Transformation of sugar maple (Acer saccharum) bark through organosolv biorefinery

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Sustainable transformation of solid bark residue

- Solid bark residues are generated in huge amounts by forest industry
- Usually burnt for energy recovery or in landfill
- Various extractable bioactive molecules are contained in bark, dominated by poyphenols
- We propose integrated biorefinery process for conversion of sugar maple bark residue into valuable new products
- Structural complexity of bark is to be taken into account for any conversion process

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Organosolv process- a forest biorefinery

- Forests -50% of the total lignocellulosic biomass on Earth
- Source of major lignocellulosic polymers: cellulose hemicelluloses and lignins
- New catalytic organosolv process presented here
    - Transformation of sugar maple (*Acer saccharum*) bark into organosolv cellulosic pulp, lignin along with phenolic extractives
    - An example of forest biorefinery

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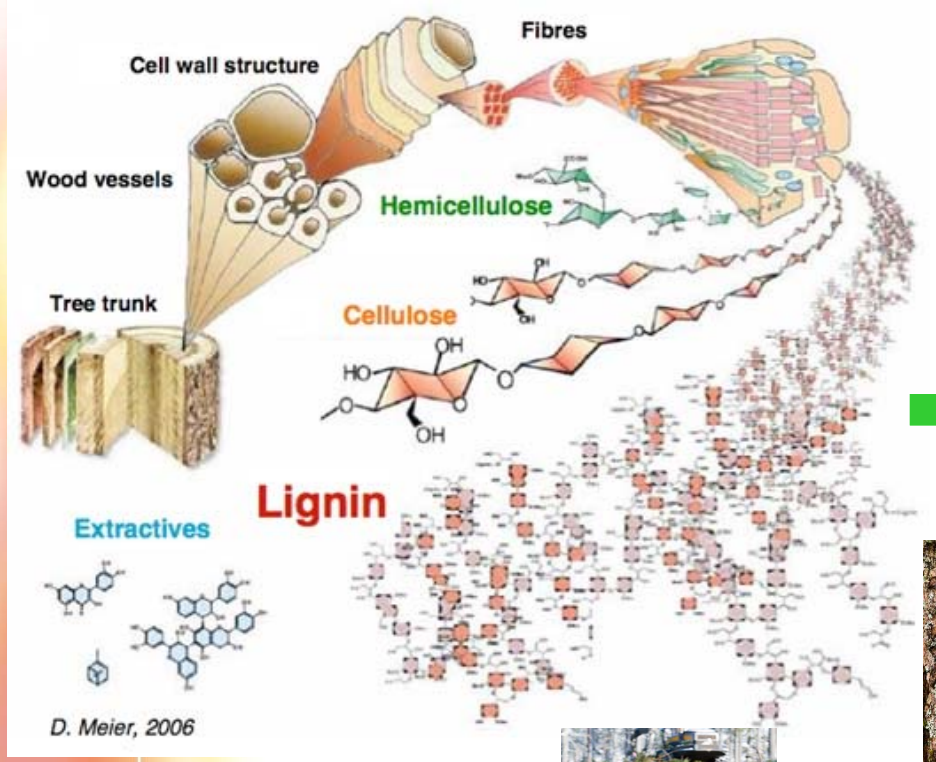
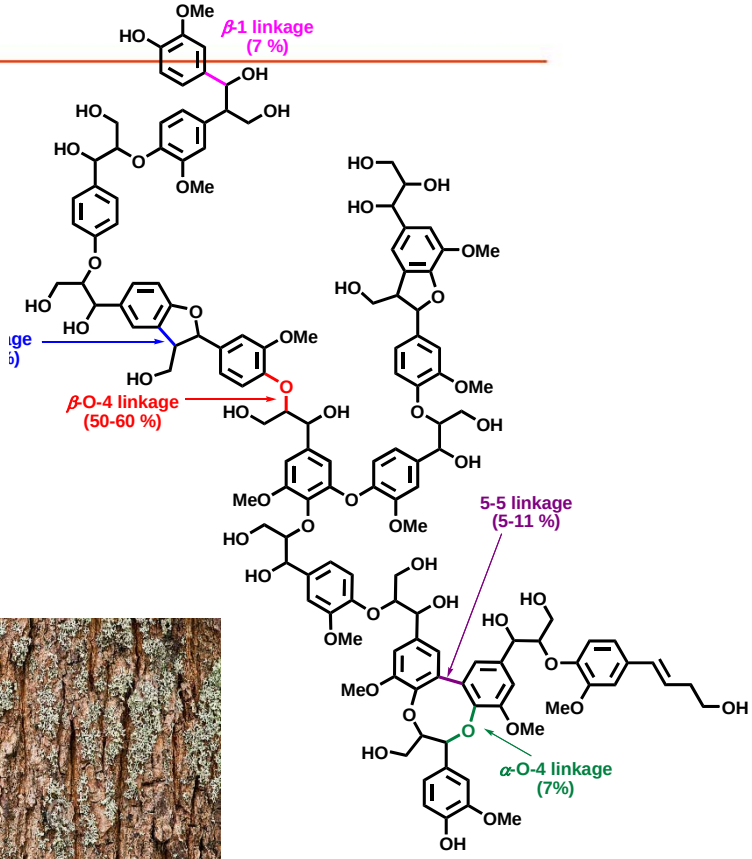
Constituents of lignocellulosics

Lignocellulosic biomasses





Lignin structure: heterogeneous aromatic polymer

Forest trees

Sugar Maple Bark

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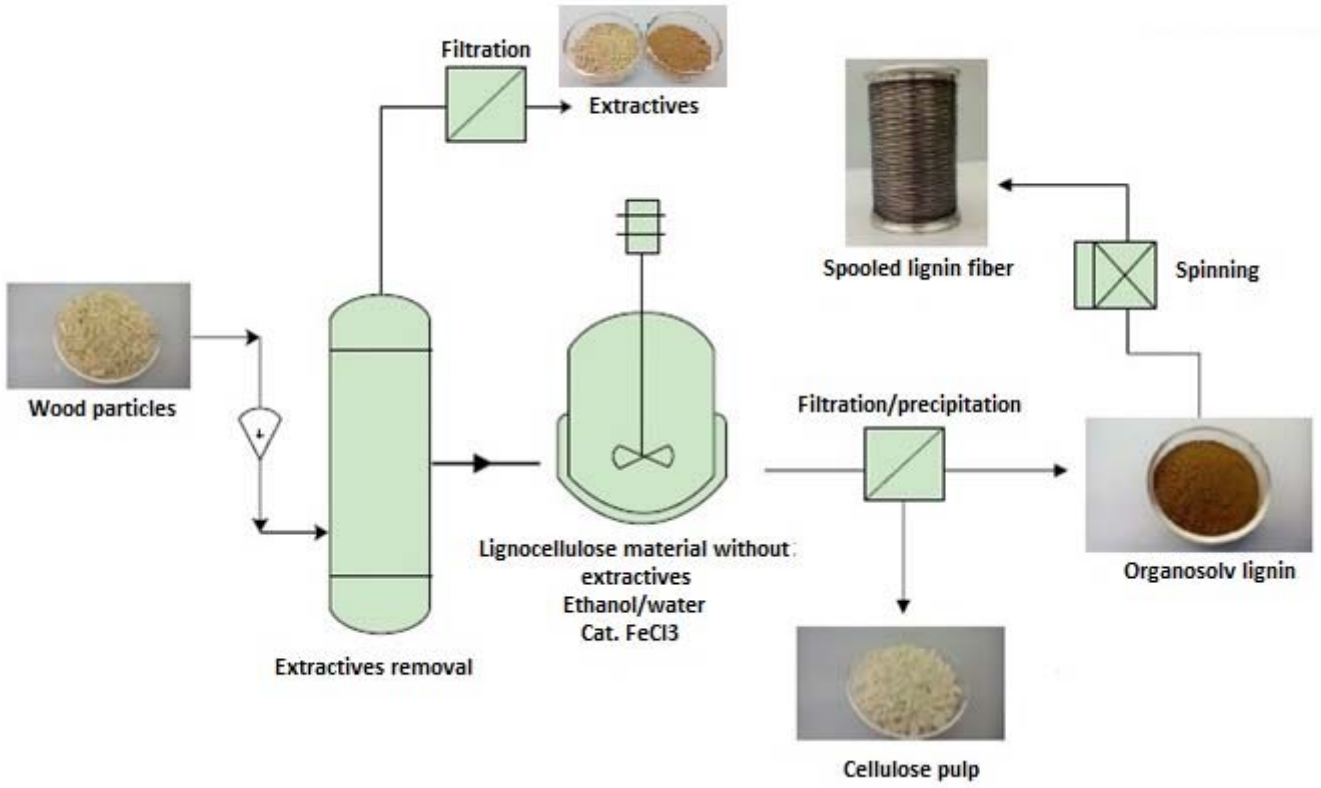
Patented catalytic organolv process: applied for sugar maple bark biorafining



Stages of organosolv refining of sugar maple bark

- Pre-extraction step - ethanol- water with ethanol-water mixture (1:1, v/v) at 80 ° C for 6 hours.
- Removal of extractives in order to protect the efficiency of catalyst used in delignification step
  - natural antioxidants based on their polyphenolic constituents
- Second delignification step with the same solvent system, using ferric chloride as catalyst, at 190°C

Chemical composition of sugar maple bark

Sugar maple bark constituent	%, on OD bark
Extract in ethanol-toluene	4.9
Extract in 1% aqueous NaOH	21.8
Total extractives	28.7
Klason lignin	27.1
Acid soluble lignin	2.5
Nitrogen content (protein)	0.39 (2.44)
Glucan	23.7
Xylan	15.9
Ash	5.2

Pre-extraction step of organosolv refining of sugar maple bark

- Extractives removal with ethanol-water mixture (1:1, v/v) at 80 ° C for 6 hours
- Thus obtained crude ethanol-water extract was fractionated with methanol into
  - Methanol soluble fraction
  - Methanol insoluble fraction, added to methanol- water mixture (9/1, v/v)- precipitation of crystals of halite NaCl- confirmed by XRD
  - Both fractions analysed for total phenols and proanthocyanidin by colorimetry

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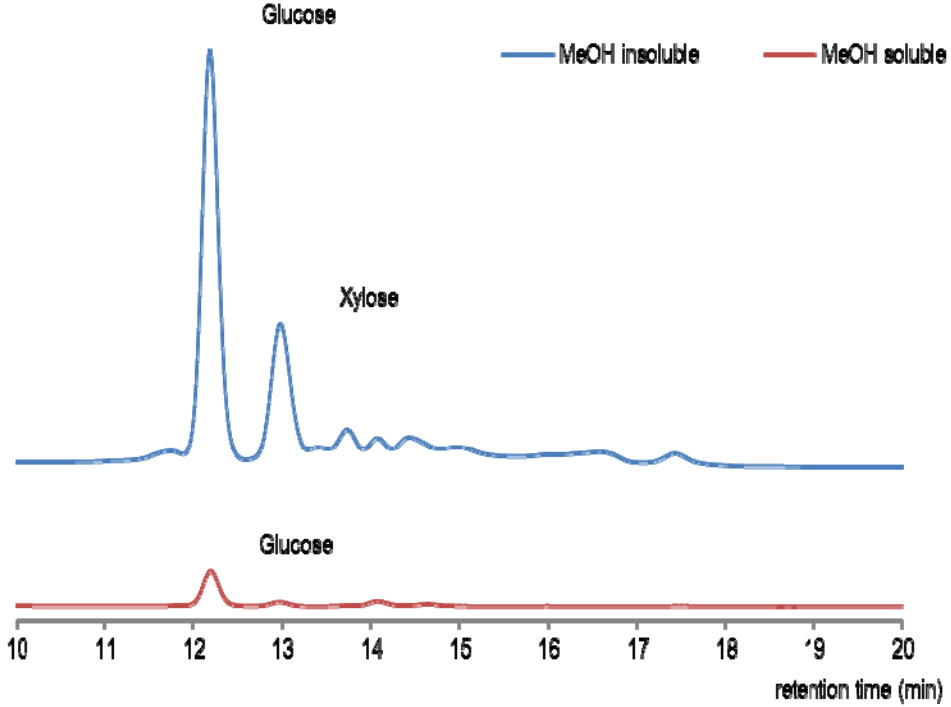
Ethanol-water bark extract

Extract	Yield, %	Total phenols; mgEGA/g bark	Proanthocyanidins, mgE CCl/g bark
Ethanol-water	5.2**		
Halite (crystal fraction)	9.1*		
Methanol insoluble	54.7*	130.1	
Methanol soluble	36.2*	212.7	50.6

** on OD mass bark basis

* on OD Ethanol-Water extract

Ethanol-water bark extract: sugars in methanol soluble and insoluble fraction



HPLC sugar analysis of methanol fractions after acid hydrolysis

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Organosolv pulping of pre-extractd sugar maple bark with ferric chloride as catalyst

- 50 g pre-extracted of bark, with 0.5 L of ethanol-water mixture , in Parr reactor with ferric chloride as catalyst at 190 ° C for 90 min
- After cooling, solid bark organosolv pulp was separated by filtration from black liquor and washed three times with ethanol (200 mL)
- Washing with water induced precipitation of Ca- oxalate
- After removal of ethabol, the oganosolv bark lignin was precipitated from dark-brown liquor (filtrate) by acidification with 2M HCl to pH = 1.5.

Chemical composition of sugar maple bark organosolv pulp

Conditions	Pulp yield (wt. % of O.D.)	KL* (%)	ASL (%)	Glucose (%)	Xylose (%)	Calcium oxalate (%)	Nitrogen content % (Protein %)	Ash (%)
EtOH/H_2O (1:1; v/v): $FeCl_3$ (cat.)	42.3	27.5±0.5	4.3±0.1	43.2±0.8	N.D.	10.3±0.1	0.57 (3.5)	9.2±0.9

Ca-oxalate precipitated upon washing organosolv bark pulp with water at yield of 10.3%

*High lignin content of pulp , even after correction for protein content

Organosolv lignin from sugar maple bark

- Obtained from spent black liquor after vaccuum removal of ethanol, by precipitation with HCl
- Separated by filtartion, oven dried
- Analysed for total lignin (Klason plus acid soluble), ash and residual sugar coontent
- Analyzed by ^{31}P NMR spectroscopy for phenolic and aliphatic hydroxyls in comparison with organosolv lignin isolated from sugar maple wood

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Chemical composition of organosolv lignin from sugar maple bark

Pulping Conditions	Lignin yield** (wt. % of O.D.)	KL* (%)	ASL* (%)	Glucose* (%)	Xylose* (%)	Ash* (%)	Nitrogen content % (Protein %)
EtOH/H_2O (1:1; v/v); $FeCl_3$ (cat.)	24.4	92.6±0.5[a]	3.5±0.1	1.5±0.7	N.D.	0.08±0.9	0.29 (1.78)

Little residual sugar in organosolv lignin; nitrogen content important

*Klason lignin corrected for nitrogen content

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^{31}P NMR spectroscopic analysis of different OH groups in organosolv lignins from sugar maple of organosolv lignins from sugar maple (mmol/g)

Entry	Functional group	Wood lignin	Bark lignin
1	Aliphatic	0.15	**1.37**
2	Syringyl	2.12	**1.59**
3	Guaiacyl	1.01	**1.61**
4	p-Hydroxyl	N.D	**0.09**
5	Carboxylic	0.01	0.34

Higher content of aliphatic hydroxyls in bark organosolv lignin than in wood

Higher guayacyl and lower syringyl in bark than in wood- more condensed?

Comparative XPS analysis of sugar maple wood and bark

Entry	Name	Bond type	Binding energy	Atomic %	
				Wood	Bark
1	C_1	C-C, C-H	285	42.42	69.91
2	C_2	C–O, C–O–C	287	47.76	24.38
3	C_3	O–C–O, C=O	288	5.20	2.84
4	C_4	O-C=O	289	3.07	2.88

No nitrogen detected in wood, while nitrogen (0.46%) and iron (0.08$) determined in sugar maple bark

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Analysis of residual liquor after lignin precipitation

Conditions	Water soluble fraction (wt %	Glucose (%)	Xylose (%)	Furfural (%)	HMF (%)
EtOH/H_2O (1:1; v/v); $FeCl_3$ (cat.)	22.9	0.91±0.6	2.1±0.3	0.35±0.1	0.74±0.2

Glucose in hydrolysate probable for other glucan than cellulose, seems to be preferentially dehydrated into HMF

Higher xylose in hydrolysate, less in cellulosic pulp

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Conclusions: a new organosolv biorefinery is available for bark residue transformation

- a new catalytic bio refinery concept
  - yielding organosolv lignin containing nitrogen and minor glucan and little ashes
  - along with co-production of
    - extractives from pre-extraction step
    - solid cellulosic pulp from deligninfication step, rich in glucose but containing high residual lignin due to protein poresence in bark
    - carbohydrates and products of their acid transformation from residual liquor for various applications.

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Thanks for your attention!

AND YOUR QUESTIONS?

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