WORKSHOP

2021

BIOBASED MATERIALS RESEARCH: ADVANCES FROM ECOFUNCO AND BIONTOP EUROPEAN PROJECTS

This project has received funding from the Bio Based Industries Joint Undertaking (JU) under grant agreement No 837863. The JU receives support from the European Union's Horizon 2020 research and innovation programme and the Bio Based Industries Consortium.

Microwave and ultrasound-assisted extraction as potential green techniques for obtaining valuable compounds from agro-food waste valorization

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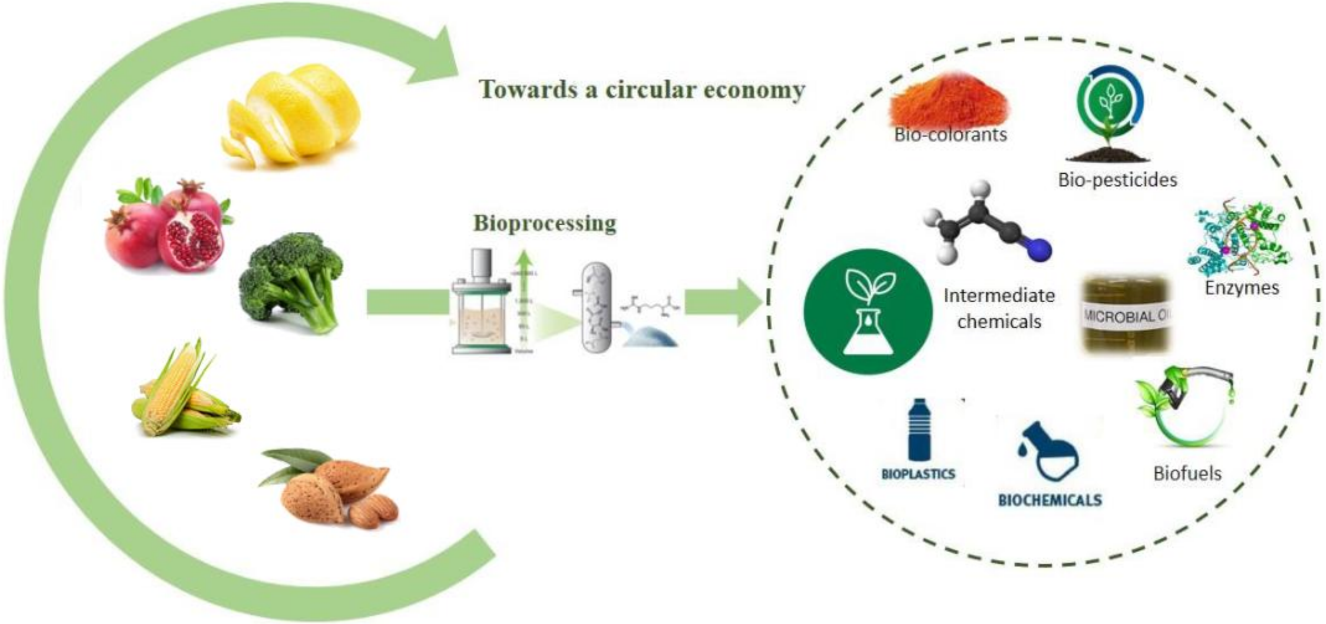
NBP
Grupo de análisis de polímeros y nanomateriales

Bioprocessing of food waste for the production of high value-added products

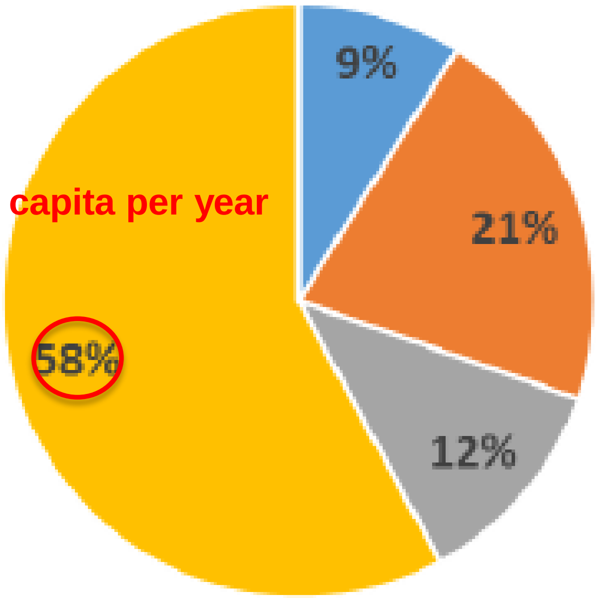


Colorants, essential oils, lipids, polyphenols and **phenolic acids** are one of the most significant examples of **high added value compounds** obtained from many different **agro-food residues and by-products.**

Food waste

Van Holsteijn et al., 2017

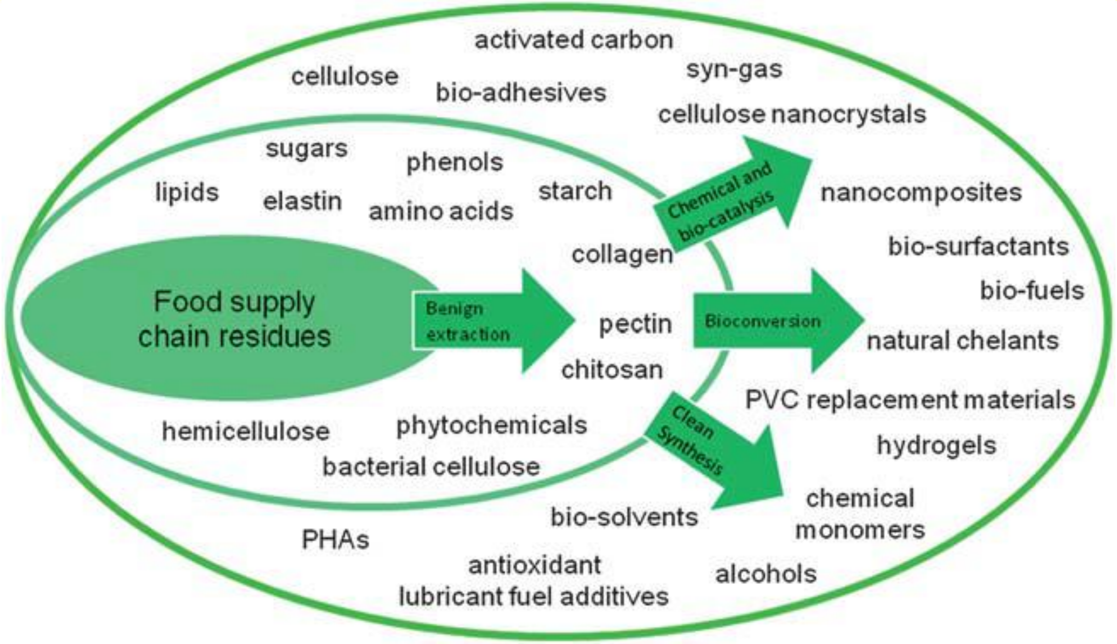
kg per capita per year

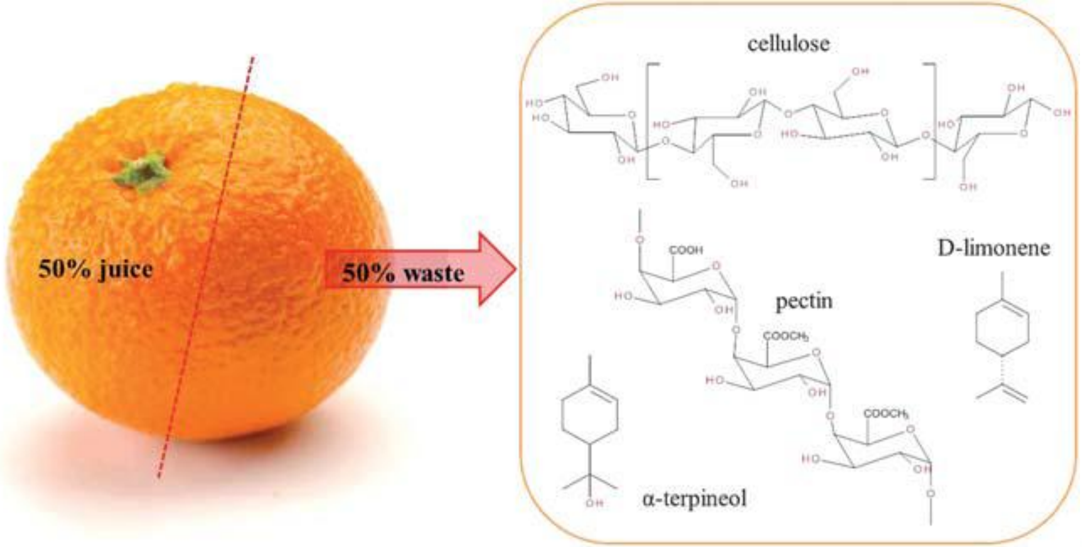


Total FW: 290 kg p^{-1} y^{-1}

- Primary production and post-harvest
- Manufacturing
- Distribution
- Consumption

The number of potentially valuable compounds in food waste is huge!!!





Extraction methods

Main challenges for valorization of food residues and by-products lies on the optimization of efficient and sustainable extraction methods and techniques

Conventional extraction

Solid-liquid extraction:
- High temperatures and long times
- Maceration at room T for days

PROBLEMS
Long extraction times
Thermal degradation
High amount of organic solvents

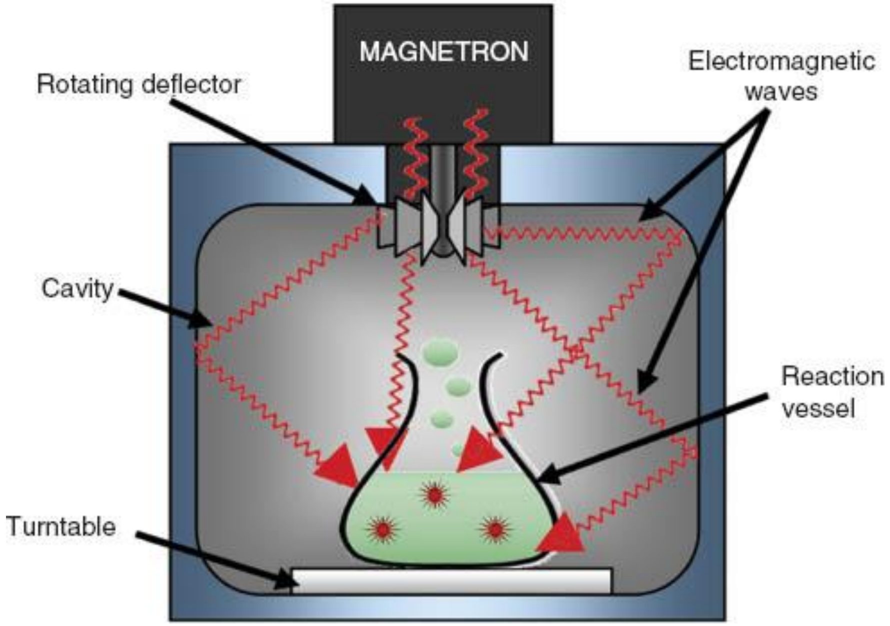
Alternative green extraction

Supercritical fluid extraction (SFE)
Pressurized liquid extraction (PLE)
Microwave-assisted extraction (MAE)
Ultrasound-assisted extraction (UAE)
Subcritical water extraction (SWE)

Short extraction times
Low amount of organic solvents
Higher selectivity and extraction yields

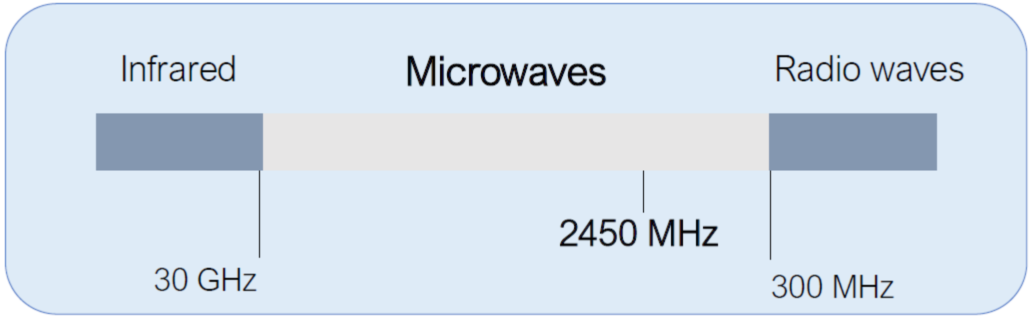
Green extraction methods

Microwave-assisted extraction (MAE)

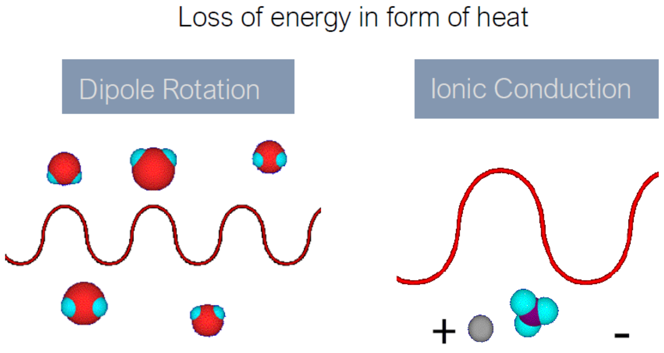


Heat release = Rupture of hydrogen bonds in dipolar molecules

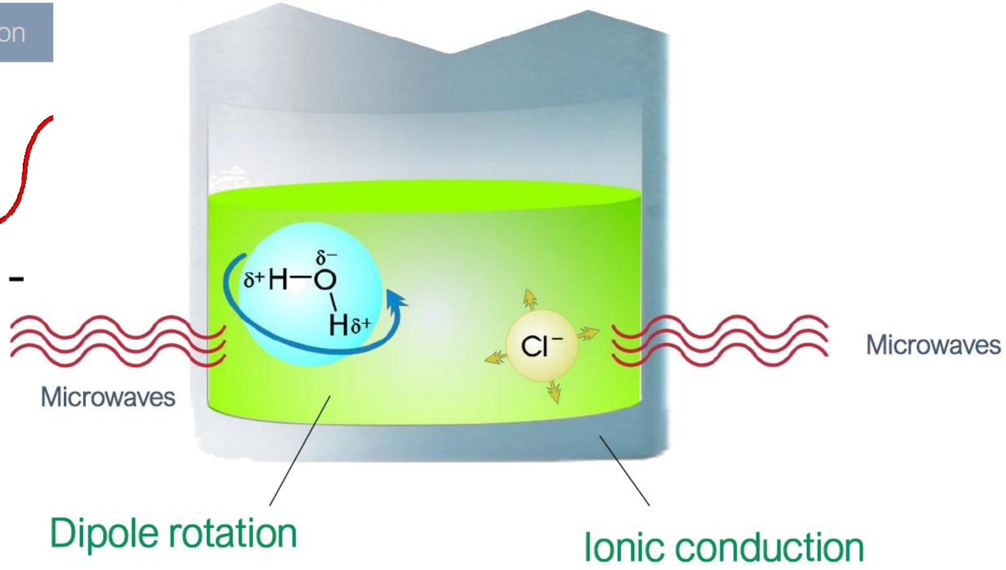
Pressure = physical modification; Good penetration of solvents through the molecular structure



MW: ionizing radiation causing molecular movement by ions migration and dipolar rotation



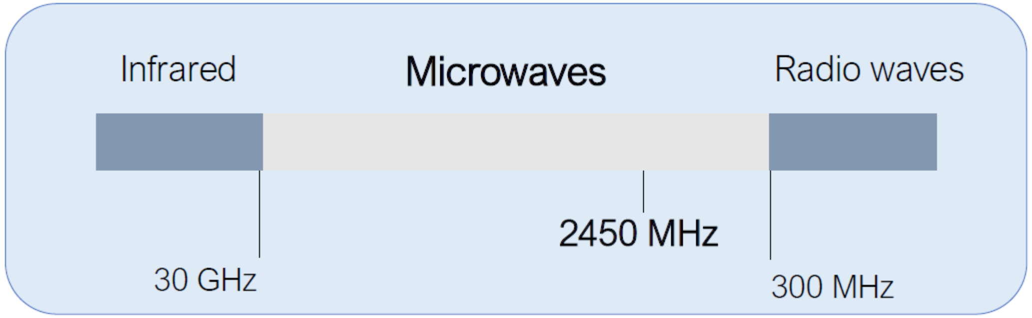
⇒ Dipole-Dipole type thanks to Polar Molecules



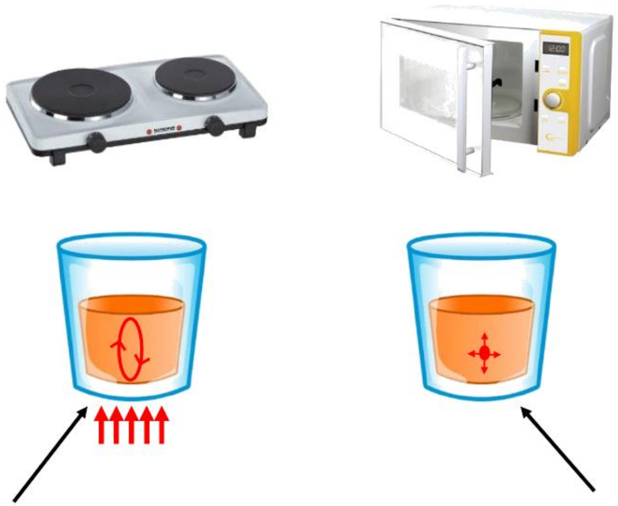
Solvent should absorb MW radiation

Green extraction methods

Microwave-assisted extraction (MAE)



CONVENTIONAL VS. MICROWAVE HEATING



⇒ Indirect heating

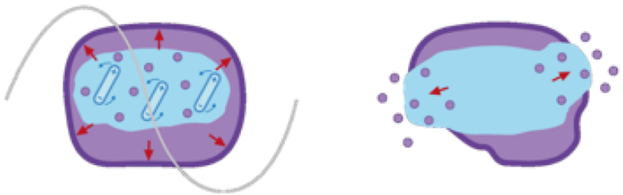
- Convection currents
-T (°C) on the outside surface is greater than that of the contents

⇒ Direct heating

- Localized "hot spots"
-T (°C) of the inside is greater than the outer surface

⇒ Inverted temperature gradients

MICROWAVE ADVANTAGES IN NATURAL PRODUCTS PROCESSING

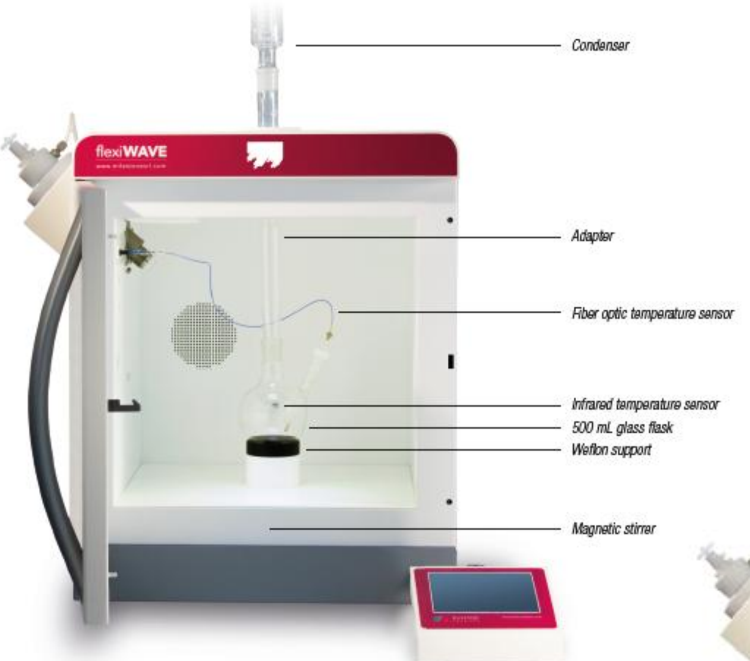


- Direct heating of cell *in natura* water
- Short processing times
- Less heating exposure
- High efficiency
- Low energy consumption
- Green process

Green extraction methods

Microwave-assisted extraction (MAE)

- ✓ Uniform heating
- ✓ High reproducibility

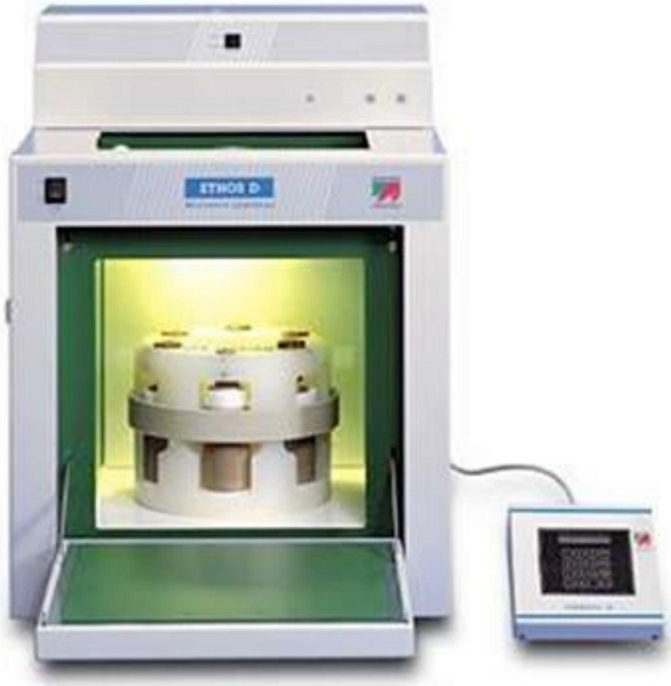


Open system
(atmospheric pressure)

Solid-phase synthesis
reactor

Microwave assisted hydrodistillation
MAHD (without solvent)

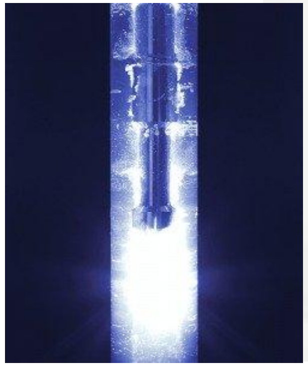
Closed system
(high T, P)

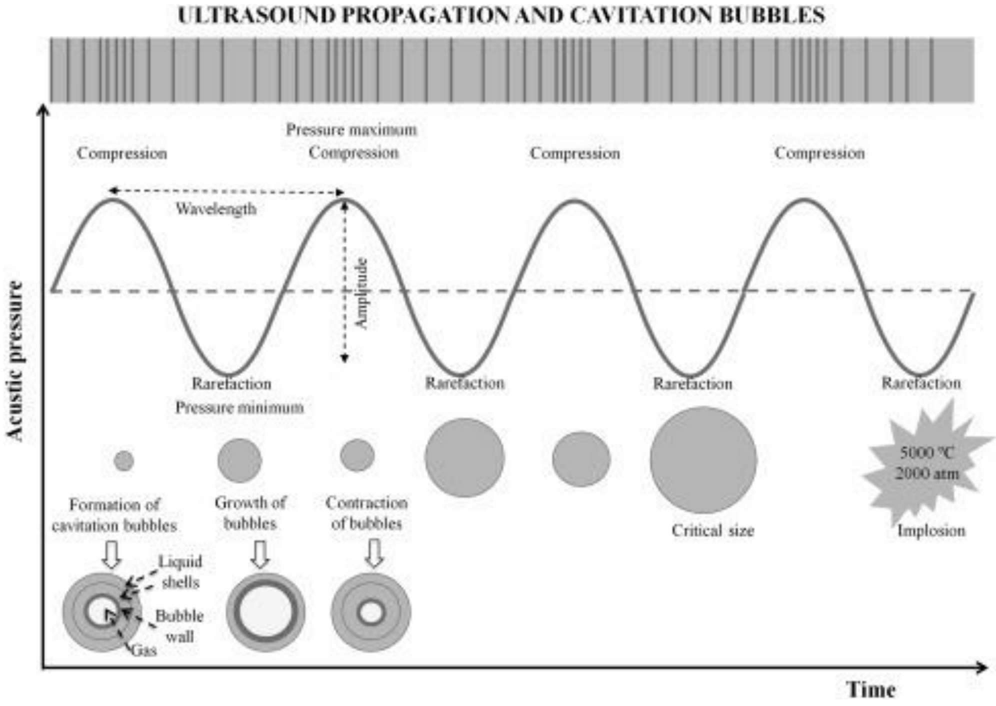


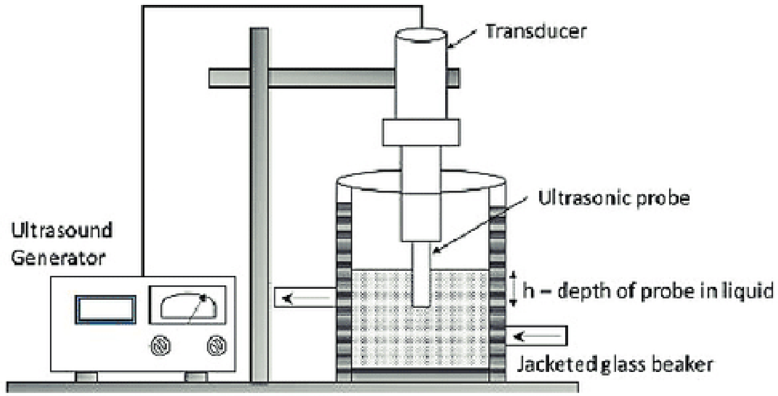
Green extraction methods

Ultrasound-assisted extraction (UAE)

- High extraction rate.
- Excellent reproducibility
- Reduced solvent consumption
- Simple manipulation
- High purity of extracts
- No need of post-treatment



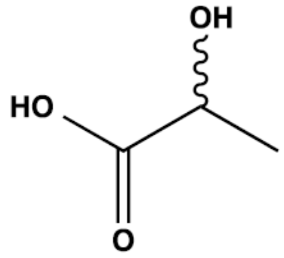




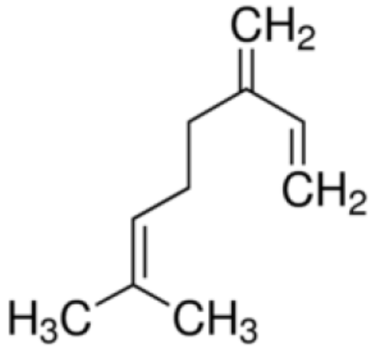
Cavitation phenomena leads to high shear forces in the extraction media. The implosion of cavitation bubbles on a product's surface results in micro-jetting which generates several effects such as surface peeling, erosion and particle breakdown

APPLICATIONS

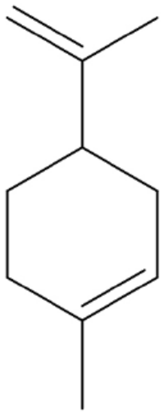
EXTRACTION OF VALUABLE MOLECULES



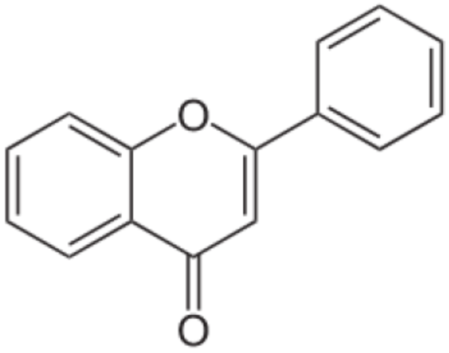
Lactic Acid



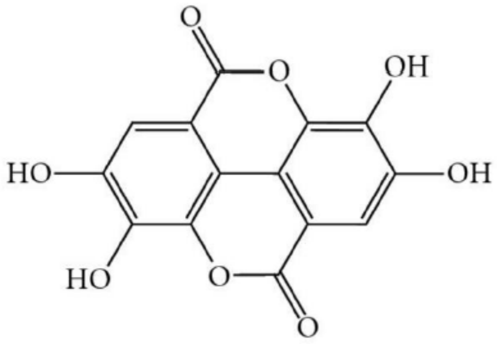
Beta-Myrcene



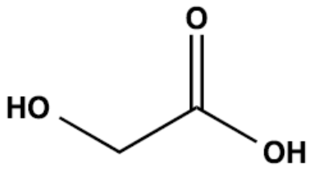
Limonene



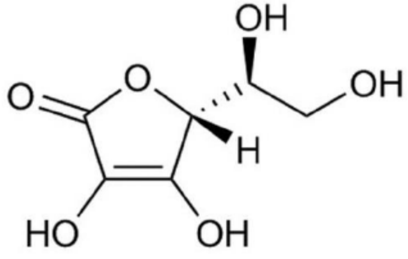
Flavonoid



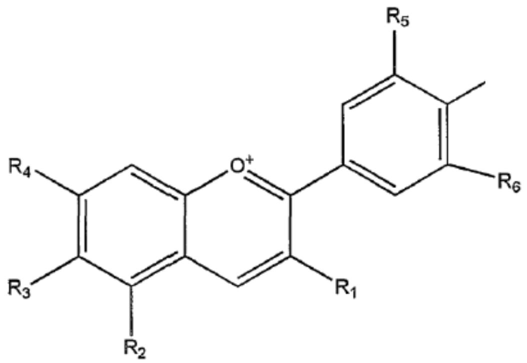
Ellagic Acid



Glycolic Acid



Ascorbic acid



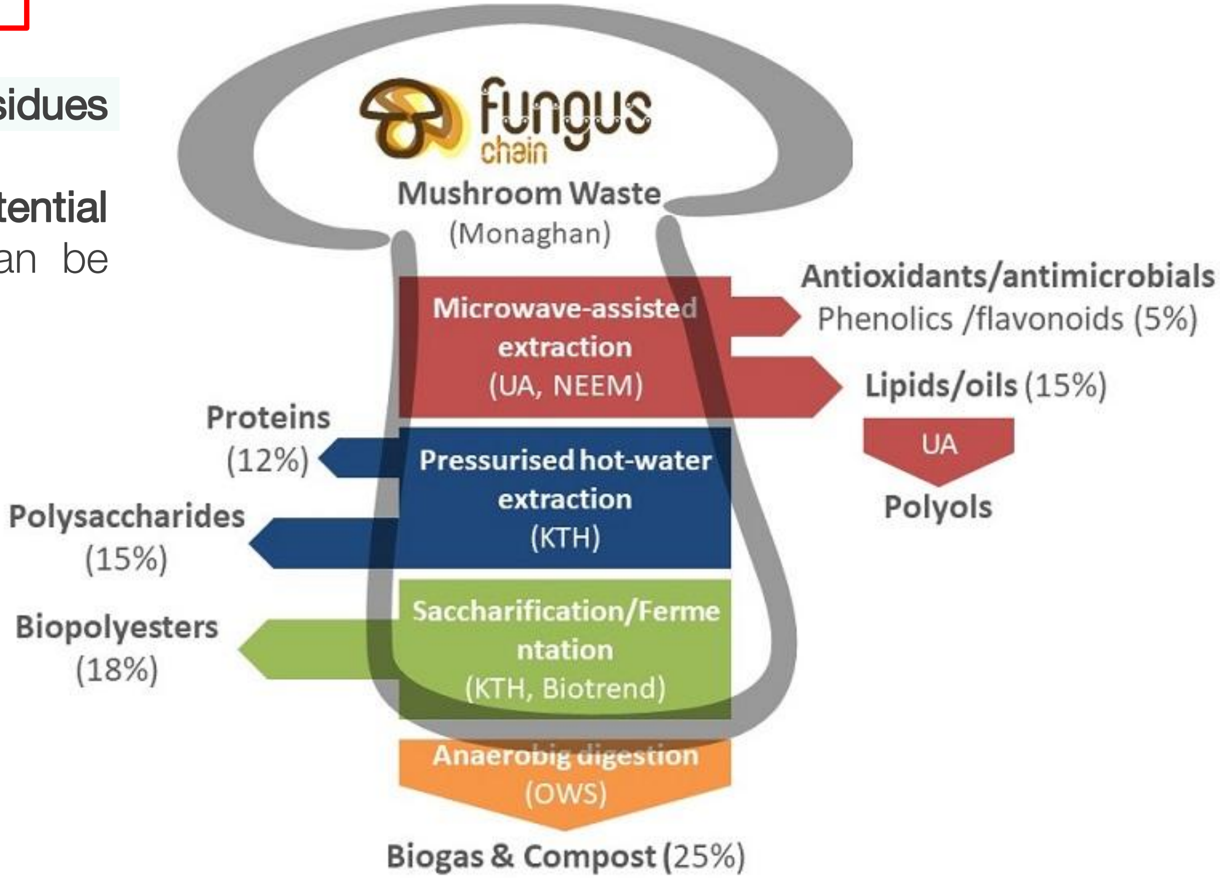
Anthocyanins

Biorefinery approach

15 tons per week

- Huge amounts of **agricultural residues are underutilized**.
- White button mushrooms are a **potential rich source of ingredients** that can be used in bio-based products

Biorefining and cascading approach for mushroom residues and by-products



Biorefinery approach

Lipids/oils

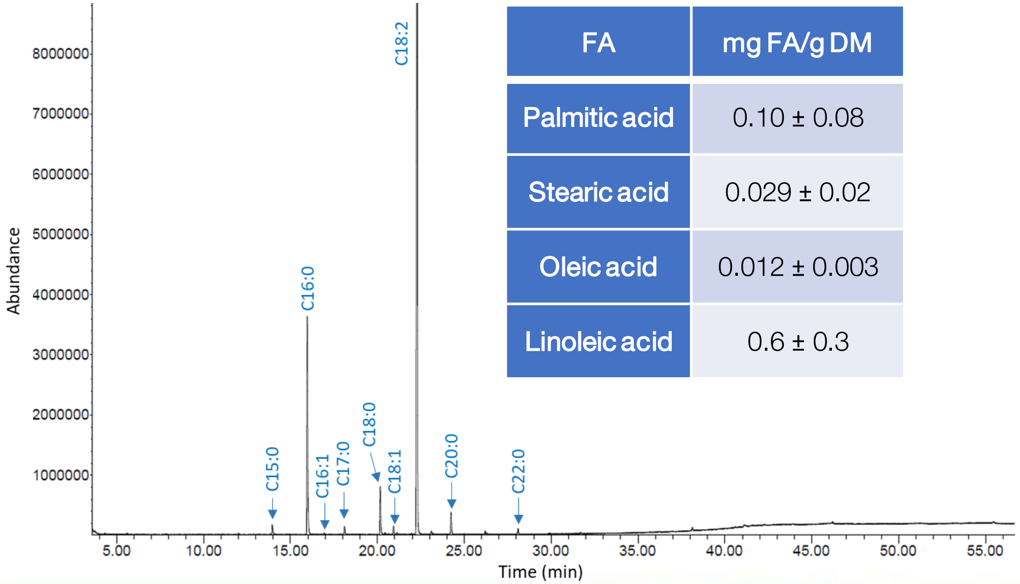
MAE
Ethyl acetate:EtOH
(2:1)

Freeze-drying

Pure extract

FAMEs

Lipids profile (GC-MS)

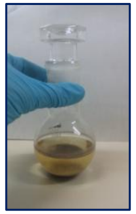


FA	mg FA/g DM
Palmitic acid	0.10 ± 0.08
Stearic acid	0.029 ± 0.02
Oleic acid	0.012 ± 0.003
Linoleic acid	0.6 ± 0.3

Polyphenols

MAE

- 2 g sample
- Ethanol/water (70/30, v/v)
- 80 °C, 10 min



Lyophilisation

Yield after MAE	TPC	DPPH	ABTS	FRAP
%	(mg GAE g^{-1} dried mushroom)	(mg TE g^{-1} dried mushroom)		
42.0 ± 0.9	4.17 ± 0.15	5.04 ± 0.24	10.58 ± 0.40	6.15 ± 0.46

Biorefinery approach

Demonstrators and future applications

These high value molecules from the fungal residue will be applied to a wide range of end-user products like:

Cleaning

A bio antimicrobial solution eco-friendly for house cleaning products.

Food

Proteins will be used as complements to enrich food suplments for the elderly and sportsmen.

Plastic

Bioplastic film to be used as bag, mulching and gloves.

Cosmetic products

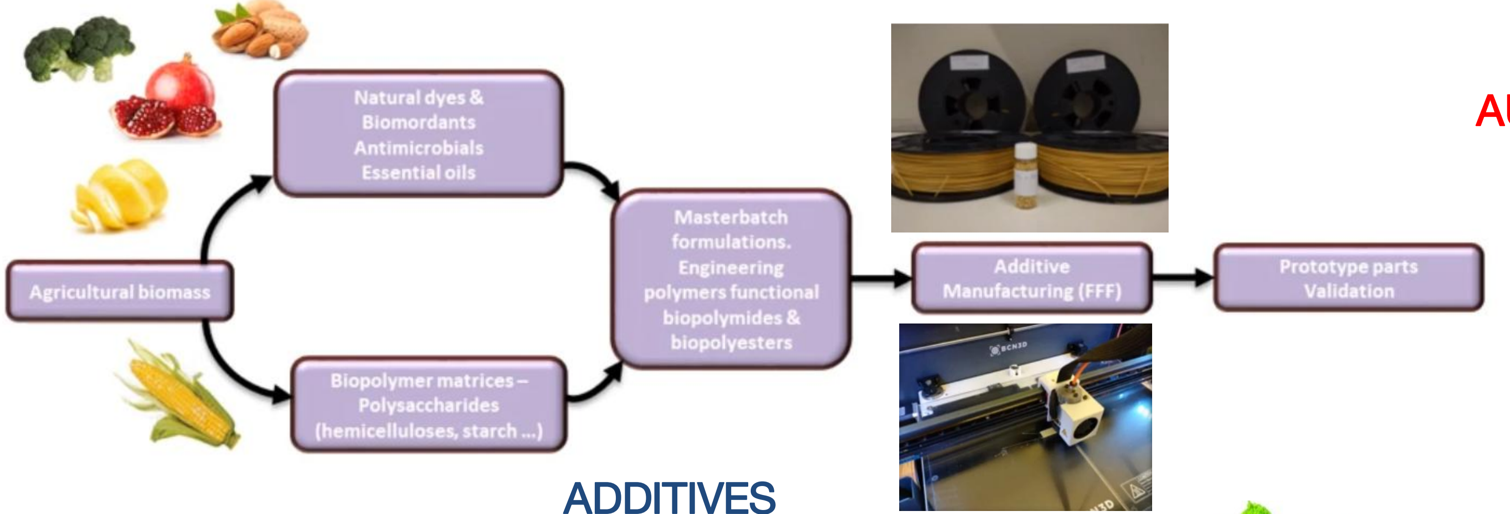
Food products

soil mulch films

Biorefinery approach

Biomass Resources → Extraction/modification bio-based components → Formulations/processing → Validation and Others

MAE



AUTOMOTIVE

ADDITIVES

Natural dyes

Fragrances

Antimicrobials

CONSTRUCTION

Biorefinery approach

A. Martínez-Abad et al. Foods 9 (2020) 1493
B. Micó-Vicent et al. Polymers 12 (2020) 1451

BARBARA

Overall process for the sequential extraction of essential oil and pigment from lemon waste

Essential oil
Fragrance
Antimicrobial
Pigments

(MAHD)

Microwave assisted hydrodistillation

essential oil

1. Extraction of essential oil

EO yield : 4%

Peel residue (MAE)

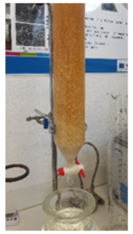
ETHANOL

Identified major metabolites

Eriocitrin
Diosmin
Hesperidin

3.3% flavonoids

Pigment extract



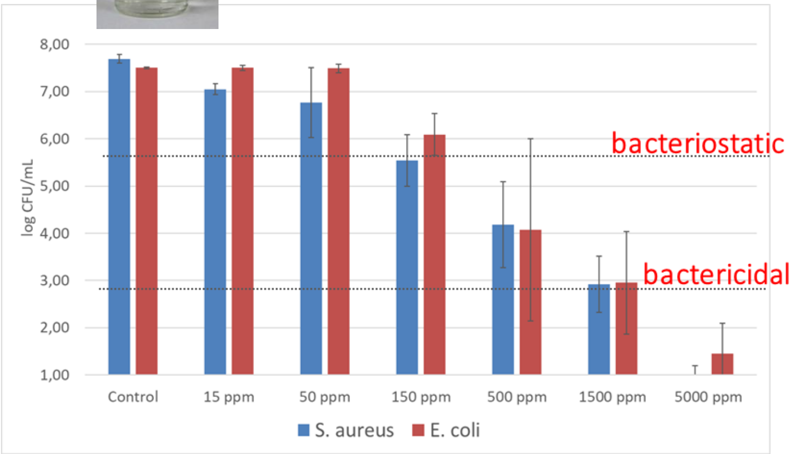
14.75% flavonoids

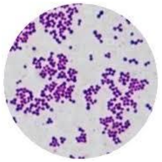
2. Extraction of pigment

Pigment powder yield : 1.5%

Amberlite XAD-16N

EO showed excellent antimicrobial performance against both Gram positive and Gram negative bacteria





S. aureus

E. coli

Biorefinery approach

B. Micó-Vicent et al. Polymers 13 (2021) 1966

BARBARA

Overall process for extracting pigments and antimicrobials/biomordants from pomegranate residues

Arils, juice

Juice filtering

Amberlite XAD-7HP

Pigment powder

yield : 20% (juice DW)

27.7% anthocyanins

Cyanidine-3,5-glucoside
Delphinidine-3,5-glucoside
Delphinidine-3-glucoside

Peels drying

MAE, ethanol/water (50/50)

Tannins extract

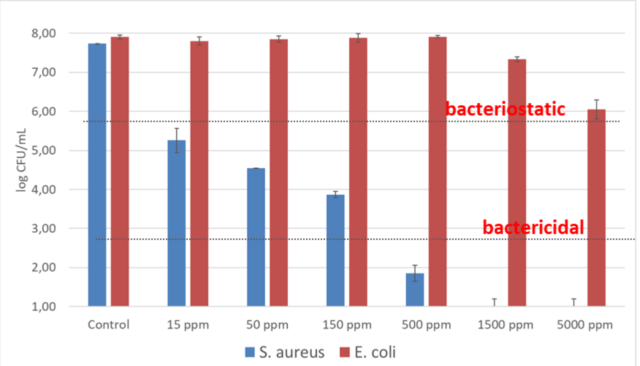
Amberlite XAD-16N

Biomordant yield : 6.4% (dried peels)

37.8% punicalagins

Punicalagins (A and B)
Punicalins (A and B)

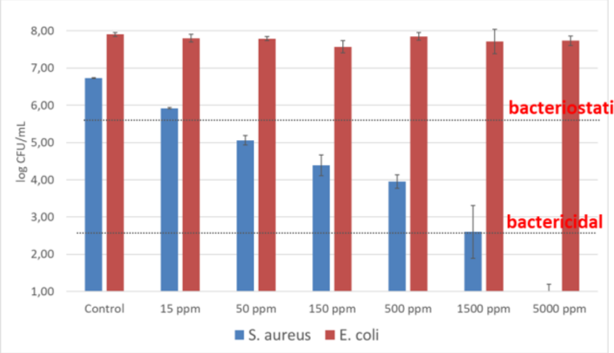
Pomegranate peel extract



Bacteriostatic effect at conc ≤ 15ppm against *S. aureus*

Extract inactive against Gram negative *E. coli*

Pomegranate pigment



Same spectrum of action as peel extract but less power

BBI JU

Biorefinery approach

MAE of Aloe Vera Agrowastes and elestrospun PEO nanofibers

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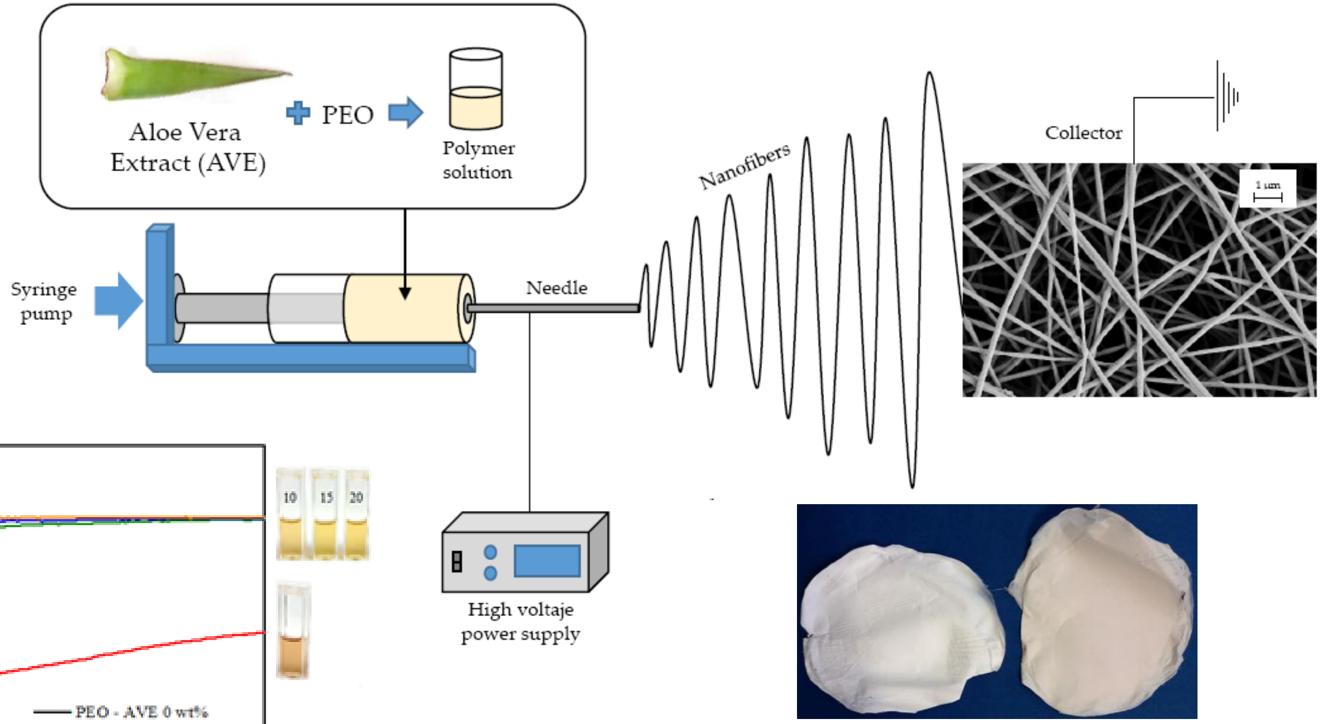
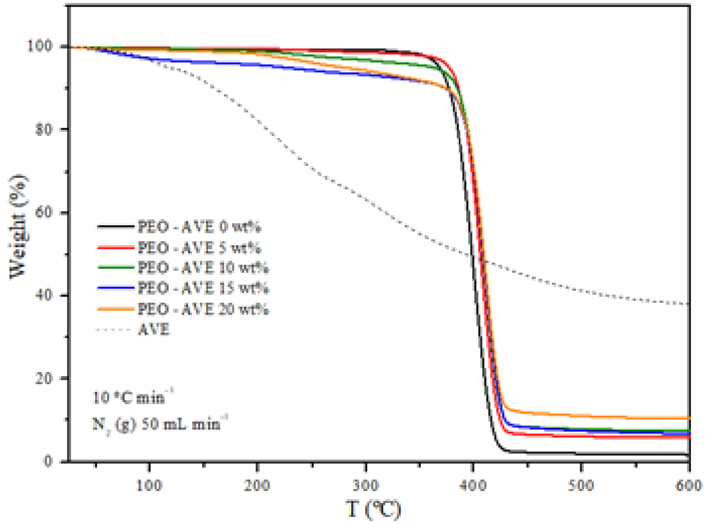
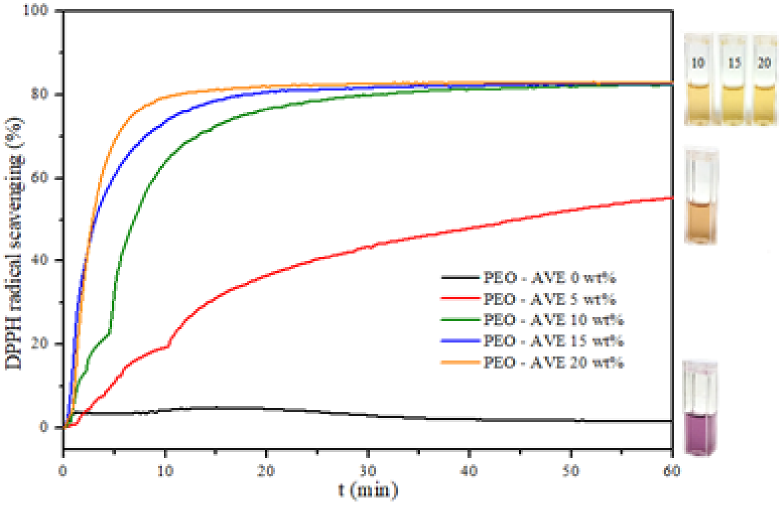
I. Solaberrieta et al. Polymers 12 (2020) 1323







AVE was successfully included in the fibrous materials after the electrospinning process, keeping its intrinsic antioxidant activity

Biorefinery approach

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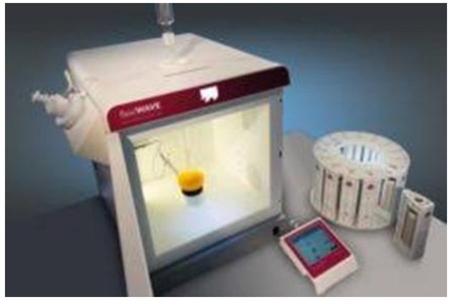
MAE synthesis of SeNPS using cocoa bean shell waste

A.C. Mellinas et al. Molecules 24 (2019) 4048



CCD, 23 Experiments (9 central points)

Factor	-α	-1	+1	+α
Time (min)	1.6	5.0	15.0	18.4
Power (W)	263.3	400.0	800.0	936.4
Amount of Selenite (g)	0.06	0.15	0.40	0.48

Reducing +stabilizing agent

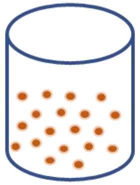
CBS extract pH=2: Polyphenols, pectin and protein

Na_2SeO_3

Plant extracts

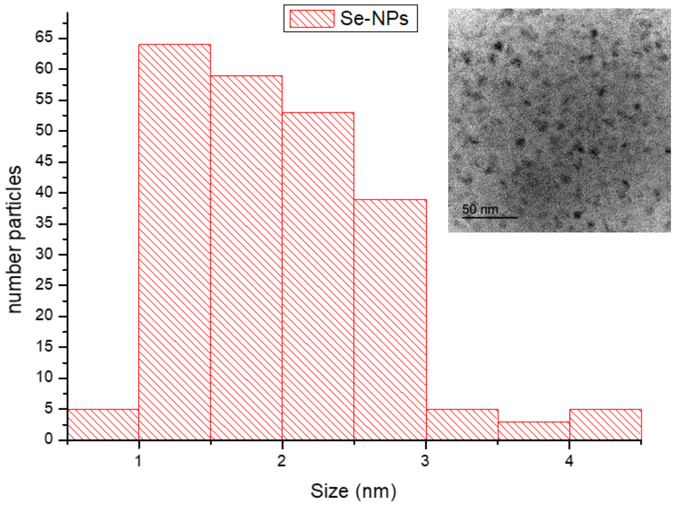
Metallic precursor

No need of toxic reducing and stabilising agents



Se nanoparticles

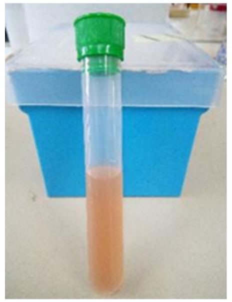
Spherical SeNPs
1-3 nm diameter



SeNPs: high antioxidant capacity and stable for more than 2 months at 4 ºC

Day	Sample	FRAP	ABTS
	mg Trolox/g dried sample		
0	CBSE-2	12.4 ± 0.2	28.6 ± 0.1
	Se-NPs	49.2 ± 0.1	67.3 ± 0.4
55	Se-NPs	47.2 ± 0.3	68.1 ± 1.2

Day O



Day 55

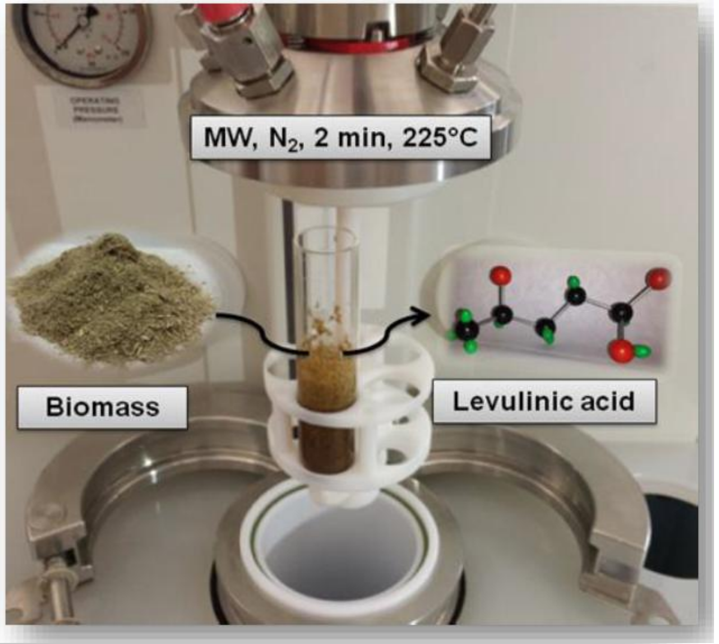
Biorefinery approach

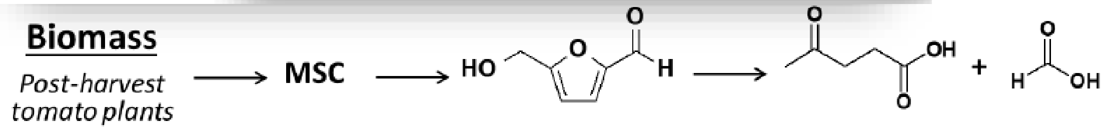
MILESTONE
HELPING CHEMISTS

Conversion of lignocellulosic biomass to valuable molecules

MW-ASSISTED FLASH CONVERSION OF POLYSACCHARIDES TO LEVULINIC ACID

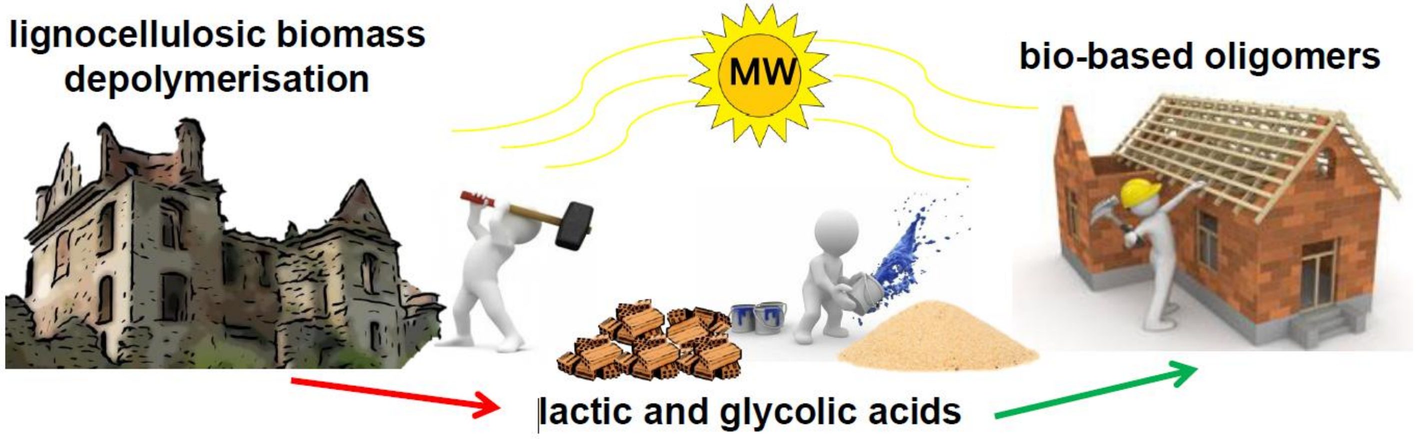
S. Tabasso et al. Green chem 16 (2014) 73





FROM LIGNOCELLULOSIC BIOMASS TO LACTIC AND GLYCOLIC ACID

D. Carnaroglio et al. ChemSusChem 8 (2015) 1342



MW heating
2 min, 220°C

Conventional heating
4 h, 190°C

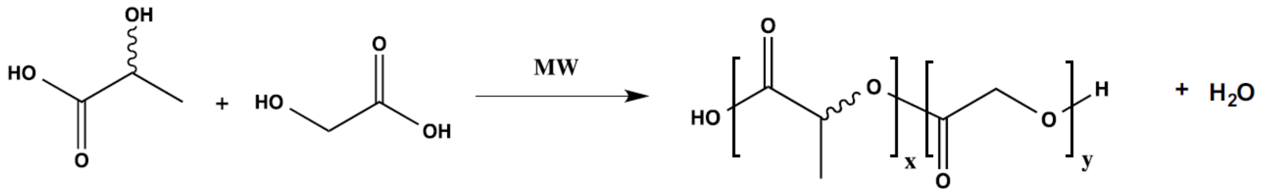
Biorefinery approach

Conversion of lignocellulosic biomass to valuable molecules

MILESTONE HELPING CHEMISTS

D. Carnaroglio et al. ChemSusChem 8 (2015) 1342

MW-ASSISTED POLY-CONDENSATION



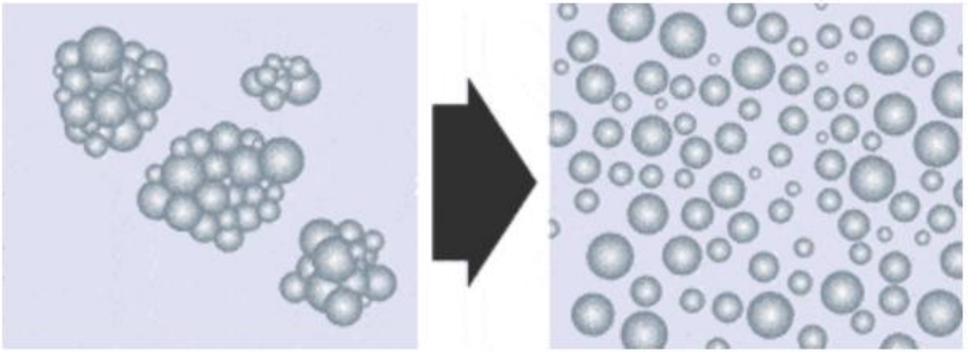
Lactic acid Glycolic acid poly(lactic-co-glycolic acid)

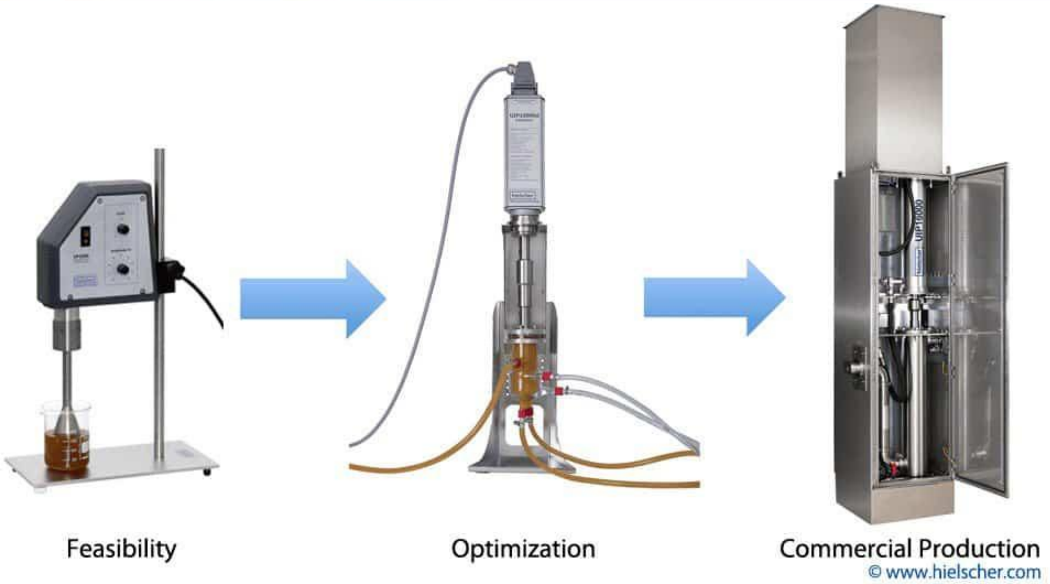
Entry	Feed (mol %) LA/GA	Yield (%)	Polymer composition LA/GA[b]	Mn[c]	Mw/Mn[c]	T_d (°C)[d]
1	100/0	80	100/0	2229	1.53	362
2	50/50	75	53/47	2923	1.47	365
3	70/30	77	69/31	2510	2.00	359

[a] 130 °C, 3h, 70 mbar,
[b] Estimated from the integral height of hydrogen in ^{1}H-NMR spectra
[c] Determined by GPC analysis
[d] Determined by TGA

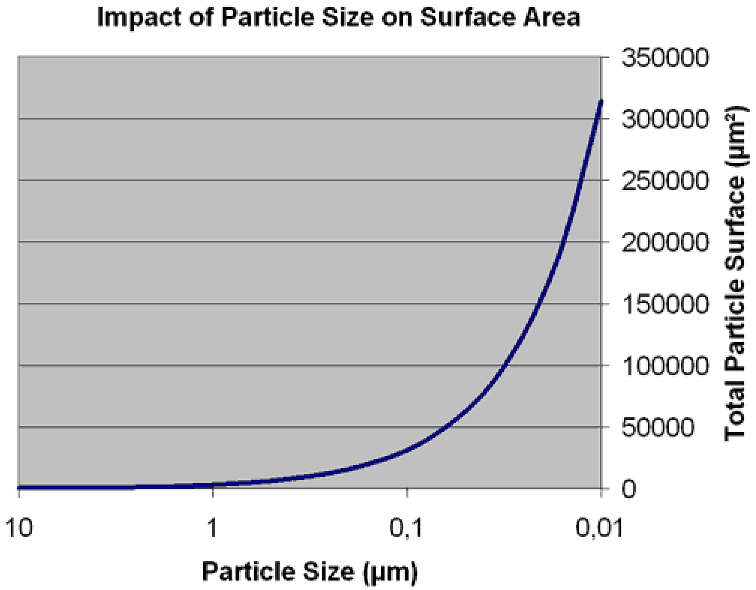
Biorefinery approach

Powerful Ultrasonic Cavitation in Liquid



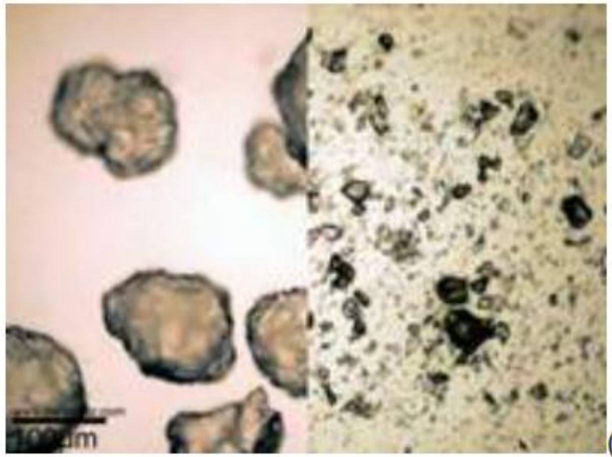


- Homogenizing
  - Dispersing and Deagglomeration
  - Emulsifying
  - Wet-Milling and Grinding
- Disintegration
  - Cell Extraction
  - Hot Water Disinfection
- Sonochemistry
  - Transesterification (Biodiesel)



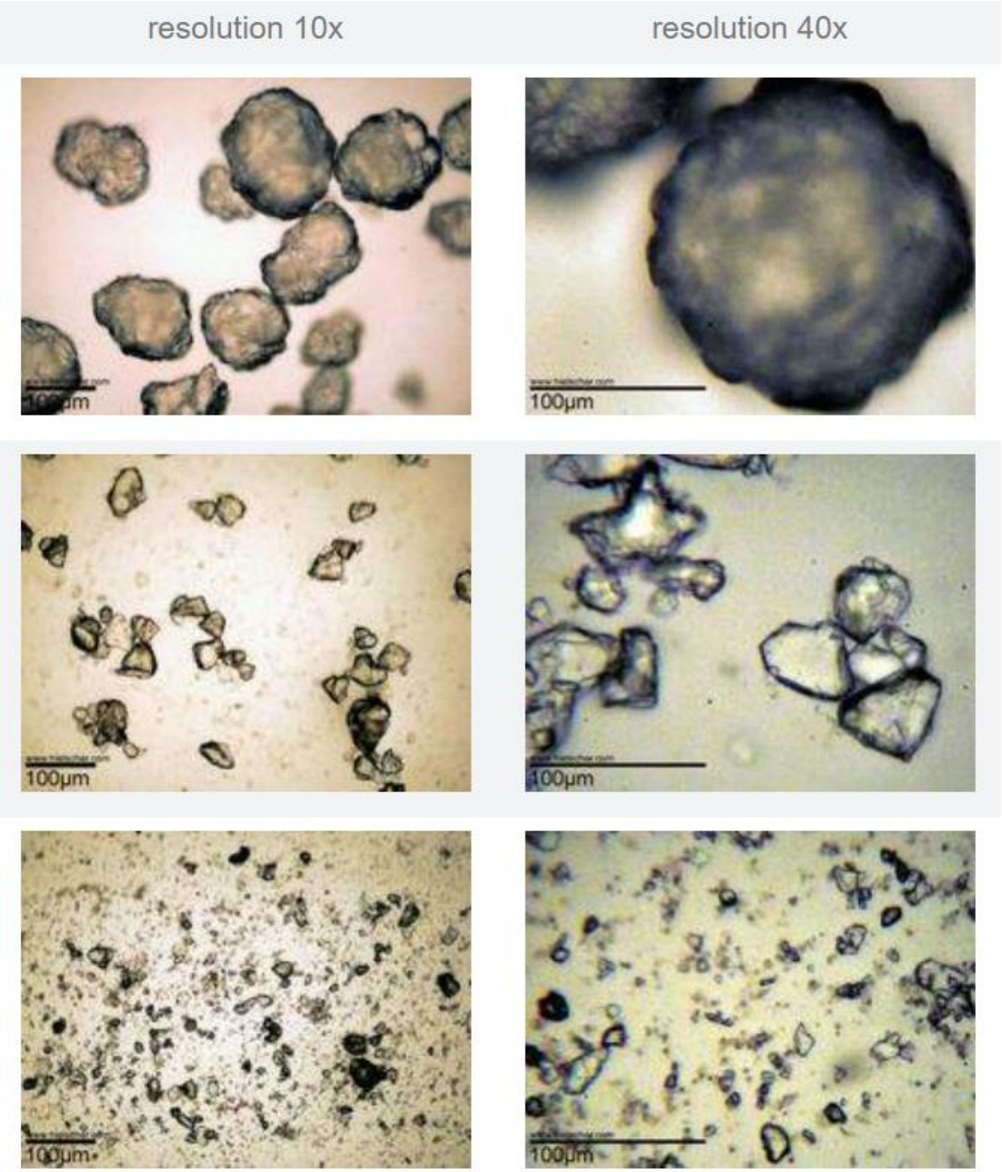
Biorefinery approach

Ultrasonic Wet-Milling and Micro-Grinding



(before)

AL(OH)3 (after)



Biorefinery approach

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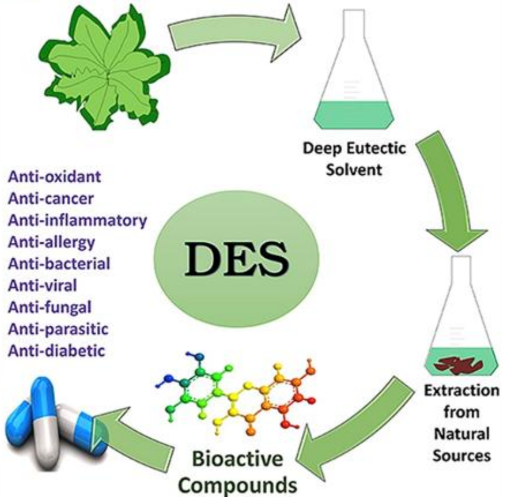
Horchata de chufa by-products valorization

Polyphenols



DES-MAE
DES-UAE

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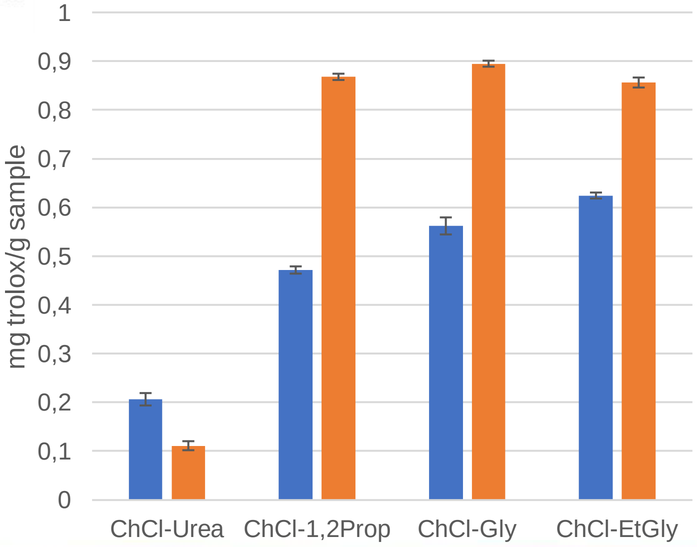
DPPH (mg trolox/g sample)	Plant residue	Tuber residue
MAE	0.489 ± 0.01^{a}	0.64 ± 0.02^{a}
UAE	0.34 ± 0.05^{a}	0.49 ± 0.09^{b}

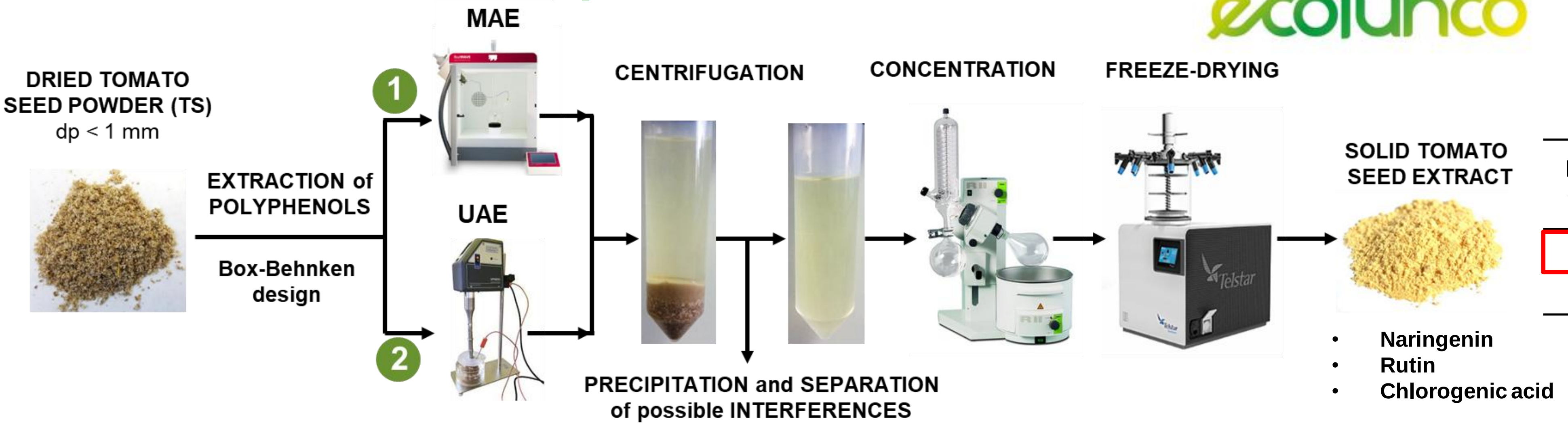
- ✓ Increased antioxidant capacity with tuber residue extractions
- ✓ Improved antioxidant activity vs. ethanolic extractions with MAE and UAE

Hydrogen bond acceptor (HBA)	Hydrogen bond donor (HBD)	Molar relation
Choline chloride (ChCl)	Urea	1:2
	1,2-Propanediol	
	Glycerol	
	Ethylene glycol	

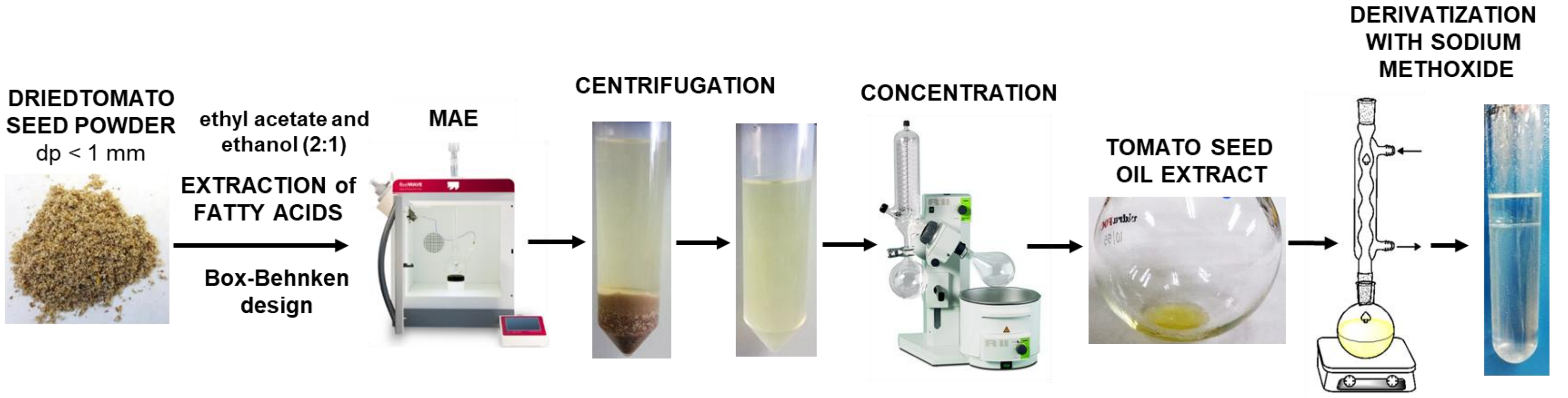


Antioxidant capacity (DPPH, 517 nm mg Trolox/g sample)

Biorefinery approach



Extraction technique	TPC (mg_{GAE}/g_{TS})	DPPH (mg_{TE}/g_{TS})
MAE	1.72 ± 0.04	1.46 ± 0.02
UAE	1.61 ± 0.03	1.25 ± 0.01



C16:0 (mg/g_{TS})	C18:0 (mg/g_{TS})	C18:1 (mg/g_{TS})	C18:2 (mg/g_{TS})
31.8 ± 1.0	12.6 ± 0.4	48.5 ± 1.4	121.7 ± 3.8

γ-tocopherol (mg/kg_{TS})	α-tocopherol (mg/kg_{TS})
260.3 ± 0.6	6.53 ± 0.12

CONCLUSIONS

Valorisation of agro-food residues and by-products is a field with high potential to develop new sustainable biomaterials with advanced functionalities.

The development of innovative, fast and efficient methods for the extraction of high value chemicals from agro-food residues are necessary to obtain high added value compounds, such as polyphenols, flavonoids, proteins, lipids and building blocks for biopolymers and biocomposites.

Extraction conditions in MAE and UAE are essential for the development of efficient methods to obtain high extraction yields.

Agro-food residues and by-products have shown their potential for the development of functional systems with multiple applications.

Thank you!

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