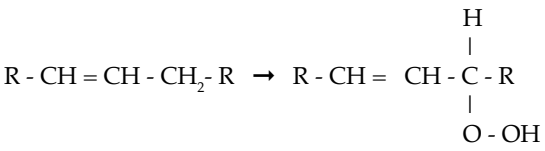
Feature Article

Mongana Basics: Part 17 - Oxidation of Oil**

N Ravi Menon*

SIMPLIFIED THEORY

Olefinic chains in contact with air undergo a slow oxidation process (becoming rancid). The primary degree of this deterioration is the formation of hydroperoxides which attach themselves to the carbon atom adjacent to the double bond:



The early part of the reaction (A – B) is autocatalytic and may be represented graphically in *Figure 1*.

Only the first part of the curve is representative of the degree of oxidation of the material.

The determination of peroxide value has made it possible to study the stability of palm oil in relation to oxidation. However, the correlation between peroxide value and the degree of oxidation of the oil applies only in the early stage of oxidation because peroxides are very unstable (decomposition accompanied by release of energy).

PEROXIDE VALUE OF FRESHLY PREPARED OIL

All results are expressed as milliequivalents per kilogramme of the material. A peroxide value of 1 corresponds to 0.008 g of oxygen per kg.

The determination procedure gives an accuracy of 0.5 peroxide value. It should be noted that the Wheeler value is expressed as millimoles of peroxide per kilogramme (a wheeler value of 1 corresponds to 0.016 g of oxygen per kilogramme of material).

Several other methods of assessing the oxidation status of oil have been tried, among which only the thiobarbituric acid (TBA) method deserves further consideration. The procedure is however difficult to use and less straightforward than the iodometric method which is the popular method currently used by the industry.

The pattern of oxidation as assessed by the determination of peroxide value according to Wheeler is not identical to that obtained by the TBA method as shown by the oxidation curves of oil in the course of time as illustrated in *Figure 2*.

Oil in the fresh fruit has a peroxide value lower than 1. After extraction under

* *Malaysian Palm Oil Board, P. O. Box 10620, 50720 Kuala Lumpur, Malaysia.*

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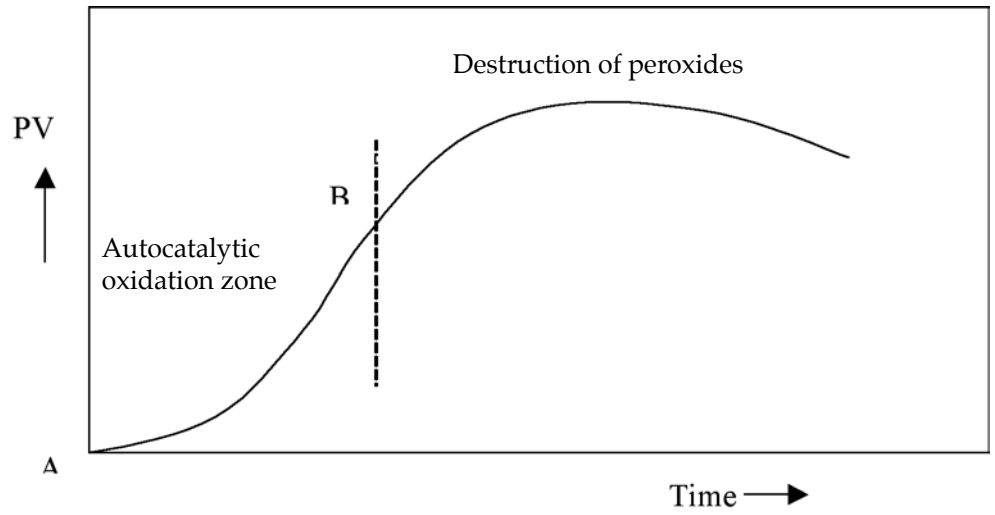

Figure 1. The autocatalytic oxidation zone.

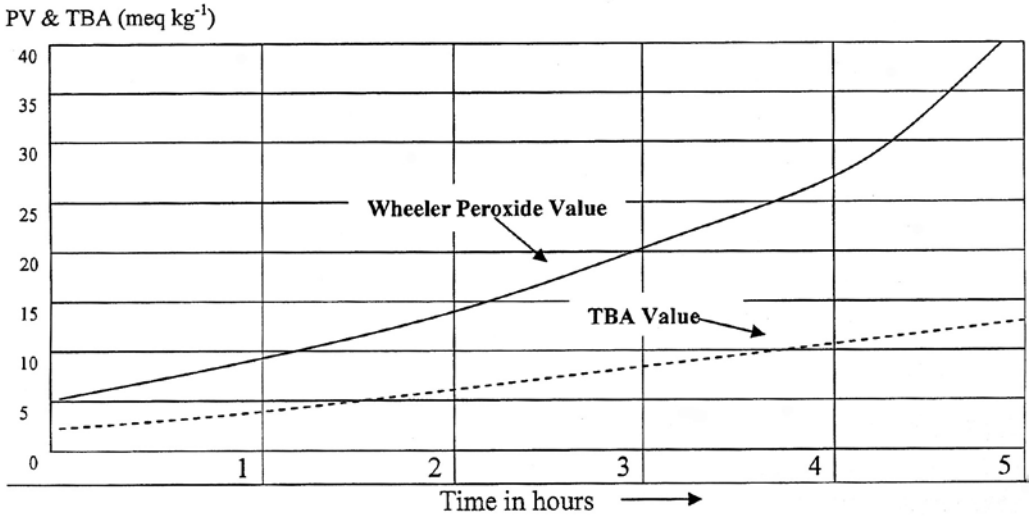

Figure 2. Oxidation at 105°C of oil as measured by the peroxide value and thiobarbituric acid (TBA) values (meq kg^{-1}).

favourable conditions, the peroxide value is lower than 2. After storage in the country of production, handling and transport to Europe or America, the peroxide value ranges between 1 and 12. Of the samples drawn ex-ship's tanks in the port of discharge, 81% had a peroxide value of 5 or lower. No specifications as regards peroxide value of palm oil have been published in the technical literature. However, Hadorn and Jungkuntz recommend the following general specifications for oil:

Peroxide value between 0 & 3 = the oil can be stored.
Peroxide value between 3 & 6 = the oil can be stored for a limited period.
Peroxide value between 7 & 10 = the oil must be refined without delay.

An exception is made for olive oil for which a peroxide value of 8 to 10 is considered normal.

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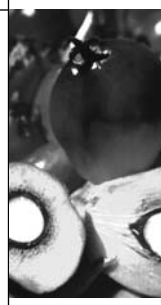

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The increase in peroxide value of oil in bulk of large tonnage is perceptible only after several weeks of storage. Small amounts of oil, for which the ratio of surface to volume is of consequence, show a sharper increase in peroxide value. *Table 1* shows the pattern of oxidation on samples of approximately 100 g stored in 250 ml beakers at ambient temperature. In order to shorten the time of recording, that is to accelerate the oxidation process, a storage temperature of 60°C is normally used. At that temperature, the oxidation process is about eight times faster.

FACTORS AFFECTING PEROXIDE VALUE

Laboratory Tests

The following factors were studied:

- drying;
- heating under inert atmosphere;
- washing;
- de-gumming;
- carotene content; and
- initial peroxide value.

The experimental procedure consists in the determination at periodical intervals of the peroxide value of oil stored at 60°C. In some series of experiments, the samples were kept in darkness as carotene exerts a pro-oxidizing effect in the presence of light and an antioxidizing influence in darkness. Numerous treatments were applied. The conclusion was reached that they are very seldom beneficial to the storage of oil and that in certain instances, they are markedly deleterious. The washing with surfactant for instance (quaternary ammonium and various alkyl-aryl-sulphonates) is clearly unsuitable.

Only the storage in sealed tubes of oil with or without prior treatment leads to a remarkable stability as regards peroxide value. A marked bleaching (destruction of the carotene) is however apparent.

Table 2 gives a summary of the results obtained through the following treatments:

- control;
- oil dried during 1 min at 110°C;
- oil stirred with water in a turbo mixer for 15 s at 50°C;
- oil stirred as in treatment No. 3 but solution of A.A.S. (alkyl-aryl-sulphate) in a turbo mixer; and
- oil treated as in treatment No. 5 but subsequently dried.

Washing with citric acid and sodium ethylene-diamine-tetracetate does not lead to improve keep ability.

TABLE 1. PEROXIDE VALUE OF OIL STORED AT AMBIENT TEMPERATURE

Type of oil	Time (days)				
	0	6	27	53	71
Crude oil obtained by centrifugal extraction	0.7	1.1	1.0	1.9	2.0
Crude oil extracted by pressing	1.3	6.7	13.1	12.9	17.1
Water washed crude oil	1.1	2.1	4.3	3.0	4.2
Oil extracted with trichloroethylene	1.3	2.4	3.5	3.8	3.3
Oil extracted with xylene	1.1	1.9	2.3	2.1	3.0

Note: Crude oil extracted by pressing contains a large amount of water, impurities and ferments during storage.

TABLE 2. PEROXIDE VALUE AND COLOUR OF TREATED OIL STORAGE AT 60°C

Day of storage	Treatment					
	1	2	3	4	5	6
Initially	1.7	3.2	-	3.1	2.2	3.2
4 days (open container)	7.3	12.0	10.2	-	9.0	8.2
14 days (open container)	37.5	39.2	40.5	-	56.0	41.1
5 days in sealed container	1.1	1.1	1.4	0.7	1.0	1.2
	Colour expressed as optical density					
Initially	87	91	90	86	89	87
4 days	81	78	79	70	75	76
10 days	49	28	20	5	7	2.6

The drying of oil, its effect on peroxide value and on the ability to withstand storage have been studied with the Swift apparatus using samples containing 0.3% moisture. Air insufflations at 80°C, 100°C, 120°C and 140°C was used.

In all cases, air bubbling was continued until moisture content had been reduced to 0.05%. As shown in *Table 3,* the drying induces an increase in peroxide value but very small magnitude.

Although peroxide value remains fairly steady during drying, it was necessary, however to ascertain whether the drying did not make the oil susceptible to post oxidation during subsequent storage, that is if oxidation did not become prevalent for the treated samples. The storage of oil in thin layer in petri dishes showed no difference between the treated and untreated oil. On the contrary, the partial oxidation sustained by oil during drying appears to slow down further oxidation to the point that the untreated oil eventually catches up with the oxidized oil (*Table 4).*

Similar experiments were carried out at various temperatures with identical results. It may be concluded therefrom that the drying of oil by air bubbling, although detrimental a priori, does not impair the quality of oil in the course of storage. The point was important because a deterioration would have prevented the used of air drying and would have made it mandatory to use vacuum drying for instance.

Absorption of Air

Whilst very little oxygen is taken up at low temperature during contact between oil and air, a marked absorption of the latter takes place. The removal of air from oil at high temperature enables the absorbed constituents to be titrated. The rate of absorption can be measured in the Warburg apparatus. In the course of an ageing test over 50 hr at 80°C, oil takes up a little more than 100% of its volume, therefore about 0.1% of its weight. Only a fraction of the oxygen of the absorbed air is combined in the form of peroxide. *Table 5* give values of the following against time: peroxide value, volume of absorbed oxygen, the corresponding milli equivalent value of oxygen per kg of oil and the ratio of combined to absorbed oxygen (temperature 80°C).

De-gumming appears to intensify the increase of peroxide value during storage.

TABLE 3. EVOLUTION OF PEROXIDE VALUE AS A RESULT OF DRYING WITH AIR

Time	80°C		100°C		120°C		140°C	
	% moisture	Peroxide value	% moisture	Peroxide value	% moisture	Peroxide value	% moisture	Peroxide value
Initial	0.30	3.5	0.30	3.5	0.30	3.5	0.30	3.5
30 s	-	-	-	-	-	-	0.13	3.9
60 s	-	-	-	-	0.09	4.0	0.08	4.0
2 min	-	-	-	-	0.04	4.2	-	-
3 min	-	-	-	-	0.03	4.0	-	-
4 min	-	-	-	-	0.01	4.5	-	-
5 min	0.19	3.5	0.04	4.5	-	-	-	-
10 min	0.04	3.6	0.02	4.9	-	-	-	-
15 min	0.07	4.0	0.02	5.0	-	-	-	-
20 min	0.01	4.1	0.02	5.9	-	-	-	-

TABLE 4. STORAGE OF DRY OIL AT 60°C

Time lapse	Initial oil	Oil dried at			
		80°C	100°C	120°C	140°C
Moisture content	0.30	0.03	0.05	0.05	0.06
Initial peroxide value	3.5	4.1	5.0	4.4	4.4
After 3 days	5.5	6.0	6.5	6.1	6.3
After 8 days	7.7	8.0	9.2	9.1	8.3
After 17 days	13.0	12.8	13.0	12.8	14.0

On the other hand, oil containing added mucilages shows improved stability.

Heating in an inert atmosphere reduces the peroxide value of oil. From an initial level of 8.5, peroxide value decreases to 5.6 after 30 min of heating at 115°C and 1.3 if 130°C is used. A portion of carotene is destroyed by the treatment (10% to 12%).

The effect of iron, whether in the form of metal or of soap is hardly noticeable or non-existent.

The initial peroxide value governs the pattern of the oxidation curve. The fact has been observed on sample of oil of vary different peroxide values as has been recorded in technical publications. The results of a few observations made on samples of oil with low peroxide value are collected in *Table 6.*

Industrial Trials

The washing of oil with detergents has been used extensively. This technique had

TABLE 5. ABSORPTION OF OXYGEN DURING STORAGE

Time (hr)	Initial peroxide value	Peroxide value increase	Volume of oxygen absorbed per unit volume oil	Milliequivalents of absorbed oxygen	Ratio of fixed to absorbed oxygen
0	6.7	0	0	0	-
6	10.9	3.2	0.81	57.2	16%
21 – 25	14.5	7.8	0.96	79.0	18%
47 – 49	24.7	18.0	1.07	88.8	20%

TABLE 6. EVOLUTION OF PEROXIDE VALUE AS A FUNCTION OF THE INITIAL PEROXIDE VALUE

Initial PV	After 4 days	After 8 days	After 17 days	% FFA	mg of carotene for 100 g of oil
0.3	0.9	1.5	5.8	1.1	34.6
0.5	0.9	2.3	5.0	2.6	40.1
3.6	9.1	12.7	13.4	5.1	65.5
4.2	11.6	14.0	10.4	1.3	37.6
4.8	10.9	14.8	16.1	1.3	39.4
5.1	13.2	19.2	21.5	1.0	61.8

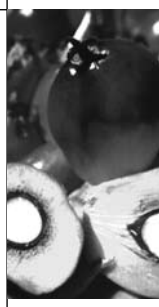
Note: PV – peroxide value. FFA – free fatty acid.

been adopted as a result of the beneficial affect reported by users, particularly in the USA, Following a large number of shipments of Congo oil to Europe and the USA. has been possible to establish that the use of detergents made the oil sensitive to oxidation. No difference in peroxide value is detectable immediately after the treatment but after a few weeks, the oxidation of oil increases sharply that seems to tend towards limit of 12 to 15. The washing of oil with detergents has consequently been stopped in Africa but still prevails in the USA for oil used in metallurgy.

NATURE OF THE PEROXIDES OF PALM OIL

The study required complex techniques. It was not our intention to investigate the composition of the peroxides formed in the course of storage. We proposed however, to find out whether the peroxides of palm oil were peroxides of the unsaturated fatty acids or carotene. With this objective in view, the peroxides were isolated by chromatography. The technique was tested on groundnut oil that applied to palm oil.

The use of a solution of oil in chloroform on a Brockmann alumina column and elution with chloroform lead to no retention of peroxide and hardly any of coloured substances. On the other hand, when a solution in petroleum ether is used, the peroxide value of the elute is nil and various coloured bands appear. Elution with chloroform, after drying under nitrogen, of these coloured bands leads to the observation that none of these bands has a



special status as regards peroxide retention. The distribution appears to be uniform.

The use of Filtrol instead of alumina leads to marked retention with petroleum ether solution and elution with chloroform. The retention is less intense for the chloroformic solution and elution by the same solvent.

In order to separate the carotenes from the peroxides, use has been therefore made of the petroleum ether solution, which removed the corotenoids leaving the peroxides, the latter being recovered by successive elutions with chloroform.

Table 7 gives the results of the technique applied to palm oil with a peroxide value of 24.7 and ground-nut oil with a peroxide value of 21.8.

In the case of palm oil, the carotenoid bands are practically eliminated by the petroleum ether. In the case of ground-nut oil, the yellow band is eluted in the three fraction. The carotenoid content of the various fractions was determined through measurement of the optical density.

Table 8 gives the results of this test and *Figure 3* gives the spectrum of the first four fractions.

TABLE 7. PEROXIDE VALUE OF DIFFERENT FRACTIONS

	Petroleum ether	Chloroform				
	1	**2**	**3**	**4**	**5**	**Total**
Palm oil	0	20.2	0.7	3.2	0.7	25.5
Ground-nut oil	0	16.9	3.2	1.2	1.0	22.4

TABLE 8. PEROXIDE VALUE AND OPTICAL DENSITY OF VARIOUS FRACTIONS

Type of solvent	**Petroleum ether**				**$CHCl_3$**		
Fraction of solvent	1	2	3	4	5	6	7
Peroxide value	0	5.7	5.1	2.3	2.3	5.2	0.6
Optical density at 420 μm	16.5	10.2	01.5	0.4	1.7	5.2	0.6

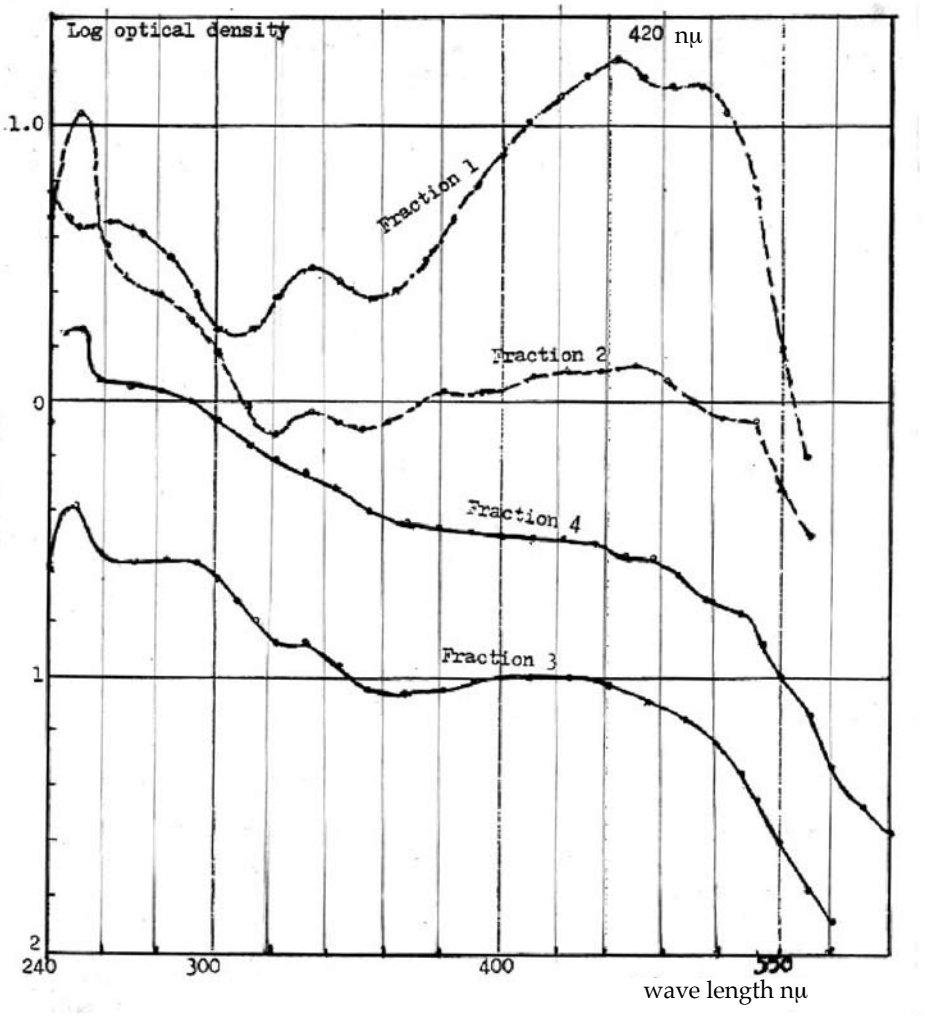


Figure 3. Absorption spectrum of fraction of palm oil of 24.7 peroxide value obtained by chromatography on Brockmann alumina using petroleum ether as eluting medium.

It may be concluded that although the elution of peroxides overlaps that of the various coloured bands of the oil, it is however, possible to modify these overlaps by suitable selection of the eluting solvents. There existing, therefore, a strong probability that peroxide which do not give the typical spectrophotometric curve are not proxides of carotenoids.

The similarity between the results obtained for palm oil and ground-nut oil respectively makes it possible to be identical in both cases. This leads to the conclusion that the peroxides of palm oil are indeed derived from fatty acids and not from carotene.