J. of Supercritical Fluids 122 (2017) 35–42

Contents lists available at ScienceDirect

The Journal of Supercritical Fluids

journal homepage: www.elsevier.com/locate/supflu

Purification of sclareol by supercritical CO_2 fractionation process

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ARTICLE INFO

Article history:
Received 29 August 2016
Received in revised form 7 December 2016
Accepted 7 December 2016
Available online 7 December 2016

Keywords:
Supercritical CO_2 fractionation
Sclareol
Response surface methodology
Continuous process
Counter-current column
Internal reflux

ABSTRACT

The implementation and optimization of continuous supercritical CO_2 fractionation of a clary sage extract containing 25 wt% of sclareol were performed in order to increase its sclareol content. After preliminary experiments confirming the feasibility of the process, different operating conditions were studied: CO_2-over-feed mass ratio from 25 up to 115, and pressure between 11 and 13 MPa, with an internal reflux due to a thermal gradient 323–338 K along the column, through an experimental design. Four responses were highlighted: sclareol mass fraction in the raffinate, sclareol mass fraction in the extract, sclareol yield in the raffinate, and the amount of an undesirable compound exhibiting a similar behaviour to sclareol and thus, hard to separate from sclareol by conventional techniques. This work allowed us to highlight the best operating conditions: a pressure of 12.6 MPa and a CO_2-over-feed mass ratio of 114.5 leading to a sclareol mass fraction in raffinate and extract of 75.3% and 4.6% respectively, to a sclareol yield of 82.4% in the raffinate, and to an amount of 0.08% of the undesirable compound in the raffinate.

1. Introduction

Clary sage (*Salvia sclarea* L.) is a biennial perennial herb in the genus salvia [1], grown in Provence in the South of France. This plant contains about 1–4% of sclareol (mostly located in the calyx of the flowers) [2]. This natural molecule is used in perfumery as a raw material for the production of a semisynthetic molecule named Ambrox® or Ambroxan® [3,4] and is employed as a fixative base note in replacement of natural ambergris (which is a whale secretion). The aim of this study was the implementation and optimization of continuous supercritical CO_2 fractionation of a liquid feed containing 25 wt% of sclareol, preliminarily obtained by extraction with an apolar solvent from clary sage, in order to increase its sclareol content.

The supercritical fractionation process allows the separation of compounds contained in a liquid mixture by using a solvent under supercritical conditions. This process is based on the solubility difference of the feed's components in the supercritical solvent. Such fractionation can be implemented in continuous mode. In order to put the liquid feed and the supercritical solvent into contact, a counter-current column setup is generally used [5]. In this configuration, the more soluble compounds in supercritical solvent are recovered on top of the column. Depressurization of the overhead produces the extract condensation, whereas the raffinate, corresponding to the highest density phase (a liquid one), is recovered directly at the bottom of the column [6,7]. CO_2 is generally the most common solvent used for the supercritical fractionation process. Supercritical CO_2 fractionation combines many advantages when compared to conventional processes. Above all it is a continuous process involving a green and recyclable solvent allowing easy and efficient separation. Supercritical fractionation is performed under pressure but it can be economically viable because it is compact and flexible. Moreover, it is a low temperature operation which adds the possibility to process thermolabile compounds. Thus, the supercritical fractionation process might be an interesting alternative for difficult separations or as a separation technique coupled with others to improve the overall separation efficiency.

Recently, Bejarano et al. [6] have published a review on fractionation technologies for liquid mixtures using dense CO_2. In this article, 41 references are listed on edible oils and 13 on essential oils.

In this work, preliminary experiments were performed to determine the experimental domain (pressure, temperature, CO_2 and feed flow rates) where the separation is feasible. In a first step, supercritical CO_2 extractions from dry clary sage straw and flowers were performed to determine pressure and temperature domain where sclareol is soluble in supercritical CO_2. In a second step, high-pressure fluid phase equilibrium measurements were performed to delimit the pressure and composition domain where the system (CO_2-feed) is biphasic liquid/vapor at temperatures between 323

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http://dx.doi.org/10.1016/j.supflu.2016.12.001
0896-8446/

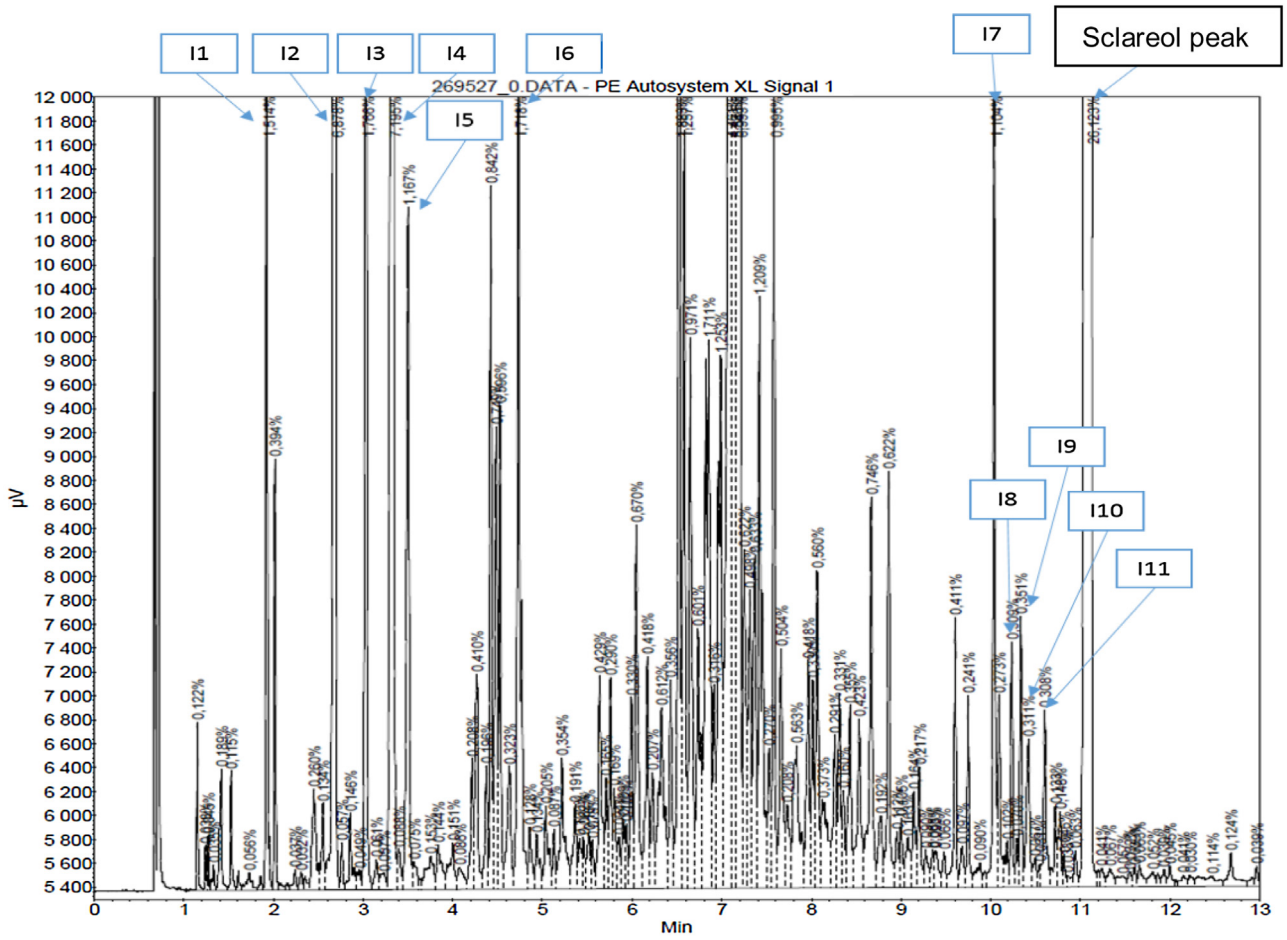

Fig. 1. Chromatogram of the feed containing 24 wt% of sclareol with the identification of the targeted compounds to separate from sclareol.

and 338 K. Finally, supercritical fractionation process was implemented. It is worth noting that due to its solubility properties, we targeted to concentrate sclareol in the raffinate. Indeed, the operating conditions for fractionation were chosen in order to avoid or limit the solubilisation of sclareol, except when an internal reflux was implemented. In a third step, supercritical fractionation tests were thus performed at a pressure fixed at 12 MPa and at different temperatures in the column, 313 and 338 K, and with a gradient temperature along the column of 323–338 K to determine the column temperature recommended for the experimental design.

Finally, an experimental design was applied to identify the optimal operating conditions for the targeted application. The influence of the variation of two parameters was studied: CO_2-over-feed mass ratio from 25 up to 115 (four levels), and pressure between 11 and 13 MPa (three levels), with an internal reflux due to a temperature gradient of 323–338 K along the column. Four responses were highlighted: sclareol mass fraction in raffinate and in extract, sclareol yield in the raffinate, and the amount of an undesirable compound, maybe due to the degradation of sclareol during the storage, having a behaviour similar to the sclareol and difficult to separate by conventional methods.

2. Materials and methods

2.1. Materials

The feed used for supercritical fractionation essays was the lightest fraction of an extract obtained with an apolar solvent (short chain volatile hydrocarbon) on clary sage by the company Bontoux SAS. This liquid mixture contained about 25 wt% of sclareol and more than 160 other components. Fig. 1 shows the chromatogram of the feed with the identification of the 11 targeted compounds to separate from sclareol and Table 1 shows the main compounds and their corresponding name (when identified) and % area in the feed. Most of the compounds were not identified, nevertheless impurities from I7 to I11 are known to be particularly difficult to separate from sclareol using classical techniques.

The clary sage straw used for supercritical extraction essays was harvested in July 2014 at Montboucher-sur-Jabron (Drôme, South of France). It was constituted of dried flowers, leaves and stems.

CO_2 was supplied by Linde Gaz (France) with a purity of 99.7%.

Table 1
Main compounds contained in the feed and the corresponding % area in the feed (NI: non identified).

Code Name	Compound name	% area in the feed
I1	Linalol	1.36
I2	Alpha terpineol	7.14
I3	Nerol	1.87
I4	Linalyl acetate + geraniol	7.64
I5	NI	1.16
I6	NI	1.89
I7	NI	0.99
I8	NI	0.31
I9	NI	0.37
I10	NI	0.31
I11	NI	0.29