



32 **Keywords:** globe artichoke; levulinic acid; microwaves; process intensification;  
33 delignification.

34

## 35 **1. Introduction**

36 In recent years, food science has expanded the scope of research investigations leading to  
37 new achievements in the field of valorization, mainly from the wide range of by-products  
38 generated during industrial processing. The renewable C-based nature of agri-food  
39 matrices represents an alternative route to high-added-value compounds that can act as  
40 alternatives to fossil sources, paving the way for the bio-economy era (Liu *et al.*, 2023).

41 Of all the by-products that derive from the processing of edible plants with functional  
42 properties, those of the globe artichoke (GlobART) (*Cynara scolymus L.*) are particularly  
43 promising for further valorization. This industrial crop originates from the Mediterranean  
44 area, and is widely cultivated in some countries, such as Italy and Spain. Generally,  
45 GlobART by-products from artichoke processing represent 80-85 % of its fresh weight,  
46 and mainly involve the heads, leaves, stalks and roots, which have a lignocellulosic  
47 composition (Francavilla *et al.*, 2021). This waste is unsuitable for human consumption  
48 and further contributes to environmental issues, meaning that an alternative exploitation  
49 route should be explored.

50 GlobART is a well-known source of biologically active compounds (BACs), and their  
51 recovery is considered to be an economically viable solution for the valorization of by-  
52 products. Of these BACs, the significant presence of phenols with therapeutic action  
53 (Ferioli and D'Antuono, 2022; Salata *et al.*, 2022b, 2022a), and proteins (Órbenes *et al.*,  
54 2021; Ruiz-Cano *et al.*, 2014) is particularly worthy of note. These BACs can be easily  
55 recovered with improved efficiency and sustainability using process-intensification  
56 technologies and green solvents, according to Green Extraction principles (Chemat *et al.*,  
57 2020; Mariatti *et al.*, 2021). For instance, subcritical water extraction (SWE) is a  
58 superheated water process at temperatures ranging from water's boiling point to its  
59 critical point (100-373 °C), combined with high pressures to keep it in a condensed state.  
60 The dielectric constant of water decreases with increasing temperature, and reaches  
61 values close to organic solvents, such as ethanol or methanol, thus facilitating the  
62 recovery of mid- and less-polar bioactive compounds (Órbenes *et al.*, 2021; Özkaynak  
63 Kanmaz, 2018). These enabling extraction conditions provide an improvement in terms

64 of mass transfer and wetting, thanks to the lower water surface tension and viscosity,  
65 leading to the matrix undergoing valuable structural modifications, and further solvent  
66 penetration (Bursać Kovačević *et al.*, 2018; Mariatti *et al.*, 2021). Moreover, higher  
67 temperatures cause intermolecular interactions to weaken, thus linking metabolites to the  
68 matrix and facilitating solubilization into water through an efficient and fast extraction  
69 process (Plaza and Marina, 2019).

70 Moreover, most valorization processes for GlobArt by-products also focus on biofuel  
71 production because of the significant carbohydrate and ethanol-soluble fractions present,  
72 which account for 70-75 % of its fresh weight (Biel *et al.*, 2020; Lutz *et al.*, 2011; Órbenes  
73 *et al.*, 2021). The hydrolysis and fermentation of inulin, a water-soluble fiber commonly  
74 extracted from GlobART residues, provides bioethanol, and thus represents a significant  
75 upgrade for this matrix (Hughes *et al.*, 2017; Zayed and Farag, 2020). However, the  
76 conversion of the sugar fraction towards bio-derived platform chemicals has not yet been  
77 reported, to the best of our knowledge. In this context, the production of LevA would be  
78 a valuable accomplishment, from an innovation point of view, in valorizing the majority  
79 of this fraction.

80 LevA, or 4-oxovaleric acid, is a recognized bio-based building block widely obtained  
81 from biomass conversion, mainly via the acidic hydrolysis of cellulose and hemicellulose  
82 fractions in lignocellulosic waste (Salgado-Ramos *et al.*, 2022c; Tabasso *et al.*, 2014). Its  
83 versatility is mainly attributed to its high functionalization thanks to the presence of both  
84 a keto and a carboxylic group. Therefore, multiple high-end products, with applications  
85 as solvents, fuels, pharmaceuticals and food additives, can be obtained from its  
86 conversion (Badgajar *et al.*, 2020).

87 LevA production can be enhanced by means of process-intensification techniques as well.  
88 The use of microwave (MW) heating for this transformation is particularly noteworthy  
89 (Aliko *et al.*, 2020; di Menno Di Bucchianico *et al.*, 2022). The selective absorption of  
90 this radiation by polar molecules, along with ionic conduction, provides superior  
91 efficiency to conventional heating, where heat is transferred via conduction from the flask  
92 wall to the sample (de la Hoz *et al.*, 2005; Lucas-Torres *et al.*, 2016). Thus, a considerably  
93 lower number of side reactions occur and fewer undesired by-products are formed, with  
94 higher product yields in shorter residence times.

95 Furthermore, MW treatment also promotes delignification via MW-assisted extraction  
96 (MAE). This step is crucial not only in terms of biomass valorization, where some  
97 hemicellulose and BACs can be easily recovered as well (Lauberte *et al.*, 2021; Salgado-  
98 Ramos *et al.*, 2022a), as some authors have reported that cellulose accessibility can be  
99 enhanced in the remaining solid fraction after processing, favoring the subsequent  
100 transformation to LevA (Rapado *et al.*, 2021; Zhao *et al.*, 2017).

101 Delignification can also be intensified by means of ultrasound (US)-assisted extraction  
102 (UAE) (Salgado-Ramos *et al.*, 2022c). The cavitation effect in US favors mass transfer  
103 because of the implosion of microbubbles in the liquid phase. These bubbles grow and  
104 collapse, creating high-energy microenvironments in the reaction medium via the  
105 generation of microjet streams, shock waves and shear forces, which induce mechanical  
106 effects such as the breakdown of tissues into small fragments and intensive mixing and  
107 heating (Calcio Gaudino *et al.*, 2021; Verdini *et al.*, 2021). This phenomenon  
108 subsequently favors cell-wall rupture, and furthers the release of the desired compounds  
109 compared to conventional methods.

110 Based on this background, a multi-step green protocol with enabling technologies has  
111 been developed for the valorization of GlobART food-processing residues towards BAC  
112 recovery and sugar conversion into LevA, and is presented in this article. The post MW-  
113 assisted -SWE (MA-SWE) matrix was either directly transformed via MW-assisted acidic  
114 conversion into LevA or subjected to a previous delignification step under either MW or  
115 US to enhance LevA recovery.

116

## 117 **2. Material and methods**

### 118 **2.1. Chemicals**

119 All chemicals and solvents were purchased from Sigma-Aldrich and used without further  
120 purification.

### 121 **2.2. Feedstocks**

122 Untreated GlobART food-processing residues were purchased from a local market  
123 (Turin-Italy) and freeze-dried until use. They were then cryo-milled to provide a  
124 homogeneous matrix for the experiments. Untreated GlobART was subsequently mildly  
125 dried at 40-50°C to remove the high amount of water remaining after cryo-milling.

126 The MA-SWE GlobART matrix was mildly dried at 40-50°C after being recovered and  
127 then blade-milled for further experiments.

### 128 **2.3. MW-assisted, subcritical water extraction of GlobART food-processing waste**

129 MA-SWE was carried out on the lab-scale in a high-pressure-resistant professional  
130 multimode MW reactor (Synthwave Milestone, Srl, MLS GmbH, Bergamo, Italy).  
131 GlobART biomass (8 g) was mixed with the desired amount of water in a 1:50 solid/liquid  
132 (S/L) ratio. The mixture was left to moisturize for 5 min in a 1 L Teflon vessel, which  
133 was then introduced into the pressure-resistant MW multimodal reactor equipped with an  
134 external inert gas feed (N<sub>2</sub>). For each MA-SWE test, appropriate purging with N<sub>2</sub> was  
135 performed three times to remove oxygen traces from the system, reducing oxidative stress  
136 on the GlobART biomass. The reaction chamber was then pressurized with N<sub>2</sub> to avoid  
137 water ebullition (40 bars). The samples were heated at 125°C for 15 min (Cravotto *et al.*,  
138 2022). The resulting extraction mixture was filtered under vacuum, and the residual  
139 biomass was thoroughly washed with fresh water. The dry extract was recovered by  
140 freeze-drying (LyoQuest-85, Telstar, Madrid, Spain), weighed, and stored at 4 °C for  
141 further conversion. Each extraction was performed in triplicate to validate the  
142 reproducibility of the experimental results.

### 143 **2.4. Recovery of biologically active compounds (BACs)**

#### 144 *2.4.1. Antioxidant activity*

145 The scavenging activity for the liquid extract after MA-SWE was determined using a  
146 DPPH assay and a Cary 60 UV-VIS spectrophotometer (Cary 60, Agilent Technologies,  
147 Santa Clara, CA, USA). Experiments were carried out at 515 nm, and the results are  
148 expressed in terms of IC<sub>50</sub> (mg/mL), with respect to C<sub>0</sub> (mg/mL), according to previous  
149 works (Salgado-Ramos *et al.*, 2022a, 2022c). The liquid fraction was freeze-dried, and  
150 then solubilized in a 50% v/v MeOH/H<sub>2</sub>O solution.

#### 151 *2.4.2. Polyphenol analysis*

152 Total polyphenol content (TPC) was determined, using the Folin-Ciocalteu method in the  
153 same UV-VIS equipment as described above, at 765 nm. The results are expressed as mg  
154 gallic acid equivalents (mg GAE) / g dry weight (g DW) (Salgado-Ramos *et al.*, 2022b).

155 The MA-SWE GlobART extracts were also analyzed by HPLC-MS using a Waters 2525  
156 pump linked to a Column Fluidics Organizer (Waters Corp., Singapore, Singapore)

157 combined with a 2767 Sample Manager (Waters) coupled with a 2487 dual Abs detector  
158 and a Micromass ZQ. The column used was a Synergi Hydro-RP C18 column (250 mm,  
159 4.6 mm, 4  $\mu$ m; Phenomenex, Torrance, CA, USA), with 2% AcOH (A) and 2% MeCN  
160 (B) as the mobile phases (1 mL/min). The monitored wavelengths were 280 and 340 nm.  
161 Elution was performed using a gradient program starting from 0% B (maintained for 6.5  
162 min), to 50% B in 30 min, and from 50% to 100% B from 30 to 36 min, followed by a  
163 100% B step for a further 6 min.

## 164 **2.5. Characterization of GlobART biomass**

### 165 *2.5.1. Proximate and ultimate analyses*

166 Proximate analysis for both GlobART and post-MA-SWE GlobART biomass was  
167 performed using thermogravimetric analysis (TGA) (Perkin Elmer Thermogravimetric  
168 Analyzer TGA 4000) at temperatures of 25-800°C and a heating rate of 10°C/min. Inert  
169 conditions were used for organic matter and an oxidizing atmosphere for ash. Differential  
170 thermogravimetric (DTG) curves were recorded in OriginLab 2019b software (OriginLab  
171 2019b Graphing and Analysis software, Northampton, Massachusetts, USA).

172 Ultimate analysis was carried out according to the ASTM D-5373 norm. Both oxygen  
173 percentage and ratio O/C were calculated according to a previous work (Salgado-Ramos  
174 *et al.*, 2022b).

### 175 *2.5.2. Fiber analysis*

176 Fiber and extractive composition were determined for untreated- and MA-SWE-treated  
177 GlobART using the National Renewable Energy Laboratory (NREL) procedure,  
178 according to a previous work (Salgado-Ramos *et al.*, 2022b) and using the standard  
179 protocol reported by Sluiter *et al.*, 2008.

180

### 181 *2.5.3. FT-IR analysis*

182 FT-IR spectra were recorded in a Spectrum Two ATR (Perkin Elmer, Waltham, MA,  
183 USA) in transmittance mode with 16 scans and a resolution of 2  $\text{cm}^{-1}$ . The frequency  
184 range was from 4000 to 500  $\text{cm}^{-1}$ .

## 185 **2.6. Microwave- and ultrasound-assisted delignification (MAD, UAD) of post-MA- 186 SWE GlobART biomass**

187 The delignification percentage was calculated in consideration of the amount of MA-  
188 SWE GlobART used, and the weight of the cellulose-rich solid fraction obtained after the  
189 procedure (**Equation 1**):

$$190 \quad \% \text{ delignification} = \frac{m(\text{MA-SWE GlobART}) - m(\text{cellulose-rich fraction})}{m(\text{MA-SWE GlobART})} \times 100 \quad (\text{Eq. 1})$$

191 MAD was carried out in the same professional multimode MW reactor (2.45 GHz, 1500  
192 W), with a multi-rack position tool for simultaneous reactions. 7.5 g of MA-SWE  
193 GlobART was placed into five 40 mL MW glass vials (20 mL maximum liquid volume)  
194 along with an NaOH solution (10 % with respect to the dry matter). Experiments were  
195 carried out in duplicate, at 120°C for 30 min, according to previous studies (Salgado-  
196 Ramos *et al.*, 2022a).

197 US-assisted delignification (UAD) was performed in a 5 L stainless steel tank high-power  
198 US bath, equipped with three probes that are screwed-fixed into the bottom (Weber  
199 Ultrasonic AG, Karlsbad, Germany). The bath was set to operate at a frequency of 40 kHz  
200 and 200 W power. 7.5 g of MA-SWE GlobART was placed into a 250 mL round-  
201 bottomed flask, along with 480 mg of NaOH (10 %) and 100 mL of deionized water  
202 (solid:liquid ratio 1:20). Experiments were carried out in duplicate, at 50°C for 60 min  
203 (Salgado-Ramos *et al.*, 2022c).

## 204 **2.7. Conversion of post-extraction MA-SWE GlobART biomass into Levulinic acid** 205 **(LevA)**

206 LevA production was performed via MW-assisted acidic conversion in the MW reactor  
207 described above (Synthwave Milestone, Srl, MLS GmbH, Bergamo, Italy).

208 For preliminary tests, 0.50 g of post-MA-SWE GlobART were charged into a 40 mL MW  
209 glass vial. Different volumes of either HCl or *p*-toluenesulfonic acid (*p*-TsA) were added  
210 at different concentrations. When using *p*-TsA, KBr was also used as a co-catalyst to  
211 favor the process (Lorente *et al.*, 2023). Samples were previously stirred to obtain a  
212 homogeneous solution. The mixtures were irradiated at 1500 W at the pertinent  
213 temperatures (190 or 225°C) and time (2 or 20 min), under inert conditions (N<sub>2</sub>, 40 bar).  
214 Reaction workup was carried out according to a previous work (Salgado-Ramos *et al.*,  
215 2022c).

216 Either *p*-TsA (0.25 M) or HCl (2 M) were added (5 mL) to both MA-SWE + MAD- and  
217 MA-SWE + UAD-GlobART solid residues, in a solid:liquid ratio of 1:10 (0.5 g of solid).  
218 Reaction conditions and workup were similar to those already described.

219 LevA molar and ponderal yields, as well as conversions, were calculated according to the  
220 available literature (Chen *et al.*, 2020; Raspolli Galletti *et al.*, 2021) (see Supplementary  
221 Material).

## 222 **2.8. GC-MS and NMR analyses**

223 Both GC-MS and NMR were performed for LevA characterization. The analysis was  
224 carried out in accordance with our previous studies (Salgado-Ramos *et al.*, 2022c).

225 Briefly, NMR analysis was performed in a Jeol JNM-ECZ600R spectrometer (Jeol,  
226 Tokyo, Japan) operating at a frequency of 600 MHz for the <sup>1</sup>H nucleus. 600 μL of CDCl<sub>3</sub>  
227 was added to the dried samples, then filtered with a nylon syringe filter and finally added  
228 to the NMR tube.

229 GC-MS was carried out after prior derivatization, in an Agilent Technologies 6850  
230 Network GC System with a 5973 Network Mass Selective Detector and 7683B Automatic  
231 Sampler, using a capillary column (HP-5MS; length, 30 m; i.d., 0.25 mm; film thickness,  
232 0.25 μm) (Agilent Technologies, Santa Clara, CA). In a typical experiment, the dried  
233 crudes were dissolved in 1.5 mL of CHCl<sub>3</sub>. Subsequently, 80 μL of BSTFA ((N,O-  
234 bis(trimethylsilyl)trifluoroacetamide) were added to the solution as a derivatizing agent.  
235 The mixture was kept under magnetic stirring for 45 min at a temperature of 65 °C.

236

## 237 **3. Results and discussion**

### 238 **3.1 MW-assisted extraction of BACs from GlobART leftovers**

#### 239 **3.1.1 Preliminary characterization of raw GlobART leftovers**

240 In order to thoroughly understand the suitability of GlobART waste for biorefinery  
241 purposes, it was fully characterized using proximate, ultimate and fiber analyses (**Table**  
242 **1**).

243



244 **Table 1.** Preliminary characterization of GlobART leftovers using proximate, ultimate  
 245 and fiber analyses.

<b>GlobART waste</b>	
<b>Proximate analysis (%)</b>	
Organic matter	91.74
Volatile content	67.83
Fixed carbon	23.91
Ash	5.99
Moisture	2.27
<b>Ultimate analysis (%)</b>	
C	42.98
H	6.04
N	1.93
O *	49.05
O/C ratio	0.86
H/C ratio	1.69
<b>HHV (MJ/kg) **</b>	<b>17.02</b>
<b>Fiber analysis (g/100g DM) ***</b>	
Extractives	
Non-polar fraction	1.38
Polar fraction	3.69
Fibers	
Cellulose	29.07
Hemicellulose + soluble polyphenols	38.68
Lignin	21.15
Total fibers	88.90
Fibers + extractives	93.97
Others	6.03

246 \* Obtained as a difference considering C, H and N percentage.

247 \*\* HHV: higher heating value (theoretical value).

248 \*\*\* g/100 g dry matter (DM).

249

250 Both the proximate and ultimate analyses provide us with information on the energetic  
 251 properties of lignocellulosic waste, with a view to an alternative and innovative means of

252 upgrading it as a bioenergy source (Ibn Ferjani *et al.*, 2019; Remón *et al.*, 2021).  
 253 However, based on the reported results for GlobART, neither its HHV (17.02 MJ/kg) nor  
 254 its O/C (0.86) and H/C ratios (1.69) make the matrix suitable for energetic purposes. For  
 255 this reason, it can be more appropriately exploited, for instance, as a source for the  
 256 recovery of BACs and the further conversion of the cellulose-rich exhausted matrix to  
 257 LevA, with this probably being the most economically viable valorization pathway. **.1.2**  
 258 ***MW-assisted Subcritical Water Extraction and characterization of BACs from***  
 259 ***GlobART***

260 The application of process-intensification technologies induces significant physical  
 261 changes in the initial matrix, with these changes due to, for instance, higher diffusivity or  
 262 viscosity variations. These enabling treatments normally convert the raw material into  
 263 products of reduced particle size, which could favor the recovery of metabolites and  
 264 further transformation steps (Osorio-Tobón, 2020; Teixeira *et al.*, 2021).

265 In this context, MW-assisted SW extraction (MA-SWE) was explored for the valorization  
 266 of GlobART by-products. Firstly, this protocol was carried out on the lab-scale (1 L  
 267 vessel), at 125°C for 15 min, according to a previous work (Cravotto *et al.*, 2022). The  
 268 liquid fraction obtained after this treatment was analyzed in terms of total polyphenol  
 269 content (TPC) and antioxidant capacity (DPPH) (**Table 2**), thus confirming the presence  
 270 of BACs. Furthermore, HPLC-MS analysis (**Figure S1**) indicates that some specific  
 271 polyphenols, such as 1-caffeoylquinic acid, chlorogenic acid, narirutin and cynarine, are  
 272 present. This experiment proved the efficiency of the intensified protocol for the  
 273 valorization of these by-products as a source of antioxidant compounds.

274

275 **Table 2.** Total polyphenol content (TPC) and antioxidant activity of the liquid fraction  
 276 obtained after microwave-assisted, subcritical water extraction (MA-SWE) from  
 277 GlobART.

Extraction conditions	DPPH (IC <sub>50</sub> based on C <sub>0</sub> <sup>a</sup> )	TPC (mg GAE/ g DW <sup>b</sup> )	Main polyphenols (HPLC-MS)
MA-SWE, 125 °C, 15 min	0.3245 ± 0.0026	24.4980 ± 0.5005	1-caffeoylquinic acid, chlorogenic acid, cynarine

278 a. C<sub>0</sub>: initial concentration for the extract.

279 b. mg GAE/ g DW: mg gallic acid equivalents / g dry weight.

280

281 Since the use of GlobART leftovers as a BACs source, in parallel with inulin extraction,  
 282 has been widely described in literature (Sałata *et al.*, 2022a, 2022b; Zayed and Farag,  
 283 2020), this work aims to valorize the solid fraction recovered after MA-SWE processing.  
 284 In this context, conversion to LevA, one of the top bio-based lignocellulosic-biomass-  
 285 derived platform chemicals, was investigated for the valorization of residual GlobART.

286 **3.1.3. Characterization of post extraction GlobART (MA-SWE) biomass**

287 As the exploitation of residual GlobART mainly focuses on the valorization of the solid  
 288 fraction that remained after MA-SWE processing, this matrix was first characterized by  
 289 means of the NREL procedure, along with starting GlobART biomass, for sake of  
 290 comparison. This procedure focused on the quantification of fibers (cellulose,  
 291 hemicellulose and lignin), and the labile polyphenols that remain after MA-SWE. Both  
 292 compositions are shown in **Table 3**.

293

294 **Table 3.** Characterization of MA-SWE globe artichoke biomass in comparison with raw  
 295 GlobART biomass using the NREL procedure.

	<b>GlobART</b> <b>(g/100g DM <sup>a</sup>)</b>	<b>(MA-SWE)-GlobART</b> <b>(g/100g DM)</b>
Cellulose	29.07	38.81
Hemicellulose + soluble polyphenols	38.68	24.43
Lignin	21.15	25.66

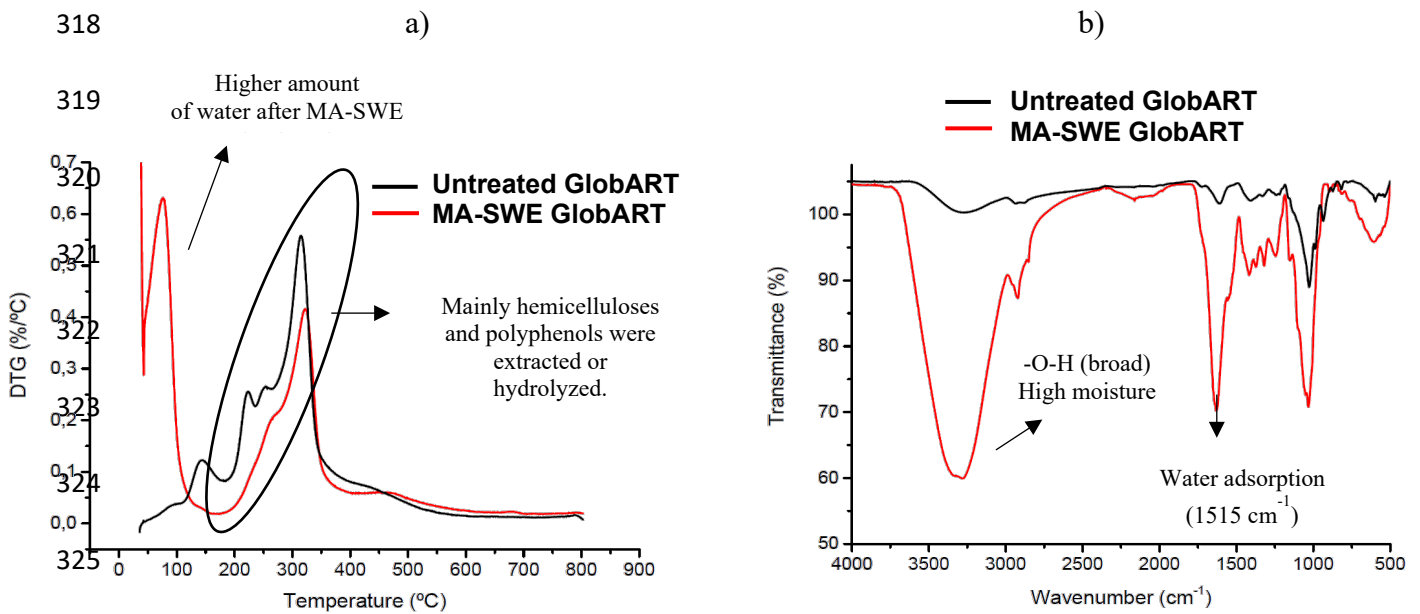
296 a. g/100g DM: g/100g dry matter

297

298 In this composition analysis, significant differences were found in terms of both relative  
 299 cellulose and hemicellulose content between these two matrices. Particularly noteworthy  
 300 is the cellulose enrichment in the post-extraction matrix (MA-SWE GlobART) (from  
 301 29.07% to 38.81%), which is then able to be better converted into the target product  
 302 (LevA). Furthermore, the significant decrease in the hemicellulosic fraction in the post-  
 303 extraction matrix from 38.68% (GlobART) to 24.43% in MA-SWE GlobART is also  
 304 important (**Table 3**). Indeed, the partial solubilization of the hemicellulose fraction  
 305 present in the starting biomass can also be expected during the MAE step in subcritical  
 306 water at 125°C in addition to the extraction of BACs from the matrix (**Table 2**). Finally,  
 307 the enrichment, albeit minimal, of the lignin fraction can be observed in the post-extracted

308 biomass (MA-SWE GlobART) (**Table 3**). In this regard, since the content of the starting  
309 matrix GlobART and that of the post-extraction recovered biomass (MA-SWE GlobART)  
310 still show lignin contents of above 20%, a prior delignification step could facilitate the  
311 subsequent conversion of both GlobART biomasses into LevA.

312 Thermogravimetric and FT-IR analyses were also recorded. Differential  
313 thermogravimetric (DTG) curves showed the efficient extraction of soluble compounds,  
314 as BACs, after the MA-SWE step, as well as a considerable increase in moisture in MA-  
315 SWE GlobART (**Figure 1a**). This fact is the main change observed in the FT-IR analysis  
316 (**Figure 1b**), and can be seen in the sharp bands related to water adsorption ( $1558\text{ cm}^{-1}$ )  
317 and -OH bonds ( $3500\text{-}3000\text{ cm}^{-1}$ , broad).



327 **Figure 1.** Differential thermogravimetric (DTG) curves (a) and FT-IR spectra (b) for  
328 untreated- and MA-SWE-GlobART.

329

### 330 3.2. MW-assisted conversion into Levulinic acid (LevA)

#### 331 3.2.1. Preliminary tests

332 According to the biorefinery approach and with the aim of valorizing all waste-biomass  
333 components, MA-SWE GlobART was selected as the starting material, in this work, for  
334 optimizing conversion into LevA after the extraction of high-added-value compounds  
335 from GlobART. Additionally, the cellulose enrichment in the extraction residue after the

336 MA-SWE process (from 29.07% to 38.81% (see **Table 3**)) makes this matrix more  
 337 suitable for the development of LevA, which is in line with the desired zero-waste  
 338 approach.

339 In this regard, we made use of a previous study of ours (Tabasso *et al.*, 2014), in which  
 340 acid-catalyzed conversion (HCl 1M) to LevA was performed under MW-assisted  
 341 radiation (225°C, 2 min), to uncover the optimized conditions for post-MA-SWE  
 342 GlobART conversion. However, two different acidic catalysts are being compared in this  
 343 present work (HCl and *p*-toluenesulfonic acid (*p*-TsA)) using different respective  
 344 amounts, biomass/acid (B/A) ratios, as well as different reaction times and temperatures.  
 345 Results are summarized in **Table 4** and compared accordingly.

346

347 **Table 4.** MW-assisted conversion of MA-SWE globe artichoke (GlobART) into LevA.

	Acid	T (°C)	Time (min)	B/A ratio <sup>b</sup>	Conversion (%)	Ponderal Yield (%)	Molar Yield (%)
<b><u>MA-SWE GlobART (this work)</u></b>							
1	HCl 1M	225	2	1:10	76.29	20.53	28.67
2	HCl 1M	225	2	1:20	78.16	23.20	32.39
3	HCl 2M	225	2	1:10	91.26	26.76	37.37
4	HCl 2M	225	2	1:20	87.65	28.54	39.85
5	<i>p</i> -TSA <sup>a</sup> 0.25 M	190	20	1:20	92.29	26.28	36.70
6	<i>p</i> -TSA <sup>a</sup> 0.25 M	225	2	1:10	90.41	26.29	37.27
7	<i>p</i> -TSA <sup>a</sup> 0.25 M	225	2	1:20	87.86	25.37	35.43
<b><u>Previous research</u></b>							
8	Post harvest tomato plant (Tabasso <i>et al.</i> , 2014)	225	2	1:10	78.00	63.00	n.d. <sup>c</sup>
9	Grape stalk (Salgado- Ramos <i>et al.</i> , 2023)	225	2	1:10	79.00	49.10	68.60

348 a. *p*-TsA: *p*-toluenesulfonic acid. 1.75 g of KBr was used as co-catalyst for these experiments.

349 b. B/A ratio: biomass/acid ratio.

350 c. n.d.: non determined.

351

352 As observed, the optimized conditions in our MW-assisted flash conversion (2 min) with  
 353 HCl (**Table 4, entry 8-9**) (Tabasso *et al.*, 2014, **Salgado-Ramos *et al.*, 2022c**) were not  
 354 highly efficient for MA-SWE GlobART, achieving only a 29% LevA molar yield and a  
 355 21% ponderal yield (**Table 4, entry 1**). It is possible that side reactions towards undesired

356 products, such as humic acids, may be triggered and thus compete with LevA formation.  
357 To avoid these side reactions, lower HCl loads were tested with the MA-SWE GlobART  
358 biomass, and these new conditions led to a significant improvement in terms of LevA  
359 (**Table S1**). Surprisingly, the use of more acidic conditions, by increasing either the B/A  
360 ratio or HCl load, also afforded better yields (**Table 4, entries 2-4**). In this context, it is  
361 worth noting that 37-40% molar yields for LevA were achieved when using HCl 2 M  
362 (**Table 4, entries 3-4**). Regarding this loading, a compromise between yields and the use  
363 of an acceptable amount of catalyst should be achieved. Therefore, a B/A ratio of 1:10  
364 could be considered in further studies.

365 On the other hand, the use of sulfonic acids, such as *p*-TsA, which has already been  
366 employed to obtain LevA from biomass (Salgado-Ramos *et al.*, 2022d; Lorente *et al.*,  
367 2023), increased the yield up to almost 37% molar and 26% ponderal, with respect to HCl  
368 1M under optimized conditions (**Table 4, entry 5**). Moreover, *p*-TsA is significantly  
369 superior in terms of sustainability to the conventional mineral acids, such as HCl, H<sub>2</sub>SO<sub>4</sub>  
370 or H<sub>3</sub>PO<sub>4</sub>, normally used for this kind of process, especially when it is employed at a low  
371 concentration (0.25 M). This can mainly be attributed to its non-corrosive character and  
372 reusability, which has been corroborated by NMR in an analysis of the aqueous phase  
373 after reaction (**Figure S2**).

374 Furthermore, for the sake of comparison, *p*-TsA was employed under the same conditions  
375 as HCl in terms of temperature (225°C) and time (2 min) (**Table 4, entries 6-7**), with the  
376 acid concentration unchanged at 0.25 M. It was observed that neither the lower B/A ratio  
377 nor changes in temperature and time significantly affected the LevA yield. Despite this,  
378 these conditions should be considered for future experiments since a B/A ratio of 1:10  
379 and the MW-assisted fast process (2 min) afforded a similar yield to the previous 20 min  
380 experiment that had used a 1:20 ratio (**Table 4, entry 5**).

381 Overall, these preliminary tests provided a LevA molar yield of slightly above 37% with  
382 HCl 2 M (**Table 4, entry 3**) and *p*-TsA 0.25 M (**Table 4, entry 6**) in a rapid, MW-assisted  
383 process (2 min). Despite the great difference observed in terms of sustainability, both  
384 catalysts were considered for further studies for the sake of comparison.

385 **3.2.2. Influence of microwave- and ultrasound-assisted delignification (MAD and**  
386 **UAD)**

387 A delignification step is commonly applied in biomass valorization prior to further  
 388 conversion to platform chemicals and biofuels (Calcio Gaudino *et al.*, 2018).  
 389 Furthermore, the lignin that was isolated after delignification can be further transformed  
 390 into added-value chemicals, such as bioaromatics and long-chain fatty acids (Salgado-  
 391 Ramos *et al.*, 2022a). This process therefore not only facilitates the next transformation  
 392 step from biomass, but also concurrently paves the way for a *zero-waste* approach.

393 The high lignin content still present in the recovered GlobART after MA-SWE (25.66%,  
 394 **Table 3**) drove us to perform separate US- and MW-assisted delignification steps (UAD  
 395 and MAD, respectively) before the subsequent conversion of this solid residue to LevA,  
 396 according to the experimental conditions described in section 2.6 (Salgado-Ramos *et al.*,  
 397 2022a, 2022c). Engaging results were obtained from both the UAD and MAD approaches  
 398 (**Table 5**), with these perhaps being favored by MA-SW pretreatment, which significantly  
 399 increased lignin accessibility compared to untreated GlobART, as already explained.  
 400 Moreover, the use of enabling technologies can intensify this step with respect to  
 401 conventional delignification procedures, as seen in the works of Demirhan *et al.*, 2017,  
 402 and Kininge and Gogate, 2022.

403

404 **Table 5.** Microwave- and ultrasound-assisted delignification (MAD and UAD) of MA-  
 405 SWE globe artichoke (GlobART).

	Conditions	MA-SWE GlobART (g)	Recovered solid fraction (g)	Delignification (%)
1	NaOH (10 %), 120°C, 30 min, MAD	7.646 ± 0.067	1.303 ± 0.052	82.97 ± 0.83
2	NaOH (10 %), 50°C, 60 min, UAD	7.561 ± 0.017	2.469 ± 0.049	67.35 ± 0.57

406

407 For the conversion of the solid into LevA, the optimal conditions determined in the  
 408 preliminary test (225°C, 2 min, B/A ratio 1:10) were applied to both delignified matrices  
 409 in separate runs with HCl 2M and *p*-TsA 0.25M, for the sake of comparison. The  
 410 recovered solid fractions, MA-SWE GlobART after MAD (SWE + MAD) and UAD  
 411 (SWE + UAD), were the starting feedstocks (**Table 6**).

412

413 **Table 6.** MW-assisted conversion of different globe artichoke (GlobART) solid residues<sup>a</sup>.

	Treatment	Acid	Conversion (%)	Ponderal yield (%) <sup>c</sup>	Molar yield (%) <sup>c</sup>
1	MA-SWE GlobART	HCl 2 M	91.26	26.76	37.37
2		<i>p</i> -TsA <sup>b</sup> 0.25 M	90.41	26.29	37.27
3	(MA-SWE+UAD)- GlobART	HCl 2 M	82.34	40.82	57.00
4		<i>p</i> -TsA <sup>b</sup> 0.25 M	91.87	39.63	55.35
5	(MA-SWE+MAD)- GlobART	HCl 2 M	70.97	51.22	71.52
6		<i>p</i> -TsA <sup>b</sup> 0.25 M	90.50	50.91	71.09

414 a. Reaction conditions: T: 225°C; t: 2 min; P: 40 bar N<sub>2</sub>; biomass/acid (B/A) ratio: 1/10.

415 b. *p*-TsA: *p*-toluenesulfonic acid. 1.75 g of KBr was used as the co-catalyst for these experiments.

416 c. Obtained considering the amount of cellulose in MA-SWE GlobART for the sake of comparison.

417

418 The considerable promotional effects that the delignification step has on LevA yields are  
419 evident. In particular, MAD (**Table 6, entries 5-6**) was the most efficient pretreatment,  
420 as it gave a molar yield of above 71% whereas only 37% was obtained without  
421 delignification (**Table 6, entries 1-2**), i.e., a boost of up to 90% in terms of LevA. The  
422 lignin fraction is known to limit contact between catalysts and feedstocks, which could  
423 hinder the hydrolysis of cellulose towards fine chemicals (Yoon *et al.*, 2014; Zhao *et al.*,  
424 2017). This step is therefore usually crucial to enhancing product yields. Moreover,  
425 partial hemicellulose degradation takes place during alkaline delignification. Thus, a  
426 significant fraction of this polymer may also be removed along with lignin, which could  
427 also facilitate further cellulose hydrolysis (Rapado *et al.*, 2021).

428 Moreover, the results obtained after UAD (**Table 6, entries 3-4**), which furnished a 55-  
429 57% LevA molar yield, were also noteworthy, with this increase also being significant  
430 compared to the results obtained in preliminary tests (50% higher). However, the more  
431 significant effect that MAD had on MA-SWE GlobART (82.97%) may explain the lower  
432 LevA yield after UAD, since delignification of only 67.35% was achieved by cavitation  
433 (**Table 5**).

434 On the other hand, no differences were found between HCl 2 M and *p*-TsA 0.25 M in  
435 preliminary tests using MA-SWE GlobART (**Table 6, entries 1-2**). In fact, a similar  
436 LevA yield was achieved after both the MAD and UAD treatments (**Table 6, entries 3-  
437 6**). Overall, the comparable results achieved using *p*-TsA are promising, as fewer  
438 degradation products are formed and fewer side reactions occur when using this acid,  
439 which is an advantage in accordance with Green Chemistry principles. Furthermore, it  
440 should be remarked that a 100 %-selective process to LevA took place when using this



441 catalyst (*p*-TsA), as observed in an analysis, by <sup>1</sup>H-NMR and GC-MS, of the organic  
442 phase after reaction (**Figure S3**). This fact would allow LevA to be employed in further  
443 transformations without a prior purification step, again an advantage according to Green  
444 Chemistry principles.

445 Finally, the reaction conditions adopted with *p*-TsA (0.25 M) were slightly modified by  
446 reducing the KBr load on (MA-SWE + MAD)-GlobART, since the optimal LevA yield  
447 was achieved after the MAD process. Despite the positive effect that halide salts have on  
448 the hydrolysis and dehydration of biomass (Lorente *et al.*, 2023), the complexity of this  
449 reaction type sometimes favors degradation or polymerization steps towards humins,  
450 especially when high amounts of salt are employed, thus negatively affecting the yield of  
451 the desired products.

452 In this context, different KBr loads were tested (**Figure 2**). Initially, the selected amount  
453 was chosen according to previous studies (Salgado-Ramos *et al.*, 2022d; Lorente *et al.*,  
454 2023), with the KBr/biomass (KBr/B) ratio kept constant at 3.5 (1.75 g KBr and 0.50 g  
455 biomass).

456 Firstly, the results obtained in the absence of salt are noteworthy; almost 55% in terms of  
457 molar yield and 39% ponderal, with 70 % conversion. However, reducing the amount by  
458 half to 1.75, compared to the initial conditions (3.5 KBr/B ratio), lead to an enhancement  
459 up to 80.26% molar, which is significantly higher than the initial 71.09% observed at a  
460 KBr/B ratio of 3.5, with no variation in terms of conversion (around 90%). Therefore, the  
461 lower amount of catalyst used to enhance the product yield also increased the  
462 sustainability of the whole process.

463

464

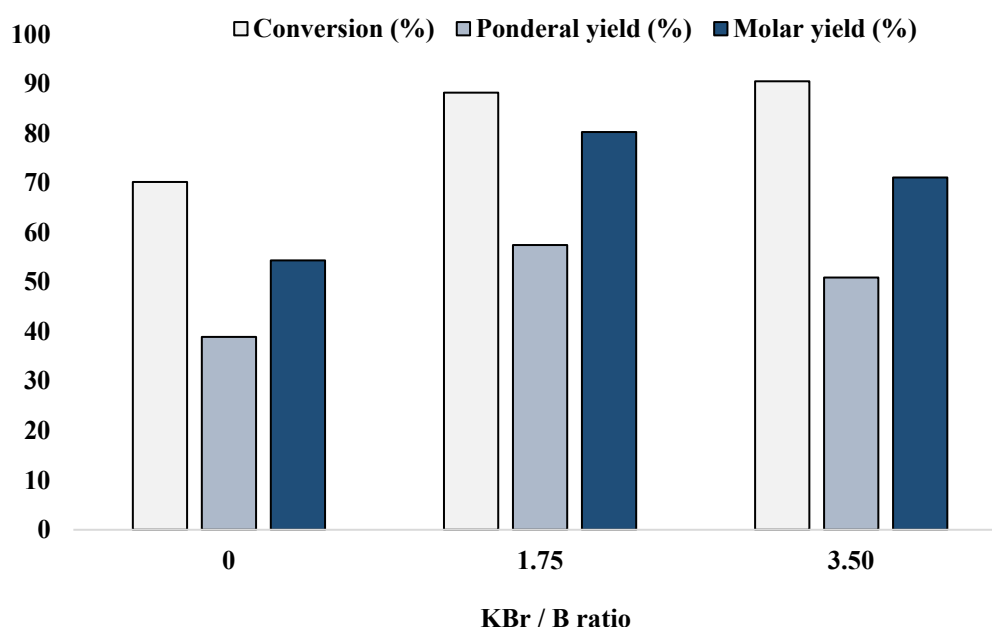
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473 **Figure 2.** Influence of KBr / biomass (KBr/B) ratio on LevA production from (MA-  
474 SWE + MAD)-(GlobART). Reaction conditions: as described in **Table 6**.

475

476 Overall, the notable influence of delignification on enhancing the LevA yield from  
477 GlobART has been demonstrated, while the use of process-intensification protocols (MW  
478 and US) and more sustainable approaches, such as the use of *p*-TsA instead of mineral  
479 acids, have also been highlighted. Furthermore, the use of a multi-step green process  
480 establishes alternative valorization pathways according to a *zero-waste* biorefinery  
481 approach.

#### 482 **4. Conclusions**

483 This work reports the first, to the best of authors' knowledge, MW-assisted valorization  
484 protocol for the production of BACs and LevA from GlobART leftovers. The solid  
485 residue remaining after MA-SWE was further pretreated via alkaline-intensified US- and  
486 MW-assisted delignification steps (UAD and MAD), which were crucial to boosting the  
487 conversion of the solid fraction GlobART into LevA. Indeed, molar yields of 57% and  
488 71% have been recorded from (MA-SWE+UAD)-GlobART and (MA-SWE+MAD)-  
489 GlobART, respectively, by means of a fast MW-assisted protocol (2 min, 225°C) that  
490 makes use of *p*-TsA as a more sustainable acid catalyst. Finally, reducing the KBr/B ratio  
491 when starting from (SWE + MAD)-GlobART by half helped to increase the yield up to  
492 80% with *p*-TsA, while lowering the amount of additive. Overall, this paper has outlined  
493 a multi-step green protocol with enabling technologies for the production of high-added-  
494 value BACs and LevA from GlobART by-products, while also establishing alternative  
495 valorization pathways for the development of a *zero-waste* biorefinery.

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#### 498 **CRedit authorship contribution statement**

499 Experimental data curation, M.S-R. and E.C.G.; Conceptualization, F.J.B. and G.C.;  
500 Writing original draft preparation, M.S-R, E.C.G. and S.T.; Review and editing, S.T.,  
501 F.J.B. and G.C. All authors have read and agreed to the published version of the  
502 manuscript.

### 503 **References**

504 Aliko, K., Doudin, K., Osatiashtiani, A., Wang, J., Topham, P.D., Theodosiou, E., 2020.  
505 Microwave-assisted synthesis of levulinic acid from low-cost, sustainable feedstocks  
506 using organic acids as green catalysts. *J. Chem. Technol. Biotechnol.* 95, 2110–2119.  
507 <https://doi.org/10.1002/jctb.6484>

508 Badgujar, K.C., Badgujar, V.C., Bhanage, B.M., 2020. A review on catalytic synthesis of  
509 energy rich fuel additive levulinate compounds from biomass derived levulinic acid. *Fuel*  
510 *Process. Technol.* 197, 106213. <https://doi.org/10.1016/j.fuproc.2019.106213>

511 Biel, W., Witkowicz, R., Piątkowska, E., Podsiadło, C., 2020. Proximate composition,  
512 minerals and antioxidant activity of artichoke leaf extracts. *Biol. Trace Elem. Res.* 194,  
513 589–595. <https://doi.org/10.1007/s12011-019-01806-3>

514 Bursać Kovačević, D., Barba, F.J., Granato, D., Galanakis, C.M., Herceg, Z., Dragović-  
515 Uzelac, V., Putnik, P., 2018. Pressurized hot water extraction (PHWE) for the green  
516 recovery of bioactive compounds and steviol glycosides from *Stevia rebaudiana* Bertoni  
517 leaves. *Food Chem.* 254, 150–157. <https://doi.org/10.1016/j.foodchem.2018.01.192>

518 Calcio Gaudino, E., Cravotto, G., Manzoli, M., Tabasso, S., 2021. Sono- and  
519 mechanochemical technologies in the catalytic conversion of biomass. *Chem. Soc. Rev.*  
520 50, 1785–1812. <https://doi.org/10.1039/D0CS01152E>

521 Calcio Gaudino, E., Tabasso, S., Grillo, G., Cravotto, G., Dreyer, T., Schories, G.,  
522 Altenberg, S., Jashina, L., Telysheva, G., 2018. Wheat straw lignin extraction with bio-  
523 based solvents using enabling technologies. *Comptes Rendus Chim.* 21, 563–571.  
524 <https://doi.org/10.1016/j.crci.2018.01.010>

525 Chemat, F., Abert Vian, M., Fabiano-Tixier, A.S., Nutrizio, M., Režek Jambrak, A.,  
526 Munekata, P.E.S., Lorenzo, J.M., Barba, F.J., Binello, A., Cravotto, G., 2020. A review  
527 of sustainable and intensified techniques for extraction of food and natural products.  
528 *Green Chem.* 22, 2325-2353. <https://doi.org/10.1039/c9gc03878g>

529 Chen, W., Hu, H., Cai, Q., Zhang, S., 2020. Synergistic effects of furfural and sulfuric  
530 acid on the decomposition of levulinic acid. *Energy Fuels* 34, 2238–2245.  
531 <https://doi.org/10.1021/acs.energyfuels.9b03971>

532 Cravotto, C., Grillo, G., Binello, A., Gallina, L., Olivares-Vicente, M., Herranz-López,  
533 M., Micol, V., Barraión-Catalán, E., Cravotto, G. Bioactive antioxidant compounds from  
534 chestnut peels through semi-industrial subcritical water extraction. *Antioxidants* 11,  
535 2022, 988. <https://doi.org/10.3390/antiox11050988>.

536 de la Hoz, A., Díaz-Ortiz, À., Moreno, A., 2005. Microwaves in organic synthesis.  
537 Thermal and non-thermal microwave effects. *Chem. Soc. Rev.* 34, 164–178.  
538 <https://doi.org/10.1039/b411438h>

539 Demirhan, H., Fauzi, A., Skoulou, V.K., Haywood, S.H., Zein, S.H., 2017. Wheat straw  
540 bio-refining. Part I: Optimization of the microwave radiation process with sulphuric acid  
541 pre-treatment. *Curr. Microw. Chem.* 4, 205–218.  
542 <https://doi.org/10.2174/2213335604666170719113659>

543 di Menno Di Bucchianico, D., Wang, Y., Buvat, J.-C., Pan, Y., Casson Moreno, V.,  
544 Leveneur, S., 2022. Production of levulinic acid and alkyl levulinates: a process insight.  
545 *Green Chem.* 24, 614–646. <https://doi.org/10.1039/D1GC02457D>

546 Ferioli, F., D’Antuono, L.F., 2022. Phenolic compounds in local Italian types of  
547 cultivated cardoon (*Cynara cardunculus* L. var. *altilis* DC) stalks and artichoke (*Cynara*  
548 *cardunculus* L. var. *scolymus* L.) edible sprouts. *J. Food Compos. Anal.* 106, 104342.  
549 <https://doi.org/10.1016/j.jfca.2021.104342>

550 Francavilla, M., Marone, M., Marasco, P., Contillo, F., Monteleone, M., 2021. Artichoke  
551 biorefinery: From food to advanced technological applications. *Foods* 10, 112.  
552 <https://doi.org/10.3390/foods10010112>

553 Hughes, S.R., Qureshi, N., López-Núñez, J.C., Jones, M.A., Jarodsky, J.M., Galindo-  
554 Leva, L.Á., Lindquist, M.R., 2017. Utilization of inulin-containing waste in industrial  
555 fermentations to produce biofuels and bio-based chemicals. *World J. Microbiol.*  
556 *Biotechnol.* 33, 78. <https://doi.org/10.1007/s11274-017-2241-6>

557 Ibn Ferjani, A., Jeguirim, M., Jellali, S., Limousy, L., Courson, C., Akrou, H., Thevenin,  
558 N., Ruidavets, L., Muller, A., Bennici, S., 2019. The use of exhausted grape marc to  
559 produce biofuels and biofertilizers: Effect of pyrolysis temperatures on biochars

560 properties. *Renewable Sustainable Energy Rev.* 107, 425–433.  
561 <https://doi.org/10.1016/j.rser.2019.03.034>

562 Kininge, M.M., Gogate, P.R., 2022. Intensification of alkaline delignification of  
563 sugarcane bagasse using ultrasound assisted approach. *Ultrason. Sonochem.* 82, 105870.  
564 <https://doi.org/10.1016/j.ultsonch.2021.105870>

565 Lauberte, L., Telysheva, G., Cravotto, G., Andersone, A., Janceva, S., Dizhbite, T.,  
566 Arshanitsa, A., Jurkjane, V., Vevere, L., Grillo, G., Gaudino, E.C., Tabasso, S., 2021.  
567 Lignin – Derived antioxidants as value-added products obtained under cavitation  
568 treatments of the wheat straw processing for sugar production. *J. Clean. Prod.* 303,  
569 126369. <https://doi.org/10.1016/j.jclepro.2021.126369>

570 Liu, Z.; de Souza, T.S.P.; Holland, B.; Dunshea, F.; Barrow, C.; Suleria, H.A.R., 2023.  
571 Valorization of food waste to produce value-added products based on its bioactive  
572 compounds. *Processes* 11, 840. <https://doi.org/10.3390/pr11030840>

573 Lorente, A., Huertas-Alonso, A.J., Salgado-Ramos, M., González-Serrano, D.J.,  
574 Sánchez-Verdú, M.P., Cabañas, B., Hadidi, M., Moreno, A., 2023. Microwave radiation-  
575 assisted synthesis of levulinic acid from microcrystalline cellulose: Application to a  
576 melon rind residue. *Int. J. Biol. Macromol.* 237, 124149.  
577 <https://doi.org/10.1016/j.ijbiomac.2023.124149>

578 Lucas-Torres, C., Lorente, A., Cabañas, B., Moreno, A., 2016. Microwave heating for the  
579 catalytic conversion of melon rind waste into biofuel precursors. *J. Clean. Prod.* 138, 59–  
580 69. <https://doi.org/10.1016/j.jclepro.2016.03.122>

581 Lutz, M., Henríquez, C., Escobar, M., 2011. Chemical composition and antioxidant  
582 properties of mature and baby artichokes (*Cynara scolymus* L.), raw and cooked. *J. Food*  
583 *Compos. Anal.* 24, 49–54. <https://doi.org/10.1016/j.jfca.2010.06.001>

584 Mariatti, F., Gunjević, V., Boffa, L., Cravotto, G., 2021. Process intensification  
585 technologies for the recovery of valuable compounds from cocoa by-products. *Innov.*  
586 *Food Sci. Emerg. Technol.* 68, 102601. <https://doi.org/10.1016/j.ifset.2021.102601>

587 Órbenes, G., Rodríguez-Seoane, P., Torres, M.D., Chamy, R., Zúñiga, M.E., Domínguez,  
588 H., 2021. Valorization of artichoke industrial by-Products using green extraction  
589 technologies: Formulation of hydrogels in combination with paulownia extracts.  
590 *Molecules* 26, 4386. <https://doi.org/10.3390/molecules26144386>

591 Osorio-Tobón, J.F., 2020. Recent advances and comparisons of conventional and  
592 alternative extraction techniques of phenolic compounds. *J. Food Sci. Technol.* 57, 4299–  
593 4315. <https://doi.org/10.1007/s13197-020-04433-2>

594 Özkaynak Kanmaz, E., 2018. 5-Hydroxymethylfurfural (HMF) formation during  
595 subcritical water extraction. *Food Sci. Biotechnol.* 27, 981–986.  
596 <https://doi.org/10.1007/s10068-018-0328-y>

597 Plaza, M., Marina, M.L., 2019. Pressurized hot water extraction of bioactives. *Trends*  
598 *Analyt. Chem.* 116, 236–247. <https://doi.org/10.1016/j.trac.2019.03.024>

599 Rapado, P., Faba, L., Ordóñez, S., 2021. Influence of delignification and reaction  
600 conditions in the aqueous phase transformation of lignocellulosic biomass to platform  
601 molecules. *Bioresour. Technol.* 321, 124500.  
602 <https://doi.org/10.1016/j.biortech.2020.124500>

603 Raspolli Galletti, A.M., Licursi, D., Ciorba, S., di Fidio, N., Coccia, V., Cotana, F.,  
604 Antonetti, C., 2021. Sustainable exploitation of residual *Cynara cardunculus* L. to  
605 levulinic acid and n-butyl levulinate. *Catalysts* 11, 1082.  
606 <https://doi.org/10.3390/catal11091082>

607 Remón, J., Latorre-Viu, J., Matharu, A.S., Pinilla, J.L., Suelves, I., 2021. Analysis and  
608 optimisation of a novel ‘almond-refinery’ concept: Simultaneous production of biofuels  
609 and value-added chemicals by hydrothermal treatment of almond hulls. *Sci. Total*  
610 *Environ.* 765, 142671. <https://doi.org/10.1016/j.scitotenv.2020.142671>

611 Ruiz-Cano, D., Pérez-Llamas, F., Frutos, M.J., Arnao, M.B., Espinosa, C., López-  
612 Jiménez, J.Á., Castillo, J., Zamora, S., 2014. Chemical and functional properties of the  
613 different by-products of artichoke (*Cynara scolymus* L.) from industrial canning  
614 processing. *Food Chem.* 160, 134–140. <https://doi.org/10.1016/j.foodchem.2014.03.091>

615 Sait, H.H., Hussain, A., Salema, A.A., Ani, F.N., 2012. Pyrolysis and combustion kinetics  
616 of date palm biomass using thermogravimetric analysis. *Bioresour. Technol.* 118, 382–  
617 389. <https://doi.org/10.1016/j.biortech.2012.04.081>

618 Sałata, A., Lombardo, S., Pandino, G., Mauromicale, G., Buczkowska, H., Nurzyńska-  
619 Wierdak, R., 2022a. Biomass yield and polyphenol compounds profile in globe artichoke  
620 as affected by irrigation frequency and drying temperature. *Ind. Crops Prod.* 176, 114375.  
621 <https://doi.org/10.1016/j.indcrop.2021.114375>

622 Sałata, A., Nurzyńska-Wierdak, R., Kalisz, A., Kunicki, E., Ibáñez-Asensio, S., Moreno-  
623 Ramón, H., 2022b. Effects of organic cropping on phenolic compounds and antioxidant  
624 capacity of globe artichoke herbs. *Agronomy* 12, 192.  
625 <https://doi.org/10.3390/agronomy12010192>

626 Salgado-Ramos, M., Mariatti, F., Tabasso, S., Sánchez-Verdú, M.P., Moreno, A.,  
627 Cravotto, G., 2022a. Sustainable and non-conventional protocols for the three-way  
628 valorisation of lignin from grape stalks. *Chem. Eng. Process. - Process. Intensif.* 178,  
629 109027. <https://doi.org/10.1016/j.cep.2022.109027>

630 Salgado-Ramos, M., Martí-Quijal, F.J., Huertas-Alonso, A.J., Sánchez-Verdú, M.P.,  
631 Barba, F.J., Moreno, A., 2022b. Almond hull biomass: Preliminary characterization and  
632 development of two alternative valorization routes by applying innovative and sustainable  
633 technologies. *Ind. Crops Prod.* 179, 114697.  
634 <https://doi.org/10.1016/j.indcrop.2022.114697>

635 Salgado-Ramos, M., Tabasso, S., Calcio Gaudino, E., Moreno, A., Mariatti, F., Cravotto,  
636 G., 2022c. An innovative, green cascade protocol for grape stalk valorization with process  
637 intensification technologies. *Appl. Sci.* 12, 7417. <https://doi.org/10.3390/app12157417>

638 Salgado-Ramos, M., Martí-Quijal, F.J., Huertas-Alonso, A.J., Sánchez-Verdú, M.P.,  
639 Barba, F.J., Moreno, A., 2022d. Microwave heating for sustainable valorization of  
640 almond hull towards high-added-value chemicals. *Ind. Crops Prod.* 189, 115766.  
641 <https://doi.org/10.1016/j.indcrop.2022.115766>

642 Sluiter, A., Hames, B., Ruiz, R., Scarlata, C., Sluiter, J., Templeton, D., Crocker, D.,  
643 2008. Determination of structural carbohydrates and lignin in biomass. *Laboratory*  
644 *analytical procedure* 1617, 1–16.

645 Tabasso, S., Montoneri, E., Carnaroglio, D., Caporaso, M., Cravotto, G., 2014.  
646 Microwave-assisted flash conversion of non-edible polysaccharides and post-harvest  
647 tomato plant waste to levulinic acid. *Green Chem.* 16, 73–76.  
648 <https://doi.org/10.1039/c3gc41103f>

649 Teixeira, G.L., Maciel, L.G., Mazzutti, S., Barbi, R.C.T., Ribani, R.H., Ferreira, S.R.S.,  
650 Block, J.M., 2021. Sequential green extractions based on supercritical carbon dioxide and  
651 pressurized ethanol for the recovery of lipids and phenolics from *Pachira aquatica* seeds.  
652 *J. Clean. Prod.* 306, 127223. <https://doi.org/10.1016/J.JCLEPRO.2021.127223>

653 Verdini, F., Calcio Gaudino, E., Grillo, G., Tabasso, S., Cravotto, G., 2021. Cellulose  
654 recovery from agri-food residues by effective cavitation treatments. *Appl. Sci.* 11, 4693.  
655 <https://doi.org/10.3390/app11104693>

656 Yoon, S.-Y., Han, S.-H., Shin, S.-J., 2014. The effect of hemicelluloses and lignin on acid  
657 hydrolysis of cellulose. *Energy* 77, 19–24. <https://doi.org/10.1016/j.energy.2014.01.104>

658 Zayed, A., Farag, M.A., 2020. Valorization, extraction optimization and technology  
659 advancements of artichoke biowastes: Food and non-food applications. *LWT* 132,  
660 109883. <https://doi.org/10.1016/j.lwt.2020.109883>

661 Zhao, W., Li, Y., Song, C., Liu, S., Li, X., Long, J., 2017. Intensified levulinic acid/ester  
662 production from cassava by one-pot cascade prehydrolysis and delignification. *Appl.*  
663 *Energy* 204, 1094–1100. <https://doi.org/10.1016/j.apenergy.2017.03.116>