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# Molecular Distillation of Palm Oil Distillates: Evaporation Rates, Relative Volatility, and Distribution Coefficients of Tocotrienols and other Minor Components

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**Abstract:** The effects of feed flow rate and temperature of distillation on extraction of minor components from PFAD were studied in terms of concentration, distribution coefficient and relative volatilities. The order of volatilities for tocotrienols, based on the distribution coefficients, was desmethyl tocotrienols ($\delta$-T3) > $\gamma$-tocotrienols ($\gamma$-T3) > $\alpha$-tocotrienols ($\alpha$-T3). The separation of tocotrienols from FFA approached maximum values only at low temperatures and fell drastically as the temperature increased. FFA and squalene evaporate at lower temperatures than tocotrienols, $\alpha$-tocopherol, and sterols. Based on these properties, it was possible to separate the tocotrienols, $\alpha$-tocopherol, and sterols from FFA by molecular distillation using low temperatures.

**Keywords:** Evaporation, extraction, free fatty acids, molecular distillation, palm oil, squalene, sterol, tocotrienols, volatility

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## INTRODUCTION

Many procedures have been used to recover minor components from crude palm oil but most are dependent on the chemical transformation of the triacylglycerol (e.g. saponification or transesterificatin) or on adsorption by adsorbent materials (1). The transesterification reaction converts palm oil triglycerides into fatty acid esters, leaving the minor components intact. Chemical transformation is, however, undesirable because the glyceride structure of the oil changes limiting its use as foodstuff. Palm fatty acid distillate (PFAD) is a better choice. Palm fatty acid distillate (PFAD) recovered from the doeorderization process is a better source.

PFAD is the volatile organic material recovered as a valuable by-product in the deodorization of palm oil. Deodorization at high temperature and high vacuum is a steam distillation process that improves the taste, odor, color, and stability of oils by removing undesirable volatiles (e.g. free fatty acids, aldehydes, and ketones) and pigments (2). In addition to the undesirable components, valuable minor components are concentrated in the PFAD such as tocopherols, tocotrienols, sterols, and squalene. Several processes have been proposed for recovering tocopherols and tocotrienols from PFAD. There is, however, just one product available commercially, which was developed by The Malaysian Palm Oil Board (MPOB) and is called "Palm Vitee" (3).

Distillation is a unit operation used for the separation of the constituents of mixtures by partial evaporation. It is based on the fact that the vapor is relatively richer in the component with the highest vapor pressure, i.e. the more volatile component. Distillation at moderate vacuum is characterized by the use of conventional distillation equipment. Its lowest pressure limit is on the order of 1 torr, i.e. one mm-Hg. When the distance of transfer is comparable with the mean free path of the vapor molecules, the distillation is known as molecular distillation.

Mean free path is defined as the average distance a molecule will travel in the vapor phase without colliding with another vapor molecule (4). This implies that, in molecular distillation, the vapor molecules can reach the condenser without intermolecular collisions. A dynamic equilibrium can not, therefore, be established between the vapor and the liquid (4). As well, concepts like theoretically plates, stages, and other common distillation terminology do not apply. There is, however, no certainty that an individual molecule that has evaporated will be able to travel any distance without a collision.

Molecular distillation occurs at low temperatures and, therefore, reduces the problem of thermal decomposition. High vacuum also eliminates oxidation that might occur in the presence of air. In molecular distillation, the rate of evaporation is controlled by the rate at which the molecules escape from the free surface of the liquid and condense on the condenser. For this separation process, it is necessary to reveal the behavior of target components in the evaporation process. The objective of this study was to

determine the evaporation and volatility properties of tocotrienols and other minor components such as tocopherols, sterol and squalene from palm fatty acid distillates (PFAD).

## MATERIALS AND METHODS

### Material

Palm fatty acid distillates (PFAD) used in this study was supplied by Acegrasas, Bogotá, Colombia. Table 1 shows their average composition of palm fatty acid distillates from Colombia. Myristic (Applied Science Laboratories, Inc., USA), palmitic, oleic, and linoleic (Sigma-Aldrich Co., USA), and stearic (Serdary Research Laboratories, USA) acids standards were used to



***Table 1.*** Composition of PFAD

| Component | Weight percent |
|---|---|
| Squalene | 1.03 |
| Vitamin E | 0.50 |
| Sterols | 0.24 |
| Free fatty acids | 90.03 |
| Glycerides | 7.33 |
| Unknown[a] | 0.88 |
| Vitamin E composition (weight percent) | |
| $\alpha$-Tocopherol | 23.79 |
| $\alpha$-Tocotrienol | 23.76 |
| $\gamma$-Tocotrienol | 38.76 |
| $\delta$-Tocotrienol | 13.69 |
| Sterol composition (weight percent) | |
| Campesterol | 24.24 |
| Stigmasterol | 18.07 |
| $\beta$-Sitosterol | 57.68 |
| Free fatty acid composition (weight percent) | |
| Myristic acid | 1.31 |
| Palmitic acid | 50.00 |
| Stearic acid | 4.39 |
| Oleic acid | 36.48 |
| Linoleic acid | 7.82 |
| Glycerides composition (weight percent) | |
| Triglycerides | 2.78 |
| Mono- and diglycerides | 97.22 |

[a]Unknown may include other hydrocarbons such as phytoene and aliphatic hydrocarbons, glycerol, and low-volatility compounds such as ketones and aldehydes.

determine retention times and response factors. Other chemicals are all analysis grade.

## Molecular Distillation Apparatus and Operation

The apparatus used was a KDL4 Laboratory UIC Short Path Distillation System (UIC INC., SP440-003, Joliet, USA). This system is a falling film evaporator capable of varying flow rates from 0.4 to 1 kg/h. Distillations were carried out at pressures below 1 mtorr, with temperatures ranging from 110 to 160°C, and three different levels of feed flow rates: 0.1 kg/h, 0.25 kg/h and 0.4 kg/h. The wiper basket speed was set for 425 RPM according to the equipment manufacturer's recommendation (UIC INC., SP440-003, Joliet, USA). After distillation, the residue and distillate fractions were weighed and transferred to containers, which were covered with aluminum foil. They were stored at 7°C until further analysis.



## Determination of Component Concentrations

Capillary gas chromatography was performed with an Agilent 6890 Series GC System equipped with a flame-ionization detector (FID) and a 30-m DB-5, 0.25-μm film thickness, 0.25 mm internal diameter capillary column, to quantify the amount of individual tocopherols, tocotrienols, sterols, and squalene in PFAD and in the fractions obtained after molecular distillation, i.e. distillate and residue (5). Hydrogen was the carrier gas with a flow rate of 0.6 mL/min and a split ratio of 65:1. The column was heated from 140 to 300°C at a rate of 10°C/min, held at 300°C for 6 min, then heated to 320°C at 5°C/min and held for 10 min. The injector port was maintained at 240°C and the FID port at 345°C. Hydrogen with a flow of rate of 0.6 mL/min was used as the carrier gas, and the split ratio was 65:1. Colombian palm oil was analyzed according to AOCS official Method Ce8-89 with *d*-α-tocopherol as the primary standard. The HPLC analysis was performed with a Waters 700 Series Satellite WISP equipped with a UV Waters 486 Tunable Absorbance Detector set at 292 nm.

Colombian palm oil was analyzed according to AOCS Official Method Ce 8-89 (6) with *d*-α-tocopherol as primary standard, HPLC was performed with a Waters 700 Series Satellite WISP equipped with a UV Water 486 Tunable Absorbance Detector set at 292 nm. The separation was done with a Resolve Silica, 5-μm particle size, 3.9 × 150 mm HPLC column. Isopropanol in hexane (0.6:99.4, v/v) with a flow rate of 0.8 mL/min was used as the mobile phase. 20 μL of palm oil diluted in hexane (8% w/v) were injected into the column.

The AOCS Recommended Practice Ce 7-87 (5) which is intended for quantification of tocopherols in deodorized distillates, was adapted to

simultaneously quantify the amount of individual tocopherols, tocotrienols, sterols, and squalene in PFAD and in the fractions obtained after molecular distillation, i.e. distillate and residue. This method separates the silylated compounds by capillary gas chromatography. Heptadecanyl stearate was used as the internal standard.

Response factors for squalene, $\alpha$-tocopherol, and stigmasterol were determined by injecting known amounts of pure standards (Sigma-Aldrich Co). Response factors for the tocotrienols and the other sterols were assumed to be the same as, $\alpha$-tocopherol and stigmasterol respectively. Retentions times for sterols (i.e. stigmasterol, campesterol, and $\beta$-sitosterol) were determined after injecting a standard sterol mixture (Matreya Inc.). Assignment of tocotrienol peaks was made by comparing the percent areas obtained after injecting a Colombian palm oil sample to the percent tocotrienol areas obtained after the analysis of the same sample by HPLC according to the AOCS Official Method (Ce 8-89).

The same conditions used for the simultaneous analysis of tocopherols, tocotrienols, sterols, and squalene by the above capillary gas chromatography procedure were also used to determine the composition of the FFA in the PFAD. Myristic (Applied Science Lab Inc.), palmitic, oleic, and linoleic (Sigma-Aldrich Co.) and stearic acid (Serdary Research Laboratories) standards were used to determine retention times and response factors.

Acid value was determined according to AOCS Official Method Cd 3a-63. Results were transformed to percent FFA by dividing the acid value by 2.1, the average molecular weight of the FFA in the sample. Mono-, di- and triacylglycerols in the PFAD were separated by silica gel column chromatography according to AOCA Recommended Practice Cd 11c-93. A sample dissolved in chloroform was transferred to the top of a silica gel column (70–230 mesh). The triacylglycerols were eluted with 10% diethyl ether in petroleum ether, diglycerides with 25% diethyl ether in petroleum ether and monoglycerides with 100% diethyl ether. Each fraction was collected in sequence, evaporated to dryness and weighed.



## Determination of Rate of Evaporation

The theoretical evaporation rate in molecular distillation is defined by the Langmuir-Knudsen equation, which is derived from kinetic theory considerations (7):

$$\dot{G}_T = P^O \sqrt{\frac{M}{2\pi RT}} \tag{1}$$

where $\dot{G}_T$ is the theoretical rate of evaporation in $kg/m^2$ s, $P^O$ is the equilibrium vapor pressure in Pa at absolute temperature $T$ in Kelvin (K), $M$ is the molecular weight of the substance, and $R$ is the universal gas constant

in J/kmol K. It is interesting to note that Eq. (1) indicates that molecular distillation is a function of the molecular species and the surface temperature. It is, therefore, a surface phenomenon (8).

If the conditions in the vapor space are such that an appreciable number of collisions can occur, the probability is good that some of the molecules will return to the liquid. This leads to a decrease in the number of molecules that reach the condensation surface. This quantity divided by the time and area of evaporation gives the actual rate of evaporation $\dot{G}$. The Langmuir-Knudsen equation, therefore, provides a limiting value for the rate of molecular distillation (7, 8). The ratio of the actual to the theoretical rate of evaporation is defined as the evaporation coefficient $f$:

$$f = \frac{\dot{G}}{\dot{G}_T} \tag{2}$$

The coefficient $f$, which represents the fraction of vaporized molecules that reach the condenser, can be calculated as follows (9):

$$f = F + (1 - F)\left(2e^{-N} - e^{-2N}\right) \tag{3}$$

where

$$F = \frac{A_C}{A_C + A_E} \quad \text{and} \quad N = \frac{h}{k\beta}$$

$A_C$ is the condensation surface area in $m^2$, $A_E$ is the evaporation surface area in $m^2$, $h$ is the distance between the evaporator and condenser in m, $k$ is a factor that has to be determined experimentally, and $\beta$ is the mean free path at equilibrium conditions in m (9). The following empirical equation is used to calculate $k$ for a short path falling film evaporator (10):

$$\log k = 0.2F + 1.38\,(F + 0.1) \tag{4}$$

The mean free path is defined by the following equation, which is derived from the kinetic theory of ideal gases (11):

$$\beta = \frac{RT}{\sqrt{2}\pi\sigma^2 N_A P^O} \tag{5}$$

where $\sigma$ is the diameter of a molecule in m, and $N_A$ is the Avogadro constant ($6.023 \times 10^{23}$ $mol^{-1}$). When a multi-component mixture is distilled, the more volatile components evaporate faster, and the rate of evaporation can be calculated as follows (10):

$$\dot{G} = \sum_{i=1}^{n} m_i \dot{G}_i \tag{6}$$

where $m_i$ and $\dot{G}_i$ are the weight fraction and the rate of evaporation of the component $i$.

In a mixture of two components, the relative volatility $\alpha$, which is also called the separation factor, represents the ratio of the observed volatility of component 1, i.e. the more volatile, to that of component 2. It is expressed as (9):

$$\alpha = \frac{y_1}{x_1}\frac{x_2}{y_2} \tag{7}$$

where $x$ and $y$ are the mol fractions in the liquid and vapor phases, respectively. Further consideration shows that, if a mixture of two components obeys Raoult's law, their relative volatility is equal to $P_1^O/P_2^O$, i.e. the ratio of their equilibrium vapor pressures in the pure state at the prevailing temperature. The ratio $y/x$ is the distribution coefficient (when equilibrium conditions are present it is the equilibrium distribution constant) and might be designated by the letter $\kappa$. Therefore, the relative volatility, according to Eq. (7), is:

$$\alpha = \frac{\kappa_1}{\kappa_2} \tag{8}$$

At high rates of evaporation under high vacuum, i.e. molecular distillation, the relative volatility becomes (12):

$$\alpha = \frac{P_1^O}{P_2^O}\sqrt{\frac{M_2}{M_1}} \tag{9}$$

where $M_1$ and $M_2$ are the molecular weights of component 1 and 2, respectively.

Vapor pressure data were for $\alpha$-tocopherol, tripalmitin, tristearin, palmitic acid, stearic acid and monopalmitin shown in Table 2. These data were fitted to the following model using the generalized least squares method (15):

$$LnP^O = -\frac{A}{T} + B \tag{10}$$

where $P^O$ is the equilibrium vapor pressure in Pa at absolute temperature $T$ in K, and $A$ and $B$ refer to regressed parameters. The model was used to estimate

***Table 2.*** Component parameters for the vapor pressure model (13, 14)

| Component | A | B |
|---|---|---|
| $\alpha$-Tocopherol | 14,886 | 34.230 |
| Palmitic acid | 11,365 | 30.663 |
| Stearic acid | 11,841 | 30.819 |
| Tripalmitin | 19,131 | 35.450 |
| Tristearin | 19,710 | 35.646 |
| Monopalmitin | 11,365 | 28.393 |

the equilibrium vapor pressures of the components at the temperatures of distillation.

## RESULTS AND DISCUSSIONS

### Identification and Quantification of Tocotrienols and other Minor Components

Figures 1 and 2 show the typical chromatogram of a simultaneous analysis of FFA, tocopherols, tocotrienols, sterols and squalene in a residue fraction. All compounds were baseline resolved and eluted under 24 min. Due to the lack of standards for the tocotrienols, a palm oil sample was analyzed by HPLC to determine its tocopherol and tocotrienol pattern. Using the HPLC pattern and relative composition of palm oil tocotrienol from literature, the assignment of the tocotrienol peaks in the GC chromatogram were made. Using the integrated areas from the GLC analysis, the weight% composition for all the minor components were calculated. The composition of the palm fatty acid distillate is given in Table 1. The major component are the FFA (90%) followed by the glycerides (7.3%). Although the levels of squalene, vitamin E and sterols were 1% or less, they still represented a good source of these nutritionally important compounds.



### Evaporation Rate

Table 3 displays theoretical and expected evaporation rates in a falling film short path evaporator (i.e. $\dot{G}_T$ and $\dot{G}$ respectively), and the mean free path at

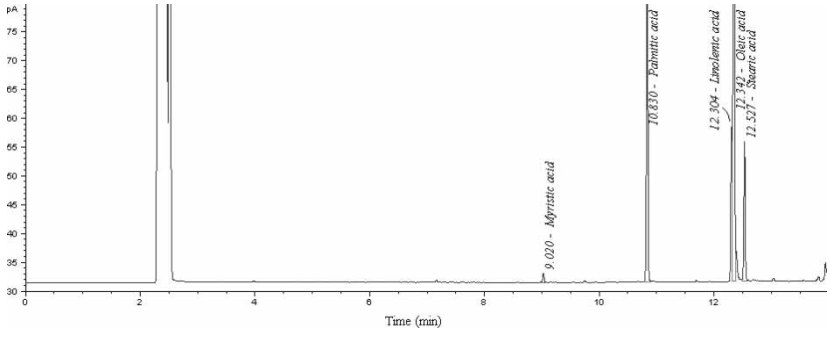


***Figure 1.*** GC chromatogram of simultaneous analysis of FFA, tocopherols, tocotrienols, sterols and squalene. Conditions as mentioned in Materials and Methods. Peak $\delta$-T3, $\delta$-tocotrienol; $\gamma$-T3, $\gamma$-tocotrienol; $a$-T, $\alpha$-tocopherol; $a$-T3, $\alpha$-tocotrienol; HDS, heptadecanyl stearate.

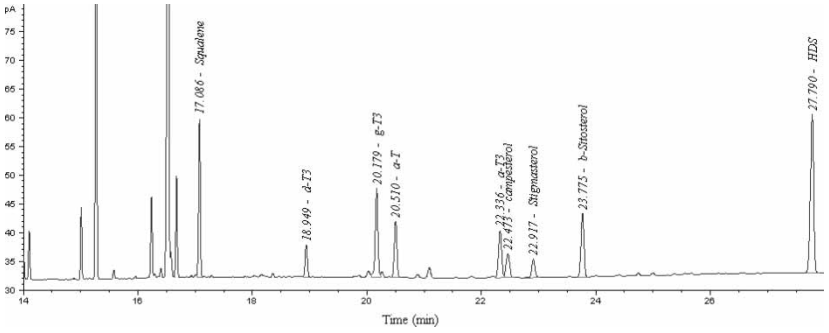


***Figure 2.*** GC chromatogram of simultaneous analysis of FFA, tocopherols, tocotrienols, sterols and squalene.



equilibrium conditions (i.e. $\beta$). According to Kapłon et al. (7), Langmuir-Knudsen's formula, which has been proved experimentally, gives the maximum theoretical rate of evaporation. In practice this theoretical value can never be reached in molecular distillation. The real rate of molecular distillation is the difference of the rate defined by Langmuir-Knudsen's formula and that of the return of evaporated molecular onto the surface of the evaporator. Theoretical evaporation rates were calculated at temperatures from 110 to 160°C using the Langmuir-Knudsen equation, Equation (1). Because of lack of vapor pressure data for most of the minor components, the vapor pressure of $\alpha$-tocopherol was used instead. Expected evaporation rates were calculated by means of Eqs. (2) to (6). They increased as temperature increased according to Table 3.

Expected evaporation rates could have been reduced during experimentation because of possible effects from the feed flow rate or the presence of mass or heat transfer resistances in the liquid phase. The actual evaporation rates should have been calculated from the results obtained in the trials. Unfortunately, calculating actual evaporation rates in the short path evaporator was not possible since there was no certainty about where on the heated length of the evaporator the evaporation process ended. There was, therefore, no knowledge of the actual evaporation surface area, which was necessary in the calculations. Nevertheless, since the short path evaporator was designed

***Table 3.*** Theoretical and expected evaporation rates, and mean free path at equilibrium

| Temperature (°C) | 110 | 120 | 130 | 140 | 150 | 160 |
|---|---|---|---|---|---|---|
| $\dot{G}_T$ (kg/m$^2$ s) | 0.00895 | 0.0188 | 0.0380 | 0.0744 | 0.141 | 0.259 |
| $\dot{G}_T$ (kg/m$^2$ s) | 0.00314 | 0.00635 | 0.0129 | 0.0251 | 0.0476 | 0.0875 |
| $\beta$ (cm) | 0.0577 | 0.0283 | 0.0144 | 0.00759 | 0.00412 | 0.00230 |

to maintain flow rates up to 1 kg/h (UIC INC., SP440-003, Joliet, USA), it was possible to calculate a maximum evaporation rate as $1\ \text{kg}/3600\ \text{s}/0.043\ \text{m}^2 = 0.0065\ \text{kg}/\text{m}^2\ \text{s}$. Therefore, the short path evaporator could have only reached the expected evaporation rates at 110 and 120°C (Table 3).

The mean free path at equilibrium conditions, calculated using equation (5), went from 0.00230 to 0.0577 cm (Table 3). These dimensions were small compared to the distance between the evaporator and condenser surface, i.e. 1.25 cm, and lots of intermolecular collisions would have been expected during the flight of the molecules from the evaporator to the condenser surfaces. There was, however, no dynamic equilibrium between the vapor and liquid phases at molecular distillation conditions, and the mean free path calculated could have been quite far from reality. The number of collisions, therefore, could have been much less than the calculated values.



## Concentrations in the Liquid and Vapor Phases

Figures 3 to 17 display the concentration of all the components in the liquid and vapor phases, i.e. the residue and the distillate respectively, as a function of temperature and feed flow rate. The feed was degasified PFAD without preliminary treatments. In all these figures the dotted lines are polynomial trends that were adjusted using the least square method.

Figure 3 shows the concentration of tocotrienols in the liquid phase. The Gaussian distribution-like shape of the curves can be explained by reference to the Langmuir-Knudsen equation, Eq. (1). At low temperatures, the vapor pressure of the tocotrienols was lower than the vapor pressure of other components, particularly FFA and squalene, and, consequently, the evaporation

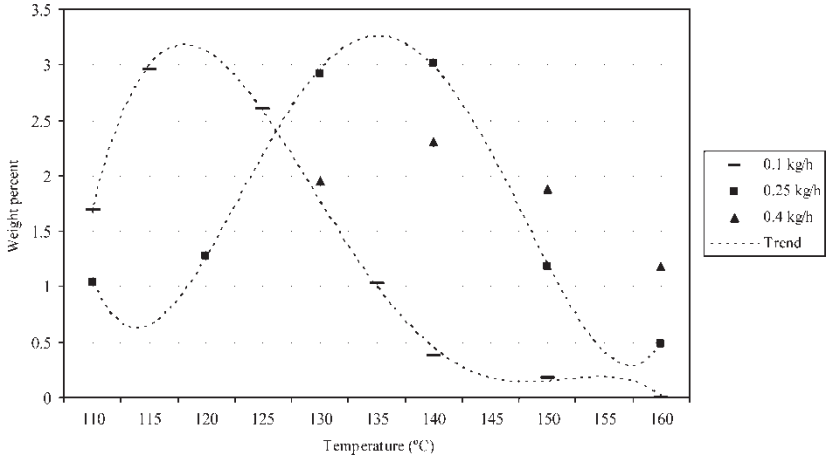


***Figure 3.*** Concentration of tocotrienols in the liquid phase at different flow rates.

rate of the tocotrienols was slower than the FFA and squalene. This produced an increase in the concentration of tocotrienols in the liquid phase, which reached a maximum at higher temperatures. Above this temperature, the vapor pressure of tocotrienols was significant, and their rate of evaporation became comparable to the other components. Under these conditions, the concentration of tocotrienol in the liquid phase decreased.

As shown in Fig. 3, the temperature that produced maximum concentration of tocotrienols was affected by the feed flow rate. At a feed flow rate of 0.1 kg/h, this temperature was about 118°C; while at 0.25 kg/h, it was about 135°C. In other words, the curve moved to the right when the feed flow rate increased. Also, the width of the curve increased with an increase in the feed flow rate. In addition, at higher feed flow rates such as 0.4 kg/h, the concentrations of tocotrienol became smaller. This observation is important because it shows that the feed flow rate has an effect on the concentration of tocotrienol in the liquid phase, and ultimately on its evaporation rate.

Figures 4 and 5 display the concentration of $\alpha$-tocopherol and sterols in the liquid phase, respectively. These figures show similar behavior to that of the tocotrienols (Fig. 3). The maximum concentrations of $\alpha$-tocopherol and sterols were also reached at the same temperatures than tocotrienols. Figures 6 and 7 show the concentration of squalene and FFA in the liquid phase, respectively. Although it was not possible to see the whole curves in the range of temperatures displayed, they seem to have the Gaussian distribution-like shape as well. At a feed flow rate of 0.25 kg/h, both squalene and FFA reached their maximum concentrations at about 115°C (Figs. 7 and 8). This temperature was lower than the one for tocotrienols, $\alpha$-tocopherol and sterols, which was 135°C. The reason for the difference in these temperatures was that the squalene and FFA started to evaporate at lower temperature



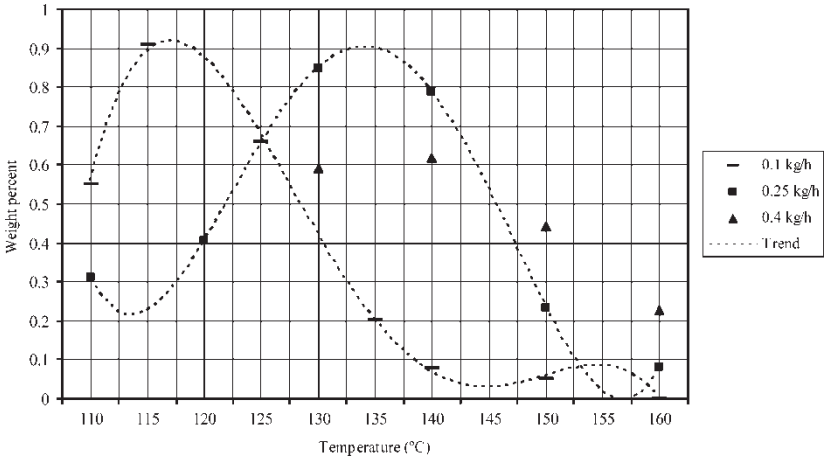


***Figure 4.*** Concentration of $\alpha$-tocopherol in the liquid phase at different flow rates.

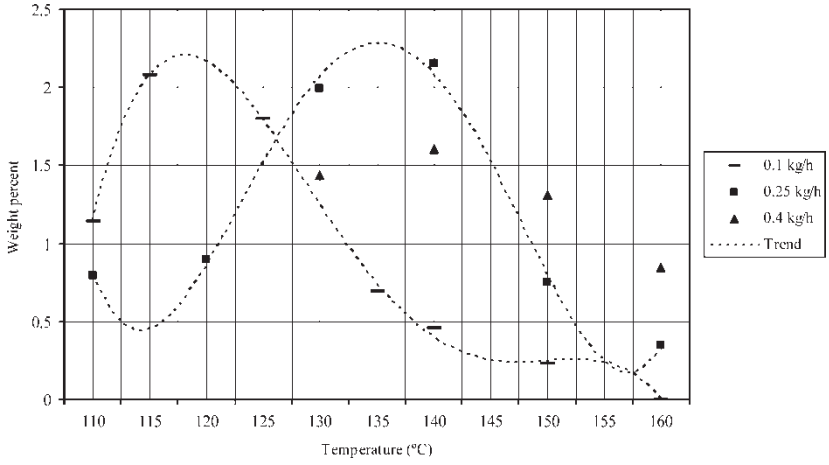


***Figure 5.*** Concentration of sterols in the liquid phase at different flow rates.



than the tocotrienols, $\alpha$-tocopherol and sterols since their vapor pressures were much higher.

Figure 8 displays the concentration of other compounds in the liquid phase. These other compounds are mono-, di-, and tri-glycerides, and unknown compounds, which probably include phytoene, aliphatic hydrocarbons, and glycerol. The curves on Fig. 8 shows that this liquid phase was composed of components with higher distillation temperatures. At 160°C, the concentration of these compounds was around 90% in the liquid phase for all of the three feed flow rates; this percentage might be due to the high

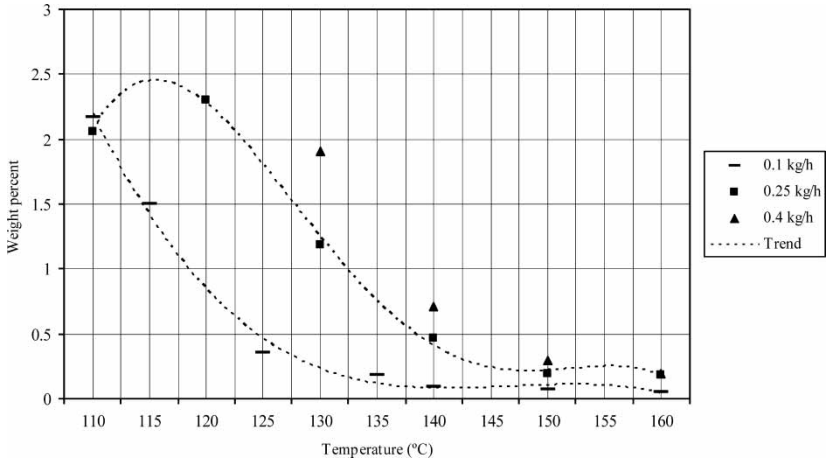


***Figure 6.*** Concentration of squalene in the liquid phase at different flow rates.

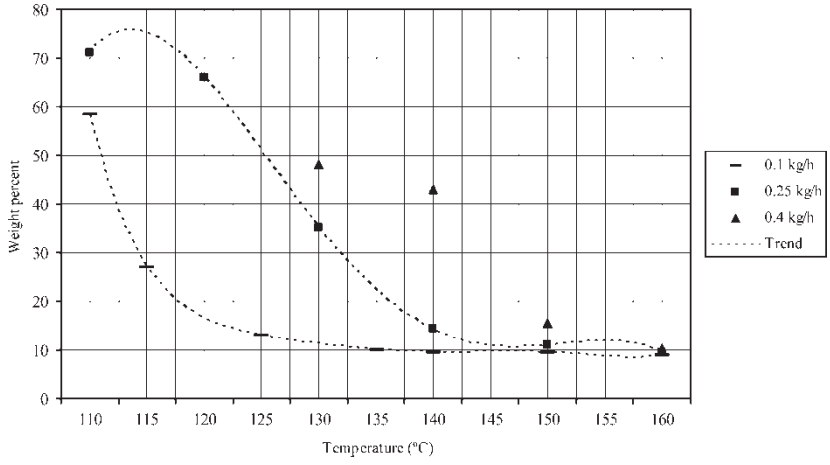


***Figure 7.*** Concentration of FFA in the liquid phase at different flow rates.



boiling triglycerides that were present in the PFAD. At the lowest flow rate (0.1 kg/h), the more volatile components were removed more quickly at the lower temperatures.

Figure 9 shows the concentration of tocotrienols in the vapor phase. The concentration of the tocotrienols in this phase was affected by the temperature of distillation and the feed flow rate. If the temperature increased and the feed flow rate held constant, the concentration of tocotrienols increased. If the feed flow rate increased and the temperature held constant, the

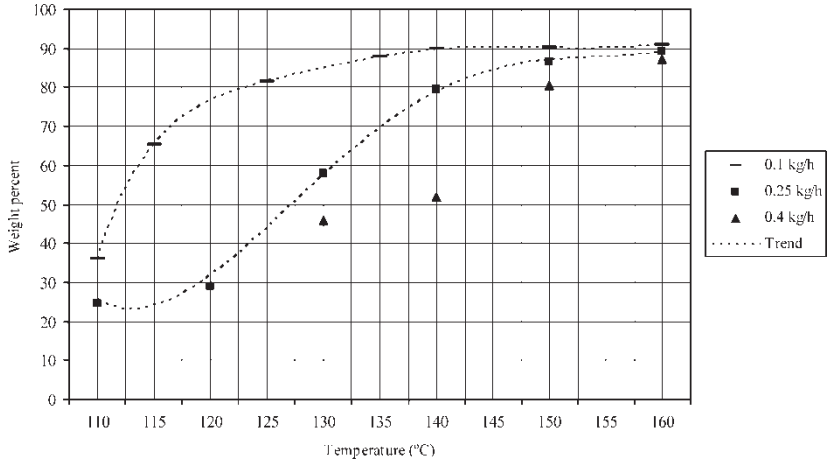


***Figure 8.*** Concentration of other compounds in the liquid phase at different flow rates.

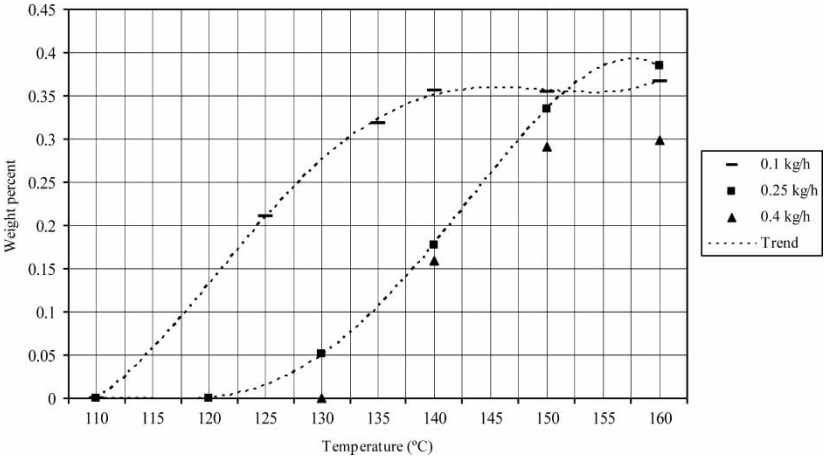


***Figure 9.*** Concentration of tocotrienols in the vapor phase at different flow rates.



concentration of tocotrienols decreased. Figures 10 and 11 show the concentration of $\alpha$-tocopherol and sterols in the vapor phase, respectively. These figures show similar behavior to that of the tocotrienols (Figure 9), which was expected.

Figures 12, 13, and 14 display the concentration of squalene, FFA and other compounds in the vapor phase, respectively. Squalene (Fig. 12) shows similar behavior to that of the tocotrienols, $\alpha$-tocopherol, and sterols at low temperatures (Figs. 9, 10, and 11). The concentration of FFA (Fig. 13) remained high at low temperatures (110–130°C): at a feed flow rate of

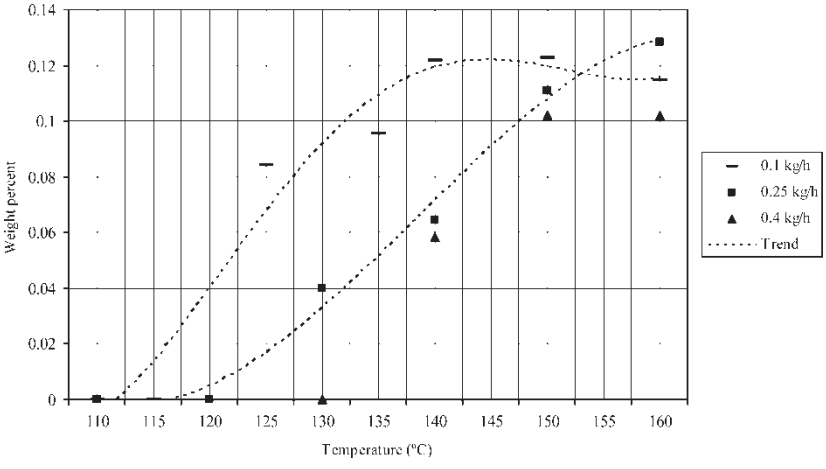


***Figure 10.*** Concentration of $\alpha$-tocopherol in the vapor phase at different flow rates.

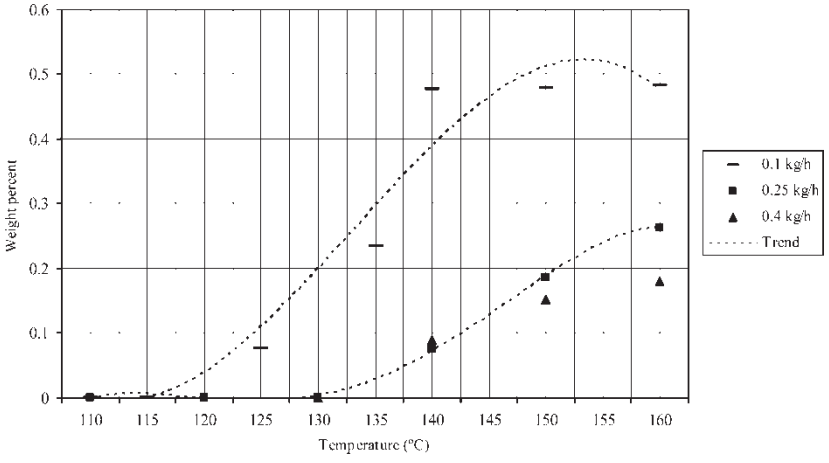


***Figure 11.*** Concentration of sterols in the vapor phase at different flow rates.



0.1 kg/h, it was around 99%; at a feed flow rate of 0.25 kg/h, it was between 96 and 97%. The concentration of other components (Fig. 14) was just the opposite to that of FFA at low temperatures since these other components and the FFA were the two main components present in the vapor phase. Interestingly, there was a particular behavior for each of these compounds at higher temperatures: the concentration of squalene (Fig. 12) tended to reach a constant value just above 1%; the concentration of FFA (Fig. 13) decreased as temperature increased; and the concentration of the other compounds (Fig. 14) increased as temperature increased.

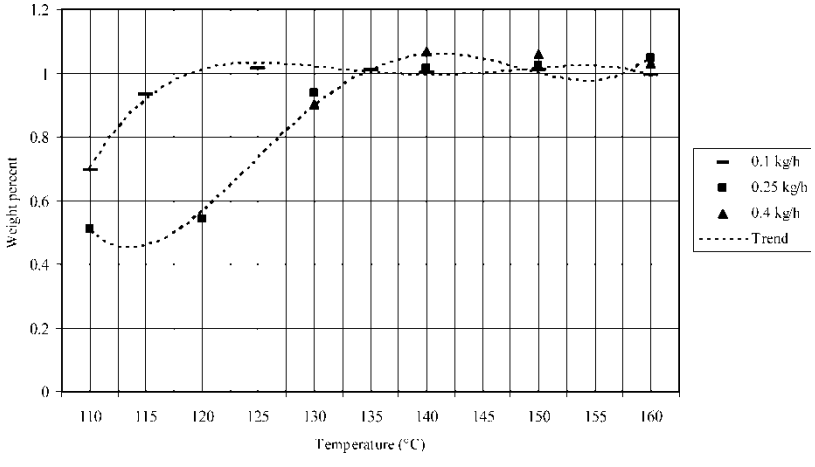


***Figure 12.*** Concentration of squalene in the vapor phase at different flow rates.

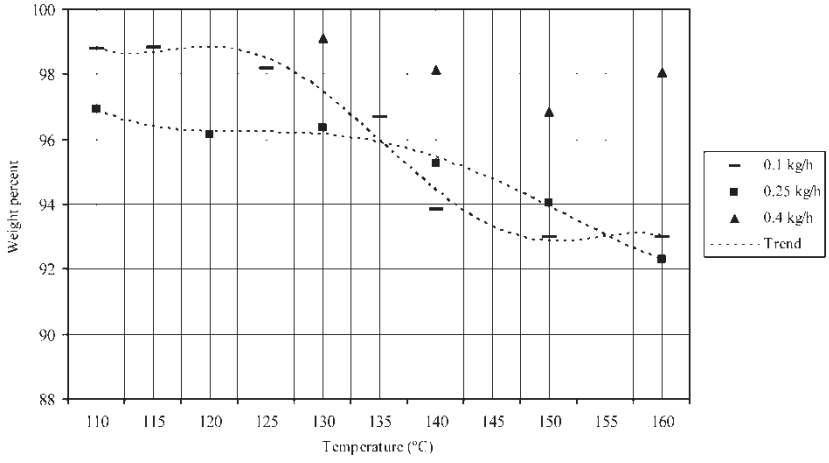


***Figure 13.*** Concentration of FFA in the vapor phase at different flow rates.



## Relative Volatility

Since the PFAD was composed of 90% free fatty acids (Table 1), and the other minor components, i.e. squalene, sterols, and $\alpha$-tocopherol, do not damage the tocotrienols (they may even add additional value to a commercial tocotrienol product), the main purpose of the molecular distillation process would be to separate the tocotrienols from the undesirable fatty acids. The effectiveness of this separation was evaluated using the relative volatility concept, which

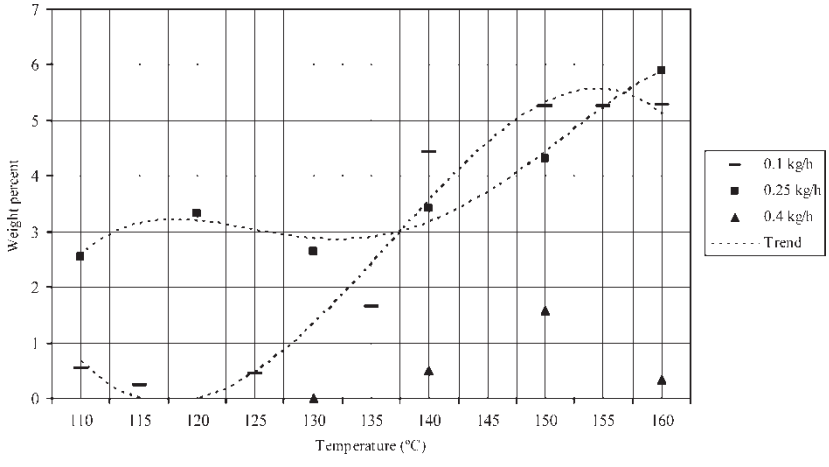


***Figure 14.*** Concentration of other compounds in the vapor phase at different flow rates.

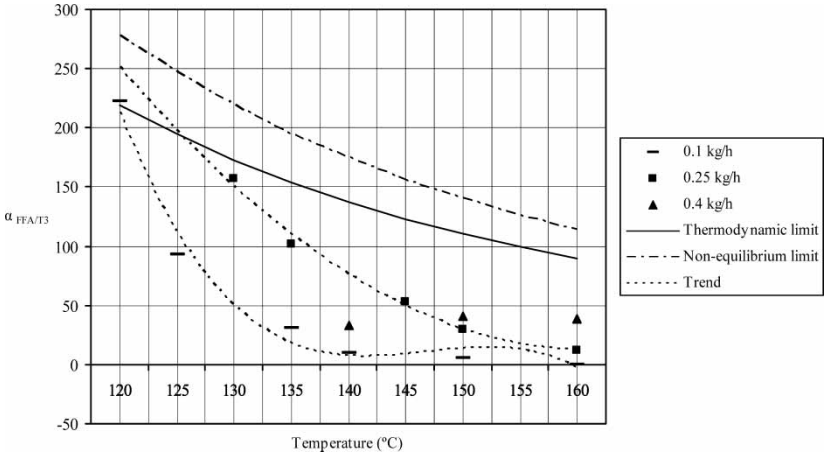


***Figure 15.*** Relative volatility of FFA with respect to T3 at different flow rates.



in this case, was expressed as the relative volatility of FFA to tocotrienols (T3), i.e. $\alpha_{FFA/T3}$, because tocotrienols are less volatile than the FFA.

Two theoretical relative volatilities were defined, one calculated using the ratio $P^O_{FFA}/P^O_{T3}$, the other one calculated by means of Eq. (9), i.e. $(P^O_{FFA}/P^O_{T3})(M_{T3}/M_{FFA})^{1/2}$. The former represented the thermodynamic separation limit since it was obtained assuming the dynamic equilibrium between the liquid and vapor phases; the latter, which was deduced from the kinetic theory (9), represented the non-equilibrium separation limit. Since tocotrienols have the higher molecular weight, the influence of the kinetic theory was to increase the degree of separation over that expected from equilibrium

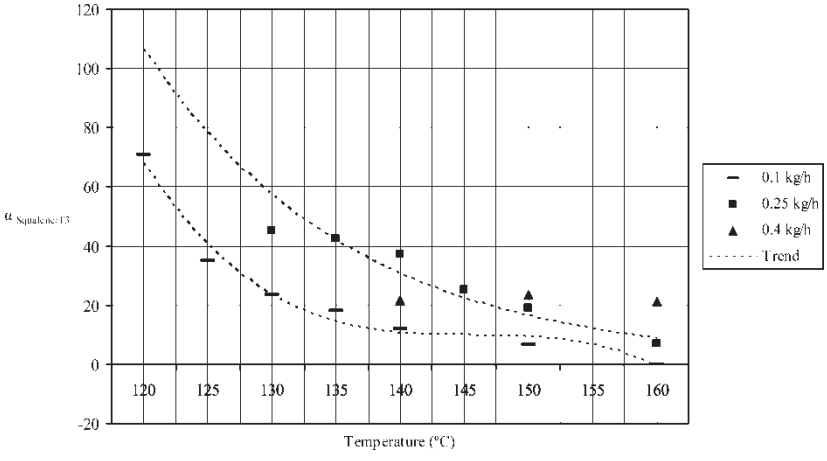


***Figure 16.*** Relative volatility of squalene with respect to T3 at different flow rates.

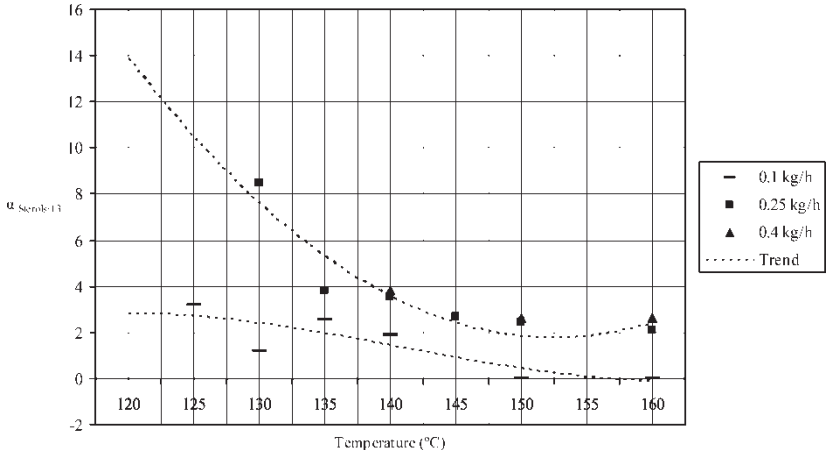


***Figure 17.*** Relative volatility of sterols with respect to T3 at different flow rates.



considerations. Both of these relative volatilities were deduced assuming that the components obeyed Raoult's law. It was, therefore, expected that the real relative volatilities were smaller than the theoretical ones since only a few mixture of substances follows Raoult's law (e.g. some mixtures of hydrocarbons of the same series), and because of possible mass and heat transfer resistances in the liquid phase that would not allow a perfect separation. Also, any intense collision of molecules in the gap between evaporator and condenser would have been detrimental to the separation results. Nevertheless, the equilibrium and non-equilibrium relative volatility limits were used to evaluate the actual separation during the trials in the short path evaporator. In all calculations, the vapor pressure of $\alpha$-tocopherol was used instead of the vapor pressure of tocotrienols. Table 4 shows the theoretical relative volatilities calculated at temperatures between 110 to 160°C.

Figure 15 displays the $\alpha_{FFA/T3}$ results, calculated by means of Eq. (7), as a function of temperature and the feed flow rate. The top line is the non-equilibrium limit; the solid line below is the thermodynamic limit; and the dotted lines are polynomial trends adjusted using the least square method. It was expected that all experimentally obtainable relative volatilities would

***Table 4.*** Theoretical relative volatilities

| Temperature (°C) | 110 | 120 | 130 | 140 | 150 | 160 |
|---|---|---|---|---|---|---|
| Thermodynamic $\alpha_{FFA/T3}$ | 282.5 | 219.5 | 172.8 | 137.5 | 110.7 | 90.0 |
| Non-equilibrium $\alpha_{FFA/T3}$ | 358.1 | 278.3 | 219.0 | 174.4 | 140.3 | 114.1 |

have lay between the kinetic and thermodynamic limits. However, that was not the case as can be seen in Fig. 15. Relative volatilities approached non-equilibrium and thermodynamic limits only at low temperatures, and they fell off drastically as temperature was increased.

There was, surprisingly, an agreement between the behavior show in Fig. 15 and the results of previous studies on molecular distillation using mixtures of pure compounds (7, 8, 12). Those studies showed that, at high temperature, the distillation rate and the relative volatilities (called separation factor) decreased. This phenomenon was probably caused by two effects related to the resistance to heat and mass transfer in a multicomponent film evaporating under high vacuum. The self-cooling effect of the interface resulting from poor heat transfer from the bulk of liquid to its surface (7, 8). Depletion at the surface in the more volatile component, because of the low diffusion rate of this component from the interior of the film to the interface (12).

Figure 15 shows the effect of feed flow on $\alpha_{FFA/T3}$ as well. A feed flow rate of 0.1 kg/h produced lower $\alpha_{FFA/T3}$ than feed flow rates of 0.25 and 0.4 kg/h. This was explained again by the retention time of tocotrienols on the evaporation surface. At low feed flow rates, tocotrienols have more time to reach the surface of the liquid and escape into the vapor phase. Therefore, the separation at low flow rate was not as good as expected. A high feed flow rate had the opposite effect.

Figures 16 and 17 display relative volatilities of squalene and sterols, respectively, with respect to tocotrienols as a function of temperature and feed flow rate. It was found that squalene and sterols were more volatile than tocopherols under molecular distillation conditions. In addition, the same effects of temperature and feed flow rate discussed above were present.



## CONCLUSIONS AND DISCUSSIONS

The volatility order of the tocotrienol, which was based on distribution coefficients, was $\delta$-T3 > $\gamma$-T3 > $\alpha$-T3, which corresponded to their molecular weights of 396, 410, and 424. No relationship between volatility order of sterols and their molecular weights was observed. Feed flow rate affected the relative volatilities of all components during the molecular distillation of palm fatty acid distillates (PFAD). As the feed flow rate decreased, the relative volatilities of FFA, squalene, and sterols to tocotrienols decreased. Concentrations of tocotrienols, $\alpha$-tocopherol, and sterols behaved similarly in both liquid and vapor phases. FFA and squalene evaporated at lower temperatures than tocotrienols, $\alpha$-tocopherol, and sterols. The concentration of FFA in the vapor phase was high at all molecular distillation conditions. Therefore, it was possible to separate the tocotrienols, $\alpha$-tocopherol, and sterols from FFA by molecular distillation using low temperatures. This effect was related to the retention time of tocotrienols in the evaporator.

The best feed flow rate for the separation of tocotrienols from PFAD was 0.25 kg/h. The relative volatilities of FFA to tocotrienols approached theoretical limits only at low temperature, and they fell off drastically at higher temperatures. This phenomenon was probably caused by the resistance to heat and mass transfer of the liquid that was evaporated under high vacuum conditions.

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