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Thermomechanical process intensification for oil extraction from orange peels.

S.-A. Rezzoug\textsuperscript{1*} and N. Louka\textsuperscript{2}

\textsuperscript{1}\textsuperscript{*}Laboratoire d’Etude des Phénomènes de Transferts et de l’Instantanéité, Agro-Industrie et Bâtiment, LEPTIAB (EA 4226), Pôle Sciences et Technologies, Avenue Michel Crépeau, Université de La Rochelle, 17042 La Rochelle, France


\textsuperscript{*}Corresponding author : Tel : +33 5 46 45 86 15 ; fax : +33 5 46 45 86 16
E-mail address : sarezzou@univ-lr.fr
**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.
World production of citrus fruit has experienced continuous growth in the last decades of the XX century. Total annual citrus production was estimated at over 105 million tons in the period 2000-2004 (http://www.unctad.org/infocomm/anglais/orange/market.htm). Oranges constitute the bulk of citrus fruit production, accounting for more than half of global citrus production in 2004. Thus, the quantities of generated by-products are very important. In this study, extraction of oil from orange peel was performed through a termomechanical process developed in our laboratory (Rezzoug, Boutekedjiret & Allaf, 2005). We report on some results obtained using this process as well as others comparing extraction kinetics when using a conventional steam distillation process and the proposed extraction process. One of advantages of the described method is the short contact of extracted oil with the heated zones in the apparatus resulting in a lower heating of the product compared to steam distillation. At industrial scale, this is interesting regarding oil quality and energy saving.

1- Introduction

Peel of citrus fruits is one of the by-products of fruit processing which provides a great potential for further commercial use. The various species of citrus elaborate and stock essential oils in schizolysigen pockets localized in the external part of the mesocarpe of fruit (flavedo). These oils are used as flavouring ingredients in a variety of foods such as soft drinks or ice cream as well as in formulation of several products in parapharmacy and perfume industry (Raeissi, Diaz, Espinosa, Peters & Brignole, 2008). Another application makes use of germicidal properties of some of their components. Redd and Hendrix (1993) reported that a small amount of the d-limonene was very effective in the germicide treatment of waste water. It is well known that 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 (Díaz, 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, Boutekejdjiret & 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 \(\text{Citrus sinensis}\) and to determine the optimum conditions using RSM analysis.

2- Experimental procedures

2.1- Plant material

Oranges used in this study were \textit{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 H\(_2\)O 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 CO\(_2\) 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
decompression, orange peels are recovered and analyzed. In order to quantify the essential oil remaining in orange peels, a classical extraction procedure of steam distillation was used. Two distinct phases were obtained, an organic phase (isolated oil) and an aqueous phase containing a small part of oil. The organic phase was separated from the aqueous phase with 10 ml of hexane and then analyzed by gas chromatography. Procedures of steam distillation and gas chromatography are described hereafter.

b- Gas chromatography (GC)

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

c- Steam distillation (S.D)

Classical S.D method of extraction was used with 50 g of orange peel treated by D.I.C process and 350 ml of water. The duration of extraction by steam distillation was 2 hours. As extraction solvent, 10 ml of distilled hexane was used. Identified compounds and their yield are grouped in table 1. The yields of identified compounds are close to those reported by Lawrance (1990) about Portuguese and Argentinean orange peel oil, by Buldish, Ullrich, Jung & Brunner (1997), and by Mira, Blasco & Subirats (1996) for orange peel oil obtained by supercritical fluid extraction.
From Table 1, it is clear that orange peel oil obtained by S.D is composed in large part of limonene. As monoterpenes, we also identified, α-pinene, β-pinene, and myrcene and as oxygenated compounds, linalool have been identified.

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

\[
\text{oil yield (\%) } = \left( \frac{\text{2.06 g extract in treated peels}}{\text{2.06 g peels treated in extract}} \right) \times 100
\]  

[1]

2.4- Experimental design

A response surface methodology was employed for optimizing the operating conditions of the D.I.C process to give high yield of liquid extract i.e. to minimize the quantity of essential oil which remains in orange peels. This quantity is assumed to be affected by three independent variables, \( \xi_i \) (processing pressure \( \xi_1 \), initial moisture content of orange peel \( \xi_2 \) and processing time \( \xi_3 \)). It is also assumed that the response \( \eta \) (oil yield), which was experimentally measured, defined the system.

\[
\eta = f(\xi_1, \xi_2, \xi_3)
\]  

[2]

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

\[
\eta = \beta_0 + \sum_{i=1}^{3} \beta_i x_i + \sum_{i=1}^{3} \beta_{ii} x_i^2 + \sum_{i=1}^{9} \sum_{j=i+1}^{3} \beta_{ij} x_i x_j
\]  

[3]

where \( \beta_0, \beta_i, \beta_{ii} \) and \( \beta_{ij} \) are regression coefficients, and \( x_i \) are the coded variables linearly related to \( \xi_i \). The coding of \( \xi_i \) into \( x_i \) is expressed by the following equation:

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

[4]
where $\xi_i = $ actual value in original units; $\xi_i^* = $ mean of high and low levels of $\xi_i$; and $d_i = $
difference between the low and high levels of $\xi_i$.

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.
According to table 4, the yield $\eta$ is given by Eq.5:

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

[5]

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

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

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

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

From fig.4a, it can be seen that for a processing time and initial moisture content of orange peel fixed at their central values (2 min. and 35% respectively), extraction yield increased from 49.4% 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 micrographs 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,

\[
\ln\left(\frac{y_\infty}{y_\infty-y(t)}\right) = k_i t + a
\]

where \(y_\infty\) is the yield at end of process, \(y(t)\) extraction yield at “t” time, \(k_i\) 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 (\(k_1=0.755\) min\(^{-1}\)) and slower beyond this period before reaching an equilibrium value (\(k_2=0.095\) 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 CO$_2$/g of extracted oil) than for the proposed D.I.C extraction process (from 12.5 to 13.7 g CO$_2$/g of extracted oil), for 7 bar as processing pressure. These calculations were preformed 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 CO$_2$ 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 R$^2$ 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
processing time. The kinetic study performed on the thermomechanical proposed process (D.I.C) and conventional steam distillation process indicated that for both methods the extraction process can be divided in two steps and that in the two cases the amount of oil recovered in the first step was about 90% of available orange peel oil. However, the first step represents 2 minutes for the proposed thermomechanical extraction process and 80 minutes for steam distillation process. Thus, using this method, a reproducible extraction can be achieved in few minutes without adding any solvent, representing economic and ecologic advantages.
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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 3.

Dried orange peel (*Citrus sinensis*)

Humidification/moisture equilibration

D.I.C extraction

Steam distillation of residual treated peels

Organic phase (oil) → Aqueous phase + oil → Solvent extraction → GC analysis
Figure 4.
Figure 5

Yield of extracted orange peel oil (g of E.O./100 g of d.m.) vs. Extraction time (min)

- Steam distillation
- Proposed extraction process
Figure 6
Figure 7

\[ \ln \left( \frac{\gamma_0}{\theta_0 - \gamma(t)} \right) \]

- Processing time (min)

(a) (1) (2) (3) (4)

(b)
Figure 8

Processing pressure (bar) vs. Initial moisture content (%) graph.
Table 1. Percentage composition of orange peel oil isolated by steam distillation

<table>
<thead>
<tr>
<th>Constituents</th>
<th>g/100 g of E.O</th>
<th>Rt *</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-pinene</td>
<td>0.5</td>
<td>2.87</td>
</tr>
<tr>
<td>β-pinene</td>
<td>0.38</td>
<td>3.76</td>
</tr>
<tr>
<td>myrcene</td>
<td>1.3</td>
<td>4.24</td>
</tr>
<tr>
<td>limonene</td>
<td>94.4</td>
<td>5.63</td>
</tr>
<tr>
<td>linalool</td>
<td>0.39</td>
<td>7.28</td>
</tr>
</tbody>
</table>

*Retention time; E.O: extracted oil
Table 2. Coded levels for independent variables used in developing experimental data and the temperature corresponding to processing pressure

<table>
<thead>
<tr>
<th>Coded level</th>
<th>−α</th>
<th>-1</th>
<th>0</th>
<th>1</th>
<th>+α</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure (bar)</td>
<td>0.97</td>
<td>2.2</td>
<td>4.0</td>
<td>5.8</td>
<td>7.02</td>
</tr>
<tr>
<td>(Corresponding temperature °C)</td>
<td>100</td>
<td>123.3</td>
<td>143.6</td>
<td>158</td>
<td>165</td>
</tr>
<tr>
<td>Moisture content (%)</td>
<td>9.8</td>
<td>20</td>
<td>35</td>
<td>50</td>
<td>60.2</td>
</tr>
<tr>
<td>Processing time (min)</td>
<td>0.32</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>3.7</td>
</tr>
</tbody>
</table>

\[ \alpha(\text{axial distance}) = \sqrt[4]{N} \], \( N \) is the number of experiments of orthogonal design, i.e. of the 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.

<table>
<thead>
<tr>
<th>Run</th>
<th>$x_1$</th>
<th>$x_2$</th>
<th>$x_3$</th>
<th>Experimental (%)</th>
<th>Predicted (%)</th>
<th>Deviation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
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Mean absolute error for replications = 0.95 %
Table 4. Regression coefficients for the response surface and p-values

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<th>Regression coefficients of the model</th>
<th>P-value</th>
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Table 5. Analysis of variance for the fit of experimental data to response surface model

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<th>Source</th>
<th>Degrees of freedom</th>
<th>Sum of square</th>
<th>Mean square</th>
<th>F-ratio</th>
<th>R²</th>
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\textsuperscript{a} p-value<0.01, \textsuperscript{b} p-value<0.001