

Fractionation of sustainable biomass from land and sea

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Technology development at ECN

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Wageningen

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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

Lignocellulosic biorefinery

Biomass – a diverse energy source

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



waste



wood



(agricultural) residues



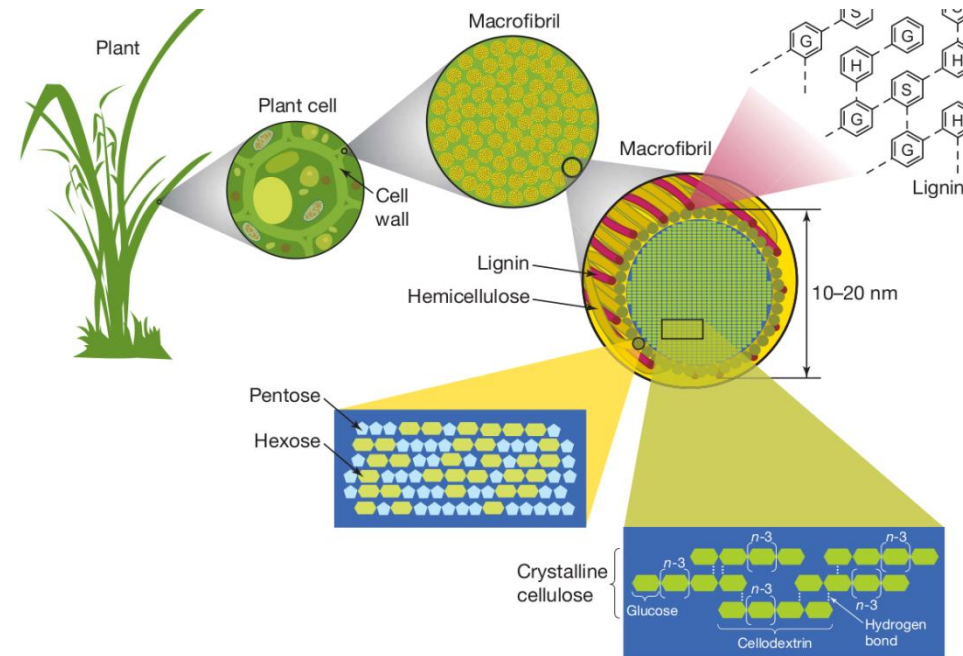
energy crops



aquatic biomass

Lignocellulose Constituents

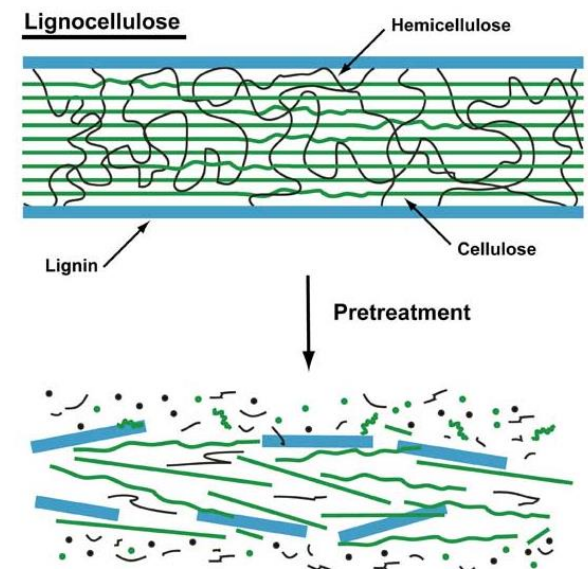
- Sugar polymers:
 - Cellulose, linear polymer of glucose.
 - Hemicellulose, branched copolymer of C5 and C6 sugars.
- Lignin:
 - Polymer of aromatic compounds.
- Factors influencing composition:
 - Plant species.
 - Part of plant (bark, stem, ...).
 - Location of cultivation,



Source: University of North Dakota.

Saccharification Cellulose

- Hydrolysis of cellulose into glucose: enzymatic or chemocatalytic.
 - Benefit enzymatic hydrolysis: selectivity to glucose.
- Direct enzymatic saccharification of lignocellulose not feasible:
 - Structural components linked (physically & chemically).
 - Cellulose protected against decay by lignin.
 - Crystallinity cellulose.
- Pretreatment: overcoming biomass 'recalcitrance' by e.g.:
 - Removing hemicellulose and lignin to improve accessibility for hydrolytic enzymes.
 - Removing / altering lignin to reduce non-productive cellulase binding.
 - Reducing crystallinity of cellulose.



Source: USDA Agricultural Research Service.

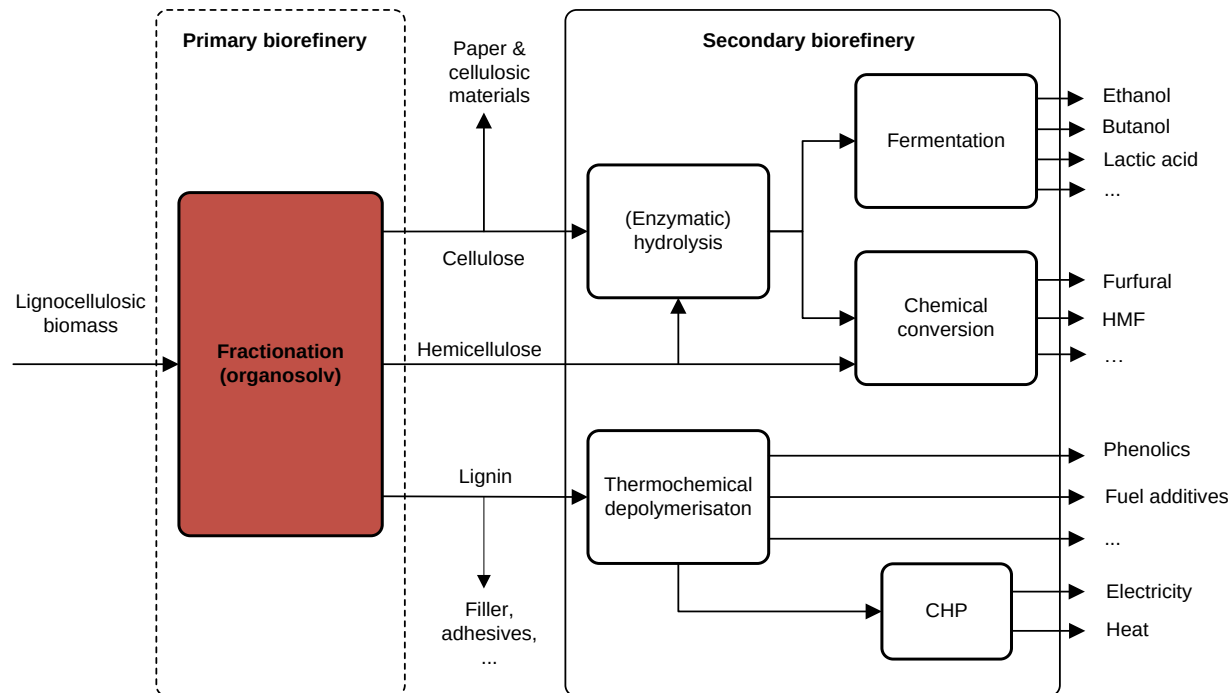
Pre-treatment

- Several physical-chemical pre-treatment routes under development.
- Main pretreatment routes (pilot-scale)¹:
 - (Dilute) acid pre-treatment
 - Steam explosion
- Routes effective for cellulose, however:
 - Lignin ends up in residue (with unconverted sugars, process chemicals, ash, etc).
 - Residue generally only suitable for CHP.
- Alternative:
 - Separation of lignin prior to enzymatic hydrolysis.
 - Preserving chemical structure of lignin & enabling higher value applications.
→ Organosolv.

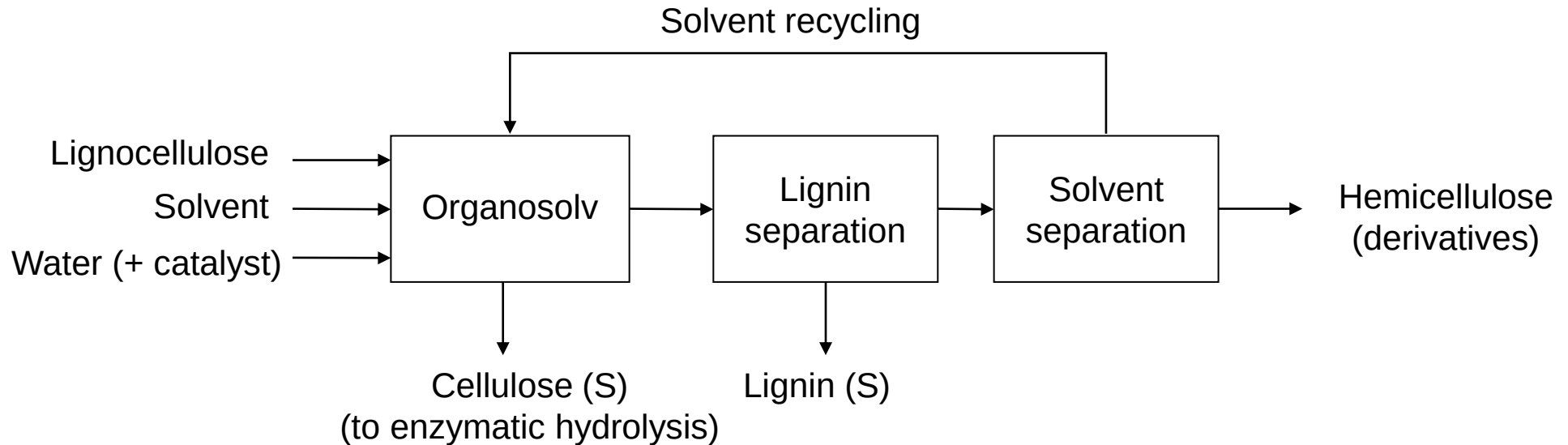
¹ Harmsen et al. (2010), Literature review of physical and chemical pretreatment processes for lignocellulosic biomass, report ECN-E--10-013.

Lignocellulose Biorefinery

- Why organosolv?
 - Fractionation of all major constituents in a sufficient quality for valorisation.
 - Including extraction of high-quality lignin for production of chemicals.



Organosolv Process



- Solvents: aqueous ethanol, acetone, ...
- Catalyst: H_2SO_4 , ...
- Typical process conditions: 160-200 °C, 30-120 min.

General information: Reith et al. (2011) A step towards the development of a Biorefinery, NPT procestechologie, 18(1), 26-28

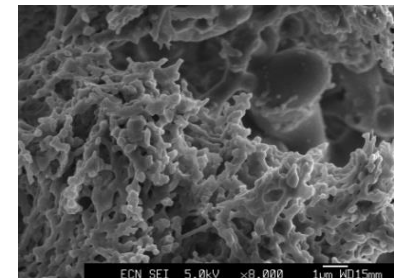
Effect of biomass source

- Optimisation towards different products possible.
- Example from published results: enzymatic digestibility.

Feedstock	T (°C)	Solvent (% w/w)	Catalyst	Enzymatic digestibility (%)
Wheat straw	205	50% acetone	Auto	80
Wheat straw	210	50% EtOH	Auto	86
Olive tree	210	43% EtOH	Auto	90
Wheat straw	190	60% EtOH	HCl (20 mM)	99
Wheat straw	190	60% EtOH	H ₂ SO ₄ (30 mM)	89
Willow	190	60% EtOH	H ₂ SO ₄ (10 mM)	87
Wheat straw	175 & 220	H ₂ O & 60% EtOH	Auto	93

Lignin Isolation & Characterisation

- Lignin isolation:
 - Insoluble in H_2O , soluble in ethanol & acetone.
 - Precipitation lignin from organosolv liquor.
 - Lignin isolation efficiency >90%.
- Lignin characteristics:
 - Light brown to black (compacted) powder.
 - High purity (>>90 wt%).
 - Main contaminant oligomeric xylose (hemicellulose).
 - Lignin sulphur and ash free (max 0.1 wt% S).
 - Molecular weight (relative to other types of lignins):
 - Low average (2000-3500 g/mol).
 - Narrow distribution.



Ongoing and Future Work

- Lignin application tests with industrial partners.
- Construction bench-scale continuous organosolv reactor.
- Partnering for further technology development & commercialisation.

2007



0.1 L



0.5 & 2 L

09/04/2013

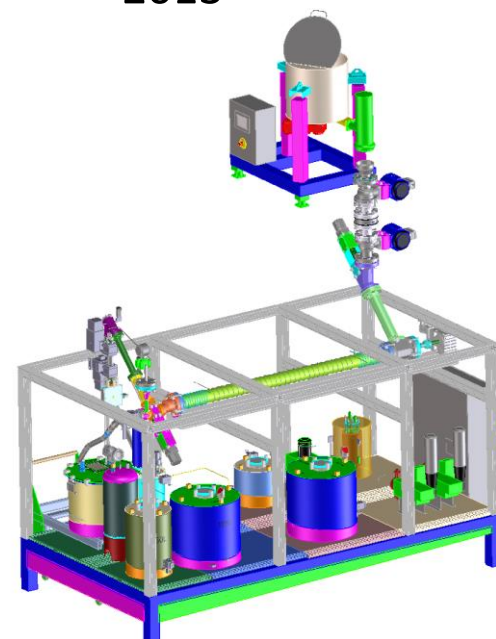
2010



20 L

BFF ECN Jaap van Hal

2013



*Continuous biomass
pretreatment reactor*

Seaweed biorefinery

Parts of seaweed plant



Blade

Stipe

Holdfast

Why seaweeds

- Does not compete with food
- Does not compete with any other land use
- Grows in cold seawater
- The fastest growing biomass at our latitude
 - The Netherlands is as far north as New Foundland
- Biochemical composition: complementary (for fuel/chemicals production) to micro-algae
 - Comprised of carbohydrates, protein and ash

Seaweed species native to the North Sea



Latissima saccharina



Laminaria digitata



Laminaria hyperborea
(Perez)



Ulva sp.



Alaria esculenta (Irish
Seaweed Centre)

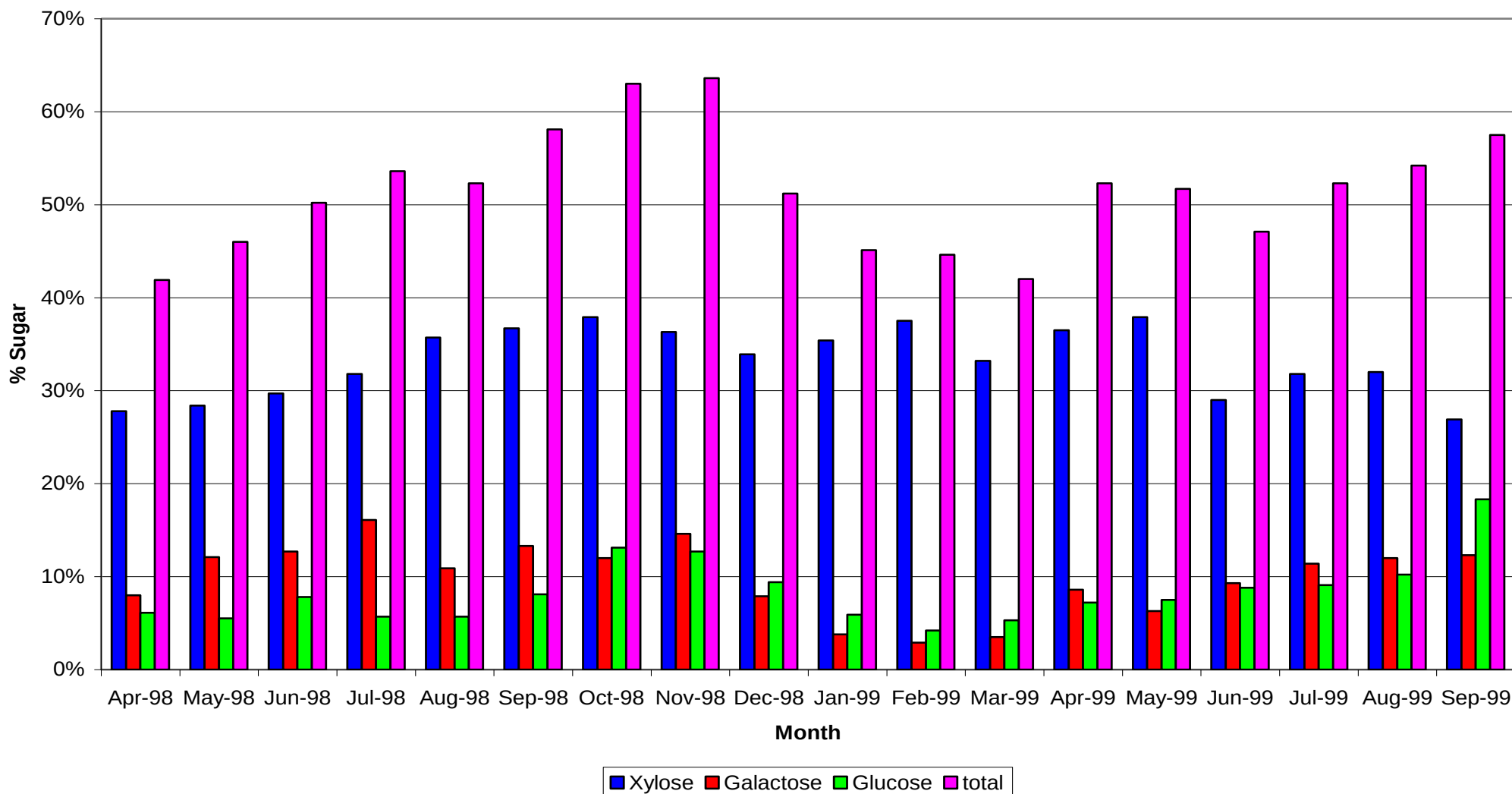


Palmaria palmata
(AWI)

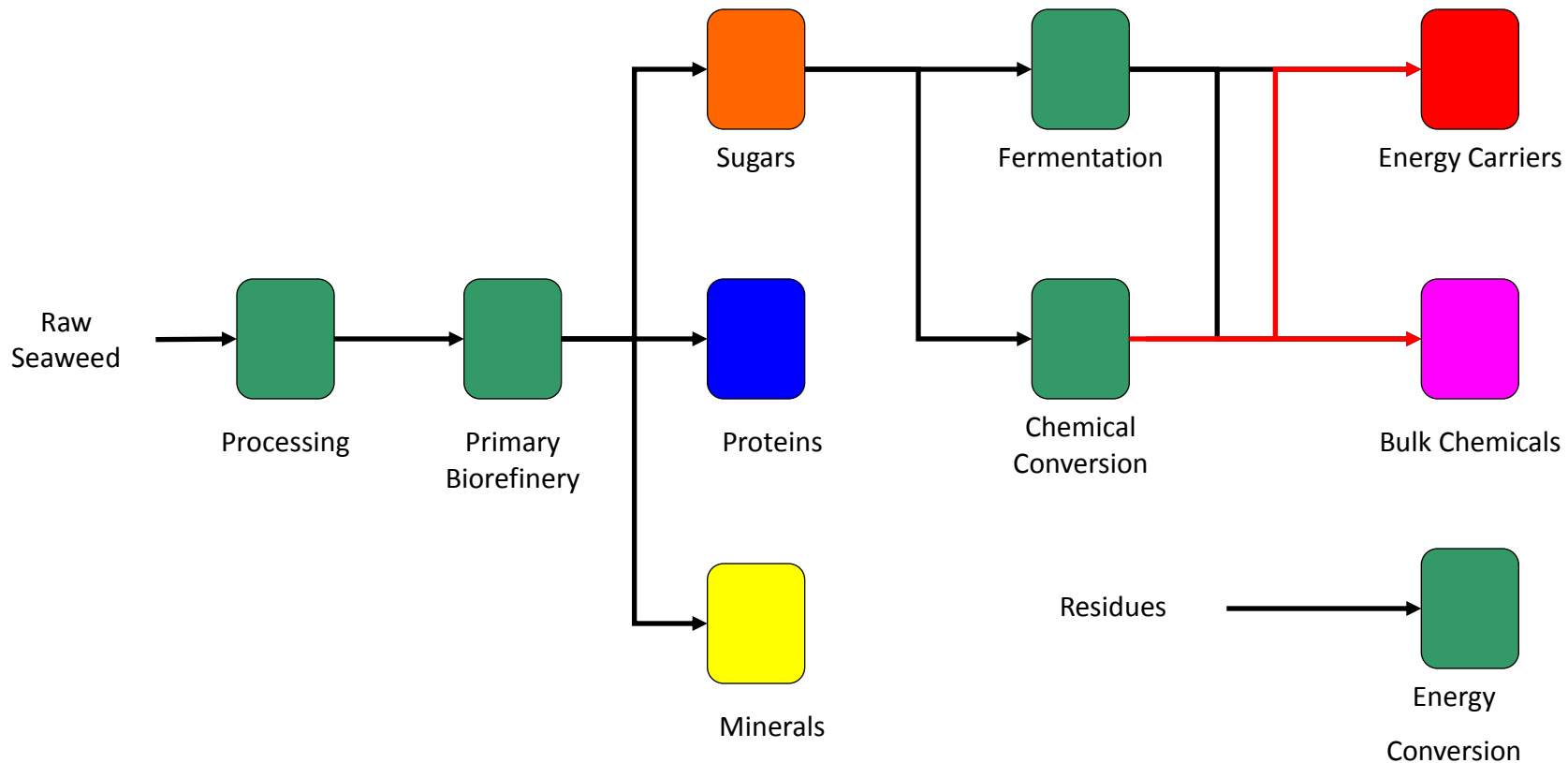
Differences between biomass from land and sea

- Lignocellulosic biomass:
- Cellulose
 - Extremely recalcitrant
- Lignine
 - 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 and location
- Extreme differences between seasons

Total Carbohydrate composition of Palmaria Palmata



Seaweed biorefinery process concept



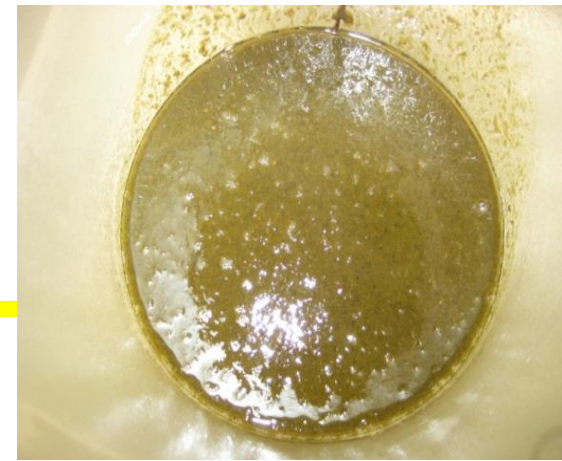
Fresh *Palmaria* tests

- Two tests in 20L autoclave (1 kg dw seaweed).
- >10 kg received, 5 kg wet per test.



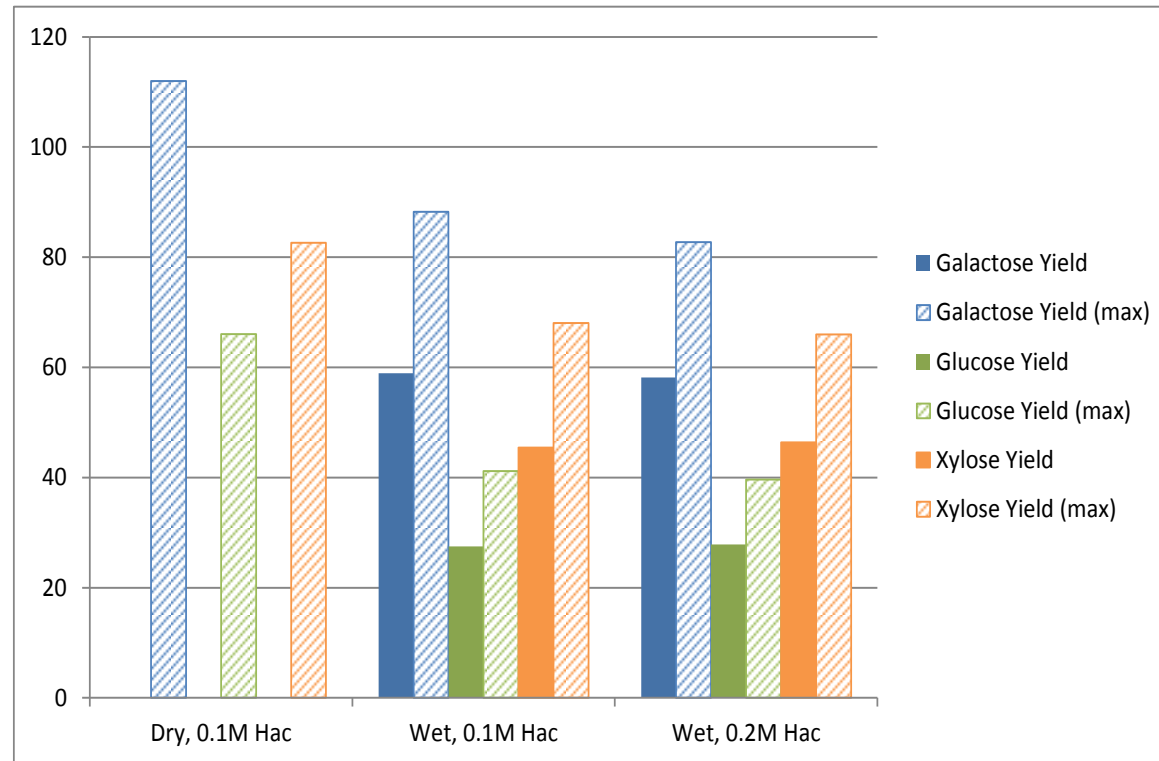
Mild acid pretreatment

- 0.1M acetic acid, 100C, 2h, 9 L/kg dw seaweed.
- Red seaweed turned into green 'soup'.
- After centrifugation, ~6L viscous liquid, ~ 4kg solid product.
- pH ND, solids recovery 51.6% dw.



Yields sugars

- Yields based on amount of extract.
- Max. achievable yield based on liquor starting amount.
- Yield xylose: ~45%.
- Optimization of separation extracted *Palmaria* / extract might increase yield to max ~65%.
- Future work: optimisation of process conditions.



Summary

- Organosolv effective fractionation of lignocellulose to obtain
 - Cellulose with enhanced enzymatic digestibility
 - High-purity lignin
 - Hemicellulose syrup
- Development towards a continuous process
- Organosolv can be adapted to different lignocellulosic biomass sources

- Seaweeds can be fractionated into
 - Their composite carbohydrate molecules
- Seaweeds can be hydrolysed under mild conditions

Question?

Further information



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