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Thermomechanical process intensification for oil extraction from orange peels.

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Abstract

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

Keywords : orange peel, extraction, oil, Controlled Instantaneous Pressure Drop (D.I.C 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

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

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

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

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

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

2- Experimental procedures

2.1- Plant material

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

2.2- Instantaneous controlled pressure drop apparatus

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

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

a- Isolation of essential oil

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

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

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

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

3- RESULTS AND DISCUSSION

3.1- Model fitting

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

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

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

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

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

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

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

3.3- Kinetics of oil extraction from orange peel

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

$$\ln\left(\frac{y_{\infty}}{y_{\infty}-y(t)}\right)=k_1t+a \quad (6)$$

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

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

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

4- Conclusion

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

319 REFERENCES

- 320 Allaf, K. Maache-Rezzoug, Z. Louka, N. Debs-Louka, E. Abraham, G. Rezzoug, S.A., Habba, A
321 (1998). French patent WO/1999/042003.
- 322 Arce, A., Pobudkowska, A., Rordíguez, O., Soto, A. (2007). Citrus essential oil terpenless by
323 extraction using 1-ethyl-3-methylimidazolium ethylsulfate ionic liquid: Effect of the
324 temperature. *Chemical engineering journal*, 133, 213-218.
- 325 Benoist, D., Tourbier Y., and Germain-Tourbier S. (1994). Plan d'expériences: construction et
326 analyse". *Lavoisier TEC & DOC*. Chapter 5, 208-389
- 327 Berna, A., Tárrega, Blasco, M., Subirats. (2000). Supercritical CO₂ extraction of essential oil
328 from orange peel; effect of the height of the bed. *Journal of supercritical fluids*, 18, 227-
329 237.
- 330 Bousbsia, N., Vian, M.A., Ferhat, M.A., Meklati, B.Y., Chemat, F. (2008) A new process for
331 extraction of essential oil from citrus peels: microwave hydrodiffusion and gravity. *Journal*
332 *of Food engineering*. doi: 10.1016/j.foodeng.2008.06.034.
- 333 Buldish, M., Ullrich, J., Jung, S. and Brunner, G. (1997). Multistage Counter-Current Extraction
334 of Orange Peel Oil Using Supercritical Carbon Dioxide. *Proc. of First European Congress*
335 *on Chemical Engineering*, ECCE-1, Florence, Italy, May 4-7, 2703-2706
- 336 Chen, S. S., and Spiro, M. (1995). Kinetics of microwave extraction of rosemary leaves in
337 hexane, ethanol and a hexane+ethanol mixture. *Flavour and Fragrance Journal*, 10, 101-
338 112.
- 339 Danielski, L., Brunner, G., Schwänke, C., Zetzi, C., Hense, H. and Donoso, J.P.M. (2008).
340 Deterpenation of mandarin (*Citrus reticulata*) peel oils by means of countercurrent
341 multistage extraction and adsorption/desorption with supercritical CO₂. *Journal of*
342 *supercritical fluids*, 44, 315-3240.
- 343 Diaz, S., Espinosa, S. and Brignole, E.A. (2005). Citrus oil deterpenation with supercritical
344 fluids. Optimal process and solvent cycle design. *Journal of supercritical fluids*, 35, 49-61
- 345 Dugo, P., Mondello, L., Bartle K.D., Clifford, A.A., Breen, D.G.P.A. and Dugo, G. (1995).
346 Deterpenation of sweet orange and lemon essential oils with supercritical carbon dioxide

347 using silica as an adsorbent. *Flavour and Fragrance Journal*, 10, 51-58

348 Ferhat, M.A., Meklati, B.Y., Smadja, J. and Chemat, F. (2006). An improved microwave
349 Clevenger vapparatus for distillation of essential oils from orange peel. *Journal of*
350 *Chromatography A*, 1112, 121-126

351 Fleisher, A. (1990). The Poroplast Extraction Technique in the Flavor and Fragrance Industry.
352 *Perfumer & Flavorist*, 15, 27-36

353 Ghodke, S.K., Ananthanarayan, L. and Rodrigues, L. (2009). Use of response surface
354 methodology to investigate the effects of milling conditions on damaged starch, dough
355 stickiness and chapatti quality. *Food Chemistry*, 112, 1010-1015.

356 Lawrence, B.M. (1990). Progress in Essential Oils. *Perfumer & Flavorist.*, 15, 45-62

357 Mellouk, H., Khezami, L., Rezzoug, S.A. and Capart. R. (2008). Total Valorisation of red cedar
358 sawmills wastes by Instantaneous controlled pressure drop process. Isolation of extractives
359 and production of activated carbon from the solid residue. *Bioresources*, 3 (4), 1156-1172

360 Nouviaire, A., Louka, N., Rezzoug, S.-A. and Allaf, K. (2001). Séchage-texturation des fraises
361 par le procédé de détente instantanée contrôlée couplé au séchage par convection.
362 Optimisation à l'aide de la méthodologie des plans d'expériences. *Sciences des Aliments*,
363 21, 177-192

364 Mira, B. Blasco, M. and Subirats, S. (1996). Supercritical CO₂ extraction of essential oils from
365 orange peel. *Journal of Supercritical Fluids*, 9, 238-243

366 Pare, J., Sigomin, M. & Lapointe, J. (1991). US Patent n° 5.002.784

367 Pernice, R., Boriello, G., Ferracane, R., Borrelli, R.C. and Cennamo, F. (2009). Bergamot: A
368 source of natural antioxidant for functionalized fruit juices. *Food Chemistry*, 112, 545-550.

369 Raeissi, S. and Peters, C.J. (2005). Liquid–vapor and liquid–liquid–vapor equilibria in the
370 ternary system ethane + limonene + linalool. *Journal of supercritical fluids*, 33, 201-208

371 Raeissi, S., Diaz, S., Espinosa, S., Peters, C.J. and Brignole, E.A. (2008). Ethane as an
372 alternative solvent for supercritical extraction of orange peel oils. *Journal of Supercritical*
373 *Fluids*, 45, 306-313

374 Redd, J.B. and Hendrix, C.M. In Fruit Juice Processing Technology. S. Nagy, C.S. Chen, P.E.

375 Shaw, Eds. Ag. Science: Florida. Chapter 4. 1993.

376 Rezzoug, S.A., Louka, N., Maache-Rezzoug, Z., Nouviaire, A. & Allaf, K. (1998). Présentation du
 377 séchage couple a la texturation par détente instantanée contrôlée. Application aux produits agro-
 378 alimentaires en morceaux. *10^{èmes} Rencontres Scientifiques et Technologiques des Industries*
 379 *Alimentaires*. AGORAL. Ed. Lavoisier, Paris. 319-324.

380 Rezzoug, S. A., Maache-Rezzoug, Z., Mazoyer, J., Jeannin, M. and Allaf, K. (2000). Effect of
 381 instantaneous controlled pressure drop process on hydration capacity of scleroglucan.
 382 Optimisation of operating conditions by response surface methodology. *Carbohydrate*
 383 *polymers*, 42, 73-84

384 Rezzoug, S.A., Baghdadi, M.W., Louka, N., Boutekedjiret, C. and Allaf, K. (1998). Study of a
 385 New Extraction Process : Instantaneous Controlled Decompression. Application for
 386 Extraction of Essential Oil from Rosemary Leaves. *Flavour and Fragrance Journal*, 13,
 387 251-258

388 Rezzoug, S.A., Boutekedjiret, C. & Allaf, K. (2005). Optimization of operating conditions of
 389 rosemary essential oil extraction by a fast controlled pressure drop process using response surface
 390 methodology. *Journal of Food Engineering*, 71, 9-17

391 Salib, A.G., Saleh M.A., Abdel-Malik, G.S. (1978). Chemical and physical Studies on peel
 392 essential oils of some Egyptian citrus fruits. *Annals of Agriculture Science*, 9, 65-71

393 Sonsuzer, S., Sahin S. and Yilmaz, L. (2004). Optimization of supercritical CO₂ extraction of
 394 *Thymbra spicata* oil, *Journal of Supercritical Fluids*, 30, 189–199.

395 Spiro, M., and Chen, S. S. (1994). Kinetics of solvent extraction of essential oil from rosemary
 396 leaves. *Flavour and Fragrance Journal*, 10, 187-200.

Spiro, M., and Selwood, R. M., (1984). The kinetics and mechanism of caffeine infusion from
 coffee: The effect of particle size. *Journal of the Science of Food and Agriculture* 35, 915-
 924

397 Statgraphics Plus for Windows 5.1. Experimental Design. Manugistics, Inc. 1994

398 Statgraphics Plus for Windows 5.1. User Manual. Manugistics, Inc. 1994

399 Tateo. F. (1990). Production of Concentrated Orange Oils Using a Thin Film Evaporator.

Journal of essential oil research, 2, 7-13

Temelli, F. Chen, C.S. and Braddock, R.J. (1988). Supercritical Fluid Extraction in Citrus Oil Processing. High-pressure CO₂ system concentrates aroma and flavor compounds in citrus oils. *Food Technogy*, 42, 145-150

Viuda-Matros, M., Ruiz-Navajas, Y., Fernández-López, J. and Pérez-Álvarez, J. (2008). Antifungal activity of lemon (*Citrus lemon* L.), mandarin (*Citrus reticulata* L.), grapefruit (*Citrus paradisi* L.) and orange (*Citrus sinensis* L.) essential oils., *Food Control*, 19, 113-1138.

Wang, L., Yang, B., Du, X., Yang, Y. and Liu, J. (2008). Optimisation of conditions for extraction of acid-soluble collagen from grass carp (*Ctenopharyngodon idella*) by response surface methodology. *Innovative food science and emerging technologies*, 9, 604-607.

Wu, Y., Cui, S.W., Tang, J. and Gu, X. (2007). Optimisation of extraction process of crude polysaccharides from boat-fruited *sterculia* seeds by response surface methodology. *Food Chemistry*, 105, 1599-1605.

Yu, J., Dandekar, D.V., Toledo, R.T., Singh, R.K. and Patil, B.S. (2007). Supercritical fluid extraction of limonoids and naringin from grapefruits (*Citrus paradisi*, Macf.) seeds. *Food Chemistry*, 105, 1026-1031.

Zeboudj, S., Belhanèche-Bensemra, N. and Belabbès, R. (2005). Use of surface response methodology for the optimization of the concentration of the sweet orange essential oil of Algeria by wiped film evaporator. *Journal of food engineering*, 67, 507-512

Zia-ur-Rehman. (2006). Citrus peel extract - A natural source of antioxidant. *Food Chemistry*, 99, 450-454

Figure captions

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

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

Fig.3. Characterization procedure of isolated orange peel oil

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

Fig.5. Kinetics of orange peel oil extracted by steam distillation (—○—) and by D.I.C extraction process (—●—) at 7 bar, 35 % d.m

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

Fig.7. First-order plots for the two stages of oil isolation orange peel by the thermomechanical process (a) and by steam distillation (b). The semi-empirical factors were obtained as 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) $k_2=0.090 \text{ min}^{-1}$

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

Figure 1.

Figure 2

Figure 3.

Figure 4.

Figure 5

451

Figure 6

452

Figure 7

Figure 8

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 $\alpha = 1.6818$.

Table 3. Experimental data and yield for orange peel essential oil with different combinations of processing pressure (x_1), initial moisture content of peels (x_2) and 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