J. Chem. Chem. Eng. 5 (2011) 706-710

Modeling of Molecular Distillation Parameters: Case Study of Green Coffee Oil (*Coffea arabica*)

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Received: March 26, 2011 / Accepted: May 06, 2011 / Published: August 10, 2011.

Abstract: In principle, the free fatty acids, diterpene fatty acid esters and triglycerides from green coffee oil can be separated effectively, by a suitable separation process, due to the differences between molar mass and vapor pressures. In addition, in the case of component separation by molecular distillation, boiling point is replaced by evaporation rate at a given temperature. Several experiments and theoretical analyses have been carried out to identify the impact of important parameters (mean free path, evaporation rate, relative volatility and Knudsen number), which determine the performance of these processes and degree of separation. In this work, a process development based on molecular distillation, for the enrichment of coffee diterpenes from green coffee oil is presented. The distillates were enriched in diterpene fatty acid esters and free fatty acids, while the residues were enriched in high molar mass triglycerides.

Key words: Diterpenes fatty acid esters, *Coffea arabica*, molecular distillation, mean free path, cafestol palmitate.

1. Introduction

Green coffee oil from coffee Arabica (*Coffea arabica*) is a mixture of free fatty acids (FFA), mono-, di-, and triglycerides, diterpene fatty acid esters, phosphatides, pigments, sterols and tocopherols [1, 2]. The unsaponifiable fraction of green coffee oil is rich in diterpene alcohols, mostly cafestol and kahweol, which are mainly esterified with various fatty acids (mainly palmitic and linoleic acids), and only a small amount of the diterpenes is present in the free form [3]. To diterpenes, have been attributed hypercholesterolemic effects, and coronary heart disease risk [4] due to the ingestion of unfiltered coffee drink. On the other hand, various studies have provided further support for the chemoprotective, hepatoprotective, antioxidative, antiinflammatory, and anticancerigenic effects of cafestol and kahweol [5, 6]. Coffee diterpenes are valuable in the cosmetic and pharmaceutical industries. In this case, molecular distillation technology (MD) has been studied as an alternative technique for recovering and concentrating valuable compounds such as diterpene fatty acid esters from green coffee oil [7].

The molecular distillation process is characterized by direct transfer of molecules from evaporator to condenser without the possibility of come back to evaporator [8-10]. Molecular distillation occurs at low temperatures, high vacuum and short residence times [8], hence reduces the thermal decomposition and eliminates oxidation of the green coffee oil. In a molecular still the condenser is separated from the evaporator a distance less than the mean free path of light molecules (λ_L), but greater than the mean free path of heavy molecules (λ_H). Therefore, with the increase of the evaporator

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temperature, the light molecules content is increased in the distillate. It is known that when the distilling temperature increases, the vapor pressure rapidly increases; at the same time, the mean free path of the molecule becomes larger [11]. Then, the light molecules (as diterpene fatty acid esters and FFA) in the vapor are condensed on the cooling surface without intermolecular collisions; hence vapor-liquid phase equilibrium cannot be reached. In contrast, the heavy molecules (as triglycerides) cannot reach the condenser and return to the evaporator [11]. Schematic representation of molecular distillation is shown in Fig. 1.

The objective of this work is to modeling the molecular distillation parameters in the case of concentration of diterpenes fatty acid esters from green coffee oil. This permits the proposition of suitable operational strategies to separate the desired products and to carry out calculation and evaluation of the evaporation rate and separation efficiency.

2. Materials and Methods

2.1 Material

The crude green coffee oil was obtained from the industry (Linax, Votuporanga-Brazil), where it was obtained by mechanical pressing of arabica coffee beans.

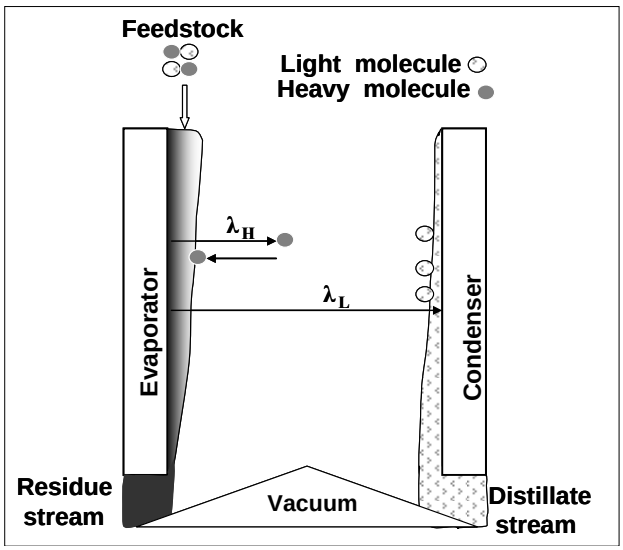

Fig. 1 Schematic representation of molecular distillation.

2.2 Molecular Distillation Equipment

The distillation was performed using a laboratory wiper-film molecular still model KDL 5, GmbH UIC (Alzenau, Germany). The distance between evaporation and condensation surfaces (h) is 0.02 m. The surface area of the evaporator is 0.048 m^2 and the surface area of internal condenser is 0.065 m^2. The operational temperature was up to 250 °C, and the pressure inside the evaporator achieved up to 0.1 Pa.

2.3 Analysis of Diterpene Fatty Acid Esters

For this purpose, a VISCOTEK GPC/SEC TDAmaxTM chromatograph with a refractive index detector was utilized. Samples of green coffee oil and fractions obtained of molecular distillation were dissolved in HPLC grade tetrahydrofuran (THF) and analyzed using THF as the mobile phase at flow rate of 0.8 mL/min. Three GPC/SEC Phenogel analytical columns (Phenomenex, Torrance, CA) with different pore sizes (50-100 Å), dimension of (300 mm × 7.8 mm, 5 μm). Sample injection volume was 20 μL, and analyses were carried out at 40 °C.

2.4 Determination of Mean Free Path, Effective Evaporation Rate, Relative Volatility and Knudsen Number under Molecular Distillation

The Eqs. (1)-(5) represent the mean free path, Knudsen number, theoretical evaporation rate, effective evaporation rate, and relative volatility, respectively. Those are given in Table 1.

The Knudsen number (Kn) expresses a ratio of the mean free path (λ) of vapor molecules to the distance between the evaporator and condenser (h), and is useful for determining the range of high-vacuum distillation. At Kn>10, evaporation proceeds at the maximal rate (molecular distillation). The intermediate range (0.05<Kn<10) is the best to run the process because of the proper distillation rate. At Kn<0.05, the distillation is under equilibrium conditions [13, 14].

Table 1 Molecular distillation parameters for components of green coffee oil.

Parameter	Equation	
Mean free path [11]	$\lambda=RT/(2\pi\sigma^2 N_A P^0)^{\wedge}0.5$	(1)
Knudsen number [12]	$Kn=\lambda/h$	(2)
Theoretical evaporation rate [12]	$G_T=P^0(M/2\pi RT)^{\wedge}0.5$	(3)
Effective evaporation rate [12]	$G=(G_T)(f)$	(4)
Relative volatility [13]	$\alpha=(y_1/x_1)/(y_2/x_2)$	(5)

Where: R(universal gas constant), T(absolute temperature), σ(molecular diameter), N_A(Avogadro constant), P^0(vapor pressure)[7], f(evaporation coefficient), M(molar mass), h(distance between the evaporator and condenser), α(relative volatility), y(mol fraction in the liquid phase), x(mol fraction in the vapor phase).

3. Results and Discussions

The composition of original green coffee oil by GPC showed that about 72.2% are triglycerides, 24.8% are diterpene fatty acid esters, and 3% are (FFA and monoglycerides). Fig. 2 shows the mean free path (λ) and Knudsen number at equilibrium conditions for cafestol palmitate (554.84 g/mol), palmitic acid (256.42 g/mol) and PLL (dilinoleoyl palmitoyl glycerol, 854.74 g/mol), as representative components of green coffee oil in this work. The free fatty acids, diterpene fatty acid esters and triglycerides can be separated effectively due to the differences between mean free path and molar mass. The distillation at 0.1 Pa, is in the intermediate range (0.05<Kn<10), see Fig. 2b. In these conditions, the process reduces the thermal decomposition of green coffee oil and becomes the proper distillation rate [13]. Fig. 3a shows the effect of temperature on effective evaporation rate (G) for palmitic acid, cafestol palmitate and PLL. The order of volatilities for representative components of green coffee oil based in the effective evaporation rate, was palmitic acid > cafestol palmitate > PLL.

The experimental relative volatility (α) for cafestol palmitate to PLL obtained in the molecular distillation may be observed in Fig. 3b. The separation of cafestol palmitate from PLL approached maximum value in the distillate fraction at 210 ºC and 6 mL/min of feed flow rate, as shown in Fig. 4. It was found that diterpenes fatty esters (ex. cafestol palmitate) were more volatile than triglycerides (ex. PLL) under molecular distillation conditions.

The diterpene fatty acid esters were concentrated in distillate fractions at 210 ºC, which were the highest values all the fractions, could achieve about 42.8%. This can be explained by increases of mean free path (λ) of the diterpene esters, causing a high amount of molecule passing to condenser. This is the purpose of the molecular distillation process, in this case to enrich the diterpene esters from green coffee oil.

4. Conclusions

The order of volatilities for representative components of green coffee oil based in the effective evaporation rate was palmitic acid > cafestol palmitate > PLL. The present work has shown that, fractionation of green coffee oil by molecular distillation is an effective tool for yielding several fractions enriched in diterpenes esters which differ markedly in their properties. The best results were obtained for a composition of diterpene fatty acid esters of 42.8% of distillate fractions at 210 ºC and 6 mL/min of feed flow rate by molecular distillation. Moreover, the molecular distillation improved the enrichment of the coffee diterpenes as a result of high vacuum and low distillation temperature, since these are components of interest for cosmetic and pharmaceutical industries. The distillation at 0.1 Pa, is

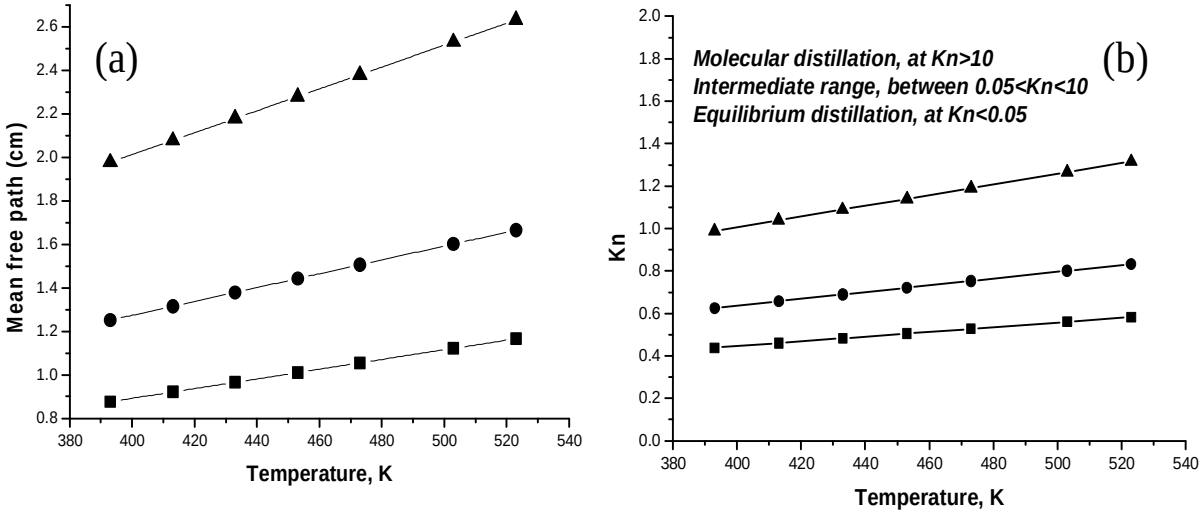

Fig. 2 Effect of temperature on (a) mean free path and (b) Knudsen number for (▲) Palmitic acid, (●) Cafestol palmitate, and (■) PLL at 0.1 Pa.

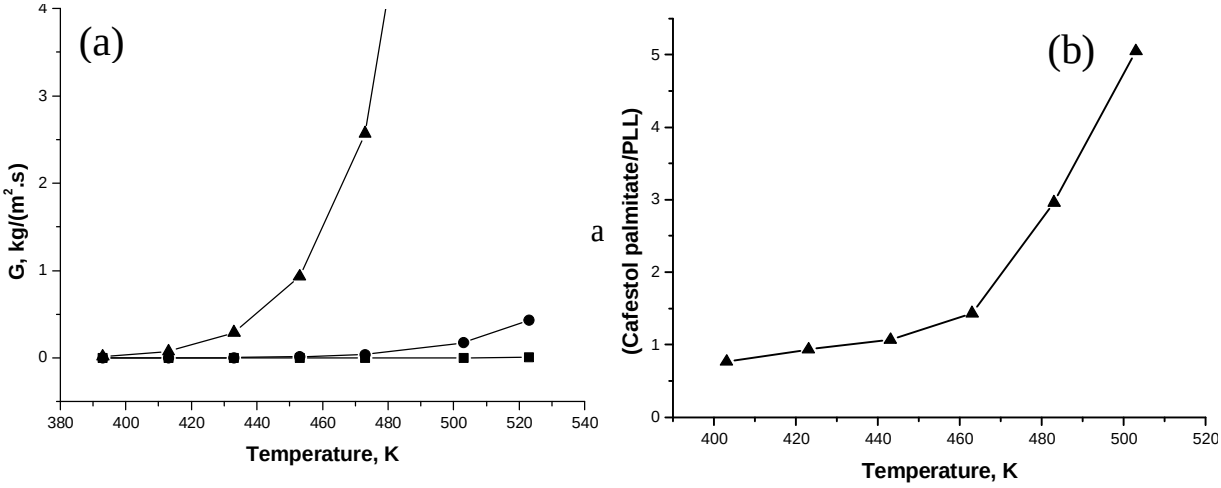

Fig. 3 Effect of temperature on (a) effective evaporation rate for (▲) Palmitic acid, (●) Cafestol palmitate, and (■) PLL, and (b) experimental relative volatility (α) for cafestol palmitate to PLL obtained in the molecular distillation at 0.1 Pa.

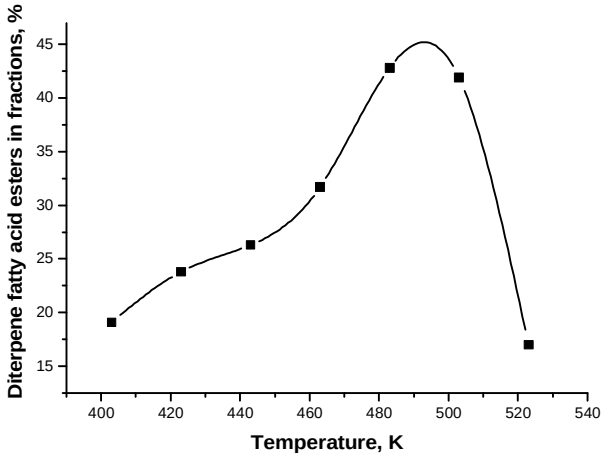

Fig. 4 Effect of distillation temperature on the percentage diterpenes fatty acid esters in the distillate fraction, at 0.1 Pa.

in the intermediate range (0.05<Kn<10). In these conditions, the process does not lead to the thermal decomposition of green coffee oil. The diterpene fatty acid esters and triglycerides can be separated effectively due to the differences between mean free path, Knudsen number and relative volatility.

Acknowledgements

The authors gratefully acknowledge the support of the Technological University of Pereira (UTP) and the Laboratory of Optimization, Project and Advanced Control (LOPCA) at the School of Chemical Engineering of State University of Campinas (UNICAMP).

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