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Condensation of extractive compounds in fresh wood

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Aalto University
School of Chemical
Engineering

2nd IFBC, Thunder Bay

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Photo: Valeria Azovskaya

What did we do?

Raw material

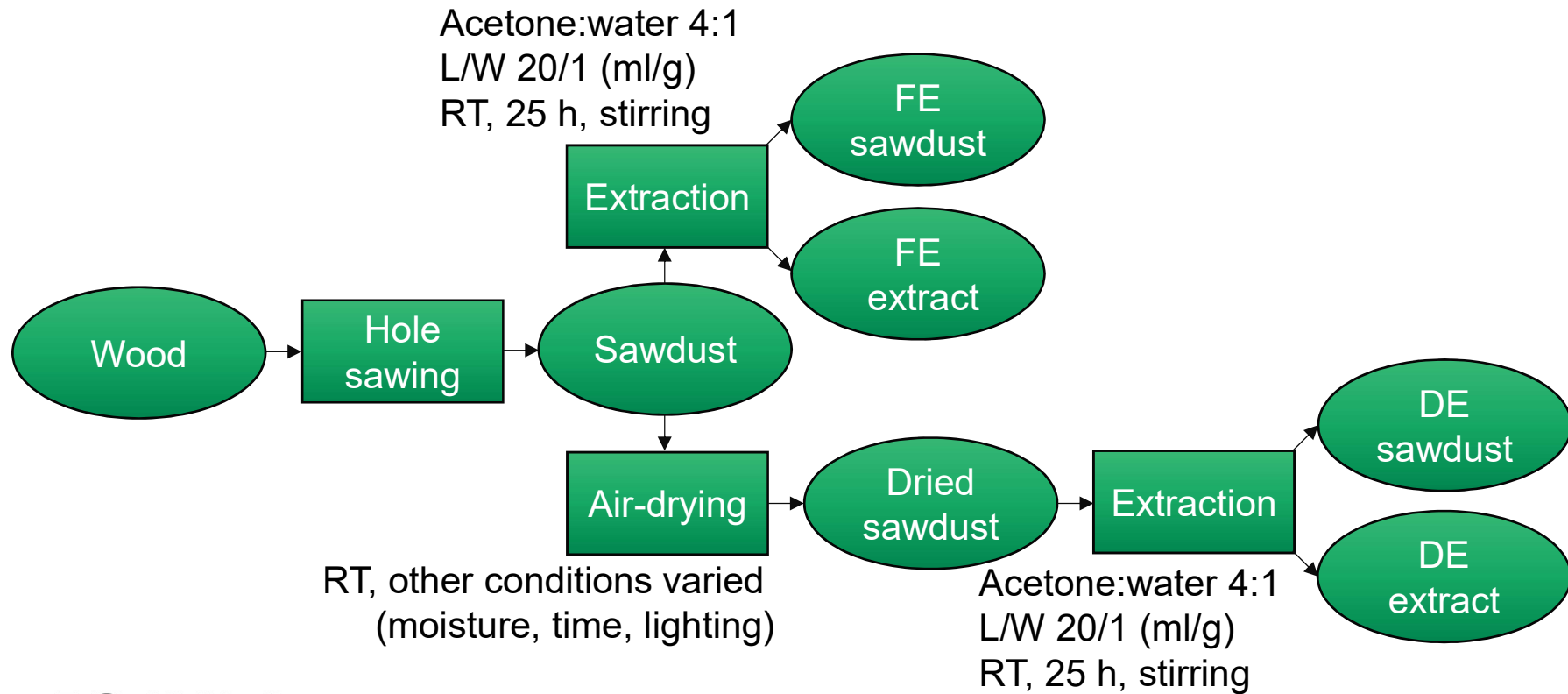
Birch tree (*Betula sp.*) with a diameter of ca. 13 cm, felled in Western Finland in late autumn

- Packed airtight and stored in a freezer below -18 °C

Sawdust prepared directly from frozen wood with a hole saw



Procedure



Methods and analyses

Extract

1. Separated from sawdust with filtration & centrifugation
2. Rotary evaporation
3. Lyophilization
 - HPAEC-PAD, UV-vis, GC/MS, GC/FID

Sawdust

1. Air-drying after filtration
 - Color measurement (CIELab*)
2. Autohydrolysis
 - P factor 800 (205 °C)
 - Mass balance: acetone-soluble lignin, hydrolysate, hydrolyzed solids, extractives

What did we see?



0.17

0.05

0.12

0.03

Photo: Valeria Azovskaya

Color difference!

Fresh-extracted (FE) sawdust brighter in color than dry-extracted (DE) sawdust

- Acetone did not extract the colored components

Effect of drying conditions

- Drying with a delay gave the darkest color
- Drying in darkness gave the same result as drying under fluorescent tube light



L*	89.2
a*	-0.9
b*	10.2

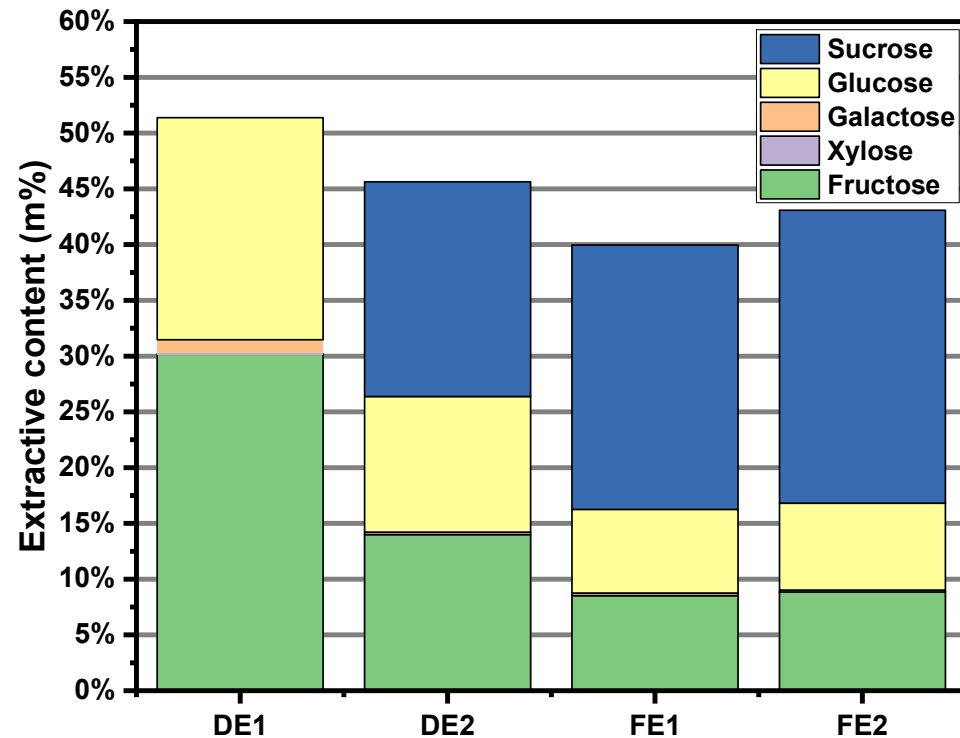
L*	80.9
a*	1.1
b*	21.9

Extracted sugar contents

(m-% of total extractives)

Less sucrose, more glucose and fructose in DE samples compared to FE samples

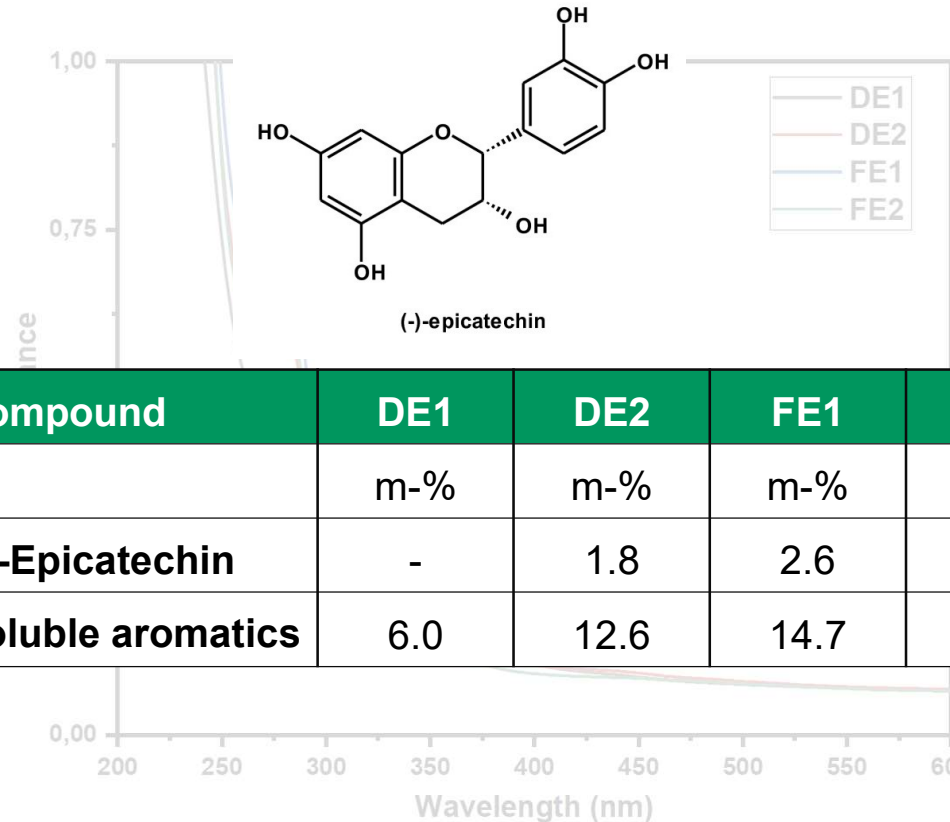
- Analyzed with HPAEC-PAD (High Pressure Anion Exchange Chromatography with Pulsed Electrochemical Detection)



Extracted phenolics contents

UV-vis analysis shows that total phenolics content is higher in FE samples compared to DE samples.

GC/MS and GC/FID results indicate that (-)-epicatechin amount decreases in the same order as the amount of total phenolics.

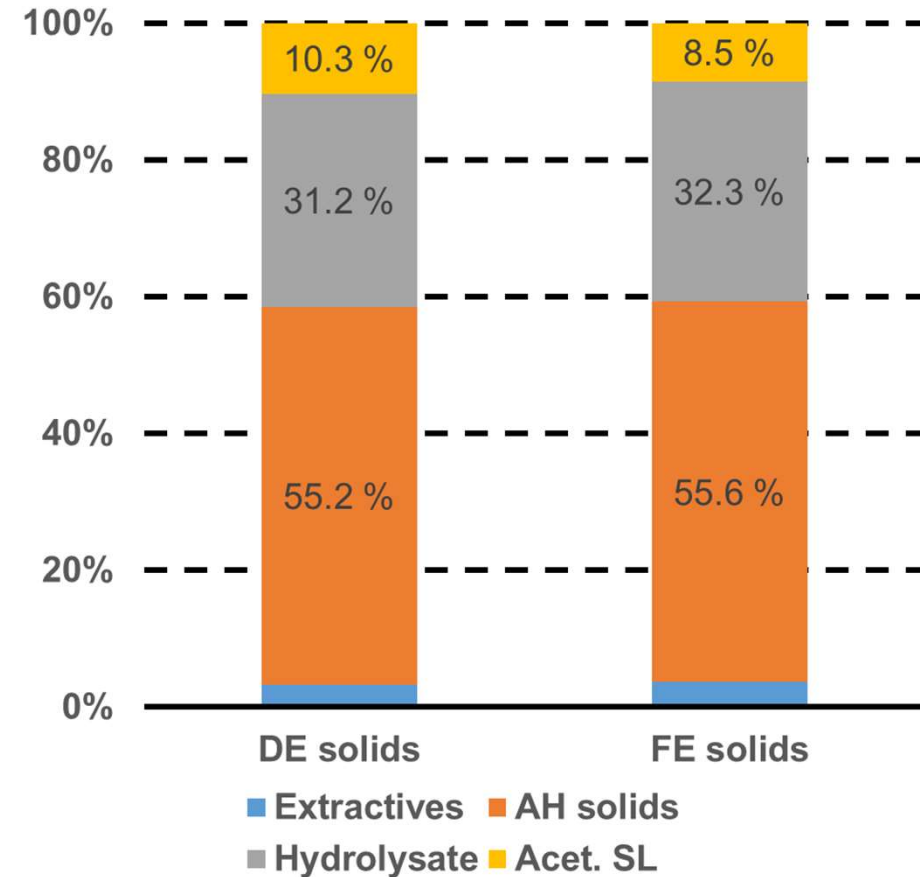


Compound	DE1	DE2	FE1	FE2
	m-%	m-%	m-%	m-%
(-)-Epicatechin	-	1.8	2.6	3.0
Soluble aromatics	6.0	12.6	14.7	15.6

Autohydrolysis material balance

(% of original wood material)

After autohydrolysis (AH; P factor 800), more acetone soluble lignin (Acet. SL) could be isolated from DE solids than FE solids.



What did we learn?



Photo: Valeria Azovskaya

Discussion

Discoloration of sawdust occurs during air-drying

- The effect most pronounced in the DE sawdust
- The formed colored compounds are not soluble in acetone

During air-drying the amounts of sucrose and (-)-epicatechin decrease

Drying the sawdust with a delay gave the darkest color

Drying in darkness gives the same result as drying under fluorescent tube light

Conclusions

Hypothesis:

Phenolic extractives in wood undergo condensation and polymerize in the presence of oxygen and enzymes when cell walls break. This will make the wood less reactive.

- + **Decrease in the amount of phenolic extractives and sugars correlate positively with the discoloration.**
- + **Moisture enhances the discoloration.**
→ enzymatic reaction?
- + **“Polyphenolic” material is formed during air-drying.**
- **Reactivity decrease of wood material doubtful.**
- **Role of auto-oxidation compared to enzyme activity?**
- **What is the structure of our “polyphenolic” material?**

Related literature

J. Dou *et al.* (2018): (+)-epicatechin condenses with hydroxymethylfurfural (HMF), formed from fructose, in acidic conditions.

A. Yamamoto *et al.* (2013): Color development in fresh birch xylem sap probably due to enzymatic activity and oxygen.

- polyphenol oxidase (PPO) causes transformation of (–)-epicatechin into colored components
- inhibition of the color development with Na_2SO_3 and with N_2 gas

S. von Schoultz (2015, 2016): Wood fractionation into carbohydrates and lignin can be made selectively in oxygen-deprived conditions.

J. Dou et al., ACS Sustainable Chem. Eng., 2018, 6(4), 5566-5573

A. Yamamoto et al., ACS Sustainable Chem. & Eng., 2013, 1(9), 1075-1082

S. von Schoultz, US patents US2015/0167234 A1 and US2016/0326203 A1

Future

Continued work in a project funded by *FinnCERES Materials Bioeconomy Ecosystem* together with VTT

Research on:

- Role of oxygen and enzymes on the color formation
- Structure of the products from extractives' reactions
- Effect of the condensation products on the wood reactivity
- Seasonal variation of the extractives in birch sap

Acknowledgements

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THANK YOU FOR THE ATTENTION! KIITOS!