Obtaining of Extracts from *Origanum vulgare* and *Cordia verbenacea* Via Supercritical Technology and Steam Distillation: Process and Economical Study

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ABSTRACT

The possibility of using supercritical fluid extraction (SFE) technology as an ecologically correct alternative for industrial processes has been long discussed in recent years. The relatively high cost of SFE processes has been a major obstacle in the widespread use of this technology. In the present study, extracts from oregano (*Origanum vulgare*) and *Cordia verbenacea* leaves collected during the vegetative phase of the plants were isolated using SFE and steam distillation (SD). Oregano is well known for its antioxidant activity and antimicrobial properties. *C. verbenacea* is used in Brazilian folk medicine for its anti-rheumatic, anti-inflammatory, analgesic and healing properties. A comparative study of the cost of manufacturing (COM) of the two extraction methods is presented. The cost estimation was done using a class 5 methodology that defines COM as a weighed sum of five factors: fixed cost of investment, cost of operational labor, cost of raw material, cost of waste treatment and cost of utilities. The operational data used were obtained from literature (*C. verbenacea* SFE) and laboratory experiments (*O. vulgare* SFE and SD and *C. verbenacea* SD). The scale-up procedure assumed that both yield and extraction time of the industrial process are equal to the laboratorial scale if the ratio between the solvent flow rate and the mass of particles inside the extractor is kept constant.

Key-words: *Cordia verbenacea*, Manufacturing cost, *Origanum vulgare*, Steam distillation, Supercritical extraction

INTRODUCTION

The name "oregano" is given to many species of a variety of genera, but usually refers to the genus *Origanum*. Within this genus there are both morphological and chemical differences and many transitional forms occur worldwide. Using the widely accepted Ietswaart's classification system, 43 species and 18 hybrids have been recognized [1]. The *Origanum vulgare* specie is a native plant of the Mediterranean region that has been successfully inserted by Andean region countries into South America crops and markets; however the local food, cosmetic and pharmaceutical industries do not take full advantage of its well know potential. Functional properties like antioxidant and antimicrobial activities of the extracts from *Origanum* genus plants have been long studied with positive results [1-4]. The extracts chemical composition, functional properties and yield can vary, depending on the *Origanum* species [2], the populations within the same specie [5] and the extraction method used for the recovery [6]. Dried aerial parts of *Origanum vulgare* (Chilean origin) were used in this study.

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Known popularly in Brazil as “erva baleeira”, *Cordia verbenacea* is found in the country from the Amazon region up to the state of Rio Grande do Sul [7]. The aerial parts of this plant have strong and durable fragrance. The extract obtained from the leaves is used in folk medicine for its anti-rheumatic, anti-inflammatory, analgesic and healing activities [8]. The biological properties cited in literature include antimicrobial [9] and anticancer [10] activities and protective effect on the gastric mucosa [11]. The major compounds found in *C. verbenacea* vary with the extraction procedure [12]. The main components in volatile fraction are α-pinene, 1,8 cineol, aloaromadrene, β-caryophyllene and α-humulene [9]. As for ethanol extraction, α-santalene and β-caryophyllene are the major compounds present on the extracts [12]. Supercritical fluid extraction (SFE) under different conditions leads to extracts with the same qualitatively chemical profile, but with different concentrations of the main compounds; by this technique, all compounds found in volatile oil obtained by hydrodistillation and ethanol extraction are found [12].

The traditional extraction methods for *O. vulgare* are Soxhlet using ethanol, hydrodistillation and steam distillation (SD) [2] and for *C. verbenacea* are Soxhlet using ethanol, ketone or dichloromethane, and hydrodistillation [10]. In general, the active compounds present in plants are in low concentrations and thus it is desirable to use a methodology that results in maximum yields with minimum changes in functional properties of the extract. SFE represents an alternative for the conventional processes. This technology exploits the high solvation power, low viscosity and high mass diffusivity presented by supercritical fluids [13]. SFE has been shown as a technically viable process to obtain a series of high quality extracts [14], and more recently, it was also shown as an economically viable process [15-20].

The objective of the present work was to carry out a technical evaluation of *O. vulgare* extraction by SD and SFE and *C. verbenacea* by SD. An economical evaluation for both raw materials was also conducted.

MATERIALS AND METHODS

Steam Distillation

The SD of whole leaves of *O. vulgare* (85 g) previously dried (12.6% of humidity) were carried out for 70 minutes collecting fractions of the volatile oil during this time. The distillation time was set according to previous experiments showing that no more *O. vulgare* essential oil was recovered after this period no matter how much longer the process was continued (180 min). It was used superheated steam (435 K) flowing at a rate of 1.7×10^{-4} kg/s. The apparent bed density in the extraction column was 102 kg/m^3.

The *C. verbenacea* used in the present work was the same from a previous study on SFE [20]. Dry (5.8% of humidity) aerial parts of the plant (77 g) were used for SD, with an apparent bed density of 123 kg/m^3. Superheated steam (421 K) flowed at 1.7×10^{-4} kg/s through the extraction bed. Fractions of volatile oil were collected during 300 min.

Supercritical Fluid Extraction

The same leaves of *O. vulgare* used for SD were grinded and sifted out to 24-32-48 and 80 mesh in a 3:3:3:1 proportion. Ninety five grams of these leaves (11.5% of humidity) were used for carbon dioxide (CO_2) SFE at 323 K and 20 MPa. The extraction conditions were chosen based on global yield (X_0) results for a two temperatures five pressures combination and on the antioxidant activity presented on the X_0 extracts. The CO_2 flow rate was 1.4×10^{-4}

kg/s and the apparent bed density was 387 kg/m^3. The kinetic experiments were performed collecting fractions of the extract during 480 minutes.

Cost of Manufacturing

The experimental data were used for cost of manufacturing (COM) estimation. The COM of *O. vulgare* extract (obtained by SFE) and *O. vulgare* and *C. verbenacea* volatile oils (obtained by SD) was estimated using the methodology described by Rosa and Meireles [15], which is based in the expression proposed by Turton et al. [21] (Eq. 1). This expression defines COM as a weighed sum of five main costs: fixed cost of investment (FCI), cost of operational labor (COL), cost of utilities (CUT), cost of waste treatment (CWT) and cost of raw material (CRM).

$$COM = 0.304\ FCI + 2.73\ COL + 1.23\ (CRM + CUT + CWT) \quad (1)$$

For SFE fixed cost of investment (FCI), it was considered an industrial scale unit equipped with a CO_2 recycling system. It is composed by two 0.4 m^3 columns, one flash tank separator, one CO_2 reservoir, one CO_2 condenser, one pump and one heat exchanger, and costs around US$ 2,000,000.00. For SD FCI, it was considered an industrial unit composed by two 0.5 m^3 distillation columns, one shell and tube condenser and one separator, which costs US$ 50,000.00. Annual depreciation was considered to be 10% for both units.

The operational labor cost (COL) was calculated using information of man-hour per operation-hour according to the tables presented by Ulrich [22]. Two and three operators per shift are needed to work in the SFE and SD units, respectively, at a cost of US$ 3.00/hour. The total operational time of both extraction units was considered as 7920 h per year, which corresponds to 330 days per year with three 8-hour shifts a day.

The raw material cost (CRM) includes the cost of the solid substrate and the cost of the solvent lost during the process. The CO_2 (US$ 100.00/ton) loss was assumed to be 2%. The pre-processing cost (drying and grinding) was estimated by Rosa and Meireles [15] using the SuperPro Designer software as US$ 30.00/ton. The commercial price of raw material were determined as US$ 2,135.00/ton and US$ 9,480.00/ton for *O. vulgare* and *C. verbenacea*, respectively.

The utilities cost (CUT) for SFE was estimated considering the energy involved in the CO_2 cycle, using the temperature-entropy diagram. The utilities used were steam (US$ 0.0133/Mcal), cold water (US$ 0.0837/Mcal) and electricity (US$ 0.0703/Mcal). For SD, the steam (US$ 16.22/ton) and cold water (US$ 0.0148/ton) costs were based on the values proposed by Turton et al. [21].

The cost of waste treatment (CWT) was neglected, since the only accumulated waste in SFE and SD are the exhausted solid and the wet solid, respectively, which may both be sold to make fertilizer or incorporated to the soil, considering they are harmless residues. The CO_2 that is lost during the process in SFE does not need any treatment, since in small quantities it is not harmful.

The mass of feed in the industrial extraction vessel was determined according to apparent bed density. For SD and SFE the scale-up procedure assumed that both yield and extraction time of the industrial process will be the same as the ones obtained in laboratorial scale if the ratio between the solvent mass and the mass of particles inside the extractor is kept constant [15].

RESULTS AND DISCUSSION

In Figures 1(a) and 1(b) are presented the variation with time of extraction yields and COM estimations for *O. vulgare* SD and SFE, respectively. In SD more than 90% of the total essential oil obtained is collected after 20 minutes; after 30 minutes the yield becomes approximately constant. The values of the COM estimation decrease with time until a minimum of US$ 450.00/kg at 25 minutes (0.95% yield); after that time, the COM starts to increase again. The COM of oregano SFE extract reaches its minimum value at 150 minutes (US$ 202.00/kg) corresponding to 2.4% yield.

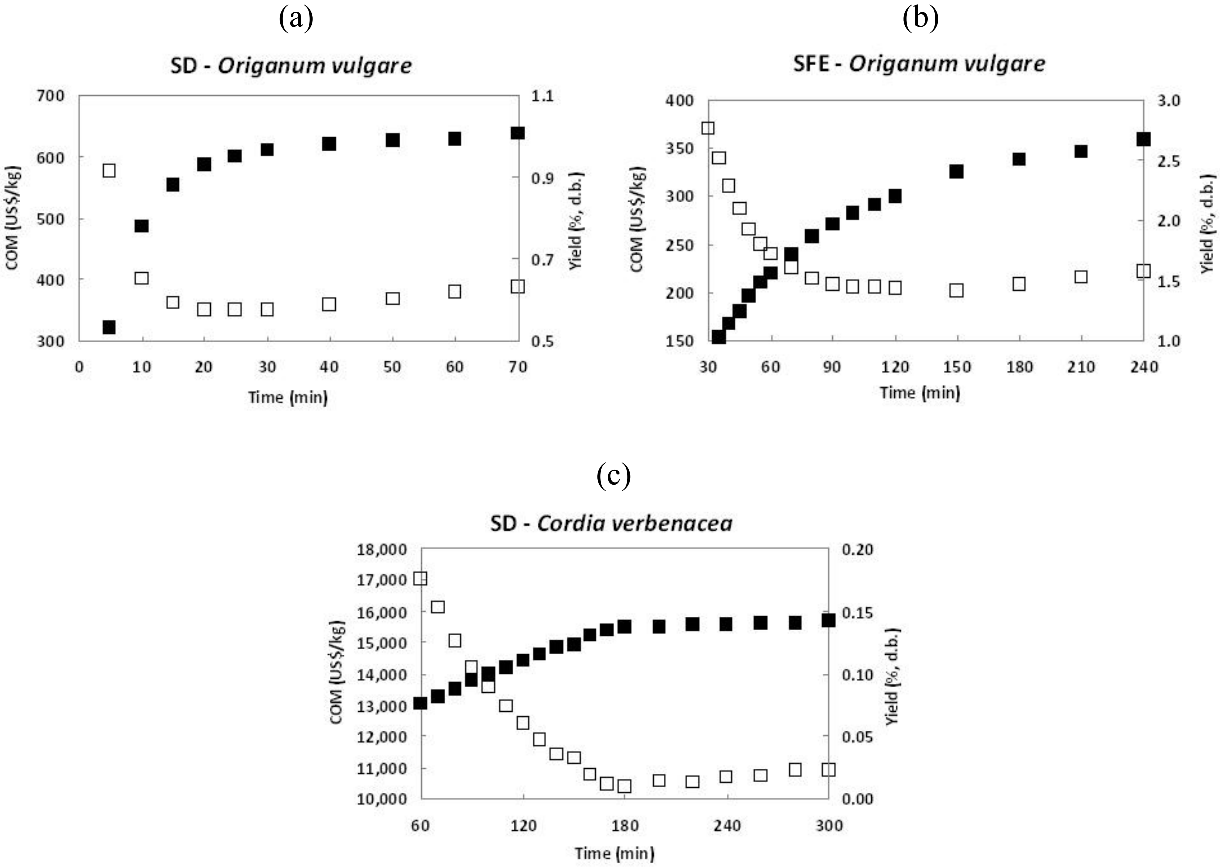

Figure 1: COM estimations for Oregano SD and SFE and *Cordia verbenacea* SD (■ = yield, □ = COM).

Since both SD and SFE used the same *O. vulgare* as feed, the difference in the COM estimations resides in the different extraction yields, maximum values of 1% and 3% for SD and SFE, respectively. The phases are different for both extracts, while SD essential oil has liquid phase the SFE extract presents a solid one. Another difference is the color, the *O. vulgare* essential oil has a translucid yellow color and the SFE extract is solid dark yellow.

It is important to note that in the conditions above mentioned for the minimum COM, the estimated mass of *O. vulgare* essential oil (8,060 kg/yr) obtained by SD was not very distant from the estimated mass of the *O. vulgare* extract (10,400 kg/yr) obtained via SFE. This fact can be related to the extraction time proportion between both processes. *O. vulgare* SD time was 6 times shorter than SFE time.

The variations of the cost fractions that compose the COM of *O. vulgare* SD were from 1% to 5% for CUT, from 2% to 17% for COL, and the FCI never exceed 2%. An inversely proportion with time variation was presented for the CRM fraction (78-98%). For *O. vulgare* SFE the COM fraction variations had larger amplitude. The CUT fraction ranged from 1% to 4%, the COL fraction from 1% to 10%, the FCI fraction from 2% to 51% and again the CRM fraction was inversely proportional with time, but with a huge drop from 98% to 36% due to FCI increase.

It is interesting to observe that even though the investment cost is much larger for SFE process when compared to SD, the minimum COM obtained by SFE is half the one obtained by SD for *O. vulgare*.

Figure 1(c) presents the COM estimations for *Cordia verbenacea* SD. The yield becomes constant from 180 min of extraction on, which corresponds to a COM of US$ 10,380.00/kg. This high COM is due to elevated raw material cost and low volatile oil yield (maximum of 0.14%). Leal et al. [20] used the same raw material for SFE. They obtained a minimum COM of US$ 667.00/kg, since the yield was much higher (2.5%). The raw material difference lays in the fact that while Leal et al. [20] used comminuted *C. verbenacea* leaves, the present work used whole leaves in order to prevent the steam head loss through the extraction bed, which is a common practice in industrial SD process.

Despite the economical and yield advantage presented by SFE, the chemical composition of extracts obtained by SD and SFE is different for *C. verbenacea*; the β-caryophyllene content on SD and SFE extracts is 22% and 2.5%, respectively [12]. Therefore, the target compound should determine the best extraction method for processing *C. verbenacea*.

The CRM was the major fraction in COM (80-99%); it was inversely proportional with time. The CUT fraction was no over 6%, while COL increased with time, from 1% to 14%. The FCI fraction stayed below 2% of COM.

Even though the investment costs still are pointed as the major limitation factor to SFE spread, recent studies have been showing its economical viability [15-20], when all the costs associated to COM are considered. It is important to remember, though, that the choice of the extraction technique to be applied to a specific raw material should take into account three factors: (i) product quality, which may be determined by chemical composition, biological activity, stability, etc.; (ii) lower cost of manufacturing, which can be associated to higher yield, lower processing time, etc.; (iii) ambient impact reduction. The careful analysis of all those parameters should lead to the choice of the best extractive technique.

CONCLUSION

The lower COM of *C. verbenacea* volatile oil was US$ 10,380.00/kg; for *O. vulgare* volatile oil it was US$ 450.00/kg and for *O. vulgare* supercritical extract it was US$ 202.00/kg. In spite of COM estimations can not be used as a the only argument for the widespread and use of SFE technology, it has been demonstrated here that large capacity plants, with optimized design and operation, lead to prices that are of the same order of magnitude or lower than those related to a classical clean process like SD.

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