Investigation of the pork adipose tissue's autoxidation

Á. Juhász

Hungarian Meat Research Institute, Budapest, Hungary

When storing lard, fat and meat products rich in fat the autoxidation of fatty acids is a serious problem. During this procedure a considerable amount of different bad flavoured products are developing consequently the organoleptic quality is decreased. In our experiments the autoxidation /rancidity/ of porcine adipose tissue /back-fat/ was studied. According to the industrial practice the pork adipose tissue was stored in salted state at 6 C°. The autoxidation processes were characterised by the production of primary and sencondary products of oxidation /peroxides and malonaldehyde/. The coloured polimerized products as supposed by-products of rancidity were also studied.
The quality of primary and secondary oxidative products showed a periodic change and the by-products increased monotonously, which could be the effect of the non-lipid -type components. As a consequence of periodic alterations of primary and secondary oxidative products the peroxide value and the Kreiss reaction sometimes may not be characteristic to the degree of autoxidation in meat products.

Untersuchung des Autoxydationsprozesses der Fettgewebe von Schweinen

Á. Juhász

Ungarisches Forschungsinstitut für Fleischwirtschaft, Budapest, Ungarn

Während der Lagerung der zum menschlichen Verzehr geeigneter Fette, fettreichen Gewebe und Fleischprodukte mit hohem Fettgehalt bedeutet die Autoxydation der Fettsäuren ein sehr grosses Problem. Während dieses Prozesses entstehen nämlich zahlreiche unangenehm schmeckende und riechende Verbindungen, die die organoleptischen Eigenschaften des Produktes nachteilig beeinflussen. In unserer Arbeit wurden die Autoxydationprozesse der Fettgewebe von Schweinen studiert.

Die Fettgewebe wurden der industriellen Praxis entsprechend eingesalzen und bei 6 C° gelagert. Die Autoxydationsprozesse wurden durch Untersuchung der primären und sekundären Produkte d.h. Peroxyd und Malonaldehyd, sowie der als Endprodukte betrachteten farbigen Polymerverbindungen studiert.

Es wurde festgestellt, dass sich die Menge der primären und sekundären Oxydationsprodukte im Laufe der Lagerungszeit periodisch ändert, wobei die Bildung des Endproduktes kontinuierlich verläuft. Diese Erscheinung ist in erster Linie auf die Anwesenheit von Nicht-Lipid-Verbindungen zurückzuführen. Aufgrund der Ergebnisse kann festgestellt werden, dass die in der Praxis allgemein benutzten Ranzigkeitsindexe -z.B. die Peroxydzahl, Kreiss-Reaktion usw. -den Oxydationsgrad der Produkte nicht befriedigend charakterisieren.

9.I

L'étude des procédés d'autooxydation dans les tissus adipeux du porc

Á. Juhász

Institut de Recherches sur la Viande, Budapest, Hongrie

L'autooxdation des acides gras soulève un grand problème au cours du stockage du saindoux, des tissus adipeux et des produits de la viande ayant un grand teneur en matière grasse. L'autooxydation provoque des goûts et des odeurs désagréables qui diminuent la qualité sensorielle des produits pendant le stockage. Dans ce travail nous avons étudié les procédés d'autoxydation des tissus adipeux du porc. Selon la pratique industrielle les tissus adipeux présalés ont été entreposés à une température de +6 C°. Les procédés d'autooxydation furent étudiés, examinant les produits primaires, secondaires et les polimaires colorés. Nous avons constaté que la quantité des produits primaires et secondaires de l' autooxydation changent en fonction du temps et la formation des polimaires colorés montre une augmentation monotone.
Sur la base des résultats on peut conclure qu 'au cas de tels systèmes complexes les indices de la rancissure, généralement appliqués - comme l'indice de peroxyde ou la réaction de "Kreiss" - ne caractérisent pas le degré d'oxydation de ces produits d'une manière convenable.

Изучение процесса самоокисления свиных жировых тканей

А.ЮХАС

Государственный исследовательский институт мясной промышленности,г.Будапешт,Венгрия

При хранении пищевых жиров, жировых тканей и мясных продуктов, содержащих большое количество жира, немалую проблему представляет собой самоокисление жировых кислот (жиров).-
При таком процессе образуются многочисленные продукты, неприятные по запаху и вкусу, которые снижают качество пищевых продуктов. В процессе нашей работы были изучены процессы самоокисления свиных жировых тканей.
Свиные жировые ткани в соответствии с промышленной практикой хранились при температуре 6°С в солёном виде. Процессы самоокисления были изучены на основании первичных.) (перекисных) и вторичных(малональдегидных), а также цветных, полимерных соединений, которые могут считаться конечным продуктом.
Было установлено, что количество продуктов первичного и вторичного окисления в зависимости от времени изменяется периодично, в то же время как образование конечного продукта характеризуется монотонным ростом.
Это явление вызвано в первую очередь присутствием нелипидных компонентов системы.
На основании результатов видно,что в таких сложных системах общеиспользуемые показатели (число перекиси, реакция Крейса) не характеризуют в достаточной мере степень окисления (величину самоокисления) продукта.

9.I

Study of the autooxidation of swine adipose tissues

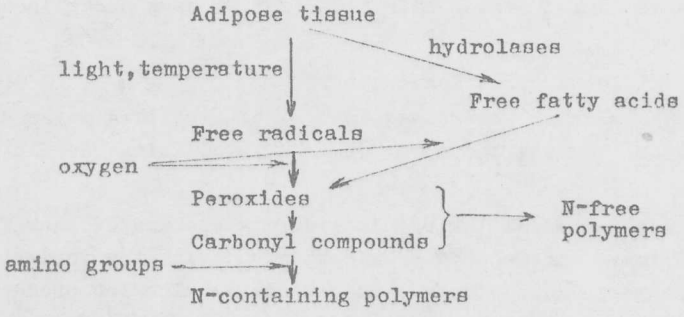
Á.JUHÁSZ

Hungarian Meat Research Institute

One of the greatest problems in the storage of meat products is the oxidative deterioration of lipids. As a result of this deterioration compounds of undesirable taste, colour and odour are formed. The rate of formation and the amount of these compounds have a great influence on keeping quality of the products.

The sensitivity of meat products to oxidative changes may be different even if their fat content is the same, since the rate of autoxidation depends on the composition of fats too. The composition of the adipose tissue added to meat products is influenced by many factors, such as the age, sex, bread of the animal as well as the composition of the feedstuffs / MYRES, BOWLAND /1975/ /.

The rancidity of adipose tissue is consequently a much more complex chemical process than that of the pure fatty acids. This is because these tissues consist of triglycerides, connective tissue proteins, enzymes /lypase, hydrolase/ free amino acids, phospho- and glycolipids, vitamins and other compounds as well /PEARSON /1968//. The following scheme shows the main reactions of the rancidity process:



As a consequence of the autoxidation process - as shown in the above scheme - several oxidation products are formed. Out of these products the different pigments and carbonyl compounds are mainly responsible for quality deterioration of foodstuffs. The carbonyl compounds are alcanals, 2-alcenals, 2,4,dialcenals /MOSITO, FUJUMAKI/1972//. These compounds are necessary in small quantities for forming the flavour of meat products, nevertheless they can be deterimental to taste and odour when being present in larger amount /KIMOTO, GADDIS/1974//. The polymers, which are considered the end products of the autoxidation are either yellow or brown in color thus undesirable in foods. The process during which polymers are formed as a result of reaction between carbonyl compounds and compounds containing amino groups - i.e. proteins, amino acids, some phospholipids - is called non-enzymic browning /POKORNY, JANICEK/ 1973//.

It is rather difficult to characterize the degree of autoxidation of adipose tissues and meat products because of the great number and variability of oxidation products. Under industrial conditions the rancidity is determined by a number of easily performed tests, i.e. peroxide value, Kreiss test, Swift test etc. The result of these tests are valid

only in certain phases of the autoxidation process.

In our present work the autoxidation of the adipose tissue has been studied on the basis of its three main intermediate processes - products of primary and secondary oxidation and polimerization - under storage conditions responding to industrial practice.

Methods

Determination of peroxide value

The peroxide value has been determined iodometrically according to the Hungarian Standard /MSZ 19823/. The results were expressed as meqv peroxide/kg sample.

Determination of the malonaldehyde concentration

The malonaldehyde content was determined according to the method of TAI KWON and WATTS /1963/ by UV absorption. The results were expressed as malonaldehyde mg/kg sample.

Determination of polymer compounds

The quantity of coloured polymers which are considered as end products of autoxidation and which are formed during rancidity process was measured according to the method of POKORNY /POKORNY et al /1974/ by absorbance at 400 nm. The degree of absorbance is in direct relation to the quantity of polymers. The method is not suitable for quantitive measurement in lack of standard.

Sampling

The autoxidation processes have been studied on samples taken from the back fats of 22 swines. The samples were taken at random from daily production of Budapest slaughter-house, the samples were stored salted at 6 ± 2°C for 90 days under industrial conditions.

Modell systems

Control Trioleate / BDH Chemicals LTD /

Sample 25mg glycine was solved in 1 ml of distilled water and emulsified in 200 gr trioleate. / The samples were put in crystallizing cups in 3 cm layers/

Results

The autoxidation processes taking place during storage of back fat were studied on the products of primary and secondary oxidation and with the formation of end products. Peroxide as primary, malonaldehyde as secondary oxidation product has been chosen. The amount of oxidation products was determined an hour after slaughter. This was considered as 0 point of storage. Following this the peroxide and malonaldehyde concentration as well as the absorbance of polymer compounds were measured at 15 days intervals. The results were represented as a function of storage time. /Fig.1.//Fig.1. shows the means of the 22 samples/. It can be seen that the peroxide concentration increases monotonously during storage /Fig.1./ This increase however is neither linear, nor exponential, because the peroxide-time curve has inflexion points every 15 days. The malonaldehyde concentration changes periodically during storage. The malonaldehyde-time curve has local extreme values every 15 days. On the basis of standard deviations /Fig.1./ it can be seen that the periodicity of the autoxidation is not due to standard deviation of the samples since the difference of the concentration of the extreme values is larger than the standard deviation.

The increase of the amount of polymers is almost linear during storage.

The periodicity of the time curves of autoxidation products is not in agreement with the literature data according to which the oxidation products increase exponentially in time /REICH /1969/. Since the time-dependent change of the autoxidation products was studied on the oxidation of pure fatty acids and/or their esthers, we presumed that the periodicity of autoxidation of adipose tissues is due to proteins, amino acids and other compounds.

To prove this postulation model experiments were carried out.

The control and model samples were stored for 90 days at 6 ± 2°C according to industrial practice. The concentration of peroxide and malonaldehyde and the amount of coloured polymers were determined.

The results were represented as a function of storage time /Fig. 2., 3., 4./

Fig 2. and 3. shows that the peroxide and malonaldehyde concentration of the samples containing glycine changes similarly to that of the back fats. The peroxide - time curve have inflexion points every 15 days intervals, and the malomaldehyde - time curve has local extreme value. The concentration of the control peroxid and malomaldehyde increases monotonously.

The absorbance at 4oo nm of the polymers showed linear increase during storage /Fig.4./ The increase was greater in experimental samples than in the control.

Discussion

The autoxidation process of swine back fat taking place during storage were studied on primary /peroxide/ on sencondary /malonaldehyde/ oxidation products chosen arbitrarily and by the absorbance of polymers that were considered as end product of oxidation.

On the basis of the results it can be stated the followings:

- The autoxidation of adipose tissue shows periodicity
- The oxidation product - time curves show the relationship between the changes in concentration of intermediates of oxidation.

In the time curves of the primary and secondary oxidation products there are inflexion points and local extreme values at every 15 days intervals. This phenomenon is not due to the standard deviation of the samples or the errors of measurements. It was proved by model experiments that one of the causes of the periodicity of autoxidation is the presence of compounds containing amino groups. This compounds - proteins, amino acids, some phospholipids - react with the carbonyl compound formed in the secondary processes of rancidity. The compounds formed as a result of this reaction are inactive in terms of autocatalytic oxidation.

On the basis of model experiments it can be seen that the time of periods /15 days/ is not altered by the fatty acid composition or by the quantity and quality of compounds containing amino groups in the standard condition of oxidation. The above mentioned periodicity relates only to the change in concentration of the primary and secondary oxidation products, for the quantity of the end-product of rancidity shows a linear increase.

Furthermore it is supposed that the periodicity of the oxidation is also due to physical factors, such as diffusion of oxygen, temperature etc. It is possible that one or more part- reaction of the oxidation process is an oscillating reaction. The type of concentration - time surves determined by us has only been observed namely in case of oscillating reactions. Further experiments are necessary to clarify the role played by the factors as well as the mechanism of autoxidation.

The oxidation products- time curves show that there is a very close relationship between the changes of peroxide and malonaldehyde concentrations, since the latter are formed in two successive phases of the autoxidation process. The amount of the polymers end products of rancidity showed and almost linear increase, during storage. It seemed that this increase was independent to the quantity of primary and secondary products. This is due to the colourless fluorescent compounds formed in the first steps of the reaction between carbonyl and amino groups. The yellow polymers /the amount of which can be determined by absorbance at 400 nm/ are formed in the next steps as a result of consecutive reactions /Tappel et al/1973./

To sum up the results it can be stated that the autoxidation of lipids in the presence of amino groups shows periodicity which can be measured by the change in concentration of oxidation products.

Therefore in determining the rancidity of adipose tissues not only the rode but also the time of sampling is essential. On the 15th day the back fats can be qualified as moderate rancid according to its peroxide and malonaldehyde concentration, but this is not true if the same samples are studied on the 30th day. Therefore the peroxide value and Kreiss test used in the industry is not suitable for estimating the rancidity of materials containing amino groups /adipose tissue, fats, bacon etc./ The peroxide value gives an estimation of process of rancidity only, while the Kreiss test is suitable only for determining the presence of carbonyl compounds, and it does not permit quantitative measuring. To characterize the autoxidation of these substances of the above mentioned composition the measurement of - peroxide value, TBA number / malonaldehyde content / and polymers of the same sample is necessary.

References

KIMOTO,W.J., GADDIS,A.M.; J. Am. Oil Chem.Soc.,51, 307.

MOSITO,M., FUJUMAKI,M; /1972/: Agr.Biol.Chem., 36/12/, 2263.

MYRES,A.W., BOWLAND,J.P.,; /1975/: Can.J.Amer.Sci.; 55/3/, 316.

PEARSON,D.; /1968/: J.Sci.Food.Agric.,19,553.

POKORNY,J., JANICEK,G.; /1973/: Nahrung, 17/7/,713.

POKORNY,J.,EL ZEANY,E.H.,KOLALOWSKA,A.,JANICEK,G;/1974/:Z.Lebensm.Unters.u.Forsch.,151, 305

REICH,L.;/1969/: Autoxidation of Hydrocarbons and Polyolefins. Kinetics and Mechanism. Ed.by Marcell Dekker Ins., New York.

TAPPEL,A.lL., FLETCHER,B.S., REDDY,K., TAPPEL,A.N.;/1973/: J.Nutr., 103, 988.

FIG.1. Back fats: Changes of the concentration of products of autoxidation as a function of storage time

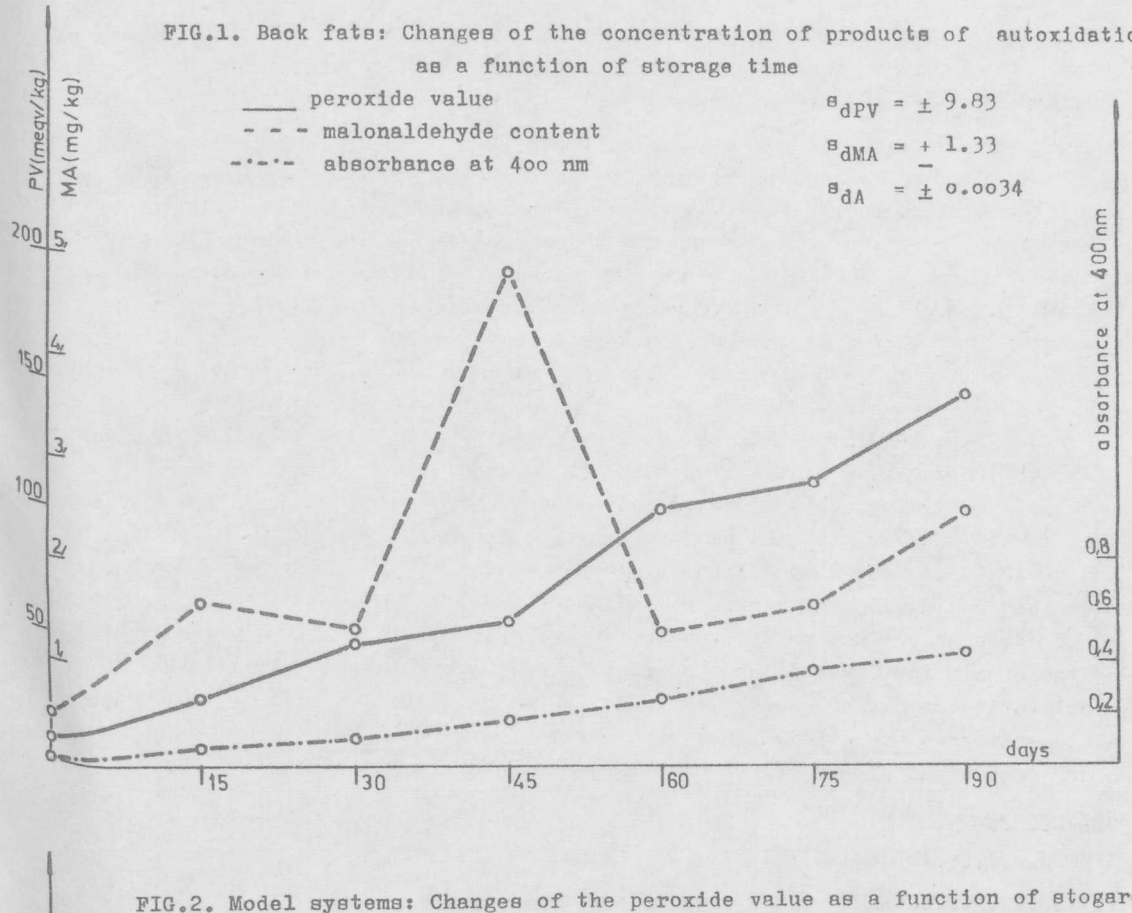


FIG.2. Model systems: Changes of the peroxide value as a function of stogare time

$s_{dPV} = \pm 1.7$

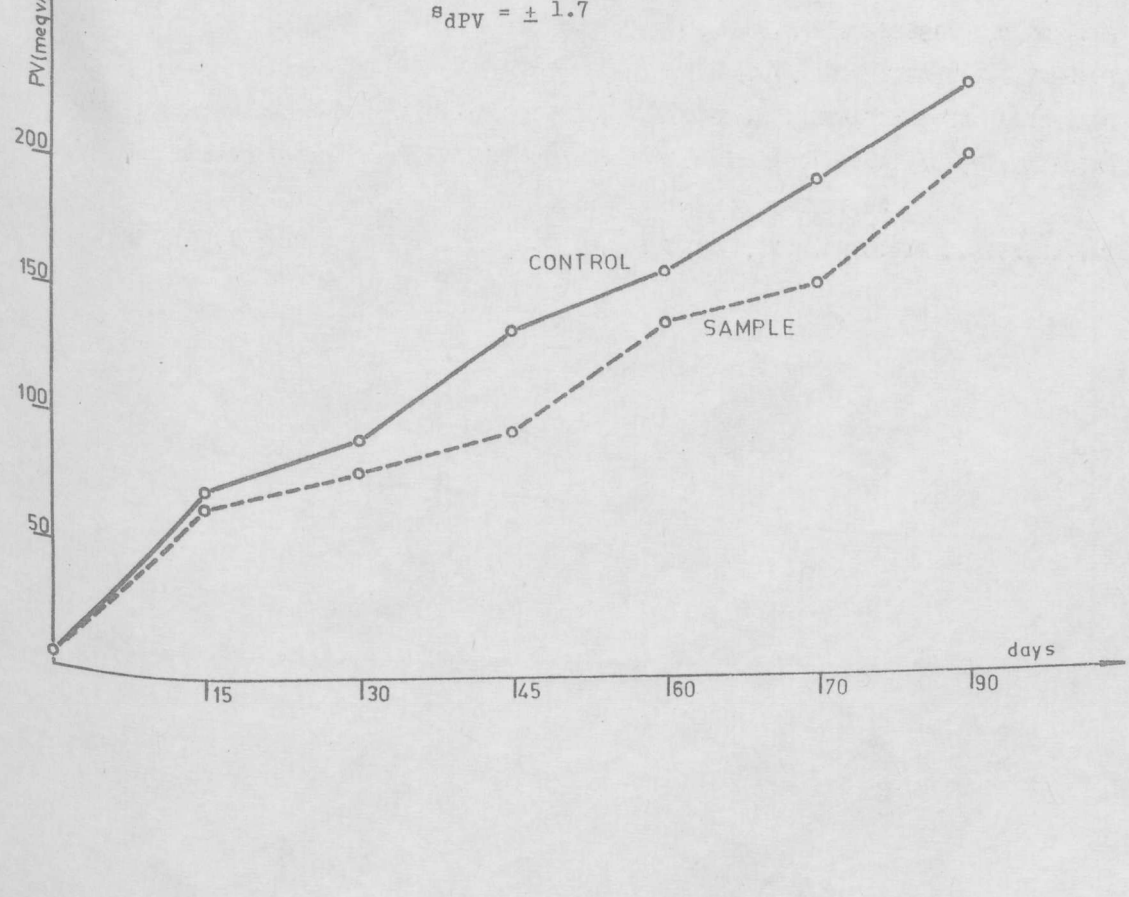


FIG.3. Model systems: Changes of the malonaldehyde concentration as a function of storage time

$s_{dMA} = \pm 0.14$

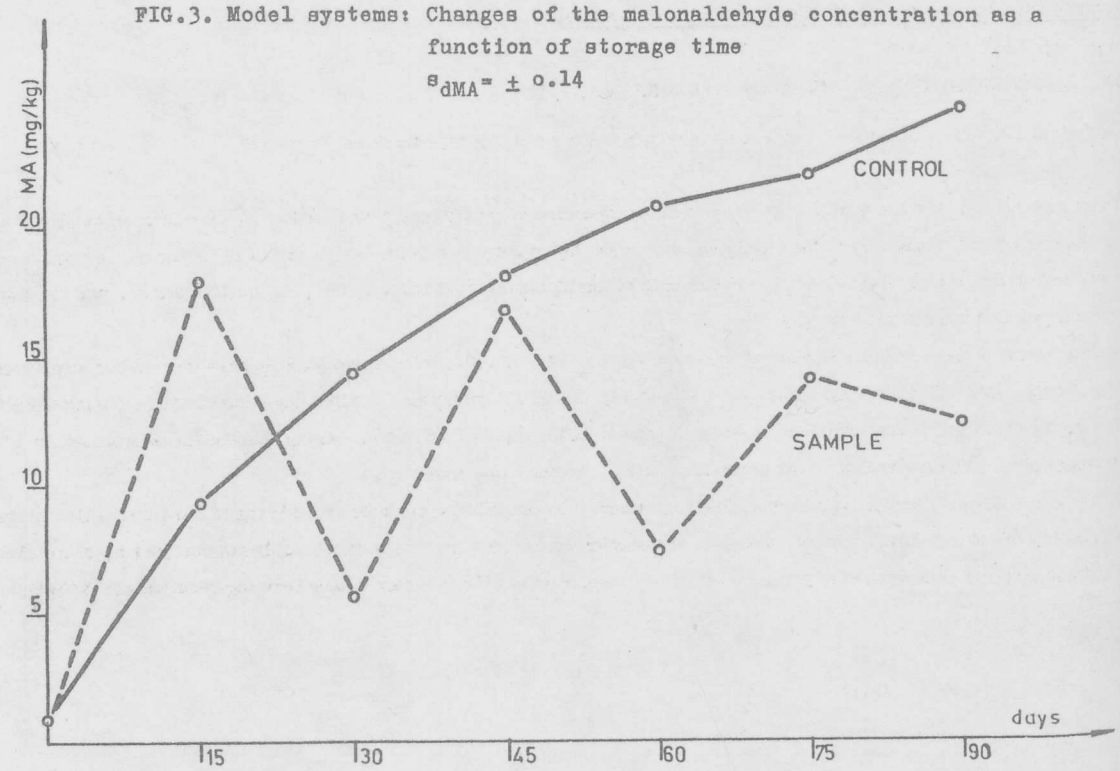


FIG.4. Model systems: Changes of the absorbance of polymer compounds at 400 nm

$s_{dA} = \pm 0.002$