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The role of bleaching clays and synthetic silica in palm oil physical refining

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Abstract

The adsorption characteristics of three bleaching clays having different degrees of activation were studied in a palm oil physical refining process. Different clay types and concentrations were used in combination with a fixed amount of synthetic silica. The analytical characteristics of crude, degummed, bleached and steam-refined oils were compared. The isotherms of colour removal vs. clay concentration demonstrated that acid-activated clays were more efficient than natural clay in removing carotene pigments. The phosphorus adsorption capacity of clay seemed also to be positively affected by acid activation. However, no relationship was observed between acid activation and copper, lead or iron adsorption; the adsorption of these metal ions seemed more probably related to the presence of synthetic silica in the bleaching mixes. Although the tested clays had different activities, the analytical characteristics of the corresponding refined palm oil samples were similar. This can be explained by the fact that synthetic silica, due to its synergic action with clays, smoothes the differences between the performances of the various clays.

Keywords: Adsorption; Bleaching; Carotene; Clay; Metals; Palm oil; Phosphorus; Synthetic silica

1. Introduction

In edible oil refining, either by chemical or physical process, the bleaching treatment is a critical step. The adsorbents used for bleaching can remove pigments and other impurities, such as soaps, trace metals, phospholipids, oxidation products, and polyaromatics (Mag, 1990). The removal of these impurities improves the sensory quality and the oxidative stability of the deodorized oil (De Greyt & Kellens, 2000).

Activated adsorbents are hydrated aluminium silicates, commonly known as bleaching clays. They are purified and activated by a mineral acid treatment, resulting in the de-lamination of the structure, thus increasing clay specific surface and adsorption capacity.

The acidity of bleaching clays depends on the degree of activation (technical document, Engelhard Italiana S.p.A., Italy; technical document, Caffaro S.p.A., Italy): the higher the degree of activation, the higher the degree of cation substitution (Ca, Mg, Al, Fe) in the clay structure interlamellar layer by the H^+ ions of the acid used for the treatment. Clay producers control clay acidity in order to guarantee the highest activity degree while maintaining the lowest levels of acidity (about 0.1% HCl). The aim is to avoid the hydrolysis of triacylglycerols by acid catalysis in the presence of moisture originating from the oil or the clay itself (technical document, Caffaro S.p.A., Italy). However, Mag (1990) observed that the increase of free fatty acids (FFA) during bleaching is more probably to be ascribed to the high temperature used, rather than to acidity or moisture levels.

Neutral clays, which are naturally active, are also used for bleaching. They are excellent metal adsorbents, able to decrease the levels of chlorophyll and colour bodies, to remove soaps and phospholipids and to minimize free fatty acid increase during bleaching (technical document, Oil-Dri S.A., France).

Besides clays, other adsorbents, such as activated carbon and synthetic silica hydrogel, are also used. Nowadays, synthetic silica, in particular, is commonly used in edible oil bleaching. Though synthetic silica has

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a moderate capacity for pigment removal, small amounts of it are used in combination with bleaching clay, their synergic action reducing the amount of clay needed to optimize the bleaching process. Silica adsorbs the compounds, such as soaps and phospholipids in particular, which are present in the oil and impair the action of bleaching clays (technical document, Grace Italiana S.p.A., Italy).

Siew, Tan, and Tang (1994) studied colour, phosphorus, and iron removal from palm oil using blends of a bleaching earth and synthetic silica. Silica had the capability of enhancing the earth's ability to remove colour bodies, phosphorus and other minor components that affect the colour stability of the oil.

Adsorption is a surface phenomenon which depends on the specific affinity between solute and adsorbent. The bleaching capacity of an adsorbent and its characteristic manner of adsorption may be described, respectively, by the K and n parameters defined by Freundlich (1926).

For a given temperature, the Freundlich equation relates the specific adsorption (x/m), i.e. the amount of substance adsorbed per unit of adsorbent weight, to residual solute concentration, at the equilibrium:

$$\frac{x}{m} = Kc^n$$

where: x = quantity of substance adsorbed; m = quantity of adsorbent; c = quantity of residual substance dissolved; K and n are constants unrelated to the amounts of solute and adsorbent. The equation may also be written in the logarithmic form:

$$\log\frac{x}{m} = \log K + n\log c$$

A plot of (x/m) vs. c on a log–log scale will produce a straight line with a slope equal to n and an intercept equal to K. The value of K determines the adsorption capacity of the adsorbent for a specific solute, and the value of n determines the range of bleaching in which the adsorbent shows its greatest effect. If n is high, the adsorbent will be effective for removing the first portions of colour, but less efficient for reaching highest bleaching degrees. If n is low, the reverse is true.

The values of K and n depend on the kinds of adsorbent and oil, and on the operative conditions of bleaching. The Freundlich equation is valid for any method of colour measurement, as long as the units of measurements are additive and proportional to the actual concentration of the colouring substances in oil.

The aim of the present study was to investigate the adsorption performances of three clays, having different activation levels, used in combination with synthetic silica, for physical refining of palm oil. Carotene, phosphorus, metal ions, acidity and oxidation products removal during bleaching and deodorizing steps were evaluated, besides the oxidation stability of the finished palm oil. Experiments were carried out on pilot plants under standard operative conditions and by varying clay concentration and type.

2. Materials and methods

2.1. Materials

Indonesian crude palm oil (5.02% FFA) was used for experiments. After acid degumming (30 min at 90 °C with 0.1–0.2% of 60% phosphoric acid) in an industrial plant, 10 kg oil batches were treated on a pilot plant consisting of a bleaching vessel and a steam physical refining vessel (Gianazza, 1996). Operative conditions were 110 °C for 20 min under vacuum (70–80 mm Hg) for bleaching, and 250 °C for 2.5 h at 2–3 mm Hg for physical refining. The pilot plant was located at an oil refining factory, and was connected to the steam and water pipelines of the industrial plant.

Five concentrations (from 0.5 to 1.0% of oil mass) of one natural and two acid-activated clays mixed with 0.125% (of oil mass) synthetic silica were used for bleaching, thus obtaining 15 samples of bleached oil and as many bleached, steam-refined oil samples (from now on called RBD or refined samples). The adsorbent concentrations chosen for the experiments were close to the values used in the industrial process, corresponding to 0.75% activated clay + 0.125% synthetic silica. Table 1 reports the characteristics of the adsorbents used.

2.2. Total carotene

For total carotene analysis, sample absorbance at 450 nm was measured using a Perkin-Elmer Lambda 3 spectrophotometer (The Perkin-Elmer Co., Norwalk, CT). Results were expressed as β-carotene equivalents after comparison against a calibration curve prepared with 0–10 mg/l β-carotene (Merck, Darmstadt, Germany) solutions in petroleum ether.

2.3. Acidity

For acidity measurement, the N.G.D. C10-1976 method was used, based on titration with a sodium hydroxide solution (phenolphthalein as indicator) of the fat suitably diluted with an ethyl alcohol–ethyl ether mix. Results are expressed as oleic acid (g/100 g).

2.4. Peroxide value (PV) and anisidine value (AV)

For PV measurement, the N.G.D. Db6-1989 method was used, based on titration with a sodium thiosulfate solution of the iodine released by the fat diluted with an acetic acid–chloroform mix and then treated with potassium iodide. Results are expressed as active oxygen milliequivalents per kilogramme of oil.

AV analysis was performed following the N.G.D. Db8-1989 method, based on absorbance measurement at 350 nm of the fat diluted with isooctane and treated with an acetic acid solution of *p*-anisidine.

2.5. Totox value

Totox is an oxidation index, calculated from PV and AV by applying the following equation:

$$\mathrm{TOTOX} = 2\mathrm{PV} + \mathrm{AV}$$

2.6. Rancimat test

The finished oil oxidation stability was measured using a Rancimat 617 instrument (Metrohm, Herisau, Switzerland). The analytical conditions were: sample weight, 2.5 g; temperature, 120 °C; air flow rate, 18–20 ml/min. Rancimat induction period was expressed as resistance time (h) of the oil to oxidation.

2.7. Total phosphorus analysis

Total phosphorus analysis was carried out by direct graphite furnace atomic absorption spectrometry. The A.O.C.S. official method Ca12b-92 (1998), modified in the programme for the graphite furnace atomizer, was used for analysis. Crude and degummed palm oil samples were diluted 1:5 (w/w) with blank oil, while bleached and refined oil samples were not diluted. Determinations were performed in triplicate on a Perkin-Elmer 1100B atomic absorption spectrophotometer, equipped with a Perkin-Elmer AS 70 automatic sample injector, a Perkin-Elmer HGA 700 graphite furnace atomizer, an appropriate electrode-less discharge lamp (Perkin-Elmer System 2), and a deuterium arc background corrector.

2.8. Analysis of trace metals

Copper, iron and lead levels were determined by direct graphite furnace atomic absorption spectrometry. The A.O.C.S. official method Ca18-79 for copper and iron (1998), also recommended for lead by Martin-Polvillo, Albi, and Guinda (1994), was used for the analysis. Determinations were performed in triplicate on a Perkin-Elmer 1100B atomic absorption spectrophotometer, equipped with a Perkin-Elmer AS 70 automatic sample injector, a Perkin-Elmer HGA 700 graphite furnace atomizer, an appropriate multielement hollow catode lamp for Cu and Fe, an E.D.L. lamp for Pb, and a deuterium arc background corrector.

All the earlier analyses were performed in duplicate unless otherwise specified.

3. Results and discussion

Fig. 1 shows the carotene adsorption isotherms obtained for the three clays tested. The natural clay (C3) is the least effective in terms of carotene adsorption, and

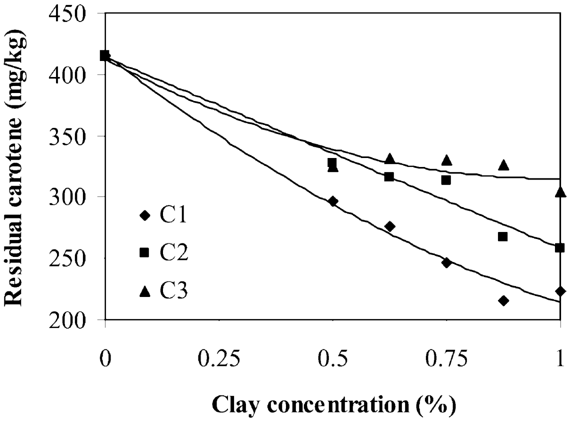

Fig. 1. Carotene adsorption isotherms for the three clays mixed with 0.125% synthetic silica.

Table 1
Principal characteristics of the utilized adsorbents

Product	Code	Type	pH[a]	Moisture (g/100 g)[b]
Fulmont XMP4[c]	C1	Activated earth	2.5	12 max.
Engelhard F-105 SF[d]	C2	Activated earth	3.2	15 max.
Pure-flo Neutral B-80[e]	C3	Nnatural earth	6–7	13 max.
Grace Trisyl[f]	S	Synthetic silica	4.5	60–68

[a] Measured in a 5% water dispersion.
[b] Measured at 950 °C.
[c] Caffaro S.p.A., Italy.
[d] Engelhard Italiana S.p.A., Italy.
[e] Oil-Dri S.A., Switzerland.
[f] Grace Italiana S.p.A., Italy.

the bleaching effect shows almost no correlation with clay concentration. For the activated clays, the trend of the curves shows a clear dependence of pigment reduction on clay concentration, more evidently for C1.

The values of K and n coefficients for each clay were calculated by applying the Freundlich equation to the interpolation curves of Fig. 1, and relating the logarithm of the specific adsorption (x/m) to the logarithm of residual carotene (c) (Table 2). Considering the K and n values obtained, it can be inferred that C1 has the highest adsorption capacity for carotene and is more efficient in reaching high bleaching degrees, while C2 shows lower adsorption performances. The non-activated C3 clay has even a negative K value, thus indicating no colour removing capacity. This is consistent with the isotherm of Fig. 1, showing that the small amount of colour removed by C3 has practically no correlation with clay concentration. The constant level of synthetic silica mixed with clay is likely to account for the minor activity observed in the C3 bleaching mix in Fig. 1. It must be underlined that the values reported in Table 2 for K and n do not characterize the performances of the single clays, but they are indices of the bleaching properties for carotene of the clay–silica mixes used.

Table 2
K and n values for the three clays mixed with 0.125% synthetic silica

Clay	K	n
C1	1.62	0.28
C2	0.82	0.61
C3	−1.65	1.57

Table 3
Effects of acid degumming and bleaching, in palm oil physical refining, on oil acidity and variables linked to lipid oxidation

Palm oil	Acidity (g oleic acid/100 g)	PV (meq O_2/kg)	AV	TOTOX
Crude	5.02	3.2	8.3	14.7
Degummed	6.26	1.0	8.4	10.4
Bleached with C1 + 0.125% S				
0.5%	6.32	0.1	8.8	10.0
0.625%	6.32	0.1	6.0	6.2
0.75%	6.37	0.1	5.8	6.0
0.875%	6.26	0.1	9.9	10.1
1.00%	6.26	0.1	4.3	4.5
mean	*6.31*	*0.1*	*7.0*	*7.4*
Bleached with C2 + 0.125% S				
0.5%	6.37	0.1	5.6	5.8
0.625%	6.26	0.1	4.3	4.5
0.75%	6.20	0.1	4.1	4.3
0.875%	6.32	0.1	6.3	6.5
1.00%	6.66	0.1	5.8	6.0
mean	*6.36*	*0.1*	*5.2*	*5.4*
Bleached with C3 + 0.125% S				
0.5%	6.26	0.1	7.2	7.4
0.625%	6.15	0.1	7.5	7.7
0.75%	6.26	0.1	7.6	7.8
0.875%	6.32	0.1	8.4	8.6
1.00%	6.32	0.1	6.1	6.3
mean	*6.26*	*0.1*	*7.4*	*7.6*

Table 3 shows the effects of acid degumming and bleaching on oil acidity and variables linked to lipid oxidation. Traces of phosphoric acid remaining in the oil after acid degumming treatment are responsible for the increase of acidity observed in the degummed oil. This is confirmed by comparison of the phosphorus levels measured in crude and degummed oil, as reported in Table 5. The bleaching treatments, on the contrary, show no further effect on oil acidity.

Peroxide value, already reduced by degumming, is further lowered to 0.1 meqO_2/kg after the bleaching process, regardless of clay type and concentration. Clays can both adsorb peroxides and catalyze peroxide degradation into secondary oxidation products. However, clays also have adsorption capacity for the products of

Table 4
Effects of palm oil steam refining on oil acidity and variables linked to lipid oxidation

Palm oil	Acidity (g oleic acid/100 g)	PV (meg O_2/kg)	AV	TOTOX	Rancimat 120 °C
RBD (from C1 + 0.125% S)					
0.5%	0.05	0.1	2.9	3.1	9 h 02′
0.625%	0.08	0.1	4.4	4.6	9 h 39′
0.75%	0.05	0.1	5.8	6.0	7 h 57′
0.875%	0.05	0.1	1.9	2.1	8 h 15′
1.00%	0.05	0.1	1.9	2.1	8 h 03′
mean	*0.06*	*0.1*	*3.4*	*3.6*	*8 h 35′*
RBD (from C2 + 0.125% S)					
0.5%	0.05	0.1	1.4	1.6	9 h 21′
0.625%	0.05	0.1	3.1	3.3	9 h 36′
0.75%	0.05	0.1	3.5	3.7	8 h 42′
0.875%	0.05	0.1	1.8	2.0	9 h 03′
1.00%	0.05	0.1	2.8	3.0	7 h 51′
mean	*0.05*	*0.1*	*2.5*	*2.7*	*8 h 55′*
RBD (from C3 + 0.125% S)					
0.5%	0.05	0.1	1.5	1.7	9 h 48′
0.625%	0.05	0.1	1.9	2.1	9 h 36′
0.75%	0.05	0.1	2.8	3.0	8 h 09′
0.875%	0.05	0.1	1.6	1.8	8 h 36′
1.00%	0.05	0.1	1.4	1.6	9 h 39′
mean	*0.05*	*0.1*	*1.8*	*2.0*	*9 h 10′*

secondary oxidation, depending on clay concentration (Mag, 1990). This capacity accounts for the AV reduction observed in most bleached samples (Table 3). The AV values for the different clays reach a maximum at a clay concentration of about 0.9%. The maximum observed corresponds to a clay concentration at which, under the operative conditions applied, the peroxide degradation, catalyzed by clay, exceeds the clay adsorption capacity for secondary oxidation products.

Table 4 shows the effects of steam refining on oil acidity and variables linked to lipid oxidation. The process causes the removal of FFA, thus reducing the acidity of RBD palm oil to 0.05 g/100 g. Also the products of secondary oxidation are stripped away under the operative conditions applied (250 °C, 2–3 mm Hg), and consequently AV is reduced in RBD oil samples. No correlations were observed between the Rancimat induction period and any of the oxidation indices in RBD oil samples, including totox.

In Tables 5 and 6 the effects of the various steps of the refining process on metals and phosphorus contents in palm oil samples are reported as function of clay type and concentration. Acid degumming tends to increase the levels of lead and phosphorus. This increase is due to the ions brought into the oil by the phosphoric acid and water used as degumming media (Ranghetti, 1995). The bleaching treatment has a minor effect on the already low copper level, while it considerably reduces iron concentration and depresses lead to values below the detection limit. Copper, iron, and lead reductions show no correlation with clay type and concentration. Phosphorus adsorption has no correlation with clay concentration either, but the average phosphorus values obtained with each tested clay indicate a positive dependence of phosphorus adsorption on clay acidity, although a significant difference ($P < 0.05$) exists only between C1 and C3.

Steam-refining does not change the levels of copper and lead (Table 6). The levels observed for these metals in the refined oils are anyhow below the limit of 0.1 mg/kg suggested by the Codex Alimentarius (1993). No relationship can be observed between iron levels in the refined and the corresponding bleached oil samples. Actually, two phenomena, having counteracting effects on iron level, can take place during the steam-refining step: the stripping of iron ions in the form of free fatty acid soaps, and an increase of iron due to a new supply, originated by steam. Phosphorus is steam-stripped, together with the compounds bearing it, and the residual phosphorus levels in the refined oil samples are positively correlated ($r = 0.994$; $P < 0.001$) with the phosphorus levels in the corresponding bleached oil samples.

Table 5
Effects of acid-degumming and bleaching, in palm oil physical refining, on metals and phosphorus contents

Palm oil	Cu (mg/kg)	Fe (mg/kg)	Pb (mg/kg)	P(mg/kg)
Crude	0.06	62	0.012	116
Degummed	0.06	66	0.049	230
Bleached with C1 + 0.125% S				
0.5%	0.05	1.08	<0.005[a]	41
0.625%	0.04	0.91	<0.005[a]	10
0.75%	0.04	1.49	<0.005[a]	10
0.875%	0.04	1.45	<0.005[a]	8
1.00%	0.03	0.37	<0.005[a]	16
mean	*0.04*	*1.06*	*<0.005*[a]	*17*
Bleached with C2 + 0.125% S				
0.5%	0.04	1.42	<0.005[a]	25
0.625%	0.04	1.10	<0.005[a]	40
0.75%	0.04	0.67	<0.005[a]	28
0.875%	0.04	1.84	<0.005[a]	28
1.00%	0.04	0.76	<0.005[a]	37
mean	*0.04*	*1.16*	*<0.005*[a]	*32*
Bleached with C3 + 0.125% S				
0.5%	0.03	0.77	<0.005[a]	42
0.625%	0.03	0.83	<0.005[a]	21
0.75%	0.04	1.46	<0.005[a]	46
0.875%	0.03	0.99	<0.005[a]	44
1.00%	0.04	0.89	<0.005[a]	56
mean	*0.03*	*0.99*	*<0.005*[a]	*42*

[a] Detection limit.

Table 6
Effects of palm oil steam refining on metals and phosphorus contents

Palm oil	Cu (mg/kg)	Fe (mg/kg)	Pb (mg/kg)	P (mg/kg)
RBD (from C1 + 0.125% S)				
0.5%	0.04	2.07	<0.005[a]	32
0.625%	0.05	1.60	<0.005[a]	9
0.75%	0.05	0.90	<0.005[a]	10
0.875%	0.03	1.48	<0.005[a]	8
1.00%	0.04	2.40	<0.005[a]	12
mean	*0.04*	*1.69*	*<0.005*[a]	*14*
RBD (from C2 + 0.125% S)				
0.5%	0.04	1.43	<0.005[a]	20
0.625%	0.04	2.07	<0.005[a]	31
0.75%	0.04	1.13	<0.005[a]	22
0.875%	0.04	1.00	<0.005[a]	21
1.00%	0.04	1.63	<0.005[a]	29
mean	*0.04*	*1.45*	*<0.005*[a]	*25*
RBD (from C3 + 0.125% S)				
0.5%	0.04	0.80	<0.005[a]	32
0.625%	0.04	1.18	<0.005[a]	15
0.75%	0.04	0.27	<0.005[a]	35
0.875%	0.04	0.68	<0.005[a]	34
1.00%	0.04	1.05	<0.005[a]	47
mean	*0.04*	*0.80*	*<0.005*[a]	*33*

[a] Detection limit.

4. Conclusion

Data demonstrate that acid-activated clays are more efficient than natural clay in removing carotene pigments. Adsorption capacity for phosphorus also seems to be positively affected by acid clay activation. However, no similar relationship exists for clay adsorption capacities for copper, lead and iron: the adsorption of these ions seems more probably related to the presence of synthetic silica in the bleaching mixes.

It has been reported that the colour of the finished palm oil obtained by physical refining has no correlation with the bleaching capacity of the clays used in the process (Rossi, Gianazza, Alamprese, & Stanga, 2001), because carotene is more efficiently reduced by heat-bleaching during the deodorization step. Therefore, a global efficiency rating of the clays used in the process must consider refined oil quality parameters other than colour, as well as cost considerations. Actually, refined palm oils of similar quality are also achievable at lower costs, since less active and cheaper clays may be used, even at small concentration, without reducing the quality of the finished oil. The combination of clays with synthetic silica probably accounts for this result: synthetic silica, due to its synergic action with clays, smoothes the differences between the performances of the various clays.

References

A.O.C.S. official method Ca12b-92. (1998). *Phosphorous by direct graphite furnace atomic absorption spectrophotometry*.

A.O.C.S. official method Ca18-79. (1998). *Analysis for chromium, copper, iron, nickel and manganese in triglyceride oils by atomic absorption spectrophotometry with a graphite furnace*.

Codex Alimentarius. (1993). *Fats, Oils and Related Products (Vol. 8)* (2nd ed.). Rome: Food and Agricultural Organization of the United Nation World Health Organization.

De Greyt, W., & Kellens, M. (2000). Refining Practice. In W. Hamm, & R. J. Hamilton (Eds.), *Edible Oil Processing* (pp. 79–128). Sheffield: Sheffield Academic Press Ltd.

Freundlich, H. (1926). In H.S. Hatfield (Ed.), *Colloid and Capillary Chemistry*, translated from the 3rd deutsche edition. London: Methuen.

Gianazza, M. (1996). *Raffinazione Fisica dell'Olio di Palma: Messa a Punto di un Impianto Pilota e Studio della Fase di Decolourazione*. Thesis, University of Milan, Italy.

Mag, T. K. (1990). Bleaching - Theory and Practice. In D. Erickson (Ed.), *World Conference Proceedings on Edible Fats and Oil Processing. Basic Principles and Modern Practices* (pp. 107–116). Champaign: A.O.C.S.

Martin-Polvillo, M., Albi, T., & Guinda, A. (1994). Determination of trace of elements in edible vegetable oils by atomic absorption spectrophotometry. *Journal of the American Oil Chemists Society*, *71*, 347–353.

N.G.D. method C10-1976. (1976) Determinazione dell'acidità. In *Norme Grassi e Derivati*. Milano: Stazione Sperimentale Oli e Grassi.

N.G.D. method Db6-1989. (1989). Determinazione del numero di perossidi. In *Norme Grassi e Derivati*. Milano: Stazione Sperimentale Oli e Grassi.

N.G.D. method Db8-1989 (1989). Determinazione dell'indice di anisidina. In *Norme Grassi e Derivati*. Milano: Stazione Sperimentale Oli e Grassi.

Ranghetti, P. (1995). *Influenza delle Diverse Fasi di Raffinazione sul Contenuto di Metalli e su Alcuni Indici di Ossidazione di Oli di Palma e di Cocco*. Thesis, University of Milan, Italy.

Rossi, M., Gianazza, M., Alamprese, C., & Stanga, F. (2001). The effect of bleaching and physical refining on colour and minor components of palm oil. *Journal of the American Oil Chemists Society*, *78*, 1051–1055.

Siew, W. L., Tan, Y. A., & Tang, T. S. (1994). Silica refining of palm oil. *Journal of the American Oil Chemists Society*, *71*, 1012–1016.