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Fractionation of Green Coffee Oil by Molecular Distillation: Modeling and Simulation

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Abstract: This work describes a non-equilibrium mathematical model and simulation procedures for the fractionation of green coffee oil via molecular distillation. The simulation results were in quantitative agreement with previously reported experimental. Green coffee oil makes up to 18% (w/w) of coffee beans (Coffea arabica). The main components of the coffee's lipids are triglycerides accounting up to 80% w/w, diterpene fatty acid esters amounting up to 18% w/w. The large amount of diterpene fatty acids renders Green Coffee Oil unsuitable for use as an edible vegetable oil. The majority of these lipids can be found in liquid form inside the cells of the coffee beans. Fractionation of green coffee oil by molecular distillation offers an avenue to improve the quality of green coffee oil allowing its use in nutritional, cosmetic and pharmaceutical applications. Molecular distillation also provides a viable process to purify valuable products such as diterpene esters which has been reported to exhibit anticarcinogenic properties.

Key words: Green coffee oil, molecular distillation, simulation, modeling, coffee diterpenes.

1. Introduction

Vegetable oils have important market in nutritional, biochemical, cosmetic, pharmaceutical and bioenergy processes. Crude vegetable oils are subject to purification processes before consumer use in order to remove undesirable substances that may influence undesirable taste, appearance, odor, color, etc.. Green and roasted coffee oil has a high price in the market and it is commonly obtained by mechanical cold-pressing and/or solvent extraction procedures. The content of triglycerides in the oil originated from green and roasted coffee beans (Coffea arabica) are no significantly different [1]. Crude green coffee oil obtained by cold pressing exhibits a dark green color with a cloudy aspect and slight vegetable odor as well as an excessive amount of diterpenes of the kaurane family, mainly cafestol and kahweol. The large amount of diterpenes makes green coffee oil unfit for direct consumer use.

Green coffee oil consists mainly of lipid components such as free fatty acids (1% w/w), free sterols (1.5% w/w), triglycerides(75% w/w), sterol esters (1% w/w), partial glycerides (5% w/w), diterpene fatty acid esters (14% w/w) and polar lipids (<1% w/w) [2]. Diterpenes are receiving significant attention due their demonstrated emollient properties, their ability to increase serum cholesterol and block solar radiation as well as potential anticarcinogenic properties [3]. Diterpenes (cafestol and kahweol) are present in the unsaponifiable lipid fraction of coffee oil [4]. Cafestol and kahweol are mainly esterified with various fatty acids, mainly palmitic and linoleic acids, hence only a small amount of the diterpenes is present in the free form [5]. It is well documented that coffee roasting has little influence on the percentage compositions of the

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diterpene ester fractions [6].

Molecular distillation is well known fractionating process usually used for concentrating vitamins, essential fatty acids, antioxidants and minor components from crude vegetable oils [7-10]. Several studies indicate that fractionation of the triglyceride constituents of vegetable oils via molecular distillation is less effective than chromatography or low-temperature crystallization [9]. However, molecular distillation offers an easier method for the separation of the unsaponifiable fractions and the removal of the free fatty acids without the use of solvents [8, 11, 12]. Molecular distillation occurs at low temperatures, high vacuum, and short residence times, hence reducing thermal decomposition and eliminating oxidation of the oil. During molecular distillation vapor molecules can reach the condenser without intermolecular collisions hence vapor-liquid phase equilibrium can not be reached [7, 8, 12].

The objective of this work is to model and simulate a fractionation process for the concentration of diterpenes fatty acid esters from green coffee oil via molecular distillation. The modeling steps included the generation of property data for compounds found in the green coffee oil. The needed properties such as normal boiling point and vapour pressure as a function of temperature for the triglycerides and diterpene fatty acids esters were generated using the Marrero and Gani group contribution model [13]. An extrapolative method based on experimental data of vapor pressure for short-chain triglycerides was used to estimate the vapor pressure of coffee oil triglycerides at low temperatures.

2. Characterization of Green Coffee Oil

We consider that green coffee oil is formed by three key compounds representing its most abundant groups: triglycerides, diterpenes fatty acid esters, and free fatty acids. These are complex compounds and many of their key physical properties are currently not available in the literature. Only the properties of free fatty acids are currently available in the database of Aspen-Plus® process simulation software. Green coffee oil was modeled as a mixture of triglycerides (93.66%), diterpene fatty acid esters (5.84%), and free fatty acids (0.5%), with an average molar mass of 818.57 kg $kmol^{-1}$. The triglycerides profile of green coffee oil has been previously studied [1]. These triglycerides are composed of fatty acids (L, linoleic acid, C18:2; Ln, linolenic acid, C18:3; O, oleic acid, C18:1; P, palmitic acid, C16:0; S, stearic acid, C18:0; M, myristic acid, C14:0). Table 1 shows composition of the triglycerides fraction of the green coffee oil used in this work.

Cafestol is the primary diterpene component in arabica coffee, with kahweol making up to 50% of the cafestol [14, 15]. Diterpenes such as cafestol and kahweol are mainly esterified with palmitic acid (46-50%), linoleic acid (25-29%), stearic acid (8-11%), oleic acid (8-12%), arachidic acid (3-6%), and behenic acid (0.7-1,3%) [6]. Our approach considers that diterpene fatty acid esters are formed by four main components: cafestol palmitate, cafestol linoleate, kahweol palmitate and kahweol linoleate as shown in Table 2.

Table 1 Triglycerides composition in green coffee oil.

Triglycerides	Molar mass (kg/kmol)	Composition % (w/w)
LLL	879.38	7.13
PLLn	852.72	2.45
OLL	881.40	4.49
PLL	854.74	28.59
OLO	882.77	1.57
PLO	856.75	13.28
SLL	882.77	3.91
PLP	830.73	25.64
POP	832.7	5.61
SOS	889.46	0.99

Table 2 Composition of diterpene fatty acid esters in green coffee oil.

Diterpenes fatty acid esters	Molar mass (kg/kmol)	Composition % (w/w)
Cafestol palmitate	554.84	2.54
Cafestol linoleate	578.86	1.31
Kahweol palmitate	552.82	1.31
Kahweol linoleate	576.84	0.68

Finally, in this work the free fatty acids composition of green coffee oil was set to be palmitic acid 0.35% and linoleic acid 0.15% according to previously reported experimental data [16].

3. Computational Model

Advances in the theoretical modeling of this molecular distillation have been reported by several authors [7-10, 17-20] with most of the reported models developed only for binary mixtures. Molecular distillation is characterized by direct transfer of molecules from the evaporator to the condenser with no possibility of return of them to evaporator. Under these circumstances there is no equilibrium between the vapour and the liquid phases and no true equilibrium pressure of the distilling molecules in the space between evaporator and condenser [7-10, 12, 22].

The proposed model comprises the following three steps:

- The creation of a property database with the main compounds of green coffee oil;
- Steady state simulation of the molecular distillation process using Aspen-Plus®;
- Model validation with experimental data.

3.1 Creating Database for Simulation

Physical property data for many of the key components of green coffee oil are not available. Only the properties of free fatty acids (palmitic and linoleic acids) are included in the database of Aspen-Plus®. Many of the physical properties of green coffee oil components can not be determined experimentally due to thermal decomposition of the components at temperatures below their normal boiling point. Aspen-Plus® requires the knowledge of the molecular structure, vapour pressure as a function of temperature, normal boiling point, liquid density, critical temperature, critical pressure, critical volume, and acentric factor. Fortunately in cases in which not all of these properties are available Aspen-Plus® can provide accurate estimates using classical group contribution methods.

Prediction of the normal boiling point, which depends only on the molecular structure of pure organic chemicals, was carried out through the Marrero and Gani group contribution method [13]. The estimation of vapour pressure of liquids as a function of temperature was done through the extended Antoine equation with data estimated by the Ceriani and Meirelles group contribution method [14].

3.2 Modeling the Molecular Distillation Process

The non-equilibrium model, (also denoted as rate-based model), was initially presented by Krishnamurthy and Taylor [23] for conventional distillation process and consists of a set of mass and energy balances for vapor and liquid phases, along with rate equations for the evaluation of mass and heat transfer rates. This model use the Maxwell-Stefan equations for description of vapor-liquid mass transfer [23], and it requires information about parameters such as mass and heat transfer coefficients and vapour-liquid interfacial area. The method requires the evaluation of the mass and heat transfer processes for both phases separately. These parameters are usually obtained from semi-empirical correlations.

The following assumptions were made to simplify the rate-based model:

- The molecular distillation process is represented by a distillation column with only one tray and reboiler;
- The process is in steady state;
- Each phase is perfectly mixed in each segment;
- The assumption of phase equilibrium is made only at the vapor-liquid interface. The thermodynamic model UNIQUAC (for liquid phase activity coefficient calculation) is used in this research;
- Chemical reactions are not considered in this process;
- The finite-flux mass transfer coefficients are assumed to be the same as the low-flux mass-transfer coefficients;
- The heat transfer coefficients are assumed to be constant for all segments;

- The reboiler is treated as equilibrium stage.

Fig. 1 shows the rate-based concept for a column segment (a stage). In the rate-based model, thermodynamic equilibrium is assumed only at the vapour-liquid interface. The bulk phases of both vapour and liquid are assumed to be perfectly mixed, and the resistance to mass and heat transfer is located in tow films next to the phase boundary. Mass transfer rates are calculated by Maxwell-Stefan equations.

The component molar balance for the vapour and liquid phases are:

$$L_{j-1}x_{i,j-1} - L_j x_{i,j} + N^L_{i,j} = 0 \quad (1)$$

$$V_{j+1}y_{i,j+1} - V_j y_{i,j} - N^V_{i,j} = 0 \quad (2)$$

$$N^V_{i,j} = N^L_{i,j} \quad (3)$$

where $N_{i,j}$ and E_j are the interfacial mass and heat transfer rate of component i on stage j ,where i=1,2,…,c-1. L_j and V_j are the liquid and vapour molar flowrates leaving stage j. $x_{i,j}$ and $y_{i,j}$ are the mole fractions of component i in the liquid and vapour streams leaving stage j. $H_{L,j}$ and $H_{V,j}$ are the liquid and vapour phase enthalpies and $T_{L,j}$ and $T_{V,j}$ are the liquid and vapour phase temperatures. The $N_{i,j}$ are related to the chemical potential gradient in either phase by the Maxwell-Stefan equations [24].

$$\frac{x_{i,j}}{RT_j}\frac{\partial \mu^L_{i,j}}{\partial \eta} = \sum_{k=1}^{c}\frac{x_{i,j}N^L_{k,j} - x_{k,j}N^L_{i,j}}{c^L_{t,j}(k^L_{i,k}A)_j} \quad (4)$$

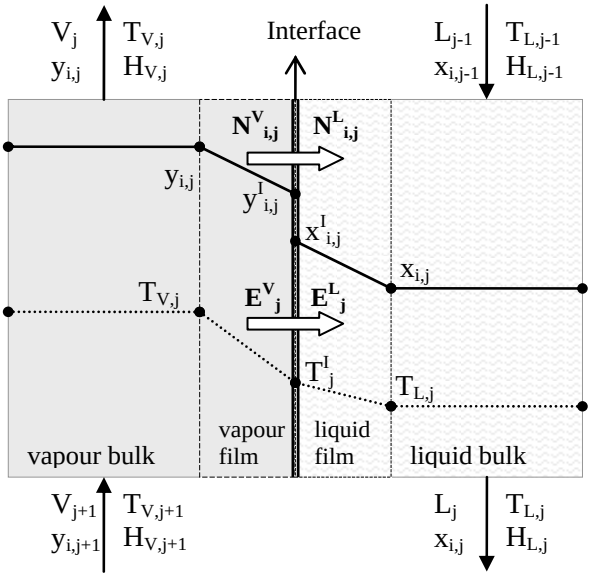

Fig.1 Schematic diagram of rate-based segment.

$$\frac{y_{i,j}}{RT_j}\frac{\partial \mu^V_{i,j}}{\partial \eta} = \sum_{k=1}^{c}\frac{y_{i,j}N^V_{k,j} - y_{k,j}N^V_{i,j}}{c^V_{t,j}(k^V_{i,k}A)_j} \quad (5)$$

In these equations, R is the ideal gas constant, μ_i is the chemical potential of species i, η is a dimensionless film coordinate, $c^V_{i,j}$ the total vapour phase concentration and $c^L_{i,j}$ is the total liquid phase concentration. The $k^V_{i,k}$ and $k^L_{i,k}$ represent the mass transfer coefficients of the i-k pair in the liquid and vapour phase. A is the total interfacial area.

The heat balances for both vapour and liquid phases becomes:

$$L_{j-1}H^L_{j-1} - L_j H^L_j + E^L_j = 0 \quad (6)$$

$$V_{j+1}H^V_{j+1} - V_j H^V_j - E^V_j = 0 \quad (7)$$

$$E^V_j = E^L_J \quad (8)$$

The heat transfer rates consist on conductive and convective contributions.

$$E^L_j = -h^L_j A\frac{\partial T^L}{\partial \eta} + \sum_{i=1}^{c}N^L_{i,j}H^L_{i,j} \quad (9)$$

$$E^V_j = -h^V_j A\frac{\partial T^V}{\partial \eta} + \sum_{i=1}^{c}N^V_{i,j}H^V_{i,j} \quad (10)$$

Here h^L_k and h^V_k are the transfer coefficients for the liquid and vapour phases. Thermodynamic equilibrium is assumed only at the interface. $K_{i,j}$ is the vapour-liquid equilibrium ratio for component i in the segment j.

$$y^I_{i,j} - K_{i,j}x^I_{i,j} = 0 \quad (11)$$

The rate-based model has been implemented into the commercial Aspen-Plus® software package in the separation module RateFrac. The process is modeled by simultaneously solving the mass and heat balances, equilibrium equations (interface) and mass transfer rate equations. The heat transfer coefficient in the vapour phase was calculated by the Chilton-Colburn analogy [25] and the mass transfer coefficient was calculated by the correlations of Scheffe and Weiland [26].

4. Results and Discussion

4.1 Estimation of Vapour Pressure of Components of Green Coffee Oil

Eq. (12) represents the extended Antoine equation used in this study to extrapolate the available estimated data to the temperatures of interest.

$$\ln P^{sat} = A + \frac{B}{T} + CT + D\ln T \quad (12)$$

where P^{sat} is vapour pressure in (kPa), temperature T is in (K), and A-D refer to regressed parameters for the extended Antoine equation. The parameters for the extended Antoine vapour pressure equation are summarized in Table 3.

Only limited vapour pressure experimental data could be found for tripalmitin (PPP), tristearin (SSS), and trimyristin (MMM) in the open literature. The predicted vapour pressures were compared to reported experimental data of literature [22] to assess the accuracy of this method. Table 4 illustrates the predicted parameters for the extended Antoine equation of tripalmitin, tristearin, and trimyristin.

Fig. 2 shows the fitting vapour pressure curves obtained for these compounds.

It can be noted that the estimated vapour pressures for these triglycerides were in quantitative agreement with the experimental data with an average relative deviation ($ARD = \frac{\sum \left| (P_i^{sat,\exp} - P_i^{sat,predic}) / P_i^{sat,\exp} \right|}{N} \cdot 100$) of 8.1%.

4.2 Validation of the Fractionation Process

The equilibrium model and rate-based models were compared with experimental data from literature. Table 5 provides a comparison between the cumulative mass percentage of distillate of coffee oil reported in the literature [27] and that predicted by the equilibrium and rate-based models. The equilibrium model used in this paper consists of the conventional MESH (Mass, Equilibrium, Summation and Heat) equations for evaporation process using the UNIQUAC model for the calculation of the liquid phase activity coefficient.

The cumulative mass percentage of distillate predicted using the rate-based model agrees quantitatively with the experimental data of Khan and Brown [27]. The calculated ARD were 2.65% for the rate-based model, and 33.89% for the equilibrium model.

In Fig. 3, the predicted and reported data for percent cumulative distilled of coffee oil as a function of distillation temperature at 0.0015 mmHg are highlighted.

Most of the unsaponifiable matter is recovered in the third distillation fraction at 483 K, together with considerable amounts of triglycerides, while free fatty acids were removed in the first and second fractions. It indicates that molecular distillation process would constitute a satisfactory procedure for separation of diterpene fatty acid esters from green coffee oil.

4.3 Evaluation of Fractionation Performance

The two models were used for study the influence of pressure. The distillation temperature and distillation

Table 3 Pure component parameters for the extended Antoine equation.

Component	A	B	C	D
LLL	23.275	-15762.405	-7.1088792E-06	6.5817175E-03
PLLn	23.344	-15665.966	1.6706963E-08	-1.9010551E-05
OLL	23.292	-15771.513	-1.9035309E-06	2.5597721E-03
PLL	23.302	-15678.897	-6.0311229E-06	6.6242770E-03
OLO	23.300	-15780.231	1.6752738E-08	-1.9061677E-05
PLO	23.343	-15694.472	1.6730396E-08	-1.9040678E-05
SLL	23.301	-15780.231	1.6752738E-08	-1.9061677E-05
PLP	23.278	-15551.269	-5.2015317E-06	6.8921692E-03
POP	23.329	-15573.868	1.6820643E-08	-1.9140037E-05
SOS	23.275	-15801.088	1.6670462E-08	-1.8964202E-05
Cafestol palmitate	20.866	-12184.586	1.9669248E-08	-2.2378719E-05
Cafestol linoleate	21.129	-12520.333	1.9391296E-08	-2.2067425E-05
Kahweol palmitate	20.760	-12048.815	1.9695586E-08	-2.2397744E-05
Kahweol linoleate	21.024	-12386.029	1.9342710E-08	-2.1993897E-05

Table 4 Pure component parameters for the extended Antoine equation of tripalmitin, tristearin, and trimyristin.

Component	A	B	C	D
Tristearin	26.637	-18665.869	1.3029228E-08	-1.4812750E-05
Tripalmitin	26.628	-18168.876	1.3265935E-08	-1.5087987E-05
Trimyristin	25.780	-16946.721	1.4332342E-08	-1.6314572E-05

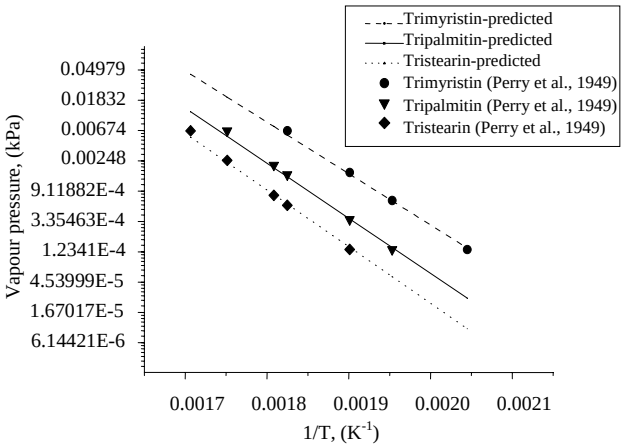

Fig. 2 Predicted and experimental vapour pressure of trimyristin, tripalmitin, and tristearin.

pressure are two major factors affecting the simulation process.

The pressure sensitivity of the molecular distillation process can be analyzed through simulation with different pressure profiles. For that purpose, we performed simulations of the molecular distillation process using a pressure ranging from 0.001 mmHg to 0.01 mmHg at 463 K as illustrated in Fig. 4.

The simulation results of the molecular distillation process using a rate-based model depend on the availability and precision of input data. At 463 K, the percentage of distillate yield decreases as the pressure increases, due to increase the collisions between evaporated molecules. When the pressure is increased, the percent yield of distillate is reduced and the molecular distillation (rate-based model) approximates to a conventional high-vacuum evaporation with an equilibrium model. The yield of distillate at 463 K is

Table 5 Fractionation process by molecular distillation: comparison of experimental data with equilibrium model and rate-based model.

Fraction	Temperature (K)	Cumulative mass distilled (%)		
		Equilibrium model -	Rate-based model	Experimental data (Khan and Brown, 1953)
1	423	0.429	0.800	0.809
2	448	1.379	2.170	2.226
3	483	15.466	19.548	20.242
Residue	---------	100	100	100

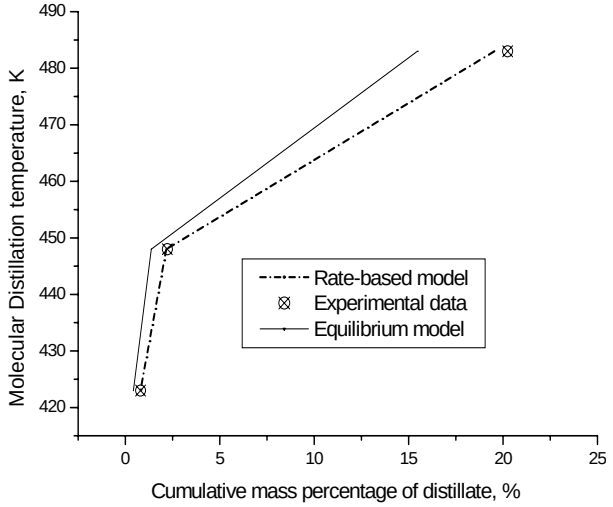

Fig 3 Comparison of experimental data with equilibrium model and rate-based model at 0.0015 mmHg.

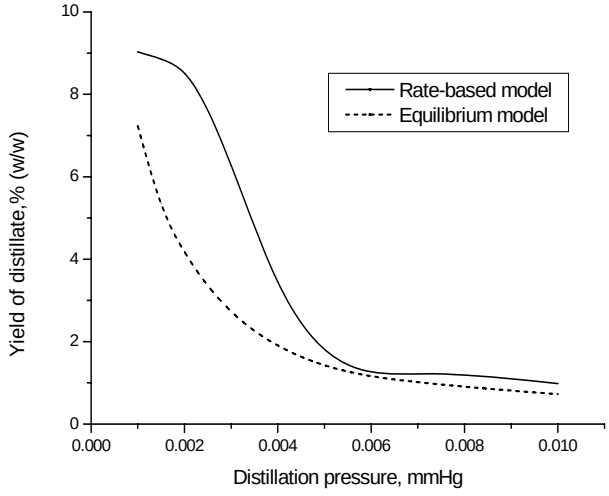

Fig. 4 Predicted effect of distillation pressure on the yield of distillate, % (w/w) at 463: equilibrium model vs. rate-based model with Maxwell–Stefan equations.

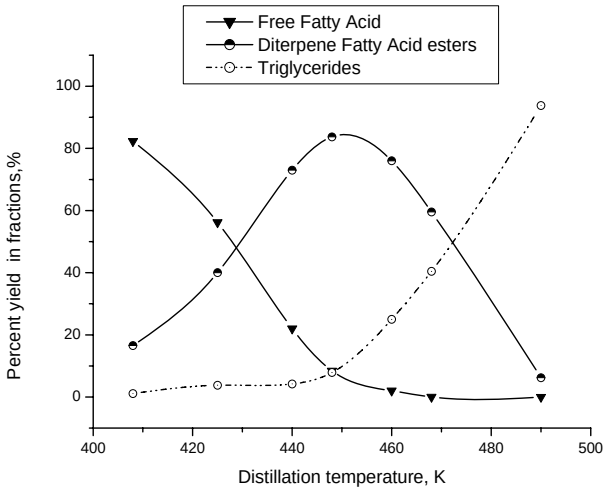

Fig. 5 Predicted effect of distillation temperature on diterpene fatty acid esters recovery in fractions (0.0015 mmHg).

appears constant as the distillation pressure increases from 0.001 mmHg to 0.003 mmHg, and then decreases from 0.003 mmHg to 0.01 mmHg, because of greater proportions of the evaporated molecules are returned to the evaporator by intermolecular collisions, and the process is approached to equilibrium.

4.4 Elimination Curve with Rate-Based Model

The simulation of the fractionation process for green coffee oil was conducted at 0.0015 mmHg. The influence of distillation temperature ranging from 408 K to 490 K on the contents of diterpene fatty acid esters in distillates is shown in Fig. 5.

The distillation temperature of 453 K became a turning point for the changes in diterpenes fatty acid esters content in the distillates. At temperatures lower than 453 K, the diterpenes content in distillates decreased slightly while the content of free fatty acids increased. As shown in Fig. 5, at 463 K the yield of distillate is 8.85% (w/w) and, content of diterpene fatty acid esters are about to 60%, what means increasing ten times over that in the raw green coffee oil. When the temperature was above 483 K, the content of large molecules such as triglycerides increased in the distillates and percent yield of diterpene fatty acid esters is less than 20% w/w. This behavior indicates that when mass in the distillated fractions is increased, the content of diterpene fatty acid esters diminish due to increase in the content of triglycerides. The components with larger molecular weights such as triglycerides are more difficult to evaporate; these components consisted of a larger proportion in residues than in distillates.

5. Conclusions

A steady-state equilibrium model and a rate-based model were compared with experimental data for fractionation process of green coffee oil. In general, the predictions from the rate-based model were the best ones. The availability of the rate-based model to represent the non-equilibrium process of molecular distillation for green coffee oil was demonstrated through a quantitative agreement between the experimental and simulated data. Specifically, the rate-based model was able to adequately predict the fractionation of green coffee oil in the temperature range of 408 K to 490 K and at pressures of between 0.001 and 0.01 mmHg, which are commonly used operating conditions for molecular distillation process. The purity of diterpenes fatty acid esters of green coffee oil was increased from 5.84% to 60% (w/w) in the fraction to 463 K and 0.0015 mmHg.

The results indicate that molecular distillation process can be effective method for separation of diterpene fatty acid esters of green coffee oil. The characterization of green coffee oil mixture, likewise the estimation of pure component vapour pressure and creation of non-databank compounds into Aspen-Plus® is a reliable alternative for predicting the behavior of green coffee oil. Distillation temperature and distillation pressure have important effect on the purification process by molecular distillation process. When distillation pressure increased, yield of distillates and the total diterpenes fatty acid esters decreased. In these conditions, the process is approximated to high-vacuum evaporation. The use of thermodynamic models and regression algorithms implemented in commercial Aspen-Plus® software package would

expedite design calculations for chemical process development.

Molecular distillation is characterized by a direct transfer of molecules from evaporator to condenser without possibility of return to evaporator Due to this fact, the system cannot reach equilibrium state and a non-equilibrium model is needed to correctly simulate the process. For the specific case considered, the rate-based model with the Maxwell–Stefan equations is able to simulate the molecular distillation process of coffee oil, better than the equilibrium model.

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