Extraction and degradation kinetics of pectic oligosaccharides (POS) from onion skin wastes using subcritical water

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CONTENTS

Pectin

Onion Skin Wastes

Subcritical Water Extraction

- Pectin yield & molecular weight
- Degradation products
- Kinetic Model

Conclusions

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BACKGROUND

CIRCULAR ECONOMY

Transition form a model based on:

TAKE – MAKE – DISPOSE to **REDUCE – REUSE – RECYCLE**

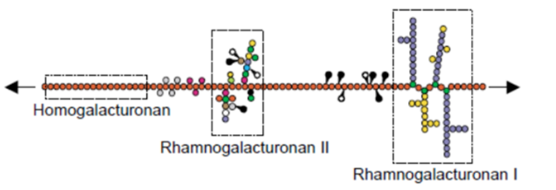
Valorization of Agroindustrial Products: BIOACTIVE COMPUNDS

PECTIN

Set of complex heteropolysaccharides present in plant cell walls

Monomer: Galacturonic Acid

Worldwide growing demand: 40,000 t/y (+5% annual)



1) **Homogalacturonan (HG)**, linear polymer of 1,4-D-GalA
2) **Rhamnogalacturonan I (RG-I)**, repeating disaccharide (GalA – Rha) to which a variety of different glycan chains (arabinan and galactan) are attached to rhamnose
3) **Rhamnogalacturonan II (RG-II)**

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BACKGROUND

PECTIN

Set of complex heteropolysaccharides present in plant cell walls

Monomer: Galacturonic Acid

Worldwide growing demand: 40,000 t/y (+5% annual)

PECTIN SOURCES

85%, citrus peels - 14%, apple pomace

Minor fraction from sugar beet

PECTIN POTENTIAL USES

High molecular weight: Additive (>65% GalA) to improve some technological aspects in formulations (E440)

Low molecular weight pectin: pecto-oligosaccharides (POS)

- prebiotic, increasing demand
- RG-I domain
- CONTROLLED HYDROLYSIS

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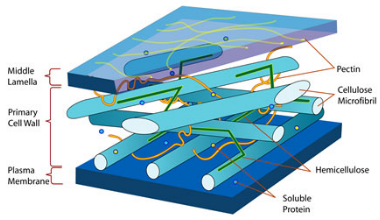
BACKGROUND

Pectin Extraction Process

- Acid Extraction (90 °C, pH 2)
- Alcohol Precipitation
- COMPLEX DOWNSTREAM

Promote the hydrolysis of the protopectin



TWO ACTIONS

NEW RAW MATERIAL
Onion skin wastes

NEW EXTRACTION METHOD
Subcritical Water

DOWNSTREAM PROCESS
Membrane technology

RAW MATERIAL

Onion Skin Wastes

HIGH CONTENT IN PECTIN

> 26%

AVAILABLE IN LOCAL INDUSTRIES

Key Ingredient for blood sausage production

Local Company: Embutidos Cardeña (http://www.morcilladeburgos.com/)

Uses 350 t/year of onion, producing 11 t/year of external skin

RICH IN BIOACTIVE COMPOUNDS

Quercetin and derivatives

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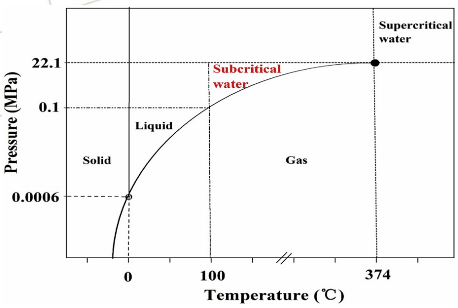
SUBCRITICAL WATER



Water at temperature ranging from 100 °C (boiling point) to 374 °C (critical point); remains in a liquid state due to the application of pressure

CHANGE IN PHYSICAL PROPERTIES

Viscosity, surface tension and dielectric constant

MASS TRANSFERS ENHANCEMENT

PROMOTION OF THE HYDROLYSIS REACTIONS

- Molecular weight loss
- Formation of degradation products

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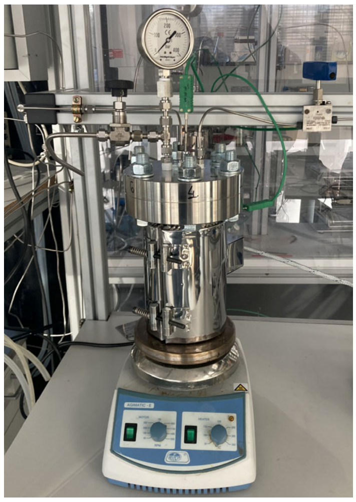
EXTRACTION EXPERIMENTS

BATCH EXTRACTOR

- 0.5 L
- Heating rate: 5 °C/min
- 105 – 165 ° C
- 180 min, samples taken periodically
- Severity factor: heating + isothermal

$$logR_0 = log\left[\int_0^{t_H} exp\left(\frac{T(t)-100}{14.75}\right)\cdot dt + t\cdot exp\left(\frac{T(t)-100}{14.75}\right)\right]$$



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EXTRACTION EXPERIMENTS

ANALYTICAL METHODS

HPLC

Galacturonic acid

Monomeric

Oligomeric (pectin)

Monosaccharides

Organic Acids

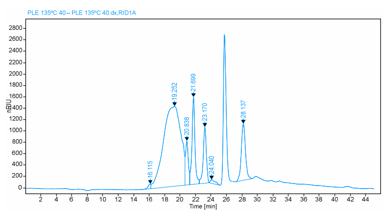
Formic

Degradation products

Furfural

GPC

Oligomeric galacturonic acid molecular weight



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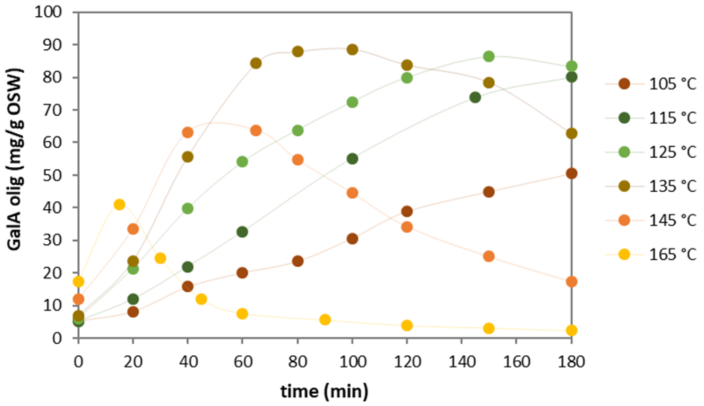
EXPERIMENTAL RESULTS: Pectin



- **Effect of Temperature**
  Promotes the extraction
- **Effect of time**
  Maximum yield, then decreases

The maximum is reached sooner and is lower as the temperature increases

- Kinetic Study

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EXPERIMENTAL RESULTS: Pectin – kinetic study

$$\text{PROTOPECTIN} \xrightarrow{k_{ext}} \text{PECTIN} \xrightarrow{k_{deg}} \text{DEGRADED PECTIN}$$

$$\frac{dY_p(t)}{dt} = -k_{ext} \cdot Y_p(t)$$

$$\frac{dY_e(t)}{dt} = k_{ext} \cdot Y_p(t) - k_{deg} \cdot Y_e(t)$$

$$Y_e(t) = A_0 \cdot \frac{k_{ext}}{k_{deg} - k_{ext}} \cdot \left(e^{-k_{ext} \cdot t} - e^{-k_{deg} \cdot t}\right)$$

$$t_{max} = \frac{ln\left(k_{ext}/k_{deg}\right)}{k_{ext} - k_{deg}}$$

The relationship between rate constants and the temperature was established by the Arrhenius law

$$Y_{e,max} = A_0 \cdot \left(\frac{k_{deg}}{k_{ext}}\right)^{\left(\frac{k_{deg}}{k_{ext}}\right)/\left(1-\frac{k_{deg}}{k_{ext}}\right)}$$

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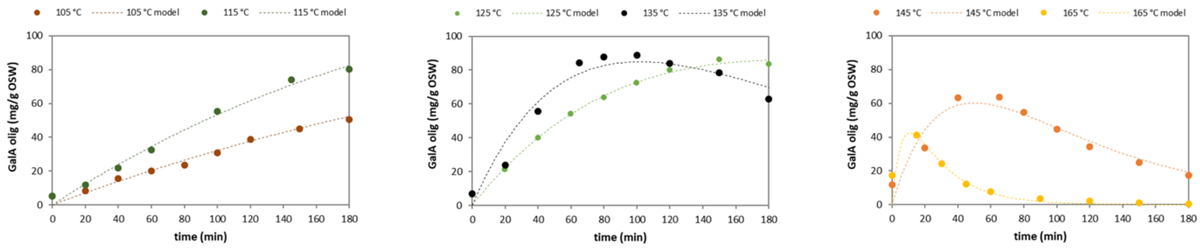
EXPERIMENTAL RESULTS: Pectin – kinetic study



Low T (105-115 °C)	Mid T (125-135 °C)	High T (145-165 °C)
$K_{ext} > k_{deg}$	$K_{ext} \approx k_{deg}$	$K_{ext} << k_{deg}$
105 °C: 1.4 > 1.0	125 °C: 4.6 ≈ 6	145 °C: 13 < 30
115 °C: 2.4 > 1.4	135 °C: 8.5 ≈ 11	165 °C: 43 < 168

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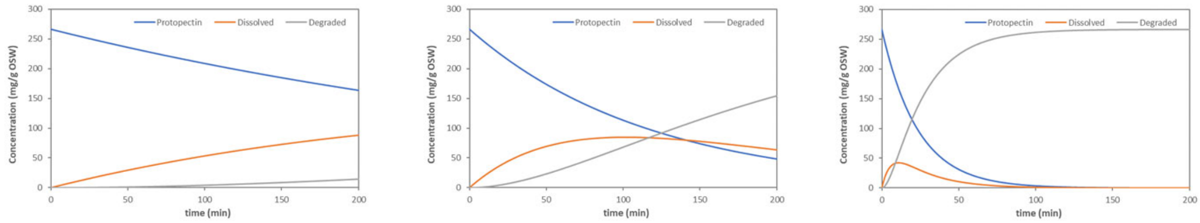
EXPERIMENTAL RESULTS: Pectin – kinetic study



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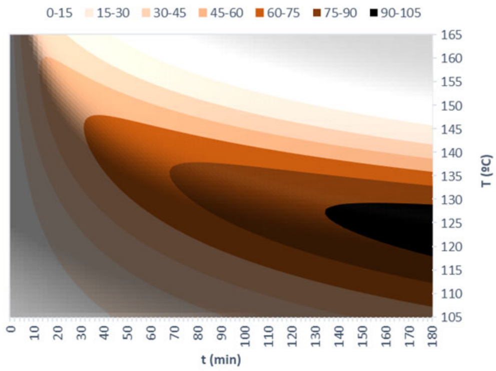
EXPERIMENTAL RESULTS: Pectin – kinetic study

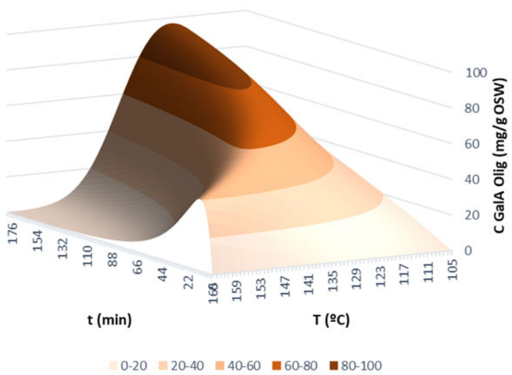
Kinetic Model application



T (°C)	$k_{ext}\cdot10^3$ (min^{-1})	$k_{deg}\cdot10^3$ (min^{-1})	R^2	t_{max} (min)	C_{max} (mg/g OSW)	$yield_{max}$ (%)
105	1.38±0.13	1.09±0.11	0.992	697	94	35.3
115	2.4±0.2	1.4±0.9	0.990	533	125	47.0
125	4.6±0.2	6.0±0.5	0.992	189	86	32.2
135	8.5±0.8	11±1	0.945	102	85	31.9
145	13±1	30±2	0.887	50	60	22.6
165	43±12	168±25	0.785	11	43	16.0

EXPERIMENTAL RESULTS: Pectin – kinetic study

Kinetic Model application



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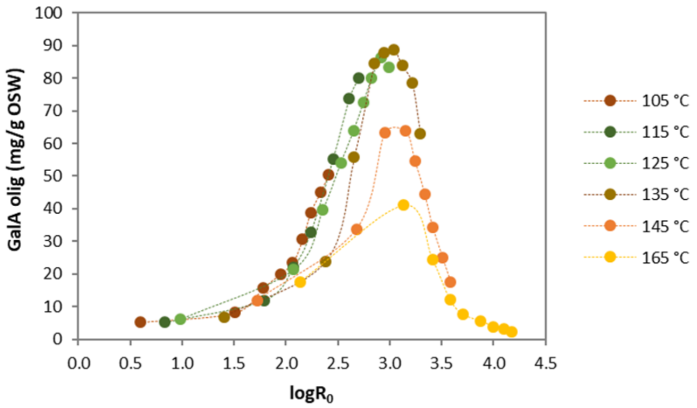
EXPERIMENTAL RESULTS: Severity Factor

Oligomeric GalA recovery



- **Maximum**

  Log R_0 2.8-3.1
  Narrow window

- Sharp decrease when increasing severity factor

  Maximum yield, then decreases

- Careful selection of the extraction conditions

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EXPERIMENTAL RESULTS: Severity Factor

Degradation products: furfural and formic acid

- **GalA main degradation products**

  Previous work

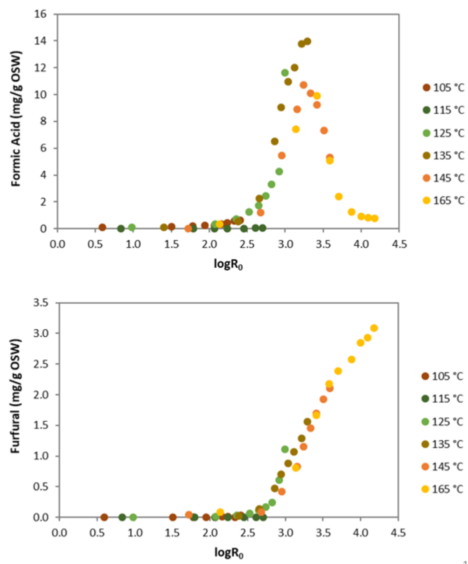
- **Formic Acid**

  Maximum
  Log R_0 3.2-3.3

- **Furfural**

  Keeps increasing as the extraction intensity increases

- **Molecular weight of the extracted pectin?**



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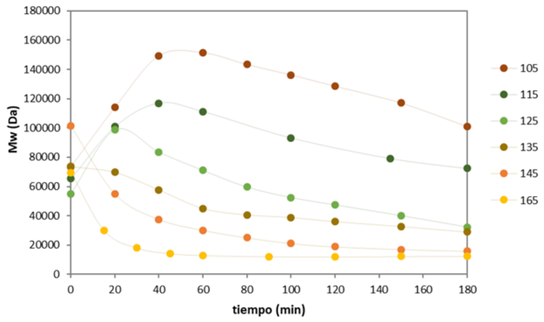
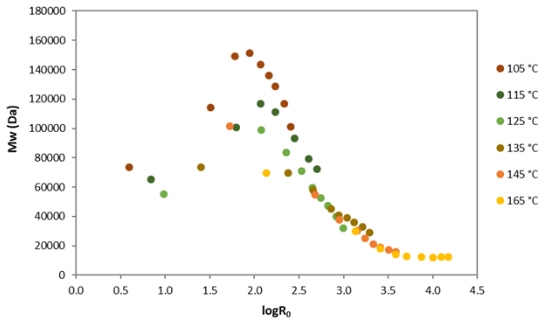
EXPERIMENTAL RESULTS: Molecular weight





Decreases as the extraction progresses
How does the MW distribution looks like?

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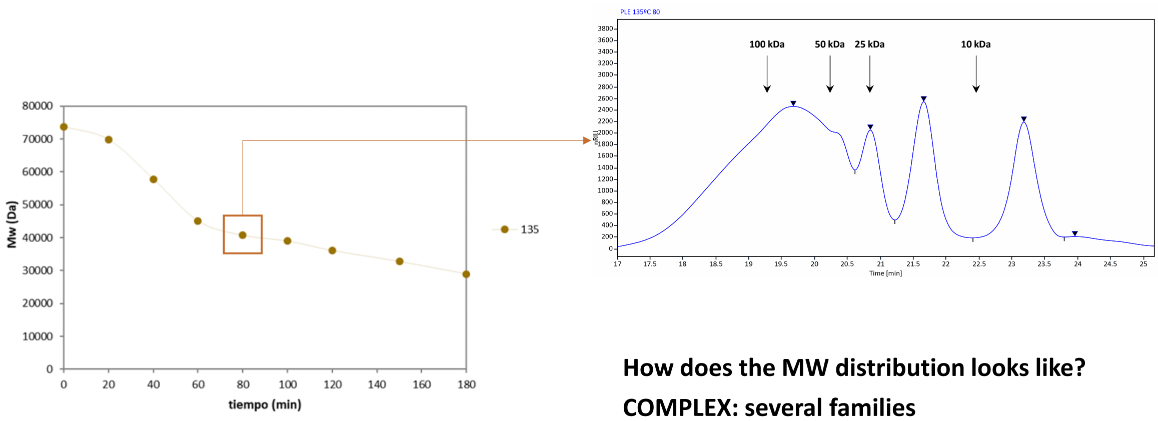
EXPERIMENTAL RESULTS: Molecular weight



How does the MW distribution looks like?

COMPLEX: several families

- Most abundant 85 kDa
- T promotes the appearance of lower MW populations

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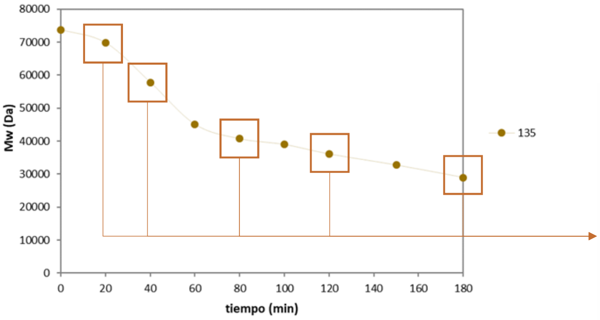
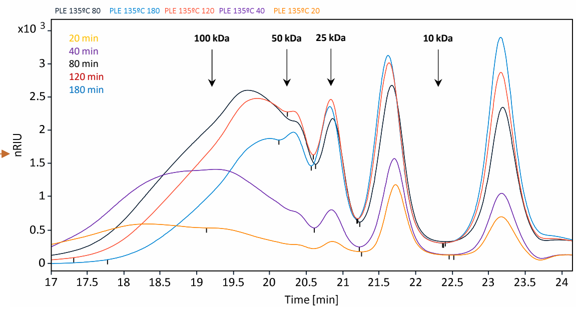
EXPERIMENTAL RESULTS: Molecular weight

How does the MW distribution looks like?

COMPLEX: several families, that change throughout the extraction





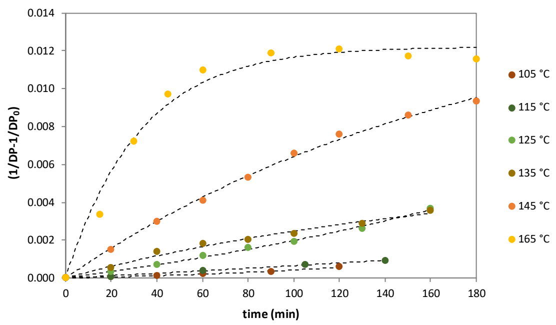
EXPERIMENTAL RESULTS: Molecular weight

MW modelling: Emsley equation

$$\frac{1}{DP} - \frac{1}{DP_o} = \frac{k_{1_0}}{k_2} \cdot \left(1 - e^{-k_2 \cdot t}\right)$$

k_{10}: initial degradation rate constant and
k_2: rate of k_1 changing

$$DP = \frac{M_n}{194.14 - 18.02}$$



T (°C)	$k_{10} \cdot 10^5$ (min^{-1})	$k_2 \cdot 10^3$ (min^{-1})	DP_0	Mn_0 (kDa)	R^2
105	0.25±0.02	-9.9±1.4	860	151	0.996
115	0.61±0.06	-1.6±0.1	664	117	0.996
125	1.6±0.1	-4.0±0.7	561	97	0.997
135	3.3±0.3	5.8±1.7	396	70	0.980
145	8.4±0.3	5.5±0.6	576	101	0.998
165	38±4	31±4	395	69	0.973

EXPERIMENTAL RESULTS: Conventional Process

➢ **Extraction Yield**

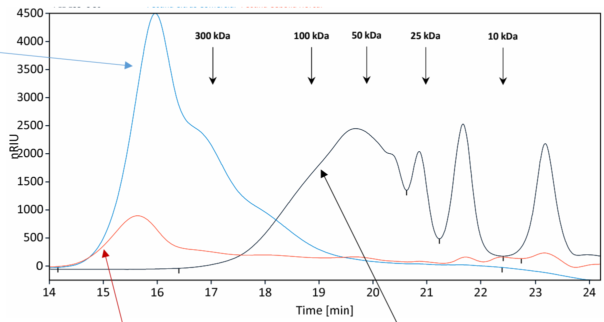
Lower (32% vs 10%)

➢ **MW**

One single family

> 300 kDa

Citrus Commercial
Conventional



OSW
Conventional
90 °C, pH 2, 100 min

OSW
SubW 135 °C, 100 min

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EXPERIMENTAL RESULTS: Conventional Process

	Conventional	Subcritical Water
	85 °C, pH 2 (HCl)	135 °C, 100min
HG (mol %)	80.3±1.6^{C}	71.7±2.4^{B}
RG-I (mol %)	10.8±0.9^{A}	21.1±1.1^{B}
Rha/GalA	0.02	0.08
(Gal+Ara)/Rha	5.9	1.4

$$HG\ (\%, mol) = GalA - Rha$$

$$RG - I\ (\%, mol) = [GalA - HG] + Rha + Gal + Ara$$

➢ SubW:

- Increases the RG-I domain
  - RG-I: Prebiotic function
  - HG: Gelling ability
- Branched structure
- Lower MW

N.H. M'sakni et al. Eur. Polym. J. 42 (2006) 786–795. https://doi.org/10.1016/j.eurpolymj.2005.09.014.

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CONCLUSIONS

SUBW IS AN EFFICIENT REACTION MEDIUM

to promote the solubilization of pectin

NARROW WINDOW TO RECOVER PECTIN

- Severity Factor 2.9-3.1
- 125 – 135 °C and 100 min
- Fast degradation (formic acid & furfural)
- MW decrease

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CONCLUSIONS

MODELING

- Control the extraction conditions to maximize both yield and MW

HYDROTHERMAL PROCESS

- Allows to obtain, at temperatures between 125-135 °C, with MW in the range 7-110 kDa, in contrast to the high MW (>300 kDa) conventional acid water extraction processes
- Structural differences
- To be coupled with membrane technology to purify and fractionate POS, in a water-based process

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ACKNOWLEDGEMENTS

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EXPERIMENTAL RESULTS: Molecular

How does the MW distribution looks like?: COMPLEX: several families that change throughout the extraction process