Evaluation of Physicochemical Changes in Cooking Oil During Heating

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Rice bran oil and double fractionated palm olein (DF palm olein) were heated at 180 C for 50 hr to measure lipid deterioration in the oils. Free fatty acid content of both oils increased during heating; however, iodine value and smoke point decreased. Solid fat contents of both oils were unaffected by heating time. Cloud point of rice bran oil was much lower than that of palm olein. Color of oils changed gradually to dark brown from light yellow with increased heating time. Absolute content of polyunsaturated fatty acid, such as linoleic acid, reduced more than that of monounsaturated fatty acid, such as oleic acid, in both oils. In both oils, iodine value correlated very well with linoleic acid content, with correlation coefficient higher than 0.96.

Cooking and salad oils are used widely in homes and institutionally. They constitute 34% of total fats and oil production in the United States (1). Cooking and salad oils are subdivided into salad dressings, household oils, and institutional and commercial frying fats and oils. Household cooking oils are mostly used for cooking and pan frying (2). During cooking or pan frying, various reactions such as oxidation, polymerization, pyrolysis and hydrolysis occur in the cooking oil itself; complicating reactions also occur between the oil and the food (3). Because of this complexity, no single method measures all qualities of oil.

Cooking oils have been known to have different characteristics in physical appearance from those of frying fats. In other words, the cooking oil should remain clear and transparent at room temperature and for some time even at or below 0 C during low temperature storage. In frying fats, clarity and transparency are not problems. Frying fats are absorbed in the food after cooking (4).

In recent years, production of palm oil, long used as a cooking oil in tropical and semitropical areas, has increased year by year. Total world production of palm oil reached 6.2 million metric tons (MT) in 1984 and is expected to continue upward (5). Although a few papers have reported use of palm oil as a cooking oil and frying medium (6,7), data about the characteristics of palm oil as a cooking oil are not readily available. The same is true for rice bran oil, one of the major cooking oils in Korea.

In this study, attempts were made to characterize palm oil liquid fraction and rice bran oil during heating by a combination of chemical, physical and chromatographic analyses and to evaluate analytical methods by correlation studies.

MATERIALS AND METHODS

Materials. Refined, bleached, deodorized (RBD) and winterized rice bran oil and DF palm olein were obtained from local refineries in Korea and Malaysia, respectively. All reagents were of analytical grade unless otherwise specified.

Heating and sampling method. Oil was heated at 180 C for 50 hr without forced agitation. Oil was not replenished after sampling. Heating and sampling methods were as described previously (8).

Analytical methods. Free fatty acid, iodine value, cold test, cloud and smoke points were determined according to AOCS methods (9). The color of oil was measured by Lovibond Tintometer (Model E) using a 5.25″ cell.

Solid fat content of the oil was measured by wide-line nuclear magnetic resonance (NMR) (Newport Analyzer, MK III A). Operation conditions of NMR were gate width, 1 1/2 Gauss; RF level, 45 μA; AF gain, 7.53; integrator, 32 sec.

Fatty acid and triglyceride compositions of oils were obtained by gas chromatography (GC) (10).

RESULTS AND DISCUSSION

Appearance of cooking oil. To maintain rice bran oil and

TABLE 1

Effect of Heating Time on Color of Rice Bran Oil and Double-Fractionated Palm Olein

	Rice bran oil			DF Palm olein		
Heating time (hr)	Red	Yellow	Blue	Red	Yellow	Blue
0	4.3	40	—[a]	3.1	30	—
10	10.3	60	—	7.2	40	—
20	17.1	60	—	10.2	40	—
30	23.0	20	2	17.0	20	—
40	36.0	30	4	30.0	20	2
50	38.0	30	5	32.4	25	2

[a]Not detected.

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palm oil clear and transparent at room temperature and at 5 C, commercial RBD rice bran oil was winterized at 4 C, and RBD palm oil was fractionated at 25 and 15 C in series. Solid fat content of fresh rice bran oil was nearly zero at 5 C, whereas that of DF palm olein was 11.8%. Solid fat was not detected in rice bran oil during heating, whereas 10.7% of solid fat was observed in DF palm olein at 5 C and 4.8% at 10 C. In both rice bran oil and DF palm olein the heating period did not significantly affect the solid fat content of either oil. Cloud points of fresh rice bran oil and DF palm olein were −5 C and 3.6 C, respectively. Rice bran oil passed a cold test and remained clear longer than 6 hr. DF palm olein, however, did not pass the cold test. The measurements of solid fat content, cloud point and cold test are principally based on detection of fat crystals solidified at low temperature. At a cloud point of 3.6 C, it was determined that the solid fat content of DF palm olein was higher than 11.8%.

In addition to transparency, color is an important physical characteristic of oil. It is reported that cooking and frying oils become darker as heating proceeds (11). The change from the light yellow of fresh oil through amber and reddish brown is the result of oxidation, as shown in Table 1. Rice bran oil showed more red, yellow and blue colors throughout the heating period than those of DF palm olein.

Physicochemical properties of cooking oil. Free fatty acid of fresh rice bran oil was 0.17 and reached 0.64 after 50 hr of heating, whereas that of DF palm olein increased from 0.23 to 1.30 in the same period (Fig. 1). The rate of free fatty acid increase of DF palm olein was higher by more than two times that of rice bran oil.

It is well known that the iodine value of oil decreases as heating time increases (3), and the same trend was observed in both rice bran oil and DF palm olein, as shown in Figure 2. Iodine values of fresh rice bran oil and DF palm olein were 101.2 and 61.5, respectivley. After 50 hr of heating, these values declined to 79% of initial values, to 80.4 and 48.6. The larger decrease of iodine value of rice bran oil compared to DF palm olein is thought to be because more double bonds are present in rice bran oil than in DF palm olein.

The smoke point of rice bran oil was found to be higher than that of DF palm olein throughout the heating period (Fig. 3). There was a progressive drop of smoke point in DF palm olein during heating, whereas in rice bran oil, smoke point decreased rapidly in the first 5 hr and slowly thereafter. The smoke point of oil is usually proportional to the concentration of accumulated low molecular weight decomposition products such as free fatty acids and partial glycerides. Hence, DF palm olein, which had a higher free fatty acid than rice bran oil, should have had a lower smoke point than that of rice bran oil.

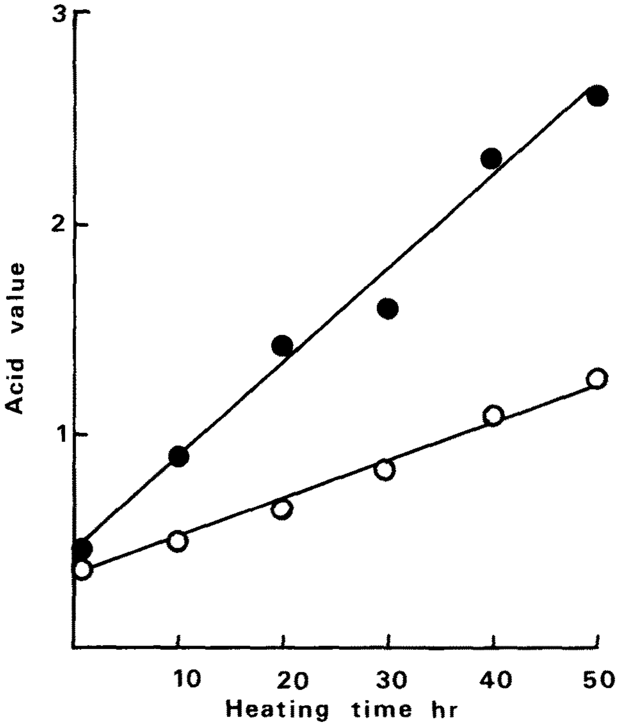

FIG. 1. Effect of heating time on free fatty acid of rice bran oil (○) and double-fractionated palm olein (●).

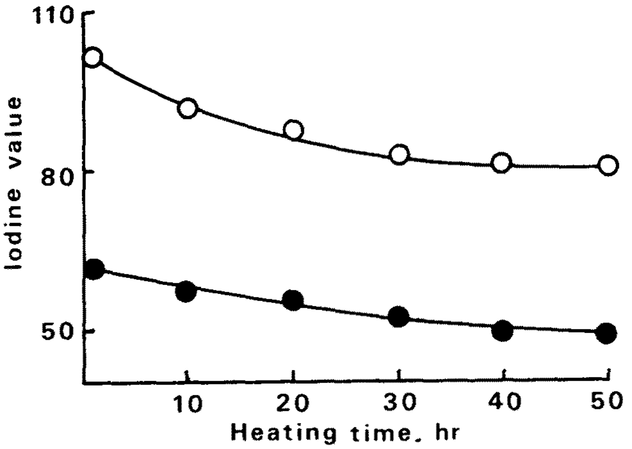

FIG. 2. Effect of heating time on iodine value of rice bran oil (○) and double-fractionated palm olein (●).

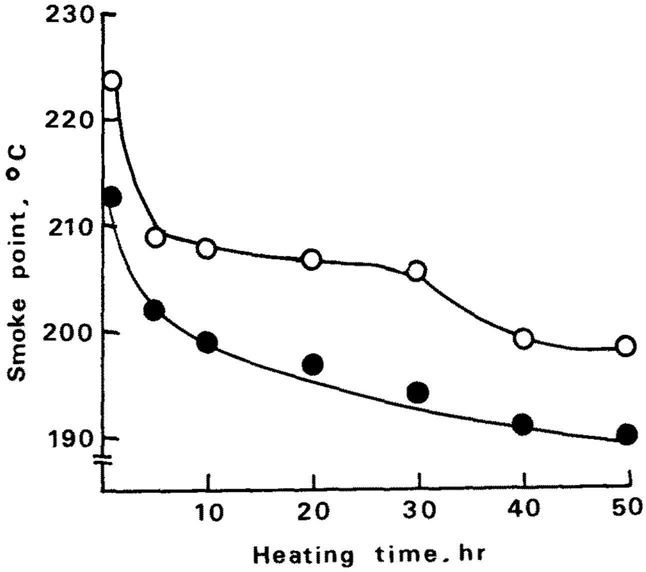

FIG. 3. Effect of heating time on smoke point of rice bran oil (○) and double-fractionated palm olein (●).

TABLE 2

Change of Fatty Acid Composition of Rice Bran Oil During Heating

Heating time (hr)	C_{14}	C_{16}	C_{18}	$C_{18:1}$	$C_{18:2}$	$C_{18:3}$	Total loss
0	0.3	18.7	1.6	44.6	33.1	1.4	0
10	0.3	18.7	1.6	43.3	29.9	1.2	5.0
20	0.3	18.7	1.6	42.2	26.4	1.0	9.8
30	0.3	18.7	1.6	42.2	24.0	0.7	12.5
40	0.3	18.7	1.6	40.8	20.5	0.5	17.6
50	0.3	18.7	1.6	33.9	19.2	0.5	19.8

TABLE 3

Change of Fatty Acid Composition of Double-Fractionated Palm Olein During Heating

Heating time (hr)	C_{12}	C_{14}	C_{16}	C_{18}	$C_{18:1}$	$C_{18:2}$	Total loss
0	0.2	1.2	37.4	4.0	44.8	11.8	0
10	0.2	1.2	37.4	4.0	42.9	10.1	4.2
20	0.2	1.2	37.4	4.0	41.4	8.5	7.3
30	0.2	1.2	37.4	4.0	39.6	7.0	10.6
40	0.2	1.2	37.4	4.0	36.6	4.8	15.8
50	0.2	1.2	37.4	4.0	36.6	4.5	16.1

Change in fatty acid and triglyceride composition. The changes in fatty acid composition of rice bran oil and DF palm olein were determined by GC. In both oils, there was an apparent increase in saturated fatty acid content and a decrease in polyenoic acid as heating time increased. In the actual sample, however, there was no such increase. It was therefore assumed that there was no change in the contents of saturated fatty acids such as palmitic and stearic acid. The fatty acid compositions of rice bran oil and DF palm olein recalculated are shown in Tables 2 and 3, respectively.

Palmitic and oleic acids initially constituted 18.7 and 44.6%, respectively, in fresh rice bran oil. After 50 hr of heating, GC showed that palmitic acid content apparently increased from 18.7 to 22.9%, and oleic acid also increased from 44.6 to 48.8%. It was assumed that palmitic acid content did not change during heating, and the actual content of oleic acid was calculated as 33.9%. Table 2 shows that polyenoic acids such as linoleic and linolenic acid decreased obviously during heating. Initial oleic (22%), linoleic (42%) and linolenic acid (64%) were shown to disappear, and 19.8% of mono- and polyenoic acids in rice bran oil disappear after 50 hr of heating. The data obtained from GC of DF palm olein were also corrected and are shown in Table 3. Oleic and linoleic acid percentages of 44.8 and 11.8 decreased to 36.6 and 4.5% after 50 hr of heating. Total loss of mono- and polyenoic acids in DF palm olein was 16.1%, which is lower than that of rice bran oil.

The changes of triglyceride composition of rice bran oil and DF palm olein are indicated in Tables 4 and 5. It is reported that major components of C50 triglyceride of rice bran oil are dipalmityloleyl glyceride, myristyldioleyl glyceride and dipalmityllinoleyl glyceride (12). The apparent increase of C50 triglyceride was therefore considered to be due primarily to the apparent increase of palmitic acid content. The major components of C52 triglyceride are palmityloleyllinoleyl, palmityldioleyl and palmityldilinoleyl glycerides, and the C52 decrease is the result of the significant decrease of linoeic acid in spite of the slight apparent increase of palmitic and oleic acid. The decrease of C54 triglyceride, which is composed of trioleyl, dioleyllinoleyl, oleyldilinoleyl and trilinoleyl glycerides, seems to be the result of linoleic acid content decrease. The C52 triglyceride content of DF palm olein decreased significantly (25.4%) with increased heating time. However, C50 and C54 contents did not decrease as much (11.5–13.5%) compared with that of C52 triglyceride. The major components of C52 triglyceride of palm oil have been identified as palmityllinoleylstearyl, dioleylpalmityl and palmityllinoleyloleyl glycerides (13). The decrease of C52 triglyceride content was attributed to the decrease of linoleic acid, which could compensate for the apparent increases of palmitic and oleic acid contents. In both C50 (primarily dipalmityloleyl and dipalmityllinoleyl glycerides) and C54 (primarily stearyllinoleyloleyl and trioleyl glycerides) triglycerides, the decrease could be explained similarly.

Relationships between analytical methods. The calculated correlation coefficients between every two analytical values are shown in Table 6. For the determination of degree of hydrolysis, free fatty acid content was determined. Iodine value and linoleic acid content were used as a measure of oxidation. The degree of pyrolysis could be predicted by the determination of smoke point. As mentioned earlier, the free

TABLE 4

Effect of Heating Time on Changes of Triglyceride Composition of Rice Bran Oil

Heating time (hr)	C_{42}	C_{44}	C_{46}	C_{48}	C_{50}	C_{52}	C_{54}	C_{56}	C_{58}	C_{60}
0	—[a]	—	—	4.2	8.6	34.6	46.2	3.5	1.1	0.9
10	—	—	—	4.5	9.1	32.8	42.1	5.1	1.4	1.3
20	—	—	—	5.9	9.6	30.3	37.0	5.5	1.6	1.9
30	—	—	—	5.8	9.5	30.1	36.3	6.1	1.7	2.2
50	4.4	3.5	3.6	6.8	9.9	28.1	32.1	7.2	1.9	2.5

[a] Not detected.

TABLE 5

Effect of Heating Time on Changes of Triglyceride Composition of Double-Fractionated Palm Olein

Heating time (hr)	C_{42}	C_{44}	C_{46}	C_{48}	C_{50}	C_{52}	C_{54}	C_{56}
0	—[a]	—	—	2.6	31.9	48.8	15.6	0.4
10	—	—	—	3.1	31.2	46.1	14.3	1.7
20	—	—	—	3.6	29.7	42.4	14.1	2.3
30	—	—	—	3.7	29.6	40.9	14.1	2.7
50	2.9	2.4	2.5	4.4	27.6	36.4	13.8	3.3

[a] Not detected.

TABLE 6

Correlation Coefficients Between Analytical Values of Rice Bran Oil and Double-Fractionated Palm Olein

	Rice bran oil			
Double fractionated palm olein	Free fatty acid	Iodine value[a]	Smoke point[a]	$C_{18:2}$ content[a]
Free fatty acid	—	0.8789	0.8431	0.6954
Iodine value[a]	0.9840	—	0.9462	0.9619
Smoke point[a]	0.8592	0.9472	—	0.9137
$C_{18:2}$ content[a]	0.9721	0.9979	0.9763	—

[a] Decreases of analytical values were correlated with others.

fatty acid increased with increased heating time, whereas iodine value, smoke point and linoleic acid content decreased.

All analytical methods given in Table 6 discriminated clearly between the two oils.

The correlation coefficients of every two analytical values were calculated and are shown in Table 6. The decrease of iodine value, smoke point and linoleic acid content was correlated with the increase of free fatty acid. For DF palm olein, linoleic acid content was shown to have correlation coefficients higher than 0.97 with other analytical values. In both oils, iodine value correlated well with linoleic acid content with correlation coefficients of 0.9979 in DF olein and 0.9619 in rice bran oil.

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