Fat Autoxidation and Related Subjects: A Review of the 2nd International Congress of Food Science and Technology

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The 2nd International Congress of Food Science and Technology took place Aug. 22–27, 1966 in Warsaw, Poland. It was attended by about 1200 participants from countries throughout the world.

Papers were allotted to eight sections. Those of either direct or indirect interest in regard to fat autoxidation were in the following sections: B) chemical and biological deteriorative changes in food; C) technological advances in food processing; E) technical problems of safety and purity of foods; and F) advances in methods for assessment of food quality.

The papers of direct interest with regard to fat autoxidation may be divided into five groups: 1) kinetics and mechanism of fat autoxidation in general; 2) kinetics and mechanism of fat autoxidation in special cases; 3) nutritional aspects of fat autoxidation; 4) fat autoxidation at low oxygen pressure; 5) inhibition of fat autoxidation by antioxidants.

Kinetics of Autoxidation, General

In the first group, a paper was given by Niewiadomski, Zwierzykowski and Budney of the Technological University of Gdansk, on the kinetics of methyloleate autoxidation. The course of autoxidation was followed by determination of iodine values and peroxide values as well as disappearance of double bonds. The reaction order, rate constant and activation energy as well as other values for formation and breakdown of peroxides were calculated on the basis of the maximum peroxide value and the length of time before this maximum was reached.

An example of research on mechanisms by determination of the products of oxidation was the paper by Sokolow and co-workers from the All-Union Fat Research Institute in Leningrad. This paper dealt with oxidation products of fatty acid methyl esters studied by the counter-flow-distribution method. The oxidation products, dissolved in a petroleum ether-methanol system, were separated by 1200 transfers. The isolated substances were identified by chemical methods, polarography and spectral analysis.

Further, a paper by Rosenthal and Seidner of Schwarz Bio Research, Inc., Tuxedo, N.Y., entitled "Peroxidation—Key Step in the Maillard Reaction," illustrated a very important secondary reaction of fat oxidation in systems (food) containing proteins (amino acids), resulting in nonenzymatic browning (Maillard reaction). The observed darkening represents the terminal step of several chemical reactions initiated by the condensation of an aldehyde with an amino group. It was found that the rate-determining step in the browning reaction is controlled by the rate of oxygen diffusion into the medium and formation of peroxides. The breakdown of peroxides coincided with the appearance of brown polymers.

Similar aspects were treated in a paper given by Pokorny, Zwain and Janicek, Institute of Chemical Technology, Prague: "Evaluation of Color Changes Caused by Autoxidation and Condensation Reactions in Fatty Foods." Initially, autoxidizing fatty material may become pale because of destruction of pigments. Later on the color darkens because of the formation of dark oxidation products, particularly conjugated ones. Polymeric derivatives of highly unsaturated fatty acids are mostly dark. Colored products are also formed by reaction of oxidized lipids with proteins or polyphenolic compounds, this process being enhanced by trace metals. Color changes were determined by extraction followed by maesuring of UV and visible spectra. Fractions with different spectral properties may be obtained by chromatography.

Kinetics of Autoxidation, Exceptions

2) Meat color changes due to rancidity are chiefly connected with oxidation and reduction of metamyoglobin. These relationships have been studied by Watts et al., Florida State University, by the use of reflectance spectrophotometry and determination of oxygen consumption and oxidation reduction potentials. Oxygen is utilized almost entirely by way of the electron transport chain, the hydrogen being derived from NAD dependent reactions. The reducing capacity of meat is positively correlated with the retention of ferrous pigment during storage while the formation of ferric pigment during storage is positively correlated with lipid oxidation as determined by malonaldehyde production.

Another problem concerning meat, due at least in part to fat autoxodiation, is the change of organoleptic properties during and after irradiation. P. I. E. Hansen of the Danish Meat Research Institute at Roskilde has examined the effect of some physical means on this organoleptic change, e.g., high dose rate and a combined heat and irradiation treatment. By the use of high dose rates considerable improvement was achieved, while irradiation at higher temperatures resulted in a very uneven energy distribution. A compensation for this uneven distribution was obtained by also depositing the dose of ionizing radiation in an uneven way throughout the sample. Canned luncheon meat has been irradiated in this way so that the dose in the center was 2–2.5 times higher than in the periphery of the can.

An example of research on oxidation in vegetable oils was given by H. Niewiadomski and Stolyhwo, Technological University, Gdansk. Investigations were carried out at various stages of refining of rapeseed oil in order to examine the influence of hydrolysis and oxidation. The composition of the low-molecular fatty acids which appear, as the acid value and the peroxide value increase, was studied by GLC. It could be concluded that certain technological steps—due to oxidation and hydrolysis—have a particularly unfavorable influence upon quality and stability.

Nutritional Aspects

3) The importance of fat autoxidation upon the quality of fats and fatty foods has hitherto mainly been regarded from the viewpoint of organoleptic properties. Another aspect of increasing interest is the nutritional one, especially the nutritional aspect of accelerated oxidation due to thermal treatment. Several studies in this regard were reported by Kadykov and co-workers of the All-Union Fat Research Institute in Leningrad. Oils which have been "overstored" or heated may show changes of their nutritive value which are regarded to be due to oxidation products, especially those of polyunsaturated fatty acids. In order to study these relationships "linoleic acid dioxide" (with 2 epoxy groups) was isolated and—in various dosages—added to the diet of young white rats. While a small dose of "linoleic acid dioxide" (0.7%) caused a certain stimulating effect, a dose of 2.5% had a clearly inhibiting effect.

In a similar study, the influence of oxidation products which accumulate in vegetable oils during heat treatment at 180–200C, were examined with regard to their influence upon nutritive value and biological effects. While 0.5% oxidation products in oils had no harmful effect, 1% brought about a certain delay of growth and 2% caused more severe biological effects. The oxidative changes occurring at a certain heat treatment depend, to a great extent, upon the initial quality of the fat.

Further, the protective effect of thiamine and α-tocopherol on rats fed with overheated sunflower seed oil was studied. It was not clear whether tocopherol had any protective effect. However, this should be the case. At any rate, it could be shown that slight increases of thiamine in the diet had a favorable effect by restricting the effect of overheated oil on the organism.

Autoxidation at Low Pressure

4) An increasing interest could be noted with regard to low oxygen treatment as a means of protecting fat and fatty food against oxidation. In our contribution, "Inhibition of Fat Rancidity at Low Oxygen Pressure" (Marcuse and Fredriksson), we reported kinetic studies on emulsions of fatty acids and fatty acid esters, based upon measurement of oxygen consumption. A special apparatus working at a constant pressure of oxygen and permitting automatic recording had been developed for this purpose. The results so far show that diffusion of oxygen is of decisive importance in the decreasing effect of lowered oxygen pressure upon the rate of oxidation. Therefore various systems will be variously affected by lowering oxygen pressure. Systems where oxygen diffusion is more or less eliminated as in dehydrated foods require much more rigorous lowering of oxygen pressure to achieve effective protection. The effect of low oxygen pressure was further studied in the case of a) added antioxidants and b) added metal ions.

Applied research in this regard, conducted at the German Bundes forschungsanstalt für Lebensmittelfrischhaltung at Karlsruhe, was reported by Spiess: "Quality Changes in Freeze-Dried Vegetables During Storage in an Atmosphere of Different Oxygen Content." As already mentioned, such products are especially sensitive to oxidation. (The changes of quality—at least in part—may be due to the deterioration of other substances than fats, but fats and lipoids in general are thought to play a more or less important part in this connection, too.) Among the vegetables studied were carrots, paprika, spinach, green beans, asparagus, cauliflower and mushrooms. After freeze-drying they were stored at different pressures of oxygen and analyzed at certain time intervals, for about one year, mainly by organoleptic means, but also by determination of oxygen consumption and content of β-carotin and ascorbic acid. β-carotin could be shown to be more sensitive to oxygen than ascorbic acid. The decrease of β-carotin and ascorbic acid was always correlated to oxygen consumption while the decrease of organoleptic quality was different for the different vegetables studied: e.g., carrots required very low xoygen pressure; green beans and asparagus were somewhat less sensitive; while cauliflower indicated very slight sensitivtiy.

In another paper, Palmer and Kramer, University of Maryland, described experiments on changes in flavor and chemical composition of raw vegetable food materials stored in the almost complete absence of oxygen. These experiments were carried out with potatoes and apples where fat oxidation is not an important problem. Although only of preliminary nature, the experiments showed a favorable effect of low oxygen pressure also in this connection.

In order to protect freeze-dried products in this way against oxidation, freeze-drying may be conducted in the presence of an inert gas and the vacuum be broken by admission of such a gas. In experiments with shrimp on the influence of inert gases during freeze drying upon the microbial survival, Sinskey, Pablo, Silverman and Goldblith could show that survival in a helium atmosphere was 90%, in a carbon dioxide atmosphere only 52%, apparently due to carbon dioxide toxicity for the microorganisms present. The relative survival in nitrogen was not mentioned.

In this connection the permeability of the packaging material for oxygen and water vapor is of primary importance. Studies were carried out by Lempka and Prominski of the Central Laboratory of the Food Concentrates Industry at Poznan, Poland, on the utility of plastics as wrapping materials for lyophilized food products as carrots, tomatoes, cauliflower, parsley and celery. The packaging was made of films prepared from conventional (paper, parchment, cellophane, aluminum) as well as modern synthetic (polyethylene, polypropylene, polystyrene, etc.) materials, tested separately and in the form of laminates. Laminates proved to be satisfactory provided the inner layer consisted of conventional material and the outer of modern synthetic material.

The difficulty in achieving and maintaining low oxygen pressure has received much attention. One possibility is to consume residual oxygen by means of glucose oxidase. However, hydrogen peroxide is produced which, among other compounds, may attack ascorbic acid and anthocyans. Enzyme preparations containing catalase are often used to decompose the hydrogen peroxide; but these have proved ineffective. This problem has been investigated by Rogatchov and Erofeev of the All-Union Research Institute of the Canning and Vegetable-Drying Industry, Moscow, USSR. As a result of the experimental work, the effectiveness was found to depend on the degree of catalase inactivation, which is dependent on the chemical composition, especially the content of organic acids, of the product to be packaged. It was established that the optimal ratio glucose oxidase:catalase varies within 1:2 and 1:6.

Finally to be mentioned in this connection is a paper on polarographic oxygen determination by Lipis and coworkers of the Moldavian Food Research Institute, USSR. Various *solid electrodes*—of Pt, Au and Ag—have been tested for use in wines and fruit juices and the experiences were reported. The sensitivity was reported to be 0.1 mg/liter and the accuracy 0.2 mg/liter, which was regarded as satisfactory.

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Fat Autoxidation and Related Subjects

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The last group of papers on fat autoxidation comprises reports on research concerning the effect of antioxidants. The contribution of Mitsuda, Yasumoto and Iwami of the Department of Agricultural Chemistry of the University of Kyoto, Japan, treated the mechanism of antioxidative effects of amino acid. Experiments were carried out with linoleic acid in model systems and with whole and dried raw milk. TBA-values, peroxide values and content of remaining linoleic acid were determined. The antioxidative effect could also be confirmed in the case of hemoglobin-catalyzed oxidation, but the effect of lipoxidase was not inhibited. The mechanism was supposed to be either chelation of trace metals or breakdown of peroxides or radicals. Aromatic amino acids as tryptophan were found to be especially effective (histinine was not mentioned) and a certain relation seems to exist between antioxidative capacity and electron donation liability. The formation of oxidative breakdown products of tryptophan could be confirmed. Besides the scavenging of free radicals, there may be a formation of charge transferring complexes with lipids or products of lipid oxidation.

Olcott, University of California, Berkeley, reported new results of experiments on the synergistic-antioxidative effect of phospholipids on oxidation of menhaden oil and squalene and gave a hypothetical interpretation.

Several papers treated aspects connected with the antioxidative effect of tocopherols. In a second paper Olcott discussed the antioxidative effectiveness of the various tocopherols which is known to differ. As to the lack of parallelism between in vitro antioxidant effectiveness and in vivo vitamin E-activity, this probably is due to different penetrability through living membranes. The results indicate that the hydrocarbon side chain is relatively unimportant for the antioxidant activity per se.

Experiments on the protective effect of α-tocopherol for the stability of margarine, lard, butter and certain vegetable oils were reported by Telegdy-Kovats, Institute of Food Chemistry, University of Technical Science, Budapest, and Markuze, State Institute of Hygiene, Warsaw. Besides lengthening the induction period, tocopherols were found to protect A-vitamin and particularly the provitamines.

Finally to be mentioned is a paper by Johnson of the Commonwealth Scientific and Industrial Research Organization, Ryde, N.S.W. Australia, on the effect of the antioxidant BHA on lipid metabolism of the rat. Owing to previously published work by this author (as well as others) the use of BHT as a food additive has been restricted. The experiments reported now showed again a reduction in growth rate of animals fed BHT. This reduction was greater when the animals were fed lard than in the case of animals on a lard-free diet.

After the congress visits were paid to some institutions in Warsaw, the Institute of General Chemistry and the Agricultural University, as well as the Agricultural University at Olsztyn and the Technical University in Gdansk.

Professor Rutkowski provided a tour of the Department of Chemistry and Analysis of Fats of the Institute of General Chemistry. He is director of research, while head of the department is Docent H. Grynberg. The department, which does not deal with problems on food, is part of a large complex of institutions under the directorship of the Ministry of Chemical Industries. Professor Rutkowski is also director of the Department of Food Technology at Olsztyn (see below).

Other Polish Institutes of fat chemistry and technology are the Institute of the Meat Industry (director: A. Borys), and the Institute of the Fat and Oil Industry (director: A. Jakubowski), both belonging to the Ministry of Food Industries (president: F. Pisula, MSc).

After this visit the group met at the institute of Professor Pijanowski, who is head of the Department of Food Industry Technology of the Agricultural University of Warsaw. An interesting review was given by Professor Pijanowski on the development of the college and the faculty and on educational and research items. The department has laboratories of dairy technology, fruit and vegetable technology and food radiology. It has 5 professors, 2 associate professors and 510 students (besides nonresident ones). The total number of students is 650. Up to 1965, 400 engineering degrees and 45 Master of Science degrees have been granted.

On the way to Olsztyn the group visited a large dairy factory at Mława. Technical and economical aspects of dairy production were outlined by the director. The plant processes 60–120,000 liters milk daily. It consists of 118 collecting units and receives milk from 7,000 farms with 19,000 cows (1–8 cows/farm). A total of 235 people are employed, including a profesisonal staff of 10–20 persons. The organization might be called a state cooperative. The main products are milk powder and butter. Ten per cent of the output is exported.

At Olsztyn a reception was given by the deputy rector Prof. J. Budsławski, who is head of the Department of Milk and Dairy Products Chemistry, and the dean of the Faculty of Food and Dairy Science, Prof. B. Imbs. Also present were Professor Rutkowski, head of the Department of Food Storage and Technology and Professor Karnicka, head of the Department of Technical Microbiology.

The college has 4,000 students and 6 faculties, including the Faculty of Dairy and Food Technology with 500 students, 5 professors (Budsławski, Eisele, Karnicka, Rutkowski and Dziama), 3 associate professors and 5 lecturers (among them Dr. Babuchowski and Dr. Chudy). The course consists of 4 years of fundamental studies and 1 year for preparation of a thesis (based on 7 months' work in the laboratory and 3 months' practical work outside the college). Altogether the Faculty of Dairy Science consists of 3 physiochemical and 7 technological departments.

The group visited some of the dairy departments as well as the Department of Food Storage and Technology.

In general the research of the department includes chemistry and technology of fats and oils, of animal products and of protein fodder, and further examination of the nutritive value of protein and fat products by physiological methods. The following people outlined their work:

Dr. Chudy, working on the nutritional value of rapeseed oil;

Dr. Kozłowska, working on the nutritional value of rape products, with special regard to the goitrogenic effect of certain components in rapemeal;

Dr. Korzeniowski, working on animal fats and meat products, with special regard to phospholipids and the effect of storage and treatment upon phospholipid composition;

Dr. Babuchowski, working on storage of rapeseed and especially the influence of chemical changes during storage upon the technological properties;

Dipl. Ing. Baturo, working on projects in the field of fat technology and analysis, especially in regard to refining of animal waste products;

Dipl. Ing. Mzyk, working on the properties and analysis of tocopherols.

Finally a visit was paid to Gdansk to visit the Technological University Politechnica Gdanska, especially the Department of Fat Technology, head: Professor Niewiadomski and the Department of Animal Food Products Technology, head: Professorr Tilgner. Professor Tilgner is known as an expert on organoleptic analysis.

Most of the time at Gdansk was spent together with Prof. Newiadomski and his co-worker Docent W. Zwierzykowski. The research carried out here is concerned with the chemistry and technology of edible and technical fats, the chemistry and the transformations during processing of minor constituents such as phospholipids and tocopherols and especially the chemistry and technology of fish oils and the theory of autoxidation of fats.

The laboratories for technological education and scientific research are well equipped. Various projects going on were discussed, especially methods of analysis and items of kinetics.

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