Research article

The Effect of Heating on Vitamin E Decomposition in Edible Palm Oil

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Abstract Currently, palm oil is popular in consumption, and vitamin E in palm oil has been used to indicate the quality. In addition to complexity processing of crude palm oil to edible oil that loses vitamin E, the use of high-heat for cooking, can cause vitamin decay. Therefore, this research aims to study the limit of how much heat affects on vitamin E decomposition; and this result will bring useful information to apply in cooking. This investigation was performed with oil having vitamin E concentration at 80 mg l^{-1} to be heated. Samples were collected when the oil was heated and started smoking and samples were collected every 15 minutes. Then, the samples were analyzed for the vitamin E through the extraction process of a solid phase extraction (SPE), which uses C18 as solid sorbent and dichloromethane as eluent Gas chromatography equipped with flame ionization detector (GC- FID) was operated under the temperature programming mode for quantitative analysis. The results show that the percentage of vitamin E degradation would continuously increase in temperatures ranging from 210 ℃ to 278 ℃ and this degradation rate still constant after a half of hour expansion for oil heating at 278 ℃. So, it's concluded that longer time used in the heating process could affect less to the vitamin E decomposition than increasing the temperature.

Keywords edible palm oil, vitamin E decomposition, SPE, GC - FID

INTRODUCTION

Vitamin E under the term of α - tocopherol is a powerful biological antioxidant. The major biological role of vitamin E is to protect unsaturated fatty acids contained in vegetable oils from oxidation by free radicals (Gordon and Kourimska, 1995). It's believed to reduce the risk of cardiovascular diseases and of certain types of cancer. The main sources of vitamin E in the human diet are vegetable fats and oils. Due to that palm oil contains more saturated fatty acids (up to 50%) and is rich in vitamin E, it can be resistant to the high heat and is resistant to oxidation (Burton and Traber,1990). So for this reason, palm oil is currently the most consumed edible oil in the world. The refining process of edible palm oil industry affects the breakdown of vitamins, so industrial palm oil has added vitamin E before bringing it to the market (Clegg, 1973). Although, vitamin E is relatively resistant to heat and insoluble in water, the high heat cooking such as frying oil can cause a loss of vitamin E. In addition the cooking time and cooking method affect loss vitamins E as well.

Sample treatment for vitamin E analysis often includes saponification, of an isolated lipid fraction. Saponification prior to the extraction is classically performed by heating with potassium hydroxide in ethanol or methanol and analyzed directly. Solid phase extraction (SPE) is a well established method for the concentration and extraction of matrices in various samples. In addition,

the use of SPE has also proven to be an efficient technique for simplifying sample clean- up (Bonvehi, Coll and Rius, 2000).

The tocopherol content of oil and fat can be determined by a wide range of analytical techniques such as spectrophotometer, chromatographic techniques such as supercritical fluid chromatography (Manninen, Laakso and Kallio,1995), gas chromatography (Lechner, Reiter and Lorbeer,1999; Demirkaya and Kadioglu,2007), high performance liquid chromatography (Rupe´rez and et. al., 2001; Schwartza and et. al., 2008). Gas chromatography with flame ionization detection (GC-FID) has been used at a lesser extension to determine vitamin E compare with high performance liquid chromatography. The GC analysis of tocopherols normally implies warm saponification prior to the chromatographic injection (Rupe´rez and et. al., 2001).

This research aims to study the limit of how much heat affects vitamin E decomposition and this result will bring useful information to apply in cooking.

OBJECTIVES

The objectives of this study are;
1. To determine Vitamin E from heated oil using SPE and GC-FID
2. To identify of how much temperature affects vitamin E decay

METHODOLOGY

Reagents and Standard Solutions

Vitamin E (DL- α – tocopherol), n - hexane, methanol and dichloromethane were purchased from Merck (Darmstadt, Germany). Standard stock solution of vitamin E was prepared in hexane to a concentration 500 mg l^{-1} and stored in the dark under refrigeration. Working standard solutions at 30, 40, 50, 80, 100 and 120 mg l^{-1} concentrations were prepared freshly by diluting with hexane. Commercially edible palm oil sample was bought from the local market.

Sample Preparations

Due to the complex composition of edible oil, it was necessary to eliminate large molecular compounds via saponification method for investigation of the performance of analysis method. For saponification, 21.25 g of edible palm oil was placed in an Erlenmeyer flask to which the mixture of 15.5 g l^{-1} 800 ml ascorbic acid solution and 10% w/v potassium hydroxide in 200 ml ethanol were added. After heating the mixture solution to 70 °C in oven for 30 min, the saponification solution was allowed to cool down and 25 g NaCl was added to accelerate phase separation. The upper layer was extracted repeatedly with n–hexane and an aliquot of n–hexane was spiked of 70 mg l^{-1} vitamin E before analysis method that included of SPE followed by GC–FID.

For the study of heat affect to vitamin E decomposition, 0.3333 g. of vitamin E was directly added to 500 ml of edible palm oil (approximately 80 mg l^{-1} concentration). The oil sample was heated until start to smoke and immediately collected 1.2 ml of oil and then diluted to 10 ml. with hexane. Thereafter the sampling was done in the same manner by continuing to keep every 15 minutes until the oil temperature remains constant and the sampling continued for another 3 times then each sampling oil was analyzed method for vitamin E determination.

Instrumentation and Analytical Conditions

Chromatographic analysis was carried out on Varian CP 3800 gas chromatography system equipped with a flame ionization detector. ZB - 5 capillary column (30 m x 0.25 mm I.D. x 0.25 µm. film thickness, USA) was used. H_2 gas was used as carrier gas at a flow–rate of 4 ml min^{-1} and splitless injection was used. The injector and detector temperatures were 255 °C and 300 °C. The oven temperature set at 200 °C held for 1 min then increase to 300 °C at rate 25 °C min^{-1} and held

at 300 °C for 5 min. Quantitative analysis of vitamin E in edible palm oil was performed using standard addition technique, from the standard curve of peak area vs. concentration.

In all SPE experiments, C18 cartridges were conditioned with 6 ml of distilled water, methanol, isopropanol and dichloromethane, respectively. The amount of 1 ml of edible oil solution with 70 mg l^{-1} of vitamin E concentration was twice loaded to SPE cartridge (1 ml per each) and soaking for about 5 minutes and then letting it flow out under the atmospheric flow rate. After loading oil sample, the cartridge was dried under vacuum, to elute vitamin E from cartridge with the same manner as in loading step except soaking time was performed at 30 min. Then this solution was injected to GC – FID for analysis.

RESULTS AND DISCUSSION

Validation of the Analysis Method

For GC - FID analysis, the chromatogram show the retention time of vitamin E in standard solution at 5.735 min. The linearity of the peak area response versus concentration was obtained in the concentration range between 30 to 120 mg l^{-1} (r^2 = 0.995). Precision was determined both within-day and between-day. Repeatability or within - day precision was tested by 7 times analysis of 100mg l^{-1} standard vitamin E solution. The intermediate precision (between – day) was set 3 times analysis of the same concentration as above. The repeatability express as relative standard deviation (% RSD) was 3.11% and the intermediate precision (% RSD) was 2.84%. The limit of detection (LOD) was determined from the intercept of the regression line of the calibration graph using a 30 to 120 mg l^{-1} concentration range. The LOD was set equal to three times the standard deviation of the area at the intercept and illustrated approximately 8.01 mg l^{-1}.

For the evaluation of the extraction recovery, palm oil was spiked with 70 mg l^{-1} vitamin E. The recovery was calculated by comparing the quantitative results obtained by SPE - GC analysis and actual spiked concentration. The percentage recovery was found between 80.1- 86.9% with relative deviations 3.1 (n=5). The results of recovery and validation values are shown in Table 1. Quantification of Vitamin E in edible palm oil was determined via standard addition method and the vitamin E content found in oil was 25.36 mg l^{-1}.

Table 1 Linearity, precision (%RSD), LOD of GC – FID analysis and %recovery of the analysis SPE – GC-FID analysis

GC – FID analysis				SPE – GC-FID analysis	
Concentration range of Linearity(mg l^{-1})	% RSD Within – day (n=7)	% RSD Between – day (n =3)	LOD (mg l^{-1})	% Recovery	% RSD (n= 5)
30 - 120	3.11	2.84	8.01	80.1 – 86.9	3.1

Heat Affecting Decomposition of Vitamin E in Edible Palm Oil

The results of vitamin E decomposition on heating oil was found that the first sampling of oil sample start at 210 ºC. Vitamin E was reduced approximately 6.38% compare with the amount of vitamin E before heated. The heating oil sample still collected continuity every 15 minutes until reach to constant temperature (278 ºC). At this temperature, the sample was further collected for 3 times (15 minutes/each). The decay rate of vitamin E increased rapidly up to 60.70% at the highest temperature (278 ºC) and the decay rate of vitamin E did not significantly increase after expansion of heated time (Table 2). Fig. 1 shows the vitamin E concentration at various heating temperature and sampling time. This result illustrated that oil heated to 278 ºC is not sufficient to completely decompose vitamin E. From the previous research, thermal decomposition of vitamin E in edible oil was completely at about 773 K (500 ºC) (Arora, Bagoria, and Kumar, 2010). It can be noticed that the heating temperature is a more significant factor than the heating time. Generally, the most of food cooking needs high heat, which influences the breakdown of vitamin E during the cooking

process.

Table 2 Heating time, heating temperature and Vitamin E decay after heated

Sampling number and time(min)	Temperature (°C)	Vitamin E concentration (mg l^{-1})	Concentration of vitamin E decay (mg l^{-1})	% Vitamin E decay (mg l^{-1})
1 (Spiked solution)	30	79.9	0	0
2 (0 min)	215	74.8	5.1	6.4
3(15 min)	255	64.1	15.8	19.8
4 (30 min)	261	46.7	33.2	41.6
5 (45 min)	278	31.4	48.5	60.7
6 (60 min)	278	30.9	49	61.3
7 (75 min)	278	30.3	49.4	61.8

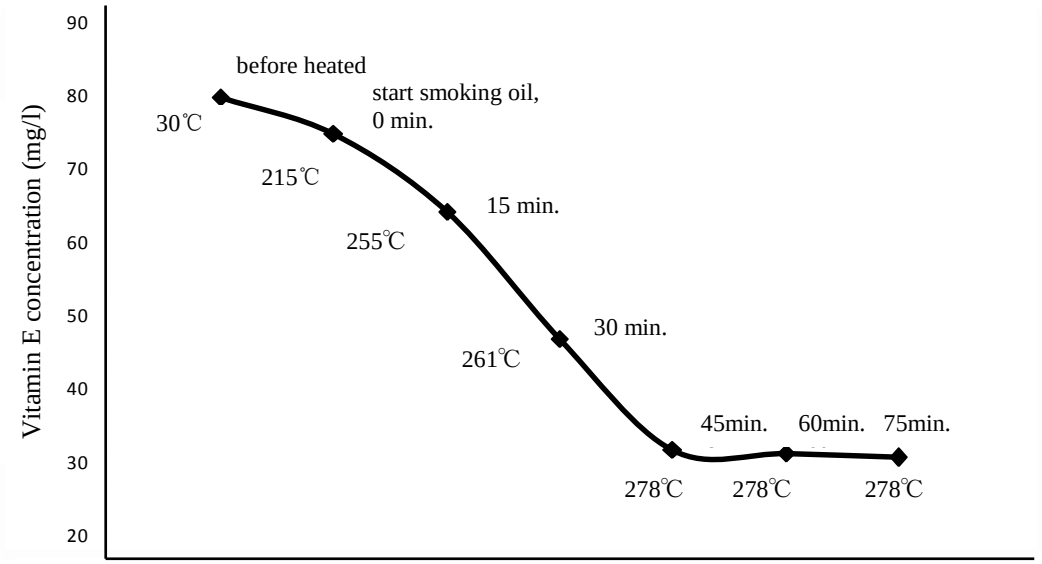

Fig. 1 Vitamin E concentration at various heating temperature and sampling time

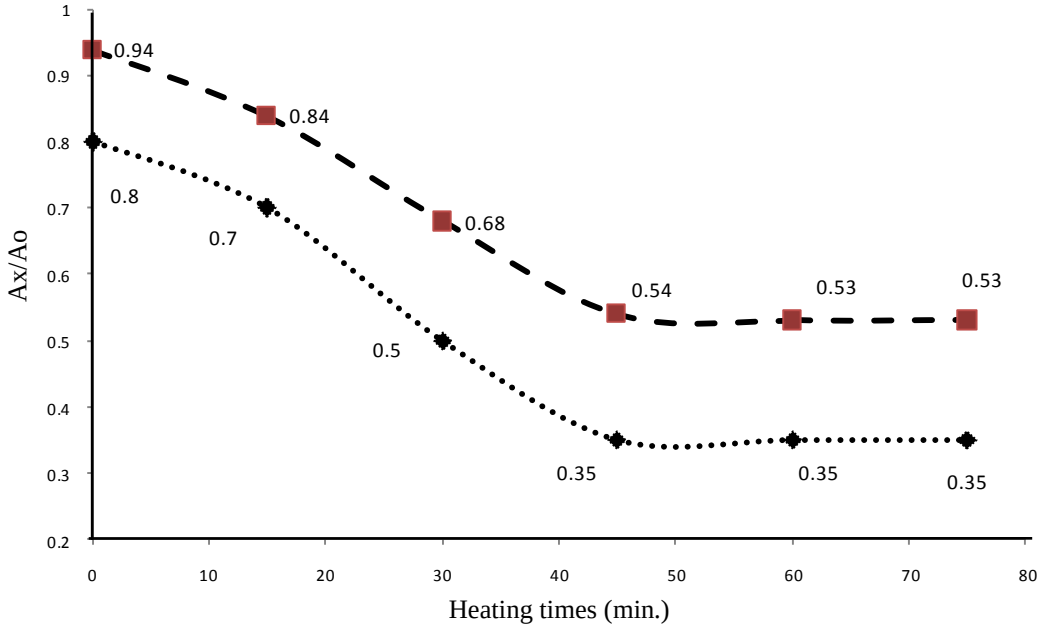

Fig. 2 Comparison of the ratio of the peak area of vitamin E in oil after heated (Ax) to a peak area of vitamin E in oil before heated (Ao) of oils with and without vitamin E added

This work was created in the trial to confirm that vitamin E that is already present in edible palm oil has degraded as well by heating palm oil samples without added vitamin E. The results were expressed by using the ratio of the peak area of vitamin E in oil after heated (Ax) to a peak area of vitamin E in oil before heated (Ao) of both oils (with and without vitamin E added). Those of experiments were shown in Fig. 2 and it can be noticed that vitamin E decay rate of oil with and without vitamin E added were similar.

CONCLUSION

In conclusion, the analysis method to determine vitamin E in edible palm oil was completely validated by using linearity, precision, limit of detection and accuracy in term of percentage of recovery. Vitamin E in edible palm oil can be decomposed during high heat cooking process and the time used to heat oil was less affect to vitamin E decomposition than temperature increasing.

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