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Conversion of artichoke leftovers to levulinic acid: A biorefinery approach

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ABSTRACT

The valorization of agrifood leftovers from an herbaceous plant widely cultivated in Mediterranean areas (Italy and Spain), *Cynara scolymus L.*, is reported here as part of a zero-waste biorefinery approach. The Globe artichoke (GlobART) variety was selected as the source of artichoke leftovers, which were valorized using the following cascade approach: (i) the recovery of antioxidant compounds (AC) still present in the matrix through sustainable microwave-assisted subcritical water extraction (MA-SWE); and, (ii) the subsequent production of levulinic acid (LevA) via the MW-assisted conversion (225°C, 2 min, 1500 W) of the cellulosic fraction recovered after initial extraction. Preliminary MW-assisted conversion tests on the post MA-SWE GlobART matrix yielded about a 37% yield of LevA (molar yield) using HCl and *p*-toluenesulfonic acid (*p*-TsA). Furthermore, performing a delignification step, mediated by either ultrasound (UAD) or MW (MAD), on the post-MA-SWE GlobART matrix before conversion considerably increased LevA yield (55% and 71% from post-UAD and post-MAD GlobART matrices, respectively, with *p*-TsA). Finally, reducing the KBr/biomass ratio, when using *p*-TsA, by half afforded an enhancement in LevA yield up to 80% when starting from the post-extraction and delignified (post MA-SWE-& MAD) GlobART matrix.

1. Introduction

In recent years, food science has expanded the scope of research investigations leading to new achievements in the field of valorization, mainly from the wide range of by-products generated during industrial processing. The renewable C-based nature of agri-food matrices represents an alternative route to high-added-value compounds that can act as alternatives to fossil sources, paving the way for the bio-economy era [1].

Of all the by-products that derive from the processing of edible plants with functional properties, those of the globe artichoke (GlobART) (*Cynara scolymus L.*) are particularly promising for further valorization. This industrial crop originates from the Mediterranean area, and is widely cultivated in some countries, such as Italy and Spain. Generally, GlobART by-products from artichoke processing represent 80–85% of its fresh weight, and mainly involve the heads, leaves, stalks and roots, which have a lignocellulosic composition [2]. This waste is unsuitable for human consumption and further contributes to environmental issues, meaning that an alternative exploitation route should be explored.

GlobART is a well-known source of biologically active compounds (BACs), and their recovery is considered to be an economically viable solution for the valorization of by-products. Of these BACs, the significant presence of phenols with therapeutic action [3-5], and proteins [6, 7] is particularly worthy of note. These BACs can be easily recovered with improved efficiency and sustainability using process-intensification technologies and green solvents, according to Green Extraction principles [8,9]. For instance, subcritical water extraction (SWE) is a superheated water process at temperatures ranging from water's boiling point to its critical point (100–373 °C), combined with high pressures to keep it in a condensed state. The dielectric constant of water decreases with increasing temperature, and reaches values close to organic solvents, such as ethanol or methanol, thus facilitating the recovery of mid- and less-polar bioactive compounds [6, 10]. These enabling extraction conditions provide an improvement in terms of mass transfer and wetting, thanks to the lower water surface tension and viscosity, leading to the matrix undergoing valuable structural modifications, and further solvent penetration [9,11]. Moreover, higher temperatures cause intermolecular interactions to weaken, thus

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linking metabolites to the matrix and facilitating solubilization into water through an efficient and fast extraction process [12].

Moreover, most valorization processes for GlobArt by-products also focus on biofuel production because of the significant carbohydrate and ethanol-soluble fractions present, which account for 70–75% of its fresh weight [6,13,14]. The hydrolysis and fermentation of inulin, a water-soluble fiber commonly extracted from GlobART residues, provides bioethanol, and thus represents a significant upgrade for this matrix [15,16]. However, the conversion of the sugar fraction towards bio-derived platform chemicals has not yet been reported, to the best of our knowledge. In this context, the production of LevA would be a valuable accomplishment, from an innovation point of view, in valorizing the majority of this fraction.

LevA, or 4-oxovaleric acid, is a recognized bio-based building block widely obtained from biomass conversion, mainly via the acidic hydrolysis of cellulose and hemicellulose fractions in lignocellulosic waste [17,18]. Its versatility is mainly attributed to its high functionalization thanks to the presence of both a keto and a carboxylic group. Therefore, multiple high-end products, with applications as solvents, fuels, pharmaceuticals and food additives, can be obtained from its conversion [19].

LevA production can be enhanced by means of process-intensification techniques as well. The use of microwave (MW) heating for this transformation is particularly noteworthy [20,21]. The selective absorption of this radiation by polar molecules, along with ionic conduction, provides superior efficiency to conventional heating, where heat is transferred via conduction from the flask wall to the sample [22,23]. Thus, a considerably lower number of side reactions occur and fewer undesired by-products are formed, with higher product yields in shorter residence times.

Furthermore, MW treatment also promotes delignification via MW-assisted extraction (MAE). This step is crucial not only in terms of biomass valorization, where some hemicellulose and BACs can be easily recovered as well [24,25], as some authors have reported that cellulose accessibility can be enhanced in the remaining solid fraction after processing, favoring the subsequent transformation to LevA [26,27].

Delignification can also be intensified by means of ultrasound (US)-assisted extraction (UAE) [17]. The cavitation effect in US favors mass transfer because of the implosion of microbubbles in the liquid phase. These bubbles grow and collapse, creating high-energy microenvironments in the reaction medium via the generation of microjet streams, shock waves and shear forces, which induce mechanical effects such as the breakdown of tissues into small fragments and intensive mixing and heating [28,29]. This phenomenon subsequently favors cell-wall rupture, and furthers the release of the desired compounds compared to conventional methods.

Moreover, literature encompasses a wide number of works in which scaling-up processes have been successfully developed using MW and US technologies. As Belwa et al. noted, [30] they are the second and third most commonly used technologies at the industrial level (15% and 14% of all studies, respectively). Based on this background, a multi-step green protocol with enabling technologies has been developed for the valorization of GlobART food-processing residues towards AC recovery and sugar conversion into LevA, and is presented in this article. The post MW-assisted -SWE (MA-SWE) matrix was either directly transformed via MW-assisted acidic conversion into LevA or subjected to a previous delignification step under either MW or US to enhance LevA recovery.

2. Material and methods

2.1. Chemicals

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

2.2. Feedstocks

Untreated GlobART food-processing residues were purchased from a local market (Turin-Italy) and freeze-dried until use. They were then cryo-milled to provide a homogeneous matrix for the experiments. During storage and pretreatment, efforts were made to avoid microbiological deterioration, which could affect the final results and hinder the exploitation of artichoke residues in future biorefineries. Untreated GlobART was subsequently mildly dried at 40–50ºC to remove the high amount of water remaining after cryo-milling.

The MA-SWE GlobART matrix was mildly dried at 40–50 ºC after being recovered and then blade-milled for further experiments.

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

MA-SWE was carried out on the lab-scale in a high-pressure-resistant professional multimode MW reactor (Synthwave Milestone, Srl, MLS Gmbh, Bergamo, Italy). GlobART biomass (8 g) was mixed with the desired amount of water in a 1:50 solid/liquid (S/L) ratio. The mixture was left to moisturize for 5 min in a 1 L Teflon vessel, which was then introduced into the pressure-resistant MW multimodal reactor equipped with an external inert gas feed (N_2). For each MA-SWE test, appropriate purging with N_2 was performed three times to remove oxygen traces from the system, reducing oxidative stress on the GlobART biomass. The reaction chamber was then pressurized with N_2 to avoid water ebullition (40 bars). The samples were heated at 125ºC for 15 min [31]. The resulting extraction mixture was filtered under vacuum, and the residual biomass was thoroughly washed with fresh water. The dry extract was recovered by freeze-drying (LyoQuest-85, Telstar, Madrid, Spain), weighed, and stored at 4 °C for further conversion. Each extraction was performed in triplicate to validate the reproducibility of the experimental results.

2.4. Recovery of biologically active compounds (BACs)

2.4.1. Antioxidant activity

The scavenging activity for the liquid extract after MA-SWE was determined using a DPPH assay and a Cary 60 UV–VIS spectrophotometer (Cary 60, Agilent Technologies, Santa Clara, CA, USA). Experiments were carried out at 515 nm, and the results are expressed in terms of IC_{50} (mg/mL), with respect to C_0 (mg/mL), according to previous works [17,25]. The liquid fraction was freeze-dried, and then solubilized in a 50% v/v MeOH/H_2O solution.

2.4.2. Polyphenol analysis

Total polyphenol content (TPC) was determined, using the Folin-Ciocalteu method in the same UV–VIS equipment as described above, at 765 nm. The results are expressed as mg gallic acid equivalents (mg GAE) / g dry weight (g DW) [32].

The MA-SWE GlobART extracts were also analyzed by HPLC-MS using a Waters 2525 pump linked to a Column Fluidics Organizer (Waters Corp., Singapore, Singapore) combined with a 2767 Sample Manager (Waters) coupled with a 2487 dual Abs detector and a Micromass ZQ. The column used was a Synergi Hydro-RP C18 column (250 mm, 4.6 mm, 4 μm; Phenomenex, Torrance, CA, USA), with 2% AcOH (A) and 2% MeCN (B) as the mobile phases (1 mL/min). The monitored wavelengths were 280 and 340 nm. Elution was performed using a gradient program starting from 0% B (maintained for 6.5 min), to 50% B in 30 min, and from 50% to 100% B from 30 to 36 min, followed by a 100% B step for a further 6 min

2.5. Characterization of GlobART biomass

2.5.1. Proximate and ultimate analyses

Proximate analysis for both GlobART and post-MA-SWE GlobART

biomass was performed using thermogravimetric analysis (TGA) (Perkin Elmer Thermogravimetric Analyzer TGA 4000) at temperatures of 25–800ºC and a heating rate of 10ºC/min. Inert conditions were used for organic matter and an oxidizing atmosphere for ash. Differential thermogravimetric (DTG) curves were recorded in OriginLab 2019b software (OriginLab 2019b Graphing and Analysis software, Northampton, Massachusetts, USA).

Ultimate analysis was carried out according to the ASTM D-5373 norm. Both oxygen percentage and ratio O/C were calculated according to a previous work [32].

Protein content was measured with a Kjel Line reactor (Buchi, Flawil, Switzerland), according to Kjeldhal method, developed by Lynch et al. [33]

2.5.2. Fiber analysis

Fiber and extractive composition were determined for untreated- and MA-SWE-treated GlobART using the National Renewable Energy Laboratory (NREL) procedure, according to a previous work [32] and using the standard protocol reported by [34].

2.5.3. FT-IR analysis

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

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

The delignification percentage was calculated in consideration of the amount of MA-SWE GlobART used and the weight of the post-extraction remaining solid fraction recovered after treatment, which entails a higher cellulose content, considering only a mass difference between them (Eq. 1):

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

	GlobART waste
Proximate analysis (%)	
Organic matter	91.74
Volatile content	67.83
Fixed carbon	23.91
Ash	5.99
Moisture	2.27
Ultimate analysis (%)	
C	42.98
H	6.04
N	1.93
O *	49.05
O/C ratio	0.86
H/C ratio	1.69
HHV (MJ/kg) **	17.02
Fiber analysis (g/100 g DM) ***	
Extractives	
Non-polar fraction	1.38
Polar fraction	3.69
Proteins (%N * 6.25)	12.06
Fibers	
Cellulose	29.07
Hemicellulose + soluble polyphenols	38.68
Lignin	21.15
Total fibers	88.90
Fibers + extractives	93.97
Others	6.03

* Obtained as a difference considering C, H and N percentage.
** HHV: higher heating value (theoretical value).
*** g/100 g dry matter (DM).

$$\%delignif. = \frac{m(MA-SWE\quad GlobART) - m(post-extraction\quad remaining\quad solid(cellulose-rich))}{m(MA-SWE\quad GlobART)}\ x100 \tag{1}$$

MAD was carried out in the same professional multimode MW reactor (2.45 GHz, 1500 W), with a multi-rack position tool for simultaneous reactions. 7.5 g of MA-SWE GlobART was placed into five 40 mL MW glass vials (20 mL maximum liquid volume) along with an NaOH solution (10% with respect to the dry matter). Experiments were carried out in duplicate, at 120ºC for 30 min, according to previous studies [25].

US-assisted delignification (UAD) was performed in a 5 L stainless steel tank high-power US bath, equipped with three probes that are screwed-fixed into the bottom (Weber Ultrasonic AG, Karlsbad, Germany). The bath was set to operate at a frequency of 40 kHz and 200 W power. 7.5 g of MA-SWE GlobART was placed into a 250 mL round-bottomed flask, along with 480 mg of NaOH (10%) and 100 mL of deionized water (solid:liquid ratio 1:20). Experiments were carried out in duplicate, at 50ºC for 60 min [17].

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

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

For preliminary tests, 0.50 g of post-MA-SWE GlobART were charged into a 40 mL MW glass vial. Different volumes of either HCl or *p*-toluenesulfonic acid (*p*-TsA) were added at different concentrations. When using *p*-TsA, KBr was also used as a co-catalyst to favor the process [35]. Samples were previously stirred to obtain a homogeneous solution. The mixtures were irradiated at 1500 W at the pertinent temperatures (190 or 225 ºC) and time (2 or 20 min), under inert conditions (N_2, 40 bar). Reaction workup was carried out according to a previous work [17].

Either *p*-TsA (0.25 M) or HCl (2 M) were added (5–10 mL) to both MA-SWE + MAD- and MA-SWE + UAD-GlobART solid residues, in a solid:liquid ratio of 1:10 or 1:20 (0.5 g of solid). Reaction conditions and workup were similar to those already described.

LevA molar and ponderal yields, as well as conversions, were calculated according to the available literature [36,37] (see Supplementary Material).

2.8. GC-MS and NMR analyses

Both GC-MS and NMR were performed for LevA characterization. The analysis was carried out in accordance with our previous studies [17].

Briefly, NMR analysis was performed in a Jeol JNM-ECZ600R spectrometer (Jeol, Tokyo, Japan) operating at a frequency of 600 MHz for the ^1H nucleus. 600 μL of $CDCl_3$ was added to the dried samples, then filtered with a nylon syringe filter and finally added to the NMR tube.

GC-MS was carried out after prior derivatization, in an Agilent Technologies 6850 Network GC System with a 5973 Network Mass Selective Detector and 7683B Automatic Sampler, using a capillary column (HP-5MS; length, 30 m; i.d., 0.25 mm; film thickness, 0.25 μm) (Agilent

Technologies, Santa Clara, CA). In a typical experiment, the dried crudes were dissolved in 1.5 mL of $CHCl_3$. Subsequently, 80 μL of BSTFA ((N,O-bis(trimethylsilyl)trifluoroacetamide) were added to the solution as a derivatizing agent. The mixture was kept under magnetic stirring for 45 min at a temperature of 65 ºC.

3. Results and discussion

3.1. MW-assisted extraction of BACs from GlobART leftovers

3.1.1. Preliminary characterization of raw GlobART leftovers

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

Both the proximate and ultimate analyses provide us with information on the energetic properties of lignocellulosic waste, with a view to an alternative and innovative means of upgrading it as a bioenergy source [38,39]. However, based on the reported results for GlobART, neither its HHV (17.02 MJ/kg) nor its O/C (0.86) and H/C ratios (1.69) make the matrix suitable for energetic purposes. For this reason, it can be more appropriately exploited, for instance, as a source for the recovery of ACs and the further conversion of the cellulose-rich exhausted matrix to LevA, with this probably being the most economically viable valorization pathway.

3.1.2. MW-assisted subcritical water extraction and characterization of ACs from GlobART

The application of process-intensification technologies induces significant physical changes in the initial matrix, with these changes due to, for instance, higher diffusivity or viscosity variations. These enabling treatments normally convert the raw material into products of reduced particle size, which could favor the recovery of metabolites and further transformation steps [40,41].

In this context, MW-assisted SW extraction (MA-SWE) was explored for the valorization of GlobART by-products. Firstly, this protocol was carried out on the lab-scale (1 L vessel), at 125 °C for 15 min, according to a previous work [31]. The liquid fraction obtained after this treatment was analyzed in terms of total polyphenol content (TPC) and antioxidant capacity (DPPH) (Table 2), thus confirming the presence of ACs. Furthermore, HPLC-MS analysis (Fig. S1) indicates that some specific polyphenols, such as 1-caffeoylquinic acid, chlorogenic acid, narirutin and cynarine, are present. This experiment proved the efficiency of the intensified protocol for the valorization of these by-products as a source of antioxidant compounds.

Since the use of GlobART leftovers as a ACs source, in parallel with inulin extraction, has been widely described in literature [4,5,16], this work aims to valorize the solid fraction recovered after MA-SWE processing.

In this context, conversion to LevA, one of the top bio-based lignocellulosic-biomass-derived platform chemicals, was investigated for the valorization of residual GlobART. The conditions initially applied are indeed severe enough to remove the inulin from the original matrix, as it is normally extracted at lower temperatures [2].

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

Extraction conditions	DPPH (IC_{50} based on C_0^a)	TPC (mg GAE/ g DW[b])	Main polyphenols (HPLC-MS)
MA-SWE, 125 ºC, 15 min	0.3245 ± 0.0026	24.4980 ± 0.5005	1-caffeoylquinic acid, chlorogenic acid, cynarine

a. C_0: initial concentration for the extract.
b. mg GAE/ g DW: mg gallic acid equivalents / g dry weight.

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

	GlobART (g/100 g DM[a])	(MA-SWE)-GlobART (g/100 g DM)
Cellulose	29.07	38.81
Hemicellulose + soluble polyphenols	38.68	24.43
Lignin	21.15	25.66

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

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

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

In this composition analysis, significant differences were found in terms of both relative cellulose and hemicellulose content between these two matrices. Particularly noteworthy is the cellulose enrichment in the post-extraction matrix (MA-SWE GlobART) (from 29.07% to 38.81%), which is then able to be better converted into the target product (LevA). Furthermore, the significant decrease in the hemicellulosic fraction in the post-extraction matrix from 38.68% (GlobART) to 24.43% in MA-SWE GlobART is also important (Table 3). Indeed, the partial solubilization of the hemicellulose fraction present in the starting biomass can also be expected during the MAE step in subcritical water at 125 °C in addition to the extraction of ACs and inulin from the matrix (Table 2). Finally, the enrichment, albeit minimal, of the lignin fraction can be observed in the post-extracted biomass (MA-SWE GlobART) (Table 3). In this regard, since the content of the starting matrix GlobART and that of the post-extraction recovered biomass (MA-SWE GlobART) still show lignin contents of above 20%, a prior delignification step could facilitate the subsequent conversion of both GlobART biomasses into LevA.

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

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

3.2.1. Preliminary tests

According to the biorefinery approach and with the aim of valorizing all waste-biomass components, MA-SWE GlobART was selected as the starting material, in this work, for optimizing conversion into LevA after the extraction of high-added-value compounds from GlobART. Additionally, the cellulose enrichment in the extraction residue after the MA-SWE process (from 29.07% to 38.81% (see Table 3)) makes this matrix more suitable for the development of LevA, which is in line with the desired zero-waste approach.

In this regard, we made use of a previous study of ours [18], in which acid-catalyzed conversion (HCl 1 M) to LevA was performed under MW-assisted radiation (225ºC, 2 min), to uncover the optimized conditions for post-MA-SWE GlobART conversion. However, two different acidic catalysts are being compared in this present work (HCl and *p*-toluenesulfonic acid (*p*-TsA)) using different respective amounts, biomass/acid (B/A) ratios, as well as different reaction times and temperatures. Results are summarized in Table 4 and compared accordingly.

As observed, the optimized conditions in our MW-assisted flash conversion (2 min) with HCl (Table 4, entry 12–13) [17,18] were not highly efficient for MA-SWE GlobART, achieving only a 29% LevA molar

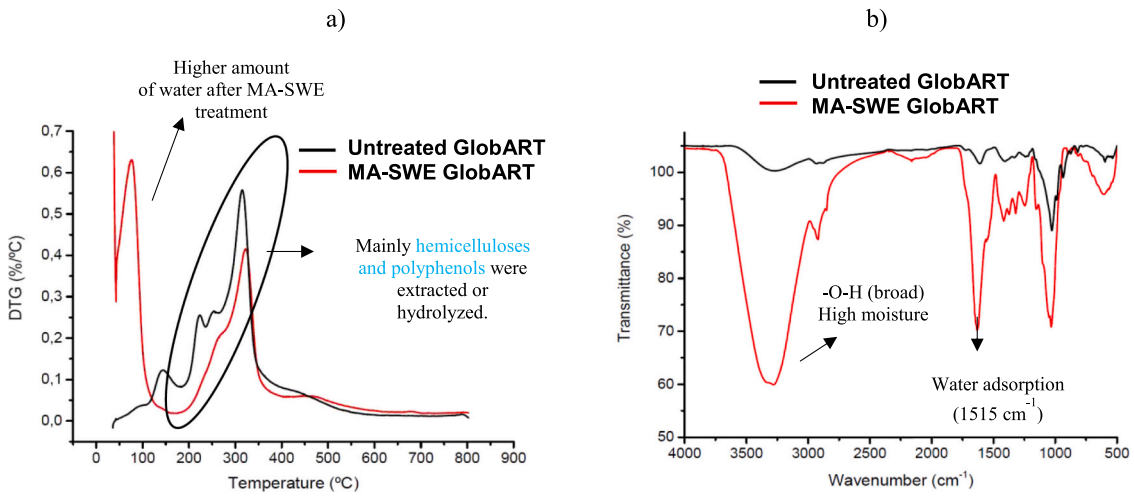

Fig. 1. Differential thermogravimetric (DTG) curves (a) and FT-IR spectra (b) for untreated- and MA-SWE-GlobART.

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

	Acid	T (ºC)	Time (min)	B/A ratio[b]	Conversion (%)	Ponderal Yield (%)	Molar Yield (%)
MA-SWE GlobART (this work)							
1	HCl 1 M	225	2	1:10	76.29	20.53	28.67
2	HCl 1 M	225	2	1:20	78.16	23.20	32.39
3	HCl 2 M	225	2	1:10	91.26	26.76	**37.37**
4	HCl 2 M	225	2	1:20	87.65	28.54	39.85
5	*p*-TSA[a] 0.25 M	190	20	1:20	92.29	26.28	36.70
6	*p*-TSA[a] 0.25 M	225	2	1:10	90.41	26.29	**37.27**
7	*p*-TSA[a] 0.25 M	225	2	1:20	87.86	25.37	35.43
8	HCl 0.25 M	225	2	1:10	87.19	4.93	6.88
9	HCl 0.25 M	225	2	1:20	92.72	18.26	25.50
10	HCl 0.5 M	225	2	1:10	87.96	21.51	30.04
11	HCl 0.5 M	225	2	1:20	88.47	18.51	25.84
Previous research							
12	Post harvest tomato plant[18]	225	2	1:10	78.00	63.00	n.d.[c]
13	Grape stalk [25]	225	2	1:10	79.00	49.10	68.60

a. *p*-TsA: *p*-toluenesulfonic acid. 1.75 g of KBr was used as co-catalyst for these experiments.
b. B/A ratio: biomass/acid ratio.
c. n.d.: non determined.

yield and a 21% ponderal yield (Table 4, entry 1). It is possible that side reactions towards undesired products, such as humic acids, may be triggered and thus compete with LevA formation. To avoid these side reactions, lower HCl loads were tested with the MA-SWE GlobART biomass (0.25–0.5 M), although these new conditions in any case lead to any improvement in terms of LevA (Table 4, entries 8–11).

Surprisingly, the use of more acidic conditions, by increasing either the B/A ratio or HCl load, afforded better yields (Table 4, entries 2–4). In this context, it is worth noting that 37–40% molar yields for LevA were achieved when using HCl 2 M (Table 4, entries 3–4). Regarding this loading, a compromise between yields and the use of an acceptable amount of catalyst should be achieved. Therefore, a B/A ratio of 1:10 could be considered in further studies.

On the other hand, the use of sulfonic acids, such as *p*-TsA, which has already been employed to obtain LevA from biomass in previous work [35,42], increased the yield up to almost 37% molar and 26% ponderal, with respect to HCl 1 M under optimized conditions (Table 4, entry 5). Moreover, *p*-TsA is significantly superior in terms of sustainability to the conventional mineral acids, such as HCl, H_2SO_4 or H_3PO_4, normally used for this kind of process, especially when it is employed at a low concentration (0.25 M). This can mainly be attributed to its non-corrosive character and reusability, which has been corroborated by NMR in an analysis of the aqueous phase after reaction (Fig. S2).

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

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

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

A delignification step is commonly applied in biomass valorization prior to further conversion to platform chemicals and biofuels [43]. Furthermore, the lignin that was isolated after delignification can be further transformed into added-value chemicals, such as bioaromatics and long-chain fatty acids [25]. This process therefore not only facilitates the next transformation step from biomass, but also concurrently paves the way for a *zero-waste* approach.

The high lignin content still present in the recovered GlobART after

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

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

MA-SWE (25.66%, Table 3) drove us to perform separate US- and MW-assisted delignification steps (UAD and MAD, respectively) before the subsequent conversion of this solid residue to LevA, according to the experimental conditions described in Section 2.6 [17,25]. Engaging results were obtained from both the UAD and MAD approaches (Table 5), with these perhaps being favored by MA-SW pretreatment, which significantly increased lignin accessibility compared to untreated GlobART, as already explained. Moreover, the use of enabling technologies can intensify this step with respect to conventional delignification procedures, as seen in the works of [44], and [45].

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

The considerable promotional effects that the delignification step has on LevA yields are evident. In particular, MAD (Table 6, entries 5–6) was the most efficient pretreatment, as it gave a molar yield of above 71% whereas only 37% was obtained without delignification (Table 6, entries 1–2), i.e., a boost of up to 90% in terms of LevA. The lignin fraction is known to limit contact between catalysts and feedstocks, which could hinder the hydrolysis of cellulose towards fine chemicals [27,46]. This step is therefore usually crucial to enhancing product yields. Moreover, partial hemicellulose degradation takes place during alkaline delignification. Thus, a significant fraction of this polymer may also be removed along with lignin, which could also facilitate further cellulose hydrolysis [26].

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

On the other hand, no differences were found between HCl 2 M and *p*-TsA 0.25 M in preliminary tests using MA-SWE GlobART (Table 6, entries 1–2). In fact, a similar LevA yield was achieved after both the MAD and UAD treatments (Table 6, entries 3–6). Overall, the comparable results achieved using *p*-TsA are promising, as fewer degradation products are formed and fewer side reactions occur when using this acid, which is an advantage in accordance with Green Chemistry principles. Furthermore, it should be remarked that a 100%-selective process to LevA took place when using this catalyst (*p*-TsA), as observed in an analysis, by ^{1}H NMR and GC-MS, of the organic phase after reaction

Table 6
MW-assisted conversion of different globe artichoke (GlobART) solid residues[a].

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

a. Reaction conditions: T: 225ºC; t: 2 min; P: 40 bar N_2; biomass/acid (B/A) ratio: 1/10.
b. *p*-TsA: *p*-toluenesulfonic acid. 1.75 g of KBr was used as the co-catalyst for these experiments.
c. Obtained considering the amount of cellulose in MA-SWE GlobART for the sake of comparison.

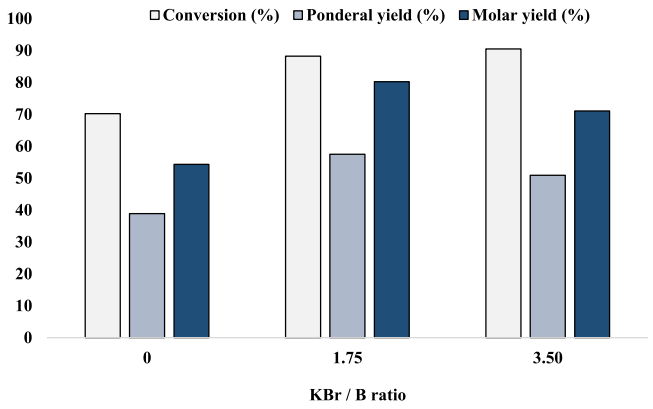

Fig. 2. Influence of KBr / biomass (KBr/B) ratio on LevA production from (MA-SWE + MAD)-(GlobART). Reaction conditions: as described in Table 6.

(Fig. S3). This fact would allow LevA to be employed in further transformations without a prior purification step, again an advantage according to Green Chemistry principles.

Finally, the reaction conditions adopted with *p*-TsA (0.25 M) were slightly modified by reducing the KBr load on (MA-SWE + MAD)-GlobART, since the optimal LevA yield was achieved after the MAD process. Despite the positive effect that halide salts have on the hydrolysis and dehydration of biomass [35], the complexity of this reaction type sometimes favors degradation or polymerization steps towards humins, especially when high amounts of salt are employed, thus negatively affecting the yield of the desired products.

In this context, different KBr loads were tested (Fig. 2). Initially, the selected amount was chosen according to previous studies [35,42], with the KBr/biomass (KBr/B) ratio kept constant at 3.5 (1.75 g KBr and 0.50 g biomass).

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

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

4. Conclusions

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

waste biorefinery. In this context, the non-conventional technologies used could be considered mature enough to convert large quantities of artichoke waste into platform chemicals quickly and efficiently.

CRediT authorship contribution statement

Manuel Salgado-Ramos: Investigation, Methodology, Writing – original draft. **Silvia Tabasso**: Data curation, Validation, Writing – original draft. **Emanuela Calcio Gaudino:** Analysis, Conceptualization, Supervision. **Francisco J. Barba:** Conceptualization, Methodology, Supervision. **Giancarlo Cravotto**: Writing – review & editing, Conceptualization, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

No data was used for the research described in the article.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jece.2023.111390.

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