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1 **Quantitative modelling approaches for ascorbic acid degradation and non-**
2 **enzymatic browning of orange juice during ultrasound processing**

3
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24 **Abstract**

25 The objective of this study was to develop a deterministic modelling approach for non-
26 enzymatic browning (NEB) and ascorbic acid (AA) degradation in orange juice during
27 ultrasound processing. Freshly squeezed orange juice was sonicated using a 1,500 W
28 ultrasonic processor at a constant frequency of 20 kHz and processing variables of
29 amplitude level (24.4 – 61.0 μm), temperature (5 – 30 $^{\circ}\text{C}$) and time (0 – 10 min). The rate
30 constants of the NEB and AA were estimated by a primary model (zero and first order)
31 while their relationship with respect to the processing factors was tested for a number of
32 models, i.e., second order polynomial, different types of Ratkowsky-type model, and an
33 Arrhenius-type model. The non-monotonic behaviour of NEB has been described more
34 accurately by the use of a polynomial model. The rate constants of AA were described by
35 a similar type of model having a monotonic behaviour. A synergistic effect of
36 temperature for different amplitudes on the rate constant of both NEB and AA was
37 observed, while an antagonistic effect of amplitude on the rate of NEB was evident. The
38 models with the best fit were integrated to produce contour plots for the combined
39 amplitude and temperature. The constructed contour plots illustrate that low temperatures
40 and intermediate amplitudes, i.e., 42.7 μm , result in lower NEB and AA deterioration and
41 consequently better quality orange juice. The overall developed modeling approaches
42 exploit quality data in order to identify the optimal processing regions for eliminating
43 quality deterioration of orange juice during ultrasound processing which is of high
44 importance to the food industry.

45

46 **Keywords: Ultrasound, Ascorbic acid, non-enzymatic browning, modelling**

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55 **Introduction**

56 The use of ultrasound within the food industry has been a subject of research and
57 development for many years with applications in both food analysis (diagnostic
58 ultrasound) and food processing (power ultrasound). Power ultrasound has been
59 recognized as a promising processing technology to replace or complement conventional
60 thermal treatment in the food industry. When high power ultrasound propagates in a
61 liquid, cavitation bubbles are generated due to pressure changes. These micro bubbles
62 collapse violently in the succeeding compression cycles of a propagated sonic wave
63 resulting in localised high temperatures up to 5000 K, pressures up to 50,000 kPa, and
64 high shearing effects (Suslick, 1988). Consequently, the intense local energy and high
65 pressure bring a localised pasteurisation effect. Advantages of sonication include reduced
66 processing time, higher throughput and lower energy consumption while reducing
67 thermal effects (Zenker et al. 2003; Knorr et al. 2004). Various research groups have
68 demonstrated the inactivation of pathogenic and spoilage microorganisms (*Escherichia*
69 *coli*, *Listeria*), spoilage enzymes (pectin methyl esterase, polyphenol oxidase) with
70 reduced effects on quality or nutritional parameters including ascorbic acid in orange
71 juice (Tiwari et al. 2008a), ascorbic acid and anthocyanins content in strawberry (Tiwari
72 et al. 2008b) and blackberry juice (Tiwari et al. 2009b). Power ultrasound has been
73 employed for inactivation of *E. coli* in apple cider (Baumann et al. 2005) and orange juice
74 processing (Valero et al. 2007; Tiwari et al. 2008a). Similarly, enzymes such as
75 peroxidase (De Gennaro et al. 1999), proteases and lipases (Vercet et al. 2001) were
76 reported to be inactivated.

77 The nutritional quality of orange juice is primarily related to the ascorbic acid
78 content (Zerdin et al. 2003). Ascorbic acid is thermolabile and highly sensitive to various
79 processing conditions. The mechanism of vitamin C degradation follows aerobic and/or
80 anaerobic pathways and depends upon several processing conditions (Tannenbaum 1976;
81 Vieira et al. 2000). Ultrasound treatment of orange juices is reported to have a minimal
82 effect on the ascorbic acid content during processing and results in improved stability
83 during storage when compared to thermal treatment (Tiwari et al. 2009a). This positive
84 effect of ultrasound is assumed to be due to the effective removal of occluded oxygen
85 from the juice (Knorr et al. 2004), a critical parameter influencing the stability of ascorbic

86 acid (Solomon et al. 1995). Tiwari et al. (2009a) reported a maximum degradation of 5
87 % in the ascorbic acid content of orange juice when sonicated at the highest acoustic
88 energy density (0.81 W/mL) and treatment time (10 min). During storage at 10 °C
89 sonicated juice was found to have a higher retention of ascorbic acid compared to
90 thermally processed and control samples. Several studies have shown that non-thermal
91 process technologies including high pressure, pulsed electric fields and sonication retain a
92 higher level of ascorbic acid relative to thermally processed juices (Yeom et al. 2000;
93 Torregrosa et al. 2006; Cheng et al. 2007; Tiwari et al. 2009a). Non-enzymatic browning
94 (NEB) significantly influences the commercial value of citrus products, as it is the first
95 visible quality defect to be detected during ambient temperature storage. In citrus juices,
96 NEB may result from reactions of sugars, amino acids and ascorbic acid.
97 Kinetic models can be used for objective, fast and economic assessments of food quality.
98 Kinetic modeling may also be employed to predict the influence of processing on critical
99 quality parameters. The objective of this study was to develop integrated deterministic
100 modeling approaches of both quality indices, i.e., AA and NEB, to identify the optimal
101 processing conditions for producing orange juice with minimal quality deterioration.
102 Therefore, the kinetics of the quality indices of NEB and AA are described quantitatively
103 in order to evaluate the combined effect of the extrinsic parameters of amplitude and
104 temperature on them. The developed deterministic modeling approaches of both quality
105 indices are integrated in order to identify the optimal conditions for producing an orange
106 juice with minimal quality deterioration.

107

108

109 **Materials and methods**

110

111 **Juice preparation**

112 Oranges (*Citrus sinensis* cv. *Valencia*) were purchased from a local fruit supplier (Reilly
113 Wholesale Ltd., Dublin Ireland). Fresh juice was squeezed using a household table top
114 citrus juice extractor (BRAUN GmbH, Kronberg, Germany) and filtered using a double
115 layer cheese cloth to remove pulp. Orange juice extraction and filtration were performed

116 in a cold room maintained at 3 ± 1 °C. Juice obtained was immediately frozen at -25 °C.
117 Frozen juice samples were processed within one month of juice preparation.

118

119 **Ultrasound treatment**

120 A 1,500 W ultrasonic processor (VC 1500, Sonics and Materials Inc., Newtown, USA)
121 with a 19 mm probe was used for sonication (Fig. 1). Samples were processed at a
122 constant frequency of 20 kHz. The energy input was controlled by setting the amplitude
123 of the sonicator probe. Extrinsic parameters of temperature (5, 10, 15, 20, 25, 30 °C),
124 amplitude (24.4, 42.7, 61.0 μ m) and treatment time (2, 4, 6, 8, 10 min) were varied with
125 pulse durations of 5 s on and 5 s off. Eighty mL orange juice samples were placed in a
126 100 mL jacketed vessel through which water at a flowrate of 0.5 L/min was circulated
127 (Fig. 1). Sonication at the desired amplitude level was started once the set temperature
128 was reached in the jacketed beaker. The ultrasound probe was submerged to a depth of 25
129 mm in the sample. All treatments were carried out in triplicate.

130

131 **Determination of non-enzymatic browning**

132 Non-enzymatic browning was measured using the method of Meydavi et al. (1977). Ten
133 mL orange juice samples were centrifuged for 10 min; 756 *g* and 20 ± 0.5 °C (Sigma 1A,
134 AGB Scientific Ltd, Dublin, Ireland) to remove coarse particles. Five mL of ethyl alcohol
135 (95%, Sigma-aldrich, Dublin, Ireland) was added to 5 mL of juice supernatant and
136 centrifuged as above. The absorbance of the supernatant was obtained at 420 nm using a
137 Unicam UV-VIS (UV2) spectrophotometer with distilled water as blank. Measurements
138 were taken in triplicate and mean value reported. s

139

140 **Determination of ascorbic acid**

141 Ascorbic acid content was determined following the HPLC (Shimadzu Model no: SPD -
142 M10AVP, Shimadzu Co., Japan) analytical procedure outlined by Lee and Coates (1999).
143 To prepare the sample, 25 mL of the juice samples were added into 50 mL centrifuge
144 tubes containing 5 mL of 2.5% metaphosphoric acid. Samples were centrifuged for 10
145 min; 2000 *g* and 4 °C. Then, 5 mL of the supernatant was filtered through PTFE syringe
146 filters (0.45 μ m, Phenomenex, U.K) and placed in an autosampler vial. Ten μ L aliquot of

147 samples were injected onto a Shimadzu C18 (15cm × 4.6cm, pore size 5µm) coupled with
148 HyperODS guard column. The mobile phase was 25 mM KH₂PO₄ (adjusted to pH 3.0
149 with phosphoric acid) at a flow rate of 1 mL/min. Eluate was monitored by UV detection
150 at 245 nm. Chromatograms were recorded and processed with EZStart Chromatography
151 Software V.7.2.1. Results were reported as g of ascorbic acid/L of orange juice.

152

153 **Overall experimental design**

154 A general factorial design (SAS V.9.1, SAS Institute, NC, USA) consisting of 180
155 experimental trials (including the 3 replicates) was employed. During ultrasound
156 treatment, the effects of amplitude (µm), temperature (°C) and treatment time (min) were
157 studied. Analysis of variance (ANOVA) was carried out to determine any significant
158 differences ($P < 0.05$) among the applied treatments.

159

160 **Model development**

161

162 The rate constants for NEB and AA were estimated by a primary model describing the
163 evolution of the concentration of a component, i.e., NEB and AA, with respect to the
164 time. A zero order and a first order model were employed for this purpose:

165

$$166 \quad C(t) = C(0) + k \cdot t \quad (1)$$

$$167 \quad C(t) = C(0) \cdot \exp(k \cdot t) \quad (2)$$

168

169 where $C(t)$ represents the AA concentration [mg/ 100 mL of orange juice] and the NEB
170 level respectively, at time t and k is the rate constant. The relationship of the rate
171 constant, k , with respect to the processing factors was tested for a number of secondary
172 models, i.e., second order polynomial, different types of Ratkowsky-type model, and an
173 Arrhenius-type model. The second-order response surface model with an interaction
174 factor is expressed as:

175

$$176 \quad k = \beta_0 + \beta_1 \cdot T + \beta_2 \cdot T^2 + \beta_3 \cdot A + \beta_4 \cdot A^2 + \beta_5 \cdot T \cdot A \quad (3)$$

177

178 where β_i are the polynomial coefficients and T and A are the temperature [$^{\circ}\text{C}$] and
179 amplitude levels [μm], respectively. Only significant parameters ($P < 0.05$) were retained
180 by performing a stepwise fit. An Arrhenius type equation inspired by the model of Cerf
181 (Cerf et al. 1996) was developed, in which the effect of the temperature and amplitude on
182 the rate constants of NEB and ascorbic acid was investigated. The model is:

183

$$184 \quad k = C_o + C_1 \cdot A^2 + \frac{C_2}{T} \quad (4)$$

185

186 Where C_o , C_1 and C_2 are the coefficients of the Arrhenius type model. This type of model
187 correlates the rate constants against the reciprocal temperature to produce a mathematical
188 structure having an Arrhenius format.

189 Two different types of the Ratkowsky type models (Ratkowsky et al. 1983) have also
190 been considered. For these equations the squared root of the rate constant has been
191 considered aiming at the stabilisation of the variance of the rate constants. These
192 transformed equations appear as follows:

193

$$194 \quad \sqrt{k} = \alpha_1 \cdot (A + \alpha_2) \cdot (T + \alpha_3) \quad (5)$$

$$195 \quad \sqrt{k} = \alpha_1 \cdot (A + \alpha_2)^2 \cdot (T + \alpha_3) \quad (6)$$

196 When Eq. (6) is compared with Eq. (5) it can be observed that the second factor of the
197 right hand side of the equation has been adjusted such as to evaluate a quadratic effect of
198 amplitude changes on the rate constants.

199 In case of the kinetics of NEB the following equation has also been employed:

200

$$201 \quad \sqrt{k} = \alpha_1 \cdot (A + \alpha_2) \cdot (1 + \exp(\alpha_3 \cdot (\alpha_4 - A))) \cdot (T + \alpha_5) \quad (7)$$

202

203 Where α_i are the coefficients of determination for these models. Observe that Eq. (7) has
204 been transformed in such a way that could take into account the antagonistic effect of
205 amplitude at different temperatures on the non-enzymatic rate constants (see constant
206 rates of NEB in Fig. 2).

207 The different secondary models are evaluated with respect to their performance and the
208 best fitted models are used to construct iso-rate contour plots that integrate both NEB and
209 AA kinetics for the combined amplitude and temperature treatments. The iso-rate contour
210 plots are further exploited for process optimisation.

211

212 **Statistical analysis**

213 Only significant parameters have been retained for the tested models ($P < 0.05$). For the
214 evaluation of the fitting capacity of the models the statistical criterion of the adjusted
215 coefficient of multiple determination R^2_{adj} and the root mean squared error $RMSE$ have
216 been used.

$$217 \quad RMSE = \sqrt{\frac{\sum_{i=1}^{n_t} (y_{\text{exp}}(t_i) - y(t_i, p_{ls}))^2}{n_t - n_p}} \quad (8)$$

218

219 Where $y_{\text{exp}}(t_i)$ denotes the experimental observations, $y(t_i, p_{ls})$ the predicted values, n_t the
220 total number of data points, n_p the number of estimated model parameters.

221

$$222 \quad R^2_{adj} = 1 - \left(\frac{n_t - 1}{n_t - n_p} \right) \cdot \frac{SSE}{SSTO} \quad (9)$$

223

224 Herein, $SSTO$ is the total sum of squared errors $\sum (y_i - \bar{y})^2$ and SSE the sum of squared

225 errors $\sum (y_{\text{exp}}(t_i) - y(t_i, p_{ls}))$.

226

227 **Software Programs**

228 For simulation, optimisation, and fitting of the data, programs were written in MatLab®
229 Version 6.5 (The MathWorks, MA, USA). The optimisation routines employed were
230 *lsqnonlin* (for the Ratkowsky type models) and *lsqin* (MatLab Optimization Toolbox).
231 The *stepwisefit* routine was employed for stepwise regression (MatLab Statistics
232 Toolbox) .

233

234 **Results & Discussion**

235

236 **Non-enzymatic browning (NEB)**

237 The NEB index followed a zero order reaction Eq (1) with respect to treatment time for
238 the different amplitudes and temperatures studied. Previous kinetics studies on browning
239 index reactions based on A420 nm measurement in citrus juices, apple juices (Burdurlu
240 and Karadeniz 2003), pear puree (Ibarz et al. 1999) and pear juice concentrate (Beveridge
241 and Harrison 1984) similarly reported zero-order reaction kinetics. The estimated
242 parameters of rate constants k , for each replicated study are illustrated in Fig. 2. Eq. (7) of
243 the modified Ratkowsky model described the observed non-linearities ($R^2_{adj} = 0.975$,
244 $RMSE = 0.0031$) better than Eqs. (5, 6), but resulted in non-accurate parameters, i.e., SE
245 errors were much higher than the estimated parameters. This may be attributed to the
246 limited amount of data describing the antagonistic behaviour of amplitude on NEB.
247 Among all the secondary models tested, the polynomial model (Eq. (3)) gave the best
248 regression performance for describing the non-monotonic behaviour of the effect of
249 amplitude on the NEB constants (Fig. 2). All its parameters appeared to be significant
250 ($P < 0.05$) (Table 1).

251 The lower P-values (so the more 'significant' the results) were obtained for the
252 coefficient of β_4 ($P=0$) (quadratic effect of Amplitude) and β_2 ($P=1.08 \times 10^{-26}$) (linear
253 effect of temperature) indicating that for the same temperature levels the NEB rate
254 constants were highly dependent on the amplitude levels followed by the temperature
255 levels. Interactive effects gave higher P values (1.36×10^{-6}). The NEB rate significantly
256 increased with processing temperature while at intermediate ultrasound amplitudes
257 appeared to have lower values indicating an antagonistic effect of amplitude on the rate
258 of NEB. More specifically, at amplitude levels of the range of 42.7 μm , the NEB rate
259 appeared to be lower than at higher or lower amplitude levels for the same temperatures.
260 The observed monotonic increase of the NEB rate with respect to temperature has also
261 been reported for the browning kinetics of apple juice and apple cider (Ugarte-Romero et
262 al. 2006; Vaikousi et al. 2008). Nonenzymatic browning may result from the
263 condensation of a carbonyl group with amino acids, reactions of sugars and ascorbic acid
264 in the absence of free amino acids (caramelization). The obtained increase of the

265 browning rate at high amplitudes can be attributed to the decrease of sugar content (Yuan
266 et al. 2009).

267

268 **Ascorbic acid degradation (AA)**

269

270 A significant ($p < 0.05$) reduction in orange juice ascorbic acid content (mg/100 mL) was
271 observed as a function of treatment time. The degradation kinetics of ascorbic acid
272 followed first order kinetics (Eq. (2)) and the estimated rate constants for each of the
273 replicates are illustrated in Fig. 3. Similar kinetic behaviour on watercress processed by
274 thermosonication was observed by other authors (Cruz et al. 2008).

275 The largest AA reduction was observed at the highest amplitude (61.0 μm) and
276 processing temperature (30 $^{\circ}\text{C}$), . However this reduction was less than 15% loss of the
277 initial ascorbic acid content of the unprocessed juice. The ascorbic acid rate constant with
278 respect to the amplitude and the temperature was described more accurately by
279 employing the polynomial model (Eq. (3)) (Table 2).

280 The lower P-values were obtained for the coefficient of β_3 ($P=0$) (linear effect of
281 amplitude) followed by β_5 ($P=6.16 \times 10^{-8}$) (interactive effect of amplitude and
282 temperature). Fig. 3 illustrates that increase of temperature and increase of amplitude
283 resulted in higher ascorbic acid loss. This indicates a synergistic effect of temperature for
284 different amplitudes and temperatures on the AA rate constant.

285 Several mechanisms can act concurrently when ultrasound is applied in liquid systems,
286 i.e., thermal effects produced by bubble implosion, mechanical stresses produced
287 microstreaming and implosion shock waves, and free radical production. Nevertheless,
288 radical productions have been considered the most probable mechanism (Portenlanger
289 and Heusinger 1992; Vercet et al. 2001). The degradation of ascorbic acid divides into
290 two sections corresponding to aerobic and anaerobic degradation (Nagy 1980;
291 Eisonperchonok and Downes 1982; Robertson and Samaniego 1986; Kennedy et al.
292 1992; Ariaahu et al. 1997; Blasco et al. 2004). Sonication results in a reduction of
293 dissolved oxygen, a critical parameter influencing the stability of ascorbic acid (Solomon
294 et al. 1995). Hydroxyl radical formation is found to increase with degassing. Sonication
295 cavities can be filled with water vapour and gases dissolved in the juice such as O_2 and

296 N₂ (Korn et al. 2002). The interactions between free radicals and ascorbic acid may occur
297 at the gas–liquid interfaces. In summary ascorbic acid degradation may follow one or
298 both of the following pathways:

299 Ascorbic acid → thermolysis (inside bubbles) and triggering of Maillard reaction

300 Ascorbic acid → reaction with OH⁻ → HC–OH and production of oxidative products on
301 the surface of bubbles

302 Thus sonication can be related to advanced oxidative processes since both pathways are
303 associated with the production and use of hydroxyl radicals (Petrier et al. 2007). Previous
304 publications have shown that vitamin C degradation in different type of processes was
305 following first order kinetics independently of the pathway followed (Nisha et al. 2004;
306 Vikram et al. 2005).

307

308 **Contour design**

309 An analysis of amplitude and temperature diagrams was performed based on the best
310 fitted mathematical expressions (see previous Sections). Iso-rate contour plots integrating
311 NEB and AA information were developed (Fig. 4). The constructed contour plots
312 illustrate that low temperatures and intermediate amplitudes, i.e., 42.7 μm, result in lower
313 NEB and AA deterioration and consequently better quality of orange juice. Non
314 enzymatic browning effects appear to be more sensitive to ultrasound processing than
315 ascorbic acid degradation (Fig. 4). Based on the obtained contour plots is suggested that
316 NEB could be more appropriate to determine the intensity of an ultrasound processing
317 during commercial applications. This is in line with the fact that browning reactions of
318 ascorbic acid are among the browning indexes while measuring the overall NEB effects.
319 Nevertheless the importance of using the ascorbic acid as a quality and shelf life indicator
320 of orange juice in the juice processing is evident and will have to be considered for
321 performing additional shelf life studies.

322

323

324 **Conclusion and future work**

325 The modeling approaches developed in this study exploit data in order to identify the
326 optimal processing regions for eliminating quality deterioration of orange juice during

327 ultrasound processing which is of high importance in food industry. The non-monotonic
328 behaviour of NEB has been described more accurately by the use of a polynomial model.
329 The rate constants of AA were described by a similar type of model having a monotonic
330 behaviour. A synergistic effect of temperature for different amplitudes on the rate
331 constant of both NEB and AA was observed, while an antagonistic effect of amplitude on
332 the rate of NEB was evident. Ultrasound was found to have more drastic effect on NEB
333 than AA degradation of orange juice.

334 The implemented modelling approaches could be further developed for incorporating a
335 prior knowledge of the kinetic process during the parameter estimation as this approach
336 was previously suggested and applied (Geeraerd et al. 2004; Valdramidis et al. 2007).
337 This would require the collection of additional biochemical information on the browning
338 and ascorbic acid dynamics of different juice products during ultrasound processing.
339 Consequently mathematical terms under the form of partial derivatives that describe
340 monotonic or non-monotonic quality kinetics can be developed and used for the
341 parameter estimation of the suggested model structures. Additional biochemical studies
342 e.g., enzymatic browning, formation of browned polymers, may also be exploited to carry
343 out multi-objective optimisations of fruit juice processing aimed at the production of high
344 quality sonicated fruit products..

345

346

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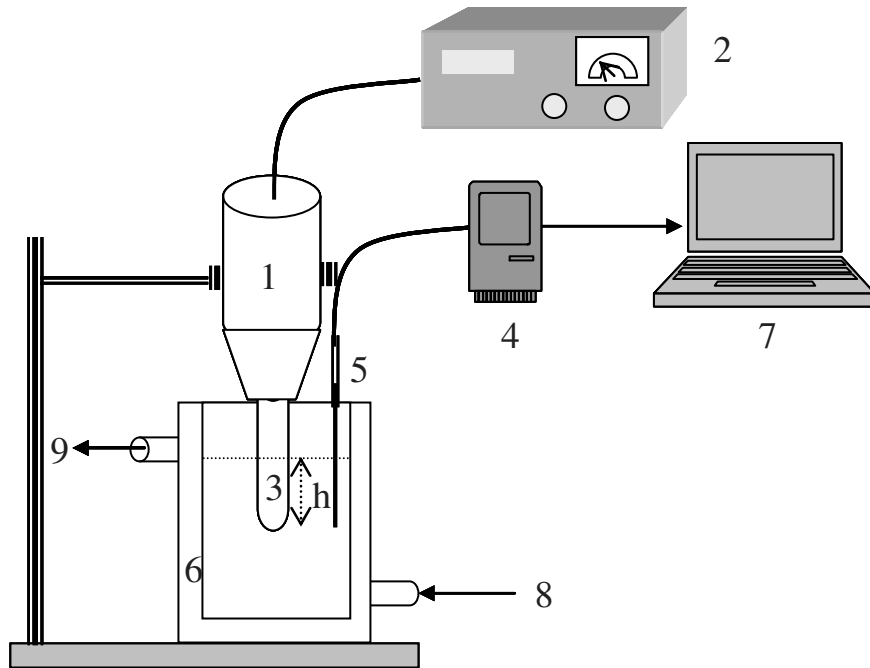
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470 Figure 1. Experimental setup (1) ultrasound transducer; (2) ultrasonic generator; (3)
471 ultrasound probe (19 mm); (4) data logger; (5) temperature probe; (6) jacketed beaker; (7)
472 computer; (8) water inlet; (9) water outlet; (h) depth of probe in to the sample (25 mm)

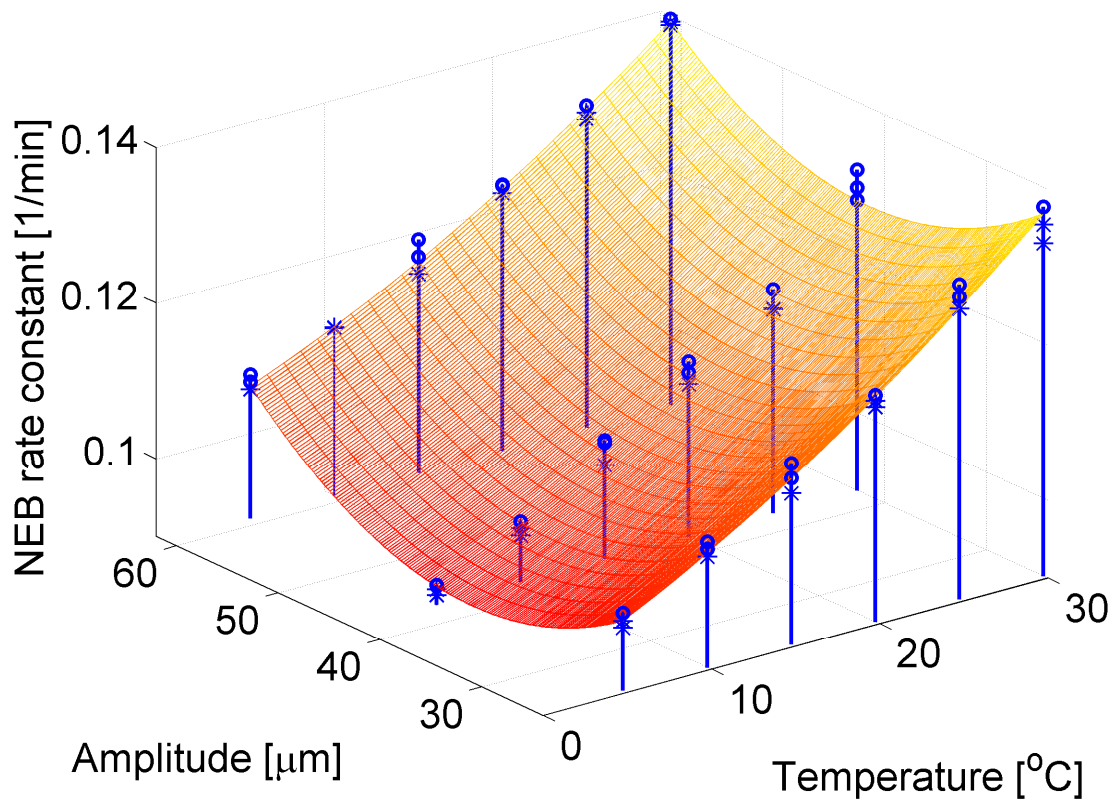
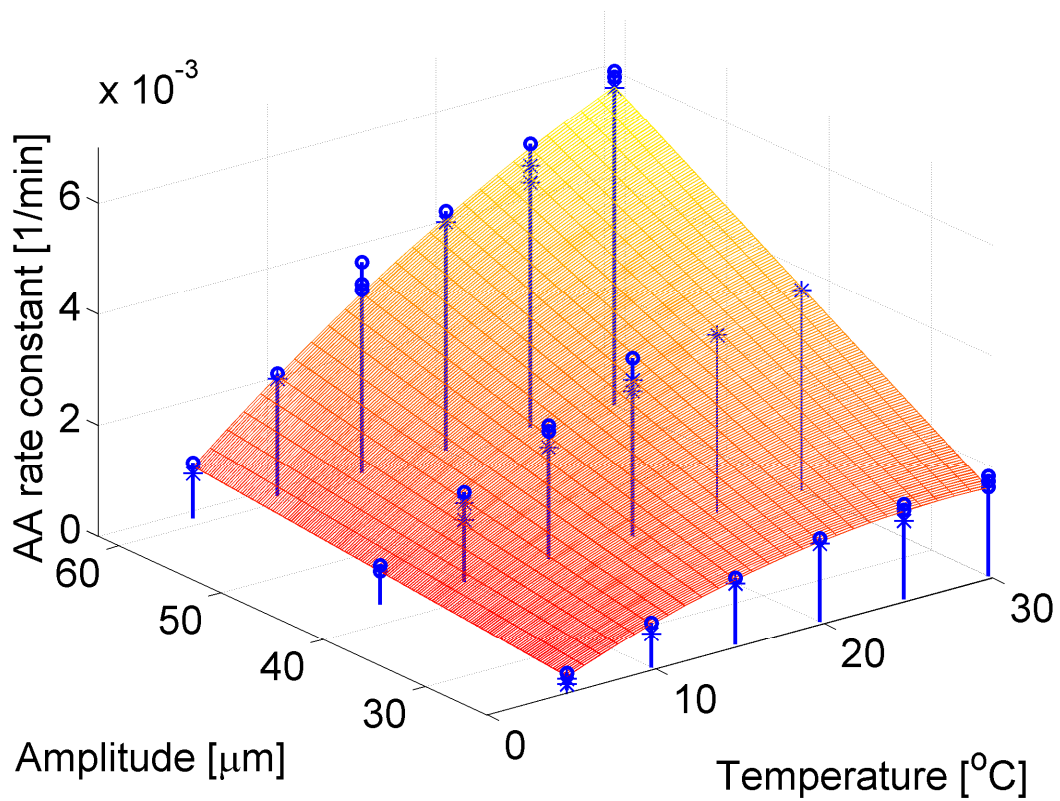


Figure 2. Modelling the non enzymatic browning rate constant, k (Eq. (3), Table 1). (o): experimental data points above the surface, (*): experimental data points under the surface.



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506 Figure 3. Modelling the ascorbic acid rate constant, k (Eq. (3), Table 2). (o):

507 experimental data points above the surface, (*): experimental data points under the

508 surface.

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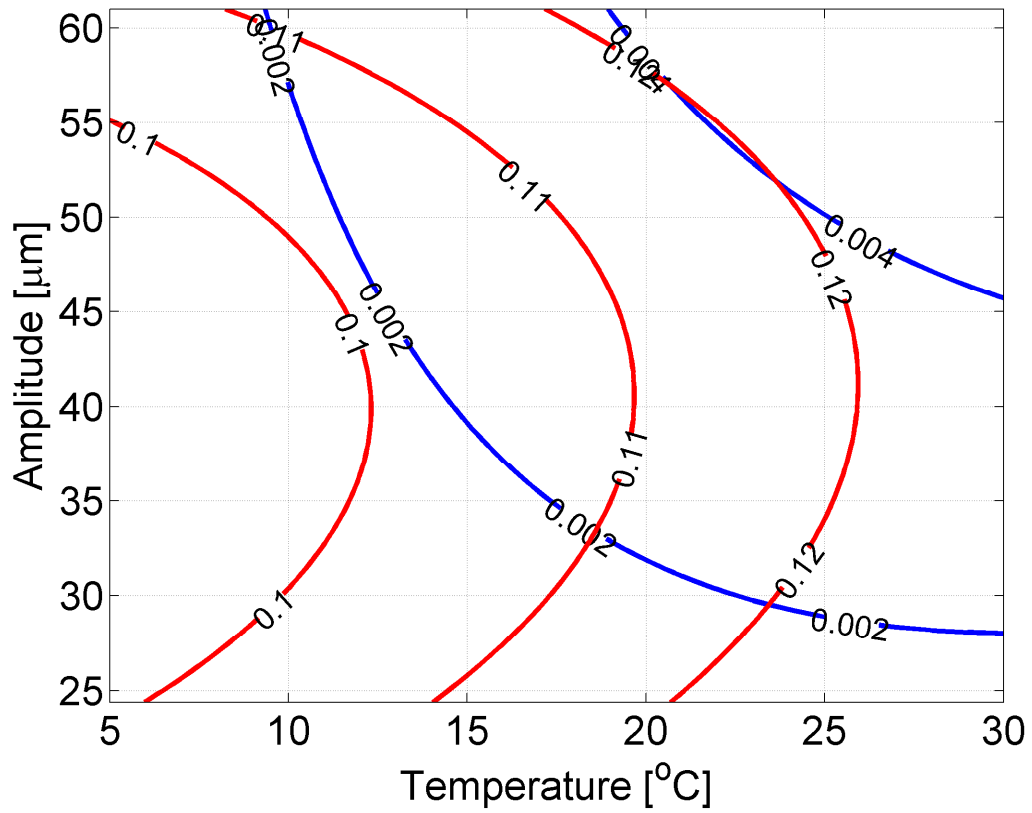


Figure 4. Non enzymatic browning and ascorbic acid iso-rate contour plots for $k = 0.1$, 0.11 , 0.12 [1/min] and $k = 0.004$, 0.004 [1/min], respectively.

546 Table 1. Results on the parameter estimates of the secondary fitted models (Eqs. (3)- (6))
 547 for the NEB kinetics.
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Equation type	Parameters	$R^2_{adj}, RMSE$	Estimated	SE
			values	
Polynomial (Eq. (3))	β_0	0.998, 0.0015	0.135	0.003
	β_1		-2.500	1.127×10^{-4}
	B_2		1.000	1.331×10^{-4}
	β_3		-5.964	1.571×10^{-6}
	β_4		3.193	1.270×10^{-6}
	β_5		1.773	3.214×10^{-6}
Arrhenius type (Eq. (4))	C_0	0.6187, 0.072	-2.078	0.023
	C_1		1.927×10^{-5}	7.649×10^{-6}
	C_2		-1.553	0.172
Ratkowsky type (Eq. (5))	α_1	0.824, 0.0083	1.29×10^{-6}	4.64×10^{-7}
	α_2		1.54×10^3	5.58×10^2
	α_3		1.47×10^2	1.06
Ratkowsy type (Eq.(6))	α_1	0.825, 0.0083	2.076×10^{-10}	1.453×10^{-10}
	α_2		3.105×10^3	1.099×10^3
	α_3		1.417×10^{-1}	1.059×10^{-1}

549 Table 2. Results on the parameter estimates of the secondary fitted models (Eqs. (3)- (6))
 550 for the AA kinetics.
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Equation type	Parameters	$R^2_{adj}, RMSE$ Estimated values SE		
Polynomial (Eq. (3))	β_0	0.986, 0.002	-4.011×10^{-4}	1.096×10^{-4}
	β_1		-	
	β_2		5.092×10^{-5}	1.480×10^{-5}
	β_3		3.767×10^{-6}	8.595×10^{-8}
	β_4		-	
	β_5		-2.548×10^{-6}	4.010×10^{-7}
Arrhenius type (Eq. (4))	C_0	0.928, 0.229	-6.162	0.074
	C_1		3.744×10^{-4}	2.425×10^{-5}
	C_2		-11.522	0.545
Ratkowsky type (Eq. (5))	α_1	0.939, 0.004	2.09×10^{-5}	1.43×10^{-6}
	α_2		22.73	3.472
	α_3		15.747	1.589
Ratkowsky type (Eq. (6))	α_1	0.936, 0.004	7.957×10^{-8}	9.397×10^{-9}
	α_2		87.635	7.316
	α_3		15.741	1.629

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