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Effect of Iron (III) Palmitate on the Oxidation of Palm Oil

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ABSTRACT

The effect of added iron(III) palmitate on the rate of oxidative deterioration of refined, bleached and deodorized palm oil (RBD palm oil) was evaluated. Assessment of the oils included determinations of peroxide and p*-anisidine values and UV absorbances at 233 and 269 nm. It was found that the rates of increase in peroxide value and UV absorbance at 233 nm in oils without added Fe(III) palmitate were greater than those for oils with added Fe(III) palmitate. However, the increases in* p*-anisidine value and UV absorbance at 269 nm were greater in oils with added Fe(III) palmitate than in oil without added Fe(III) palmitate. The results suggested that the assessment of the extent of oxidative deterioration in oils with added Fe(III) palmitate could not be evaluated using indicators of primary oxidation alone. An overall assessment showed that added Fe(III) palmitate increases the rate of formation of secondary products of oil oxidation.*

INTRODUCTION

Trace metals, especially iron and copper, have been known to have a pro-oxidant effect in catalysing the oxidative deterioration of oils and fats

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(Labuza, 1971; Waters, 1971; Toyoda *et al.*, 1982). Although there is a need to establish the chemical form of the pro-oxidant metals in oil and the nature of the interaction between the metal and other substances in the oil, the form in which the metals occur naturally in the oils is not known (Odumosu & Hudson, 1978). It is often assumed that metals are present as soaps formed by the action of fatty acids during processing but this could not be demonstrated in plant tests (Gunstone & Norris, 1983). It has been considered most likely that the metals are in an organically bound form (other than soap) as a component of the oil seed (Gunstone & Norris, 1983). However, there is still no direct evidence about the natural form of metals in oils. It is nevertheless of interest to investigate the effect of different chemical forms of the metal on oil oxidation and stability.

There have been a number of investigations on the effect of iron on lipid oxidation (Smith & Dunkley, 1962; Eriksson *et al.*, 1971; Marcuse & Fredriksson, 1971). A study of the effect of iron contamination in palm oil has also been carried out (Yeoh, 1976). However, an understanding of the action of iron on quality deterioration of palm oil is still lacking. In this work, the effect of added iron(III) palmitate on the rate of oxidation of refined, bleached and deodorized palm oil was studied.

MATERIALS AND METHODS

Materials

RBD palm oil was obtained from Lam Soon Oil and Soap Mfg. Sdn. Bhd. Iron(III) palmitate was prepared in the laboratory. Palmitic acid (0·77 g) was dissolved in warm water containing 0·12 g sodium hydroxide. To this mixture was added 0·27 g $FeCl_3.6H_2O$ which had been dissolved in a few cubic centimetres of water. The orange–red Fe(III) palmitate salt was formed immediately. The salt was filtered and washed with water. The Fe(III) palmitate was dried in an oven at 60°C.

Preparation of RBD palm oil spiked with Fe(III) palmitate

A stock solution containing 0·442 g added Fe(III) palmitate in 200 g RBD palm oil was prepared on the day of use. Oils with different amounts of added Fe(III) palmitate were prepared by diluting the stock solution with RBD palm oil which had no added Fe(III) palmitate. The Fe contents in the oils used for storage experiments were determined by atomic absorption spectroscopy (PORIM Test Methods, 1986).

Storage experiment

Samples (100 g) of RBD palm oil without added iron and RBD palm oil with varying amounts of added Fe(III) palmitate were placed in stoppered 125 ml brown glass bottles. The bottles were stored at 65°C. At intervals during the storage period, 10 g oil was withdrawn for analysis of peroxide value (AOCS, 1974), *p*-anisidine value and $E^{1\%}_{1\text{cm}}$ at 233 and 269 nm (IUPAC, 1979). The results represent the average of analyses carried out on samples of oil stored in two separate storage bottles.

RESULTS AND DISCUSSION

Oxidation values during storage

The effects of added Fe(III) palmitate on the peroxide value, *p*-anisidine value, and UV absorbances during storage are given in Table 1.

It was noted that the peroxide value of the RBD palm oil increased during storage. The increase in peroxide value in oils without added iron was greater than the peroxide value of oils which had been spiked with Fe(III) palmitate. In addition, the increase in peroxide value was greater in oils which contained 3·3 ppm iron than in oils with higher contents of 6·6–18·4 ppm iron.

The trends for changes in $E^{1\%}_{1\text{cm}}$ at 233 nm paralleled the trends observed for changes in peroxide value. It should be borne in mind that both peroxide value and $E^{1\%}_{1\text{cm}}$ at 233 nm are indicators of primary oxidation. The similarity in trends for increases in peroxide value and $E^{1\%}_{1\text{cm}}$ at 233 nm adds confidence to the results.

The addition of Fe(III) palmitate to RBD palm oil resulted in greater increases in *p*-anisidine value as compared to that for RBD palm oil without added iron. The trend for changes in $E^{1\%}_{1\text{cm}}$ at 269 nm was similar to that observed for changes in *p*-anisidine value. Although both *p*-anisidine values and $E^{1\%}_{1\text{cm}}$ at 269 nm are indicators of secondary oxidation, it should be noted that the $E^{1\%}_{1\text{cm}}$ at 269 nm measures ethylenic diketones, conjugated ketodienes, dienals and trienals whereas the *p*-anisidine value is particularly sensitive to the presence of 2-alkenals. This accounts for differences in the magnitude of changes for these two parameters.

In separate storage experiments where 200-ml samples of RBD palm oil spiked with Fe(III) palmitate and oils without added iron were stored in 250 ml brown glass bottles at 65°C and evaluated during storage, a similar trend for changes in oxidation values was observed although the absolute increases in peroxide and *p*-anisidine values and UV absorbances at 233 and

TABLE 1

Measurements of Oxidation of RBD Palm Oil Spiked with Fe(III) Palmitate during Storage at 65°C

System	*Fe content (ppm)*	*Days of storage*						
		1	*8*	*15*	*22*	*28*	*42*	*57*
				Peroxide value (meq/kg)				
No added Fe	0·4	1·5	8·8	17·8	31·8	40·6	59·8	78·3
Added Fe (III)	3·3	4·9	14·4	21·9	23·8	41·2	45·3	60·8
palmitate	6·6	4·3	12·8	20·4	29·8	35·3	39·6	47·3
	8·9	4·5	14·3	18·1	26·1	31·6	37·8	47·6
	18·4	4·5	10·7	16·7	29·4	30·2	37·3	41·6
				p-*Anisidine value*				
No added Fe	0·4	1·0	1·2	1·9	2·6	3·8	7·2	13·0
Added Fe (III)	3·3	2·5	5·7	10·0	12·0	16·0	26·5	32·5
palmitate	6·9	2·7	6·3	11·1	13·5	17·6	25·2	33·0
	8·9	3·4	6·4	11·9	14·6	18·2	26·4	34·8
	18·4	3·8	7·0	12·6	15·8	19·1	29·6	34·6
				$E^{1\%}_{1\,cm}$ *at 233 nm*				
No added Fe	0·4	1·7	2·1	3·5	4·9	6·2	—	6·0
Added Fe (III)	3·3	2·1	3·0	4·0	5·0	5·8	—	6·7
palmitate	6·9	2·1	3·0	3·8	4·6	5·2	—	6·1
	8·9	2·1	2·8	3·4	4·2	5·0	—	6·0
	18·4	2·0	2·7	3·4	4·1	4·9	—	5·9
				$E^{1\%}_{1\,cm}$ *at 269 nm*				
No added Fe	0·4	0·51	0·51	0·54	0·56	0·59	0·75	0·97
Added Fe (III)	3·3	0·60	0·75	0·88	0·94	0·98	1·13	1·30
palmitate	6·9	0·60	0·79	0·92	0·99	1·02	1·16	1·31
	8·9	0·62	0·80	0·94	1·02	1·04	1·18	1·36
	18·4	0·63	0·83	0·97	1·04	1·07	1·22	1·33

Each value is the average result obtained from analysis of samples of oil obtained for duplicate analyses from two separate storage bottles. The average differences in the results of analysis from two separate bottles were 0·97 meq/kg for peroxide value, 0·50 for *p*-anisidine value, 0·008 for $E^{1\%}_{1\mathrm{cm}}$ at 233 nm and 0·008 for $E^{1\%}_{1\mathrm{cm}}$ at 296 nm.

269 nm were different. Differences in absolute values may be expected as a different batch of oil was used and, in addition, the oil to air ratio in the bottles during storage was different.

Correlation between indicators of lipid oxidation

There are good correlations between the indicators of primary oxidation (peroxide value and $E^{1\%}_{1\mathrm{cm}}$ at 233 nm) and between the indicators of secondary oxidation (*p*-anisidine value and $E^{1\%}_{1\mathrm{cm}}$ at 269 nm). The correlations obtained when using data obtained in this storage experiment are given in Table 2. In separate experiments where a different batch of RBD palm oil was used, it

TABLE 2
Correlation between Indicators of Lipid Oxidation for RBD Palm Oil in Storage Experiments[a]

System	*Fe content (ppm)*	*Number of values*	*Equation*	*Correlation coefficient*
		Peroxide value versus $E^{1\%}_{1cm}$ at 233 nm		
No added Fe	0·4	6	$y = 12{\cdot}44x - 20{\cdot}79$	0·867
Added Fe (III) palmitate	3·3	6	$y = 11{\cdot}44x - 21{\cdot}20$	0·984
	6·6	6	$y = 10{\cdot}65x - 19{\cdot}04$	0·997
	8·9	6	$y = 10{\cdot}31x - 16{\cdot}68$	0·990
	18·4	6	$y = 9{\cdot}54x - 14{\cdot}40$	0·985
		p-*Anisidine value versus $E^{1\%}_{1cm}$ at 269 nm*		
No added Fe	0·4	7	$y = 25{\cdot}54x - 11{\cdot}78$	0·998
Added Fe (III) palmitate	3·3	7	$y = 46{\cdot}01x - 28{\cdot}22$	0·976
	6·6	7	$y = 44{\cdot}33x - 27{\cdot}37$	0·974
	8·9	7	$y = 44{\cdot}56x - 27{\cdot}78$	0·975
	18·4	7	$y = 46{\cdot}61x - 29{\cdot}71$	0·966

[a] Values obtained in the set of experiments given in Table 1 were used.

was similarly found that there was good correlation between peroxide value and $E^{1\%}_{1\mathrm{cm}}$ at 233 nm and between *p*-anisidine value and $E^{1\%}_{1\mathrm{cm}}$ at 269 nm. However, it was noted that the equations for the regression lines for corresponding systems were different. In this system where the same batch of RBD palm oil was used, the equations for the regression lines for the system without added iron were different from those with added Fe(III) palmitate.

Assessment of the action of added Fe(III) palmitate

The results for changes in indicators of primary oxidation should be interpreted with caution. The observation of a greater increase in peroxide value of the oil without added iron as compared to oils which had added Fe(III) palmitate is not necessarily indicative of a faster rate of primary oxidation in the oil without added iron. Peroxides are only intermediates of oil oxidation which are later converted to other secondary oxidation products. It has been suggested that compounds of transition metals act as secondary catalysts by promoting rapid formation of radicals by one-electron transfer reactions. The suggested mechanisms for Fe catalysis are given below (Gutteridge, 1984).

$$\mathrm{LOOH} + \mathrm{Fe}^{3+} \longrightarrow \mathrm{LO}_2^{\cdot} + \mathrm{H}^+ + \mathrm{Fe}^{2+}$$
$$\mathrm{LOOH} + \mathrm{Fe}^{2+} \longrightarrow \mathrm{LO}^{\cdot} + \mathrm{OH}^- + \mathrm{Fe}^{3+}$$

It has been suggested that the reduced form of iron (Fe^{2+}) can also initiate lipid peroxidation (Smith & Dunkely, 1962). The suggestion that the indicators of primary oxidation cannot be taken to reflect the actual rate of primary oxidation is supported by the data on *p*-anisidine value and $E_{1\,\mathrm{cm}}^{1\%}$ at 269 nm. The observation of greater increases in *p*-anisidine value and $E_{1\,\mathrm{cm}}^{1\%}$ at 269 nm in systems with added Fe(III) palmitate as compared to that without added iron strongly suggests that the addition of Fe(III) palmitate increases the rate of formation of secondary products of oxidation. The greater increase in *p*-anisidine value and $E_{1\,\mathrm{cm}}^{1\%}$ at 269 nm in systems with added Fe(III) palmitate is due to the increased rates of formation of secondary oxidation products which form as a result of the breakdown of primary oxidation products, i.e. the peroxides. Increased rates of formation of secondary products may be attributed to (i) a faster rate of breakdown of peroxides or to (ii) the combined effect of a faster rate of formation of hydroperoxides coupled with an increased rate of breakdown of the hydroperoxides once formed. The data in these storage experiments do not allow us to distinguish between the actual rates of formation and destruction of peroxides. However, it is clear from the data that added iron palmitate has the effect of increasing the rate of formation of secondary products of oxidation.

CONCLUSION

The results showed that the addition of Fe(III) palmitate increased the rate of formation of secondary oxidation products in RBD palm oil. In addition, they showed that the evaluation of the degree of oxidation in oils with added iron palmitate, which is based on indicators of primary oxidation alone, may lead to inaccurate conclusions about the effect of added iron on the rate of oxidation of oil.

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