D-LIMONENE AND GERANIAL FRACTIONATION FROM LEMON ESSENTIAL OIL BY MOLECULAR DISTILLATION

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Abstract — D-limonene and geranial are, respectively, the most abundant terpenic and oxygenated compounds found in lemon essential oil. The main objective of this research work is to study the technical feasibility of molecular distillation, in order to separate and concentrate those thermal labile compounds of lemon essential oil and to determine the best evaporation temperature and feed flow rate values which will lead to high separation efficiency. The highest temperature analyzed allowed to obtain a residue poor in d-limonene and enriched in geraniol, with low geranial yield (between 35–50%). Regarding d-limonene, the highest temperature (30 °C) used, led to higher yields of d-limonene. Lower feed flow rate (0.6 ml min⁻¹) led to low concentrations of d-limonene (320 g kg⁻¹) and geranial (70 g kg⁻¹) in the residue, with low yield for geranial (23.5%).

A high yield of geranial in the residue (76.4%) can be obtained by using a feed flow rate of 1.3 ml min⁻¹, which leads to the highest geranial concentration (113 g kg⁻¹).

Keywords — Essential oils, lemon, molecular distillation, d-limonene, geranial

I. INTRODUCTION

In Argentina, there is a significantly important “citrus” fruits production, from which different products are obtained — mainly juices. Essential oils are the most important by-products of juice production, and they are extracted from the “citrus” peelings. Nowadays, the production of natural essential oils is being encouraged; therefore there seems to be a brilliant future concerning this economical activity (Bruzzone, 2003; Lawrence and Reynolds, 1999).

Lemon essential oil is a product of particular interest for Argentina, since it is placed in a relevant spot in the international markets. Besides that, it constitutes a versatile product since it is used as a flavored and scented agent in cosmetic, pharmaceutical and foodstuff industries.

Oils obtained from different “citrus” fruits have in common a high amount of terpenes, which are volatile-lower molecular weight compounds. The most frequent terpene found in lemon oil is d-limonene, which constitutes around 700 g kg⁻¹ of the oil weight. The remaining part of it consists of low to medium molecular weight aldehydes, unsaturated aldehydes, ketones, esters and alcohols. Given that, d-limonene can be considered as a primary solvent for scented compounds present in lemon essential oil (Buccellato, 2000).

Among the chemical substances found in the essential oil, some of them have nutraceutical properties (Miyake et al., 1998). Some isoprenoids such as d-limonene and others such as farnesol, tocotrienol and geranial have been evaluated on their chemo-protective activity. When administered to rats, dogs and humans at levels between 0.1 and 5% tumor genesis was suppressed by a direct action over carcinogens and pre-carcinogens that require activation. D-limonene was found to be the most effective chemo-protector (Wildman, 2001).

Given these important properties of the compounds found in lemon essential oil, it is necessary to study beneficial techniques of separation and concentration that allow obtaining more valuable products. Several methods exist for processing valuable compounds present in essential oils. Concentration can be carried out by vacuum fractional distillation, extraction using oxygenated solvents with diluted alcohol or other solvents, or dragging steam distillation. Despite the fact that acceptable separations are obtained using these methods, they present some disadvantages such as the formation of degradation products due to the high operation temperatures, or the presence of solvent traces in the final product (Sinclair, 1984; Haypek et al., 2000; Pino and Sanchez, 2000; Stuart et al., 2001).

In order to overcome those difficulties in the separation process, alternative separation techniques have been searched for. One of them is the molecular distillation — also called short path distillation. This operation is expected to provide satisfactory results, since it requires a short residence time and a very low operation temperature, due to the high vacuum levels in which the separation takes place. These characteristics prevent the compounds of interest from suffering thermal damage, and lead molecular distillation to become a very useful technique in the purification of thermal labile substances (Pramparo et al., 2004; Pramparo et al., 2006; Zeboudi et al., 2005).

Molecular distillation is based on the partial vaporization of the compounds of a mix, which usually moves as a falling film in contact with a heated surface, and the subsequent condensation that takes place in a very close and cold surface. The main feature of this operation is its very low operation pressure, around 10⁻⁶-10⁻⁸ atmospheres. In these conditions, relative volatility of the