Seaweed biorefinery: towards third generation biobased commodities

Jaap W. van Hal, Jip Lenstra, Hans Reith, Ana M. López Contreras
(WUR-FBR)

Presented at the Alg'n Chem 2011, Montpellier, France
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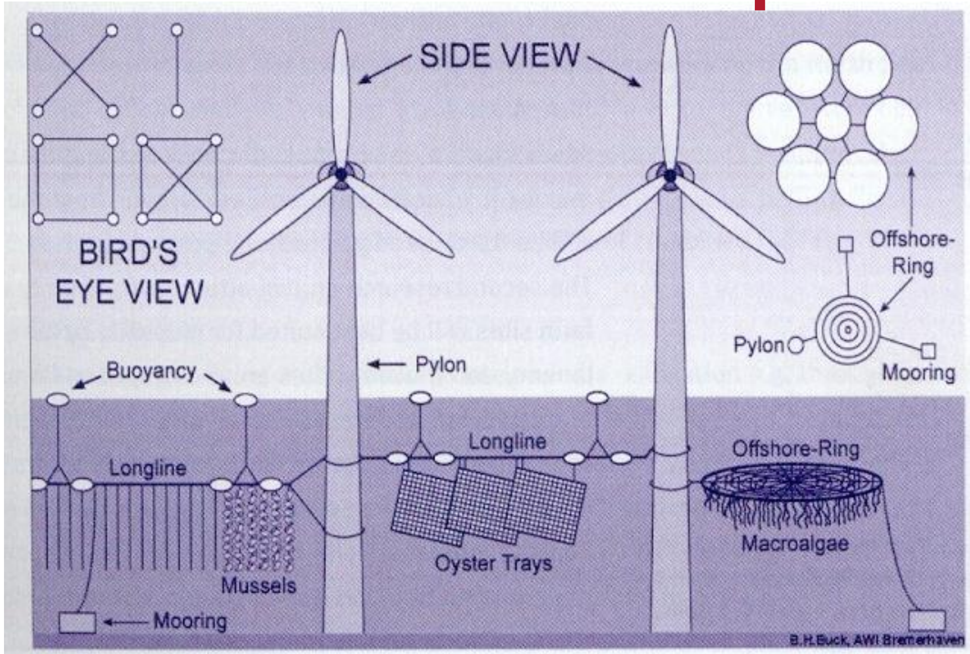
Drivers for seaweed cultivation in the Dutch North Sea

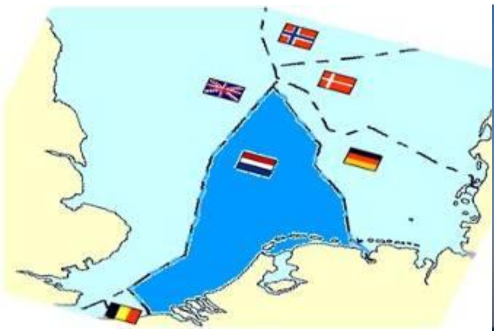
- No existing seaweed industry
- Development of biobased economy (agricultural crops, lignocellulose residues, microalgae,..)
- Interest in seaweeds:
  - No competition with food or other land use issues
  - High biomass productivity
  - Versatile feedstock: numerous options for chemicals and fuels via biorefinery
  - Biochemical composition: complementary (for chemicals/fuel production) to micro-algae
- Development offshore wind turbine parks

Seaweed cultivation in offshore wind turbine parks

- Area closed for shipping
- Multifunctional use of area and offshore constructions
- Potential combination with other aquaculture e.g. mussel cultivation
- Joint O&M: personnel, vessels, equipment
- Synergy and cost benefits

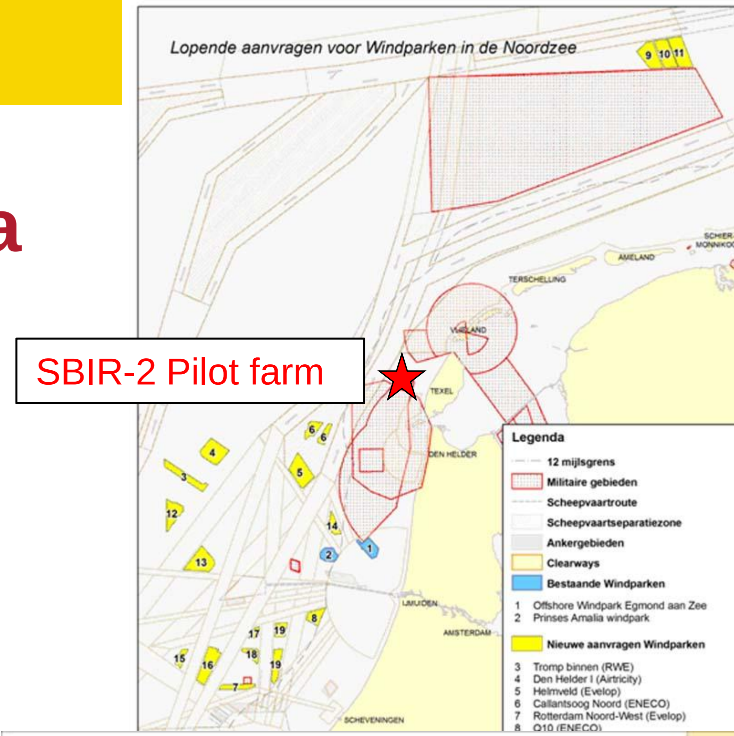


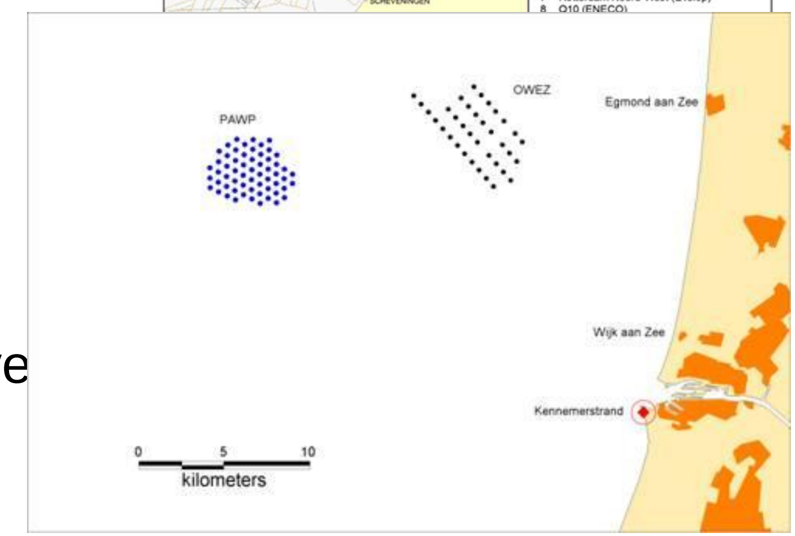
Source: Bela H. Buck, Alfred Wegener Institute, DE.



Seaweed at the North Sea

- 2 wind parks operational, 3 more planned/under construction.
- Plans for combination with wind parks (Ecofys/Eneco/ECN)
- Construction must be stable in storms, high waves, current,..
- 0.5 Hectare experimental farms (Texel, Zeeland)
  - Test cultivation concepts
  - Test harvesting concepts
  - Product quality
  - Cultivate test quantities of native seaweeds





Seaweed species native to the North Sea

Lattissima saccharina

Laminaria digitata

Laminaria hyperborea (Perez)

Ulva sp.

Alaria esculenta (Irish Seaweed Centre)

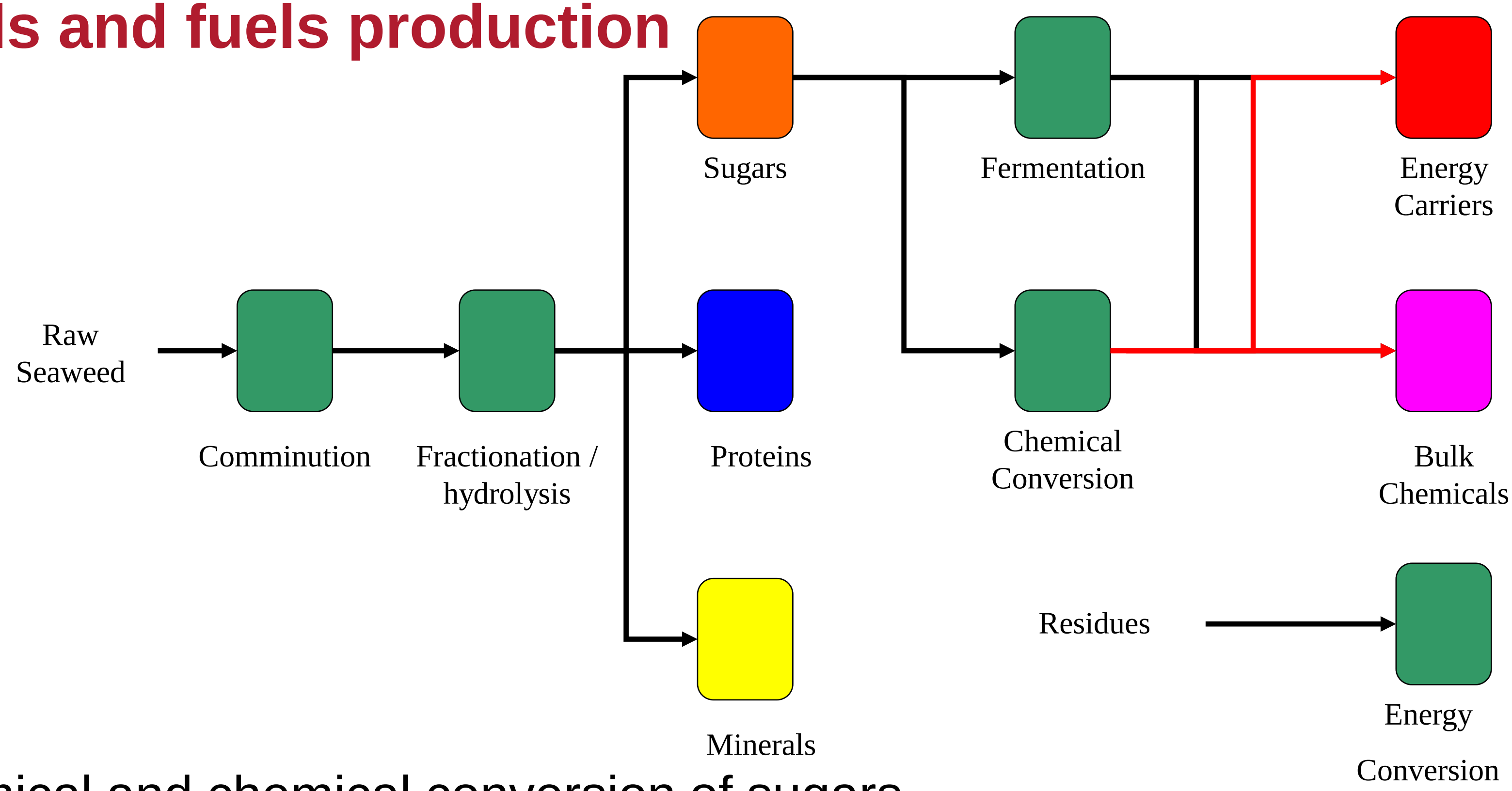
Palmaria palmata (AWI)

National research project: seaweed biorefinery (EOS LT 08027): 2009-2013

- ECN (Project coordinator)
- Irish Seaweed Center
- Wageningen University Food and Biobased Research (WUR-FBR)
- Wageningen University Plant Research International (WUR-PRI)
- ATO-NH (Technology transfer)
- Process Groningen BV (Anaerobic Digestion)

This presentation: First results

Aim: Development of biorefinery technologies for chemicals and fuels production



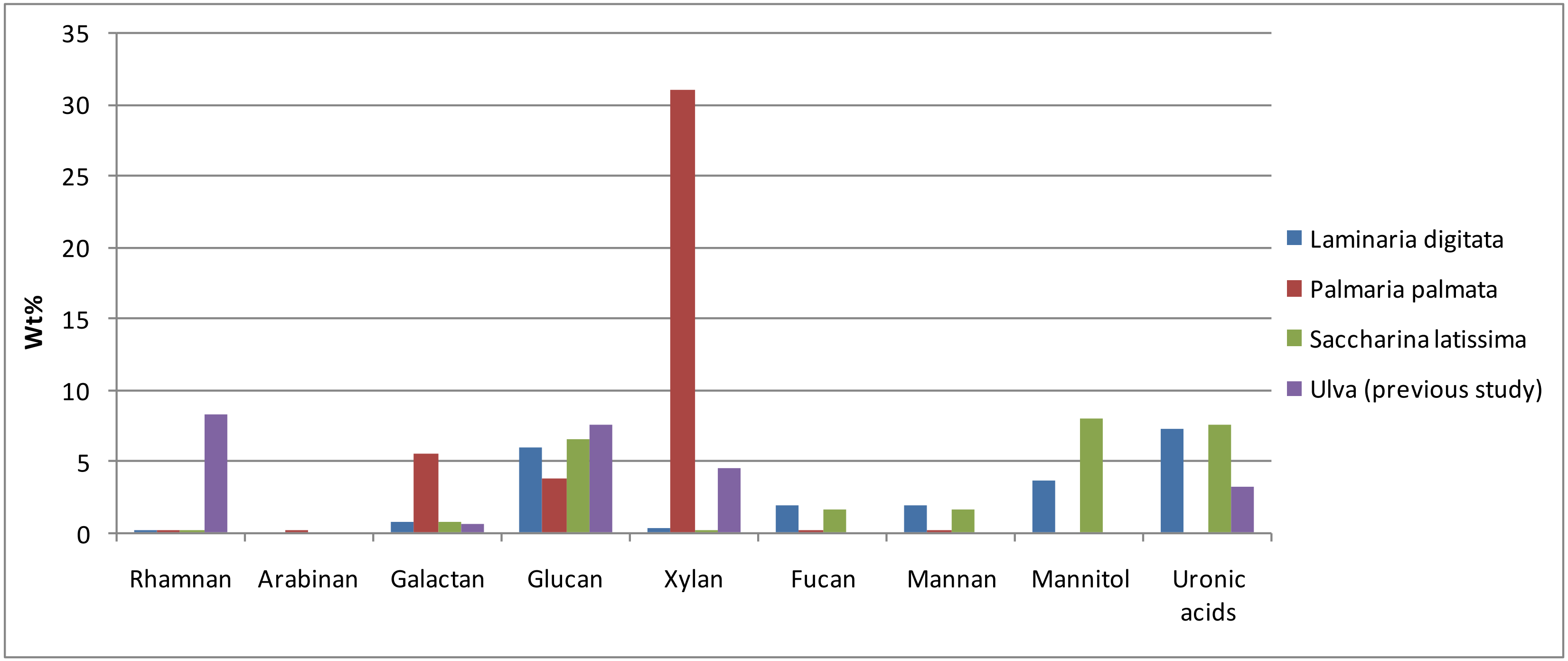
- Biochemical and chemical conversion of sugars
- Valorization remaining fractions: proteins, minerals, biogas
- Extraction of bio-actives, alginates, fucoidan,.. Not the focus
- Design, economic evaluation, LCA

Biomass characterization

basis for process development and selection of products/applications

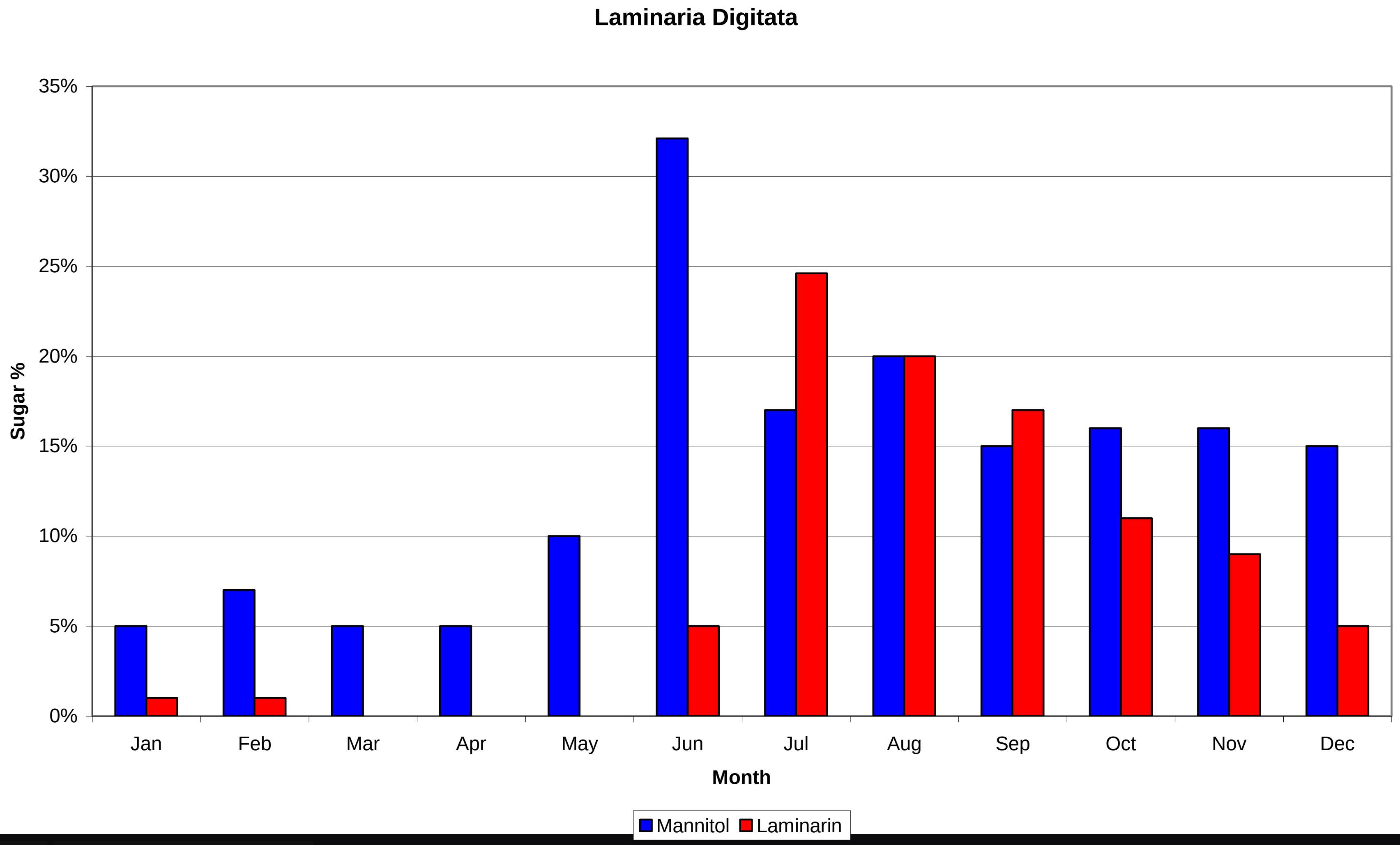
	Laminaria digitata	*Sargassum muticum*	*Saccharina latissima*	*Palmaria palmata*	*Ulva lactuca*
Harvest month	June	June	July	March	February
Sugars					
Total sugars, % d.m.	**14.5**	**7.8**	**17.6**	**40.5**	**11.3**
Glucose	5.9	2.2	6.6	3.8	5.4
Xylose	0.4	0.3	0.2	31.1	1.3
Fucose	1.9	1.1	1.6	0.0	0.0
Mannose	1.9	0.4	0.3	0.0	0.0
Arabinose	0.0	0.0	0.0	0.0	0.0
Galactose	0.7	1.0	0.8	5.5	0.5
Rhamnose	0.1	0.1	0.1	0.0	4.1
Mannitol	3.6	2.7	8.1	0.0	0.0
Total water extrac. % d.m.	25.2 (no mono-)	32.8 (mannitol)	47.9 (mannitol)	32.2(no mono-)	38.3 (no mono-)
EtOH/Toluene extract. % d.m.	3.4	7.9	6.3	6.3	2.6
EtOH extrac. % d.m.	1.3	2.5	3.3	2.0	0.2
Ash (900°C) % d.m.	22.8	22.9	25.0	9.9	18.2
Protein, % d.m. (Kjeldahl)	10.8	16.0	12.4	17.8	23.5

Carbohydrates

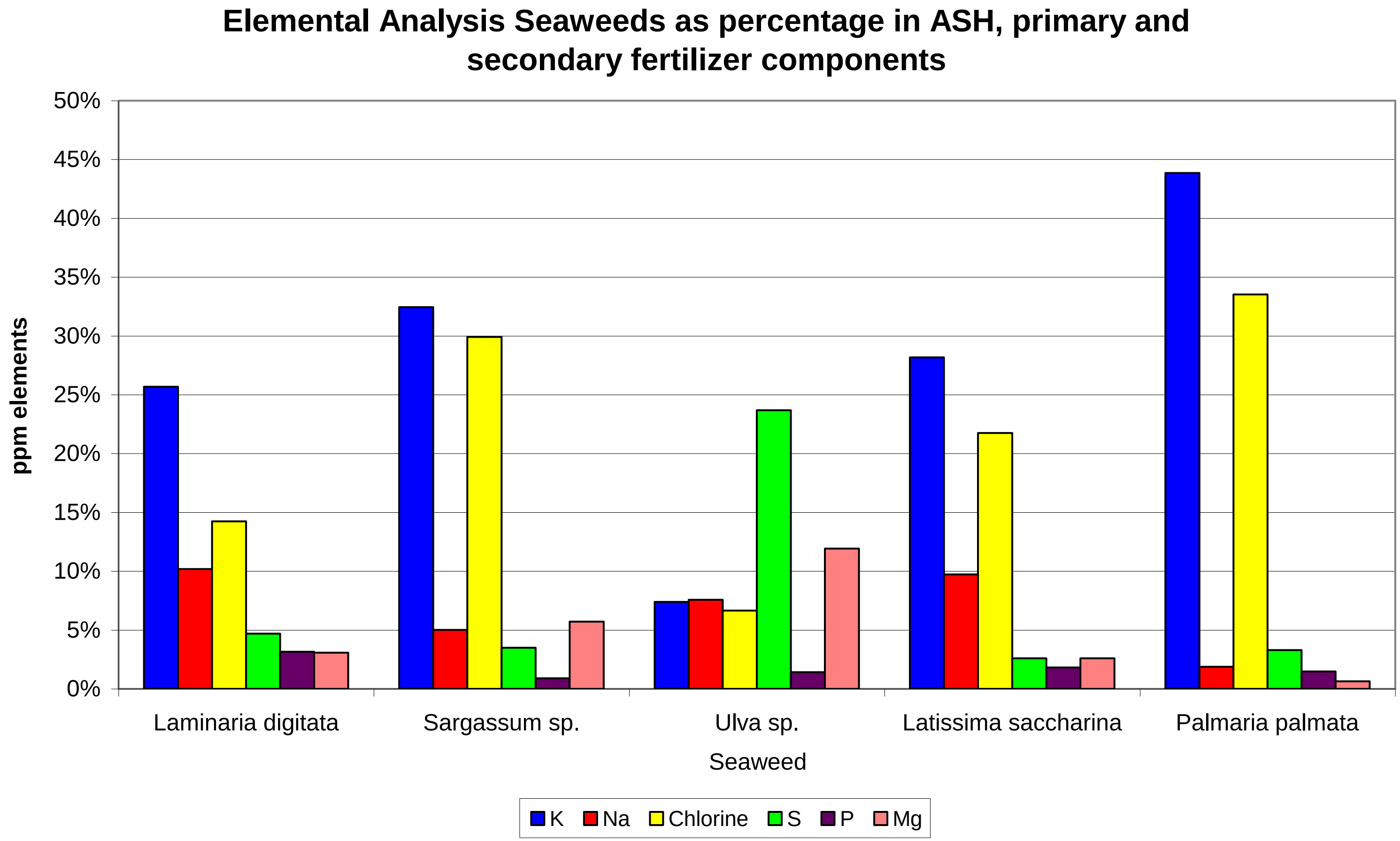


- Carbohydrate profile: species specific
- Analytic protocols for algal carbohydrate analyses seem incomplete.
- Comprehensive protocol for analysis all sugar monomers (incl. uronic acids)

Large seasonal variation

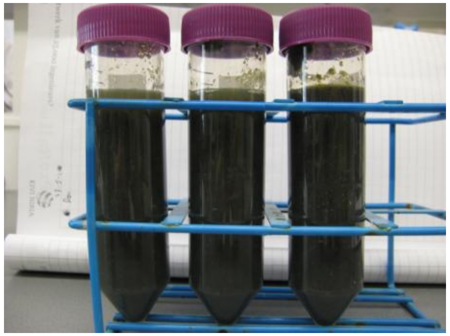


Minerals



- Plus appreciable amounts of trace elements, incl. B, Mn, Fe, Zn, Cu, Mo, Se,..
- Fertilizer ‘ore’ or recycling to sea

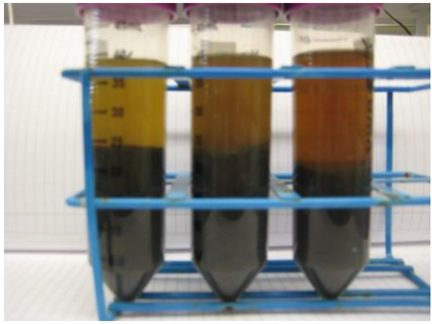
Fractionation of Laminaria



Optional
Catalyst

Water +
Seaweed

T: 120-160 °C
t: 1-4 h
Liquid:Solid=1:10
Cat: 0-1 M H_2SO_4



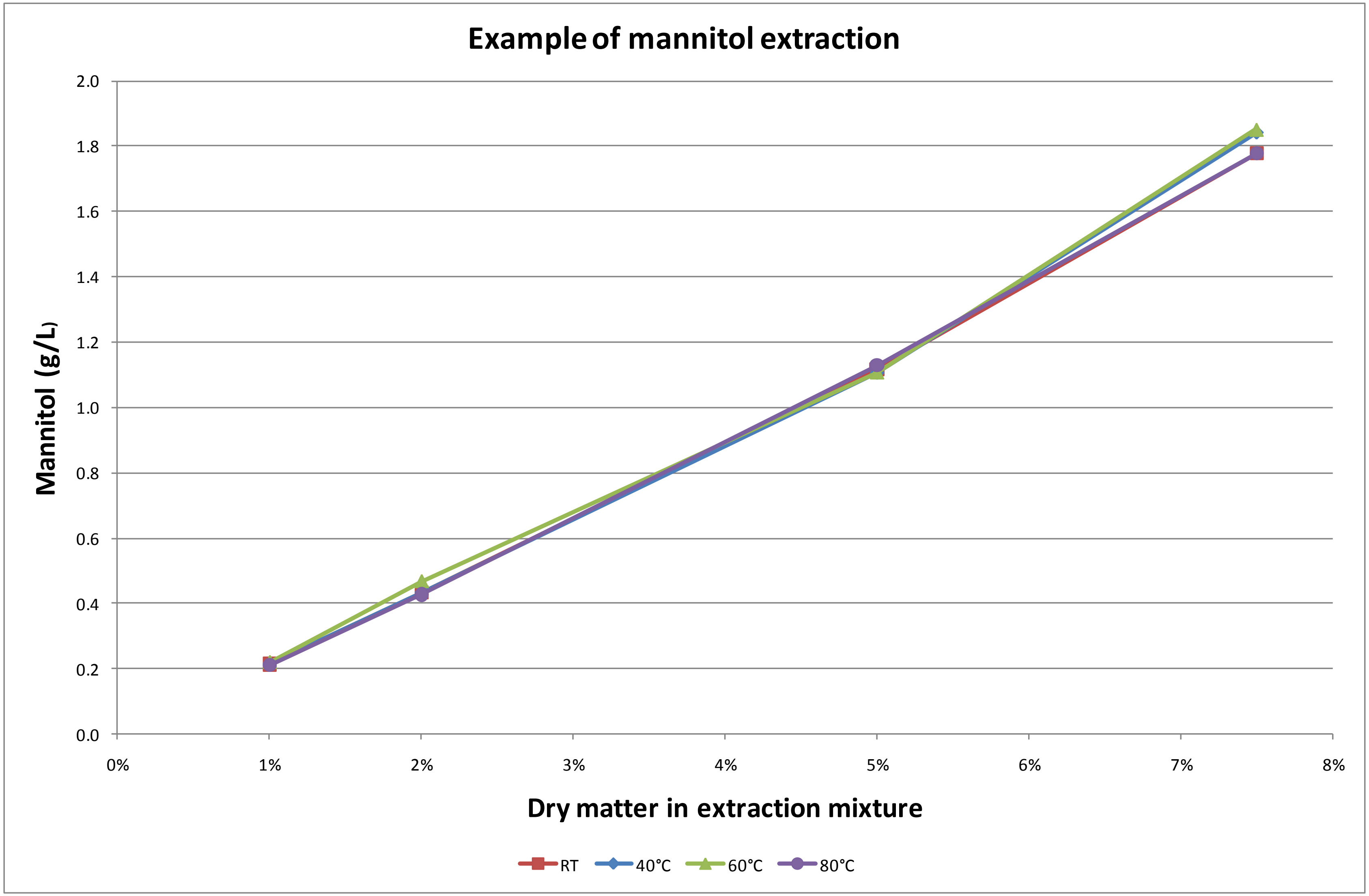
Liquid

Solid

- After reaction, separation by centrifugation (10 min, 4000 rpm) and separation of the phases.

Results

- Near-complete liquefaction occurs at relatively mild conditions
- Fractionation requires (very) mild conditions to preserve biochemical structure and functionalities of biomass components


Example of mannitol extraction
Mannitol (g/L)
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0%
1%
2%
3%
4%
5%
6%
7%
8%
Dry matter in extraction mixture
RT
40°C
60°C
80°C

Hydrolysis of alginates

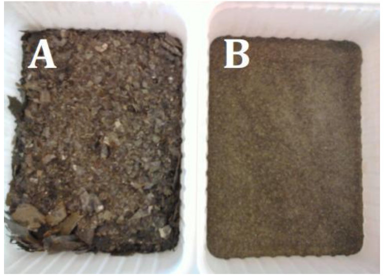
Hydrolysis of alginates into Mannuronic and Guluronic acid monomers challenging:

- Chemical hydrolysis: multi-stage approach required
- Enz. hydrolysis: Lyases perform β-scission to dimers
- Ongoing activity

Enzymatic hydrolysis

Hydrolysates of *Ulva, Palmaria* and *Saccharina* prepared by:

1) Water extraction
2) Enzymatic hydrolysis



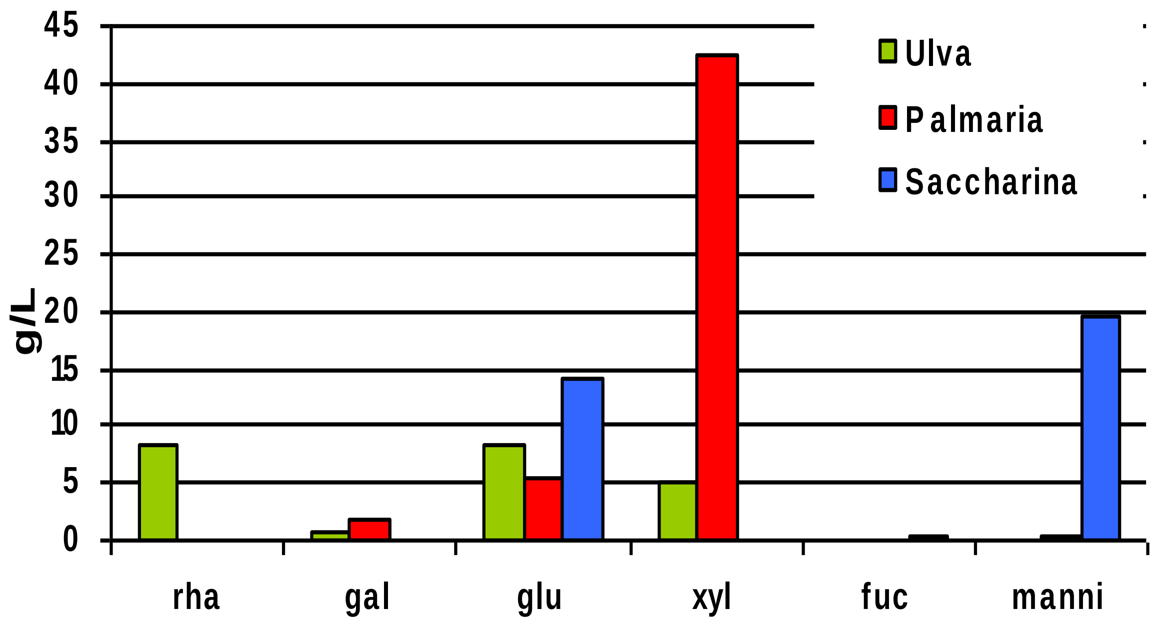
Dried, milled seaweed

Water extraction

Enzymatic hydrolysis

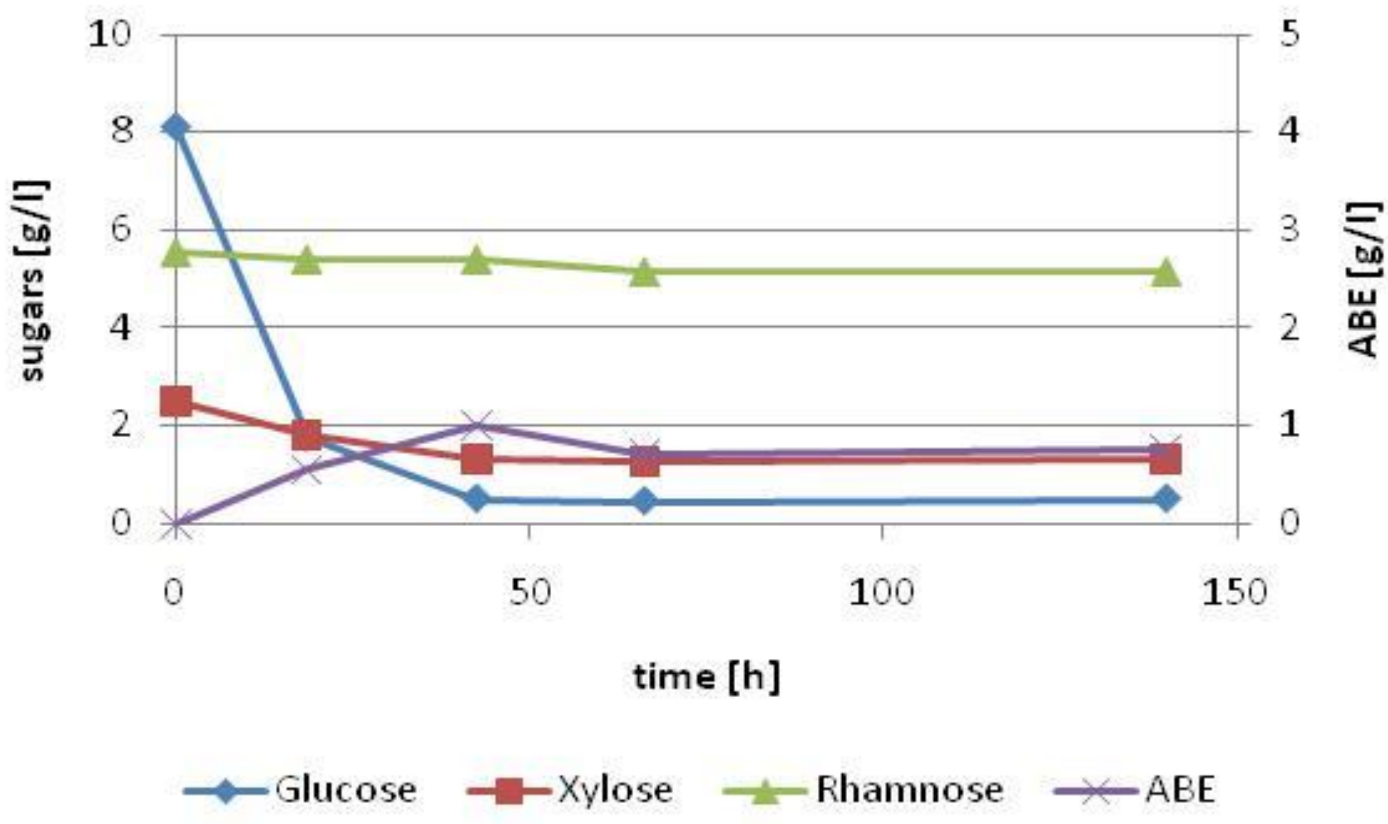
Centrifugation

Seaweed hydrolysate



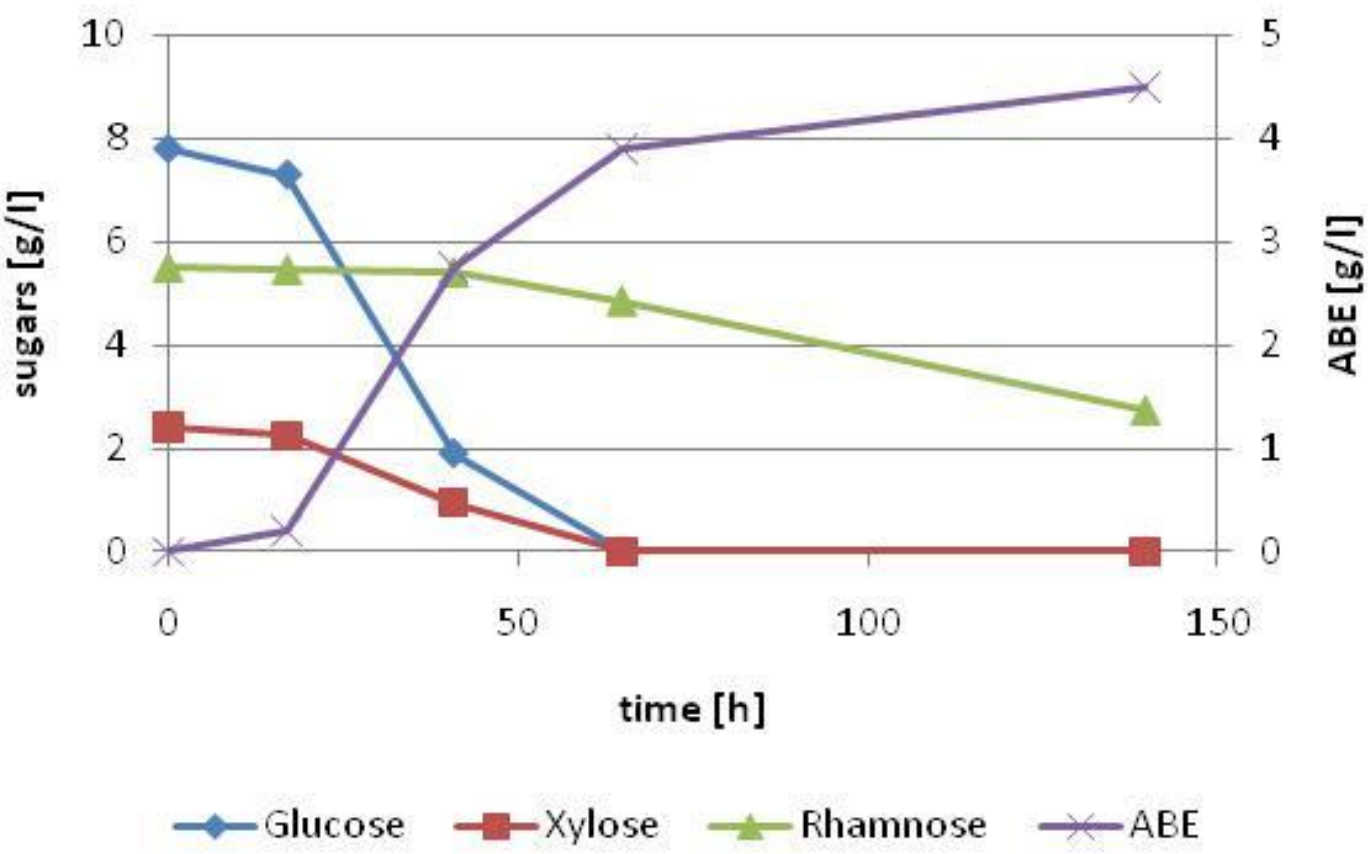
Sugar content of seaweed hydrolysates for fermentation

ABE fermentation (1)



Fermentation of Ulva lactuca hydrolysate by C. acetobutylicum to acetone, butanol and ethanol (ABE)

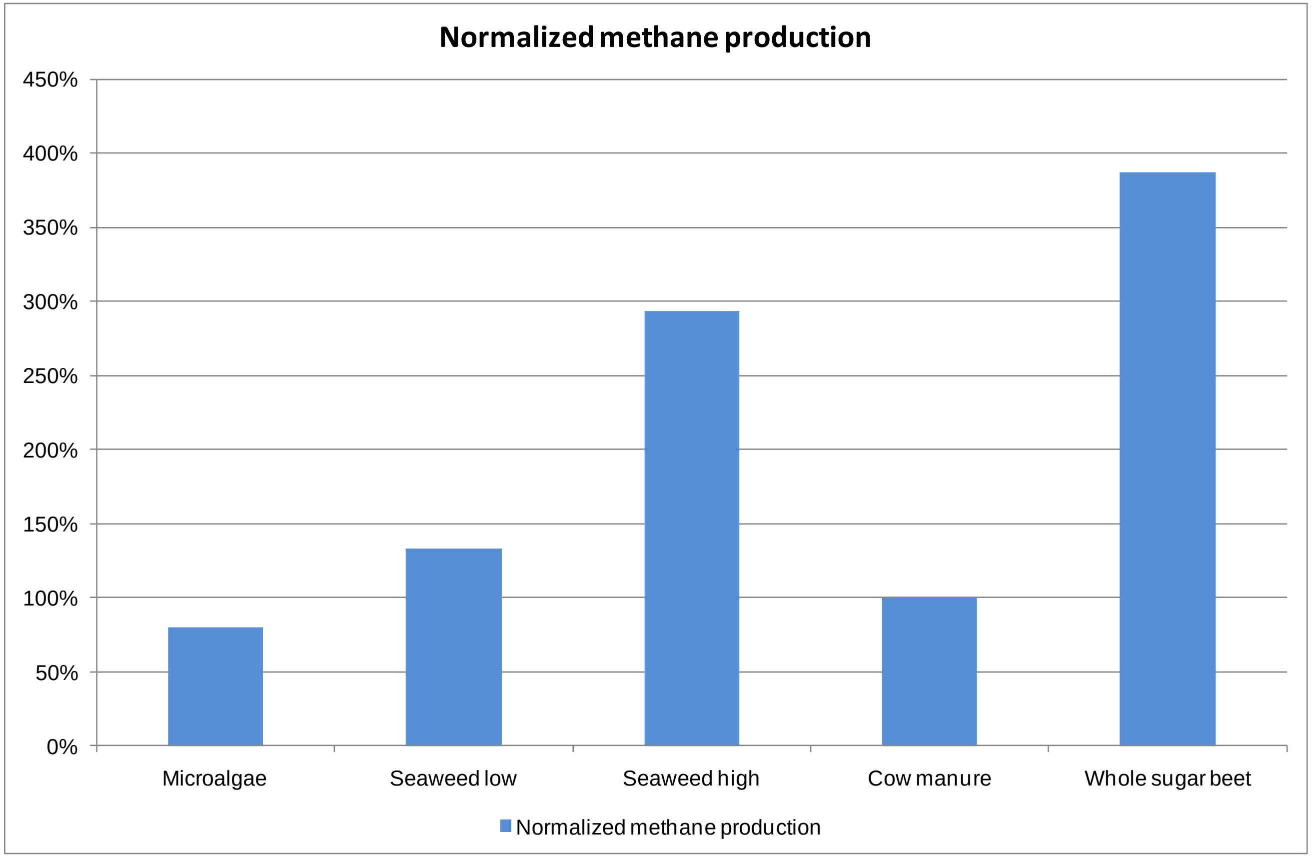
ABE fermentation (2)



Fermentation of *Ulva lactuca* hydrolysate by ***C. Beijerinckii*** to acetone, butanol and ethanol (ABE): **Higher ABE productivity, rhamnose utilised as well.**

Anaerobic digestion: first results

Literature data methane production from seaweed: 0.3 to 0.48 m3 methane per ton organic matter



Process synthesis

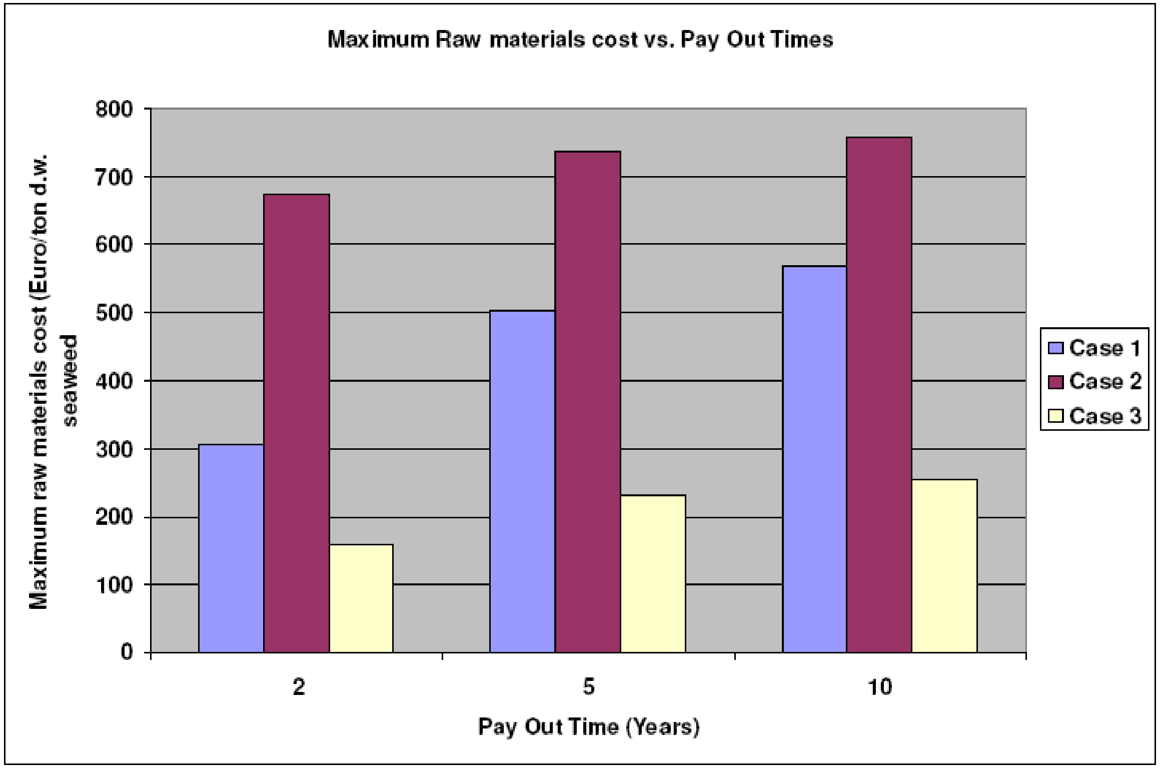
- To determine the maximum allowable raw material cost
- Compare different biorefinery options
- Methodology
  - Determine market value of potential products
  - Determine mass balance
  - Estimate CAPEX and OPEX
  - Estimate gross revenue per product
  - Evaluate market size vs plant output

ECN

Economics: Product spectrum

Product	Estimated Value (Euro/ton)
Mannitol (valued as sorbitol)	1,500
Fumaric acid (as adipic acid)	1,600
Fucoidan (as detergent)	2,900
1-Butanol (chemical grade)	1,200
Ethanol (fuel grade)	600
Protein	1,000
Fertilizer (as ore)	350
Furanics	800
Alginates	3,000

Max. allowable seaweed costs based on projected sales revenues for Pay Out Time 2, 5, 10 yrs



Scale biorefinery 330 kt/yr

= 110 km2 @ 30 ton/ha/yr

1: Full Biorefinery: mannitol, fucoidan, furanics, fumaric acid, protein, K-"ore": 300-600 €

2: Extraction of (too much) alginate, fertilizer (K,P) and energy (AD + CHP): 650- 750 €

3: Simplified Biorefinery producing butanol and fertilizer: 150 - 250 € /ton d.w

Seaweed production cost

Type of cultvation system	Productivity		Costs		Reference:
	ton daf/ ha.yrr	ton d.w./ ha.yr	$ / ton daf	$ (or €) / ton d.w.	
Chili: harvest of natural populations	-	-	-	250	Internet
Philippines: coastal cultivation; 'off-farm' price	-	-	-	80 - 160	Internet
Nearshore cultivation Macrocystis	34 50	57 83	67 42	40 25	[3]
Gracillaria/Laminaria line cultivation (offshore)	11 45	14 59	538 147	409 112	[3]
Tidal Flat farm Gracillaria/Ulva	11 23	14 30	44 28	33 21	[3]
Floating cultivation Sargassum	22 45	32 66	73 37	50 25	[3]

Indication large scale production cost (mostly from published design studies):
50 € (nearshore/floating) - 400 € (offshore) per ton dw. Verification required!
Biomass production costs depend mostly on 1) investment cultivation and harvesting system 2) achieved productivity

Summary

- Four species of seaweeds biochemically characterized for biorefinery
- Mild fractionation required to preserve chemical structure.
- Mannitol extraction from kelps possible under mild conditions.
- Seaweed carbohydrates can be hydrolyzed and fermented to ABE.
- Good Anaerobic Digestion to methane confirmed
- Monetizing of all fractions is needed for viable biorefinery

Thank you for your attention

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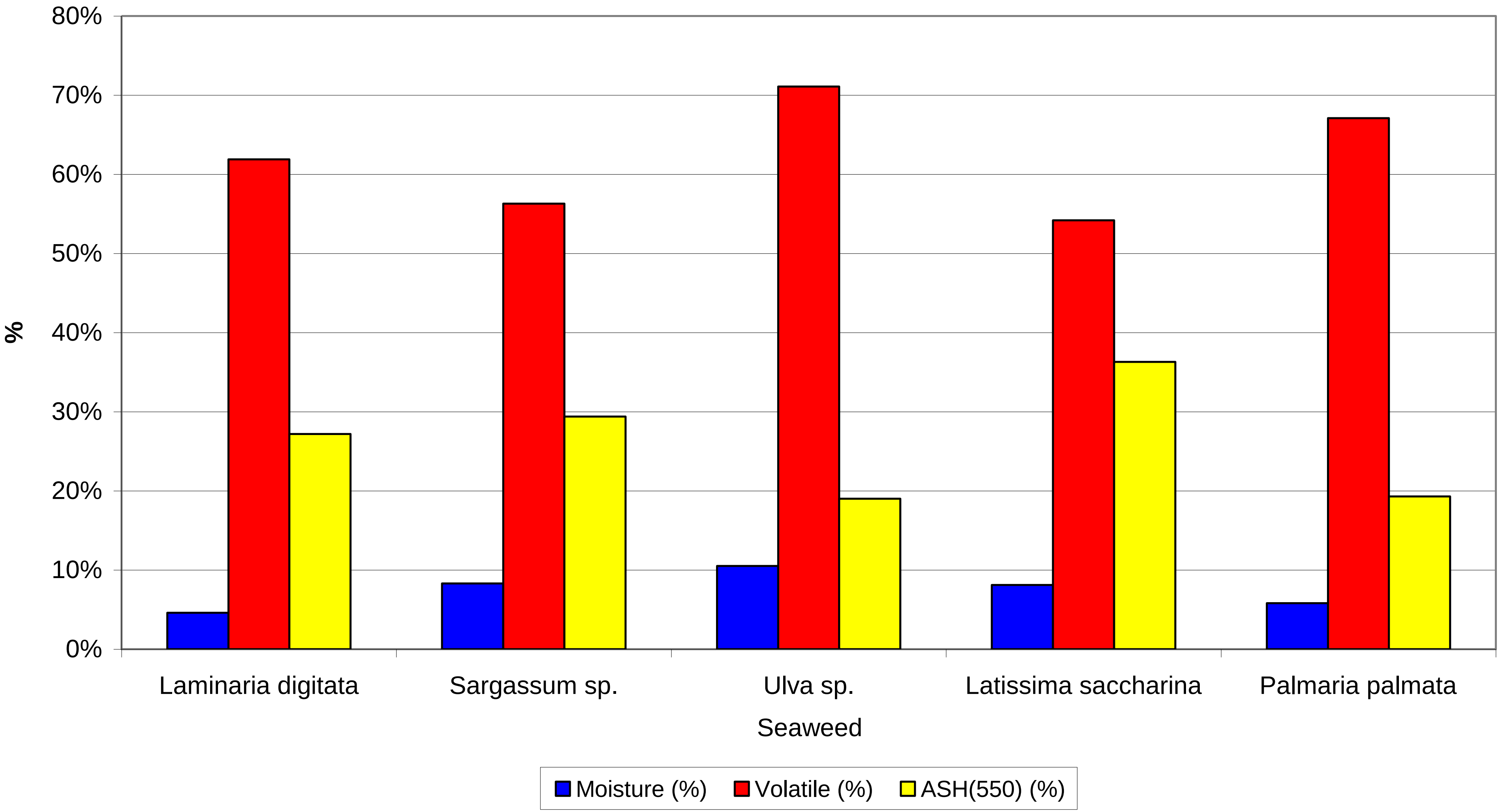
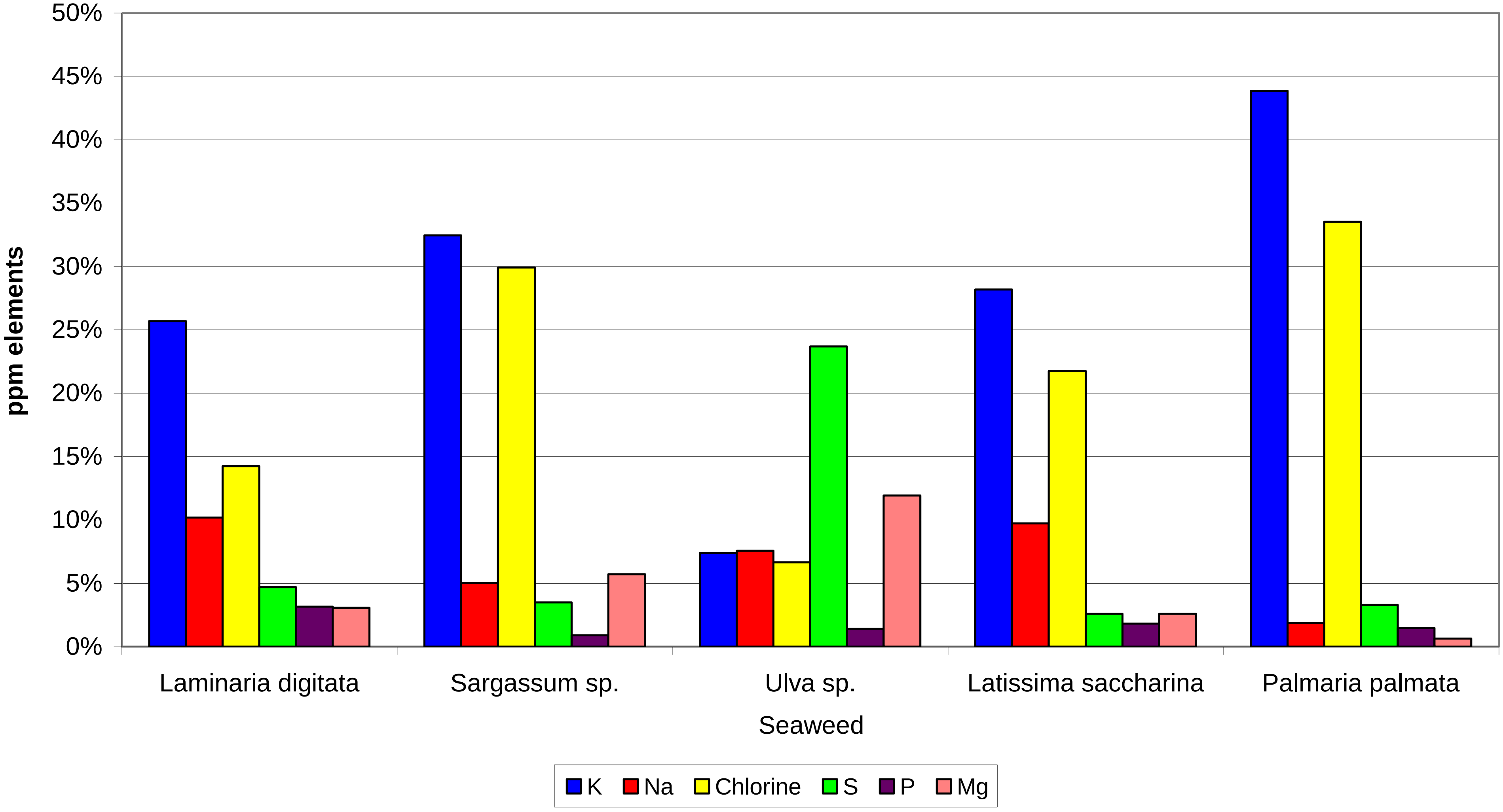
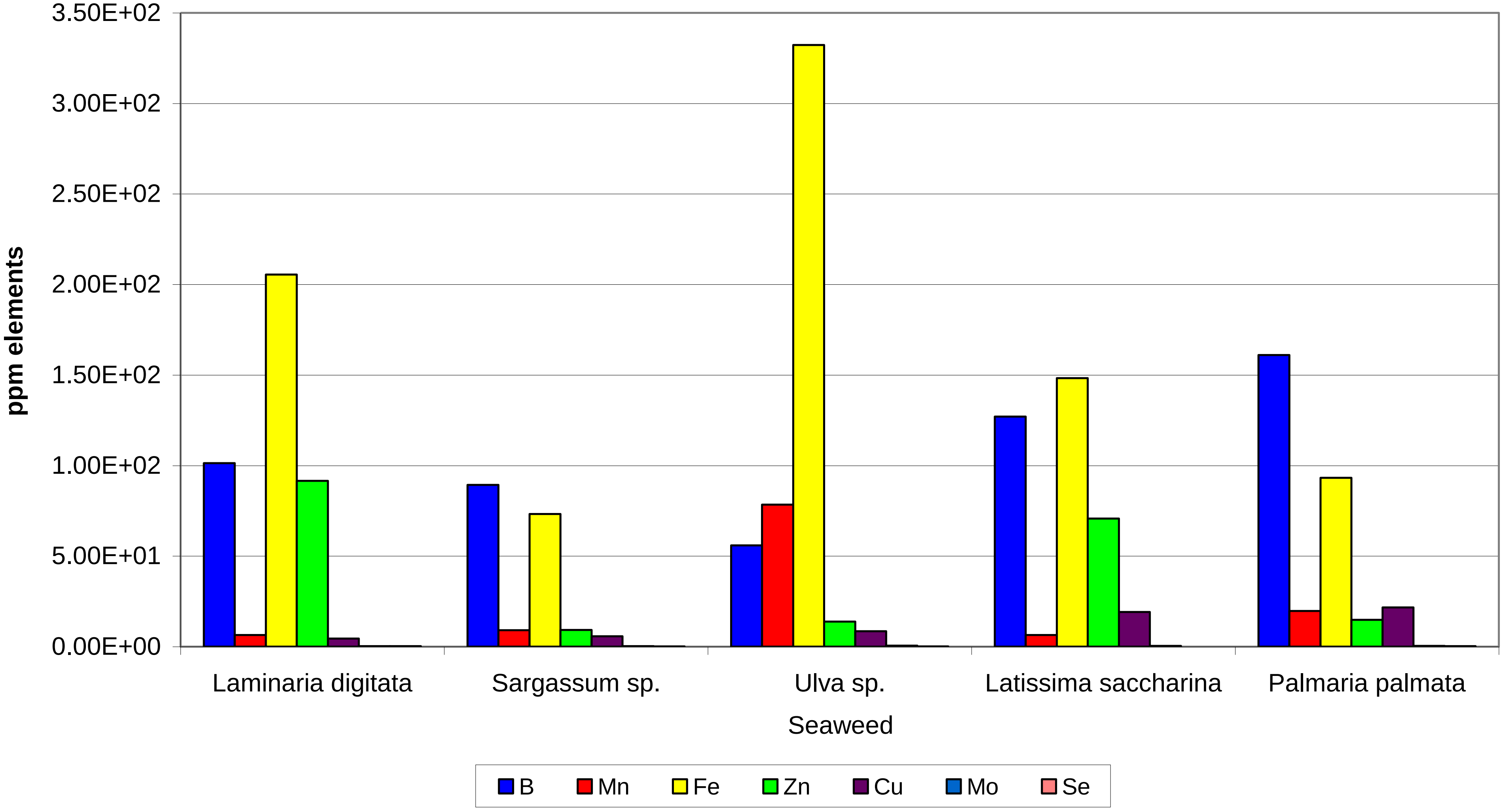
Elemental Analysis Seaweeds



Elemental Analysis Seaweeds as percentage in ASH, primary and secondary fertilizer components



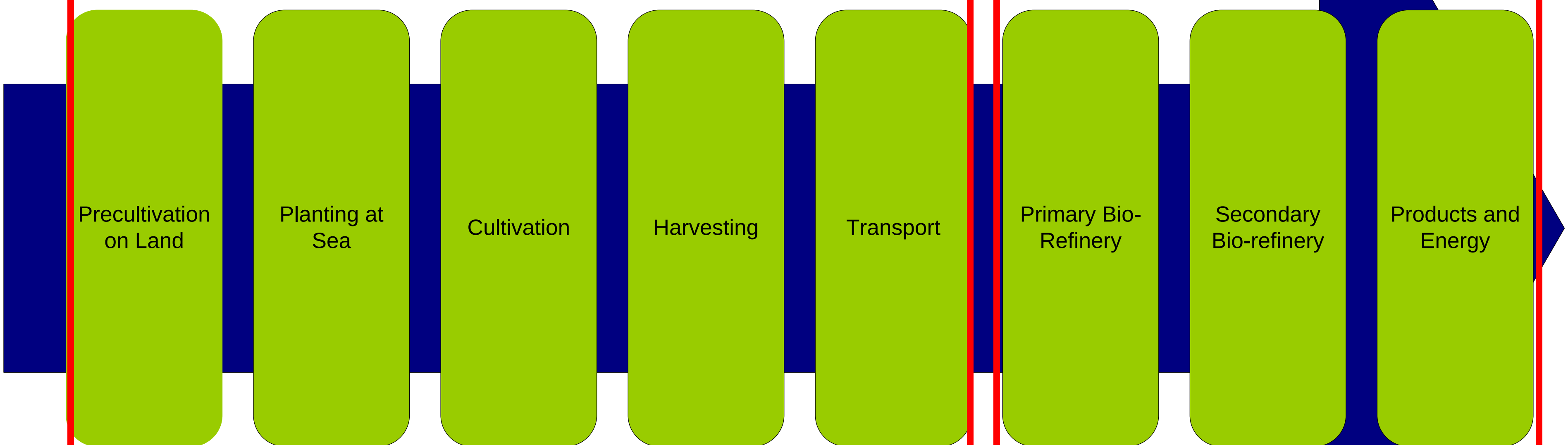
Elemental Analysis Seaweeds (trace fertilizer components)



Seaweed projects in the Netherlands

SBIR

EOS LT



Partners: Ecofys, Eneco, ECN, OceanFuel, Van Beelen, PipeLife, De Vries & Van de Wiel

Partners: ECN WUR, ISC, ATO, Process Groningen