Effect of Vacuum Frying on the Oxidative Stability of Oils

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ABSTRACT: The purpose of this study was to evaluate frying oil quality with different assessment methods during vacuum frying of carrot slices. In six consecutive days, palm oil, lard, and soybean oil were fried under vacuum at 105°C for 20 min each hour in an 8-h shift. Peroxide value, acid value, carbonyl value, total polar components, dielectric constant (Food Oil Sensor reading), viscosity, and fatty acid composition were used to evaluate the quality of these oils. Results showed that palm oil and lard possess greater thermal stability than soybean oil. The decrease in $C_{18:2}/C_{16:0}$ ratio was greater for soybean oil than the other two oils. Of the assessment methods used, peroxide value, carbonyl value, total polar components, and dielectric constant all showed good correlation with frying time and between each other. Viscosity was suitable to assess vacuum-fried lard and soybean oil, but not palm oil. The measurement of dielectric constant, on the other hand, appeared to be unsuitable to assess vacuum-fried soybean oil.

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KEY WORDS: Carrot chips, dielectric constant, frying oil assessment, food oil sensor, lard, oxidative stability, palm oil, peroxide value, soybean oil, total polar components, vacuum frying.

Deep-fat frying of food is usually performed at high temperature (about 180°C) under atmospheric pressure. Surface darkening may occur even before the food is fully cooked. Some of the fat and oil decomposition products have also been implicated in producing adverse health effects when fried oils degraded with continued use (1,2). Pressure frying is another way of deep-fat frying; food is fried in a closed system under pressure. This increases the boiling points of frying oil and moisture in food, and thus increases the rate of heat transfer to the interior of food and shortens the frying time. Food fried under pressure will usually retain more moisture and flavor. Pressure frying is conducted at high temperature and pressure, it therefore might have adverse effects on the quality of frying oils (3).

In vacuum-frying operations, food is heated under reduced pressure in a closed system that can lower the boiling points of frying oil and moisture in food. Water in the fried food can be rapidly removed when the oil temperature reaches the boiling point of water. Because food is heated at lower temperature and oxygen content during vacuum frying (4), the natural color and flavor can be preserved. Vacuum frying also has less adverse effects on oil quality (5).

Vegetables and fruits are generally dehydrated by freeze drying, a process that can maintain their original flavor and color. This operation, however, is energy and time consuming. Therefore, production of dehydrated vegetables and fruits with high quality in a short time is an important issue for food processors. Vacuum frying of fruits and vegetables slices may be a good alternative to process dehydrated fruits and vegetables.

The purpose of this study was to evaluate the stabilities of different frying oils while vacuum-frying carrot slices. Different assessment methods were employed in order to find a simple and rapid method that would be applicable to assess the oxidative stability of different oils, and to correlate the results of various analytical methods.

MATERIALS AND METHODS

Materials. Soybean oil, lard, and carrots were purchased from local market in Taiwan. Palm oil imported from Malaysia was also purchased from local market. Carrot (*Daucus carota*) root was packaged in polyethylene bags and stored at 0°C before use. The acid values (AV) of soybean oil, lard, and palm oil were 0.06, 0.06, and 0.07, respectively, while the iodine values were 123.2, 71.5, and 56.8, respectively. All other reagents used were of analytical grade unless otherwise specified.

Processing methods. Pretreatment of carrots. Washed, peeled and drained carrots were cut into 2-mm thick slices with a slicer (OMAS slicer, model VS250, Italy). Carrot slices were blanched at 95°C for 2 min, cooled, drained, and immersed in a 40% fructose solution at 50°C for 30 min. Drained slices were stored at –30°C before vacuum frying.

Vacuum frying of carrot slices. About 36 kg frying oil (palm oil, lard, or soybean oil) was placed into a vacuum fryer (Horng Yun Steel Factory, Yon Lin, Taiwan) as shown in Figure 1. In six consecutive days, a batch of 800 g carrot slices (73.2% moisture) was fried under vacuum (20 torr) at 105°C for 20 min each hour. A total of eight batches of carrot slices was fried in an 8-h shift. At the end of the day, the frying oil was cooled to room temperature and an oil sample was taken and stored at –20°C before analysis within a week.

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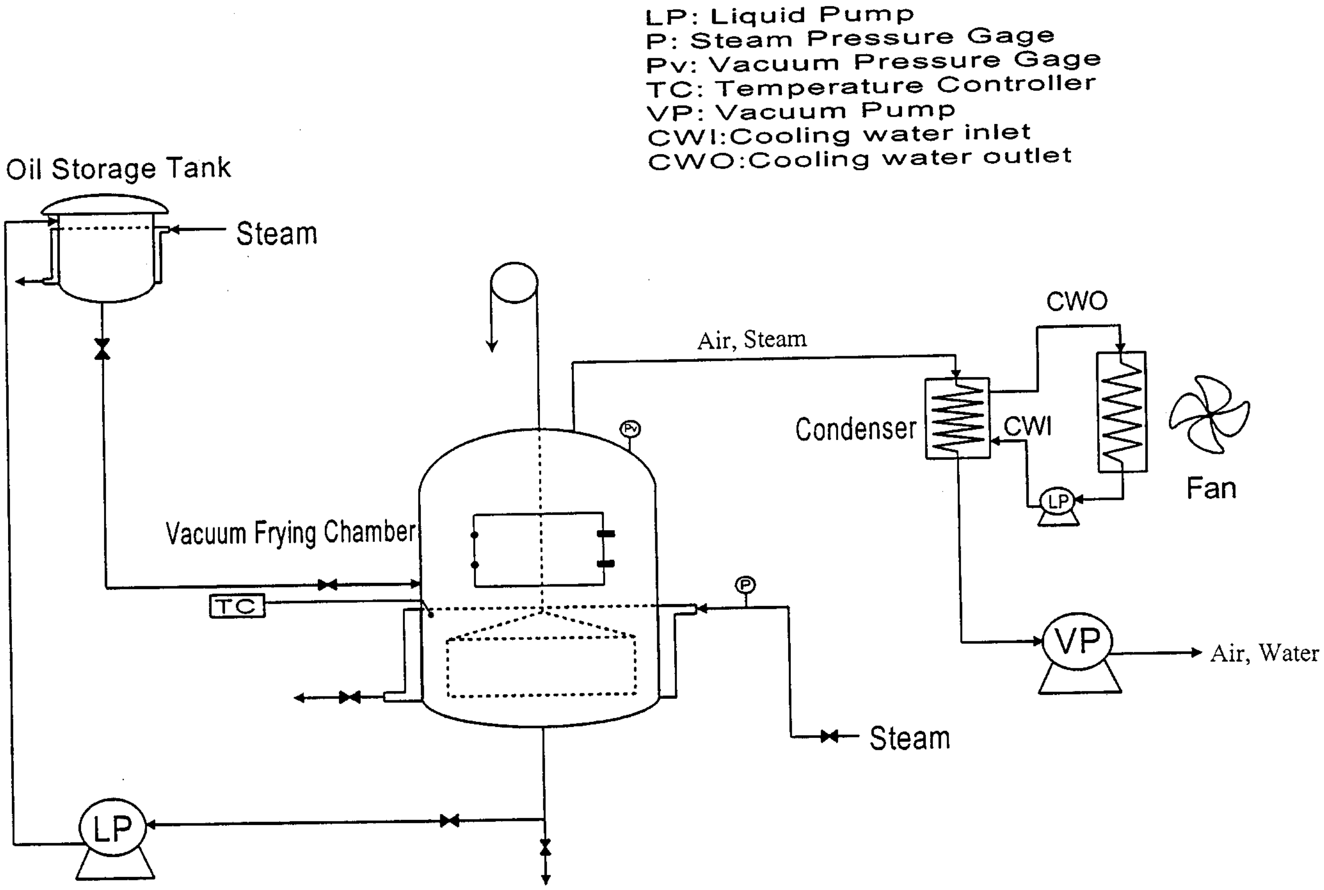

FIG. 1. The vacuum-frying system used in this experiment.

Analytical methods. American Oil Chemists' Society methods (6) were used to determine AV (Cd 3a-63) and peroxide value (POV) (Cd 8-53). Carbonyl value (CV) was determined according to Bhalerao *et al.* (7). The change in dielectric constant (DC) was measured with a Food Oil Sensor Model NI-20 (Northern Instruments Corp., Lino Lakes, MN). Viscosity (Vis) was determined with a Brookfield Synchro-Lectric Viscometer, Model RVF (Brookfield Engineering Laboratories, Inc., Stoughton, MA) at 25 (soybean oil) and 40°C (lard and palm oil).

Total polar components (TP). Polar and nonpolar components in oil samples were separated by column chromatography (8). Column-packing material used was silica gel (70–230 mesh), and the polar components were eluted with a solvent mixture composed of 87% light petroleum and 13% diethyl ether.

Fatty acid composition. Oil samples (about 20 mg) were weighed and the methyl esters were prepared with 0.5 N sodium methoxide in methanol and methylated at 60°C for 10 min as described by Christie (9). A known amount of internal standard (triheptadecanoin, triglyceride 17:0) was added. Fatty acid compositions of the methylated oil samples were determined by capillary gas chromatography (GC) analysis with an HP-5890 Series II GC equipped with a flame-ionization detector (Hewlett-Packard, North Hollywood, CA). An HP-INNOWAX column (30 m × 0.25 mm i.d., 0.5 μm film thickness; Hewlett-Packard) was employed. Column temperature was programmed from 140 to 220°C at 4°C/min, and then raised to 260°C at 5°C/min and held at 260°C for 10 min. The injector and detector temperatures were 260 and 280°C, respectively. Helium was used as carrier gas with a flow rate of 1 mL/min.

Statistical analysis. All data were analyzed using the SAS (Statistic Analysis System) package software for the analysis of variance and the least significant difference (10). Slopes were calculated for each line by linear regression using least squares technique.

RESULTS AND DISCUSSION

During frying, oil or fat is exposed to air, water, and heat. Therefore, thermal, oxidative, and hydrolytic decomposition of the oil may take place. Fats and oils are oxidized to form hydroperoxides, the primary oxidation products. These peroxides are extremely unstable and decompose *via* fission, dehydration, and formation of free radicals to form a variety of chemical products, such as alcohols, aldehydes, ketones, acids, dimers, trimers, polymers, and cyclic compounds (11–13). In this study, POV, AV, CV, TP, DC, Vis, and fatty acid compositions were employed to measure frying oil deterioration.

POV. Hydroperoxides are the primary products of lipid ox-

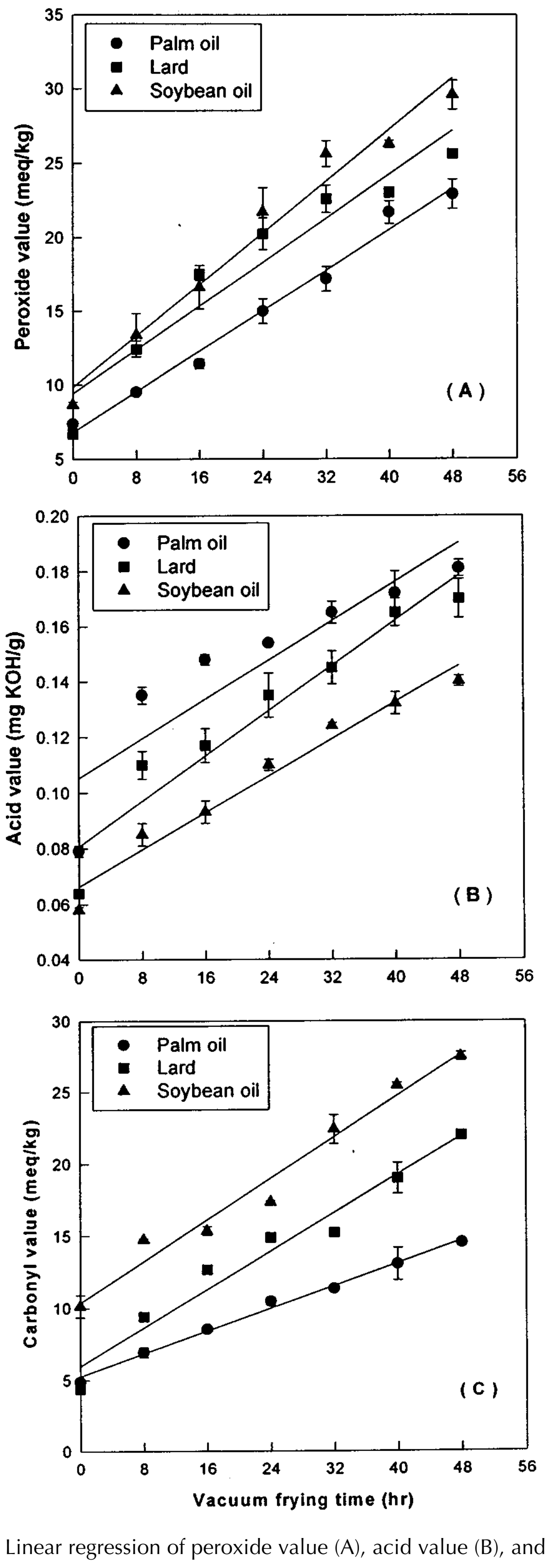

FIG 2. Linear regression of peroxide value (A), acid value (B), and carbonyl value (C) during vacuum frying of the three oils.

TABLE 1
Slope, *y* Intercept, and Correlation Coefficients for Linear Regression of Analytical Values of Frying Oils vs. Frying Time

		Analytical values vs. frying time		
Analytical values	Frying oil	Slope	*y* Intercept	Linear regression coefficient
Peroxide value	Palm	0.3423	6.7829	0.9863
	Lard	0.3699	9.4068	0.9192
	Soybean	0.4350	9.8168	0.9738
Acid value	Palm	0.0018	0.1052	0.8135
	Lard	0.0020	0.0806	0.9286
	Soybean	0.0017	0.0663	0.9665
Carbonyl value	Palm	0.1963	5.2421	0.9934
	Lard	0.3327	5.9461	0.9617
	Soybean	0.3594	10.3536	0.9731
Total polar components	Palm	0.1911	4.3786	0.9845
	Lard	0.2197	3.9536	0.9684
	Soybean	0.2743	4.6246	0.9472
Dielectric constant	Palm	0.0060	1.6007	0.9352
	Lard	0.0165	1.2336	0.9628
	Soybean	0.0122	2.1064	0.8317
Viscosity	Palm	0.1383	38.9468	0.8976
	Lard	0.1529	35.4875	0.9811
	Soybean	0.1982	47.5500	0.9858

idation, therefore, determination of POV can be used as an oxidation index for the early stages of lipid oxidation. During vacuum frying of carrot slices, POV increased linearly with frying time for all three oils under investigation (Fig. 2A). The linear regression coefficients were above 0.92, and the slopes of the POV time curves were below 0.435 (Table 1). In deep-fat frying of palm oil at 120°C for 24 h, the slope of POV was about 0.755 (14). Since the oils were heated at lower temperature (105°C) and lower oxygen content in the vacuum fryer, the formation and decomposition of hydroperoxide would be less than in deep-fat frying. In this study, palm oil POV increased slightly with frying time and was below 15 meq/kg after 24 h of frying. In deep-fat frying at 120°C under atmospheric pressure, palm oil was reported to show an increase in POV over 22 meq/kg after 24 h of frying (14). It is evident from Figure 2A that the increase in POV was fastest for soybean oil followed by lard and palm oil; this can be expected from the degree of unsaturation of the three oils. The POV in soybean oil, however, was still below 30 meq/kg even after 48 h of vacuum frying .

AV. During frying, fats and oils are oxidized to form hydroperoxides that can decompose further to yield the secondary oxidation products, such as alcohols, ketones, aldehydes, and acids. In deep-fat frying, however, acids are also produced by hydrolysis—the reaction of fat with water to form free fatty acid (15). Changes in AV of the three different oils during vacuum frying are shown in Figure 2B. AV of the three oils increased slightly with frying time. The slopes of the AV time curves for the three oils were below 0.002 (Table 1). Handel and Guerrieri (16) found that the slopes of AV of different oils (including soybean oil, corn oil, and tallow) were above 0.012 in deep-fat frying at 200°C for 24 h. Sakata *et al.* (14) also found that the palm oil AV slope was about 0.005 in deep-fat frying at 120°C for 24 h. In this study, the AV increase during vacuum frying was more significant ($P < 0.05$) for palm oil and lard than soybean oil. This may result from the fact that palm oil and lard have higher hydrolyzed saturated fatty acids that are more resistant to further degradation and remained in the oil during frying. This phenomenon was also reported by Hau *et al.* (17).

CV. Carbonyl compounds, such as aldehydes and ketones, are formed as secondary oxidation products from the decomposition of hydroperoxides during fat and oil frying. These carbonyl compounds can react with 2,4-dinitrophenylhydrazine to yield 2,4-dinitrophenylhydrazone derivatives that have a high absorbance at 440 nm. The soybean oil CV increased slowly in the early period of vacuum frying and more rapidly after 24 h, while the other two oils showed a steady CV increase (Fig. 2C). Soybean oil was also found to have a greater increase in CV than the other two oils because of its highly unsaturated nature, as evident from the slope of the plot of CV vs. frying time (Table 1).

TP. TP in fresh frying oil include sterols, tocopherols, mono- and diglycerides, free fatty acids, and other oil-soluble components that are more polar than triglycerides (12). In this study, the contents of TP in fresh oils were 5% or less (Fig. 3A). During frying, fats and oils undergo oxidation and/or hydrolysis to produce polar products, such as epoxides, aldehydes, ketones, alcohols, acids, mono- and diglycerides. Total polar lipid components therefore increased significantly ($P < 0.05$) as the frying time increased. For the three oils, the slopes of TP were below 0.2743 (Table 1). In deep-fat frying at 200°C for 24 h, the slopes of TP of different frying oils were 1.244, 1.967, and 0.501 for soybean oil, corn oil, and tallow, respectively (16). Wu and Nawar (18) also found that the slope of TP of corn oil was about 0.517 in deep-fat frying at 185°C for 40 h. As shown in Figure 3A, after 48 h of vacuum frying, the amount of polar components in soybean oil was below 20%, and the amounts in the other two oils were below 14%. A level of 25% polar components has been suggested as the limit beyond which a restaurant should discard its frying oil (19). In typical frying, soybean oil was reported to show an increase in TP of more than 18% after 16 h of frying (17). It is clear that vacuum frying can maintain better oil quality than typical frying.

DC. As frying oil degrades, an increase in the amount of polar components directly increases the DC of the frying oil. Fritsch *et al.* (20) reported that a statistically significant correlation existed between DC and the increases in TP, POV, and free fatty acids of the used frying oil. In this investigation, Food Oil Sensor was employed to measure DC of frying oil. The changes in DC of the three oils during vacuum frying are shown in Figure 3B. The three oils had large differences in DC before frying. It was 1.9, 1.6, and 1.1 for fresh soybean oil, palm oil, and lard, respectively. Generally, the DC are higher for unsaturated fats than saturated fats (15). After vacuum frying, DC of soybean oil and lard increased rapidly, but the change was very slow in palm oil (Table 1). For the three oils, the slopes of DC were below 0.0165. Fritsch *et al.* (20) found that the slope of soybean oil DC was about 0.185 in deep-fat frying at 190°C for 32 h; this slope was more than 10 times that for vacuum frying.

Vis. Polymerization reactions occur at the termination period of lipid oxidation. The reaction products consist mainly

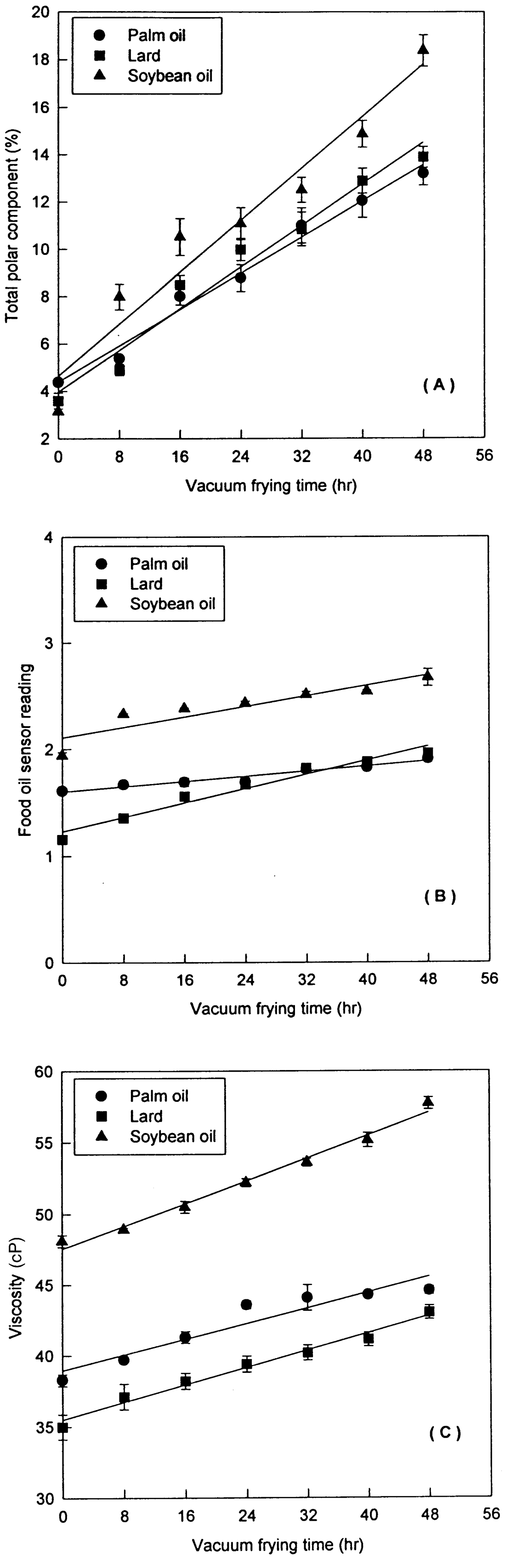

FIG. 3. Linear regression of total polar components (A), dielectric constant (B), and viscosity (C) during vacuum frying of the three oils.

of dimers, trimers, epoxides, cyclic compounds, and polymers with higher molecular weight. These compounds not only change the molecular weight, Vis, and heat transfer of frying oil but also directly affect the quality of fried food (21). Vis is therefore quite often used to estimate the degree of frying oil deterioration. The changes in Vis of the three oils during vacuum frying are shown in Figure 3C. It is evident that the Vis increase of soybean oil was the highest of the three oils (Table 1) owing to its high polyunsaturated fatty acid contents (around 60%). Also the Vis of palm oil increased rapidly in the first 24 h of vacuum frying before leveling off.

Fatty acid composition. Oxidation of oils can easily occur in the presence of oxygen. Oils become rancid as a result of oxidation; this oxidative rancidity is mainly due to the reaction of oxygen with unsaturated fatty acids to form oxidation products. The changes of fatty acid composition during vacuum frying of carrot slices are shown in Table 2. The content of polyunsaturated fatty acid in fresh soybean oil was around 60%, that in palm oil was less than 12%, while it was around 17% in lard. During vacuum frying, the decrease in linoleic and linolenic acid contents for all oils was significant ($P < 0.05$), but no apparent change in the other fatty acids was observed. When comparing the ratio of 18:2/16:0 during vacuum frying, soybean oil again showed the greatest decrease (0.35), followed by lard (0.09) and palm oil (0.06).

Correlations between assessment methods for frying oil quality. The measurement of TP in frying oil is one of the best indicators of frying oil quality (13). The analytical time for TP is lengthy, however. Assessment methods that correlate well with TP may provide alternative ways to measure frying oil quality. The correlation coefficients between the different assessment methods used in this study were obtained by linear regression analysis. For palm oil (Table 3), POV, CV, and DC had good correlation (0.92–0.98) with TP. In the case of lard, all five methods correlated well (0.92–0.98) with TP (Table 4); while in the case of soybean oil, all methods were shown to have good correlation (0.92-0.94) with TP (Table 5), but DC had a lower correlation ($r = 0.8317$) with frying time (Table 1). For the three oils, POV, CV, and DC were found to correlate well (0.92–0.98) with TP. Vis was suitable for monitoring the vacuum-fried lard and soybean oil, but not for palm oil, since the correlation with frying time (Table 1) was not as good ($r = 0.8976$). On the other hand, the measurement of DC appeared to be unsuitable for soybean oil due to low correlation ($r = 0.8317$) with frying time (Table 1).

From the results of this study, it can be concluded that vacuum frying imparted a lower oxidative degradation on the frying oil than the typical frying. During the early stage of frying, soybean oil had similar oxidative stability as lard and palm oil, but it rapidly degraded after 24 h of frying. Soybean oil would be suitable for vacuum frying if total frying time did not exceed 24 h. Further investigation on the storage stability of vacuum-fried foods is needed, however, in order to clarify this point. As for the suitable assessment methods for vacuum-fried oil, POV, CV, and DC all showed good correlation with frying time, and they also correlate well with TP.

TABLE 2
The Effect of Vacuum Frying Time on Fatty Acid Composition of The Three Oils

Frying oil	Frying time (h)	Fatty acid composition (wt %)^{a}							
		14:0	16:0	16:1	18:0	18:1	18:2	18:3	18:2/16:0
Palm oil	0	1.69^{c}	44.93^{c}	—^{b}	3.54^{c}	37.41^{c}	11.24^{c}	0.73^{c}	0.25^{c}
	8	1.44^{d}	43.93^{d}	—	3.23^{c}	37.58^{c}	10.17^{d}	0.66^{c}	0.23^{d}
	16	1.33^{d}	42.00^{f}	—	4.03^{c}	37.67^{c}	9.52^{d,e}	0.55^{d}	0.23^{d}
	24	1.33^{d}	43.02^{e}	—	3.71^{c}	37.63^{c}	9.15^{e}	0.54^{d,e}	0.21^{e,f}
	32	1.40^{d}	42.94^{e}	—	3.36^{c}	35.75^{d}	9.22^{e}	0.51^{d,e,f}	0.21^{e,f}
	40	1.69^{c}	44.36^{c,d}	—	3.26^{c}	35.66^{d}	9.07^{e}	0.46^{e,f}	0.20^{e,f}
	48	1.11^{e}	43.09^{e}	—	4.10^{c}	37.52^{c}	8.35^{f}	0.44^{f}	0.19^{f}
Soybean oil	0	—	14.89^{c}	—	3.85^{c}	21.75^{c}	52.92^{c}	6.58^{c}	3.55^{c}
	8	—	14.76^{c,d}	—	3.75^{c}	19.97^{c}	51.57^{d}	6.26^{c,d}	3.49^{d}
	16	—	14.72^{c,d}	—	3.88^{c}	21.09^{c}	51.12^{d,e}	6.16^{d}	3.47^{d}
	24	—	14.64^{c,d}	—	3.86^{c}	20.62^{c}	50.07^{e}	5.88^{d,e}	3.42^{e}
	32	—	14.76^{c,d}	—	3.67^{c}	19.83^{c}	48.67^{f}	5.69^{e,f}	3.30^{f}
	40	—	14.72^{c,d}	—	3.78^{c}	19.35^{c}	47.88^{f}	5.33^{f,g}	3.25^{g}
	48	—	14.43^{d}	—	3.41^{c}	19.88^{c}	46.19^{g}	5.29^{g}	3.20^{h}
Lard	0	3.25^{c}	31.92^{c,d}	3.80^{c,d}	6.07^{c}	38.59*c*	15.39^{c}	0.98^{c}	0.48^{c}
	8	2.67^{e}	31.88^{c,d}	3.36^{d}	5.43^{c}	38.14*c*	14.77^{c}	0.75^{d}	0.46^{c}
	16	3.10^{c,d}	30.99^{d}	3.98^{c}	5.82^{c}	36.97*c*	14.28^{c,d}	0.72^{d,e}	0.46^{c}
	24	2.88^{c,d,e}	31.47^{d}	3.70^{c,d}	5.76^{c}	38.05*c*	13.43^{d,e}	0.65^{e}	0.43^{d}
	32	2.54^{e}	30.98^{d}	3.53^{c,d}	5.58^{c}	37.23*c*	13.00^{e}	0.56^{f}	0.42^{d,e}
	40	2.61^{e}	32.78^{c}	3.60^{c,d}	6.02^{c}	37.72*c*	13.05^{e}	0.65^{e}	0.40^{e,f}
	48	2.81^{d,e}	31.94^{c,d}	3.61^{c,d}	5.92^{c}	36.91*c*	12.40^{e}	0.54^{f}	0.39^{f}

[a] The wt% of each fatty acid in the oil sample was calculated as the percentage of the sum of total wt (g/100 g oil) of fatty acids in the fresh oil samples.
[b] Not detected.
[c-h] Means within a column of the same oil followed by different letters were significantly different ($P < 0.05$).

TABLE 3
Correlation Between Analytical Values of Fried Palm Oil[a]

	AV	POV	CV	TP	DC	Vis
AV	—	0.7560	0.8523	0.8106	0.7521	0.8501
POV	0.7560	—	0.9760	0.9610	0.9132	0.8680
CV	0.8523	0.9760	—	0.9750	0.8978	0.9261
TP	0.8106	0.9610	0.9750	—	0.9169	0.9119
DC	0.7251	0.9132	0.8978	0.9169	—	0.7362
Vis	0.8501	0.8680	0.9261	0.9119	0.7362	—

[a] Abbreviations: AV, acid value; POV, peroxide value; CV, carbonyl value; TP, total polar components; DC, dielectric constant; Vis, viscosity.

TABLE 4
Correlation Between Analytical Values of Fried Lard[a]

	AV	POV	CV	TP	DC	Vis
AV	—	0.9488	0.9625	0.9198	0.9566	0.9522
POV	0.9488	—	0.9453	0.9557	0.9865	0.9441
CV	0.9625	0.9453	—	0.9628	0.9552	0.9865
TP	0.9198	0.9557	0.9628	—	0.9777	0.9546
DC	0.9566	0.9887	0.9552	0.9777	—	0.9619
Vis	0.9522	0.9441	0.9865	0.9546	0.9619	—

[a] For abbreviations see Table 3.

TABLE 5
Correlation Between Analytical Values of Fried Soybean Oil[a]

	AV	POV	CV	TP	DC	Vis
AV	—	0.9878	0.9518	0.9410	0.9148	0.9168
POV	0.9878	—	0.9383	0.9203	0.8682	0.9385
CV	0.9518	0.9383	—	0.9222	0.8274	0.9501
TP	0.9410	0.9203	0.9222	—	0.9306	0.9234
DC	0.9148	0.8682	0.8274	0.9306	—	0.7672
Vis	0.9168	0.9385	0.9501	0.9234	0.7672	—

[a] For abbreviations see Table 3.

These three simple and rapid methods can therefore be employed to monitor the quality of frying oil during vacuum-frying operation.

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