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1 **Thermomechanical process intensification for oil extraction from orange peels.**
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11 **Abstract**

12 The study investigated the intensification and improvement of oil extraction from orange peel
13 through a thermomechanical process: the Instantaneous Controlled Pressure Drop (briefly D.I.C
14 process). This process involves subjecting orange peel for a short time to steam pressure,
15 followed by an instantaneous decompression to vacuum at 50 mbar. Central composite design
16 was used to study the combined effects of processing steam pressure (1–7 bar; which
17 corresponds to a temperature ranging between 100°C and 162 °C respectively), processing time
18 (0.3 – 3.7 min.) and initial moisture content of orange peel before thermomechanical oil
19 extraction (9.8 – 60.2 % on dry material basis). The quantitative analysis, have been undertaken
20 on oil present in orange peels, after processing. Correlation analysis of the mathematical
21 regression model indicated that quadratic polynomial model could be employed to optimize the
22 extraction of oil from orange peel. From response surface plots, the three variables exhibited a
23 linear effect with the strongest effect for the processing pressure. The optimum reaction
24 conditions selected with response surface analysis were as follows: steam processing pressure:
25 6.6 bar, processing time: 3.68 min, initial moisture content: 53.6 % d.m basis. Under these
26 conditions, experimental yield of orange peel oil was close to predicted value (99 %) calculated
27 from the polynomial response surface model equation. A kinetic study indicated that extraction
28 performed by D.I.C process is clearly quicker than conventional steam distillation method.

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31

32 **Keywords :** orange peel, extraction, oil, Controlled Instantaneous Pressure Drop (D.I.C
33 extraction process), response surface methodology.

34 **Industrial relevance**

35 World production of citrus fruit has experienced continuous growth in the last decades of the XX
36 century. Total annual citrus production was estimated at over 105 million tons in the period
37 2000-2004 (<http://www.unctad.org/infocomm/anglais/orange/market.htm>). Oranges constitute
38 the bulk of citrus fruit production, accounting for more than half of global citrus production in
39 2004. Thus, the quantities of generated by-products are very important. In this study, extraction
40 of oil from orange peel was performed through a termomechanical process developed in our
41 laboratory (Rezzoug, Boutekedjiret & Allaf, 2005). We report on some results obtained using
42 this process as well as others comparing extraction kinetics when using a conventional steam
43 distillation process and the proposed extraction process. One of advantages of the described
44 method is the short contact of extracted oil with the heated zones in the apparatus resulting in a
45 lower heating of the product compared to steam distillation. At industrial scale, this is interesting
46 regarding oil quality and energy saving.

47 **1- Introduction**

48 Peel of citrus fruits is one of the by-products of fruit processing which provides a great potential
49 for further commercial use. The various species of citrus elaborate and stock essential oils in
50 schizolysigen pockets localized in the external part of the mesocarpe of fruit (flavedo). These
51 oils are used as flavouring ingredients in a variety of foods such as soft drinks or ice cream as
52 well as in formulation of several products in parapharmacy and perfume industry (Raeissi, Diaz,
53 Espinosa, Peters & Brignole, 2008). Another application makes use of germicidal properties of
54 some of their components. Redd and Hendrix (1993) reported that a small amount of the d-
55 limonene was very effective in the germicide treatment of waste water. It is well known that
56 terpenes which constitute the major part of citrus oils have a strong antifungal and antioxidant

57 activities (Ur-Rehman, 2006; Pernice, Boriello, Ferracane, Borrelli & Cennamo, 2009; Viuda-
58 Matros, Ruiz-Navajas, Fernández-López & Pérez-Álvarez, 2008). Few studies have been
59 conducted on extraction of citrus essential oils in general and oil from orange peel in particular
60 (Ferhat, Meklati, Smadja & Chemat, 2006; Berna, Tárrega, Blasco & Subirats, 2000), although
61 studies on the deterpenation or separation of the different hydrocarbons composing citrus oils are
62 more abundant (Diaz, Espinosa & Brignole, 2005; Danielski, Brunner, Schwänke, Zetzl, Hense
63 & Donoso, 2008; Arce, Pobudkowska, Rordíguez & Soto, 2007; Dugo, Mondello, Bartle,
64 Clifford, Breen & Dugo, 1995; Raeissi and Peters, 2005)

65 Supercritical fluids extraction processes have gained an increasing importance in chemical and
66 food industry since they can maximize product recovery and improve product quality (Budich,
67 Ullrich, Jung & Brunner, 1997; Grosso, Ferraro, Figueiredo, Barroso, Coelho & Palavra, 2008;
68 Yu, Dandekar, Toledo, Singh & Patil, 2007). The interest of this method lies in criteria which are
69 not fulfilled by classical extraction methods such as the solvent inertness and toxicity. In fact,
70 fractionation can be done at moderate temperatures and without remaining organic solvent
71 (Temelli, Chen & Braddock, 1988). This is important for terpenes which tend to decompose at
72 high temperatures. However, technological conditions for using supercritical fluid extraction at
73 industrial scale are restrictive and the high production costs of specific products have limited the
74 use of this process. For these reasons, several authors tried to improve the classical methods of
75 citrus oil extraction. Tateo (1990) developed a “thin film evaporator system” which has as
76 advantage to work under mild temperature conditions. Fleisher (1990), through a process called
77 “Poroplast” has tempted to minimize the quantity of solvent used in essential oil extraction of
78 different citrus products. In the last decade, there has been an increasing demand for new
79 extraction techniques enabling automation, shortening of extraction time and reducing of organic
80 solvent consumption with a special attention to energy prices and reduction of CO₂ emissions.

81 Many researchers as Bousbsia, Vian, Ferhat, Meklati and Chemat (2008) or others cited by these
82 authors focused their works on novel techniques and sustainable extraction processes.

83 The aim of this work was to provide an efficient and economically attractive process for
84 extraction of essential oil from orange peel through a thermomechanical extraction technique
85 developed in our laboratory: the Instantaneous Controlled Pressure Drop process. This process
86 known as "D.I.C", was developed and patented in our laboratory some years ago (Rezzoug,
87 Baghdadi, Louka, Boutekedjiret & Allaf, 1998; Allaf et al, 1999) initially for using in the field of
88 drying-texturation of various food products by improving hydration capacity (Rezzoug, Louka,
89 Maache-Rezzoug, Nouviaire & Allaf, 1998; Rezzoug, Maache-Rezzoug, Mazoyer, Jeannin and
90 Allaf, 2000). This process is based on a thermo-mechanical processing induced by subjecting the
91 product to a fast transition from high steam pressure to vacuum. For food products such as
92 vegetables, the aim was to improve the vaporization of water with a preservation of fragrance
93 coupled to an alveolate texture of dried product, while in the present study this process was used
94 for the separation of volatile oil from the solid material. This extraction process, successfully
95 tested on isolation of essential oil from rosemary leaves (Rezzoug et al., 1998) represents an
96 interesting alternative not only to classical processes such as extraction by solvent and steam
97 distillation, but also to more effective processes such as extraction with supercritical fluids. In
98 fact, this extraction process does not require using of any solvent and induced cooling when the
99 plant is rapidly transferred from a high steam pressure to vacuum stops all thermal degradation
100 of oil components. Due to the "flash" evaporation of bulk water present in peels, the processing
101 by instantaneous controlled pressure drop increases the global diffusivity of the product and
102 improves availability of the liquid in plant. Moreover, compared to steam distillation, the short
103 time contact (few minutes) between plant and heat avoids the loss and degradation of volatile
104 and thermolabile compounds.

105 The response surface methodology (RSM) has been successfully applied for optimizing
106 conditions in food research (Wu, Cui, Tang & Gu, 2007, Ghodke, Ananthanarayan & Rodrigues,
107 2009; Wang, Yang, Du, Yang & Liu, 2008) but few studies focused on optimization of
108 extraction of oils from various plants (Sonsuzer, Sahin & Yilmaz, 2004; Zeboudj, Belhanèche-
109 Bensemra & Belabbès, 2005). RSM is defined as a statistical method using quantitative data
110 from an appropriate experimental design to determine and simultaneously solve multivariate
111 equations. The main advantage of RSM is the reduced number of experimental trials needed to
112 evaluate multiple parameters and their interactions. This paper aims to assess the effect of the
113 main processing parameters of D.I.C extraction process, namely the processing steam pressure,
114 processing time and initial moisture content of the peels, on extraction efficiency of oil from
115 orange peel (*Citrus sinensis*) and to determine the optimum conditions using RSM analysis.

116 **2- Experimental procedures**

117 **2.1- Plant material**

118 Oranges used in this study were *citrus sinensis* L., grown in Valencia (Spain). The peels were
119 separated from the endocarp by cutting with hand knife and cut into 6-8 pieces giving yield of 17
120 % (w/w) of orange peels with respect to whole fruit. The peels were used without milling and
121 were softly dried at 40 °C in a drying oven by a flow air and then placed in hermetically sealed
122 bags and stored in a cold chamber until treatment. The moisture content of dehydrated orange
123 peels, measured by Mettler LP16 infrared balance was 0.0685 kg H₂O kg⁻¹ dm. The yield of oil
124 in raw material, as described in section 2.3.c, was 2.06 % by mass (dry basis). This value is in
125 agreement with data previously obtained by Salib, Saleh & Abdel-Malik (1978) for Egyptian
126 orange peel oil and by Dugo, Mondello, Bartle, Clifford, Breen & Dugo (1995) for extraction by
127 supercritical CO₂ processing of Sicilian orange peel oil.

128 **2.2- Instantaneous controlled pressure drop apparatus**

129 Figure 1 gives a representative diagram of used equipment and the pressure profile is presented
130 in figure 2. Humidified orange peel is firstly placed in the processing vessel (fig.1.2) at
131 atmospheric pressure before vacuum setting (~ 50 mbar) (fig.2a and 2b). Vacuum build-up is
132 obtained by communication with the vacuum tank (fig.1.4 and fig.2b). This initial vacuum
133 facilitates the diffusion of steam into product and allows its rapid heating. After closing the valve
134 (fig 1.3), an atmosphere of saturated steam under pressure is introduced in processing vessel
135 (fig.2c). The thermal processing is followed by a rapid decompression (fig.2e) insured by a
136 communication (in less than 1/10 second) between processing vessel and vacuum container
137 (fig.1.4) which has a volume (250 litres) 80 times that of processing vessel (3.2 litres). Initial
138 vacuum level in the processing vessel was maintained at 50 mbar during all experiments. This
139 transition induces a rapid modification of the thermodynamic equilibrium reached during the
140 pressurisation (P_1, T_1) towards another equilibrium state (P_2, T_2). Equilibrium pressure after
141 decompression depends on the level of processing pressure: the higher the processing pressure,
142 the higher the equilibrium pressure. In our case, it varied from 62 up to 120 mbar when
143 processing pressure increases from 1 to 7 bar. The followed vaporization, as an adiabatic
144 transformation, induces a rapid cooling of the residual product. After the vacuum phase,
145 atmospheric air is injected to return to atmospheric pressure for sample recovery (fig.2f).

146 **2.3- Procedures adopted for the characterization of isolated orange peel oil**

147 *a- Isolation of essential oil*

148 Figure 3 depicts the procedure of extracted oil characterisation. Each experiment begins with
149 humidification of the orange peel at fixed initial moisture content, followed by 12 hours
150 conservation stage in refrigerated atmosphere (4~5 °C) in order to homogenize moisture in
151 whole product. The feed reactor with typically 100 g of humidified peels undergoes a thermo-
152 mechanical treatment, at fixed processing pressure and processing time. After the rapid

153 decompression, orange peels are recovered and analyzed. In order to quantify the essential oil
154 remaining in orange peels, a classical extraction procedure of steam distillation was used. Two
155 distinct phases were obtained, an organic phase (isolated oil) and an aqueous phase containing a
156 small part of oil. The organic phase was separated from the aqueous phase with 10 ml of hexane
157 and then analyzed by gas chromatography. Procedures of steam distillation and gas
158 chromatography are described hereafter.

159 *b- Gas chromatography (GC)*

160 GC analysis was performed using a Shimadzu-GC-14A gas chromatograph. GC conditions were
161 as follows: fused silica column (12 m * 0.32 mm i.d., film thickness 0,25 mm, liquid stationary
162 phase: silicone, detection by FID, split ratio 100 : 1). Oven temperature 50 °C for 1 minute then
163 programmed from 50 to 250 °C at 5 °C/min, and 2 minutes at 250 °C. Injection temperature 200
164 °C, detection temperature 280 °C. Carrier gas nitrogen (1 ml/min). Volume of injection 0,5 ml.
165 Gas chromatograph was connected with a Merck D-2500 chromato-integrator. Identification of
166 volatile compounds was based on a comparison with injection of references compounds
167 (provided by Aldrich-Chimie, France).

168 *c- Steam distillation (S.D)*

169 Classical S.D method of extraction was used with 50 g of orange peel treated by D.I.C process
170 and 350 ml of water. The duration of extraction by steam distillation was 2 hours. As extraction
171 solvent, 10 ml of distilled hexane was used. Identified compounds and their yield are grouped in
172 table 1. The yields of identified compounds are close to those reported by Lawrance (1990) about
173 Portuguese and Argentinean orange peel oil, by Buldish, Ullrich, Jung & Brunner (1997), and by
174 Mira, Blasco & Subirats (1996) for orange peel oil obtained by supercritical fluid extraction.

175 From table 1, it is clear that orange peel oil obtained by S.D is composed in large part of
 176 limonene. As monoterpenes, we also identified, α -pinene, β -pinene, and myrcene and as
 177 oxygenated compounds, linalool have been identified.

178 The maximum oil extraction yield obtained by SD was about 2.06 g based on 100 g of dried feed
 179 material (see section 3.3). The oil yield was determined according to the quantity of oil remained
 180 in orange peel:

$$181 \quad \text{oil yield (\%)} = \left(\frac{2.06 - \text{extract in treated peels}}{2.06} \right) \times 100 \quad [1]$$

182 **2.4- Experimental design**

183 A response surface methodology was employed for optimizing the operating conditions of the
 184 D.I.C process to give high yield of liquid extract i.e. to minimize the quantity of essential oil
 185 which remains in orange peels. This quantity is assumed to be affected by three independent
 186 variables, ξ_i (processing pressure ξ_1 , initial moisture content of orange peel ξ_2 and processing
 187 time ξ_3). It is also assumed that the response η (oil yield), which was experimentally measured,
 188 defined the system.

$$189 \quad \eta = f(\xi_1, \xi_2, \xi_3) \quad [2]$$

190 Second degree polynomial equation were assumed to approximate the true function :

$$191 \quad \eta = \beta_0 + \sum_{i=1}^3 \beta_i x_i + \sum_{i=1}^3 \beta_{ii} x_i^2 + \sum_{i=1}^2 \sum_{j=i+1}^3 \beta_{ij} x_i x_j \quad [3]$$

192 where β_0 , β_i , β_{ii} and β_{ij} are regression coefficients, and x_i are the coded variables linearly related
 193 to ξ_i . The coding of ξ_i into x_i is expressed by the following equation:

$$194 \quad x_i = \frac{2(\xi_i - \xi_i^*)}{d_i} \quad [4]$$

195 where ξ_i = actual value in original units; ξ_i^* = mean of high and low levels of ξ_i ; and d_i =
196 difference between the low and high levels of ξ_i .

197 A central composite rotatable design (Benoist, Tourbier & Germain-Tourbier, 1994) was used.
198 For the three variables, the design yielded 22 experiments with eight (2^3) factorial points, six
199 axial points to form a central composite design and eight center points for replications. The range
200 and the centre point were chosen after preliminary trials (Table 2). The 22 experiments were run
201 in random order to minimize the effects of unexpected variability in observed responses due to
202 extraneous factors. Response surfaces as represented by Fig. 4 were drawn by using the *analysis*
203 *design* procedure of *Statgraphics Plus for Windows* software (5.1 version).

204 **3- RESULTS AND DISCUSSION**

205 **3.1- Model fitting**

206 In order to develop response surface equation for predicting the percentage of extracted oil in the
207 range of conducted study, the experimentally determined oil yield percentages were fitted to
208 Eq.1. The responses generated from experiments are presented in table 3 along with the
209 predicted yield values. A good fit was obtained between experimental and predicted data. It can
210 be seen that for the lower processing time (~ 18 sec) the yield was already about 37 % (run 13).

211 The regression coefficients of equation describing the responses surfaces are grouped in Table 4
212 which shows that x_1 (processing pressure) linearly and quadratically affected the oil yield (p-
213 value<0.01). However, x_3 (processing time), and in a lesser extent x_2 (initial moisture content)
214 affected only linearly the response (p-value<0.06). There were no significant two-factor
215 interactions. It should be noted that p-value indicates the statistical significance of each
216 parameter. It is based on hypothesis that a parameter is not significant, thus the more this
217 probability is close to zero, the more effect is significant..

218 According to table 4, the yield η is given by Eq.5:

$$219 \quad \eta = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{33} x_3^2 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_2 x_3, \quad [5]$$

220 where x_1 , x_2 and x_3 are the coded values for processing pressure, moisture content of peels and
221 processing time respectively.

222 A summary of variance analysis (ANOVA) is given in table 5. The Fisher's test (F-test) carried
223 out on experimental data make it possible to estimate the statistical significance of the proposed
224 model. The F-test value of the model being 6.53 with a low probability value ($p < 0.01$), we can
225 conclude that it is statistically significant at 99.9 % confidence level. As indicated by the
226 coefficient of determination R^2 in table 5, the predicted model seemed to reasonably fit to
227 experimental values, since the fitted model could explain 89 % of total variation.

228 **3.2- Effects of processing pressure, processing time and initial moisture content on oil** 229 **extraction yield**

230 Table 4 indicates that the linear terms related to processing pressure and to processing time were
231 statistically significant as proven by the low p-value (< 0.0001 and 0.0024 respectively) . This is
232 also obvious when considering Fig. 4, which shows the tri-dimensional response surface for the
233 yield in extracted oil. Both processing time and processing pressure demonstrated a linear
234 increase on extraction yield, with the strongest effect for the processing pressure which imposes
235 the ΔP of the pressure drop. In a recent work, this thermomechanical process, used in isolation of
236 extractives from red cedar wood (Mellouk, Khezami, Rezzoug & Capart, 2008), also showed a
237 strong linear effect of processing pressure.

238 From fig.4a, it can be seen that for a processing time and initial moisture content of orange peel
239 fixed at their central values (2 min. and 35 % respectively), extraction yield increased from 49.4
240 % to 73.9 % when processing pressure increased from 2.2 to 5.8 bar. On the other hand, when

241 the processing pressure and initial moisture content of orange peel were fixed at their central
242 value (4 bar and 35 % respectively), the change in the extraction rate was only from 48.4 % to
243 60.4 % when processing time increased from 1 to 3 minutes (fig 4c). This is probably the result
244 of two simultaneous effects: a free diffusion phenomenon on the peels surface and a mechanical
245 strain resulting from the drop of steam pressure with a subsequent degradation of cells. This
246 degradation therefore involves the liberation of compounds initially located in intact cells. Spiro
247 and Chen (1994) reported that the essential oil synthesized in secretory cells is not released
248 unless an external factor damages the microstructure. The same authors (Chen and Spiro 1995)
249 reported that a severe thermal stress such as irradiation with high microwave power, and the
250 build-up within the cells could have exceeded their capacity for expansion, thus causing their
251 breaking. This expansion phenomenon was also observed by Nouviaire et al, (2001) for fruits as
252 apples treated with D.I.C process. Fig. 4b also shows that it is possible to obtain a high extraction
253 yield oil for a low processing time (~1 min) but at high processing pressures (5 bar) indicating
254 that the mechanical strain induced by the rapid decompression and the brutal vaporization has as
255 effect a change in the surface tension of the glandular wall, causing it to crumble or rupture more
256 readily. Similar effects were pointed out by Pare, Sigomin & Lapointe, (1991) for microwave
257 extraction. The authors reported that an explosion at cell level occurred as a consequence of the
258 sudden temperature rise generated by microwaves. In this work, increasing of steam pressure
259 leads also to a temperature rise. The collapse and rupture phenomenon's were also confirmed by
260 scanning electron micrographs on extraction of rosemary oil by instantaneous controlled
261 pressure drop process (Rezzoug et al, 1998). Concerning effect of initial moisture content of
262 peels, it can be seen that it displays an intermediate linear effect ($p=0.0588$). This linear effect
263 can be explained by the quantity of water in orange peel. The higher is this quantity, the higher is

264 the evaporation, with intensive vapor formation and thus sweeping of orange peels oil
265 compounds.

266 **3.3- Kinetics of oil extraction from orange peel**

267 A comparative kinetic study between extraction by steam distillation which is the reference
268 method and by extraction with D.I.C process was performed. The maximum yield (2.06 g/100 g
269 d.m) for the steam distillation method was obtained after 90 to 100 minutes processing. For
270 extraction by D.I.C technique, we have studied the variation of yield versus processing time by
271 keeping constant processing pressure (7 bar) and initial moisture content of peels (35 % d.m).
272 As illustrated by figure 5, for 1 minute processing time, more than half of available oil was
273 extracted and for 4 minutes, extracted oil was equivalent to that obtained after 100 minutes by
274 steam distillation. In the two cases, oils have the same composition gathered in table 1 but for
275 steam distillation, a degradation of isolated oil, expressed by a more deepened colouring was
276 observed (Fig. 6). Oil extraction yield was assumed to obey to a first order kinetic law, an
277 assumption supported by various authors such as Spiro and Selwood (1984). In integrated form,
278 the kinetics are described by Eq. 6,

$$279 \quad \ln\left(\frac{y_{\infty}}{y_{\infty}-y(t)}\right) = k_1 t + a \quad (6)$$

280 where y_{∞} is the yield at end of process, $y(t)$ extraction yield at “t” time, k_1 a first-order rate
281 constant, and “a” the semi empirical intercept. For the two techniques, extraction of oil occurred
282 in two distinct kinetic steps as testified by the rupture of slope in the linear plots drawn in figure
283 7. Each step was characterised by its own kinetic constant. It is clear from fig.7 (a) that the
284 change in oil yield versus time was fast during the first 2 minutes of the D.I.C extraction process
285 with a high kinetic constant ($k_1=0.755 \text{ min}^{-1}$) and slower beyond this period before reaching an
286 equilibrium value ($k_2=0.095 \text{ min}^{-1}$). An inverse trend was observed for extraction by steam
287

288 distillation for which the slowest period was observed at the beginning of extraction process.
289 Figure 7 indicates that in the two periods, the kinetics constants were lower to those obtained for
290 D.I.C extraction process. This is probably due, for the thermomechanical proposed process, to a
291 combination of heat treatment provided by steam and mechanical effect provided by the sudden
292 pressure drop while for steam distillation only heat treatment is present.

293 The reduced cost of extraction is clearly advantageous for the proposed D.I.C method in terms of
294 time and energy saving. The energy required to perform the two extraction methods were
295 respectively 0.13 kWh/g of isolated oil for steam distillation, and 0.014 kWh/ g of isolated oil for
296 D.I.C extraction process. The power consumption was determined according to the quantity of
297 steam required and to vacuum pump energy consumption. Regarding the environmental impact,
298 the calculated quantity of carbon dioxide rejected in atmosphere is largely higher for steam
299 distillation (from 115.8 to 127,1 g CO₂/g of extracted oil) than for the proposed D.I.C extraction
300 process (from 12.5 to 13.7 g CO₂/g of extracted oil), for 7 bar as processing pressure. These
301 calculations were performed according to literature provided by the French Nuclear Energy
302 Society (<http://www.sfen.org/fr/societe/developpement/edf.htm>; downloaded on September 25,
303 2008): to obtain 1 kWh from coal and fuel, respectively 978 and 891 g of CO₂ is rejected in
304 atmosphere during combustion.

305 **4- Conclusion**

306 This study clearly shown that oil yield from orange peel was more influenced by the processing
307 pressure than by processing time and initial moisture content of peels. However, the three
308 variables exerted a positive linear effect. The empirical model gave R² of 0.89 and P-value of
309 less than 0.01, which implied a good agreement between the predicted values and actual values
310 of oil yield. The optimal conditions to obtain the highest yield are showed in fig.8: 6.6 bar for the
311 processing pressure; 53.6 % for the initial moisture content of peels and 3.68 minutes for

312 processing time. The kinetic study performed on the thermomechanical proposed process (D.I.C)
313 and conventional steam distillation process indicated that for both methods the extraction process
314 can be divided in two steps and that in the two cases the amount of oil recovered in the first step
315 was about 90 % of available orange peel oil. However, the first step represents 2 minutes for the
316 proposed thermomechanical extraction process and 80 minutes for steam distillation process.
317 Thus, using this method, a reproducible extraction can be achieved in few minutes without
318 adding any solvent, representing economic and ecologic advantages.

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Figure captions

428 **Fig.1.** Schematic of the apparatus used for extraction. 1. Boiler, 2. Pressure vessel, 3.Butterfly
429 valve, 4. Vacuum tank, 5. Water ring vacuum pump, 6. Extract container. All parts and
430 valves of the apparatus are made of stainless steel.

431 **Fig.2.** Typical pressure-time profile for DIC processing cycle.

432 **Fig.3.** Characterization procedure of isolated orange peel oil

433 **Fig.4.** Responses surfaces of the extracted oil yield as a simultaneous function of two operating
434 parameters. For each figure, the third variable is fixed at “0” level

435 **Fig.5.** Kinetics of orange peel oil extracted by steam distillation ($-o-$) and by D.I.C
436 extraction process ($-●-$) at 7 bar, 35 % d.m

437 **Fig.6.** Extracted oil obtained by: (a) steam distillation (80 min.); (b) D.I.C extraction process (7
438 bar and 0.35 g H₂O/ g of dm, 4 min.)

439 **Fig.7.** First-order plots for the two stages of oil isolation orange peel by the thermomechanical
440 process (a) and by steam distillation (b). The semi-empirical factors were obtained as
441 follows: (1): $k_1=0.755 \text{ min}^{-1}$; (2) $k_2=0.095 \text{ min}^{-1}$; (3) $k_1=0.033 \text{ min}^{-1}$; (4) $k_2=0.090 \text{ min}^{-1}$

442 **Fig.8.** Contours plots showing the simultaneous effects of processing pressure and initial
443 moisture content at the optimal processing time selected by the developed equation
444 (processing time: 3.68 min.)

Figure 1.

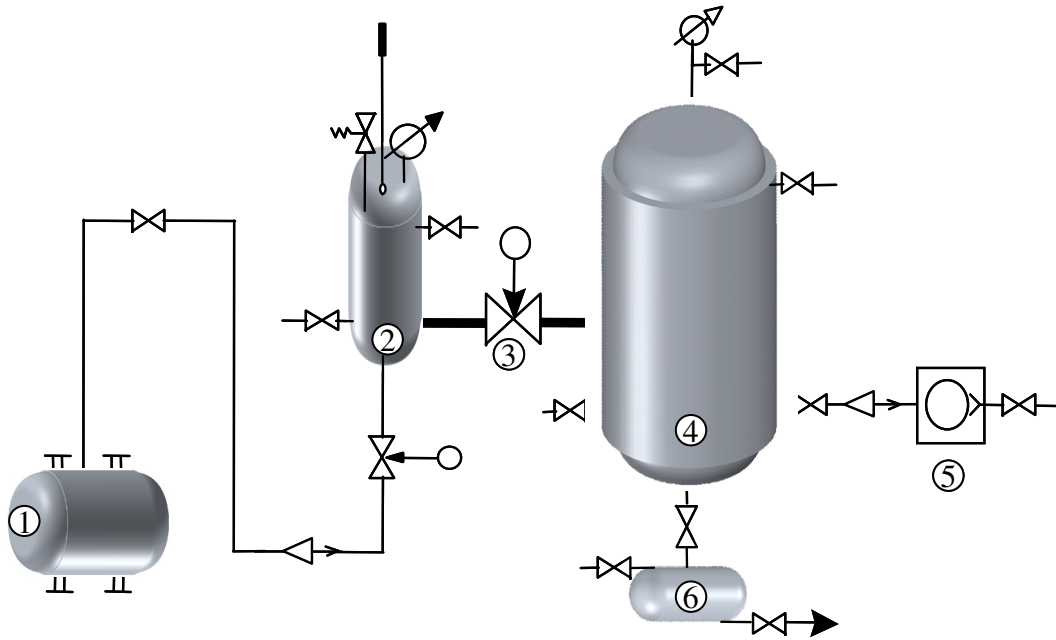


Figure 2

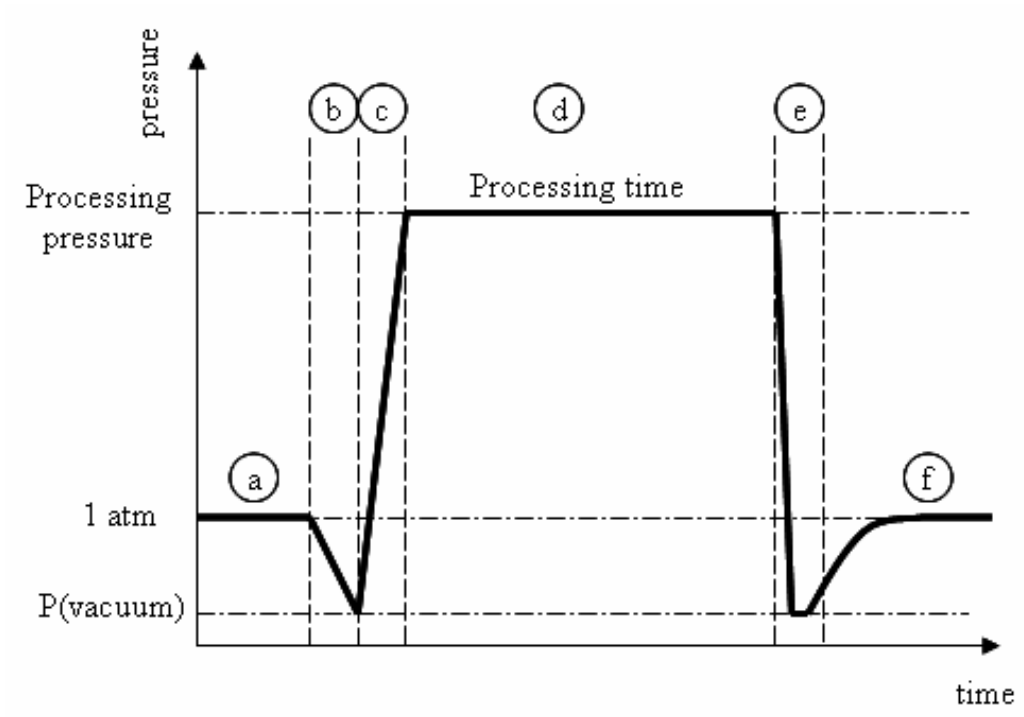


Figure 3.

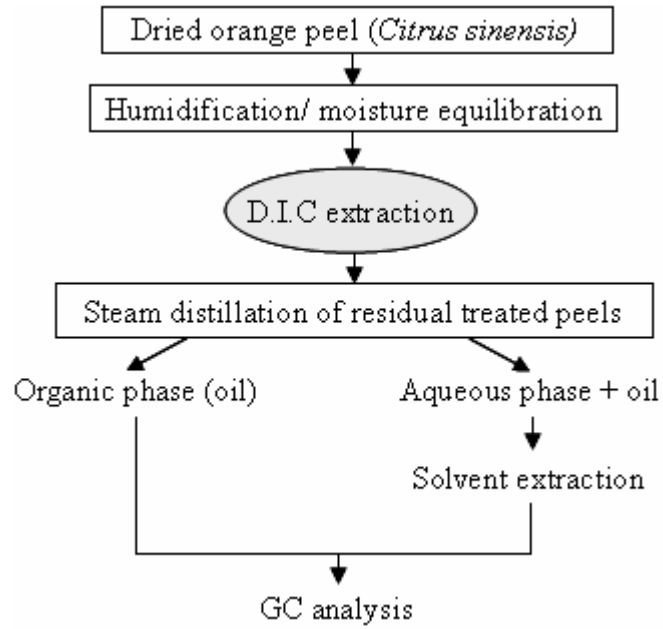


Figure 4.

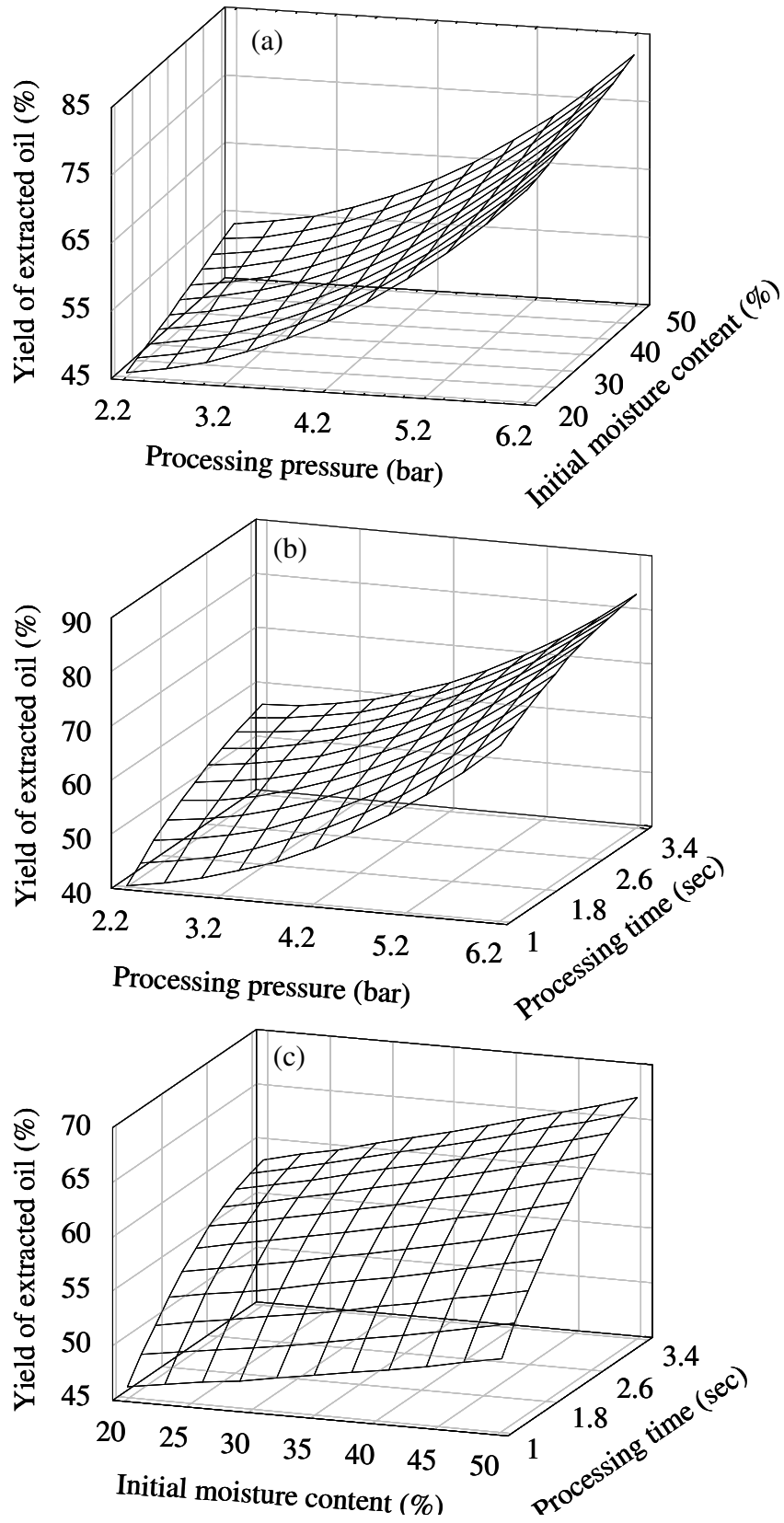
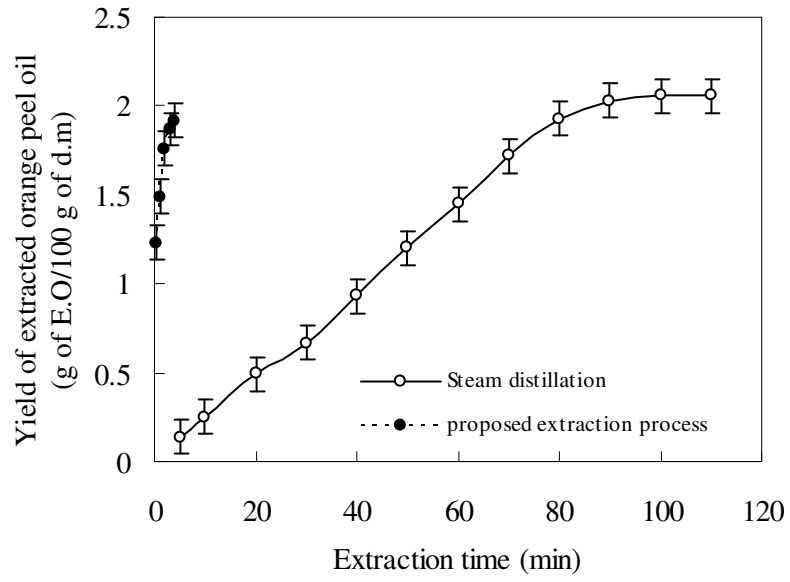
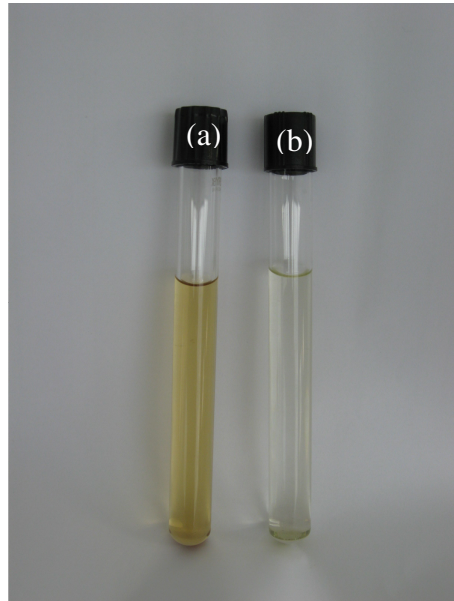


Figure 5



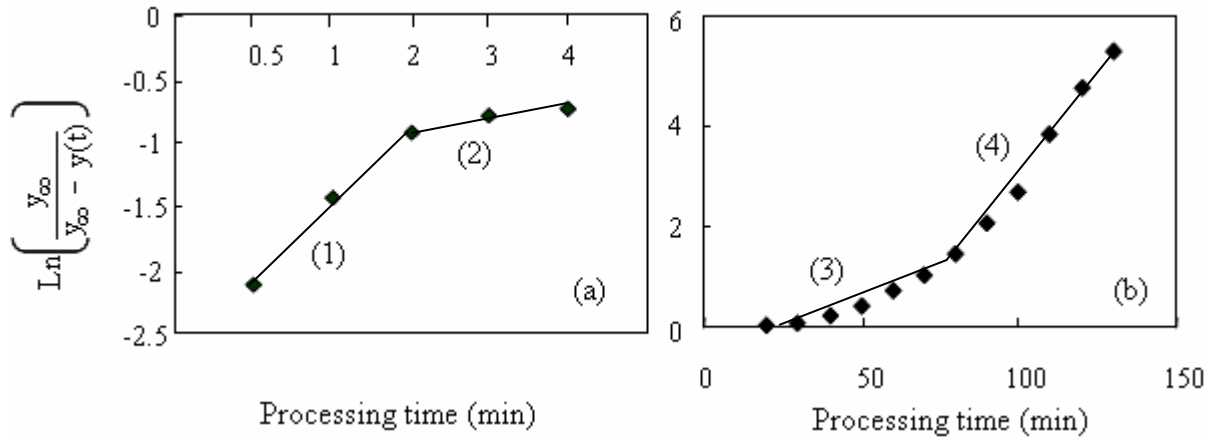
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Figure 6



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Figure 7



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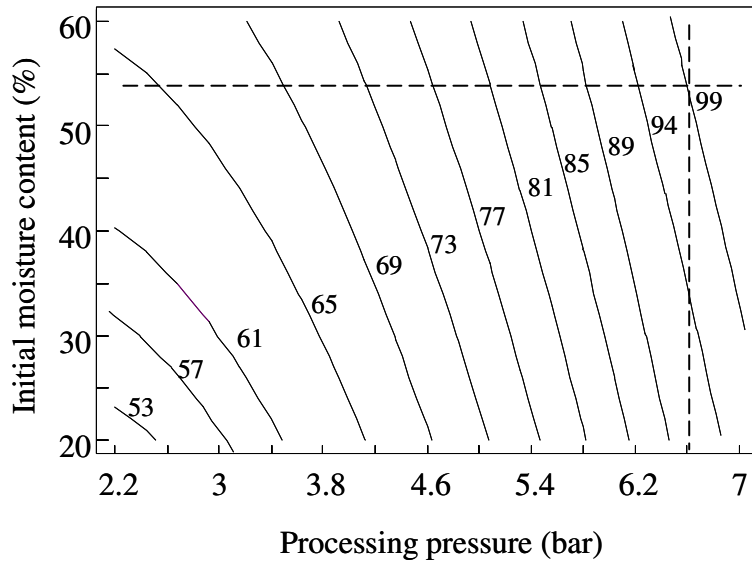
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Figure 8

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463 Table 1. Percentage composition of orange peel oil isolated by steam distillation

Constituents	g/100 g of E.O	Rt [*]
α -pinene	0.5	2.87
β -pinene	0.38	3.76
myrcene	1.3	4.24
limonene	94.4	5.63
linalool	0.39	7.28

464 ^{*}Retention time; E.O: extracted oil

465 Table 2. Coded levels for independent variables used in developing experimental
 466 data and the temperature corresponding to processing pressure

	Coded level				
	$-\alpha$	-1	0	1	$+\alpha$
Pressure (bar)	0.97	2.2	4	5.8	7.02
(Corresponding temperature °C)	100	123.3	143.6	158	165
Moisture content (%)	9.8	20	35	50	60.2
Processing time (min)	0.32	1	2	3	3.7

467 $\alpha(\text{axial distance}) = \sqrt[4]{N}$, N is the number of experiments of orthogonal design, i.e of the
 468 factorial design. In this case $\alpha = 1.6818$.

469 Table 3. Experimental data and yield for orange peel essential oil with different
 470 combinations of processing pressure (x_1), initial moisture content of peels (x_2) and
 471 processing time (x_3) used in the randomized central composite design

Run	Independent variables			responses		
	x_1	x_2	x_3	Experimental (%)	Predicted (%)	Deviation (%)
1	1	1	1	81.06	81.48	0.42
2	1	-1	1	79.61	74.11	5.50
3	1	1	-1	67.96	69.46	1.50
4	1	-1	-1	73.78	74.61	0.83
5	-1	1	1	54.85	58.06	3.21
6	-1	-1	1	56.31	56.71	0.40
7	-1	1	-1	42.23	43.77	1.54
8	-1	-1	-1	41.74	39.09	2.65
9	$-\alpha$	0	0	50.00	49.92	0.08
10	$+\alpha$	0	0	85.42	88.08	2.66
11	0	$-\alpha$	0	38.83	51.48	12.65
12	0	$+\alpha$	0	70.38	68.30	2.08
13	0	0	$-\alpha$	36.89	41.22	4.33
14	0	0	$+\alpha$	61.65	62.90	1.25
15	0	0	0	56.90	56.71	0.19
16	0	0	0	56.31	56.71	0.41
17	0	0	0	58.25	56.71	1.54
18	0	0	0	56.67	56.71	0.04
19	0	0	0	56.65	56.71	0.06
20	0	0	0	55.80	56.71	0.91
21	0	0	0	55.82	56.71	0.89
22	0	0	0	58.25	56.71	1.54

Mean absolute error for replications = 0.95 %

Table 4. Regression coefficients for the response surface and p-values

Regression coefficients of the model		P-value
β_0	58.45	-
β_1	24.43	<0.0001
β_2	6.98	0.0588
β_3	12.85	0.0024
β_{11}	8.57	0.0095
β_{12}	-0.85	0.8382
β_{13}	-2.065	0.6365
β_{22}	-0.70	0.8820
β_{23}	1.33	0.7790
β_{33}	-4.46	0.3179

473 Table 5. Analysis of variance for the fit of experimental data to response surface model

Source	Degrees of freedom	Sum of square	Mean square	F-ratio
Model	9	3146,35	349,59	6.53 ^a
Linear	3	2769,14	923.05	17.24 ^b
Quadratic	3	363,70	121.23	2.26 ^b
Interactions	3	13,51	4.50	0.084
Residual	12	642.51	53.54	-
Lack of fit	5	463.57	92.71	3.63
Pure error	7	178.94	25.56	-
R^2		0.89		

474 a : p-value<0.01, b: p-va