DEGUMMING AND BLEACHING: EFFECT ON SELECTED CONSTITUENTS OF PALM OIL

PUAH CHIEW WEI*; CHOO YUEN MAY*; MA AH NGAN* and CHUAH CHENG HOCK**

ABSTRACT

Degumming and bleaching are essential processes in palm oil refining. The purpose is the removal of gums, trace metals, pigments, peroxides, oxidation products and other breakdown products in the crude oil by adsorption on the active surface of the bleaching earth to improve colour and stability of the final oil. This paper aims to study the effect of degumming and bleaching using neutral and acid-activated clays to achieve the aforementioned objectives. It was found that valuable palm minor components, i.e. *[tocols (tocopherol and tocotrienols) were retained; no significant changes occurred in the total phytosterols, squalene, composition of acylglycerols (*i.e. *mono-, di- and triacylglycerols)] and free fatty acids by using both acid-activated and neutral clays up to 1.0%. However, acid-activated clay reduced the carotenes content. Both clays gave markedly improved oxidative stability with induction period >30 hr at 120°C. Impurities such as pro-oxidant iron, copper and phosphorus were reduced by both clays. The bleaching effect of neutral clay was relatively poor compared to acid-activated clay in the removal of unwanted compounds.*

Keywords: degumming, bleaching, acid-activated clay, neutral clay, palm oil.

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INTRODUCTION

Degumming and bleaching are important processes in the refining of palm oil. These are for the removal of unwanted constituents in the crude oil. These include hydroperoxides and their breakdown products such as ketones and aldehydes, trace metals such as iron and copper as well as phosphatides. They are essential processes in the production of stable refined edible oil with the required colour, properties and bland taste desired by consumers.

Today, emphasis is put on the minor constituents in palm oil such as carotenes, tocols, phytosterols and squalene for their possible nutritional aspects (Goh *et al.*, 1985). In addition, the composition of these constituents provides specific information on the identity of the oil.

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Palm oil is a vegetable oil rich in minor components, which have nutritional attributes. The carotenes content in palm oil varies between 500-700 ppm. The major carotenes include α- and β-carotenes that constitute to ~90% of the total carotenes. The β-carotene is important as the precursor of vitamin A. Carotenes play an important role in the prevention of cancer, cataracts and degenerative diseases such as heart disease (Choo, 2000).

Another group of components in palm oil is tocols, which consist of α-tocopherol and α-, γ- and δ-tocotrienols. These are powerful natural antioxidants in scavenging free radicals. At the same time, they possess vitamin E activity in the human body (Wang and Quinn, 1999). The concentration in crude palm oil (CPO) ranges from 600-1000 ppm.

In addition, other minor constituents such as phytosterols and squalene are present in a smaller amounts. The major phytosterols in palm oil include campesterol, stigmasterol and β-sitosterol. Phytosterols have great potential in the pharmaceutical industry when converted to steroid derivatives (Hedtmann *et al.*, 1988). Research findings show that β-sitosterol has a cholesterol-lowering effect on serum. Squalene is important as the precursor of sterols (Khor and Chieng, 1997).

In this study, the effects of degumming and bleaching on selected constituents of palm oil were investigated. The clays used included neutral and acid-activated clays. The commercial bleaching clays consisted mainly of Montmorillonite, a three-layered sheet alumino-silicate mineral (Habile *et al.*, 1992). The neutral clay was used without any chemical treatment while the acid-activated clay was produced by activating the clay using mineral acid.

EXPERIMENTAL

Samples

CPO was obtained from a local palm oil mill. The bleaching clays (acid-activated and neutral) were obtained from local palm oil refineries. Concentrated phosphoric acid (85%) was purchased from Merck, Germany.

Oil Analyses

The determination of carotenes, free fatty acids (FFA), peroxide value (PV), phosphorus, iron and copper were according to PORIM Test Methods (1995). The Rancimat induction period at 120°C was determined. The acylglycerol composition, total phytosterols and squalene were determined using GC-FID (Lau *et al.*, 2002). Tocopherol and tocotrienols were determined using HPLC with normal phase column.

Procedures

Degumming. Degumming was carried out at 90°C–100°C. Phosphoric acid was added to a concentration of 0.06 wt % of the CPO. The mixture was stirred at 900 rpm for 10 min. The oil was subjected to nitrogen blanketing for the whole experiment.

Bleaching. The degummed oil was subjected to bleaching using both acid-activated and neutral clays. The oil was heated to 110°C–120°C for 30 min with 0.1%–1.0% clay used in the experiments.

The degummed and bleached oil was filtered twice with Whatman filter paper #1 under vacuum as soon as possible to prevent any undesirable oxidation. Thereafter, the oil was flushed with nitrogen and kept in the dark at –10°C prior to analysis.

RESULTS AND DISCUSSION

Effect on Carotenes

The CPO used contained 597 ppm total carotenes. From the results, it was found that the total carotenes content was reduced proportionately to the acid-activated clay used (*Figure 1*). However, the carotene content was partially preserved with neutral clay. As suggested by Sarier and Guler (1988), the acid-activated clay adsorbed more carotene on its active sites by formation of hydrogen bonding with the Bronsted sites, or coordination bonds with the Lewis sites. The carotenes attached to the surface as carbonium ions which were fairly stable. Thus, the carotenes were chemically adsorbed on the active surface of the clay and desorption was not easy. Carotenes are degraded by acid (Chen *et al.*, 1995). Mortensen and Skibsted (2000) suggested that the mechanism for the degradation of carotenes is protonation in medium strength acid. The protonated carotenes decay slowly to species with shorter conjugated systems. Thus, the possible

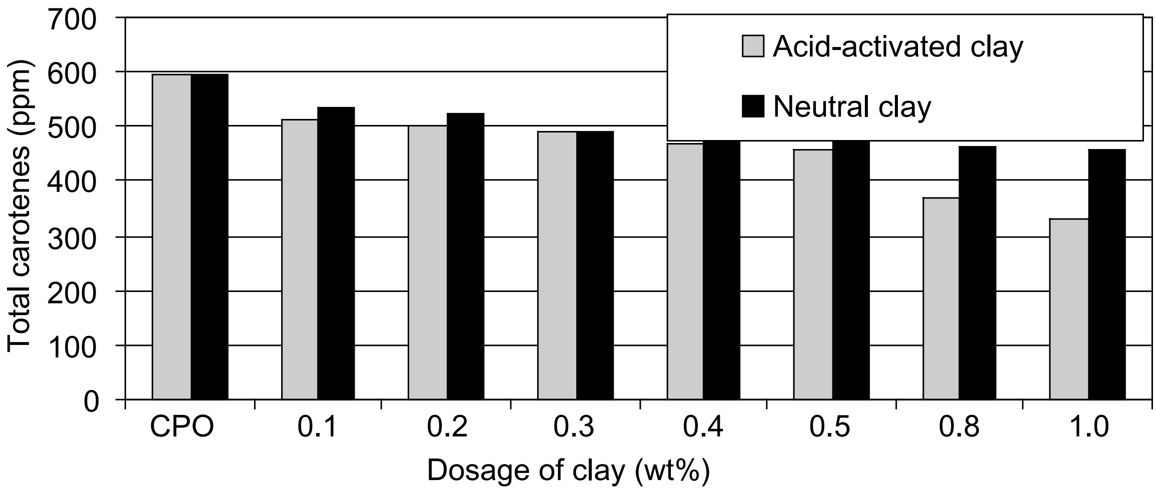

Figure 1. Effect of degumming and bleaching on the total carotenes content in crude palm oil (CPO).

destruction of carotenes by acid-activated clay may be explained by two concurrent reactions:

$$Car^{*} + [-SiO_4-AlO_3-SiO_4-AlO_2H^{+}] \rightleftharpoons [Car^{*}H^{+}.......SiO_4-AlO_3-SiO_4-AlO_2^{-}] \quad (1)$$

$$Car^{*} + 2[-SiO_4-AlO_3-SiO_4-AlO_2H^{+}] \rightleftharpoons [Car^{*}H_2^{2+}....2\{SiO_4-AlO_3-SiO_4-AlO_2\}^{-}] \quad (2)$$

Car* is carotenes

Effect on Tocols

Generally, the content of tocols (tocopherol and tocotrienols) is not significantly affected by both clays (*Figure 2*). However, the tocols level decreased by a small amount for high dosages of acid-activated clay of up to 1.0%. Thermal breakdown of tocols is only relevant for high temperatures of >260°C as reported by De Greyt *et al.* (1999). Thus, the loss of tocols from heat may be negligible.

Effect on Phytosterols

The major phytosterols in palm oil include campesterol, stigmasterol and β-sitosterol. *Figure 3* shows that no significant changes were observed in the phytosterols composition during degumming

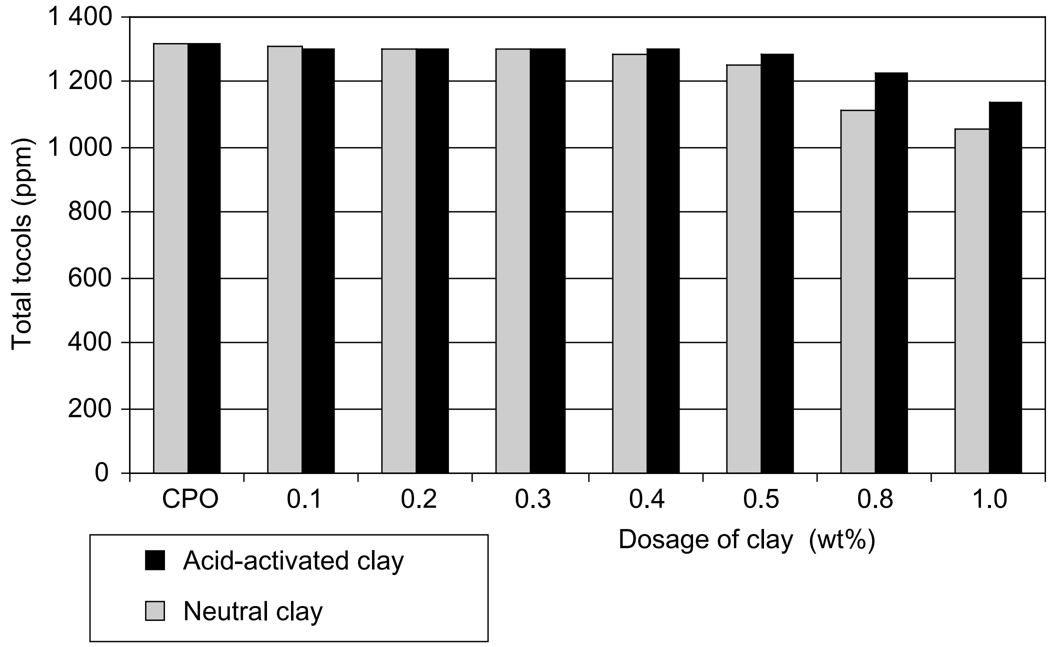

Figure 2. Effect of degumming and bleaching on the total tocols content in crude palm oil (CPO).

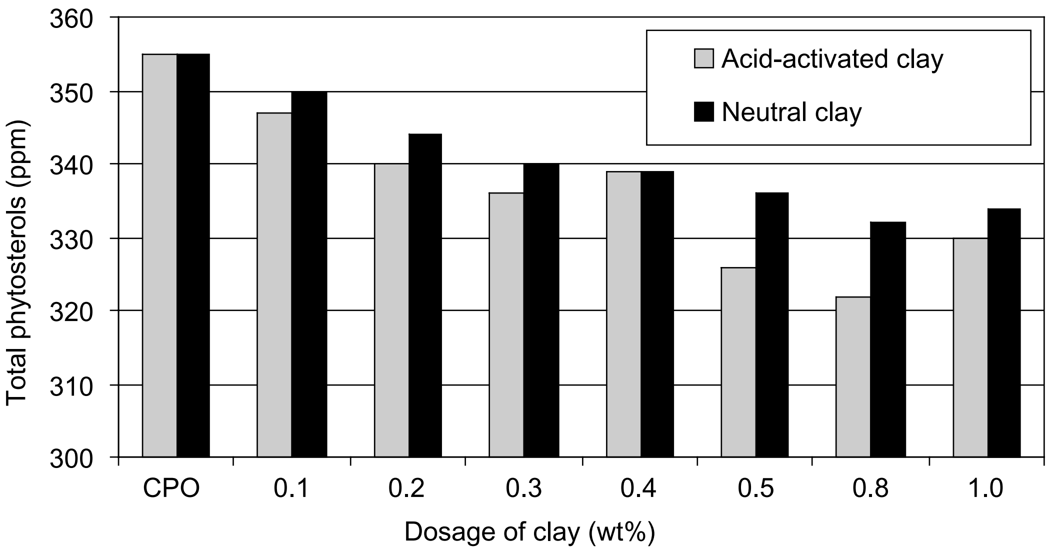

Figure 3. Effect of degumming and bleaching on the total phytosterols content in crude palm oil (CPO).

and bleaching with the dosage of clay up to 1.0%. Thus, phytosterols that are odourless and stable components and which have been found to possess a plasma cholesterol lowering effect, are retained after these processes.

Effect on Squalene

The squalene content showed very little changes as presented in *Figure 4* after degumming and bleaching with dosages of clay up to 1.0%. The contents of squalene in the degummed and bleached oil were similar to that in CPO of about 400 ppm. Thus, degumming and bleaching in the refining of palm oil do not affect the squalene content in palm oil significantly.

Effect on Phospholipids

The total phosphorus content is a measurement of the total phosphatides, such as phospholipids, or gums, in the oils and some inorganic phosphates present in the oil. The total phosphorus content (*Figure 5*) showed a slightly higher removal by the acid-activated clay. The reduction of phosphorus was proportionate to the dosage of clay used. Kheok and Lim (1982) suggested that the mechanism for phosphorus reduction was adsorption of the phosphorus ions on the lattice structure of the clay.

Effect on Trace Metals – Iron and Copper

Some of the undesirable materials to be removed during degumming and bleaching are pro-oxidants – trace metals such as iron and copper. The results shown in *Table 1* indicate better removal of the pro-oxidants using the acid-activated clay. Using 1.0% acid-activated clay, the iron and copper contents were reduced by 90% and 70%, respectively. With neutral clay, the iron and copper contents were reduced by only 80% and 40%, respectively.

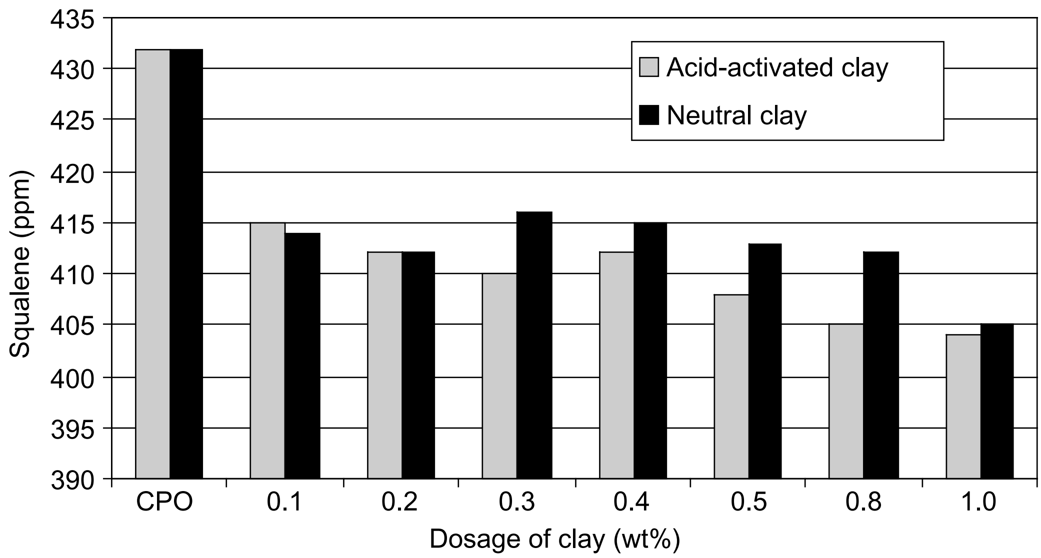

Figure 4. Effect of degumming and bleaching on the squalene content in crude palm oil (CPO).

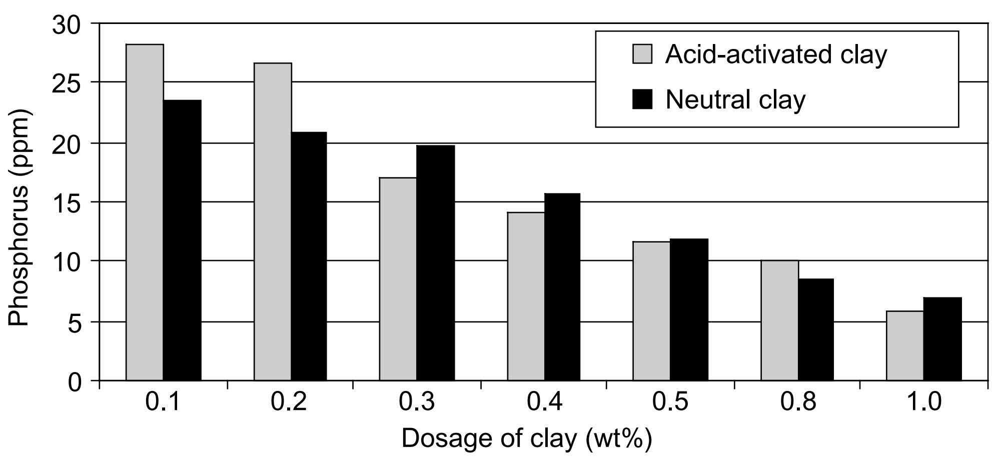

Figure 5. Effect of degumming and bleaching on the phosphorus content in crude palm oil (CPO).

TABLE 1. EFFECT OF DEGUMMING AND BLEACHING ON TRACE METALS: IRON AND COPPER IN CRUDE PALM OIL (CPO)

Dosage	Acid-activated clay		Neutral clay	
(wt %)	Iron (ppm)	Copper (ppm)	Iron (ppm)	Copper (ppm)
CPO	2.96	0.052	2.96	0.052
0.1	1.79	0.037	1.92	0.050
0.2	1.45	0.034	1.74	0.049
0.3	0.87	0.032	1.16	0.042
0.4	0.70	0.030	0.92	0.037
0.5	0.66	0.027	0.88	0.041
0.8	0.21	0.020	0.42	0.037
1.0	0.14	0.016	0.37	0.032

Effect on Free Fatty Acids

The percentages of FFA in the degummed and bleached oils for both acid-activated and neutral clays did not show any significant differences from the content in CPO as shown in *Figure 6*. Nevertheless, with the acid-activated clay, the %FFA was 0.1% higher than with the neutral clay. During refining of the oil, the FFA was removed most significantly during deodorisation at high temperature and under sparging steam.

Effects on Peroxide Value

The PV is an indicator of the primary oxidation of the oil. Both acid-activated and neutral clays reduced the PV to a non-detectable value with dosages greater than 0.8% as shown in *Figure 7*. Thus,

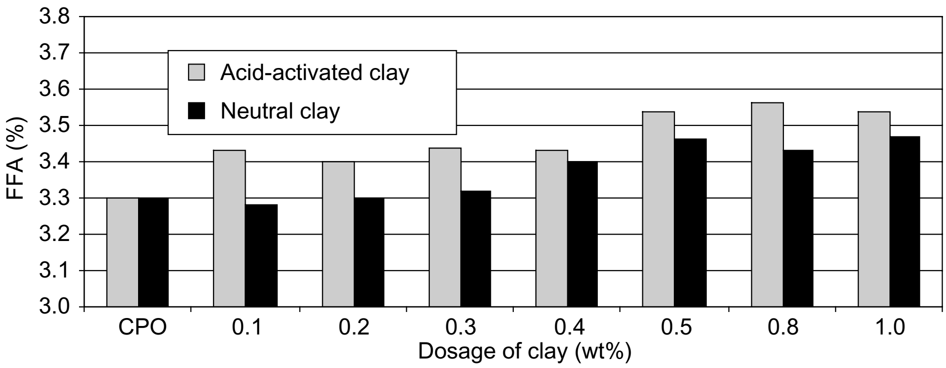

Figure 6. Effect of degumming and bleaching on free fatty acids (FFA %) in crude palm oil (CPO).

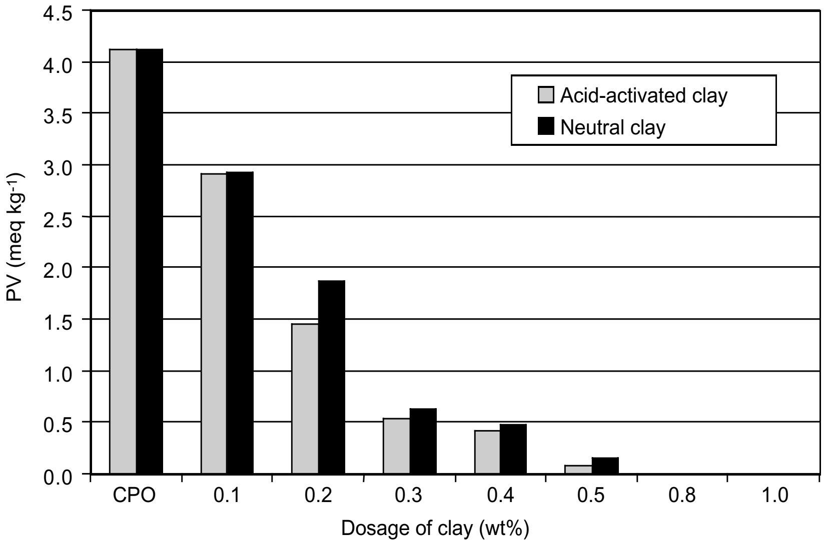

Figure 7. Effect of degumming and bleaching on peroxide value (PV) in crude palm oil (CPO).

all the primary oxidation products were removed with a clay dosage of >0.8%. The efficiency of adsorption of the oxidation products, however depended on the starting crude oil. If the content was relatively high, a greater dosage of clays was needed.

Effect on Stability of Oil

The accelerated oxidative stability of oil was investigated using Rancimat at 120°C. The results (*Table 2*) showed that the induction period for degummed and bleached oils using both clays give >30 hr stability as the dosage increased up to 0.8%. The carotenes and tocols in the oil may have contributed to the stability of the oil. As the levels of total carotenes and tocols were reduced (as shown in *Figures 1* and *2*, respectively), the stability of the oil declined.

TABLE 2. EFFECT OF DEGUMMING AND BLEACHING ON OXIDATIVE STABILITY OF CRUDE PALM OIL (CPO)

Dosage	Induction period (hr)	
(wt %)	Acid-activated clay	Neutral clay
CPO	14.3	14.3
0.1	>48	>48
0.2	>48	>48
0.3	>48	>48
0.4	39.6	42.8
0.5	38.8	35.7
0.8	33.8	30.4
1.0	24.2	24.6

CONCLUSION

Degumming and bleaching play important roles in the refining of palm oil to obtain a refined edible oil. The undesirable compounds are removed to give a final product acceptable to the consumers. This is carried out using different clays (*i.e.* neutral and acid-activated). The clays perform differently on the different constituents in the oil as their respective physico-chemical properties affect their adsorption efficiency. In general, the acid-activated clay is a more effective bleaching agent than the neutral clay. The recommended dosage of clay to use is >0.5% for effective removal of the unwanted materials.

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