

Impact of Instant Controlled Pressure Drop (DIC) Treatment on Drying Kinetics and Caffeine Extraction from Green Coffee Beans

I. Kamal

University of La Rochelle

Laboratory of Engineering Science for Environment(LaSIEFRE-CNRS 3474)

Avenue Michel Crepeau

La Rochelle 17042, cedex 01, France

E-mail: imustaph@univ-lr.fr

A. Gelicus

University of La Rochelle

Laboratory of Engineering Science for Environment(LaSIEFRE-CNRS 3474)

Avenue Michel Crepeau

La Rochelle 17042, cedex 01, France

E-mail: anthony.gelicus@univ-lr.fr

K. Allaf

University of La Rochelle

Laboratory of Engineering Science for Environment(LaSIEFRE-CNRS 3474)

Avenue Michel Crepeau

La Rochelle 17042, cedex 01, France

Tel: 33-546-458-766 E-mail: kallaf@univ-lr.fr

Received: October 19, 2011

Accepted: November 4, 2011

Published: February 1, 2012

doi:10.5539/jfr.v1n1p24

URL: <http://dx.doi.org/10.5539/jfr.v1n1p24>

Abstract

The present work is directed towards the impacts of Détente Instantanée Contrôlée DIC (French, for instant controlled pressure-drop) in terms of decaffeination and drying of Ethiopian green coffee beans (GCBs). DIC consisted in subjecting the product to a high-pressure saturated steam during some seconds and ended with an abrupt pressure drop towards a vacuum. A conventional aqueous extraction and a hot air-drying took place after DIC treatment. In this study, Response Surface Method (RSM) was used with DIC saturated steam pressure P , thermal treatment time t , and initial moisture content W as the independent variables. Both direct DIC extract recovered from the vacuum tank and the aqueous extracts were analyzed and quantified using the reversed phase-HPLC. With decaffeination ratios as dependent variables, P and W were the most significant operating parameters; while t was much weaker. Total decaffeination ratio could reach 99.5% after DIC treatment at specific conditions of $W=11.00\%$ db, $P=0.1$ MPa, and $t=35$ s while it was only 58% when achieved with untreated raw material.

The effective diffusivity D_{eff} and the starting accessibility δW_s were calculated from the diffusion/surface interaction kinetic model of hot air drying after DIC treatment. They dramatically increased with P and t while W had a weak impact. Thus, at the optimized DIC conditions, D_{eff} and δW_s increased from 0.33 to 12.60 $10^{-10} \text{ m}^2 \text{ s}^{-1}$ and from 0.75 to 11.53 g/100 g db, respectively. Drying time needed to reach 5% db became 60 min instead of 528 min for untreated raw material.

Keywords: Green coffee beans (GCBs), Instant Controlled Pressure Drop (DIC), Drying kinetics, Caffeine extraction, Reversed phase-HPLC, Response Surface Methodology (RSM)

1. Introduction

Coffee is the second popular beverage worldwide, and is one of the most important commodities in international trade. The two well-known species of coffee trees, which are Coffee Arabica and Coffee Robusta, present high commercial importance. They differ in chemical composition; Arabica contains more lipids and Robusta contains more caffeine and sucrose as well as the polyphenols antioxidant chlorogenic acid and its derivatives (Parliament and Stahl, 1995).

The term “green coffee beans” GCBs refers to un-roasted mature or immature coffee beans. Caffeine content in green coffee beans varies markedly between species and within species (Robusta vs. Arabica), mainly depending on geographic origins (Rodrigues et al., 2007). It is reported that it ranges from 1.22% in Arabica to 2.54% dry basis (or g/100 g of dried coffee) in Robusta (Kyet et al., 2001). Huge number of studies focused on coffee, its composition, flavor and quality characteristics (De Maria et al., 1996; De Maria et al., 1994; Sarrazinet al., 2000; Franca et al., 2005).

Caffeine (1,3,7-trimethylxanthine) paid lot of attention. Caffeine is one of the most notorious compounds because of its many physiological effects on the human body, and scientific studies have linked caffeine to the prevention of some related-age disease (Glade, 2010). However, caffeine acts as a central nervous system stimulant and also has negative withdrawal effects (Smith, 2002); as a result, decaffeinated coffee is being used to overcome its negative effects. Thus, from marketing point of view, the decaffeinated coffee green beans have an important economical value. Conversely, it was found that caffeine has had particular interest for pharmaceutical, cosmetic and satiety applications. Both caffeine extract and coffee intakes were modestly and inversely associated with weight gain (James et al., 2006).

Decaffeination processes are usually carried out in order to dramatically reduce the caffeine level. Decaffeinated coffee beverage should reach a caffeine level nearly 0.04 g/100 g of dried coffee (Fujioka et al., 2008). Literature survey showed huge information on the attempts used for decaffeination. Different factors having an impact on the decaffeination process include blend composition, brewing extraction rates, grind or water temperature (Maeso et al., 2006). Processes such as organic solvent extraction, with or without ultrasound treatment, have been used for decaffeination. However, it is difficult to completely remove the traces of solvent from end-decaffeinated products and the highest level admitted by the international standards is increasingly restrictive (Wang & Weller, 2006). The final distillation stage would also lead to a great loss of light compounds. Other operations have used the supercritical CO_2 as solvent (Icen & Guru, 2009). Although attractive with low operating costs, the disadvantages of this extraction process are the costly facilities required and a cumbersome installation. Note that supercritical CO_2 process as well as microbial and enzymatic methods (Gokulakrishnan et al., 2005) are not selective and can extract not only caffeine but also volatile molecules (Clarke, 2003). The energy costs, together with low kinetics, render the main part of these extraction processes unattractive from an economic point of view.

Other caffeine extraction processes such as microwave-assisted extraction have been proposed (Wang et al., 2011). They offer some advantages regarding kinetics and preservation of the chemical composition, but as far as we know, no industrial development has been achieved and all applications are still at the laboratory scale. No work has used high temperature processes for decaffeination, although such operations would be interesting in coffee industry. Conversely, no steam decaffeination process has been defined or highlighted probably because of the relatively high boiling temperature of caffeine. However, it was noted that the roasting process altered the amount of caffeine in coffee bean. A common misconception is that the darker the roast level, the lower the caffeine content. A small amount of caffeine is lost due to sublimation. This occurs in caffeine at approximately 178 °C, however, the thermodynamic parameters of caffeine have been the subject of various studies (Griesser et al., 1999; Cuong et al., 2010; Emelyanenko & Verevkin, 2008).

In this context, it was proposed to carry out a study of the possible extraction of caffeine from the Ethiopian Green Coffee Beans GCBs using the innovative technology of Détente Instantanée Contrôlée DIC (French, for instant controlled pressure-drop) through a direct DIC extraction and an intensification of the environmentally friendly aqueous extraction thanks to the DIC-expansion.

DIC was defined in 1988 (Allafet et al., 1988) as a high temperature-short time stage usually carried out by establishing high-pressure saturated steam-high temperature (0.1 to 0.7 MPa relating with 100 to 165 °C during 5 to 60 s). This is followed by an instant pressure drop towards a vacuum at about 5 kPa at a rate $\Delta P/\Delta t$ higher than 0.5 MPa s⁻¹. It simultaneously provokes an autovaporization of a part of the water and other volatile molecules within the product, and induces a swelling effect. An instant cooling of the products is capable to immediately stop

thermal degradation. Depending on the severity of the treatment, the structure can be slightly or greatly modified. Also, the operating conditions can preserve or break the cell walls. DIC has been studied, developed, optimized and used at industrial scale. DIC ensues as specific unit operations of decontamination (Mounir & Allaf, 2009), texturing (Kamal et al., 2008), and volatile compounds extraction from plants (Kristiawan et al., 2008). DIC also involves as a particular treatment achieved in order to intensify hot air drying, solvent extraction of non-volatile molecules such as flavonoids (Berka-Zougali et al., 2010), and other chemical or enzymatic reactions.

The technology was introduced to different sources of coffee beans prior to the roasting process. DIC treatment showed an interesting impact on expanding the bean microstructure (Kamal et al., 2008).

DIC has made every relevant extraction of essential oils, in spite of the high boiling point of certain molecules to about 220°C. The most instructive studies were reported by (Kristiawan et al., 2008; Berka-Zougali et al., 2010; Besombes et al., 2010), total extraction could be obtained in less than 4 min. Other research works proved that DIC used as a texturing pretreatment could dramatically intensify solvent extraction (Benamor & Allaf, 2009).

Works regarding the detection and quantification of caffeine in complex media can be found in the literature (Belay et al., 2008). Among them are the ultraviolet-visible spectroscopy and its derivatives (Belay, 2010), Liquid Chromatography (Pistos & Stewart, 2004; Hywel et al., 2010), and gas chromatography (Espinoza-Perez et al., 2007). However, these works are focused on extraction and monitoring methods.

Finally, in terms of experimental design, we did not use in this study the one-factor-at-a-time approach, because it is time-consuming, expensive and doesn't allow evaluating the interaction effects among the various operating parameters. RSM (Response Surface Methodology) could overcome these difficulties by accounting the possible interaction effects between operating parameters in terms of various outputs. RSM has been successfully used to model and optimize biochemical and biotechnological processes related to food systems (Silva et al., 2007; Pompeu et al., 2009; Berka et al., 2010).

2. Materials and Methods

2.1 Reagents and chemicals

All the materials used in this work are of analytical grade obtained from Fluka Chemie GmbH, Buchs, Switzerland.

2.2 Plant material

In this study, we used locally available Ethiopian green coffee beans. The first pretreatment involved grinding to 7-mm particles, which were then soaked in water bath at ambient temperature to reach predefined values of water content. Moisture content was measured using the oven method. The measurements were triplicated and conducted on a 3 g of GCBs, placed in a thin layer glass capsule and dried in the oven at 105.5°C for 24 h. The moisture content was determined between the initial raw material value of $11.00\% \pm 0.2\%$ db (dry basis: g H₂O/100 g dry matter) up to $35 \pm 0.2\%$ db for soaked grains.

2.2.1 Protocol of treatment

In the present study, the treatment design was achieved as illustrated in Figure 1.

2.2.2 Instant controlled pressure drop DIC treatment and equipment

DIC reactors have been presented in numerous articles (Besombes et al., 2010; Kamal and Allaf, 2011; Ben Amor et al., 2009). In the present work, the reactor used was a new developed version of DIC apparatus (Micro-DIC provided from ABCAR-DIC Process, La Rochelle, France) (Figure 2). It is a 30 cc processing vessel, a 7-liter vacuum tank connected with a water ring vacuum pump allowing the pressure to reach 5 kPa. A pneumatic valve ensures an "instant" connection between the vacuum tank and the processing vessel; it can open in less than 50 ms. Other valves control the flow of steam and compressed air within the processing vessel. Figure 3 shows the different stages of a DIC treatment.

Preliminary experiments were performed to define the range of various operating parameters such as saturated steam pressure P , total thermal treatment time t and GCB initial water content W . In a second stage, DIC extraction was carried out using a specific experimental design to identify and compare the effects of saturated steam pressure, process (heating) time and initial moisture content, chosen as operating parameters (or independent variables). The extracted product was collected as an emulsion of water and other compounds from the vacuum tank. The amount of caffeine present in this emulsion was quantified and defined as the "direct DIC extract" to be considered as a dependent variable (response) of the operation.

2.2.3 Solid – liquid extraction procedure

Reflux water distillation–extraction was used as a solid-liquid extraction technique to extract caffeine from the untreated and DIC treated GCBs. A mixture of 1 g of concerned beans, distilled water (20 ml) was heated inside a round bottom flask (50 ml) using a thermostatic bath set at 97 °C. The reflux distillation set-up was provided by magnetic agitation to ensure that the concentration of the extracted beans and the temperature of the solution were uniform within the flask. The crude extracts were filtered immediately after 20-min extraction using R-C membrane filter 0.45 µm (Sartorius Stedim Biotech GmbH/Germany) and tested for caffeine quantification using HPLC. This amount of caffeine we defined as the “20-min-97 °C aqueous extract” was considered as a dependent variable (response) of the operation.

2.2.4 Instrumentation and chromatographic conditions

A reversed phase HPLC system (Agilent Instruments, 1100 series, Massy, France) was used. The Chromatographic system consisted of a vacuum degasser on line with three solvent delivery pumps linked to a thermostatted column compartment via auto-sampler. The detection was carried out using a diode array UV detector (200–400 nm). Data was collected and processed using HPLCChemstation software program (Agilent, version B.04.01, Massy, France).

Caffeine crude extracts were separated on a Pursuit XRs Ultra C18 (2.8 µm), 150 × 2 mm (Varian - Agilent). The mobile phase A was a mixture of water/acetic acid and the mobile phase B was acetonitrile. Both of them were filtered through a 0.45 µm membrane filters. The elution program is outlined in table 1. The flow-rate was set at 0.4 ml/min and the column compartment was kept at a controlled temperature of 50±0.5 °C during all runs. The absolute pressure was 0.341MPa and the capillary voltage was 3 kV.

Quantification was carried out using calibration curve obtained with standard caffeine at 272 nm. For the spectrophotometric procedure, a standard curve was determined over y range of (0.05–9) µg/ml as analyte concentration *versus* x as the experimental measured area, with $R^2 = 0.99994$ showing good adherence to Beer's Law:

$$y = -5 * 10^{-28} x^4 + 7 * 10^{-21} x^3 + 3 * 10^{-14} x^2 + 4 * 10^{-7} x - 7 * 10^{-4} \quad (1)$$

The experimental results were mentioned as average ± standard deviation (SD) of three measurements.

2.2.5 Drying process

After DIC and aqueous extraction of GCBs, a conventional drying was achieved on a static-tray type with air flux at initial temperature of 40±1 °C, velocity of 1±0.2 m s⁻¹, and initial humidity of 265 Pa. A precision balance (Adventure Ohaus Europe GmbH, Greifensee, Switzerland) with an accuracy of 0.1 mg was used for weighing the untreated and DIC treated GCB samples. Before beginning the experiments, the dryer system was started in order to achieve desirable steady state conditions. The samples weight were measured after sequential drying intervals and the drying continued until no further changes in the sample mass were observed, e.g. to the final moisture content of about 5% db which was then taken as the equilibrium moisture content.

3. Fundamentals

3.1 High temperature volatile extraction

Some authors noted that roasting of GCBs is usually linked to a slight lose of caffeine by evaporation or sublimation. Such phenomenon never has been considered as complete heat extraction process. Fundamental approach carried by Mounir and Allaf, (2009) assumes that heat transferred into the plant considered as porous material mainly assures a phase change (liquid/vapor) with a partial pressure strictly depending on the temperature. The mass transport of volatile molecules from the grain surface to the surrounding environment can be intensified. That let the internal heat and mass transfers become the limiting process.

The internal heat transfer is mainly processed by a similar conduction phenomenon. The porous structure including air, water and volatile molecules, allows vaporization-condensation phenomena inside the product holes. The global phenomenon is a conduction-type transfer where the gradient of temperature is conducted as the driving force with a higher value of effective conductivity. The main part of such heat flow is used to evaporate water and volatile compounds within the product holes:

$$-\lambda_{eff} \vec{\nabla} \cdot \vec{\nabla} T + s_{gas} M_c L_c \frac{\partial}{\partial t} \left[\frac{p_c}{RT} \right] = 0 \quad (2)$$

The internal transfer of volatile compounds is assumed to be negligible under a liquid phase, and achieved as pure gas phase diffusion. It can be revealed by a Fick-type's law with the gradient of the partial pressure per temperature of each volatile compound as driving force. (Allaf, 1982):

$$\frac{p_c/T}{\rho_s} (\vec{v}_c - \vec{v}_s) = -D_{eff} \vec{\nabla} \frac{p_c/T}{\rho_s} \quad (3)$$

where D_{eff} is the effective mass diffusivity.

3.1.1 Paradox of coupled internal heat and gas diffusion transfers

The partial pressures of water and other volatile compounds inside the holes of the plant considered as porous material closely depend on the temperature through the thermodynamic liquid/gas equilibrium of the molecule mixture. By neglecting the possible shrinkage phenomena, one can assume:

$$(p_c/T) \vec{v}_c = -D_{eff} \vec{\nabla} (p_c/T) \quad (4)$$

The gradient of p_c/T is then the driving force of gas diffusion (which is controlled by) and the transfer of heat to

change the liquid into gas phase within the porous material, can be coupled to become, with one x dimension, as:

$$-\lambda \frac{\partial^2 T}{\partial x^2} + s_{gas} M_c L_c \frac{\partial}{\partial t} \left[\frac{p_c}{RT} \right] = 0 \quad (5)$$

$$(p_c/T) v_c = -D_{eff} \left(\frac{\partial (p_c/T)}{\partial x} \right) \quad (6)$$

However, as (p_c/T) is as higher as the temperature is higher,

$$\frac{\partial (p_c/T)}{\partial T} > 0 \quad (7)$$

the gradient of mass transfer is then directed from the surface to the sample core; the result is a paradoxical situation implying a motion completely opposite to that required for the sought extraction operation. In the usual heat extraction of volatile molecule from plant oils, the process is achieved by slow "front progression" kinetics.

3.1.2 Specificity of the DIC treatment

Depending on the high temperature level of DIC, the total pressure of the mixture vapor and volatile molecules in the porous material is, just after the pressure drops, much higher than the external vacuum pressure. Therefore, whatever the structure of the porous plant, the mass transfer operation within this porous matrix has to be performed from the core towards the surrounding medium through the gradient of the total pressures (Darcy-type law):

$$\rho_c v_c = - \frac{K}{v_c} \frac{\partial P}{\partial x} \quad (8)$$

By considering mass balance and continuity laws, and by integrating between the hole (whose radius R_o) and the external radius R_s of the spherical shape, Allaf et al., 2011 calculated the part m_m of vapor mixture removed as:

$$m_m = \frac{4}{3} \pi R_s^3 \frac{\langle M \rangle}{RT} (P_o - P_{ext}) \quad (9)$$

Usually, the time t_i of the final vacuum DIC stage just after pressure drops is defined to allow the mixture vapor to be transported towards the surrounding medium and then collected.

DIC is fundamentally relevant to remedy the disadvantages of the paradoxical stage and can greatly intensify the thermal extraction of volatile compounds.

3.2 Fundamentals of hot air drying kinetics

When external heat and mass transfers are not the limiting phenomena of the operation kinetics thanks to adequate air flow temperature and velocity, only internal transfers are considered as controlling and limiting the whole operation (Al-Haddad et al.; 2008). Mounir and Allaf (2009) have modeled such dehydration kinetics, in the case of porous medium by coupling the internal transfer processes with an initial superficial drying assumed to be the limiting process during the first part of the operation.

As usually internal mass transfer in vegetables is much slower than conduction heat transfer within the product, the drying kinetics is claimed as controlled by water diffusion within the solid structure. GCBs can be assumed as isotropic structure in terms of water flow within the material; by assuming a constant temperature and homogeneous structure, different 1-D mathematical solutions may be proposed, depending on the boundary conditions (Pakowski and Mujumdar, 2006; Crank, 1975); limited to the first term approximation, a straight-line equation may be obtained through the logarithmic transformation of the adimensional water content dry basis:

$$Y = \text{LN} \left(\frac{W_{\infty} - W_o}{W_{\infty} - W} \right) = kt + \text{cte} \quad (10)$$

GCB can be assumed to be spherical shape with d_p as radius. The effective diffusivity is:

$$D_{eff} = \frac{k d_p^2}{\pi^2} \quad (11)$$

The experimental data used to determine the effective diffusivity D_{eff} from the Fick's model exclude the ones concerning the points close to $t=0$; the extrapolation of the model thus obtained leads to evaluate W_o as, generally, distinct from the initial humidity content W_i . The difference at the starting point between W_i and W_o reveals the starting accessibility δW_s , which is the superficial water capable to be quickly removed from the surface, independently from diffusion process.

4. Statistical and Experimental Design Protocol

Several authors (Benoist et al., 1994; Kamal et al., 2008) developed RSM (response surface methodology) in order to identify the effects of each factor (independent variables or operating parameters) and target the optimal treatment conditions with the possibility of maximizing the information and obtaining the most relevant responses from the lowest number of trials. In the present work, this experimental design was defined after some preliminary trials to test the behavior of the plant (structure expansion, thermal degradation etc.) versus the operating parameters. The results of these preliminary experiments allowed us to select only three factors that seemed to have a significant influence in our case. These were saturated steam pressure P , initial water content W , and total thermal processing time t . They ranged from 0.1 to 0.6 MPa, 11 to 35% db, and 16 to 84 s, respectively (Table 1). Other parameters, such as the final pressure in the vacuum tank and the pressure drop rate were kept constant. A full central composite design with the three independent variables and seven replicates at the central point, i.e. a total of 21 trials, was employed for evaluating the effect of steam DIC treatment on GCBs decaffeination and

drying kinetics. The trials were run randomly to minimize the effects of an unexpected variability of responses due to unrelated and uncontrolled factors.

The statistical analysis of the results was carried out using the analysis design procedure of Statgraphics Plus software for Windows (1995, version 5.1, Levallois-Perret, France). Variance (ANOVA) was performed to determine significant differences between independent variables ($P \leq 0.05$). The effects of the independent variables or operating parameters on each parameter response were revealed under Pareto chart, which is usually very effective when introduced to describe a phenomenon in which 95% of the variation observed in experimental processes can be explained by a mere 5% of the causes of that variation.

Pareto chart is introduced together with the main trends, response surface, empirical model coefficients and R^2 . The response parameter (dependent variable Y) is expressed through a second-order polynomial empirical model of independent variables:

$$Y = \beta_0 + \sum_{i=1}^n \beta_i x_i + \sum_{i=1}^n \beta_{ii} x_i^2 + \sum_{i=1}^n \sum_{j=1}^n \beta_{ij} x_i x_j + \varepsilon \quad (12)$$

where β_0 , β_i , β_{ii} and β_{ij} are the regression coefficients, x_i the independent variables, ε the random error, i and j the indices of the factors. Response Surface Methodology can be used to optimize the operating parameters by coupling various studied responses. The dependent response variables were the amount of DIC-direct caffeine extract "DIC-DEC", the amount of 20-min-97 °C aqueous caffeine extract "ACE", the total decaffeination ratio "TDR", and the direct decaffeination ratio "DDR", as well as the drying kinetic parameters such as the drying time to reach a water content level of 5% db " $t_{5\%}$ ", the effective diffusivity " D_{eff} " and the starting accessibility " W_s ".

5. Results and Discussion

5.1 Extraction processes

The process of DIC-direct-extraction of caffeine should involve the autovaporization of volatile compounds. This phenomenon strictly appears when the pressure drops instantaneously. Furthermore, the increase in porosity and the appearance of holes due to the possible expansion of the matter allow water and other solvents to easily diffuse within the new structure; rupture of cell walls can occur at high severity DIC treatment.

The liquid resulted from the condensation of the vapor expelled into the vacuum tank by dropping the DIC pressure was clear, homogeneous, with a pleasant coffee odor. Caffeine present in this liquid was quantified and reported to the quantity of dry treated GCBs. The 20-min-97°C aqueous caffeine extracted from the untreated and DIC-treated GCBs was measured and quantified reported to dry matter. DIC treatment was designed to assess and identify the efficacy of the two operations by quantifying the amount of DIC-Extract Caffeine (DIC-DEC) and GCB aqueous Extract Caffeine (AEC).

5.1.1 Direct extraction of caffeine by DIC treatment

The DIC-direct extract caffeine expelled in the vacuum tank had a concentration in the condensed water between 0.005 and 0.133% db.

RSM analysis for direct DIC-DEC revealed that the effects of the processing time (t) and the saturated steam pressure (P) reflecting the processing temperature were both significant; whereas the initial water content (W) had a lower impact (Figure 4a). It is worth noting that the higher the saturated steam pressure (P) and the processing time (t), the higher the DIC-DEC value (Figure 4b).

RSM analysis generated a second order polynomial model, and estimated response surfaces shown in (Figure 4c). The regression coefficients of the model for caffeine directly expelled by DIC were obtained by multiple linear regressions. The polynomial empirical model could be estimated and expressed with $R^2 = 0.788952$ as the following:

$$(DIC - DEC)\%db = -0.037\% + 0.730\%W - 0.021\%P - 0.002\%t - 1.864\%W^2 + 0.307\%WP + 0.001\%Wt - 0.105\%P^2 + 0.003\%Pt + 1.6 \cdot 10^{-5}\%t^2 \quad (13)$$

The highest direct caffeine extraction DIC-DEC was calculated as 0.1622% db, at optimal conditions of 0.6 MPa saturated steam pressure, 27.53% db water content and 84 s thermal treatment time. This was higher than the content of lightly roasted coffee (0.06 % as was reported by Hecimovic et al., (2011). This increase can be explained by the expulsion of some volatile compounds thanks to the gradient of the total pressure between GCB

core and the surrounding vacuum medium. Indeed, in a similar situation even with essential oil extraction, Al-Haddad et al., (2007) and Besombes et al., (2010) indicated that Darcy-similar process could effectively remedy the paradoxical stage.

The values of DIC-DEC were systematically underestimated, because a certain amount of caffeine should have been retained on the vacuum tank wall and vacuum pump. However, the results proved the ability of DIC to quickly remove a certain amount of caffeine from GCBs, with low energy consumption and water vapor as proved by Mounir and Allaf (2008).

5.1.2 Aqueous extraction of caffeine

20-min-97 °C aqueous extraction was operated on untreated and DIC-treated GCBs. Each experiment treatment was carried out in triplicate and the average of aqueous extract caffeine "AEC" expressed in %db was taken as the response.

RSM analysis for aqueous extract caffeine AEC revealed that the effects of the saturated steam pressure (P) reflecting the processing temperature, and the initial water content (W) were the most significant DIC operating parameters; whereas the processing time (t) had a too low impact (Figure 5a).

In the considered ranges, the higher the values of water content (W), saturated steam pressure (P), and processing time (t), the lower the aqueous extract caffeine AEC (Figure 5b). However, at high P level (about 0.6 MPa) and at high W level (about 35% db), AEC kept constant, independently of W and P, respectively (Figure 5c).

The regression coefficients of the model for caffeine directly expelled by DIC were obtained by multiple linear regressions. The polynomial empirical model could be estimated and expressed with $R^2=0.71$ as the following:

$$AEC = (3.670 - 7.197W - 4.925P - 0.007t + 2.388W^2 + 12.642WP - 0.003Wt + 0.946P^2 + 0.005Pt + 105 \cdot 10^{-5}t^2)\% \quad (14)$$

Although increasing the DIC processing pressure is correlated with increasing the steam temperature, the dissolution and extraction of caffeine in the aqueous solution seemed to decrease with increasing DIC temperature, possibly because a higher retention of caffeine. The highest theoretical value of AEC was obtained at $P=0.1$ MPa, $W=11.0\%$ db, and $t=35$ s; its optimized value was calculated as 2.35% db.

5.2 Decaffeination process

The new decaffeination process was triggered as two stages issued from:

- DIC direct caffeine extraction; the crude directly extract was collected in the extract container of the DIC apparatus,
- Aqueous caffeine extraction.

The first stage allows a part of caffeine to be directly expelled towards the vacuum tank once the DIC pressure abruptly dropped, while the second stage was greatly intensified thanks to the DIC expanded structure. Indeed, by expanding GCBs, DIC treatment could dramatically increase water diffusion and solvation.

The average amount of total extracted caffeine in the first experimental design could then reach up to 1.891 ± 0.04 g of caffeine/100 g dry GCBs, which represented a decaffeination ratio up to 80%, while it was only 1.3640 ± 0.04 g/100 g dry matter representing a decaffeination ratio of 58% when the aqueous extraction was achieved with untreated GCBs. Research works on DIC treatment of various plants highlighted similar behavior revealing greater availability of compounds to be extracted normally because of expansion and possible broken cell walls.

Statistical analyses of total decaffeination ratio TDR illustrated in (Figure 6-a,b,c), showed the effects of DIC operating parameters such as the saturated steam pressure (P), the initial water content (W) of GCBs, and the DIC processing time t on total decaffeination ratio TDR. P and W were the most significant variables with a negative impact; that means that TDR decreased with increasing P and W. TDR were revealed through the following polynomial expression established with $R^2 = 0.70$:

$$TDR = (190.241 - 338.641W - 259.029P - 0.450t + 27.408W^2 + 678.102WP - 0.101Wt + 44.036P^2 + 0.416Pt + 0.0014t^2)\% \quad (15)$$

The optimal TDR corresponded to a complete decaffeination, which was estimated at 99.5% at optimized DIC conditions of $W=11.00\%$ db, $P=0.1$ MPa, and $t=35$ s.

Moreover, it worth to be noted that, as expected, despite its low level, the direct contribution of DIC to decaffeination by the expulsion of caffeine towards the vacuum tank should be very important because of the short operation time, the high concentration level, and the low energy consumption reported to the amount of extract.

From experimental data, it was possible to establish the response analysis as shown in (Figure 7-a,b,c), and an empirical model of the DDR versus the DIC processing parameters. The R^2 value ($R^2 = 0.789$) directly proved that the DIC treatment was a relevant extraction process with caffeine:

$$DDR = (1.926 + 38.235W - 1.105P - 0.104t - 97.635W^2 + 16.064WP + 0.070Wt - 5.487P^2 + 0.167Pt + 0.001t^2)\% \quad (16)$$

The highest value of DDR of 8.5% could be obtained with initial water content $W=27.5\%$ db, at a saturated steam pressure $P=0.6$ MPa during processing time $t=84$ s.

5.3 Drying kinetics

After the decaffeination process, and just before roasting, GCBs have to be dried. The impact of DIC on drying kinetics should be correlated with DIC-expansion. At first, it was evident to note that the drying time needed to let GCBs reach moisture of 5% db was much lower with DIC-treated grains than raw material (Table 2).

In our case, the lowest value of $t_{5\%}$ was obtained with the following values of DIC operating parameters: $P=0.6$ MPa, $W=23\%$ db and $t=50$ s with $t_{5\%}=60$ min instead of 528 min for untreated raw material.

On the other hand, response surface method RSM analysis confirmed that DIC processing pressure P and time t had negative linear effects on $t_{5\%}$ that means the higher the DIC operating parameters P and t , the more effective the drying kinetics. (Figure 8-a,b,c) displays the effects, while the empirical mathematical model was established with $R^2=68.636$ percent as following:

$$t_{5\%} = 204.006 + 980.295W + 501.661P - 5.218t - 687.756W^2 - 1655.62WP - 6.107Wt - 218.591P^2 - 4.034Pt + 0.057t^2 \quad (17)$$

5.3.1 Drying model

In the present work, the mathematical diffusion-drying model coupled with the initial surface interaction was fitted to experimental data using non-linear regression analysis techniques. The experimental data of moisture (% dry basis) versus time were used in order to assess a suitable form of the drying curve for GCBs. They allowed determining the starting accessibility W_s and the effective diffusivity D_{eff} adapted to each drying curve of untreated and DIC treated GCBs. The statistical treatment of these results revealed the remarkable improvement in the starting accessibility and the moisture diffusivity that could be achieved when coffee beans are pre-treated by DIC prior to drying. In the present case of DIC treated samples, they ranged from 5 to 17.8 g/100 g db and from 5.4 to 28.4 $10^{-10} \text{ m}^2 \text{ s}^{-1}$, respectively; as against 0.8 g/100 g db and 1.3 $10^{-10} \text{ m}^2 \text{ s}^{-1}$, respectively for the raw material. These last values correlate with those reported for coffee cherries by Sfredoet al., (2005); Hernandez-Diaz et al., (2008) of an effective moisture diffusivity between 110^{-11} and $1 \cdot 10^{-10} \text{ m}^2 \text{ s}^{-1}$ at 45 °C and between $3 \cdot 10^{-11}$ and $3 \cdot 10^{-10} \text{ m}^2 \text{ s}^{-1}$ at 60 °C.

DIC textured beans with increased pore size and greater exchange surface enhance the powerful raise of drying kinetics through effective responses. The results are in agreement with other DIC experiments carried out on various food products (Albitar et al., 2011).

It was then possible to establish the response surface analysis (Figure 9-a,b,c and Figure 10-a,b,c), and the empirical mathematical models of the effective diffusivity D_{eff} and the starting accessibility W_s versus the DIC processing parameters P , t and W . The regression coefficients of the models were obtained by the multiple linear regressions, and the polynomial equations estimated are expressed as the following:

$$D_{eff} = 13.6381 - 24.103W - 34.969P - 0.226t - 37.860W^2 + 95.280WP + 0.423Wt + 10.770P^2 + 0.303Pt + 0.001t^2 \quad (18)$$

$$\delta W_s = (9.160 + 18.213W - 27.998P - 0.068t - 79.385W^2 + 38.643WP + 0.147Wt + 27.155P^2 + 0.1Pt + 0.001t^2)\% \quad (19)$$

with R^2 values 0.72 and 0.55, respectively. Though these R^2 values of D_{eff} and δW_s reveal that these equations reflect a general trend rather than a precise relationship, but all of these relations shows the great impact of DIC pretreatment in the improvement of the drying kinetics; possibly through the porous structure.

From these second order polynomial models generated by response surface analysis, optimal drying conditions of GCBs were obtained using the predictive equations generated by RSM:

The highest values of D_{eff} at $1.9994 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ and δW_s at 13.901% were obtained at the same DIC operating parameters $P=0.6 \text{ MPa}$ and $t=84 \text{ s}$, while the water contents slightly differed to be $W=33.5\% \text{ db}$ and $25.6\% \text{ db}$, respectively.

Finally, it worth to note that the same optimal DIC treatment parameters were defined for DDR/Total extracted caffeine. General correlations (Figure 11) were recognized between D_{eff} and DDR/Total extracted caffeine with 79.5% as correlation factor. Both of these response parameters should be directly linked to porosity and porous structure.

6. Conclusions

The results obtained throughout this work conclude that a new decaffeination process could be defined and applied on green coffee beans (GCBs). It is a two-step operation of Détente Instantanée Contrôlée DIC (French, for instant controlled pressure-drop) and an aqueous extraction, normally followed by a drying step, prior to storing and roasting. The first stage of thermo-mechanical process DIC led to an expulsion of a part of caffeine possibly by autovaporization; it is the “direct decaffeination” step. DIC treatment can also allow the structure to be expanded and solvent extraction to be dramatically intensified. A “20-min-97 °C aqueous extraction” was defined as the second step of this solvent-free, environmentally decaffeination. In the present work, both operations of decaffeination and drying were achieved on Ethiopian green coffee beans. The highest value of the direct decaffeination ratio DDR could be 8.5% of total caffeine content and corresponded to a DIC saturated steam pressure $P=0.6 \text{ MPa}$, for a DIC processing time $t=84 \text{ s}$ with an initial moisture content $W=27.5\%$. Untreated and DIC-treated GCBs were then submerged for 20 min in water bath at 97 °C. Thus, a total decaffeination ratio TDR was obtained. With optimized DIC treated GCBs of $W=11.00\% \text{ db}$, $P=0.1 \text{ MPa}$, and $t=35 \text{ s}$, TDR corresponded to a complete decaffeination, which was estimated at 99.5% while only 58% could be extracted from the untreated raw materials.

Using the classical diffusion coupled with surface interaction model of hot-air drying kinetics, DIC expansion dramatically improved the drying kinetic parameters. Thus, the effective diffusivity D_{eff} and the starting accessibility δW_s increased 3780% and 1537%, respectively. Drying time needed to reach 5% db became 60 min instead of 528 min for untreated raw material.

From a technological point of view, this new route for coffee decaffeination is very promising because of various drawbacks related to the traditional decaffeination processes.

Acknowledgements

The authors would like to acknowledge the financial support from CPER/EU-FEDER. The authors wish to extend their heartfelt gratitude to Mr. Laurent Lefevre, from ABCAR-DIC Process for having contributed to the scaling up DIC treatments and for having provided them with the raw material thus contributing to perform these tests.

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Nomenclature

DIC	Détente Instantanée Contrôlée (French for "Instant controlled pressure drop")
GCB	Green coffee bean
RSM	Response Surface Method
P	DIC saturated steam pressure (in MPa)
t	DIC thermal treatment time
W	Initial moisture content of GCB
D_{eff}	Effective diffusivity from the diffusion/surface interaction kinetic model of hot air drying after DIC treatment
δW_s	Starting accessibility from the diffusion/surface interaction kinetic model of hot air drying after DIC treatment
db	Dry basis
p_c	Partial pressure of volatile compounds
R	Gas constant, ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$)
T	Temperature (K)
λ_{eff}	Effective heat conductivity ($\text{W m}^{-1} \text{ K}^{-1}$)
$\langle M_c \rangle$	Average of molar mass of volatile compounds
$\langle L_c \rangle$	Average latent heat Length of volatile compounds
v_c	Velocity of volatile compound flux
P	Total pressure
K	Darcy coefficient (m^2)
m_m	Mass of vapor removed
R_o	Pororadius
P_o	Internal total pressure
P_{ext}	External total pressure
W_∞	Equilibrium moisture content
W_o	Computed initial moisture content (hypothesis of diffusion model)
W	Moisture content at certain drying time
k	Drying rate
t	Drying time
cte	Constant
d_p	Sphere radius
ρ	Density of water (kg m^{-3})

Table 1. HPLC elution conditions

Solvent gradient (acetic acid 6.7% : acetonitrile% : water%, v/v/v)	Time (min.)
10.0% : 0.0% : 90%,	0
10.8% : 0.2% : 89%	2
11.0% : 1.0% : 88%	6
11.0% : 2.0% : 87%	10
11.0% : 4.0% : 85%	15
12.0% : 8.0% : 80%	20
12.0% : 0.0% : 88%	25
10.0% : 0.0% : 90%	40

Table 2. Independent variables and their coded and natural levels employed in a 5-level central composite design to optimize the effect of DIC on decaffeination and on drying kinetics of the green coffee beans

Trial	DIC parameters					
	Saturated steam pressure P		Water content dry basis W		Total processing time t	
	Coded level	Natural level (MPa)	Coded level	Natural level (% db)	Coded level	Natural level (s)
1	+ α	0.6	0	23.00%	0	50
2	0	0.35	0	23.00%	+ α	84
3	0	0.35	0	23.00%	0	50
4	+1	0.5	+1	30.00%	+1	70
5	0	0.35	+ α	35.00%	0	50
6	0	0.35	0	23.00%	0	50
7	+1	0.5	+1	30.00%	-1	30
8	+1	0.5	-1	16.00%	+1	70
9	0	0.35	0	23.00%	0	50
10	+1	0.5	-1	16.00%	-1	30
11	-1	0.2	+1	30.00%	+1	70
12	0	0.35	0	23.00%	0	50
13	-1	0.2	+1	30.00%	-1	30
14	-1	0.2	-1	16.00%	+1	70
15	0	0.35	0	23.00%	0	50
16	0	0.35	- α	11.00%	0	50
17	- α	0.1	0	23.00%	0	50
18	0	0.35	0	23.00%	0	50
19	-1	0.2	-1	16.00%	-1	30
20	0	0.35	0	23.00%	- α	16
21	0	0.35	0	23.00%	0	50

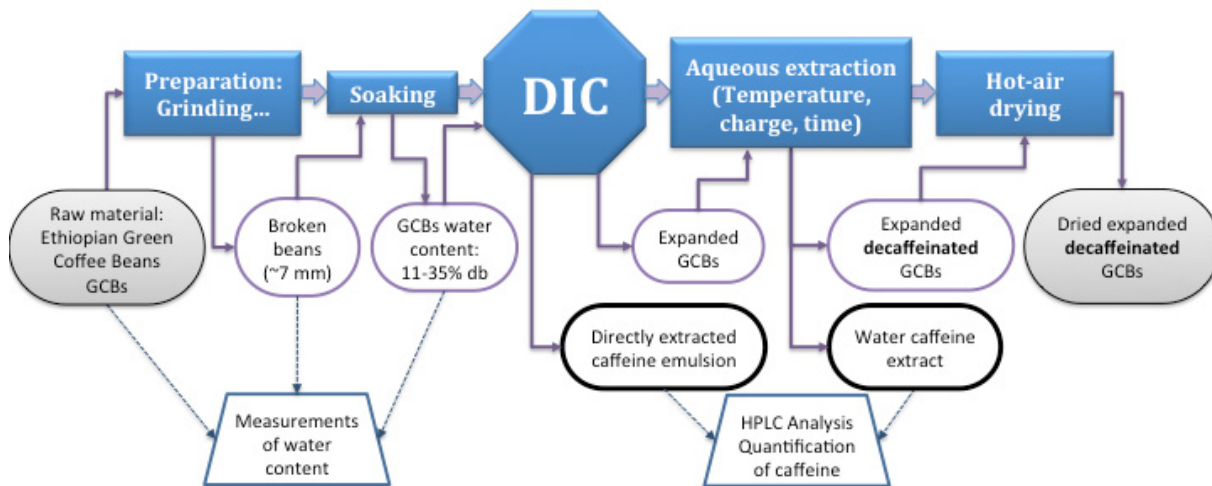


Figure 1. Treatment protocol and assessments of GCBs (Green Coffee Beans) through instant controlled pressure drop DIC

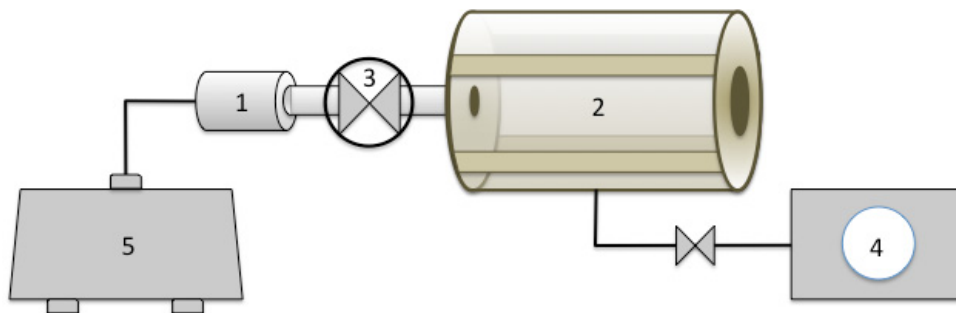


Figure 2. Schematic presentation of DIC reactor: 1- treatment vessel; 2- vacuum tank with transparent Jacket; 3- controlled instant pressure drop valve; 4- water ring vacuum pump; 5- steam generator

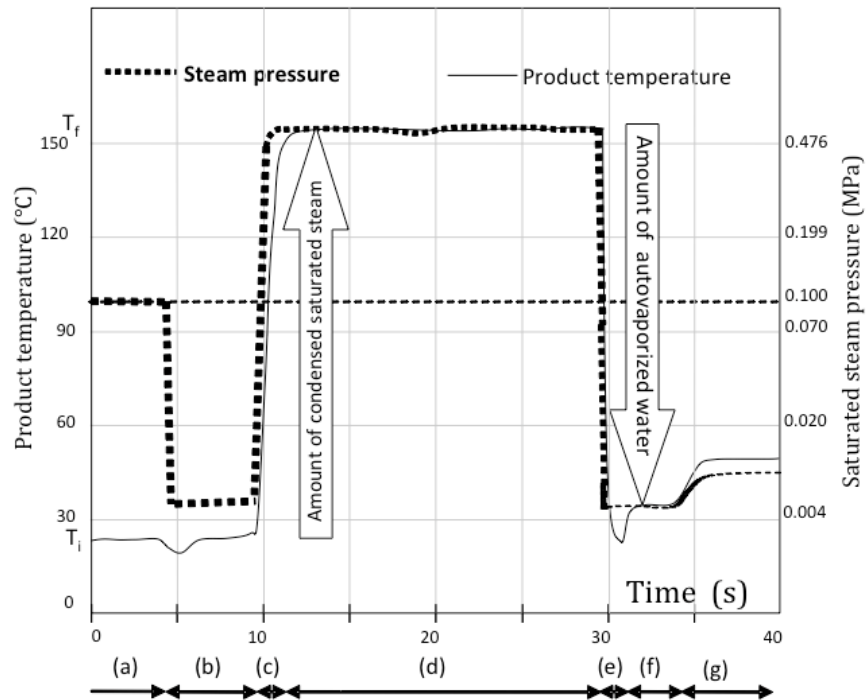


Figure 3. Different stages of a DIC treatment: a- Product to be place in the treatment vessel; b- First vacuum stage; c- saturated steam to be injected in the treatment vessel; d- High-pressure/high-temperature stage; e- Pressure to be abruptly dropped toward a vacuum; f- Second vacuum stage; g- Releasing toward Atmospheric pressure

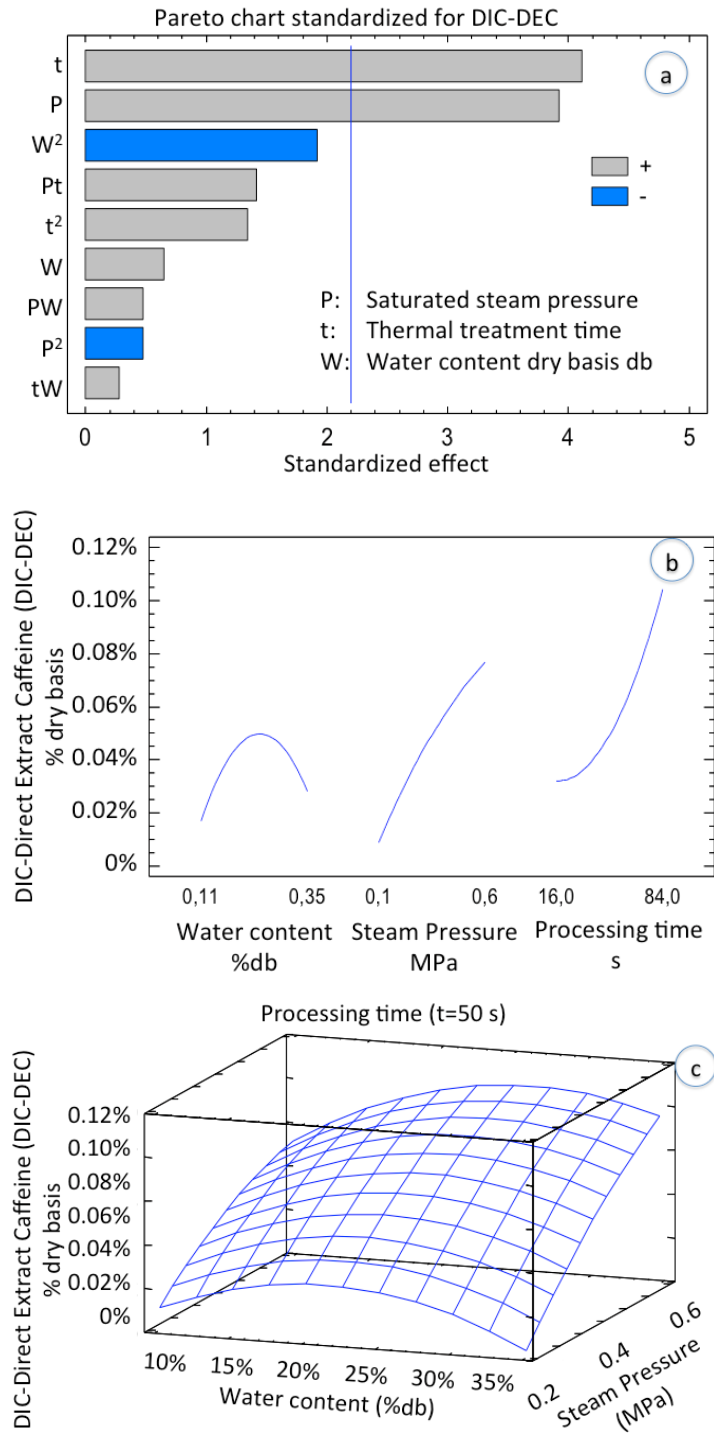


Figure 4. Pareto chart of DIC operating parameters (a), general trends (b), and response surface (c) for caffeine directly extracted by DIC (DIC-DEC)

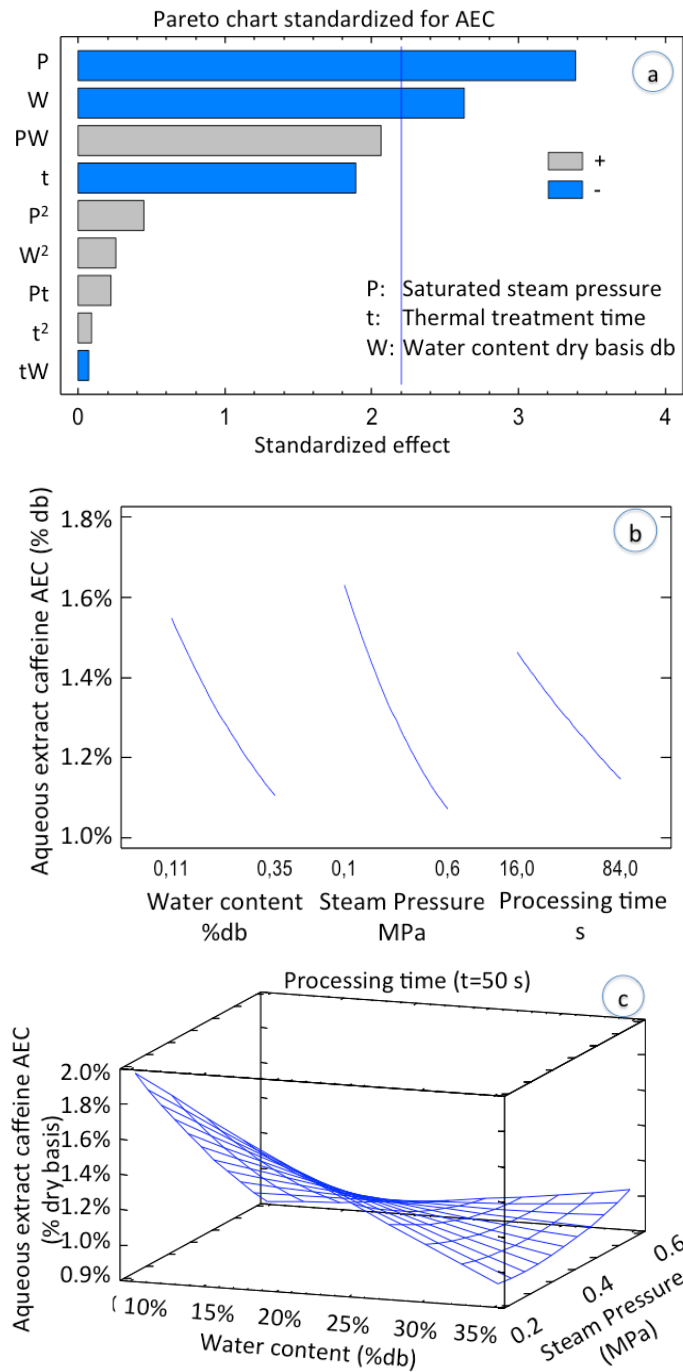


Figure 5. Pareto chart (a), general trends (b) and response surface (c) of DIC operating parameters for caffeine extracted during 20 minutes in water at 97 °C, after DIC treatments (AEC)

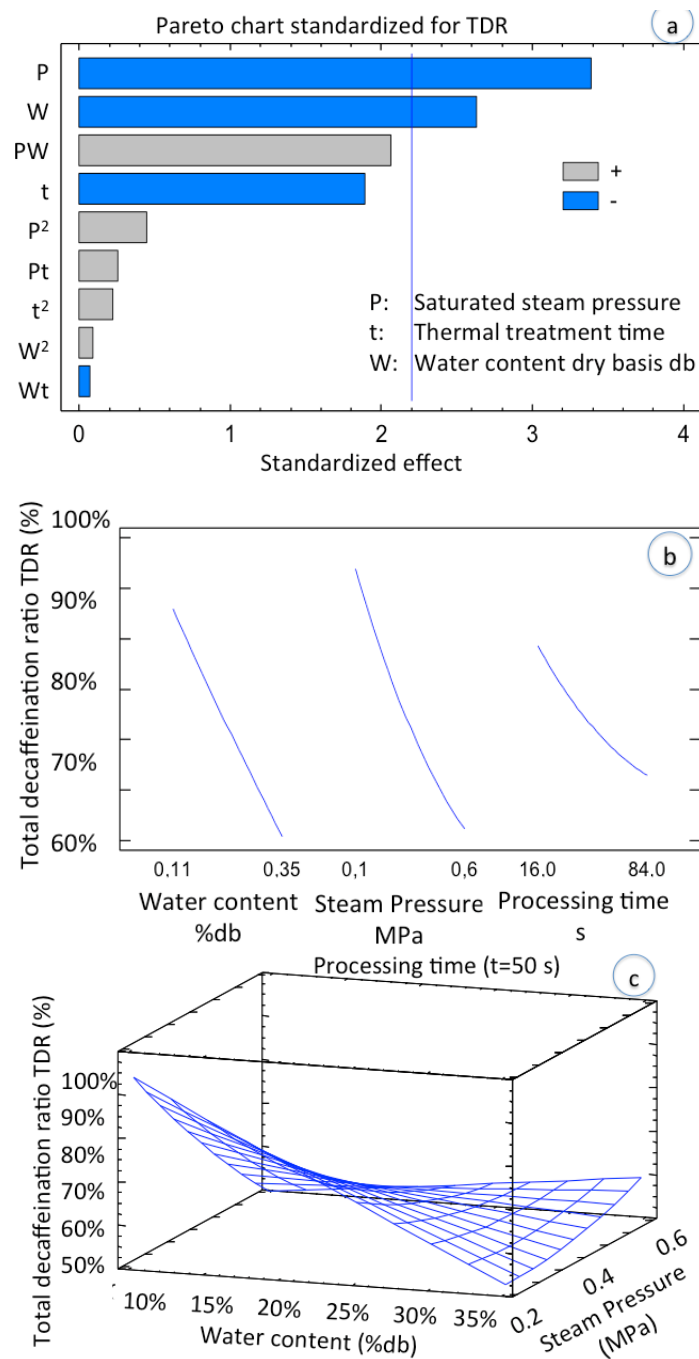


Figure 6. Pareto chart, General trends, and response surface analysis results for total decaffeination ratio (TDR)

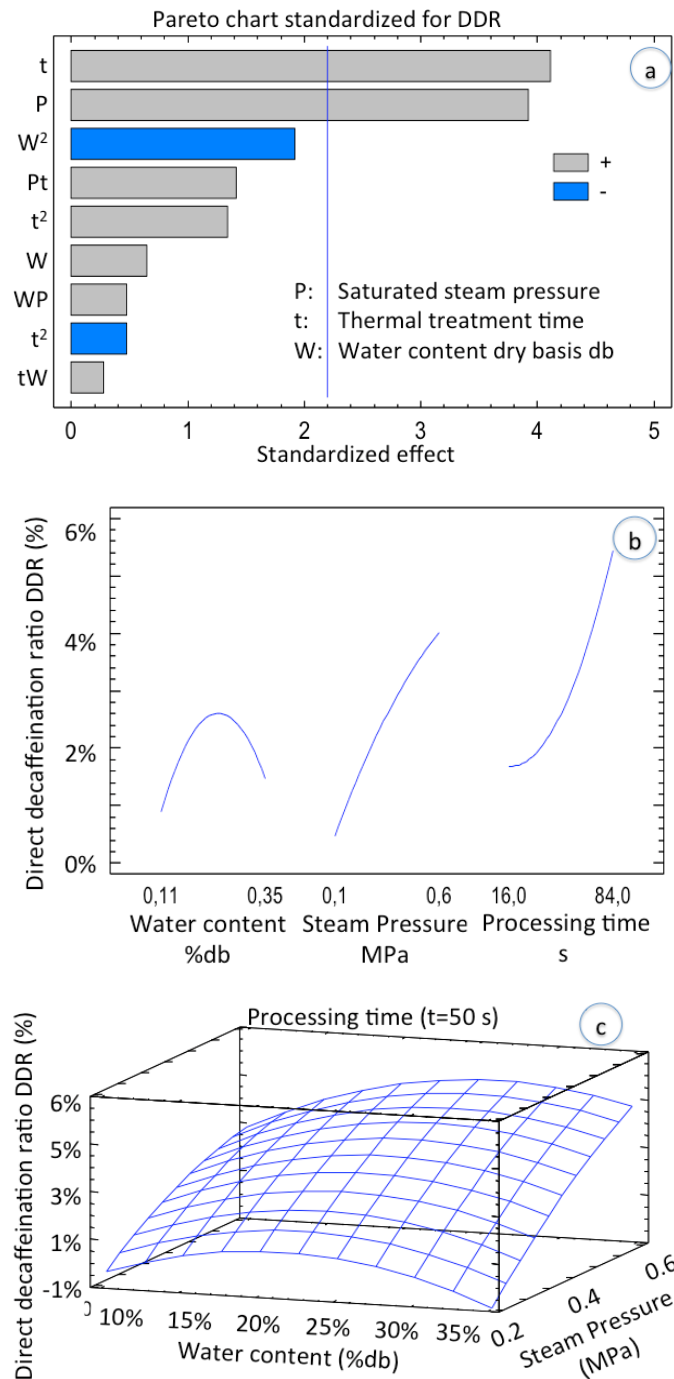


Figure 7. Pareto chart, general trends, and response surface for the DIC-Direct Decaffeination Ratio DDR

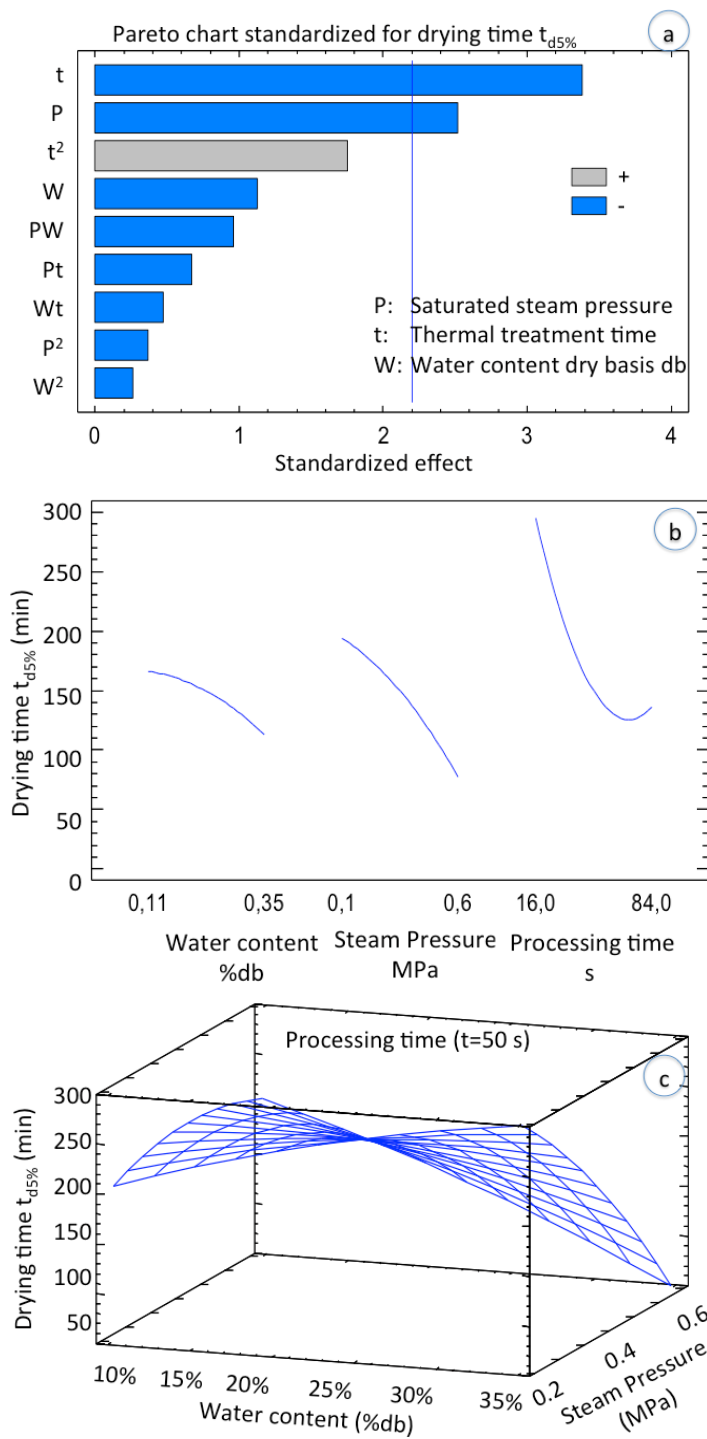


Figure 8. Pareto chart, general trends, and response surface for the drying time $t_{5\%}$ of DIC treated GCBs

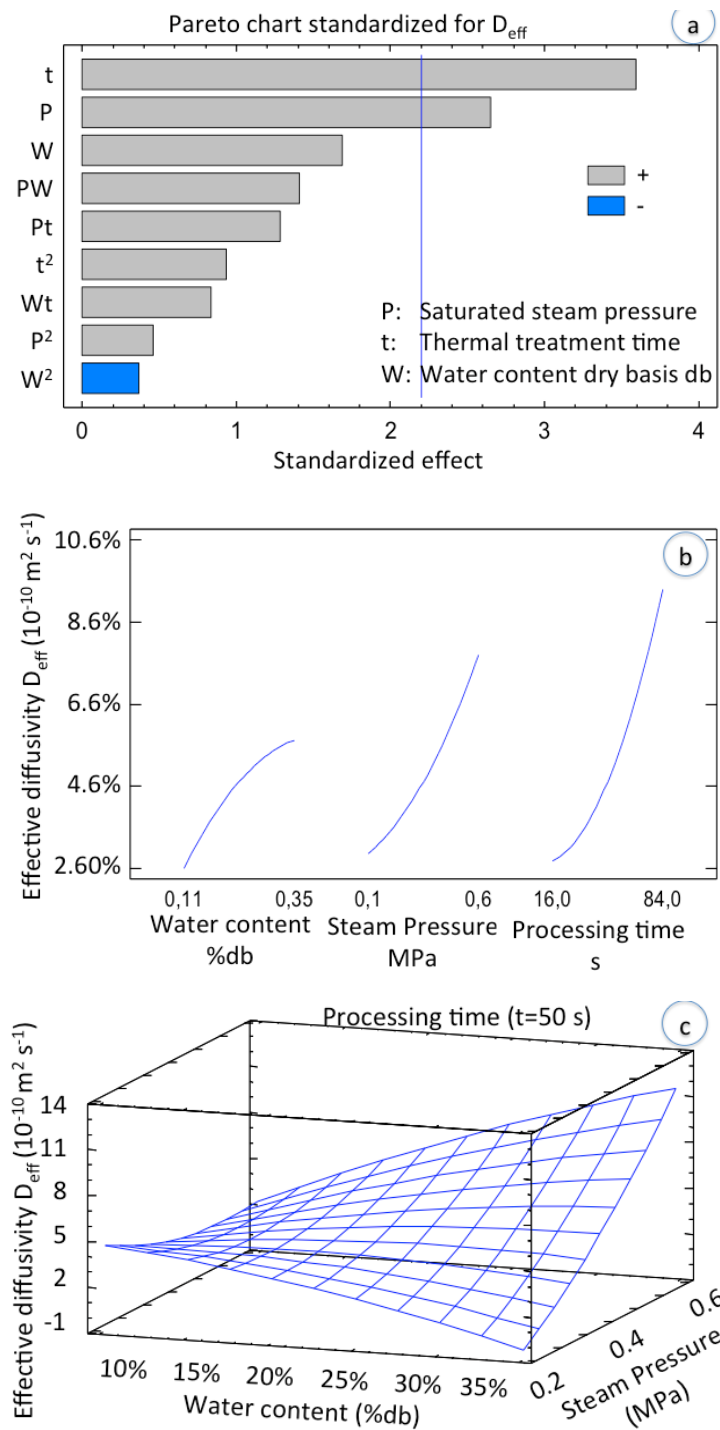


Figure 9. Pareto charts, general trends and response surfaces showing the effects of the DIC processing variables on the effective diffusivity D_{eff}

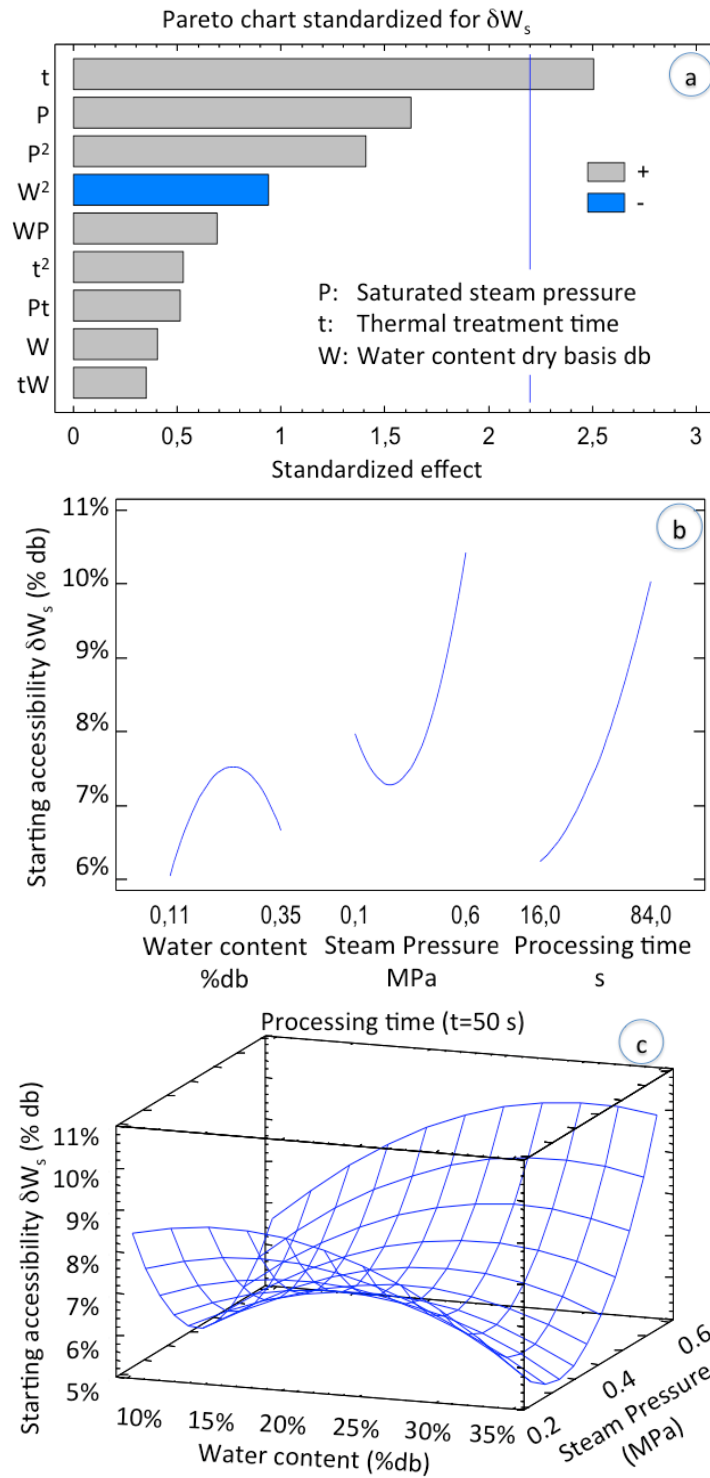


Figure 10. Pareto charts, general trends and response surfaces showing the effects of the DIC processing variables on the starting accessibility W_s

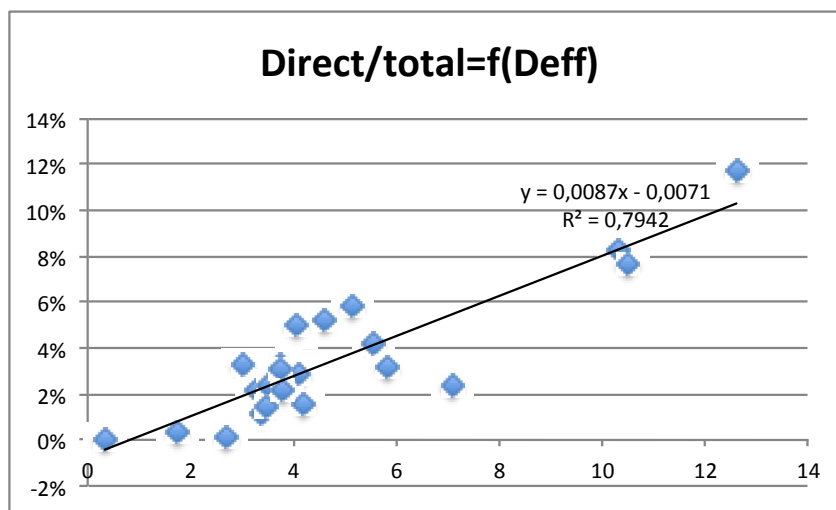


Figure 11. Correlation between drying effective diffusivity and DIC direct decaffeination to total decaffeination ratio (DDR)