INFLUENCE OF REFINING OF VEGETABLE OILS ON MINOR COMPONENTS

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ABSTRACT

Refining of crude vegetable oils involving degumming, bleaching and deodorization has a high influence on the content of functional minor components. In this study, the difference of chemical versus physical refining will be studied. Especially the reduction of the tocopherol content in refined oil is mainly due to oxidation of the tocopherol. Also the content of sterols in free and esterified form is changing during the various refining procedures. An alternative two-step deodorization is described.

Keywords: tocopherols, phytosterols, refining, deodorization, vegetable oil.

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INTRODUCTION

The traditional quality characteristics for refined vegetable oils focus on a bland taste, a light colour and a good oxidative stability. Currently, an increased interest is observed for functional minor components naturally present in oils and fats performing a beneficial nutritional effect. In this study, organic chemical aspects associated to the influence of processing on tocopherols and phytosterols are presented.

During the industrial production of vegetable oils and fats by crushing or solvent extraction, several non-glyceride constituents are incorporated into triglycerides. In order to become suitable for human consumption, crude vegetable oils have to be refined, aiming at removal of unwanted components such as partial acylglycerides, free fatty acids, waxes, metals, colouring pigments, odorous components and artefacts (Verhé *et al.*, 2000). Two alternative processes exist, the chemical and physical refining (*Figure 1*).

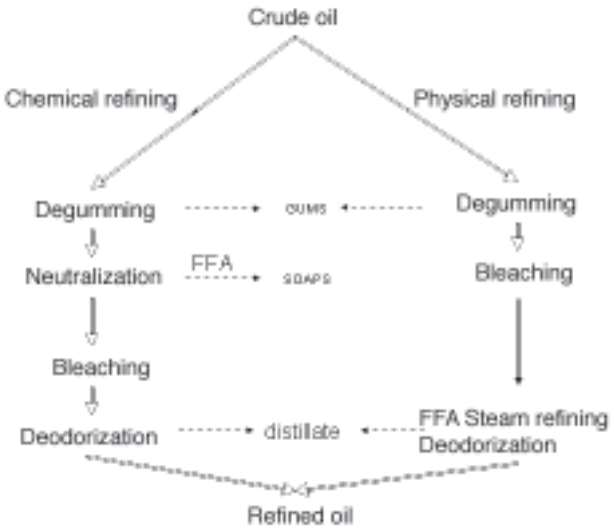

Figure 1. Schematic view of the chemical and physical refining process.

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The processes differ in the procedure to remove free fatty acids, which is performed in the chemical refining by chemical neutralization and in the physical refining by distillation. The first step in the refining process is a degumming designed to remove phospholipids by washing with water and/or acid treatment. Upon chemical refining, a weak alkali solution is added in order to neutralize free fatty acids which are washed out of the oils as soaps. This step causes a number of environmental problems. In the bleaching process using activated bleaching earth pigments, residual phospholipids, soaps and metals are removed. The last step is a deodorization which is a steam vacuum distillation, which aims the removal of odoriferous components and free fatty acids. Free fatty acids and valuable minor components such as squalene, tocopherols and phytosterols are distilled during this distillation and recovered in the deodorizer distillate. Especially the loss of tocopherols and sterols during the refining has a negative influence on the nutritional quality of the refined oil and in this study, the influence of the various process conditions on the content of tocopherols and phytosterols will be studied.

INFLUENCE OF PROCESSING ON TOCOPHEROLS

During deodorization, all tocopherols present in the bleached oil will be partitioned either in the deodorized oil or in the deodorizer distillate. A significant loss in the tocopherol mass balance in the range of 25%-35% was observed originating from technological and/or chemical origin (*Table 1*).

TABLE 1. LOSS IN TOCOPHEROL AND FREE FATTY ACIDS DURING DEODORIZATION *

Mass	0.33%
α-Tocopherol	32.9%
γ-Tocopherol	27.3%
δ-Tocopherol	31.4%
Total tocopherol	28.3%
Free fatty acids	1.5%

Note: * Physical refining of corn oil: 240°C, 2 mbar, 1.5 % steam, 80 min.

The loss of tocopherols can be caused either by a thermal breakdown at temperatures higher than 240°C, by oxidation reaction or by chemical reaction such as the formation of tocopheryl esters (Verleyen *et al.,* 2001b). Extensive analysis of vegetable oils by HPLC and comparison with synthesized tocopheryl esters did not show any adsorption in the elution region of tocopheryl esters, indicating that esters of tocopherols with fatty acids are not present in crude oils (Verleyen *et al.,* 2001c). Therefore the stability of tocopherols during deodorization has been studied under various process conditions. The presence of oxidation products has no influence on the loss of tocopherols during deodorization as during two successive deodorization steps an identical loss of tocopherols has been observed.

Experiments using spiked triolein with 2000 ppm of α-tocopherol showed that the addition of tert-butylhydroquinone (TBHQ) as a strong antioxidant reduces the loss of tocopherols with more than 50% in comparison with the reference procedure. α-Tocopherol (2000 ppm) was dissolved in triolein and heated to 254°C, 5-6 mbar, for 80 min, with no steam injection. The tocopherol loss was for the reference 9%, for the sample with 1500 ppm TBHQ, 3%. The more active TBHQ will compete with tocopherols to scavenge radicals and consequently the tocopherol loss in the mass balance is reduced as more natural tocopherols stay in the oil or in the distillate (Verlayen *et al*., 2002d; 2003a).

In vegetable oils, the addition of TBHQ from 0 to 1500 ppm establishes a gradual reduction in tocopherol loss from 26.7% to 17.6% while the concentration of tocopherols in the distillate rises from 1.85% to 2.35%.

Performing deodorization with nitrogen as stripping agent showed an important reduction in the tocopherol loss (Verleyen *et al.,* 2002d). In the model study with triolein no reduction of α-tocopherol was observed while using corn oil a reduction of 30%-50% was observed. The highest reduction was detected at severe deodorization conditions (260°C, 3 mbar) (Verleyen *et al.,* 2002d). These experiments show that tocopherols are thermally stable compounds and probably the loss of tocopherols is due to oxidation reactions (*Figure 2*).

In order to prove the oxidation reaction of tocopherols, a number of oxidation products of tocopherols have been synthesized and identified by NMR/MS (Verleyen *et al.,* 2001b) (*Figure 3*). During these experiments, the following tocopherol oxidation products have been separated by preparative HPLC and identified by NMR/MS: α-tocopherol dimer quinone, 4α, 5-epoxy-tocopherolquinone, 7, 8-epoxy tocopherol quinone, tocopherol dimer quinone, tocopherol spirotrimer and ditocopherol ethers (Verleyen *et al.,* 2001b).

In a model experiment using 3500 ppm α-tocopherol in triolein and heating at 240°C for 90 min at a reduced pressure of 6-7 mbar 4α, 5-epoxy-tocopherolquinone, 7, 8-epoxy tocopherolquinone and α-tocopherol quinone were identified as oxidation products supporting that the tocopherol loss during deodorization is mainly due to oxidative degradation (Verleyen *et al.,* 2002d).

At the high temperature of frying, it is of primary interest to know the evolution of α-tocopherol degradation in relation to the fatty acid oxidation

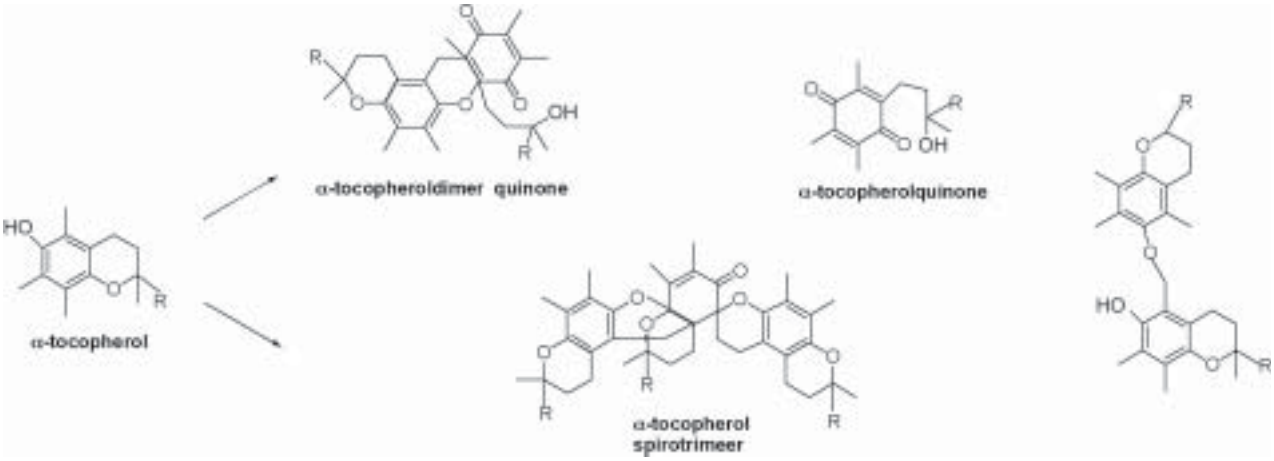


Figure 2. Oxidation products of α-tocopherols.

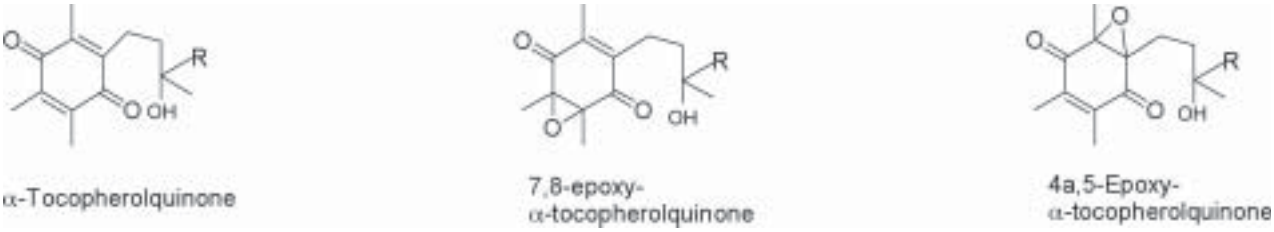


Figure 3. Isolated oxidation products of tocopherols.

status. In a model system of triolein and tripalmitin the kinetics of α-tocopherol degradation and the formation of oxidation products and polymers was studied as a function of heating time, the heating temperature and the composition of the triacylglycerol matrix (Verleyen *et al.*, 2001b; 2002d) (*Figures 4, 5* and *6*).

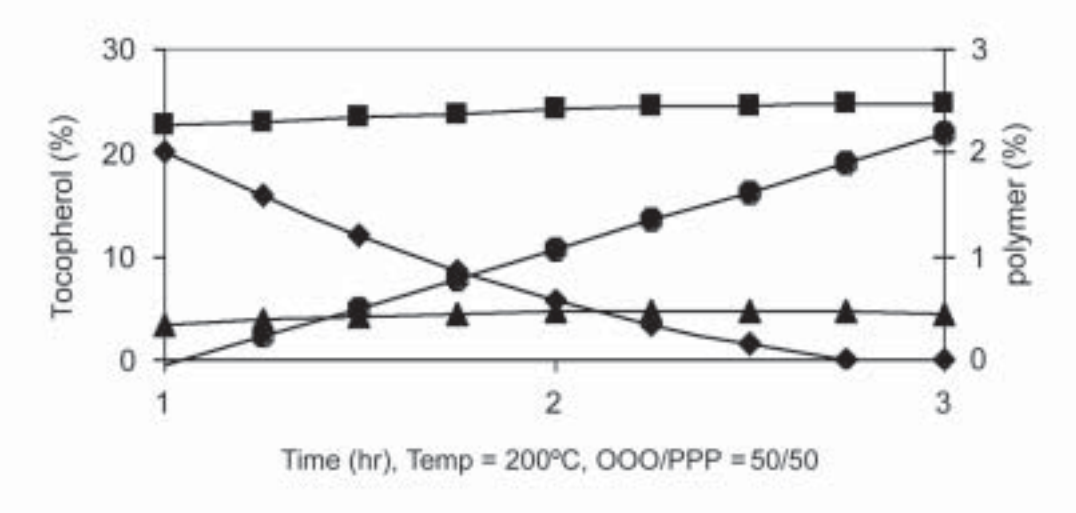


Figure 4. Influence of time on evolution of α-tocopherol (◆), epoxy-α-tocopherol quinone (■) and α-tocopherol quinone (Δ) concentration relative to initial α-tocopherol concentration of 1000 ppm, total triacylglycerol polymer content (•).

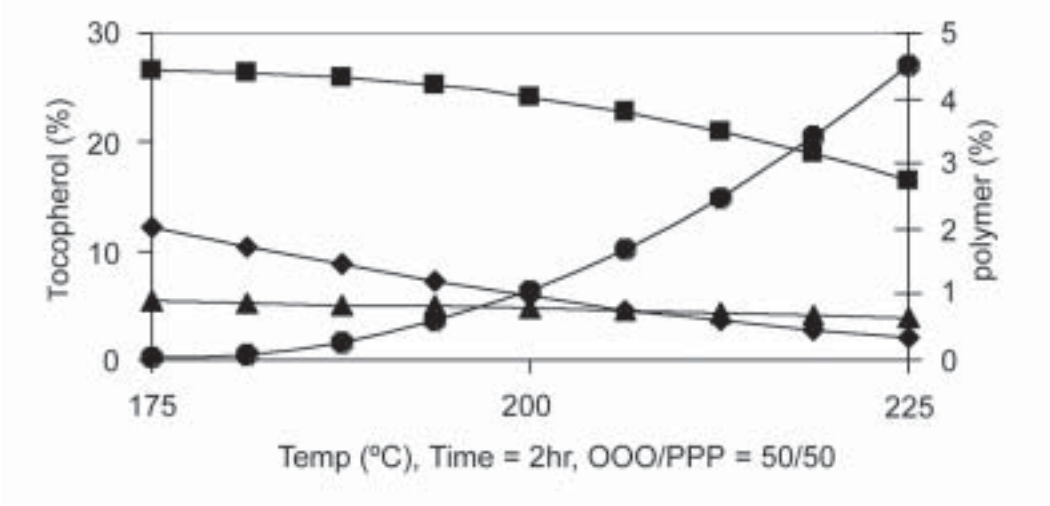


Figure 5. Influence of temperature on evolution of α-tocopherol (◆), epoxy-α-tocopherol quinone (■) and α-tocopherol quinone (Δ) concentration relative to initial α-tocopherol concentration of 1000 ppm, total triacylglycerol polymer content (•).

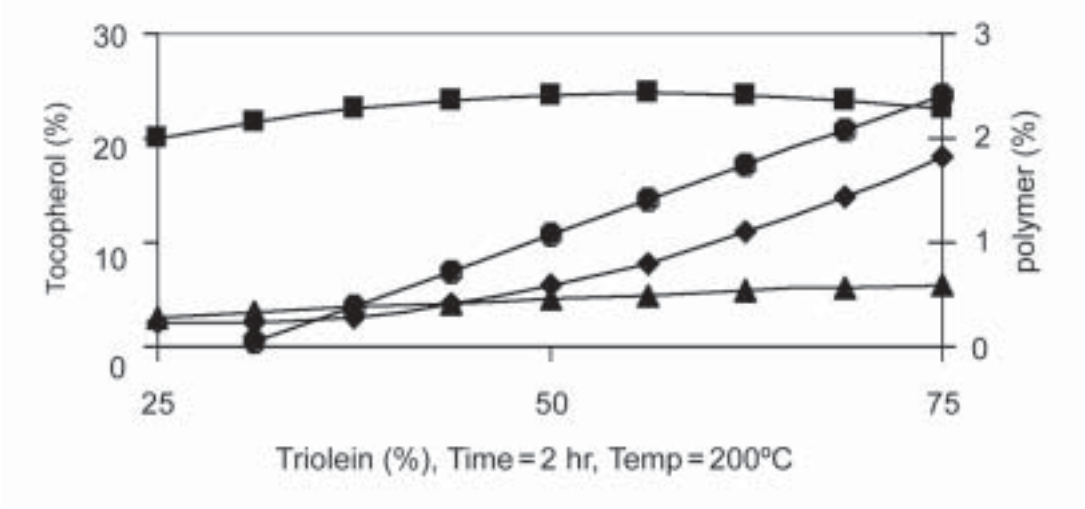


Figure 6. Influence of time, temperature and triacylglycerol composition on evolution of α-tocopherol (◆), epoxy-α-tocopherol quinone (■) and α-tocopherol quinone (△) concentration relative to initial α-tocopherol concentration of 1000 ppm, total triacylglycerol polymer content (•).

The temperature of heating has a drastic influence on the degradation of α-tocopherol. After heating a mixture of 50% tripalmitin/triolein at 200°C, the α-tocopherol content is already decreased to 20% whereas after 3 hr no residual α-tocopherol is present. Little influence on the concentration of the tocopherol quinones and epoxy tocopherol quinones is observed indicating an equilibrium of formation of new epoxyquinones and their further degradation to unknown oxidation products.

The influence of temperature was shown in experiments by heating for 2 hr from 175°C to 2 hr at 225°C resulting in a residual α-tocopherol content of 12.1% and 2% respectively. By increasing the temperature above 175°C, a gradual decrease in the epoxy quinones is observed while the level of the α-tocopherol quinone seems not to be affected by temperature. This indicates degradation of the epoxy quinones to unidentified oxidation products. At temperatures above 200°C, polymerization increased rapidly. By increasing triacylglycerol unsaturation, the rate of α-tocopherol oxidation decreased although the triacylpolymerization increased. In 100% triolein, the residual α-tocopherol concentration is 44.1% while in 25% triolein/25% tripalmitin, only 2.2% of α-tocopherol is found.

It can be concluded that α-tocopherol oxidation decreased by competitive oxidation of unsaturated triacylglycerol and was significantly increased by increased temperature.These results were confirmed by experiments in which α-tocopherol was heated at 180°C and 240°C in palm oil, high oleic sunflower oil, sunflower oil and flaxseed oil (*Figure 7*). The difference in tocopherol degradation as affected by

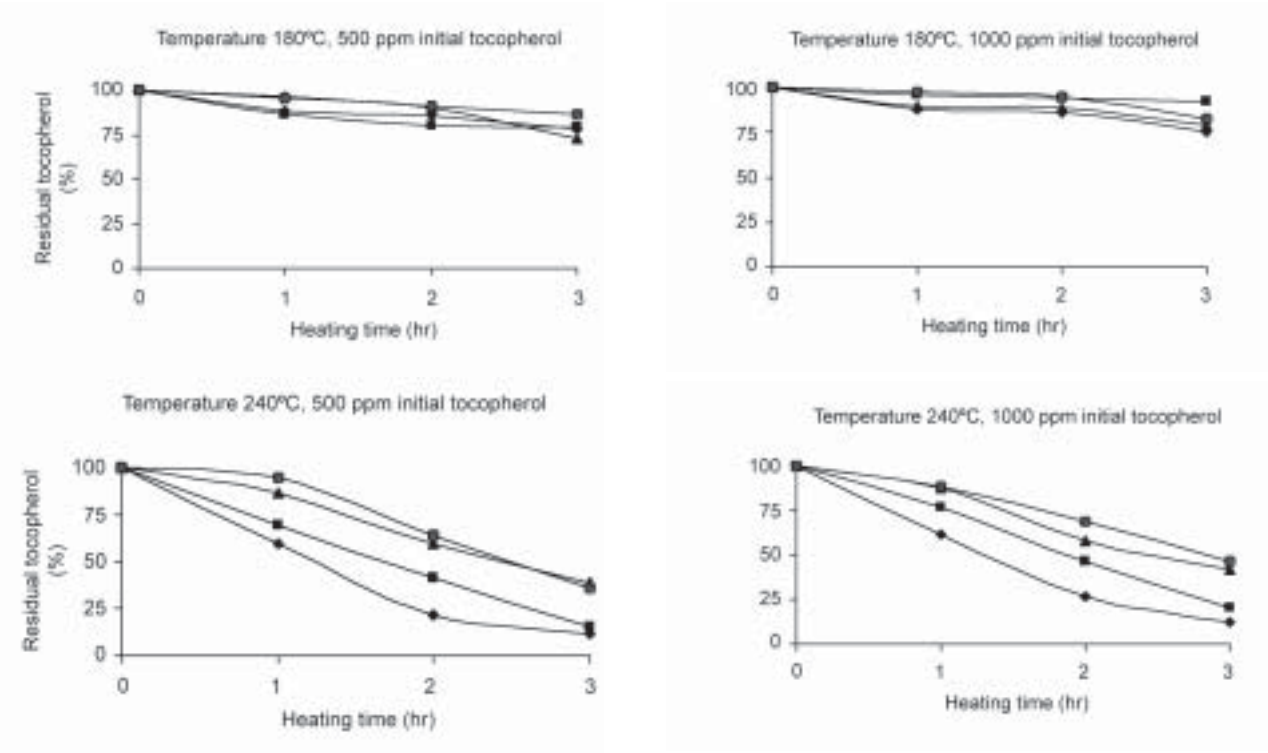


Figure 7. Degradation of α-tocopherol, at different levels, during 3 hr heating of purified triacylglycerols from four vegetable oils (• flaxseed, △ sunflower, ■ high oleic sunflower, ◆ palm).

triacylglycerol unsaturation is evident at 240°C but not at 180°C.

It can be concluded that the rate of tocopherol oxidation producing tocopherol quinones and epoxy quinones at high temperatures is reduced with the increase of the degree of unsaturation in a fatty acyl matrix.

INFLUENCE OF REFINING ON PHYTOSTEROLS

The conventional method for sterol analysis involves a saponification of the triacylglycerols and steryl esters. However, through saponification important information on the phytosterol fraction is lost, especially concerning the ratio free and esterified sterols. A new method has been developed for the analysis of free and esterified sterols based on a separation on polarity by silica gel chromatography followed by saponification and GC quantification (Verleyen *et al.*, 2002e).

A large variation in the content and distribution of the phytosterol fraction between different vegetable oils can be observed (*Figure 8*). Corn and rapeseed oil are extremely rich in sterols (800 mg/100 g oil) while palm and coconut oil are low (60-100 mg/100 g oil) (*Figure 9*).

Acid hydrolysis of steryl esters may occur upon bleaching with an acid activated bleaching earth. The slight reduction of the total sterol content is due to the formation of steradienes and disteryl ethers.

A gradual reduction in the total sterol content is observed at increasing deodorization temperature due to distillation and steradiene formation. Increasing the temperature from 220°C to 260°C resulted in a gradual reduction of the total sterol recovery from 90.4% to 67.7% in physical refining and from 93% to 62.7% in chemical refining. However in physical refining, an increase of 40% in the steryl ester fraction is observed due to an esterification reaction, promoted by high temperature between a sterol and a fatty acid. Due to the absence of free fatty acids in the chemical refining their esterification did not occur (Verleyen *et al.*, 2001a). The influence of refining on free and esterified sterols has been studied and the results are summarized in *Figures 10, 11* and *12* (Verleyen *et al.*, 2002a).

Phytosterols are progressively lost during refining while continuously altering the ratio of free and esterified sterols. During chemical neutralization, the free sterol content is significantly reduced especially upon addition of weak caustic solution due to the loss in the soapstock.

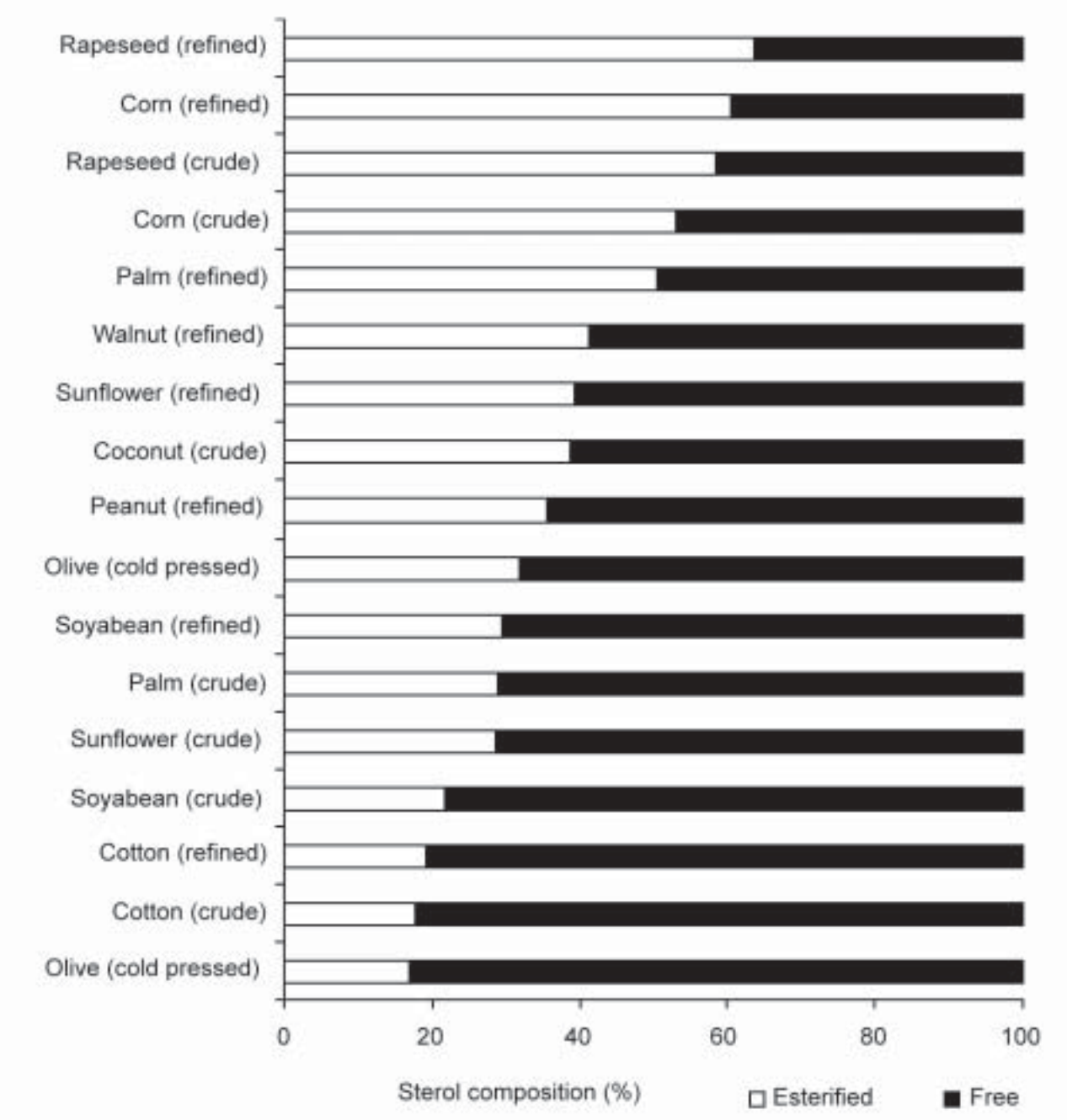


Figure 8. Schematic overview of the esterified and free sterol content (%) for several vegetable oils.

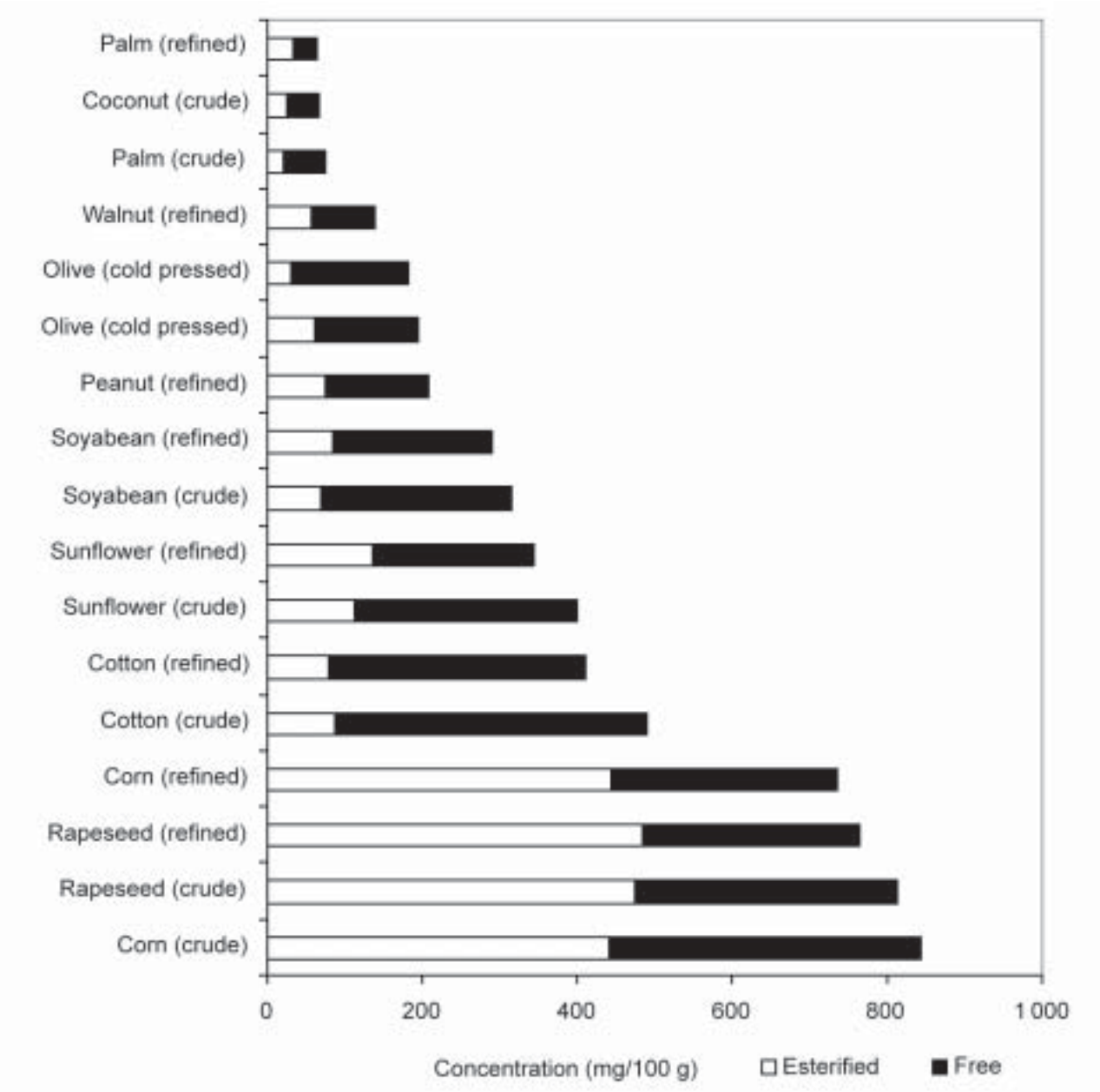


Figure 9. Schematic overview of the free and esterified sterol content (mg/100 g) for several vegetable oils.

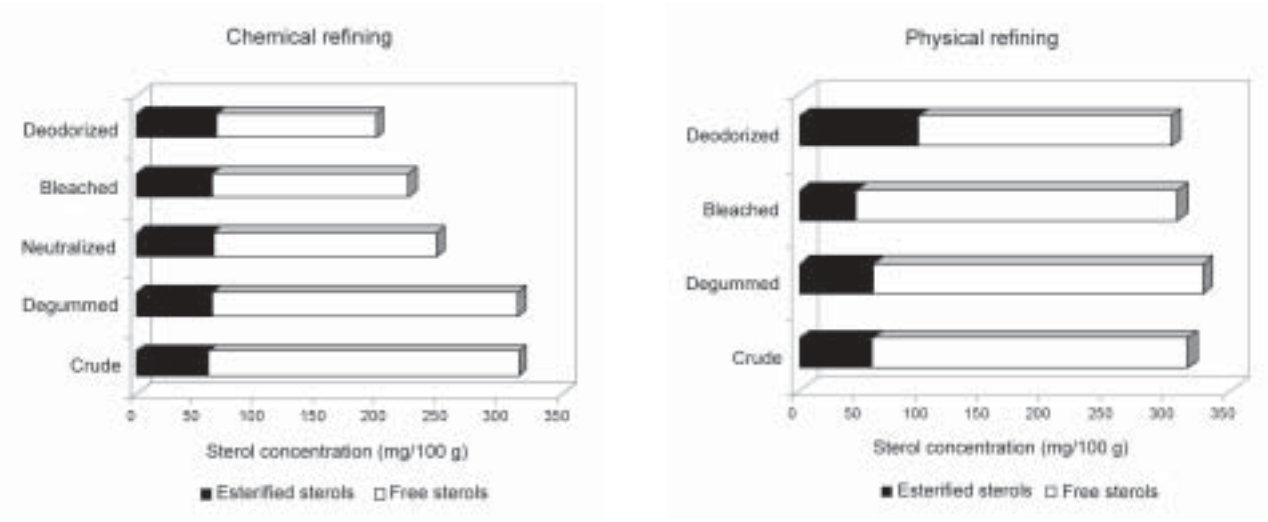


Figure 10a. Schematic overview of the free and esterified phytosterol distribution during chemical and physical refining of soyabean oil.

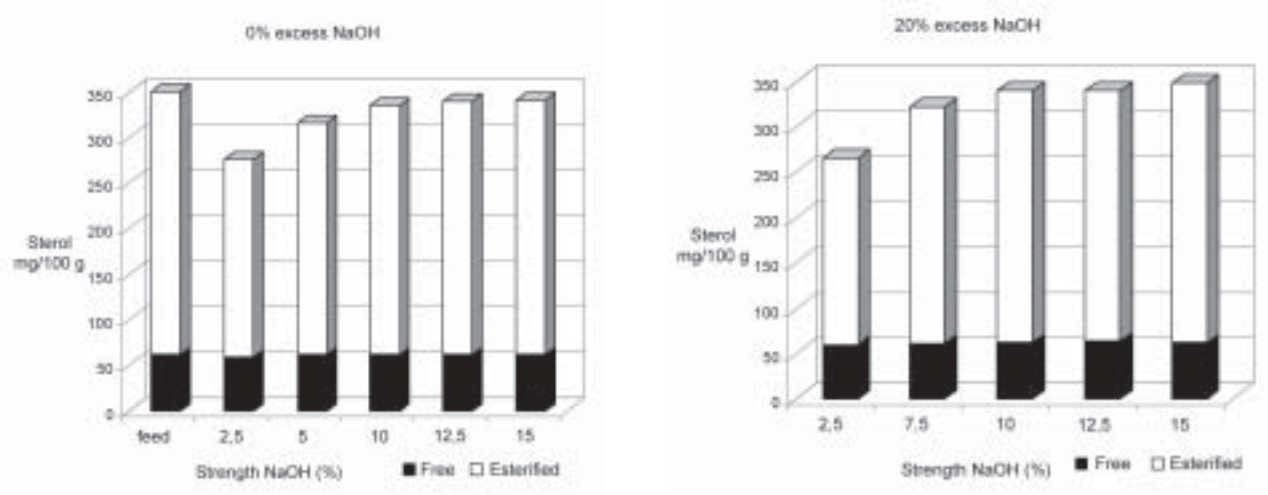


Figure 10b. Schematic overview of free and esterified phytosterol distribution after chemical neutralization in function of the NaOH strength.

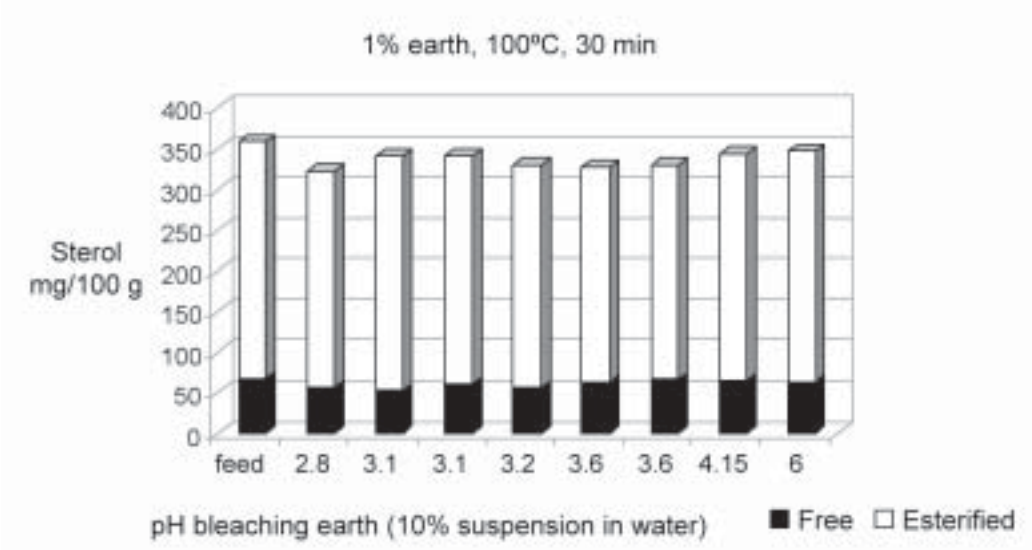


Figure 11. Schematic overview of free and esterified phytosterol distribution of soyabean oil upon bleaching with different types of bleaching earth.

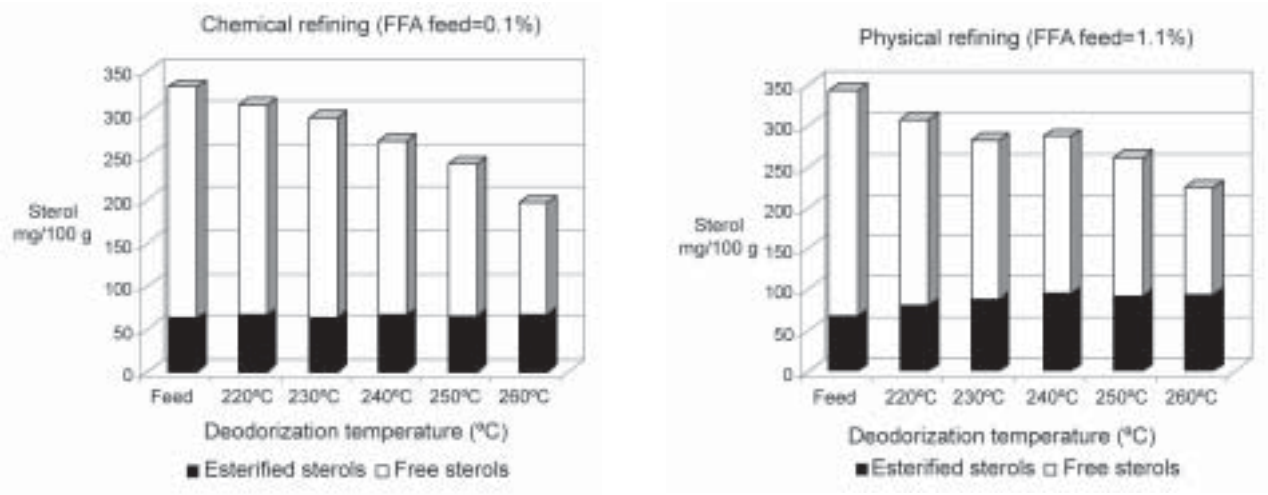


Figure 12. Schematic overview of the free and esterified phytosterol distribution of soyabean oil upon deodorization at different temperatures.

Figure 13 shows the sterol degradation products formed during refining. Steradiene formation is mainly influenced during the bleaching step by the bleaching temperature and the degree of acid activation of the bleaching earth (*Figure 14*), while during the deodorization, the degree of sterol dehydration is mainly influenced by deodorization temperature giving rise to a concentration of the steradienes in the distillate (Verleyen *et al.*, 2002a,b) (*Figure 15*).

GC-analysis of 3,5-stigmastadiene was carried out for several vegetable oils. In crude palm oil, bleached red palm olein and refined palm oil respectively 0.80, 3.07 and 5.96 ppm 3,5-stigmastadiene was detected.

These results prove that detection of steradienes is an excellent method for the level of refining of oils and fats.

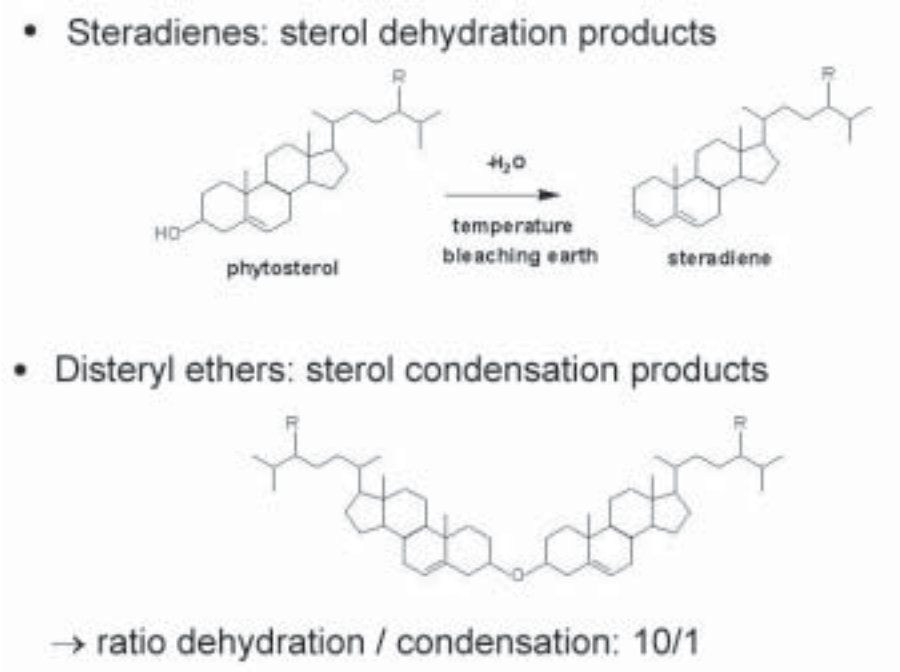


Figure 13. Reaction products of sterols during refining.

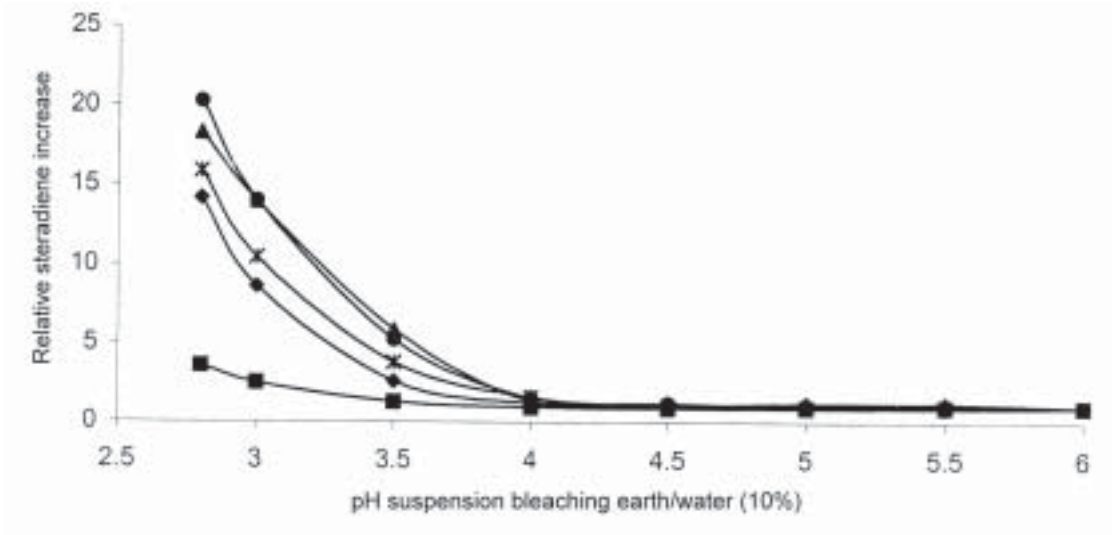
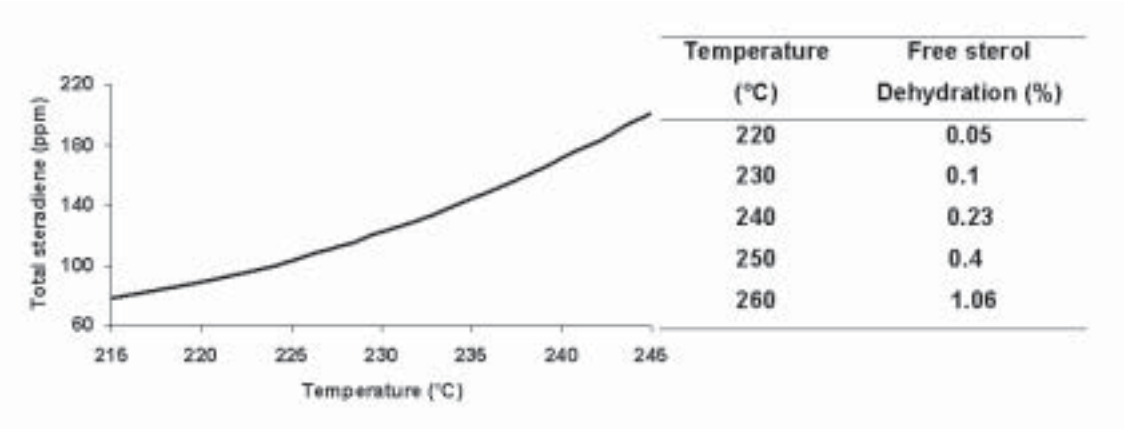


Figure 14. Influence of the acidity of bleaching earth on the formation of steradienes.



Temperature (°C)	Free sterol Dehydration (%)
220	0.05
230	0.1
240	0.23
250	0.4
260	1.06

Figure 15. Influence of temparature on steradiene formation during deodorization.

IMPROVED PHYSICAL DEODORIZATION TECHNOLOGY

The composition of the deodorizer distillate depends on a number of factors including the type of oil, mode of refining, refining conditions *etc*. The relative volatility of vegetable oil components – fatty acids, squalene, tocopherol, sterol and triacylglycerides is respectively 2.5; 5; 1; 0.6; 0.04. The economic value of the deodorizer distillate is completely determined by the content in tocopherols and sterols.

In batch deodorization experiments (temperature 220°C-260°C), physical refined oils have a higher retention of unsaponifiables in the oil compared to chemical refining. A sterol retention varying between 68%-90% in physical and 79%-87% in chemical refining is observed while a tocopherol retention between 23.5%-92.3% in physical and 20.6%-73.2% in chemical refining is found. This higher retention is attributed to the lower vapour pressure of these components due to the abundance of free fatty acids during deodorization.

Deodorizer distillates obtained from chemical refining are rich in tocopherols (9.2%-15%) and sterols (9.0%-17.6%) and contain little free fatty acids (10%-24.5%). Distillates from physical refining contain mainly fatty acids (76.2%-83.6%) and consequently little tocopherols (1.4%-4.3%) and sterols (1.8%-6.9%). In addition, a physical deodorizer distillate has two to four times higher weight fraction.

A new technology has been developed in order to improve the quality of the physical deodorizer distillate by increasing its tocopherol and sterol content. In order to separate the distillate in a fatty acid rich and an unsaponifiable rich part, the temperature and steam pattern needed to be optimized, which could be obtained either by low-high temperature or high-low temperature profile.

The first approach aims to remove fatty acids by distillation at low temperature (200°C-240°C) and little steam injection followed by stripping at higher temperature (260°C) to promote distillation of tocopherols and sterols. Both distillates were condensed separately.

In the first step, a high retention of tocopherols (65.1%-80.3%) and sterols (93.5%-99.6%) in the oil is observed. Residual free fatty acids content is 0.1%-0.28%. The distillate contains little unsaponifiables (< 2%) and consists mainly of free fatty acids (87.3%-96.3%). The second distillate fraction contains 5.7%-9.6% tocopherols, 10.8%-15.4% sterols and 37.6%-67.0% free fatty acids.

Nevertheless the first distillate is the largest fraction (0.46%-0.77% w/w); the second distillate ranges between 0.37%-0.57% w/w. The major part of tocopherols and sterols are recovered in the second step for which the working conditions are 260°C; 30 min; 1% steam; 2 mbar pressure.

In the second approach with a high-low temperature profile, the free fatty acids are distilled in a short deodorization step at 260°C for maximum 15 min and maximum 0.5% steam and 2 mbar followed by a second step for 15 min at 260°C with 0.5%-1% steam.

In the first step, the free fatty acid content is reduced to a low level below 0.15% retaining 68.7%-85.4% of sterols in the oil. The distillates have a free fatty acid content of 77.4%-88.6%, a sterol content between 1.7%-3.5% and a tocopherol content between 1.7%-3.4%.

Conditions of the second step were selected to retain as much as possible tocopherols and sterols in the oil and to complete the elimination of odour and taste components. Such a refining process is able to retain 60%-80% tocopherols and 87%-92% sterols in the oil while the free fatty acid content is lower than 0.05%.

Nevertheless the second distillate is small (0.15%-0.22%), rich in tocopherols (11.4%-13%) and sterols (12.4%-13.1%). An alternative for the second step is to perform the deodorization at higher temperature (240°C). In this way, the distillate is rich in tocopherols (11.6%-15.5%) and sterols (12.2%-17.8%).

The dual deodorization technology offers many opportunities to increase the economic value of the deodorizer distillate.

CONCLUSION

This study on the influence of refining on minor components indicates that tocopherols and phytosterols are stable components. However, several transformation reactions such as oxidation of tocopherols at high temperature and formation of steradienes can take place of which the ratio is largely influenced by the process conditions especially in the deodorization step.

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