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Free fatty acid separation from vegetable oil deodorizer distillate using molecular distillation process

P.F. Martins *, V.M. Ito, C.B. Batistella, M.R.W. Maciel

Laboratory of Separation Process Development (LDPS), School of Chemical Engineering, State University of Campinas, São Paulo, CP 6066, CEP 13081-970, Brazil

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Abstract

Distillates of the vegetable oil deodorization are composed of free fatty acids (FFA), sterols, tocopherols, sterol esters, hydrocarbons and breakdown products of fatty acids, aldehydes, ketones and acylglycerols. The content of free fatty acids in deodorizer distillates varies between 25 and 75%. Due to its high content, free fatty acid separation from deodorizer distillate is an important step to concentrate tocopherols to high purity. Tocopherols are valuable natural substances used in food, cosmetic and pharmaceutical industries. In this work, separation of free fatty acids from soybean oil deodorizer distillate (SODD) was investigated through molecular distillation, using different operating conditions. Evaporator temperature from 100 to 180 °C and feed flow rate in the range of 1.5–23.0 g min^{-1} were used in the experiments. FFA and tocopherols contents were monitored in each stream generated by the molecular distillation process (distillate and residue streams). The intention is to determine the best operating conditions to produce a material with minimum FFA content and to minimize tocopherol losses during the process. Removal of FFA in the distillate stream resulted in a preliminary concentration of tocopherols, which is removed in the residue stream of the molecular distillation. The results showed that an efficient FFA separation from SODD with the lowest loss of tocopherols requires specific operating conditions. It was possible to obtain a material with 6.4% of FFA and 18.3% of tocopherols from a raw material composed by 57.8% of FFA and 8.97% of tocopherols, using 160 °C of evaporator temperature and 10.4 g min^{-1} of feed flow rate. These results represent FFA elimination of 96.16% and tocopherol recovery of 81.23%.

Keywords: Separation process; Molecular distillation; Free fatty acids; Tocopherols; Deodorizer distillates

1. Introduction

There is a growing trend of consumer preference for natural products. The recent interest in formulate and commercialize phytochemical-based nutraceutical products has evidenciated the importance of process development to concentrate natural substances.

Natural tocopherols are recovered from vegetable oil deodorizer distillates (VODD), a valuable by-product obtained during the deodorization of vegetable oil refining.

Tocopherols, which are physiologically active as Vitamin E, are considered natural antioxidants and find extensive applications in food, cosmetics, and pharmaceutical industries. It is suggested that Vitamin E decreases the occurrence of several age-related degenerative diseases [1].

Vegetable oil deodorizer distillate from the last step of fats and oil refining, which is sold on the basis of tocopherols and sterols [2], is one of the richest sources of tocopherols [3].

Deodorizer distillate can have significantly different characteristics, uses, and value. Depending on fats and oils, it can be a good raw material for the production of Vitamin E, sterols [4] or only for fatty acid production [5].

VODD is considered a complex mixture due to the great number of its components. It is composed of free fatty acids (FFA), sterols, tocopherols, sterol esters, hydrocarbons, breakdown products of fatty acids, aldehydes, ketones and acyl glycerol [4]. Free fatty acids constitute 25–75% of the distillate depending on the raw material, the type of VODD and conditions of the refining process. Due to

* Corresponding author. Tel.: +55 19 3788 3971.
E-mail address: patricia@lopca.feq.unicamp.br (P.F. Martins).

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Table 1
Molecular weights and vapor pressures of FFA and tocopherols

Component	Molecular weight[a] ($g\,mol^{-1}$)	Vapor pressure at 200 °C[a] (Pa)
FFA	180	533.28
Tocopherols	415	20.00

[a] Ref. [5].

its high content, FFA separation from VODD is one of the steps that can be followed to concentrate tocopherols to high purity.

FFA elimination from SODD through molecular distillation to tocopherol concentration is technologically viable due to the differences between molecular weights and vapor pressures of FFA and tocopherols (Table 1).

Due to the values of molecular weights and vapor pressures, it is expected that FFA, which are the lighter substances, be removed from SODD in the distillate stream and tocopherols be concentrated in the residue stream, preferentially.

Different combinations of physical and chemical treatments have been proposed in the literature to eliminate FFA and purify tocopherols. Most of them include a preliminary chemical treatment step. Chu et al. [6,7] recommended the use of alkali neutralization and washing to remove free fatty acids as a preconcentration step prior the batch adsorption of Vitamin E from palm fatty acid distillate. Ramamurthi and McCurdy [4] studied the pretreatment of deodorizer distillate using a lipase-catalyzed esterification reaction to convert FFA into methyl esters, followed by vacuum distillation to remove them and concentrate tocopherols. Chu et al. [3] proposed an enzymatic hydrolysis using a commercial immobilized *Candida antarctica* lipase, followed by alkali neutralization and washing to remove FFA from the mixture. Buczenko et al. [8] performed the saponification of the raw material and the extraction of unsaponifiable matter as pretreatment of VODD before the procedure of Vitamin E concentration, using liquefied petroleum gas extraction. The enzymatic hydrolysis and saponification reactions convert fatty acids associated with acylglycerol molecules into FFA. These mentioned procedures are laborious and require close attention to prevent the exposure of tocopherols to molecular oxygen, to light and to temperature in order to avoid its decomposition. Therefore, the search for alternative approaches is continuing in an attempt to overcome the drawbacks of the aforementioned processes (e.g. laborious procedures and tocopherol decomposition). In this way, this work proposes the elimination of FFA from VODD through molecular distillation as a first step for tocopherol concentration.

The molecular distillation process is useful in the separation and purification of materials of high molecular weight, as well as for those that are thermally sensitive, such as vitamins, by minimizing losses by thermal decomposition. It is characterized by high vacuum in the distillation space, short exposure of the distilled liquid to the operating temperatures, and a small distance between the evaporator and the condenser (20–50 mm) [9]. Furthermore, this process has advantages over other techniques that use solvents as the separating agent, avoiding problems with toxicity.

The combination of a small distance between the evaporator and the condenser (about 2 cm) and a high vacuum in the distillation gap results in a specific mass transfer mechanism with evaporation outputs as high as 20–40 $g\,m^{-2}\,s^{-1}$ [10]. Under these conditions (e.g., short residence time and low temperature), distillation of heat-sensitive materials is accomplished without or only negligible thermal decomposition. Therefore, molecular distillation shows potential in the separation, purification and/or concentration of natural products, usually constituted by complex and thermally sensitive molecules such as tocopherols.

Molecular distillation has also been used for heavy petroleum characterization, demonstrating the potential of this separation process in other applications [11].

The objective of this work is to study free fatty acid elimination from VODD by molecular distillation, using different evaporator temperatures and feed flow rates as a preliminary step to concentrate tocopherols.

2. Experimental

2.1. Materials

Deodorizer distillates originating from industrial refining of several vegetable oils (soybean, canola and sunflower) were obtained from Bunge Alimentos S.A. (São Paulo, Brazil). All samples were stored in the refrigerator at 4 °C until analysis.

A tocopherol kit consisting of α-, β-, γ- and δ-tocopherol (purity ≥ 95%) were obtained from Calbiochem (San Diego, CA, USA) and used as reference standards for quantitative and qualitative tocopherol chromatographic analysis.

The reagents used for the free fatty acids analysis were ethyl alcohol, phenolphthalein and sodium hydroxide. These reagents were of analytical grade.

The solvents, hexane and isopropanol, for tocopherols analysis were of HPLC grade.

2.2. Molecular distillation equipment

The distillation of free fatty acids was performed using a laboratory wiped film molecular distillation model KDL 5, GmbH UIC (Alzenau, Germany) which is a variation from falling film molecular distillation with agitation. The major part of the equipment was constructed from glass. The heating of the evaporator was provided by a jacket circulated with heated oil from an oil bath. The vacuum system included a diffusion and a mechanical pump. The surface area of the evaporator is 0.048 m^2 and the surface area of internal condenser is 0.065 m^2. The roller wiper speed inside the evaporator was fixed at 350 rpm.