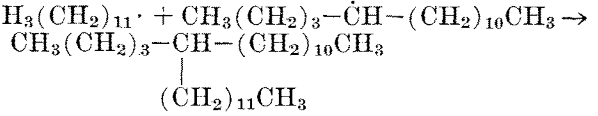
There are numerous ways in which these radicals may recombine. Some of the more likely reactions that occur on the basis of the observations made here are as follows:

Branching:



$$CH_3(CH_2)_{11}\cdot + CH_3(CH_2)_3{-}\dot{C}H{-}(CH_2)_{10}CH_3 \rightarrow CH_3(CH_2)_3{-}\underset{\displaystyle (CH_2)_{11}CH_3}{\underset{|}{CH}}{-}(CH_2)_{10}CH_3$$

Yielding gases:

$$CH_3(CH_2)_3\cdot + \cdot H \longrightarrow n{-}C_4H_{10}$$

Incorporation of nitrogen and hydrogen:

$$CH_3(CH_2)_3\cdot + CH_3(CH_2)_{11}\cdot + \dot{:}N + H\cdot \longrightarrow CH_3(CH_2)_{11}{-}NH{-}(CH_2)_{11}CH_3$$

Incorporation of oxygen:

$$CH_3(CH_2)_{11}\cdot + \cdot H + :O \longrightarrow CH_3(CH_2)_{11}OH$$

Since the system is highly dynamic, no products stay in the reaction field unchanged, but undergo branching, cracking, crosslinking and end up eventually as solid polymers. The same reactions may be expected to occur with fats, and we observe the formation of solid polymers from lard. Although discharge reactions have been used for the commercial production of acetylene, gasoline, lubricants and some simple chemicals (2), a major problem has been to control them. Since it is possible to transport methyl radicals, for example, up to 37 cm (9) an important use of discharge reactions may be for the generation of radicals for use in reactions outside the electrical field.

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REFERENCES

1. Glocker, G., and S. C. Lind, The Electrochemistry of Gases and Other Dielectrics, John Wiley & Sons, New York, 1939.
2. Thomas, C. L., G. Egloff and J. C. Morell, Chem. Rev. *28*, 1 (1941).
3. Steacie, E. W. R., Atomic and Free Radical Reactions, Reinhold, New York, 1954.
4. Houzeau, A., Compt. rend. *74*, 256 (1872).
5. Cottrell, F. G., Ind. Eng. Chem. *3*, 542 (1911).
6. Miller, S. M., J. Amer. Chem. Soc. *77*, 2351 (1955).
7. Oró, J., Nature, *197*, 862 (1963) and Nature *197*, 971 (1963).
8. Johnson, C. B., and A. T. Wilson, Nature *204*, 181 (1964).
9. Paneth, F., and W. Hofeditz, Ber. *62*, 1335 (1929).

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Effect of Moisture Level on Volatile Carbonyls in Cottonseed Oil Heated to 210C[1]

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Abstract

Cottonseed oil containing 0, 2.5, 5 and 10% added moisture was heated to simulate food-frying conditions. The volatile carbonyls from the heated oil were crystallized as 2,4-dinitrophenylhydrazones and then regenerated for separation by gas-liquid chromatography. Nineteen peaks were observed for the dry oil; oil with added moisture had fewer peaks. Oil containing added moisture produced more total carbonyl by weight than did dry oil. Maximum production of carbonyls occurred in the oil with 2.5% added moisture.

Introduction

IN RECENT YEARS the chemistry of fat deterioration at the elevated temperature of frying conditions has been the subject of considerable study (3–8). Water plays an important role in many chemical and physical reactions. Since most foods which are fried possess high concentrations of water, this moisture may affect many of the reactions which are possible.

This study was undertaken to determine the effect of water on the production of total volatile carbonyls in heated cottonseed oil and also the relative proportion of different carbonyls formed.

Experimental

Oil

Cottonseed oil representative of that used for the frying of potato chips was furnished by the Frito-Lay Company. The oil had the following characteristics: free fatty acid, <0.05%; color (Lovibond), 4.0 red; stability (AOM), 29 hr, 100 M.E. end point; moisture and impurities, nil; peroxide value, 0.5 M.E.; smoke point, >425F; cloud point, 290F. The tests above were carried out by the Procter and Gamble Co., the source of the oil. The one-gallon cans of oil were placed in storage at −35C on receipt and held at this temperature until needed.

TABLE I

Retention Times of the Volatile Carbonyl Compounds from Heated Oil and of Authentic Carbonyl Compounds on 10% LAC-446

Retention time in minutes relative to injection time						
Peak No.	Percent moisture				Authentic Compound	Identification
	0	2.5	5.0	10.0		
1	0.5	0.45	0.5	0.6		Unknown
2	0.75	0.65	0.80	0.80	0.75	α-ketoglutaric acid[b]
3	1.13	1.12	1.15	1.20	1.15	Ethanal
4	1.50	1.61	1.58	1.60	1.60	Propanal
5[a]	1.80	1.80	2.1	1.89	1.80	α-ketoglutaric acid[b]
	2.0	2.0	2.0	2.0	2.0	Acrolein
					3.4	Diacetyl
6	3.9	3.8	4.0	3.9	4.0	Pentanal, Pentanone
					5.2	Crotonal
7	7.0	6.6	7.1	7.1	7.1	Hexanal, Hexanone
8	12.2	11.6	12.2	12.2	12.2	Heptanal, Heptanone
9	16.3	16.6	16.6	16.2	16.4	Octanal
10	17.6	17.6	17.2	17.3	17.4	Octanone
11	19.2	19.2	19.0	19.0	18.8	Nonal
12	20.4	20.4	20.6	20.6	20.6	Nonanone
13	21.6	21.6	21.2		21.3	Decanal
14	22.8					Unknown
15	25.0	25.6				Unknown
16	26.7	27.0				Unknown
17	27.5					Unknown
18	28.2					Unknown
19	28.9					Unknown
20	29.6					Unknown
21	30.4					Unknown

[a] Acrolein and α-ketoglutaric acid appeared as one peak in the chromatogram.

[b] Excess α-ketoglutaric which remained after the reaction took place. Temperature: for 8 min at 60C, then temperature programmed at the rate of 6.4 C/min to 160C. Carrier gas flow rate: 112 ml/min (Nitrogen). Range, 10; attenuation, 16.

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[1] Approved as Journal Paper No. 448, College Experiment Station, University of Georgia, Athens.

TABLE II

Retention Times of the Volatile Carbonyl Compounds from Heated Oil and of Authentic Carbonyl Compounds on 30% Carbowax 20 M

Peak No.	Retention time in minutes relative to injection time					
	Percent moisture				Authentic compound	Identification
	0	2.5	5.0	10.0		
1	2.4	2.4	2.4	2.4	2.4	α-ketoglutraic acid
2	3.7	3.7	3.7	3.7	3.7	Ethanal
3	5.9	6.0	6.0	6.1	6.0	Propanal
					7.0	α-ketoglutaric acid
4[a]	6.9	7.0	6.9	7.0	7.0	Acetone
5	8.4	8.4	8.3	8.5	8.4	Acrolein
6	10.0	10.2	10.0	10.0	10.0	Butanal
					17.8	2,3-butanedione
7	18.8	19.0	18.9	19.0	19.0	2-butanone

[a] Peak No. 4 is considered to represent 3 compounds since α-ketoglutaric acid, acetone and isobutanal have the same retention time, 7.0 min under the condition used.

Column temperature: Isothermal at 75C. Carrier gas flow rate: 70 ml/min (nitrogen). Range, 10; attenuation, 16.

Chemical Reagents

Dinitrophenylhydrazine (DNPH) solution: HCl (2N) was saturated with 2,4-DNPH, brought to a boil, cooled to room temperature and filtered through Whatman #2 filter paper. This solution was prepared fresh as needed. The α-ketoglutaric acid (Calbiochem) was used directly from the bottle.

Collection of Carbonyls

Boiling chips and 2 liters of oil were placed in a 5-liter round-bottom flask. Distilled water was then added to the oil in amounts 0, 2.5, 5 and 10% by volume. The flask was then connected to a tank of nitrogen gas by Tygon tubing and a bent glass tube which extended below the surface of the oil-water mixture. Another glass tube was used to connect the flask to a series of 4 glass traps containing 2,4-DNPH solution. The oil was heated to 210C on a hot plate. Nitrogen gas bubbled through the oil at a moderate rate to aid in the removal of volatile products. The volatile carbonyl compounds produced by heating were collected as the 2,4-dinitrophenylhydrazones in the series of traps. After 48 hours of heating the traps were disconnected from the flask. The 2,4-DNPH derivatives were collected on Whatman #2 filter paper, washed thoroughly with distilled water, and dried at room temperature in a vacuum desiccator.

Regeneration of Carbonyls and Analysis

The carbonyls were regenerated by the technique of Dornseifer and Powers (1,2). The columns used for gas chromatographic analysis were ¼ ft (O.D.) x 4 ft copper tubing. Acid-washed Chromosorb W was the solid support. Except for one 30% Carbowax 20 M column, all packing materials were prepared as 10% stationary phase (w/w). The stationary phases used were: Carbowax 20 M, LAC-446, Silicone GE F 96, Ucon polar, and Ucon nonpolar.

An F & M Model 609 Gas Chromatograph with a flame ionization detector was used throughout this study. The sample size was 2 ml of vapor. Column conditions and instrument settings are given in Tables I and II.

Results and Discussion

Nineteen carbonyl compounds were separated from dry cottonseed oil heated for 48 hr at 210C. The retention times and identification of these compounds are given in Tables I and II.

Positive identification of ethanal, propanal, acrolein, butanal, butanone and heptanone was substantiated by comparison of retention times for recovered volatiles with authentic compounds on two or more columns. Tentative identification was made of acetone, pentanal, pentanone, hexanal, hexanone, octanal, octanone, nonanal, noanone, and decanal. There were seven peaks which could not be identified. These are compounds with retention times greater than decanal and may possibly be 2,3-dienals which have been reported to occur in heated oil. No authentic 2,4-dienals were available for comparison of retention time.

TABLE III

Relative Proportion of Volatile Carbonyl Compounds Formed in Heated Cottonseed Oil

Peak no.	Compound	% Moisture			
		0	2.5	5	10
1	Unknown	++	—	—	—
2	α-ketoglutaric acid	+++	++	++	+++
3	Ethanal	+	+	+	+
4	Propanal	+	+	+	+
5	α-ketoglutaric acid and acrolein	++	+++	+++	+++
6	Pentanal, Pentanone	++	++	++	++
7	Hexanal, hexanone	+++	+++	+++	+++
8	Heptanal, heptanone	+++	+++	+++	+++
9	Octanal	+	+	+	+
10	Octanone	++	+	+	+
11	Nonanal	+	+	+	+
12	Nonanone	+	+	+	+
13	Decanal	+	+	+	—
14	Unknown	+	—	—	—
15	Unknown	+	+	—	—
16	Unknown	+	+	—	—
17	Unknown	+	—	—	—
18	Unknown	+	—	—	—
19	Unknown	+	—	—	—
20	Unknown	+	—	—	—
21	Unknown	+	—	—	—

— nil; + trace; ++ moderate; +++ large

Acrolein and α-ketoglutaric acid could not be separated on the 10% LAC-446 column. These compounds when chromatographed on 30% Carbowax 20 M were resolved and from this we were able to estimate that approximately 80% of peak 3 was acrolein. Peaks 5 and 6 (Tale I) when chromatographed on 10% silicone GE F 96 were shown to be hexanal and heptanone, respectively. No column could be found that would separate pentanal and pentanone.

Table III shows that the presence of water apparently caused a decrease in the amount of carbonyls above C_8. Chromatograms run at the same sensitivity settings and column conditions established that the oil heated in the absence of moisture gave 19 peaks while oil heated with 2.5, 5.0 and 10% moisture gave 13, 11 and 10 peaks, respectively. The decrease in number of peaks with increasing moisture content does not imply the complete absence of carbonyls above decanal. By using much larger sample sizes and a 10-fold increase in sensitivity, the chromatogram of oil heated with water showed 8 more peaks corresponding to peaks No. 14–21. However, at the higher sensitivity, the peaks were barely noticeable over the background noise.

The total amount of carbonyl recovered from the heated oil was less for the dry oil than the oils containing water. The amounts were: 0.235 g total carbonyl (as DNPH's) for dry oil, 0.856 g for oil containing 2.5% moisture, 0.426 g for oil containing 5% moisture and 0.352 g for oil containing 10% moisture. Since the 2.5% moisture level yielded the greatest amount of carbonyls, the increase in carbonyls recovered from the 3 moisture levels seems not to be solely a result of steam distillation; otherwise, the 5 and 10% moisture levels should have resulted in at least as great a yield of carbonyls. The results indicate that the water affects in some manner the formation of carbonyls in heated oil.

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REFERENCES

1. Dornseifer, T. P., and J. J. Powers, Food Technol. *17*, 118 (1963).
2. Dornseifer, T. P., and J. J. Powers, Food Technol. *19*, 195 (1965).
3. Endus, J. F., V. R. Bhalerao and F. A. Kummerow, JAOCS *39*, 159 (1962).
4. Kumazawa, H., from abstract in JAOCS *40*, 472 (J. Oil Chem. Soc. Japan *10*, 531) (1963).
5. Kummerow, F. A., "Proceedings of the Flavor Chemistry Symposium." Campbell Soup Company, Camden, N.J. (1961).
6. Sahasrabudhe, M. R., and V. R. Bhalerao, JAOCS *40*, 711 (1963).
7. Tor, B., et al., from abstract in JAOCS *40*, 472. (J. Oil Chem. Soc. Japan *10*(9), 536) (1963).
8. Wishner, L. A., and M. Kenney, "Carbonyl Compounds Formed During Deep Frying," presented at Symposium on Thermal Oxidation and Polymerization, Fifty-fifth Annual Spring Meeting, American Oil Chemists Society, 1964.

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A Comparison of Nuclear Magnetic Resonance and Dilatometry for Estimating Solids Content of Fats and Shortenings

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Abstract

The percent solids values of fats and shortenings using nuclear magnetic resonance (NMR) and solid fat index (SFI) have been compared. The samples used were: blends of hard fat and safflower oil, safflower oil hydrogenated to varying degrees, and different types of shortenings.

This investigation demonstrated the empirical nature of the SFI technique and shows the nature of the deviations from the solids content determined by the NMR method. The magnitude of the deviation of SFI from the NMR solids content increased with the level of the solids. The SFI values and the NMR solids content were similar at the lower levels (SFI values of 10) but at the upper limit for the SFI method (SFI values of 50) the solids content by the NMR method can be 80% or more, a difference of 30 units.

Although the determination of solids content by NMR is reliable, the relationship between SFI values and NMR values for different types of samples is so variable that the calculation of the SFI value from percent solids by NMR, or percent solids from SFI values from prediction equations is not very reliable.

Since NMR measures the solids content more accurately than SFI and is applicable over the entire range of solids, 0 to 100%, it will be very useful in fat and oil research and control.

Introduction

THE OFFICIAL AOCS METHOD for SFI (1) or one of many modifications is used extensively to evaluate shortenings and blends of fats for their relative consistency and plastic properties. In its original form the solids content of a sample at a given temperature was estimated from the difference between the specific volume at a point on the curve at that temperature (for example B, in Figure 1) and the corresponding point on the extrapolated liquid curve, at the same temperature (for example A), divided by the difference between the specific volume at A on the extended liquid curve and C on the extended solids curve.

Because of the time required to establish both the liquid and solid portions of the curve, and the fact that the solids curve is relatively constant, it was decided by those concerned with these measurements to establish only the liquid curve and use the difference between the specific volume of the liquid curve and the specific volume at a point on the dilatometer curve as an index of the solid fat present at that temperature. The solid fat index (SFI) is a purely empirical value which has been very useful in research and for control of processes and quality of the finished product, although it is limited to evaluation at levels below 50 units.

The development of a broad line nuclear magnetic resonance (NMR) instrument offered a new approach to the determination of the solids in fats, blends and shortenings. It appeared to offer a means of measuring the solid fat content with greater accuracy and over the entire range from 0–100% solids. This technique was applied to a stabilized and unstabilized margarine oil by Chapman (3) and to soybean oil hydrogenated to varying degrees by Ferren (4). Both suggested using the technique for measuring the solids content of fats and shortenings but did not extend their investigations into this area.

A previous investigation by the authors (2) dealt with NMR measurements on fats containing less than 50% solids and comparison with SFI values for margarine oils which were below 30. This study showed that while the values were not equal, a prediction

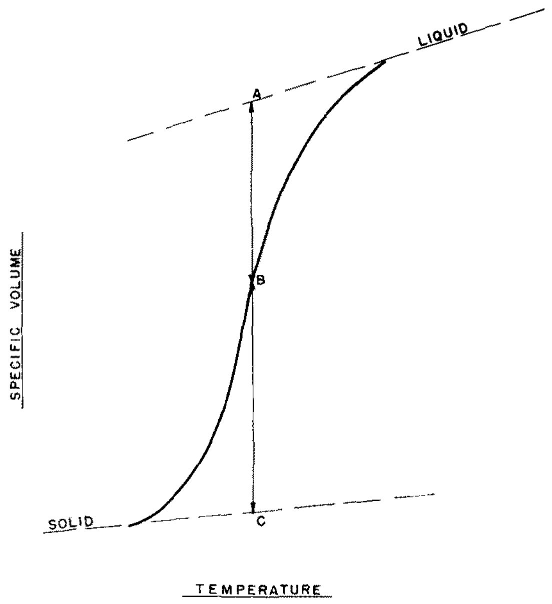

FIG. 1. Example of a dilatometer curve.