

Liquefied gas extraction: A new method for the recovery of terpenoids from agroindustrial and forest wastes



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ABSTRACT

Terpenoids are important ingredients in perfumery, and terpene residues have shown potential as new sources of these compounds. This study aimed to apply gas extraction with liquefied petroleum gas (butane/propane) as a clean technology to extract terpenes from agroindustrial and forest wastes. The extracts obtained were characterized by gas chromatography–mass spectrometry (GC–MS), and compared to extracts obtained using traditional organic solvent extraction (hexane and dichloromethane:*n*-pentane). The oil extraction yields were 5.36% for the orange waste, 2.1% for the apple pomace, 2.32% for the pine needle and 0.6% for the pine wood shavings. The extract obtained using this new method on orange waste contained the highest concentration of limonene (95.32 g/100 g of extract), α -pinene (0.40) and β -pinene (0.23) among all of the solvents as well as the largest extracted amount (0.051 g/g of dry substrate). Based on the GC–MS analyses, the LPG extraction displayed less decomposition or modification of the compounds.

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1. Introduction

Solvent extraction has been widely used for the separation, purification, and recovery of substances due to the simplicity of its equipment and operation. However, the disadvantages of traditional solvent extraction have been recently recognized. The main disadvantages of conventional Soxhlet extraction include (1) a long extraction time, (2) the use of a large amount of solvent, (3) an inability to accelerate the process using agitation, (4) an evaporation or concentration process being necessary due to the high quantity of solvent used in the process and (5) the possibility of thermal degradation of the targeted compounds occurring during extractions over a long period of time at the solvent boiling point [1]. Most of these disadvantages are applicable to other extraction methods, such as the amount of solvent used. Dichloromethane:*n*-pentane (DMP) extraction is fast and simple but the low boiling point of the solvents can be a problem during

the analysis even though it makes the sample easier to concentrate after the extraction. Thermal degradation is a major issue for the extraction of terpenoids. α -Pinene, limonene, camphor, citronellol, carvacrol, camphene, Δ^3 -carene, and *r*-terpinene have high degradation indices at temperatures above 100 °C, under subcritical water conditions [2] and in the presence of hot air [3]. Due to their limited water solubility, terpenoids are commonly extracted on a large scale with methanol or 2-propanol, ethyl acetate and light petroleum (1:1:1) at temperatures that range from 40 °C to 190 °C [4].

The use of supercritical fluids is an alternative that replaces or supplements traditional industrial methods similar to using solvent extraction and pressing in oil extraction. This technique has several advantages over conventional methods due to the absence of retained solvent in the extracts. These advantages include low temperature extraction, elevated product quality and decreased energy usage [5]. Despite the method using liquefied petroleum gas (LPG) not under supercritical fluid conditions, the advantages are the same as those described for this method due to its general similarities. In addition, the extractor designed to pressurized LPG extraction is suitable for use in a fast, clean and cheap method for the extraction of terpenes and their derivatives. Pressurized LPG extraction has been rarely studied but has been previously employed for steroid extraction from fruits of the pepper family [6]

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and to enhance the enzymatic hydrolysis of sugarcane bagasse [7]. The current method does not exhibit the main recurring problem in terpene extraction and offers a series of advantages regarding ecological and technical issues. Therefore, this method offers a solution that can be applied for the recovery of terpenes in industrial processes and on the laboratory scale.

Currently, environmental pollution has become an important issue due to increasing global ecological concerns. New substrates for extraction, trade and use of byproducts as substrates in processes are an emerging issue not only due to environmental concerns but also for financial reasons. Therefore, the determination of the profiles of volatile waste enables several options including seeking grants to create new technologies that employ these promising substrates.

Citrus fruits have high concentrations of limonene [8–11]. Therefore, its wastes may be of great interest to various areas that can take advantage of this terpene. The processing of orange juice is one of the most important industries in the world, producing an enormous amount of process residues. This residue constitutes approximately 50% of the weight of the fruit and provides excellent models for value-added products. According to Mahmood [12], bagasse orange, bark and seeds comprises approximately 46% of the fruit with the juice making of 54% of the fruit.

Different conifer species have high concentrations of terpenes [13,14]. An industrial waste rich in α -pinene and β -pinene is produced by paper industries, and pine needles (*Pinus* leaf), *Pinus* bark and sawdust from the timber industry are also natural sources of these terpenes. α -Pinene and β -pinene are monoterpenes that are widely distributed in nature as well as in industrial wastes with minimal commercial value [15]. *Pinus* bark represents approximately 10–15% of the total weight of the tree [16]. The discarded *Pinus* bark from production processes is still an attractive and important renewable source of biomass. However, this material has a high content of polyphenols and low carbohydrate concentration [17].

The main byproduct of apple agribusiness (apple bagasse) can represent 20–40% of the total apple quantity processed and is currently being used as animal feed or organic fertilizer [18]. Some terpenes are found on apples (i.e., limonene) [19,20], and other terpenes, such as α -pinene, β -pinene and linalool, have been reported [21].

Other terpenes are present in many plant species and part of the main composition of many essential oils. Therefore, orange waste, apple pomace and pine substrates, terpenes, such as camphene, myrcene, p-cymene, terpinolene, cadinene, sabinene, longifolene, germacrene, linalool, terpinene, β -phellandrene, 3-carene, spathulol, α -farnesene and citral have been found [8–10,13–15,19–21]. In addition to those previously mentioned, many of these terpenes have important biological properties and can be used as precursors to products of interest in various industrial fields. Despite the fact that the agro-industrial wastes involved in this study predominantly contain limonene, α -pinene and β -pinene, a large number of other terpenes were detected at lower concentrations.

The main objective of this study was to apply pressurized liquefied petroleum gas extraction (butane/propane) as an alternative to the use of traditional solvents for the recovery of terpenoids from agroindustrial and forest wastes and confirm the use of these wastes as a source of terpenoids.

2. Materials and methods

2.1. Residues

The residues from the extraction of orange juice (peel and pulp) were obtained from a canteen located at the Federal University

of Paraná (Curitiba, PR, Brazil). *Pinus* needles and bark were collected at the forestry area of Arauco Forest of Brazil (Campo do Tenente, PR, Brazil). The *pinus* samples collected belong to the species *Pinus taeda*. Pine wood shavings were acquired from Aliança Ltda. (Curitiba, PR, Brazil). The collected *pinus* belongs to the species *Pinus ellioti*. These shavings are residues that are larger in size than that of sawdust particles resulting from cutting wood. The apple pomace used in this study was donated by Agrícola Fraiburgo S.A. (Videira, SC, Brazil) and consisted of a mixture of Fuji and Gala apples with a minor component consisting of *Granny Smith*, *Pink Lady*, *Colorida*, *Imperial*, *Catarina*, *Joaquina* and *Eva* apples. All of the materials were dried in an oven with circulating air at 60 °C, milled in a Willey-type knife mill (De Leo Equipamentos para Laboratório Ltda) and classified granulometrically below 0.8 mm.

2.2. LPG extraction

The extraction was performed in a portable extractor for use with liquefied gases developed by Oliveira [22]. Liquefied petroleum gas (LPG), which consists of a mixture of butane and propane, was used as the extractor solvent. The used gas consisted of propane 25 ± 5% and iso-butane + n-butane 75 ± 5% w/w. The liquid-phase solvent was transferred into the equipment vessel where it came into contact with 5 g of dried material. The equipment extraction flowchart is shown in Fig. 1. The extraction was performed using the liquefied form of butane/propane. The vapor pressure of the LPG was estimated to be 544.93 ± 43.4 kPa.

Each cycle of extraction used 15 g of LPG (Volcano Isqueiros Ltda, São Paulo, SP, Brazil). The exposure time of the sample material was set to 20 min per cycle at 35 °C in an oven. The required number of cycles was previously determined according to efficiency assays where five cycles was considered to be 100%. The extract was transferred to a sealed vial without contact with the environment using a needle attached to the extractor. Then, the LPG was evaporated under atmospheric pressure. All of the assays were performed in triplicate for each of the extraction methods.

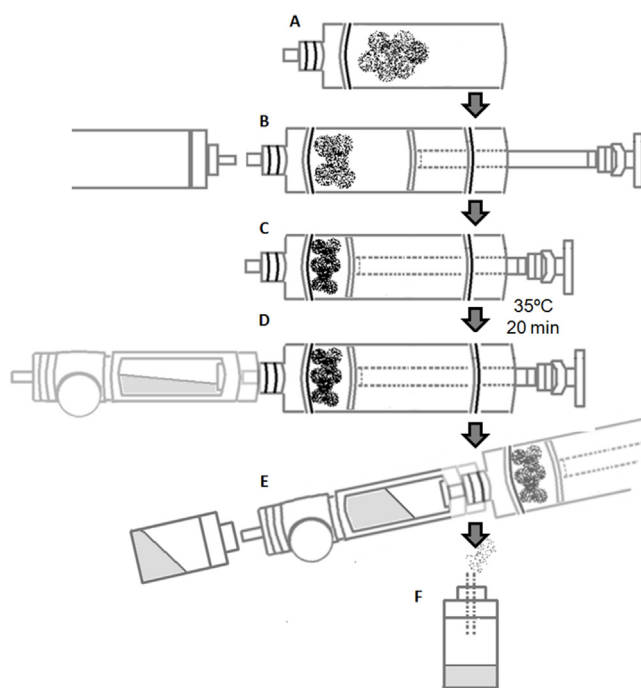


Fig. 1. LPG extractor flow chart: (A) Sample Filling. (B) Coupling of the container and LPG injection. (C) Plunger compression. (D) Recovery compartment coupling and extract recuperation. (E) Extract transfer to a vial. (F) Solvent flash evaporation.

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