# Preliminary investigation of the production of 1,6-anhydro-β-d-glucofuranose by wood pyrolysis

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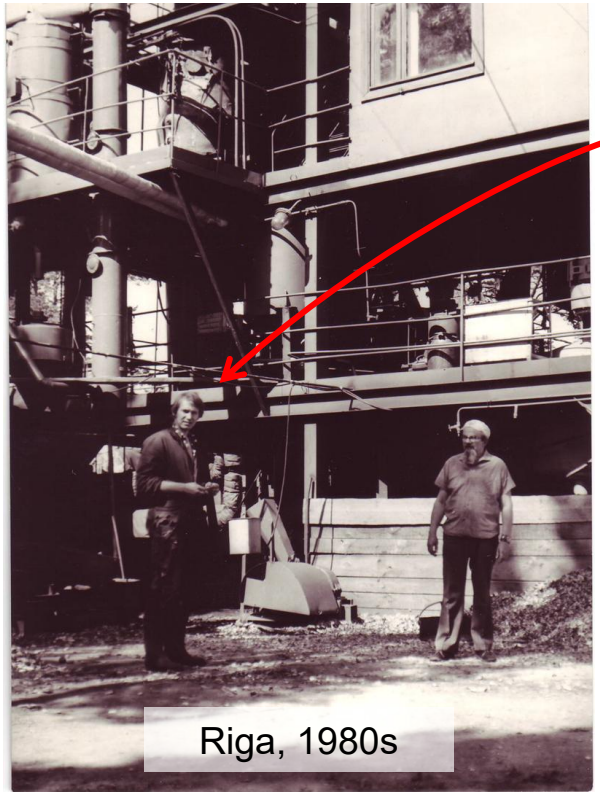
NACIONĀLAIS ATTĪSTĪBAS PLĀNS 2020

EIROPAS SAVIENĪBA
Eiropas Reģionālās attīstības fonds

IEGULDĪJUMS TAVĀ NĀKOTNĒ

# Introduction, literally

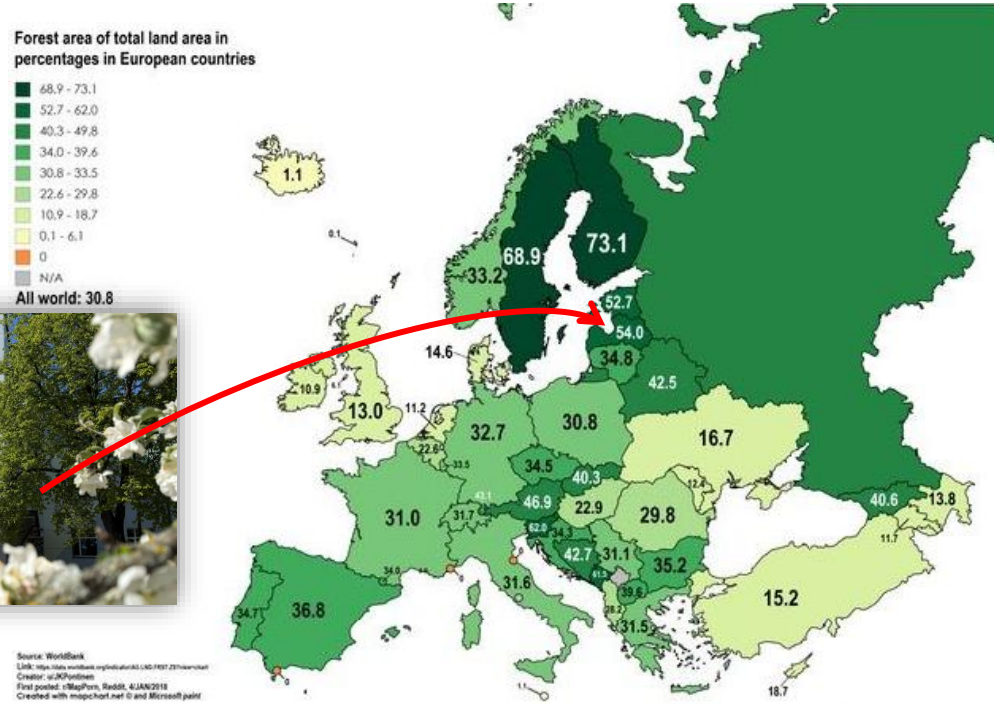
- Latvian State Institute of Wood Chemistry
  - Wood materials
  - Green chemistry
  - Biorefinery
- Thermochemical process group



Riga, 1980s

*Dr.sc.ing.*
Aivars Zhurinsh

Nova Pangaea Technologies, UK, 2022




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

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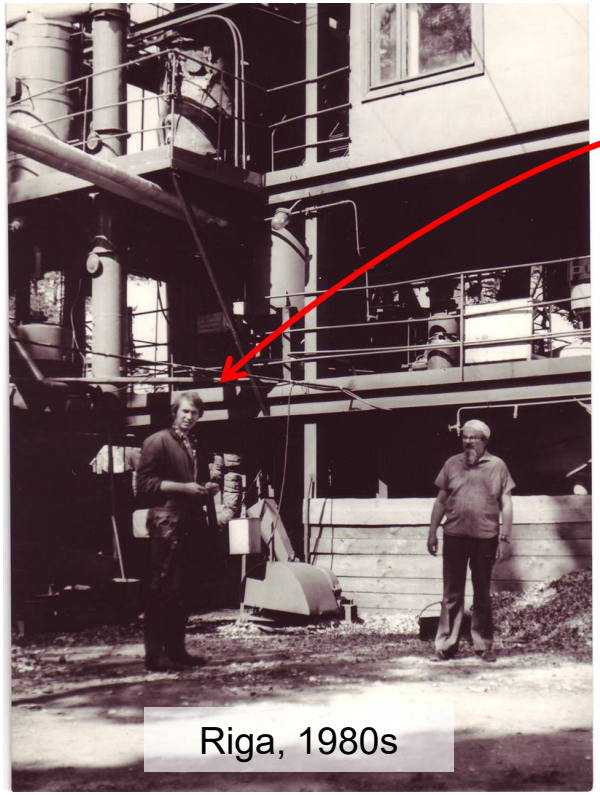

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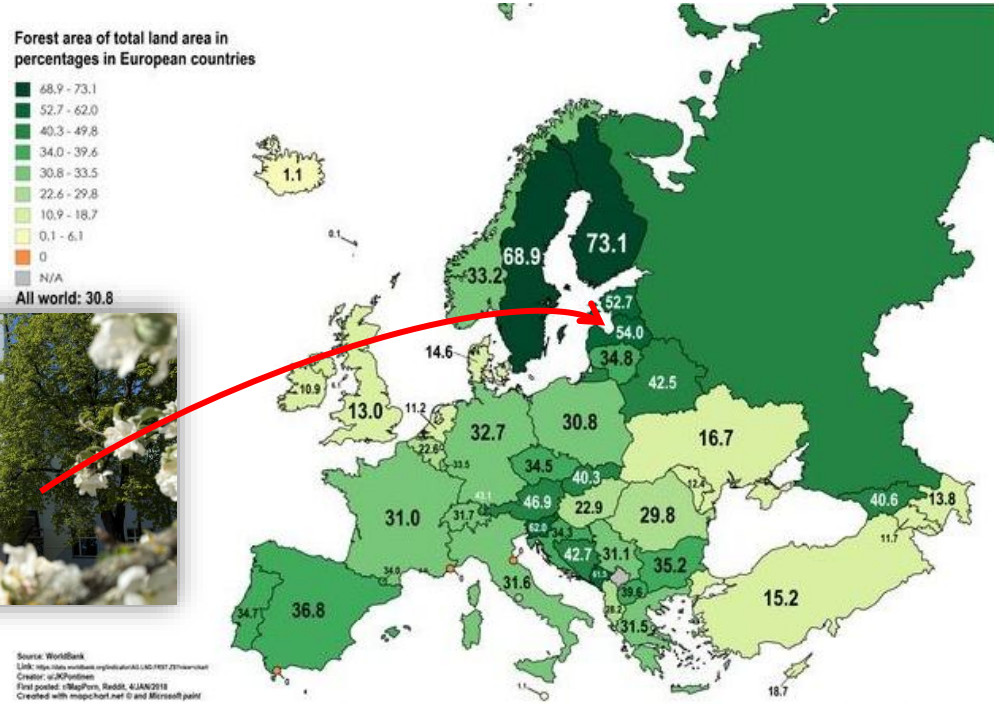


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Analytical chemist on an industrial site...

# Presentation over-view

- «Levoglucosan: a promising platform molecule?»
- Meet the gang: anhydrosugars in pyrolysis products
- 1,6-anhydro-β-D-glucofuranose sightings
- Py-GC/MS screening and a case of up-scaling

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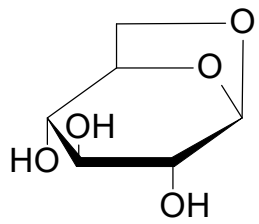
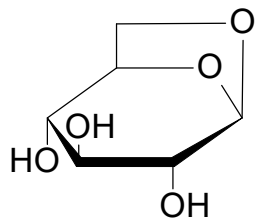
# «Levoglucosan: a promising platform molecule?»

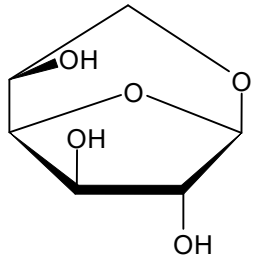

**1,6-anhydro-β-D-glucopyranose**
**Levoglucosan**
**LG**

- ✓ Biomass (cellulose) origin
- ✓ Established technology to obtain a reasonably high yield
- ✓ Appealing chemical structure (chirality)
- ✓ Many different chemical and biochemical conversion pathways
- ✓ When all else fails - source of glucose

# «Levoglucosan: a promising platform molecule?»


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




**1,6-anhydro-β-D-glucofuranose AGF**

- ✓ Biomass (cellulose) origi
- ✓ Established techn
- ✓ Appealing chemica
- ✓ Many different chemical and biochemical conversion pathways
- ✓ When all else fails - source of glucose

**Could AGF be a promising platform molecule?**

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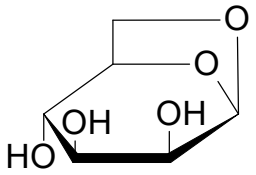
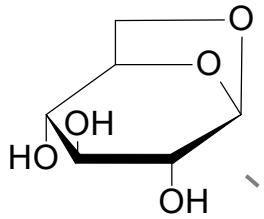
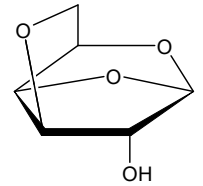
# Meet the gang: anhydrosugars in pyrolysis products



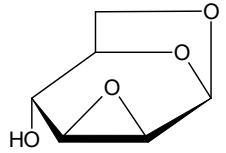
1,6-Anhydro-d-mannopyranose
Mannosan



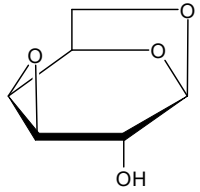
1,6-Anhydro-d-glucopyranose
Levoglucosan, LG



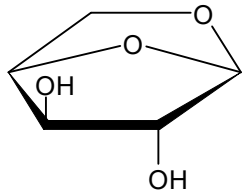
1,4;3,6-Dianhydro-.alpha.-d-glucopyranose



2,3-Anhydro-d-mannosan

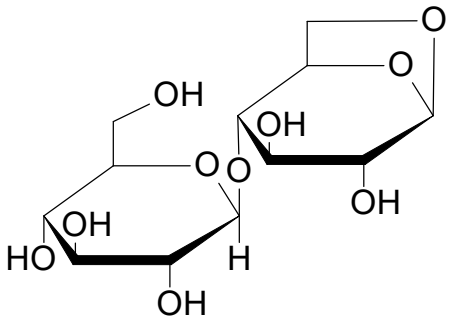


3,4-Anhydro-d-galactosan



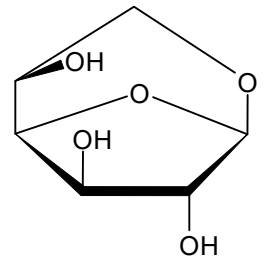
1,4-Anhydro-d-xylopyranose
Xylosan

*From hemicelluloses*

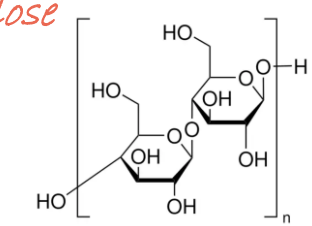


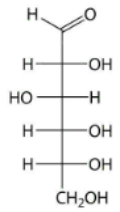
1,6-Anhydro-d-cellobiose
Cellobiosan...

*From cellulose*



1,6-Anhydro-d-glucofuranose
Levoglucosan, LG





*From acyclic d-glucose?*

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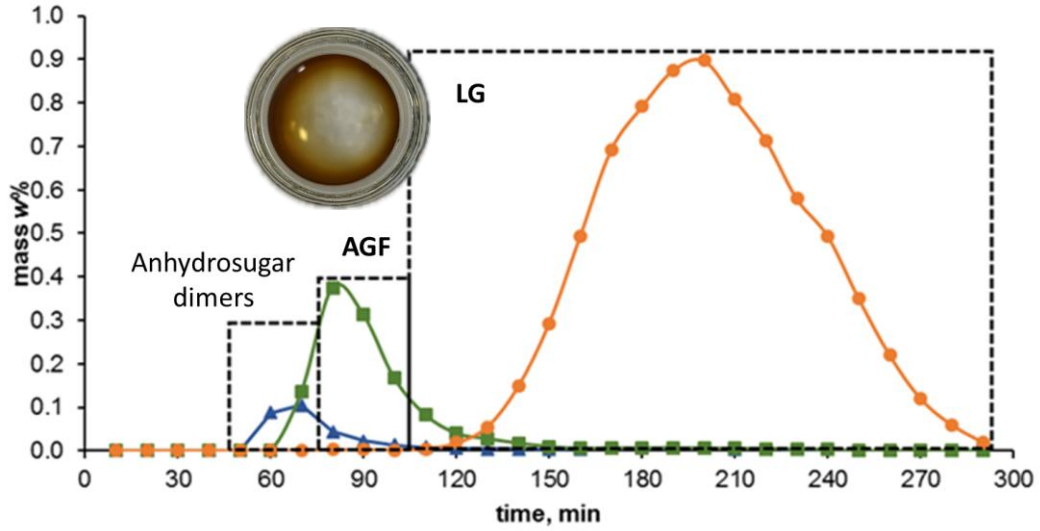
# 1,6-anhydro-β-D-glucofuranose sightings

- 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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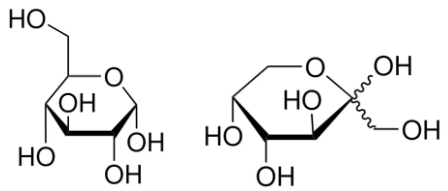
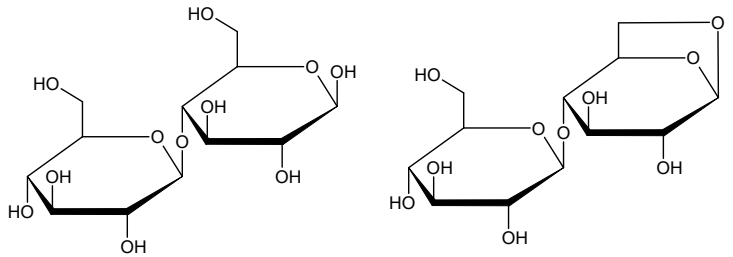
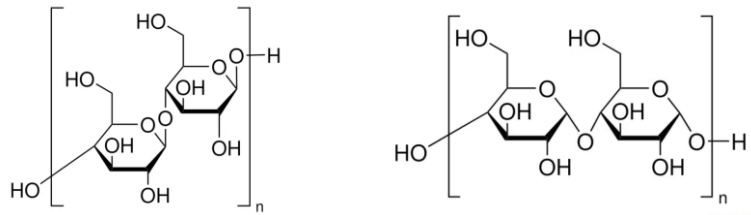
# Py-GC/MS screening and a case of up-scaling




Monosaccharides

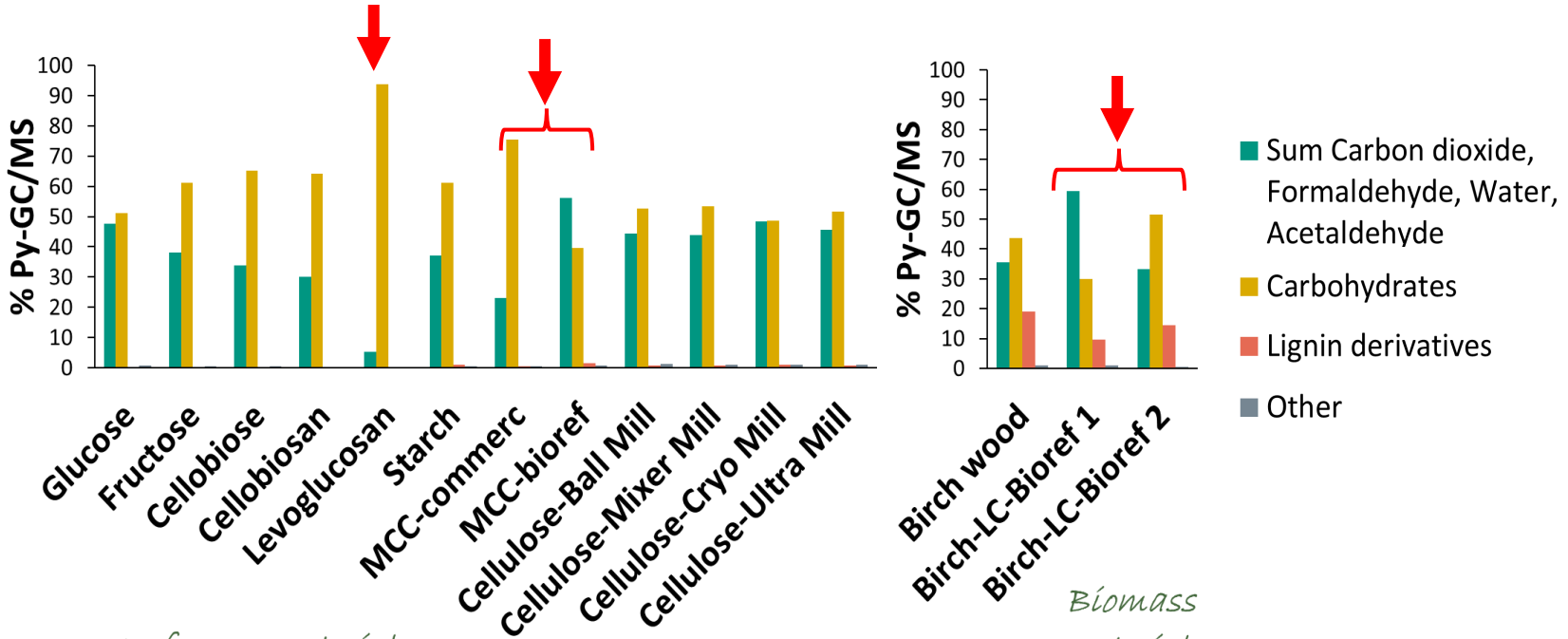



Disaccharides




Polysaccharides


Biomass




Reference materials

Biomass materials

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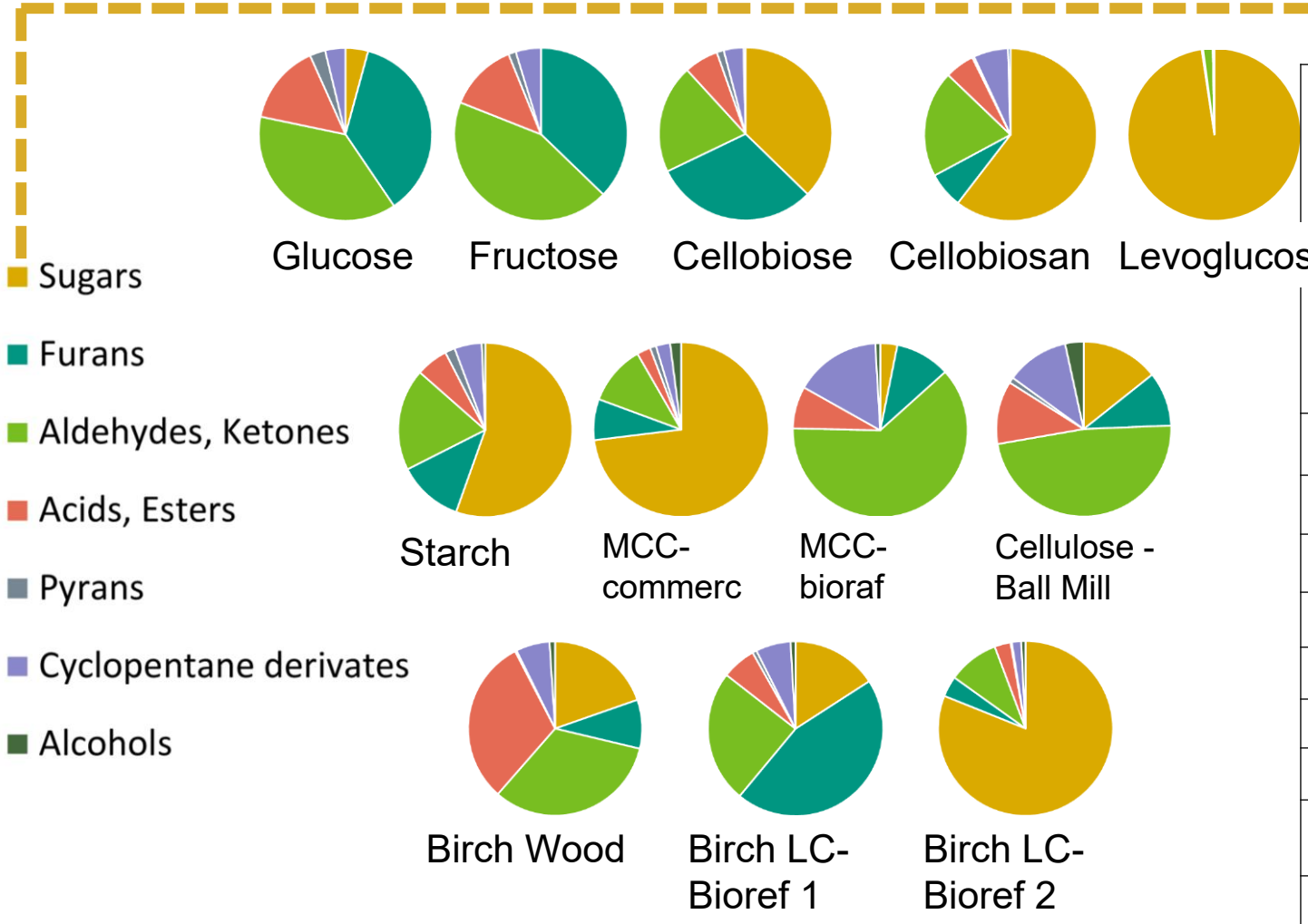


| Feed-stock → / Products ↓ | Glucose | Fructose | Cellobiose | Cellobiosan | Levoglucosan | Starch | MCC-commerc | MCC-bioref | Cellulose-Ball Mill | Birch wood | Birch-LC-Bioref 1 | Birch-LC-Bioref 2 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2-Deoxy-D-galactose | | | | 1.2 | | | | | | | | |
| 2,3-Anhydro-d-mannosan | | | | 2.0 | 1.1 | 0.6 | 0.4 | | 0.3 | 0.2 | | 0.2 |
| 1,4;3,6-Dianhydro-.glucopyranose | | | 0.6 | 2.0 | | 0.7 | 0.5 | 0.1 | 0.4 | 0.3 | 2.4 | 0.4 |
| 2,3-Anhydro-d-mannosan | | | | 0.8 | 0.1 | 0.1 | 0.08 | | | | | |
| 3,4-Anhydro-d-galactosan | | | | 1.5 | 0.2 | | | | | | | |
| Ribopyranoside, methyl, 3-acetate | | | | | | | | | | 0.2 | | |
| 1,3-Di-O-acetyl-ribopyranose | | | 0.3 | 1.2 | 0.3 | 0.5 | 0.4 | | 0.2 | 0.5 | | |
| **LG** | **2** | **Trace** | **22** | **29** | **90** | **32** | **53** | **1** | **7** | **7** | **2** | **39** |
| 1,3-Di-O-acetyl-.ribopyranose | | | 0.2 | 0.3 | | 0.3 | | | 0.1 | 0.3 | | 0.1 |
| **AGF** | | | **1** | | | | **1** | | | | | **2** |

*no oligomers

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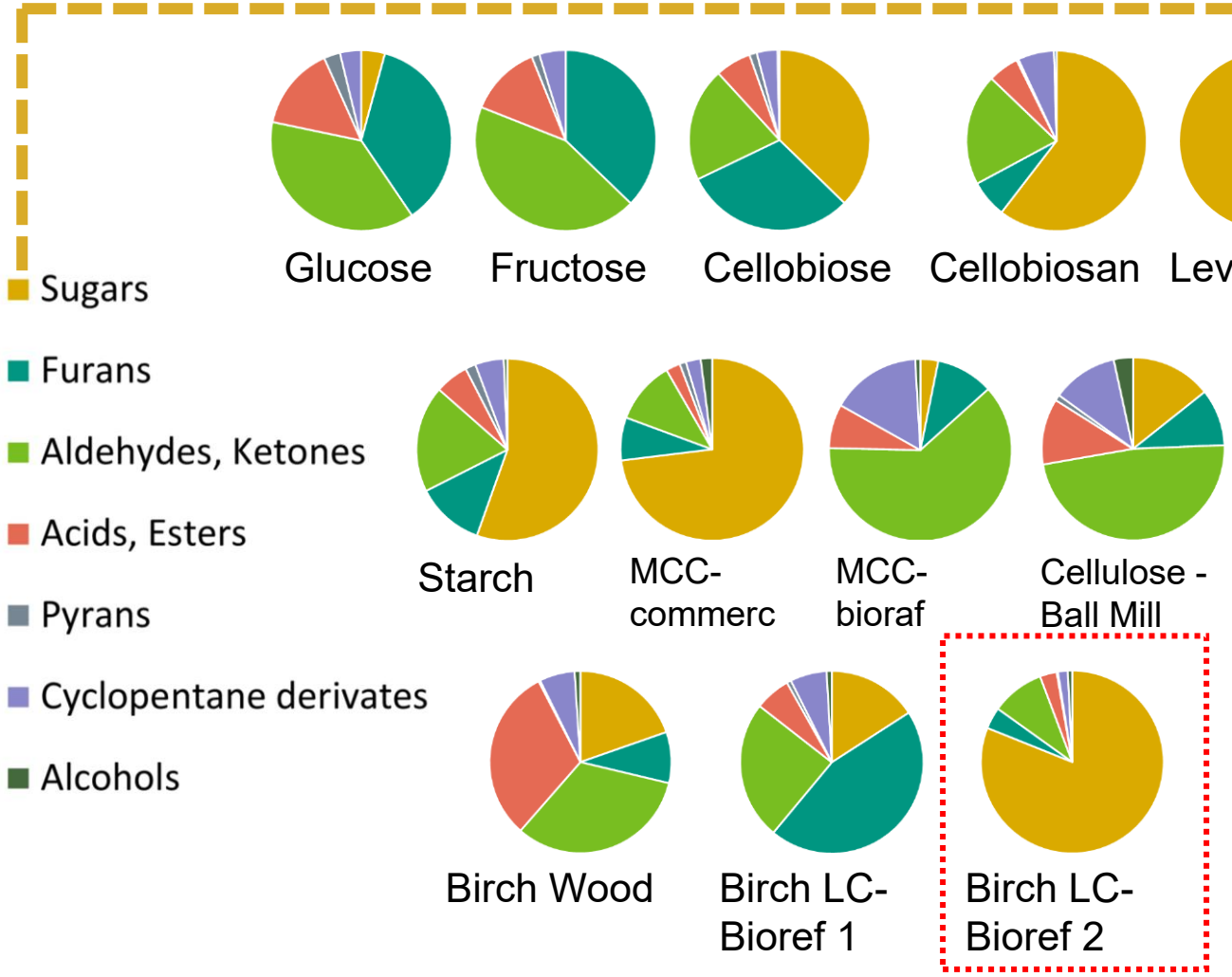
**Summary of carbohydrate derivatives in Py-GC/MS**

# Py-GC/MS screening and a case of up-scaling




| Feed-stock → / Products ↓ | Glucose | Fructose | Cellobiose | Cellobiosan | Levoglucosan | Starch | MCC-commerc | MCC-bioref | Cellulose-Ball Mill | Birch wood | Birch-LC-Bioref 1 | Birch-LC-Bioref 2 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2-Deoxy-D-galactose | | | | 1.2 | | | | | | | | |
| 2,3-Anhydro-d-mannosan | | | | 2.0 | 1.1 | 0.6 | 0.4 | | 0.3 | 0.2 | | 0.2 |
| 1,4;3,6-Dianhydro-.glucopyranose | | | 0.6 | 2.0 | | 0.7 | 0.5 | 0.1 | 0.4 | 0.3 | 2.4 | 0.4 |
| 2,3-Anhydro-d-mannosan | | | | 0.8 | 0.1 | 0.1 | 0.08 | | | | | |
| 3,4-Anhydro-d-galactosan | | | | 1.5 | 0.2 | | | | | | | |
| Ribopyranoside, methyl, 3-acetate | | | | | | | | | | 0.2 | | |
| 1,3-Di-O-acetyl-ribopyranose | | | 0.3 | 1.2 | 0.3 | 0.5 | 0.4 | | 0.2 | 0.5 | | |
| **LG** | **2** | **Trace** | **22** | **29** | **90** | **32** | **53** | **1** | **7** | **7** | **2** | **39** |
| 1,3-Di-O-acetyl-.ribopyranose | | | 0.2 | 0.3 | | 0.3 | | | 0.1 | 0.3 | | 0.1 |
| **AGF** | | | **1** | | | | **1** | | | | | **2** |

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**Summary of carbohydrate derivatives in Py-GC/MS**

# Py-GC/MS screening and a case of up-scaling

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

Solid phase extraction with a strongly basic anion exchange resin

75% of the condensate recovered in the anhydrosugar fraction, while the other 25% (phenols) adsorbed on the resin

Recrystallised LG with purity >95%

Mother liquor with a reduced LG ratio in the anhydrosugar mixture

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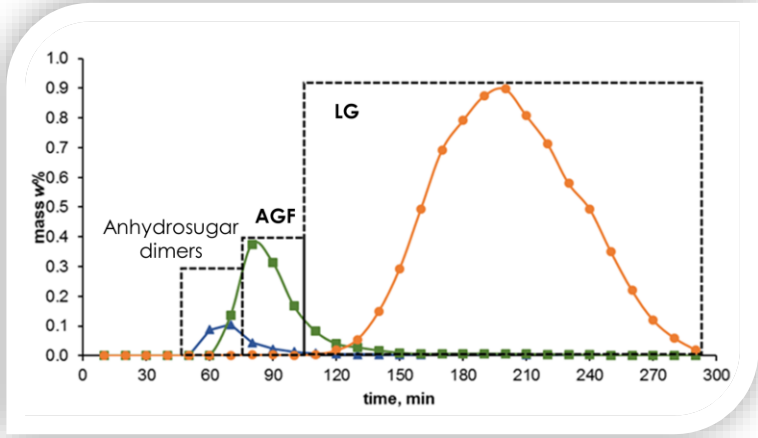


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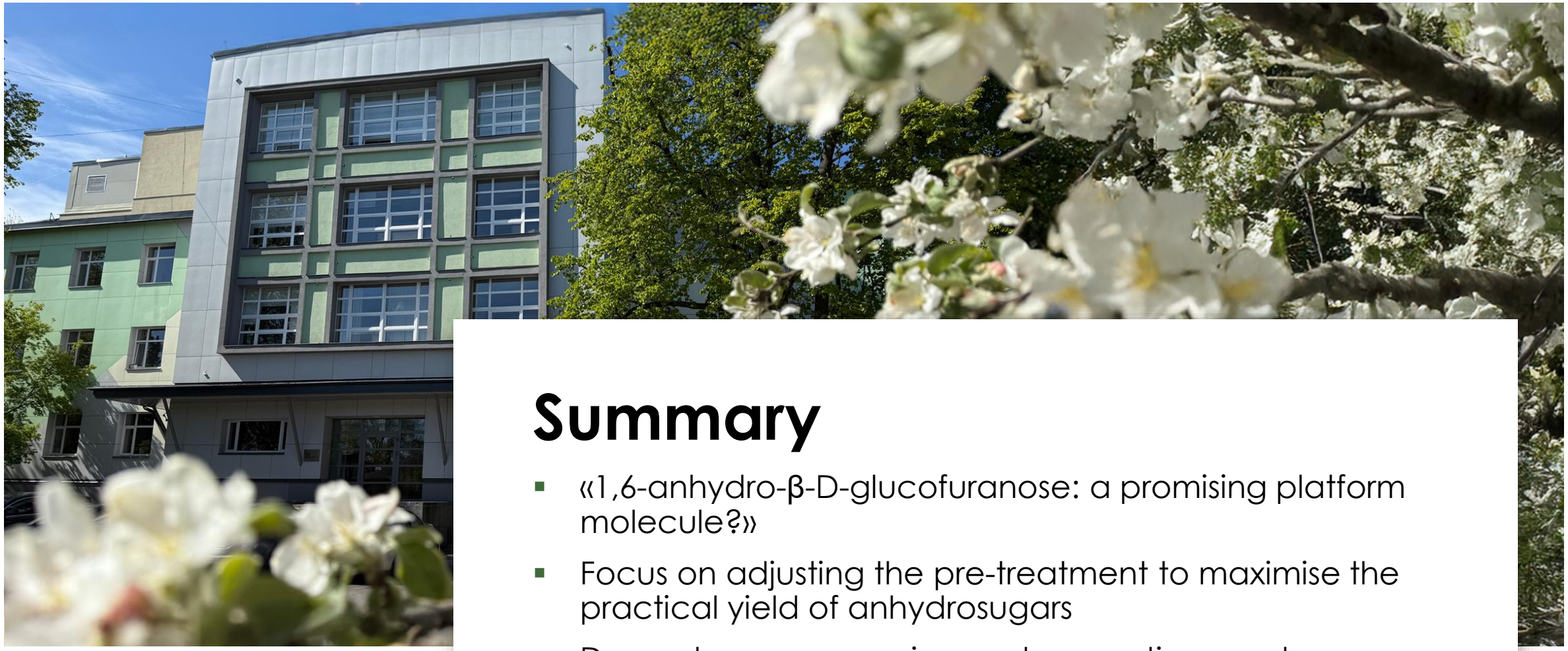

# Summary

- «1,6-anhydro-β-D-glucofuranose: a promising platform molecule?»
- Focus on adjusting the pre-treatment to maximise the practical yield of anhydrosugars
- Down-stream processing and separation can be a make-or-break moment

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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

***Dr. chem.* Kristīne Meile**
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Biorefinery laboratory

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