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Bench Scale Production of Vitamin E from Crude Palm Oil

Amnart Soontornchatchawate, Santi Wattananusorn, Prakob Kitchaiya*

Department of Chemical Engineering, School of Engineering, King Mongkut's Institute of Technology Ladkrabang, Bangkok 10520, Thailand
prakob.ki@kmitl.ac.th

Vitamin E (VitE) from palm oil is usually separated from palm fatty acid distillate. VitE separation from crude palm oil (CPO) has been rarely reported. This work presents a separation of VitE from CPO in a bench scale process to attain a high concentration of VitE oil by methanol extraction, followed by fatty acid esterification and glycerides transesterification in the extract, and finally concentrated by high vacuum evaporation of fatty acid methyl esters. The starting content of VitE in CPO was 887 ppm, which was first extracted with an equal mass of methanol and evaporated to gain 4,515 ppm of VitE in the evaporated extract. The extract was esterified and transesterified to convert free fatty acids and glycerides into fatty acid methyl esters. The bulk of methyl ester was evaporated under high vacuum using Kugelrohr apparatus and the oil residue contained 69,950 ppm VitE, which was 80 times the original amount in CPO. By this development, 80 wt.% of VitE remains in the extracted CPO as a natural antioxidant and the CPO can be normally purified as edible palm oil or used as feed stock for biodiesel production.

1. Introduction

Natural oil soluble antioxidants found in edible oils are carotenoids and VitE. These antioxidants are available in vegetable oils such as palm oil, annatto oil and rice bran oil, etc (Ahsan et al., 2015). VitE has been reported to function against free radical-mediated degenerative diseases, such as cancers and neurological diseases (Ahsan et al., 2015; Aggarwal et al., 2019). VitE is always recovered from fatty acid distillates due to the amount of VitE in them, which is 5 to 10 times higher than in crude oils (Chu et al., 2005). There are many publications on VitE separation from fatty acid distillates. Adsorption chromatography, molecular distillation, and supercritical fluid extraction are the three main techniques applied to separate VitE from fatty acid distillates (Liu et al., 2008; Hiromori et al., 2016; Posada et al., 2007; Mendes et al., 2005; Ng et al., 2018). Separation of VitE from CPO has been rarely reported (Ng et al., 2004; Gasta et al., 2005; Chuang and Brunner, 2006). Ng et al. (2004) obtained 13,780 ppm VitE in phytonutrient concentrate as the residue from vacuum distillation of CPO methyl esters. Gasta et al. (2005) applied supercritical carbon dioxide at 66.85 and 96.85 ^{o}C and pressures between 20 and 30 MPa to separate VitE from CPO. They attained 3,200 ppm VitE in the extract, 10 times increasing from the original CPO. Chuang and Brunner (2006) converted deacidified CPO to methyl ester and extracted VitE by supercritical carbon dioxide.
This process was repeated 3 times and they achieved at 6 wt.% VitE oil. CPO is the raw material for palm olein, palm stearin, oleochemicals, and biodiesel. Production of edible palm oil and biodiesel always has palm fatty acid distillate as a low revenue by product. The distillate is used as animal feed stock. CPO is composed of over 90 wt.% of the mixture of triglycerides, 4 to 7 wt.% of diglycerides and below 1 wt.% of monoglycerides (Sambanthamurthi et al., 2000). Free fatty acids content in CPO varies from 3 to 6 wt.%. CPO contains 600 to 1000 ppm VitE in the two main aspects, namely tocotrienols and tocopherols (Sambanthamurthi et al., 2000; Ng et al., 2004). Goncalves et al. (2007) investigated tocopherol distribution between ethanol and palm olein in deacidification of palm oil. Tocopherol distribution coefficient was found to be 0.75 between ethanol and palm oil. Batista et al. (1999) deacidified oleic acid from canola oil by using methanol extraction and the distribution coefficient of the acid was closed to unity. Publications of VitE separation from CPO are rare and there was Brunner group that applied supercritical fluid extraction to separate VitE from CPO (Gasta et al., 2005; Chuang and Brunner, 2006). Supercritical fluid equipment is expensive.

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It requires high pressure operating cost. Supercritical fluid extraction may not be practical to separate VitE from the large bulk of CPO. Therefore, a simple process is demonstrated here to separate VitE from CPO. The present paper will separate VitE from 1 kg of CPO in a bench scale process by using methanol solvent. Methanol is more polar than ethanol, which will selectively extract more VitE than triglycerides. Free fatty acids and mono- and di-glycerides will be coextracted and need to be removed by evaporation after they are converted to fatty acid methyl esters achieving a high concentrated VitE oil.

2. Materials and Methods

2.1 Materials

Degummed CPO was a gift from Suksomboon Vegetable Oil Co., Ltd., Chonburi, Thailand. There were 887 ppm VitE and 6.1 wt.% free fatty acids in the CPO. Methanol (99.5 vol.%) and sodium methylate (30 wt.%) were commercial grade available in Thailand. Other chemicals were HPLC grade from RCI Labscan Co., Ltd. 3 liters jacketed glass reactor with overhead stirrer and 300 ml jacketed and 500 ml baffled jacketed glass reactor mixed by magnetic stirrer, from SP Glass Thailand, were used for extraction and chemical reactions, respectively. Temperature inside reactors was controlled by a circulating bath, PolyScience model 9602. Buchi rotary evaporator and an in-house Kugelrohr distillation apparatus set were used to evaporate methanol or water and methyl ester, respectively, as shown in Figure 1.

(a) (b)

Figure 1: Photo of (a) Buchi rotary evaporator and of (b) in-house Kugelrohr distillation apparatus set

2.2 Methods

2.2.1 Extraction of VitE in crude palm oil with methanol

1 kg of degummed CPO was molten and mixed with 1 kg of methanol inside the 3-liter jacketed glass reactor at 50 ^{o}C under nitrogen atmosphere. The mixture was well mixed at 150 rpm for 5 minutes, and then left for phase separation for 2 hours. Top layer was rich with methanol and the bottom was oil layer. Both layers were separated, and the separated oil layer was repeatedly extracted with 1 kg of methanol for 4 times. Samples from oil and methanol layers for each extraction were taken to determine VitE and free fatty acids contents. Methanol layers for each extract were evaporated by applying the rotary evaporator under vacuum and the weight of the residue oils were determined.

2.2.2 Esterification

Free fatty acids in the residual oil of the previous first methanol extract was esterified to methyl esters by reacting with 100 g of methanol inside the 500 ml baffled glass reactor. 0.07 ml of sulfuric acid was added as catalyst into the reactor after the temperature of the mixture reached 60 ^{o}C. The reaction time was 8 hours, and the remaining content of free fatty acids in the bottom oil after esterification was less than 1 wt.%. The oil was cooled down, washed with water, and dried inside the rotary evaporator.

2.2.3 Transesterification

After the esterification, glycerides in the residue oil were converted to methyl esters by transesterification with 10 ml methanol catalyzed by 0.35 ml of sodium methylate solution at 65 ^{o}C for 1 hour in 300 ml reactor.

After settle for 6 hours, bottom glycerine-rich layer was removed, and the oil layer was washed with 1 vol.% phosphoric acid solution 2 times following by washing with water for 2 more times. The oil was dried inside the rotary evaporator under vacuum.

2.2.4 Methyl esters evaporation

Kugelrohr distillation set was applied to evaporate methyl esters from the reacted oil under 50 Pa at 150 ^{o}C. The residual oil was analyzed to determine the amount of VitE.

2.2.5 Analytical Procedure

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

3. Results and Discussion

3.1 Degummed crude palm oil extraction using methanol

CPO contains 10 to 50 ppm of sticky phospholipid gum. Phospholipids interfere with later steps of palm oil purification and need to be removed. Degummed CPO with less than 1 ppm gum was used in this research. Methanol can be used to extract VitE from this CPO along with other species such as free fatty acids, monoglycerides, diglycerides, sterol glycosides, and sterols, etc. Degummed CPO was extracted 5 times using methanol and the amount of oil extract after methanol evaporation is shown in Figure 2. Mass of extract oil decreases stepwise, from 38.6 to 9.9 g from the first to the fifth extract step. Free fatty acid and VitE content in extract and raffinate oils of each step are shown in Figure 3 and 4, respectively. Fatty acids is one of the most polar species in the oil and methanol is a polar solvent, thus smaller amount of free fatty acids being left in the raffinate CPO in later step. Free fatty acids concentration in CPO decreases from original 6.1 to 0.24 wt.% in the fifth raffinate. Methanol extraction is a technique that may be used to deacidify CPO. Recently, it has been proposed to have a treatment that can lower the amount of free fatty acid in CPO before deodorization to prevent glycidyl ester formation, a carcinogenic relating compound found in edible oils (Cheng et al., 2017). The major component in the extract oil is obviously free fatty acids which is 68 wt.% in the first extract and decreases to 24 wt.% in the fifth extract. VitE concentration in CPO decreases from 887 ppm to 741 and 330 ppm in the first and fifth raffinate, respectively. Since free fatty acids are more polar than VitE, less free fatty acids are available in later CPO raffinates while more concentrated VitE (4,500 to 7,200 ppm) is found in later extracts. However, less oil is extracted in later steps causing lower amount of VitE being extracted. Thus, only one step of methanol extraction is more economics in terms of energy consumption in methanol recovery and CPO usage as raw material for edible oil or biodiesel production with high VitE content as a natural antioxidant.

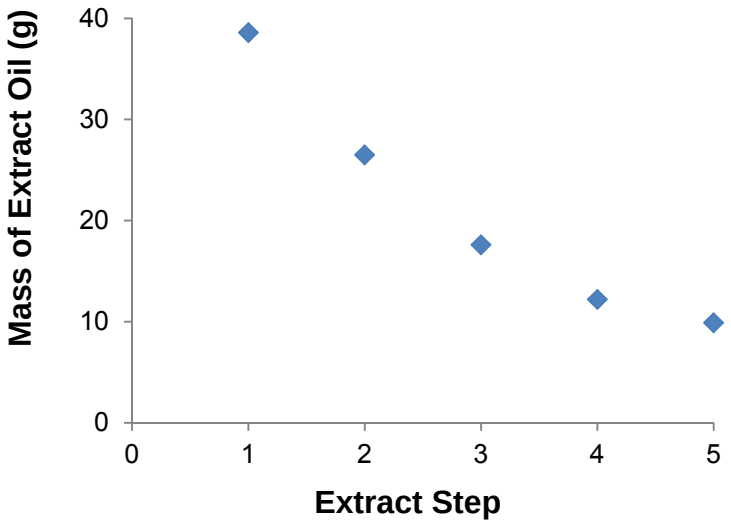

Figure 2: Mass of extract oil in each step

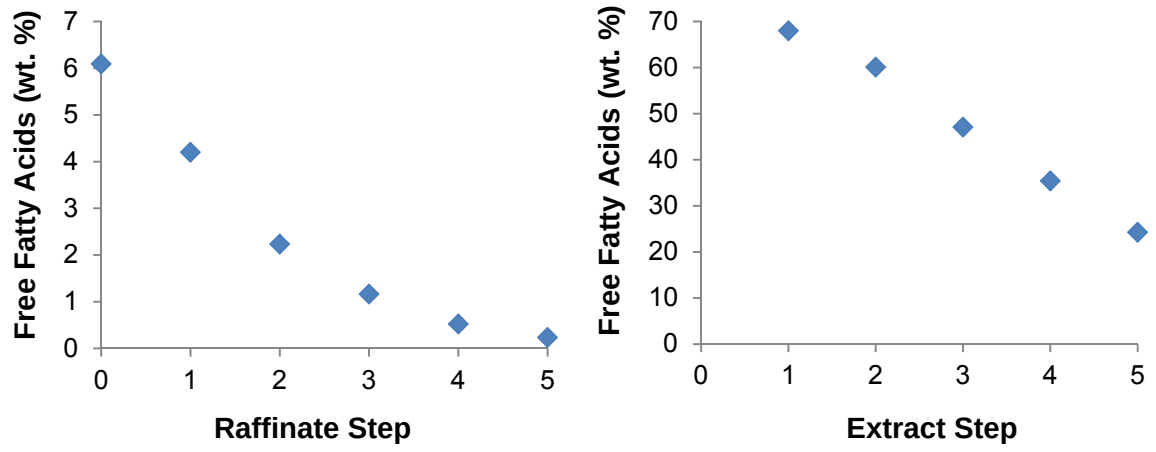

Figure 3: Free fatty acid content in extract and raffinate oils of each step

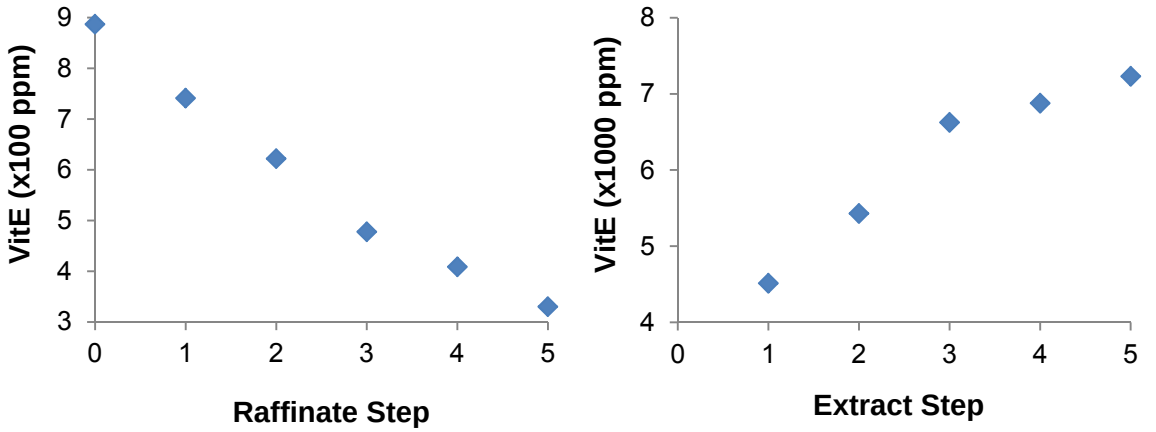

Figure 4: Amount of VitE in extract and raffinate oils of each step

(a) (b)

Figure 5: Photo of (a) CPO after methanol extraction and of (b) oil residue after methyl ester evaporation

3.2 Esterification and Transesterification

Methanol extract oil from the first step contains 68 wt.% free fatty acids and some glycerides. Fatty acids and glycerides removal from the methanol extract oil can considerably enhance VitE concentration in the oil. Therefore, fatty acids in the oil were first converted to methyl esters by esterification with methanol catalyzed by sulfuric acid as explained above. Later, the esterified oil bottom product was further transesterified with methanol catalyzed by sodium methoxide.

Transesterification is applied to convert glycerides to methyl esters and glycerine is produced as a bottom byproduct. VitE in the oil product from esterification and transesterification was monitored and found to be 3,915 and 3,375 ppm, respectively. It is lower than 4,500 ppm in the previous methanol extract. Esterification needs methanol as the reactant, and unreacted methanol can extract some VitE to the upper layer. Transesterification medium is base, causing a fraction of VitE which has hydroxyl group to be present in the ionized form and to be lost to the bottom product. To sacrifice VitE by these reactions, it will be boost up in the next evaporation step.

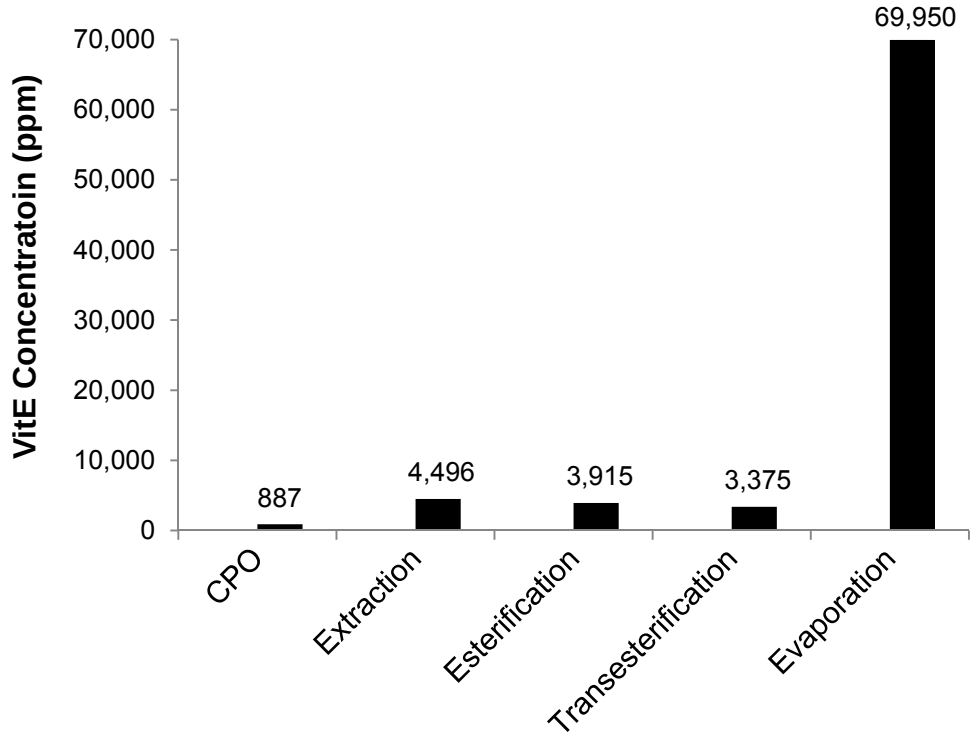

Figure 6: VitE concentration in the presented bench scale process

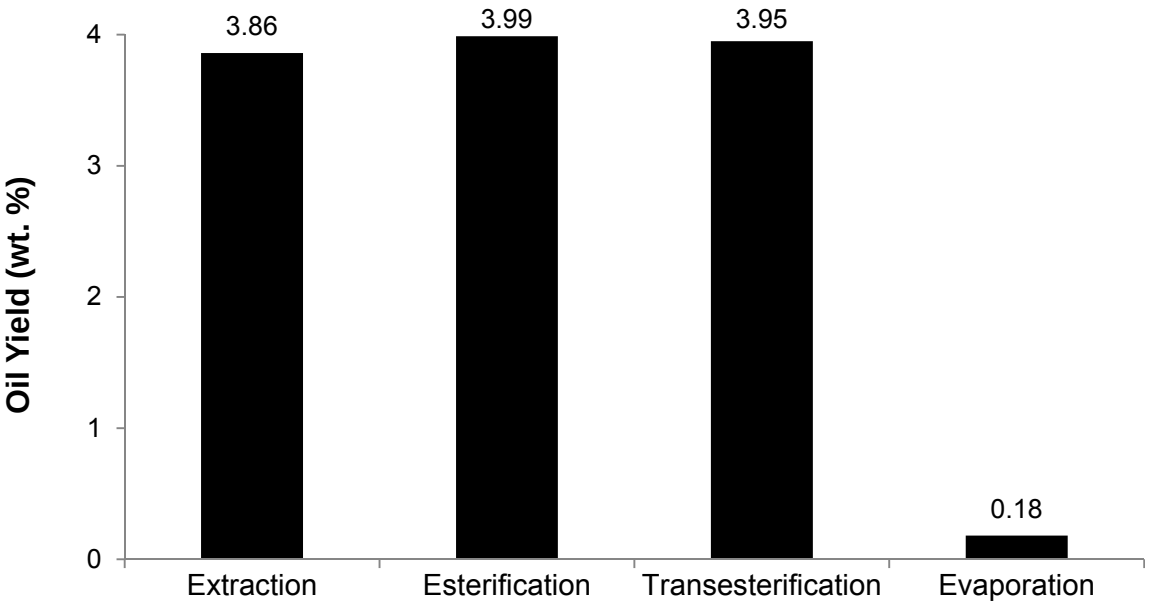

Figure 7: Concentrated VitE oil yield from each process

3.3 Methyl ester evaporation and VitE concentration

Methyl esters containing VitE from previous step was evaporated under high vacuum using the Kugelrohr apparatus leaving a concentrated VitE oil residue. VitE content in the unevaporated oil (residue) was determined to be 69,950 ppm. This residue is shown in Figure 5 along with CPO after methanol extraction. Concentration of VitE and oil yield from each process are depicted in Figure 6 and 7, respectively. Starting from 1 kg of CPO with 887 ppm of VitE, this bench scale process could produce 1.82 g of residue oil which contains 7.9 wt.% of VitE. This concentration is approximately 80 times higher than that found in CPO.
Yield of VitE in the residue is calculated to be 14 wt.% while 80 wt.% of VitE remains in CPO after the first methanol extraction.

4. Conclusions

VitE separation from CPO in a bench scale process presented in this work provides an oil containing 7.9 wt.% VitE. The concentrated VitE oil yield was 0.18 wt.% with respect to CPO. 80 wt.% of VitE remaining in CPO could preserve the antioxidant activity for further process to produce edible oils and biodiesel. In addition, a decrease of 2 wt.% of free fatty acids in CPO for one step methanol extraction will ease the later processing of CPO, especially a large reduction on the load of deodorizer for free fatty acids removal. Separation of methanol residue in CPO could be simply performed by water washing. It may be noted that this concentrated VitE oil contains sterols, another valuable semipolar phytonutrient.

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