Scrubbed Palm Fatty Acid Distillate as Vitamin E Concentrate

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Abstract: Vitamin E (VitE) production from crude palm oil (CPO) has been extensively studied and industrially conducted. VitE in CPO is in the range of 600 to 1,000 ppm, and is usually produced from one of the main by-products of edible palm oil production, namely palm fatty acid distillate (PFAD). PFAD contains 4,000 to 5,500 ppm of VitE, and is produced from deodorization process of palm oil purification. This paper presents an innovative process of VitE concentrate production from CPO. A scrubber was designed and installed between the deodorizer and conventional PFAD scrubber. The main objective of this new scrubber was a recovery of glycerides from PFAD. This new scrubber is operated at 150 to 160°C. The scrubbed oil is named as Scrubbed Palm Fatty Acid Distillate (S-PFAD). This simple and efficient modified process can retrieve glycerides as S-PFAD at 0.3% recovery and it enhances VitE concentration in S-PFAD to the range of 28,000 to 32,000 ppm, which is the highest concentration of VitE that has ever been produced in the palm oil production. Fatty acids and glycerides in S-PFAD were esterified and transesterified to methyl esters. The methyl esters were evaporated from S-PFAD, and S-PFAD residue oil contained 24.7% VitE.

Key words: vitamin E, tocopherol, tocotrienol, scrubbed palm fatty acid distillate, methyl esters

1 Introduction

VitE, an oil soluble potent antioxidant, is classified into two tocols, namely tocopherol and tocotrienol, as shown in Fig. 1. Tocopherol or tocotrienol is composed of a chromanol ring which is connected by phytyl or isoprenoid tail at the carbon 2 position on chromanol ring, respectively. The unsaturated isoprenoid chain is more rigid than the saturated phytyl chain which affects tocotrienol absorption and the availability in the human body. The three double bonds, at the position of 3, 7, and 11 carbon in tocotrienol, are not conjugated that give rise to color of VitE as pale yellow, while most natural antioxidants are colorful. The chromanol ring serves as the free radical scavenger, that possess antioxidant activity of tocols. Phenolic group of the chromanol ring donates hydrogen to the attack peroxyl and alkoxyl radicals generated during lipid peroxidation and VitE molecules become a stabilized resonance radical form of quinone. This radical combines with other attack radicals or another molecule of tocol to form tocol dimer. This chain-breaking process can terminate the free radical causing diseases. Therefore, VitE can heal many symptoms relating to health. 

In 1922, α-tocopherol was discovered as an essential chemical required in reproduction. VitE is a substance necessary for proper body and brain function. VitE has also been shown as a protective agent in bone, cardiovascular, eye, nephrological and neurological diseases, apart from cancer. VitE exerts various beneficial health promoting properties especially against chronic diseases, including cancer. Tocotrienols can suppress the growth of different malignancies of breast, lung, ovary, prostate, liver, brain, colon, myeloma, and pancreas. Recently, a combination of δ-tocotrienol and bevacizumab is effective in chemotherapy refractory ovarian cancer in a phase II trial. γ-Tocotrienol, a member of the VitE, owes anti-proliferative and anticarcinogenic potential due to its effective cellular inflammatory.

The growing pervasiveness of target diseases including cancer, kidney diseases, and diabetes, and the benefit of brain health and functionality, superior antiglycemic, anti-
inflammatory, neuroprotective, and cardioprotective and cholesterol-lowering properties by the introduction of advanced tocotrienol administration. Recently, Delgado et al.\textsuperscript{8} contributed a review of the significance of tocols as food sensorial properties, stability, and overall quality. It is estimated that tocotrienols market size was US Dollars 321.5 million in 2018\textsuperscript{9}. It is forecasted that tocotrienols global trade value will reach US Dollars 522 million by the year 2026 at the growth of 6.7\textsuperscript{ˊ} annually.

\(\alpha\)-Tocopherol has been the most commonly studied form of VitE\textsuperscript{3}, since 1966 only 3\textsuperscript{ˋ} of all VitE research papers are publications of tocotrienol. However, tocotrienols are more potent than \(\alpha\)-tocopherol, especially \textit{in vitro} studies\textsuperscript{10}. Despite their high therapeutic benefits, tocotrienols have a very short elimination half-life. Tocotrienols have lower binding for the \(\alpha\)-tocopherol transfer protein (ATTP), the protein that maintains the plasma level of tocols. Therefore, they have a longer residence time in the liver and being metabolized and biliary excreted\textsuperscript{11}. This low affinity of tocotrienols to ATTP was postulated to come from the rigidity of isoprenoid tail in tocotrienols comparing with the more flexible phytol tail in tocopherols. Compadre \textit{et al.}\textsuperscript{11} proposed a new tocol, namely Tocoflexol, which has 2 double bonds at the position of 3’ and 11’ carbon in tocotrienols. Tocoflexol was 5 times more effective than \(\alpha\)-tocopherol to quench oxidative damage in microsomes. Ng \textit{et al.}\textsuperscript{12} discovered \(\alpha\)-tocomonoenol 3 - 4\% (40 ± 5 ppm) of VitE content in CPO. \(\alpha\)-Tocomonoenol has one double bond on the isoprenoid tail of VitE, which has more molecular flexibility comparing with tocotrienol for the affinity to ATTP. \(\alpha\)-Tocomonoenol is superior to \(\alpha\)-tocopherol on better distribution in the cell membranes with saturated fatty layers which can more easily be incorporated into cells\textsuperscript{10}. Separation of tocotrienol racemic mixture at carbon 2 position was achieved by HPLC on a chiral phase of adsorbent cellulose derivated with 3,5-dimethyl phenyl carbamate. Only R, E-E isomer of tocotrienols (as shown in Fig. 1) is naturally found in palm oil\textsuperscript{15}. Durazzo \textit{et al.}\textsuperscript{14} provided an update of current databases of tocols occurrence in foods, such as fruits, grains, and oils. Tocotrienols are uncommonly found in nature and occur at very low concentration. They are found in palm, rice bran, and barley oils as well as wheat germ and oats. Palm oil is the most concentrated natural source of tocotrienols after annatto seeds oil which contains more than 5\% of \(\delta\)-tocotrienol\textsuperscript{15}. To have beneficial effects of VitE on health, ones need to consume an entire cup of palm oil each day. While many people take vitamin E supplements, it most only contains \(\alpha\)-tocopherol. CPO is a rich source of nutraceuticals which are VitE, carotenoids, squalene, and sterols. Concentration of these nutraceuticals is available in the range of 700 to 1000 ppm in CPO. VitE in CPO are composed of \(\alpha\)-tocopherol (420 ppm), \(\alpha\)-tocomonoenol (40 ppm), \(\alpha\)-tocotrienol (260 ppm), \(\gamma\)-tocotrienol (360 ppm), and \(\delta\)-tocotrienol (80 ppm)\textsuperscript{12}. PFAD, derived from CPO by deodorizing process, is a rich source of VitE. Generally,
PFAD contains mainly fatty acids (80 - 85%), glycerides (10 - 12%), nutraceuticals (1.5 - 1.8%), aldehyde and ketone odor compounds and others.

Hoe et al. and Malekbalaa et al. recently reviewed VitE extraction technologies from palm oil (such as CPO and PFAD) and other natural resources. Several techniques have been studied which are molecular distillation, adsorption, liquid-liquid extraction, supercritical-fluid extraction (SFE), membrane processing, and a novel SFC which combines adsorption and SFE. These techniques usually require oil pretreatments to convert the main components which are glycerides and fatty acid to compounds that ease the separation of each technique. In term of high concentration of VitE product, molecular distillation and SFE are the most effective process with low and clean solvent consumption, respectively.

In this work, a new scrubber was installed to scrub glycerides from conventional PFAD. Inside the new scrubber, there is a structural packing and a distributor. Fatty acid distillate or conventional PFAD from the deodorizer is fed into this scrubber. The scrubbed glycerides are called S-PFAD, and it is returned as the feed of the deodorizer to increase the yield of neutral oil. S-PFAD has some significant unsaponification matters, such as VitE, sterols and squalene. To produce oil that has such a high VitE content, S-PFAD was esterified and transesterified to convert fatty acid and glycerides to methyl ester. Methyl ester evaporation significantly enhanced VitE concentration in the residue oil.

2 Materials and Methods

2.1 Materials

Degummed CPO and S-PFAD were a gift from Suksomboon Vegetable Oil Co., Ltd., Chonburi, Thailand. Methanol (99.9%) and other chemicals were HPLC grade from RCI Labscan Co., Ltd. 500 mL baffled jacketed glass reactor mixed by magnetic stirrer, from SP Glass Thailand, was used for chemical reactions. Temperature inside both reactors was controlled by a circulating bath, PolyScience model 9602. Buchi rotary evaporator and in-house Kugelrohr distillation apparatus set were used to evaporate methanol or water and methyl ester, respectively.

2.2 Methods

2.2.1 Extraction of VitE in CPO as S-PFAD

500 Tons of degummed CPO is daily fed into a deodorizer to produce refined palm oil (RPO) and fatty acid deodorized distillate. The fatty acid distillate is fed into a new installed scrubber, namely S-PFAD scrubber, and the fatty acid distillate was scrubbed as S-PFAD. Vapor from S-PFAD scrubber is further scrubbed in the following PFAD scrubber as shown in Fig. 2. Cooled S-PFAD product is used to scrub the deodorized fatty acid distillate inside S-PFAD scrubber, while the cooled PFAD product is returned to scrub vapor from S-PFAD scrubber in PFAD scrubber.

2.2.2 Esterification of free fatty acid

Free fatty acid in S-PFAD 212 g was esterified to methyl ester by reacting with 100 g of methanol inside the 500 mL baffled glass reactor. 0.27 mL of concentrated sulfuric acid was added as catalyst into the reactor after the temperature of the mixture reached 60°C for 12 hours. The oil was cooled down, washed with water, and dried inside the rotary evaporator.

2.2.3 Transesterification of glycerides

Glycerides in the dried esterified oil were converted to methyl ester by transesterification with 80 mL methanol catalyzed by 1 g of sodium hydroxide at 60°C for 2 hours. After settling overnight, glycerine-rich layer was removed, and the oil was washed with 1% phosphoric acid solution twice, followed by washing with water 2 more times. The oil was vacuum dried inside the rotary evaporator.

2.2.4 Methyl ester evaporation

Methyl ester was evaporated using Kugelrohr distillation under 50 Pa at 150°C. The S-PFAD residual oil was analyzed to determine the content of VitE.

2.2.5 Analytical Procedure

Samples was diluted in isopropanol and determined for VitE concentration by High Performance Liquid Chromatography of Thermo Separation Products Model 3200 with TSK-GEL column, type ODS-100S, size 4.6 mm (ID) × 25.0 cm (L), using UV detector at the wavelength of 295 nm. The mobile phase was acetonitrile : methanol : dichloromethane mixture at 65 : 30 : 5 volumetric ratio. The mobile phase flow rate was 1 mL/min.

3 Results and Discussion

3.1 Extraction of VitE in CPO as S-PFAD

500 T/d of degummed CPO is deodorized using steam in
the deodorizer at temperature higher than 220°C to produce refined palm oil at Suksumboon Vegetable Oil, Co. Ltd. The deodorized distillate is scrubbed by its product, S-PFAD, at 150 - 160°C in S-PFAD scrubber. S-PFAD is produced by this scrubber at 1,400 to 1,500 kg/d which is estimated to be 0.3% recovery of glycerides and it is returned to the deodorizer to enhance VitE content in RPO and produce higher RPO yield. S-PFAD is composed of glycerides, 20 - 25% free fatty acids, 2.5 - 3.2% VitE, and others. This new installation of S-PFAD scrubber provides such a high concentration level of VitE that has never been reported by a simple modification in the real world edible oil refining process. Unscrubbed vapor from S-PFAD unit is scrubbed by PFAD at 90 to 100°C. Free fatty acid and VitE content in this PFAD is in the range of 88 - 91% and 3,000 - 3,500 ppm, respectively. Suksumboon PFAD has higher free fatty acid and lower VitE concentration than general PFAD, since some glycerides and VitE have been scrubbed into S-PFAD.

3.2 Esterification of free fatty acid
S-PFAD was esterified by reacting with methanol. Free fatty acid in S-PFAD was dropped from 23 to 0.51% after 12 hours. Concentration of VitE in S-PFAD was 3.1% after esterification. There is no loss of VitE in esterification since it is quite stable to heat\(^1\). Extraction of VitE into methanol phase was very limited, since there was a large amount of water produced in esterification that occluded nonpolar compounds to dissolve into methanol\(^{19}\).

3.3 Transesterification
The esterified S-PFAD was transesterified with methanol catalyzed by sodium hydroxide. Transesterification was applied to convert glycerides to methyl ester and glycerine. VitE in the transesterified S-PFAD was determined to be 2.7%. Since transesterification is base in polar phase, a fraction of VitE has lost into the bottom that is rich in methanol and glycerine. Hydroxyl group at the chromanol ring of VitE presents in the ionized form in base medium and dissolves into the bottom product.

3.4 Methyl ester evaporation and yield of VitE concentrate
Fatty acid and glycerides in S-PFAD were transformed to methyl esters. This methyl ester was evaporated under high vacuum using the Kugelrohr apparatus. This oil residue is shown in Fig. 3 along with 2 fractions of methyl ester distillate. The oil residue has 24.7% of VitE, which is 8 times higher than VitE in S-PFAD. Concentration of VitE from each step in all extraction process is illustrated in Fig. 4. Yield of VitE and VitE oil are 82.7 and 10.4%, respectively. Ng et al.\(^{12}\) reported a change of mass ratio of tocols in phytonutrient concentrate (contained 1.37% of VitE and produced by CPO conversion to methyl ester and followed by vacuum distillation) from that found in CPO, and postulated that it was caused by esterification, transesterification, and vacuum distillation. From this experimental result, there is no different of the tocols mass ratio resulting from the reactions and evaporation in all steps. Vacuum distillation of methyl ester is usually operated at above 200°C, while evaporation in this work was conducted at 150°C at high vacuum (below 50 Pa).

4 Conclusions
VitE from CPO is extracted as a concentrate in S-PFAD by a simple scrubber installed between the conventional deodorizer and PFAD scrubber. S-PFAD has 6 times higher VitE concentration than conventional PFAD. VitE concentration in S-PFAD was further enhanced by methyl ester formation from other main components and methyl ester evaporation. The concentrate residue oil has a quarter of mass as VitE which it is 280 times more concentrate than CPO. The relative content of active tocotrienols was well preserved by this process without any change of the mass percent of each tocol.
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