rates ~ 1.19). This could be ascribed to the fact of the change in lipase or the acid chain length. Because of the importance of interesterification chemistry to possible commercial processes, a more detailed investigation of the stereochemical consequences of this process seems warranted and is under way. In addition, we have made use of lypase stereobias in esterification and interesterification to synthesize insect sex attractants (20).

REFERENCES

1. Luddy, F.E., J.W. Hampson, S.F. Herb and H.L. Rothbart, *J. Amer. Oil Chem. Soc. 50*:240 (1973).
2. Kozempel, M.F., J.C. Craig Jr., W.K. Heiland, S.Elias and N.C. Aceto, *Ibid. 58*:921 (1981).
3. Luddy, F.E., J.W. Hampson, S.F. Herb and H.L. Rothbart, U.S. Patent 4,072,766, Feb. 7, 1978.
4. Perkins, E.G., J.E. Bauer, N. Pelick and A. El-Hamdy, in *Dietary Fats and Health*, edited by E.G. Perkins and W.J. Visek, AOCS Monograph 10, AOCS, Champaign, IL, 1983, pp. 184-208.
5. Pan, W.G., and E.G. Hammond, *Lipids 18*:882 (1983).
6. Posorske, L.H., *J. Amer. Oil Chem. Soc. 61*:1758 (1984).
7. Linfield, W.M., D.J. O'Brien, S. Serota and R.A. Barauskas, *Ibid. 61*:1067 (1984).
8. Linfield, W.M., S. Serota and L. Sivieri, *Ibid. 62*:1152 (1985).
9. Macrae, A.R., *Ibid. 60*:291 (1983).
10. Wisdom, R.A., P. Dunnill, M.D. Lilly and A. Macrae, *Enz. and Microb. Tech. 6*:443 (1984).
11. Muderhwa, J.M., R. Ratomahenina, M. Pina, J. Graille and P. Galzy, *J. Amer. Oil Chem. Soc. 62*:1031 (1985).
12. Brockerhoff, H., and R.G. Jensen, in *Lipolytic Enzymes*, Academic Press, New York, N.Y., 1974, p. 56.
13. Iriuchijima, S., and N. Kojima, *J. Chem. Soc., Chem. Commun.*, 185 (1981).
14. Ladner, W.E., and G.M. Whitesides, *J. Am. Chem. Soc. 106*:7250 (1984).
15. Cambou, B., and A.M. Klibanov, *Appl. Biochem. and Biotech. 9*:255 (1984).
16. Martin, V.S., S.S. Woodard, T. Katsuki, Y. Yamada, M. Ideda and K.B. Sharpless, *J. Am. Chem. Soc. 103*:6237 (1981).
17. Cambou, B., and A.M. Klibanov, *Ibid. 106*:2687 (1984).
18. Linfield, W.M., R.A. Barauskas, L. Sivieri, S.Serota and R.W. Stevenson Jr., *J. Amer. Oil Chem. Soc. 61*:191 (1984).
19. Morita, S., H. Narita, T. Matoba and M. Kito, *Ibid. 61*:1571 (1984).
20. Sonnet, P.E., and M.W. Baillargeon, *J. Chem. Ecol.* (In press).

[Received February 10, 1986]

Improving the Quality of Used Frying Oils by Treatment with Activated Carbon and Silica

John McNeill[a], Yukio Kakuda*,[a] and Basil Kamel[b]
Department of Food Science, University of Guelph, Guelph, Ontario, Canada N1G 2W1, and [b]Atkemix Inc., Brantford, Ontario.

This study was undertaken to investigate the effectiveness of activated carbon and silica in removing the degradation products present in used frying oils. Two batches of canola oil were treated with mixtures of activated carbon and silica. Three levels of activated carbon (3%, 6%, 9%, wt/wt) were blended with three levels of a silica compound (2%, 4%, 6%, wt/wt) in all nine possible combinations. Oil 1 was prepared by continuous heating in the lab, and oil 2 was obtained from a small potato-frying operation. For each treatment combination of silica and carbon, the average percent decrease for acid value, peroxide value, photometric color, polar compounds, saturated carbonyls and unsaturated carbonyls was 53.9%, 39.4%, 38.3%, 27.5%, 54.0% and 27.3%, respectively, for oil 1, and 51.1%, 53,5%, 49.7%, 16.3%, 58.9% and 39.0%, respectively, for oil 2. The levels of oleic, linoleic and linolenic acids decreased by 28%, 33% and 35%, respectively, following heat treatment but were shown to increase by 1 to 5% after adsorbent treatment. The yield of treated oil ranged from 56 to 83%.

Deep fat frying is an important processing procedure used worldwide for the preparation and production of foods. During the deep fat frying process, oil is continuously or repeatedly subjected to high temperatures in the presence of air and moisture. Under these conditions a variety of degradation reactions can occur, such as autoxidation, thermal polymerization, thermal oxidation, isomer cyclization and hydrolysis.

The degradation products formed by these reactions include both volatile and non-volatile compounds (1). Although most of the volatiles are lost through steam distillation during the frying process, some remain in the oil and may be consumed with the fried food (2). The non-volatile decomposition products are produced primarily by thermal oxidation and polymerization of unsaturated fatty acids (3,4). These compounds are of particular concern because they accumulate in the frying oil where they promote further degradation and may be absorbed by the fried food and enter the diet of the consumer (5).

The overuse of frying oils will noticeably affect the flavor, flavor stability, color and texture of fried foods

TABLE 1

Oil Quality Before Adsorbent Treatment

Quality attributes	Oil 1[a]	Oil 2[b]
Acid value	1.4	0.7
Peroxide value	13.9	11.6
Photometric color	6.0	13.7
Polar compounds (%)	24.8	29.0
Non polar compounds (%)	73.1	72.8
Saturated carbonyl (μmol/g)	13.8	16.5
Unsaturated carbonyl (μmol/g)	22.1	26.0

[a]Heated 72 hr at 180 C.
[b]Potato-fried oil, 4 hr/day for 1 wk at 180 C.

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*To whom correspondence should be addressed.

(1). The oil itself will undergo a number of chemical and physical changes resulting in increased smoking, foaming, color and viscosity, accompanied by the formation of free fatty acids, hydroperoxides, carbonyls and high molecular weight polymerized compounds. The nutritional value and toxicity of the oil also may be affected if the oil is severely abused. (1,6,7).

In order to reduce these detrimental effects and prolong the useful life of frying oils, regular cleaning and maintenance of equipment and utilization of proper frying conditions are required (5). One commonly used method of maintaining oil quality is to add fresh oil periodically (8,9). Another procedure to control the rate and degree of oil breakdown involves filtering the oil on a daily or continuous basis. Food particles, if not removed by filtration, may burn and develop undesirable flavors and odors and increase the rate of oil deterioration (10).

Filtering aids capable of extending the cooking life of frying oils also are available. These adsorbent materials improve oil quality by reducing the levels of free fatty acids and colored compounds (11). One such adsorbent material consists of a mixture of diatomaceous earth and calcium and magnesium silicates. The daily use of 1% of the mixture based on the weight of oil has been shown to increase the frying life of oils (12). However, care should be taken when selecting these products, as some of them have been shown to reduce oil stability (11).

The major focus of much of the published work on used frying oil quality has been concerned with the identification, quantitation and toxicity of degradation products. Considerably less work has been published on procedures to clean or purify these oils. The ability of activated carbon and silica to improve the quality of used frying oils was investigated in this study.

TABLE 2

Effect of Adsorbents on Oil No. 1

			Mean percent decrease[a]					
Treatment	Carbon %	Silica %	AV[b]	PV[c]	PCOL[d]	PC[e]	SC[f]	UC[g]
1	3	2	46.3	39.1	30.4	16.9	39.1	24.0
2	3	4	48.9	36.4	33.4	28.4	49.1	24.2
3	3	6	52.6	31.1	39.5	37.7	39.6	29.2
4	6	2	55.5	35.6	34.5	29.0	52.9	26.4
5	6	4	43.1	39.7	51.4	31.4	56.1	27.5
6	6	6	59.9	37.1	36.7	31.6	58.0	29.4
7	9	2	56.2	35.6	36.6	20.6	61.8	23.6
8	9	4	56.2	29.5	36.2	25.8	68.4	32.4
9	9	6	66.4	58.9	46.4	26.1	61.3	28.6
Mean of 9 treatments			53.9	39.4	38.3	27.5	54.0	27.3

[a] Mean % decrease = (initial − final)/(initial) × 100 (mean of 2 determinations).
[b] Acid value.
[c] Peroxide value.
[d] Photometric color.
[e] Polar compounds.
[f] Saturated carbonyls.
[g] Unsaturated carbonyls.

TABLE 3

Effect of Adsorbents on Oil No. 2

			Mean percent decrease[a]					
Treatment	Carbon %	Silica %	AV	PV	PCOL	PC	SC	UC
1	3	2	44.3	42.8	39.3	19.7	52.2	34.6
2	3	4	47.9	53.3	69.3	10.3	78.3	34.7
3	3	6	55.7	52.1	38.6	32.9	59.5	36.8
4	6	2	44.3	56.5	36.8	16.4	49.1	40.6
5	6	4	45.0	42.2	45.5	18.1	57.9	38.3
6	6	6	46.7	60.1	75.9	9.1	57.5	40.5
7	9	2	56.6	60.6	50.3	13.7	54.8	40.6
8	9	4	41.4	58.1	48.3	9.1	53.9	44.6
9	9	6	62.7	56.4	43.4	17.7	66.9	40.2
Mean of 9 treatments			51.1	53.5	49.7	16.3	58.9	39.0

[a] For abbreviations see Table 2.

MATERIALS AND METHODS

Oil samples. Two batches of canola oil were used in this study. One batch was obtained from a small scale potato fryer (2 kg oil, one week of frying at 180 C for approximately 4 hr per day). The second batch was prepared by continuously heating 2 kg of oil for 72 hr at 180 C.

Adsorbents. "Silasorb," a silica-based compound supplied by Manville Products Corp., and activated carbon (Darco KB-B), supplied by ICI Americas Inc., Marshall, Texas, were used without further treatment.

Oil treatments. Aliquots of 100 g each were taken from the two batches of heated oil and treated with a mixture of activated carbon and silica. Three levels of carbon (3%, 6%, 9%, wt/wt) and silica (2%, 4%, 6%, wt/wt) in all nine possible combinations of carbon/silica (3%/2%), (3%/4%), (3%/6%), (6%/2%), (6%/4%), (6%/6%), (9%/2%), (9%/4%), (9%/6%) were used. The treatments were replicated twice on each oil for a total of 36 treatments.

Activated carbon, silica and oil slurried in a 250-ml centrifuge bottle and agitated for 20 min in a shaking water bath maintained at 80 C. Following centrifugation at 8,000 g for 15 min, the oil was filtered through two layers of Whatman No. 1 filter paper in a 100 C oven. The filtered oil was stabilized with 0.02% (wt/wt) Tenox BHA (Eastman Kodak, Rochester, New York) and stored at 4 C in 50-ml screw capped test tubes until analyzed.

Polar and nonpolar compounds. The column chromatographic procedure of Billek et al. (13) was used to determine the percentages of polar and nonpolar compounds.

Carbonyl compounds. Saturated and unsaturated carbonyls were quantified by the method of Henick et al. (14) as modified by Fioriti (15). The reaction was carried out at 60 C for 30 min using redistilled solvents. Our experimentally determined molar extinction coefficients for hexanal ($E_{430} = 18240$, $E_{460} = 19668$) were in close agreement with those given by Henick et al. (14); therefore, the equations derived by those authors were used to calculate the levels of saturated and unsaturated carbonyls.

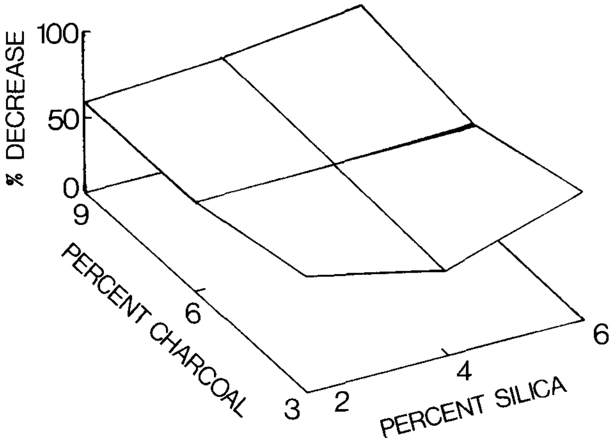

FIG. 1. Effect of activated carbon and silica on the reduction of acid value for oil 1.

Gas liquid chromatography. Fatty acid methyl esters were prepared by base catalyzed transesterification. The transesterification reagent, 2N methanolic KOH, was prepared fresh daily. Approximately 0.5 g of oil was accurately weighed into a glass-stoppered test tube and dissolved in 10 ml of heptane. Methanolic KOH (0.5 ml) was added, the tube contents mixed by inversion and then allowed to stand until the upper phase became clear. A 5.0-ml aliquot of the clear heptane phase was removed and quantitatively spiked with 2.0 μl of methyl nonanoate (PolyScience, Niles, Illinois). The methyl esters were found to be stable for several days when stored at 4 C.

Methyl nonanoate was used as the internal standard for calculation of absolute fatty acid percentages in the oil samples. Response factors were determined from known weights of standard fatty acid methyl esters. Methyl palmitate, stearate, oleate and linoleate were purchased from PolyScience (Niles, Illinois) and used without further purification. Methyl linolenate (Eastman Kodak Co., Rochester, New York) was purified by the method outlined by Erwin and Block (16).

The analysis was performed on a Hewlett Packard 5830 A gas chromatograph equipped with a six-ft glass column packed with 10% Silar 9CP on acid washed Chromasorb W. The flame ionization detector (FID) and injector ports were maintained at 230 C and 200 C, respectively. The chromatograph was temperature programmed from 70 C to 180 C at 10 C per min and held at 180 C for 60 min. The carrier gas was nitrogen at a flow rate of 30 ml/min.

Acid value, peroxide value and photometric color. The acid and peroxide values were determined by AOCS Official Methods [Cd 3a-63 and Cd 8-53 (17)]. The photometric color was determined by AOCS Method Cc 13c-50 with the following changes: in order to lower viscosity and speed filtration, samples were diluted 1:1 (v/v) with heptane, then filtered through 0.45 μM Millipore membrane filters (Millipore Co., Bedford, Massachusetts). The filtered samples were placed in a vacuum desiccator to remove hexane and the absorbance values of the solvent-free oils were measured on a Beckman model 35 spectrophotometer (Irvine, California).

RESULTS AND DISCUSSION

The quality attributes of the two heated oils prior to adsorbent treatment are shown in Table 1. The two oils were similar in all respects except for acid value and color. The acid value for oil 1 (heated 72 hr at 180 C) was twice that of oil 2 (potato-fried oil), while the color for oil 1 was half that of oil 2. Losses of volatiles by steam distillation may account for the lower acidity of oil 2, while solubilization of food lipids and colored compounds and reactions of food components may have contributed to the darker color in the potato fried oil.

Treatment of the oils with mixtures of activated carbon and silica was effective in reducing acid value, peroxide value, saturated and unsaturated carbonyls, polar compounds and photometric color. The results were expressed as percent decrease (value for untreated oil—value after treatment)/(value for untreated oil) × 100, and subjected to the analysis of variance procedure

(SAS Institute Inc., SAS Circle, Cary, North Carolina). Each treatment level was replicated twice and the average percent decrease calculated. Tables 2 and 3 contain the average percent decrease data for oils 1 and 2. Significant differences between treatment levels were observed for acid value and unsaturated and saturated carbonyls. In the case of acid value (AV), increasing levels of both activated carbon and silica were significant ($P < 0.05$). The highest levels of carbon (9%) and silica (6%) resulted in a 66% decrease in AV for oil 1 (Fig. 1) and a 63% decrease in AV for oil 2. Silica proved to be more effective than carbon in reducing acidity.

Conversely, activated carbon was shown to be more effective than silica in reducing the levels of saturated and unsaturated carbonyls in oils 1 and 2. Silica showed a significant effect only on unsaturated carbonyls. Perhaps this difference may be explained by the unique adsorptive characteristics of these two compounds. Carbon removes impurities by occlusion and by adsorption based on chemical properties, while silica's adsorptive qualities are based primarily on interaction with exposed silanol groups.

The analysis of the remaining quality attributes showed no significant differences between treatments. The percent decrease in peroxide value, photometric color and polar compounds was approximately the same regardless of the levels of carbon and silica used. It would appear that under our experimental conditions the levels of each adsorbent compound used were in excess of their equilibrium concentration. In addition, since greater amounts of oil were being adsorbed by increasing levels of carbon and silica, further removal of degradation products may have been obscured.

To assess the effectiveness of the adsorbents on reducing the levels of peroxides, color and polar compounds, the overall percent decrease (mean of 9 treatments) was calculated. These values are shown on the bottom of Tables 2 and 3. The results show that for oil 1, peroxide value (39.4%), color (38.3%) and polar compounds (27.5%) were substantially reduced. Oil 2 showed slightly better reductions for peroxide value (53.5%) and color (49.7%), and only a 16.3% decrease in polar compounds.

In general, no major differences were observed between the two oils. The carbon/silica mixtures were most effective in reducing acid value and saturated carbonyls and least effective in removing total polar compounds.

Changes in the fatty acid composition of oil 1 were determined by GLC analysis. The absolute percentages of fatty acids (weight of fatty acid/weight of sample) × 100 were calculated by the internal standard method. The results are shown in Table 4. The concentration of the three main unsaturated fatty acids, linolenic, linoleic and oleic, decreased by 35%, 33% and 28%, respectively. Following carbon/silica treatment a 1 to 5% increase in the levels of these fatty acids was observed. This increase is likely due to the removal of polymerized and oxidized compounds and indicates an overall improvement in the quality of the oil.

TABLE 4

Fatty Acid Composition of Oil 1

Sample	16:0	18:0	18:1	18:2	18:3
Fresh	3.3	1.4	47.5	21.0	10.4
Heated	2.6	1.1	34.4	14.2	6.7
Adsorbent treated	2.9	1.2	39.5	16.3	7.6

Percentages based on 18 determinations.
Percent fatty acid = wt fatty acid/total wt of sample.

As expected, the yield of treated oil was reduced by increasing levels of both silica and carbon. The percent yield ranged from 56 to 83% for oil 1 and 50 to 78% for oil 2. Yields of 50% may be uneconomical for practical application, but they were observed at the highest levels of carbon and silica. Lower levels of adsorbents and longer contact times may increase the yield values without diminishing the removal of degradation products. Perhaps some type of flow-through cartridge system would be more efficient and allow greater throughput while minimizing oil losses.

ACKNOWLEDGMENTS

This research was funded in part by Kraft, Limited and the Ontario Ministry of Agriculture and Food. Sandra Wachnuik did preliminary studies on this project.

REFERENCES

1. Chang, S.S., R.J. Peterson and C.T. Ho, *J. Amer. Oil Chem. Soc. 55*:718 (1978).
2. May, W.A., R.J. Peterson and S.S. Chang, *Ibid. 60*:990 (1983).
3. Perkins, E.G., *Food Technol. 21*:125 (1967).
4. Paulose, M.M., and S.S. Chang, *J. Amer. Oil Chem. Soc. 55*:375 (1978).
5. Stevenson, S.G., M. Vaisey-Genser and N.A.M. Eskin, *Ibid. 61*:1102 (1984).
6. Perkins, E.G., and F.A. Kummerow, *J. Nutr. 68*:101 (1959).
7. Alexander, J.C., *J. Amer. Oil Chem. Soc. 55*:711 (1978).
8. Robertson, C.J., *Food Technol. 21*:34 (1967).
9. Thompson, L.U., and R. Aust, *Can. Inst. Food Sci. Technol. J. 16*:246 (1983).
10. Weiss, T.J., in *Food Oils and Their Uses*, The AVI Publishing Co., Inc., Westport, CT, 2nd edn., 1983, pp. 157-180.
11. Jacobson, G.A., *Food Technol. 21*:43 (1967).
12. *Food Eng. 50*:191 (1978).
13. Billek, G., G. Guhr and J. Waibel, *J. Amer. Oil Chem. Soc. 55*:728 (1978).
14. Henick, A.S., M.F. Benca and J.H. Mitchell Jr., *Ibid. 31*:88 (1954).
15. Fioriti, J.A., *Ibid. 42*:743 (1965).
16. Erwin, J., and W. Block, *J. Biol. Chem. 238*:1618 (1963).
17. *Official and Tentative Methods of the American Oil Chemists' Society*, 3rd edn., Champaign, IL, Method Cd 3a-63.

[Received March 21, 1986]