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Additional Information

1 **Influence of high-intensity ultrasound application on the kinetics of sugar release**
2 **from acid suspensions of artichoke (*Cynara scolymus*) biomass**

3

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24 **Abstract:** The study of sugar release kinetics is an essential step prior to developing new
25 technologies for applying in the bioethanol industry. To this end, the kinetics of reducing
26 and total sugar release (extraction/hydrolysis) from artichoke waste were obtained in
27 different conditions to evaluate the solubility of free sugars from raw matter and the
28 hydrolysis of larger chain molecules separately. Thus, experiments of extraction with
29 water (WE), hydrolysis (HY) in acid solutions and a conventional industrial hydrolysis
30 (IHY), which combines dissolution and hydrolysis effects, were carried out. All of the
31 treatments were studied with ultrasound application (US) or with conventional agitation
32 (AG). Compared to AG experiments, US application accelerated the sugar dissolution
33 reducing 50% the time to reach the equilibrium. The decrease in the biomass
34 concentration in the suspensions increased the US effects in HY experiments. In IHY
35 experiments, US was also able to enhance the final yield of sugars achieving relative
36 reducing sugar and total sugar amounts 213% and 175%, significantly higher than AG
37 experiments. The rheological changes in the suspensions during treatments can explain
38 the different magnitude of ultrasound effects. The acoustic field characterization and the
39 measurement of viscosity in the acid suspensions agreed with these results.

40 **Keywords:** hydrolysis, pretreatment, modeling, phosphoric acid, fermentable sugar.

41

42

43 **1. Introduction**

44 The environmental concerns about the use of fossil fuels have been the driving force
45 behind exploratory research into the use of emerging technologies for the purposes of
46 improving the conversion of alternative renewable resources into biofuels. Most of these
47 resources are biomass from agro-industrial processes and agricultural residues. Their use
48 as raw material for bioethanol production can aggregate value to the by-product, reduce
49 the costs regarding waste storage and disposal and provide a sustainable alternative to
50 fossil fuels. Moreover, it can contribute to reducing the use of crops for food production
51 purposes, e. g. corn, as biofuel sources.

52 Biomass structures are rich in cellulose and hemicellulose, polymers of pentose and
53 hexose. Their large molecular chain can be broken down and converted by fermentation
54 into bioethanol and other feedstock chemicals. In this sense, the residue from artichoke
55 (*Cynara scolymus*) processing is an interesting raw material to be studied for bioethanol
56 production. Artichoke production in only the main producer countries (Italy, Egypt, Spain
57 and Argentina) reaches approximately 900,000 tons per year [1]. Artichoke is rich in
58 antioxidant compounds and has many beneficial health properties [2]. The industrial
59 processing of artichoke involves the separation of outer bracts, stem and tip from the
60 pieces in order to obtain the artichoke heart, which is the edible fraction. This means that
61 more than 50% of the raw matter which is industrially processed is converted into waste,
62 leading to a biomass generation of over 500,000 tons per year. This by-product is rich in
63 cellulose (>75%), hemicellulose, fructosans and pectic polysaccharides –18% of the
64 fibers composition, excluding ashes and lignin – that can be converted into fermentable
65 sugars [3, 4]. Moreover, in its composition, it can be found reducing sugar (as monomers
66 of xylose, fructose, glucose, arabinose and disaccharides of cellobiose) as well as non-

67 reducing saccharides, such as disaccharides of sucrose, and several oligomers without
68 reducing end, as raffinose or starchyose [5].

69 The pretreatment of lignocellulose is one of the main challenges to second-generation
70 ethanol production. At this stage, the carbohydrate polymers of cellulose and
71 hemicellulose are prepared to be converted into short chain carbohydrates and, even into
72 monomer molecules. In addition to partial hydrolysis, pretreatments can also affect the
73 arrangement and accessibility of cellulose fibers and, consequently, enhance further
74 processing [6-9]. The magnitude of each effect is dependent on some variables, e. g.
75 treatment temperature, type and concentration of catalyst, reaction time or the application
76 of alternative technologies. The different pretreatments include conventional methods,
77 such as acid and alkaline hydrolysis under mechanical agitation (AG), steam explosion
78 or oxidative treatments, and emerging techniques, such as microwaves, ozone, irradiation
79 by gamma rays, supercritical CO₂ or ultrasound application [10-12]. In this sense, the use
80 of high-intensity ultrasound (US), characterized by operating at acoustic intensity higher
81 than 1 W·cm⁻² in the frequency range of 10–100 kHz, has shown itself to be an efficient
82 tool for intensifying the treatment of biomass in combination with conventional processes
83 [13-16]. Moreover, the application of US in an alternative primary pretreatment could
84 enhance the sugar release using milder conditions in terms of temperature, type of acid or
85 acid concentration [17]. Thus, instead of the conventional acids, e. g. sulfuric acid, it can
86 allow the use of other with lower corrosive potential, like phosphoric acid, for example,
87 also reducing the sugar degradation into inhibiting compounds to microorganisms growth
88 [18]. Moreover, it can promote cellulose and hemicellulose retrieval in the solid fraction,
89 a reduction of further enzyme loadings during enzymatic hydrolysis or higher
90 accessibility of solid fraction to microorganisms [7].

91 Recent studies with the assistance of ultrasound have been focused on determining
92 kinetics of sugar production by enzymatic [13, 19, 20] or alkaline methods [21]. However,
93 little information has been reported about the kinetics of ultrasound-assisted sugar release
94 in diluted acid medium in comparison with, e. g. conventional agitation [22]. The
95 quantification of the process variable effects can provide useful information about the
96 efficiency of the sugar release [23].

97 Thus, the aim of this study was to evaluate the kinetics of both reducing and total sugar
98 release from artichoke waste (AW) by conventional agitation (AG) in acid solution and
99 assess the influence of ultrasound application (US).

100

101 **2. Materials and Methods**

102 **2.1. Sample preparation**

103 Fresh artichokes (*Cynara scolymus*) were bought in a local market in Valencia, Spain.
104 The outer bracts, one of the main by-products generated during artichoke processing,
105 were manually removed, cleaned and placed in a convective oven at 60 °C until reaching
106 constant weight (24 h approx.). The dried product was then milled and sieved to obtain a
107 powder of artichoke waste (AW) with a particle size of under 1 mm. Moreover, the
108 moisture content of the dried samples were determined by drying the samples in a vacuum
109 oven at 70 °C until constant weight (24 h approximately). The average moisture content
110 obtained was 4.92% ± 0.04% (w.b.). Then, the AW was packed in polypropylene bags
111 for later use.

112

113 **2.2. Experimental plan**

114 The experimental plan included three sets of experiments, summarized in Table 1. In the
115 first one, the extraction of soluble sugars of AW with water was studied (WE); in the

116 second, the hydrolysis process in acid solution (HY) after the WE process; and finally,
117 the third set consisted of the simultaneous application of the previous two processes (WE
118 and HY), that is the study of the direct treatment of AW in acid solution (IHY). This last
119 one was applied to simulate an industrial hydrolysis process in which the artichoke waste
120 is directly added into the acid solution. Each condition considered was tested at least three
121 times.

122 The conventional conditions for hydrolysis include the application of high temperatures
123 and strong and corrosive acids. However, because the goal of this study was to enhance
124 the process by means of ultrasound application in mild conditions, an acid solution of
125 10% w·w⁻¹ of metaphosphoric acid (GPR Rectapur; VWR Chemicals, Lutterworth, UK)
126 in distilled water and a temperature of 50 °C were used, being in the range applied by
127 other authors [17, 24]. This acid, in contrast to the conventional acids, is reported to be
128 less corrosive with high conversion efficiency and has low formation of inhibiting
129 compounds such as acetic acid and furfural [18, 25]. To control this temperature, all the
130 experiments were carried out in a jacketed vessel circulating a cooling liquid through the
131 jacket from a thermostatic bath (Frigedor, J.P. Selecta, Barcelona, Spain). Next, the
132 experimental conditions of each set of experiments are described in detail.

133

134 **2.2.1. Extraction of soluble sugars with water (WE)**

135 Initially, aqueous suspensions (distilled water) containing 5% (w·w⁻¹) of AW were
136 maintained at 50 °C for 2 h in order to determine the total amount of free sugars that can
137 be directly extracted by solubilization with water. These experiments were carried out
138 through the agitation of the suspension (B5AG0) or ultrasound application (B5US0).

139

140 **2.2.2. Hydrolysis in acid suspensions (HY)**

141 This set of experiments consists of a previous phase where the soluble sugars were
142 extracted in a similar way to how they were in WE experiments (aqueous suspensions
143 continuously agitated at 50 °C) for 120 min (time to reach equilibrium). In this case, two
144 different biomass concentrations, 2.5 or 5% w·w⁻¹, were tested. After that, hydrolysis in
145 acid medium was carried out (10% w·w⁻¹ of phosphoric acid). The conditions were
146 maintained for 60 min at 50 °C under conventional agitation (B2.5AG10-A, B5AG10-A)
147 or with ultrasound application (B2.5US10-A, B5US10-A). The goal of this set of
148 experiments was to differentiate the effects of the solubilization of free sugars from the
149 actual hydrolysis in acid medium.

150

151 **2.2.3. Simulation of an industrial hydrolysis (IH) process.**

152 Finally, to assess a more realistic approach to an industrial process, a set of experiments
153 was carried out including, in one simultaneous step, the sugar solubilization and actual
154 hydrolysis. Experiments B5AG10 and B5US10 consisted of directly submitting AW to
155 the treatment in a (5% w·w⁻¹) suspension of phosphoric acid (10% w·w⁻¹) at 50 °C for 60
156 min under conventional agitation or ultrasound application, respectively (Table 1).

157

158 **2.3. High-intensity ultrasound (US) system**

159 The experimental set-up used to carry out ultrasound experiments is shown in Figure 1.
160 An ultrasonic probe-type system (UP400S, Dr. Hielscher GmbH, Teltow, Germany)
161 supplied with a probe of 2.2 cm diameter of the emitter surface was used to generate a
162 high intensity ultrasonic field. To standardize the ultrasonic treatment, the ultrasonic
163 probe was immersed 1 cm into the different suspensions.

164 As stated before, during the experiments, the suspension's temperature was maintained
165 constant at 50 ± 2 °C. For this purpose, a K type thermocouple immersed in the suspension

166 was connected to a process controller (E5CK, Omron, Hoofddorp, Netherlands). This
167 controller drove a peristaltic pump (302 S, Watson-Marlow, Postfach, Germany) to
168 recirculate a glycol solution (30% glycol) at $-10\text{ }^{\circ}\text{C}$, from a refrigerated bath (Frigedor,
169 J.P. Selecta, Barcelona, Spain), through the jacketed vessel (250 mL of capacity).
170 The maximum electric nominal power (400 W) was applied to the ultrasonic system in
171 pulses way: 0.6 s on followed by 0.4 s off. This was the longer period of ultrasound
172 exposure that could be applied without overheating the solution, including with the help
173 of the cooling system.

174

175 **2.4. Conventional agitation (AG) system**

176 Experiments under conventional agitation (AG) were carried out in a similar set-up to
177 that shown in Figure 1, but changing the ultrasonic probe for an agitator (Heidolph RZR1;
178 Heidolph Instruments GMBH & Co., Schwabach, Germany). A detail of the agitator and
179 different shape factors (F_1 , F_2 , F_3 , F_4 and F_5) calculated to characterize the agitation are
180 shown in Figure 2. The agitator consisted of a rectangular impeller, inclined at 45° .
181 Suspensions were stirred at 1000 rpm.

182

183 **2.5. Sugar determination**

184 Aliquots of approximately 3 mL were taken from the suspensions at preset times. In the
185 case of acid suspensions, the aliquots were immediately neutralized with NaOH 2.5 M.
186 After that, all the samples were centrifuged at 8000 rpm for 10 min at $5\text{ }^{\circ}\text{C}$ and filtered
187 with PTFE micro filters ($0.45\text{ }\mu\text{m}$, 25 mm diameter; LabBox, Barcelona, Spain) to
188 proceed to the sugar determinations.
189 The reducing sugars (S_R) were determined using the DNS method, as used by Kassaye et
190 al. [8]. This is a fast and practical method for determining reducing sugars, which is based

191 on the reduction, in alkaline medium, of the 3,5-dinitrosalicylic acid in the presence of
192 reducing sugars. From this reaction, 3-amino-5-nitrosalicylic acid is produced in the same
193 stoichiometric proportion, presenting stability and being orange-red in color. For this, 200
194 μL of neutralized and properly diluted aliquots were mixed with 200 μL of DNS solution
195 and subsequently boiled for 5 minutes. After cooling, 1.6 mL of distilled water were
196 added to the orange-red solution. The absorbance was measured at a wavelength of 540
197 nm using a spectrophotometer (Helios Gamma, Thermo Spectronic, Cambridge, UK).
198 The analyses were carried out in triplicate. The results were expressed as kg of reducing
199 sugar (glucose equivalent) per 100 kg of dried matter using a previously determined
200 standard curve of anhydrous glucose.

201 To measure the total amount of the total hydrolysable sugars (S_T) present in the samples,
202 the aliquots were previously hydrolyzed, as done by Ramón et al. [24]. The neutralized
203 aliquots (0.5 mL) were hydrolyzed using 2 mL of HCl 2 M under boiling for 30 min, then
204 cooled and neutralized again with NaOH 2.5 M. Then, the hydrolyzed samples were
205 submitted to the DNS method and the amount of total fermentable sugar was also
206 expressed as kg of glucose equivalent per 100 kg of AW dried matter (kg gl-eq·100 kg
207 AW^{-1} d.b.).

208

209 **2.6. Mathematical modeling**

210 The kinetics of sugar release during the treatments was described mathematically by an
211 adaptation of the Naik model [26], given by Eq. (1), in this case considering the relative
212 sugar release (Y):

$$213 \quad Y = \frac{Y_{\infty} t}{(B + t)} \quad (1)$$

214 Y is calculated by Eq. (2):

$$215 \quad Y = \frac{([S]_t - [S]_{t=0})}{[S]_{t=0}} \quad (2)$$

216 Where $[S]_t$ is the sugar production at time t (kg gl-eq·100 kg AW⁻¹ d.b.); $[S]_{t=0}$ the initial
 217 sugar content (kg gl-eq·100 kg AW⁻¹ d.b.); t is the treatment time (min), Y_∞ is the relative
 218 difference of sugar production at equilibrium and B (min) is the time needed to reach half
 219 of Y_∞ .

220 In order to determine the goodness of the fit of the experimental data, the adjusted
 221 determination coefficient (R_{adj}^2) and the root-mean-square error ($RMSE$) given by Eq. (3)
 222 and Eq. (4), respectively, were used:

$$223 \quad R_{adj}^2 = 1 - \frac{n-1}{n-(k+1)}(1-R^2) \quad (3)$$

$$224 \quad RMSE = \sqrt{\frac{\sum_{n=1}^n (y_p - y_{exp})^2}{n}} \quad (4)$$

225 where n is the number of observations, k is the number of parameters in the model
 226 (excluding the constant), R^2 is the determination coefficient, y_p is the predicted value and
 227 y_{exp} is the experimental value.

228

229 **2.7. Changes of viscosity throughout the acid hydrolysis**

230 The viscosity of acid suspensions was measured before and after the treatment, under
 231 agitation or under sonication, to quantify possible changes induced by the process. For
 232 this purpose, a rotational rheometer, AR-G2 (TA Instruments, USA), was used coupled
 233 with the Starch Pasting Cell geometry (gap 5500 μ m) in order to avoid particle
 234 sedimentation. Approximately 28 mL of each sample were inserted into the equipment to
 235 take measurements in triplicate of the shear stresses for the range of shear rate from 1 up
 236 to 265 s⁻¹. A thermostatic bath included in the equipment maintained the temperature at a

237 constant 50 °C, simulating the same conditions employed during the acid hydrolysis. The
238 results were exported by the Universal Analysis 2000 version 4.7 (TA Instruments, USA)
239 data acquisition system.

240

241 **2.8. Acoustic field characterization**

242 The actual acoustic power applied was determined to characterize the ultrasound
243 influence in the acid hydrolysis of AW. The experimental measurements were taken in
244 the same experimental set-up used for hydrolysis experiments, using a calorimetric
245 method. Specifically, the temperature of the different suspensions was measured every
246 second for the first 60 s of ultrasound application. These measurements were taken with
247 the help of a type K thermocouple (± 0.1 °C) placed 2 cm from the tip of the ultrasonic
248 probe and connected to a PC through a process controller (E5CK, Omron Spain, Spain).
249 There, a software developed in LabVIEW (LabVIEW Run-Time Engine 7.0, National
250 Instruments, USA) allowed the temperature to be recorded every second. The acoustic
251 power applied was determined using Eq. (5) [27]:

$$252 \quad P = mc_p \frac{dT}{dt} \quad (5)$$

253 where P is the acoustic power (W), m is the acid solution mixture mass (kg), c_p is the
254 specific heat capacity of the acid solution ($4064.8 \text{ J}\cdot\text{kg}^{-1}\cdot\text{°C}^{-1}$, determined by differential
255 scanning calorimetry) and dT/dt is the heating rate ($\text{°C}\cdot\text{s}^{-1}$). The rise in temperature was
256 recorded in triplicate for each condition tested, before and after the hydrolysis
257 experiments. Thus, the influence of the changes produced in the acid solution mixture
258 during treatment on the ultrasonic power applied could be studied.

259 The acoustic density (D ; $\text{kW}\cdot\text{kg}^{-1}$ of AW) was given by the relationship between the
260 acoustic power and the particles loading in the suspensions being treated.

261

262 3. Results and discussions

263 3.1. Extraction of soluble sugars with water

264 The extraction kinetics of total and reducing sugars from artichoke waste (AW) using
265 water in a conventional agitation system (B5AG0 experiments) were determined over 2
266 hours. This was long enough to reach equilibrium and to obtain the total amount of sugar
267 that can be dissolved. As can be observed in Figure 3, after 60 min of extraction, both
268 curves reached an asymptotic value of 5.78 (kg gl-eq·100 kg AW⁻¹ d.b.) for reducing
269 sugar and 8.29 (kg gl-eq·100 kg AW⁻¹ d.b.) for total sugar.

270 For this reason, experiments with ultrasound application (B5US0) were only carried out
271 for 60 min. In fact, these experiments exhibited a faster and greater dissolution of soluble
272 sugars when compared to experiments carried out with agitation (B5AG0) only, as can
273 be observed in Figure 4. Although the differences between both kinds of experiments
274 were not significant, probably due to the great natural variability, US application seemed
275 to increase the extraction kinetics of sugar release. In these treatment conditions (non-
276 acid aqueous suspensions at a moderate temperature), no hydrolysis occurred and sugar
277 degradation was not evidenced. Therefore, the mechanical effects of US application can
278 be related to the improvement in the mass transfer. In the solid material, the compression
279 and decompression zones contributed to the sponge effect, promoting the release of the
280 compounds trapped into the solid matrix. Regarding the liquid phase, the collapse of the
281 cavitation bubbles caused the formation of micro-jets and turbulences in the solid-liquid
282 interface, leading to the reduction in the diffusion boundary layer, disruption of the cell
283 walls and creation of microscopic channels [5, 28]. Ultrasound is also able to produce
284 H₃O⁺ and OH⁻ in aqueous medium under cavitation that act oxidizes the plant tissues
285 [29]. All these effects enhance the release of extra and intracellular content towards the
286 dispersant which, in fact, occasioned the faster dissolution [30]. US could also facilitate

287 sugar dissolution by enhancing the contact between the liquid and the solid due to the
288 solvent penetrating into areas where conventional agitation is not efficient [31]. Some
289 authors have stated that aqueous treatment with US has more effects on the physical
290 structure, such as biomass accessibility and cellulose crystallinity, than on the chemical
291 reaction [16]. Thus, the B5US0 experiments reached dissolution equilibrium faster than
292 the B5AG0 experiments, US being more efficient for the purposes of extracting soluble
293 sugars already existent in biomass.

294

295 **3.2. Hydrolysis in acid suspensions**

296 Taking into account the results shown in the previous section and in order to differentiate
297 the hydrolysis treatment from the sugar dissolution process, hydrolysis experiments were
298 carried out on AW previously treated in water. For this purpose, after treating AW in
299 agitated aqueous suspensions for 120 min to ensure the total dissolution of the soluble
300 sugars, phosphoric acid was added until there was 10% ($w \cdot w^{-1}$) of acid in the dispersant.
301 These final suspensions were submitted to hydrolysis under mechanical agitation or US
302 irradiation.

303

304 **3.2.1 Hydrolysis kinetics**

305 Figure 5 shows the kinetics of both reducing and total sugar relative release from HY
306 experiments of 5% ($w \cdot w^{-1}$) AW suspensions carried out with (B5US10-A) and without
307 (B5AG10-A) ultrasound application. As can be observed, no significant differences
308 ($p < 0.05$) were found between the relative release of total sugars obtained with ultrasound
309 application and with suspension agitation. On the contrary, the release of reducing sugars
310 was greater for conventionally agitated experiments when compared to US-assisted ones.
311 These results can be attributed to the changes in the viscosity of the suspensions produced

312 by the prior soluble sugar extraction with water. Thus, after this stage, suspensions
313 showed a paste-like appearance, probably as a consequence of particle swelling. This
314 could increase their volume and reduce the amount of free dispersant. In these conditions,
315 the conventional mechanical agitation seemed to be more efficient at enhancing the rate
316 of hydrolysis. According to Loow et al. [7], mechanical agitation generally promotes
317 adequate heating and acid-biomass contact to recover fermentable sugars. On the
318 contrary, the viscous behavior of the suspensions can prevent the effects of ultrasound
319 from being significant. Thus, viscous forces between particles can make the transmission
320 of mechanical vibration difficult. In this case, it is very difficult for cavitation to take
321 place and the micro-agitation phenomena could be quite limited. As a consequence, the
322 ultrasound effects on acid hydrolysis at the intensity applied was limited.

323 Despite the differences in the hydrolysis rate, both conventional agitation and ultrasound
324 application contributed to hydrolyzing the fermentable matter during the treatment time.
325 These results indicate the possibility of using diluted acid solutions to produce a
326 continuous amount of sugar without sugar decomposition. Lenihan et al. [23] also found
327 similar results as the hydrolysis was carried out in mild concentrations of acid. Moreover,
328 it must be highlighted that the curves of sugar production under these conditions did not
329 attain asymptotic behavior at the time tested. Thus, at the end of 60 min, a total sugar
330 production of 12.16 kg per 100 kg of dried AW was observed, while the reducing sugar
331 content reached 11.29 kg per 100 kg of dried AW. Karimi et al. [32] encourage the use
332 of two-stage hydrolysis or enzymatic hydrolysis if the main objective is to obtain greater
333 amounts of total sugars. When analyzing the hydrolysis of rice straw, the same authors
334 noticed that the first stage has a greater effect on xylan depolymerization, while
335 significant amounts of glucose were observed after the second stage as a consequence of
336 cellulose digestion.

337

338 **3.2.2. Influence of the decrease of artichoke waste (AW) concentration in HY** 339 **treatments**

340 The effect of decreasing the biomass content in the HY treatments was also studied. For
341 this purpose, the results obtained in the 5% (w·w⁻¹) AW suspensions were compared with
342 those of a new set of experiments considering suspensions with 2.5% (w·w⁻¹) AW content
343 (B2.5AG10-A and B2.5US10-A experiments). Thus, contrary to the 5% (w·w⁻¹) AW
344 experiments (Figure 5-a), no differences were found between the experiments carried out
345 with agitation and those performed with ultrasound application in the case of 2.5% (w·w⁻¹)
346 AW experiments. In fact, as can be observed in Figure 6-a, both US and AG kinetics
347 overlapped. As regards the appearance, 2.5% (w·w⁻¹) of AW suspensions seemed to be
348 less viscous than 5% (w·w⁻¹), qualitatively. This is coherent with the explanation of the
349 negative influence that the viscosity of the suspensions exerts on ultrasound effects. Thus,
350 the reduction in biomass concentration from 5% (w·w⁻¹) to 2.5% (w·w⁻¹) in the US
351 treatments led to an increase in relative reducing sugar release from 40% up to 80% after
352 60 min of treatment. This was the same value as that attained in AG experiments.

353 On the other hand, the relative sugar release in AG experiments was quite similar for the
354 two AW concentrations of suspensions tested (B5AG10-A and B2.5AG10-A
355 experiments). Higher concentrations have to be tested to determine the maximum
356 concentration to be used in these kinds of treatments in order to process higher amounts
357 of biomass with the minimum usage of chemicals and water.

358 The HY experiments also showed that after 60 min of treatment, the hydrolysis was a
359 long way from reaching equilibrium (Figures 5 and 6). This fact is particularly evident in
360 the case of total sugar release, mainly in the 2.5% (w·w⁻¹) AW suspensions where only a
361 linear trend was observed. In this case, it must be highlighted the increase in the acid-

362 biomass ratio (from 1.9 in the 5% (w·w⁻¹) AW suspensions to 3.9 in the 2.5% (w·w⁻¹) AW
363 suspensions) that can produce a more intense contact between acid and biomass.
364 Moreover, the less qualitative viscosity of these suspensions may favor the appearance of
365 significant ultrasound effects (Figure 6-b). Thus, after 60 min of treatment, the relative
366 total sugar release of B2.5US10-A experiments was 87% higher than that of B2.5AG10-
367 A experiments. When studying dilute acid hydrolysis of biomass, Germec et al. [33]
368 found an increase of 69% in the total fermentable sugar production from tea processing
369 waste in the cases ultrasound was applied. Werle et al. [17] and Ramón et al. [24] also
370 found increases up to 96% in ultrasound-assisted acid hydrolysis of lignocellulosic and
371 starchy biomass, respectively. The application of acoustic fields in these conditions could
372 promote the formation of microjets from the asymmetrical implosion of cavitation
373 bubbles which hits the crystalline cellulose, besides the erosion in the solid material by
374 the shockwaves (Alvira et al., 2010). According to Luo et al. [15], it can lead to the pre-
375 fractionation of the raw material, the opening of the crystalline structure of cellulose and
376 the intensification of the mass transfer process to release more fermentable sugars during
377 the treatment when compared to AG experiments.

378

379 **3.3. Industrial approach application**

380 The application of an industrial approach should obtain the greatest sugar release in the
381 minimum time possible, regardless of whether the sugar release is due to the dilution of
382 the sugars present or hydrolysis. For this reason, a new set of experiments considering
383 this fact was carried out (B5AG10 and B5US10), in which the biomass was directly
384 suspended in the acid medium to be treated.

385 The results (Figure 7) showed that acid suspensions directly treated with US (B5US10
386 experiments) produced relative reducing sugar and total sugar amounts of 213% and

387 175%, significantly higher than what was obtained through the agitation of suspensions
388 (B5AG10 experiments). The less qualitative viscosity at the beginning of the treatments
389 can favor the mechanical effects of ultrasound not only by producing an intense
390 microstirring in the suspension but also by providing the energy needed to produce
391 cavitation. Yunus et al. [16] related the US application to the enhancement of acid
392 penetration in order to convert cellulose and hemicellulose into fermentable sugars of low
393 molecular weight. In addition to hydrolysis, there is a significant combined effect of acid
394 and ultrasound on the extraction of the pectin in plant tissue cells [34]. The presence of
395 pectin in the acid solution makes its depolymerization easier, leading to higher rates of
396 reducing sugar production when compared to total sugars. At the same time the US-
397 assisted treatments permit the recovery of carbohydrates and hydrolyze lignocellulose,
398 modifications in the biomass surface can be obtained for the purposes of improving its
399 accessibility to enzymes and microorganisms for further additional stages [22].

400

401 **3.4. Mathematical modeling**

402 The mean experimental data of relative sugar release were fitted to the Naik model for
403 the different experiments to quantify the differences among the tested treatments. The
404 fitting parameters of each condition are shown in Table 2.

405 On the whole, the Naik model adequately fitted the experimental data as shown by the
406 high determination coefficient values (R_{adj}^2), greater than 0.93 in every case, and the low
407 root-mean-square error value ($RMSE$), lower than 0.093. Moreover, the curves calculated
408 using the model followed the same trend as those of the experimental data in every
409 condition studied (Figure 4, Figure 5, Figure 6 and Figure 7). According to Gaméz et al.
410 [25], representative kinetic equations are useful for economical estimations in the
411 conversion industry.

412 As far as the WE set of experiments is concerned, the B parameter was 80% for reducing
413 sugars and 60% for total sugars, lower in the US-assisted experiments than in the AG
414 ones. On the other hand, the estimated sugar release at equilibrium (Y_{∞}) was greater in
415 the US experiments than in the AG for the extraction of both reducing (35%) and total
416 sugars (39%). These parameters indicate that the application of US was a more efficient
417 means of dissolving the soluble sugars present in artichoke waste than applying AG.

418 As regards the hydrolysis of 5% ($w \cdot w^{-1}$) AW suspensions (HY experiments), higher
419 values were observed for the release of total and reducing sugars at equilibrium (Y_{∞}) in
420 the AG experiments (B5AG10-A) than in the US (B5US10-A). This means that acid
421 hydrolysis under AG was more efficient at converting fermentable matter into reducing
422 sugar in concentrated suspensions. As for the B parameter, the lower values obtained in
423 the US experiments seemed to indicate a faster process. However, because this parameter
424 represents the time needed to release half of the sugar at equilibrium (Y_{∞}), which was
425 lower for US experiments, it is not possible to extract a clear difference between AG and
426 US application.

427 The decrease in AW concentration from 5% ($w \cdot w^{-1}$) to 2.5% ($w \cdot w^{-1}$) led to very similar
428 kinetic parameters, B and Y_{∞} , for the reducing sugar release of B2.5AG10-A and
429 B2.5US10-A. On the contrary, in the case of the total sugar release, the values obtained
430 in US experiments were higher than those obtained under AG. The high values of B found
431 for the total sugar release indicated that equilibrium was far from reached in these
432 conditions.

433 Finally, in IHY experiments, the application of US increased both the total and the
434 reducing sugar release at equilibrium, these values being 110% and 186% higher than in
435 the AG experiments, respectively. As regards the B parameter, it was quite similar in
436 both cases.

437

438 3.5. Viscosity of the acid suspensions

439 As stated before, the differences between the influence of US application in WE and HY
440 experiments can be attributed to the influence of changes in the apparent viscosity of
441 suspensions during the HY process. Thus, the qualitative increase in apparent viscosity
442 could hinder ultrasound transmission and, therefore, its effects. Hou et al. [35] stated that
443 hydrolysis produces changes in the rheological properties of acid suspensions. Thus, the
444 viscosity of suspensions before and after the HY treatment was measured to quantify these
445 changes

446 In the studied conditions, the resulting rheograms showed the absence of yield stress and
447 a linear dependence of the shear stress (mPa) on the shear rate (s^{-1}). Thus, the Newton
448 model could be fitted to the experimental data to provide the Newtonian viscosity values
449 (mPa·s) of the suspensions.

450 As can be observed in Table 3, the HY treatment produced an increase in the viscosity of
451 the suspensions. The viscosity of 5% AW suspensions (B5AG10-A) was 53% higher after
452 HY treatments and it rose by 70% in the case of 2.5% ones (B2.5AG10-A). The
453 application of US during treatments brought about a greater increase in the viscosity when
454 compared to the treatments with AG (Table 3). Thus, in B5US10-A the viscosity had
455 increased by 360% at the end of the HY treatment and 326% in the case of B2.5US10-A.
456 These results were coherent with the findings of Koppram et al. [36], who stated that
457 rheological properties of treated suspensions containing biomass depend on the type of
458 raw material and the pretreatment conditions. In all likelihood, US application was more
459 efficient at retrieving hemicellulose and lignin from the solid phase than AG. It may have
460 increased the viscosity of the dispersant with the same degree of particle-particle

461 interactions as the initial suspensions, leading to an increased flow resistance of the
462 resulting acid suspension.

463

464 **3.6. Characterization of the acoustic fields**

465 As stated in previous papers, the magnitude of the ultrasound effects depends on the
466 acoustic energy that is effectively applied [30, 37]. In this sense, the sonication of the
467 suspensions leads to difficulties if compared to the processing of liquids. The presence of
468 heterogeneous systems influences cavitation activity and transport phenomena [38]. The
469 combination of the suspension's properties and sonication parameters can affect the
470 intensity of diverse chemical and mechanical effects [39]. Therefore, every modification
471 of the viscous properties of suspensions can also influence the transmission of the acoustic
472 energy and so the magnitude of the ultrasound effects.

473 In this way, the actual power applied in the acid suspensions was determined by using a
474 calorimetric method. Due to the significant change in the viscosity observed during the
475 acid hydrolysis of suspensions, the ultrasonic power measurements were taken before
476 processing and after 1 hour of HY treatment. It must be highlighted that every condition
477 was tested in triplicate.

478 The results (Table 4) indicated that the acoustic density was greater in the diluted
479 suspensions than in the concentrated ones. Thus, the acoustic density measured in the 5%
480 (w·w⁻¹) AW suspensions was 43% lower than that measured in the 2.5% (w·w⁻¹) AW
481 suspensions. This means that when applying the same input power, the sonochemical
482 effects generated in suspensions with a lower solid content were more intense than those
483 induced in the more concentrated suspensions. This was coherent with the sugar release
484 results from the HY experiments, where the influence of US application was more
485 enhanced in the 2.5% (w·w⁻¹) AW suspensions than the 5% (w·w⁻¹) ones. Higher

486 concentrations of lignocellulosic biomass in suspensions generally caused an increase in
487 the apparent viscosity when compared to diluted suspensions, probably as a consequence
488 of the particle-particle interactions [40]. Therefore, in order to obtain similar
489 sonochemical effects in concentrated solutions, it will be necessary to apply more energy,
490 not only to overcome the frictional forces but also to supply more energy per unit of mass.
491 The significant differences in the acoustic energy at the beginning and at the end of both
492 processes also indicated the changes that took place in the suspension during the process.
493 Specifically, the acoustic density decreased by 34% in the case of the 5% (w·w⁻¹) AW
494 suspensions and by 49% in the case of the 2.5% (w·w⁻¹) AW suspensions after 60 min of
495 HY treatments. In addition to the particle swelling, the intensification of the acid action
496 brought about by US could hydrolyze hemicellulose more easily than cellulose, and broke
497 the linkages between xylan and lignin [41, 42]. It may have provoked the release of lignin
498 fragments and the consequent increase observed in the medium viscosity (Table 3),
499 leading to difficulties in ultrasound propagation. Moreover, acid treatment can affect the
500 particles surface and consequently modify how they interact with each other to form
501 agglomerates during longer holding times [43]. These phenomena could be more
502 significant in the 2.5% (w·w⁻¹) AW suspensions than in the 5% (w·w⁻¹) ones due to a
503 better initial transmission of acoustic energy that enhanced ultrasound effects, leading to
504 a greater reduction in acoustic density after 60 min of treatment in the first case.

505

506 **4. Conclusions**

507 The processes of sugar release from artichoke waste by dissolution in water or by
508 hydrolysis in acid suspensions were studied. In the first case, ultrasound application
509 enhanced the kinetics of soluble sugar release when compared to conventional agitation
510 extraction. As to the hydrolysis in acid suspensions, the effectiveness of ultrasound

511 applications was greater in the lower artichoke waste concentration suspensions tested
512 (2.5% of AW w·w⁻¹). The greater viscosity of the more concentrated suspensions (5% of
513 AW w·w⁻¹) could limit the ultrasound effects. Actual acoustic field measurements
514 concurred with this being the acoustic density obtained in the 5% (w·w⁻¹) AW suspensions
515 lower than that measured in the 2.5% (w·w⁻¹) ones. In addition, changes in the rheological
516 properties of the suspensions during the acid hydrolysis could be linked to the decrease
517 in the acoustic density at the end of the processes.

518 Simulating a practical approach, in which biomass particles are directly treated in acid
519 medium, ultrasound-assisted experiments provided sugar release equilibrium values
520 higher than those obtained in experiments carried out with conventional agitation. In
521 addition to the enhanced release of sugars from biomass, ultrasound could have effects
522 on the structure of lignocellulose that may be worthy of research in the further enzymatic
523 and/or fermentative processes involved in bioethanol production.

524

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530

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671 **Table Captions**

672 **Table 1.** Conditions of the total set of experiments.

673 **Table 2.** Kinetic parameters of the adapted Naik model for the different treatments tested:
674 extraction of soluble sugars with water (WE); hydrolysis in acid suspensions (HY) and
675 simulation of industrial hydrolysis (IHY).

676 **Table 3.** Viscosity of the AW acid suspensions before and after HY treatments carried
677 out with agitation (AG) or with ultrasound (US) application.

678 **Table 4.** Acoustic density measured in 5 and 2.5% (w·w⁻¹) AW suspensions before and
679 after 1 h of HY treatment.

680

681 **Figure Captions**

682 **Figure 1.** Scheme of the set-up used in ultrasound-assisted experiments.

683 **Figure 2.** Geometrical characteristics (distances shown in cm) of the agitation system
684 with the corresponding shape factors.

685 **Figure 3.** Extraction kinetics with water of reducing and total sugar release from AW.
686 Experiments carried out with conventional agitation (B5AG0).

687 **Figure 4.** Kinetics of (a) reducing sugar and (b) total sugar release fitted to the Naik
688 model for experiments B5AG0 and B5US0.

689 **Figure 5.** Kinetics of (a) reducing sugar and (b) total sugar release fitted to the Naik
690 model for experiments B5AG10-A and B5US10-A.

691 **Figure 6.** Kinetics of (a) reducing sugar and (b) total sugar release fitted to the Naik
692 model for experiments B2.5AG10-A and B2.5US10-A.

693 **Figure 7.** Kinetics of (a) reducing sugar and (b) total sugar release fitted to the Naik
694 model for experiments B5AG10 and B5US10.

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697 **Table 1.** Conditions of the total set of experiments.

Set	Code	AW concentration (% w·w ⁻¹)	H ₃ PO ₄ concentration (% w·w ⁻¹)	Previous agitation in aqueous medium (2 h)	Technology applied
Extraction with water (WE)	B5AG0	5	0	No	Agitation
	B5US0	5	0	No	Ultrasound
Hydrolysis (HY)	B5AG10-A	5	10	Yes	Agitation
	B5US10-A	5	10	Yes	Ultrasound
	B2.5AG10-A	2.5	10	Yes	Agitation
	B2.5US10-A	2.5	10	Yes	Ultrasound
Industrial hydrolysis (IHY)	B5AG10	5	10	No	Agitation
	B5US10	5	10	No	Ultrasound

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718 **Table 2.** Kinetic parameters of the adapted Naik model for the different treatments tested:
 719 extraction of soluble sugars with water (WE); hydrolysis in acid suspensions (HY) and
 720 simulation of industrial hydrolysis (IHY).

	EW		HY				(IHY)	
	B5AG0	B5US0	B5AG10-A	B5US10-A	B2.5AG10-A	B2.5US10-A	B5AG10	B5US10
	Reducing sugars							
Y_{∞}	0.854	1.157	2.019	0.958	1.274	1.148	2.411	6.900
B	22.870	5.154	88.735	78.856	41.686	33.986	26.162	29.274
R_{adj}^2	0.994	0.994	0.995	0.998	0.999	0.999	0.999	0.996
$RMSE$	0.010	0.027	0.018	0.006	0.007	0.006	0.012	0.093
	Total sugars							
Y_{∞}	0.726	1.009	0.673	0.294	1.579	5.911	1.918	4.040
B	8.516	3.461	123.863	68.343	406.882	918.091	13.495	11.556
R_{adj}^2	0.999	0.995	0.992	0.934	0.986	0.988	0.992	0.995
$RMSE$	0.008	0.022	0.006	0.012	0.008	0.012	0.044	0.078

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735 **Table 3.** Viscosity of the AW acid suspensions before and after HY treatments carried
 736 out with agitation (AG) or with ultrasound (US) application.

Experiment	Viscosity (mPa·s)	
	Before	After
B5US10-A	180.1 ± 0.1 ^d	834.2 ± 0.4 ^a
B5AG10-A		276.9 ± 0.1 ^c
B2.5US10-A	83.3 ± 0.1 ^f	355.9 ± 0.2 ^b
B2.5AG10-A		142.83 ± 0.01 ^e

737 Means and standard deviations followed by the same lowercase letters represent no significant
 738 differences were found between the measurements according to the Fisher test at the 95%
 739 confidence level.

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759 **Table 4.** Acoustic density measured in 5 and 2.5% (w·w⁻¹) AW suspensions before and
 760 after 1 h of HY treatment.

Experiment	Acoustic density (kW·kg ⁻¹ of dried AB)	
	Before	After 1 h HY treatment
B5US10-A	21.1 ± 0.1 ^b	14 ± 2 ^d
B2.5US10-A	37.0 ± 0.5 ^a	19 ± 1 ^c

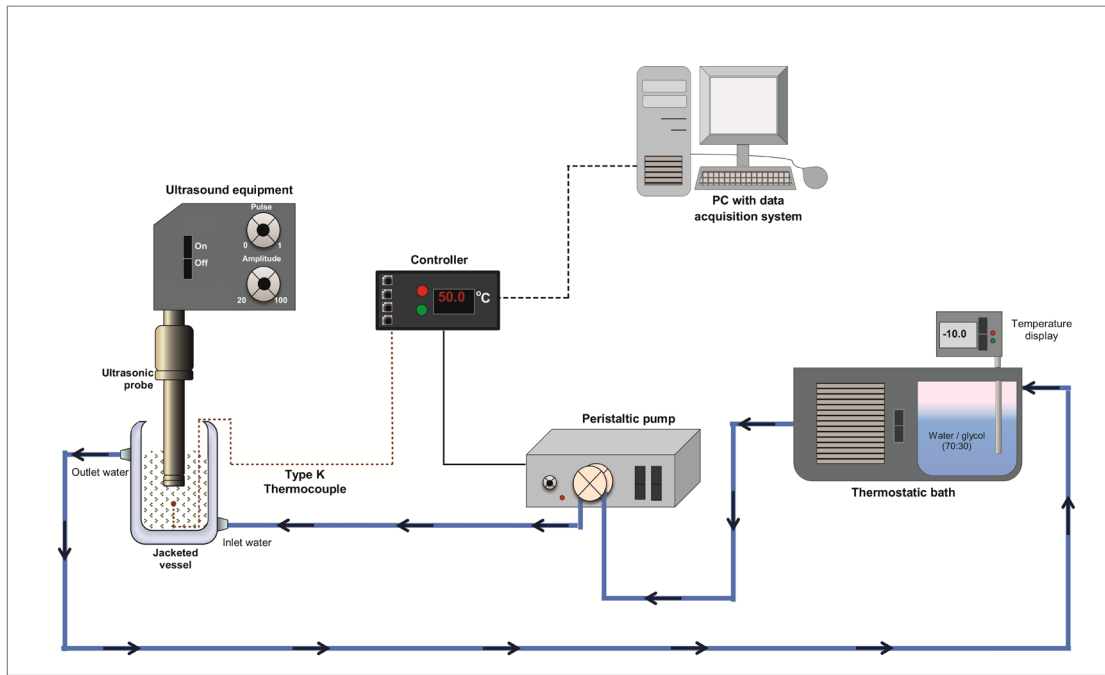
761 Means and standard deviations followed by the same lowercase letters represent signify that no
 762 significant differences were found between the measurements according to the Fisher test at the
 763 95% confidence level.

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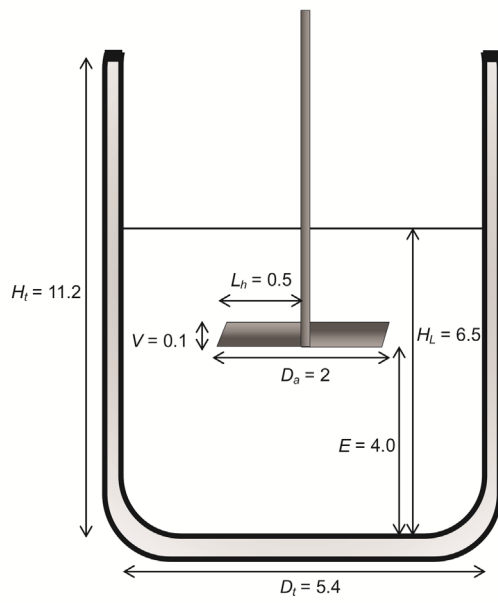


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769 Figure 1

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$$F_1 = \frac{D_t}{D_a} = 2.7$$

$$F_2 = \frac{E}{D_a} = 4$$

$$F_3 = \frac{L_h}{D_a} = 0.25$$

$$F_4 = \frac{V}{D_a} = 0.05$$

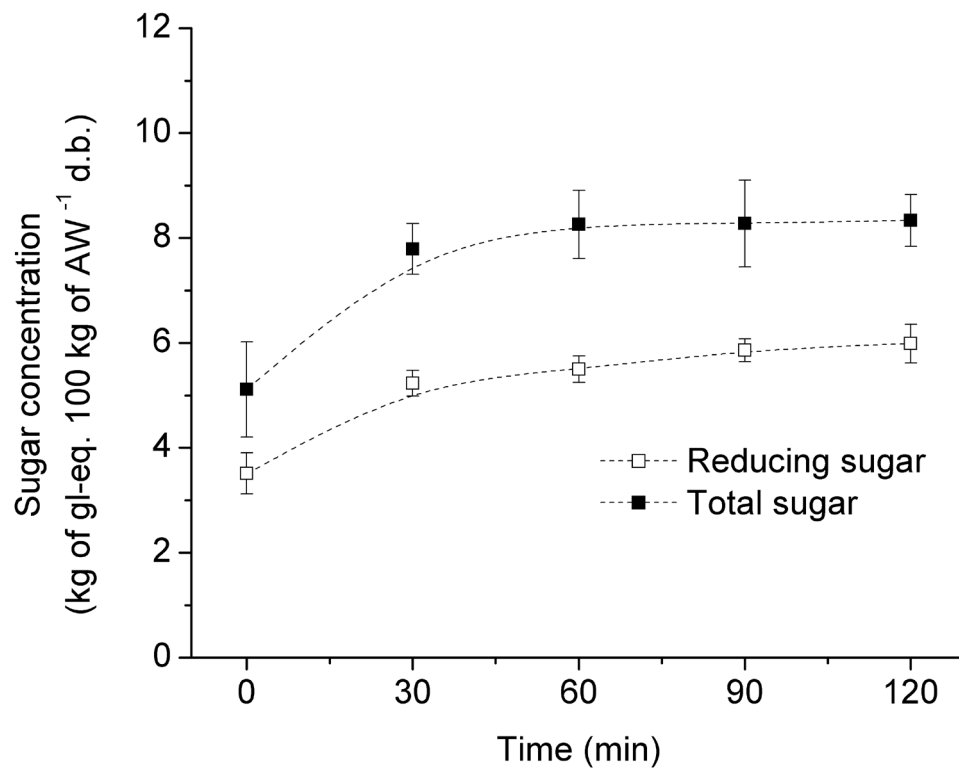
$$F_5 = \frac{H_L}{D_t} = 1.2$$

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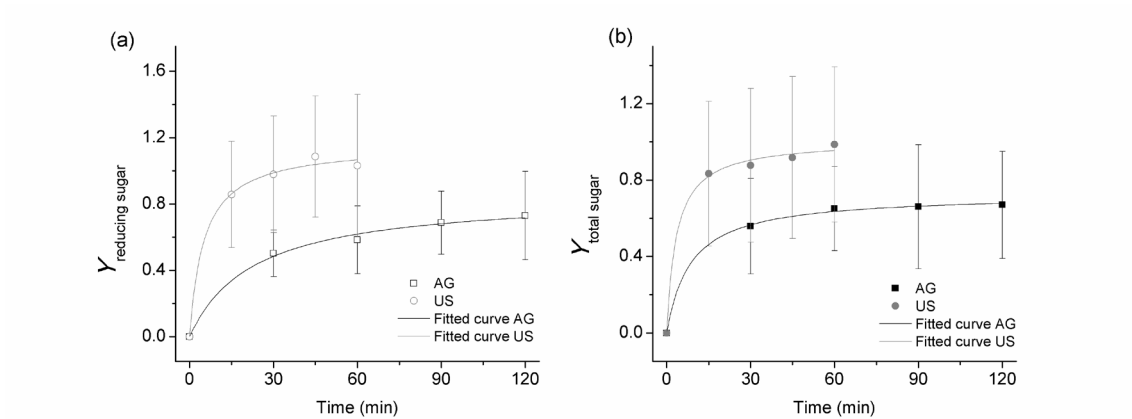


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777 Figure 3

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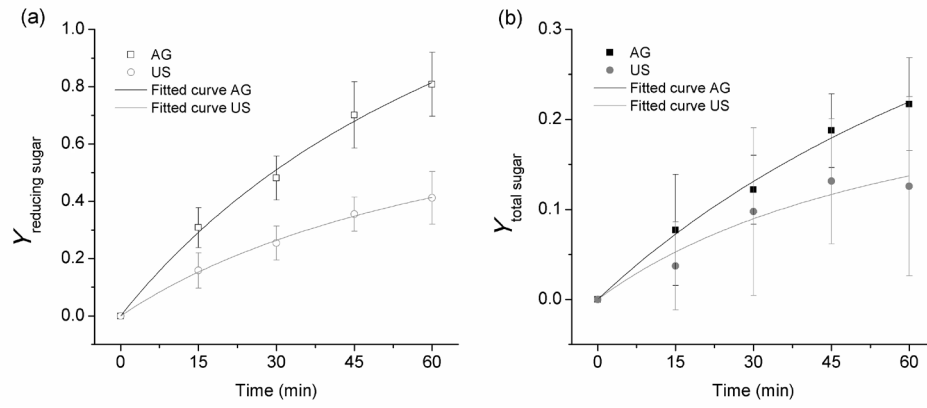


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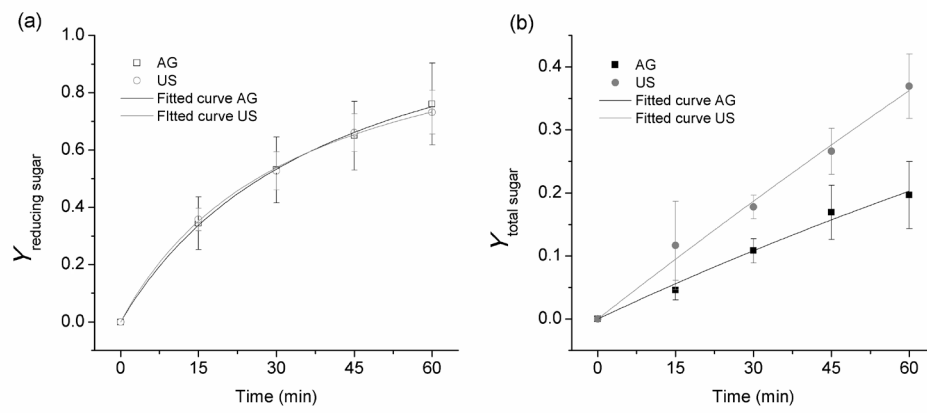


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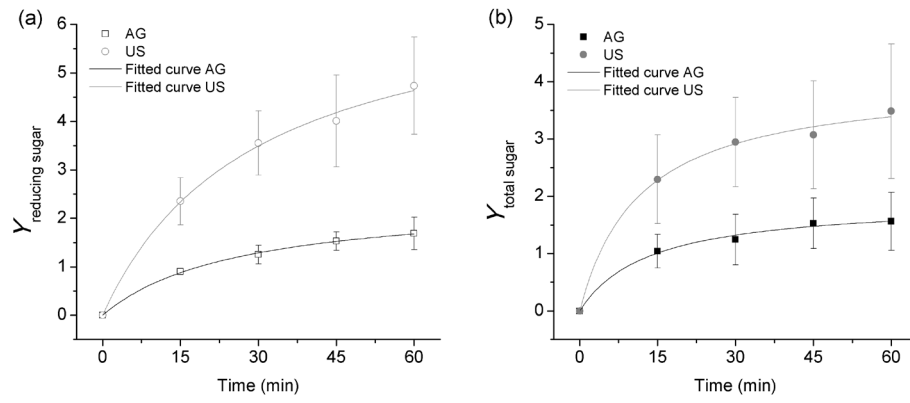


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789 Figure 6

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793 Figure 7

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