

A Comparative Study of Analytical Methods for Evaluation of Soybean Oil Quality

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This study is focused on the improvement of soybean oil stability by addition of additives and blending with more stable oils. The methods for evaluation of oil deterioration include changes in dielectric constant (DC), total polar (TP) compounds, refractive index (RF), fritest (FT), acid value (AV), iodine value (IV), anisidine value (AnV), carbonyl value (COV), viscosity and color. Statistically significant correlations were obtained between changes in DC and increase in the TP compounds, RF, FT, AV, AnV, COV and the decrease in the IV, respectively. Food oil sensor reading of 4 as a measure of changes in DC of oil has been suggested as the criterion of low oil quality. Consequently, the cut-off level for straight and blended soybean oils were thereby identified by using the above parameters.

KEY WORDS: Dielectric constant, oil deterioration, total polar compounds.

Soybean oil is an excellent dietary source of linoleic acid, the primary dietary essential fatty acid, and it also contains significant levels of tocopherols (1). However, a high level of linolenic acid (7–8%) is responsible for oxidation and flavor deterioration (2). Soybean oil is more susceptible to rancidity than most other oils such as rice, peanut, corn and sesame oils. Stability and quality of oil are of great interest to oil processors and commercial frying operators for good oil performance at elevated temperatures. Hydrogenation and addition of additives are the major treatments used to maintain oil quality during frying (3,4). Antioxidants under scrutiny in this study included propyl gallate (PG), butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), tertiary butylhydroquinone (TBHQ) and α -tocopherol (5,6). Maximum levels of antioxidants, alone or in combination, are 0.02% in fats and oils (7,8). Silicon oil, especially methyl or ethyl polysiloxanes with a viscosity of 1,000 to 100,000 centistokes are able to reduce or inhibit the smoking tendencies of vegetable oil at high temperatures. Five to twenty-five ppm of silicon oil added to vegetable oil gives a satisfactory effect on stabilization (9). Citric, phosphoric, ascorbic and tartaric acids are considered as synergists for antioxidants in vegetable oil (5). The proper formulation of antioxidants and synergists to achieve high oil stability might become an alternative to hydrogenation. Several methods were used by researchers to assess the oil quality. For instance, the measurements of dielectric constant, total polar compounds, fritest (10), refractive index, iodine value, carbonyl value, anisidine value, viscosity and color were often used as quality control tests for deep frying operation. The purpose of this

TABLE 1

Rancimat Values of Oils^a

Sample	Rancimat (hr)
Soybean oil (SBO)	2.7
Sesame oil (SSO)	20.6
Rice bran oil	3.7
Peanut oil	3.9
Corn oil	3.3
Palm olein (PO)	14.1
Lard olein	3.7
SBO + SSO (6:4)	9.0
SBO + PO (6:4)	6.2
SBO + ascorbyl palmitate (AP) (500)	6.4
SBO + TBHQ (120) + AP (500)	8.0
SBO + α -tocopherol (500) + AP (500)	6.7
SBO + PG (100) + AP (500)	7.5
SBO + rosemary (500) + AP (500)	6.8
SBO + lecithin (1000) + AP (500)	5.2

^aUnit of additives—ppm.

TABLE 2

Effect of Silicon Oil on Defoaming of Soybean Oil

Silicon oil (ppm)	Foam volume (mL)
0	111
1	102
2	98
5	88
6	92
10	96
15	94
20	90
25	88

study was to find out the relationship between each test method and in turn the cut-off value of each test for straight and blended soybean oils.

MATERIALS AND METHODS

Materials. RBD (refined, bleached and deodorized) soybean oil and palm olein were purchased from local markets. Unrefined sesame oil was made in our pilot plant. Antioxidants, including TBHQ, PG, BHA, BHT and lecithin; synergists including ascorbyl palmitate, ascorbic acid, tartaric acid, etc., were obtained from Fluka Co. (Buchs, Switzerland). Dimethyl polysiloxane was purchased from Sigma Chemical Co. (St. Louis, MO). α -Tocopherol was obtained from Eastern Kodak Co. (Rochester, NY). Rosemary concentrate was obtained from a local company.

Methods. A variety of combinations of antioxidants and synergists were added into soybean oil (SBO). Blended soybean oils such as SBO/palm olein and SBO/sesame oil were prepared in the ratio of 6:4. These oils were used to

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determine their respective oxidative stability during heating and frying.

Heating and frying tests. In the heating test, oil samples were heated to 185°C for eight hours each day. At the end of the day the heat was shut off and samples were taken. This procedure was repeated each day for 10 days. In the frying test, oil samples were heated to 185°C and temperature was allowed to rise to 190°C before the next batch was fried. The oil was sampled every 2 hr. This frying process was performed continuously for 8 hr/day on two consecutive days. Oil sampling (5 mL) from heating and frying tests were taken for analyses.

Analyses of oils. AOCS official methods were used for the determination of acid value (AV), iodine value (IV), refractive index (RF) and color. Fatty acid compositions were determined by gas liquid chromatography of methyl esters on a 30 m × 0.25 mm (ID) SP 2330 fused silica

capillary column. Methyl esters of fatty acids were prepared by refluxing the oil with 0.2% sodium methoxide and excess methanol for 1 hr. The changes in dielectric constant was measured with a Food Oil Sensor (Model NI-20 (Northern Instruments Corp., Lino Lakes, MN) (11) and expressed as Food Oil Sensor (FOS) readings. The percentage of total polar compounds was determined by using column chromatography (12). Anisidine value was measured by the method of List *et al.* (13). Fritest based on the reaction of oxidative products, i.e., aldehyde with alkali solution, was measured by spectrophotometer at 520 nm (10). Carbonyl compounds were estimated according to Bhalerao *et al.* (14). Viscosity was determined by using VT-03 portable viscometer (Rion Co., Tokyo, Japan). The induction periods of a variety of oils were measured by the Rancimat at 120°C (15).

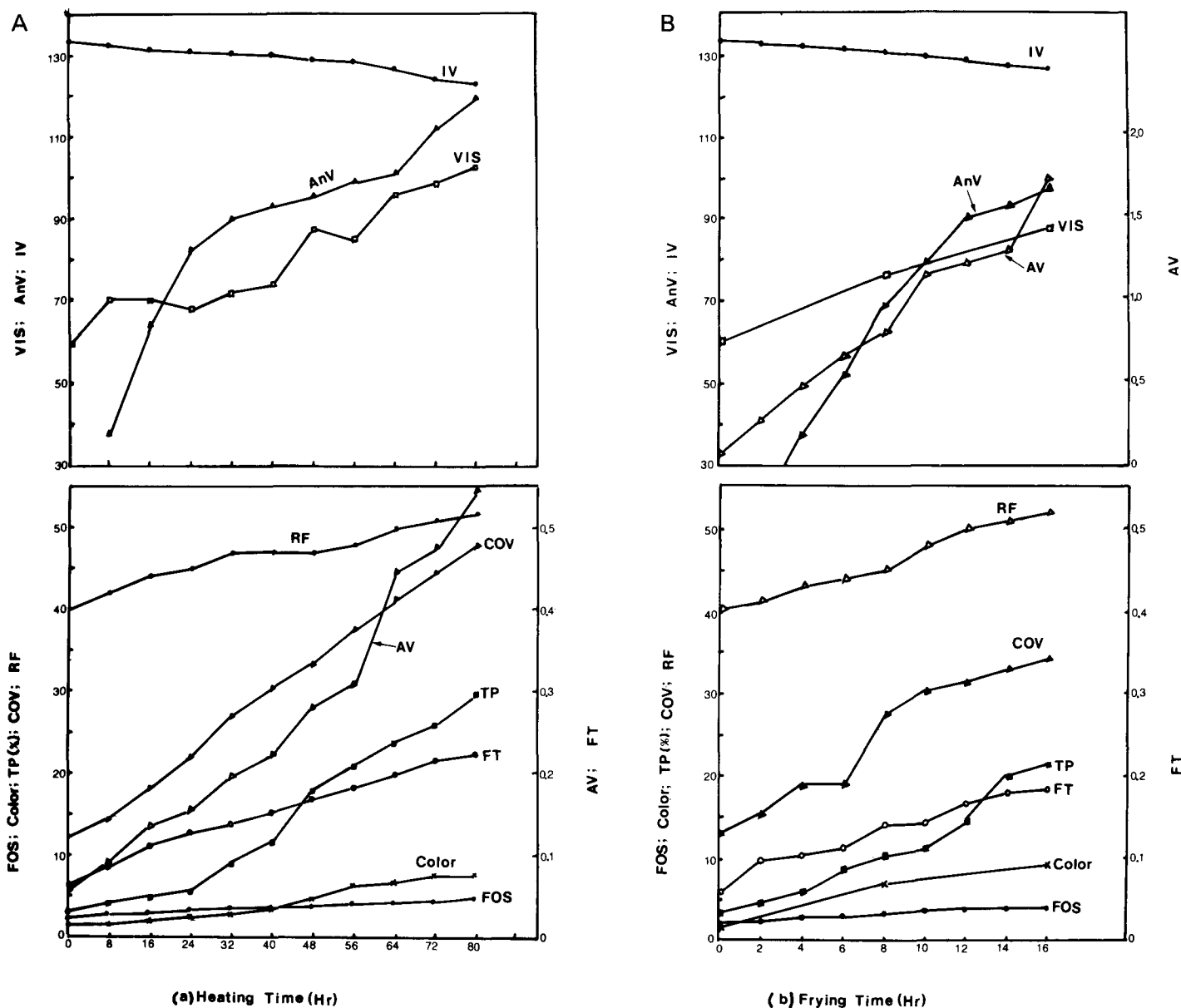


FIG. 1. Physical and chemical change of control SBO during a, heating; and b, frying.

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RESULTS AND DISCUSSION

Effects of various additives and oil blending on the stability of soybean oil. The induction periods of soybean oil treated by additives or blended with other oils are shown in Table 1. Unhydrogenated soybean oil (control SBO) is the most unstable oil among all the oils due to the high amount of linolenic acid. Sesame oil and palm olein containing low amounts of linolenic acid (16) are more stable than control SBO and they were selected as blending oils. In the study of antioxidants, TBHQ, PG, rosemary concentrate, α -tocopherol and lecithin were used to determine their effects on the oxidation stability of soybean oil during heating and frying. It was found that TBHQ (120 ppm) and PG (100 ppm) in low concentrations were effective on the prevention of oil oxidation at 120°C. The maximum amount of lecithin added into SBO is limited to 0.1% of oil to prevent emulsification of oil. α -Tocopherol and rosemary had similar Rancimat values at 500 ppm concentration in the oil. Among the synergists, ascorbyl palmitate (AP), which has good oil solubility and high stability, was used as the main synergist in this experiment. Dimethyl polysiloxane, a foam suppressor, showed the lowest foam volume of frying oil at a concentration of 5 ppm (Table 2).

Comparative study of various soybean oil formulations

by ten test methods during heating and frying. Heating and frying practices were studied for their effects on the susceptibility of SBO to oxidation. The results of ten analyses vs time between heating and frying practices for control SBO are shown in Figure 1. From these test methods, we found that the oil showed an increase in the readings of FOS, TP, RF, AV, AnV, COV and FT, whereas the IV decreased with heating and frying time. By comparing SBO plus additives to blended SBO with control SBO, both SBO plus additives and blended SBO showed less increase in FOS, TP compounds and RF. They also showed less decrease in IV than control SBO during heating and frying (Tables 3 and 4). However, the effects of additives or blending oils on the oxidation stability of soybean oil cannot be completely observed from the determinations of AnV, COV and FT.

The oil color and the concentration of secondary compounds in SBO/SSO and SBO/lecithin are the factors that effect the COV and FT readings. For oil color, the original dark color of sesame oil and the darkening of oil color caused by the browning reaction of phospholipids during heating and frying interfered with the measurement of carbonyl or secondary compounds in frying oil, which accounted for the increase in COV and FT readings. Although lecithin in SBO had an adverse effect on oil color, the antioxidant effect still can be observed from the

TABLE 3

Physical and Chemical Change for Various Soybean Oil Treatments During Heating

HR	Analysis ^a									
	DC	FT	TP	RF	VIS	C	AV	IV	AnV	COV
Control										
0	2.24	.060	3.19	1.4740	60	1.3	0.05	133.3	1.4	11.7
40	3.52	.151	11.52	1.4747	74	3.3	0.22	130.2	93.3	30.4
80	4.84	.223	29.59	1.4754	103	7.8	0.54	122.6	119.3	48.1
TBHQ 120 + AP 500 (ppm)										
0	2.29	.072	3.54	1.4740	62	1.3	0.06	133.5	2.2	11.2
40	2.72	.125	6.09	1.4742	58	1.7	0.23	131.2	71.4	20.8
80	3.07	.164	11.15	1.4746	72	3.4	0.29	128.7	103.2	37.4
PG 100 + AP 500 (ppm)										
0	2.19	.065	3.06	1.4740	62	1.2	0.07	132.9	1.4	12.0
40	2.62	.116	8.36	1.4742	75	2.6	0.22	129.9	83.1	22.1
80	3.29	.211	12.04	1.4745	85	5.3	0.33	125.3	125.3	36.6
Rosemary 500 + AP 500 (ppm)										
0	2.24	.075	4.26	1.4740	60	2.3	0.06	133.3	1.5	12.4
40	2.61	.125	12.08	1.4743	74	2.1	0.20	130.1	78.7	22.7
80	3.06	.157	15.00	1.4745	78	3.5	0.31	126.6	105.1	36.1
Lecithin 1000 + AP 500 (ppm)										
0	2.26	.097	3.64	1.4744	63	0.5	0.07	133.1	2.5	10.7
40	2.69	.233	9.97	1.4742	80	6.0	0.33	129.3	66.4	28.4
80	3.21	.292	18.55	1.4743	87	6.2	0.41	126.2	79.2	42.7
Palm olein:soybean oil (4:6)										
0	2.12	.066	5.14	1.4704	59	2.1	0.06	101.2	2.1	10.0
40	2.59	.113	9.03	1.4706	67	2.4	0.17	97.3	47.7	20.3
80	3.15	.182	19.70	1.4710	83	7.2	0.34	93.5	76.6	36.7
Sesame oil:soybean oil (4:6)										
0	2.34	.257	6.06	1.4733	75	8.6	1.35	123.8	10.3	13.2
40	2.60	.343	10.03	1.4736	81	18.0	1.80	122.0	36.6	28.4
80	2.89	.655	17.33	1.4738	85	20.0	2.44	117.6	61.8	54.1

^aDC, changes in dielectric constant; FT, fritest; TP, total polar compounds (%); RF, refractive index; VIS, viscosity; C, color; AV, acid value; IV, iodine value; AnV, anisidine value; and COV, carbonyl value.

TABLE 4

Physical and Chemical Changes for Various Soybean Oil Treatments During Frying

HR	Analysis ^a									
	DC	FT	TP	RF	VIS	C	AV	IV	AnV	COV
Control										
0	2.16	.058	3.20	1.4740	60	1.4	0.05	133.3	2.7	12.9
8	3.11	.140	11.11	1.4748	76	6.8	0.81	130.5	69.1	27.3
16	3.82	.182	21.23	1.4752	88	9.3	1.74	126.7	97.5	34.2
TBHQ 120 + AP 500 (ppm)										
0	2.23	.075	3.53	1.4740	62	1.4	0.06	133.6	1.4	11.4
8	2.45	.114	10.12	1.4741	75	5.2	0.81	132.7	47.1	18.7
16	2.80	.158	14.08	1.4745	85	9.0	1.68	130.8	77.4	30.1
PG 100 + AP 500 (ppm)										
0	2.17	.069	3.16	1.4740	62	1.7	0.07	132.9	1.0	10.1
8	2.80	.128	8.02	1.4742	75	5.7	0.98	131.9	56.9	23.7
16	3.15	.161	14.95	1.4743	78	11.0	2.05	130.1	95.6	32.8
Rosemary 500 + AP 500 (ppm)										
0	2.24	.073	4.21	1.4740	60	2.3	0.06	133.3	3.0	12.1
8	2.85	.131	8.75	1.4741	72	8.2	0.78	132.2	4.8	28.8
16	3.20	.169	14.88	1.4845	76	13.0	1.85	130.3	43.8	35.4
Lecithin 1000 + AP 500 (pm)										
0	2.27	.092	3.52	1.4740	63	0.7	0.07	133.1	2.5	10.6
8	2.92	.369	9.64	1.4742	75	12.0	1.66	131.6	58.6	22.1
16	3.40	.423	17.89	1.4745	82	14.0	2.90	129.6	90.9	36.6
Palm olein:soybean oil (4:6)										
0	2.14	.068	5.11	1.4704	60	1.8	0.06	101.2	2.2	10.1
8	2.83	.141	9.91	1.4709	80	4.9	0.85	99.4	20.1	16.1
16	3.28	.178	14.08	1.4715	85	8.4	1.52	97.1	52.4	33.3
Sesame oil:soybean oil (4:6)										
0	2.33	.255	6.12	1.4732	75	9.7	1.34	122.0	10.3	13.0
8	2.55	.457	10.38	1.4736	82	13.0	1.78	117.0	24.4	20.8
16	2.90	.568	14.62	1.4742	85	20.0	2.79	115.9	55.8	40.2

^aAbbreviations are as in Table 3.

TABLE 5

Correlation Between Changes in Dielectric Constant and Other Analyses of the Combined Data of Soybean Oil with Different Additives During Heating and Frying

Analyses ^a	Number of samples	Correlation coefficient
FT	80	.887
TP	100	.871
RF	100	.920
IV	100	.802
AnV	100	.816
COV	100	.870

^aAbbreviations are as in Table 3.

lower TP, FOS and RF values; as well as the higher IV values as compared to control SBO. In regards to carbonyl or secondary compounds, the initial readings of AnV and FT of SBO/SSO were different from those of SBO with or without additives due to the difference in the initial concentration of these compounds. In addition, upon heating or frying, the formation rate of these secondary compounds also varied with the kinds of oils.

For the AV analysis, the rate of FFA increase was higher in control SBO and SBO/SSO during heating but showed almost no difference for all the oils during fry-

ing, which indicated that the frying oil quality is difficult to evaluate with only the AV test.

Both the measurements of viscosity and color cannot be used adequately as indications of oil deterioration during frying. The red color formation showed either no difference among all the SBO with and without additives or showed even higher value than control SBO during frying. For the viscosity analysis, control SBO showed a slightly higher increase in viscosity but the increase was not obvious compared to SBO/additive or blended SBO after two 8-hr frying periods.

Correlation between changes in dielectric constant and other analyses. The change in the dielectric constant measured by the Food Oil Sensor has been used as an indicator of the extent of oil deterioration due to its reproducibility and the simplicity of the measuring procedure. A FOS reading of 3.7 or higher also has been suggested to represent low quality oil (17,18). In this study, the FOS value of 4.0 is selected as the discarded value of oil and the other values of TP, IV, RF, FT, AV, AnV and COV are thereby derived from the respective linear equation between the changes in DC and the respective test method. As shown in Table 5, the correlations between changes in DC and other analyses for straight SBO are highly significant ($p < 0.001$) when the combined data for all SBO/additives are considered together. For blended

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TABLE 6

Cut-Off Values of Eight Analyses for SBO/Additives, SBO/SSO and SBO/PO

	Cut-Off Value		
	SBO/additives	SBO/SSO ^b (6:4)	SBO/PO ^c (6:4)
DC ^a	4	4	4
TP	22.33 ± 1.88	41.82 ± 0.94(H) 30.99 ± 0.91(F)	29.99 ± 0.86(H) 25.10 ± 3.26(F)
IV	126.23 ± 1.80	108.06 ± 0.61(H) 106.07 ± 0.71(F)	86.62 ± 0.31(H) 94.46 ± 0.18(F)
RF	1.4750 ± 0.0002	1.4750 ± 0.0001(H) 1.4763 ± 0.0001(F)	1.47140 ± 0.00004(H) 1.47220 ± 0.00004(F)
AnV	154.59 ± 15.32	158.66 ± 2.67(H) 138.62 ± 3.88(F)	132.26 ± 2.90(H) 79.62 ± 1.55(F)
COV	42.16 ± 3.74	120.93 ± 3.15(H) 87.04 ± 7.95(F)	58.06 ± 0.58(H) 44.02 ± 0.86(F)
AV	0.45 ± 0.13(H) 2.70 ± 0.56(F)	4.34 ± 0.08(H) 5.24 ± 0.29(F)	0.54 ± 0.007(H) 2.53 ± 0.045(F)
FT	0.2175 ± 0.0130	1.63 ± 0.04(H) 1.27 ± 0.05(F)	0.2708 ± 0.0045

^aAbbreviations are as in Table 3.^bSSO, sesame oil.^cPO, palm olein.

TABLE 7

Time Required for Each Soybean Oil Formulation to Reach Respective Cut-Off Value of DC and TP Tests During Frying

	SBO/Additives ^a						
	Control SBO	TBHQ 120 + AP 500	Rosemary 500 + AP 500	PG 100 + AP 500	Lecithin 1000 + AP 500	SBO/SSO	SBO/PO
DC	16.11	49.61	26.97	28.42	23.13	47.19	26.53
TP	17.71	25.61	26.95	28.11	21.33	32.69	25.96

^aUnit of additives—ppm.

SBO, the correlation coefficients are above 0.950 for both heating (n=11) and frying (n=9) practices. Among these test methods, the measurement of TP compounds which correlated well with FOS test is a highly reliable method for oil assessment (17). A study showed that the corn oil sample with 27% polar compounds gave a 3.7 FOS reading (18). In our experiment, we found that FOS reading of 4 had corresponding polar compounds of 22.33%, 25–30% and 31–42% for SBO/additives, SBO/palm olein and SBO/SSO, respectively (Table 6). The high reading of polar compounds in SBO/SSO resulted from the high initial concentration of unsaponifiable matter in fresh sesame oil. Although the determination of total polar compounds in a frying fat provided a highly reliable measure of the extent of deterioration in most cases, this complex and tedious procedure cannot be used as the method of routine quality control for oil quality.

Endpoint of oil quality evaluated by changes in DC (FOS), TP, IV, RF, FT, AnV, COV and AV. The mean value of each test is considered the cut-off level among SBO with additives, SBO/palm olein and SBO/sesame oil during heating and frying (Table 6). For straight SBO, the

oil is considered to have deteriorated in the frying system as FOS readings reach 4, which corresponds to the average values of 22% TP, 0.2175 FT, 1.4750 RF, 126.2 IV, 154.6 AnV, 42.2 COV and 2.7 (frying) AV. All these mean values (except AV) were obtained by combining the data of SBO with a variety of additives both in heating and frying systems (n=100). Due to the small variation of each test value, these results are adequately used as indicators of SBO quality assessment during frying. For blended SBO, the cut-off value of each test was different between heating and frying systems. In the frying system, the values of most tests, *i.e.*, TP, IV, AnV, COV and FT reached the limits of low oil quality more rapidly than that in the heating system which excluded the effect of food on oil quality. Therefore, the values obtained from the heating system can be suggested as the lowest limits for oil discarding during frying.

Comparison in oxidation stability between SBO plus additives, SBO/palm olein and SBO/sesame oil. Determination of the endpoint of a frying fat is based on the frying operation, the nature of the deep frying fat and the advantages and limitations of the analytical procedures

employed. There is no single procedure which will produce reliable results in all cases. For instance, some of the test methods in our experiment such as color, AV, AnV, COV and FT have some factors which affected the results, as mentioned previously. Therefore, by using one of these methods, it was difficult to judge the oil quality. However, among these tests, we found that FOS, TP, RF and IV were more reliable than the rest of the methods for the assessment of oil quality. The previous report (17) also pointed out the determination of TP compounds in a frying fat provided the most reliable measure of the extent of oil deterioration and the measure of changes in DC by FOS was the simplest methods of all. By determining changes in DC and TP compounds of straight and blended SBO at the frying stage, the frying life of each oil, as shown in Table 7, was thereby evaluated from the relationship between frying time and respective DC and TP compound determination. From all these oils, we found that SBO/SSO, which had the longest frying life, is the most stable amongst all the oils. This indicated that soybean oil blended with highly stable oil is more effective than the addition of antioxidants. This is due to the instability and volatility of such additives at high temperatures. The high stability of sesame oil is ascribed to the high amount of powerful antioxidants such as sesamol, sesamol dimer (19) and tocopherol. As regards to antioxidants, the choice of TBHQ is more suitable than the other additives. However, SBO with added antioxidants is preferably used as a means to extend the shelf life of oil during storage.

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