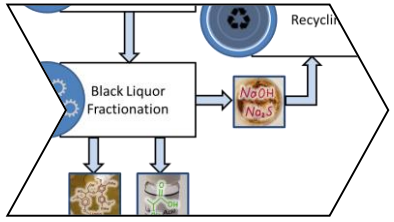
Kraft Black Liquor as Biorefinery Feedstock - The Role of Hemicellulose

Silvia Maitz
silvia.maitz@tugraz.at
Institute of Chemical Engineering and Environmental Technology (CEET)
Graz University of Technology

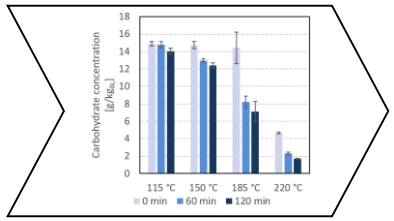
EPNOE Webinar, 02/02/2023

Agenda

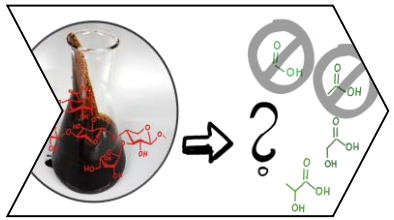
- Introduction



- Kraft Mill Biorefinery

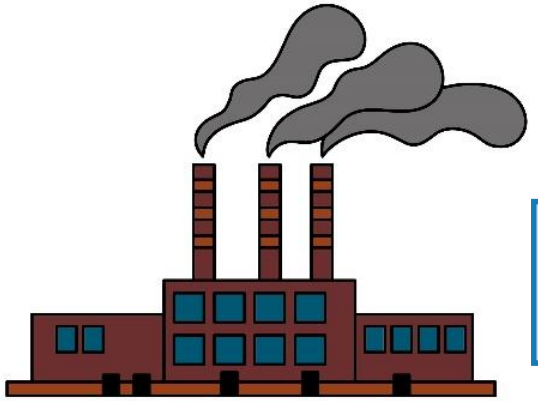


- Hemicellulose Quantification in Black Liquor



- Hemicellulose Conversion in Black Liquor

Kraft Mill Biorefinery



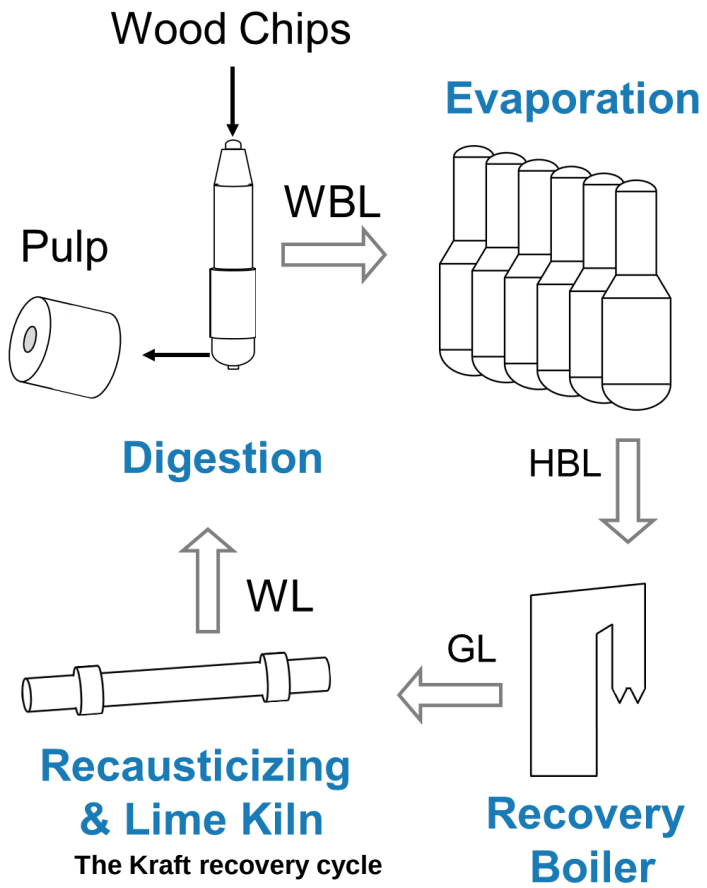
Conventional pulp mill

Biorefinery

- Materials
- Chemicals
- Energy

from **renewable resources**

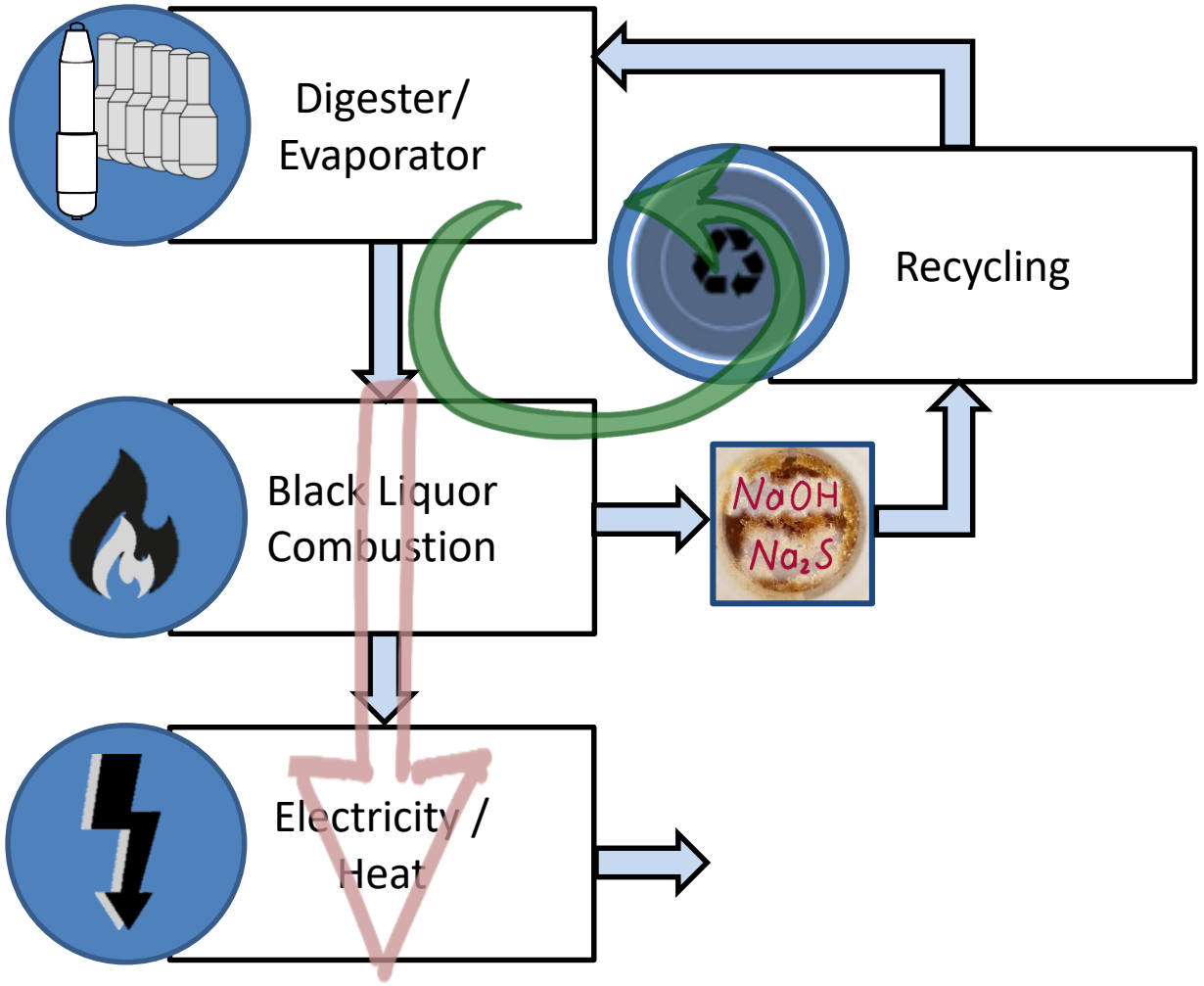
The Kraft Pulp Mill



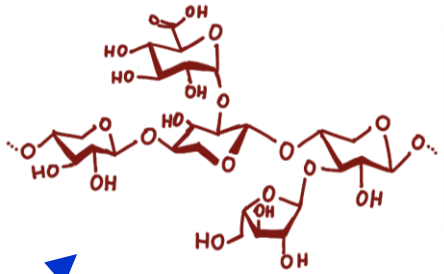
The Kraft recovery cycle

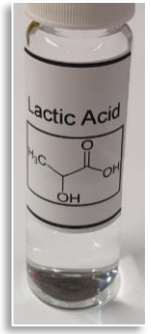
WBL - *Weak Black Liquor*
HBL - *Heavy Black Liquor*
GL - *Green Liquor*
WL - *White Liquor*

The Kraft Pulp Mill – Black Liquor Utilization

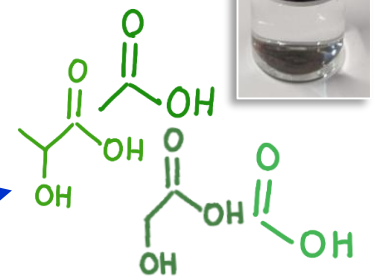


The Kraft Pulp Mill – Black Liquor

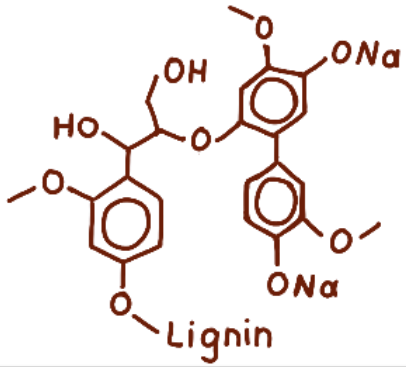




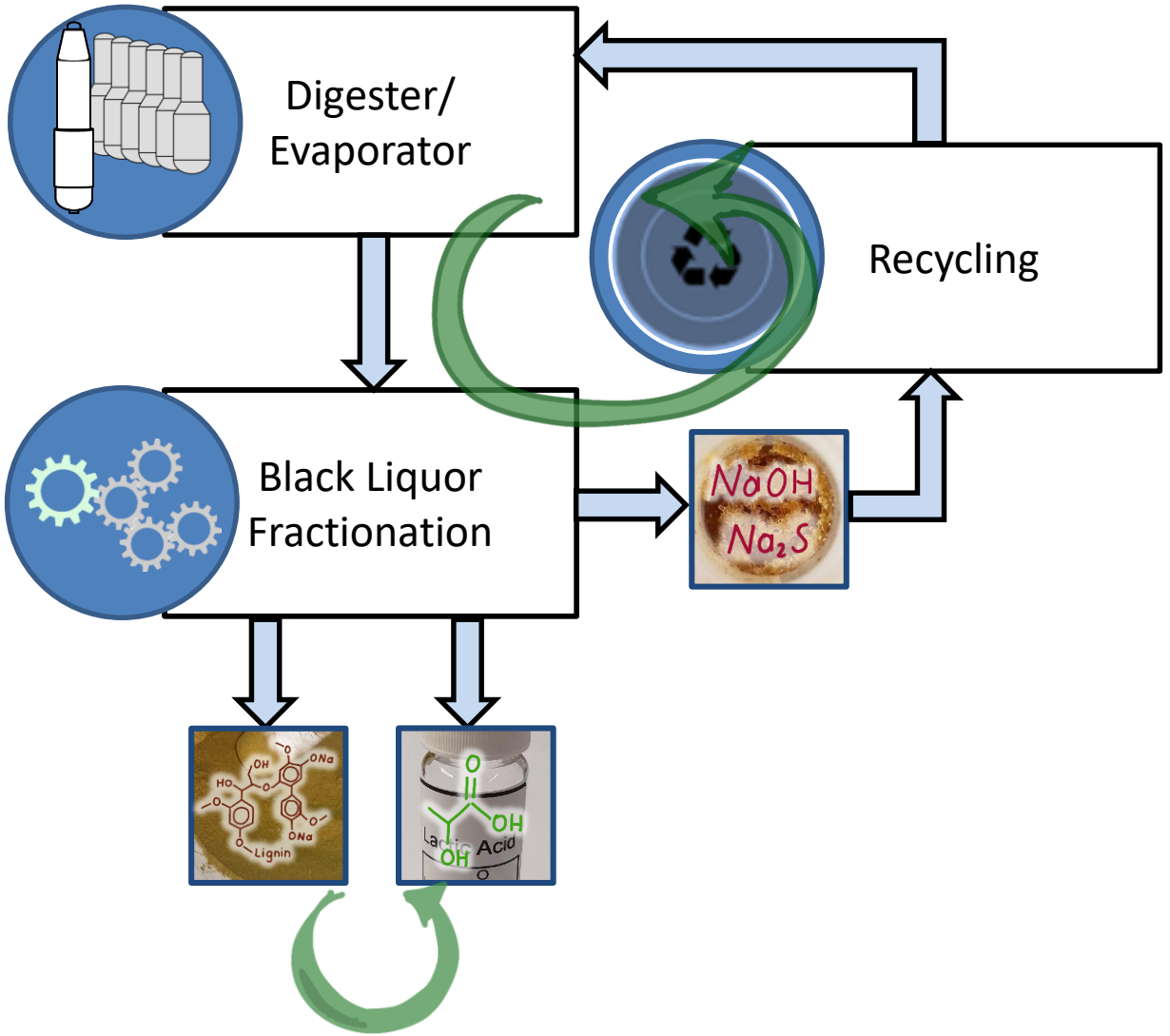
H_2O



$NaOH$
Na_2S



The Kraft Pulp Mill – Black Liquor Utilization



My research project

- Fractionate kraft black liquor (BL)
- Isolate carboxylic acids and lignin
- Recycle pulping chemicals
- Maintain mill operation

Hemicellulose Conversion in Black Liquor

Our hypothesis

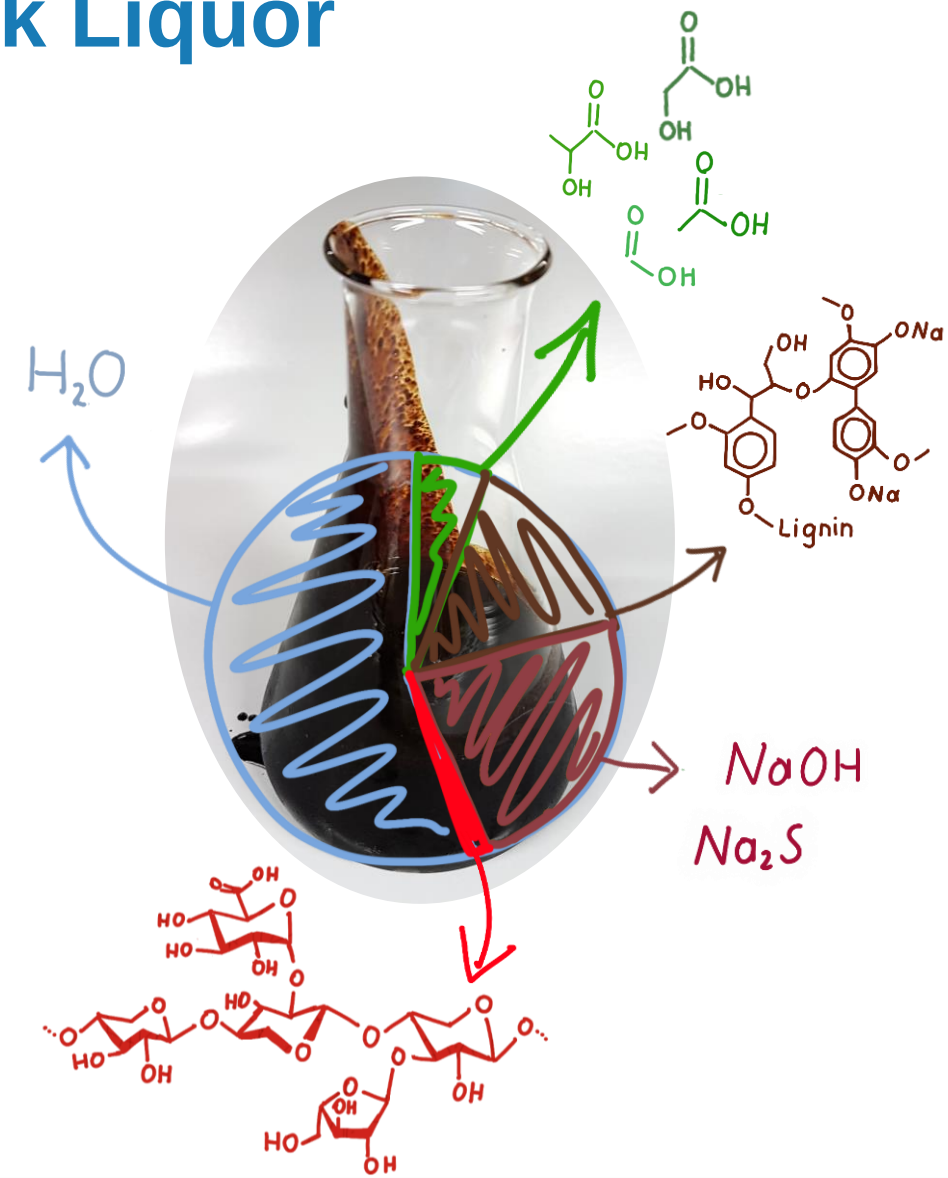
- Carbohydrates can be degraded to carboxylic acids by hydrothermal treatment / oxidation

  → Increases acid concentration
  → Reduces viscosity
  → Improves lignin properties

Our feedstock material

- Concentrated industrial hardwood BL

  - 57 % water
  - 6 % carboxylic acids (formic, acetic, glycolic, lactic)
  - 17 % lignin
  - 0.5-3 % carbohydrates



Hemicellulose Quantification

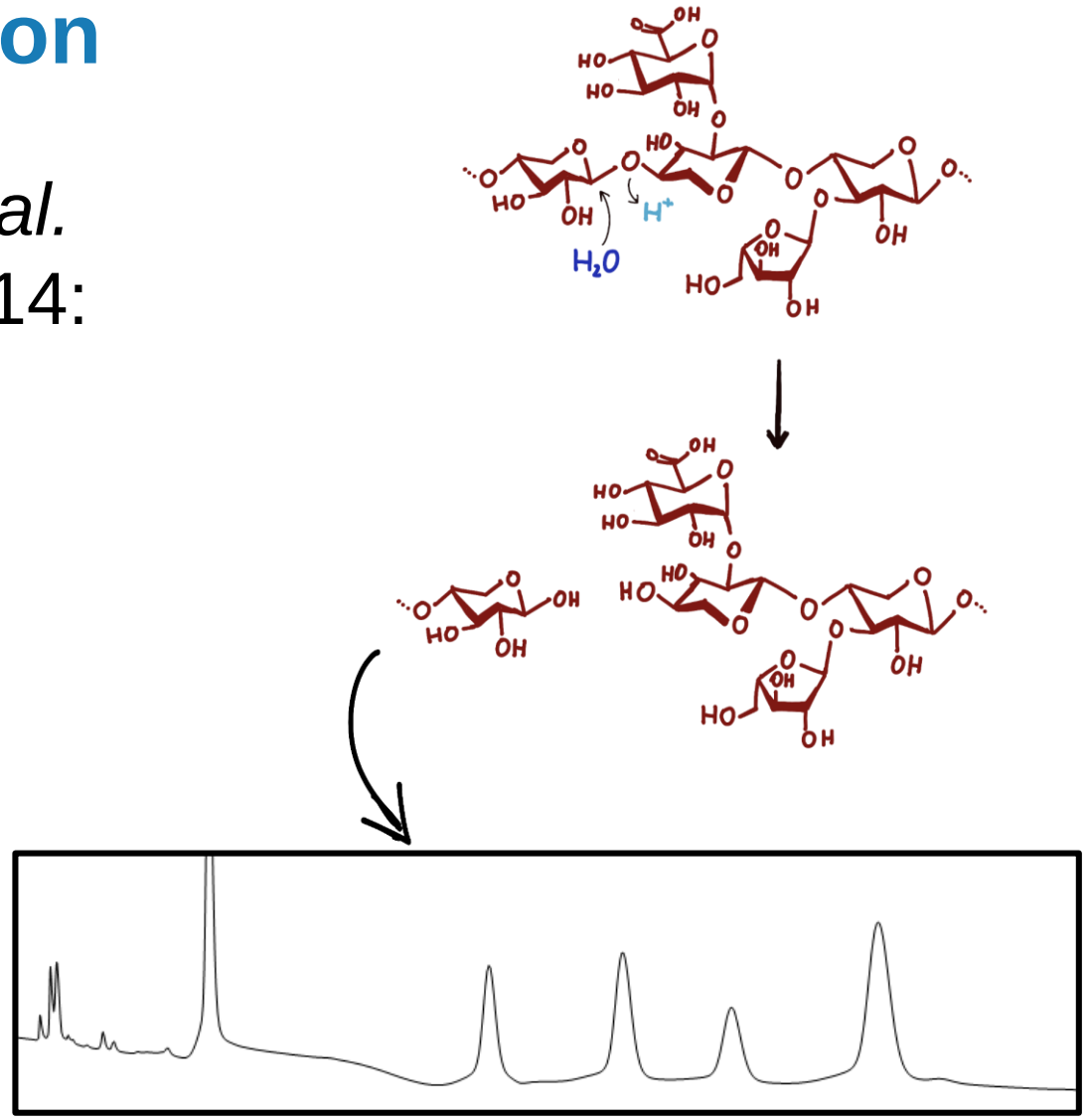
Standard procedure: Sluiter *et al.* 2008, NREL/TP-510-42623 1–14:

1. Acid hydrolysis, 4 % H_2SO_4

Hemicellulose Quantification

Standard procedure: Sluiter *et al.* 2008, NREL/TP-510-42623 1–14:

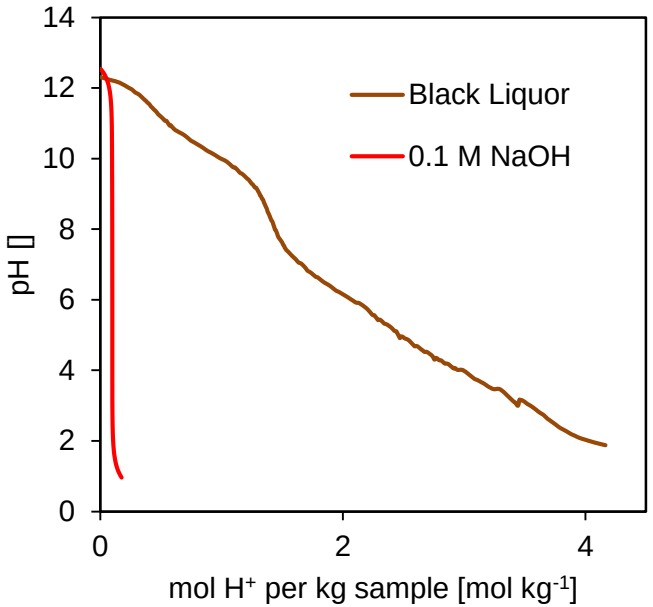
1. Acid hydrolysis, 4 % H_2SO_4
2. Liberation of monosaccharides
3. Quantification by HPIC



Hemicellulose Quantification

Standard procedure: Sluiter *et al.* 2008, NREL/TP-510-42623 1–14:

1. Acid hydrolysis, 4 % H_2SO_4
2. Liberation of monosaccharides
3. Quantification by HPIC

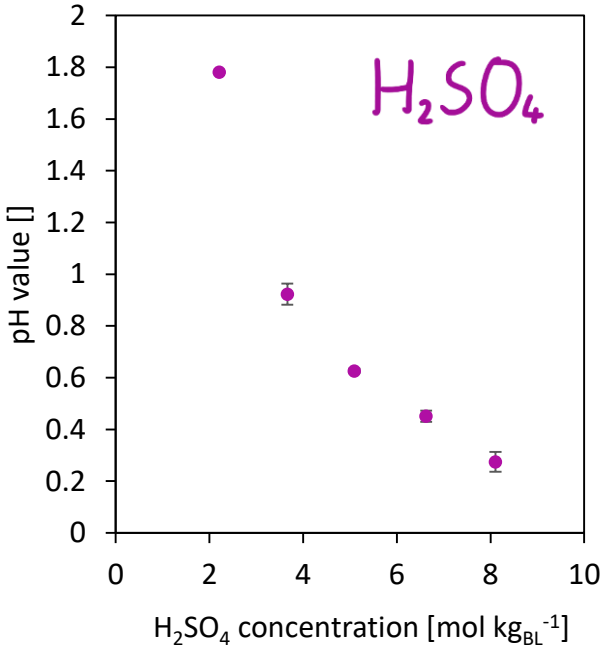


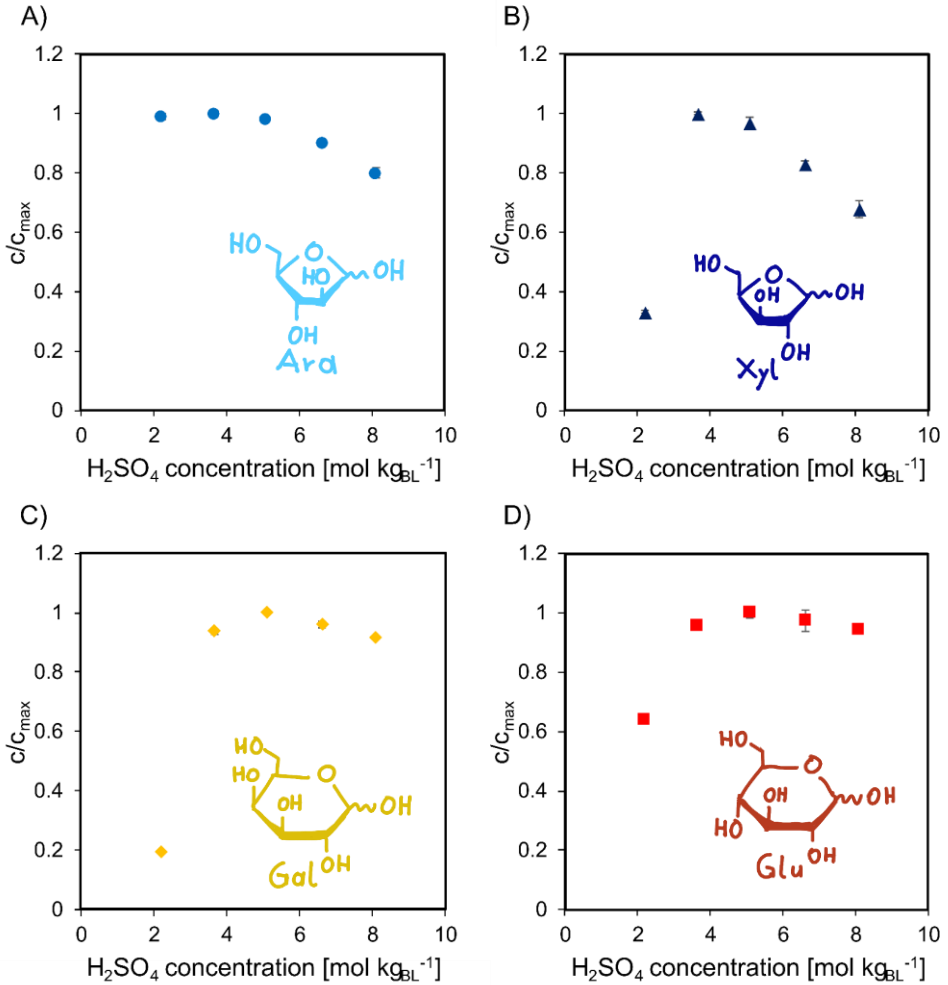
not directly applicable to concentrated BL!

Adjust Acid concentration and BL dilution

Hemicellulose Quantification – Hydrolysis Conditions

Influence of acid concentration

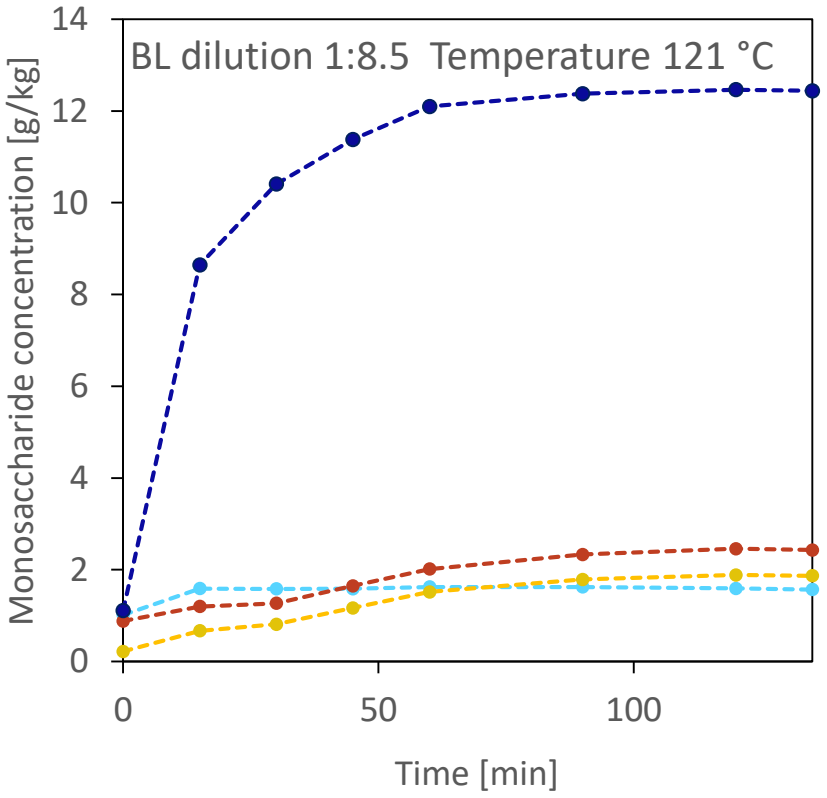


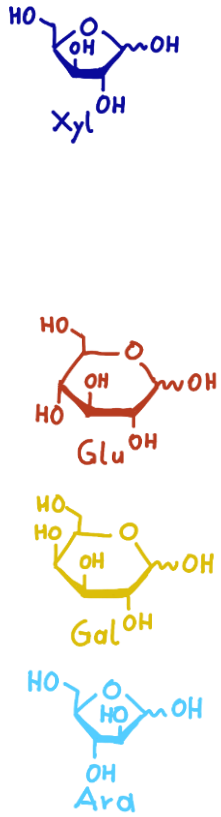


Maitz, S. M., and Kienberger, M. (2021). Investigation of acid hydrolysis for carbohydrate analysis in kraft black liquor. *Holzforschung*, *76*(1), 49-59

Hemicellulose Quantification – Hydrolysis Conditions

Liberation of sugars over hydrolysis time





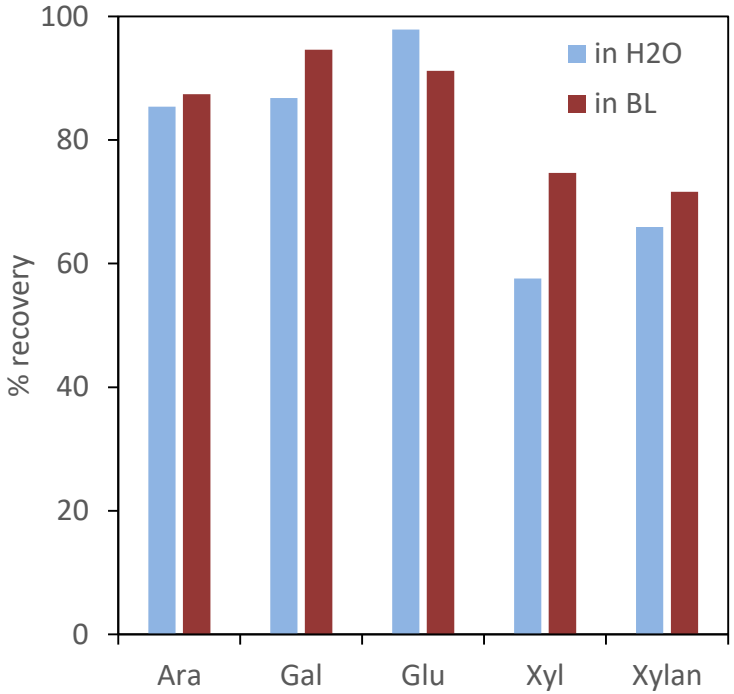
Maitz, S. M., and Kienberger, M. (2021). Investigation of acid hydrolysis for carbohydrate analysis in kraft black liquor. *Holzforschung*, *76*(1), 49-59

Hemicellulose Quantification – Recovery Standards

Sluiter *et al.* 2008: Treat monosaccharide recovery standards together with liquid samples

Our recommendation

- Add standard directly to a BL sample
- Use hemicellulose recovery standard



Maitz, S. M., and Kienberger, M. (2021). Investigation of acid hydrolysis for carbohydrate analysis in kraft black liquor. *Holzforschung*, *76*(1), 49-59

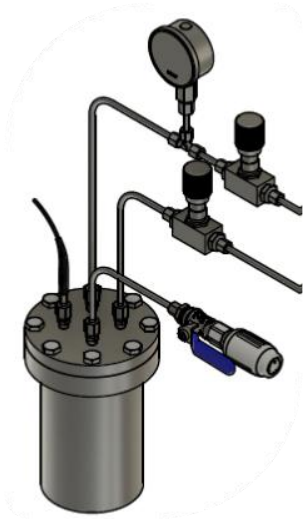
Hemicellulose Quantification

Conclusions and recommendations

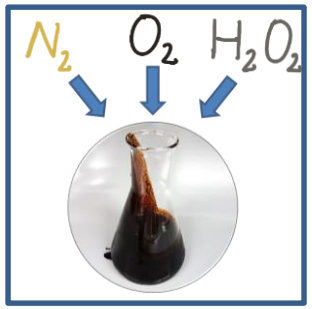
- Pentoses require shorter hydrolysis times and lower acid concentrations compared to hexoses
- Pentoses are less stable than hexoses
- pH value after hydrolysis should be between 0.5 and 1
- Add recovery standards directly to BL samples
- Use standards similar to the expected hemicellulose
  - Arabinoxylan for hardwood
  - Galactoglucomannan for softwood

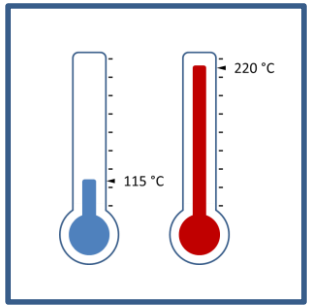
Black Liquor Hydrothermal Treatment and Oxidation

- Investigate the influence of treatment conditions on carbohydrate conversion by variation of:
  - Oxidants
    - N_2, O_2, H_2O_2
  - Temperature
    - 115-220 °C
  - Time
    - Up to 2 h



Treatment reactor

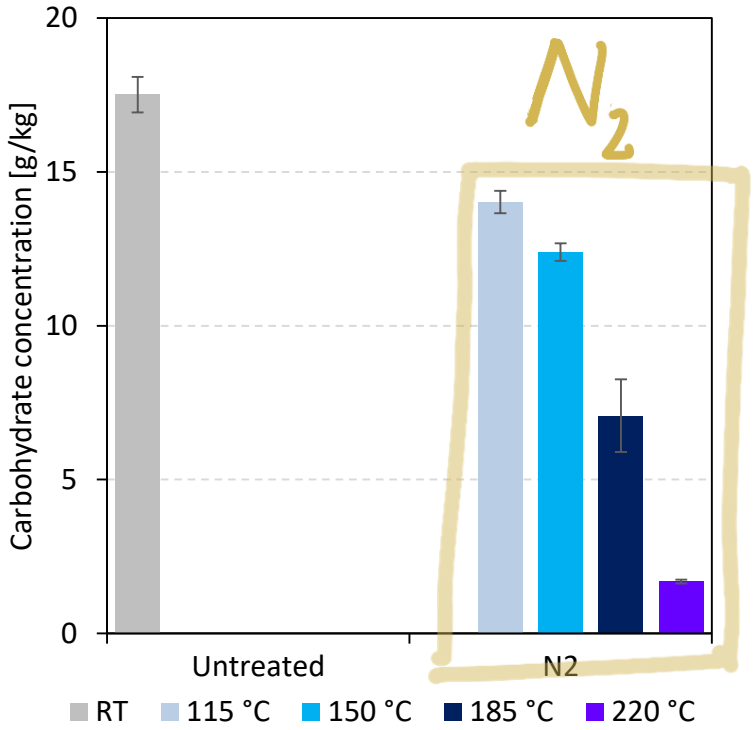




Maitz, S., Siebenhofer, M. and Kienberger, M. (2022). Conversion of carbohydrates to carboxylic acids during hydrothermal and oxidative treatment of concentrated kraft black liquor, *Bioresource Technology Reports*, 19, 101148

Carbohydrate Degradation: Inert Atmosphere

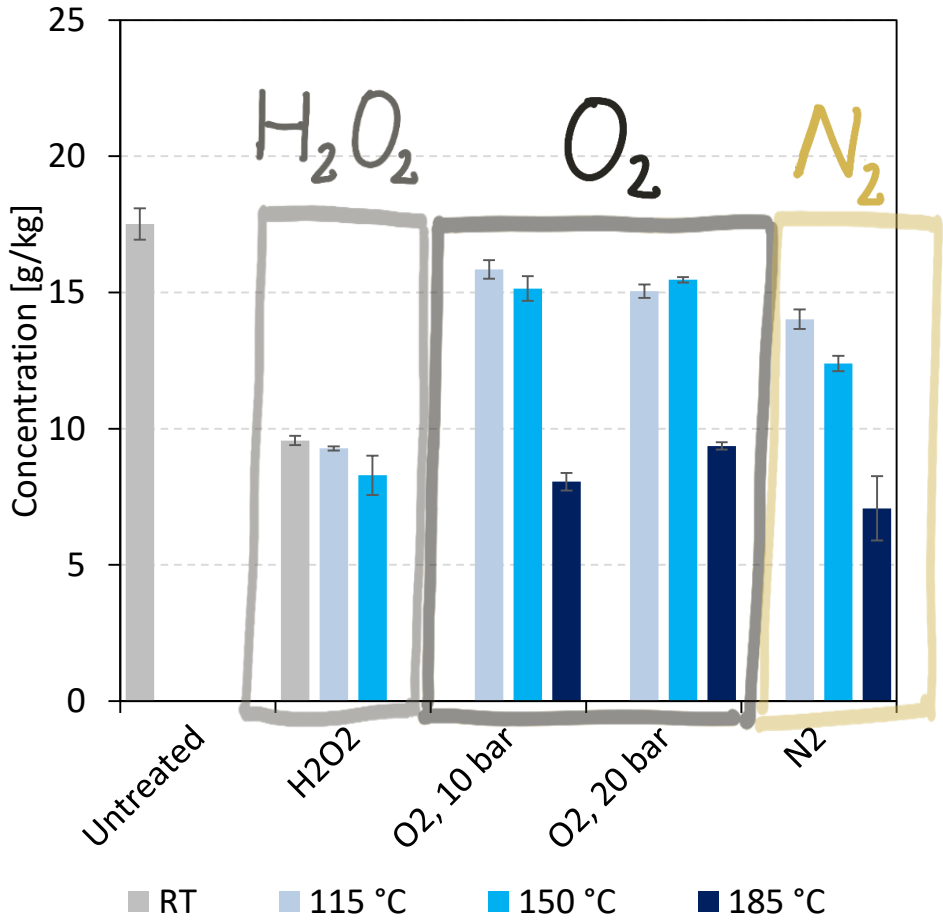
- Higher treatment temperature
  - ► accelerates carbohydrate degradation
  - ► decreases pH value
    - by up to 1.7 pH units
  - ► decreases TOC
    - by up to 3 %



Maitz, S., Siebenhofer, M. and Kienberger, M. (2022). Conversion of carbohydrates to carboxylic acids during hydrothermal and oxidative treatment of concentrated kraft black liquor, *Bioresource Technology Reports*, 19, 101148

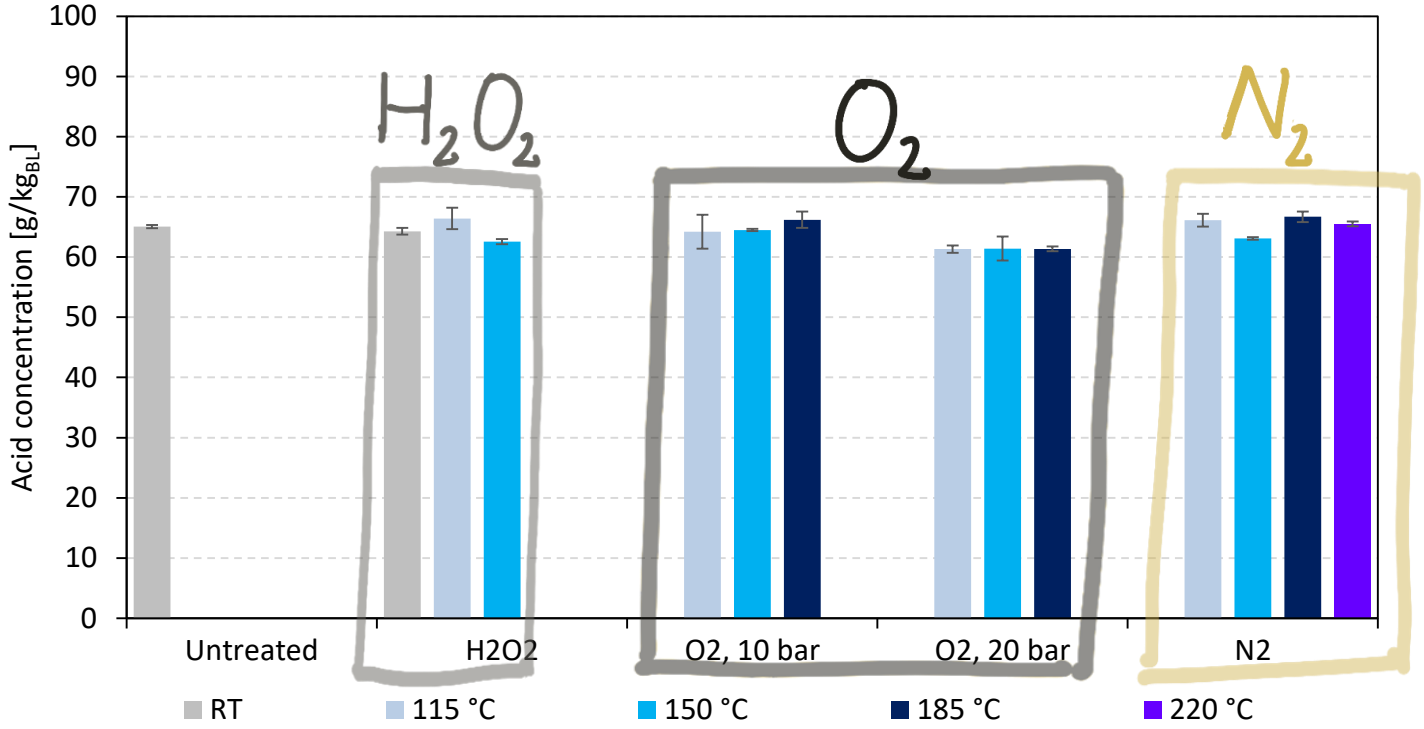
Carbohydrate Degradation: Effect of Oxidants

- Addition of oxygen
  - ► stabilizes carbohydrates
  - ► decreases pH value
    - ○ by up to 2.3 pH units
  - ► decreases TOC content
    - ○ by up to 8 %
- Addition of H_2O_2
  - ► immediate exothermal oxidation
  - ► Significant degradation of carbohydrates without heating



Maitz, S., Siebenhofer, M. and Kienberger, M. (2022). Conversion of carbohydrates to carboxylic acids during hydrothermal and oxidative treatment of concentrated kraft black liquor, *Bioresource Technology Reports*, 19, 101148

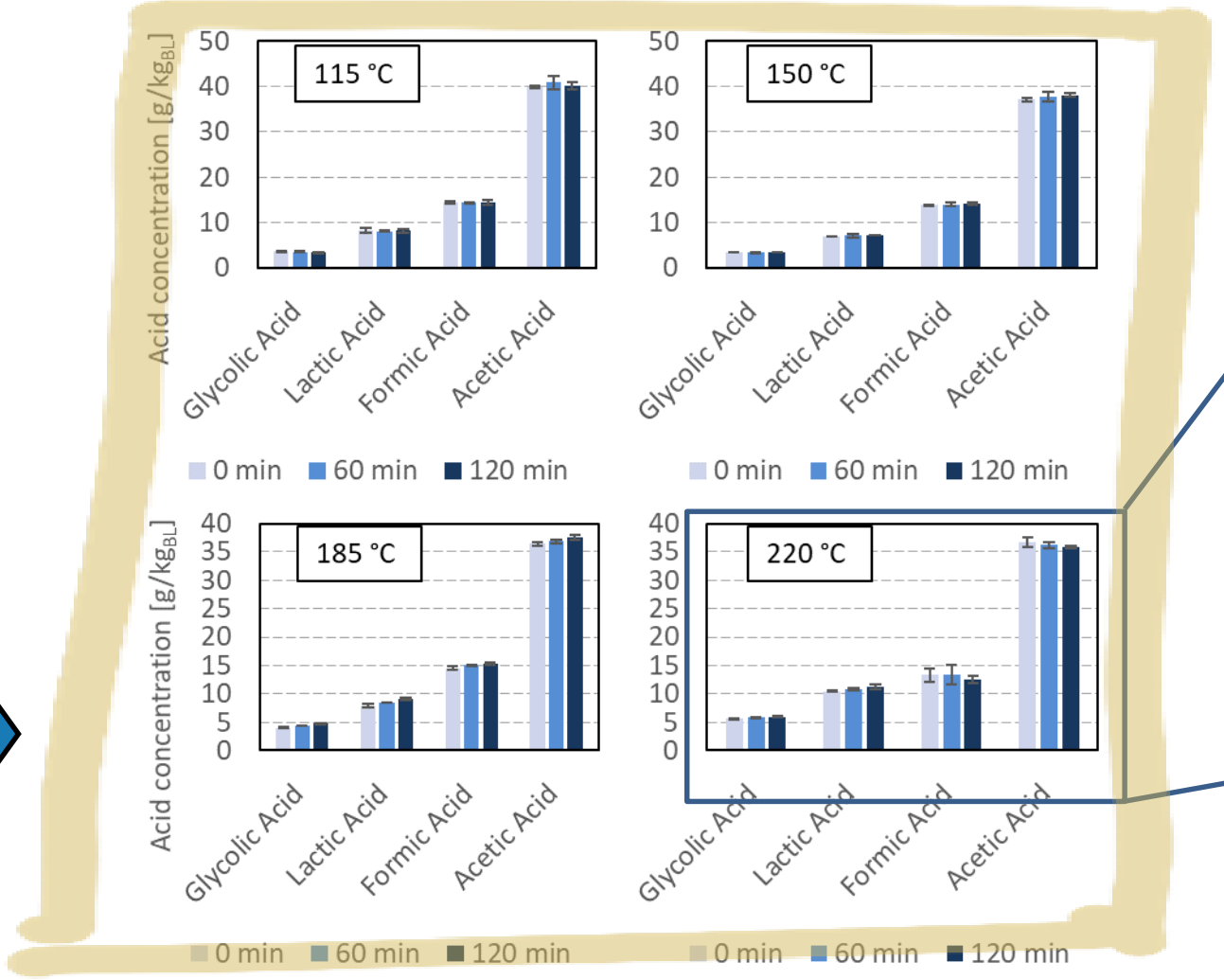
Acid Formation



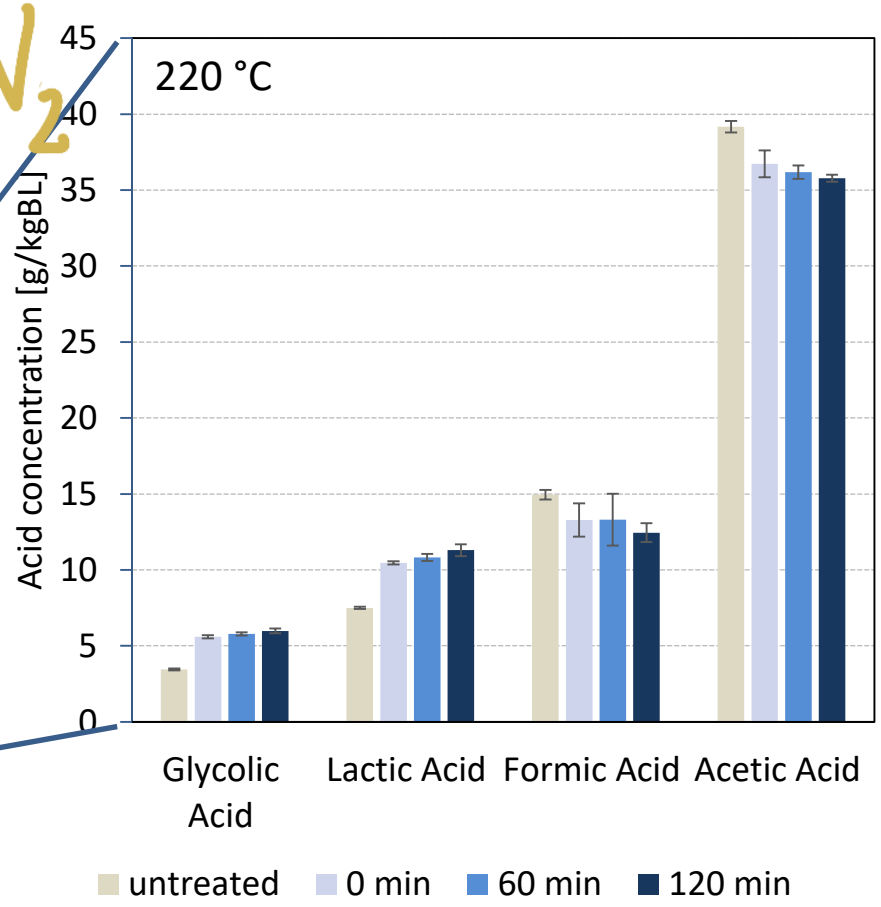
- Total acid concentration hardly affected by treatments!

Maitz, S., Siebenhofer, M. and Kienberger, M. (2022). Conversion of carbohydrates to carboxylic acids during hydrothermal and oxidative treatment of concentrated kraft black liquor, *Bioresource Technology Reports*, 19, 101148

Effects of Treatment Time

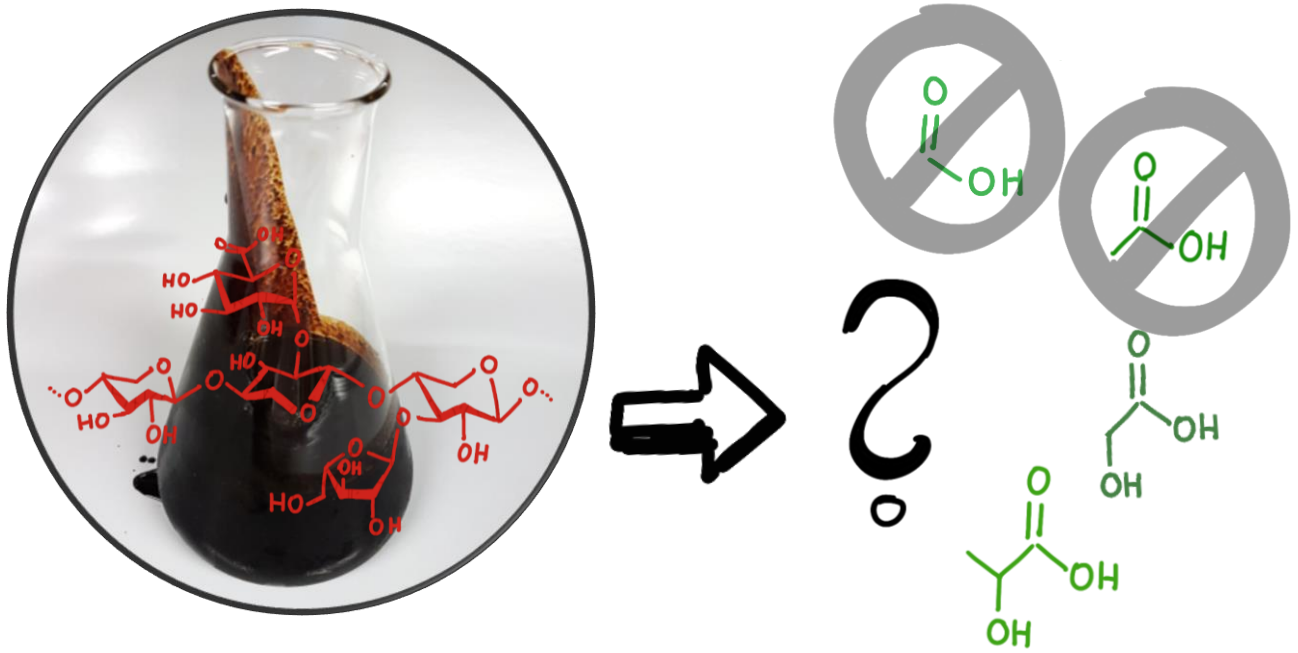


N_2



Maitz, S., Siebenhofer, M. and Kienberger, M. (2022). Conversion of carbohydrates to carboxylic acids during hydrothermal and oxidative treatment of concentrated kraft black liquor, *Bioresource Technology Reports*, 19, 101148

Conversion of Carbohydrates to Carboxylic Acids



- Carbohydrate conversion to hydroxy acids with 32 % carbon conversion efficiency

Maitz, S., Siebenhofer, M. and Kienberger, M. (2022). Conversion of carbohydrates to carboxylic acids during hydrothermal and oxidative treatment of concentrated kraft black liquor, *Bioresource Technology Reports*, 19, 101148

Hemicellulose Conversion

Conclusions and recommendations

- Higher treatment temperatures accelerate carbohydrate degradation
- O_2 treatment leads to carbohydrate conservation
- H_2O_2 treatment induces carbohydrate degradation
- At 220 °C, 2 h, 0.61 moles of hydroxy acids formed per mole sugar
  → carbon conversion of 32 %

Summary and Outlook

- Carbohydrate quantification in BL still challenging
  → use recovery standards
- Efficient degradation of hemicellulose at elevated temperatures in inert atmosphere or upon addition of H_2O_2
  - Formation of hydroxy carboxylic acids, degradation of volatile acids

Carbohydrate conversion as pre-treatment for BL fractionation:

→ only reasonable in broader context, if also other BL properties shall be modified

→ further studies on BL fractionation without pre-treatment

Kraft Black Liquor as Biorefinery Feedstock - The Role of Hemicellulose

Contact:
Silvia Maitz
Biorefinery Engineering Group
Institute of Chemical Engineering and Environmental Technology (CEET)
Graz University of Technology
silvia.maitz@tugraz.at
+43 316 873 - 7967