Deep Eutectic Solvent Pretreatment of Cork Dust

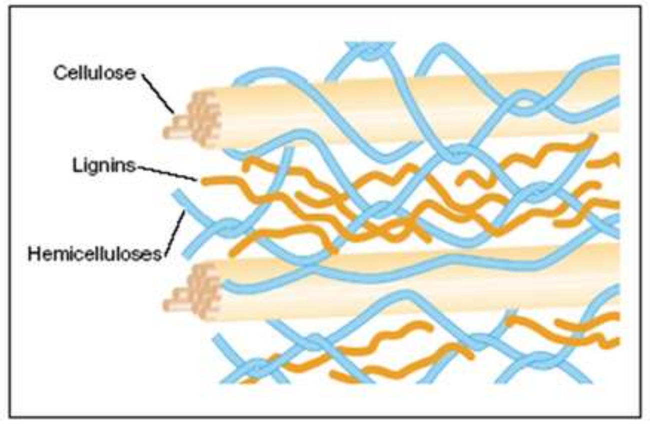
Simel BAGDER ELMACI[1*], Jana SCHULTZ[2], Asli ISCI[1], Marvin SCHERZINGER[2], Dicle Delal ASLANHAN[1], Miyase Deniz CAM[1], Ozge SAKIYAN[1], Martin KALTSCHMITT[2]

[1] Ankara University, Food Engineering Department, 06830 Golbasi, Ankara, Turkey
[2] Hamburg University of Technology (TUHH), Institute of Environmental Technology and Energy Economics (IUE), Eissendorfer Straße 40, 21073 Hamburg, Germany

Content

Background

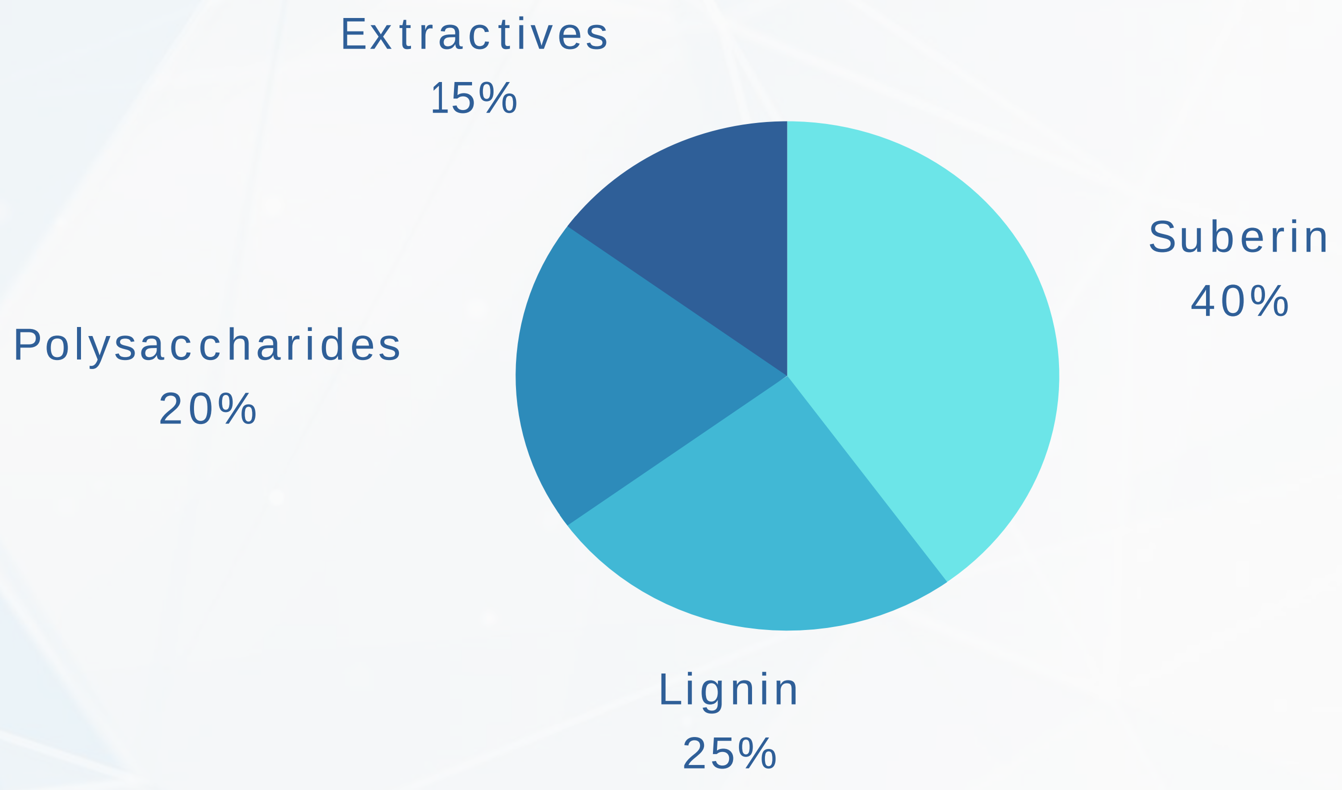
- ✓ Lignocellulosic materials (such as wood and stalky biomass) are present in nature in huge quantities and offer a high potential as alternative resources for energy, materials and chemical production.
- ✓ One of the major lignocellulosic residues generated in the Mediterranean region is cork waste.
- ✓ This waste stream could be utilized using different valorization technologies to produce value-added products and energy within an integrated biorefinery process.

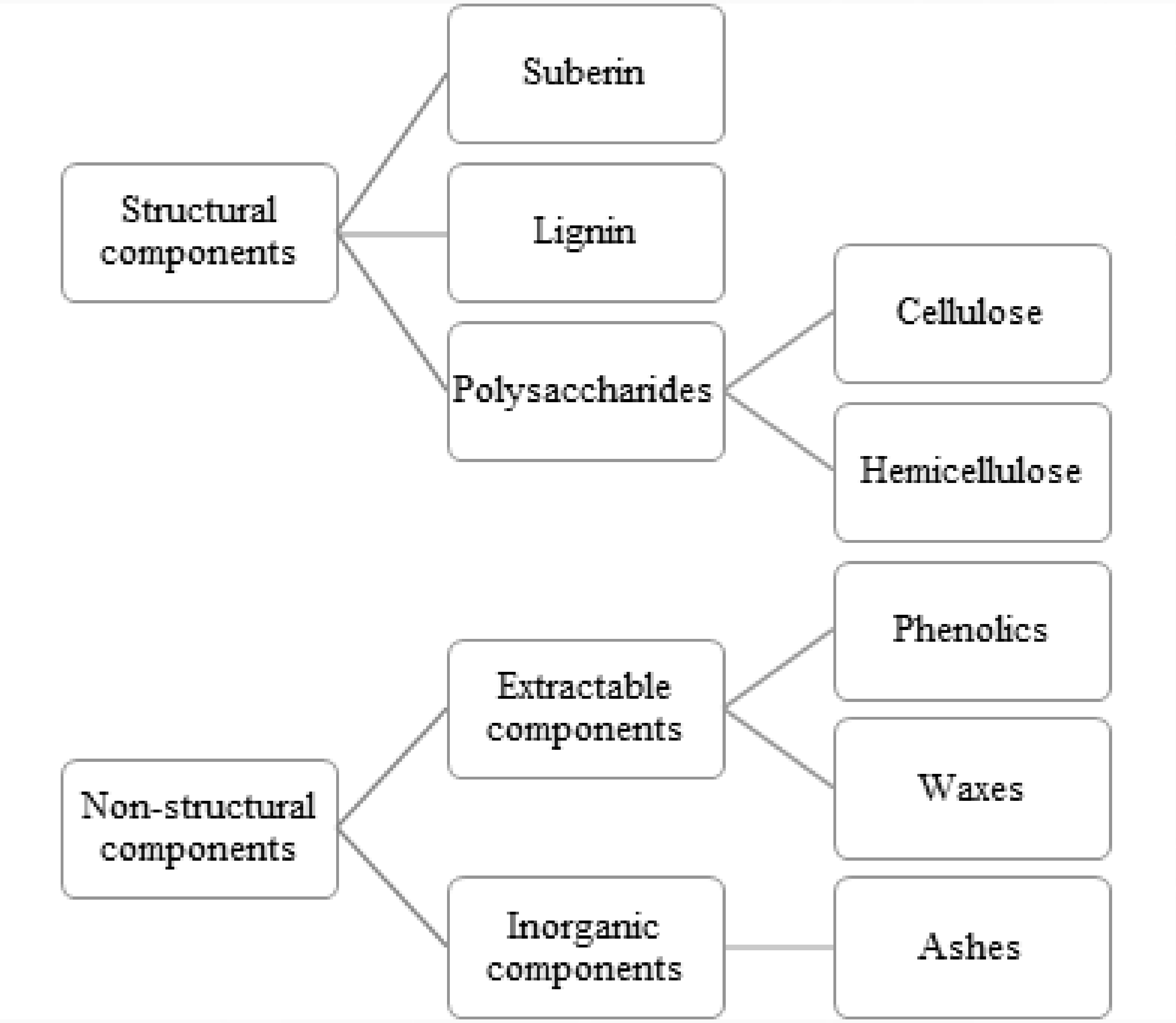


Introduction

Cork

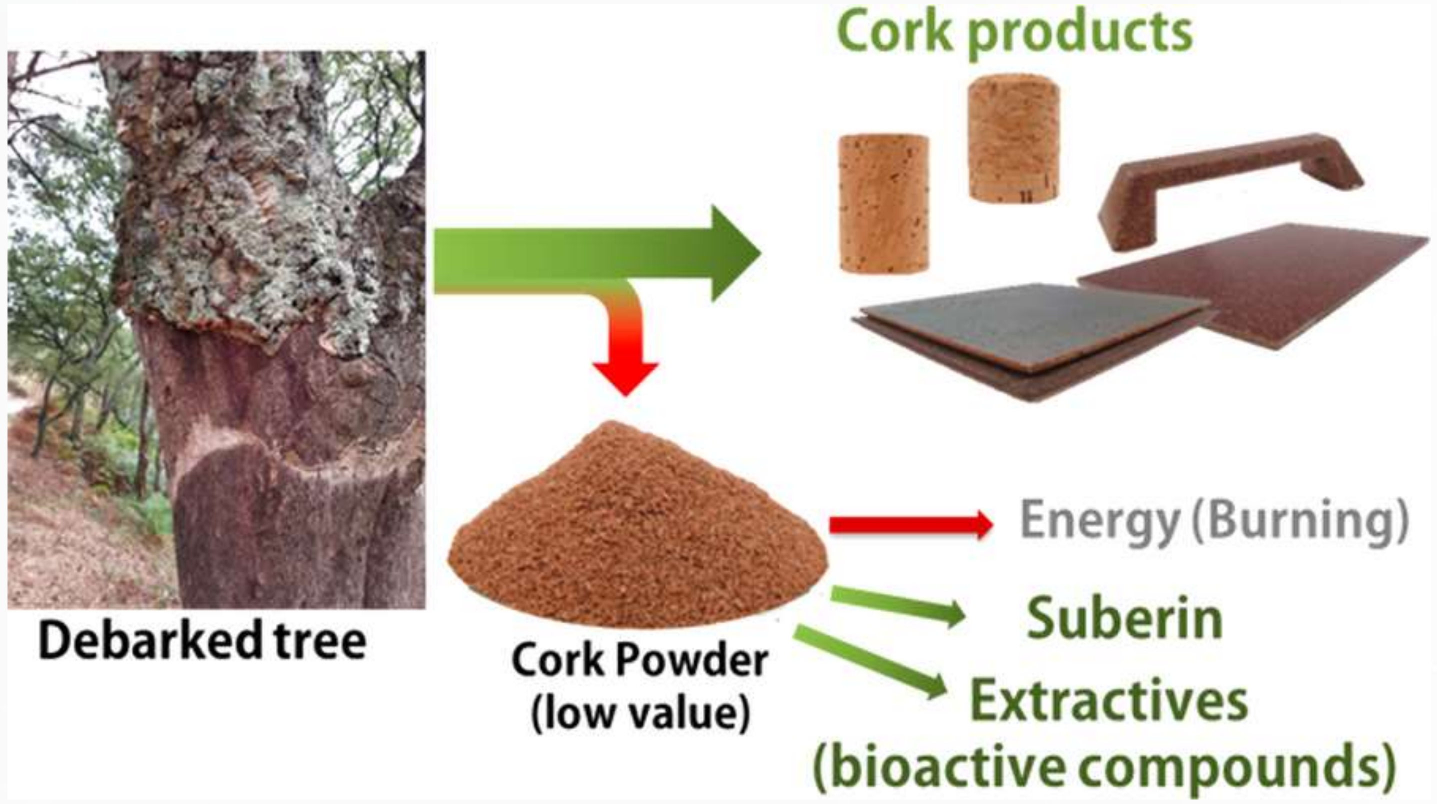
- ✓ Cork is the outer bark of *Quercus suber L.*, the cork oak tree .
- ✓ It is a natural, renewable, and sustainable raw material.



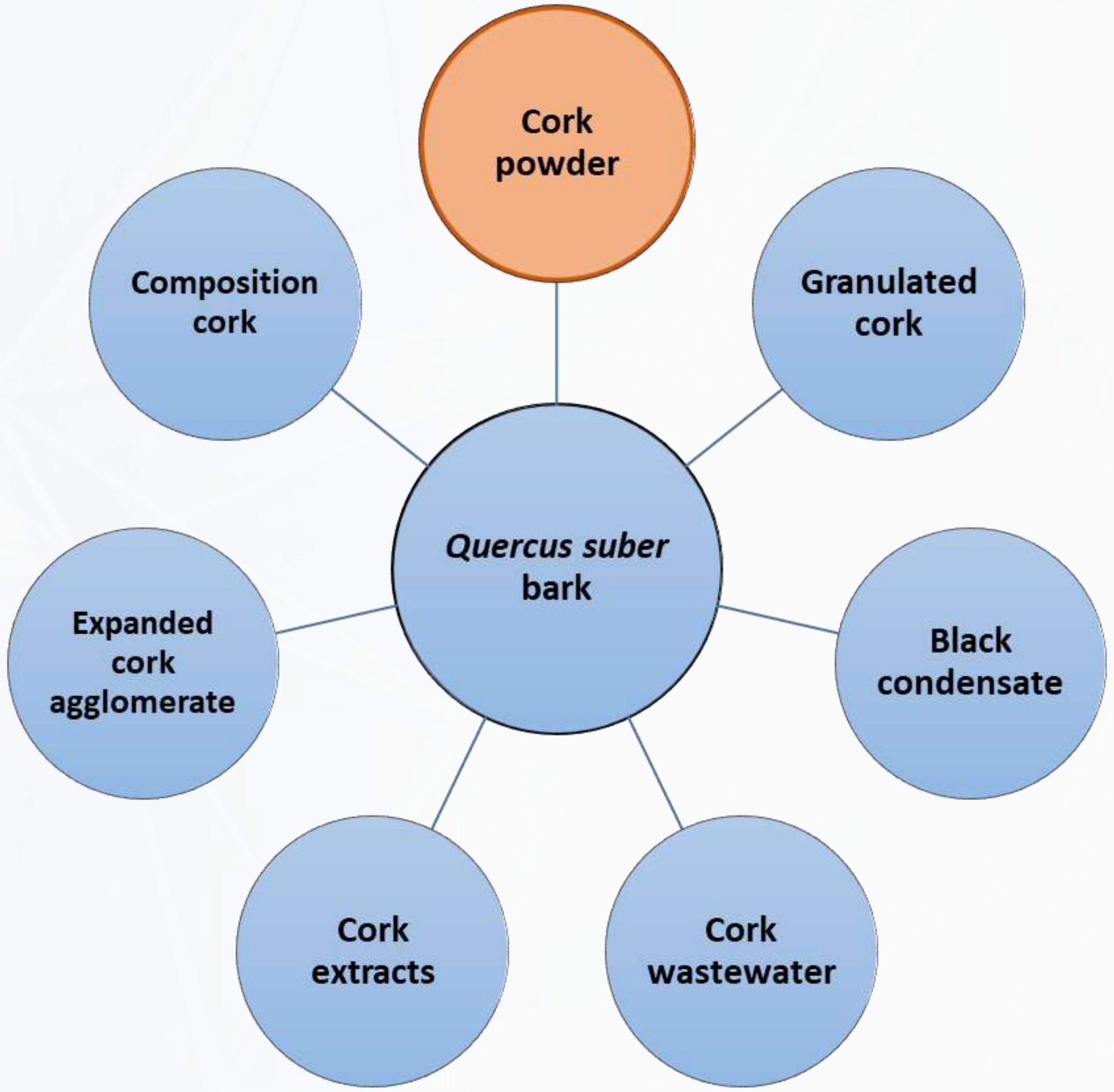


Cork

- ✓ Wide range of applications: the production of wine stoppers, applications in thermal and/or acoustic insulation materials
- ✓ The cork industry: Portugal, Spain
- ✓ Industrial processing of raw cork yields 20 % to 30 % residue, primarily in the form of cork powder/dust with low commercial value.



Cork by-products

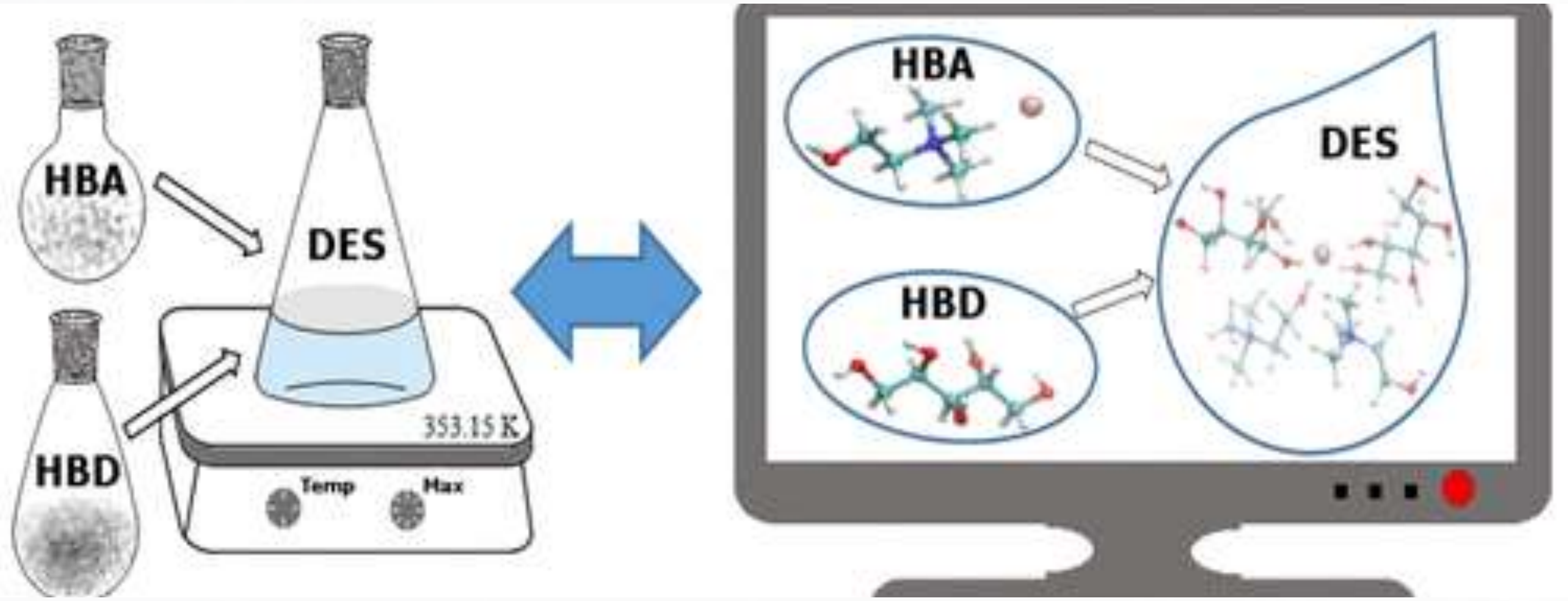


Cork dust / Cork Powder

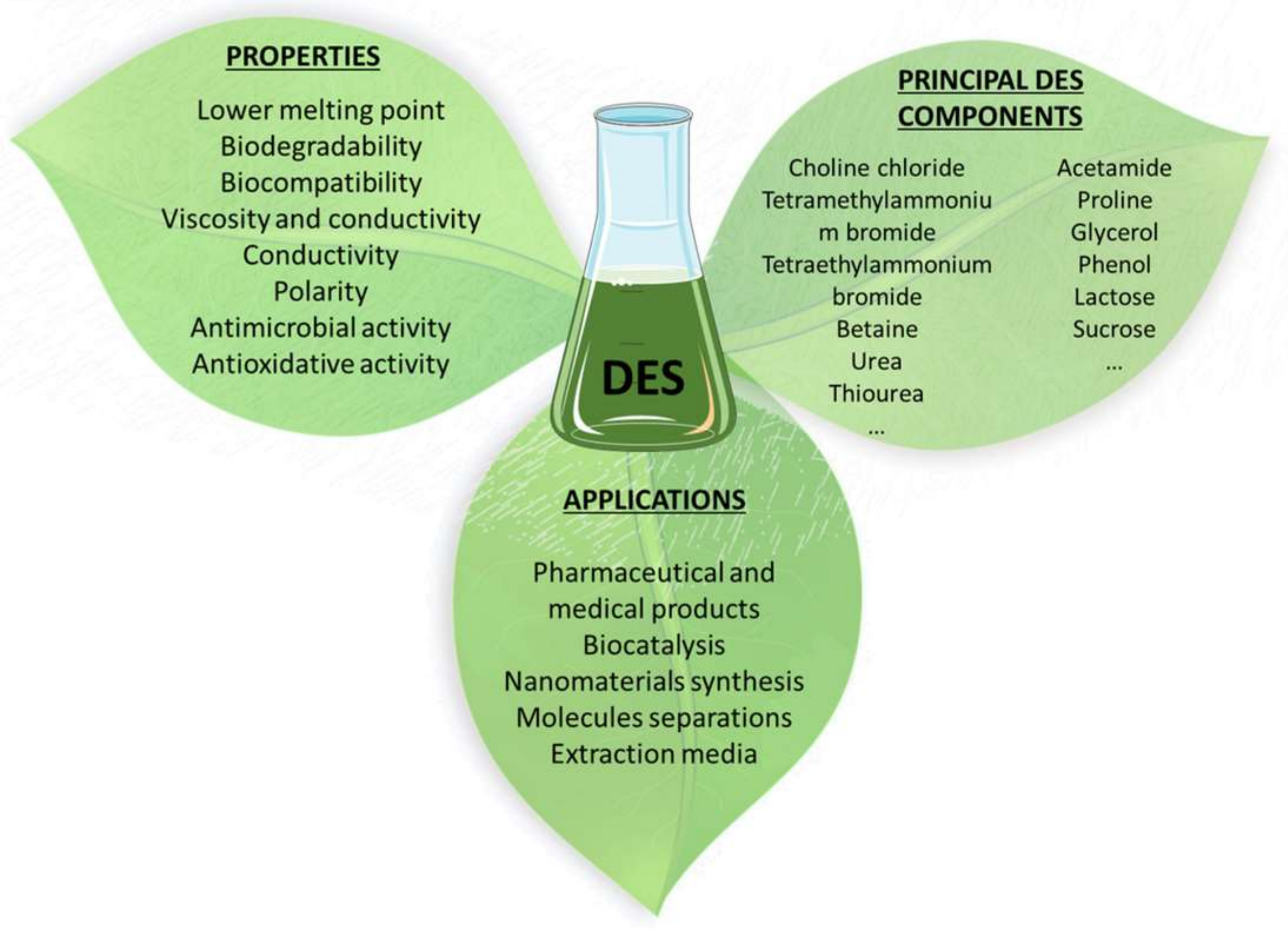
- ✓ Cork powder is also a residue from the industrial transformation of cork.
- ✓ Due to its low economic value and high heating value, it is currently used for combustion and energy production.
- ✓ This by-product is the major waste from cork industry, originating from grinding, cutting and finishing processes.
- ✓ Usually cork powder is composed by particles with sizes inferior to 0.25mm.
- ✓ In cork stopper production, cork powder corresponds to 25–30% of the raw material.

Deep Eutectic Solvents (DES)

- ✓ Deep eutectic solvents (DES) are one of the "green" solvents.
- ✓ They can be synthesized by mixing a hydrogen bond donor (HBD) and a hydrogen bond acceptor (HBA) at a specific molar ratio capable of forming eutectic mixtures.



Deep Eutectic Solvents (DES)



- ✓ Deep eutectic solvents might also be a proper extraction medium for phenolic compounds due to their relatively low cost, their biodegradability and their non-toxic nature.

- ✓ Deep eutectic solvents can donate and accept protons, which enables them to form hydrogen bonds with other compounds. Hence, they have high solvation properties and could provide higher yields in phenolic extractions .

Literature Review

- Various studies related to deep eutectic solvent extraction of phenolic compounds from different biomass sources are available.
- However, utilization of deep eutectic solvents for the extraction of phenolic compounds from cork dust is very scarce (only two articles) in literature.

01 *Freitas et al. (2022)* extracted bioactive compounds (such as phenolic acids, terpenoids, and tannins) from cork with higher yields using DES compared to harsh solvents such as dioxane.

02 *Rocha et al. (2023)* used the DES-extracted bioactive compounds of cork in cosmetic formulations and cotton fabric coloration.

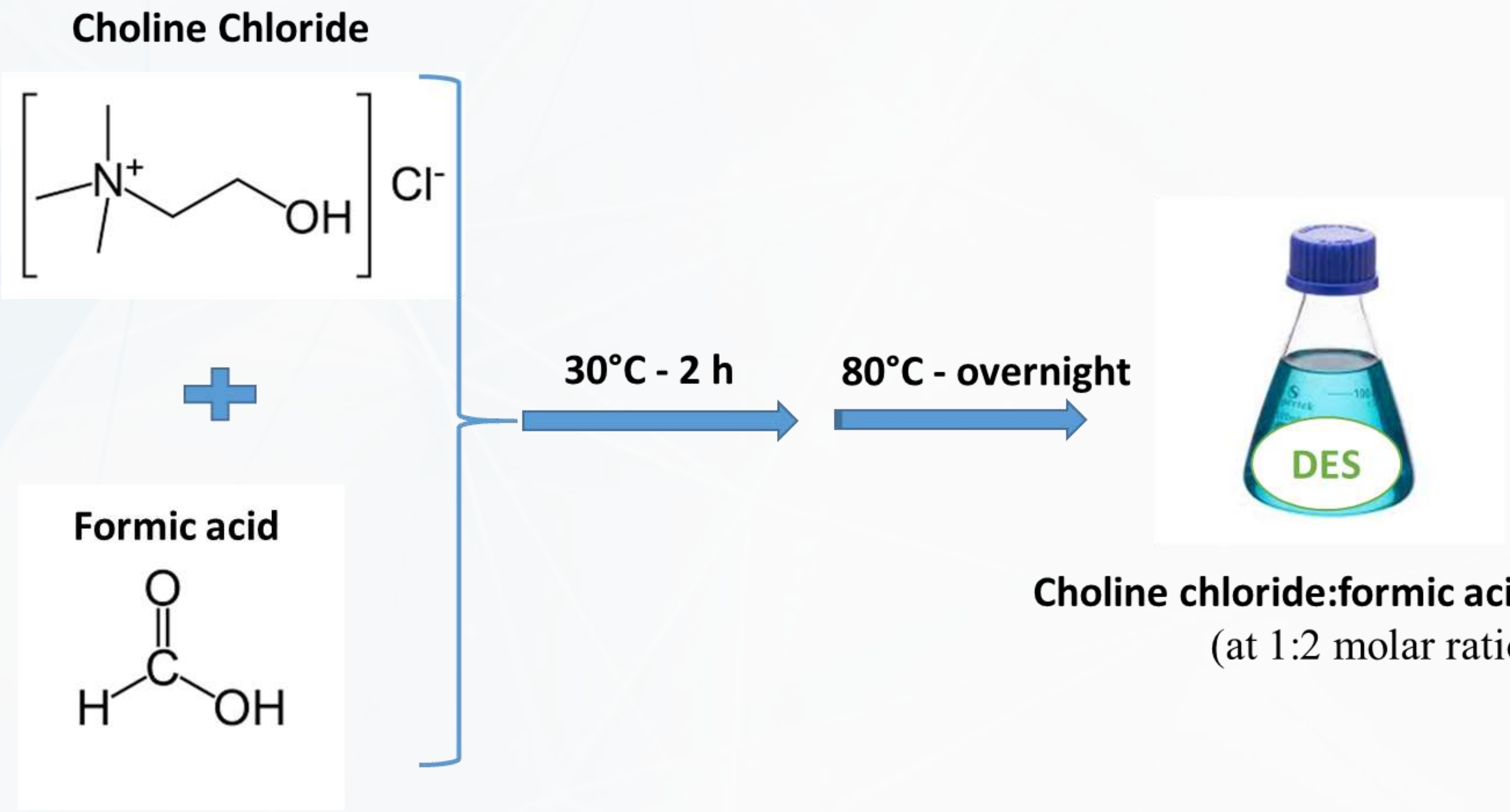
Objective of the Study

- ✓ to study the use of DES as solvent for phenol extraction from cork dust
- ✓ to study the effect of the DES pretreatment on the solubilization of carbohydrates

Feedstock

- ✓ The cork dust was supplied by an industrial cork producer in Ponte de **Sôr** (Portugal) in the form of fine powder in the year 2022.
- ✓ It was shipped to Turkey in July 2022 for DES pretreatment and subsequent analysis.

Synthesis of DES



Choline chloride:formic acid (ChCl:FA)
(at 1:2 molar ratio)

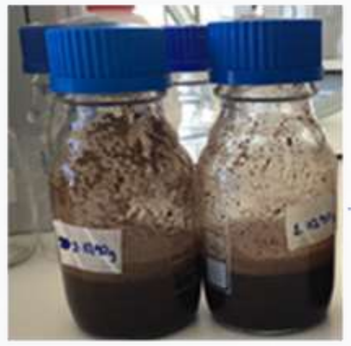
DES Pretreatment

Feedstock
(cork dust)

+

-Pretreatment conditions-

Temperature (°C)	Time (min)
90	20
90	40
90	60
110	20
110	40
110	60
130	20
130	40
130	60



Feedstock + DES
(1:10 g/mL)

Coarse filter paper

Filtration

Washing with water

Solid Fraction

Liquid Fraction

Material and Methods

Liquid Phase Investigations

- **Sugar Profile** → Determination of monosaccharides (glucose, xylose, arabinose, galactose and mannose) by Dionex ICS-6000 system (Thermo Scientific, USA) with pulsed amperometric detection (HPAEC–PAD)
- **Total Phenolic Content** → Folin-Ciocalteu method
- **Phenolic Profile** → Recovery of phenolic compounds from DES extracts using Amberlite XAD-16 resin → Elution of the Amberlite XAD-16 resin-bound phenolics with ethanol → Quantification of phenolic compounds using a Shimadzu (Shimadzu LC-20A, Japan) liquid chromatography system-equipped with a photodiode array detection (PDA)
- **Antioxidant Capacity** → DPPH (1,1-diphenyl-2-picrylhydrazyl) method

Sugar content of the liquid phase

Results and Discussion

Sugar yields in liquid fraction of cork dust samples after pretreatment

Temp. (°C)	Time (min)	Arabinose (%)	Galactose (%)	Glucose (%)	Xylose (%)	Mannose (%)
90	20	15.2	NA	NA	NA	NA
90	40	39.8	3.1	NA	NA	NA
90	60	48.0	7.2	NA	NA	NA
110	20	70.1	15.7	NA	2.3	NA
110	40	58.8	12.6	NA	3.5	NA
110	60	67.8	21.0	NA	5.4	NA
130	20	34.8	24.2	1.6	6.7	NA
130	40	31.1	26.0	1.9	8.4	NA
130	60	23.5	21.5	1.8	8.8	4.5

The sugar yields (YS,l in %) in the liquid fraction

$$Y_{S,l}\ (\%) = \frac{m_{S,l}\ (g)}{m_{S,0}\ (g)} 100\ \%$$

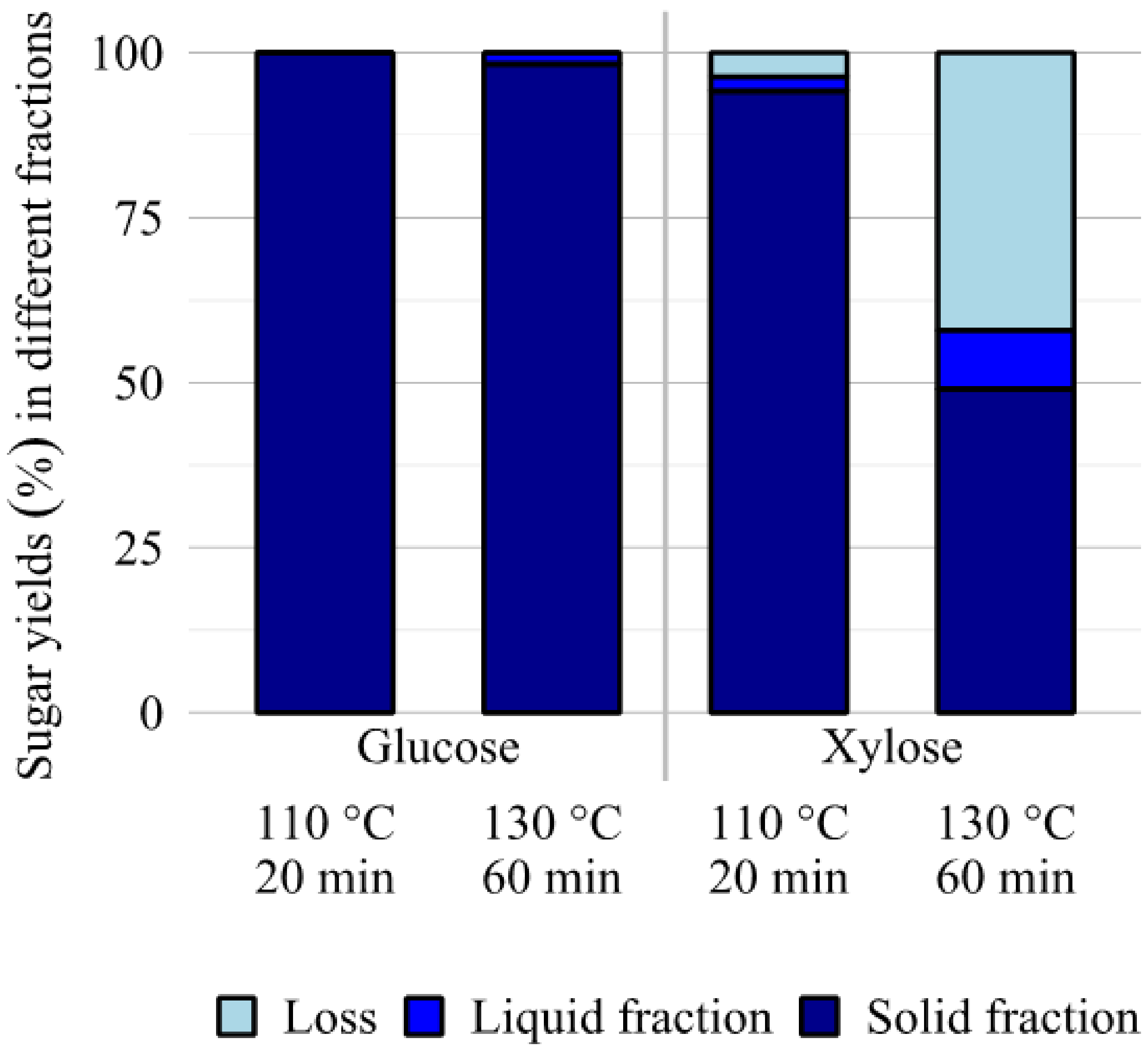
mS,l (g): amount of sugar in the liquid fraction
mS,0 (g): amount of sugar in the original sample

- ✓ **Hydrolysis products** → monomers of hemicellulose (arabinose, galactose and xylose).
- ✓ **Solubilization of glucose:** ↓
- ✓ Depolymerization of glucan during DES pretreatment is known to be low.
- ✓ Pretreatment time positively impacted xylose hydrolysis.
- ✓ Pretreatment temperature ↑, galactose and xylose ↑
- ✓ Concentrations of arabinose in the liquid fraction reached its maximum at 110 °C, decrease afterwards

Sugar content of the liquid phase

Results and Discussion

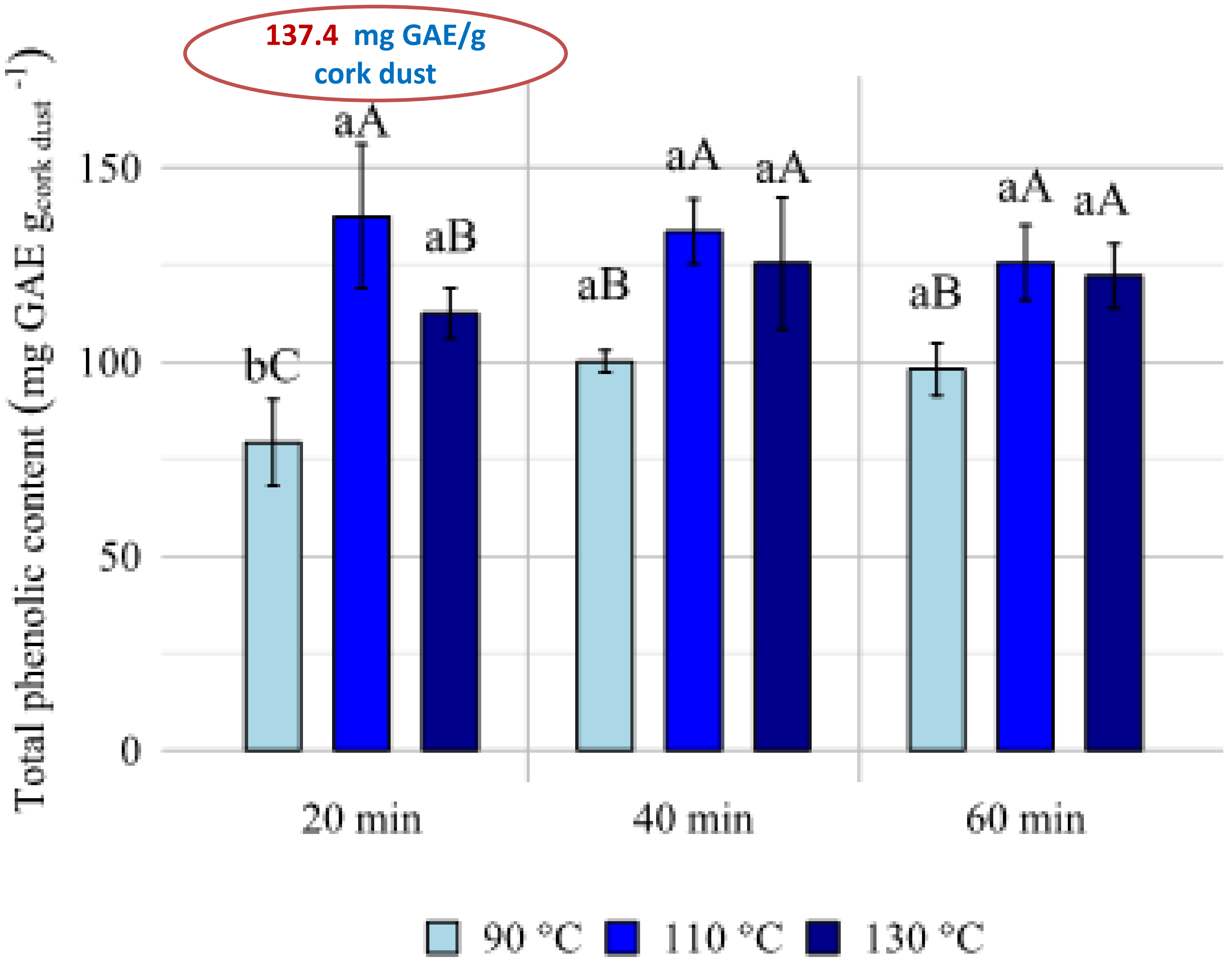
Sugar yields in solid and liquid fraction of cork dust samples after pretreatment



- ✓ All of the glucose and most of the xylose have remained in the solid fraction after pretreatment at 110 °C.
- ✓ Temperature ↑, 42 % of the initial xylose was loss/degraded.
- ✓ It is a fact that under high temperature and acidic environment xylose dehydration reactions can occur.
- ✓ In contrast, no loss of glucose was observed at high temperature and long pretreatment time, supporting the idea that DES treatment does not affect the glucan fraction of lignocellulosic materials.

Total Phenolic content of the liquid phase

Results and Discussion



- ✓ The total phenolic content yield in the liquid fractions was increased with **pretreatment time** at low pretreatment temperature.
- ✓ No statistically significant difference ($p < 0.05$) was observed between pretreatment times at higher temperatures.

- ✓ **Pretreatment temperature** had also significant impact on the release of phenolic compounds from cork dust.
- ✓ The impact of temperature was more pronounced at short pretreatment times.
- ✓ However, a further increase in the pretreatment temperature did not enhance the yield significantly.

Phenolic profile of the liquid phase

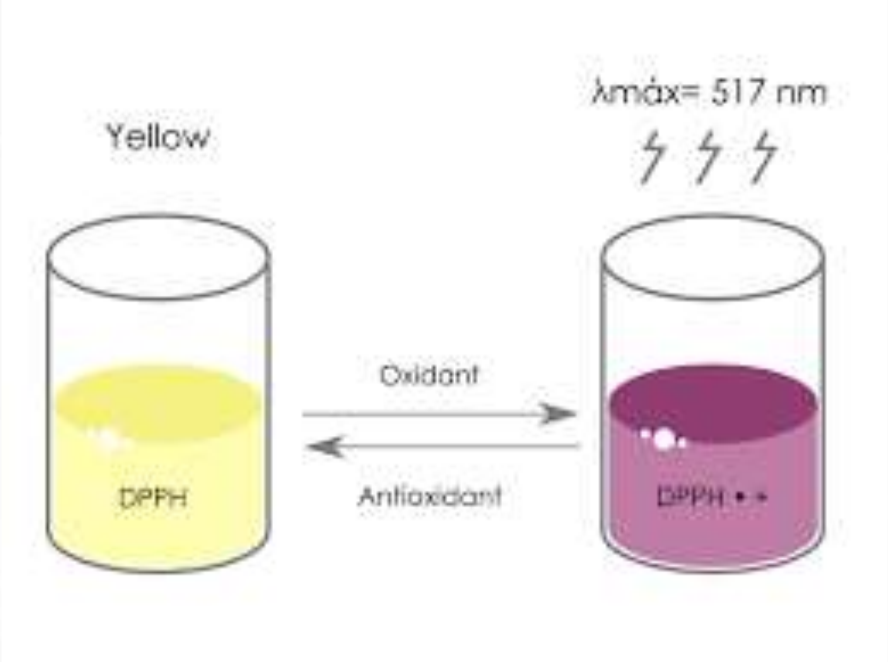
Phenolic compounds (mg kg-1 dry cork dust) in liquid fraction of cork dust samples after DES pretreatment

Compound name	130 °C / 60 min	110 °C / 20 min
Gallic acid	412.10	555.50
4-Hydroxybenzoic acid	4120.10	321.50
Chlorogenic acid	15.60	6.30
Vanillic acid	120.30	0.00
Caffeic acid	96.00	0.00
Ellagic acid	3.30	0.00
p-Cumaric acid	0.00	27.90
Ferrulic acid	132.40	8.40
Catechin	29639.80	31595.30

Antioxidant Capacity

Results and Discussion

- ✓ The **antioxidant capacities** of DES extracts pretreated at the selected conditions (110 °C / 20 min and 130 °C / 60 min) were **56.3 ± 3.1** % and **47.6 ± 5.3 %** of DPPH inhibition (using a dilution rate of 100).
- ✓ In agreement with the total phenolic content, the antioxidant capacity was found in higher amounts in the DES extracts pretreated at 110 °C for 20 min.



Conclusion

01 A non-toxic and environmentally friendly pretreatment method based on DES was applied for the extraction and recovery of bioactive phenolic compounds from cork dust.

02 The maximum phenolic extraction yield (137 mg GAE g cork dust-1 (dry matter basis)) was achieved when the cork dust samples were treated with choline chloride and formic acid (1:2 molar ratio) at 110 °C / 20 min at a solid to solvent ratio of 1:10 (g mL-1).

03 Catechin, 4-hydroxybenzoic acid, and gallic acid were the most abundant phenolics in DES extracts.

04 Overall, DES pretreatment was effective at extracting phenolic compounds from cork dust.

Thank You

TÜBİTAK

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Question and Answer...