Ulvan as a versatile biobased polysaccharide for textile and plastic applications

4th International Conference on Bio-based and Biodegradable Textiles and Plastics

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Biobased and Circular Technologies Group, TNO

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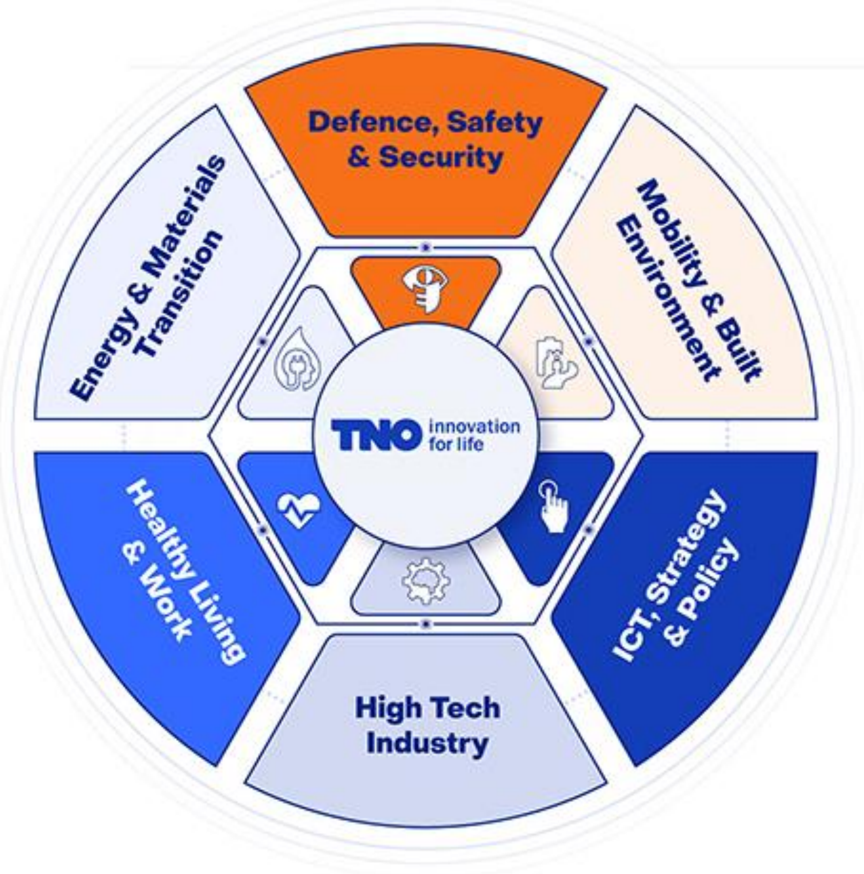
TNO innovation for life

Agenda

1. Introduction
2. Green seaweed & ulvan
3. Ulvan applications
4. Biorefinery development: Ulvan
5. Biorefinery development: Residue valorisation
6. Concluding remarks

Our organisation

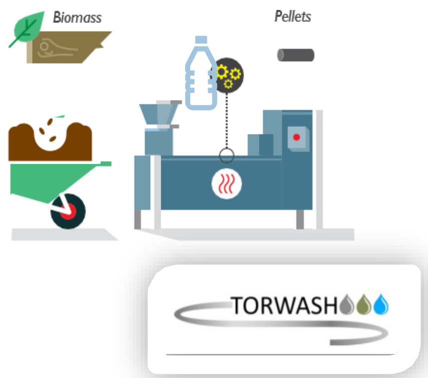


Biobased & Circular Technologies Group

- Knowledge and technology for biomass conversion into energy, chemicals and materials
- Our partners:
  - Technology suppliers, knowledge institutes
  - Biomass/waste streams producers
  - Biobased products producers

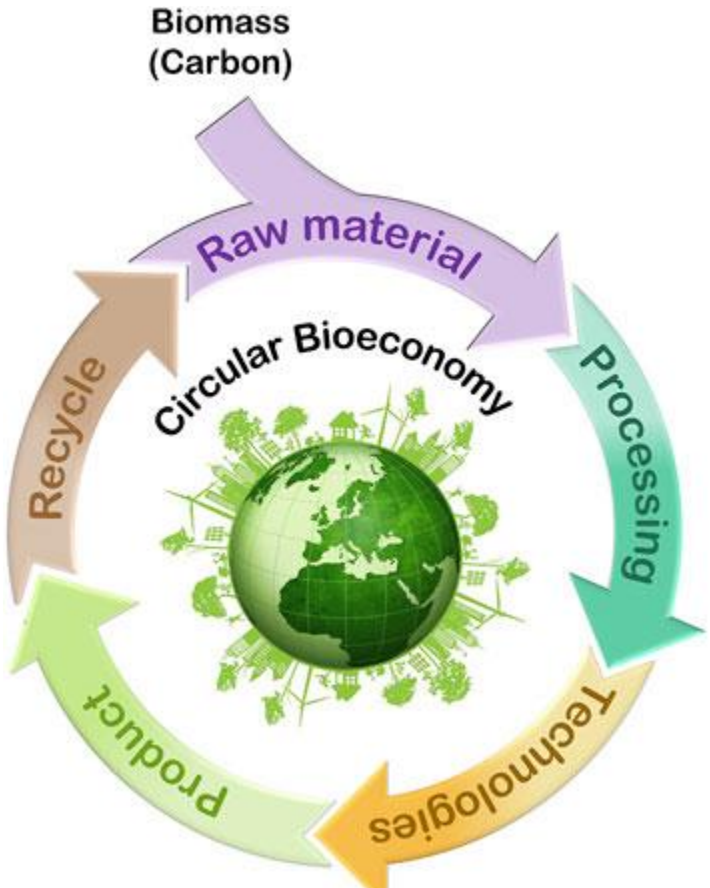
Biorefinery

Upgrading



Introduction
Circular & Biobased Economy

- EU climate strategy: 40% emission reductions by 2030, climate neutrality by 2050
- Bioeconomy strategy:
  - Sustainable use of natural resources
  - Reduce dependency on non-renewable, unsustainable resources
  - Strengthen EU competitiveness
- Important elements:
  - Sustainable, renewable biomass
  - Resource efficiency
  - Integrated biorefineries

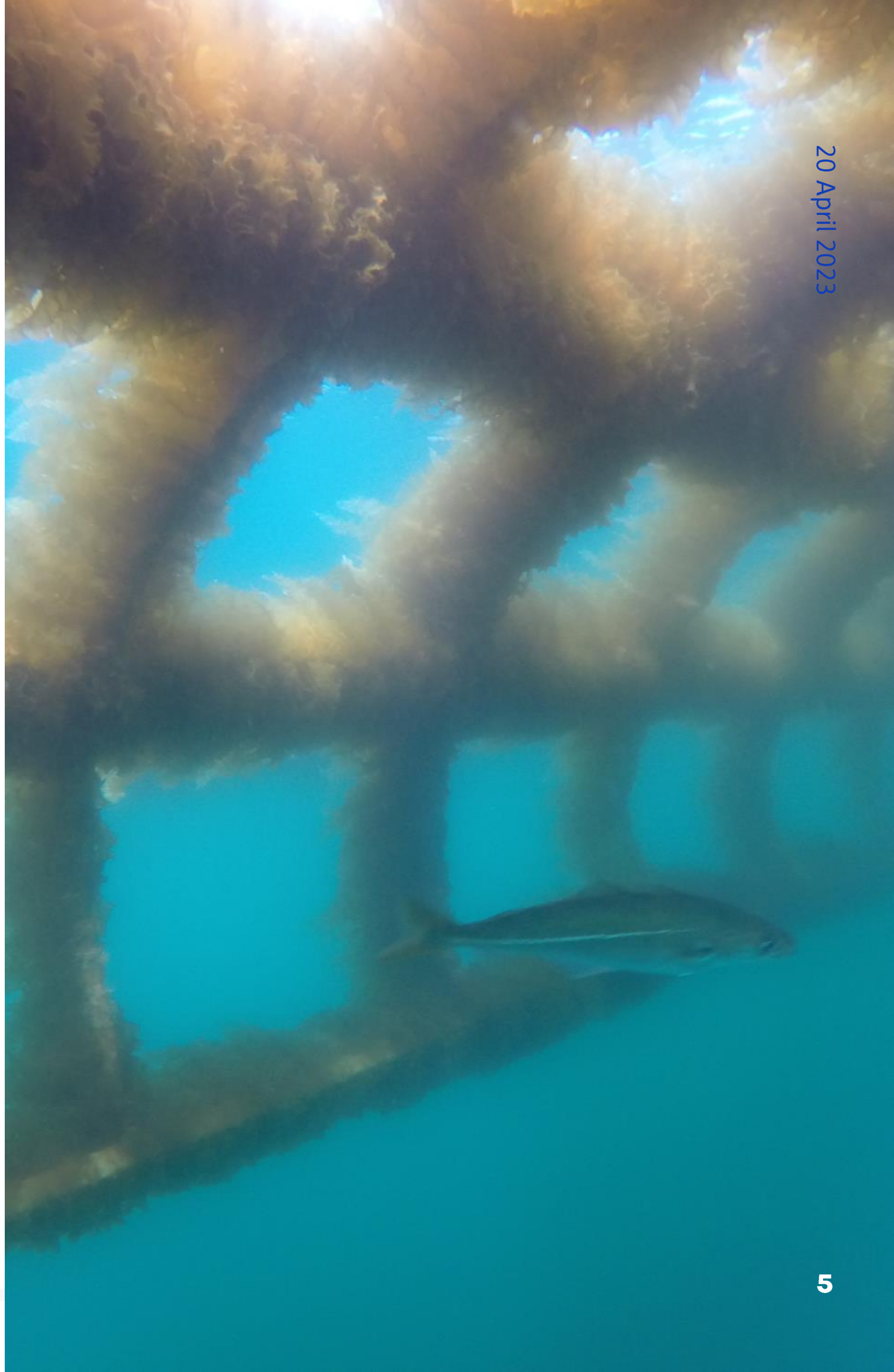


Caetano et al., doi: 10.3389/fenrg.2022.851047

Seaweed for a sustainable future

- Fast growing biomass in European climates
- Large availability of marine environment, no land competition
- Integration with offshore sites, multi-renewable energy platforms and multi-trophic aquaculture
- Richness in (specialty) carbohydrates, protein, bioactives and minerals: Opportunities for biorefining

Contribution to UN Sustainable Development Goals



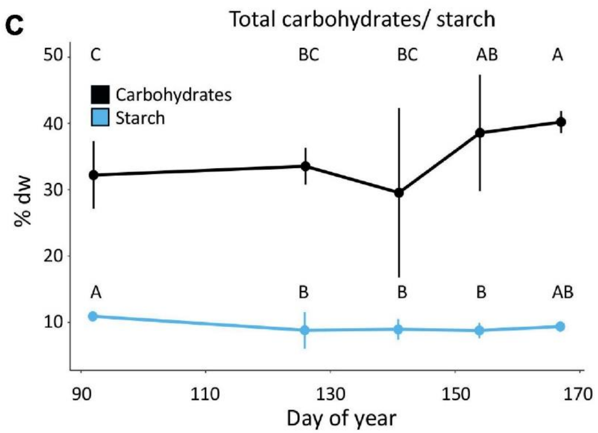
Green seaweed as biomass

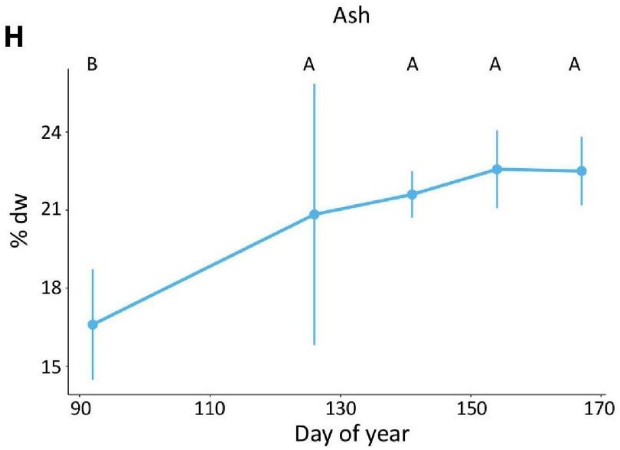
- Commonly known as *sea lettuce*, incl. *Ulva lactuca* and *Ulva fenestrata*
- Highly attractive in the aquaculture sector
- Land-based cultivation: Control over quality, year round supply, high yields, higher costs
- Near/off-shore: Capitalising on the ocean, cost efficient, larger scale production, more challenging control
- Environmental benefits:
    - Ecosystem and bioremediation services
    - Removal of green tides

Seaweed Harvest Holland B.V., Seagriculture 2018

Green seaweed as biomass

- High carbohydrate content but depending on cultivation/harvest
- Land-based: Control over nutrient and cultivation conditions
- Sea-based: Highly dependant on site and harvest time





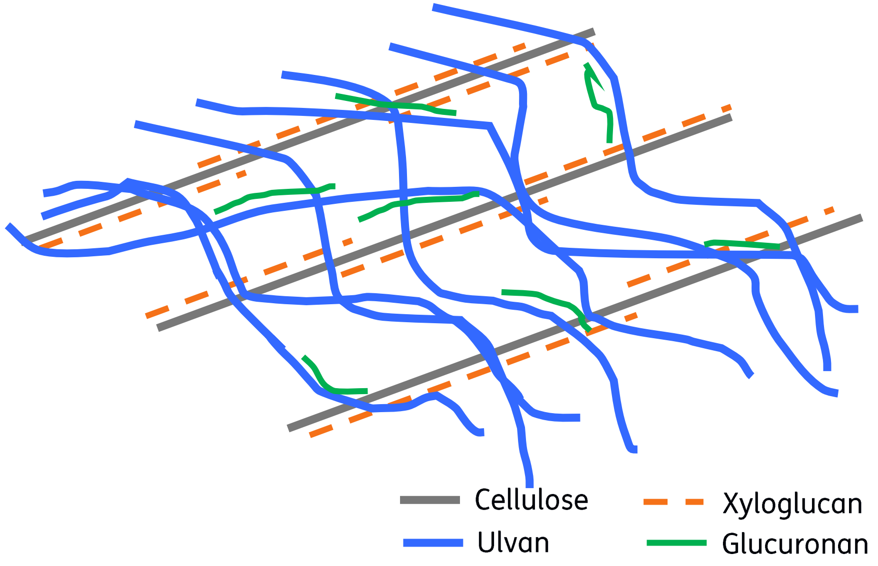
Steinhagen et al. 2022, doi: 10.3389/fmars.2022.816890

Composition, dw basis	Range
Rhamnan	5-10%
Xylan	1-8%
Uronic acids	2-7%
Glucan	10-30%
Protein	5-30%
Ash	20-50%

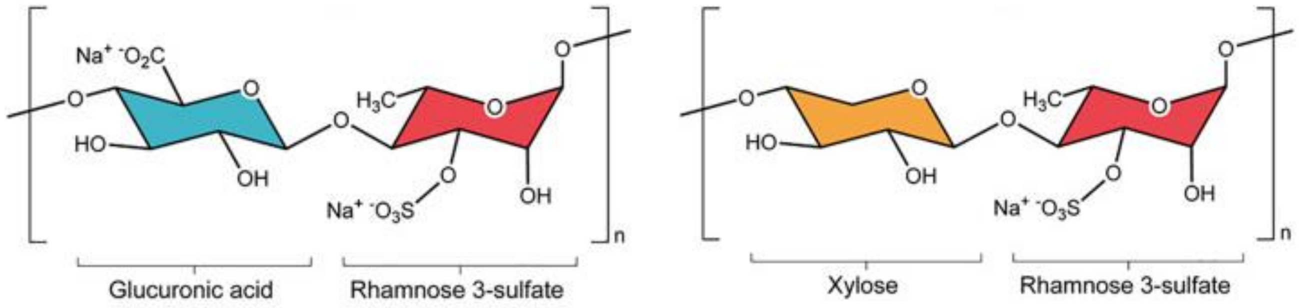
TNO data, Phyllis2 database, https://phyllis.nl/

Ulvan as new biobased polysaccharide

- Water-soluble fraction in cell wall of green seaweeds
- Building blocks: Rhamnose, uronic acids, xylose, glucose, sulphate
- Diverse properties and activities:
  - ✓ Unique composition
  - ✓ Mw ranges: 300-1000 kDa
  - ✓ Rheological activity
  - ✓ Biological activities:
    - Non toxic, antioxidant, therapeutical
    - Plant defence & stress response



Adapted from Lahaye et al, doi: 10.1021/bm061185q



Adapted from Lahaye et al, doi: 10.1021/bm061185q

Ulvan in material applications Thickening agent & hydrogels

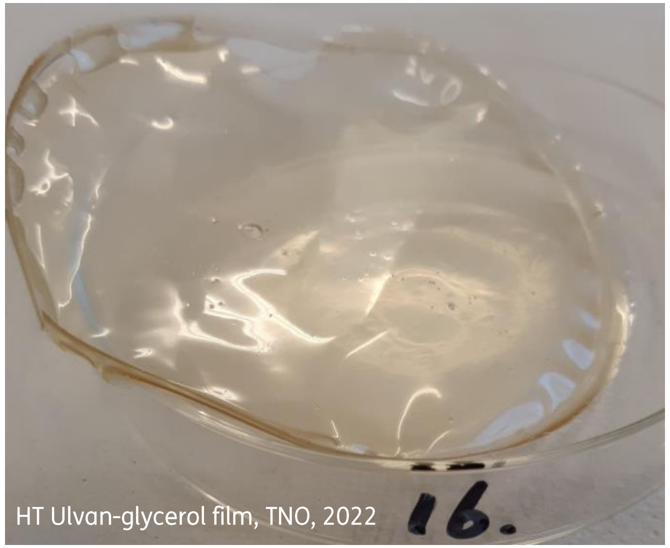
- Gel formation behaviour at high concentrations and enhanced with other agents
- High affinity to bind heavy metal ions and compound carrier/delivery
- Diverse partial or fully biobased potential formulations
- Applications:
  - Medical
  - Personal care
  - Environmental
  - Agriculture


Whalstrom, N., KTH-TNO, 2019

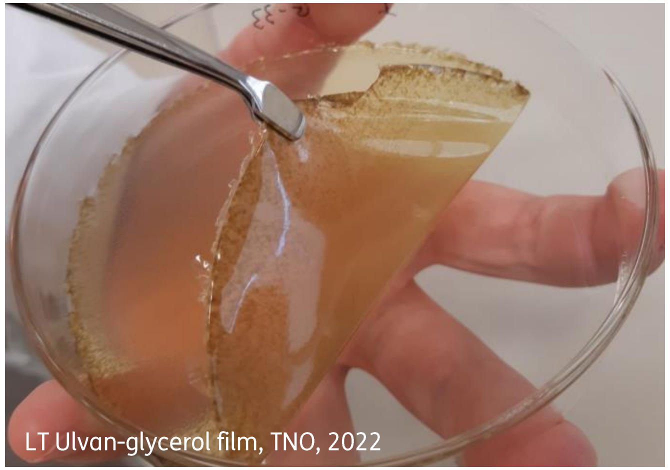
ZCORE, TNO, 2021

Ulvan in material applications
Biobased plastics

- Natural polymer for solution casting
- Biobased, active, potentially biodegradable
- Plasticizing additives to improve elasticity
- As additive on cellulose based films
- Applications:
  - Edible films and coatings in food packaging
  - Biobased composites

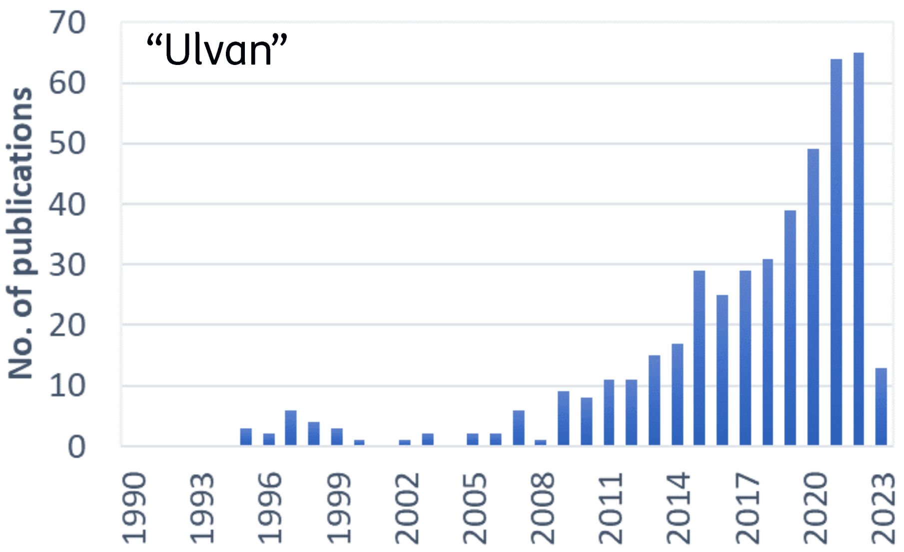


HT Ulvan-glycerol film, TNO, 2022


LT Ulvan-glycerol film, TNO, 2022

Ulvan in material applications Untapped potential

- Functional textiles:
  - Spinning/incorporation into fibres for added functionalities[1]
  - Technical and biomedical applications
- Biocomposites:
  - New renewable source of natural polymers
  - Blending with other polymers[2]
- Biobased chemicals for materials:
  - High value compounds: rhamnose, uronic acids
  - Feedstock for production of furanics and organic acids[3]



1 Toskas, et al. doi: 10.1016/j.carbpol.2010.12.075
2 Kikionis, et al. doi: 10.1002/app.42153
3 Podolean et al. doi: 10.1016/j.cattod.2020.06.086, van Hal, et al. H2020 MacroFuels project, 28th European Biomass Conference and Exhibition

Biorefinery development: Ulvan extraction

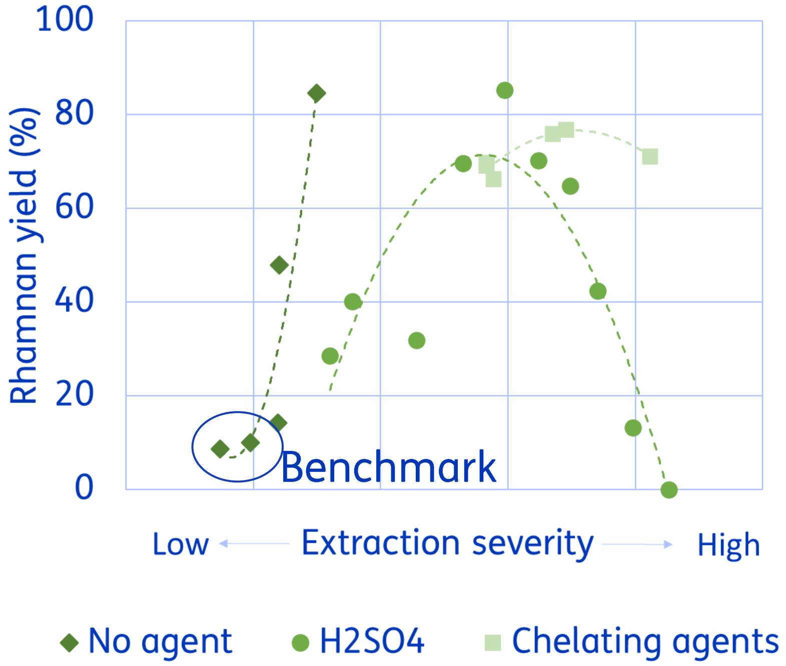
Process development

- Challenges:
  - Biomass novelty
  - Availability of ulvan
  - Variability in terms of origin, extraction, purification
- Opportunities:
  - Effect of extraction conditions on ulvan characteristics
  - Downstream processing requirements
  - Seaweed residue valorisation
  - Scale up

Biorefinery development: Ulvan extraction

Process development

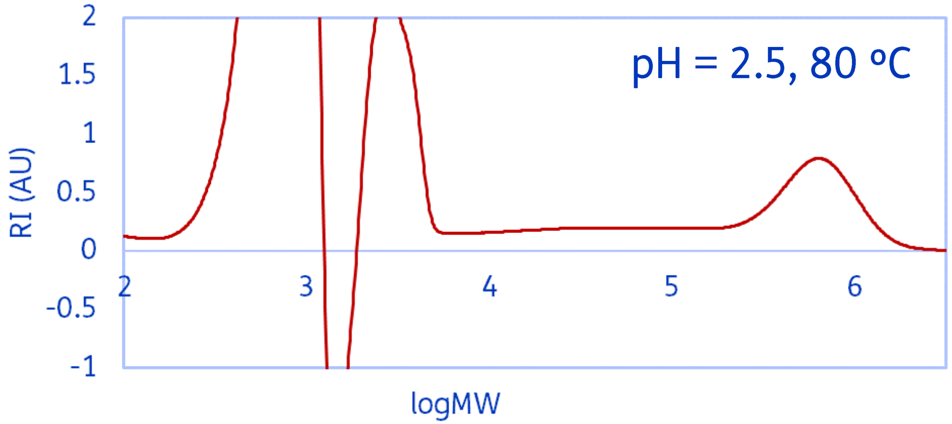
- Extraction in aqueous phase at low temperatures
- Parametric screening combining effects of temperature, time and pH (extracting agent)
- Focusing on extraction selectivity (rhamnan yield)
- Severity and extracting agent can improve extraction efficiency

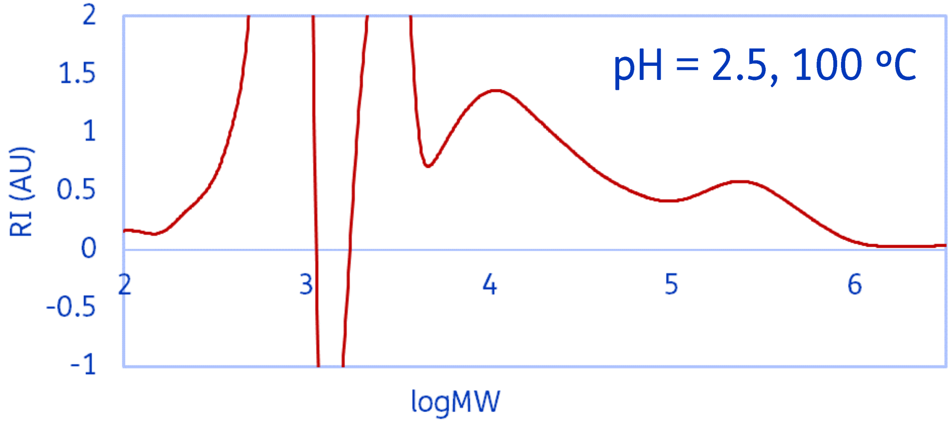


Biorefinery development: Ulvan extraction

Process development

- Increasing severity releases more ulvan
- Trade-off in extraction: Higher yield, different MW distribution
- Other effects in terms of functional units (uronic acids, sulphate, xylan)



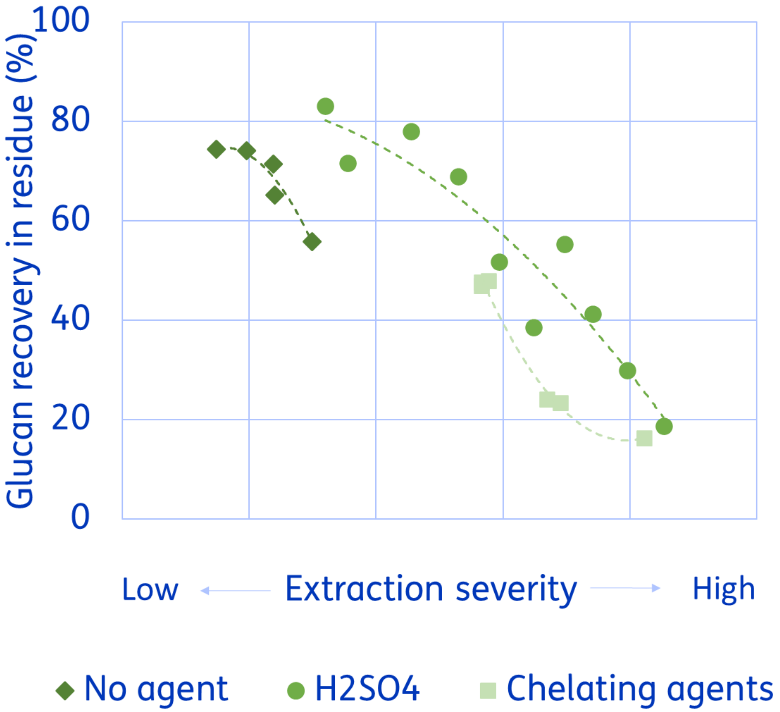


Biorefinery development: Cellulose from residue valorisation

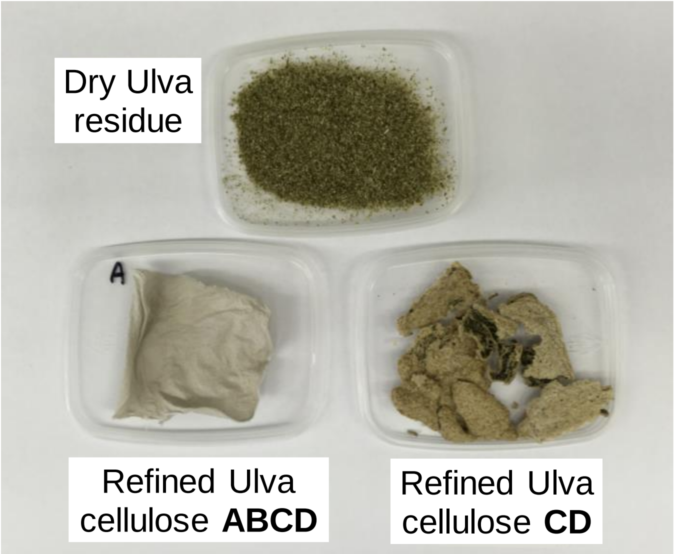
Process development

- Extraction impacts residue quality: Cellulose extracted in proportion with extraction severity
- Cellulose content in residues depend on starting seaweed composition and extraction conditions
- Cellulose recovery: Targeting removal of remaining fractions

Components	Green seaweed residues
Glucan	10-39%
Other saccharides	10-20%
Protein	5-7%
Ash	10-26%

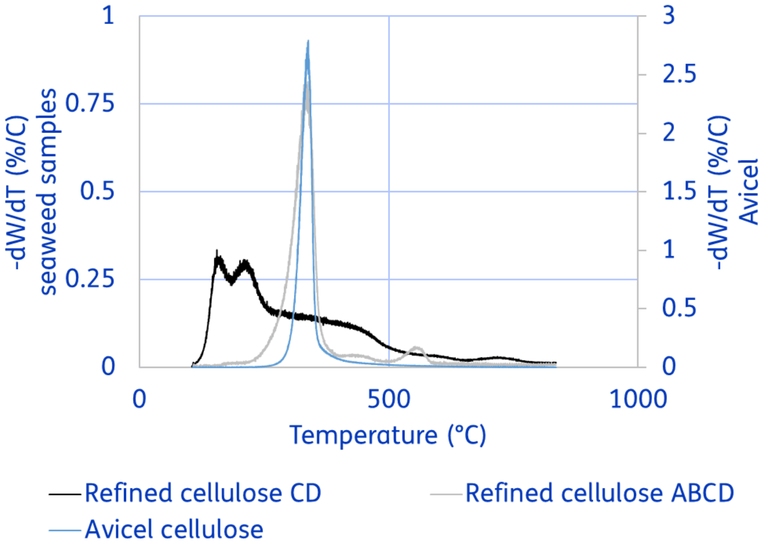


Biorefinery development: Cellulose from residue valorisation



Process development

- Low yields and minerals difficult to remove selectively
- Cellulose purity achieved when incl. solvent extraction and oxidative treatment
- Chemically-intensive processing steps:
  - Further optimisation for suitable applications



Pigments/extractives	Protein	Minerals
•Treatment AB •Solvent + oxidative	•Treatment C •Alkaline	•Treatment D •Low pH leaching

Biorefinery development: Upscaling

Process development

- Upscaling from g to kg scale: 100L total volume
- Batch wise incorporating relevant downstream separation processes
- Challenges:
  - Higher fraction of degradation products
  - Solid-liquid separations

	Rhamnan yield % Poly / Mono	Residue yield % dw	Glucan recovery %
g-scale	85 / 9	50	52
Kg-scale	67 / 20	19	28

Grinding/ milling

Hydrothermal processing (20-100L)

Solid-liquid continuous separation

Membrane filtration

Concentration & stabilisation

Concluding remarks

- Green seaweed: New biomass value chain for a sustainable European bioeconomy
- Opportunities in the implementation of polysaccharide ulvan in material applications due to its functionalities and properties
- Green seaweed biorefinery opportunities:
    - Ulvan extraction approach: Process efficiency, DSP & product properties
    - Upscaled extraction: Relevant for advancement of applications
    - Cellulose refining: Intensive and low yields, thus alternative valorisation routes for residues are desirable

Acknowledgements

HEREWEAR

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Thank you

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