Volatile Compounds in Oils After Deep Frying or Stir Frying and Subsequent Storage

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Soybean oil (900 g) was heated by deep frying at 200°C for 1 h with the addition of 0, 50, 100, 150 and 200 mL water, and then stored at 55°C for 26 weeks. Soybean oil, corn oil and lard were heated by stir frying and then stored at 55°C for 30 weeks. The volatiles and peroxide values of these samples were monitored. All samples contained aldehydes as major volatiles. During heating and storage, total volatiles increased 260–1100-fold. However, aldehyde content decreased from 62–87% to 47–67%, while volatile acid content increased from 1–6% to 12–33%; especially hexanoic acid which increased to 26–350 ppm in the oils after the storage period was completed. Water addition to the oils heated by deep frying tended to retard the formation of volatile compounds. The total amount of volatile constituents of lard heated by stir frying increased more during storage than that of corn oil or soybean oil. Peroxide values did not reflect the changes of volatile content in the samples.

KEY WORDS: Corn oil, deep frying, lard, peroxide value, soybean oil, stir frying, storage, volatiles, water.

Deep-fat frying is a universal cooking method. Stir frying is common in some areas, especially in Chinese cooking. Edible oils are heated for both methods. Autoxidation of unsaturated fatty acids in stir frying and aging was the main cause of changes in volatile compounds of stir-fried bell peppers (1). Oxidative degradation of deep-fried oils or heated fatty acid esters has also been reported (2–4). Volatile compounds can be used as a measure of rancidity of foods (5,6). Both cooking methods have rancidity problems, especially when the foods are for sale in commercial channels that require a minimum storage of at least several months.

The presence of water in foods relates to autoxidation of such foods. In previous work we found that water in soybean oil cans caused the production of a significant amount of volatiles just after sterilization. However, during storage soybean oil cans without water had a higher rate of volatile compound production (7). The rancid taste developed most slowly in noodles at $a_w = 0.3$, which was equivalent to 5.16% moisture (8). Hexanal concentration in noodles was a good indicator of the development of oxidative rancidity. Therefore, a suitable amount of water in foods may retard lipid oxidation.

In this study, soybean oil was heated by deep frying, with different amounts of water addition. Also, soybean oil, corn oil and lard were heated by stir frying. All the samples were then stored at 55°C. Changes in volatile compounds and peroxides of the oils during storage were studied.

EXPERIMENTAL PROCEDURES

Deep frying. The apparatus shown in Figure 1 was used for the oils heated by deep frying. Soybean oil (900 g) was poured into a 3-L three-necked round-bottom flask. The flask was heated by a silicon-oil bath to 200°C, and heating was continued for 1 h. Water was added drop by drop within 1 h for a total amount of either 0 g, 50 g, 100 g, 150 g or 200 g. The temperature was kept at 200 ± 5°C, with air passing through the apparatus at a flow rate of 20–30 mL/min during heating, with moderate

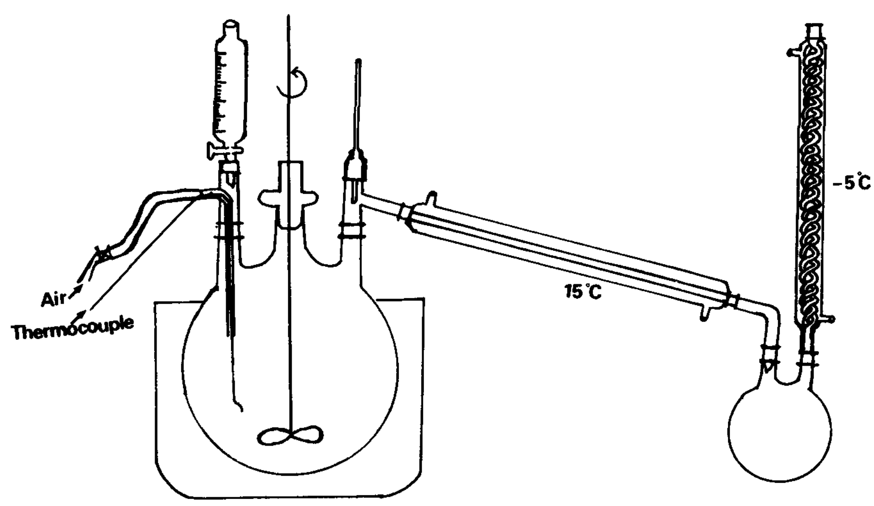

FIG. 1. Apparatus used for oil heated by deep frying.

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stirring. Heated oils from several batches receiving the same treatment were mixed together, cooled and then poured into 500-mL plastic bottles. Each bottle contained 315 g heated oil. The bottles were closed tightly with a plastic cover, there was no special headspace gas treatment, and storage was at 55°C. One bottle sample, selected at random, was used for each volatile and peroxide value (PV) determination during storage.

Stir frying. A Chinese wok 40 cm in diameter was used. The wok was dried by heating, then 300 g commercial edible oil (soybean oil, corn oil or lard), bought from the market, was added and heated to around 200°C within 3 min under constant stirring with a hand-held spade. A thermocouple wire was placed on the wok to measure the temperature. The heated oils from many batches were cooled down to room temperature, mixed together and then poured into 500-mL plastic bottles, closed tightly and stored at 55°C. Monitoring was as described for the deep frying method.

Flavor isolation. Volatile compounds of the oils were extracted for 2.0 h in a Likens-Nickerson apparatus (9). The 5-L sample flask contained 300 g heated oil and 300 mL distilled water. Redistilled pentane and diethyl ether (1:1) were used as the extracting solvent. Tridecane (Merck, Darmstadt, Germany) was added as an internal standard to the solvent after extraction. The volatile extracts were dried with anhydrous Na_2SO_4 and concentrated to about 0.5 mL by using a spinning-band distillation apparatus (Kontes Co., Vineland, NJ). The concentrate was then transferred to a one-ended, sealed, glass capillary tube and heated in a water bath at 40°C to a small volume.

Gas chromatography and gas chromatography-mass spectrometry. The procedure of our previous study was followed (1).

Peroxide value (PV). PVs were determined by the AOAC procedure (10).

RESULTS AND DISCUSSION

Table 1 shows the changes in volatile compounds generated from soybean oil heated by deep frying, without the addition of water, during storage at 55°C for 26 weeks. This was one sample from a series of soybean oils without heating or heated at 200°C for 1 h with the addition of 0 mL, 50 mL, 100 mL, 150 mL or 200 mL water, respectively. The samples were then stored and monitored. Table 2 compares the important fatty acid degradation volatiles of these samples. Tables 3–5 show changes in volatile compounds generated from soybean oil, corn oil and lard, respectively, heated by stir frying during storage at 55°C. Figure 2 is the gas chromatogram corresponding to the volatile sample of soybean oil heated by stir frying after storage of 15 weeks.

Forty-seven volatile compounds were identified in the above samples, including 23 aldehydes, 11 acids, 6 alcohols, 5 ketones, 1 ester and 1 furan. There are quantitative differences, but no qualitative differences, among samples. All these volatiles are the oxidation products of unsaturated fatty acids and have been reported in many studies (11–13). Soybean oil, which contains 53.2% linoleic acid, 23.4% oleic acid and 7.8% linolenic acid, is a common unsaturated edible oil, and it was chosen as the main sample. Corn oil, which contains 57% linoleic acid and 27.5% oleic acid, is also a common unsaturated edible oil, but with no linolenic acid. Lard is a more saturated edible oil, which contains 45.1% oleic acid and 9.9% linoleic acid. From the volatiles identified we can conclude that the cleavage of fatty acids into aldehydes, and subsequent oxidation to the corresponding acids, was the main pathway for changes in volatile compounds of heated oils during storage. Aldehydes, including propanal, pentanal, 2-pentenal, hexanal, 2-hexenal, 2-heptenal, 2-octenal, nonanal, 2-nonenal, 2-decenal and 2-undecenal were found in the samples. The corresponding acids included propanoic acid, pentanoic acid, 2-pentenoic acid, hexanoic acid, 2-hexenoic acid, 2-heptenoic acid, nonanoic acid and 2-octenoic acid, but not 2-nonenoic acid, 2-decenoic acid and 2-undecenoic acid. Low volatility of these latter acids caused low recovery during isolation of volatile compounds. In addition, low concentration of the compounds and long retention times and broad peaks in GC analysis may be reasons for being unable to detect theoretically existing acids.

The content of volatiles in the unheated oils was low in the beginning but increased 260–1100-fold during heating and storage. However, aldehyde content decreased from 62–87% to 47–67%, while volatile acid content increased from 1–6% to 12–33%, especially hexanoic acid, which reached 26–350 ppm in the oils at the final storage period. Other acids increased also, but their content was much less than that of hexanoic acid. The major aldehydes in the heated oils after storage were hexanal, *(E)*-2-heptenal, *(E)*-2-octenal and 2,4-decadienals.

Hexanal has a powerful, penetrating, fatty-green, grassy odor (14). Hexanal is easily oxidized to hexanoic acid, which is mainly responsible for the "rancid" note. Hexanoic acid has a heavy, acrid-acid, fatty rancid odor, often described as "sweat-like" (14). The concentrations of these compounds in the stored oils were high; both reached 100–300 ppm in oils at the final storage period.

Water addition in the oils during deep frying had the tendency to retard the formation of volatile compounds, as shown in Table 2. Total volatiles, hexanal and hexanoic acid contents in the oils with water addition were only 20–30% compared to the oils without water addition, both immediately after heating and after storage.

The increase in aldehyde and acid contents during storage was significant for all three edible oils heated by stir frying but the total amount of volatile constituents of lard increased more than that of corn oil or soybean oil. Lard contains more saturated fatty acids than the other two vegetable oils, but less natural antioxidants such as tocopherols. The reason for the contradiction that more saturated fatty acids produce more degraded volatile compounds is not clear.

Contents of decadienal isomers were lower in lard, possibly due to its lower linoleic acid content. Soybean oil has a high linolenic acid content. This was postulated to be the reason for having a higher content of heptadienal isomers.

Table 6 compares soybean oils heated by deep frying and stir frying. The heat energy applied to soybean oil heated by deep frying was more than 20-fold that applied by stir frying. However, the total volatile compounds produced after 26 weeks storage were only 2.5-fold higher. Also, stir-fried soybean oil had a higher hexanoic acid content in the volatiles. Actually, it is hard to compare these two processes fairly, but that stir frying causes more

TABLE 1

Changes of Volatile Compounds in Soybean Oils Generated by Deep Frying Without Water Addition, and Stored at 55°C

Peak no.	Compound[a]	Storage time (weeks)[b]						
		0	2	6	10	14	22	26
1.	Ethanal	27.16	3.00	91.40	65.57	41.15	77.70	389.57
2.	*n*-Propanal	2.12	54.12	26.41	80.17	70.38	506.50	1120.99
3.	*(E)*-2-Propenal	n.d.[c]	23.76	49.93	50.81	43.01	175.84	341.93
4.	Ethyl acetate	17.24	60.56	87.12	38.56	102.58	147.24	141.26
5.	*n*-Pentanal	59.60	211.89	460.04	428.22	334.30	1345.38	1726.76
6.	*n*-Hexanal	383.93	718.07	1548.86	1977.08	2409.36	11976.14	16282.64
7.	*(E)*-2-Pentenal	51.08	123.07	322.21	306.65	318.90	1406.13	2157.49
8.	1-Penten-3-ol	257.41	402.66	834.05	685.66	599.00	2116.57	4994.31
9.	2-Heptanone	44.99	91.41	127.59	148.79	184.63	1106.44	1203.94
10.	2-Pentyl furan	24.85	186.98	254.52	289.12	260.57	1959.36	2549.35
11.	*(E)*-2-Hexenal	57.90	358.94	571.58	470.31	362.30	1474.95	1747.24
12.	*n*-Pentanol	174.56	289.84	466.34	350.85	438.10	1303.00	1500.92
13.	Tridecane	i.s.[d]	i.s.	i.s.	i.s.	i.s.	i.s.	i.s.
14.	2-Octanone	115.65	135.46	117.03	134.09	165.56	474.64	342.20
15.	*(Z)*-2-Heptenal	n.d.	n.d.	56.36	39.69	59.94	96.47	96.06
16.	*(Z)*-2-Penten-1-ol	96.33	135.46	106.22	84.29	92.37	219.72	372.48
17.	*(E)*-2-Heptenal	3056.70	3820.31	5228.21	5124.79	4381.15	13812.16	10388.41
18.	*n*-Hexanol	77.89	83.57	102.62	75.24	125.20	336.88	336.69
19.	*n*-Nonanal	525.54	517.00	421.77	326.68	305.88	448.59	314.96
20.	*(Z)*-2-Octenal	35.28	104.51	127.95	118.61	144.36	224.49	158.80
21.	3-Octen-2-one	22.85	26.83	85.78	117.51	171.44	616.86	411.95
22.	*(E)*-2-Octenal	1262.50	1093.31	1440.82	1648.96	2592.75	6365.71	4936.43
23.	1-Octen-3-ol	1036.60	1159.42	1706.28	2045.43	2062.41	5497.65	4230.75
24.	*n*-Heptanol	n.d.	11.54	45.75	49.79	32.71	116.34	64.76
25.	*(E,Z)*-2,4-Heptadienal	695.03	939.96	1217.65	1513.59	1443.35	2378.48	1734.90
26.	*(E,E)*-2,4-Heptadienal	2976.40	3025.69	3625.31	3526.04	3361.58	5130.10	3680.68
27.	*n*-Propanoic acid	n.d.	15.33	27.35	43.90	71.22	113.73	360.80
28.	*(E)*-2-Nonenal	93.80	118.75	163.92	168.51	206.76	571.34	2241.00
29.	3,5-Octadien-2-one	38.50	21.42	40.73	74.61	115.21	320.40	306.09
30.	*n*-Butanoic acid	n.d.	n.d.	n.d.	n.d.	n.d.	71.29	76.98
31.	*(E)*-2-Decenal	377.23	346.15	361.42	320.60	373.23	497.49	557.51
32.	2,3-Octadione	29.92	14.14	31.72	61.57	129.71	431.22	430.43
33.	*(E,Z)*-2,4-Nonadienal	12.71	23.62	28.97	50.34	103.79	204.98	218.24
34.	*(Z,E)*-2,4-Nonadienal	21.32	2.39	16.10	27.90	59.16	121.29	132.16
35.	*(E,E)*-2,4-Nonadienal	33.56	45.77	93.58	125.15	174.33	270.47	340.83
36.	*n*-Pentanoic acid	n.d.	11.55	44.75	91.29	253.55	584.35	770.24
37.	*(E)*-2-Undecenal	183.26	196.60	187.90	152.19	183.91	202.43	283.57
38.	*(E,Z)*-2,4-Decadienal	955.20	815.49	940.06	852.91	1036.24	668.25	1435.41
39.	*(Z,Z)*-2,4-Decadienal	n.d.	57.04	44.83	36.57	44.91	23.51	55.25
40.	*(E,E)*-2,4-Decadienal	3547.80	3389.06	3561.95	3354.83	4191.69	5067.65	7443.14
41.	*n*-Hexanoic acid	45.13	143.74	392.90	786.13	2429.88	5708.76	8543.17
42.	*(E)*-2-Pentenoic acid	71.86	79.33	70.08	75.86	7.61	84.93	150.54
43.	*n*-Octanoic acid	n.d.	23.95	35.93	55.62	113.21	207.21	189.55
44.	*(E)*-2-Hexenoic acid	n.d.	8.04	18.26	13.19	114.66	120.87	71.61
45.	Unknown	n.d.	n.d.	8.06	7.18	6.32	39.43	26.45
46.	*n*-Nonanoic acid	n.d.	4.94	13.00	27.58	53.46	219.04	184.88
47.	*(E)*-2-Heptenoic acid	n.d.	27.78	7.90	16.52	44.99	97.59	117.73
48.	*n*-Decanoic acid	n.d.	n.d.	3.84	5.86	15.44	3.78	23.82
49.	*(E)*-2-Octenoic acid	n.d.	n.d.	26.36	13.47	38.44	42.18	60.49
Total		16411.90	18922.45	25241.41	26058.28	29870.70	74985.53	85245.36
Total aldehyde		14358.12	15988.50	20587.23	20766.17	22242.43	50346.05	57783.97
Total acid		116.99	314.66	640.37	1129.42	3142.46	7253.73	10549.81
Aldehyde (%)		87.49	84.49	81.56	79.69	74.46	70.74	67.79
Acid (%)		0.71	1.66	2.54	4.33	10.52	9.67	12.38

[a]Numbers refer to Figure 2. [b]Unit is 10^{-6} g/100 g wet basis. [c]n.d. = not detectable. [d]i.s. = internal standard.

TABLE 2

Comparisons of Hexanal, Hexanoic Acid, *(E)*-2-Heptenal, Heptadienals, Decadienals and Total Volatile Compounds Generated from Soybean Oils Heated by Deep Frying and Stored at 55°C

Storage time (weeks)	Control[b]	Water added during heating[a] 0 mL	50 mL	100 mL	150 mL	200 mL
Hexanal						
0	20	383	121	62	184	33
2	390	718	135	586	219	94
6	1014	1548	225	653	462	352
10	4817	1977	9522	1904	1109	1361
14	5182	2409	3781	1042	3339	2454
22	9213	1176	7000	8048	8177	7159
26	27932	16282	29205	16420	5074	3042
Hexanoic acid						
0	0	45	13	10	42	6
2	94	143	0	0	21	12
6	115	392	48	67	48	60
10	1031	786	2349	2641	195	753
14	3176	2429	3516	586	956	2536
22	4710	5708	3384	5778	4738	4776
26	14262	8543	4961	11703	7837	2560
(E)-2-Heptenal						
0	3	3057	494	142	186	131
2	286	3820	146	766	295	99
6	932	5284	526	860	575	528
10	2426	5164	3168	1630	1458	982
14	3641	4441	2745	1244	1943	1945
22	6102	13918	5457	6624	7795	6834
26	15683	10484	13639	9581	5531	2482
Heptadienals						
0	3	3671	593	198	128	69
2	160	3966	165	672	300	123
6	735	4843	656	1076	835	806
10	2440	5040	2851	1913	2012	1257
14	2955	4805	2460	1567	2417	2142
22	4516	7509	3393	4533	4667	4697
26	6566	5415	5393	5295	3870	2386
Decadienals						
0	3	4503	1340	1757	1093	526
2	52	4262	644	833	1118	835
6	829	4546	1112	1431	1189	1040
10	2729	4244	1763	2200	1920	1494
14	6709	5273	2454	2246	3568	3180
22	7734	5759	2404	5454	5526	4274
26	21565	8834	6656	8129	7298	6177
Total volatiles						
0	114	16411	3842	2802	2415	1321
2	2439	18922	2093	4483	3221	1894
6	6159	25241	3970	6362	4929	4120
10	19818	26058	30990	16754	10012	9204
14	29974	29870	25182	9857	19781	18747
22	47862	74985	37003	50735	50250	45792
26	125731	85245	106326	82229	48074	23595

[a]Unit: 10^{-6} g/100 g oil. [b]Control is soybean oil without frying.

TABLE 3

Changes of Volatile Constituents of Soybean Oil Heated by Stir Frying During Storage at 55°C

Peak no.	Compound[a]	Control[b]	Storage time (weeks)[c]								
			0	1	3	6	9	15	18	24	30
1.	Ethanal	0.50	7.73	9.13	3.07	0.99	13.69	5.65	13.79	8.79	36.55
2.	*n*-Propanal	1.25	6.70	4.21	2.67	47.49	8.06	265.57	106.94	13.17	105.03
3.	*(E)*-2-Propenal	n.d.[d]	1.24	n.d.	n.d.	3.87	n.d.	11.97	13.16	n.d.	n.d.
4.	Ethyl acetate	n.d.	14.15	15.70	3.65	10.74	29.85	39.18	38.74	41.92	90.22
5.	*n*-Pentanal	16.70	24.18	48.70	47.20	174.44	87.51	296.19	325.14	90.34	292.07
6.	*n*-Hexanal	13.26	122.00	165.40	100.83	1781.00	541.53	3938.52	2367.56	5013.80	4228.87
7.	*(E)*-2-Pentenal	n.d.	21.86	17.90	25.68	141.40	38.79	230.01	314.56	52.00	453.55
8.	1-Penten-3-ol	n.d.	20.45	11.20	9.17	206.42	53.63	376.55	511.61	99.89	781.98
9.	2-Heptanone	23.24	6.62	18.00	10.77	89.35	61.38	236.41	261.52	49.75	764.19
10.	2-Pentyl furan	n.d.	20.91	19.60	3.11	130.80	38.05	318.82	252.39	41.63	2108.06
11.	*(E)*-2-Hexenal	1.51	32.04	21.60	11.68	122.74	29.33	191.96	246.65	30.26	565.03
12.	*n*-Pentanol	0.29	42.67	29.21	15.52	127.20	103.70	208.93	320.59	85.74	976.71
13.	Tridecane	i.s.[e]	i.s.	i.s.	i.s.	i.s.	i.s.	i.s.	i.s.	i.s.	i.s.
14.	2-Octanone	0.88	167.33	3.25	4.11	78.41	88.10	204.12	191.48	64.38	386.07
15.	*(Z)*-2-Heptenal	0.26	3.47	3.50	5.23	27.10	10.17	30.74	38.68	14.32	52.24
16.	*(Z)*-2-Penten-1-ol	n.d.	13.95	3.40	7.84	23.01	n.d.	30.10	33.27	6.31	70.26
17.	*(E)*-2-Heptenal	n.d.	431.67	316.30	404.43	1193.78	544.64	1596.69	2143.56	468.61	6899.54
18.	*n*-Hexanol	n.d.	n.d.	1.71	10.04	21.95	13.91	41.50	67.09	24.62	142.56
19.	*n*-Nonanal	1.20	82.67	84.70	73.13	216.70	201.74	303.89	197.58	101.59	324.14
20.	*(Z)*-2-Octenal	0.56	7.72	8.42	8.49	56.27	20.08	71.37	65.48	23.39	106.79
21.	3-Octen-2-one	n.d.	1.56	8.93	11.26	43.38	35.67	205.26	81.18	25.17	559.50
22.	*(E)*-2-Octenal	1.51	38.33	37.30	285.93	735.63	461.34	1128.80	1339.49	687.82	5969.10
23.	1-Octen-3-ol	n.d.	128.00	133.30	n.d.	594.60	419.20	748.58	1071.91	466.40	3735.90
24.	*n*-Heptanol	0.44	2.90	3.96	2.95	21.51	38.51	40.68	48.17	22.26	102.47
25.	*(E,Z)*-2,4-Heptadienal	n.d.	76.00	64.00	151.29	377.36	184.25	226.11	517.96	140.22	712.20
26.	*(E,E)*-2,4-Heptadienal	1.94	234.66	215.70	370.12	729.17	418.06	490.79	982.63	362.16	4921.12
27.	*n*-Propanoic acid	1.44	20.91	22.70	24.18	36.98	32.21	44.33	31.92	26.57	79.05
28.	*(E)*-2-Nonenal	1.25	7.50	8.56	22.97	41.92	77.28	175.45	151.03	91.42	834.70
29.	3,5-Octadien-2-one	0.25	4.68	n.d.	19.72	21.32	29.62	69.02	49.14	17.55	241.27
30.	*n*-Butanoic acid	n.d.	n.d.	n.d.	3.56	4.00	1.78	7.52	14.22	3.32	78.33
31.	*(E)*-2-Decenal	0.36	12.04	12.40	25.89	79.86	91.58	151.09	121.04	114.87	377.29
32.	2,3-Octadione	0.17	3.68	1.58	9.75	63.82	37.32	120.16	99.16	53.40	533.04
33.	*(E,Z)*-2,4-Nonadienal	0.12	n.d.	6.30	25.05	18.53	80.78	34.97	111.59	65.96	441.22
34.	*(Z,E)*-2,4-Nonadienal	0.37	n.d.	2.31	11.06	10.91	31.81	14.79	44.06	23.07	185.38
35.	*(E,E)*-2,4-Nonadienal	0.24	3.89	5.41	15.11	56.54	52.22	62.23	68.52	61.91	211.46
36.	*n*-Pentanoic acid	0.43	n.d.	n.d.	4.77	28.90	90.52	93.06	198.84	113.78	874.57
37.	*(E)*-2-Undecenal	n.d.	6.22	5.95	8.65	42.68	40.92	77.11	59.35	62.79	181.31
38.	*(E,Z)*-2,4-Decadienal	1.67	17.45	26.00	80.05	187.73	156.85	144.13	196.09	293.80	722.45
39.	*(Z,Z)*-2,4-Decadienal	2.65	n.d.	n.d.	2.88	6.46	n.d.	3.66	9.70	8.88	32.74
40.	*(E,E)*-2,4-Decadienal	0.87	179.33	215.30	366.83	1160.08	1203.40	961.16	1733.07	1669.71	4494.21
41.	*n*-Hexanoic acid	0.44	1.74	9.52	38.81	48.72	1490.20	1157.75	1870.97	1760.93	10295.30
42.	*(E)*-2-Pentenoic acid	0.38	n.d.	n.d.	2.45	28.93	21.57	14.95	36.85	11.54	60.10
43.	*n*-Octanoic acid	n.d.	n.d.	n.d.	9.22	21.90	57.92	52.89	105.50	118.37	421.16
44.	*(E)*-2-Hexenoic acid	n.d.	n.d.	n.d.	2.87	6.37	n.d.	4.92	24.45	5.67	99.56
45.	Unknown	n.d.	n.d.	n.d.	n.d.	14.56	11.19	11.08	4.06	10.95	60.66
46.	*n*-Nonanoic acid	n.d.	n.d.	n.d.	0.49	11.91	70.20	46.71	74.00	104.10	317.54
47.	*(E)*-2-Heptenoic aci	n.d.	n.d.	n.d.	n.d.	20.91	25.61	27.62	29.06	35.05	166.89
48.	*n*-Decanoic acid	n.d.	n.d.	n.d.	n.d.	5.88	n.d.	n.d.	23.88	26.92	71.35
49.	*(E)*-2-Octenoic acid	n.d.	n.d.	n.d.	n.d.	9.32	n.d.	16.16	15.91	13.12	115.25
Total		74.18	1766.25	1561.15	2242.48	8883.54	7044.17	14529.15	16623.54	12628.22	55278.98
Total aldehydes		46.22	1316.70	1279.09	2048.24	7212.65	4294.03	10409.21	11167.63	9390.00	32146.99
Total acids		2.69	22.65	32.22	86.35	223.82	1790.01	1465.91	2425.60	2219.37	12579.10
Aldehyde (%)		62.31	74.55	81.93	91.35	81.19	60.96	71.64	67.18	74.36	58.15
Acid (%)		3.63	1.28	2.06	3.85	2.52	25.41	10.09	14.59	17.57	22.76

[a]Numbers refer to Figure 2.

[b]Soybean oil without stir frying and storage.

[c]Unit is 10^{-6} g/100 g.

[d]n.d. = not detectable.

[e]i.s. = internal standard.

TABLE 4

Changes of Volatile Constituents of Corn Oil Heated by Stir Frying During Storage at 55°C

Peak no.	Compound[a]	Control[b]	Storage time (weeks)[c]								
			0	1	3	6	9	15	18	24	30
1.	Ethanal	0.23	4.12	n.d.[d]	1.87	11.78	15.29	3.48	28.79	33.38	10.78
2.	*n*-Propanal	1.14	25.93	35.00	7.86	37.70	17.09	59.39	154.07	118.01	156.56
3.	*(E)*-2-Propenal	n.d.	n.d.	3.60	0.84	5.14	0.73	9.29	20.32	n.d.	n.d.
4.	Ethyl acetate	1.57	14.10	37.60	7.73	65.04	40.04	32.37	64.33	243.92	52.78
5.	*n*-Pentanal	8.85	45.67	144.33	80.89	244.00	138.13	261.76	545.16	661.97	466.94
6.	*n*-Hexanal	35.77	283.00	691.30	346.09	2914.70	1109.70	3116.11	5555.00	5431.31	8011.84
7.	*(E)*-2-Pentenal	0.81	n.d.	8.11	10.54	53.55	7.58	31.17	79.84	62.84	86.94
8.	1-Penten-3-ol	0.15	4.19	5.02	14.73	21.99	10.81	40.80	122.41	94.67	123.06
9.	2-Heptanone	5.28	26.15	35.00	25.01	168.24	93.16	222.09	361.22	337.62	150.48
10.	2-Pentyl furan	6.80	91.33	116.67	78.21	29.37	75.68	291.68	401.61	524.67	1935.16
11.	*(E)*-2-Hexenal	2.61	49.67	131.67	44.21	134.23	51.12	224.42	388.56	330.19	666.22
12.	*n*-Pentanol	2.33	128.00	170.67	64.57	251.44	189.18	326.17	607.15	914.03	1306.20
13.	Tridecane	i.s.[e]	i.s.	i.s.	i.s.	i.s.	i.s.	i.s.	i.s.	i.s.	i.s.
14.	2-Octanone	2.25	25.70	8.91	22.83	104.05	91.77	70.49	90.11	67.45	265.40
15.	*(Z)*-2-Heptenal	0.78	11.53	15.08	15.92	41.73	23.19	29.97	39.30	38.59	66.52
16.	*(Z)*-2-Penten-1-ol	0.24	10.45	n.d.	10.73	41.25	14.20	32.59	50.24	48.93	89.77
17.	*(E)*-2-Heptenal	5.30	848.00	1126.00	788.80	1320.90	887.04	2653.22	3908.19	3336.06	8627.34
18.	*n*-Hexanol	0.15	12.90	13.60	16.34	23.17	24.91	70.66	141.81	181.94	369.81
19.	*n*-Nonanal	2.95	296.00	236.00	212.12	265.46	245.15	199.85	229.02	234.90	272.34
20.	*(Z)*-2-Octenal	1.87	41.01	25.37	16.51	71.17	38.59	129.15	157.41	149.32	200.47
21.	3-Octen-2-one	0.41	18.63	16.85	13.42	45.56	39.49	107.84	170.90	302.87	742.46
22.	*(E)*-2-Octenal	1.23	209.33	138.30	305.71	683.34	604.73	1635.08	2380.87	3767.05	7891.11
23.	1-Octen-3-ol	2.58	248.00	262.00	137.24	785.20	546.95	1366.15	1810.35	2848.00	3952.07
24.	*n*-Heptanol	n.d.	11.56	n.d.	5.14	30.97	35.66	28.92	43.10	50.26	77.43
25.	*(E,Z)*-2,4-Heptadienal	0.81	22.13	32.73	26.40	41.90	44.32	122.82	169.45	102.15	149.13
26.	*(E,E)*-2,4-Heptadienal	0.65	72.00	68.67	71.36	78.13	83.44	160.66	253.48	212.82	317.66
27.	*n*-Propanoic acid	0.17	n.d.	n.d.	n.d.	n.d.	1.94	4.43	3.70	7.72	n.d.
28.	*(E)*-2-Nonenal	1.24	20.84	11.32	20.01	27.53	47.64	112.58	168.22	347.06	596.58
29.	3,5-Octadien-2-one	0.37	4.25	3.68	3.58	33.47	7.31	14.09	21.05	31.09	44.77
30.	*n*-Butanoic acid	n.d.	n.d.	n.d.	n.d.	n.d.	1.14	n.d.	5.58	3.10	29.42
31.	*(E)*-2-Decenal	0.29	78.00	21.90	26.05	48.15	69.37	92.40	121.76	231.32	386.89
32.	2,3-Octadione	0.67	13.25	2.59	11.97	56.00	51.07	133.56	299.77	279.75	699.87
33.	*(E,Z)*-2,4-Nonadienal	0.24	4.95	n.d.	n.d.	n.d.	4.86	4.70	8.55	10.37	52.16
34.	*(Z,E)*-2,4-Nonadienal	0.06	n.d.	n.d.	n.d.	0.16	4.34	7.32	9.57	18.09	26.15
35.	*(E,E)*-2,4-Nonadienal	0.38	20.98	19.60	27.11	54.59	119.99	224.54	294.44	374.30	433.66
36.	*n*-Pentanoic acid	n.d.	1.36	n.d.	6.26	38.79	106.96	160.78	409.12	462.54	761.88
37.	*(E)*-2-Undecenal	0.09	44.33	12.34	10.60	17.69	28.25	47.97	71.35	92.04	199.23
38.	*(E,Z)*-2,4-Decadienal	1.40	230.67	55.33	75.10	83.38	142.37	400.07	447.52	985.28	711.21
39.	*(Z,Z)*-2,4-Decadienal	n.d.	7.37	2.28	1.10	1.85	1.49	8.61	13.67	23.44	49.01
40.	*(E,E)*-2,4-Decadienal	3.88	1196.00	436.33	425.06	553.79	1126.70	2098.87	2682.37	4225.95	6514.24
41.	*n*-Hexanoic acid	4.34	11.73	31.41	77.68	34.12	1575.50	1784.52	3818.20	8057.59	12658.06
42.	*(E)*-2-Pentenoic acid	1.43	7.76	n.d.	8.69	8.88	2.28	8.23	15.52	43.00	61.89
43.	*n*-Octanoic acid	0.42	n.d.	n.d.	7.86	27.72	71.84	71.06	135.24	184.46	313.22
44.	*(E)*-2-Hexenoic acid	n.d.	n.d.	n.d.	n.d.	n.d.	2.27	9.08	17.95	21.63	19.45
45.	Unknown	n.d.	n.d.	n.d.	n.d.	n.d.	4.08	4.85	10.83	8.59	87.58
46.	*n*-Nonanoic acid	n.d.	n.d.	n.d.	n.d.	9.47	53.51	53.00	99.43	143.44	191.82
47.	*(E)*-2-Heptenoic acid	n.d.	n.d.	n.d.	n.d.	4.64	21.60	25.86	49.73	94.33	209.27
48.	*n*-Decanoic acid	n.d.	n.d.	n.d.	n.d.	n.d.	12.10	22.98	49.60	126.99	94.42
49.	*(E)*-2-Octenoic acid	n.d.	27.78	n.d.	n.d.	n.d.	n.d.	23.28	45.83	56.03	193.63
Total		99.74	4168.67	3919.26	3026.14	8470.24	7884.56	16538.91	26571.69	35921.06	60322.88
Total aldehyde		70.58	3511.53	3215.26	2514.15	6648.97	4811.11	10985.46	17472.44	20786.44	36486.31
Total acid		6.36	48.63	31.41	100.49	123.62	1849.14	2163.22	4649.90	9200.83	14533.06
Aldehyde (%)		70.76	84.24	82.04	83.08	78.50	61.02	66.26	65.76	57.87	60.48
Acid (%)		6.37	1.16	0.80	3.32	1.46	23.45	13.08	17.50	25.61	24.09

[a] Numbers refer to Figure 2.
[b] Corn oil without stir frying and storage.
[c] Unit is 10^{-6} g/100 g.
[d] n.d. = not detectable.
[e] i.s. = internal standard.

TABLE 5

Changes of Volatile Constituents of Lard Heated by Stir Frying During Storage at 55°C

Peak no.	Compound[a]	Control[b]	Storage time (weeks)[c]								
			0	1	3	6	9	15	18	24	30
1.	Ethanal	n.d.[d]	15.19	5.74	10.17	9.39	20.63	13.22	28.43	436.02	26.99
2.	*n*-Propanal	15.53	n.d.	16.90	42.66	34.29	63.02	217.43	281.22	2350.05	1329.00
3.	*(E)*-2-Propenal	n.d.	n.d.	n.d.	n.d.	2.74	16.68	n.d.	n.d.	n.d.	37.18
4.	Ethyl acetate	5.90	7.28	n.d.	8.70	24.48	52.67	38.67	78.93	793.09	336.52
5.	*n*-Pentanal	5.47	58.00	65.30	68.53	98.01	160.19	370.28	352.86	2543.37	1419.80
6.	*n*-Hexanal	38.76	247.00	208.00	569.49	440.37	1808.25	3143.80	4685.70	30145.36	18835.30
7.	*(E)*-2-Pentenal	12.46	8.13	10.50	36.40	40.07	54.61	122.63	139.75	535.55	364.58
8.	1-Penten-3-ol	1.29	5.01	11.84	14.97	17.95	107.39	391.93	390.06	1316.60	778.14
9.	2-Heptanone	14.11	106.30	68.33	122.07	72.36	166.28	356.61	502.03	2282.65	2327.50
10.	2-Pentyl furan	6.76	64.33	47.67	93.49	n.d.	184.20	324.15	961.49	5060.04	7952.75
11.	*(E)*-2-Hexenal	9.93	43.00	25.13	61.20	72.91	86.96	244.16	274.75	2282.65	739.82
12.	*n*-Pentanol	22.22	87.33	60.33	85.27	91.73	296.01	383.08	561.53	3760.66	2439.00
13.	Tridecane	i.s.[e]	i.s.	i.s.	i.s.	i.s.	i.s.	i.s.	i.s.	i.s.	i.s.
14.	2-Octanone	13.47	103.33	64.67	136.32	137.53	241.48	533.88	814.13	1794.93	3722.83
15.	*(Z)*-2-Heptenal	2.43	21.58	12.34	24.07	17.49	48.72	64.88	102.99	199.80	n.d.
16.	*(Z)*-2-Penten-1-ol	n.d.	31.68	8.44	34.30	13.77	43.36	49.81	79.42	109.65	205.28
17.	*(E)*-2-Heptenal	80.33	619.00	389.00	1207.83	596.77	1622.18	2258.27	3313.50	5723.86	8794.28
18.	*n*-Hexanol	3.19	7.25	8.60	23.29	20.83	31.12	56.02	91.57	318.49	159.22
19.	*n*-Nonanal	42.31	490.66	423.70	555.46	459.58	592.83	710.88	1046.41	3046.57	4073.45
20.	*(Z)*-2-Octenal	0.75	35.33	26.61	44.63	40.86	99.79	89.45	165.14	295.23	330.93
21.	3-Octen-2-one	0.75	23.73	39.67	143.69	92.42	458.93	215.12	931.69	2114.62	3119.38
22.	*(E)*-2-Octenal	25.46	126.66	104.33	688.89	466.69	1216.27	1203.91	3729.25	8331.85	11793.02
23.	1-Octen-3-ol	22.92	204.00	166.00	321.38	476.62	1556.70	1171.17	1851.82	4146.28	3544.79
24.	*n*-Heptanol	4.63	32.01	21.98	42.83	70.56	124.50	98.50	164.28	393.49	465.09
25.	*(E,Z)*-2,4-Heptadienal	5.07	44.67	31.82	79.82	39.80	83.20	75.10	108.46	109.85	98.09
26.	*(E,E)*-2,4-Heptadienal	22.37	157.00	104.67	264.60	42.54	369.68	44.45	342.04	302.97	457.22
27.	*n*-Propanoic acid	n.d.	n.d.	4.04	35.77	14.30	95.10	19.54	61.74	130.01	29.87
28.	*(E)*-2-Nonenal	12.12	48.33	51.67	116.51	129.09	407.32	337.50	1266.17	3471.02	4294.40
29.	3,5-Octadien-2-one	4.10	3.45	29.51	84.04	20.63	207.44	74.25	225.78	363.68	292.07
30.	*n*-Butanoic acid	n.d.	n.d.	n.d.	2.50	3.32	n.d.	1.16	n.d.	35.13	127.20
31.	*(E)*-2-Decenal	32.18	n.d.	141.00	200.08	218.45	442.90	302.63	657.40	1826.63	1839.34
32.	2,3-Octadione	n.d.	137.67	6.54	28.92	29.37	92.47	87.26	295.36	589.87	893.73
33.	*(E,Z)*-2,4-Nonadienal	n.d.	n.d.	n.d.	2.43	0.39	8.13	n.d.	n.d.	7.32	212.11
34.	*(Z,E)*-2,4-Nonadienal	n.d.	n.d.	n.d.	n.d.	1.54	3.52	n.d.	2.20	19.93	n.d.
35.	*(E,E)*-2,4-Nonadienal	0.69	n.d.	9.31	24.52	25.70	115.53	42.11	185.12	522.16	441.00
36.	*n*-Pentanoic acid	n.d.	2.22	2.41	8.37	24.56	114.25	119.99	348.56	1048.56	2083.86
37.	*(E)*-2-Undecenal	15.72	87.33	87.33	99.42	118.27	248.59	170.34	362.56	1018.15	1047.62
38.	*(E,Z)*-2,4-Decadienal	8.48	42.00	41.00	62.27	40.77	147.06	52.00	177.79	523.49	237.36
39.	*(Z,Z)*-2,4-Decadienal	1.05	2.89	3.02	5.03	5.41	11.37	1.75	20.72	29.52	72.52
40.	*(E,E)*-2,4-Decadienal	45.93	442.00	428.00	542.00	503.33	1362.16	750.41	1842.36	3391.60	3015.54
41.	*n*-Hexanoic acid	1.16	14.03	11.05	119.29	376.98	2366.90	1274.45	5797.22	27631.58	35042.78
42.	*(E)*-2-Pentenoic acid	2.00	4.40	7.61	11.85	10.95	18.25	14.09	50.66	213.38	187.01
43.	*n*-Octanoic acid	n.d.	n.d.	0.63	9.82	27.77	95.31	111.52	265.91	899.42	1276.39
44.	*(E)*-2-Hexenoic acid	n.d.	n.d.	n.d.	0.81	3.14	10.25	5.41	14.56	46.58	17.40
45.	Unknown	6.32	n.d.	0.70	20.02	29.59	6.33	29.33	17.14	42.89	72.72
46.	*n*-Nonanoic acid	n.d.	n.d.	29.72	6.69	24.25	49.46	123.19	246.47	881.45	1364.44
47.	*(E)*-2-Heptenoic acid	n.d.	n.d.	n.d.	8.33	18.69	68.30	47.49	154.54	580.84	720.86
48.	*n*-Decanoic acid	n.d.	n.d.	13.18	n.d.	n.d.	46.85	34.45	137.67	405.92	455.32
49.	*(E)*-2-Octenoic acid	n.d.	n.d.	3.07	n.d.	n.d.	n.d.	27.20	98.31	141.40	311.76
Total		485.86	3322.79	2791.36	6068.10	5006.26	15423.14	15803.47	33225.69	122214.16	127385.46
Total aldehyde		377.04	2488.77	2185.37	4706.01	3404.60	8989.59	10215.20	19084.82	67112.95	59459.55
Total acid		3.16	20.65	71.71	203.43	503.96	2864.67	1778.49	7175.64	32014.27	41616.89
Aldehyde (%)		77.60	74.90	78.29	77.55	68.01	58.29	64.64	57.44	53.37	46.68
Acid (%)		0.65	0.62	2.57	3.35	10.07	18.57	11.25	21.60	25.46	32.67

[a]Numbers refer to Figure 2.

[b]Lard without stir frying and storage.

[c]Unit is 10^{-6} g/100 g.

[d]n.d. = not detectable.

[e]i.s. = internal standard.

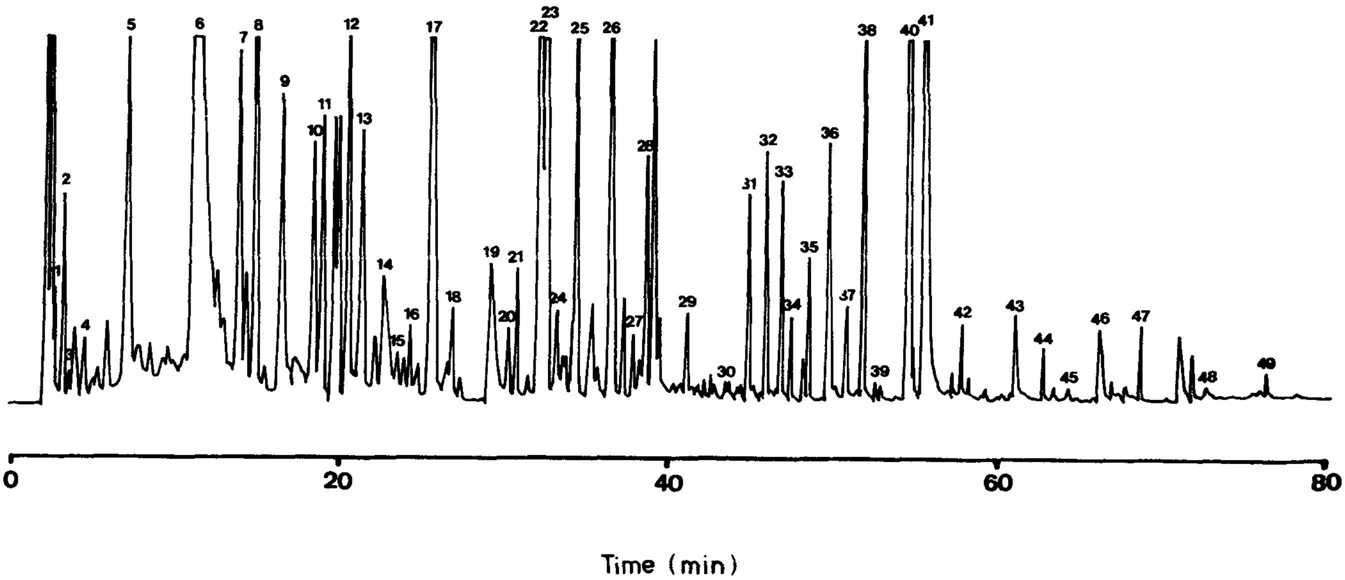

FIG. 2. Gas chromatogram of volatile compounds in soybean oil heated by stir frying after 15 week storage at 55°C.

TABLE 6

Comparisons of Volatile Compounds in Soybean Oil Generated by Deep Frying and Stir Frying After 26 Weeks Storage at 55°C

Samples	Heat applied	Heat applied ratio	Total volatiles produced after 26 weeks storage	Hexanoic acid/total volatiles percentage
Soybean oil heated by deep frying	200°C × 3 min[a]	20	85.24 mg/100 g oil	10
Soybean oil heated by stir frying	200°C × 3 min[b]	1	33.95 mg/100 g oil	16

[a]Heat energy applied to soybean oil before temperature reached 200°C was not included.

[b]Final temperature was 200°C for a total 3 min of stir frying, therefore; heat applied was much less than this value.

autoxidation can be fairly proposed. Smaller compounds such as hexanal and hexanoic acid were more abundant in the stir-fried samples' volatiles after storage, which indicates that secondary degradation occurred.

PVs of samples were also studied. In the first 10 weeks of storage, PVs increased, but after that the values decreased or then increased again or they fluctuated. Changes of PVs were not consistent with volatile compounds during storage. As we reported earlier (7), PVs do not reflect the changes of volatile compounds in oil samples.

This study reports the significant amount of aldehydes, acids and other volatiles produced from heated edible oils during storage. This may explain the deterioration of foods heated with oils.

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