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Procedia Engineering 42 (2012) 1061 – 1078

**Procedia  
Engineering**[www.elsevier.com/locate/procedia](http://www.elsevier.com/locate/procedia)

20<sup>th</sup> International Congress of Chemical and Process Engineering CHISA 2012  
25 – 29 August 2012, Prague, Czech Republic

## Instant controlled pressure drop combined to ultrasounds as innovative extraction process combination: fundamental aspects.

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### Abstract

To entirely recover and value orange peels by extracting both essential oils and antioxidant compounds, hydrodistillation and standard solvent extraction are usually used. These treatments are known as long, fastidious, and energy-consuming processes mainly because of a low diffusivity coupled with a low starting accessibility. Various innovative processes were recently proposed, studied and optimized. They could have their own advantages. By analyzing the fundamental aspects of different processes, it was possible to recognize the limiting phenomena. Therefore, combining adequate innovative processes intensified the whole operation. This will increase heat and mass transfers; both process performance and extract quality could be dramatically improved. DIC (Détente Instantanée Contrôlée), instant controlled pressure-drop treatment enhances autovaporization, which results in an expansion of the sample. The autovaporization enables a direct extraction of essential oils simultaneously triggering expansion, which enhances the availability of some molecules and also increases solvent diffusivity within the plant matrix. Ultrasound extraction process is fast in comparison with standard methods, thanks to a greater contact surface area between solid and liquid phase. It was possible to compare the effect of ultrasound-assisted extraction to standard solvent extraction in terms of fundamental aspects, highlighted with a former experimental study. Fundamentals enabled the study and comprehension of the extraction modelling. As an example, orange peel extraction has been studied. In order to achieve innovative extraction, we combined and associated these two

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techniques. We carry out the treatment by DIC to extract the essential oils and at the same time to obtain a textured vegetal material. Followed by ultrasound assisted solvent extraction, a great intensification of antioxidants extraction is generated. It was possible to compare the effect of ultrasound assisted extraction to standard solvent extraction both achieved on dried orange peels as raw material and DIC treated material. Combining DIC to ultrasounds enabled enhancing yields and extraction kinetics of antioxidant.

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*Keywords: Extraction; instant controlled pressure drop (DIC); ultrasound; intensification; by-product; recovery*

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## 1. Introduction

Solvent extraction processes have been largely used in various industries. They recently were improved through new physical concepts such as CO<sub>2</sub> Supercritical Fluid Extraction[1-5], Ultrasound assisted process[6, 7], Micro-Waves[8, 9]... Systematically, a pretreatment stage of grinding takes place in order to improve the exchange surface and reduce the thickness of solvent diffusion within the solid matrix[10]. A new concept of expanded products has recently been defined using Instant Controlled Pressure Drop DIC technology. Whatever the type of solvent is, such a structure expansion can dramatically intensify the kinetics by improving diffusivity of solvent within the solid. Coupled to ultrasound, the internal transfer of solute within the pore solvent can likewise be intensified by replacing convection transfer instead of diffusion[11, 12].

In this work, we carried out a first approach of modeling of solvent extraction kinetics of expanded granules involving higher exchange surface and greater internal diffusion process.

The main objective of different research works carried out on industrial unit operations is to improve both process performance and final product quality[13]; this aims at reducing the treatment time, decreasing the energy consumption, preserving and even improving multidimensional quality. Global intensification philosophy consists in listing different processes, determining their possible interaction and considering between the main successive processes, the limiting phenomena. This last should be intensified to improve the global kinetics of the operation.

In the case of solvent extraction, it is well known that four mass transfer mechanisms should take place[13]:

1. Solvent transfer within the product; it is carried out in liquid form by various processes including capillarity, molecular diffusivity; the gradient of solvent content is the driving force.
2. Solute transfer in the solvent within the product; it is carried out by molecular diffusivity with the gradient of solute concentration in the solvent as the main driving force.
3. Solvent interaction between the material exchange surface and the contacting solvent.
4. Solute transport outside the product surface to external solvent; when no external agitation is done, this transport takes place by diffusion with the gradient of solute concentration in the solvent as the driving force.

The type of solvent (polarity...) is defined depending on the solute to extract, and the temperature limited by boiling temperature and thermal sensitivity of various compounds. Thus, we normally assume the interaction between solvent and product to instantaneously let the solute be present at equilibrium level; the solute is transferred within the surface solvent in both external medium and pores.

The agitation of the external environment solvent allows the part of the solute  $m_A$  accessible at the exchange surface to be easily and quickly extracted and transported far from the exchange surface; this is the first intensification of the solvent extraction process instead of natural convection.

Then, the internal solvent diffusion within the matrix becomes the limiting process; DIC expansion of such a natural structure can be a very relevant solution for intensifying the whole operation. DIC can also ensure a complete extraction of volatiles such as essential oils

The solute diffusion within the material inside the pore solvent is normally considered to usually be the limiting process within the expanded structure. By using ultrasonic treatment, one can imply an internal motion/agitation of the liquid within the pores, leading the solute transfer to be achieved by convection instead of or coupled to diffusion [14]. This is the third intensification process.

Ultrasound irradiation (20–100 kHz) [15–17] is one of the upcoming extraction techniques that can offer high reproducibility in shorter time, lower temperature, reduced solvent consumption and less energy input [18]. Oscillatory particle motion produced by high-intensity ultrasonic waves can also induce secondary flows, known as acoustic streaming. Such an agitation should realize an internal convection motion of solute within the solvent inside holes of porous material. Moreover, cavitation produces micro-jets at the surface of the food material that may improve the exchange surfaces which has to be revealed globally through a high starting accessibility. Both effects can increase mass transfers of solvent within the solid and solute within the solvent [14, 19].

The intensification of the solvent extraction operation implies:

1. A grinding process, which normally allows the exchange surface to increase as well as the surface solute to be more accessible. Normally, granules are supposed to be spherical and compact.
2. An agitation allowing solute transport from the product surface to outside to be carried out by convection
3. A new texturing in order to expand the granules. An increasing of porosity to improve solute transfer in the solvent within the product; indeed, natural structure of vegetables and more specifically the cytoplasmic membrane and the cellular wall should not support the liquid transfer processes. The structure resistance often seems to be the principal restrictive factor of the operation kinetics.
4. In the expanded matrix, the use of ultrasonic treatment for solvent extraction should be a very relevant process for intensifying the whole operation.

Industries are willing to recover and value wastes. Citrus by-products are a good representation of this trend. Indeed, annual citrus production has doubled over the last 5 years and is now estimated at over 100 million tons, inducing a dramatic amount of wastes. Citrus by-products (peels) have interested several fields (agro-industry, cosmetics, flavoring, pharmaceutical...) in which their uses are diverse such as essence and fragrances [20], aromatherapy [21] and food flavoring [22].

Through several extraction steps it is possible to recover essential oils, antioxidant, pectin, etc. However, several matters regarding extraction could be listed mainly when performed on citrus peels. As a matter of fact citrus fruit outer peel, called flavedo, has a large number of very small glands, each containing a minute drop of essential oils. The common commercial techniques to produce essential oils from citrus peels are mechanical expression (cold pressing) or distillation (hydrodistillation or steam-distillation). Whether ancient or new techniques, it is mainly used to grounding the product before extraction [10] because of its structure permeability, which prevents an easy essential oil removal.

#### Nomenclature

$\langle T_v - T \rangle_{LN}$  the logarithmic mean of the difference of temperature between steam ( $T_v$ ) and product ( $T$ )

$v_d$	the velocity of the solid dry material ( $m \cdot s^{-1}$ )
$v_d$	the velocity of the solid dry material ( $m \cdot s^{-1}$ )
$v_s$	the velocity of the solute ( $m \cdot s^{-1}$ )
$\rho_d$	the apparent density of the solid dry material ( $kg \cdot m^{-3}$ )
$\rho_s$	the apparent density of the solute within the solid matrix ( $kg \cdot m^{-3}$ )
$c_e$	the specific heat of liquid essential oils in the material ( $J \cdot kg^{-1} \cdot K^{-1}$ )
$c_{pp}$	the specific heat at constant pressure of the product ( $J \cdot kg^{-1} \cdot K^{-1}$ )
$c_s$	the specific heat of dry material ( $J \cdot kg^{-1} \cdot K^{-1}$ )
$c_w$	the specific heat of liquid water in the material ( $J \cdot kg^{-1} \cdot K^{-1}$ )
$D_{eff}$	the effective diffusivity of liquid water within the solid medium ( $m^2 \cdot s^{-1}$ )
$h$	the coefficient of heat transfer by condensation and convection ( $W \cdot m^{-2} \cdot K^{-1}$ )
$K$	the permeability of the essential oil and water vapor mixture within the porous medium ( $m^2$ )
$L_e$	the essential oil vaporization latent heat ( $J \cdot kg^{-1}$ )
$L_m$ :	the mean of the specific latent heat of the essential oil and water mixture evaporation ( $J \cdot kg^{-1}$ )
$L_w$ :	the water vaporization latent heat ( $J \cdot kg^{-1}$ )
$M_e$ :	the Molar mass of essential oils ( $kg \cdot mol^{-1}$ )
$m_m$	the mass of evaporated essential oil and water mixture of per DIC cycle (kg)
$M_w$ :	the Molar mass of water ( $kg \cdot mol^{-1}$ )
$P$ :	the total pressure of the vapor of the mixture of water and essential oil (Pa)
$p_e$ :	the partial pressure of essential oils in the material (Pa)
$p_w$ :	the partial pressure of vapor in the material (Pa)
$Q_c$ :	the quantity of heat furnish by the steam to the surface of the product
$S$ :	the exchange surface ( $m^2$ )
$t$	the time (s)
$t_c$	the duration time of the heating stage (d) of a DIC cycle
$T_f$ & $T_i$	the product's final and initial temperatures, respectively; they usually are $T_f = T_v$ the temperature of saturated steam, and $T_i = T_e$ the "equilibrium temperature"
$V_m$	the velocity of the essential oil and water vapor mixture within the porous medium ( $m \cdot s^{-1}$ )
$V_s$	the absolute velocity of solid medium ( $m \cdot s^{-1}$ )
$V_s$	the absolute porous medium velocity ( $m \cdot s^{-1}$ )
$v_w$	the absolute velocity of liquid water flow within the porous medium ( $m \cdot s^{-1}$ )
$\lambda$	the effective conductivity of material ( $W \cdot m^{-1} \cdot K^{-1}$ )
$\nu_m$	the kinematic viscosity of the mixture of essential oils and water ( $m^2 \cdot s^{-1}$ )
$\rho_e$	the apparent density of liquid essential oils in the material ( $kg \cdot m^{-3}$ )

$\rho_m$	the apparent density of the essential oil and water vapor mixture ( $\text{kg m}^{-3}$ )
$\rho_s$	the apparent density of dry material ( $\text{kg m}^{-3}$ )
$\rho_w$	the apparent density of liquid water in the material ( $\text{kg m}^{-3}$ )
$\varphi$	the heat flow within the porous material ( $\text{W m}^{-2}$ )
A	a constant depending on the shape of solid material
X	the amount of solute extracted at time t ( $\text{mg.g}^{-1}$ dry material)
$X_\infty$	the amount of solute extracted at $t \rightarrow \infty$ ( $\text{mg.g}^{-1}$ dry material)
k	the transfer coefficient ( $\text{s}^{-1}$ )
$r_p$	a characteristic length depending on the shape of the product (half the thickness in the case of a plaque)
RM-SE	raw material extracted by solvent extraction;
RM-UAE	raw material extracted by ultrasound-assisted extraction;
DIC-SE	DIC treated material extracted by solvent extraction;
DIC-UAE	DIC treated material extracted by ultrasound-assisted extraction

## 2. Fundamentals:

### 2.1. Volatile compound extraction

#### 2.1.1. Steam extraction

Drying and extraction of volatile molecules from plants are normally considered as coupled heat and mass transfer processes taking place within the plant tissues as porous medium and at the exchange surface with the surrounding environment. The main part of the heat providing from the external medium is used to for a phase change (liquid-vapor) with a partial pressure, which is a temperature function. Heating is usually delivered at the exchange surface by convection (hot air, contact, overheated steam, IR...) and/or by condensation of saturated steam. Internal heat transfer is done through effective conduction. An internal evaporation takes place within the pores, with the partial pressure gradient as the driving force of the migration of various volatile molecule compounds.

In steam extraction, one can intensify the driving force in the surrounding atmosphere, which is normally the gradient of partial pressure, by increasing the ratio of the difference of temperature between the exchange surface of the material and the condenser over the distance between them. However, various mixing and mechanical motions can noticeably intensify much more such a transport of the volatile molecules.

At the surface, the temperature increases very rapidly the steam level, and will then gradually growths within the solid. The internal heat transfer is mainly processed by a similar conduction process with an effective conductivity as coefficient of the gradient of temperature. This effective conductivity of the porous structure closely depends on the whole porosity and pore size (which are revealed through the absolute expansion ratio  $\epsilon$ ), and water content. It is also closely linked to the phenomenon of evaporating/condensation taking place inside the holes.

$$\operatorname{div} \vec{\varphi} + (\rho_s c_{p_s} + \rho_e c_{p_e} + \rho_w c_{p_w}) \frac{\partial T}{\partial t} + \frac{\partial \left( p_e \varepsilon \frac{M_e L_e}{RT} + p_w \varepsilon \frac{M_w L_w}{RT} \right)}{\partial t} = 0 \quad (1)$$

As the interne transfer is carried out by conduction:

$$\operatorname{div} \left( -\lambda \cdot \vec{\operatorname{grad}} T \right) + (\rho_s c_{p_s} + \rho_e c_{p_e} + \rho_w c_{p_w}) \frac{\partial T}{\partial t} + \frac{\partial}{\partial t} \left[ \frac{\varepsilon}{RT} (p_e M_e L_e + p_w M_w L_w) \right] = 0 \quad (2)$$

The main part of such heat flow is “only” used for evaporating essential oils and water; the repartition of temperature may be assumed to be stationary during the main part of the operation:

$$\operatorname{div} \left( -\lambda \cdot \vec{\operatorname{grad}} T \right) + \frac{\partial}{\partial t} \left[ \frac{\varepsilon}{RT} (p_e M_e L_e + p_w M_w L_w) \right] = 0 \quad (3)$$

The internal evaporation inside the holes closely depends of temperature through the partially pressure of water and each volatile compounds. The saturation state of water leads to study the operation, a thermodynamic balance of water; only the essential oil partially pressure would take place:

$$-\lambda \vec{\nabla} \cdot \vec{\nabla} T + \varepsilon M_e L_e \frac{\partial}{\partial t} \left[ \frac{p_e}{RT} \right] = 0 \quad (4)$$

A liquid water transfer process may be conducted by complex phenomena of liquid/solid interaction (permeability, capillary force, molecular diffusivity...) depending on the nature of the solid in which the migration is done. In steam extraction, it can be assumed negligible the transfer of essential oils under the liquid phase. The migration of volatile molecules is a general operation, which may be conducted by diffusion of the gas phase gradient (interaction gas/solid). It also depends on several factors, including temperature, but also the matter structure (porosity ratio, permeability, secretion element walls...). Water liquid and vapor and essential oil mass transfers within the plant as a porous medium, should be assumed to be the limiting process because it would be much slighter than the heat transfer. The transfer of essential oils, assumed to be a diffusion of gas phase, can be considered as a similar Fick's diffusion of gas phase, with an effective diffusivity  $D_{eff}$  and the partial pressure gradient of each volatile compound as driving force:

The Allaf's [13] formulation of Fick-type law can be:

$$\left( \frac{p_e}{\rho_s} \right) (\vec{v}_e - \vec{v}_s) = -D_{eff} \vec{\nabla} \left( \frac{p_e}{\rho_s} \right) \quad (5)$$

By neglecting the possible shrinkage or expansion phenomena during this operation, one can assume that  $\rho_s$  = constant and  $v_s = 0$ ; the equation (5) becomes

$$p_e \vec{v}_e = -D_{eff} \vec{\operatorname{grad}} p_e \quad (6)$$

As the external water vapor partial pressure is saturated, one can assume the internal vapor partial pressure  $p_w$  within the porous material as approximately constant, it can be postulated:

$$-\lambda \operatorname{div}(\vec{\operatorname{grad}} T) + \varepsilon M_e L_e \frac{\partial}{\partial t} \left[ \frac{p_e}{RT} \right] = 0 \quad (7)$$

With one dimension  $r$ , it is possible to have:

$$(p_e/T) V_e = -D_{eff} \left( \frac{\partial (p_e/T)}{\partial r} \right) \quad (8)$$

$$-\lambda \frac{\partial^2 T}{\partial r^2} + \varepsilon M_e L_e \frac{\partial}{\partial t} \left[ \frac{p_e}{RT} \right] = 0 \quad (9)$$

On the other hand, as  $(p_e/T)$  is as higher as the temperature is higher:

$$\frac{\partial (p_e/T)}{\partial T} > 0 \quad (10)$$

The values of  $(p_e/T)$  are then higher at the exchange surface than in the granule heart, and the essential oil flow obviously follows the temperature flux. This conclusion reveals the **paradox** of Al-Haddad et al.; the gradient of mass transfer is directed from the surface to the sample core with a motion of essential oils completely opposite to that required for the sought extraction operation. In the usual steam extraction of essential oils, the process is achieved by normally time-consuming progressive front kinetics.

This justifies why to reduce the granule size. Nevertheless, it is possible to remedy this paradoxical situation by using microwave heating and/or transferring volatile molecules by the Total Pressure Gradient TPG (Darcy's law) as a driving force issued from DIC process; it makes a notable improvement in the kinetics.

## 2.1.2. Instant Autovaporization of Essential oil

### 2.1.2.1. General approach

As extraction process, DIC is based on the phenomenon of **autovaporization** of volatile compounds. It is to subject the raw material for a short period of time to high-pressure saturated steam with almost 0.1 to 0.9 MPa according to the product; temperature is identified to be between 100 and 175°C. Water and essential oil vapors get then **an internal total pressure** normally equal to the surrounding environment total pressure. Indeed, after this high-temperature/short-time stage, an abrupt pressure drop towards a vacuum of about 5 kPa happens with a rate  $\Delta P/\Delta t$  usually higher than 0.5 MPa/s. It simultaneously provokes an abrupt autovaporization as well as an instantaneous cooling of the residual solid. The thermal degradation of the product immediately stops. Rheological behavior of this material allows swelling even breaking the cell and likely secretion element walls. The new porous structure enhances mass transfer through higher permeability and diffusivity. However, the main transfer of

essential oil vapor occurs just after the instant pressure drop from the core of material to its surface with the gradient of total pressure as driving force (Darcy-type law) [19].

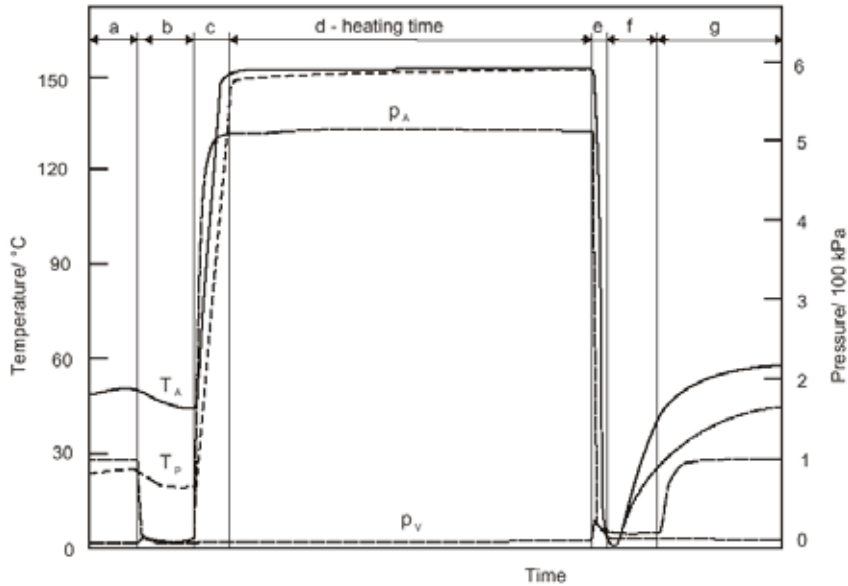


Fig. 1. Temperature and pressure evolutions during a DIC processing cycle.  $P_A$  steam pressure in autoclave,  $P_V$  pressure in vacuum tank,  $T_A$  temperature in autoclave,  $T_p$  temperature of product: (a) sample at atmospheric pressure; (b) initial vacuum; (c) saturated steam injection to reach the selected pressure; (d) constant temperature corresponding to saturated steam pressure; (e) abrupt pressure drop towards vacuum; (f) vacuum; (g) releasing to the atmospheric pressure

#### 2.1.2.2. Usual analysis of various DIC stages

During the heating stage (Fig. 1. d) of DIC cycle, the coefficient of heat transfer mainly by condensation and by convection  $h$  expressed on ( $W m^{-2}K^{-1}$ ) of saturated steam has a very great value, and the exchange surface final temperature is reached in very short time. Therefore, the heat flux from the steam to the product is:

$$\varphi = hS(T_v - T) \quad (12)$$

and the quantity of heat during the thermal treatment time of a cycle is:

$$Q_c = hS \langle T_v - T \rangle_{LN} t_c \quad (13)$$

As it takes place after an initial vacuum stage (Fig. 1.b), the closer contact between the external product surface and steam ensures higher value of the exchange surface  $S$ ; thus intensifying this process. During this same stage, the heat and liquid transfers within the product are carried out by conduction (a Fourier-type law) and diffusion (Fick's type law), respectively:

$$\varphi = -\lambda_{eff} \cdot \vec{grad}T \quad (14)$$



$$\frac{\rho_w}{\rho_s}(\vec{v}_w - \vec{v}_s) = -D_{eff} \vec{\nabla} \left( \frac{\rho_w}{\rho_s} \right) \quad (15)$$

[23] During this stage (d), no expansion is noted;  $\rho_s$  keeps constant with  $v_s = 0$ . The equation (15) becomes:

$$\rho_w \vec{v}_w = -D_{eff} \vec{\nabla} \rho_w \quad (16)$$

And with one-dimension radial transfer:

$$\rho_w v_w = -D_{eff} \frac{\partial \rho_w}{\partial r} \quad (17)$$

By using mass conservation and the continuity, the second Fick law becomes:

$$\frac{\partial \rho_w}{\partial t} = \frac{\partial}{\partial r} \left( D_{eff} \frac{\partial \rho_w}{\partial r} \right) \quad (18)$$

Thus, the diffusivity  $D_{eff}$  can be assumed as constant since the both internal structure and temperature are supposed homogeneous. The second Fick's law becomes:

$$\frac{\partial \rho_w}{\partial t} = D_{ws} \frac{d^2 \rho_w}{dr^2} \quad (19)$$

The time  $t_c$  of such a stage (d) must generally be defined to avoid any thermal degradation while getting the homogeneity and uniformity of both temperature  $T$  and moisture content  $\rho_w$  in the product. Usually, the product quickly reaches the steam temperature while the amount of added moisture absorbed by the product from the surrounded saturated steam during this (d) stage will be:

$$m_v = Q/L = m_s (c_{ps} + \langle Wc_{pw} \rangle) (T_f - T_i) \quad (20)$$

After the pressure drop stage (e) and during the vacuum stage (f), the deep total pressure in the porous medium is mainly due to the water and essential oil vapor. The internal gas transfer is carried out in a homogeneous and isotropic medium. The main driving force of such a transfer from the core towards the surface of the porous plant and then the transport to the surrounding medium is the gradient of the total pressures; Allaf's formulation of Darcy's law is:

$$\rho_m (\vec{V}_m - \vec{V}_s) = -\frac{K}{v_m} \vec{\nabla} P \quad (21)$$

One could observe that the expansion is obtained in a very short time, afterward  $V_s = 0$ . By assuming a one-dimension radial transfer within a spherical shape material, Eq. 21 becomes:

$$\rho_m V_m = - \frac{K}{v_m} \frac{\partial P}{\partial r} \quad (22)$$

By using mass conservation and the continuity, and by integrating between the hole (whose radius  $R_o$ ) and the external radius  $R_s$  of the spherical shape Eq. 23 becomes:

$$\dot{m}_m = 4\pi \frac{K}{v} \frac{(P_o - P_{ext})}{\left(\frac{1}{R_o} - \frac{1}{R_s}\right)} \quad (23)$$

The value of the total pressure  $P_o$  in the hole decreases versus the time  $t$ , depending of the flux  $\dot{m}_m$ . The time  $t_v$  of such a stage (f) must generally be defined for allowing the vapor mixture to be transferred towards the surrounding medium.

One can assume the quantity of essential oil and water vapor mixture issued from the autovaporisation to be:

$$m_m = Q/L_m = m_p c_{pp} (T_f - T_i) \quad (24)$$

DIC process seems to be a highly relevant operation for remedying the paradoxical phenomenon and greatly intensifying the internal transfer of essential oil through the Total Pressure Gradient TPG instead the normal Fick diffusion phenomenon.

## 2.2. Standard solvent extraction vs Ultrasound assisted extraction

Solvent extraction as a solid/liquid interaction aims at withdrawing soluble components out of solids. This operation is, from a technological point of view, a diffusion phenomenon of a carrier fluid (liquid) within a porous solid in order to bring out specific molecules using a solvent capable of “solubilizing” one or more components from a solid (or a liquid). The extract solution (solvent + solute) is also transferring within the porous solid through a diffusion process.

The transfer of these active molecules to the surroundings occurs through a diffusion that is mainly the result of a concentration gradient of solute between the inner solution near the solid phase (more concentrated) and the liquid phase. At the end of the operation, the system tends toward the equilibrium and the diffusion transfer becomes nil. In contrast, if the liquid phase is continuously renewed, the diffusion continues until the complete exhaustion of the solid phase.

At the end of the operation, the exhausted solid (residue), inert or insoluble, contains very little or no solute at all [13].

The whole operation with possible intensifications was studied [13].

## 2.3. Intensification processes

### 2.3.1. External transport:

Transport of solute from the surface of solid within the external solvent is usually done by **diffusion** from the high solute concentration (close contact with the solid exchange surface) toward low concentration zone with the gradient of solute concentration as the driving force.

$$\frac{\rho_{solute}}{\rho_{solvent}} (\vec{v}_{solute} - \vec{v}_{solvent}) = -D_{solute-solvent} \vec{\nabla} \left( \frac{\rho_{solute}}{\rho_{solvent}} \right) \quad (25)$$

Different methods are usually used to intensify these external transfer phenomena, such as:

- Choosing the best solvent in terms of:
  - Getting the highest desired solute solubilization
  - Getting the lowest viscosity to obtain the best diffusivity  $D$  of solute within the solvent.
- Establishing external mechanical agitation to let external mass transport to be done by **convection** instead of **diffusion**.
- Renewing external solvent to reduce solvent solute concentration:
  - improving the difference between the exchange surface and the whole solvent concentrations;
  - being as far as possible from solute saturation level in the solvent.

Once the external transport is adequately intensified, internal transfers should become the limiting processes.

### 2.3.2. Internal transfers:

Two main types of internal transfer phenomena have to be analyzed: The solvent to be transferred from the exchange surface within the solid matrix, and the solute to be transferred within the solvent situated inside the holes of the porous materials. The adequate intensification methods to be envisaged depend on these two phenomena:

1. To intensify the solvent transfer from the exchange surface within the solid matrix, one has firstly to note that the various processes (diffusion, capillarity, osmosis...) from high solvent concentration toward low solvent concentration are globally carried out with the gradient of solvent concentration as the driving force with  $D_{eff}$  as effective diffusivity.

$$\frac{\rho_{solvent}}{\rho_{solid}} (\vec{v}_{solvent} - \vec{v}_{solid}) = -D_{eff} \vec{\nabla} \left( \frac{\rho_{solvent}}{\rho_{solid}} \right) \quad (26)$$

The intensification method has then to be achieved by:

- 1.1. Expanding matrix structure by détente instantanée contrôlée DIC (French for "Instant controlled pressure drop") to let effective diffusivity  $D_{eff}$  and effective exchange surfaces be higher.
- 1.2. Selecting the lowest viscosity solvent to increase solvent diffusivity within the solid.
- 1.3. Reducing cell walls resistance through cavitation (Ultra-Sound US) with possible destruction of cell walls mainly generated through higher DIC or US severity.
2. The transfer of solute within the solvent situated inside the holes of porous materials is usually achieved by diffusion from high solute concentration toward low solute concentration zones with the gradient of solute concentration in the solvent as the driving force with  $D$  as the standard solute-solvent diffusivity.

$$\frac{\rho_{solute}}{\rho_{solvent}} (\vec{v}_{solute} - \vec{v}_{solvent}) = -D_{solute-solvent} \vec{\nabla} \left( \frac{\rho_{solute}}{\rho_{solvent}} \right) \quad (27)$$

The different intensification methods, which can be envisaged, are:

- 2.1. To expand matrix structure: since the solute-solvent process closely depends on the amount of solvent inside the porous material holes, one has to let the solvent be present in higher quantity inside the solid by increasing the porosity. This can normally be realized by DIC,
- 2.2. To ensure a solute-in-solvent **micro-convection** inside the holes instead of the **natural diffusion**: US should realize such a micro-convection in the internal solvent and the operation can be postulated by a similar diffusion model within the porous solid with an effective diffusivity  $D_{US}$  normally much higher than standard solute-solvent diffusivity  $D$  :

$$\frac{\rho_{solute}}{\rho_{solid}} (\vec{v}_{solute} - \vec{v}_{solid}) = -D_{US} \vec{\nabla} \left( \frac{\rho_{solute}}{\rho_{solid}} \right) \quad (28)$$

Thus the advantages of ultrasonic extraction are as follows: reducing both extraction temperature and time; decreasing solvent quantity; and improving solute extraction yield. Oscillatory particle motion produced by high-intensity ultrasonic waves can also induce secondary flows, known as acoustic streaming. Such an agitation should realize an internal convection motion of solute within the solvent inside holes of porous material. It has to be revealed globally through a higher effective diffusivity  $D_{US}$ .

Moreover, cavitation produces microjets at the surface of the food material that may improve the exchange surface, which has to be revealed globally through a high starting accessibility.

Both effects can increase mass transfers of solvent within the solid and solute within the solvent. Therefore, cavitation induced cell disruption and dispersion of suspended solids coupled with enhanced mass transfer rates due to acoustic streaming are believed to be responsible for the improved extraction [14, 19].

#### 2.4. Kinetic calculation: diffusivity and starting accessibility

In any solvent extraction achieved on plants (porous solid material), the main part of the operation is controlled through various penetration processes of the solvent within the material (capillarity, molecular diffusivity...), possibly coupled with convection within the holes of such a porous solid material. The driving force for global operation is the gradient of concentration and the model can be similar to Fick Law with a global effective diffusivity  $D_{eff}$  as the process coefficient [13].

$$\frac{\rho_s}{\rho_d} (\vec{v}_s - \vec{v}_d) = -D_{eff} \vec{\nabla} \left( \frac{\rho_s}{\rho_d} \right) \quad (29)$$

From the experimental data,  $D_{eff}$  has to be computed, normally using Crank calculation [24]. In our cases, it would be possible to limit this model to the first term:

$$\frac{X_{\infty} - X}{X_{\infty}} = A e^{-kt} \quad (30)$$

However, in any solvent extraction, before starting the “diffusion stage” there is the interaction between the solvent and the exchange surface of the porous solid. This first stage is not part of the

diffusion mode. One has to exclude from the total kinetic data the ones near to  $t=0$  in order to model the diffusion part.

Here, this is true at  $t \geq t_0$ . In the present case, which was assumed to be a semi infinite plaque ( $A = \frac{8}{\pi^2}$ ), we retained  $t_0 = 5 \text{ min}$ , and:

$$\frac{X_\infty - X_{t_0}}{X_\infty} = \frac{8}{\pi^2} e^{-kt_0} \quad (31)$$

and

$$\frac{X_\infty - X}{X_\infty - X_{t_0}} = e^{-k(t-t_0)} \quad (32)$$

$X_\infty$  is the maximum solute extracted with the best extraction process and  $X_{t_0}$  the solute extracted after  $t_0=5 \text{ min}$  of extraction.

The time evolution term  $k$  can be obtained as the slope of the linear model

$$\ln\left(\frac{X_\infty - X}{X_\infty - X_{t_0}}\right) = f(t) \quad (33)$$

we then can calculate the effective diffusivity  $D_{eff}$  from:

$$k = \frac{\pi^2 D_{eff}}{4r_p^2} \quad (34)$$

By extrapolating this diffusion model till  $t = 0$  one can calculate the theoretical value  $X_0 = X_{t=0}$  normally distinct from the initial value of  $X=0$ ;  $\delta X_s = X_0$  is defined as the **starting accessibility**.

### 3. Experiments

In order to illustrate fundamental aspects we gathered information from the article [25]. The following part shows the elements regarding experimental results obtained regarding instant autovaporization of essential oils and extraction of antioxidant via ultrasound achieved on DIC treated orange peel.

Within the experimental study, two main steps were performed on the dried orange peels (*Citrus sinensis*) from Burkina Faso, as shown in Fig. 2. First we achieved the extraction of essential oils by instant controlled pressure drop technology and afterwards we recovered the solid residue to realize the extraction of antioxidants via both, solvent extraction and ultrasound assisted extraction.

#### 3.1. Essential oil extraction via Instant controlled pressure drop technology

DIC lab-scale equipment was from the company ABCAR-DIC Process (La Rochelle, France). The reactor we used was a 7-liter processing vessel with a heating jacket; thermal treatment in this vessel is achieved using saturated steam with a pressure varying from 5 kPa up to 1 MPa (Fig. 2). A 0.35 m<sup>3</sup>

vacuum tank is connected to the treatment chamber via an “instant” pneumatic valve ensuring its opening in less than 0.2 s.

A DIC cycle can be fractionated through seven steps as shown in Fig. 1.: Saturated steam pressure  $P_A$  evolves in autoclave, implying a similar evolution of temperature  $T_A$  in the autoclave and the temperature of the product  $T_P$ , while  $P_V$  is the pressure in the vacuum tank. DIC cycle can be divided within the following steps:

1. inserting the product sample at atmospheric pressure in the processing vessel;
2. establishing a gradual (non-instantaneous) initial vacuum;
3. injecting a saturated steam to reach a selected pressure;
4. keeping high-pressure/high-temperature stage at a constant level during one-DIC-cycle processing time period
5. abruptly establishing pressure drop towards a vacuum;
6. maintaining the vacuum level during a defined vacuum-time;
7. releasing pressure towards the atmospheric pressure and withdraw the solid.
8. subsequently recuperating the essential oils and other expelled molecules from the condensation system

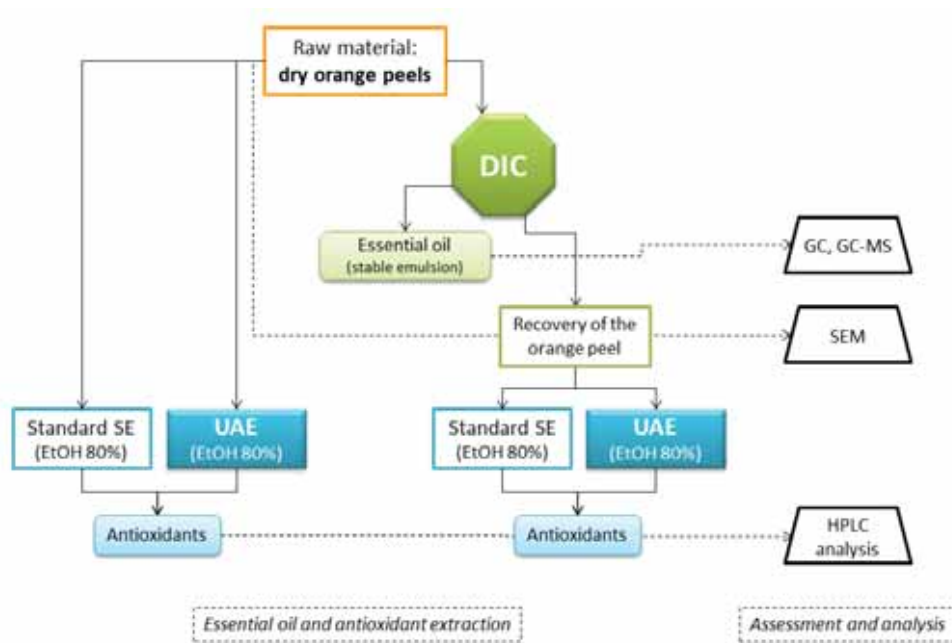


Fig. 2. Essential oil and antioxidant extraction protocol

DIC treatment enabled the extraction of  $1.66 \cdot 10^{-2}$  g/g dmof essential oil through autovaporization (Eq. 21 to 24) within 2 minutes. DIC essential oil was analyzed by gas chromatography enumerating essential oil compounds gathered in groups (oxygenated and non-oxygenated fractions). While monoterpene hydrocarbons are less valuable than oxygenated compounds in terms of their contribution to the fragrance of the essential oil, oxygenated compounds are highly odoriferous and, hence, the most valuable. Total

oxygenated compounds for DIC treatment were  $6.29 \cdot 10^{-4}$  g/g dm. Extraction efficiency of essential oil was higher than 98% of essential oil with the chosen parameter.

### 3.2. Comparative extraction yields and kinetics of SE and UAE

According to HPLC analyses, yields and kinetics of hesperidin extracted from the three products (RM and DIC treated materials) during 1 hour of SE or UAE were compared.

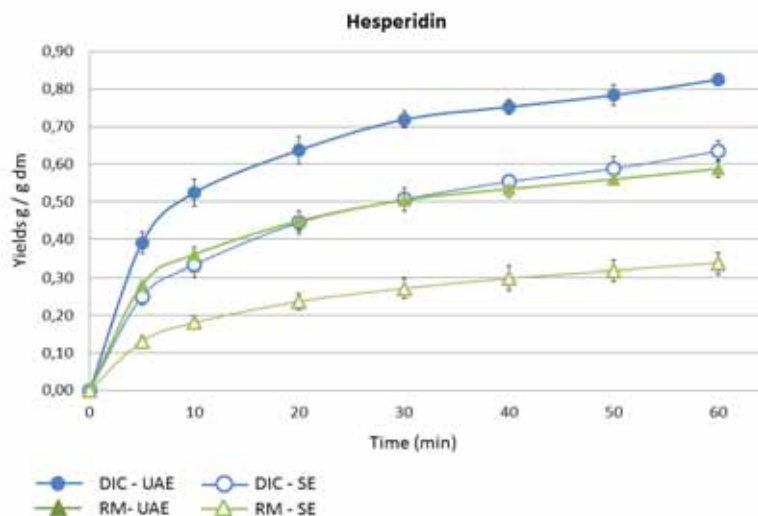


Fig. 3. Ultrasound assisted extraction and standard solvent extraction of hesperidin from DIC treated and untreated orange peel

Hesperidin kinetics was gathered in Fig. 3. Extraction kinetics of hesperidin mostly shows the same trends, which gave the possibility to perceive and deduce the action of each process used. It is however interesting to note that regarding hesperidin extraction, DIC-SE and RM-UAE have the same trends, yet combining them gave a complementary effect. Indeed, both effects were acting on two different side of the extraction enhancement. DIC opened the cells enabling an easy diffusion, ultrasound, through its agitation, generated an internal convection motion of solute within the solvent.

After 60 min of extraction, it was possible to observe important differences in terms of yields and extraction rate; With raw material, one hour standard SE generated a yield of  $0.34 \pm 2.8 \cdot 10^{-2}$  g of hesperidin/g dm. By using UAE treatment for raw material, this solvent extraction became intensified to  $0.18 \pm 1.7 \cdot 10^{-2}$  g of hesperidin/g dm. With DIC treated solid samples, one hour standard SE generated a yield of  $0.64 \pm 2.7 \cdot 10^{-2}$  g of hesperidin/g dm. By coupling DIC treated solid samples to UAE treatment, this solvent extraction became intensified to  $0.83 \pm 1.6 \cdot 10^{-2}$  g of hesperidin/g dm.

Consequently, combining DIC to UAE enabled to highly improve the antioxidant extraction yields with trends in terms of kinetics dramatically improved compared to standard processes. This is illustrated in Eq. 25 to Eq. 28.

To obtain a thorough kinetics analyses, diffusivity and starting accessibility calculation was undergone. The modeling analysis of extraction kinetics based on the surface exchanging and internal diffusion which are revealed respectively by starting accessibility and effective diffusivity enabled us to

show these aspects as shown in Table 1. The raw material extracted with standard SE (RM-SE) was taken as the comparison basis. With regards to hesperidin extraction, the effective diffusivity and starting accessibility of DIC-UAE are respectively 9.5 and 4 time higher than that of RM-SE (Eq. 29-34).

Table 1. Diffusivity and starting accessibility of solvent within different matrices

	Effective diffusivity $D_{eff}$ ( $10^{-11} m^2/s$ )	Improvement of effective diffusivity (%)	Starting accessibility $dX_s = X_0$ (g / g dry matter)	Improvement of starting accessibility (%)	Time (min) for getting 95% of final extraction $t_{95\%}$
Hesperidin					
RM-SE	2.74	100%	0.122	100%	479
RM-UAE	6.31	231%	0.270	222%	193
DIC-SE	8.91	326%	0.266	219%	150
DIC-UAE	26.10	954%	0.506	416%	49

### 3.3. Impact of treatments on microstructure

3.3.1. Micro-structures were observed using an environmental type JEOL5410LVFEI Quanta 200F Scanning Electronic Microscope (SEM) (Philips Croissy-sur-Seine; France).

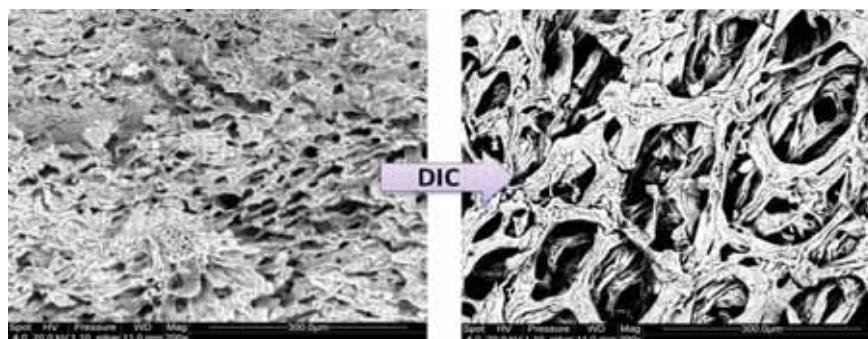


Fig. 4. Scanning electron microscopy of untreated (left) and DIC treated (right) orange peels

It is well known that DIC treatment can modify the structure of plant at various and controlled levels although this is highly dependent on the operating parameters [11, 12]. Such modifications from interstitial zone to broken cell walls can greatly modify structural characteristics. It would be then possible to control functional and technological capacities that help to greatly intensify mass transfer phenomena by improving diffusivity and permeability within the matrix. In the case of orange peel, the SEM images revealed structural differences between raw material and DIC treated samples. Before DIC treatment (Fig. 4), the product had a slightly compact and relatively well organized cell structure. On the one hand, the impact of DIC treatment, which led to an evident expansion of the structure, has kept the main part of the cells intact thus proving the great structural stability of the leaves.



## 4. Conclusion

Fundamental studies on solvent extraction allowed defining the limiting process, hence enabling to propose the expansion by instant controlled pressure drop (DIC) sequentially combined with ultrasound-assisted extraction as intensification means. Both operations were coupled generating an increase two parameters defining the kinetics: the effective diffusivity  $D_{\text{eff}}$  and the starting accessibility  $\delta X_s$ .

In order to recover and recycle wastes from citrus processing, a quite thorough study was achieved on sweet dried orange peels. We studied both, fundamental and experimental aspects regarding two innovative technologies, instant controlled pressure drop and ultrasound processes. We hence could define whether in terms of antioxidant extraction DIC and ultrasounds can be complementary. We compared the effect of Ultrasound Assisted Extraction (UAE) to standard Solvent Extraction (SE) both achieved on dried orange peels as raw material and instant controlled pressure drop (DIC) treated material.

Pre-treatment by DIC can improve antioxidant extraction yields and kinetics as well as UAE. The highest yield of hesperidin with best kinetics is obtained by coupling both treatments. We also noted that UAE treatment generated a higher antioxidant activity than standard SE and even higher when UAE is undergone on DIC treated matrix. The impact of DIC on microstructure delivered a reliable explanation regarding our results. The swelling of the cells enabled a better kinetic extraction in terms of diffusivity and starting accessibility. Accordingly, former experimental results were here highlighted and modeled via fundamental aspects.

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