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Fractionation of citrus essential oil by liquid–liquid extraction using a perforated rotating disc contactor

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ABSTRACT

Citrus essential oils are important raw materials used in the formulation of many products, including soft and alcoholic drinks, flavoring agents, cosmetics, perfumes and toiletries. With the aim of improving the quality and, consequently, the price of the product, the separation of terpenic hydrocarbons and oxygenated compounds is required. The fractionation of essential oils may be achieved using diverse techniques, including liquid–liquid extraction using the appropriate solvents. This study was aimed at the fractionation of citrus essential oil model systems, composed of limonene and linalool mixtures, and crude orange essential oil (COEO) using continuous equipment known as a perforated rotating disc contactor (PRDC), in which mixtures of ethanol and water were used as the solvent. The effect of some variables, including disc rotation speed (DRS), linalool content in the feed (%LF), water content in the solvent ($w_{4,\ S}$) and the ratio between the solvent and the feed mass flows (S/F), on process performance, using model mixtures, was studied. The fractionation process using the PRDC achieved concentration of linalool in the extract, on a solvent-free basis, 7-fold using a hydroalcoholic solvent with a water content of 30% by mass, and close to 10-fold using a solvent with 40% water by mass. With respect to the fractionation of COEO, the extraction indices reported here were in accordance with those determined for model systems, being obtained a concentration of oxygenated compounds of 10-fold using solvent with 30% of water and 15-fold using solvent with 40% of water.

1. Introduction

Essential oils, as raw materials, are an important commodity on the world market. In the last year, essential oil exportation amounted to almost 221,103 tons, corresponding to about US$ 4 billion in trade value. Nowadays, Brazil is the main essential oil producer, with close to 25% of world's exports (almost 65,103 tons). This fact is due to the wide production of citrus essential oil; Brazil is the top exporter of orange essential oil in the world (about 47% of exports) [1].

Essential oils are important constituents for the formulation of food and chemical products, mainly citrus essential oils, such as orange, lemon and lime. They are used in the preparation of soft and alcoholic drinks, flavoring and additive agents, and in the composition of perfumes, cosmetics, toiletries and others products [2–5].

Citrus essential oils are characterized as mixtures of several components, such as terpenes, sesquiterpenes, aldehydes, alcohols and esters, but can be simplified as a mixture of terpene hydrocarbons, oxygenated compounds and non-volatile residues, such as pigments and waxes [3,6,7]. The oxygenated compounds are, generally, those mainly responsible for the characteristic flavor of citrus essential oils and, unlike the hydrocarbon terpenes, present greater stability. Thus, the removal of hydrocarbons is an important step to provide better quality and stability of the product, thereby reducing the development of off-flavors [3,6–10]

In relation to trade value, the ranking of the main essential exporters is as follows: India, China, the United States of America, France, the United Kingdom and Brazil. Moreover, in the perfume, cosmetics and toiletries market, the ranking of the main exporters by trade value is: France, the United States of America, Germany, Ireland and Italy, with Brazil in the 21th position [1]. The trade value is usually related to the quality of the essential oil and its source (e.g. citrus fruit, eucalyptus leaves and flower petals). Thus, with the aim of improving the commercial value of essential oils,

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Nomenclature

w	mass fraction
F	feed mass flow (kg s^{-1})
S	solvent mass flow (kg s^{-1})
R	raffinate mass flow (kg s^{-1})
E	extract mass flow (kg s^{-1})
E_{OMB}	overall mass balance error (%)
E_{MBi}	specific component relative error in the mass balance (%)
K_E	overall mass transfer coefficient $kg_{linalool}\ m^{-2}\ s^{-1}\ (kg_{linalool}\ kg_{extract}^{-1})]^{-1}$ or m s^{-1}
$K_E \cdot a$	overall volumetric mass transfer coefficient based on the composition of the extract stream ($kg_{linalool}\ s^{-1}\ m^{-3}\ [kg_{linalool}\ kg_{extract}^{-1}]^{-1}$)
$K_R \cdot a$	overall volumetric mass transfer coefficient based on the composition of the raffinate stream ($kg_{solute}\ s^{-1}\ m^{-3}\ [kg_{solute}\ kg_{rafinatte}^{-1}]^{-1}$)
v	extraction region volume (m^3)
a	mass transfer area per extraction region volume unit ($m^2\ m^{-3}$)
N_{tEO}	mass transfer units

Abbreviations

DRS	disc rotation speed (rpm)
S/F	solvent to feed mass flow ratio
PRDC	perforated rotating disc contactor
$\%EXT_{LOL}$	total percentage of linalool or oxygenated compounds extracted from the feed (%)
$\%EXT_{LIM}$	total percentage of limonene extracted from the feed (%)
%LF	percentage of linalool or oxygenated compounds in the feed stream (%)
%LE	percentage of linalool or oxygenated compounds in the extract phase on a solvent-free basis (%)
$\%M_{SOLV}$	percentage of solvent migration to the raffinate stream (%)
$\Delta\rho$	difference between the densities of extract and raffinate streams (kg m^{-3})
$\Delta\eta$	difference between the dynamic viscosities of extract and raffinate streams (mPa s)

Subscripts

F	feed stream
S	solvent stream
R	raffinate stream
E	extract stream
1	limonene or terpene fraction
2	linalool or oxygenated compounds fraction
3	ethanol
4	water

Superscripts

′	mass fraction on a solvent-free basis
*	equilibrium conditions

and to achieve better integration in the cosmetics market, fractionation processes are required.

Nowadays, the usual industrial fractionation of citrus essential oil is by vacuum distillation, which can present some problems once the boiling points of the oxygenated compounds are generally close to the boiling points of the terpenes [2]. Moreover, this technique generally requires a complex vacuum control and can present several problems related to the start up and stabilization of the process [11]. In this case, other alternative techniques of citrus essential oil fractionation are required.

Among the several methods applied to provide separation between terpenes and oxygenated compounds, a previous study [3] focused on the thermodynamic approach in which model citrus essential oils and crude orange essential oil were used. This study showed that fractionation is possible by the use of a liquid–liquid extraction technique (or solvent extraction), using ethanol and water mixtures as the solvent. Actually, the use of ethanol and water mixtures for the fractionation of essential oils has been studied [3,6,9,10,12,13]. In these studies, was possible to obtain fractions enriched in oxygenated compounds.

Studies based on the use of solvent extraction applied to the fractionation of essential oils consist, mostly, of the experimental determination and thermodynamic modeling of liquid–liquid equilibrium data. However, studies that present experimental data of essential oil fractionation using extraction equipment which can be used in industrial scale are rare or even non-existent.

The equipment used for liquid–liquid extraction may present several configurations and must promote contact between the liquids, create droplets of a dispersed phase in a continuous phase and provide a large area of contact between the phases to improve mass transfer. In addition, the apparatus must be able to establish the separation of the phases [14]. The perforated rotating disc contactor (PRDC) is a column with inner perforated rings, which provides good dispersion between the phases. In general, the PRDC is indicated for systems with low interfacial tension [15], and has been used by several authors to promote the fractionation of different systems [15–20]. The PRDC proved to be efficient in separation processes using liquid–liquid extraction, with a good mass transfer performance and controllability [20].

The aim of this study was to use the PRDC as a novel and alternative technology to promote the fractionation of citrus essential oils, using mixtures of ethanol and water as the solvent stream. As a primary study, citrus essential oil model systems, composed of limonene and linalool were used as the feed stream. The equipment was operated continuously and in a countercurrent configuration, and the studied process variables were: (i) the disc rotation speed (DRS), (ii) solvent and feed mass flow ratio (S/F) and (iii) water content in the solvent ($w_{4,S}$), as the manipulated variables, and (iv) the linalool content in the feed (%LF), as the disturbance variable.

The effect of the variables was analyzed over the performance of the process through the calculation of extraction indices, estimation of the solute overall volumetric mass transfer coefficient and estimation of the number of mass transfer units. In addition, once physical properties such as density (ρ) and dynamic viscosity (η) of the output streams have a direct influence over the separation of the phases and the stability of the process, these variables were also measured.

Finally, crude orange essential oil (COEO) was also submitted to the fractionation process in PRDC, using the same operation procedures of model systems. In these trials, the manipulated variables DRS and S/F were maintained at pre-set values, chosen based on results from model system experiments. The extraction indices obtained herein are in accordance with those determined for model systems, being possible to obtain a concentration of oxygenated compounds of 10-fold using solvent with 30% of water and 15-fold using solvent with 40% of water.