HYDROTHERMAL FRACTIONATION OF *GELIDIUM SESQUIPEDALE* ALGA RESIDUE BY SUBCRITICAL WATER EXTRACTION

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Raw Material

INDUSTRIAL AGAR EXTRACTION:

MACROALGA *Gelidium sesquipedale*

BASIC TREATMENT

WASHING

AGAR-AGAR EXTRACTION

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SECOND EXTRACTION

MACROALGA RESIDUE

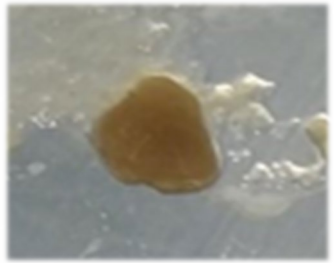
Raw Material

COMPOSITION:

G. Sesquipedale

Macroalga Residue (DMR)

	G. Sesquipedale	Macroalga Residue (DMR)
CARBOHYDRATES	**38 ± 1**	**42 ± 2**
Glucans	10.7 ± 0.3	23.4 ± 0.9
Galactans	**21.3 ± 0.5**	**10.9 ± 0.5**
Arabinans	1.4 ± 0.1	2.9 ± 0.2
Uronic acids	4.3 ± 0.1	3.8 ± 0.1
LIGNIN	**11.3 ± 1**	**12 ± 1**
Soluble	11 ± 0.1	8.7 ± 0.1
Insoluble	0.3 ± 0.1	3 ± 1
PROTEINS	**14.9 ± 0.3**	**21 ± 1**
LIPIDS	**0.7 ± 0.2**	**0.87 ± 0.09**
ASHES	**14.9 ± 0.3**	**22 ± 2**



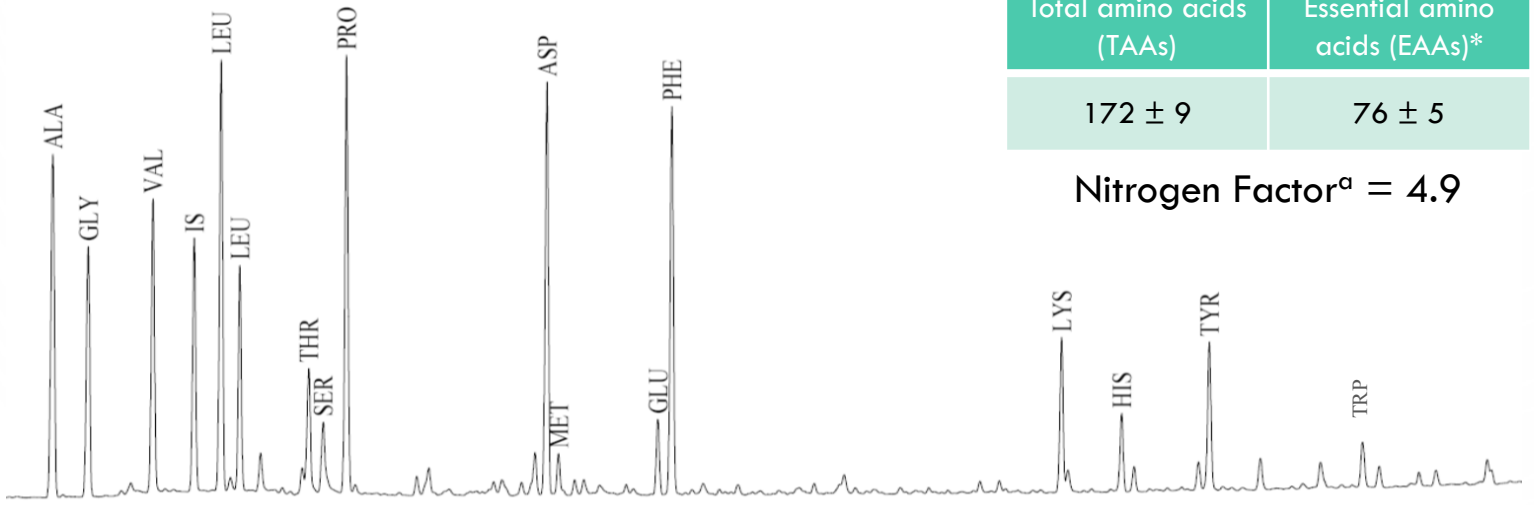
Residual Agar (≈ 7 %)

Raw Material

AMINO ACIDS PROFILE: 21 % Proteins

(mg/g dry macroalga residue)

Ala	Gly	Val*	Leu*	Ile*	Thr*	Ser	Pro	Asp	Met*	Glu	Phe*	Lys*	His*	Tyr	Trp
19.9	8.7	14	16.3	9.4	7.5	8	15.4	20.4	1.7	16.6	10.6	12	3.4	7.3	0.6



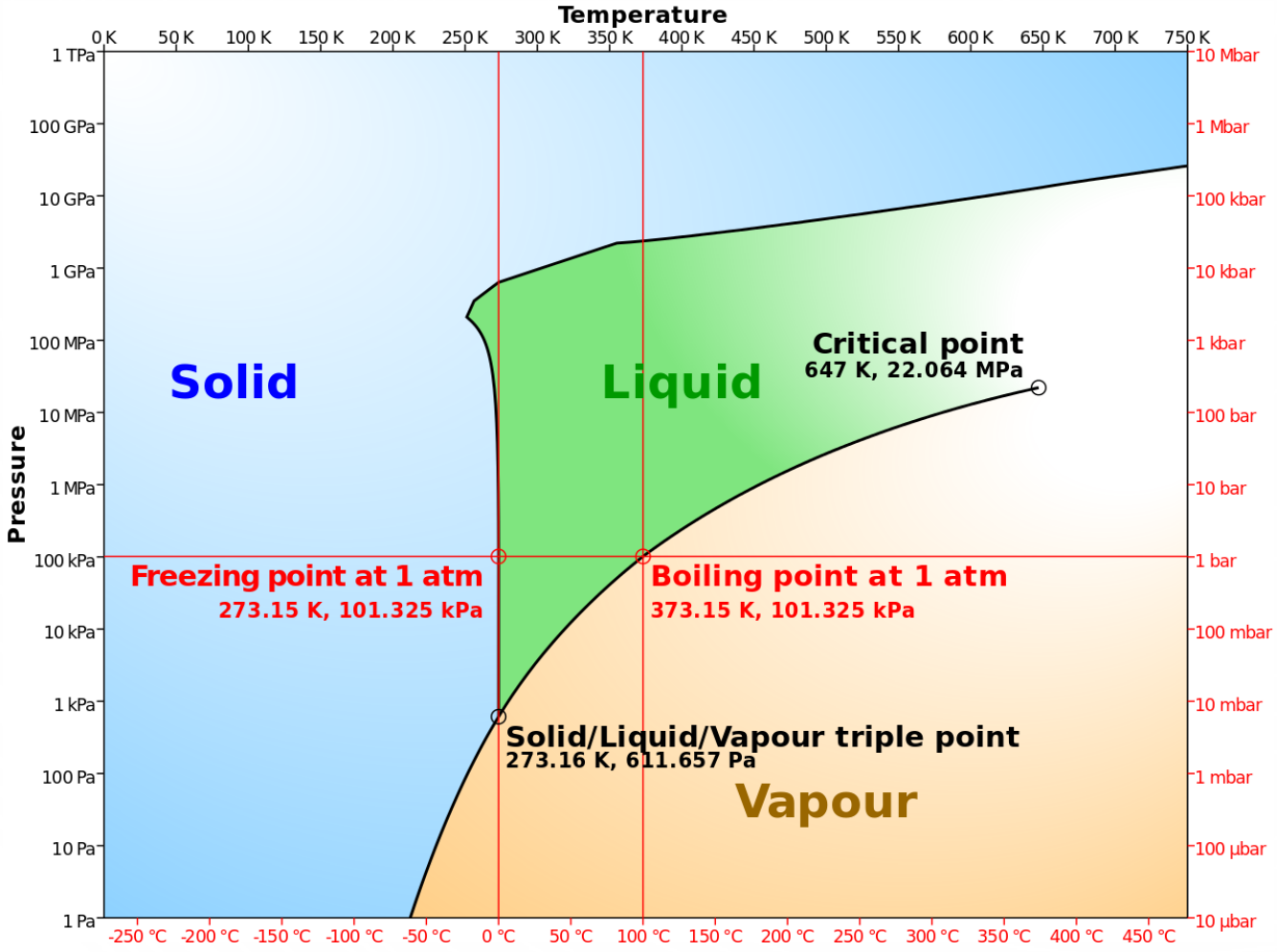
(mg/g dry macroalga residue)

Total amino acids (TAAs)	Essential amino acids (EAAs)*
172 ± 9	76 ± 5

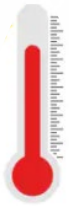
Nitrogen Factor[a] = 4.9

[a]Estimated by calculation spreadsheets provided by NREL according to amino acids sample profile (https://www.nrel.gov/)

Subcritical Water Extraction

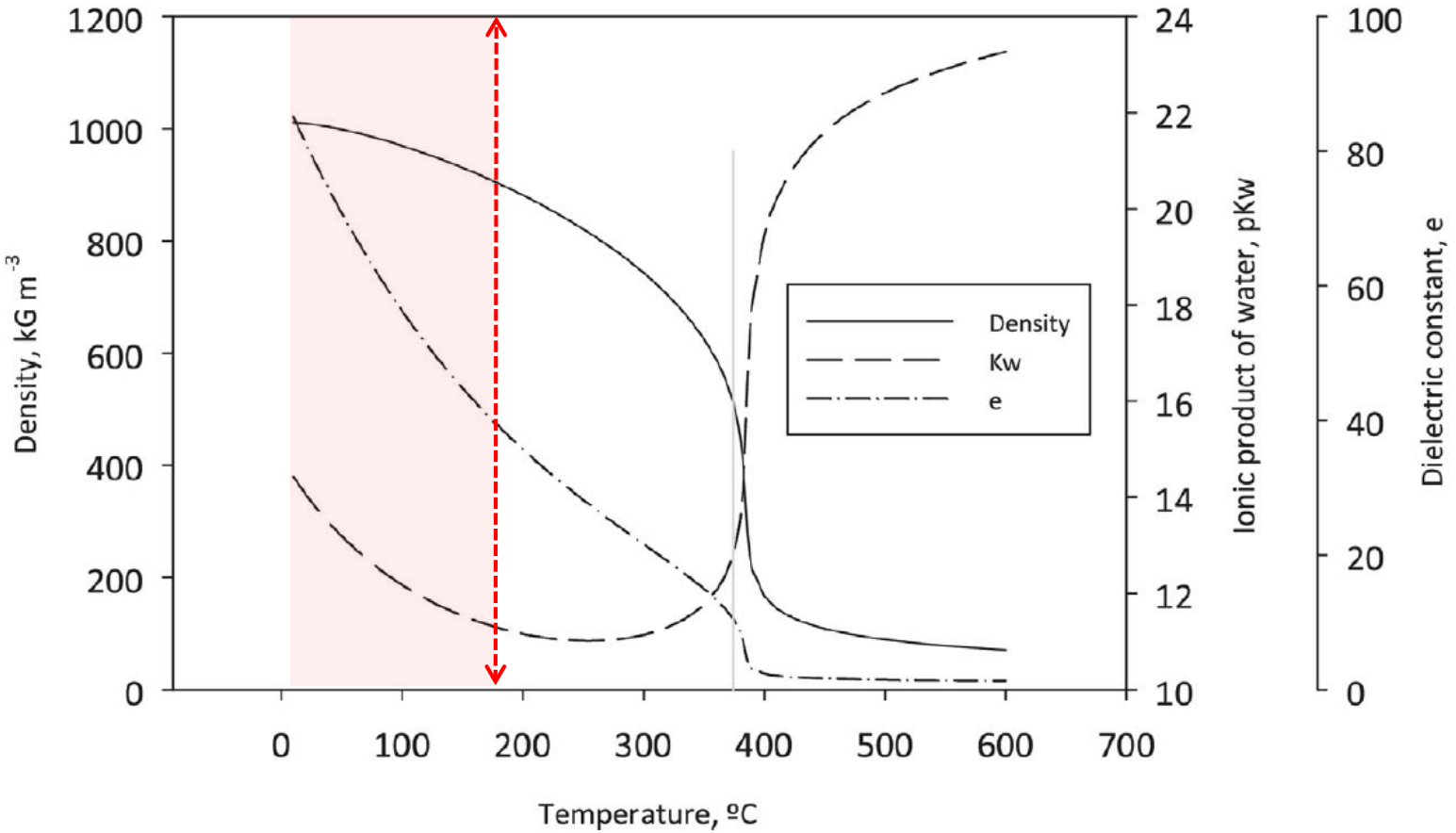


*Adapted from Plaza & Turner et al. (2015)



100 – 374 °C

Subcritical Water Extraction



*Cocero et al. (2018)

OBJECTIVES

TO EVALUATE SUBCRITICAL WATER EFFECT ON THE HYDROLYSIS / EXTRACTION OF BIOACTIVE COMPOUNDS FROM MACROALGA RESIDUE

TO STUDY THE EFFECT OF HEATING RATE

TO STUDY THE EFFECT OF RESIDENCE TIME

18th European Meeting on Supercritical fluids
May 4th-6th, 2021 - ONLINE

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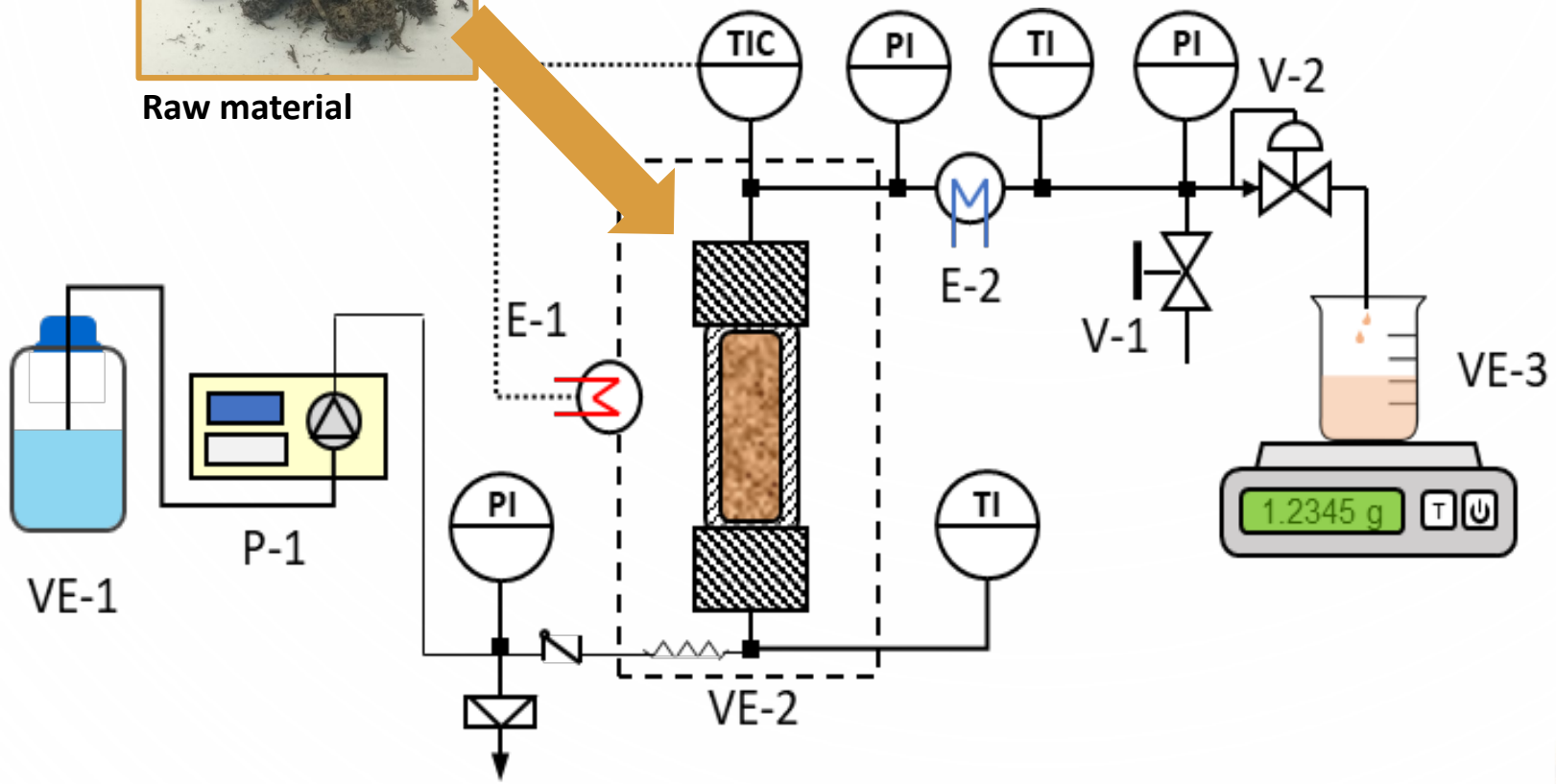
EQUIPMENT: REACTOR

Raw material

SEMICONTINUOUS FIXED-BED REACTOR



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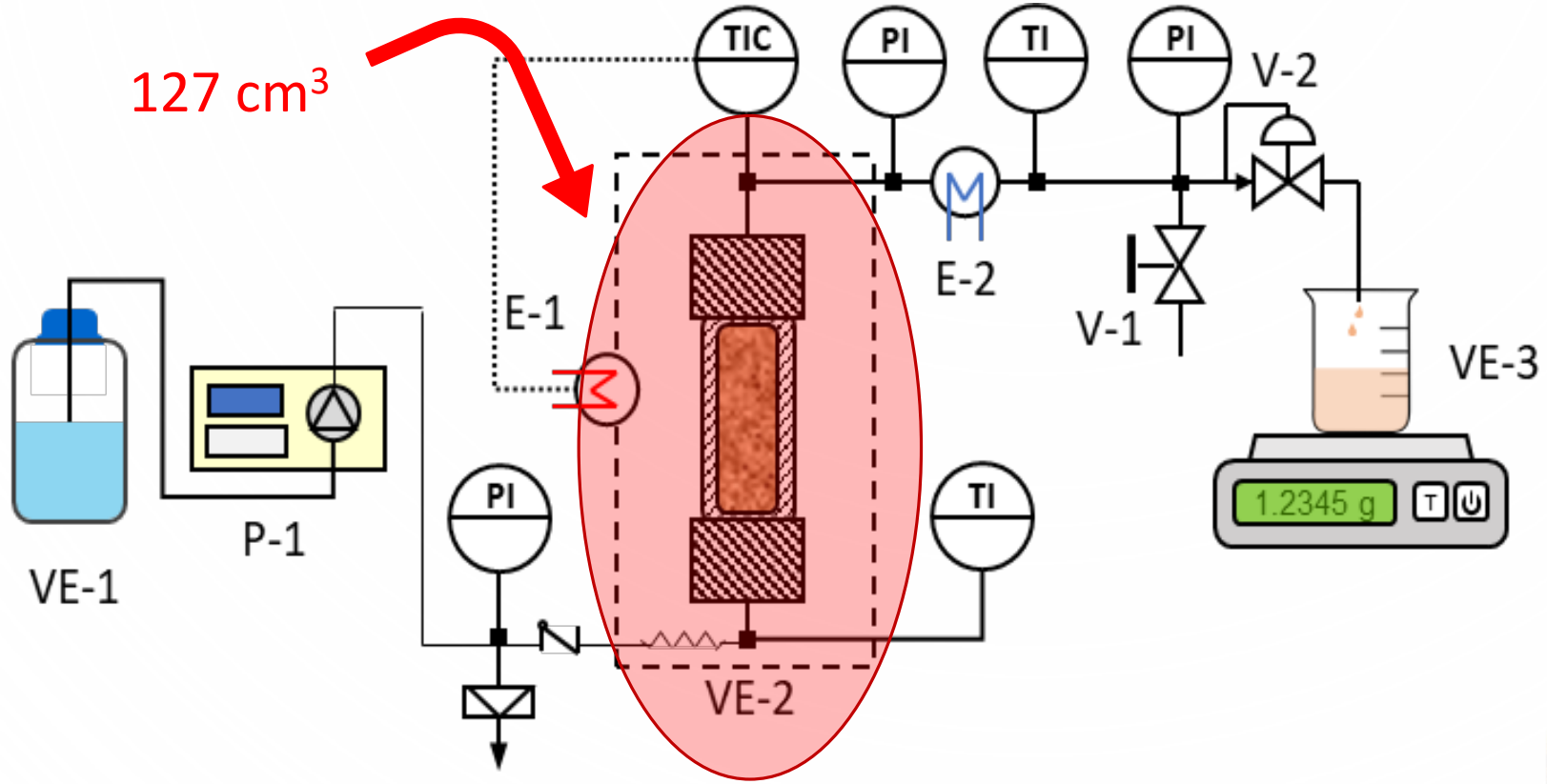
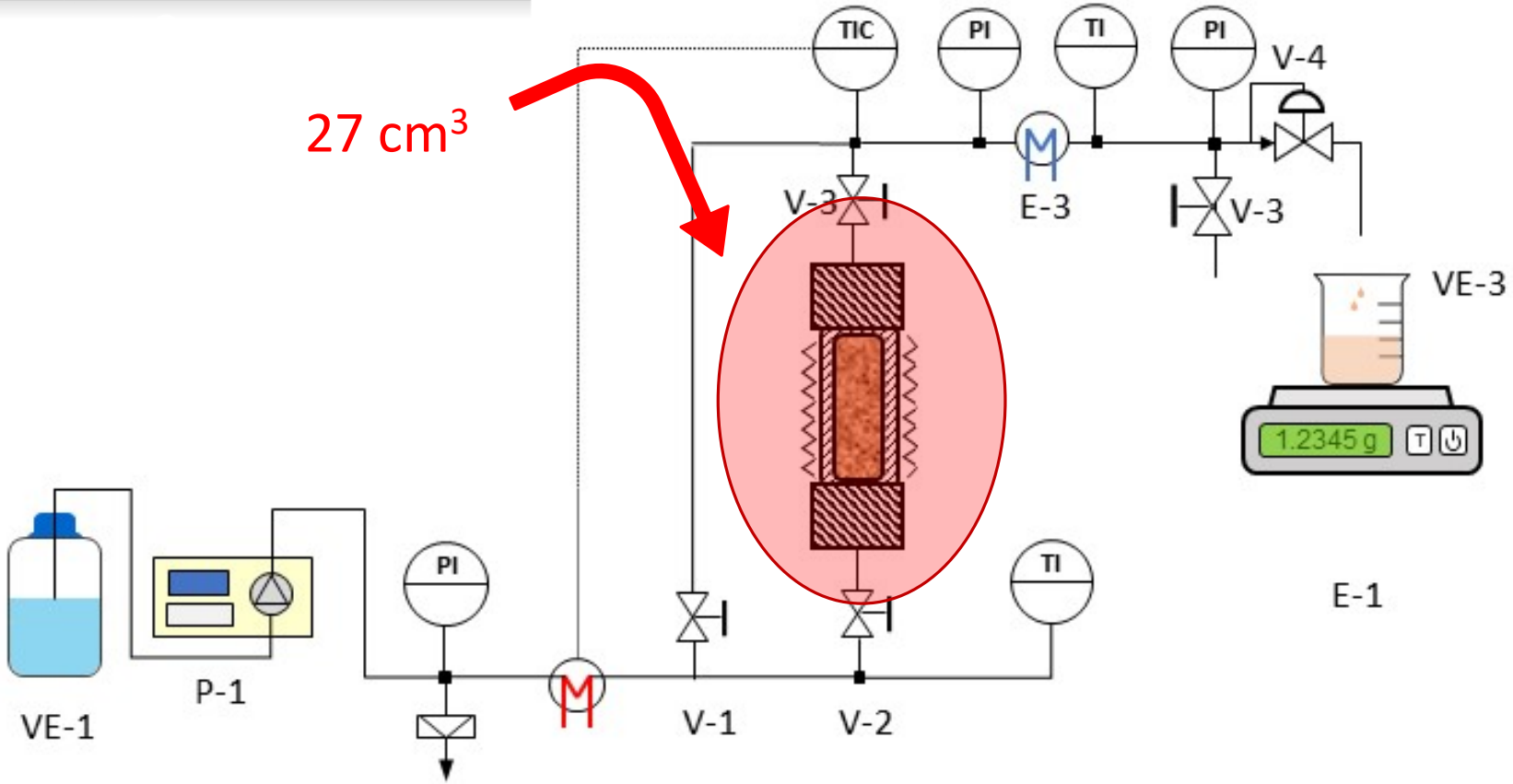
Configuration 1



EQUIPMENT: REACTOR

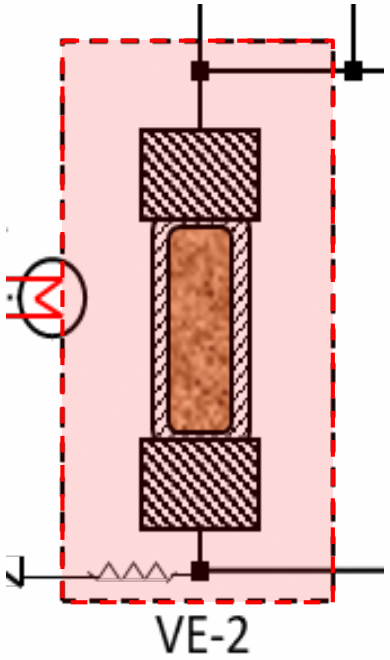
Configuration 2



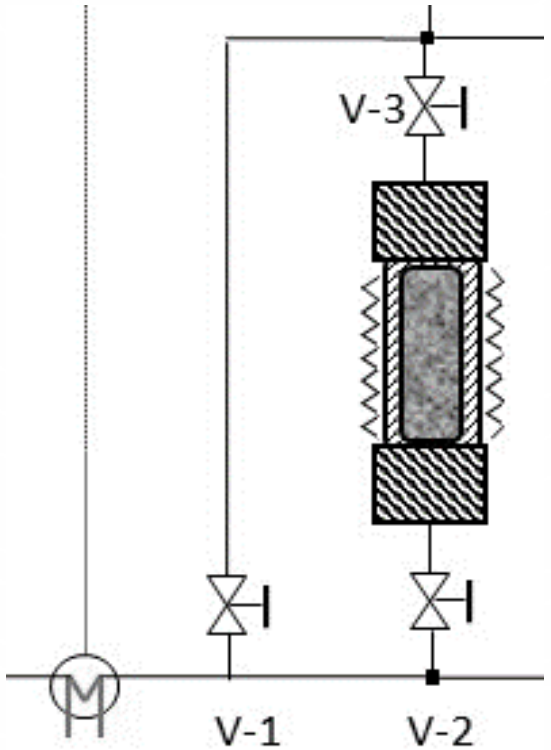
EQUIPMENT: HEATING SYSTEM

Configuration 1

HEATING SYSTEM: Oven

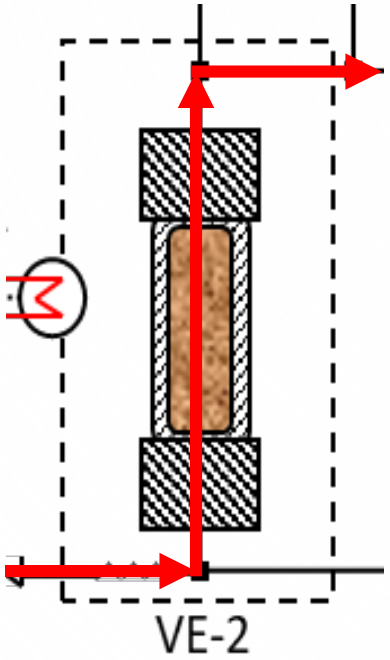


Configuration 2



Equipment: Heating system

Configuration 1



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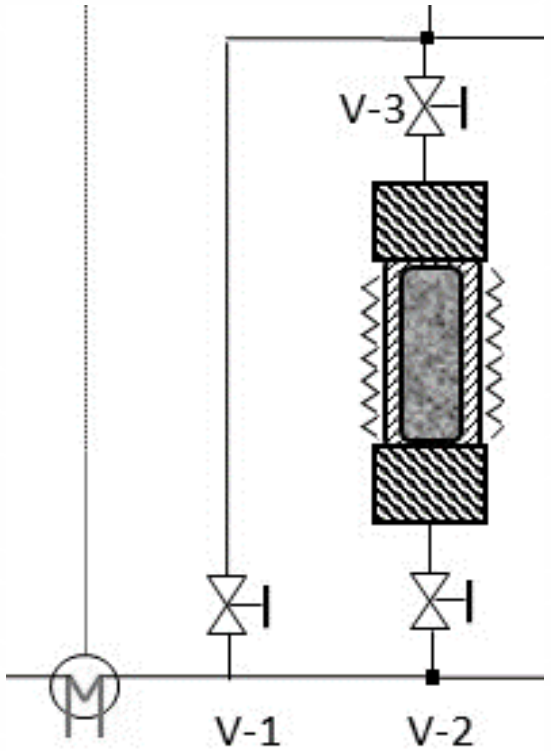

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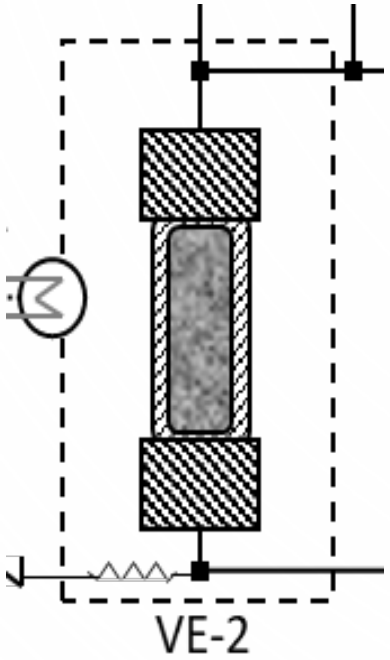
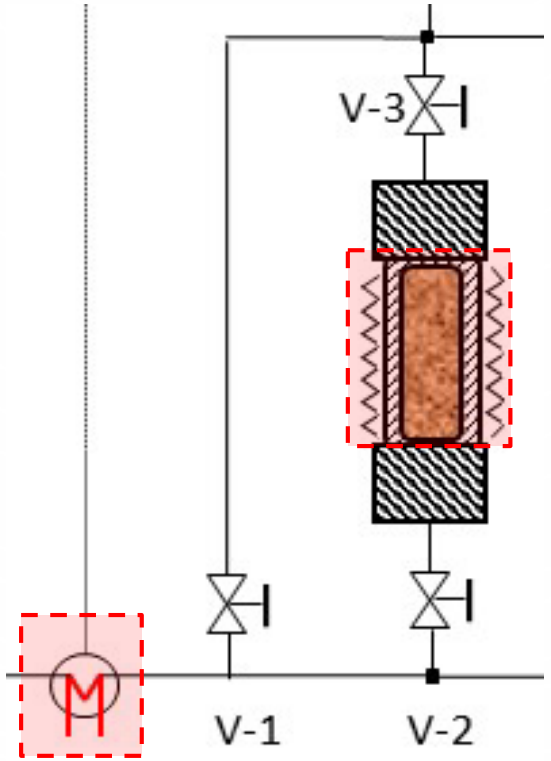


Configuration 2

HEATING SYSTEM: Heating Jacket



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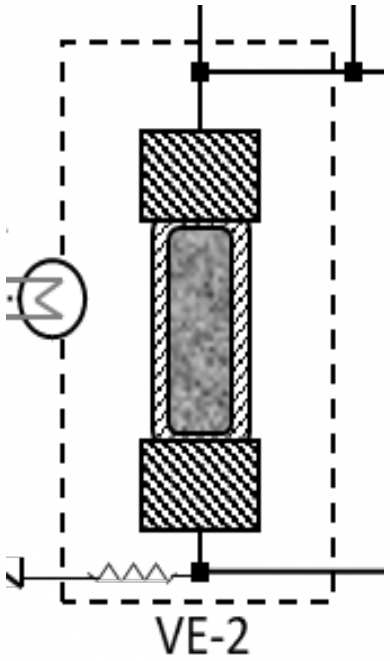

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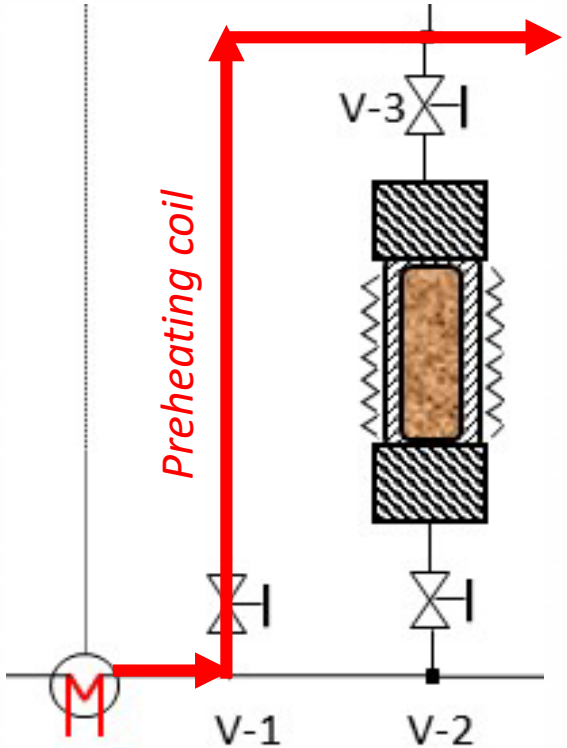

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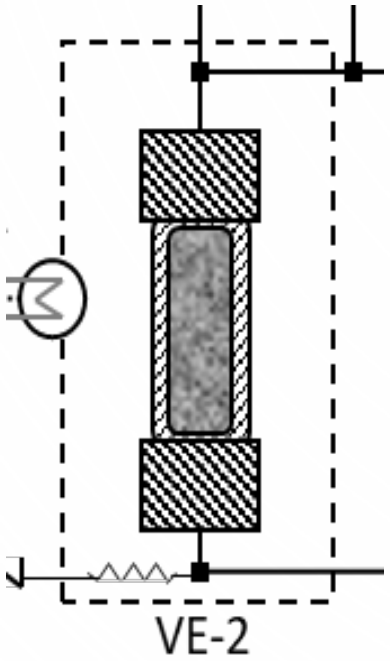
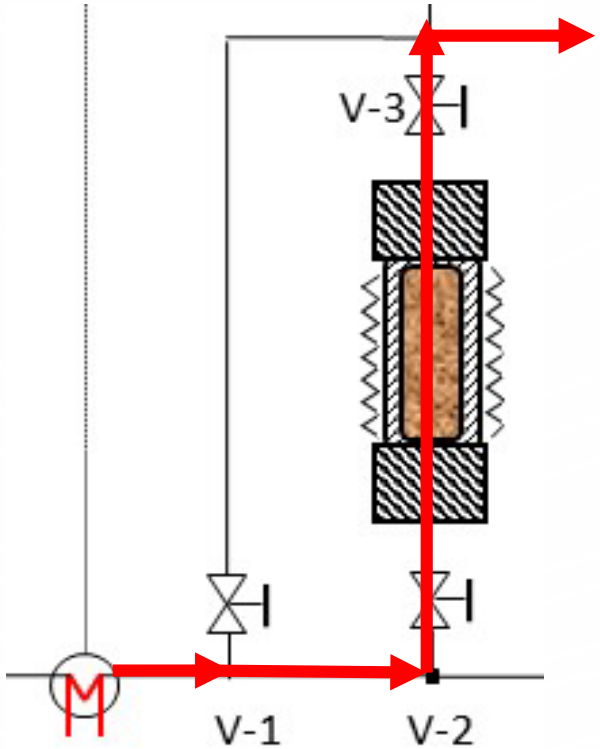
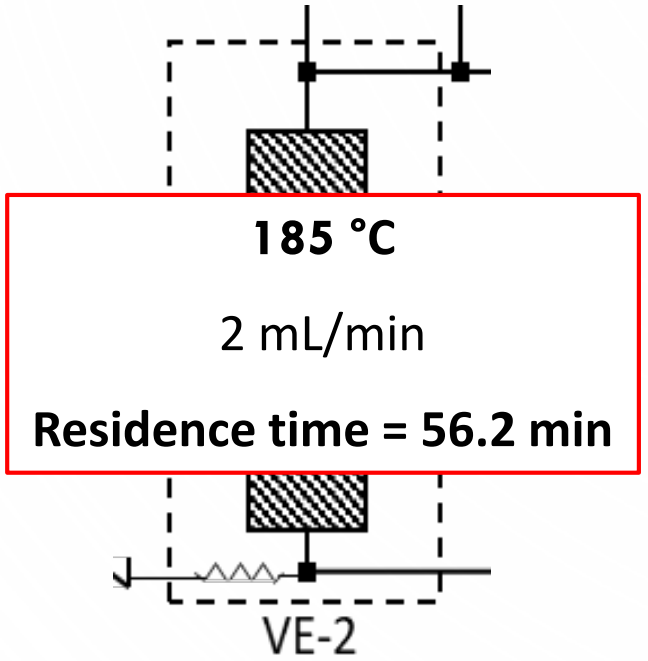


Configuration 2



EQUIPMENT: OPERATIONAL CONDITIONS

Configuration 1

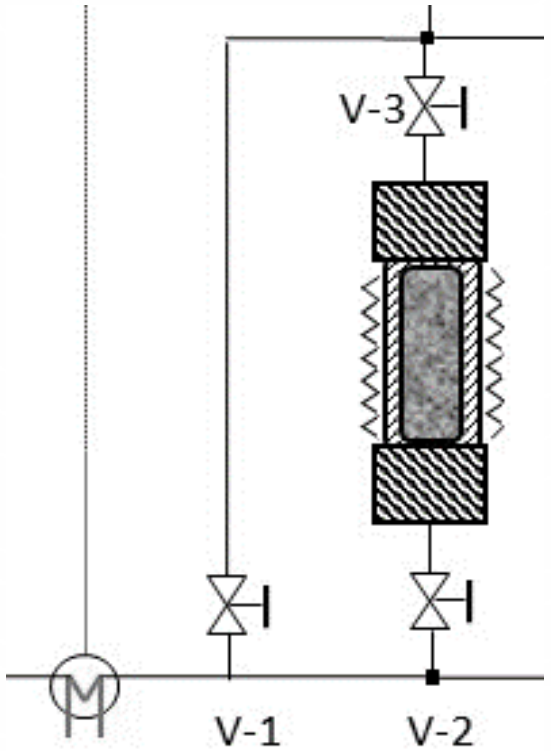


185 °C

2 mL/min

Residence time = 56.2 min

Configuration 2



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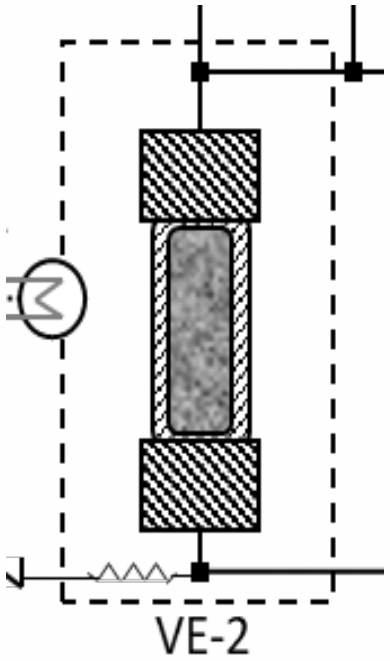
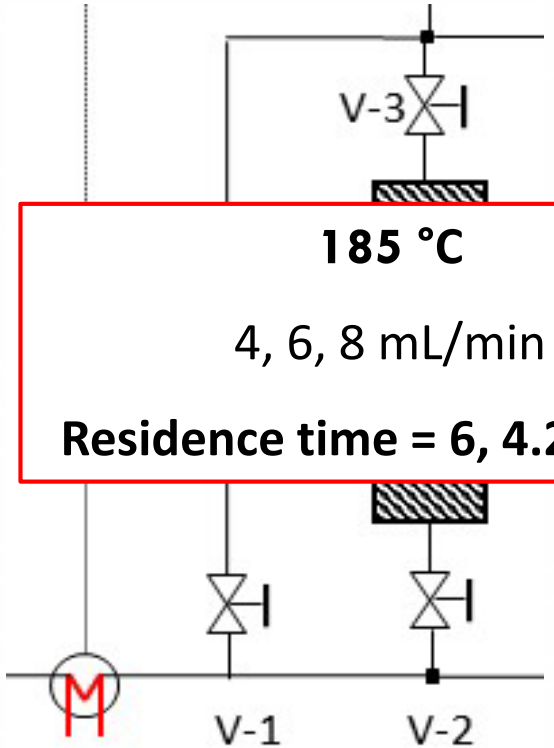
Configuration 1



Configuration 2

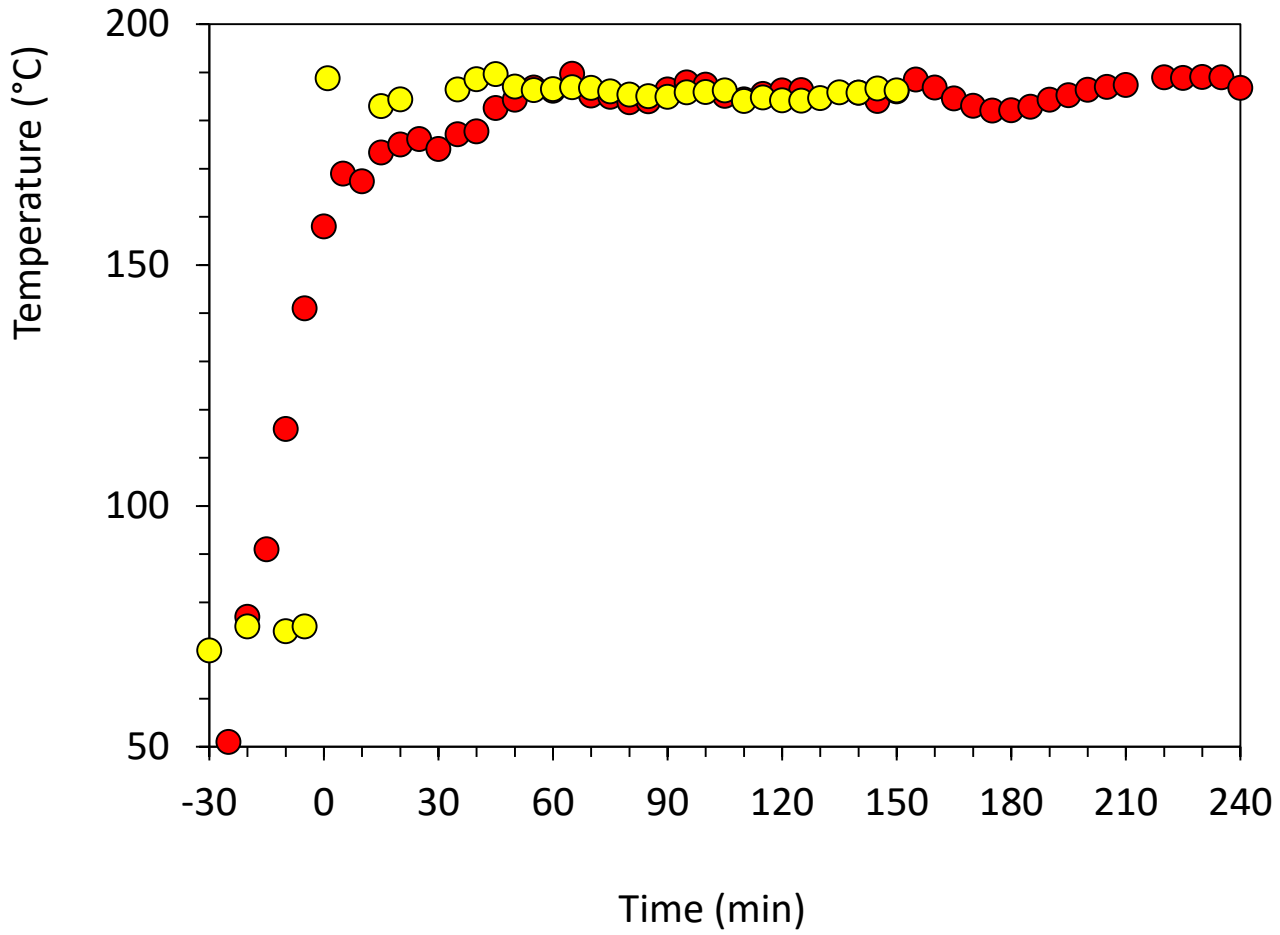


185 °C

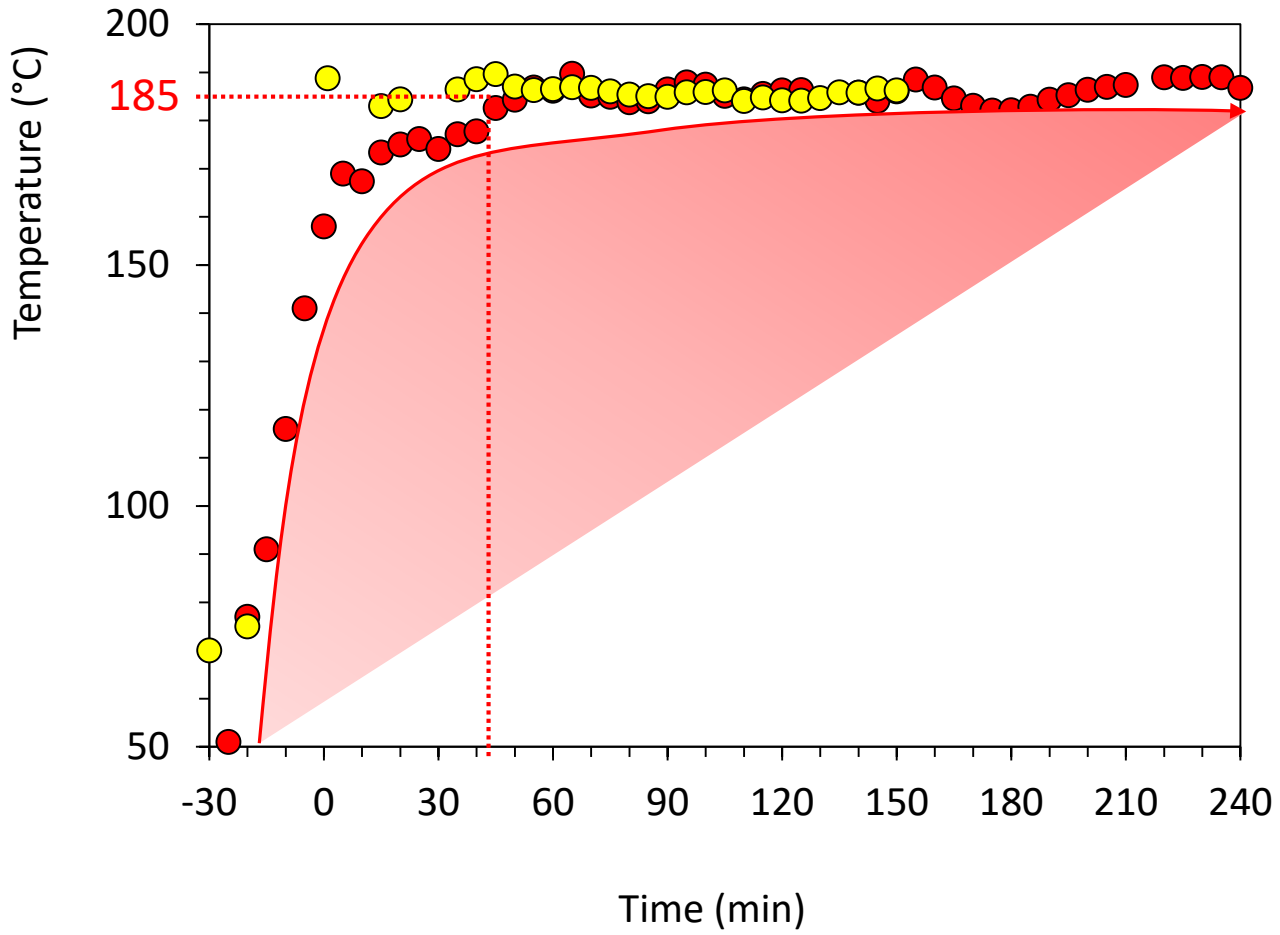
4, 6, 8 mL/min

Residence time = 6, 4.2, 3 min

TEMPERATURE PROFILE



TEMPERATURE PROFILE



Configuration 1

- Oven
- 127 cm^3

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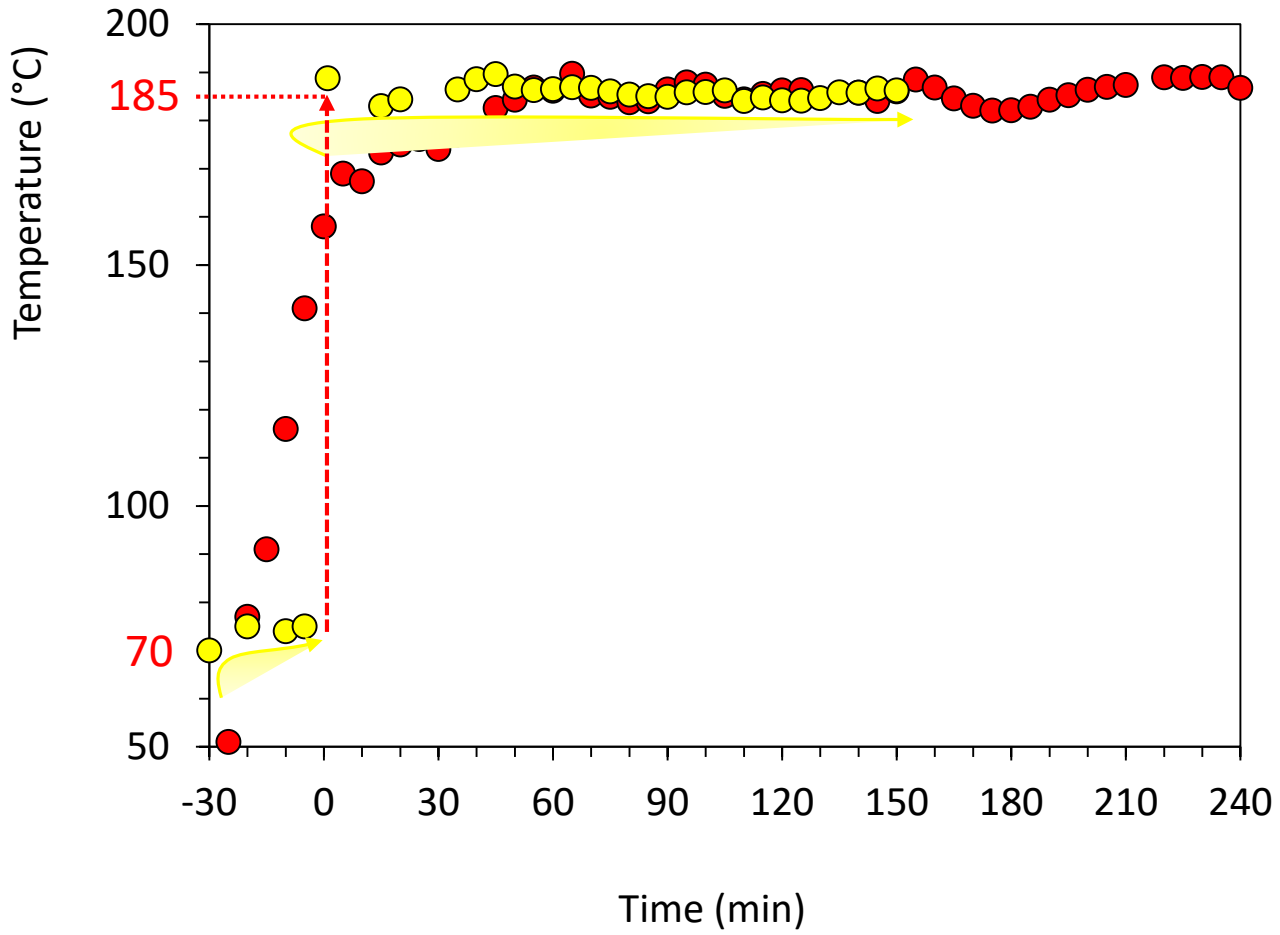
TEMPERATURE PROFILE

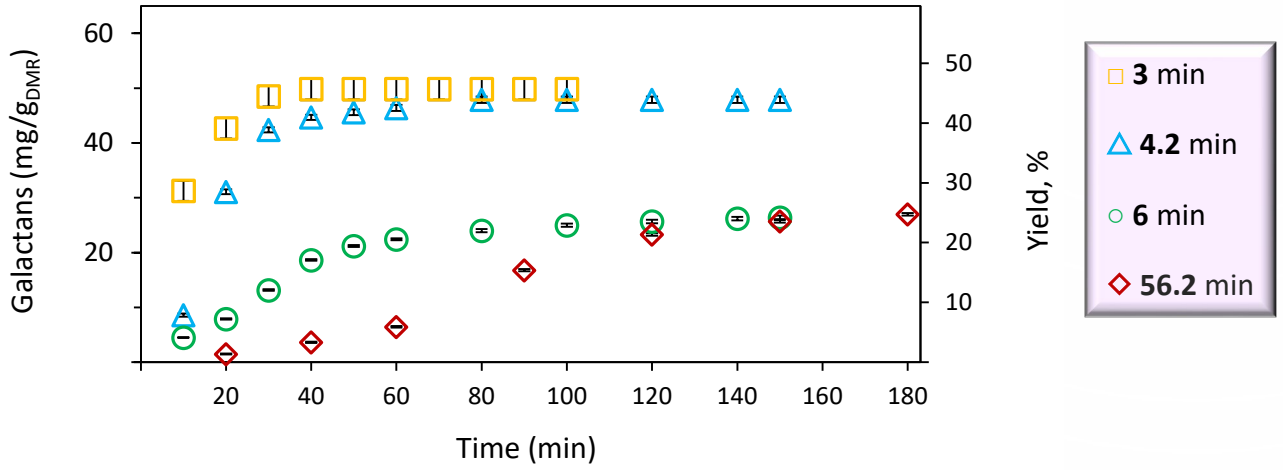


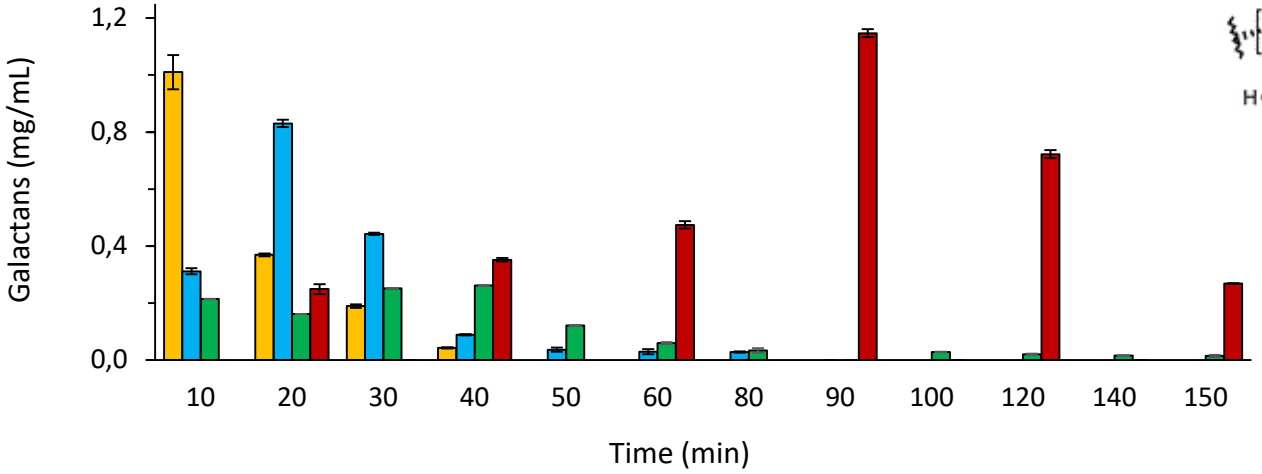
Configuration 2

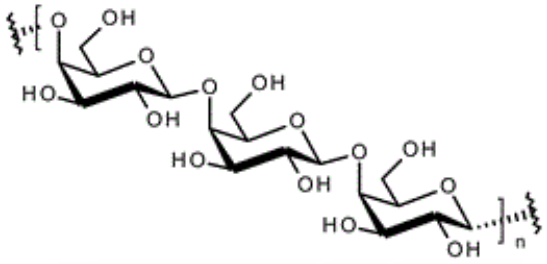
- Heating jacket
- Preheating coil
- 27 cm^3

CARBOHYDRATE FRACTION
HYDROLYSIS/EXTRACTION

GALACTANS







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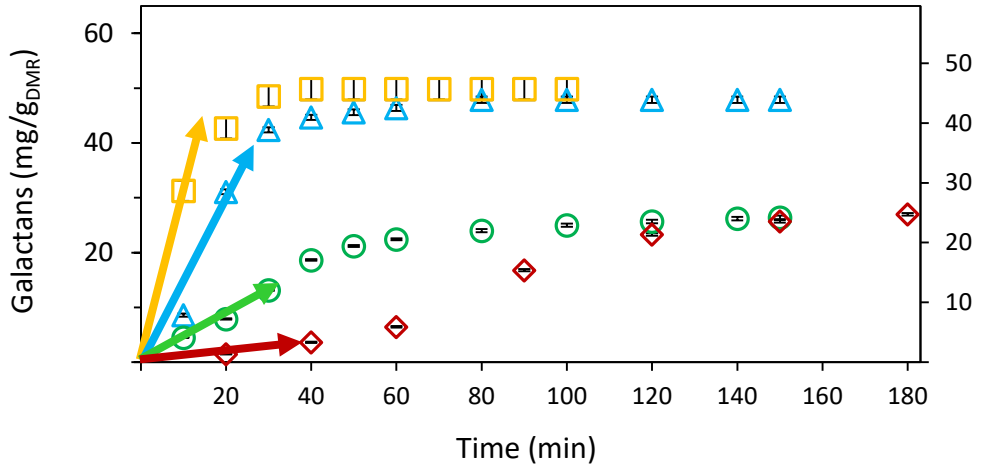
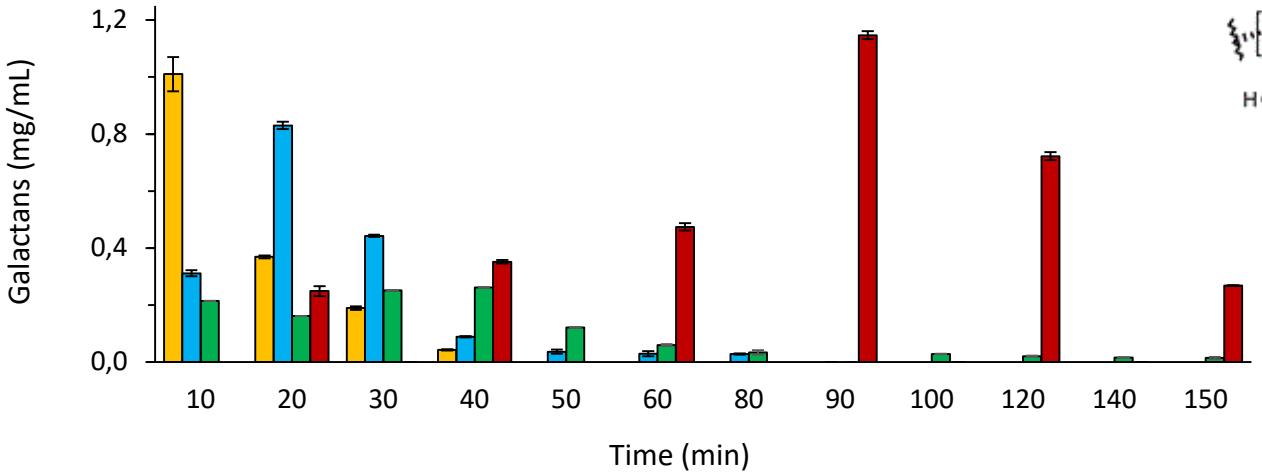
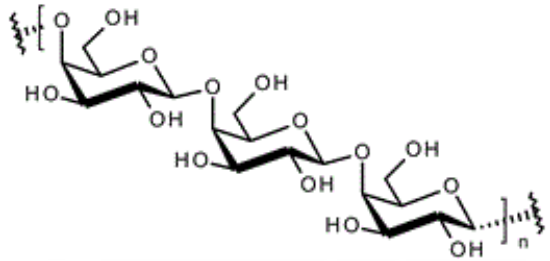


It was observed an **increase of the initial slope** of the solubilisation curve by **decreasing RT (increasing flow rate)**.





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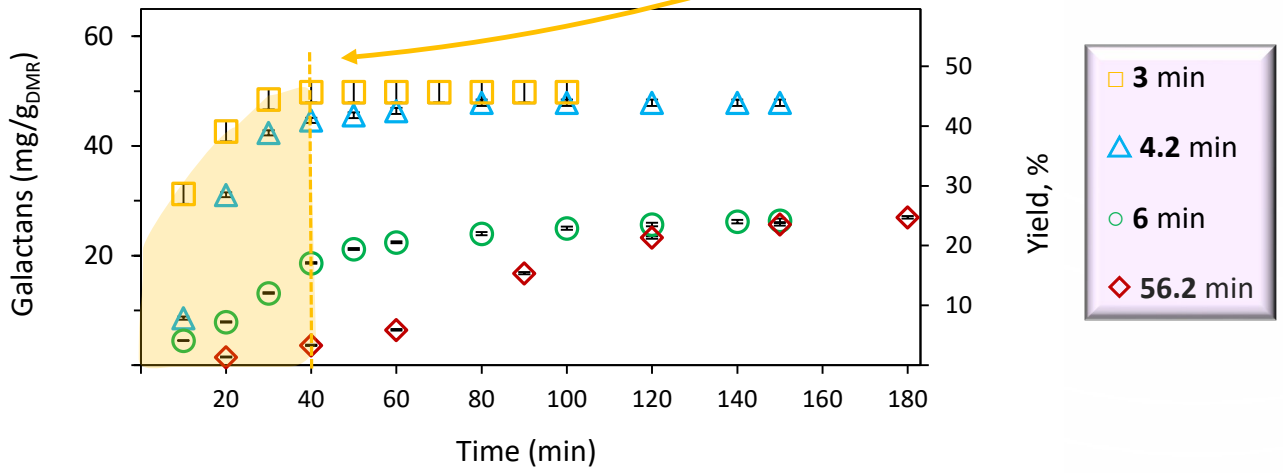
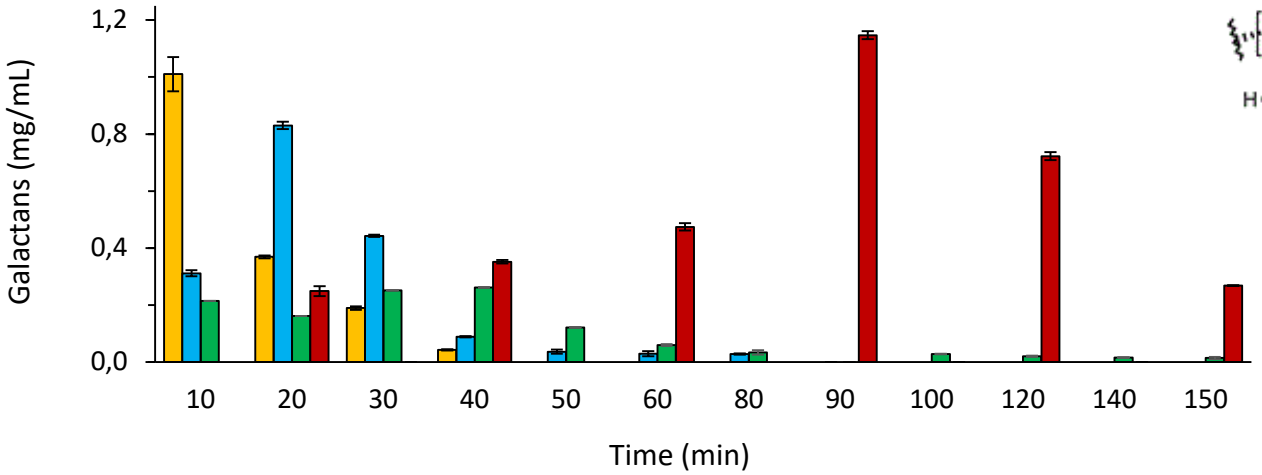
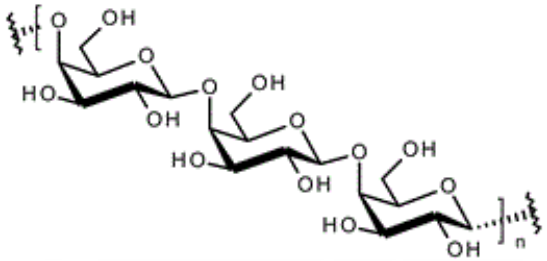


Configuration 2: [*Heating jacket*]

The maximum yield (≈ 45 %) was reached at approx. 40 min.





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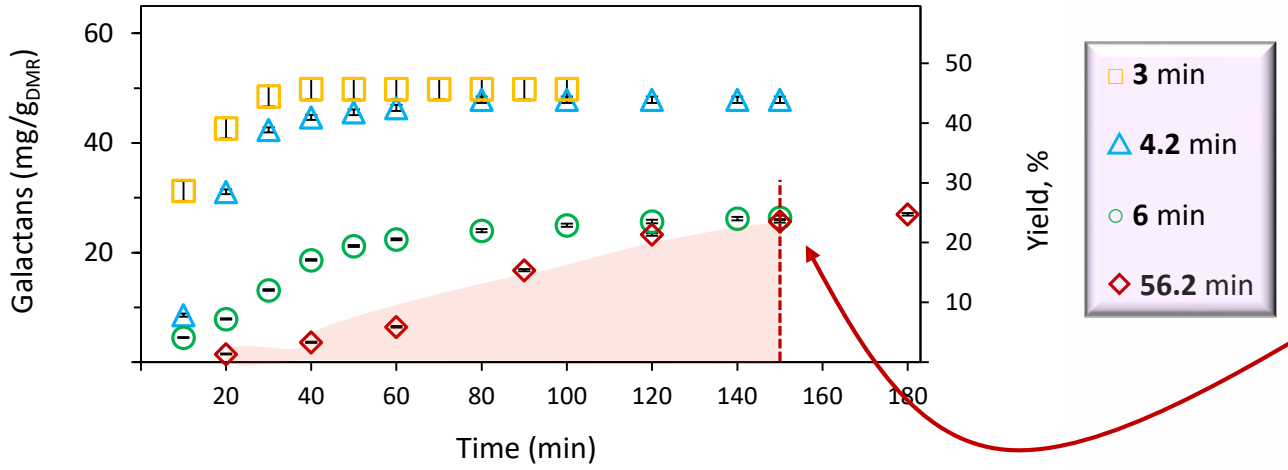
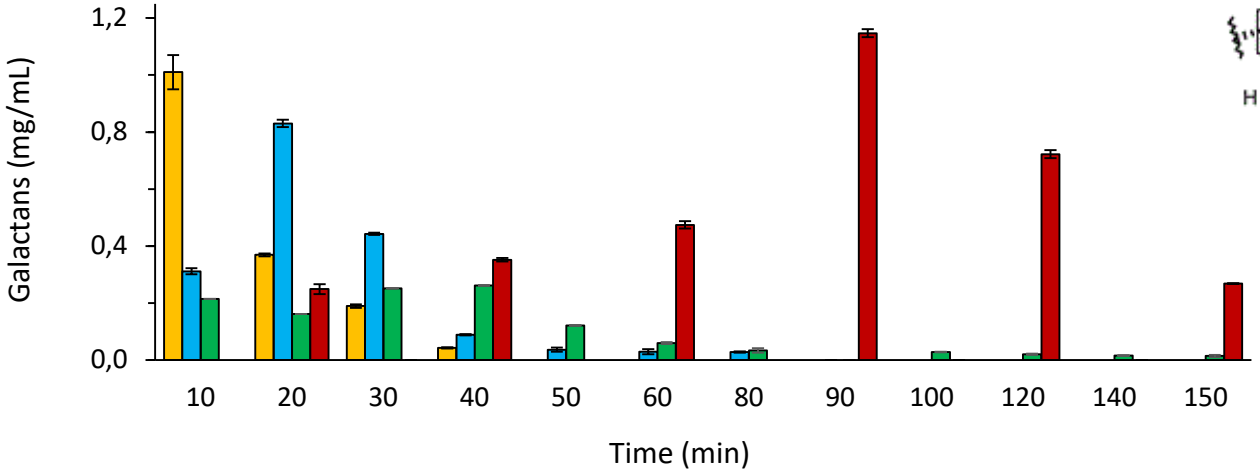
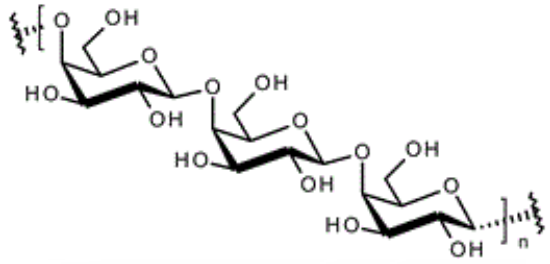


Configuration 1: [*oven*]

The maximum yield (≈ 25 %) was not reached until 140-160 min





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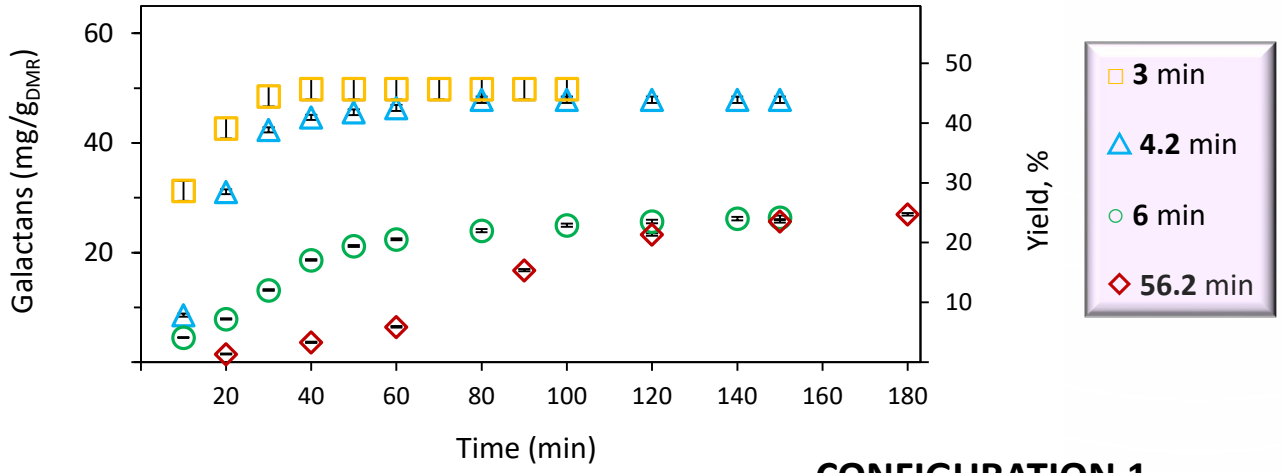
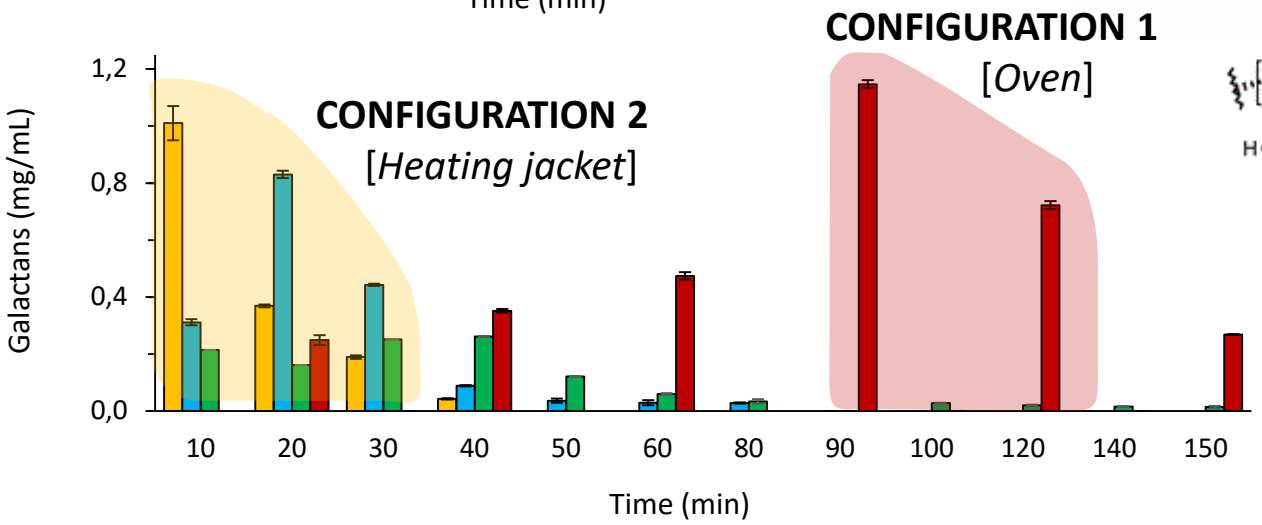
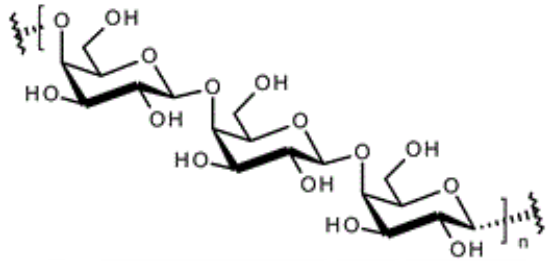
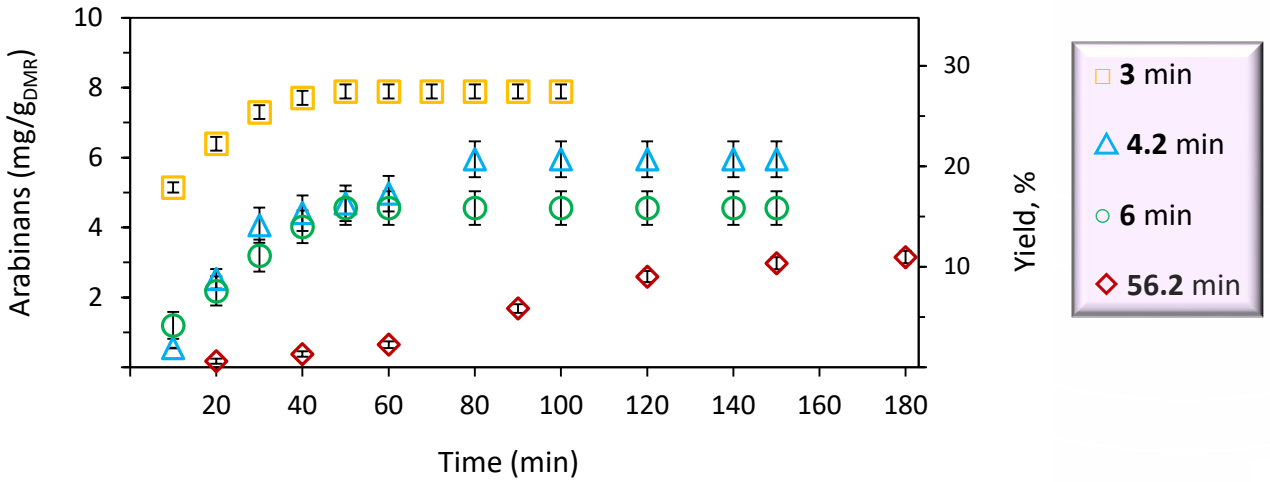


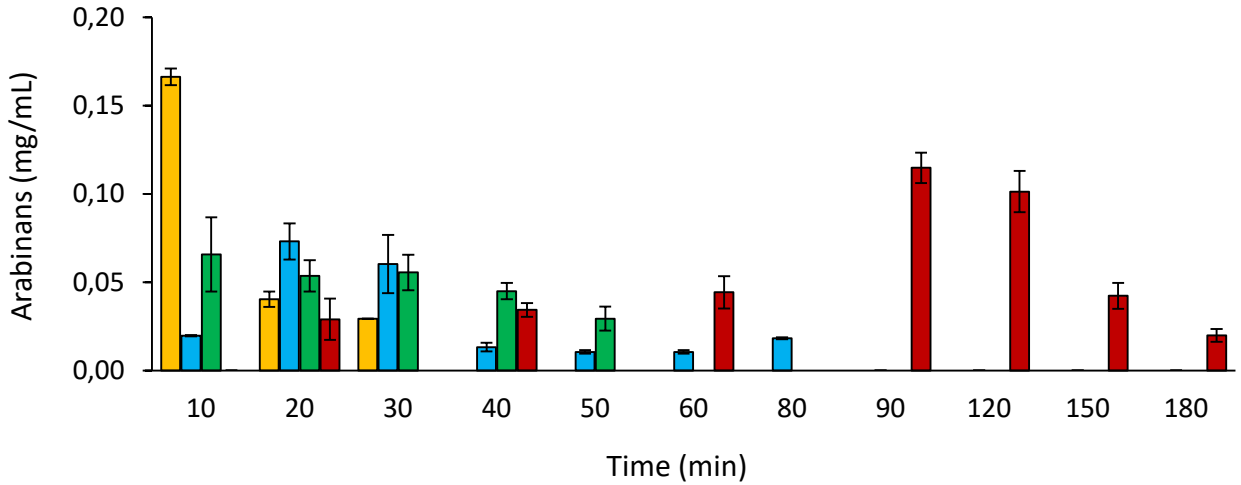


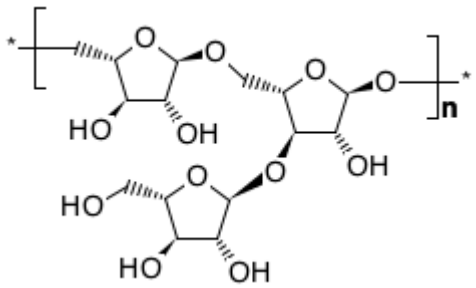


CARBOHYDRATE FRACTION
HYDROLYSIS/EXTRACTION

ARABINANS







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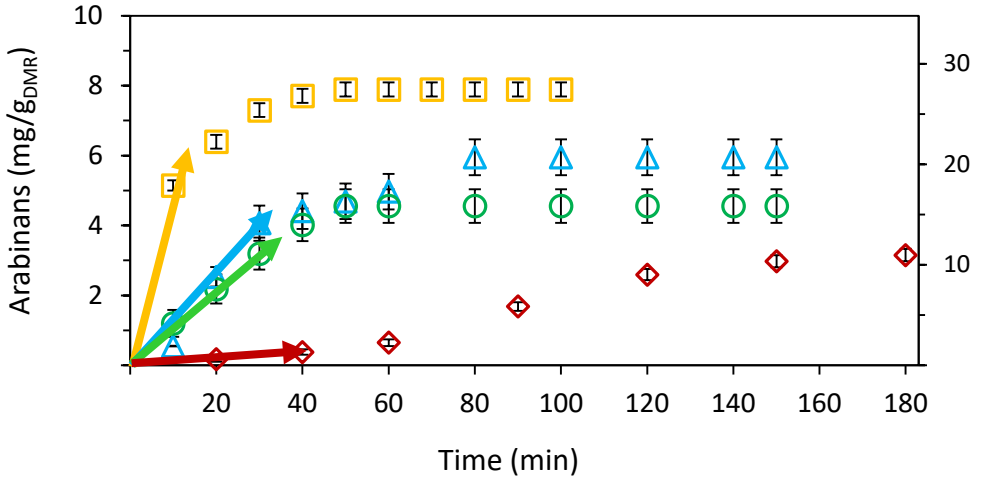
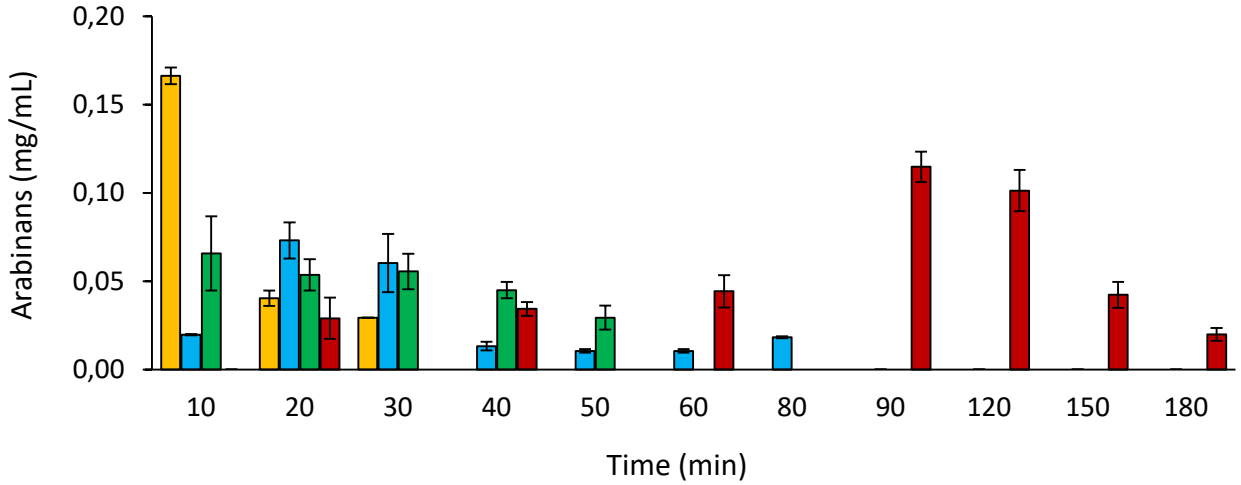
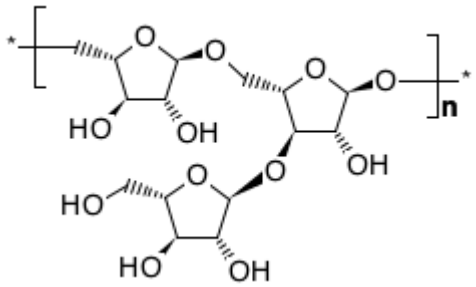


Decreasing RT by increasing flow rate results in **higher initial slope**.





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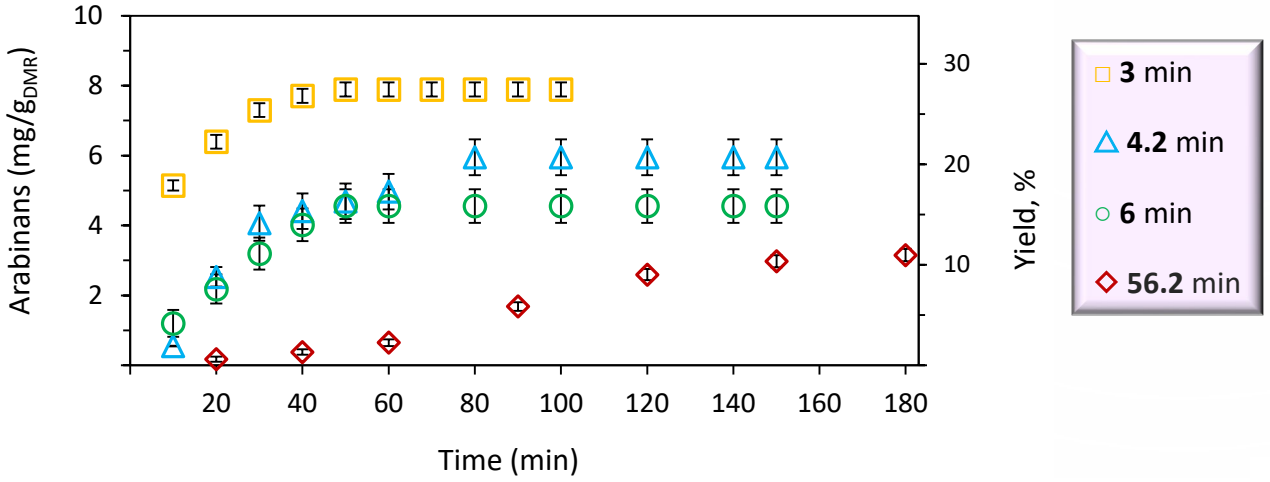

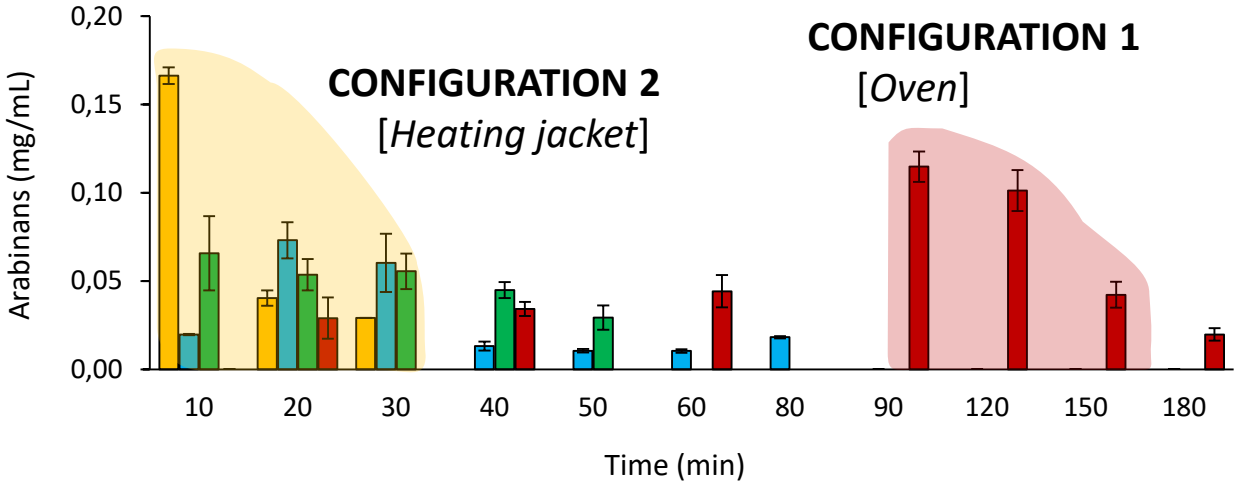

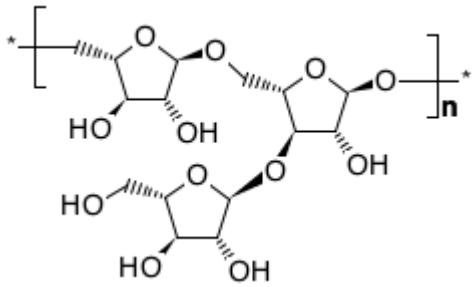

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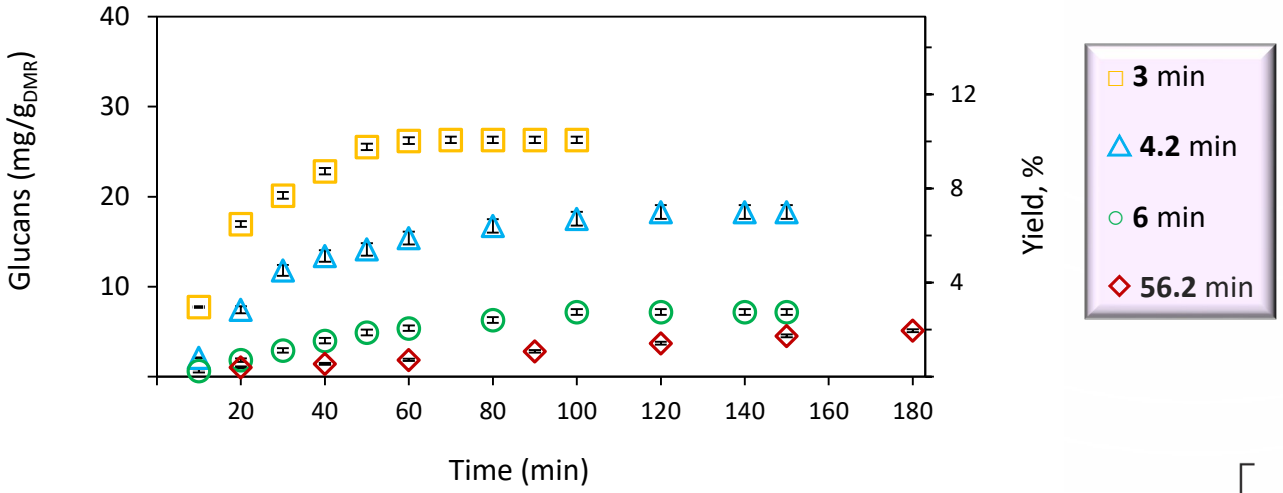
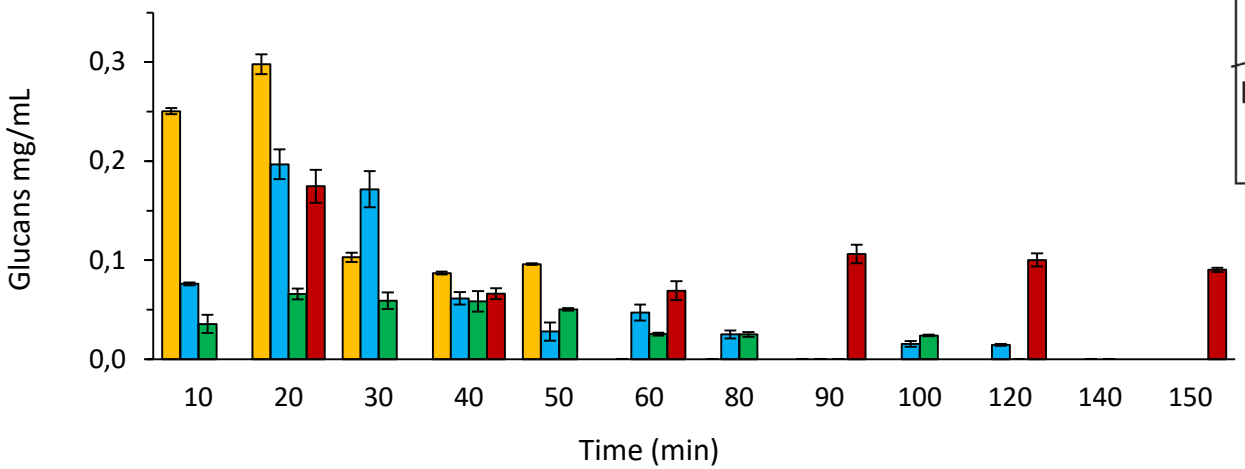
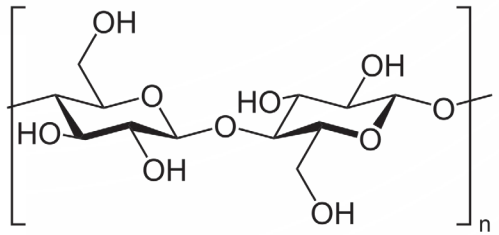
GLUCANS







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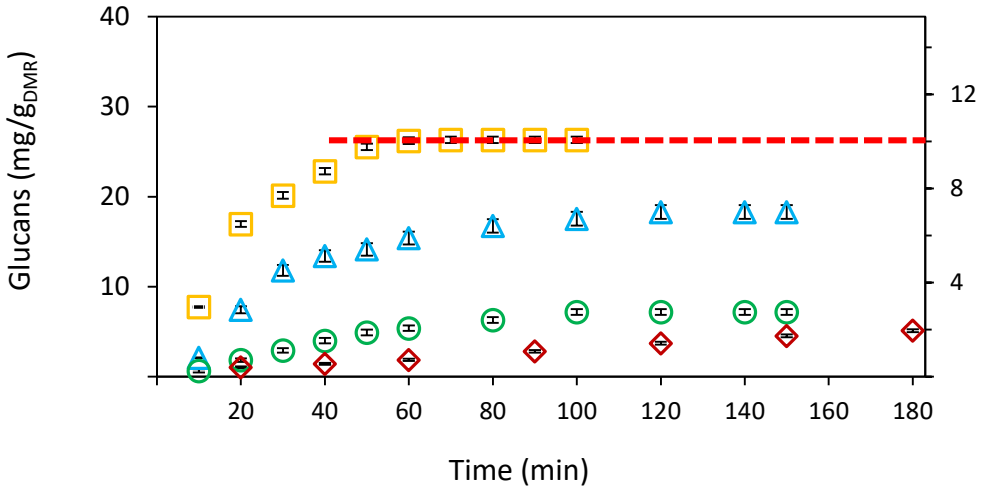
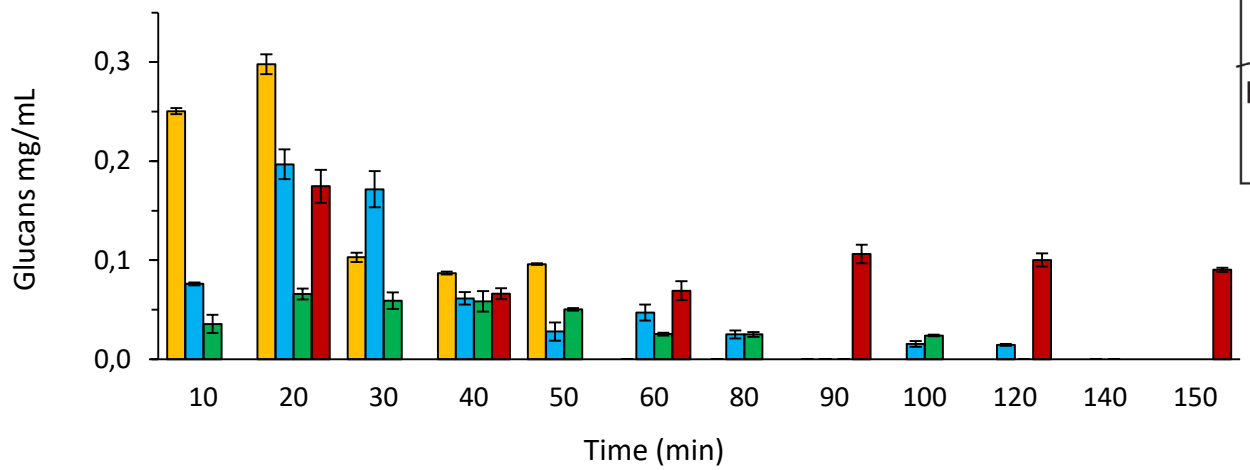
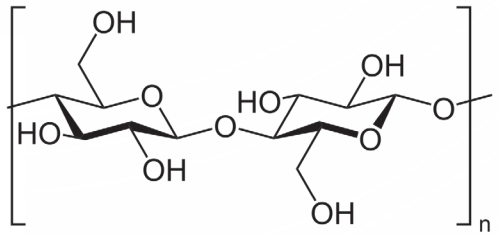


- **3** min
- **4.2** min
- **6** min
- **56.2** min

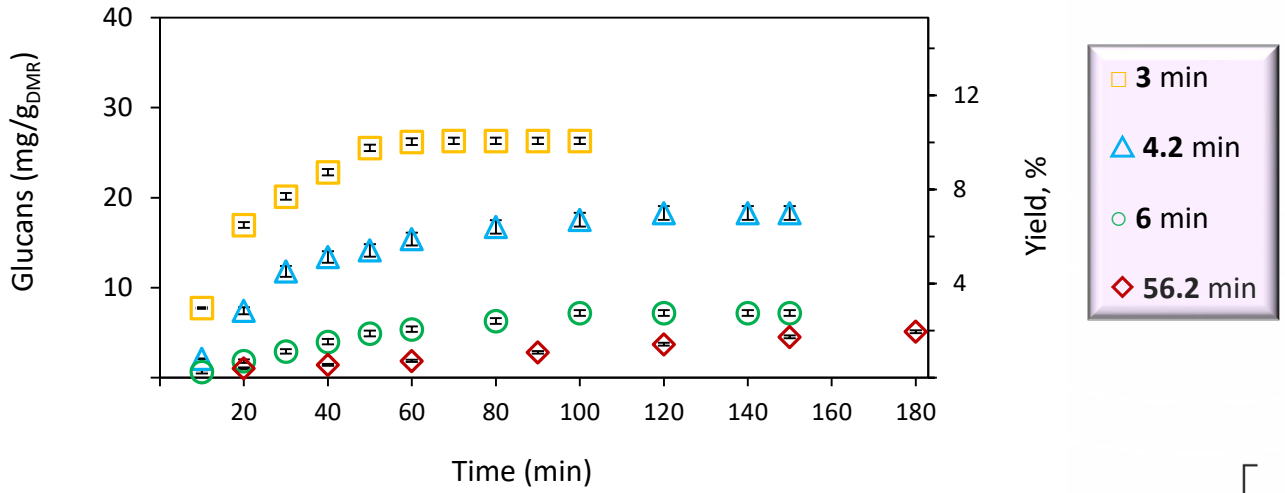
Same trend but lower extraction/hydrolysis yields (≈ 10 %) were observed for glucans fraction.

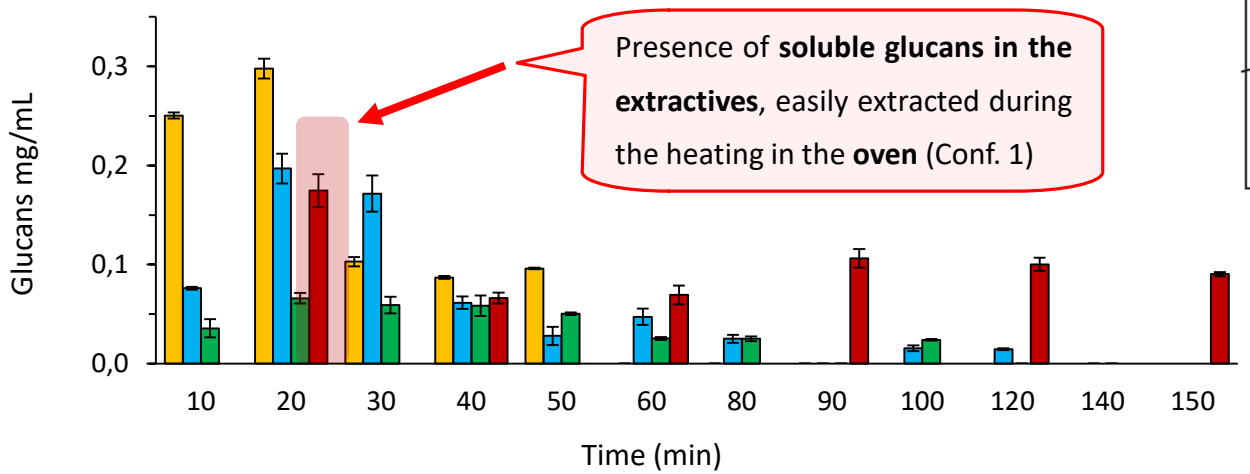


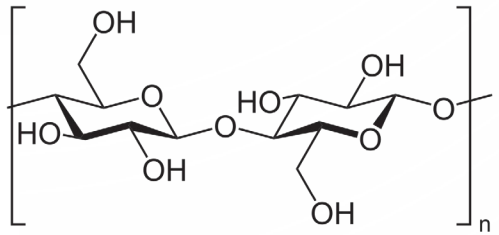


CARBOHYDRATE FRACTION
HYDROLYSIS/EXTRACTION

GLUCANS







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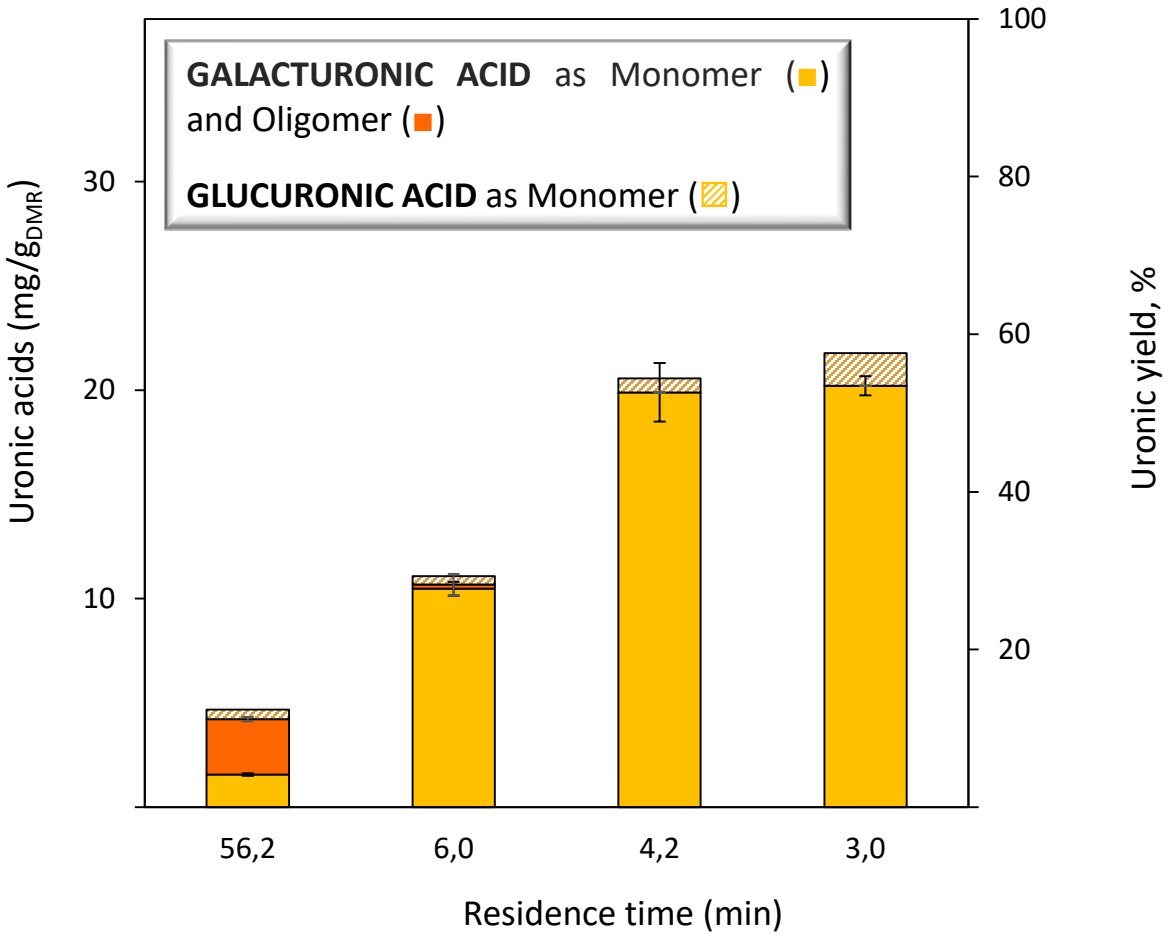
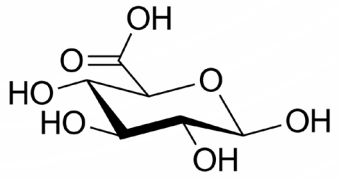
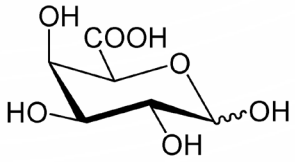
URONIC ACIDS



GLUCURONIC ACID



GALACTURONIC ACID



CARBOHYDRATE FRACTION
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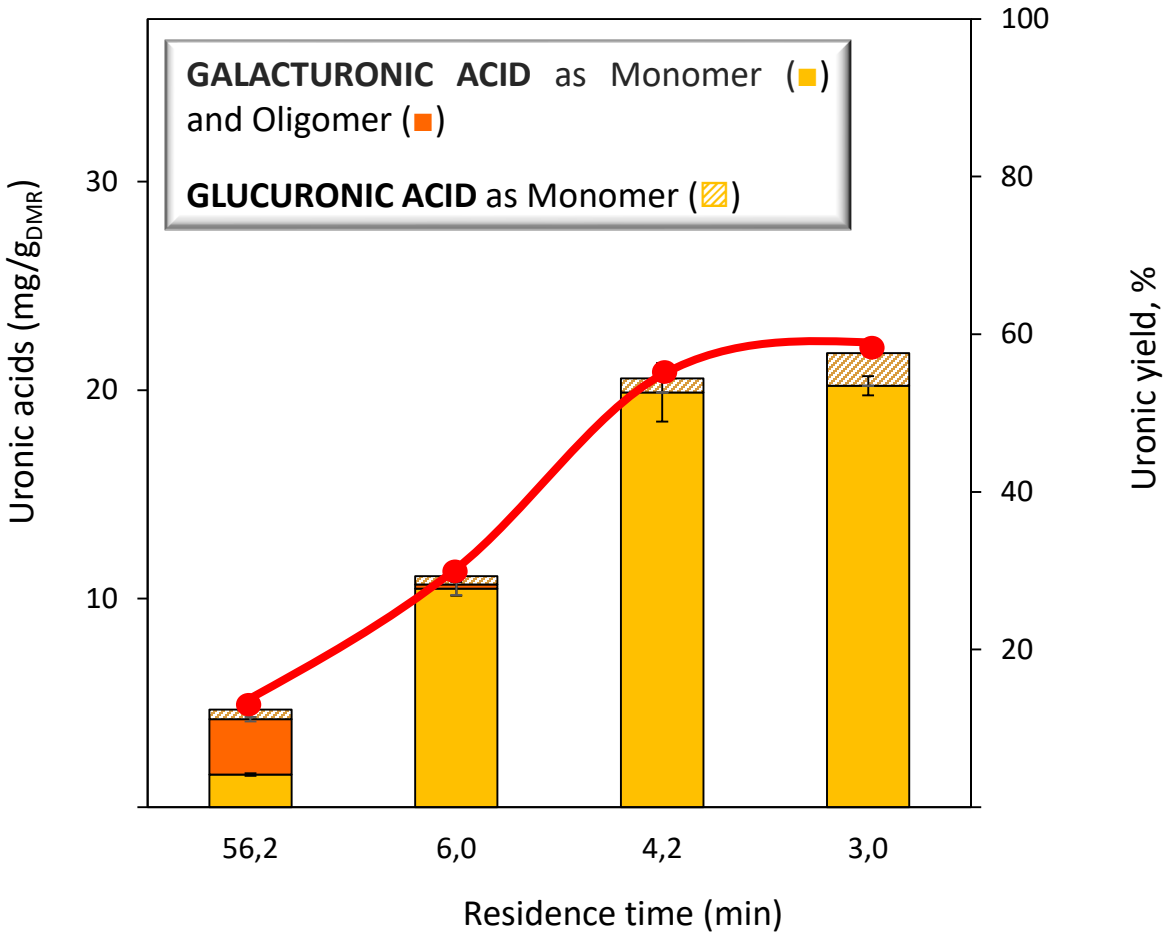
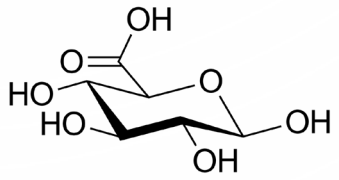
URONIC ACIDS

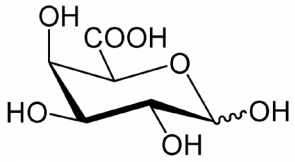


A **decrease in RT** led to an **increase in uronic acids yield**

GLUCURONIC ACID



GALACTURONIC ACID



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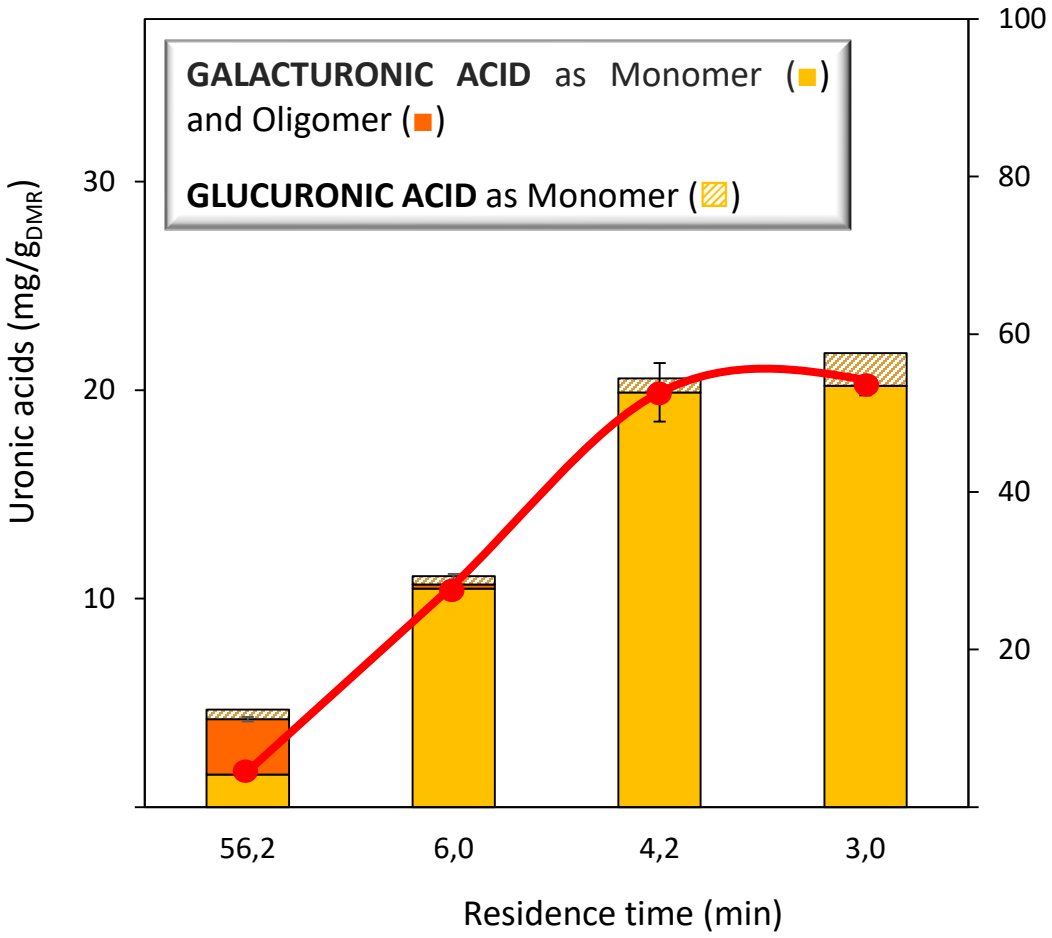
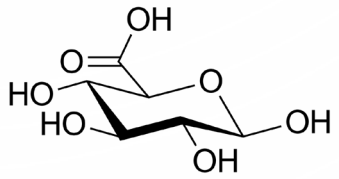
URONIC ACIDS

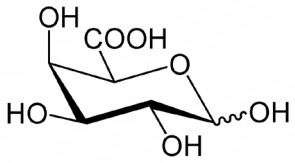


By **decreasing RT**, **Galacturonic acid** is mainly released as **monomer**.

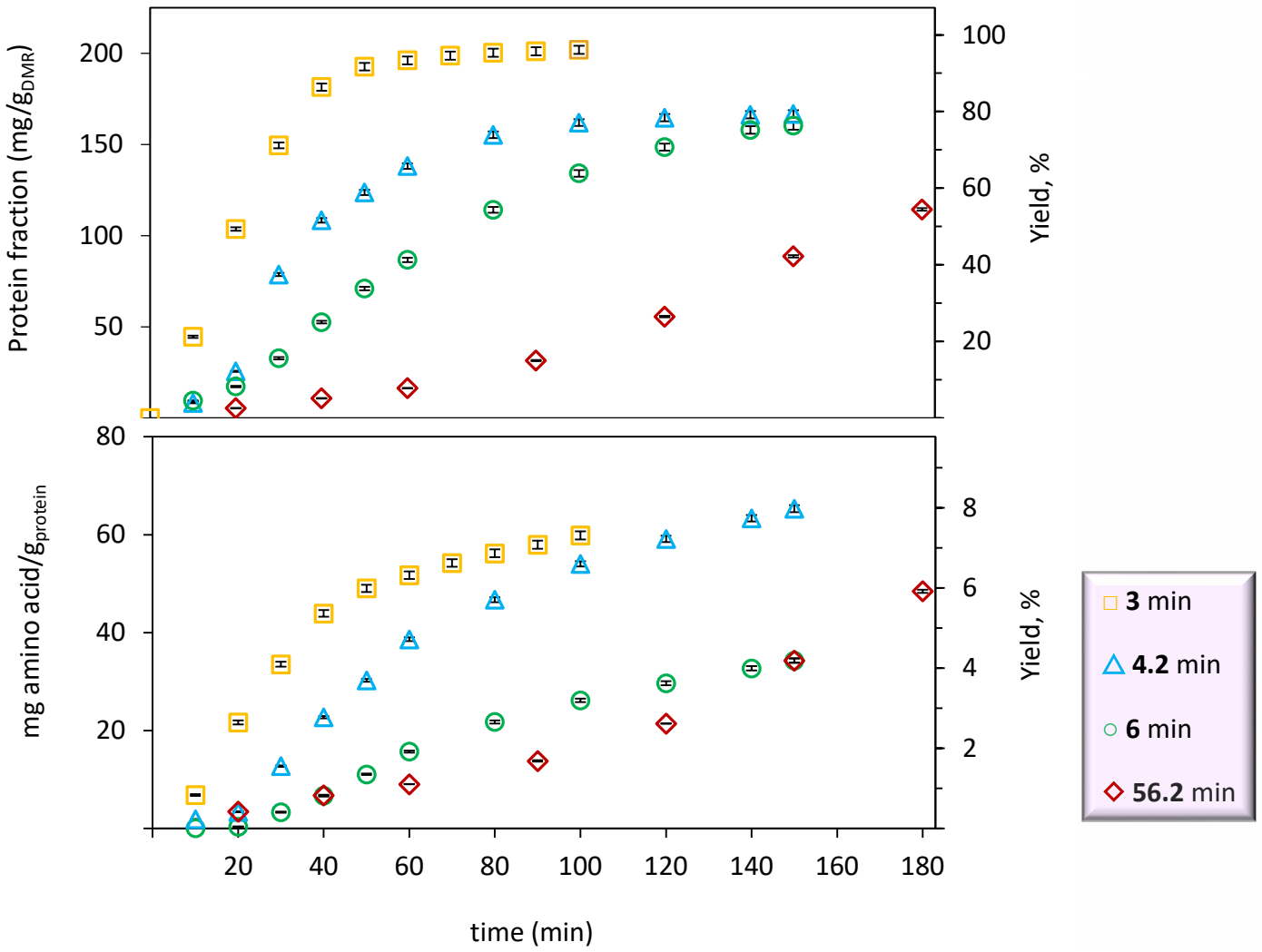
GLUCURONIC ACID



GALACTURONIC ACID



PROTEIN FRACTION HYDROLYSIS/EXTRACTION



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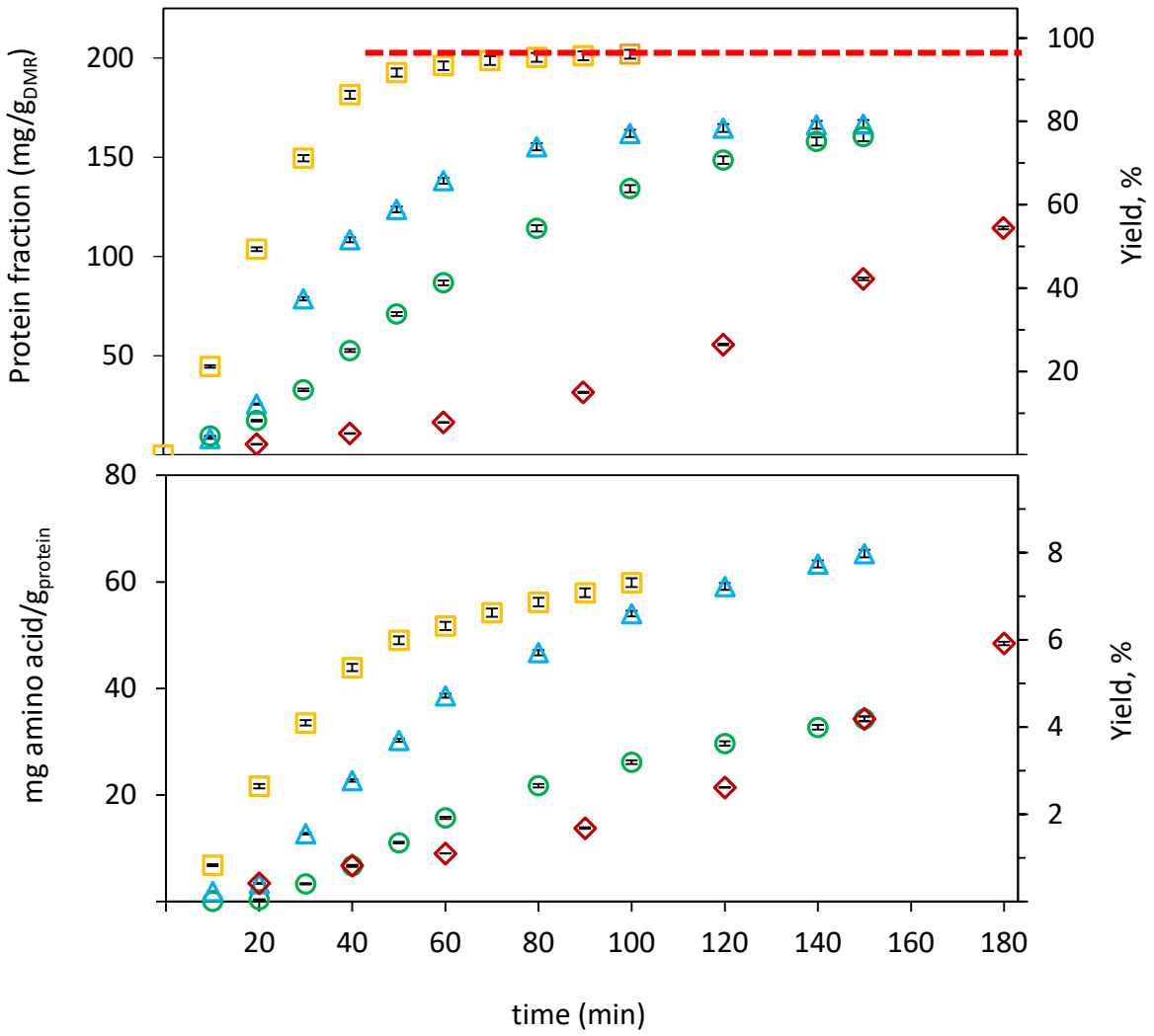
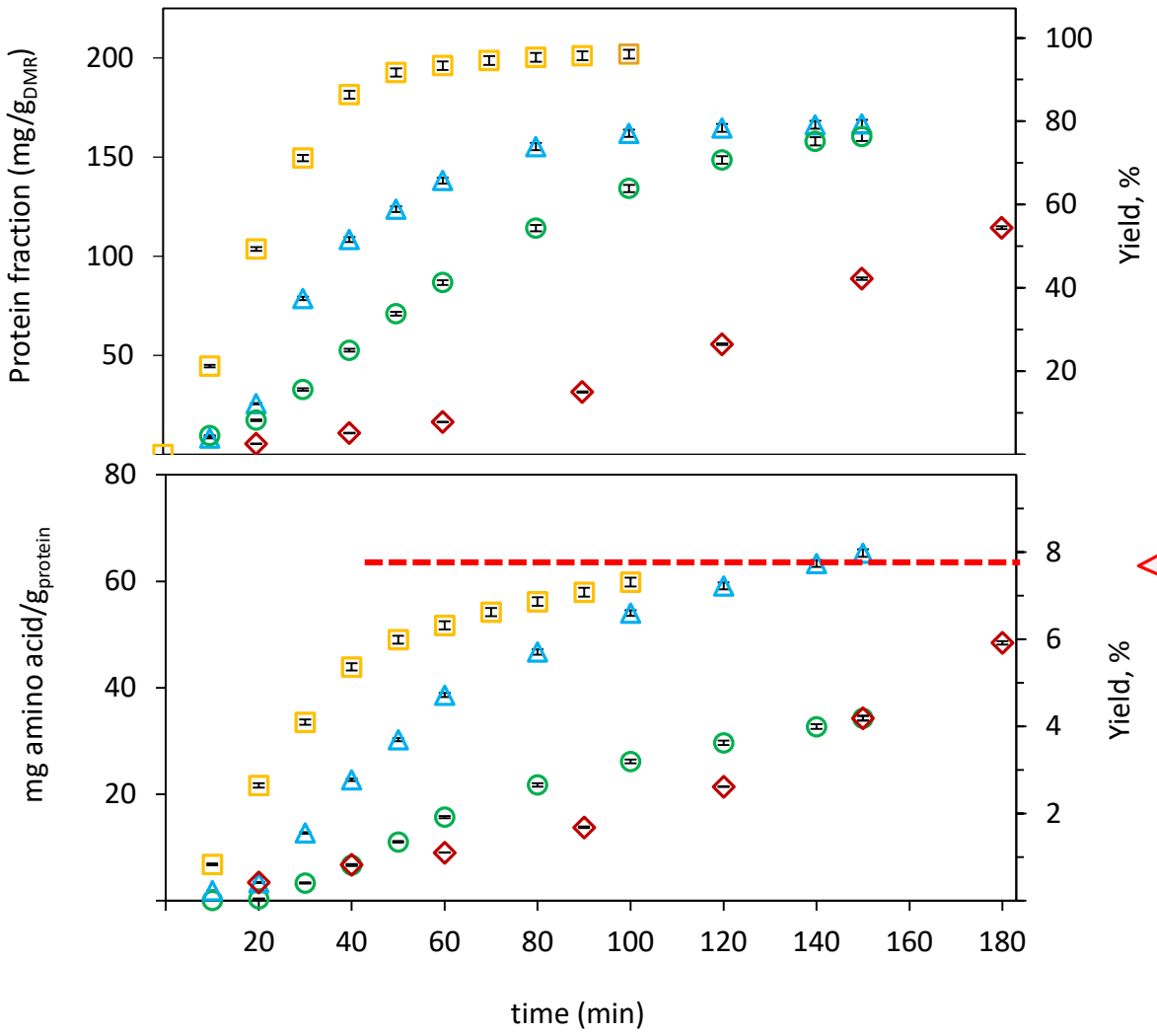
PROTEIN FRACTION HYDROLYSIS/EXTRACTION



At the **lowest RT (3 min)**, nearly **100 % of the protein** content was recovered

- **3** min
- **4.2** min
- **6** min
- **56.2** min

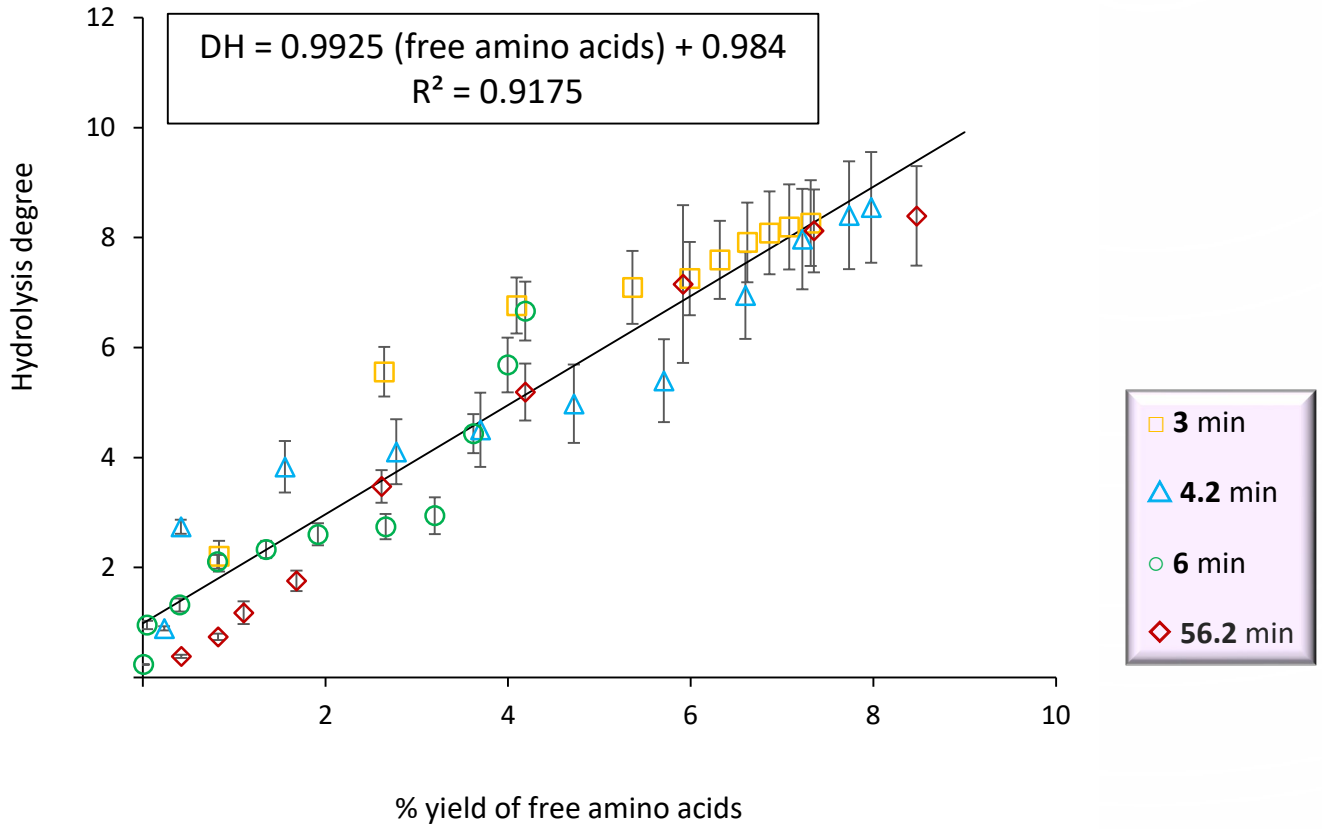
PROTEIN FRACTION HYDROLYSIS/EXTRACTION



□ **3** min
△ **4.2** min
○ **6** min
◇ **56.2** min

The **highest free amino acid yield** (≈8%) was obtained at the **lowest RT** with the **Configuration 2** (heating jacket)

PROTEIN FRACTION
HYDROLYSIS/EXTRACTION



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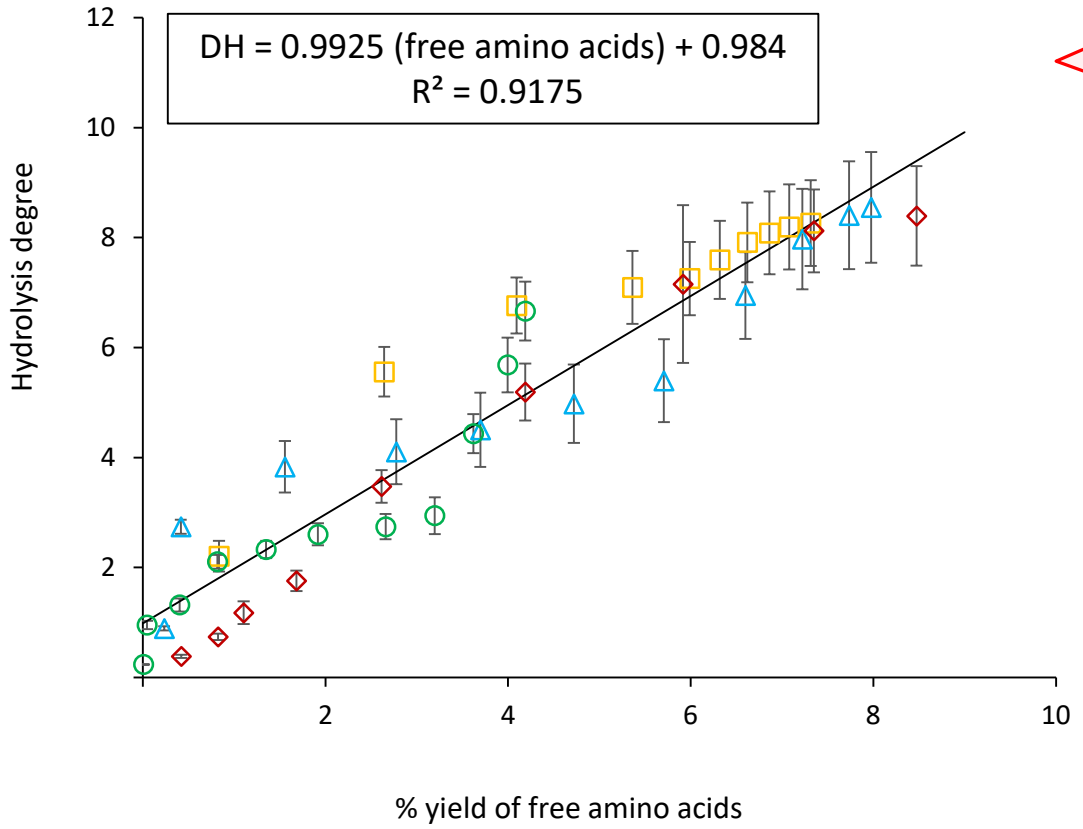
PROTEIN FRACTION HYDROLYSIS/EXTRACTION



A **good correlation** has been stablished between **hydrolysis degree** and **total free amino acids content**.

- **3** min
- **4.2** min
- **6** min
- **56.2** min

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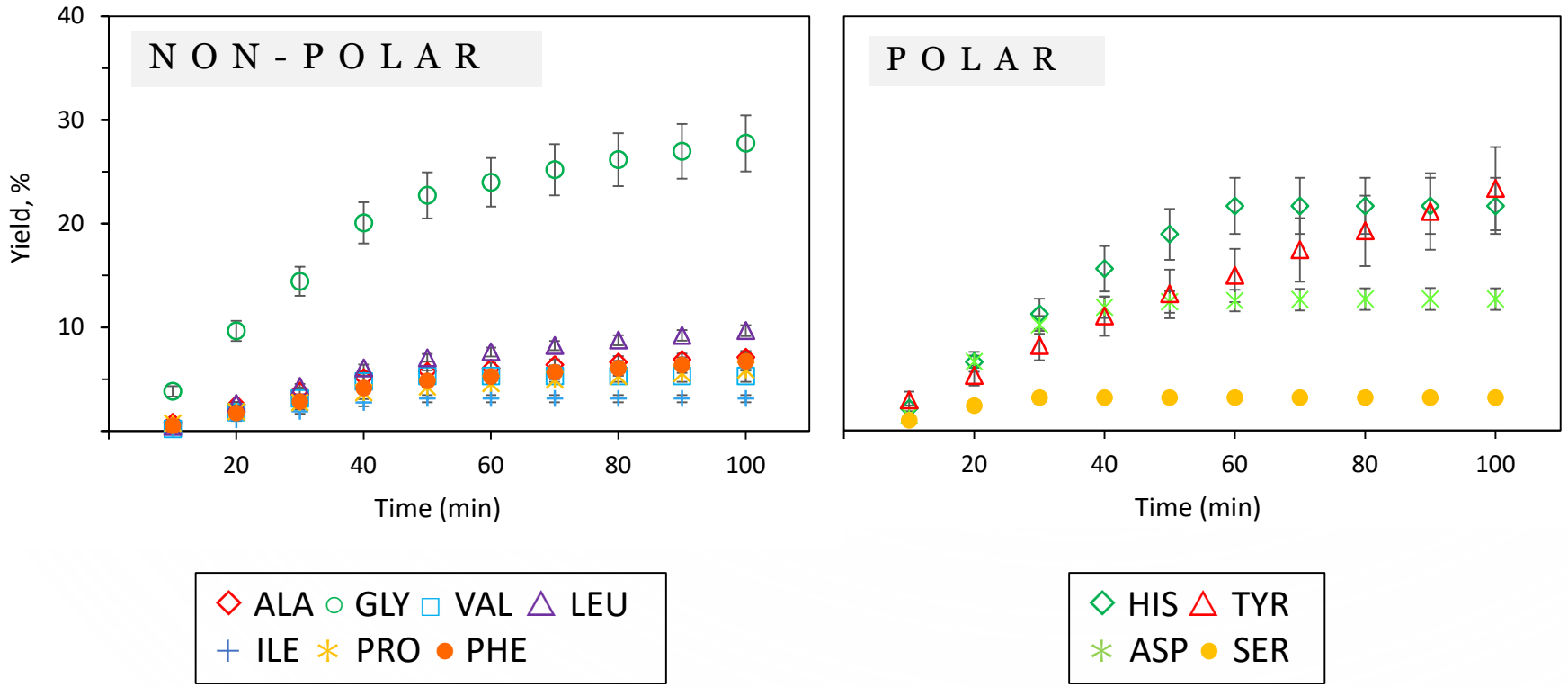
PROTEIN FRACTION
HYDROLYSIS/EXTRACTION

FREE AMINO ACIDS

→ 185 °C, **3 minutes RT**



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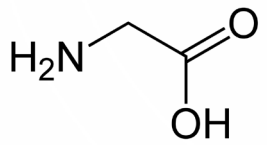
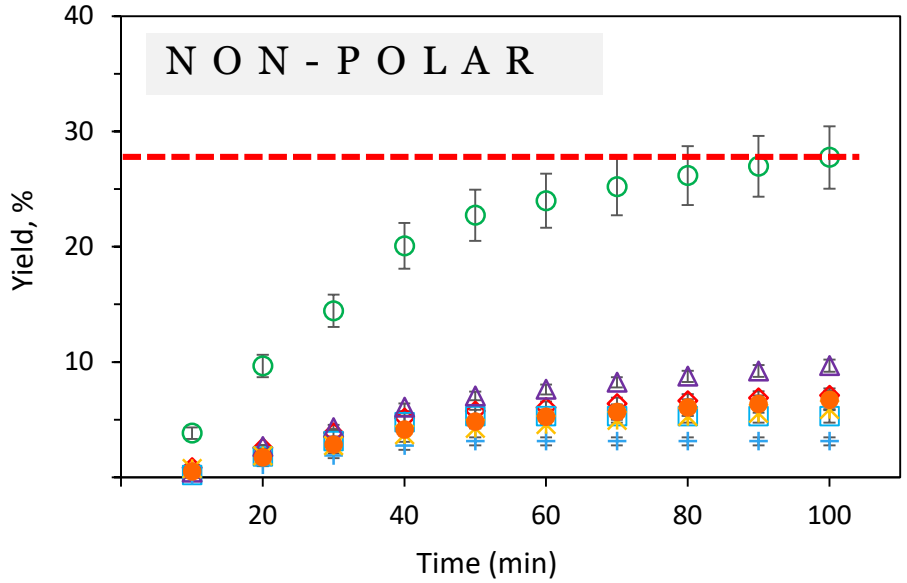
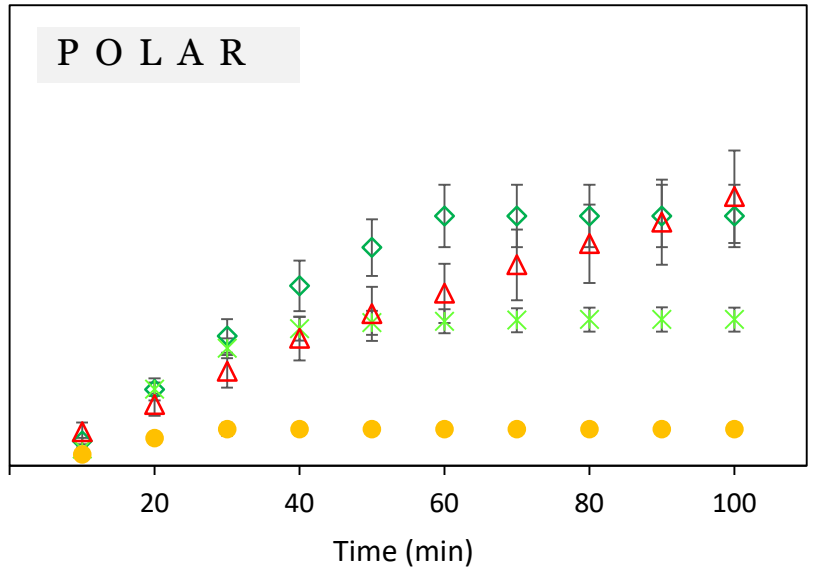
FREE AMINO ACIDS

→ 185 °C, **3 minutes RT**



The **highest free amino yield** (≈ 28 %) was obtained for the non-polar amino acid **Glycine**.





◇ ALA ○ GLY □ VAL △ LEU
+ ILE ✳ PRO ● PHE

◇ HIS △ TYR
✳ ASP ● SER

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CONCLUSIONS

- Subcritical water technology allowed hydrolysis of the solid residue generated after agar extraction from red algae.
- A bypass section (Configuration 2) before subcritical reactor allowed reaching the operating temperature avoiding the exposure of the sample to high temperatures during the heating procedure.
- By working at low residence times, higher flow rates, led to higher hydrolysis rates due to enhancing diffusion of hydrolysed biocompounds from biomass surface into the bulk solution.

CONCLUSIONS

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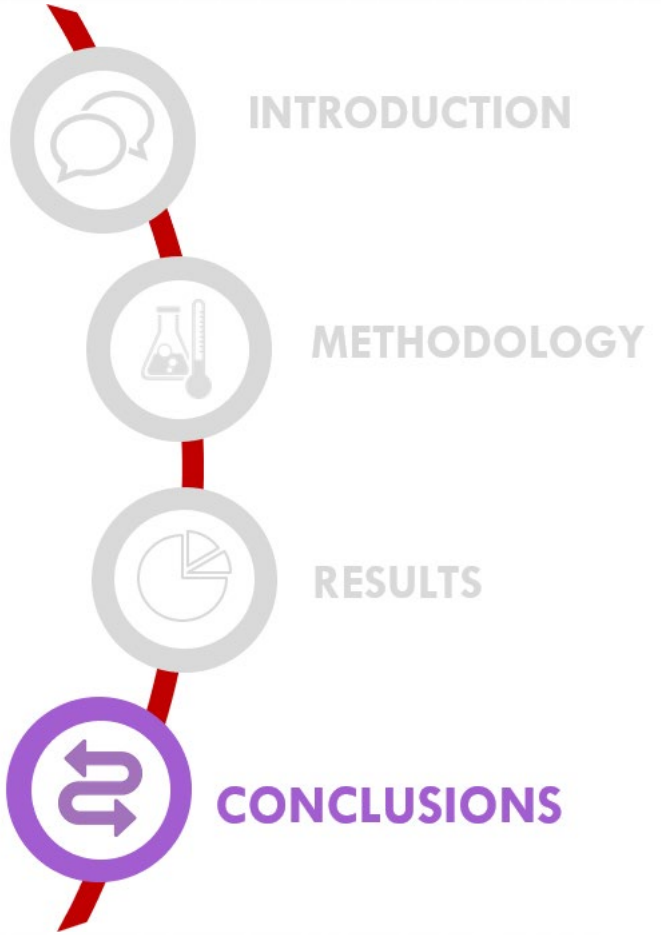

THANKS FOR YOUR ATTENTION

Junta de Castilla y León

EUROPEAN REGIONAL DEVELOPMENT FUND

EUROPEAN SOCIAL FUND

Acknowledgements

- To JCyL and ERDF for financial support of projects BU301P18 and BU050P20.
- To Agencia Estatal de Investigación for project funding PID2019-104950RB-I00/AEI/10.13039/501100011033.
- To JCyL and ESF for E. Trigueros and P. Alonso-Riaño predoctoral contracts.