MACROFUELS

Carbohydrate analysis of seaweed in the biorefinery to chemicals and fuel context

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Take home messages

- Seaweed specific protocols needed for:
  - accurate mass balances of biorefineries
  - Identification of the process bottle necks and opportunities for improvement
- Color reactions are limited by their (lack of) specificity
- Protocols are converging
- Single run HPAED possible

Who is ECN?

- 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

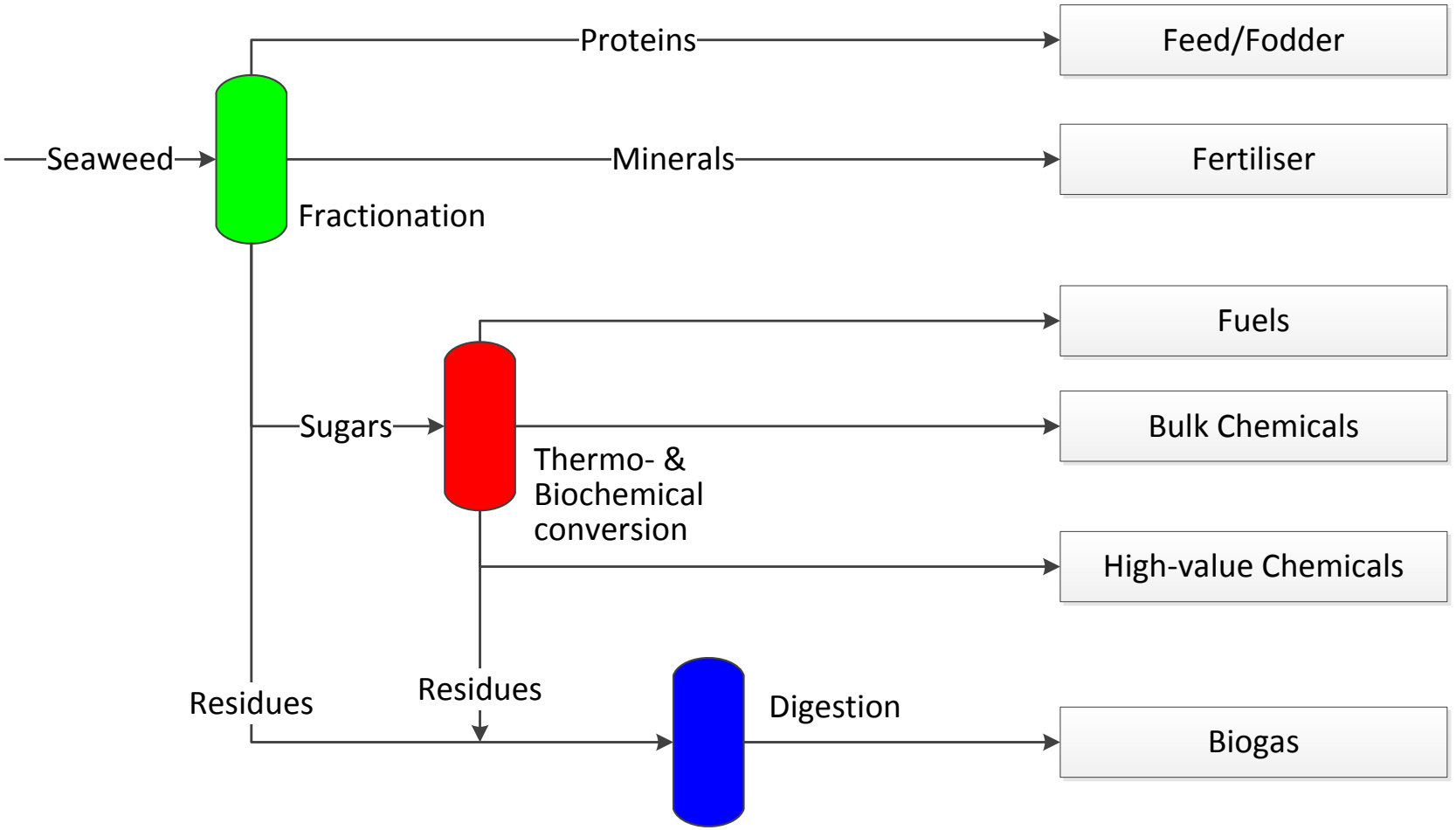
- Independent research institute
- ~500 employees
- Locations:
  - *Petten (HQ)*
  - *Amsterdam*
  - *Eindhoven*
  - *Kuala Lumpur*

The pilot/DEMO stage

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
- Crown Estate, 15,000 km^2 for biogas

Seaweed biorefinery



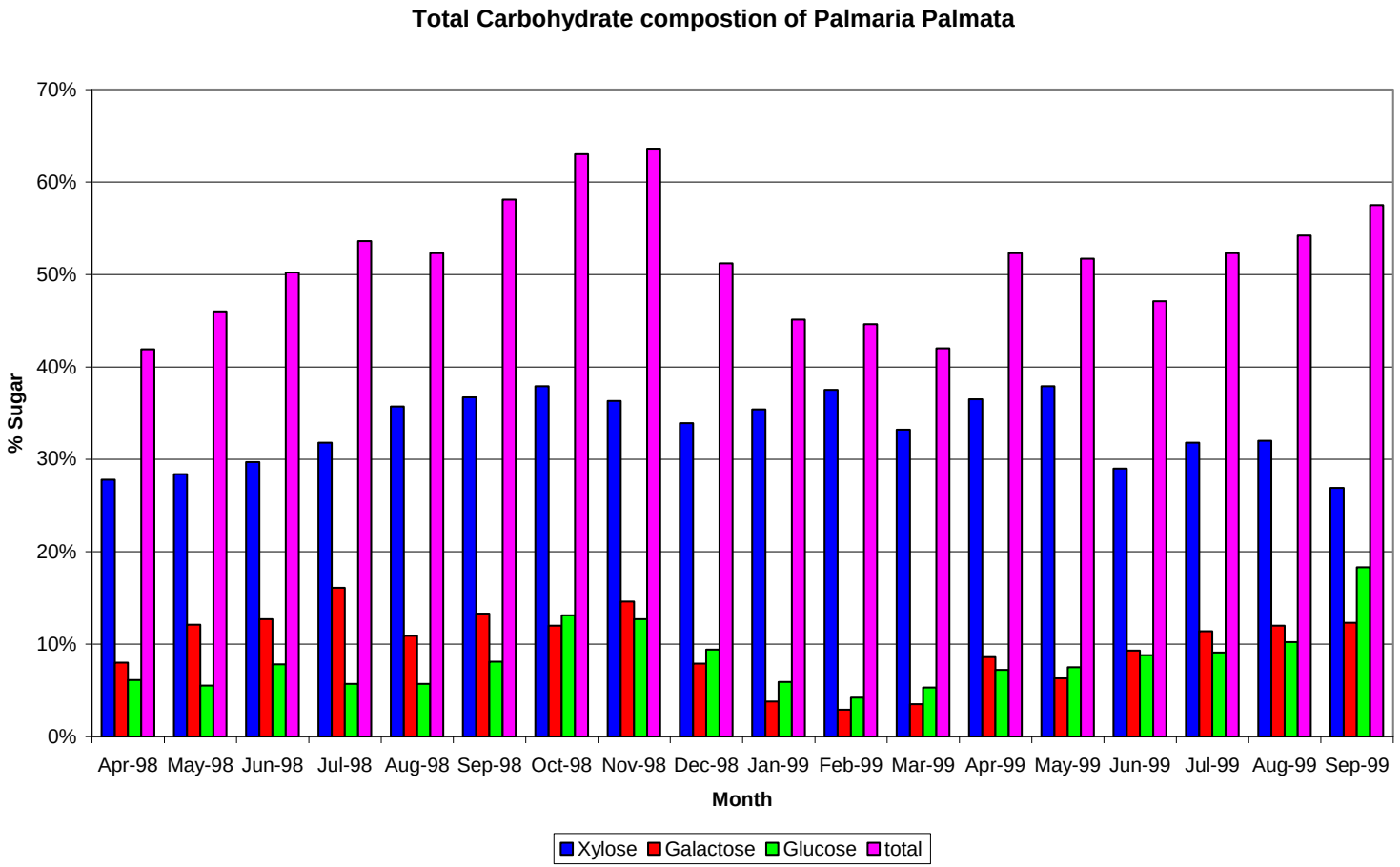
Compositional analysis of seaweed (fractions)

- Critical evalutation of the existing protocols
- Large differences between seaweeds and lignocellulosic biomass
- Large differences between species
- Large seasonal variations
- Different resilience during hydrolysis
- Identification of unknown carbohydrates in the HPAED trace

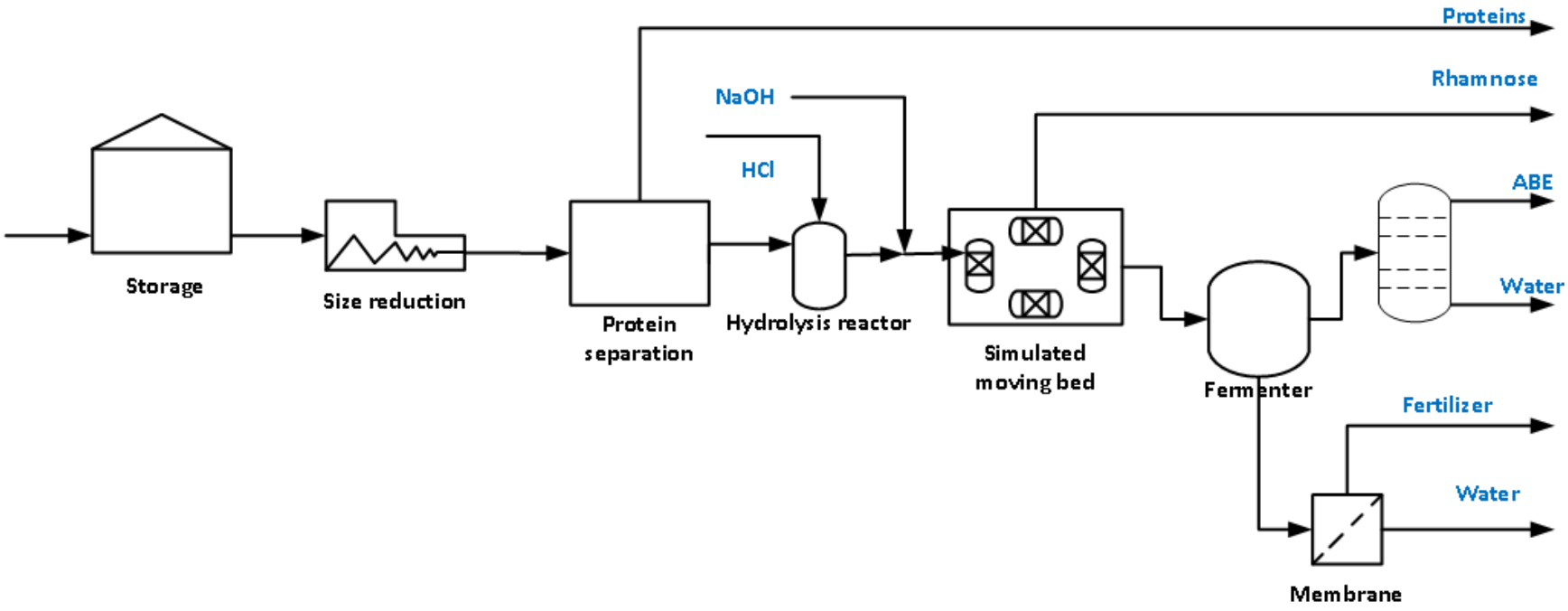
Compositional variation

Seaweed	Brown	Red	Green
Example species	*Laminaria digitata*	*Palmaria palmata*	*Ulva lactuca*
Carbohydrates in seaweed	Mannitol	Floridoside	Ulvan
	Alginate	Xylan	Cellulose
	Laminarin	Cellulose	
	Fucoidan	*Mannitol*	
	Cellulose		
Expected components in hydrolysate	Mannitol	Galactose (floridoside)	Rhamnose (ulvan)
	Glucose (laminarin/cellulose)	Glycerol (floridoside)	Glucuronic acid (ulvan)
	Fucose (fucoidan)	Xylose (xylan)	Iduronic acid (ulvan)
	Mannuronic acid (alginate)	Glucose (cellulose)	Glucose (cellulose)
	Guluronic acid (alginate)	*Mannitol*	Xylose
	Galactose	*Mannuronic acid*	*Fucose*
	Xylose	*Guluronic acid*	*Galactose*
	Galacturonic acid		

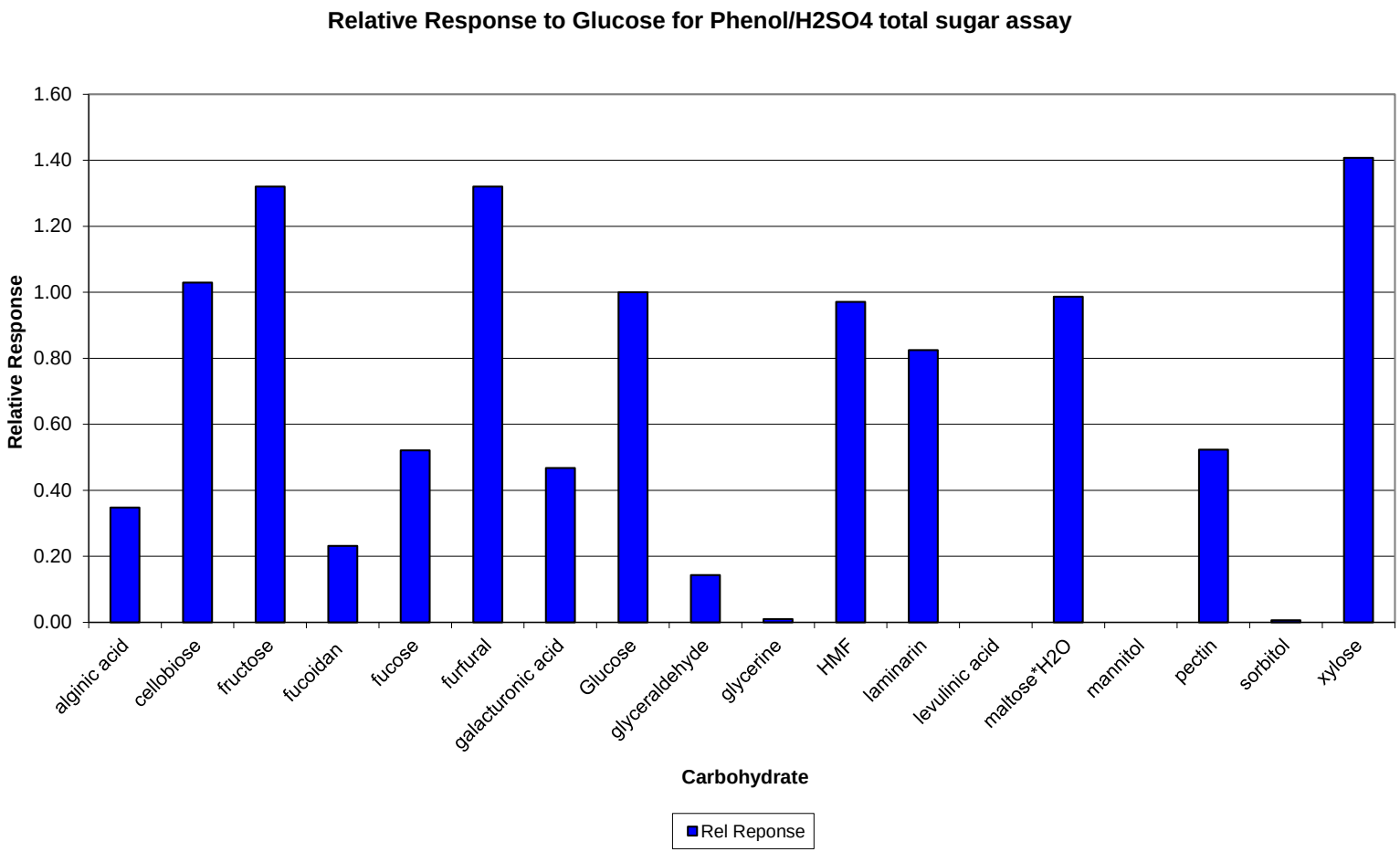
Example of seasonal variation



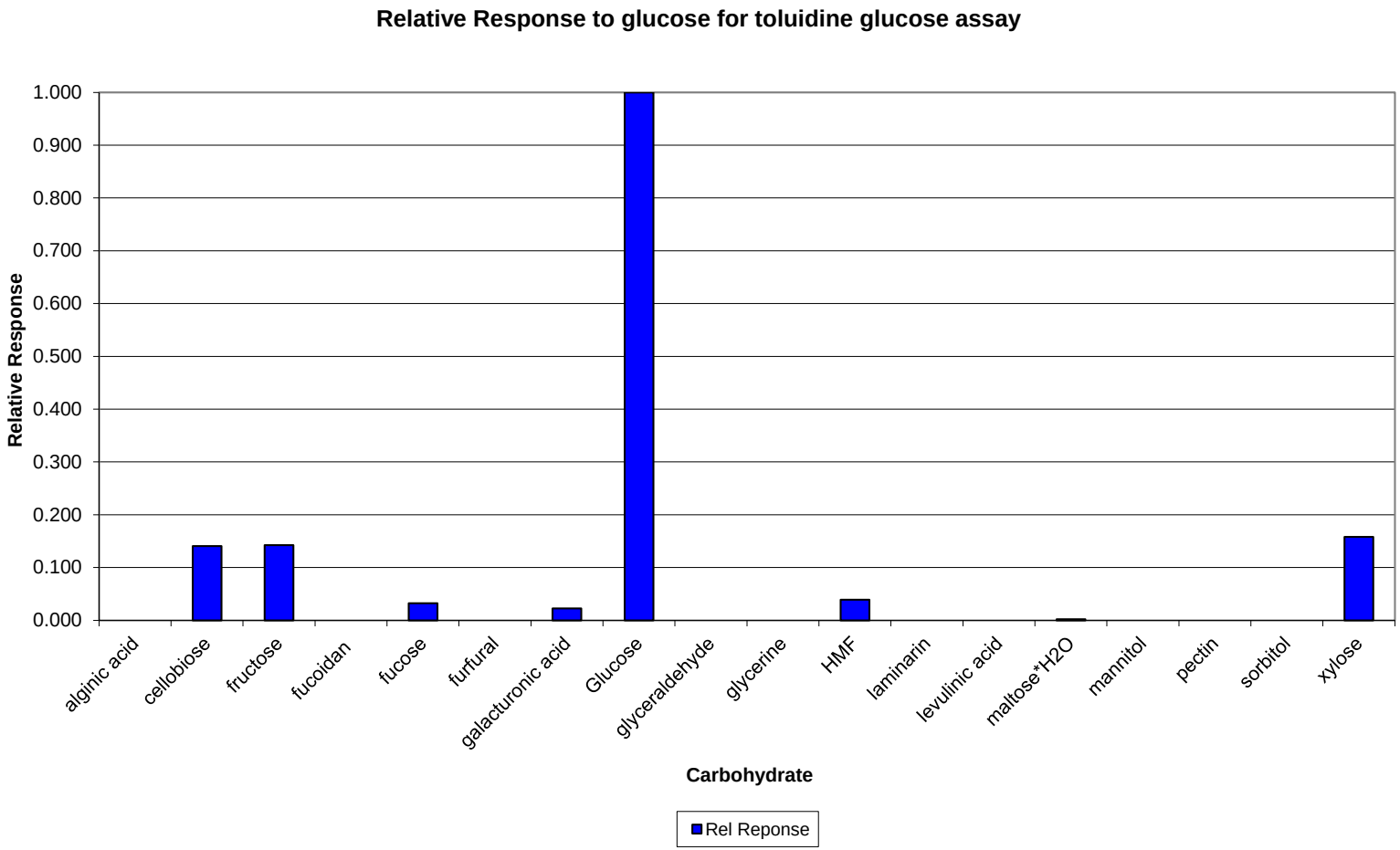
Ulva biorefinery



Limitation of color reactions

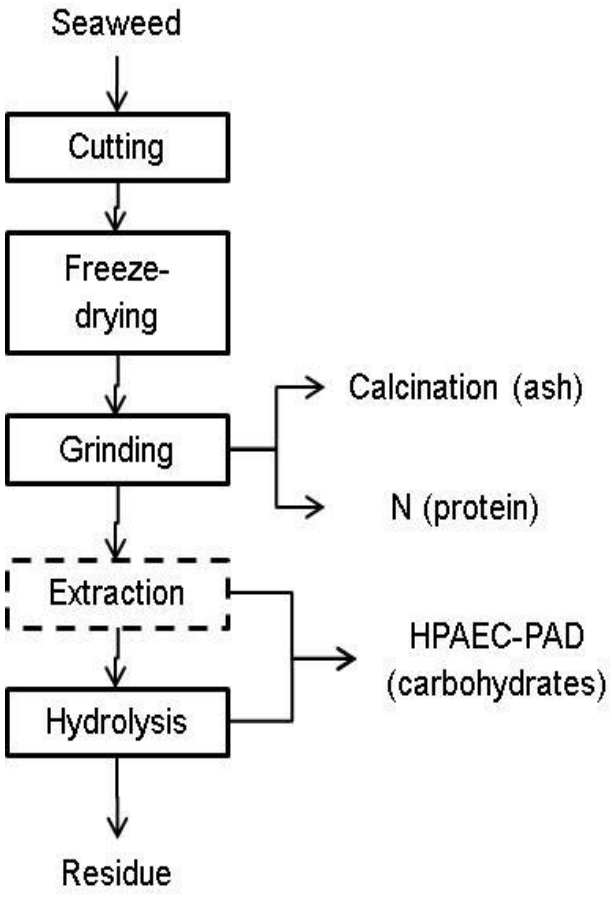


Limitation of color reactions

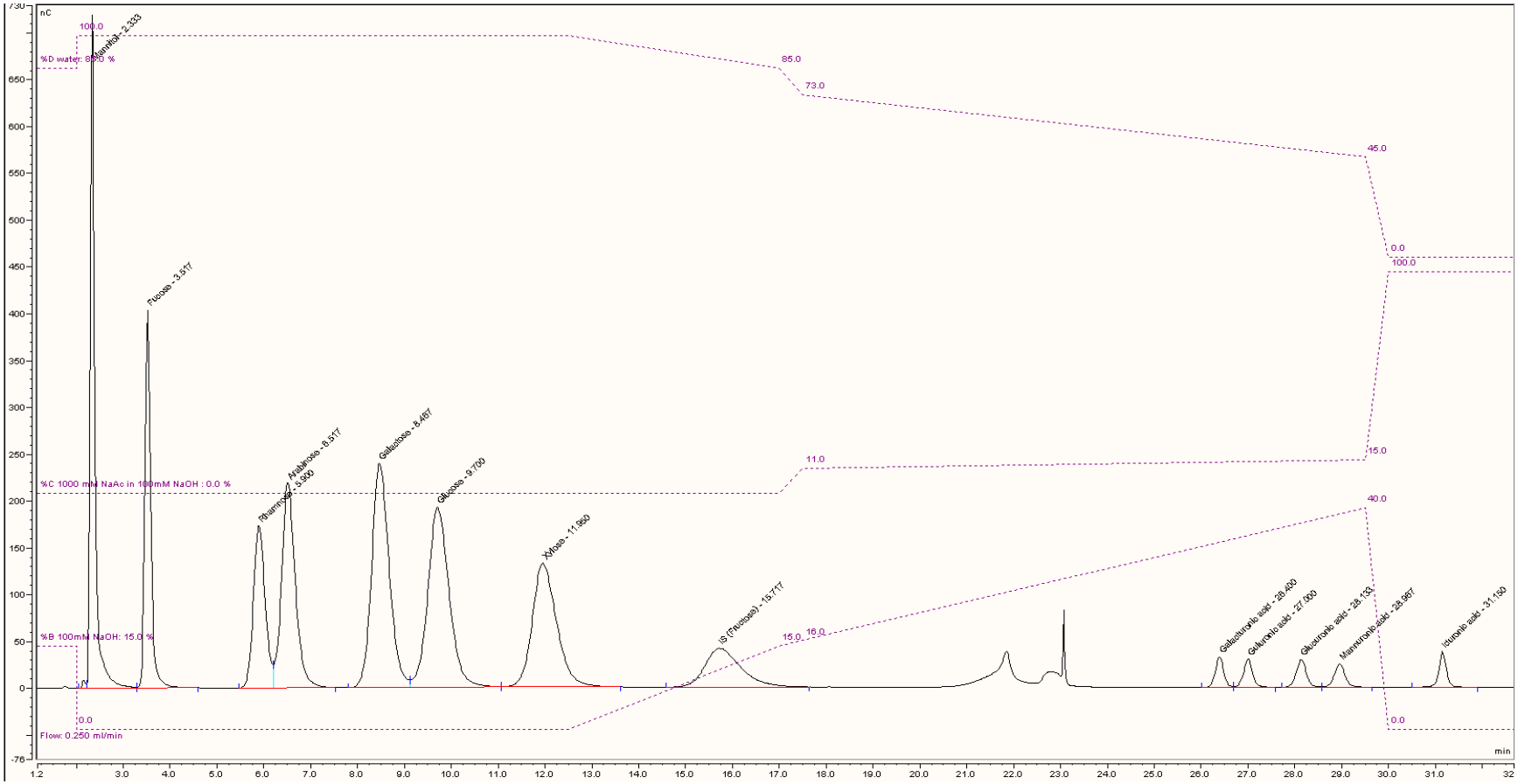


Seaweed analysis protocol

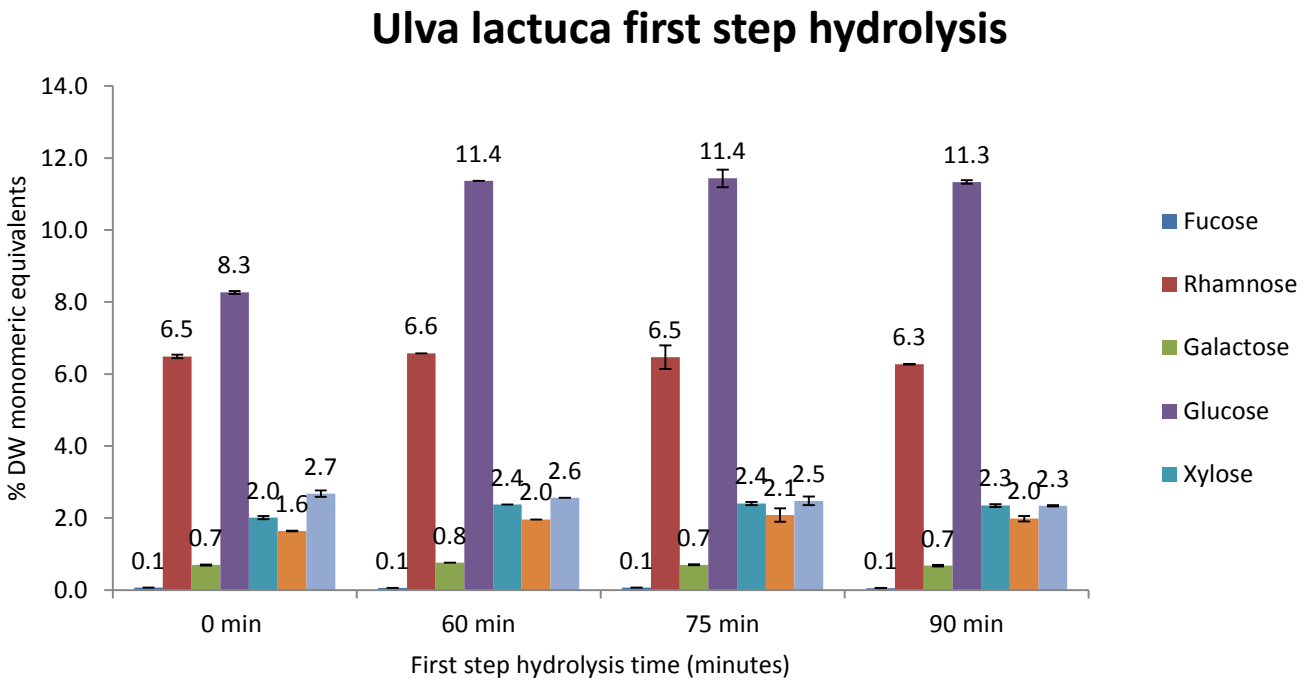
- Uniform analysis protocol for carbohydrate composition of seaweeds
- Specific hydrolysis conditions optimized per type of seaweed.
- NREL/TAPPI starting point
  - Pre-hydrolysis: 12M H_2SO_4, 30 °C, 1 hr.
  - Hydrolysis: 1.2M H_2SO_4, 100 °C, 3 hr.
  - Neutralization.
- Analysis of monomeric carbohydrates with HPAEC-PAD
- **Research questions:**
- Pre-hydrolysis step required for seaweeds?
- Optimum hydrolysis time(s) for each class of seaweeds (brown, green and red).



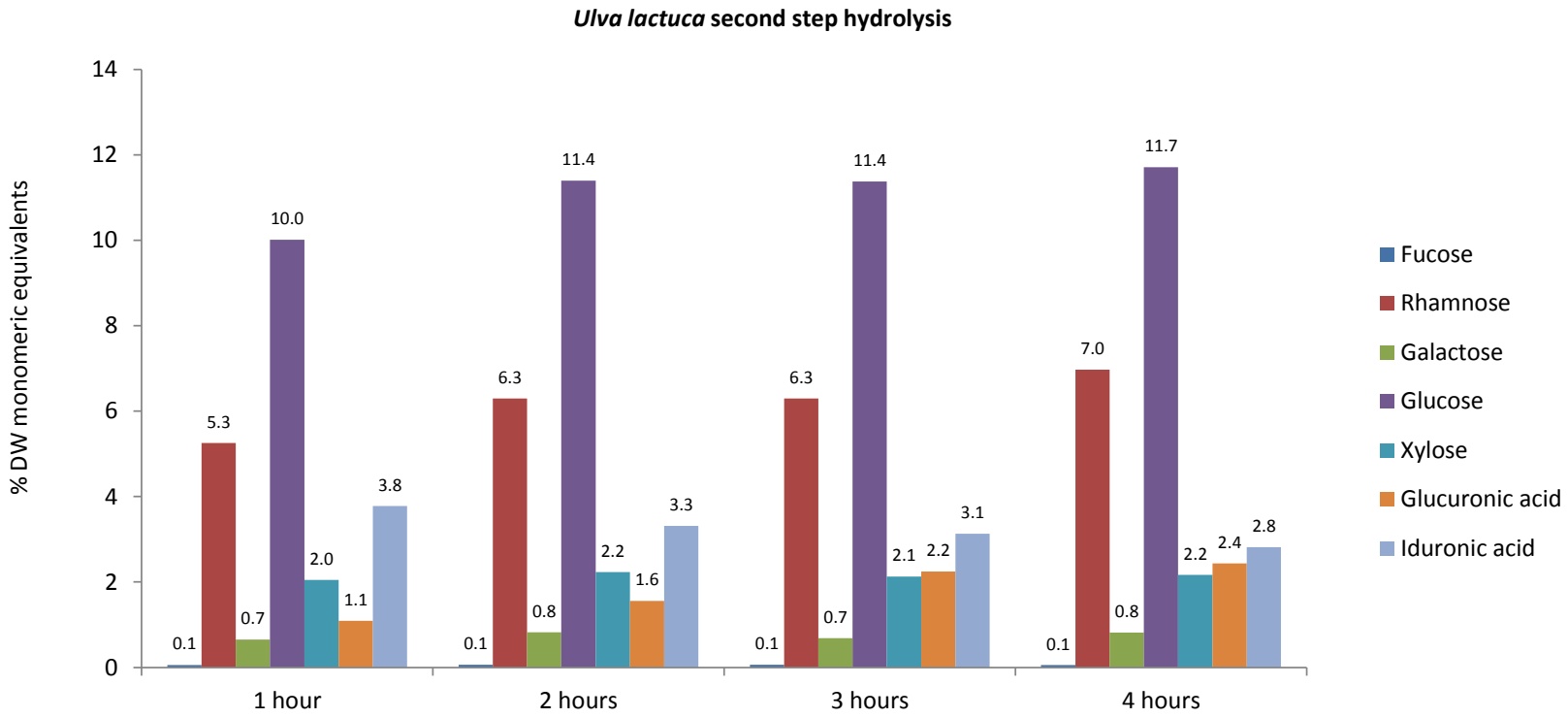
Optimised HPAED analysis



Optimized hydrolysis Ulva, 1st step



Optimized hydrolysis *Ulva*, 2nd step



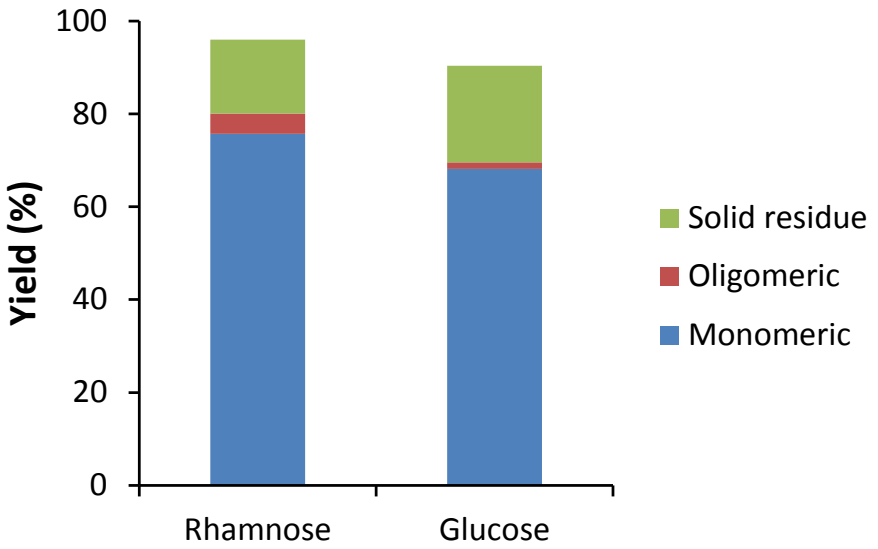
Preliminary conclusions

- Pre-hydrolysis step required for sufficient hydrolysis of seaweeds (particularly brown and green).
- Recommended pre-hydrolysis and hydrolysis times:
  - Brown (*Laminaria*): 1 hr & 4 hr.
  - Red (*Palmaria*): 0.5 hr & 2 hr.
  - Green (*Ulva*): 1 hr & 4 hr.
- All types of carbohydrate monomers in one HPAED run possible

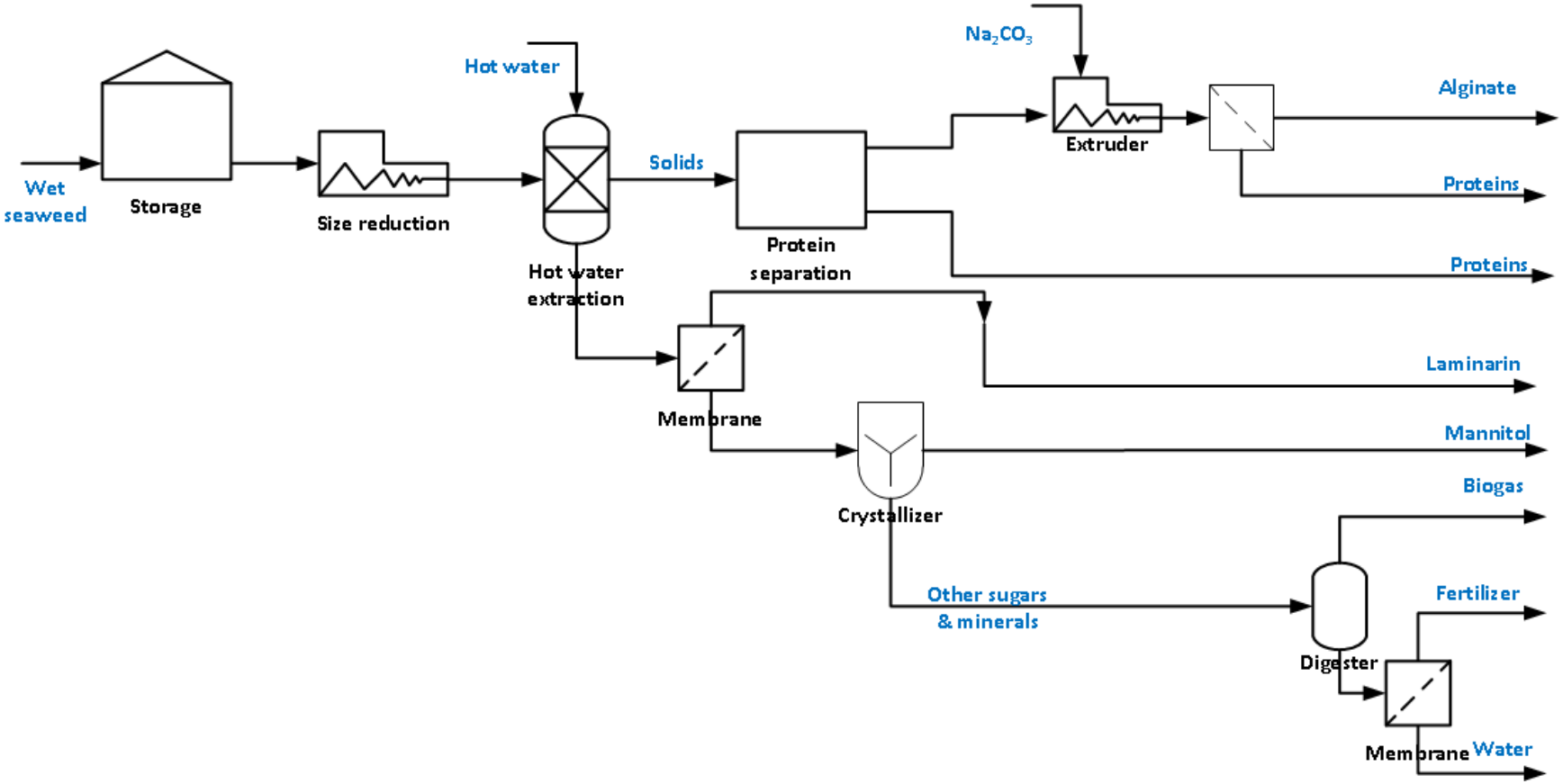
Biorefinery

Fresh Ulva

Isolated monomeric Sugars



Biorefinery Kelps



From fresh Kelp to isomannide

Outlook

- Work ongoing:
  - Extension work to other Kelps (*Alaria, Fucus, Saccharina*) & carrageenan / agar-containing red seaweeds (*Gracilaria*).
  - Pre-extraction prior to hydrolysis for determination of non-structural carbohydrates (brown: mannitol, red: floridoside).
- Converging towards reliable protocols
- Verification of the use of color reactions for example for quick screening enabled

Acknowledgement

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Thank you for your attention

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