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Volatile components of the frying process

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SUMMARY

Volatile components of the frying process

In the course of deep fat frying, food contacts oil at about 180 °C and is partially exposed to air for various periods of time. Thus frying, more than any other standard food process or handling method, has the greatest potential for causing chemical changes in fat, and sizeable amounts of this fat are carried with the food (5-40% fat by weight is absorbed).

During frying, oxidative reactions involving the formation and decomposition of hydroperoxides lead to such compounds as saturated and unsaturated aldehydes, ketones, hydrocarbons, lactones, alcohols, acids and esters. Sulfur compounds and pyrazine derivatives may develop in the food itself or from the interactions between the food and oil.

Food absorbs varying amounts of oil during deep-fat frying (potato chips have a final fat content of about 35%). The food itself can release some of its endogenous lipids (e.g., fat from chicken) into the frying fat and consequently the oxidative stability of the new mixture may be different from that of the original frying fat. The changes that occur in the oil and food during frying should not be automatically construed as undesirable or harmful. In fact, some of these changes are necessary to provide the sensory qualities typical of fried food. On the other hand, extensive decomposition, resulting from lack of adequate control of the frying operation, can be a potential source of damage not only to sensory quality of the fried food but also to nutritional value.

KEY-WORDS: Changes in food – Changes in oil – Deep fat frying – Oxidative reactions.

In the course of deep-fat frying, food contacts oil at about 180 °C and is partially exposed to air for various periods of time. Thus frying, more than any other standard food process or handling methods, has the greatest potential for causing chemical changes in fat, and sizeable amounts of this fat are carried with the food (5-40% fat by weight is absorbed). Under frying conditions reactions occur at a relatively rapid rate resulting in the formation of large numbers of reaction products which vary widely in volatility, stability, concentration and flavor characteristics.

Significance of Food Volatiles

Food volatiles are of paramount importance in relation to flavor perception. Of all the senses, smell is the major mechanism responsible for the overall flavor sensation. Receptors in the olfactory region are capable of responding to hundreds of different smells at many different levels. And, it is the components of the headspace above the food which make up the volatile pattern to which the olfactory region responds. Unlike the sense of vision, the sense of smell requires physical contact between the signal, i.e. flavor components, and the receptor, i.e. olfactory cells. For an object to be seen, there is no need for that object, or particles from it, to touch the eye. But to be able to smell an object, molecules from that object must «volatilize», travel through the headspace, and interact with cells in the olfactory region. Of course the headspace composition will reflect the qualitative composition of the food constituents. But the relative amounts of the various components in the headspace will be quite different from those in the food. The quantitative pattern of volatiles will be influenced by many factors including the vapor pressure of the individual components, the food medium in which they exist (water, fat, etc.), solubilities of these components in the food media and in each other, viscosity and temperature.

An added value of headspace volatiles is that they provide an elegant technique in food analysis. The advances in gas chromatographic and mass spectrometric analysis of the volatiles allow relatively simple means of examining the composition of the numerous components which exist in food at extremely low level.

Structural Identity and Mechanistic Pathways

The volatiles of fried food arise from several sources. Major among these are, obviously, the oxidative and non-oxidative events in the frying oil. Typically, oxidative reactions involving the formation and decomposition of hydroperoxides lead to such compounds as saturated and unsaturated aldehydes, ketones, hydrocarbons, lactones, alcohols, acids, and esters (1). Thermal decomposition of the saturated fatty acids produces aldehydes, ketones and lactones (2). Free fatty acids arise from hydrolysis of the triacylglycerols in the presence of heat and water.

Considering that frying oils are usually mixtures of several edible fats each of which contains several fatty acids, it is not surprising that the number of volatiles produced from this source alone is literally in the hundreds. In the case of olive oil for example, more than 200 volatile compounds were detected after heating for 1 hr at frying temperature (Figures 1, 2). The major peaks consisted of series of n-alkanals, 2-alkenals, l-alcohols, n-fatty acids, 2-alkanones, and n-alkanes, while the minor peaks represented series of 1-alkenes, alkadiens, n-alkyl cyclohexanes, 3-alkanones and lactones.

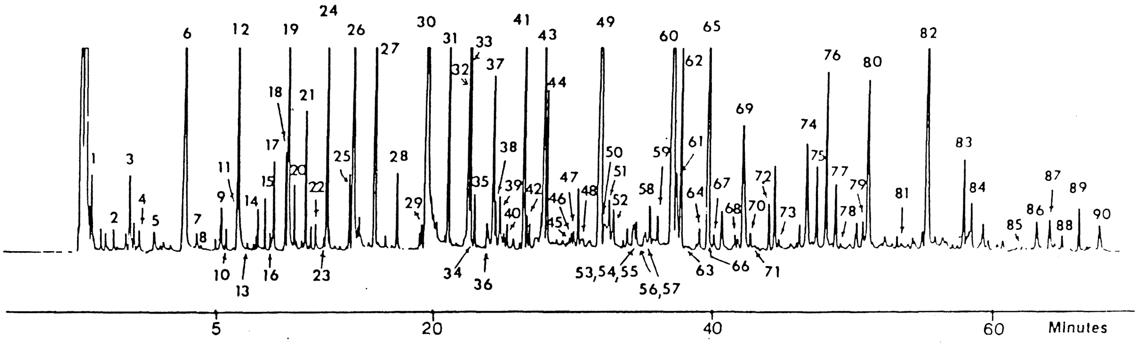

Figura 1
Gas chromatographic analysis of the polar volatile components from olive oil heated for 1 hr at 185 °C. Peak identification is given in table I.

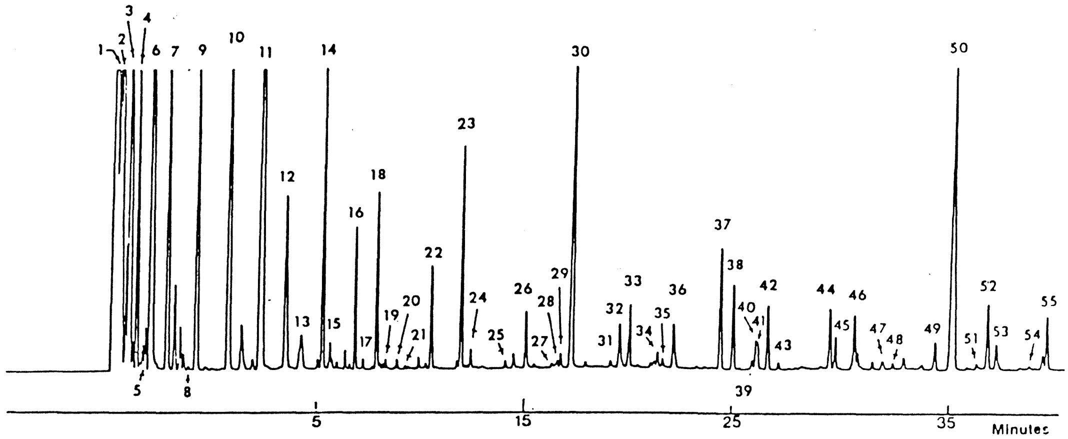

Figura 2
Gas chromatographic analysis of the nonpolar volatile components from olive oil heated for 1 hr at 185 °C. Peak identification is given in table II.

In spite of the complexity of the decomposition pattern obtained, a definite correlation could be observed between the volatiles produced and the fatty acid composition of the olive oil. The major components were those expected from simple cleavage of the monohydroperoxides formed by oxidation of the unsaturated fatty acids and the major saturated acids. Quantitatively, the volatiles produced in the largest amounts were those reflecting oxidation of oleic acid, the major fatty acid of olive oil. It can be seen that of the 2-alkenal series, 2-decenal and 2-undecenal were present in the highest amounts; of the n-alkanals, nonanal and octanal were produced in relatively large quantities; and of the n-alkanes, octane and heptane were the most abundant. Typical compounds consistent with the autoxidation of linoleic acid, e.g. hexanal and 2,4-decadienal, and linolenic acid, e.g. 2,4-heptadienal, were similarly observed.

The methyl ketones and the lactones arise from oxidation of the saturated fatty acids as observed in our work with model systems of triacylglycerols (3).

In addition to the frying oil, other sources of volatiles include oxidative and thermal decomposition of the lipids in the food itself (e.g. chicken fat, fish oil); breakdown products of certain non-lipid food components (e.g. amino acids); and the interaction among these products and/or with other food components (e.g. phospholipids, proteins). For example sulfur compounds and pyrazine derivatives may develop in the food itself or from the interactions between the food and oil.

Several events which take place during frying impact significantly on the volatiles. For example, water is continuously released from the food into the hot oil. This produces a steam-distillation effect, sweeping volatile oxidative products from the oil. The released moisture also agitates the oil and hastens hydrolysis. The blanket of steam formed above the surface of the oil tends to reduce the amount of oxygen available for oxidation.

Food absorbs varying amounts of oil during deep-fat frying (potato chips have a final fat content of about 35%), resulting in the need for frequent or continuous addition of fresh oil.

The food itself can release some of its endogenous lipids (e.g., fat from chicken) into the frying fat and consequently the oxidative stability of the new mixture may be different from that of the original frying fat.

Although the amounts of volatiles produced vary widely, depending on oil type, food type, and the heat treatment, they generally reach plateau values, probably because a balance is achieved between formation of the volatiles and loss through evaporation or decomposition.

Correlation with Flavor

In recent years we have witnessed remarkable progress in instrumentation and analytical methodology which enable us today to detect, separate and identify hundreds of compounds at concentrations in the ppm and ppb range. Unfortunately however, our ability to correlate the volatile composition with sensory attributes has not been too impressive.

The challenge here is phenomenal but understandable. The very large number and the extremely low concentration of the volatile components make it very difficult to examine the sensory properties of individual compounds. In view of the extreme sensitivity of the human nose, certain compounds known to be powerful odorants may be present in such low concentrations that they escape instrumental detection. Flavor response is not necessarily brought about by individual compounds acting separately, but rather by the combined influence of several compounds. Some flavor components exhibit additive, synergistic or masking properties. Finally, flavor response represents an exceedingly complex decision by the brain which not only depends on the sense of smell but also integrates the latter's interactions with the other senses, i.e. taste, vision, touch and hearing, as well as with various social, cultural and psychological factors. Indeed volatile analysis can be highly informative and of great significance to our understanding and control of flavors and off-flavors. On the other hand, one cannot expect the «machine» to match the ability of that formidable apparatus, the human brain.

Future Prospects

Frying is a complicated process involving a multitude of reactions and interactions and producing numerous reaction products. The volatiles from the frying process impact significantly on the flavor of fried food and provides us with significant information regarding its quality. However, as indicated above, some difficulties remain in correlating analysis of the volatiles with the flavors and off-flavors of the fried products.

I believe that a new approach and new thinking are needed in the evaluation of the volatile components of the frying process. In addition to the details already discussed, the following aspects must be considered:

1. The volatile pattern is not constant. It changes continuously. Release of fat from the food into the frying medium changes the composition of the latter. Chicken fat, which is more highly unsaturated than most of the commonly used frying oils, would make the frying medium more susceptible to oxidation resulting in a change in the volatile decomposition products of the oil. Conversely, the food being fried may contain certain components which are known to inhibit oxidation of the oil thus producing the opposite effect. Furthermore, certain compounds produced in the first stages of the frying process may themselves decompose or interact with other components. Also the volatile pattern of the final product, the fried food, continues to change due to the wide variation in the vapor pressure of its individual components.

It is obvious therefore that a single analysis of the volatiles cannot be sufficient. The volatile pattern must be monitored by repeated examination in order to reflect the continuous changes in this composition.

2. The food being fried is not a homogenous system. The food matrix consists of «regions» which actually differ in composition. Consequently, the reactions and interactions which take place may differ from region to region depending on the conditions (e.g. oxidation parameters) in each region. The conditions in each region are not static, they continue to change.

3. Certain volatiles commonly used as «key markers» of oxidation, e.g. hexanal, may be markedly reduced by facile interaction with other components from the food, e.g. compounds containing free amino groups. Their absence may thus be misleading.

4. New techniques should be developed to establish more precise relationships between volatile (and pertinent nonvolatile) lipid-derived components and specific flavors. One such approach, aimed at identifying the most important volatile oxidation products, is one in which a flavor dilution factor (FD factor) is determined by gas chromatographic analysis and effluent sniffing of a dilution series of the original aroma extract (4).

5. Much more work is needed to improve our understanding of odor sensation. Perhaps means could be found to «measure» and «integrate» the many facets that make up the «final judgement».

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