J. of Supercritical Fluids 92 (2014) 177–182

Contents lists available at ScienceDirect

The Journal of Supercritical Fluids

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

Study of candeia oil extraction using pressurized fluids and purification by adsorption process

Marielen Cozer Ribas[a], Daniel Mantovani[b], Jamal Abd Awadallak[a,*], Rafael Luan Canevesi[a], Nilson Marcos Tazinafo[b], Lúcio Cardozo Filho[b], Fernando Palú[a], Edson Antonio da Silva[a]

[a] Department of Chemical Engineering, Universidade Estadual do Oeste do Paraná, Toledo, Brazil
[b] Department of Chemical Engineering, Universidade Estadual de Maringá, Maringá, Brazil

ARTICLE INFO

Article history:
Received 4 July 2013
Received in revised form 15 April 2014
Accepted 19 April 2014
Available online 1 May 2014

Keywords:
Candeia oil
Supercritical extraction
Adsorption
Sovavá model

ABSTRACT

The extraction of oil from wood Candeia (*Eremanthus erythropappus*) was evaluated using CO_2 and propane as solvents. Experiments were carried out under the following conditions: $T = 40\,^{\circ}C$, $P = 200$ bar, $T = 60\,^{\circ}C$, $P = 120$ bar, $T = 50\,^{\circ}C$, $P = 200$ bar and $T = 60\,^{\circ}C$, $P = 245$ bar for carbon dioxide, yield was from 0.30 to 0.72. For propane, the temperature conditions studied were 30, 55 and 80 °C and pressures of 80, 100 and 120 bar, the yield was from 0.44 to 0.59. The α-bisabolol content of oil was evaluated and it was found that the operating conditions of extractions interfere in your concentration. The purification of the candeia oil was evaluated by the combined extraction and adsorption in fixed bed column using silica gel and alumina as the adsorbents. The separation was more efficient when used silica gel as adsorbent.

1. Introduction

α-Bisabolol has been used in pharmaceutical and cosmetic industries as an active ingredient of some formulations. It presents anti-inflammatory, anti-irritant, anti-bacterial, and anti-allergic features [1], which are its most important biological activities. In addition to this, α-bisabolol has anti-carcinogenic properties, being able to reduce cancer cell proliferation, as shown in recent studies [2].

Bisabolol (Fig. 1) is formally known as (−)-α-Bisabolol and also known as levomenol, its official nomenclature is 6-methyl-2-(4-methylcyclohex-3-en-1-yl)hept-5-en-2-olis. It is a natural monocyclic sesquiterpene alcohol, presenting a tertiary hydroxyl group, a six-member carbon ring and two trisubstituted unsaturations. Its minimal molecular formula is $C_{15}H_{26}O$, it presents molar mass of 222.37 g, CAS (*Chemical Abstracts Service)* number of (−) [23089-26-1] and racemate of (±) [515-69-5]. Its density is 0.9223 g/mL and its boiling point is 153 °C at 12 mmHg. Bisabolol is a natural substance, extracted from several species of plants, shrubs and trees. In nature, it is found in (+) and (−) enantiomeric forms, but only the (−) enantiomer shows biological activity (LOPES, 2010) [2,3].

α-Bisabolol can be extracted from the essential oil of several plants such as *Matricaria chamomilla*, *Salvia runcinata*, *Myoporum grassifolium*, and *Eremanthus erythropappus* [4]. Candeia (*Eremanthus erytropappus*) is a native Brazilian tree that grows in shallow soils with low fertility. One of its main uses is the extraction of a non-timber product: a high value essential oil.

Generally, on a large scale, candeia oil is extracted by steam distillation. Galdino et al. [4] investigated the yield and content of α-bisabolol present in candeia oil obtained by steam distillation extraction under a pressure of 1.8 kg/cm^2 for a period of 2.5 h. Candeia oil extraction yields were in the range of 0.14% to 0.33% and α-bisabolol content was 63–73%. Several factors, such as luminosity, humidity, season, plant part, genetics, nutrient availability, among others, may significantly affect the synthesis of natural substances by vegetables. Each method of extraction presents a different fraction of each component, however, Nascimento et al. [5] and Mori et al. [6] determined the chemical constitution of the oil extracted from candeia wood (*Vanillosmopsis erythropappa*) by using the GC-MS method, which consists of applying both gas chromatography and mass spectrometry processes.

In the chemical industry field, compressed-fluid technology has emerged as a promising, economically viable and environmentally friendly alternative in several industrial processes. Possible applications to this technology range from toxic materials and high-value product separation to the development of entirely new products. The use of supercritical technology has several

* Corresponding author. Tel.: +55 4533797000.
E-mail address: awadallak@hotmail.com (J.A. Awadallak).

http://dx.doi.org/10.1016/j.supflu.2014.04.009
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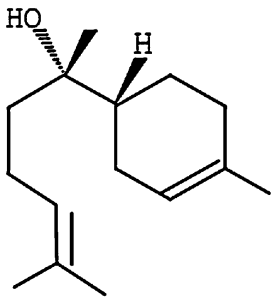

α-BISABOLOL

Fig. 1. Structural formula of α-bisabolol.

advantages, such as controlling process selectivity by a proper choice of solvent and solvent/co-solvent combination, providing mild operating temperatures, avoiding product degradation, using inert fluids that are non-toxic and do not degrade in the environment, and the possibility of carrying out the extraction and fractionation with no risk of leaving undesirable residues.

Besides being non-toxic, carbon dioxide (CO_2) is the most used supercritical fluid due to its cost, mild critical temperature and pressure. However, some studies [8–13] have shown that the use of compressed propane as a solvent has achieved extraction yields superior to those obtained with supercritical CO_2.

Extraction and fractionation using supercritical fluids can be done in two different ways: selective extraction and/or selective separation. Selective separation can also be achieved by combining the extraction process to another separation process, such as adsorption. Some researchers have studied the process of extraction followed by adsorption/desorption purification. Lucas and Cocero [14] used an integrated two-stage process. In the first stage, the extraction of coffee bean volatile components was performed by using supercritical CO_2 as a solvent. In the second stage, a selective removal of undesirable volatile (furfural) compounds was performed by adsorption on activated carbon. The authors also investigated the effect of pressure (12–17 bar), temperature (35–50 °C) and mass flow (3.5 kg/h) of the solvent on the process. After these two processes, it was found that the highest efficiency in the furfural removal was obtained under conditions of lower levels of temperature, pressure, and volumetric flow rate with carbon dioxide.

Danielski et al. [15] investigated the deterpenation of two mandarin oils (*Citrus reticulata*) obtained by cold pressing using supercritical CO_2 extraction on countercurrent, adsorption/desorption, and combination of both processes.

In particular, studies on candeia oil extraction using pressurized fluid and/or supercritical fluid, as well as this oil purification, are scarce. Souza et al. [16] studied the kinetics of candeia wood oil extraction using pressurized carbon dioxide as the solvent. The authors obtained and modeled phase equilibrium data of the CO_2 + candeia oil system. Studied temperatures were 35, 40, and 60 °C, and pressures were 100, 150, and 200 bar.

This paper investigates supercritical carbon dioxide and compressed propane as solvents in the extraction of oil from candeia wood. It also evaluates the process of oil extraction followed by purification in a fixed-bed column using different adsorbents.

2. Materials and methods

The candeia wood used in this study was provided in the form of chips by Citróleo Essential Oils Industry and Trade Ltd located in the city of Torrinha – SP – Brazil.

Table 1
Operating conditions for candeia oil extractions using supercritical CO_2 as the solvent.

Test	Temperature (°C)	Pressure (bar)
1	40	200
2	50	200
3	60	120
4	60	245

Carbon dioxide (99.5%) was provided by Guerra Gases Company and propane (99.5%, analytical grade) by Linde Company.

Other chemicals used were methylene chloride and hexane A.R. grade, which were both from Nuclear.

2.1. Wood pre-treatment

The wood was grinded in a Marconi MA-580 knife mill. After grinding, the timber was sieved and classified according to its size. Particles with a diameter between 28 and 32 mesh were used in the tests.

2.2. Candeia wood moisture content determination

Moisture determination was obtained by drying at 105 °C to constant weight [15].

2.3. Pressurized solvent extraction

2.3.1. Extraction equipment

The experimental apparatus used in solvent extraction at high pressures consisted of: a solvent reservoir, a Teledyne ISCO (model 500D) syringe pump for solvent pressurizing, two Quimis Q214M2 thermostatic baths, one for pump temperature control and the other one for the extractor temperature control, a stainless steel extractor with a capacity of 165.86 cm^3, diameter of 2.85 cm, and height of 26 cm, a furnace for heating the extracted oil, a micrometric valve from Autoclave Engineers, a CTM-04 Tholz thermoregulator, and a glass vessel collector. In the extractor output, where the oil was collected, conditions were ambient temperature and pressure.

An adsorption column made of stainless steel was connected to the experimental module in the extractions for further purification with adsorbents.

2.3.2. Experimental procedures and operating conditions

The stainless steel extractor was loaded with approximately 42 g of candeia chips, and then bath temperature was adjusted to the required extraction conditions. When thermal equilibrium was achieved, the system was gradually pressurized by the injection of solvent to achieve the desired pressure. After pressurization, candeia chips were in contact with the solvent for about 60 min. Then the micrometer valve was opened and set to the desired flow. The extracted oil was collected in preset time intervals in a glass vessel and its mass was determined on a Marte AM-220 analytical scale. The extractor was kept on until there were no significant changes in the collected oil mass.

Candeia oil extractions with propane and pressurized supercritical CO_2 were conducted under different conditions of temperature and pressure as shown in Tables 1 and 2. Extractions using supercritical CO_2 presented a volumetric flow rate of 3 ml/min while propane extractions showed a value of 2 ml/min.

A complete 2^2 factorial design with triplicate at the central point was applied for propane extractions, then the conditions in which propane was pressurized (low level) and almost at pump limit (high