PROCESS CHEMISTRY CENTRE

ÅBO AKADEMI UNIVERSITY

Acid Hydrolysis of Hemicelluloses in a Continuous Reactor

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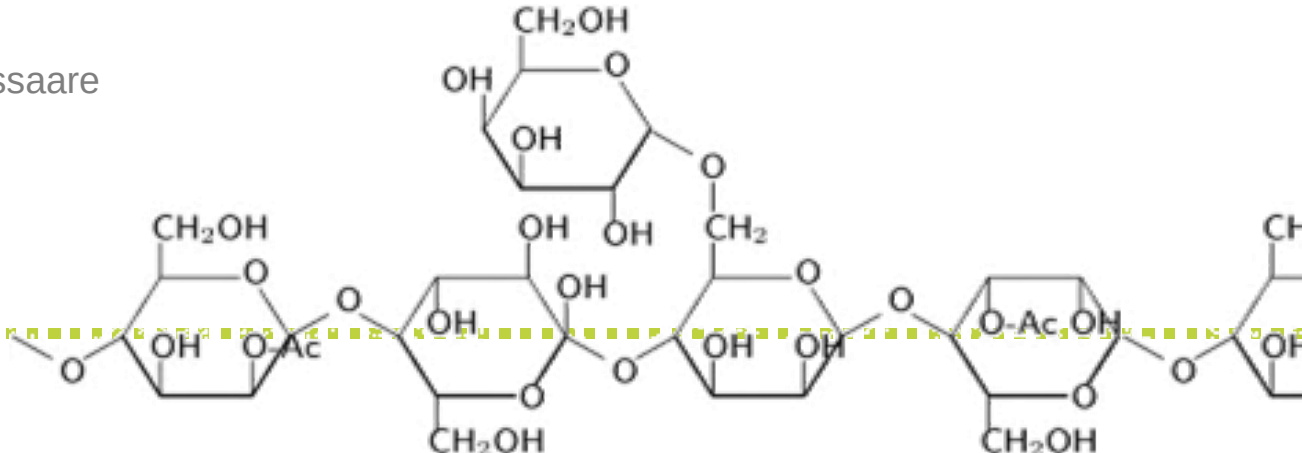

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1. Introduction - Biorefineries

SHORTAGE OF RAW MATERIALS
IN THE LONG TERM

Issue

- Energy Sector
- Environmental implications

SUSTAINABLE DEVELOPMENT

Key

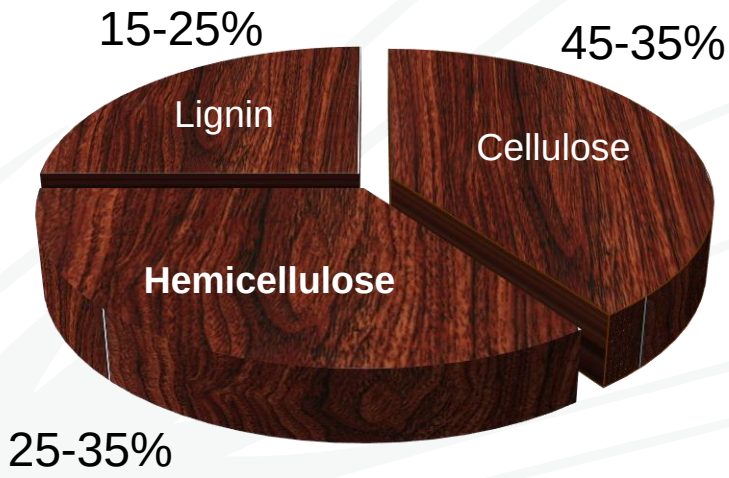
- Renewable resources
- **Biomass**

- Lignocellulosic biomass

Cellulose

Hemicellulose

Lignin



- Hemicellulose:
  - mannans, xylans, arabinans, galactans and derivatives

2. Aim of the Project

- **Continuous** production of rare sugars via acid hydrolysis of different types of hemicelluloses
- Minimizing the formation of degradation products
  - Furfural, HMF, formic acid, levulinic acid…
- Developing a mathematical model of the process

3. Hydrolysis of hemicelluloses

- Hemicelluloses are heteropolysaccharides composed of different sugar units
- **Hydrolysis**: Process for production of rare sugars
- Rare sugars: highly value-added compounds in biorefinery

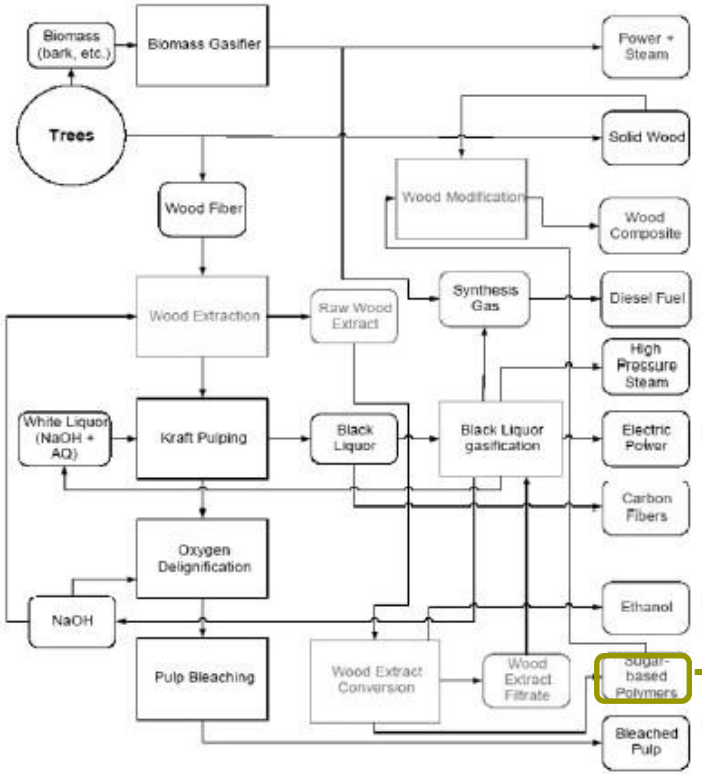
HYDROLYSIS

- Enzymatic
- Acid
  - Homogeneous
  - Heterogeneous

- Selective acid hydrolysis is more efficient than enzymatic
- Different methods: two-step method…

4. Why continuous?

- **TMP → Hydrolysis → Monomers**
- Logical next step
- Norway spruce is one of the main wood species in the Nordic countries
- Very versatile raw material

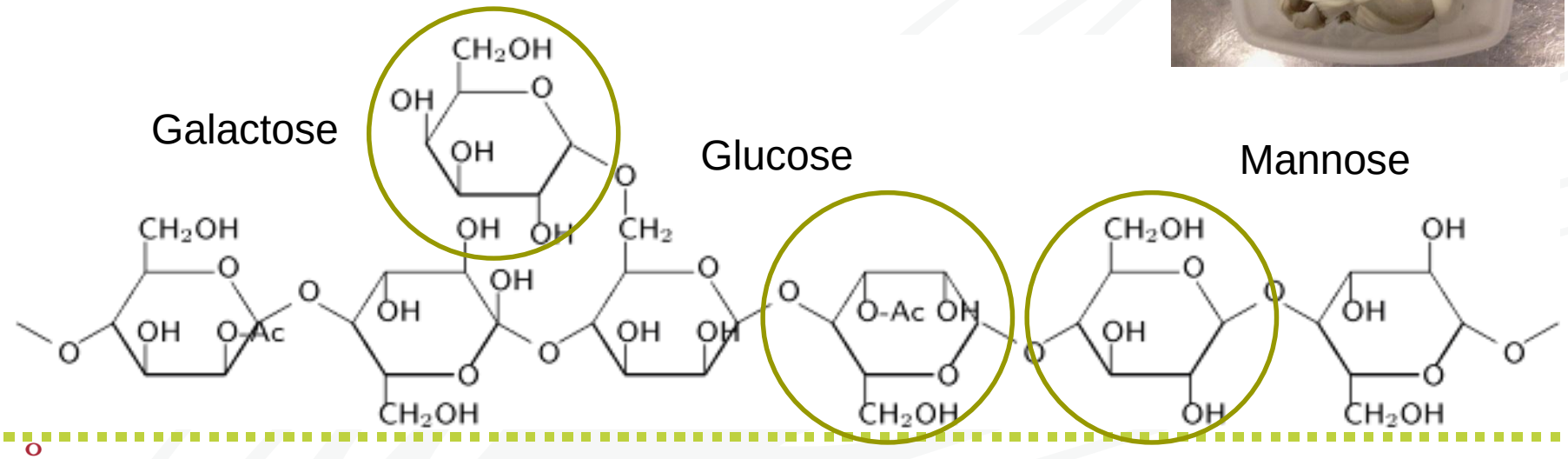


Sugar-based polymers

- Advantages of continuous reactor
  - ↑ heat transfer capacities
  - better concentration profiles
  - ↓size → ↑↑mixing rates
  - ↑operating flexibility

5. Galactoglucomannan (GGM)

- Softwood derived polysaccharide
- Extracted from TMP from Norway spruce (*Picea abies*)
- Structure:
  - (1→4)-linked β-D-mannopyranosyl
  - (1→4)-linked β-D-glucopyranosyl
  - α-D-galactopyranosyl
  - O-acetyl groups

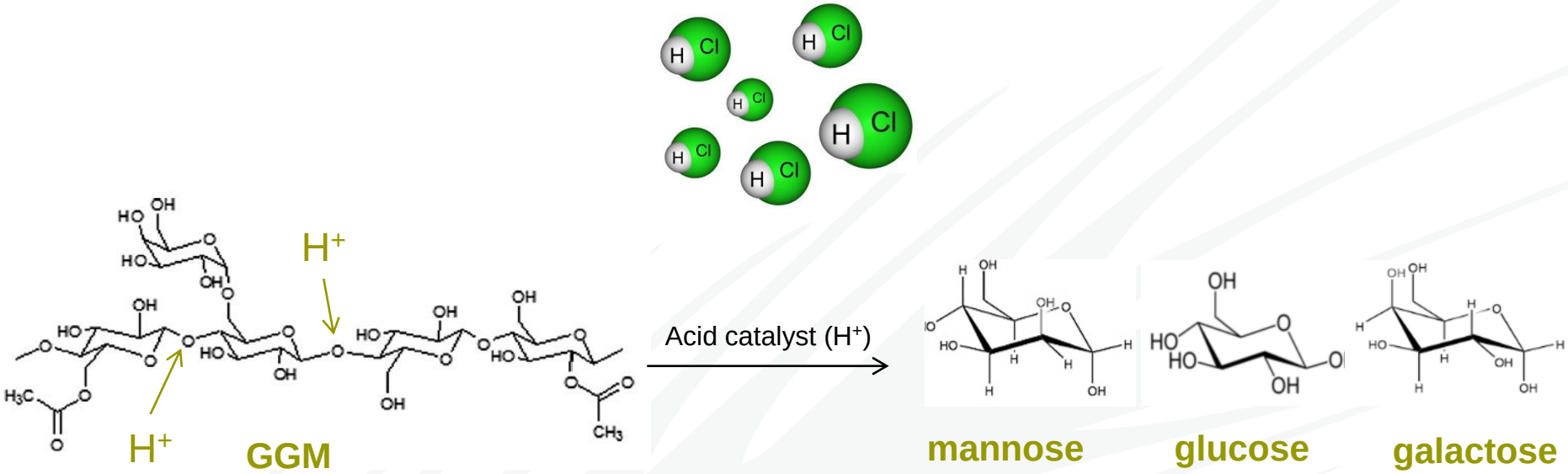


O-acetylgalactoglucomannan

6. Hydrolysis of GGM

- Protonation of the glycosidic bond

Catalyst: Hydrochloric acid (HCl)



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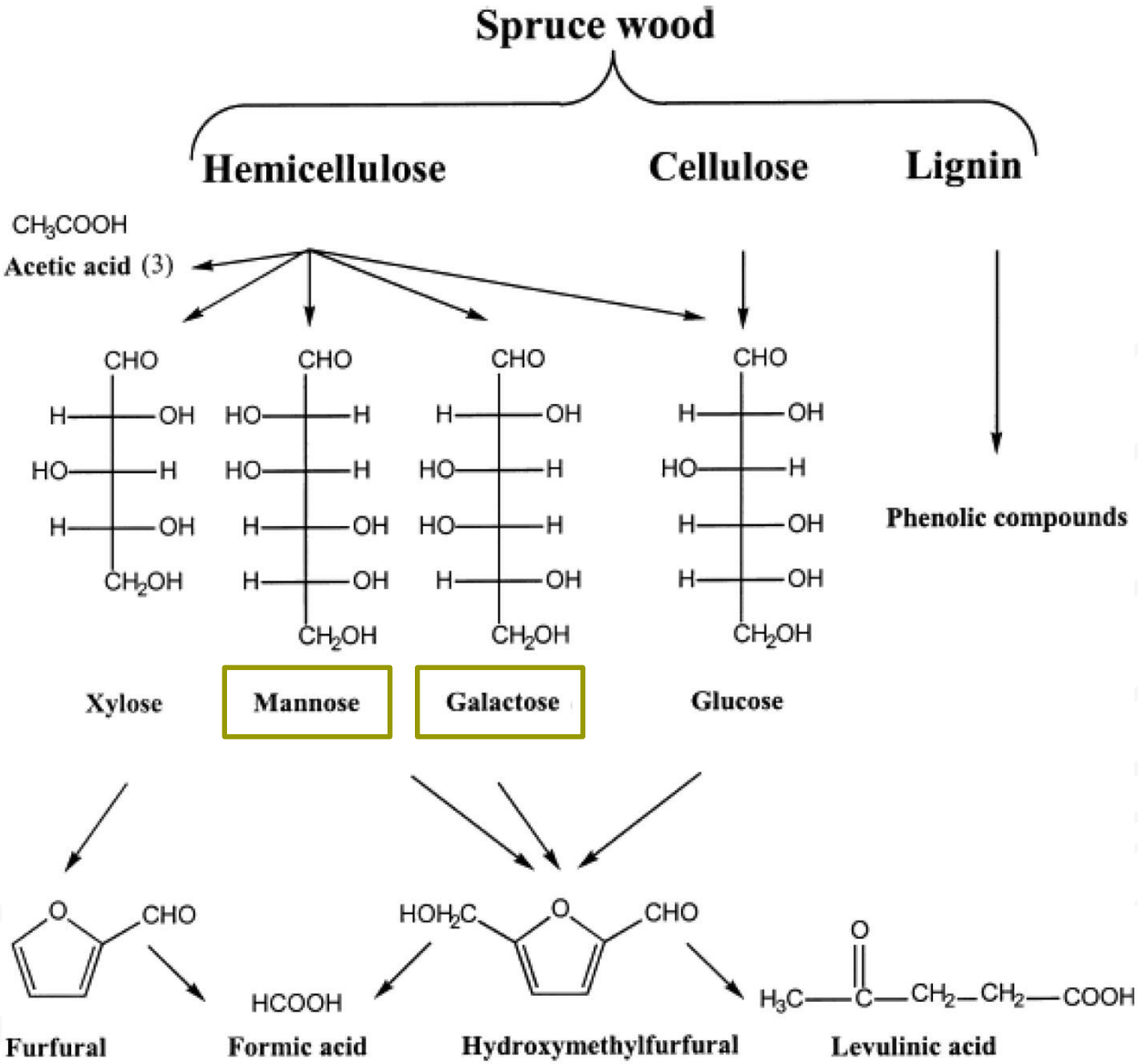
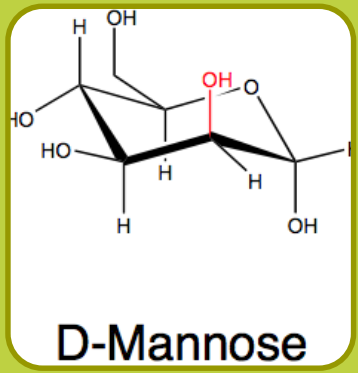
Product Applications

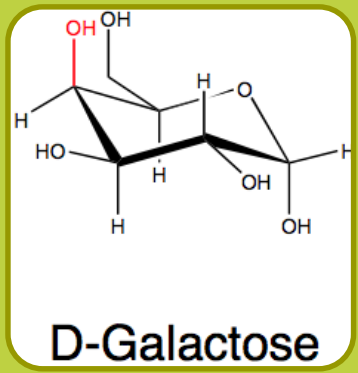


Product Applications



D-Mannose

- Production of pharmaceuticals
- Decrease of the symptoms in lower urinary tract diseases
- Growth accelerator for swine
- Hydrogenation to mannitol: further applications



D-Galactose

- Applications in the pharmaceutical and alimentary industry
- Nutrient medium for maintaining viability of neutral cells
- Use in cytotoxic and anti-inflammatory drugs
- Transformation to tagatose or fucose: further applications

7. Materials and Methods

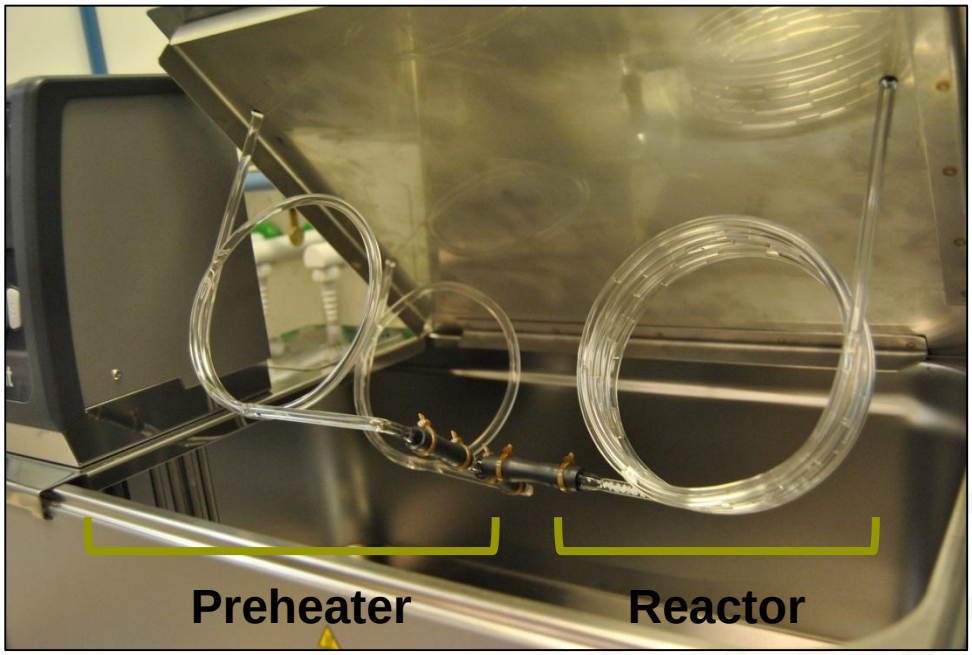
- Continuous reactor
- Isothermal conditions
- Parameters to study
  - Conversion
  - Sugar concentration

- Reaction conditions
  - pH = 0 – 2
  - T= 80 – 100 ºC
  - c_{GGM}= 0.5%wt – 6%wt

Raw Material	GGM
Catalyst	HCl

7.1. Reactor Setup

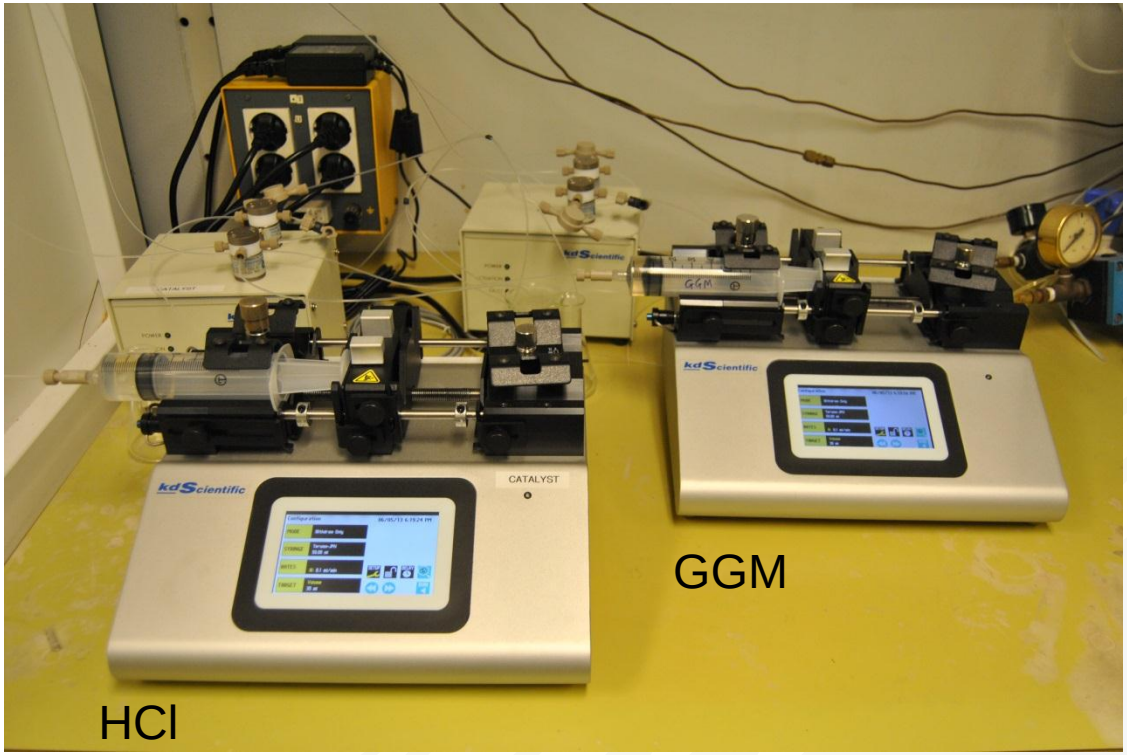
Reactor



- Characteristics
  - Glass
  - Dimensions
    - L_{ph} = 1 m
    - L_r = 3 m
    - d_t = 3 mm

7.1. Reactor Setup

Pump



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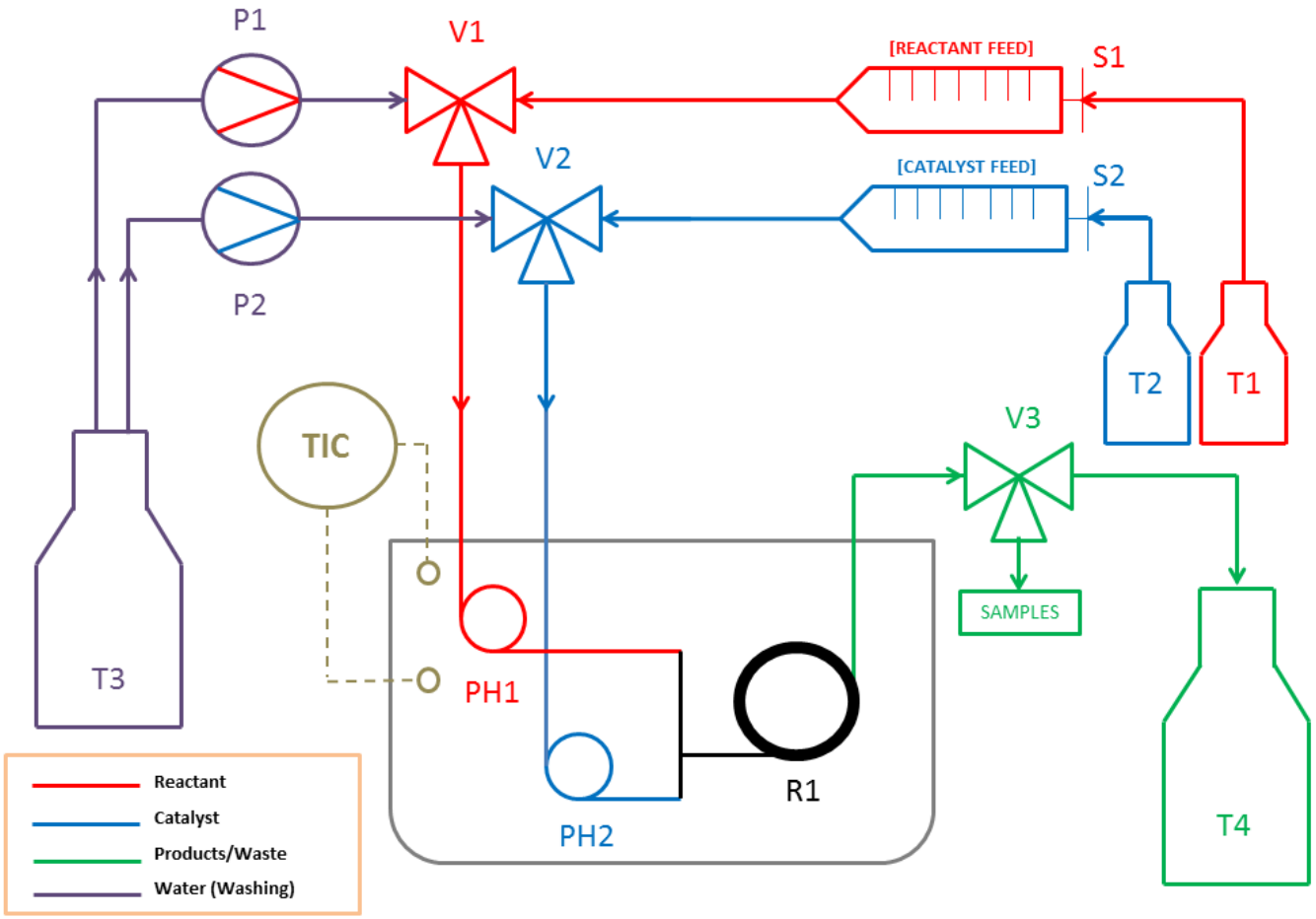
7.1. Reactor Setup

Flowsheet



7.2. Analysis

Gas Chromatography Analysis (GC)

- Total organic carbohydrate content (Methanolysis)
- Monomeric sugar content
- Oligomer content (DP<6)

Analysis:
- Quantitative
- Qualitative

- Mass balance ⟹ Conversion

⚠ Challenging and time consuming techniques

8. Results

- Residence time

		GGM		HCl		Total flow
	Flow rate	**0,1 mL/min**	**+**	**0,1 mL/min**	**=**	**0,2 mL/min**
Preheater	d_t = 3mm L = 1m V = 7,07 mL	t_r= 71 min				
Reactor	d_t = 3mm L = 3m V = 19,56 mL	**t_r=98 min**				

		GGM		HCl		Total flow
	Flow rate	**0,075 mL/min**	**+**	**0,1 mL/min**	**=**	**0,175 mL/min**
Preheater	d_t = 3mm L = 1m V = 7,07 mL	t_r= 71min t_r=94 min				
Reactor	d_t = 3mm L = 3m V = 19,56 mL	**t_r=121min**				

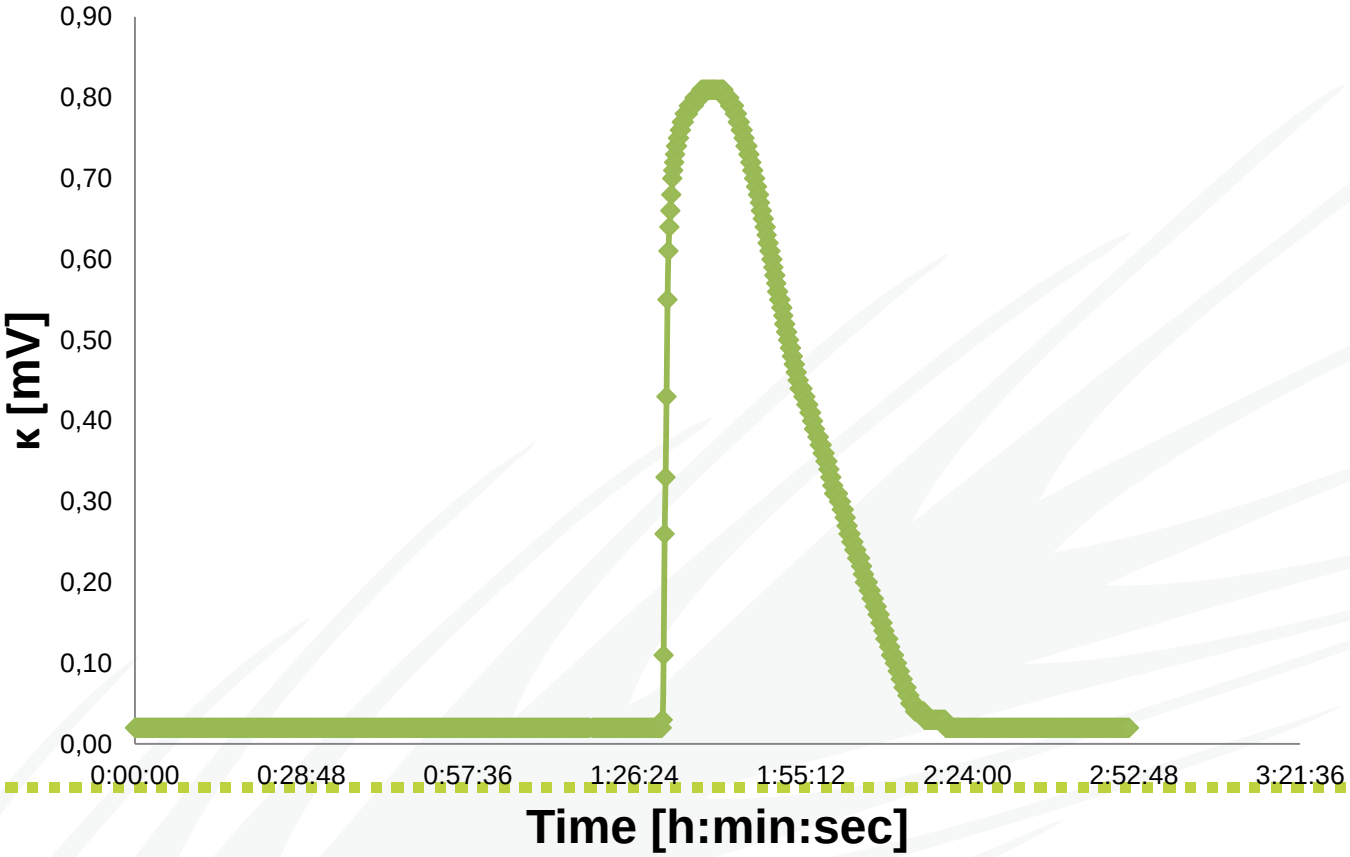
8. Results

- Residence time

Experimental Measurement

Pulse experiment

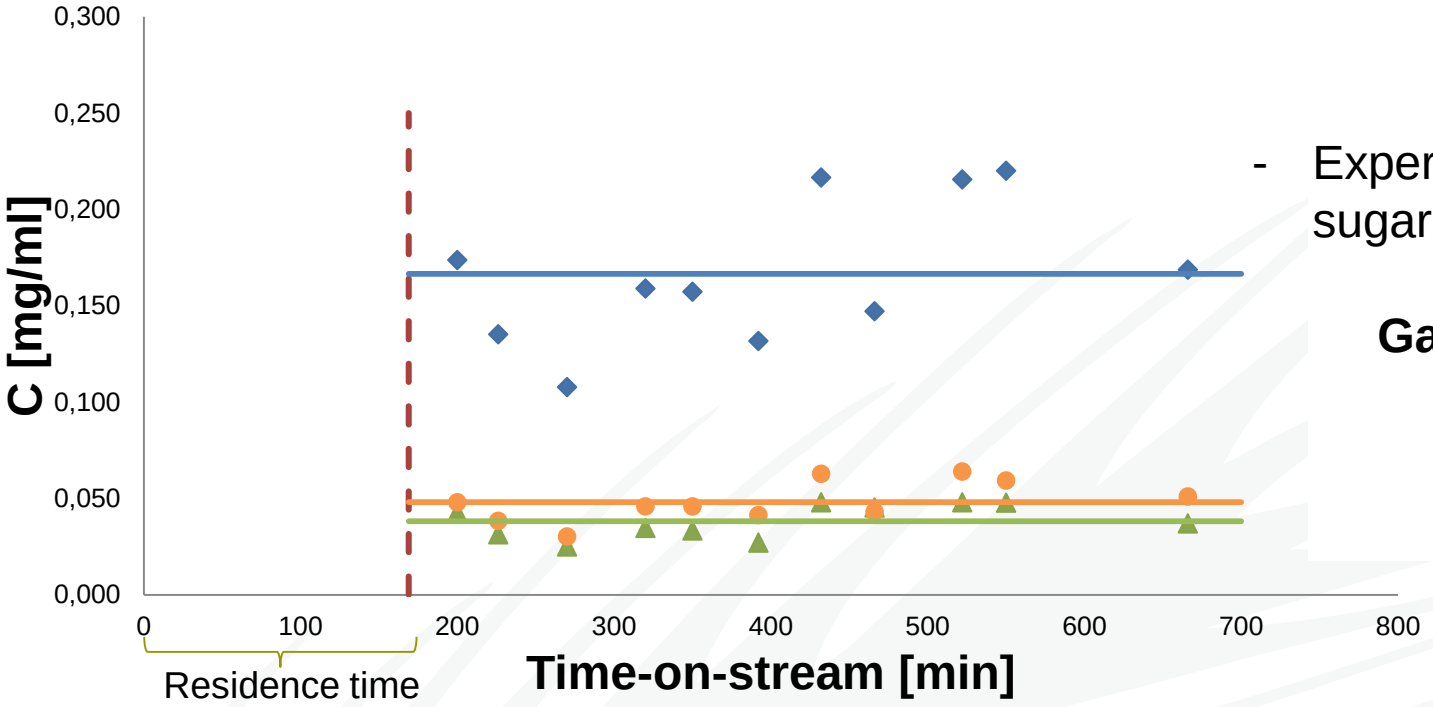
V = 19,56 mL



8. Results

- Monomer Production
- pH = 0,3 ; T = 90ºC

Initial concentration of GGM inside the reactor: C_0=0,43 mg/ml



- Experimental ratio for sugar production:

Gal:Glu:Man
1:1,5:5

- Mannose is produced in larger amounts
- Concentration in the outlet tend to be constant

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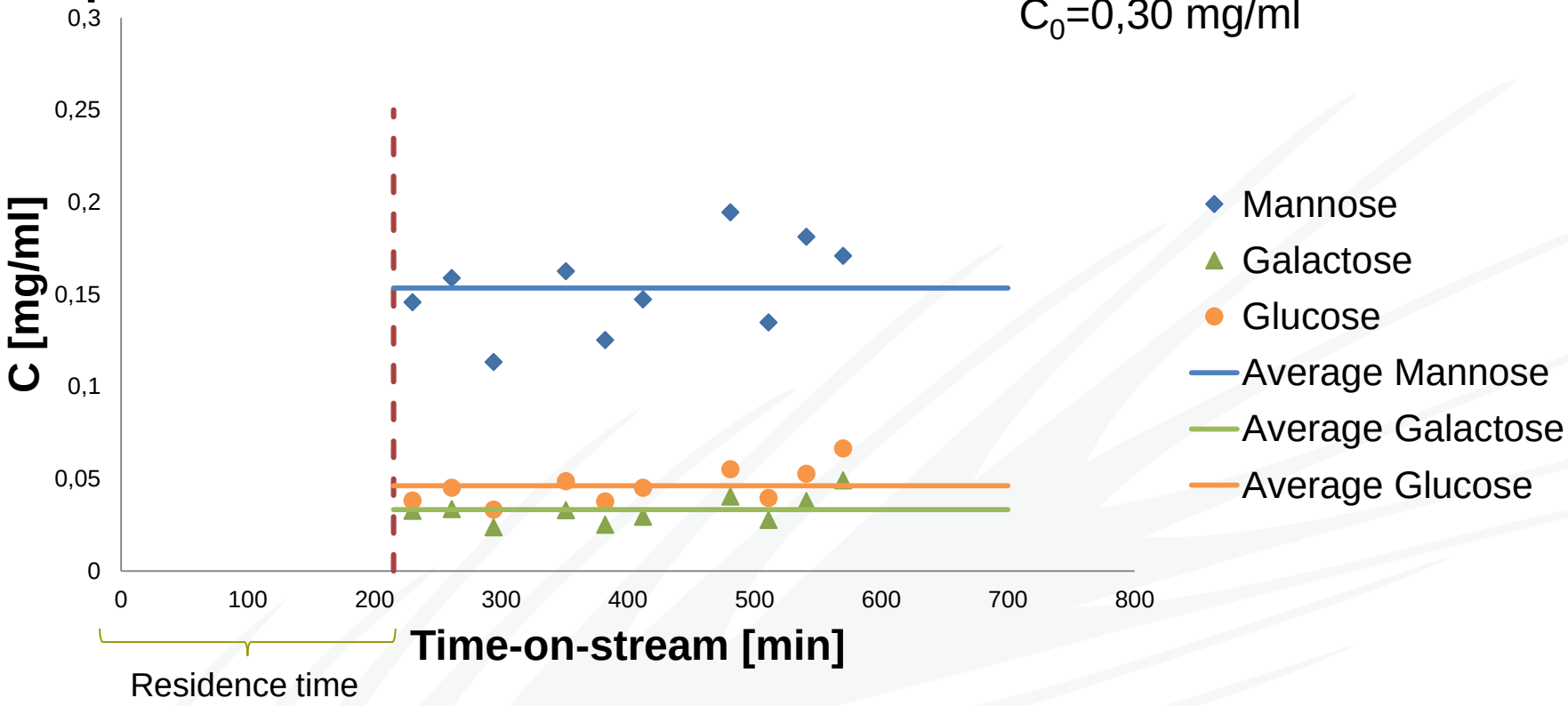
8. Results

- Monomer Production
- pH = 0,24; T=90ºC

Initial concentration of GGM inside the reactor: C_0=0,30 mg/ml



- Mannose is produced in larger amounts
- Concentration in the outlet tend to be constant

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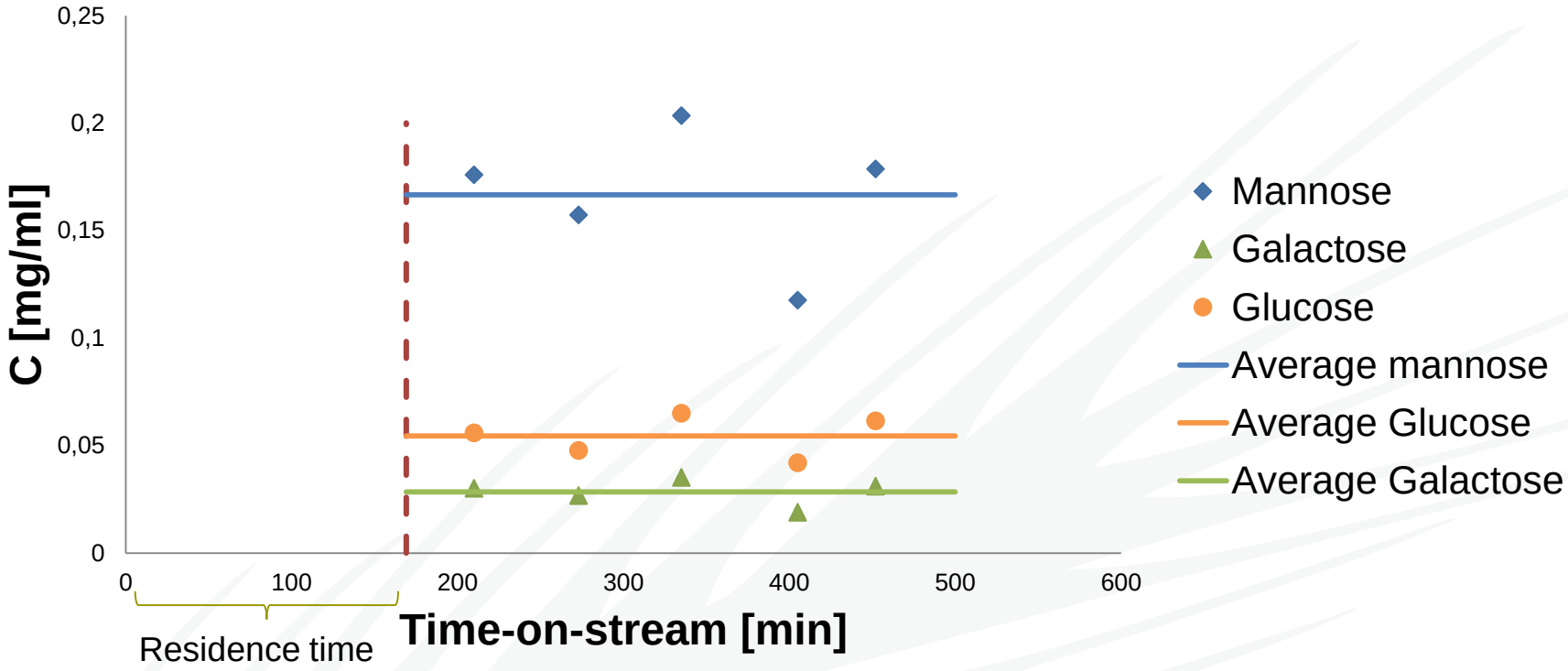
8. Results

- Monomer Production
- pH = 0,3 ; T = 95ºC

Initial concentration of GGM inside the reactor: C_0=0,32 mg/ml



- Mannose is produced in larger amounts
- Concentration in the outlet tend to be constant

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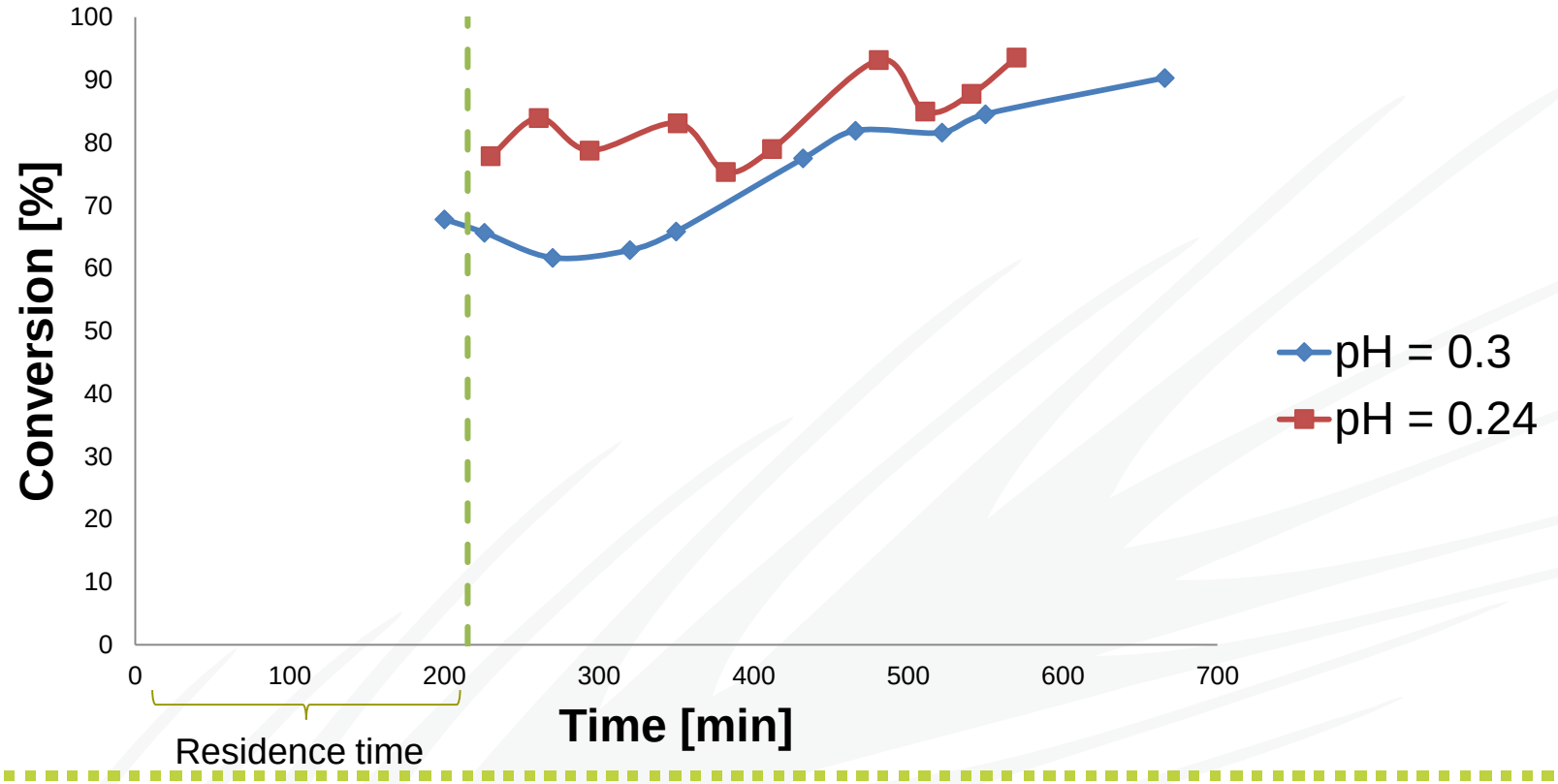
8. Results

- pH dependence



Outlet conversion: Lower pH → Higher conversion

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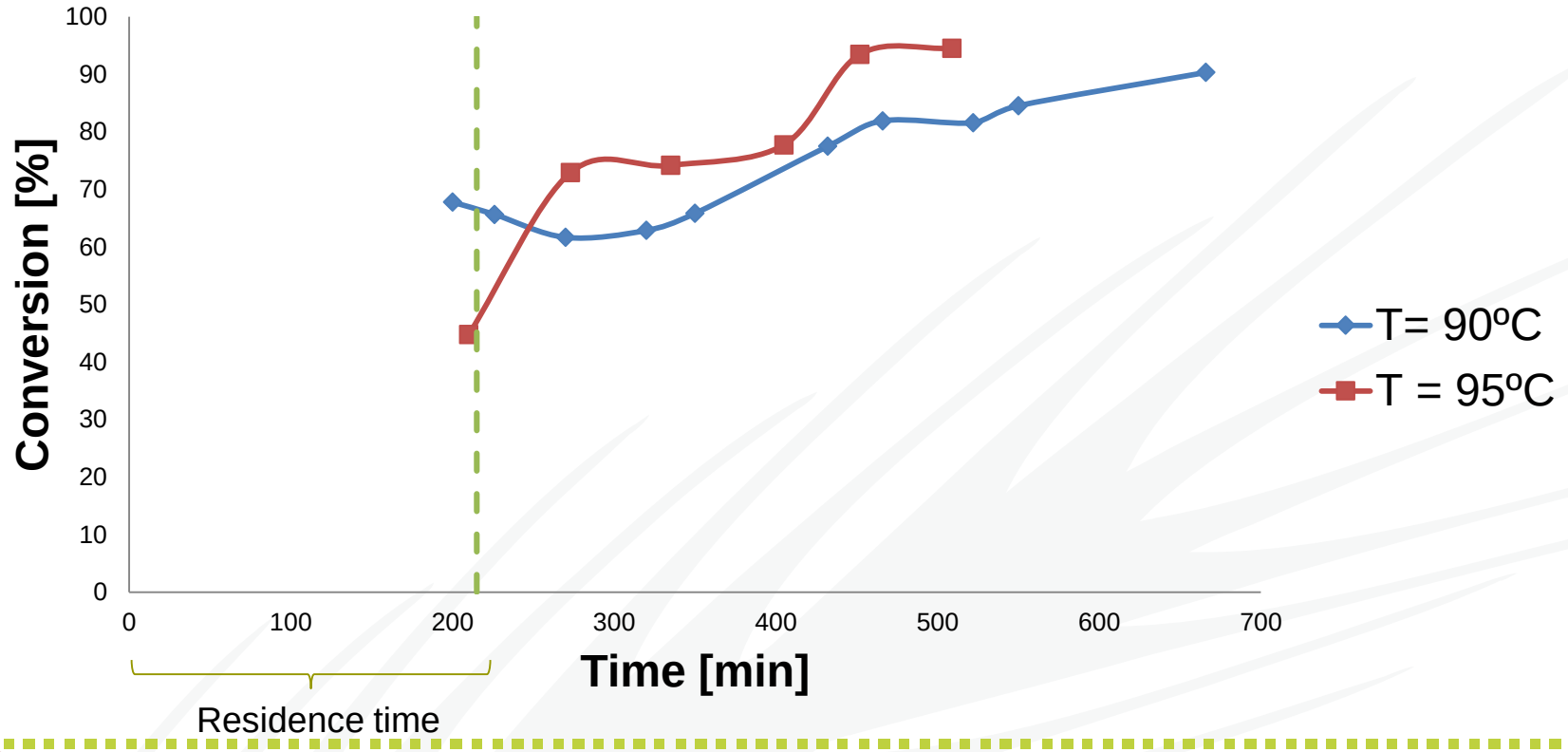
8. Results

- Temperature dependence



Outlet conversion: Higher temperature → Higher conversion

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9. Conclusions

- High production of sugars was accomplished
- < 90% conversion was reached
- No degradation products were detected
- ↓pH → ↑Conversion
- ↑T → ↑Conversion

- First time demonstration of feasibility of continuous operation mode

10. Future Work

- Hydrolysis of different hemicelluloses
  - Arabinogalactan
  - Glucuroxylan
  - Inulin
- Use of different catalysts
  - Organic acids
  - Heterogeneous catalysts – fixed bed reactor
- Optimization of reactor conditions in continuous mode
- Separation of product fractions by chromatographic techniques

Acknowledgements

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Thanks for your attention!

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