



ENFiber

European Network for Valorising Food
Processing Waste into Sustainable Fibers

Fibre solubilization and separation

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Life as we know it is ending...



Earth's ecological footprint

(measures how fast we consume natural resources and generate waste compared to how fast nature can generate new resources and absorb our waste)

is telling us we need **1.74 planets Earths** to **PROVIDE RESOURCES** and **ABSORB** our **WASTE**¹

Data from 2017 indicates we are extracting **88 billion tons/year** of **natural resources** from Earth:



- 22.5 billion tons biomass
- 15 billion tons fossil fuels
- 9.1 billion tons metal ores
- 41.7 billion tons non-metallic minerals



This will **duplicate** by **2050!**



New geological Epoch:

The Anthropocene Epoch.

aka

The Human Age or The Era of Man.

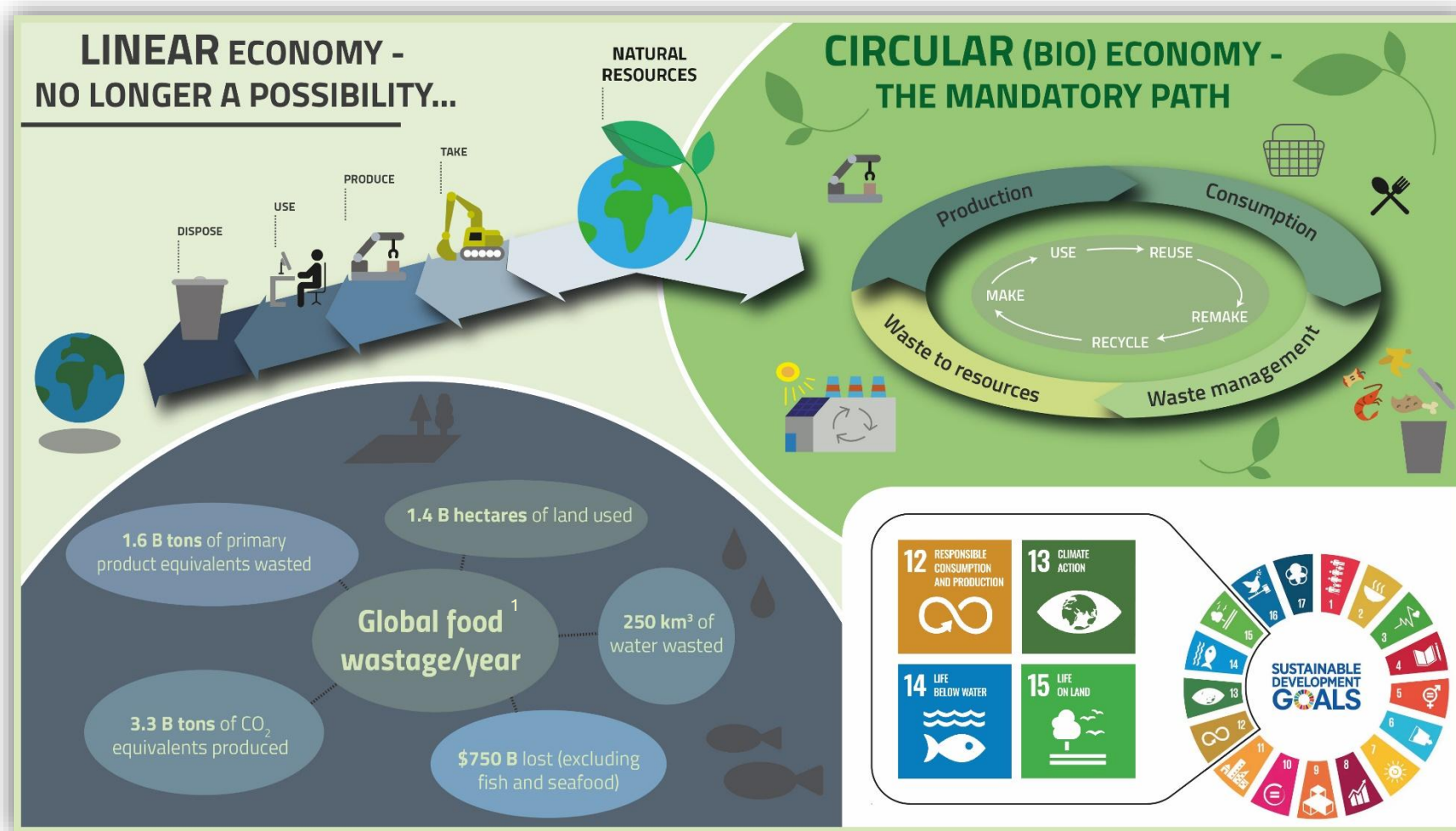


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¹ <https://www.theworldcounts.com/economies/global/effects-of-consumerism>

The imperative transition towards a Circular (Bio)Economy...



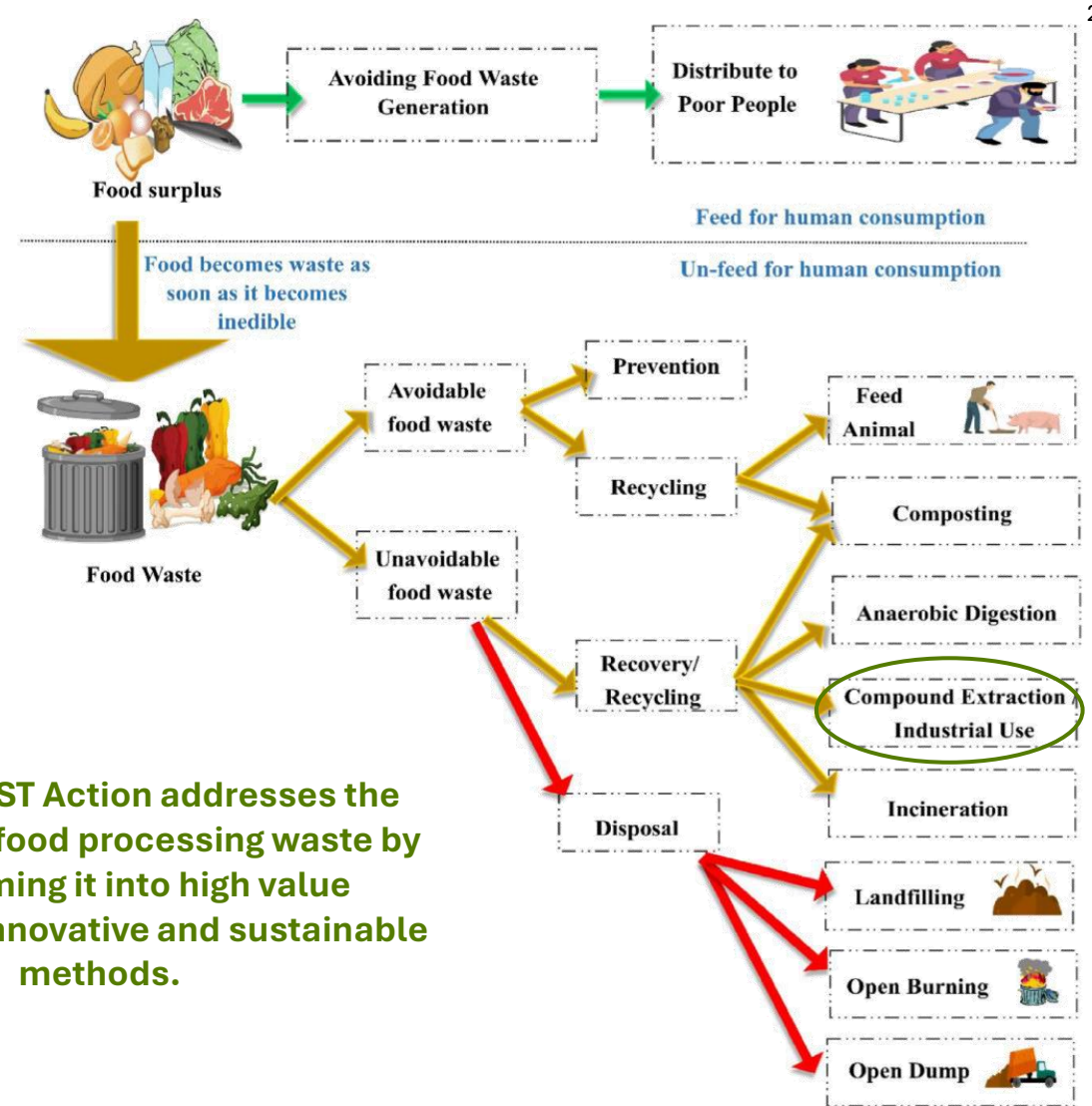
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¹ <https://www.fao.org/news/story/en/item/196402/icode/>.

Embracing new challenges...

The amended Waste Framework Directive (2018/851/EC) (European Commission, 2018) obliges Member States to monitor the generation of food waste and to take measures to limit it, positioning food waste prevention at the top of the waste hierarchy.¹



ENFiber COST Action addresses the challenge of food processing waste by transforming it into high value fibers using innovative and sustainable methods.

¹ Caldeira, C., De Laurentiis, V., Sala, S., EUR 29901 EN; Luxembourg (Luxembourg): Publications Office of the European Union; 2019, ISBN 978-92-76-12388-0, JRC118276

² M. Bigdeloo, T. Teymourian, E. Kowsari, S. Ramakrishna, A. Ehsani, Mater. Circ. Econ. 3, 3 (2021).

What are fibers?

In material and biological sciences, a fiber is a natural or synthetic substance that is **significantly longer** than it is **wide**, typically characterized by an **elongated structure**, **high aspect ratio**, and the capability to provide **structural integrity**, **reinforcement**, or **biological functionality**.

- Materials/Textiles: An elongated strand of matter (like cotton, wool, or carbon fiber) capable of being spun into yarn or used to reinforce composite materials.
- Nutrition/Biology: A diverse group of plant-derived carbohydrates (mainly polysaccharides) and lignin that are resistant to human digestive enzymes.

Cellulose fibrils (plant cell wall)	Hemicellulose microfibrils	Pectin network (plant matrix)	Chitin fibrils (crustacean shell)	Lignin-rich fibers (woody biomass)	Textile fiber (cotton)	Micro / Nano fibrils (example)
• Main structural component of plants • High crystallinity and strong hydrogen bonding • Provide strength and rigidity	• Amorphous and branched polysaccharides • Associated with cellulose • Contribute to matrix flexibility	• Gel-forming polysaccharides • Important in cell adhesion and porosity • Soluble dietary fiber	• Structural biopolymer (N-acetylglucosamine) • Forms strong, ordered fibrils • High strength and stability	• Aromatic polymer • Provides rigidity and hydrophobicity • Acts as natural adhesive in cell walls	• Natural macroscopic fiber • Spinnable, flexible and absorbent • Widely used in textiles	• Nanoscale fibrillar structures • Very high surface area • Excellent reinforcement potential

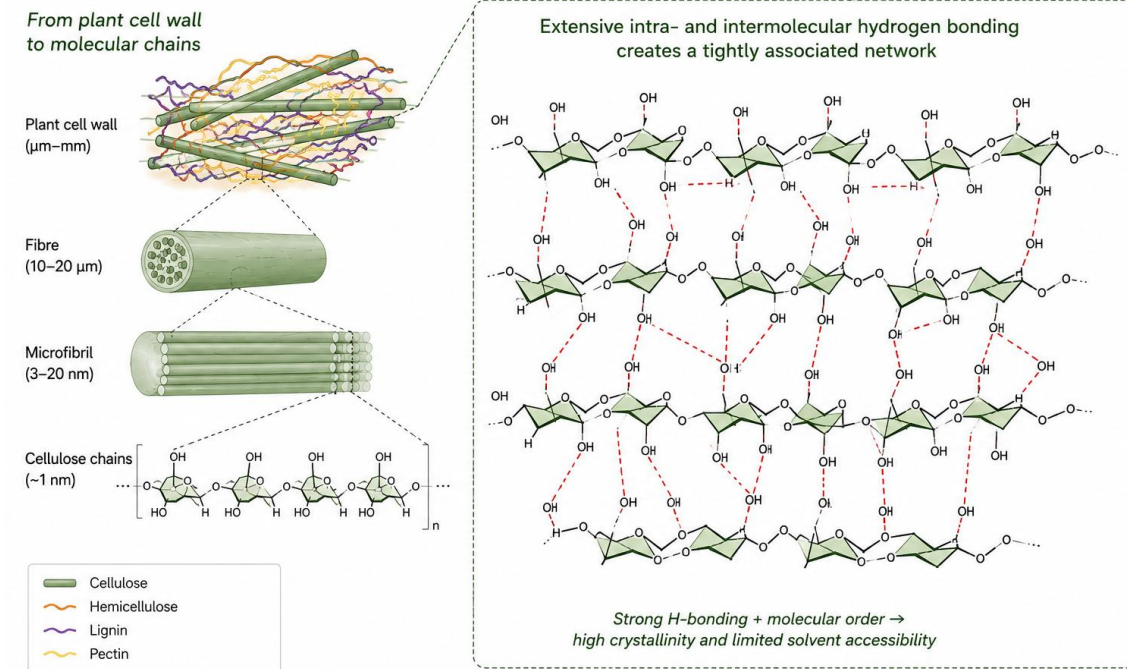


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Why is it difficult to solubilize fiber?

- **Strong inter- and intramolecular H-bonding** → tightly associated polymer chains
- **Crystallinity / molecular order** → limits solvent penetration
 - **High molecular weight** → chain interactions and entanglement
 - **Complex multicomponent matrices** → interactions between cellulose, hemicelluloses, pectin, lignin, etc.
 - **Crosslinking & supramolecular interactions** → restrict polymer-chain mobility
- **Limited accessibility** → compact structures hinder solvent diffusion



What does solubilization actually mean?

Dispersion

Particles are distributed in the liquid but remain a separate solid phase

You can often separate them physically

Swelling

Solvent penetrates the polymer structure, increasing its volume, but the polymer network remains intact

Volume changes, network remains

Dissolution

Polymer-polymer interactions are sufficiently disrupted for individual polymer chains to become molecularly dispersed in the solvent

No separate polymer-rich solid phase

Solubilization means achieving true molecular-level dissolution of the polymer in the solvent.



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What can we actually optimize?

Solvent

polarity • H-bonding • ionic character

Water

viscosity • structure • accessibility

Temperature

kinetics • viscosity • degradation risk

Time & mixing

mass transfer • equilibrium

Particle size

surface area • diffusion distance

Solid loading

capacity • viscosity • processability

Optimization is rarely finding the strongest solvent. It is finding the best combination.

Solvent strategies: different solvents for different fibers

Water / pH

Simple, scalable
limited for many structural polysaccharides

Organic / mixed solvents

Tune polarity
recovery and safety can dominate

Ionic liquids

Strong dissolution potential
viscosity + cost + recovery matter

Deep eutectic solvents

Highly tunable mixtures
water can completely change behaviour

A “green” solvent is not automatically a green process: concentration, energy and recovery still count.

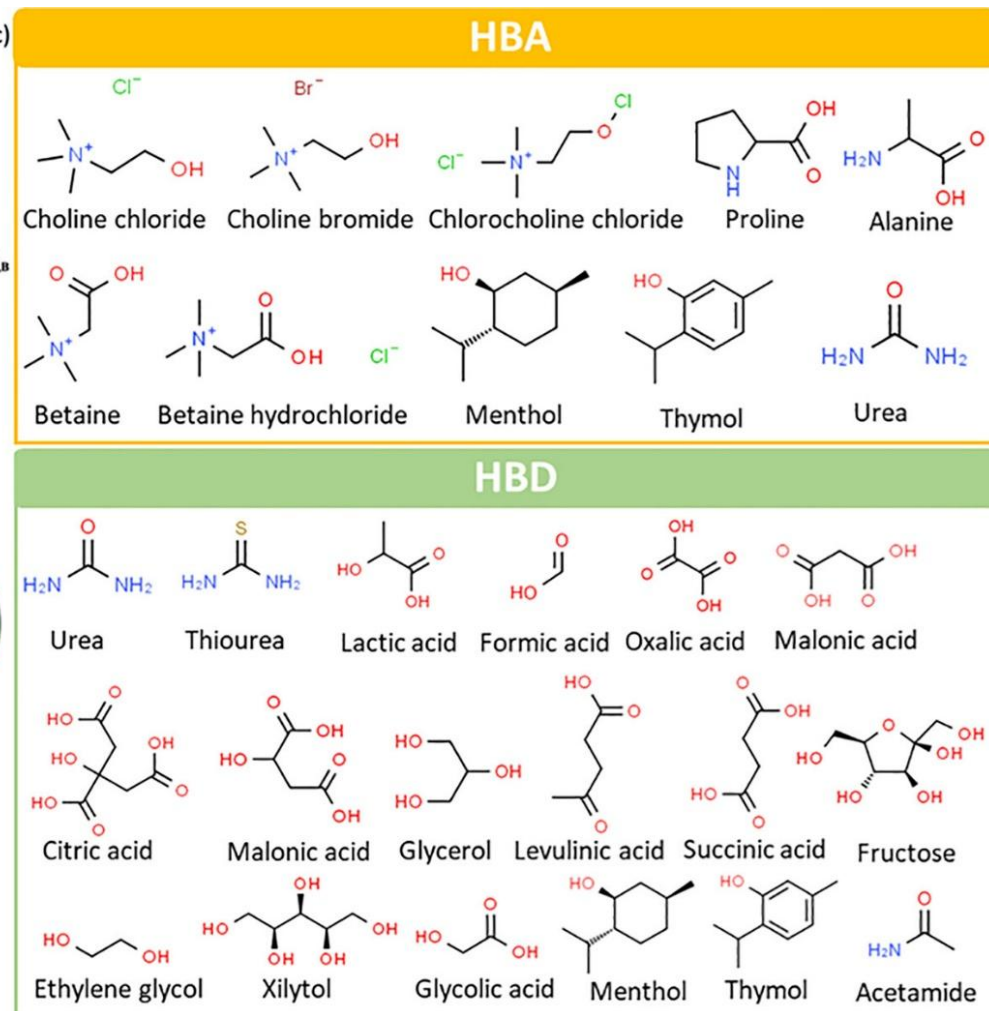
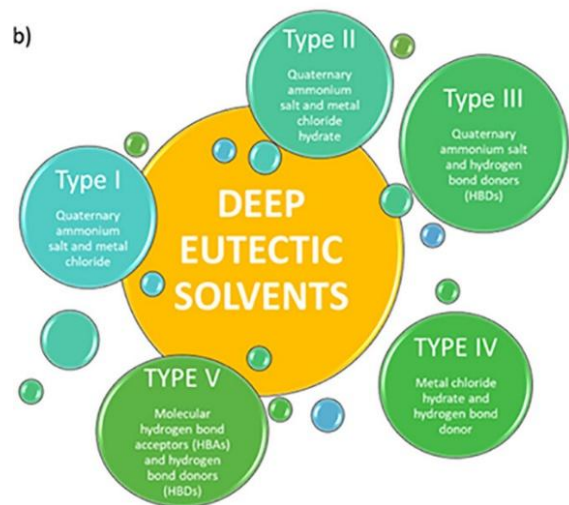
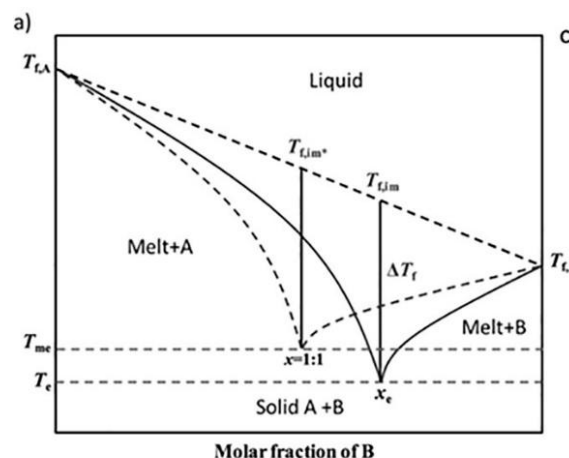


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Deep eutectic solvents (DES)

DES are defined as a mixture of pure compounds, namely Lewis or Brønsted acids and bases, displaying a small difference in their acid-base strength, in which one compound acts as a hydrogen bond acceptor (HBA) and the other as a hydrogen bond donor (HBD), and for which the eutectic temperature is significantly depressed relative to the ideal mixture.



Case study: starch solubilization and extraction from potato peels

CELLULOSE

β -D-glucose
 β -(1 $\rightarrow$ 4) linkages
Linear chains
Strong inter- and intrachain H-bonding
Highly ordered / crystalline fibrils
Difficult to solubilise

STARCH

α -D-glucose
 α -(1 $\rightarrow$ 4) + α -(1 $\rightarrow$ 6)
Amylose + amylopectin
Different chain packing
Strong inter- and intrachain H-bonding
Granular / semi-crystalline structure
Difficult to solubilise

Same glucose building block
but
different structure $\rightarrow$ different solubilisation strategy



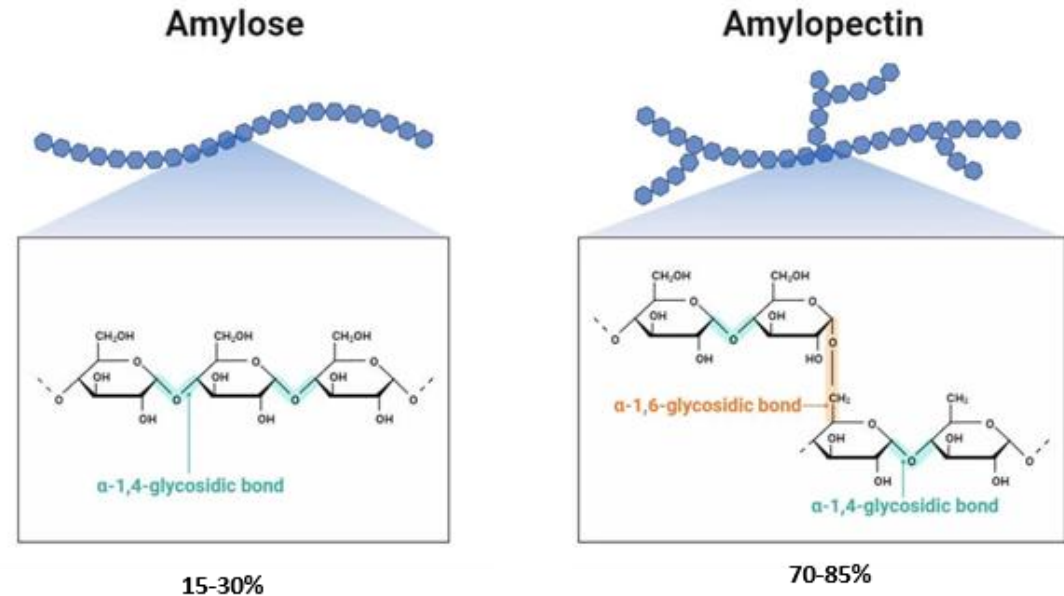
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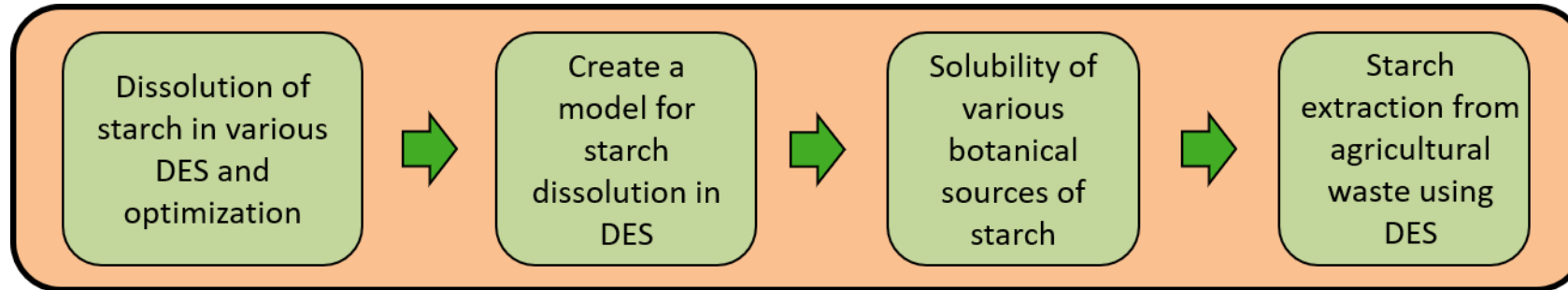
Case study: starch solubilization and extraction from potato peels

Common Solvents & Issues

- **Water:** Swells but doesn't fully dissolve starch.
- **Organic Solvents:** Minimal solubility.
- **Ionic Liquids:** Effective but can be quite costly.



Our plan:

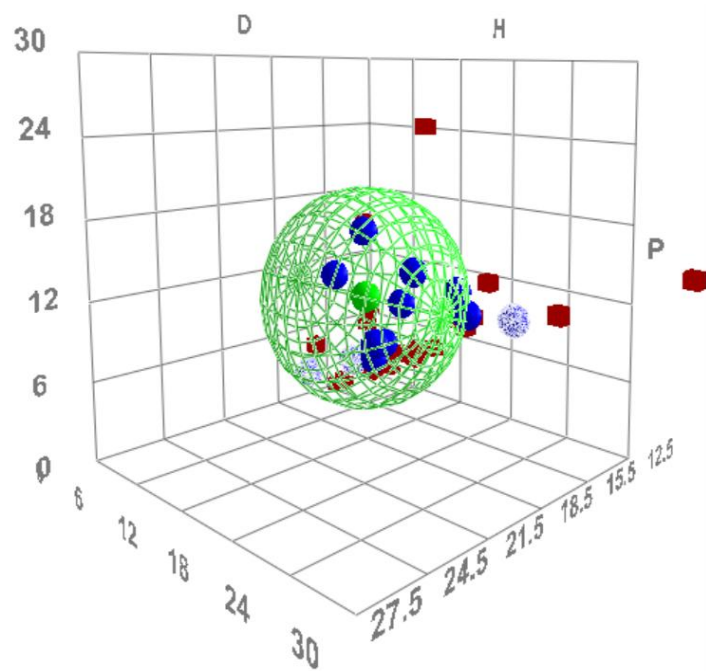


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Case study: starch solubilization and extraction from potato peels

Hansen solubility parameters (HSP)



Hansen solubility sphere obtained for corn starch at 100 °C. Score: 1 – soluble, 2 – dispersion, 3 – swell, and 0 – insoluble.

➤ **HSP describe the affinity between a solute and a solvent based on three contributions to intermolecular interactions:**

- δ_D – dispersion forces
- δ_P – polar interactions
- δ_H – hydrogen bonding

➤ The closer the solvent is to the **HSP region/sphere of the solute**, the higher the expected affinity and potential for dissolution.

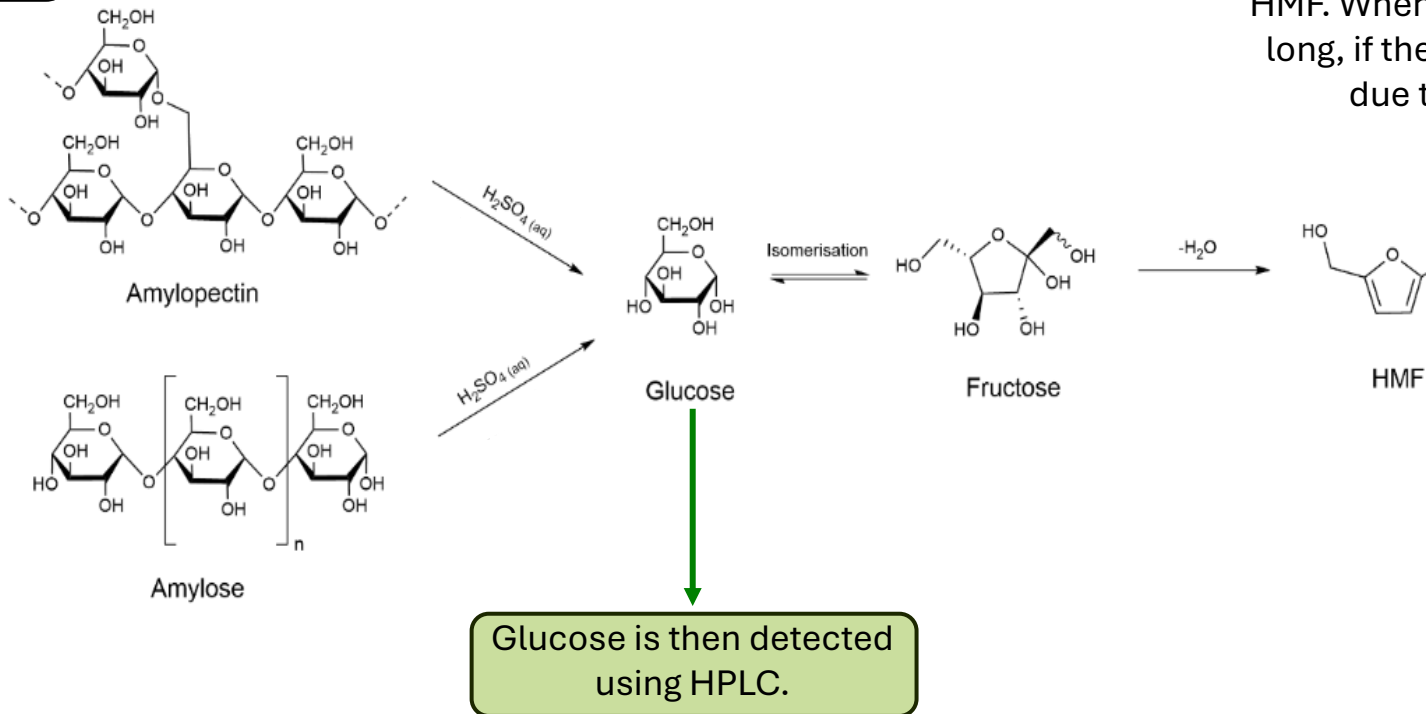
➤ For **corn starch**, the calculated HSP sphere was:
 $\delta_D = 18.9 \text{ MPa}^{1/2}$, $\delta_P = 11.8 \text{ MPa}^{1/2}$, $\delta_H = 12.9 \text{ MPa}^{1/2}$, $\delta_T = 25.7 \text{ MPa}^{1/2}$, radius = 8.4

➤ HSP analysis was used as a **screening/rationalisation tool to identify DES components with higher predicted affinity toward starch**

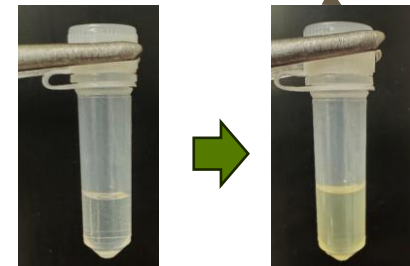
Case study: starch solubilization and extraction from potato peels

How to analyze starch

Starch can be hydrolyzed to glucose with the use of acid catalysts.

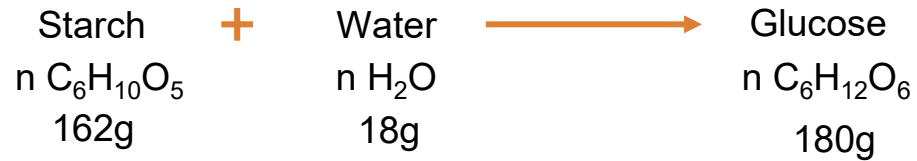


Degradation product of glucose is HMF. When we heat the mixture for too long, if there is a change in color, it is due to the HMF formation.



Case study: starch solubilization and extraction from potato peels

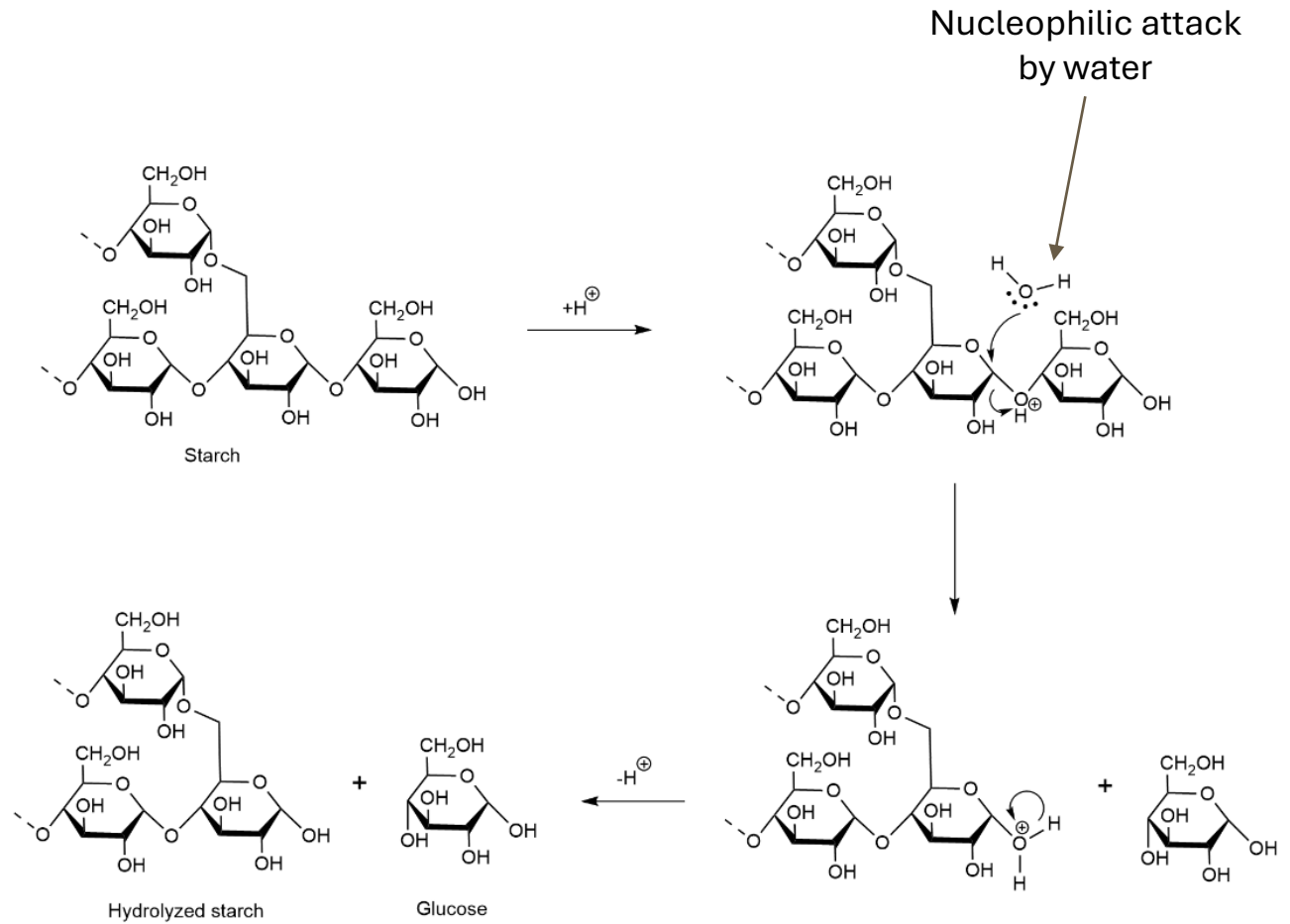
Hydrolysis of starch to glucose



- Water molecules break glycosidic bonds in starch.
- Release of glucose molecules.

$$c(\text{starch}) = c(\text{glucose}) \times 0.9$$

Molecular Mass Difference: Starch unit ($\text{C}_6\text{H}_{10}\text{O}_5$) is 90% of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) due to the absence of **one** water molecule.

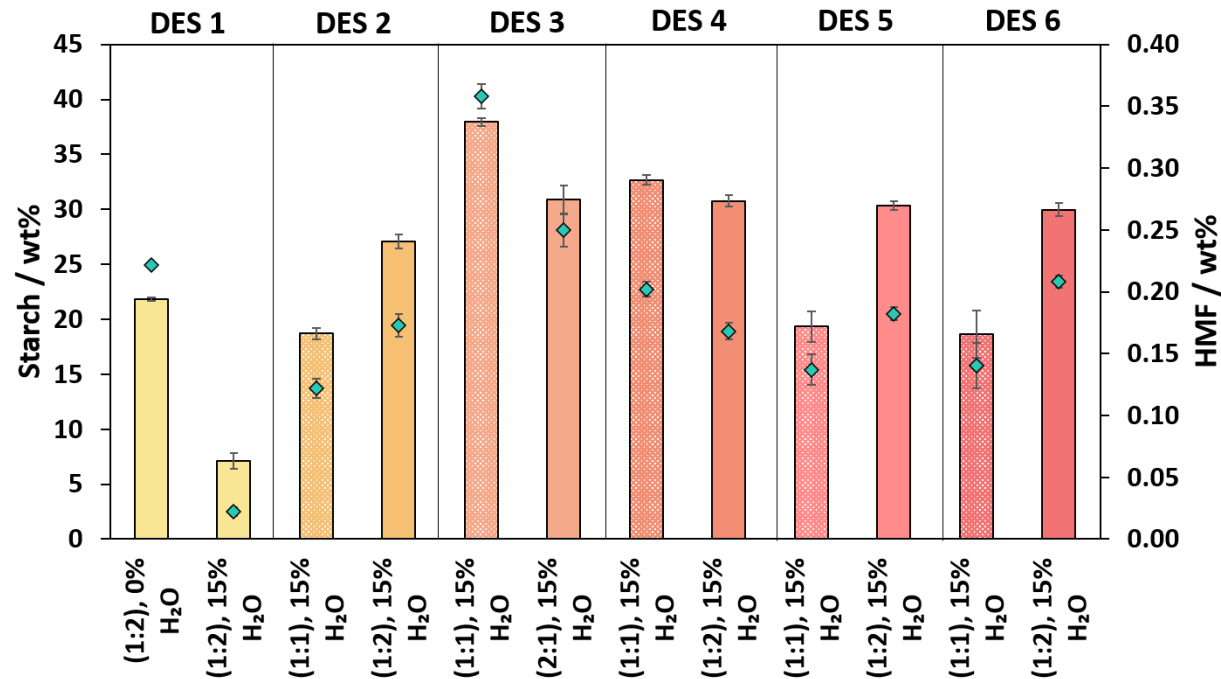


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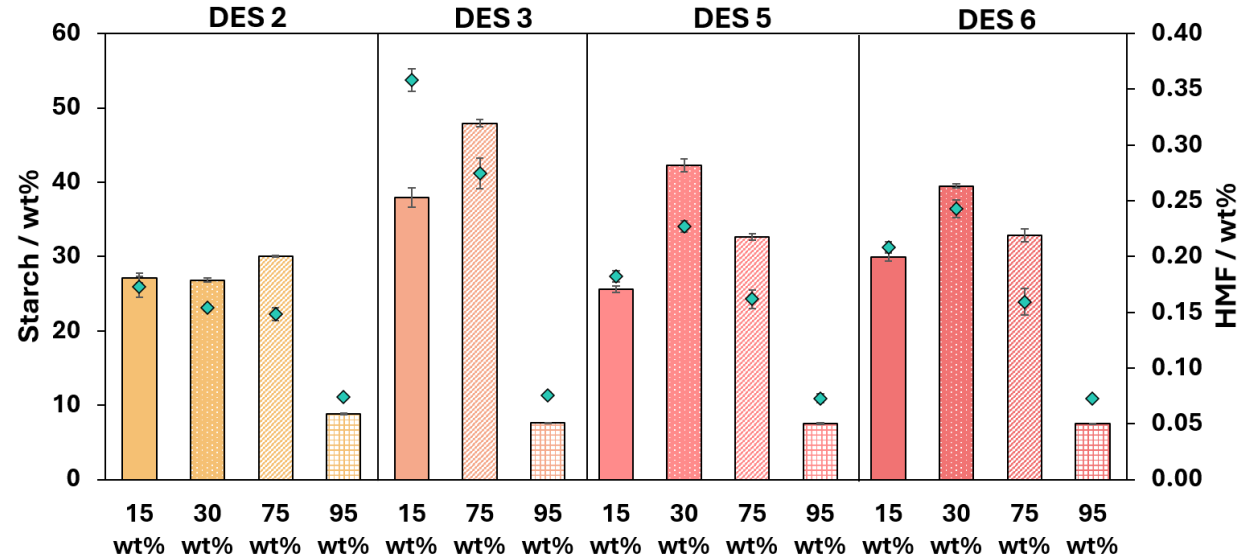
Case study: starch solubilization and extraction from potato peels

Starch dissolution optimization



➤ DES 3 has the highest solubility of starch.

Bars correspond to starch concentration; dots represent HMF concentration

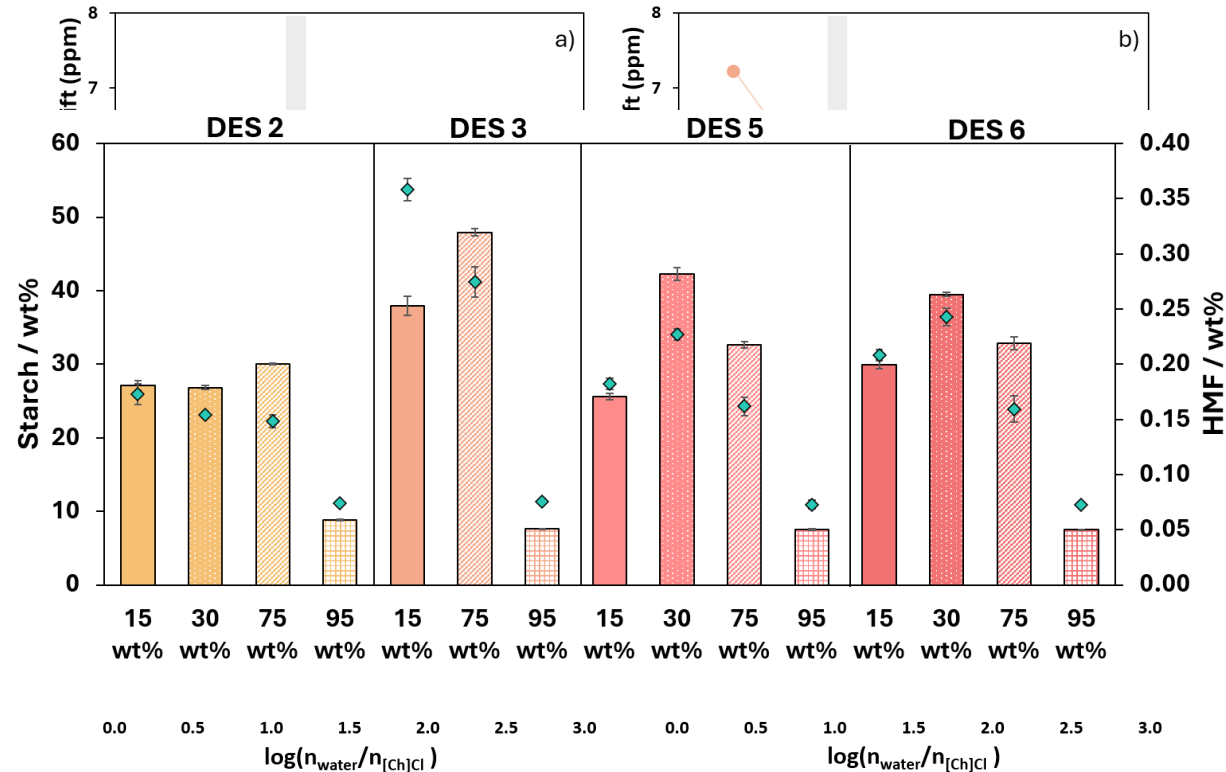


Water increase solubility of starch, why:

- Reduce **viscosity** of the DES.
- Increase in **polarity** of the solvent.
- Facilitate the **interaction** with polar molecules.
- Impact on **intramolecular interactions** between HBD and HBA.

Case study: starch solubilization and extraction from potato peels

Are DES still DES?



The “**water-in-DES**” → “**DES-in-water**” transition occurs around 35-45 wt% water

- **DES structure relies on a strong H-bond network** between the hydrogen-bond acceptor (HBA) and hydrogen-bond donor (HBD).
- **Low water content:** water is incorporated into the DES network → the characteristic **HBA-HBD interactions are largely preserved**.
- **Increasing water content:** water progressively competes for H-bonding sites and **disrupts the original DES network**.
- A transition occurs from a “**water-in-DES**” → “**DES-in-water**” regime.
- At high water contents, the DES components become increasingly **hydrated and separated** → the system behaves more like an **aqueous solution of the DES components than a genuine DES**.
- **This structural transition is crucial for starch dissolution:** water is not simply lowering viscosity; it changes the **solvent-solvent and solvent-starch interactions**.
 - The highest starch solubility occurs at an **optimal intermediate/high water content**, reflecting a balance between DES interactions, hydration, and disruption of starch H-bonding.



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Case study: starch solubilization and extraction from potato peels

Starch solubility in pure acids (HBDs) and the HBA

HBD	Starch _{aq HBD} (wt%)	HMF _{aq HBD} (wt%)
HBD 2	30.0 ± 0.3	0.15 ± 0.01
HBD 3	34.4 ± 0.1	0.16 ± 0.01
HBD 5	28.8 ± 0.1	0.15 ± 0.01
HBD 6	29.3 ± 0.1	0.15 ± 0.01

- **Aqueous solutions of the HBA and HBD (75 wt%) were tested separately** to distinguish their individual contributions to starch dissolution.
- **Aqueous solution of HBA** leads to starch gelation rather than dissolution.
- **Aqueous solutions of pure HBDs** can dissolve starch to some extent → confirming that the acids themselves contribute to starch-solvent interactions.
- Neither the **HBA nor HBD alone reproduces the dissolution achieved by the corresponding DES-water system.**
 - Combining **HBA + HBD** creates a distinct interaction environment that enhances starch dissolution beyond the contribution of the individual components.
- This demonstrates a **synergistic HBA-HBD effect** and supports the need to retain sufficient **DES-like interactions**, even in highly hydrated systems.

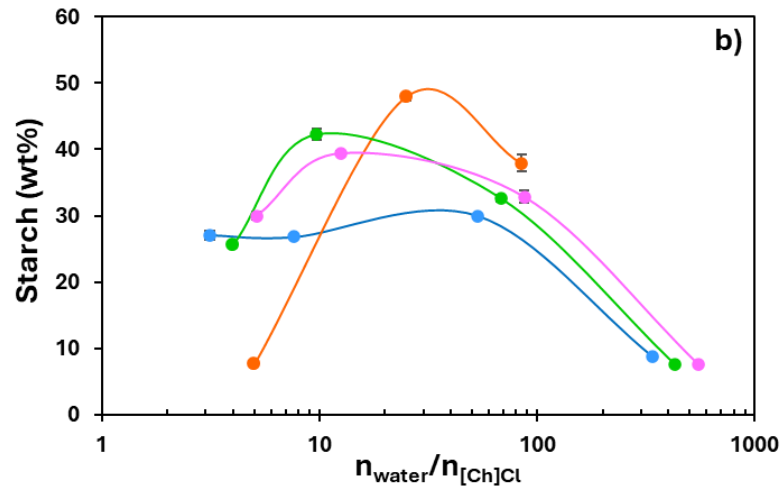
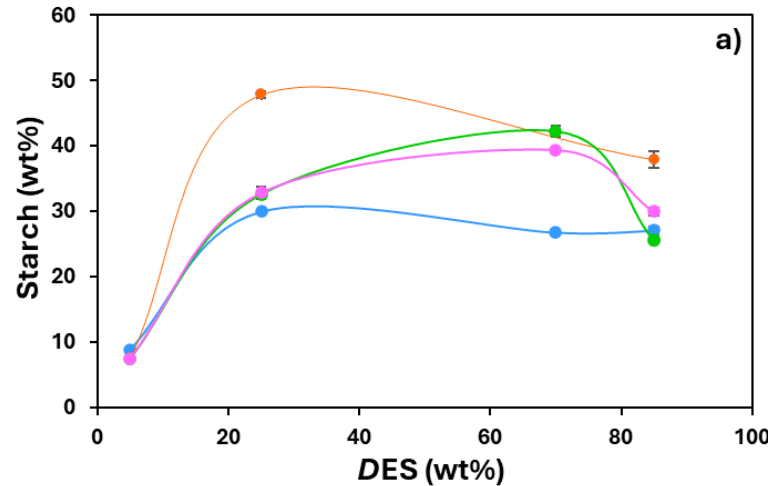


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Case study: starch solubilization and extraction from potato peels

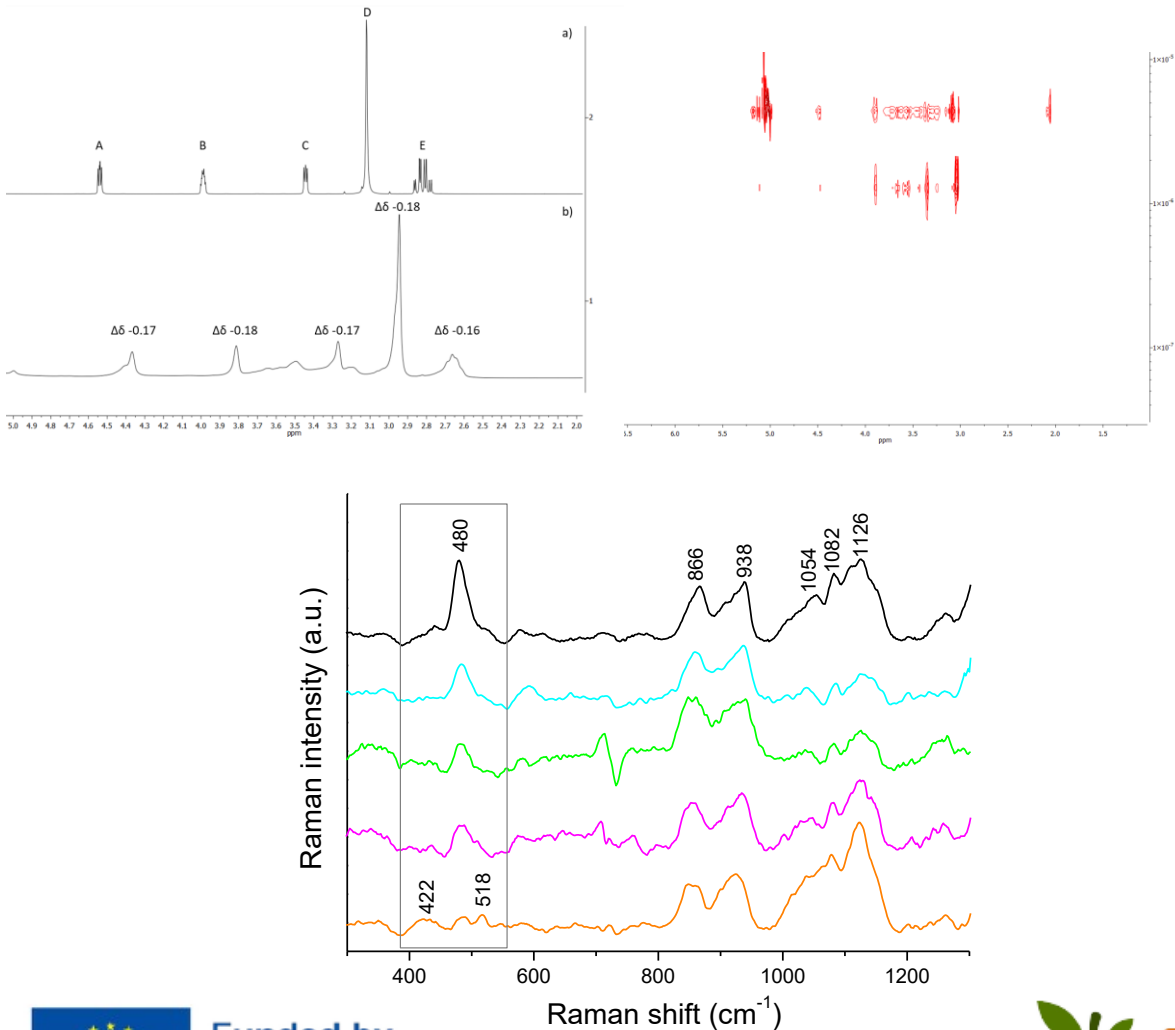
Hydrotropic effects in starch dissolution



- **Hydrotropy** = enhanced solubility caused by the presence and organization of **amphiphilic/hydrotropic molecules in water**.
- Starch dissolution shows a **non-linear dependence on DES concentration** → suggesting that simple dilution, viscosity reduction, or HSP affinity cannot fully explain the behaviour.
- The **maximum starch solubility occurs at specific DES/water compositions**, consistent with a concentration-dependent hydrotropic effect.
- At these compositions, DES components can preferentially **accumulate/interact around starch**, creating a more favourable local environment for solubilization.
- These interactions help **disrupt the extensive starch-starch H-bonding network** while stabilizing starch chains in solution.
- **Too little water:** strong DES-DES interactions and high viscosity limit effective starch solvation.
- **Too much water:** excessive dilution weakens the cooperative effect of the DES components → **starch solubility decreases again**.
- The solubility maximum reflects an **optimal balance between water, DES self-interactions and DES-starch interactions**.

Case study: starch solubilization and extraction from potato peels

Molecular insights into starch dissolution in DES.



- **¹H NMR shows systematic shifts after starch dissolution:** in DES 5 + 30 wt% H₂O, signals from both **HBD** and **HBA** shift **upfield** by **~0.16–0.18 ppm**.
- Similar chemical-shift changes are observed for the other investigated systems → **both the HBA and HBD environments are affected by starch**.
- This means starch is **not simply dispersed in the liquid**: its –OH groups perturb the interactions between the DES components and participate in a **new H-bonding environment**.
- **DOSY NMR detects starch in the liquid phase** and reveals different diffusion populations → supporting **dynamic association between dissolved starch and DES species** rather than simple physical swelling/gelation.
- **Raman spectroscopy shows changes in the characteristic starch bands** after dissolution, particularly in regions sensitive to **H-bonding and starch molecular organization**.
- At the same time, the characteristic polysaccharide vibrations remain → **the starch backbone is preserved; dissolution does not imply chemical degradation of the polymer**.
- **NMR + Raman point to the same mechanism:** native starch-starch interactions are disrupted and replaced/reorganized through interactions with **HBA + HBD + water**.



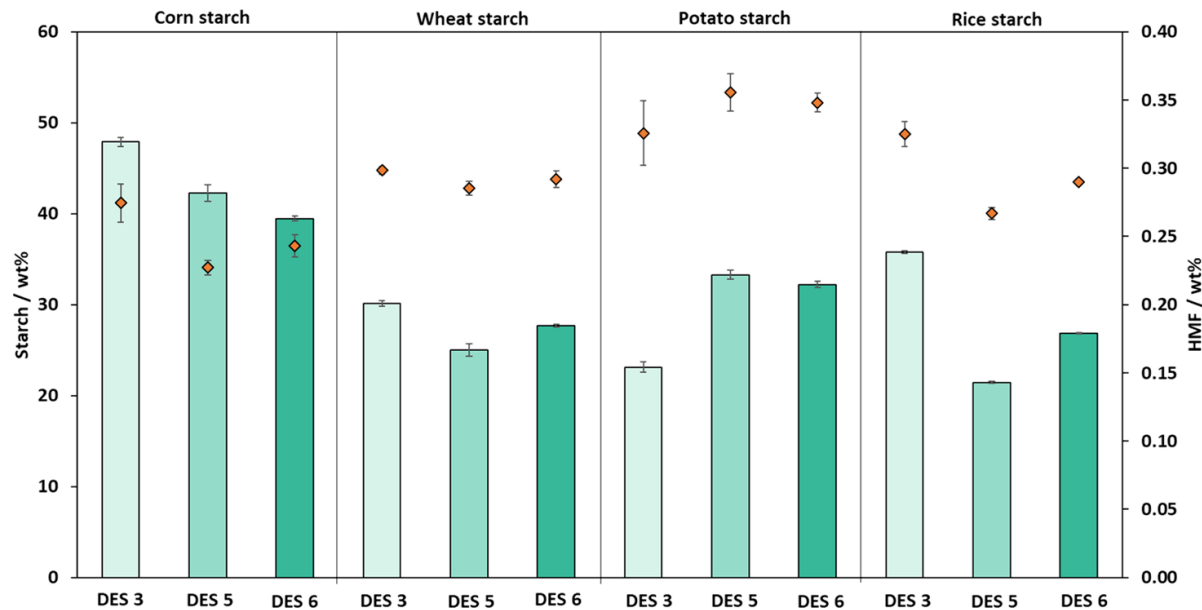
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Effect of different botanical starches on dissolution

Starch	Corn	Wheat	Potato	Rice
Granule size (um)	5-20 ^a	1.5-20 ^a	10-75 ^a	3-10 ^a
Granular shape	Round, polygonal ^a	Lenticular-shaped, small round ^a	Oval, spherical ^a	Round, angular and polygonal ^a
Amylose content (%)	22.4-32.5 ^b	18-30 ^b	20.1-31.0 ^b	5-28.4 ^b
Amylopectin content (%)	67.5-77.6 ^c	70-82 ^c	69-79.9 ^c	71.6-95 ^c
Gelation T	64.1 ^b	46.0-52.4 ^b	59.72-66.2 ^b	66.0-67.3 ^b



➤ Starch composition differs by **source**, primarily in the **amylose-to-amylopectin ratio**.

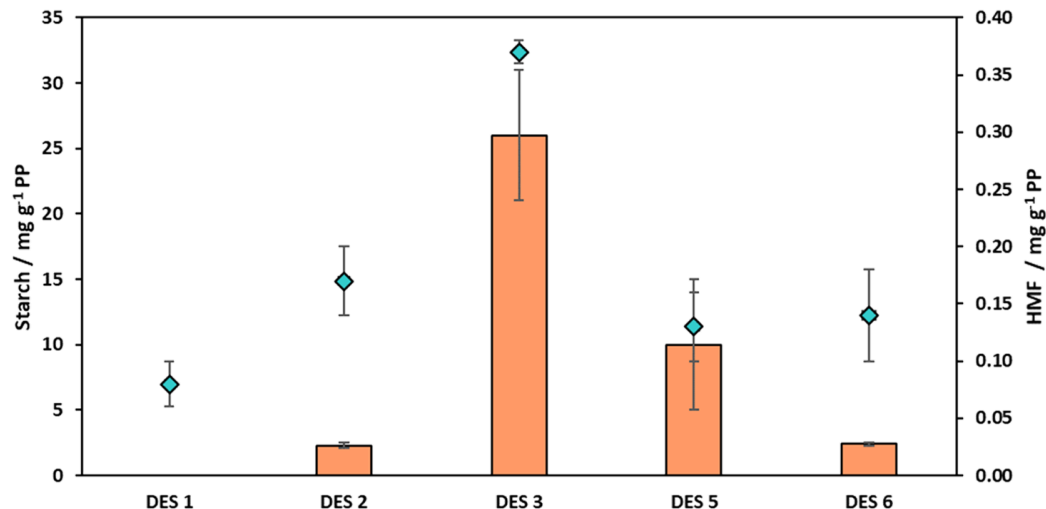
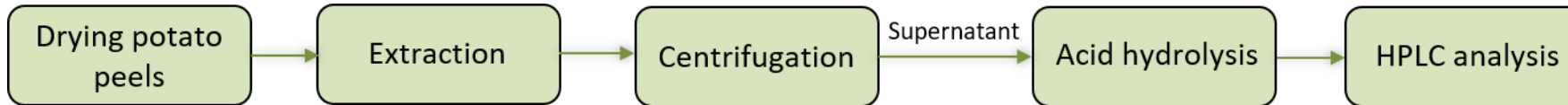
➤ This ratio impacts starch physical properties, including its solubility.

➤ The dissolution of all starches was lower compared to the values measured with corn starch.

➤ No obvious correlations were observed between the DES and starch of different botanical origins.

Case study: starch solubilization and extraction from potato peels

Starch extraction from potato peels

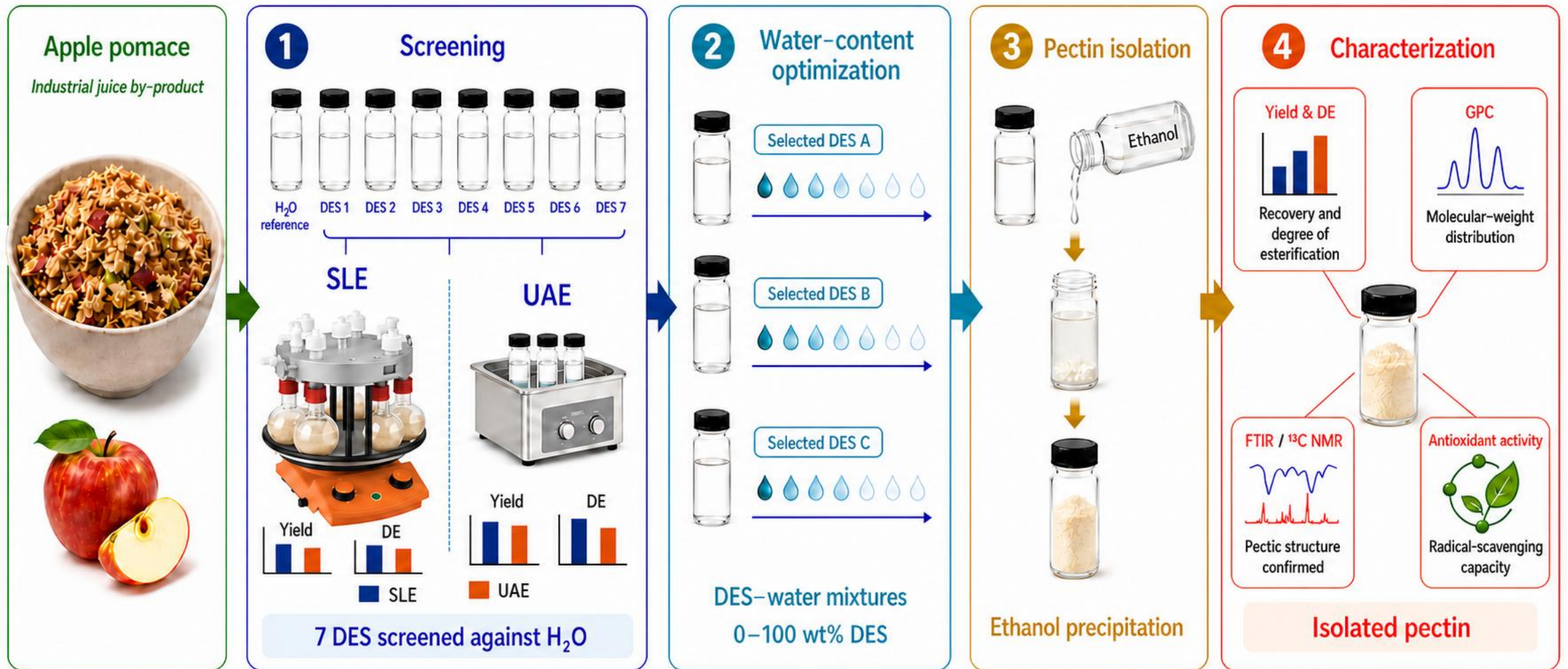


- DES with optimal molar ratios and water contents were used for starch extraction from potato peels.
- The highest solubility was achieved in DES 3 (up to 26 mg.g⁻¹ potato peels).

Future work:

- Optimization of extraction parameters to achieve higher starch yields.
- Other types of starch-containing agricultural waste could also be explored and optimized for efficient starch extraction.

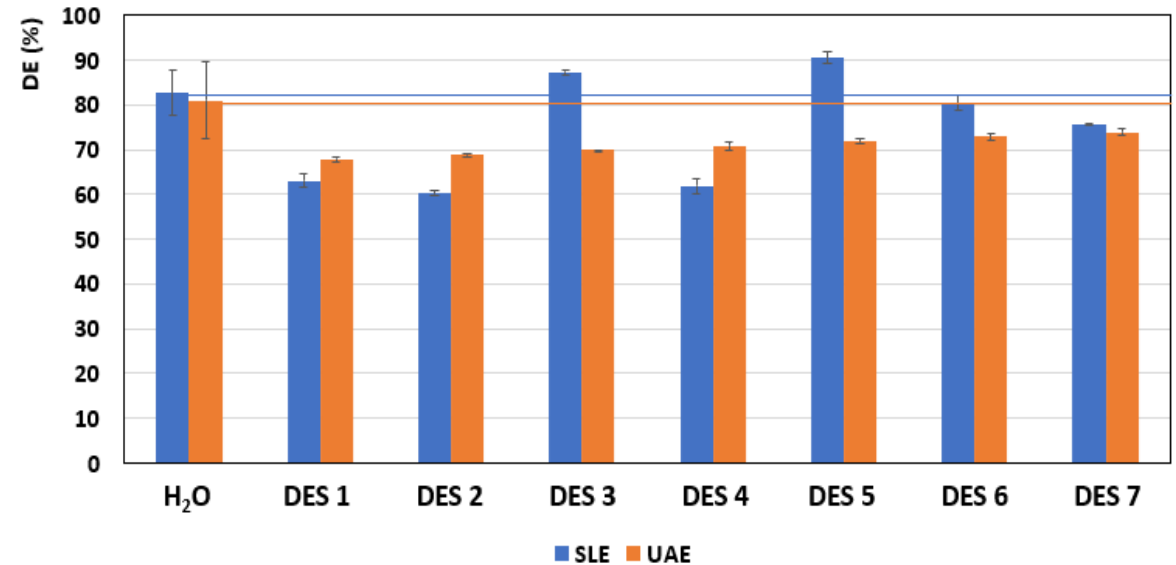
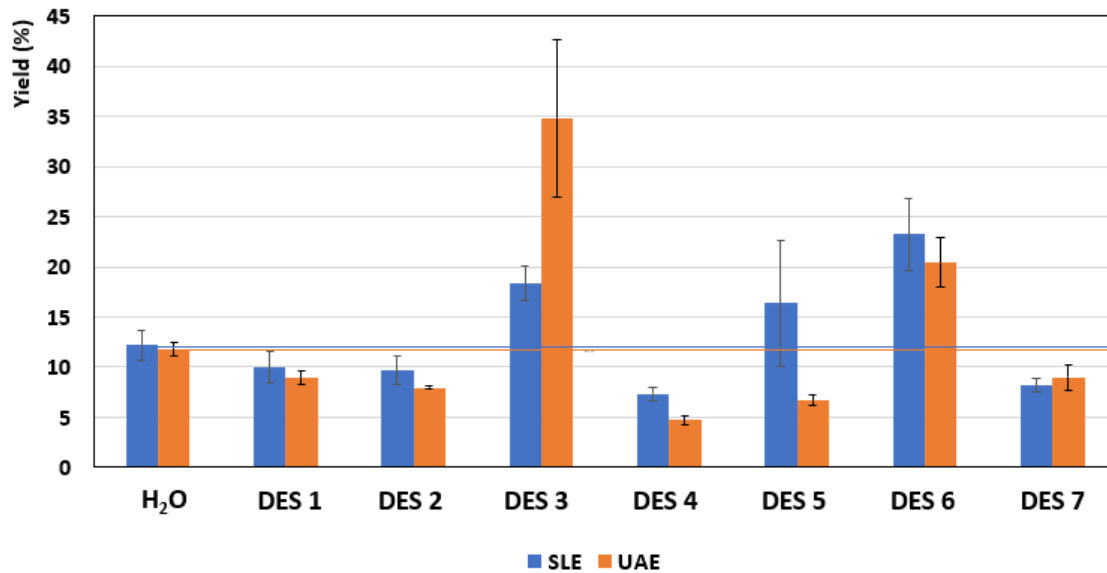
Case study: extraction of pectin from apple pomace



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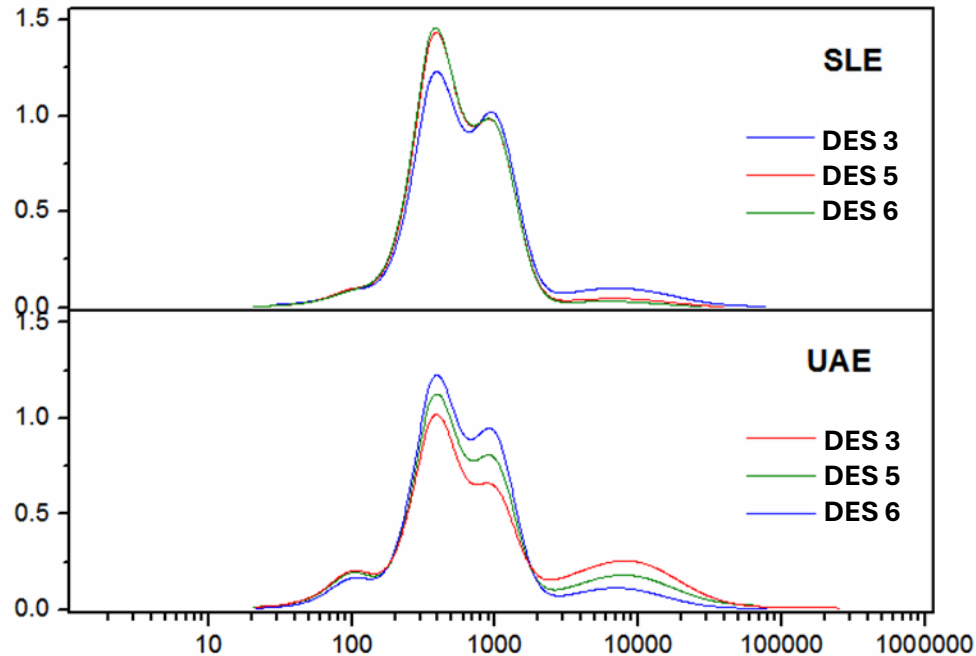


Case study: extraction of pectin from apple pomace



- **Screened 7 DES and compared it with the reference** → analysis considered in terms of extraction yield and de-esterification degree as this can determine the possible applications
- **Most promising DES: DES 3, DES 5 and DES 6** → selected for further optimization and characterization

Case study: extraction of pectin from apple pomace



- GPC shows predominantly **bimodal molar-mass distributions** dominated by fractions of approximately **100–2500 Da**.
- The recovered products are better described as **pectic oligosaccharide-rich extracts** rather than intact high-MW pectin.
- UAE produces **broader distributions**: a very-low-MW fraction **< ~130 Da** plus a more pronounced **2.5×10^3 – 4.0×10^4 Da** fraction.
- Ultrasound appears to do two things at once: **enhance release of larger cell-wall polysaccharides** + **promote partial fragmentation**.

More extraction ≠ recovery of intact pectin

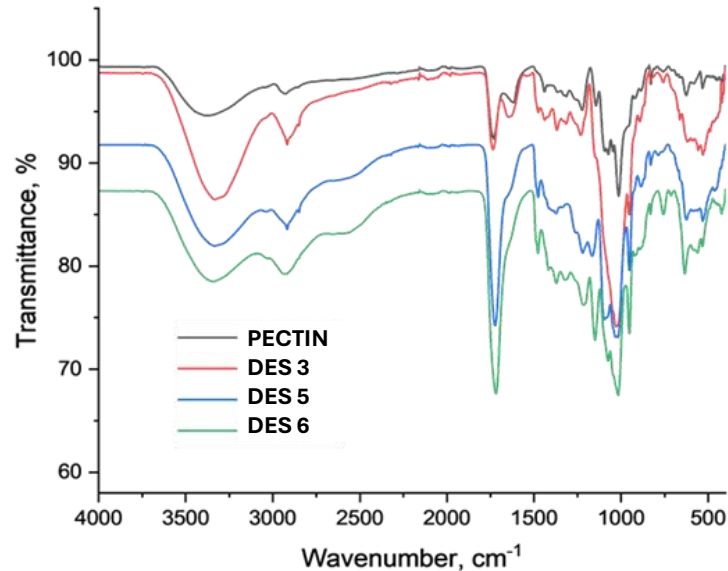


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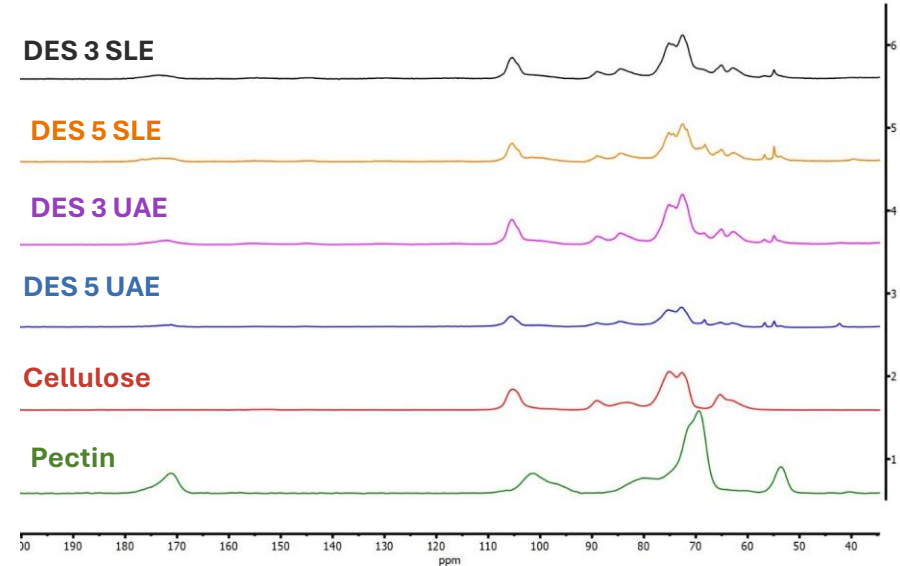


Case study: extraction of pectin from apple pomace

ATR-FTIR



Solid-state ^{13}C NMR



- Both techniques confirm **esterified pectic structural motifs** → FTIR $\sim 1733/1638\text{ cm}^{-1}$; NMR 173.46 and 54.90 ppm.
- However, intense cellulose/carbohydrate-associated signals reveal a **non-negligible lignocellulosic contribution**.
- Spectral similarity to commercial pectin does **not** mean equivalent purity or molecular weight.

Recovered fraction = pectin + pectic oligosaccharides + co-extracted lignocellulosic polysaccharides



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Case study: extraction of pectin from apple pomace

Antioxidant activity — IC₅₀

Lower IC₅₀ = stronger radical-scavenging activity

DES 3 UAE

Vitamin C

DPPH•

0.251 mg/mL

0.143 mg/mL

DES 3 UAE

Vitamin C

ABTS•⁺

0.208 mg/mL

0.137 mg/mL

At 5 mg/mL → 84.9% DPPH inhibition

- The most active extract was obtained with **DES 3 using UAE**.
- Its antioxidant potency was still **lower than vitamin C**, despite reaching a similar inhibition plateau at high concentration.
- The stronger activity may reflect the combination of **abundant low-MW pectic fractions** and **co-extracted bioactive compounds**. However, the contribution of each cannot be separated from these data.
- Extraction conditions therefore control not only **how much material is recovered**, but also **what is recovered and what it can do**.



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