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Condensation of extractive compounds in fresh wood

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School of Chemical
Engineering

2nd IFBC, Thunder Bay

June 9-12, 2019


Photo: Valeria Azovskaya

What did we do?

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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


Photo: Valeria Azovskaya

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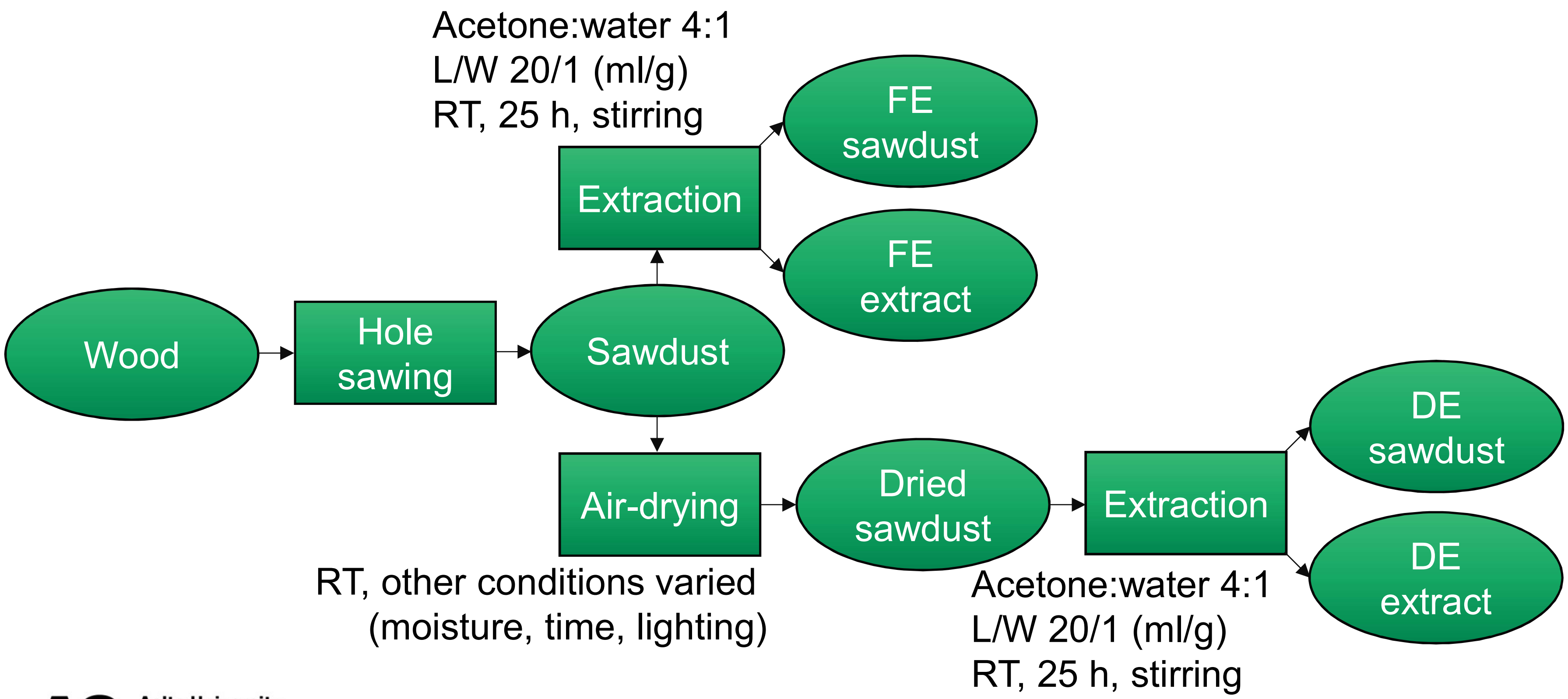
Procedure


Acetone:water 4:1
L/W 20/1 (ml/g)
RT, 25 h, stirring
FE sawdust
Extraction
FE extract
Wood
Hole sawing
Sawdust
DE sawdust
Air-drying
Dried sawdust
Extraction
DE extract
RT, other conditions varied
(moisture, time, lighting)
Acetone:water 4:1
L/W 20/1 (ml/g)
RT, 25 h, stirring

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?

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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

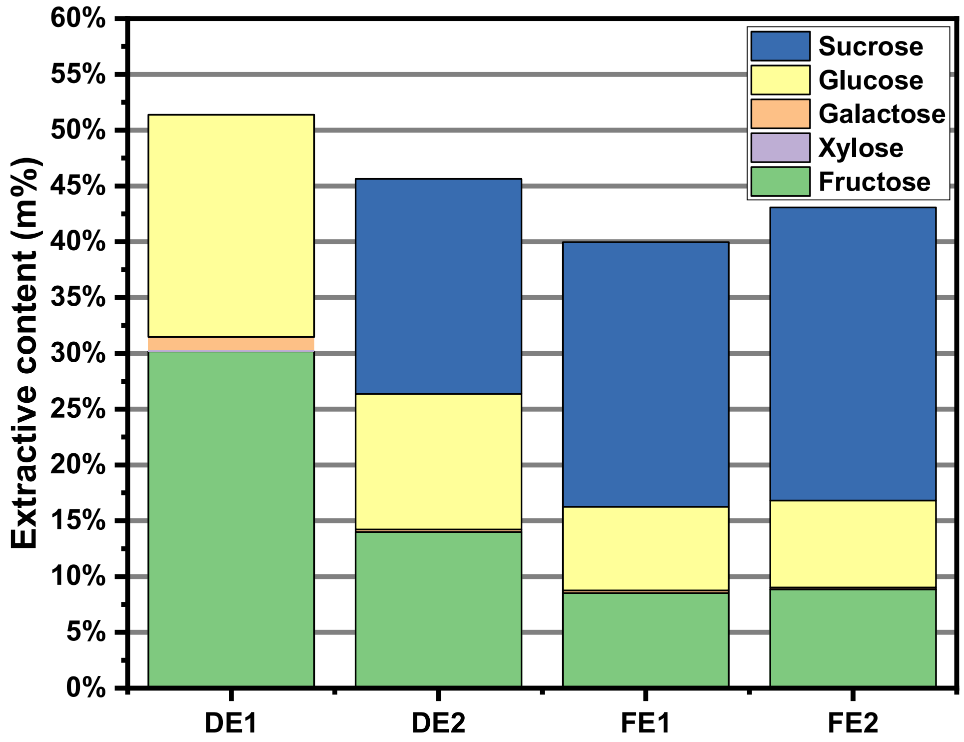
- Drying with a delay gave the darkest color
- Drying in darkness gave the same result as drying under fluorescent tube light

Photo: Valeria Azovskaya

	FE	DE
L*	89.2	80.9
a*	-0.9	1.1
b*	10.2	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)

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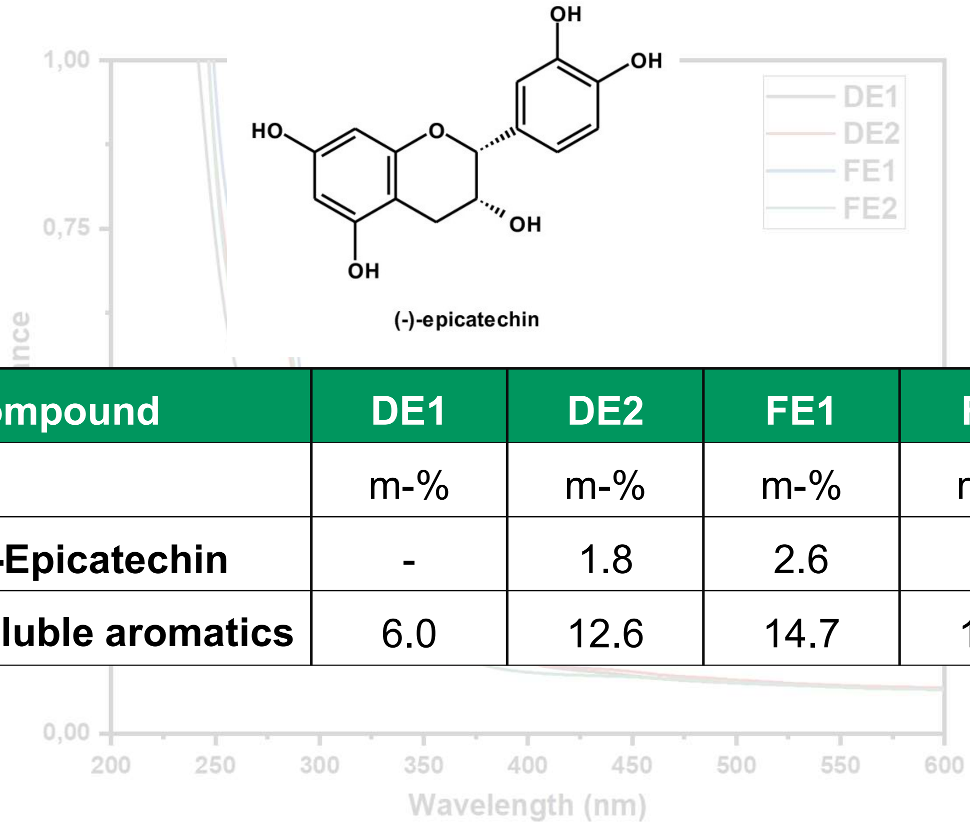
Extracted phenolics contents

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

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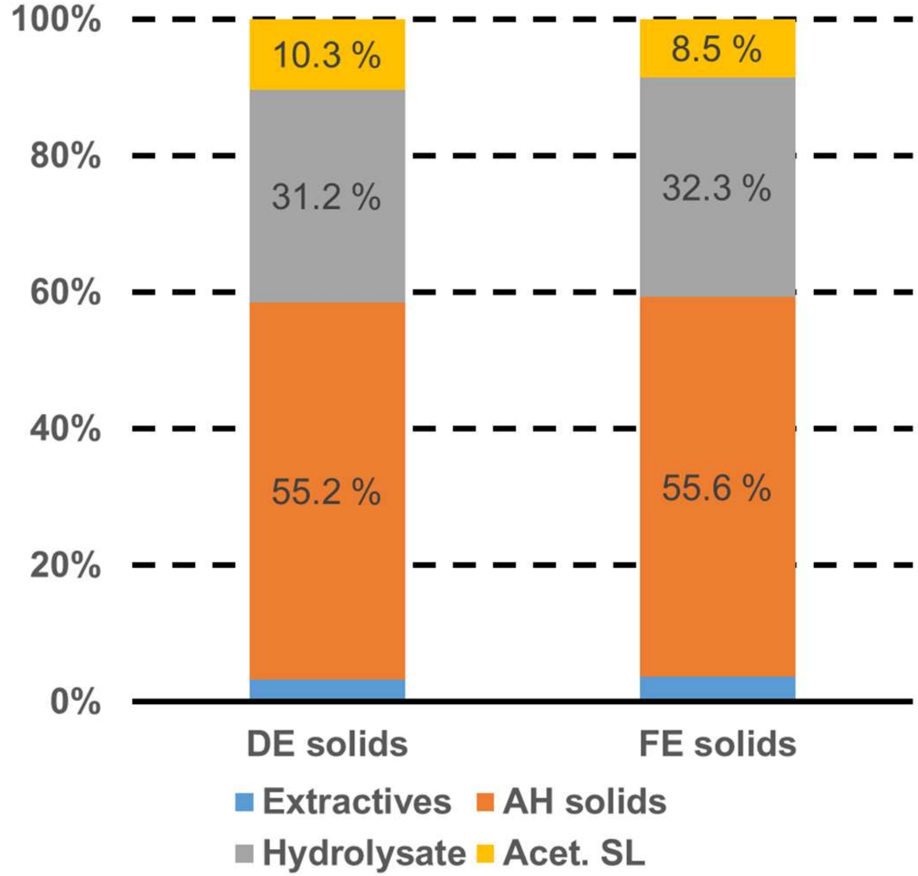
Autohydrolysis material balance

(% 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 hydroxymethyl-furfural (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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FinnCERES
Materials Cluster

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THANK YOU FOR THE ATTENTION! KIITOS!

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