DETERMINATION OF FLAVOUR STABILITY OF BLENDED COOKING OILS MADE WITH PALM OIL AND RICE BRAN OIL

Keywords: Flavour stability; Cooking oil; Palm oil; Rice bran oil

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The flavour stability of cooking oils made with palm oil and rice bran oil was assessed by gas chromatography, Rancimat, and peroxide value during storage. Double fractionated palm olein and blended oils containing more than 70% double fractionated palm olein failed in the cold test. Double fractionated palm olein was shown to be the most stable to oxidative deterioration during storage among the oil samples tested. The more super olein incorporated in blended oil, the less storage deterioration was observed in terms of development of volatile compounds, disappearance of headspace oxygen, hydrogen evolution, induction period and peroxide value. With all blending ratios tested, the analytical methods applied correlated very well with each other, with correlation coefficients above 0.92. It was shown that any one of the determinations (formation of volatile compounds, oxygen disappearance, hydrogen evolution, induction period or peroxide value) could be used for the determination of flavour stability of blended cooking oils made with double fractionated palm olein and rice bran oil.

INTRODUCTION

One of the most important qualities of cooking oil is flavour stability, which is greatly affected by the characteristics of individual oils and minor components present in them (Mounts, 1985; Min and Jung, 1989).

It is well known that blending may improve the physicochemical properties and stability of individual oils, and in fact huge quantities of blended oil are used for frying, cooking and manufacturing of salad dressings (Yoon *et al.*, 1986).

There have been many assessments of analytical methods for the determination of flavour stability of oils, and the subject has been reviewed (Min and Kim, 1985; Gray, 1985).

This paper reports i) the gas chromatographic and electrical determination of flavour stability of super olein, rice bran oil, and their blends, and ii) the effect of blending on the flavour stability of oils.

MATERIALS AND METHODS

Materials

Refined, bleached, deodorized (RBD) and winterized rice bran oil and RBD double fractionated palm olein (called super olein hereafter) were purchased from local markets in Korea and Malaysia, respectively. The two oils were blended in the desired ratios by volume with agitation under nitrogen. The blends studied were a mixture of 30% super olein and 70% rice bran oil (called 30% super olein hereafter), and a mixture of 70% super olein and 30% rice bran oil (called 70% super olein hereafter). All reagents used were of analytical grade unless otherwise specified.

Storage of Oil Samples

To test the effects of storage conditions on flavour stability super olein, rice bran oil, and the two blends were stored and analyzed. Fifteen grams of experimental sample was transferred into a 30 ml serum bottle and tightly sealed with a Teflon-coated rubber septum and an aluminum cap. The samples were stored at 60°C in a dark forced-draft air-oven (Yoon *et al.*, 1988).

Analytical Methods

AOCS methods (American Oil Chemists' Society, 1980) were used to determine acid value, iodine value, saponification value, peroxide value, refractive index at 25°C, phosphorus content, unsaponifiable matter and cloud point, and for the cold test at 0°C. Colour was measured with a Lovibond Tintometer using a 5 1/2 inch cell. Sterol content in oil was determined spectroscopically by the Liebermann-Burchard method using cholesterol as a reference material (Bartos and Pesez, 1976). Tocopherol content was determined by the Emmerie-Engel method (Tsen, 1961). Flavour stability of oil was determined by measuring volatile compound formation, hydrogen evolution and molecular oxygen disappearance in the headspace of oil in sealed, air-tight bottles. The gas chromatograph used for volatile compounds, hydrogen evolution and oxygen content measurement was a Hewlett-Packard GC HP-5880. The analytical method used was substantially the same as described in Yoon *et al.* (1988). Induction period was measured using a Rancimat E617 (Metrohm AG) at 130°C with an air flow rate of 20 l/hr (Laubli and Bruttel, 1986).

RESULT AND DISCUSSION

Characterization of Oil Samples

Several characteristics of super olein and rice bran oil are shown in *Table 1*. The iodine value, saponification value and refractive index of super olein and rice bran oil were within the normal range. The acid value and peroxide value of super olein were higher than those of rice bran oil and fresh super olein. This was considered to be due to possible lipid oxidation during transportation and storage of the super olein. Rice bran oil was darker in colour than super olein. The phosphorus content of super olein was higher than that of rice bran oil, whereas the contents of unsaponifiable matter, sterols and tocopherols in super olein were less than in rice bran oil. The cloud point of super olein was obviously higher than that of rice bran oil. Super olein did not pass the cold test at 0°C, but rice bran oil did, remaining clear even after six hours. The differences in cloud point and cold test results were attributed to differences in fatty acid composition, molecular species of triglycerides and so forth (Yoon *et al.*, 1987).

Effects of Blending and Storage Time on Flavour Stability

The changes in total volatile compounds content in the headspace of four oil samples during storage are shown in *Figure 1*. Volatile compounds in the headspace of rice bran oil increased from 28 000 to 530 000 units during 20 days' storage, whereas with

TABLE 1. CHARACTERISTICS OF SUPER OLEIN AND RICE BRAN OIL

Parameter		Super Olein	Rice Bran Oil
Acid Value		0.34	0.04
Iodine Value		59.3	106.5
Saponification Value		204	187
Peroxide Value		1.0	0.8
Refractive Index		1.4655	1.4705
Colour	Red	3.1	4.3
	Yellow	30	40
Phosphorus, ppm		11.9	5.7
Unsaponifiables, %		0.3	3.1
Sterols, ppm		3800	15000
Tocopherols, ppm		870	950
Cloud Point, °C		3.6	-5
Cold Test		Not Passed	Passed

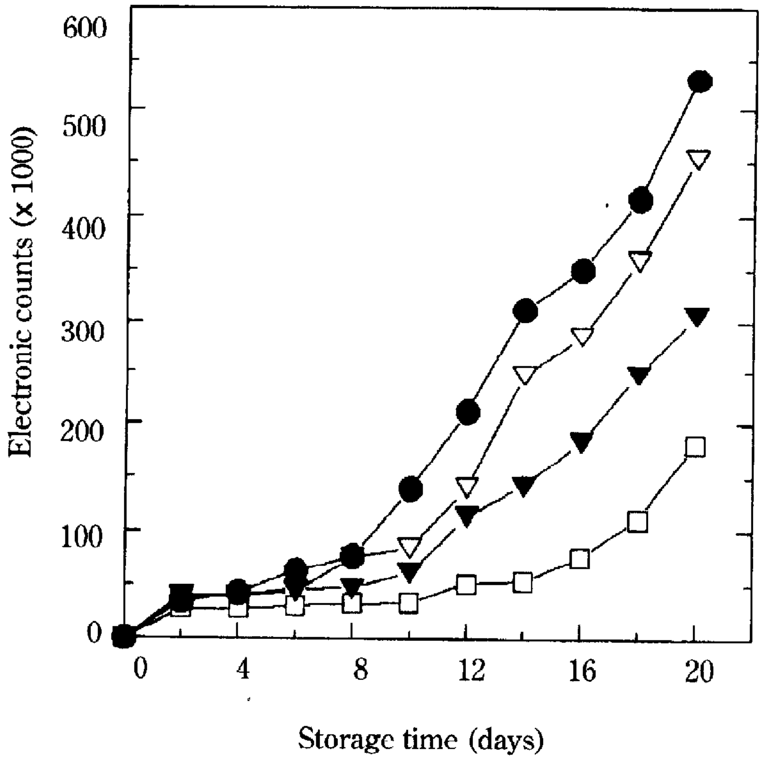

Figure 1. Effect of Storage Time on Formation of Volatile Compounds in Headspace of Oils.
●, Rice Bran; ▽, 30% Super Olein and 70% Rice Bran Oil;
▼, 70% Super Olein and 30% Rice Bran Oil;
□, Super Olein.

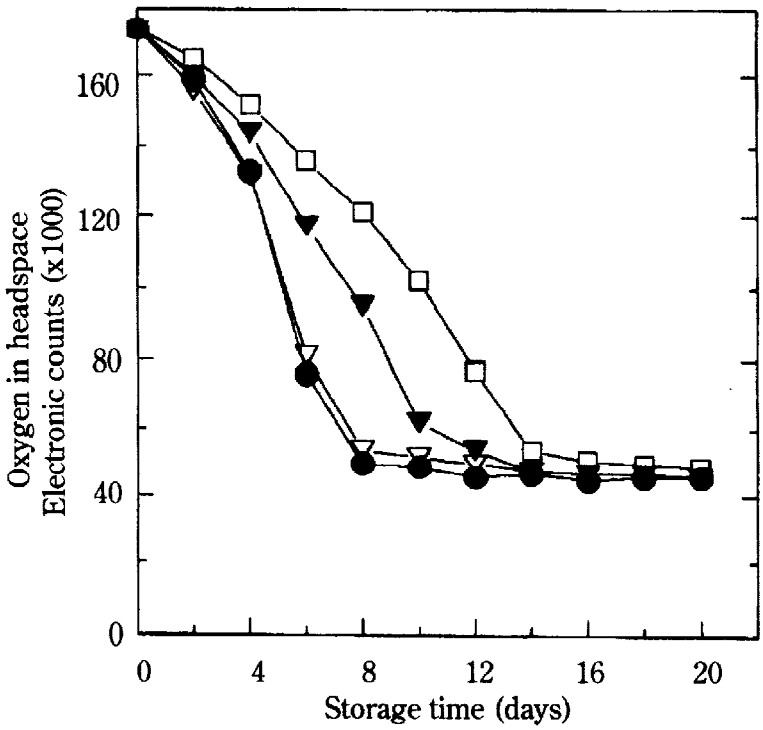

Figure 2. Effect of Storage Time on Oxygen Content in Headspace of Oils.
●, Rice Bran; ▽, 30% Super Olein and 70% Rice Bran Oil; ▼, 70% Super Olein and 30% Rice Bran Oil; □, Super Olein.

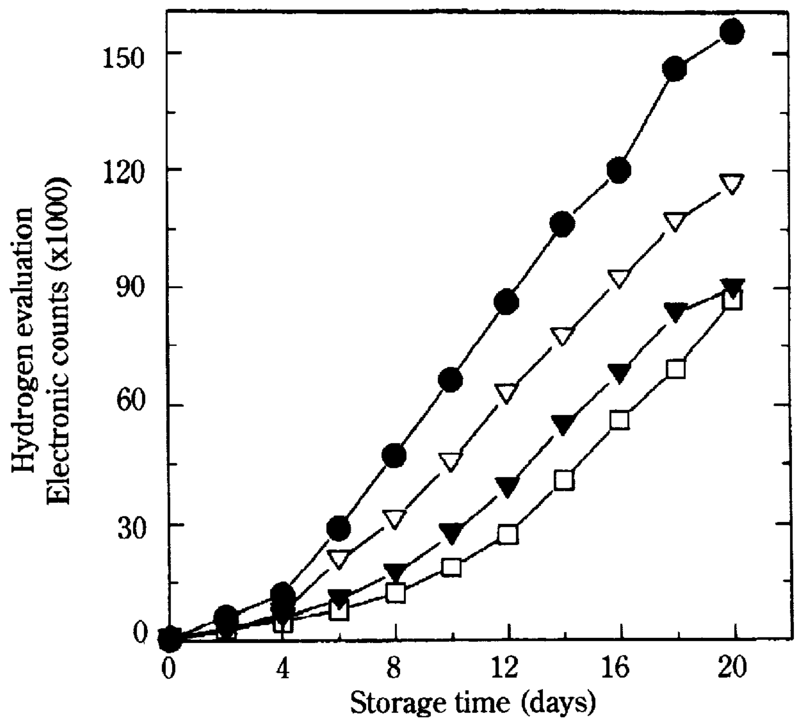

Figure 3. Effect of Storage Time on Hydrogen Content in Headspace of Oils.
●, Rice Bran; ▽, 30% Super Olein and 70% Rice Bran Oil; ▼, 70% Super Olein and 30% Rice Bran Oil; □, Super Olein.

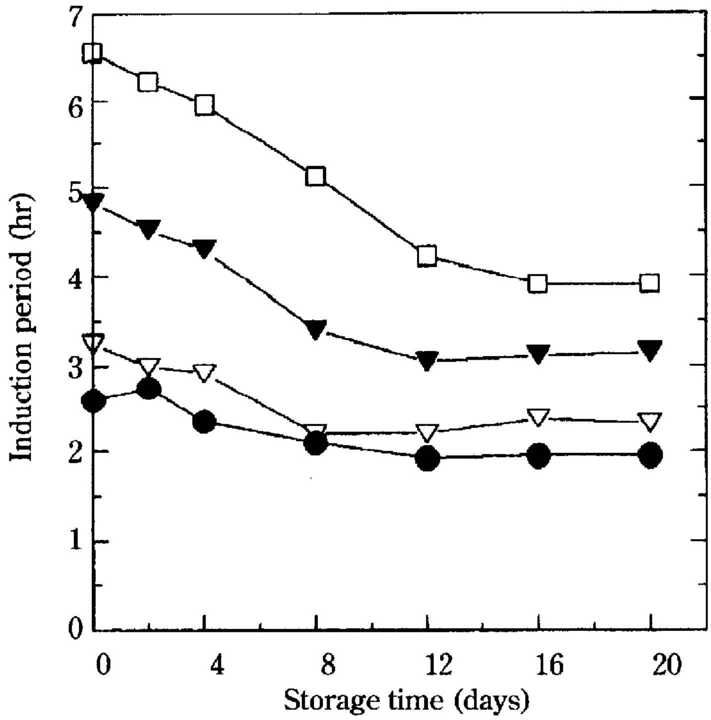

Figure 4. Effect of Storage Time on Induction Period of Oils.
●, Rice Bran; ▽, 30% Super Olein and 70% Rice Bran Oil; ▼, 70% Super Olein and 30% Rice Bran Oil; □, Super Olein.

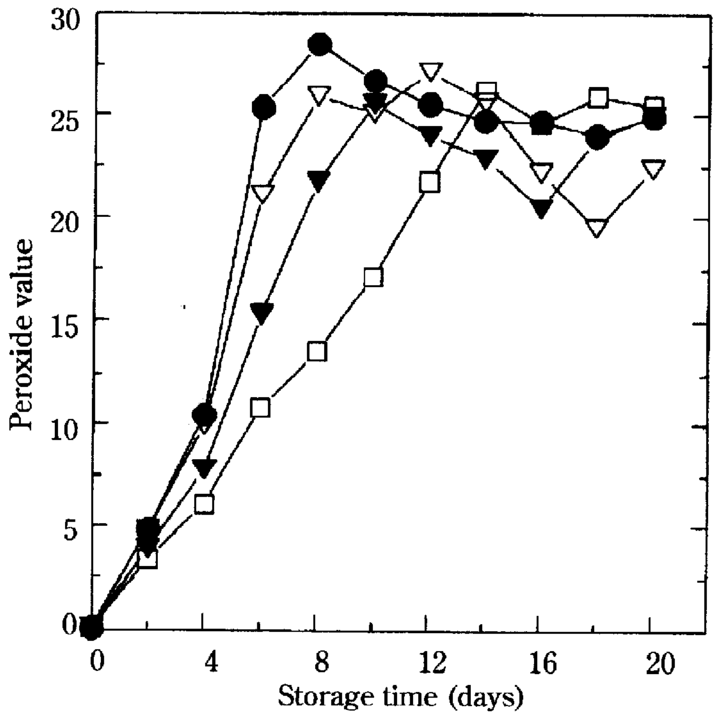

Figure 5. Effect of Storage Time on Peroxide Value of Oils.
●, Rice Bran; ▽, 30% Super Olein and 70% Rice Bran Oil; ▼, 70% Super Olein and 30% Rice Bran Oil; □, Super Olein.

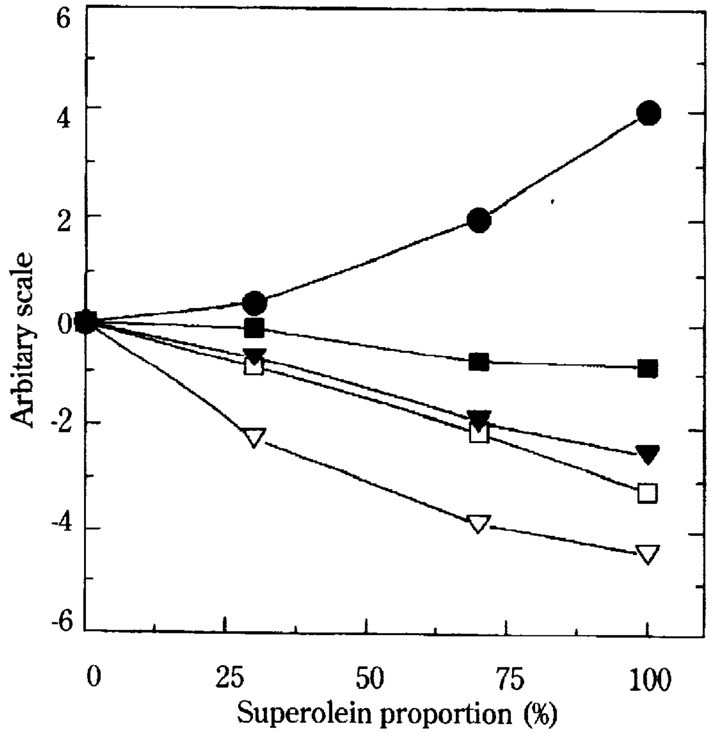

Figure 6. Effect of Proportion of Super Olein in Blended Oil on Deterioration Rate of Flavour Stability. □, Formation of Volatile Compounds; ■, Oxygen Disappearance; ▽, Hydrogen Evolution; ●, Induction Period; ▼, Peroxide Value.

super olein they increase to 181 000 units in a same storage time. Super olein showed the best flavour stability by this criterion, and 70% super olein, 30% super olein and rice bran oil showed less stability in decreasing order. Thus it was clearly shown that the more super olein in the blend, the less volatile compounds were formed. It is reported that flavour quality shows a very good inverse correlation with the content of total volatile compounds, which consist of butane, pentane, propanal and hexanal resulting from lipid oxidation (Frankel, 1985). It is also reported that as the volatile compounds in oil increase, the flavour quality declines (Yoon *et al.*, 1985).

Oxygen content in the headspace decreased rapidly in the case of rice bran oil, and with 30% super olein, 70% super olein and super olein it decreased less rapidly in order, as shown in *Figure 2*. It took eight days to fall to 28% of initial oxygen content with rice bran oil compared with about fourteen days in the case of super olein. Since the volatile compounds in the headspace increased and oxygen content decreased with storage time, a linear regression equation was developed between volatile compounds and oxygen content in the headspace. The correlation coefficient between the rate of formation of volatile compounds in the initiation stage of lipid oxidation and the decrease in molecular oxygen was 0.9768, which was considered excellent (*Table 2*). This high positive correlation strongly suggests that the volatile compounds are formed by the reaction between oil and oxygen, as was expected.

The quantitative effect of storage time on hydrogen evolution into the headspace is shown in *Figure 3*. It is well known that molecular hydrogen is released from the carboxyl group of fatty acids in the initiation step of lipid autoxidation, which results in the formation of free fatty radicals (Frankel, 1985). Subsequently, the peroxy radical abstracts a hydrogen from another unsaturated fatty acid in the propagation step. The hydrogen content in the headspace appeared less than that of volatile compounds, since hydrogen is released from fatty acids only in the initiation stage of lipid oxidation. More hydrogen was evolved from the more unsaturated rice bran oil than from the less unsaturated super olein (*Figure 3*).

The induction periods of the oils were determined graphically by the tangent method, and are shown in *Figure 4*. Super olein showed the highest initial stability of 6.6 h, and this reached about 4 h after 20 days' storage, whereas rice bran oil had an initial induction period of 2.6 h and a final induction period of two hours. Even though the initial and final induction periods were higher in super olein than in rice bran oil and the two blends, the decrease in the induction period of super olein was the largest among the oils tested.

The changes in the peroxide values of oil samples during storage are illustrated in *Figure 5*. The peroxide value of rice bran oil reached its maximum value of 28 after eight days' storage, whereas that of super olein reached its maximum of 27 after 14 days' storage. The rate of increase of peroxide value fell as the proportion of super olein in the blended oils increased.

The rates of formation of volatile compounds, of hydrogen evolution and of disappearance of oxygen in the headspace, as well as the rates of change in induction period and peroxide value are substantially dependent upon the degree of unsaturation of the fatty acids of an oil, and the contents of minor compounds and antioxidants, *etc.* (Jung *et al.*, 1989). The higher the content of unsaturated fatty acids in oils, the faster the oils are oxidized. Accordingly, rice bran oil was oxidized faster than super olein (which resulted in faster evolution of volatile compounds and hydrogen, faster disappearance of oxygen, faster decrease of induction period, and faster increase of peroxide value in rice bran oil), although the two oils have similar contents of natural antioxidants/tocopherols.

To determine the effect of blending of super olein on the deterioration of rice bran oil, the formation of volatile compounds, oxygen disappearance, hydrogen evolution, decrease in induction period value were plotted against proportion of super olein in the blended oils (*Figure 6*). As more super olein was incorporated into the blend the rates of formation of volatile compounds, of oxygen disappearance, of hydrogen evolution and of decrease in peroxide value all fell. The reverse trend, however, was observed in regard to decrease in induction period. Thus, it was demonstrated that super olein had the highest and rice bran oil the lowest flavour stability during storage. The more super olein was incorporated in a blended oil, the higher was the flavour stability observed.

The correlation coefficients between each pair of the analytical values shown in *Figure 2* were ob-

TABLE 2. CORRELATION COEFFICIENTS BETWEEN DETERIORATION RATES OF BLENDED OIL DETERMINED BY DIFFERENT ANALYTICAL METHODS

	Volatiles Formation	**Oxygen Dissapearence**	**Hydrogen Evolution**	**Induction Period**	**Peroxide Value**
Volatiles Formation	–				
Oxygen Disappearance	0.9768	–			
Hydrogen Evolution	0.9469	0.9228	–		
Induction Period	-0.9875	-0.9518	-0.8873	–	
Peroxide Value	0.9953	0.9857	0.9649	-0.9685	–

tained by linear regression analysis and are given in *Table 2.* With all the blending ratios tested, the results of the different analytical methods correlated very well, with coefficients higher than 0.92, as between hydrogen evolution and induction period, where the coefficient was -0.8873. The highest coefficient observed was 0.9953, between formation of volatile compounds and peroxide value. Consequently any one of the five analytical methods tested could be used for the determination of flavour stability of super olein, rice bran oil, or blends made with them.

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