Py-GC/MS investigation of the formation of various anhydrosugars from carbohydrates for efficient green chemical synthesis

Kristīne Meile, Gaļina Dobele, Vilhelmīne Jurkjāne, Aivars Žūriņš



LATVIAN STATE INSTITUTE OF WOOD CHEMISTRY

PostDoc Latvia

NACIONĀLAIS ATTĪSTĪBAS PLĀNS 2020

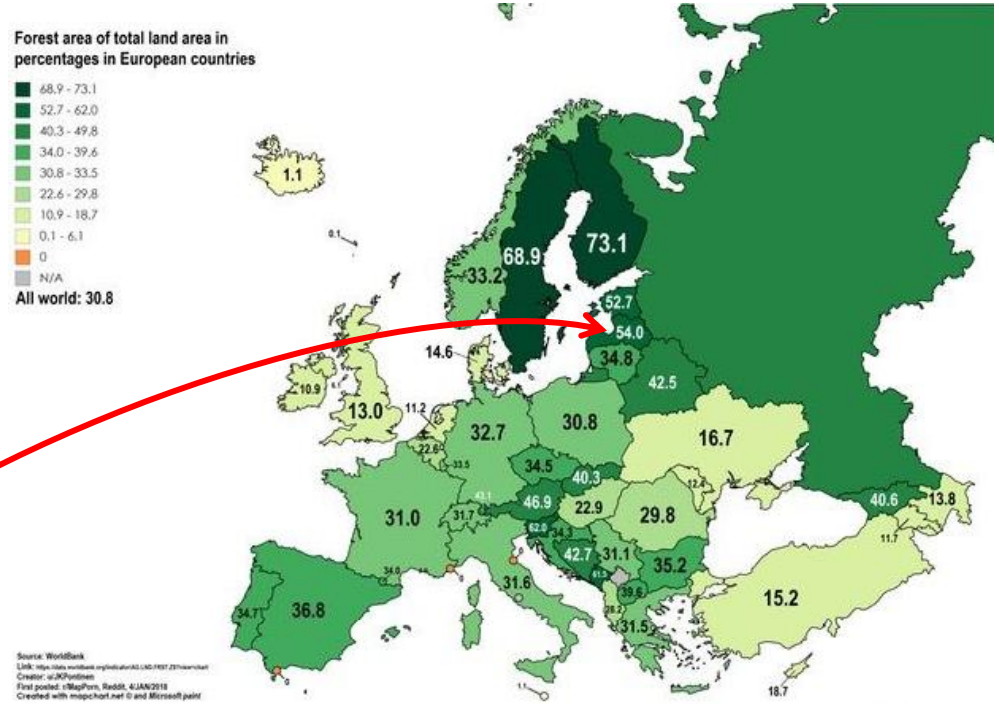
EIROPAS SAVIENĪBA
Eiropas Reģionālās attīstības fonds

IEGULDĪJUMS TAVĀ NĀKOTNĒ

Introduction

- **Latvian State Institute of Wood Chemistry**
  - Wood materials
  - Green chemistry
  - Biorefinery

- **Thermochemical process group**
  - Fast pyrolysis
  - Catalytic pyrolysis
  - Slow pyrolysis
  - High temperature carbonisation
  - Hydrothermal carbonisation
  - Chemical activation
  - Doping

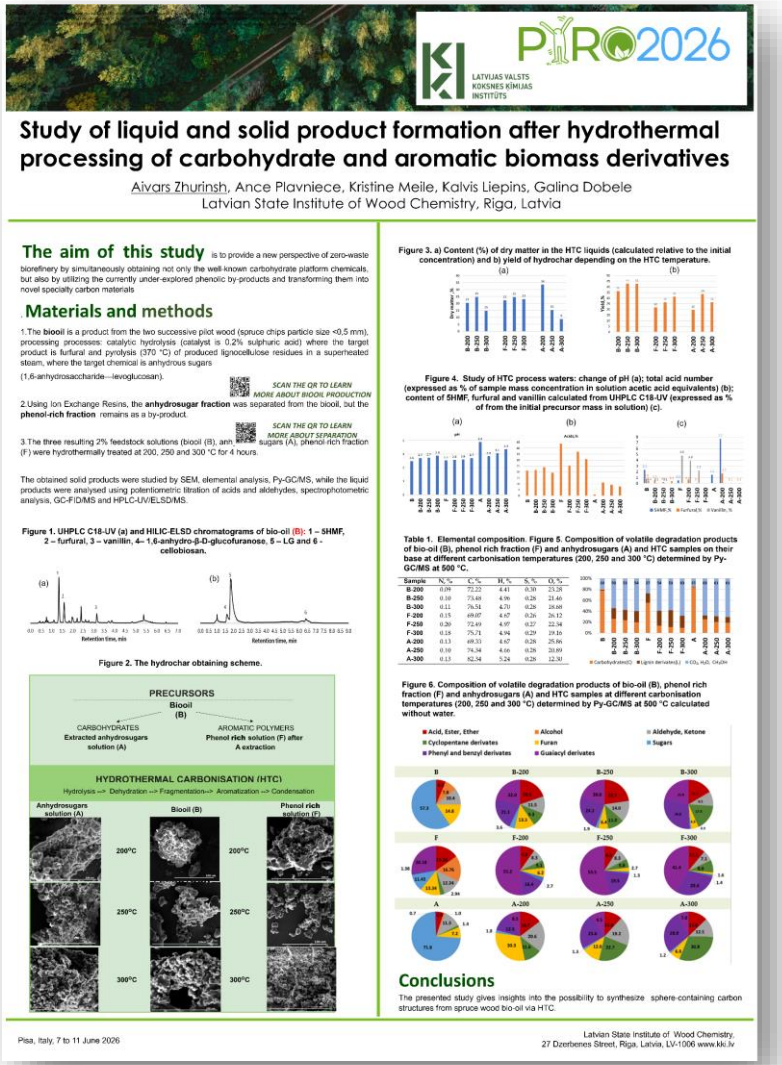




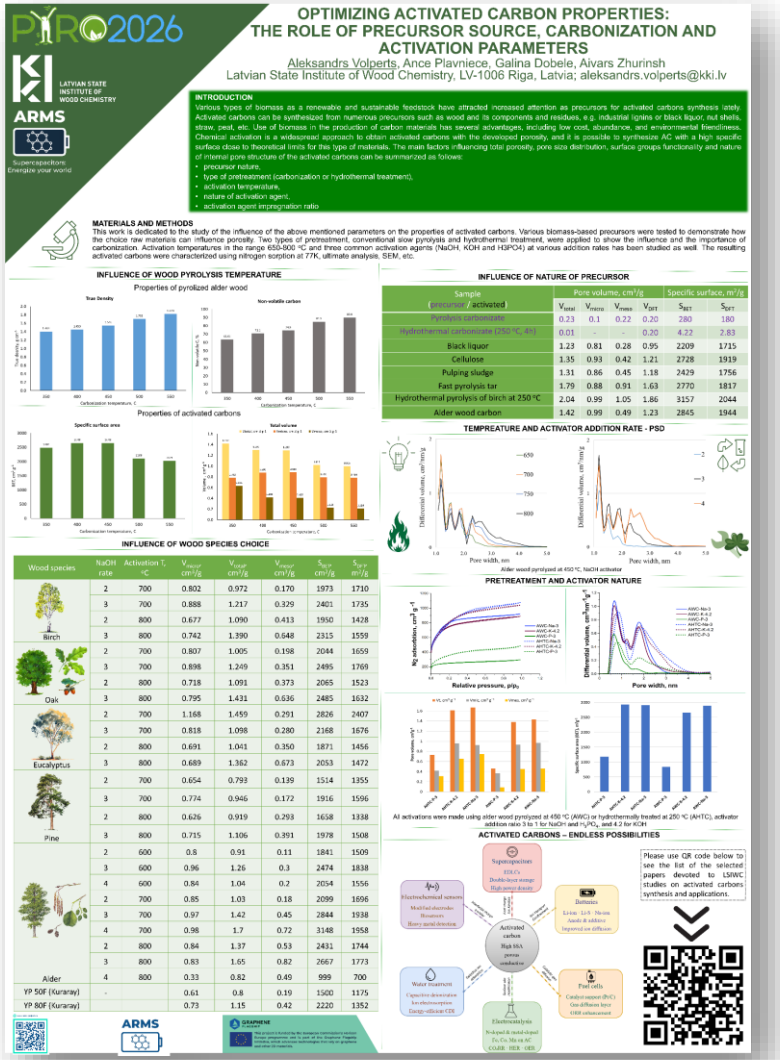
Forest area: 3.41 million ha (54%)
Forestry sector: 5.1% of GDP, 21% of export

Introduction

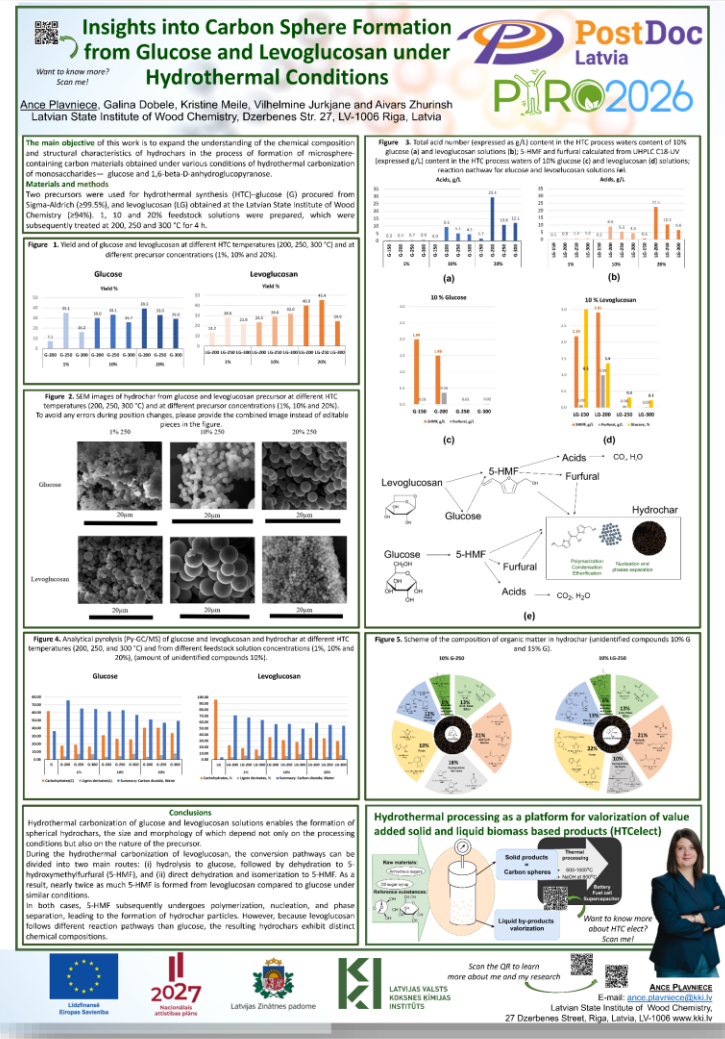
Poster Session 1, Monday
Floor 0 (P-S1F0-06)

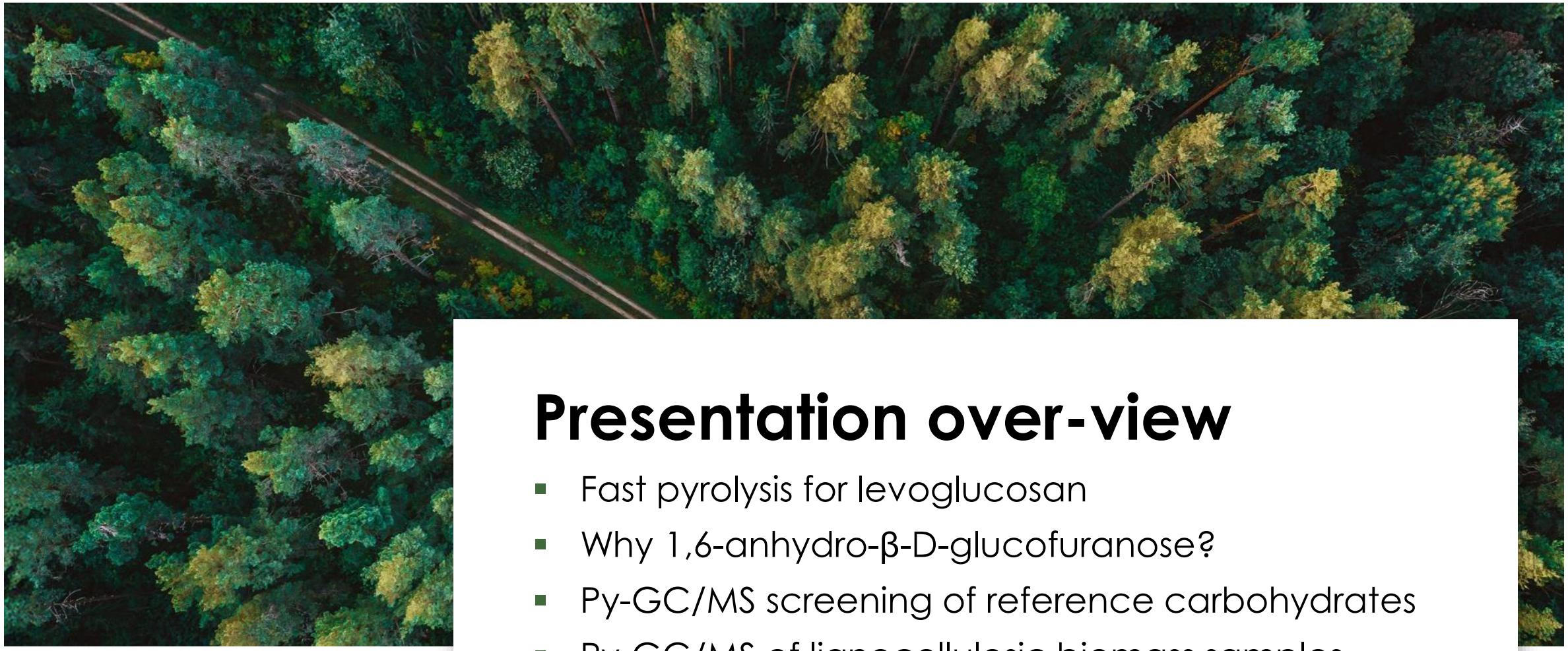


Poster Session 2, Tuesday
Floor 1 (P-S2F1-01)



Poster Session 3, Wednesday
Floor 1 (P-S3F1-19)





Presentation over-view

- Fast pyrolysis for levoglucosan
- Why 1,6-anhydro-β-D-glucofuranose?
- Py-GC/MS screening of reference carbohydrates
- Py-GC/MS of lignocellulosic biomass samples
- Future perspective

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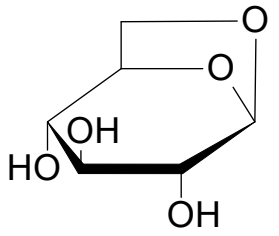
Fast pyrolysis for levoglucosan



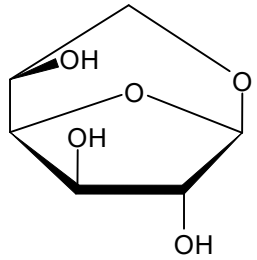


36 mg/mL non-volatiles
18 mg/mL LG
0.5 mg/mL AGF
2 mg/mL acids
<0.4mg/mL each furan
<0.2 mg/mL each phenol

700 g LC → 7.1L condensate



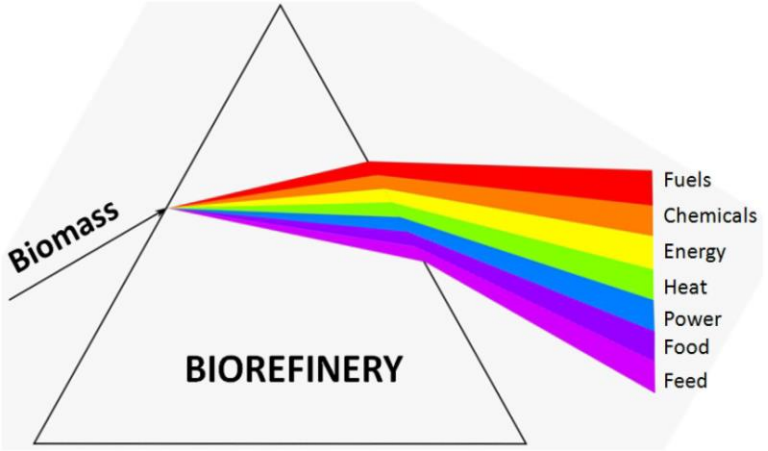
1,6-anhydro-β-D-glucopyranose
Levoglucosan
LG



1,6-anhydro-β-D-glucofuranose
AGF

Why 1,6-anhydro-β-D-glucofuranose?

	Levoglucosan	1,6-anhydro-β-D-glucofuranose
Biomass (cellulose) origin	Yes	
Established technology to obtain a reasonably high yield	Yes	
Appealing chemical structure (chirality)	Yes	
Many different chemical and biochemical conversion pathways	Yes	
When all else fails - source of glucose	Yes	

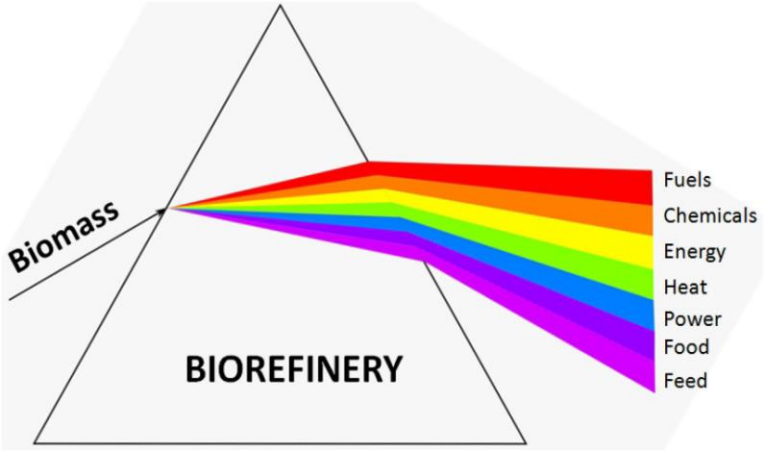


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Why 1,6-anhydro-β-D-glucofuranose?

	Levoglucosan	1,6-anhydro-β-D-glucofuranose
Biomass (cellulose) origin	Yes	Yes
Established technology to obtain a reasonably high yield	Yes	Nooo…
Appealing chemical structure (chirality)	Yes	Yes
Many different chemical and biochemical conversion pathways	Yes	Maybe
When all else fails - source of glucose	Yes	Probably



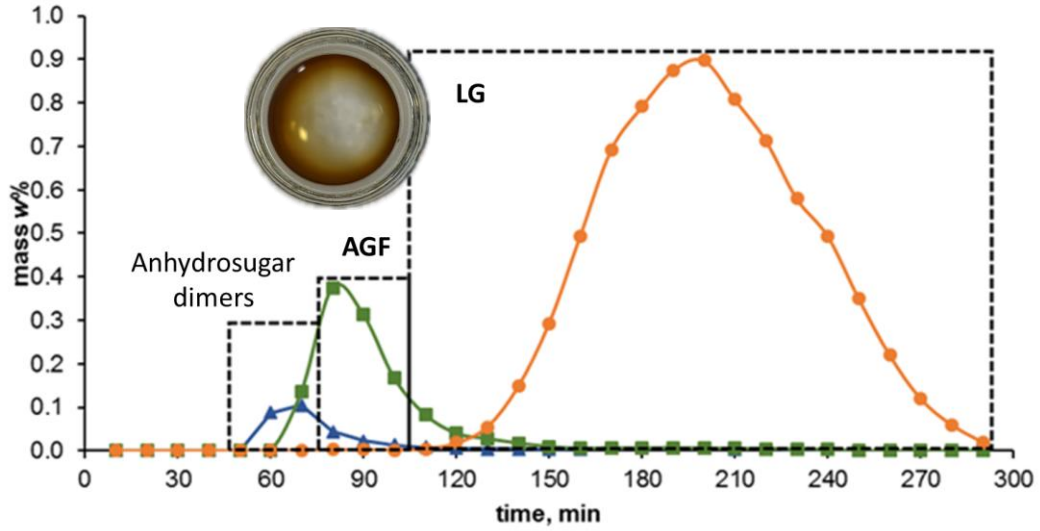
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Why 1,6-anhydro-β-D-glucofuranose?

- Sasaki, M. et al. Thermochemical transformation of glucose to 1,6-anhydroglucose in high-temperature steam, *Carb. Res.*, **2008**, 343(5), 848-854
  - ➢ **glucose 40% LG yield, and 19% AGF yield**

- Meile, K. et al. Discrimination of levoglucosan and its structural isomer in biomass pyrolysis products by iodometry, liquid chromatography, mass spectrometry, *J. Anal. Appl. Pyrolysis*, **2022**, 166, 105602
  - ➢ **9% AGF content in bio-oil and 55% AGF content in a preparative fraction of the bio-oil**

Prep LC
Strongly acidic cation exchange resin in Ca^{2+} form, eluent H_2O



No.	Sample description	AGF, wt%	LG, wt%	AGF/LG ratio
1	Paste A	9.02 ± 0.01	28.3 ± 0.6	1:3.1
2	Paste B	7.2 ± 0.2	48.6 ± 0.1	1:6.8
3	Mother liqour A-1	9.0 ± 0.1	25.2 ± 0.7	1:2.8
4	Mother liqour A-2	10.75 ± 0.03	26.1 ± 0.1	1:2.4
5	Mother liqour B	15.1 ± 0.2	63.8 ± 0.9	1:4.2
6	SPE fraction	11.2 ± 0.1	62.8 ± 0.9	1:5.6
7	prepLC fraction	55.4 ± 0.5	<LOQ	–

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Py-GC/MS screening of reference carbohydrates

LG – levoglucosan

AGF – 1,6-anhydro-β-D-glucofuranose

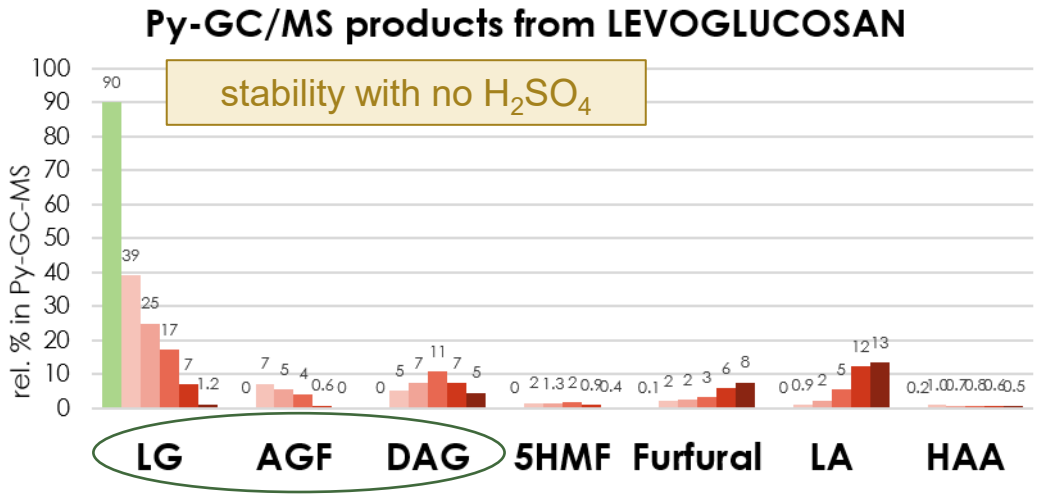
DAG - 1,4;3,6-dianhydro-a-D-glucopyranose

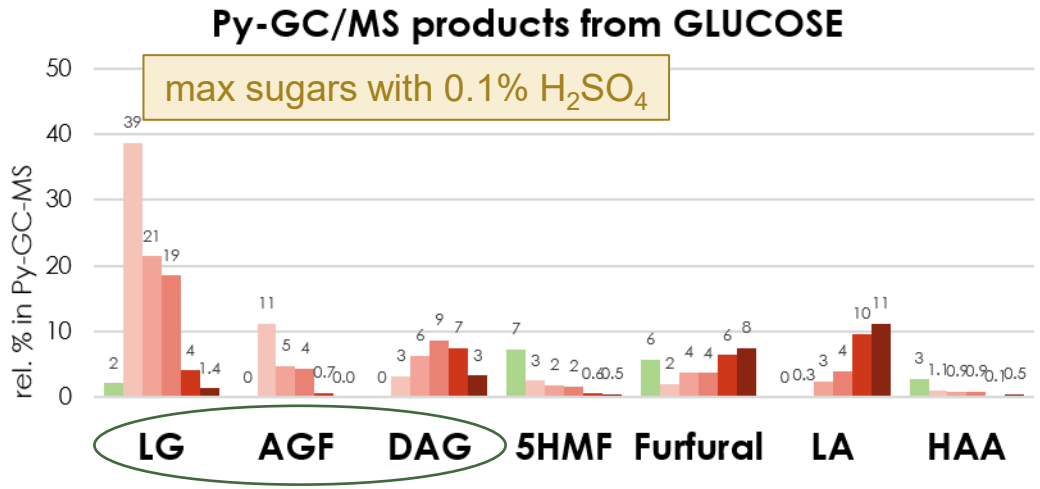
5HMF – 5-hydroxymethyl furfural

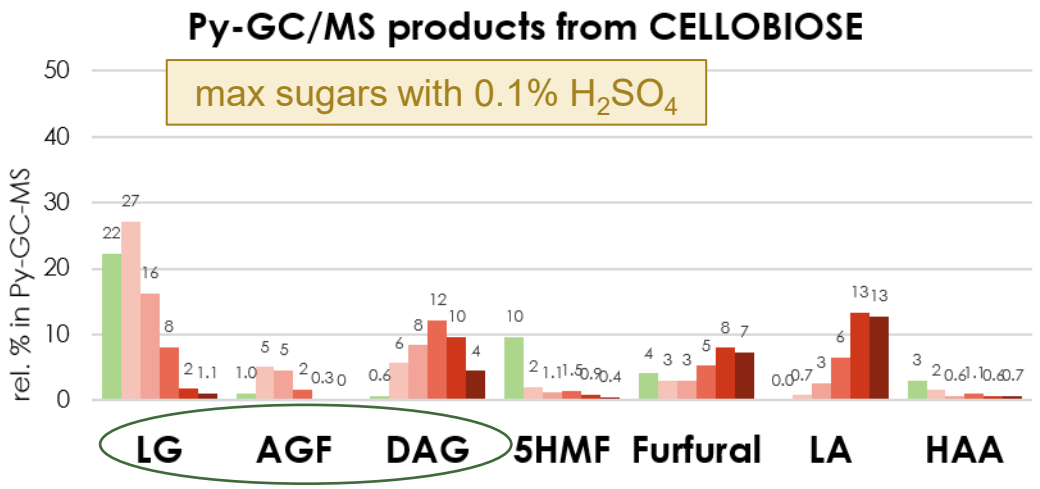
Furfural

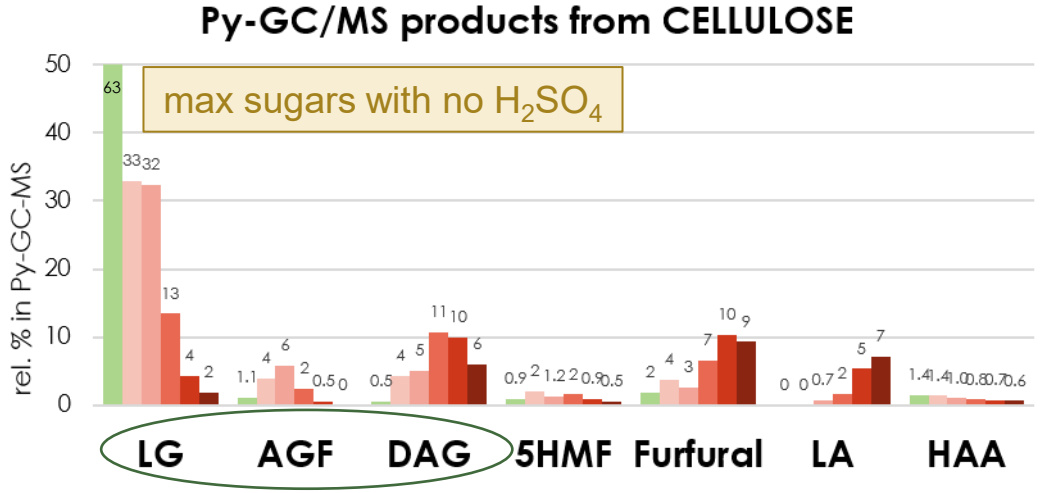
LA – levulinic acid

HAA - hydroxyacetaldehyde









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No H_2SO_4 | 0.1% H_2SO_4 | 0.2% H_2SO_4 | 0.5% H_2SO_4 | 2% H_2SO_4 | 4% H_2SO_4

Py-GC/MS of cellulose

LG – levoglucosan

AGF – 1,6-anhydro-β-D-glucofuranose

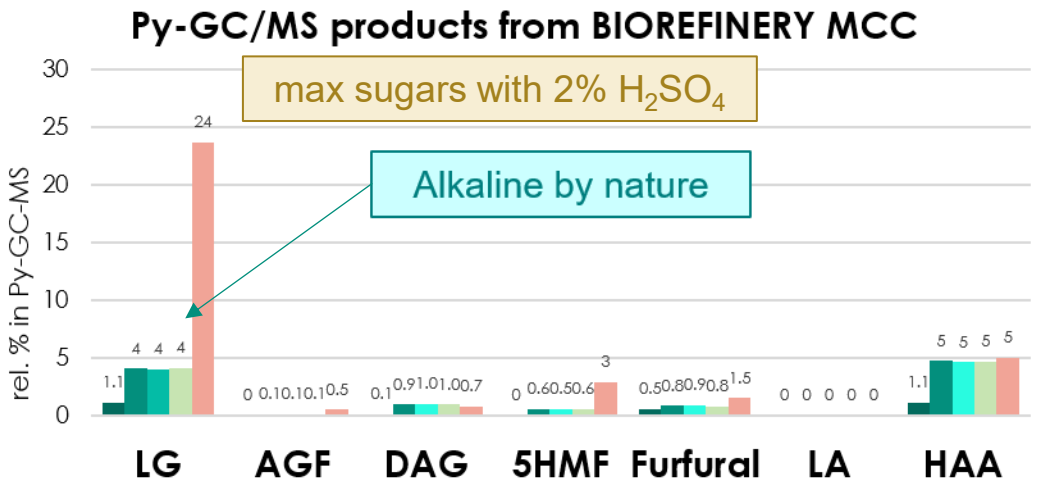
DAG - 1,4;3,6-dianhydro-a-D-glucopyranose

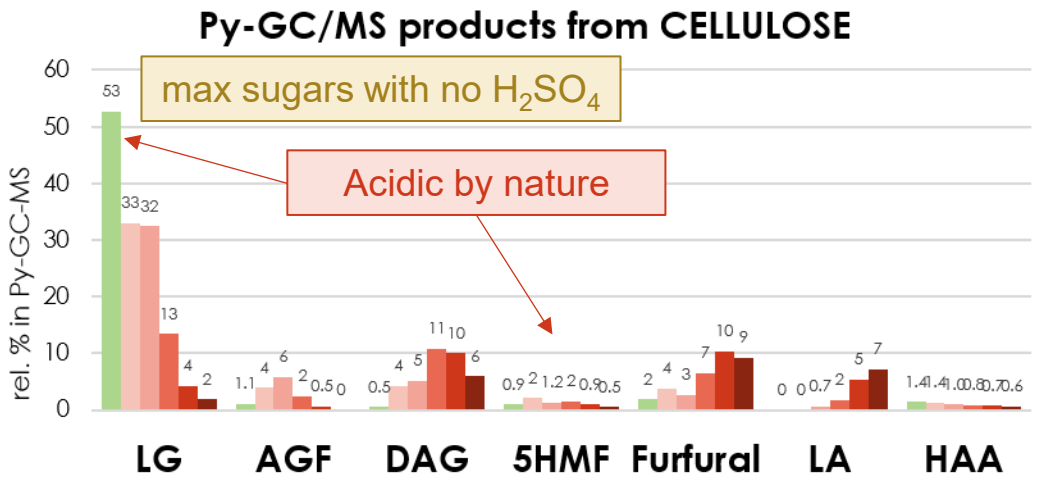
5HMF – 5-hydroxymethyl furfural

Furfural

LA – levulinic acid

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No H_2SO_4 | 0.1% H_2SO_4 | 0.2% H_2SO_4 | 0.5% H_2SO_4 | 2% H_2SO_4 | 4% H_2SO_4

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Py-GC/MS Py-GC/MS of biomass samples

LG – levoglucosan

AGF – 1,6-anhydro-β-D-glucofuranose

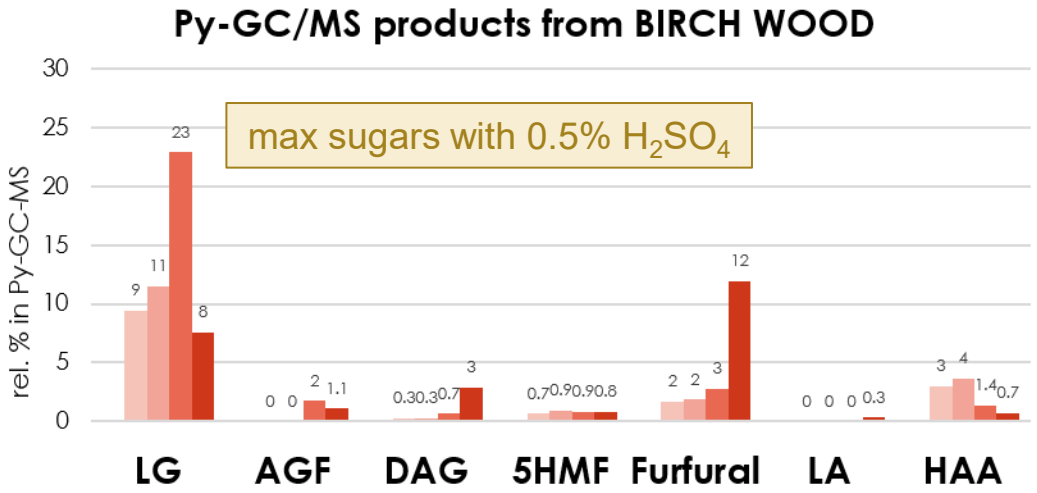
DAG - 1,4;3,6-dianhydro-a-D-glucopyranose

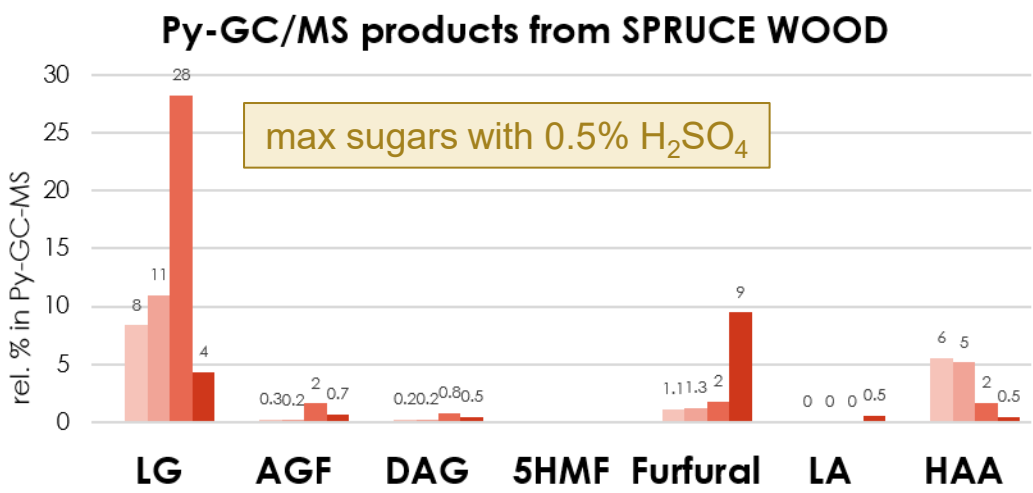
5HMF – 5-hydroxymethyl furfural

Furfural

LA – levulinic acid

HAA - hydroxyacetaldehyde



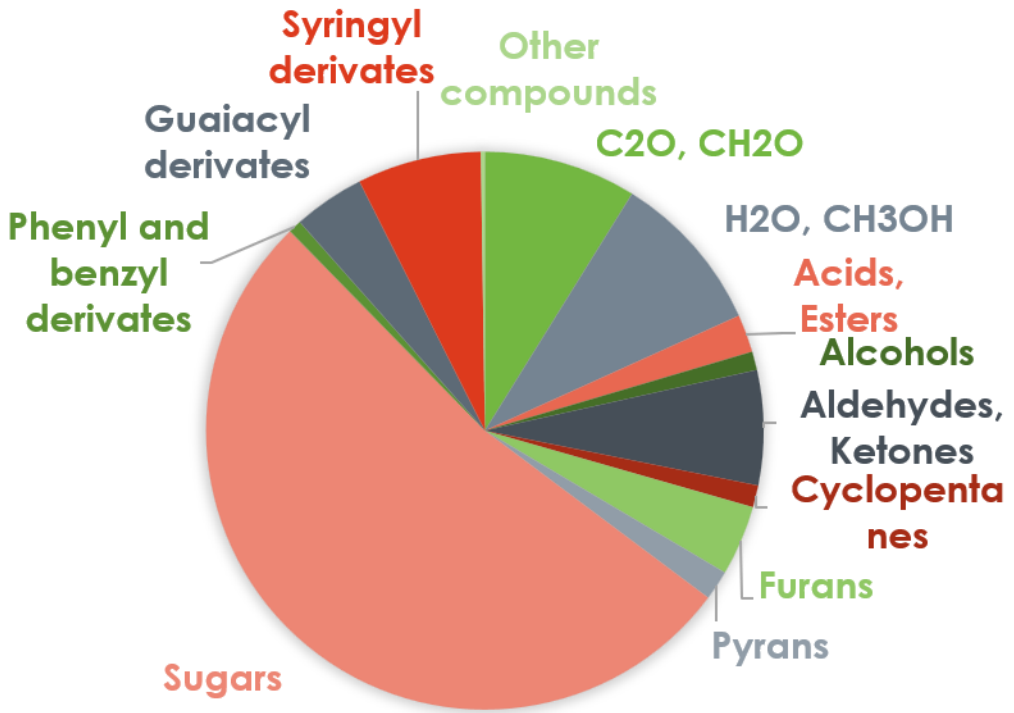


No H_2SO_4 | 0.1% H_2SO_4 | 0.2% H_2SO_4 | 0.5% H_2SO_4 | 2% H_2SO_4 | 4% H_2SO_4

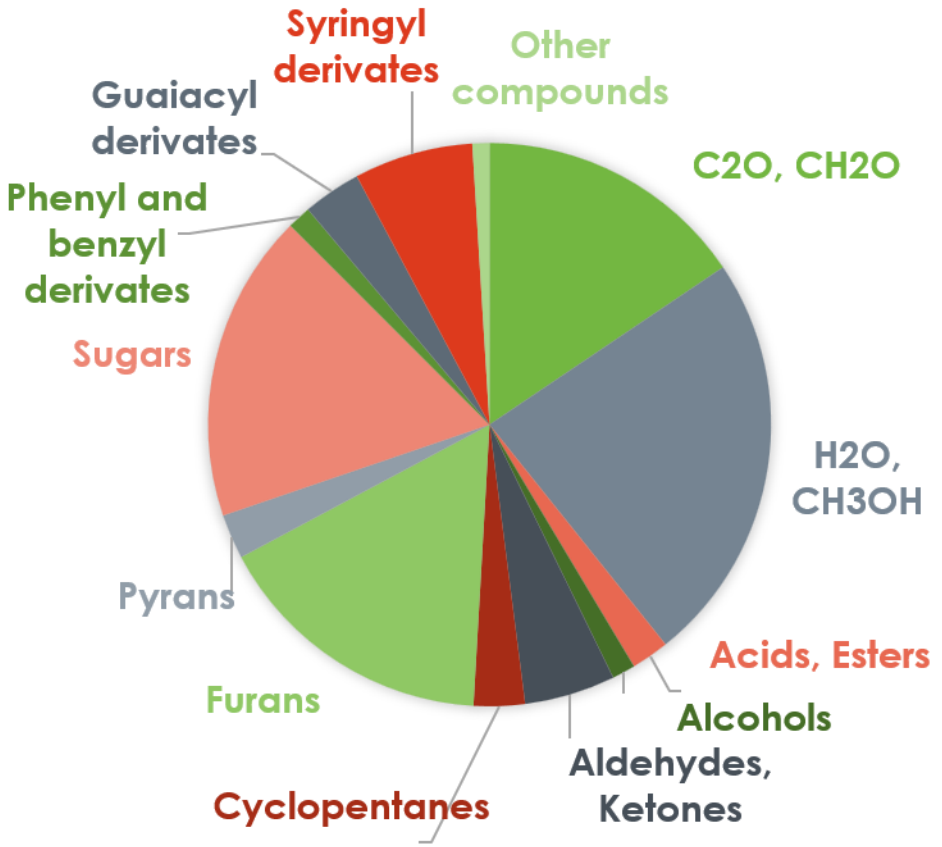
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Py-GC/MS of biomass samples

Birch lignocellulose after H_2SO_4 pre-treatment



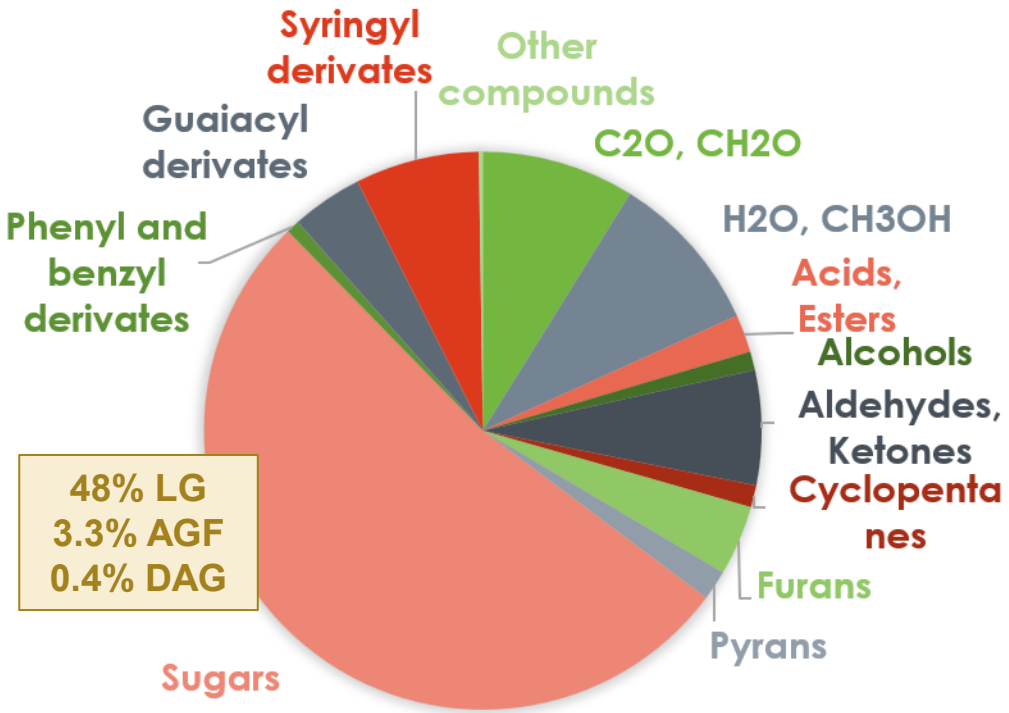
Birch lignocellulose after H_3PO_4 pre-treatment



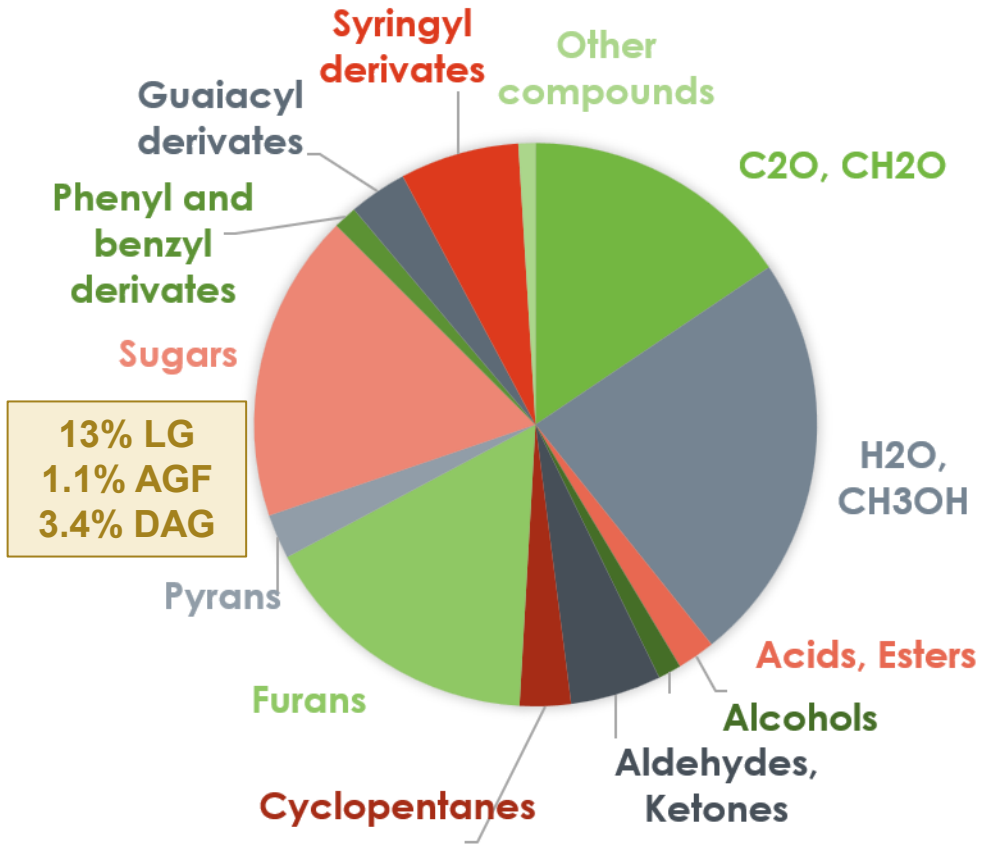
Product rel. % in Py-GC/MS

Py-GC/MS of biomass samples

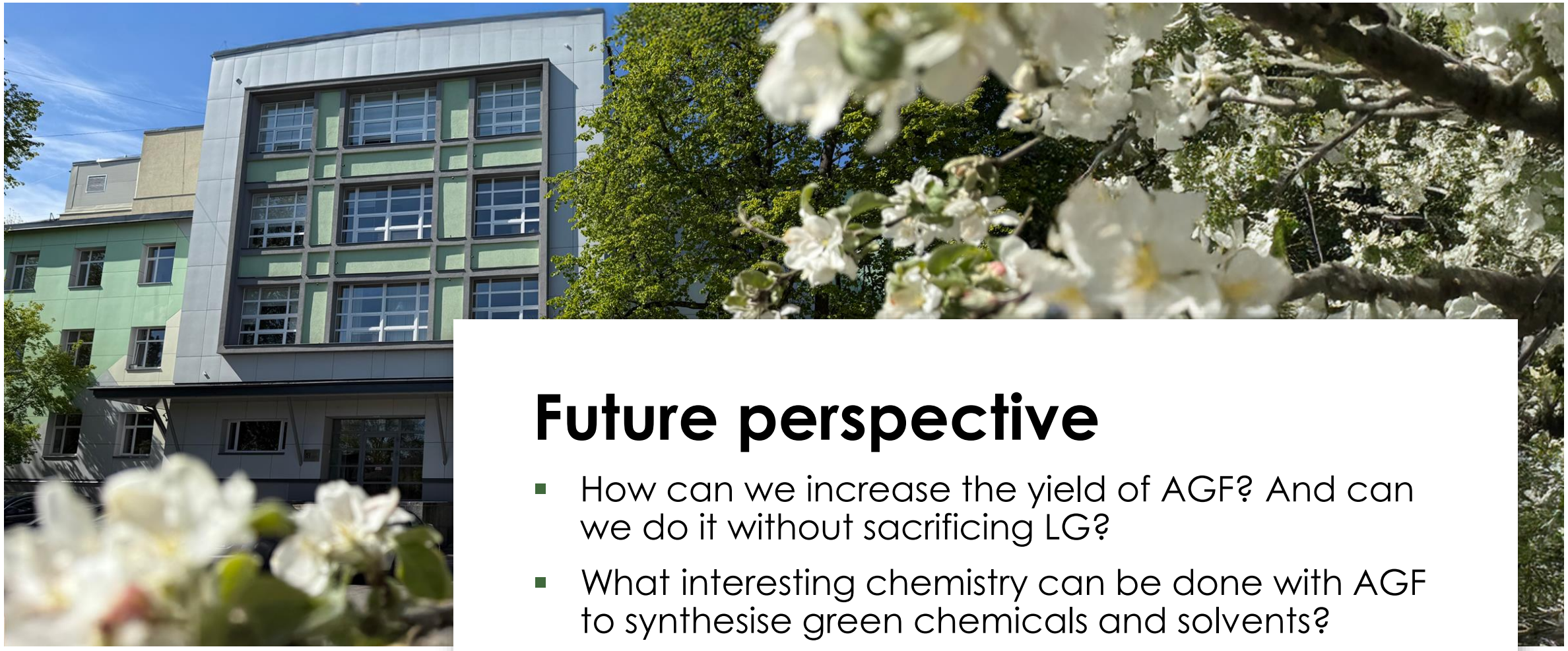
Birch lignocellulose after H_2SO_4 pre-treatment



Birch lignocellulose after H_3PO_4 pre-treatment



Product rel. % in Py-GC/MS



Future perspective

- How can we increase the yield of AGF? And can we do it without sacrificing LG?
- What interesting chemistry can be done with AGF to synthesise green chemicals and solvents?

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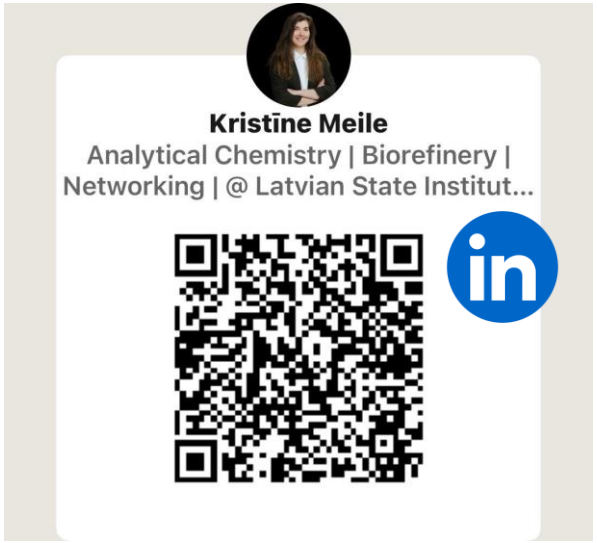
THANK YOU!

Unlocking the potential of wood pyrolysis anhydrosugars: new knowledge and value-added products (SugarPot), project No. 1.1.1.9/LZP/1/24/005

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