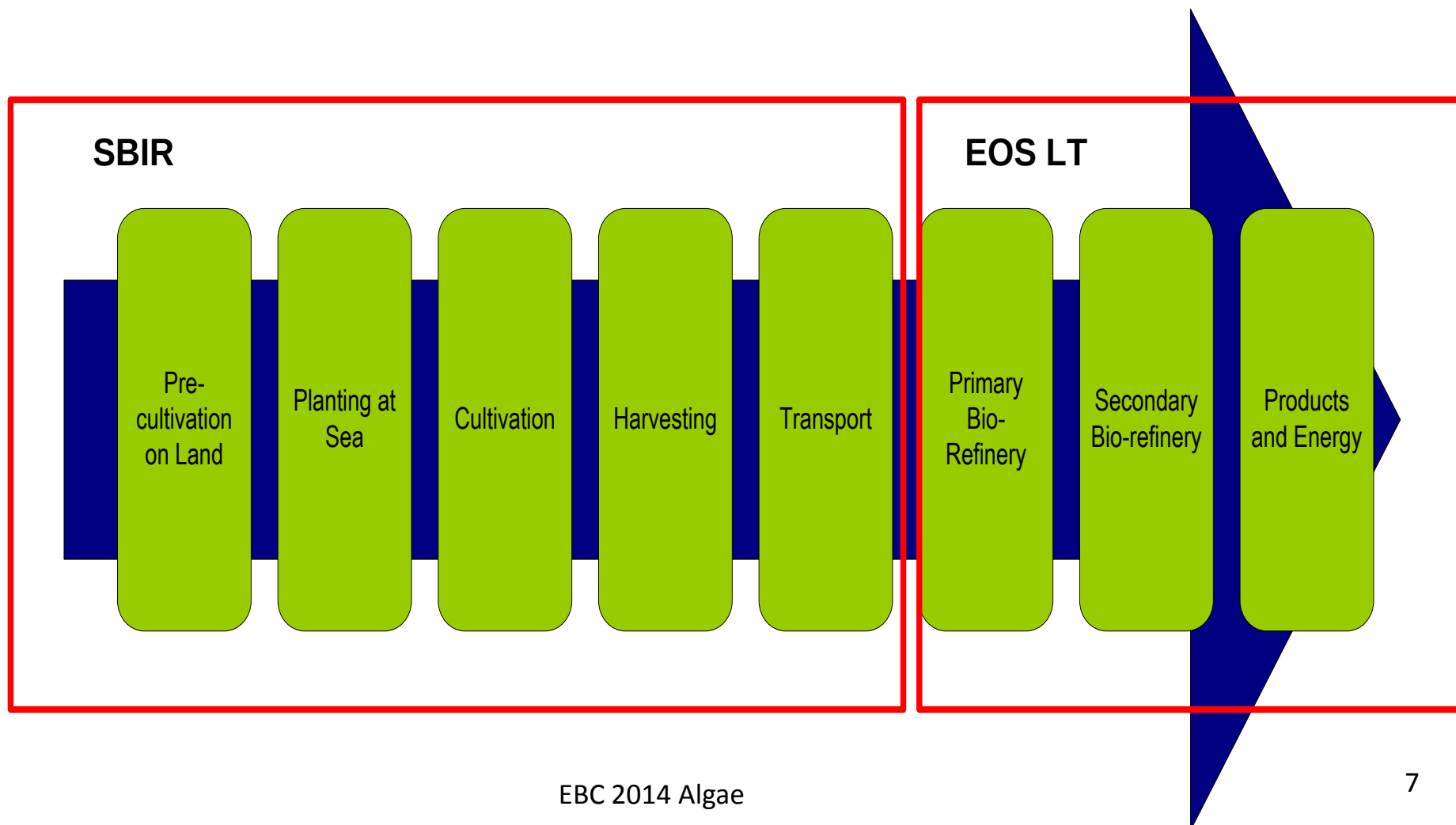


aquatic biomass

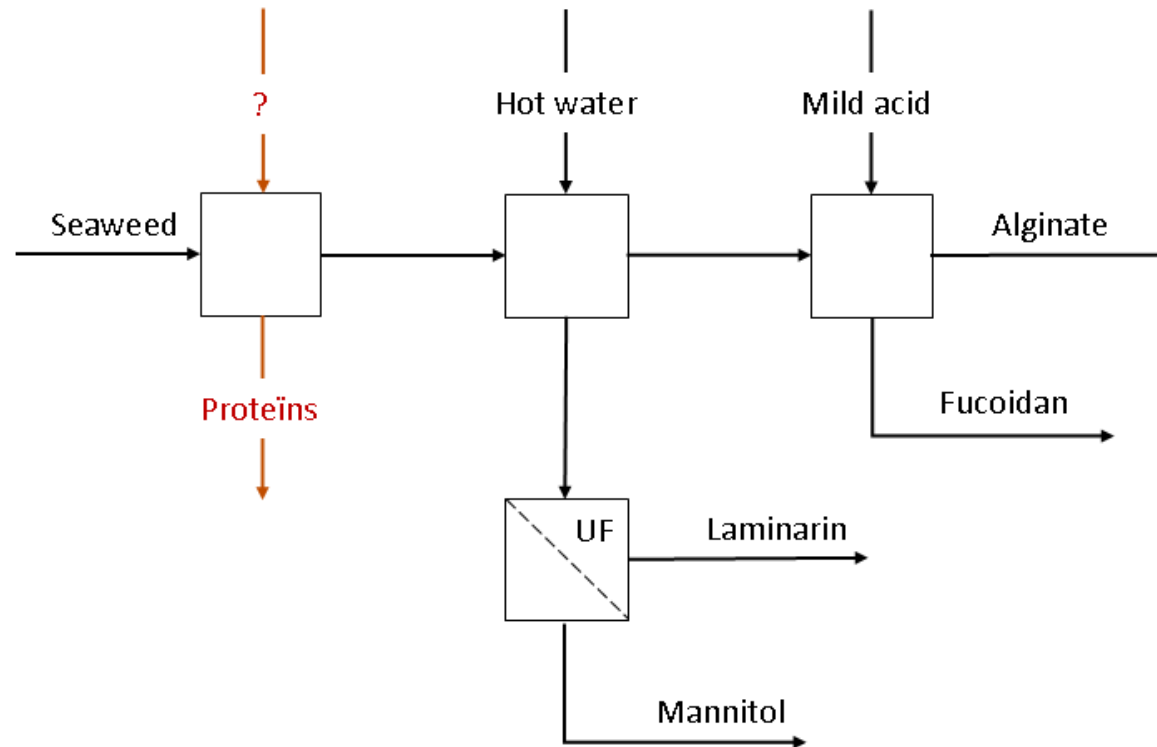


Primary Biorefinery for seaweed

Dutch National Biorefinery Project

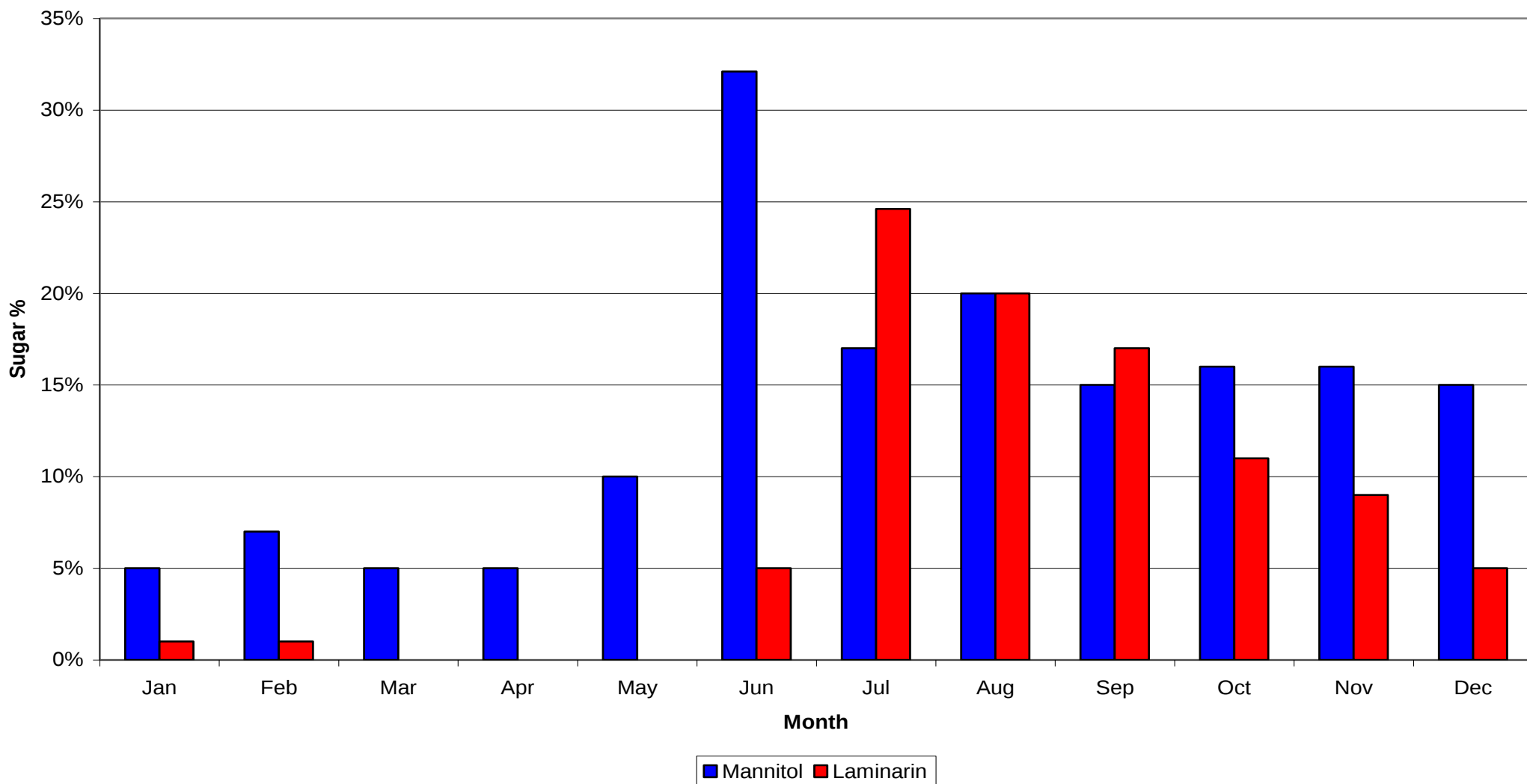


Fractionation *Laminaria* / *Saccharina*



- Potential mannitol uses: e.g., conversion to isomannide, intermediate for plasticizers, fuel additives, PET replacements, epoxy resins & PUR.
- Patent filed on mannitol extraction from brown seaweed (Sept, 2012).

Laminaria Digitata



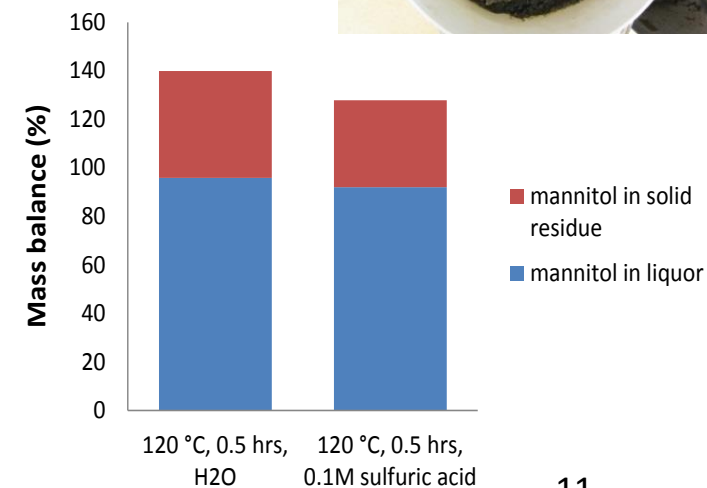
Laminaria hot water extraction

- Freeze-dried seaweed
 - Determination of optimum process conditions.
- Fresh seaweed
 - RT, 80, & 120 °C, 0.5h, H₂O.
 - Successful isolation mannitol (@ all T), but substantial mannitol losses through adhering moisture of solid residue.
 - Increase laminarin extraction with T.
 - Difficulties in separation mannitol and laminarin by UF (alginate?).
- Goal:
 - Increase mannitol yield by optimization solid-liquor product separation.



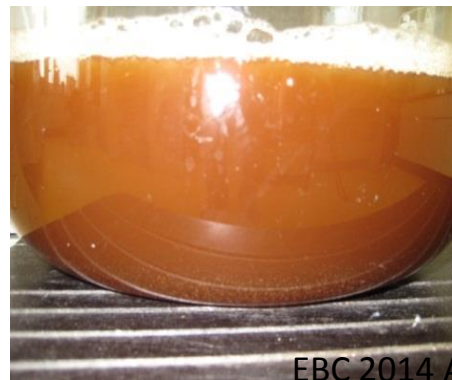
Laminaria hot water extraction

- Harvest June 2013, Galway, Ireland.
 - *Laminaria* cut to pieces of ~5cm.
 - ~84% moisture.
- Hot water extraction:
 - 120C, 0.5 hrs, H₂O
 - pH after 5.3, solid recovery: 52.7% w/w.
 - structure still intact.
- Mass balance mannitol >100%
 - Underestimation mannitol content seaweed?
 - Assuming mass balance closed → extraction ~70%.



Saccharina hot water extraction

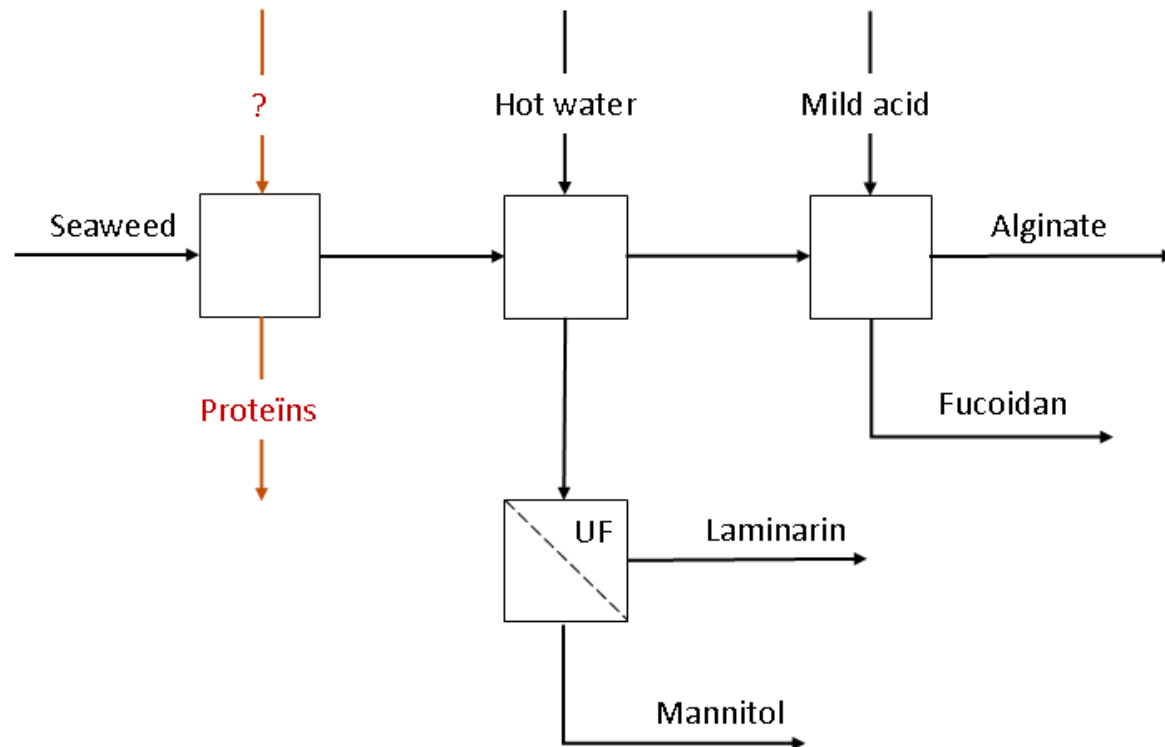
- Harvest June 2013, Galway, Ireland.
 - Huge leaves → cut to ~5 cm pieces for experiments.
 - Moisture: 82-85%.
- Same background and goals as *Laminaria*.
- Hot water extraction:
 - Extraction of mannitol (/ laminarin) with water (1:1 wet basis).



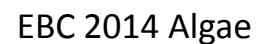
EBC 2014 Algae

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

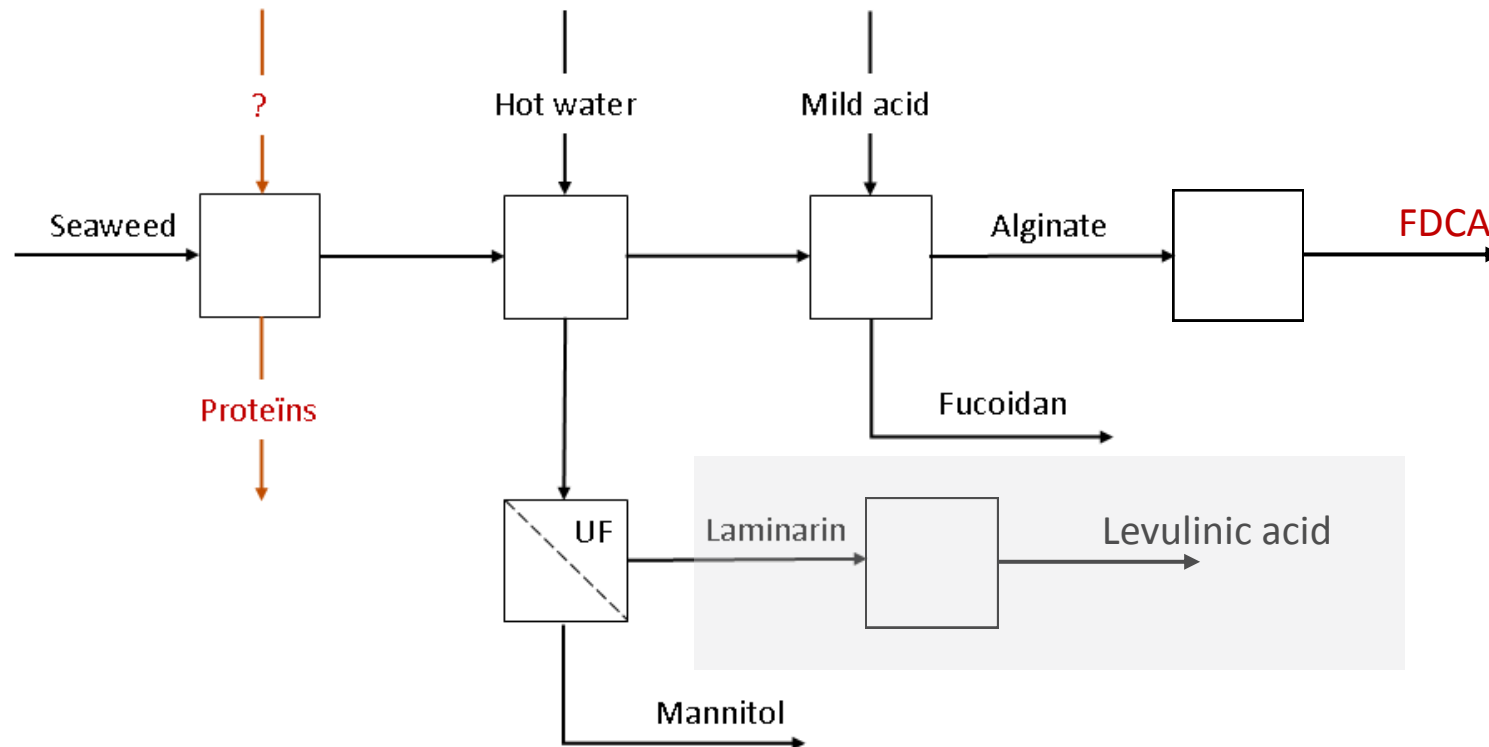
Fractionation *Laminaria* / *Saccharina*



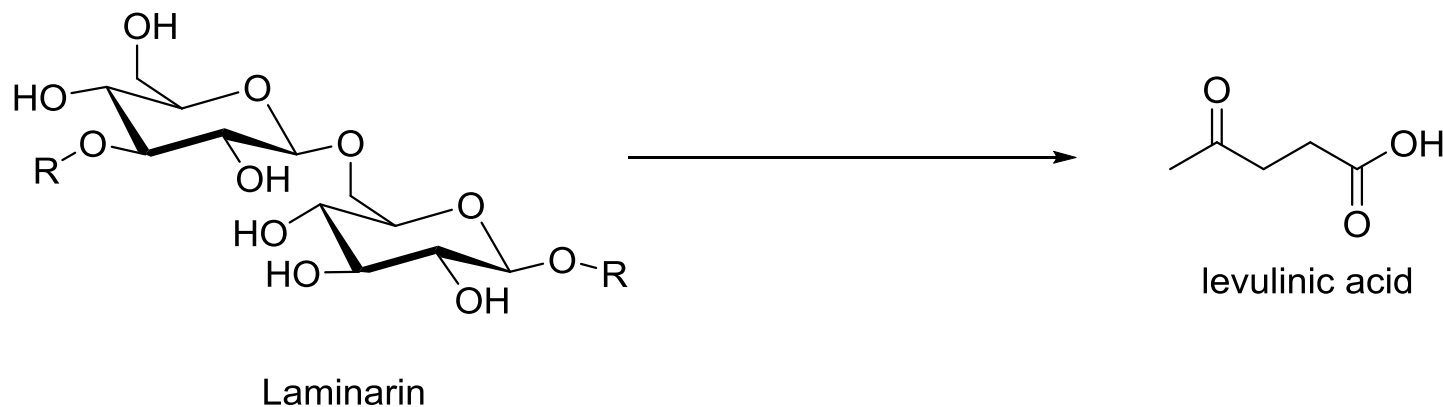
Secondary Biorefinery for seaweed



Conversion Laminarin to levulinic acid



Laminaran to levulinic acid



Tests *Laminaria* 2013

- Use of HCl to hydrolyse laminarin:
 - 120C, 0.5 hrs, 0.1M HCl
 - pH after 2.7, solid recovery: 55.2% w/w.
 - structure broken
- 0.1M HCl found not strong enough to yield monomeric Glucose.
- S/L separation of product slurry:
 - Various techniques tested (filtration, pressing, centrifugation, ...) → separation difficult.
 - Viable approaches:
 - 1 avoid separation
 - 2 washing of product slurry
 - 3 destruction of structure → centrifugation.

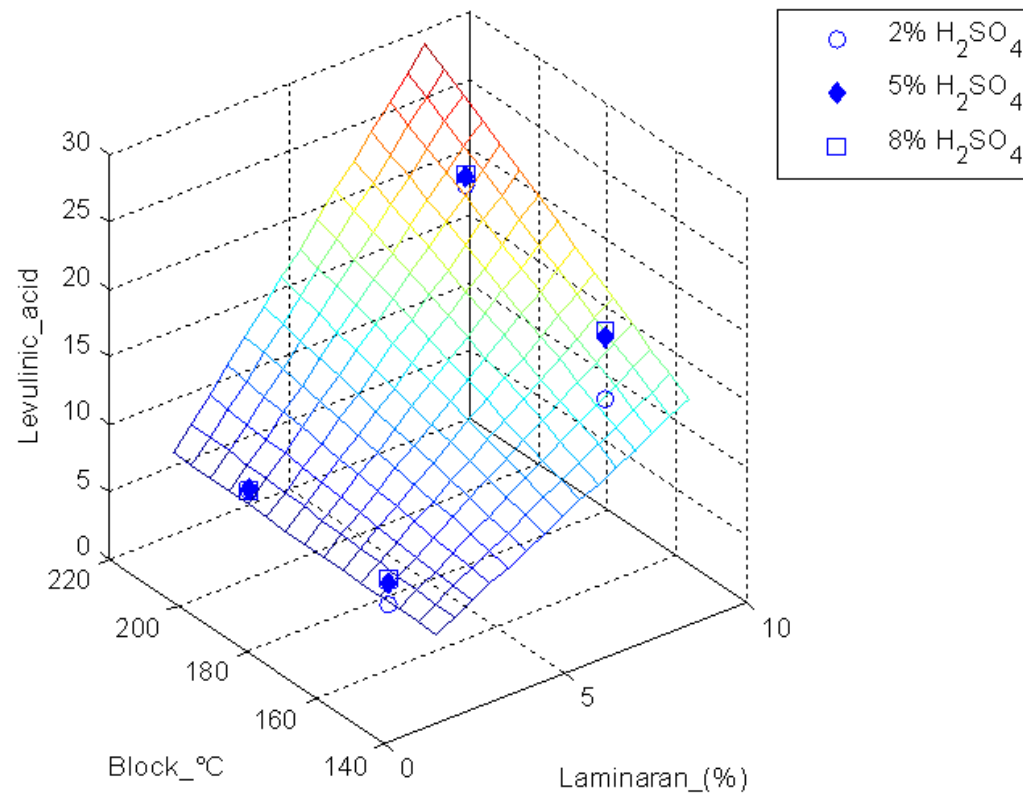


Tests *Saccharina* 2013

- Use of HCl to hydrolyse laminarin:
 - 120C, 0.5 hrs, 0.1M HCl
 - pH after 1.7, solid recovery: 54.6% w/w (structure broken)
 - Solid recovery↑ (alginate → insoluble alginic acid?, reduced solubility of proteins?)!
- Results:
 - HCl again not strong enough to substantially hydrolyse laminarin to mon. Glc (yield ~5%).



DOE for the production of levulinic acid

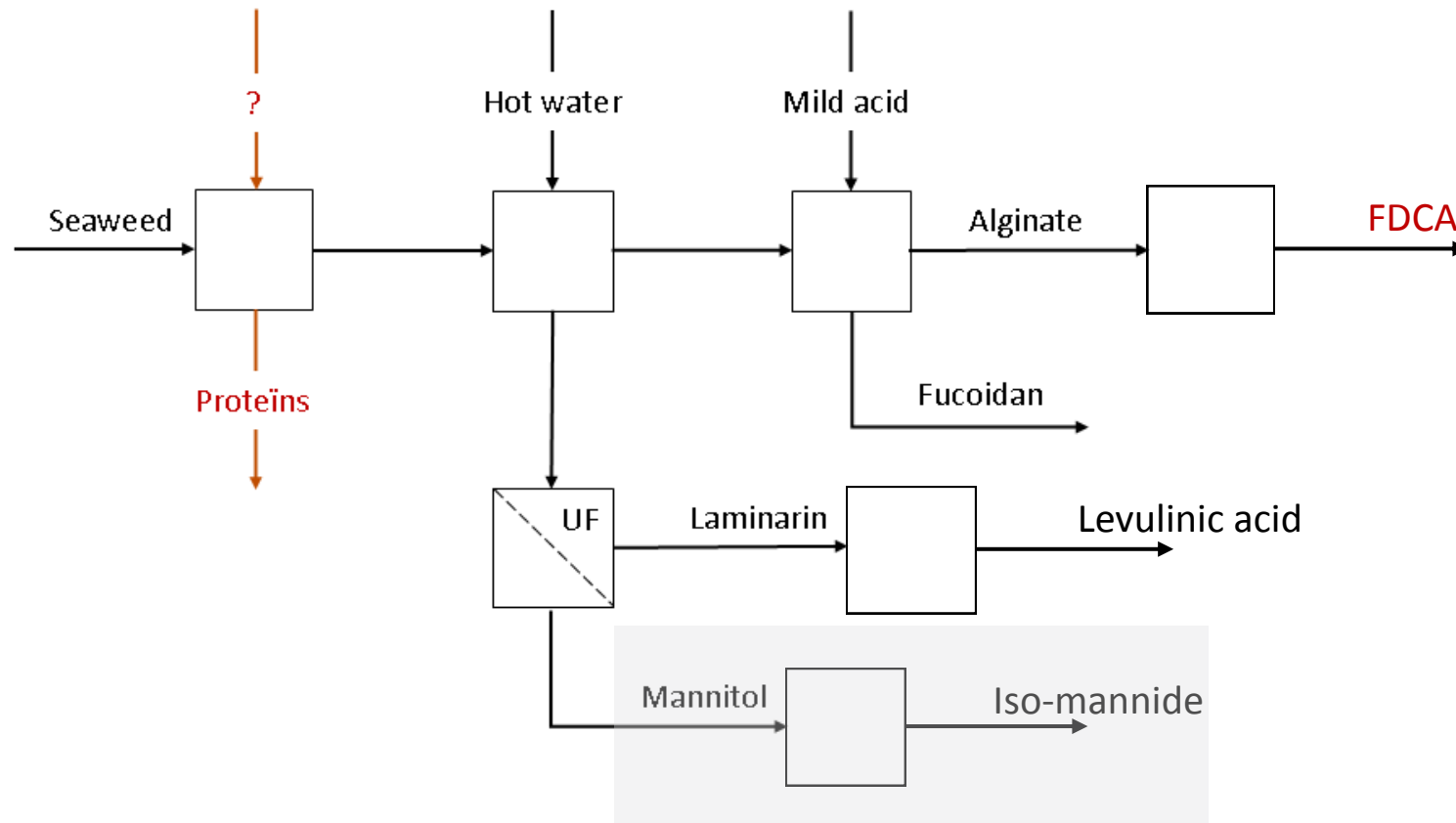


Levulinic acid

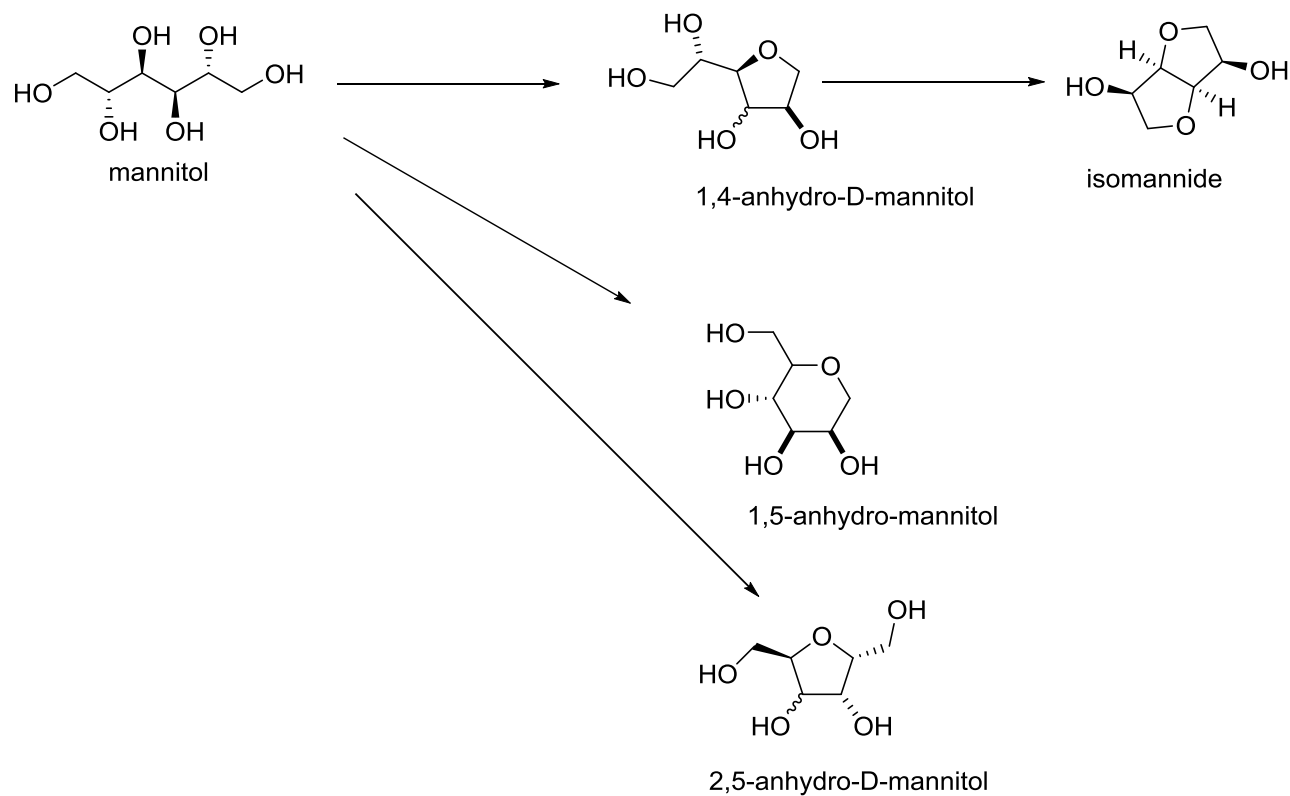


- DOE:
 - 35 % yield of levulinic acid
 - Formic/Levulinic 0.70
 - Best condition
 - 8 % laminarin, 2% H_2SO_4 , 200 °C
- Autoclave
 - 37 % yield of levulinic acid
 - Formic/Levulinic 0.67
 - Reaction is fast
- Perspective
 - Wheat bran: 35 % yield

Conversion Mannitol to Iso-mannide



Reaction steps



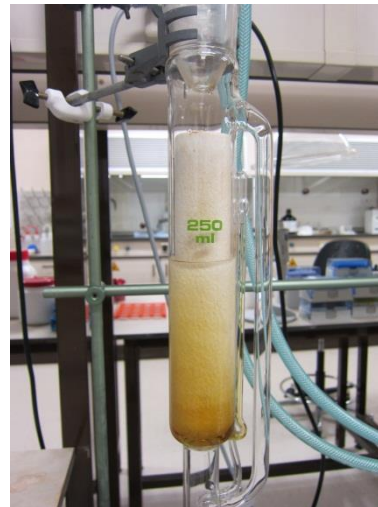
Sacchararina to Iso-mannide



Saccharina



Crude Mannitol



Purified Mannitol



Iso-mannide

Summary

Summary

- Seaweed can be fractionated in components
- Fractionated components can be converted to high value chemicals
- Seaweed can be valorised by cascading high value output chemicals

Thank you for your attention

Presentation can be downloaded from: www.ecn.nl

Acknowledgements

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Further information

Jaap W. van Hal, Seaweed research coordinator ECN

vanhal@ecn.nl

<http://seaweed.biorefinery.nl>

<http://www.atsea-project.eu>

<http://www.mermaidproject.eu>

ECN

Westerduinweg 3
1755 LE Petten
The Netherlands

P.O. Box 1
1755 LG Petten
The Netherlands

T +31 88 515 4949
F +31 88 515 8338
info@ecn.nl
www.ecn.nl

