ECN
Your energy. Our passion.

A look back at the Seaweed Biorefinery Project

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Terneuzen
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Who is ECN?

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

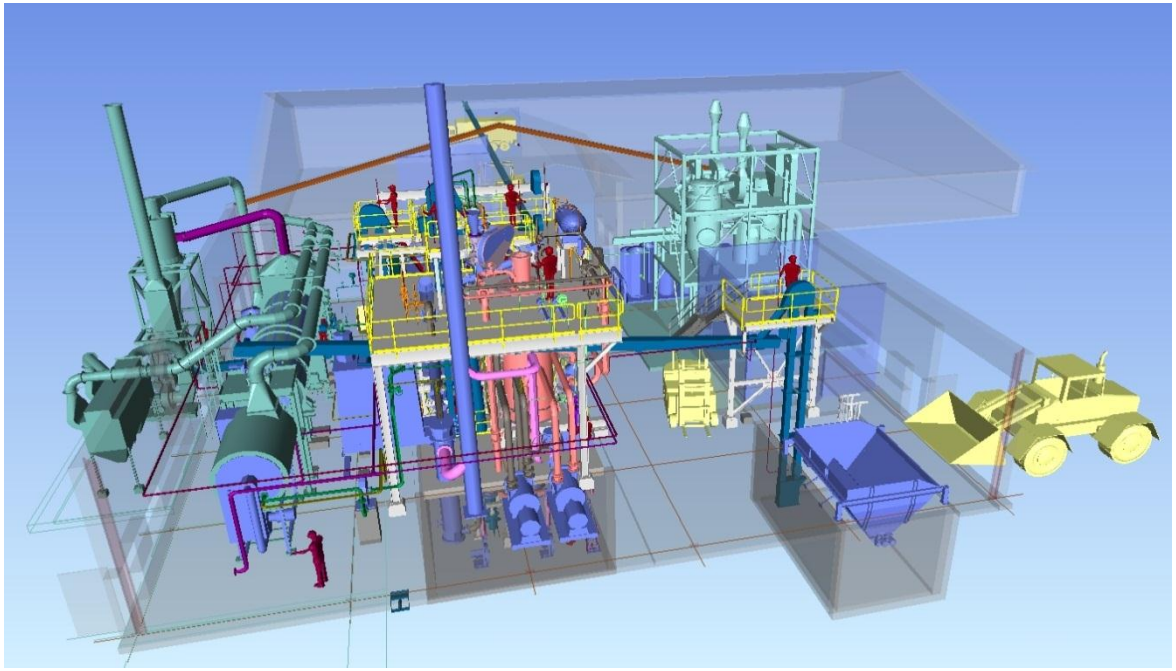
- Business units:
  - Biomass & energy efficiency
  - Solar energy
  - Wind energy
  - Policy studies
  - Environment & energy engineering

ECN

- Independent research institute
- ~600 employees
- Locations:
  - Petten (HQ)
  - Amsterdam
  - Eindhoven
  - Brussels
  - Beijing

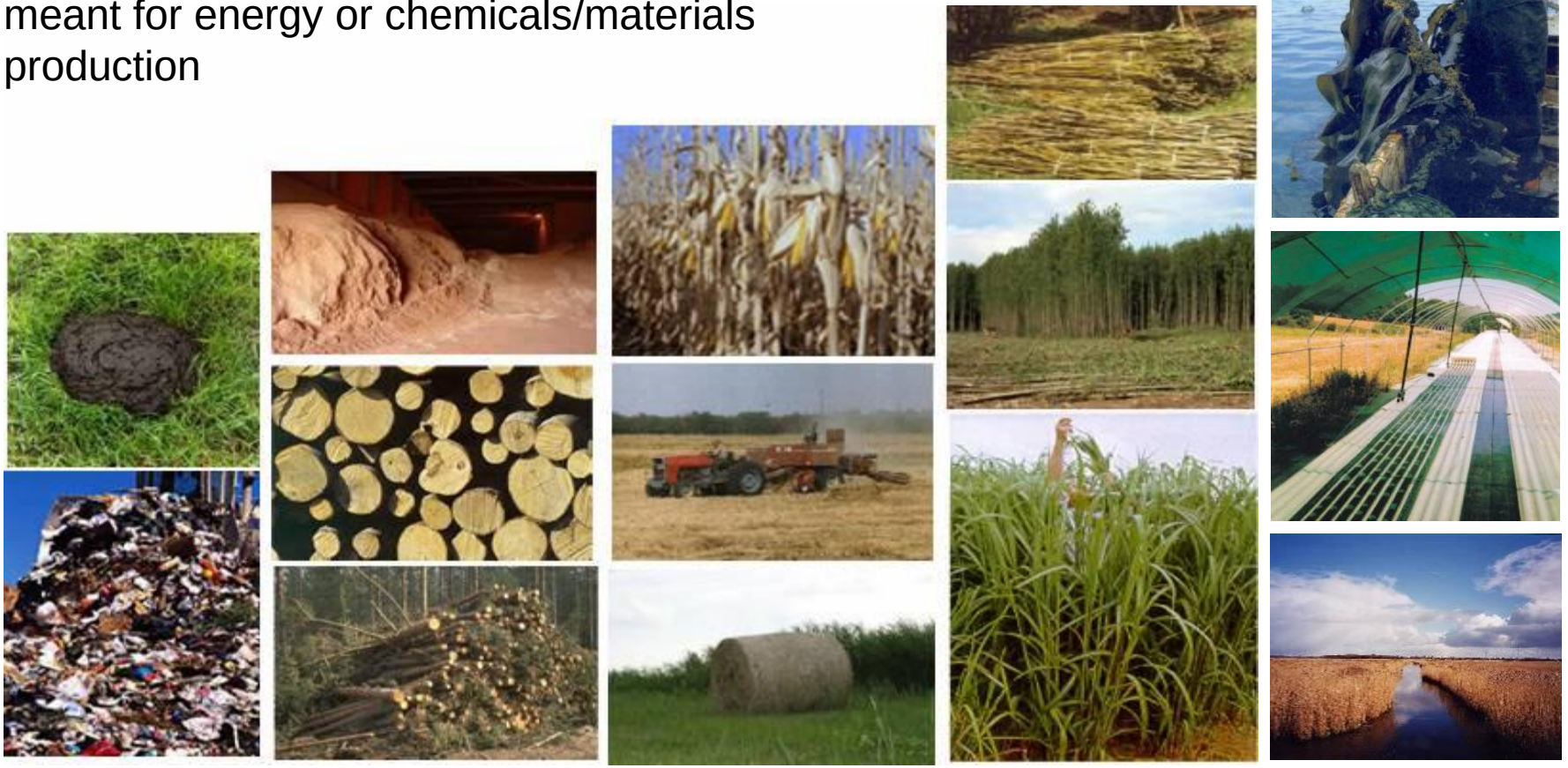
Biomass Pre-Treatment Licensees, clients

- Torrefaction technology
  - Demo plant operational



Biomass – a diverse energy source

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



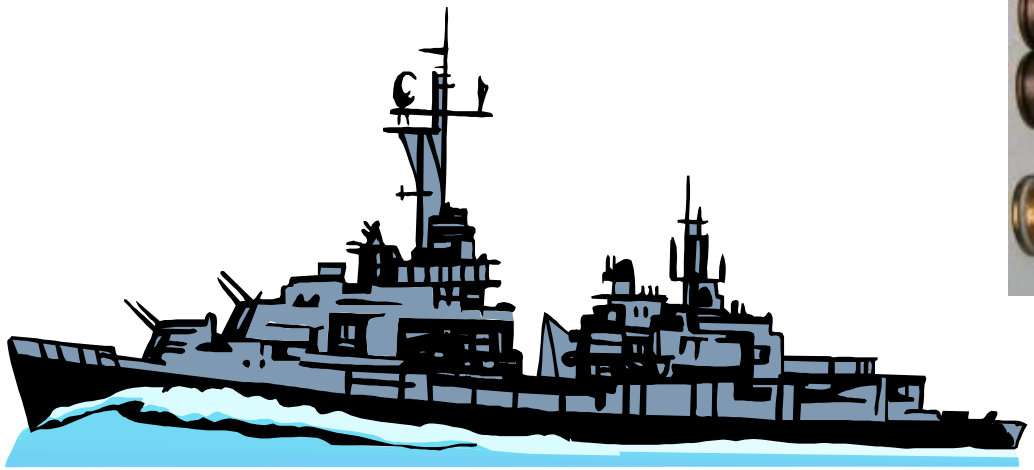
waste wood (agricultural) residues energy corps aquatic biomass

Bio-Offshore

- Seaweed cultivation area 5.000 km2 (<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)
- ECN-C—05-008

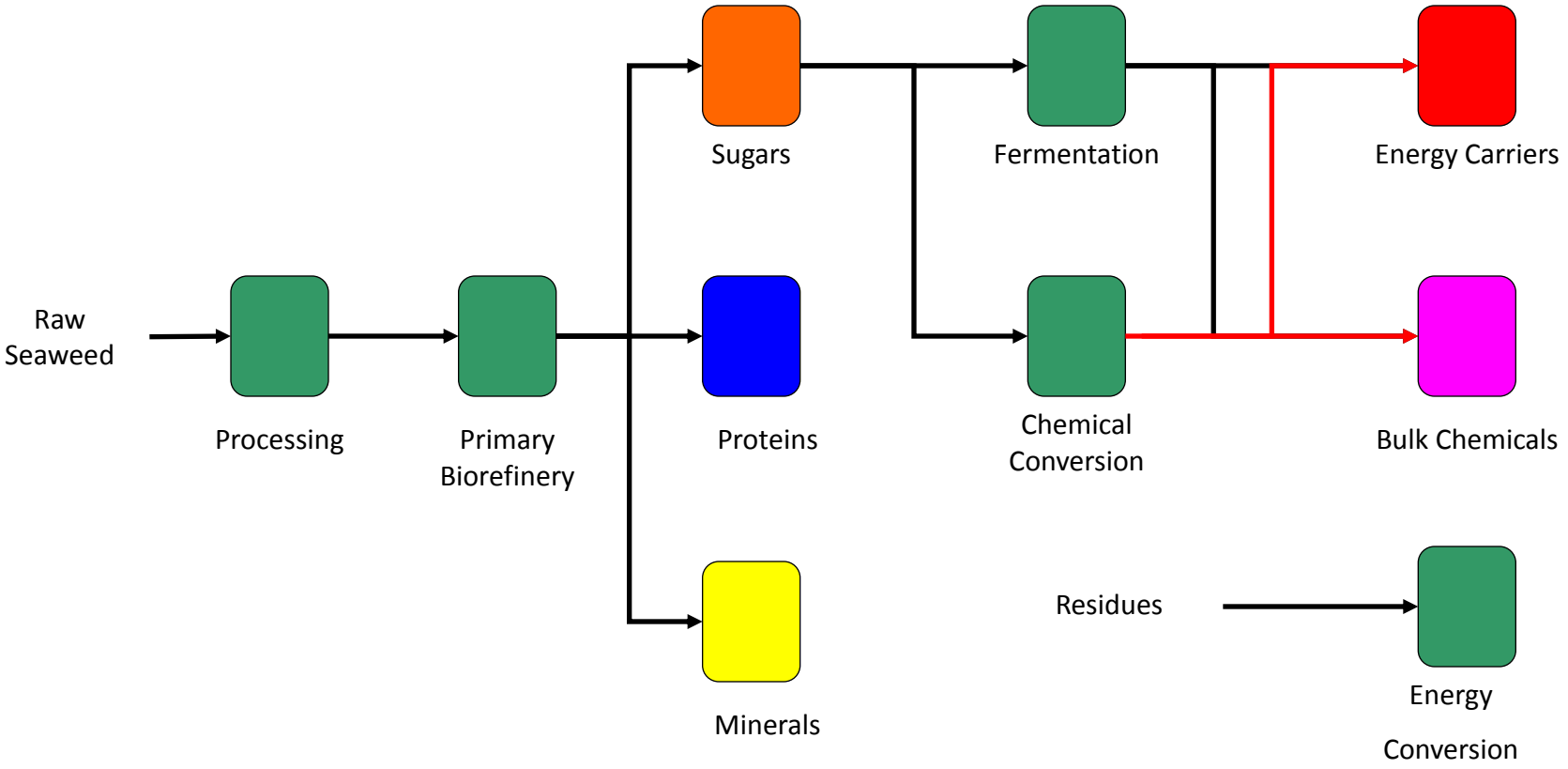
Current intiatives

- Crown Estate, 15,000 km^2 for biogas production
- Denmark, MAB3
- France, seaweed for biogas project
- Norway, Statoil initiative (seaweed to ethanol)
- India, national seaweed initiatives (seaweed to ethanol)
- South Korea, seaweed to ethanol initiative
- EU, use seaweed for biofuels
- US: PNNL-Canadian initiative
- Etc.



Cordite

Seaweed biorefinery process concept



Seaweed species native to the North Sea

Saccharina latissima

Laminaria digitata

Laminaria hyperborea

Ulva sp.

Alaria esculenta

Palmaria palmata

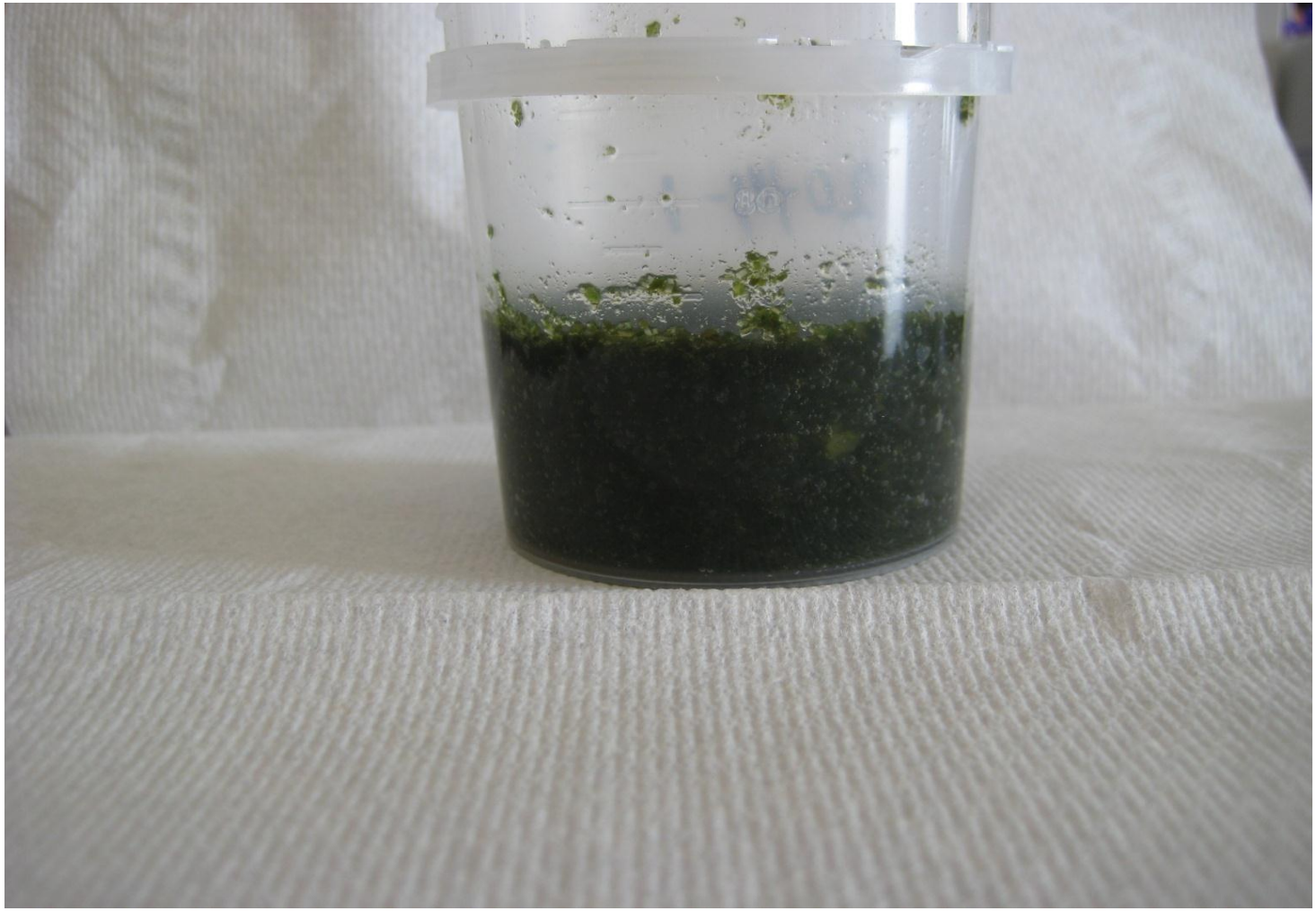
Fractionating seaweeds

Differences between biomass

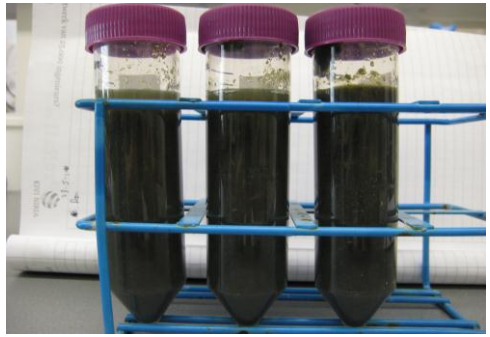
- Lignocellulosic biomass:
- Cellulose
  - Extremely recalcitrant
- Lignin
  - Heterogeneous polymer
    - Species, source and time of harvesting dependent
- Hemicellulose
  - Easy to hydrolyse
- Ash
  - Low to high
- Overall composition reasonably stable

- Seaweed biomass
- Carbohydrates
  - Type dependent on species
  - Amount dependent on season and location
- Proteins
  - Aminoacid composition dependent on species
  - Amount dependent on season and location
- Ash
  - Species dependent
  - Amount dependent on season an location
- Extreme differences between seasons

Re-hydrated Seaweed



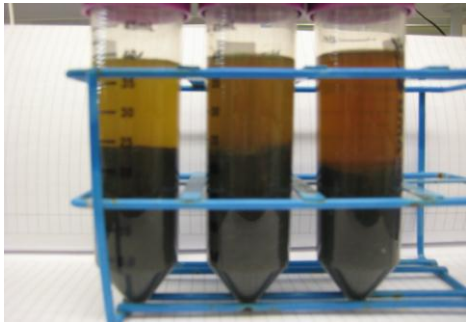
Fractionation



Water +
Seaweed

Optional
Catalyst

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

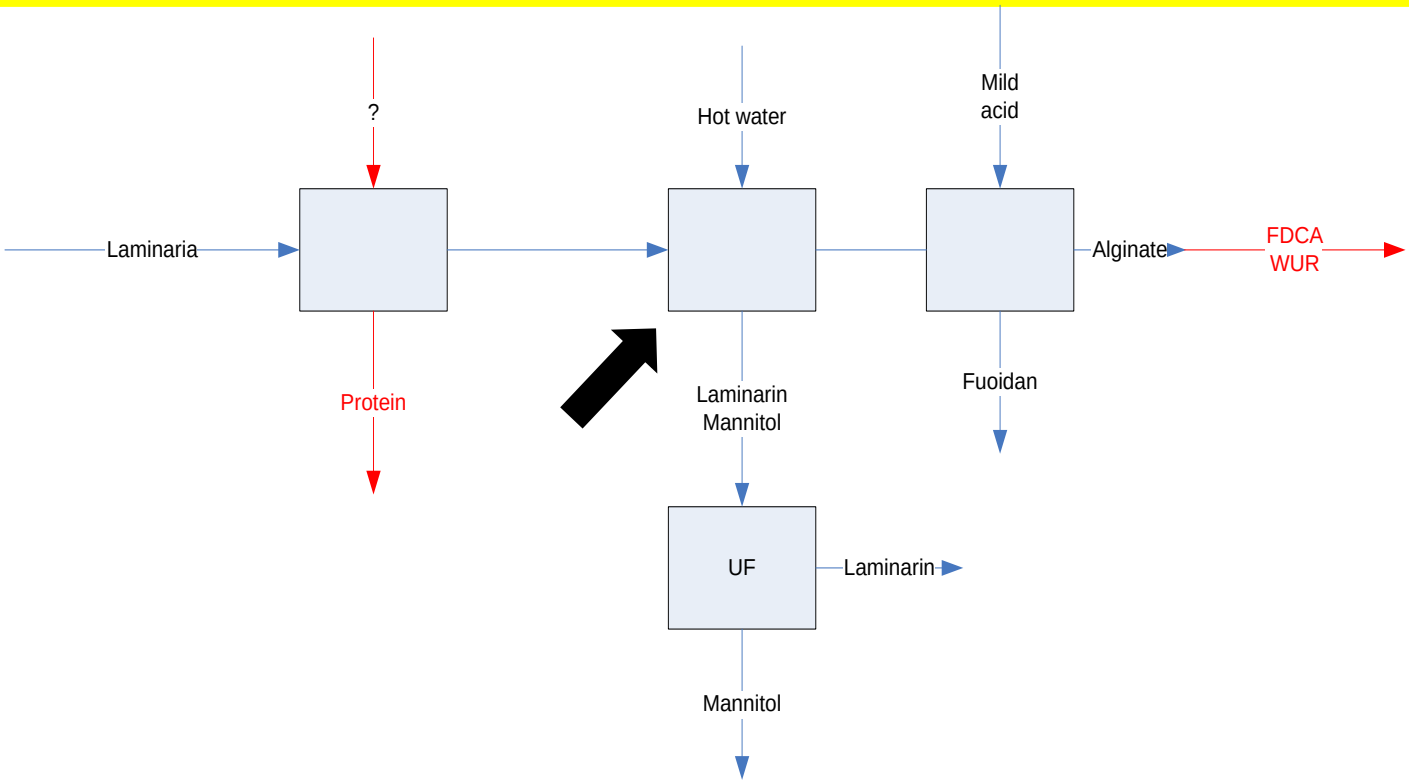


Liquid

Solid

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

Fractionation *Laminaria / Saccharina*

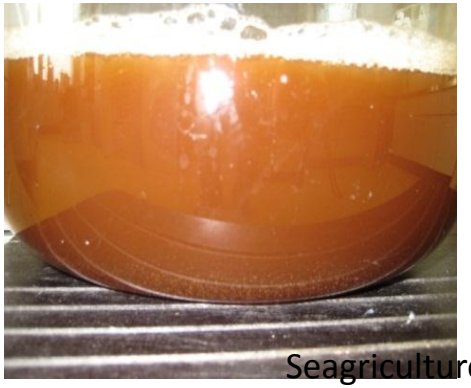


- Potential mannitol uses: e.g., conversion to isomannide, intermediate for plasticizers, fuel additives, PET replacements, epoxy resins & PUR.
- Patent filed on mannitol extraction from brown seaweed (Sept, 2012).

Saccharina tests

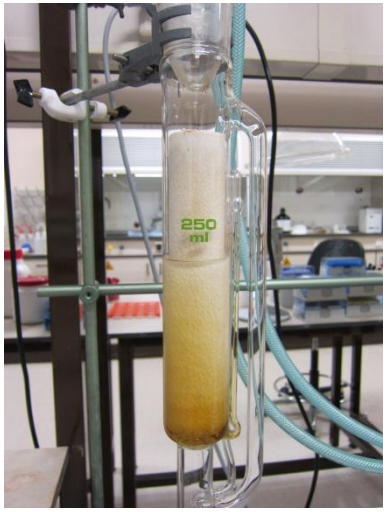
- Harvest June 2013, Galway, Ireland.
  - Huge leaves → cut to ~5 cm pieces for experiments.
  - Moisture: 82-85%.

- Obtain high mannitol & laminaran fractions
- Extract with water (1:1)
- Test fermentation/isolate mannitol

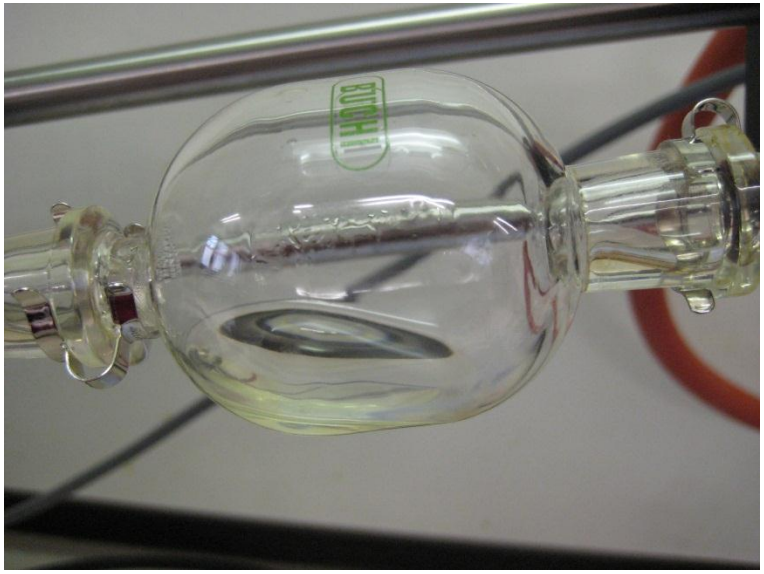


T (°C)	pH	Solids (dw%)
RT	5.0	72.2
80	5.9	70.8
120	5.6	63.2

Crude carbohydrates and isolated mannitol



Synthesis of iso-mannide

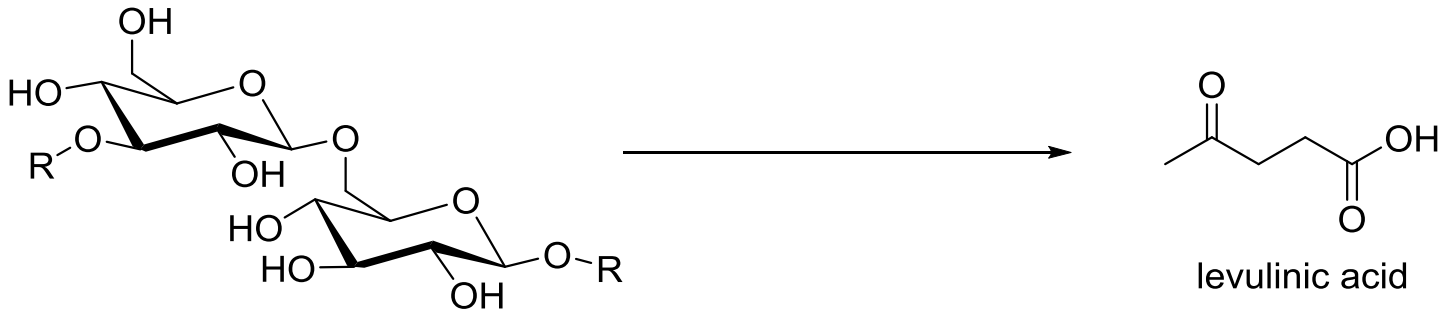


Applications of iso-mannide

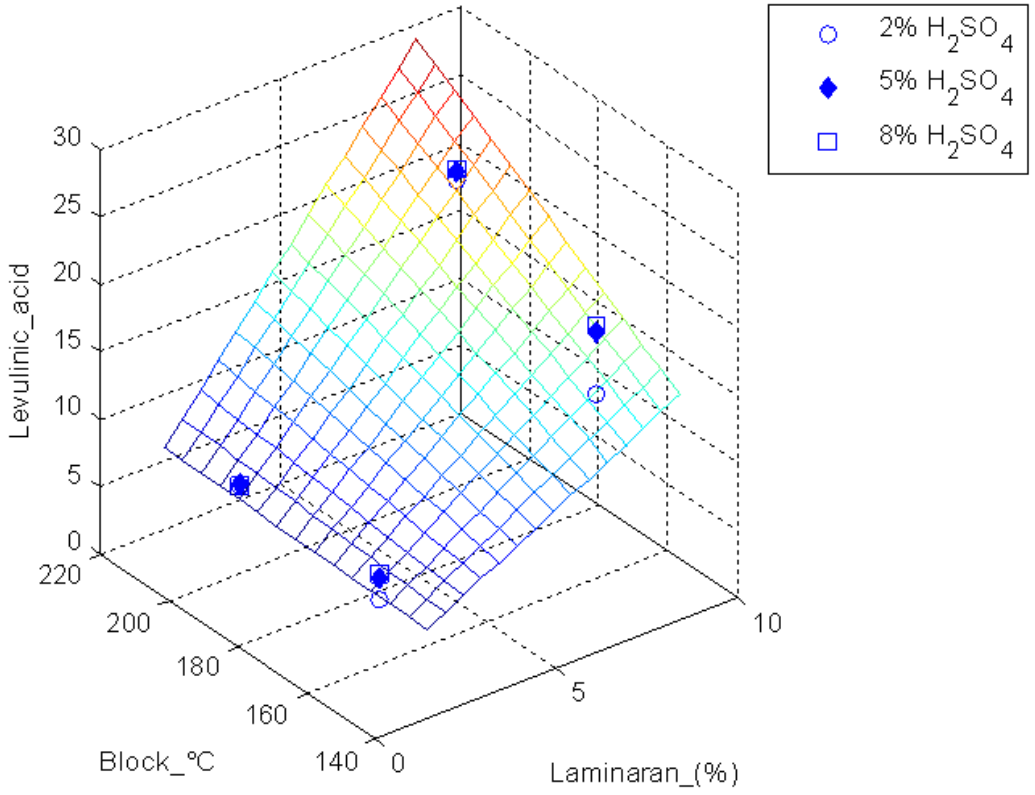
- Isomer of iso-sorbide
- Interconvertable into other isomers
- Separation based on boiling point possible
- Intermediate for
  - Plasticizers
  - Fuel additives
  - PET replacements
  - Epoxy resins
  - PUR

- Prepared isomannide from fresh seaweed!

Laminaran to levulinic acid



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

Table 5. Concentration of sugars and products of *C.beijerinckii* fermentation on *Saccharina latissima* and *Laminaria digitata* extracts.
a: (E) Cultures performed in the correspondent extract (EN) cultures performed in the correspondent extract supplemented with CM2 nutrients.

Fermentation of extracts from brown seaweeds

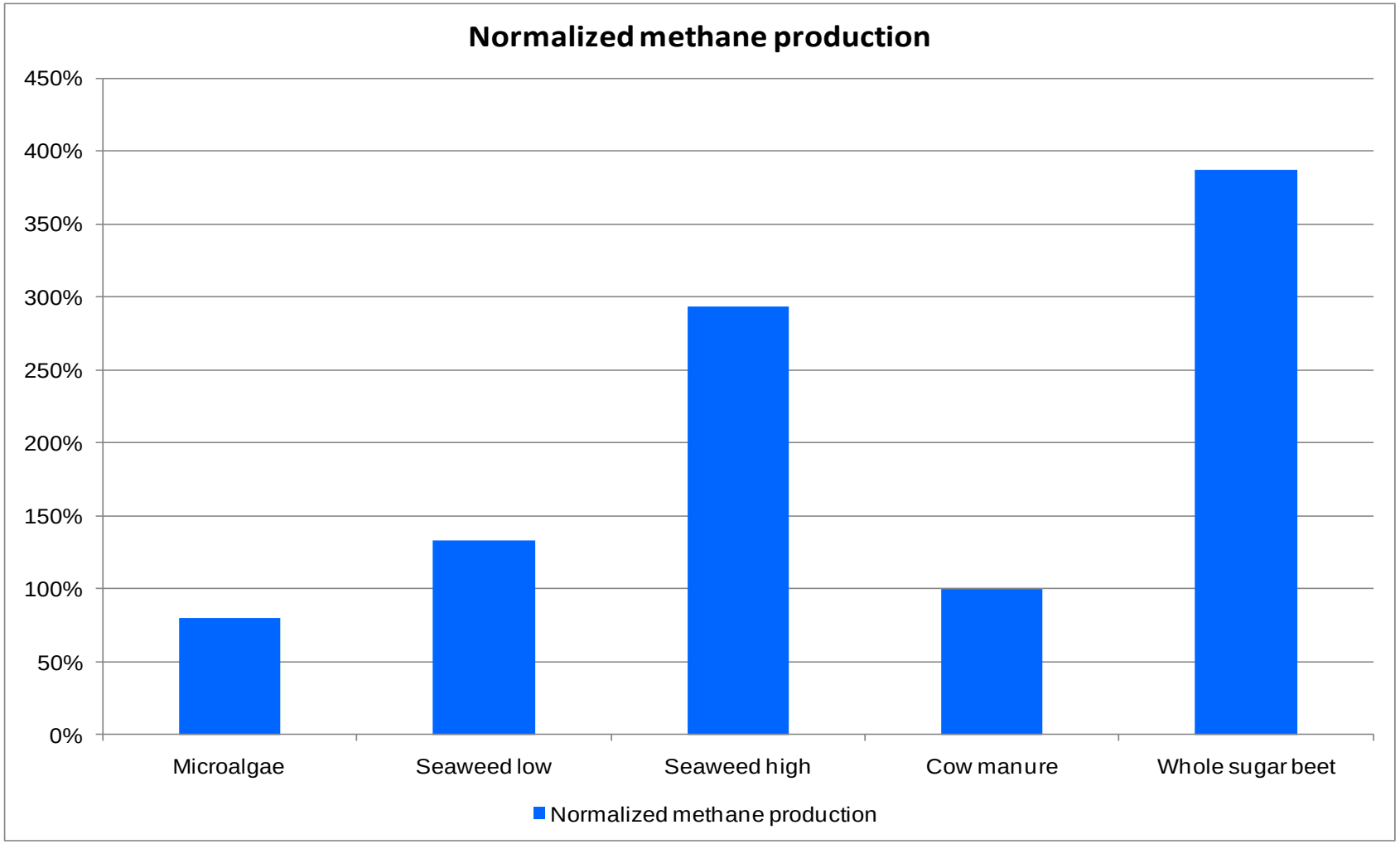
Tested 4 extracts of *Laminaria digitata* and 2 of *Saccharina latissima*

- Main sugars: Mannitol, glucose is low
- Liberation of free glucose during growth
- Extracts are fermentable
- Low ABE production,
- High acid production

	L.digitata 12080901		S.latissima 12072701		S.latissima 12073101	
Cultures[a]	E	EN	E	EN	E	EN
Sugars at t=0 h (g/L)						
Glucose	0.45	0.46	0.40	0.60	0.31	0.35
Mannitol	5.80	5.85	15.98	13.49	16.04	15.87
Total	6.25	6.31	16.38	14.09	16.35	16.22
Sugars at t=300 h (g/L)						
Glucose	0.00	0.00	7.44	0.18	6.13	5.66
Mannitol	2.48	0.00	13.68	13.68	8.37	6.31
Total	2.48	0.00	21.12	13.86	14.50	11.99
Acetic Acid						
t=0 h (g/L)	0.00	2.45	0.00	2.30	5.05	7.21
t=250 h (g/L)	0.00	0.79	0.76	1.05	1.06	1.81
Products at 300 h (g/L)						
ABE	0.27	1.04	0.63	4.33	1.31	1.07
Butyric Acid	4.26	1.14	1.15	3,64	5.4	9.95

Digesters (photos courtesy of Process Groningen)

Digestion results



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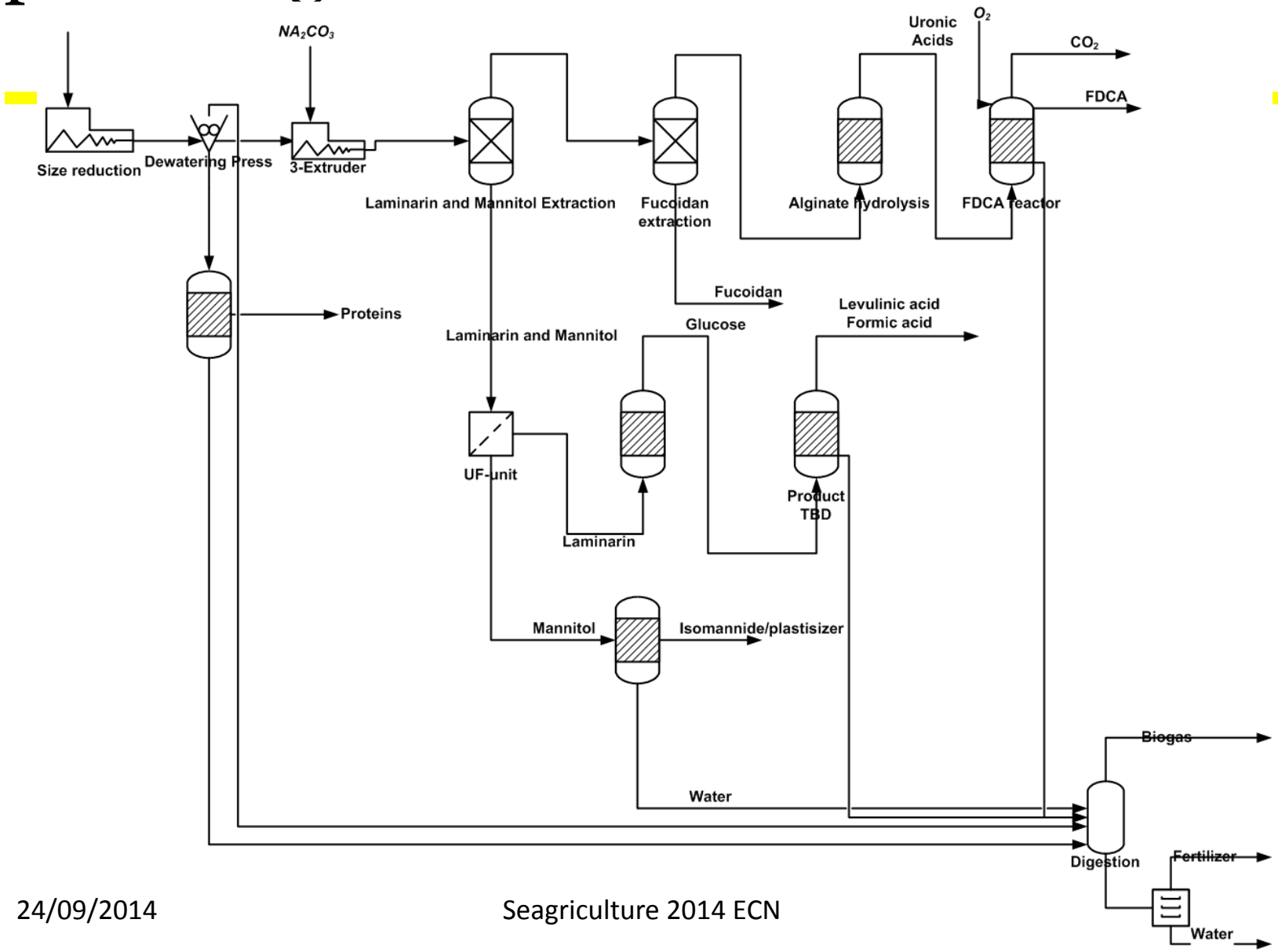
Economics

Estimate MRP seaweed when producing chemicals



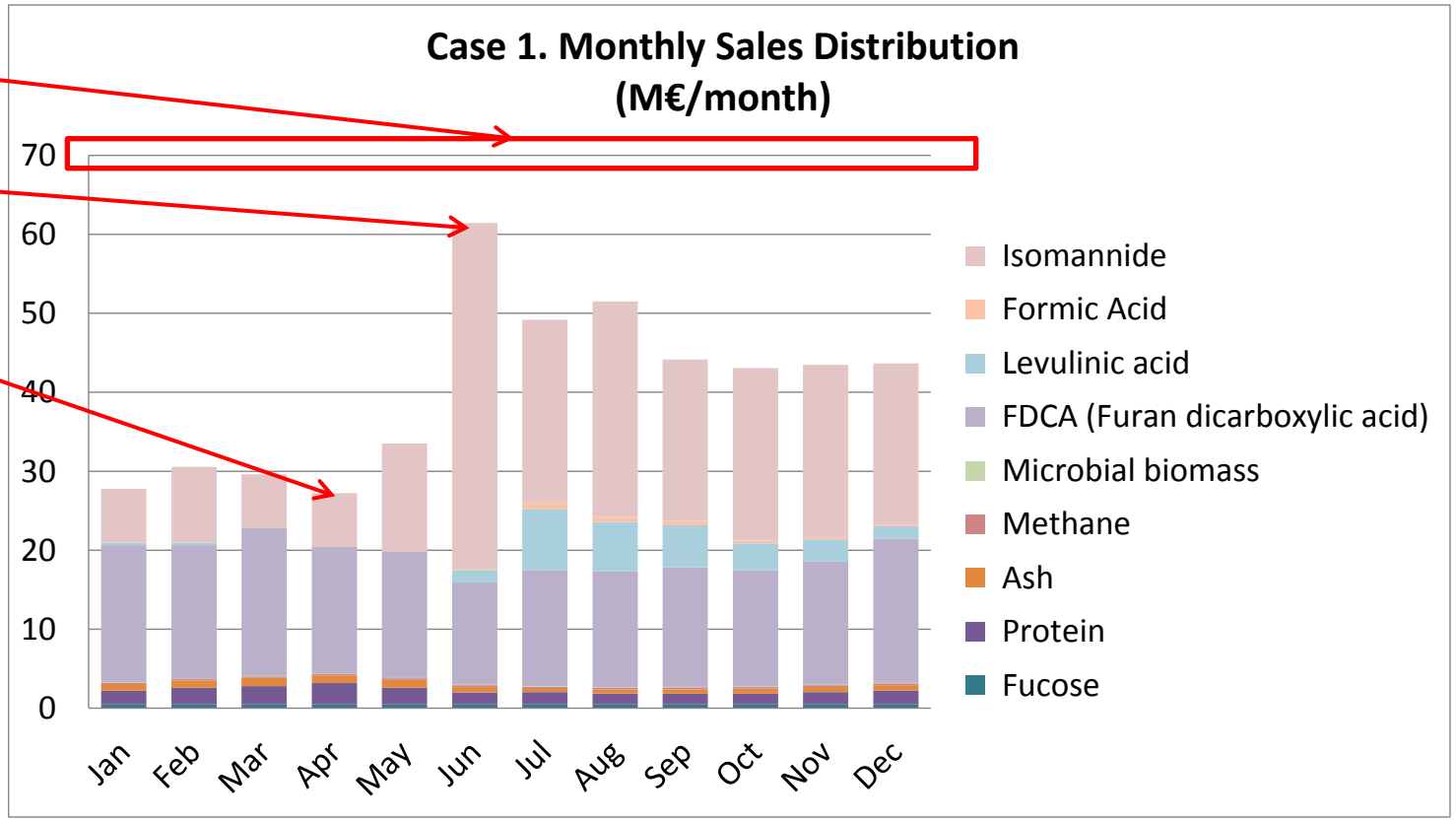
Composition: Laminaria Digitata

Harvest mont	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sept	Oct	Nov	Dec
Laminaria digitata												
% of dry weigth												
Alginic acid	39%	38%	42%	36%	36%	29%	33%	33%	34%	33%	35%	41%
Fucose	4%	4%	4%	4%	4%	4%	4%	4%	4%	4%	4%	4%
Mannitol	5%	7%	5%	5%	10%	32%	17%	20%	15%	16%	16%	15%
Glucose	1%	1%	0%	0%	0%	5%	25%	20%	17%	11%	9%	5%
Protein	9%	11%	12%	14%	11%	8%	8%	7%	7%	7%	8%	9%
Ash	28%	30%	35%	32%	33%	23%	14%	17%	19%	21%	22%	24%
Others	15%	10%	3%	9%	6%	0%	0%	0%	4%	8%	6%	3%
Elements %												
C	25%	26%	27%	25%	26%	32%	36%	35%	32%	30%	30%	31%
H	2%	2%	2%	2%	2%	4%	4%	4%	3%	3%	3%	3%
O	30%	31%	32%	29%	31%	40%	45%	44%	40%	37%	37%	38%
N	1%	2%	2%	2%	2%	1%	1%	1%	1%	1%	1%	1%
Ash	28%	30%	35%	32%	33%	23%	14%	17%	19%	21%	22%	24%
Unknown	15%	10%	3%	9%	6%	0%	0%	0%	4%	8%	6%	3%
Total	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%

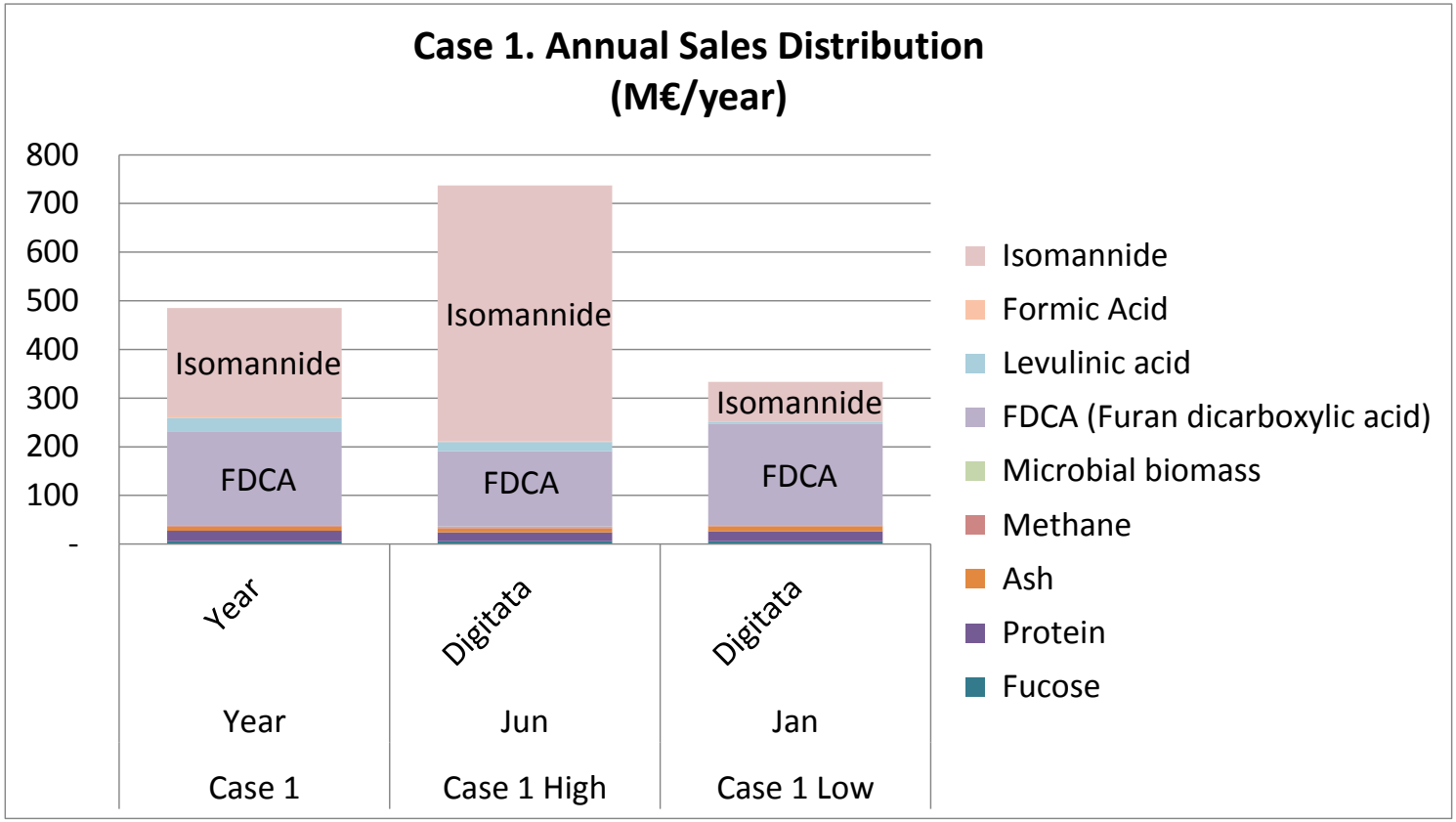
Laminarin →

Sales Revenues/Harvesting Season

- Year
- High
- Low



Profit drivers



To make a long story short

- Need to valorize all components from seaweed
- Profit drivers are the high value components
- Seaweed to biofuels not as attractive
- Seaweed can cost up to € 1000/ton (dry matter)
  - POT 2 years!
- Storing seaweed not allways necessary

Major achievements

Major achievements

- Several species specific fractionation schemes
- Fractions ferment to ABE (and precursors), residues to biogas
- Isolated pure mannitol
- Converted mannitol to isomannide
- Produced levulinic acid from seaweed
- Produced FDCA precursors from seaweed
- Develop flexible economic model
- Positive businesscases without subsidies (POT 2 years)
- Large visible dissimination efforts
- International recognition and traction


Thank you for your attention
Questions/Comments

Questions?
For more information

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