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Instant autovaporization as intensification way of classic distillation processes: fundamental and industrial applications

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Abstract

In the present work, the new extraction process of Détente Instantanée Contrôlée DIC was studied, developed, optimized and compared to the conventional hydrodistillation method for the extraction of essential oils of sandalwood. DIC was used as a thermomechanical treatment, DIC subjecting the product to a high-pressure saturated steam. The DIC cycle ends with an abrupt pressure drop towards vacuum, and this instantly leads to an autovaporization of sandalwood volatile compounds. An immediate condensation in the vacuum tank produced a micro-emulsion of water and essential oils. Thus, an ultra-rapid cooling of residual leaves occurred, precluding any thermal degradation. Response surface methodology RSM was used with a 2-parameter 5-level Design of Experiments (DoE).

The structure with a slight destruction of cell walls after DIC treatment. The operating parameters (independent variables) were the treatment time t , and the number of pressure drops C , whilst the main response was the extraction of extraction efficiency EE of volatile compounds. RSM Statistical analysis allowed comparing this process with conventional hydrodistillation unit operation in terms of total yields of essential oil. The most important differences between the two essential oils were reflected in the yields, with 1.14 as against 1.23 g EO/100 g of raw matter, and in the extraction time, with 5 min as against 24 hours for respectively the DIC and the hydrodistillation operations. These differences have been previewed through the fundamental analysis based on both concept of thermodynamics of instantaneous transformations and calculation of the volatility as well as on Darcy similar transfer law was used to explain the main results.

Keywords: Intensification; Instant Autovaporization; Volatility; Instant Controlled Pressure Drop DIC; Distillation; Paradoxical Stage

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1. Introduction

Sandalwood is considered one of the most valuable trees in the world [1], Sandalwood oil is an essential oil obtained by the distillation of the heartwood and roots of the plant *Santalum album* (family – Santalaceae). *S. album* is a hemiparasitic tree of great economic value, growing in Southern India, Sri Lanka, Australia and Indonesia. Its trunk contains resins and essential oils particularly the α and β santalols, santalenes and many other minor sesquiterpenoids [2]. These sesquiterpenoids are responsible for the unique sandalwood fragrance. A number of aromatic and phenolic compounds have also been identified in the oil *S. album* [3]. The quantity of oil produced in a tree varies considerably according to location (environmental factors) and age of the tree, even in nearly identical growing conditions [2]. It should also be noted that santalol composition can vary depending on the method of oil extraction, sections of a single tree. The international standard (ISO 3518, 2002) for sandalwood oil and similar authorities stipulate a minimum of 90% w/w santalol (as free alcohol) in the oil [4].

Sandalwood oils are essential oils commonly used as fragrances for body oils and incense as well as in medicines and cosmetics. Sandalwood oils have many well-known health benefits in traditional medicinal systems such as Ayurveda, as antiseptic, antipyretic, antiscabietic, diuretic, expectorant, stimulant, and for the treatment of bronchitis, dysuria, urinary infection, and in gonorrhoeal recovery.

Sandalwood oils are usually extracted by steam distillation [5]. However, solvent extraction can be performed on chips of sandalwood [6]. It would present numerous disadvantages [5]. Therefore, various other alternatives were tested. Thus Marongiu and al. [7], Piggott and al [8] used supercritical or subcritical fluid for extracting and fractioning essential oils. Microwave-assisted extraction was also used as new innovative techniques [9]. 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 or pilot scale.

In this context, it was proposed to carry out a comparative study of the extraction of the essential oils of the sandalwood using two different methods: traditional hydrodistillation and the innovative technology of Détente Instantanée Contrôlée DIC (French, for instant controlled pressure drop). DIC was defined in 1988 [10] and has been studied, developed, optimized and used at industrial scale for various applications such as drying and decontamination, texturing, the extraction of non-volatile molecules such as flavonoids [11] and of volatile compounds [12,13]. In the present work, we studied DIC, as essential oil extraction process. A preliminary thermodynamic study allowed us to determine the relative or absolute volatility of each compound versus temperature. The hydrodistillation was performed as references to compare the DIC extraction yields and kinetics.

2. Materials and methods

2.1. Raw Material

The bark of the sandalwood tree used in this study. Was provided by the company BAHAVE (Nantes, France). Its was originally from Australia and harvested in avril 2013. Its initial moisture content was 11 g H₂O/100 g dry matter, with average diameter of 2 mm.

2.2. Assessment protocol

In the present study we had examine the effects of the total heating time (t) and the number of cycles (C) as DIC operating parameters (independent parameters), regarding the extraction efficiency EE considered as the main response parameter (dependent variable). The principle objective was to identify separately the impacts of evaporation and autovaporization phenomena. An experimental design was built intervening t and C; the first must be correlated to the evaporation process while the second one must reveal the effect of the autovaporization by itself. This investigation was achieved according to the protocol shown in Fig. 1. The treatments by hydrodistillation were performed as references to compare

the DIC extraction yields and kinetics. An adequate statistical treatment of the data issued from the experimental work carried out in the present article allowed us to study, analyze, optimize and model the DIC extraction of essential oils.

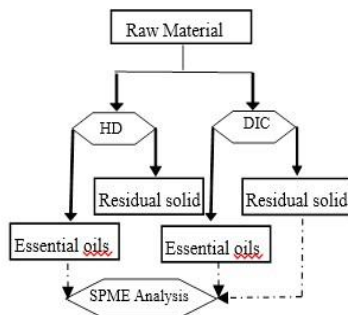


Fig. 1. Protocol treatment of sandalwood chips oil extraction.

2.3. Hydrodistillation

The hydrodistillation equipment used was a modified Clevenger, in accordance with conventional hydrodistillation protocols, 50 g of raw material was immersed in 500 mL of distilled water in a 1 L distillation flask. The extraction of essential oils was performed out from the first drop of distillate until no more essential oil was obtained. The essential oil yield (Y) is defined as the ratio of the mass of the essential oil obtained (M_{EO}) to the dry of sandalwood chips (M_{dm}):

$$Y(\%) = \frac{M_{EO}}{M_{dm}} \quad (1)$$

2.4. Laboratory scale (DIC) process

The reactor we used was a 18 l processing vessel with a heating jacket; thermal treatment in this vessel was achieved using saturated steam with a pressure varying from 0,1 MPa up to 0,6 MPa, which means a temperature between 100 and 160°C. A 1600 l vacuum tank with cooling water jacket is connected with a water ring vacuum pump allowing the vacuum to be to be maintained at 5 kPa. A pneumatic valve ensures an “instant” connection between the vacuum tank and the processing vessel; it can open in less than 0.2 s. Some other valves control the flow of steam and compressed air within the processing vessel (Fig. 2).

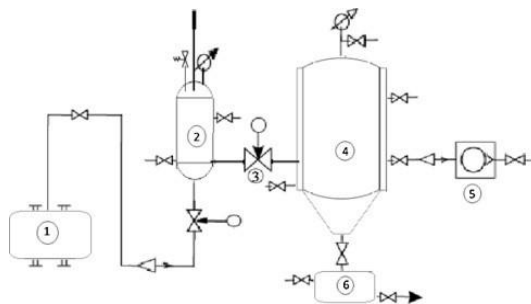


Fig. 2. Schematic diagram of DIC system. (1: boiler; 2: processing vessel; 3: quick pneumatic motion valve; 4: vacuum tank; 5: vacuum pump; 6: tank of liquid).

2.5. DIC treatment

In the present study, the raw sandalwood was directly put in the DIC reactor-processing vessel. After placing the raw material in the treatment vessel and closing it, a first vacuum stage (about 5 kPa) was

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established in order to remove the air presented in the vessel and, thus to assure close contact between the surface of the sample and the steam to be injected just after (Figure 3. phase c).

High pressure saturated steam used in our case was 0.6 MPa according to the experiment design (Table 1), and the product temperature to 160 °C. This stage lasted 10–300 s and ended by an abrupt pressure drop towards a vacuum (5 ± 0.2 kPa) by opening the pneumatic valve V3 (Fig. 2), which assured a decompression rate higher than 1 MPa s^{-1} . In our case, several DIC-cycles were carried out and atmospheric pressure was established after the final pressure drop. Fig. 3 gives the flow-sheet of this treatment. In our case, during the total thermal treatment time (phases d of various cycles), a part of essential oils must evaporate; the instant pressure drops towards a vacuum would normally simultaneously provoke an autovaporization of a part of water and volatile molecules (essential oils), and an instantaneous cooling of the product immediately stoppes its thermal degradation.

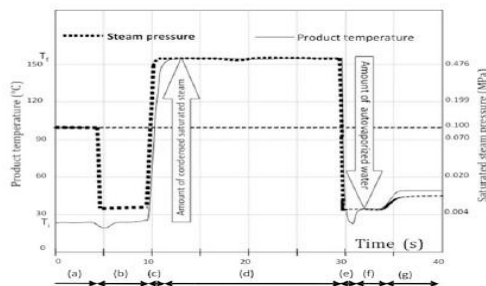


Fig. 3. Temperature and pressure history of a cycle of DIC extraction: (a) Sample at atmospheric pressure; (b) initial vacuum; (c) saturated steam injection to reach the selected pressure; (d) constant temperature corresponding to saturated steam pressure; (e) abrupt pressure drop towards vacuum; (f) vacuum; (g) releasing to the atmospheric pressure. [14].

2.6. Statistical and experimental design protocol

Response surface methodology (RSM) method with a five-level central composite rotatable experimental design method was adopted. In the present study, the saturated steam pressure used kept constant at 0.6 MPa and the two DIC operating parameters we studied were the total heating time t , and the number of pressure drops C , (Table 1). Moisture content just before DIC treatment was maintained constant (11 ± 0.3 g $\text{H}_2\text{O}/100$ g dry matter). DIC treatment experiments were then carried out using the operating conditions described in Table 2.

The statistical treatment of results was executed using the analysis design procedure of Statgraphics Plus software for Windows (1994, version 4.1, Levallois-Perret, France). Variance (ANOVA) was performed to determine significant differences between independent variables, and Pareto charts were introduced as well as general trends, response surface, empirical model coefficients, and R^2 were determined. The dependent variables had concerned process performances: the response was expressed with a second order polynomial model of independent variables :

$$Y = \beta_0 + \beta_1 t + \beta_{11} t^2 + \beta_2 C + \beta_{22} C^2 + \beta_{12} tC + \varepsilon \quad (2)$$

where Y was the response, $\beta_0, \beta_1, \beta_{11}, \beta_2, \beta_{22},$ and β_{12} were the regression coefficients, C, t were the independent variables, ε was random error. Response surface methodology could be used to optimize the operating parameters by coupling various studied responses.

Table 1. Independent variables used in response surface methodology at a fixed steam pressure value

Table 1. Independent variables used in response surface methodology at a fixed steam pressure value

| Parameters | Coded level | | | | |
|--------------------|-------------|-----|-----|-----|-----------|
| | $-\alpha$ | -1 | 0 | +1 | $+\alpha$ |
| Number of cycles | 2 | 5 | 12 | 19 | 22 |
| Treatment time (s) | 120 | 240 | 600 | 960 | 1080 |

The extraction efficiency EE considered as the main response parameter (dependent variable) was calculated from SPME analysis by summing the areas, carried out on untreated sandalwood chips (raw material) and residual solid after DIC treatments, as:

$$EE (\%) = \frac{EO \text{ in raw material} - EO \text{ in DIC solid residue}}{EO \text{ in raw material}}$$

Table 2. DIC extraction trials with extraction efficiency.

| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 |
|--------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Total time (s) | 600 | 1080 | 600 | 600 | 960 | 960 | 600 | 240 | 240 | 600 | 120 | 600 | 600 |
| Time per cycle (s) | 50 | 90 | 27 | 50 | 51 | 192 | 50 | 48 | 13 | 50 | 10 | 300 | 50 |
| Number of cycles | 12 | 12 | 22 | 12 | 19 | 5 | 12 | 5 | 19 | 12 | 12 | 2 | 12 |
| Efficiency (%) | 47.54 | 48.32 | 69.51 | 40.97 | 71.03 | 38.06 | 63.22 | 31.28 | 67.69 | 55.34 | 59.92 | 15.43 | 50.12 |

2.7. Analysis by GC/MS with solid-phase microextraction (SPME)

The volatile molecules present in the untreated solid samples, as well as in DIC treated samples were analyzed through SPME system (model CombiPal, CTC Analytics AG, Zwingen, Switzerland) connected with a GC-MS system. Comprising a Varian GC 3800. equipped with a capillary column VARIAN, with an apolar phase (polydimethylsiloxane) model VF-5ms (30m× 0,25 mm× 0,25 mm), was connected to a mass spectrometer Saturn 2100T, equipped with a sample tray of the CombiPal (Cie Varian, Les Ulis, France).

In this study, a 75µm CAR/PDMS Fuses Sillica fiber was used. The SPME parameters including the sample mass, extraction temperature, extraction time, and desorption time were respectively: 1 g, 70 °C, 30 min and 10 min. GC analysis conditions were optimized, with helium used as carrier gas, at a constant rate of 1 ml/min. The column temperature was 70 °C for 6 min; it increased to 120 °C at 15°C/min, from 120 to 200 at 3 °C/min, and 25 °C/min up to 250 °C. The detection, and transfer temperature was 230 °C and 250 °C respectively.

Compounds were identified by comparing their mass spectral fragmentation patterns with those stored in the data bank MS from National Institute of Standards and Technology (NIST). For each compound on the chromatogram, percentage of peak area relative to the total peak areas from all compounds was determined and reported as the relative amount of that compound.

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3. Results and discussion

3.1. Hydrodistillation

The study of the kinetics of extraction of essential oil by hydrodistillation reveals extraction increases with time to reach after 160 hours of extracting a level of stability (Fig.4).

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 mixture of the volatile molecules. Therefore, we sought to determine the thermodynamic properties of liquid-vapor equilibrium of each compound of sandalwood. The vapor pressure at various temperatures of the various compounds was determined using the ACD / I-Lab (ACD / Labs 2010-2014). These data then plot the relative volatility of each compound relative to the water Fig. 5. The results show a relative volatility whose evolution is significant depending on the temperature. Thus, in the field of hydrodistillation, the temperature is 100 °C, and the relative volatility is less than 0.004. This aspect of very low relative volatility explains the low kinetic evaporation extraction.

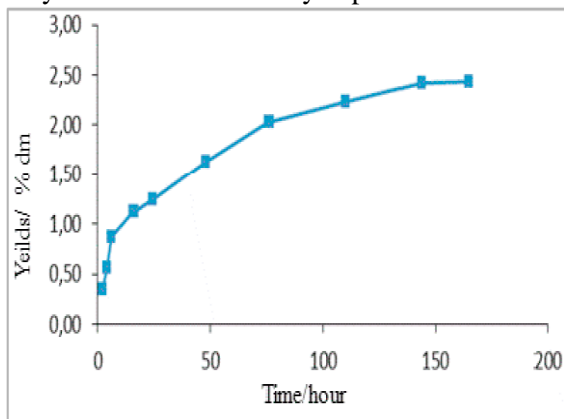


Fig. 4. Kinetics of hydrodistillation of sandalwood volatile compounds vs water.

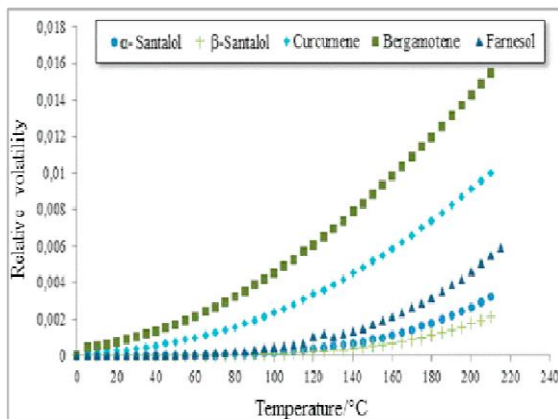


Fig. 5. Relative volatility of sandalwood

3.2. Comparative extraction yields of hydrodistillation extraction and DIC

These both values of hydrodistillation and DIC yields were sub-estimated, the first would be due to the condenser problems whereas the second would concern some amount of essential oils linked on the vacuum tank wall. However, these values were able to prove the ability of DIC to extract very quickly much higher yields of sandalwood essential oils (Table 3).

Table 3. Yield of essential oils obtained using DIC extraction in comparison with conventional hydrodistillation.

| | DIC | Hydrodistillation |
|------------------------|------|-------------------|
| Yields (g EO/100 g dm) | 1.14 | 1.23 |
| Total heating time | 5min | 24h |

3.3. DIC optimization statistical and experimental design protocol

As shown in Table 2, we performed a central composite experimental design. The number of DIC cycles and total heating time were taken as independent parameters it allowed analyzing and determining the importance of the Autovaporisation and evaporation respectively. The extraction efficiency EE%

determined on each solid residue after DIC experimental design by SPME was considered as the main response parameter.

The mathematical relationship obtained with the statistical package Statgraphics was a polynomial equation representing the quantitative effect of process variables and their interactions on the measured response EE.

The response surfaces allowed us to represent the total effect of operative parameters. RSM optimization was used to show the impact of the operative factors in terms of extraction efficiency EE (Fig. 6). Thus, it was possible to identify the highest and the quickest DIC extraction process through the operation efficiency. Here, it was clear that the number of cycles (revealing the impact of the pressure drops) was the only factor to have a profound effect. The values of the coefficients of C and t were related to the effect of these variables on the response EE (Fig. 7). A positive value represented an effect that favors the operation, while a negative value indicated an antagonistic effect.

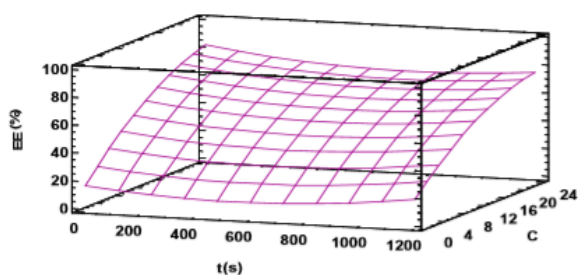


Fig. 6. The response surfaces to represent the total effect of operative parameters.

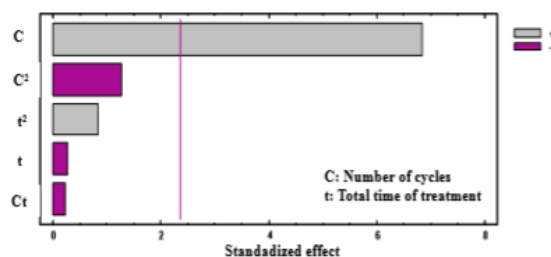


Fig. 7. Standardized Pareto chart for EE (%)

This mathematical relationship is listed below:

$$EE (\%) = 15.6644 - 0.0218008t + 4.54692C + 0.0000199396t^2 - 0.000341237tC - 0.0729185C^2$$

With $R^2 = 87.62\%$ (4)

The optimized operative conditions with the goal to maximize the extraction efficiency EE was calculated as an optimum value of 77.17%, for 120 s as a total thermal treatment time t, and 22 as a theoretical value of the number of cycles C. These t and C optimized values were substituted and used in experimental trials carried out at 0.6 MPa as saturated steam pressure P, total thermal treatment time t = 330 s, and C = 22 cycles, which means 15 s of thermal treatment time for each cycle.

4. Conclusion

The present research work confirmed the high relevance of DIC treatment as extraction process. At both fundamental and experimental points of view, this study allowed the DIC extraction process to be defined as a mainly autovaporization phenomenon; the contribution of evaporation to the extraction of essential oils was established to be very weak even negligible in the usual DIC processes. The natural structure of some plants such as sandalwood prevents an easy conventional essential oil extraction. The extraction performed by hydrodistillation (HD) showed that a slow process.

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