The influence of oxygen content on lipid oxidation in foods
A literature review

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1. Introduction

Oxidation of fat and other food ingredients (vitamins, colours and aroma compounds) is one of the most important causes of quality losses during food processing and storage. In microbiologically stable foods, such as dry and semi-moist or frozen products, lipid oxidation is the main deteriorative reaction (Lingnert and Ericsson, 1981).

Lipid oxidation is a very complex reaction system. Basically, it is a free radical reaction which is influenced by a number of factors, one of them being oxygen availability. The oxygen amounts needed to cause unacceptable oxidative changes are usually very small. However, our knowledge about which levels that can be accepted for different kinds of food and how the storage stability is related to the oxygen concentration or the oxygen amount available for oxidation is limited.

The influence of oxygen on lipid oxidation can be looked at in two ways. As oxygen is consumed during oxidation, the amount of oxygen available will limit the extent of oxidation. But, it is not only the total amount of oxygen available that influences the oxidation. The concentration of oxygen in the headspace or dissolved in the product is also important (Karel 1974), as it can influence the oxidation rate. A lower oxidation rate prolongs the time required to reach a certain degree of quality loss, in the case where the total amount of oxygen is not the limiting factor.

The relationship between the rate of oxidation and the oxygen partial pressure varies with the type of reaction, type of product and temperature (Karel, 1974). In many oxidation reactions, this relationship is of the type:

\[ R_{\text{ox}} \propto \frac{pO_2}{k_2 \cdot k_1 \cdot pO_2} \]  

(1)

where \( R_{\text{ox}} \) is oxidation rate,

\( pO_2 \) is the oxygen partial pressure and

\( k_1 \) and \( k_2 \) are constants
This behaviour is typical of oxidation of lipids (Karel, 1974) in products with little internal diffusion. The equation shows that with a high oxygen partial pressure, the oxidation rate is relatively independent of the oxygen partial pressure. On the other hand, a low oxygen partial pressure, which gives \( k_{pO_2} < k_2 \), gives an oxidation rate proportional to the oxygen partial pressure. With a lowering of the oxygen partial pressure, the oxidation rate will be more and more influenced by the oxygen partial pressure (Karel, 1974).

This relationship between oxygen partial pressure and oxidation rate explains why a lowering of the oxygen partial pressure from 2% to 1% in the headspace above a linolenic or linoleic acid emulsion, can retard the oxidation more, than a lowering from 21% to 2% (Marcuse and Fredriksson, 1968).

The aim of this report is to review what has been reported in the literature on the influence of the oxygen concentration and/or the amount of oxygen available on the lipid oxidation in food. Various types of food are treated and in chapter 6 the foods are divided into the following groups: liquid products, dehydrated products, oils, fats and emulsions, meat products, fruit and fruit products, and finally a chapter on some experiments in which computer predictions of shelf-life are compared with experimental values. The report also contains a chapter (Chapter 4) which goes deeper into elucidating the fact that the solubility and diffusion of oxygen in the food will influence the oxidation rates. In chapter 5, the influence of oxygen availability on the lipid oxidation in the cases with constant and decreasing levels of oxygen are discussed in a more generally way.

The review also contains introductory chapters on lipids (Chapter 2) and lipid oxidation (Chapter 3).
2. Lipids

It is difficult to define which compounds belong to the lipid group. One definition used by both Belitz and Grosch (1987) and Nawar (1985) is that lipids are soluble in organic solvents, but not in water. Lipids are necessary for the functioning of the body. They form the major part of adipose tissue and together with proteins and carbohydrates, they are responsible for the structure and strength of the cell (Nawar, 1985). Glycerol esters of fatty acids make up the most of the lipids in plants and animals and up to 99% of the lipids can be glycerol esters, although this figure of course differs between different species (Belitz and Grosch, 1987). The lipids can be divided into different groups depending on their physical properties or chemical composition. They may, for instance, be divided into neutral-polar lipids (Table 1) or into the groups simple, compound or derived lipids (Table 2).

Table 1. Lipid classification (Belitz and Grosch, 1987)

<table>
<thead>
<tr>
<th>A. Classification after “acyl residue” characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. Simple lipids (not saponifiable)</td>
</tr>
<tr>
<td>Free fatty acids, isoprenoid lipids (sterols, carotenoids, monoterpenes), tocopherols</td>
</tr>
<tr>
<td>II. Acyl lipids (saponifiable)</td>
</tr>
<tr>
<td>Mono-, di-, triacyl-glycerols Phospholipids (phosphatides)</td>
</tr>
<tr>
<td>Glycolipids</td>
</tr>
<tr>
<td>Fatty acid, glycerol or sphingosine, phosphoric acid, organic base</td>
</tr>
<tr>
<td>Fatty acid, glycerol or sphingosine, mono-, di- or oligosaccharide</td>
</tr>
<tr>
<td>Diol lipids</td>
</tr>
<tr>
<td>Waxes</td>
</tr>
<tr>
<td>Sterol esters</td>
</tr>
</tbody>
</table>

B. Classification after the characteristics “neutral-polar”

<table>
<thead>
<tr>
<th>Neutral lipids</th>
<th>Polar (amphiphilic) lipids</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fatty acids (&gt; C₁₂)</td>
<td>Glycerophospholipid</td>
</tr>
<tr>
<td>Mono-, di-, triacyl-glycerols</td>
<td>Glyceroglycerolipid</td>
</tr>
<tr>
<td>Sterols, sterol esters</td>
<td>Sphingophospholipid</td>
</tr>
<tr>
<td>Carotenoids</td>
<td>Sphingoglycerolipid</td>
</tr>
<tr>
<td>Waxes</td>
<td>Tocopherols*</td>
</tr>
</tbody>
</table>

* Tocopherols and quinone lipids are often considered as “redox lipids”.
Table 2. Lipid classification (Nawar, 1985)

<table>
<thead>
<tr>
<th>Major class</th>
<th>Subclass</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simple lipids</td>
<td>Acylglycerols</td>
<td>Glycerol + fatty acids</td>
</tr>
<tr>
<td></td>
<td>Waxes</td>
<td>Long-chain alcohol + long-chain fatty acid</td>
</tr>
<tr>
<td>Compound lipids</td>
<td>Phosphoacylglycerols (or glycerophospholipids)</td>
<td>Glycerol + fatty acids + phosphate + another group usually containing nitrogen</td>
</tr>
<tr>
<td></td>
<td>Sphingomyelins</td>
<td>Sphingosine + fatty acid + phosphate + choline</td>
</tr>
<tr>
<td></td>
<td>Cerebrosides</td>
<td>Sphingosine + fatty acid + simple sugar</td>
</tr>
<tr>
<td></td>
<td>Gangliosides</td>
<td>Sphingosine + fatty acid + complex carbohydrate moiety that includes sialic acid</td>
</tr>
<tr>
<td>Derived lipids</td>
<td>Materials that meet the definition of a lipid but are not simple or compound lipids</td>
<td>Examples: carotenoids, steroids, fat-soluble vitamins</td>
</tr>
</tbody>
</table>

As can be seen from the tables, fatty acids play an important role, as a constituent of many of the lipids.

2.1 Fatty acids

Fatty acids are the fundamental constituent in all acyl lipids. They usually consist of a long straight carbon chain with an acid group at one end, but branched chains also exist, being a very minor part of food (Figure 1).

![Figure 1. A saturated and an unsaturated fatty acid (Alberts et al., 1989)]
The fatty acids are usually synthesized through biosynthesis, with an even number of 2-30 carbon atoms, and exist in saturated and unsaturated forms, the double bonds normally being in the cis configuration (Table 3).

<table>
<thead>
<tr>
<th>Abbrev.</th>
<th>Systematic name</th>
<th>Common name</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saturated fatty acids</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2:0</td>
<td>ethanoic</td>
<td>acetic</td>
<td>CH3CH2COOH</td>
</tr>
<tr>
<td>3:0</td>
<td>propanoic</td>
<td>propionic</td>
<td>CH3(CH2)2COOH</td>
</tr>
<tr>
<td>4:0</td>
<td>n-butanoic</td>
<td>butyric</td>
<td></td>
</tr>
<tr>
<td>5:0</td>
<td>n-pentanoic</td>
<td>valeric</td>
<td></td>
</tr>
<tr>
<td>6:0</td>
<td>n-hexanoic</td>
<td>caproic</td>
<td></td>
</tr>
<tr>
<td>7:0</td>
<td>n-heptanoic</td>
<td>heptanoic</td>
<td></td>
</tr>
<tr>
<td>8:0</td>
<td>n-octanoic</td>
<td>caprylic</td>
<td></td>
</tr>
<tr>
<td>9:0</td>
<td>n-nonanoic</td>
<td>nonanoic</td>
<td></td>
</tr>
<tr>
<td>10:0</td>
<td>n-decanoic</td>
<td>decanoic</td>
<td></td>
</tr>
<tr>
<td>11:0</td>
<td>n-undecanoic</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12:0</td>
<td>n-dodecanoic</td>
<td>lauric</td>
<td>CH3(CH2)10COOH</td>
</tr>
<tr>
<td>13:0</td>
<td>n-tridecanoic</td>
<td></td>
<td></td>
</tr>
<tr>
<td>14:0</td>
<td>n-tetradecanoic</td>
<td>myristic</td>
<td>CH3(CH2)14COOH</td>
</tr>
<tr>
<td>15:0</td>
<td>n-pentadecanoic</td>
<td></td>
<td></td>
</tr>
<tr>
<td>16:0</td>
<td>n-hexadecanoic</td>
<td>palmitic</td>
<td>CH3(CH2)16COOH</td>
</tr>
<tr>
<td>17:0</td>
<td>n-heptadecanoic</td>
<td>margaric</td>
<td></td>
</tr>
<tr>
<td>18:0</td>
<td>n-octadecenoic</td>
<td>stearic</td>
<td></td>
</tr>
<tr>
<td>19:0</td>
<td>n-nonadecanoic</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20:0</td>
<td>n-eicosanoic</td>
<td>arachidic</td>
<td></td>
</tr>
<tr>
<td>21:0</td>
<td>n-heneicosanoic</td>
<td></td>
<td></td>
</tr>
<tr>
<td>22:0</td>
<td>n-docosanoic</td>
<td>behenic</td>
<td></td>
</tr>
<tr>
<td>23:0</td>
<td>n-tricosanoic</td>
<td></td>
<td></td>
</tr>
<tr>
<td>24:0</td>
<td>n-tetracosanoic</td>
<td>lignoceric</td>
<td></td>
</tr>
<tr>
<td>26:0</td>
<td>n-hexacosanoic</td>
<td>cerotic</td>
<td></td>
</tr>
<tr>
<td>28:0</td>
<td>n-octacosanoic</td>
<td>montanic</td>
<td></td>
</tr>
</tbody>
</table>

Branched-chain fatty acids:

<table>
<thead>
<tr>
<th>Abbrev.</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iso 14:0</td>
<td>12-methyltridecanoic</td>
</tr>
<tr>
<td>Anteiso 14:0</td>
<td>11-methyltridecanoic</td>
</tr>
<tr>
<td>Iso 15:0</td>
<td>13-methyltetradecanoic</td>
</tr>
<tr>
<td>Anteiso 15:0</td>
<td>12-methyltetradecanoic</td>
</tr>
<tr>
<td>Iso 16:0</td>
<td>14-methylpentadecanoic</td>
</tr>
<tr>
<td>Anteiso 16:0</td>
<td>13-methylpentadecanoic</td>
</tr>
<tr>
<td>Iso 17:0</td>
<td>15-methylhexadecanoic</td>
</tr>
<tr>
<td>Anteiso 17:0</td>
<td>14-methylhexadecanoic</td>
</tr>
<tr>
<td>C16</td>
<td>4,8,12-trimethyltridecanoic</td>
</tr>
<tr>
<td>C19</td>
<td>2,6,10,14-tetramethylpentadecanoic</td>
</tr>
<tr>
<td>C20</td>
<td>3,7,11,15-tetramethylhexadecanoic</td>
</tr>
</tbody>
</table>
### Monounsaturated fatty acids (MUFA)

<table>
<thead>
<tr>
<th>Chain Length</th>
<th>Fatty Acid</th>
<th>Position</th>
<th>cis-</th>
<th>Trans</th>
</tr>
</thead>
<tbody>
<tr>
<td>14:1n-5</td>
<td>9-tetradecenoic</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16:1n-7</td>
<td>9-hexadecenoic</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16:1n-10</td>
<td>6-hexadecenoic</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18:1n-12</td>
<td>6-octadecenoic</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18:1n-9</td>
<td>9-octadecenoic</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18:1n-7</td>
<td>11-octadecenoic</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18:1n-9</td>
<td>9-eicosanoic</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20:1n-9</td>
<td>9-eicosanoic</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20:1n-11</td>
<td>11-docosanoic</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>22:1n-9</td>
<td>13-docosanoic</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>24:1n-9</td>
<td>15-tetracosanoic</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Polyunsaturated fatty acids (PUFA)

#### Dienoic acids:

<table>
<thead>
<tr>
<th>Chain Length</th>
<th>Fatty Acid</th>
<th>Position</th>
<th>cis-</th>
<th>Trans</th>
</tr>
</thead>
<tbody>
<tr>
<td>16:2</td>
<td>7,10-hexadecadienoic</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18:2n-6</td>
<td>9,12-octadecadienoic</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18:2n-7</td>
<td>6,11-octadecadienoic</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

#### Trienoic acids:

<table>
<thead>
<tr>
<th>Chain Length</th>
<th>Fatty Acid</th>
<th>Position</th>
<th>cis-</th>
<th>Trans</th>
</tr>
</thead>
<tbody>
<tr>
<td>18:3</td>
<td>7,10,13-hexadecatrienoic</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18:3n-3</td>
<td>9,12,15-octadecatrienoic</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18:3n-6</td>
<td>6,9,12-octadecatrienoic</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18:3n-9</td>
<td>5,8,11-eicosatrienoic</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

#### Tetraenoic acids:

<table>
<thead>
<tr>
<th>Chain Length</th>
<th>Fatty Acid</th>
<th>Position</th>
<th>cis-</th>
<th>Trans</th>
</tr>
</thead>
<tbody>
<tr>
<td>16:4</td>
<td>6,9,12,15-hexadecatetraenoic</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20:4n-6</td>
<td>5,8,11,14-eicosatetraenoic</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20:4</td>
<td>8,11,14,17-eicosatetraenoic</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18:4</td>
<td>9,11,13,15-octadecatetraenoic</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18:4</td>
<td>6,9,12,15-octadecatetraenoic</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

#### Pentaenoic acids:

<table>
<thead>
<tr>
<th>Chain Length</th>
<th>Fatty Acid</th>
<th>Position</th>
<th>cis-</th>
<th>Trans</th>
</tr>
</thead>
<tbody>
<tr>
<td>18:5</td>
<td>3,6,9,12,15-octadecapentaenoic</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20:5n-3</td>
<td>5,8,11,14,17-eicosapentaenoic</td>
<td></td>
<td></td>
<td>trans</td>
</tr>
<tr>
<td>22:5n-6</td>
<td>4,7,10,13,16-docosapentaenoic</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>22:5n-3</td>
<td>7,10,13,16,19-docosapentaenoic</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

#### Hexaenoic acids:

<table>
<thead>
<tr>
<th>Chain Length</th>
<th>Fatty Acid</th>
<th>Position</th>
<th>cis-</th>
<th>Trans</th>
</tr>
</thead>
<tbody>
<tr>
<td>22:6n-3</td>
<td>4,7,10,13,16,19-docosahexaenoic</td>
<td></td>
<td></td>
<td>trans</td>
</tr>
</tbody>
</table>

*Note: Unless otherwise stated, all double bonds are in the cis-configuration. t = trans-configuration.*

The unsaturated fatty acids can be further divided into different groups according to where the double bonds are situated. Usually the double bonds are numbered from the carboxylic end of the fatty acid (with the carboxylic carbon atom as number one). This classification is shown by the prefix Δ. There is also a classification made from the methyl end. The classification from the methyl end is prefixed by a ω and the groups are called ω3, ω6 and ω9, depending on where, counting from the methyl end, the first double bond is situated (Table 4).
<table>
<thead>
<tr>
<th>Abbreviated designation</th>
<th>Structure</th>
<th>Common name</th>
<th>Melting point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ω9-Family</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18:1 (9)</td>
<td>CH₃·CH₂·CH·CH·CH₂·CH·H·COOH</td>
<td>Oleic acid</td>
<td>13.4</td>
</tr>
<tr>
<td>22:1 (13)</td>
<td>-CH₃·H·COOH</td>
<td>Erucic acid</td>
<td>34.7</td>
</tr>
<tr>
<td>24:1 (13)</td>
<td>-CH₃·H·COOH</td>
<td>Nervonic acid</td>
<td>42.5</td>
</tr>
<tr>
<td><strong>Ω6-Family</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18:2 (9, 12)</td>
<td>CH₃·CH₂·CH·CH·CH·CH₂·CH·H·COOH</td>
<td>Linoleic acid</td>
<td>-5.0</td>
</tr>
<tr>
<td>18:3 (6, 9, 12)</td>
<td>-CH·CH·CH·CH₂·CH·H·COOH</td>
<td>γ-Linolenic acid</td>
<td>-49.5</td>
</tr>
<tr>
<td>20:4 (5, 8, 11, 14)</td>
<td>-CH·CH·CH·CH₂·CH·H·COOH</td>
<td>Arachidonic acid</td>
<td>-49.5</td>
</tr>
<tr>
<td><strong>Ω3-Family</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18:3 (9, 12, 15)</td>
<td>CH₃·CH₂·CH·CH·CH·CH₂·CH·H·COOH</td>
<td>α-Linolenic acid</td>
<td>-11.0</td>
</tr>
<tr>
<td>16:3 (7, 10, 13)</td>
<td>-CH₃·H·COOH</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Ω9-Family</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18:1 (9)</td>
<td>CH₃·CH₂·CH·CH·CH·CH₂·CH·H·COOH</td>
<td>Oleic acid</td>
<td>13.4</td>
</tr>
<tr>
<td>16:1 (8)</td>
<td>-CH₃·H·COOH</td>
<td>Palmitoleic acid</td>
<td>0.5</td>
</tr>
<tr>
<td>14:1 (9)</td>
<td>-CH₃·H·COOH</td>
<td>Myristoleic acid</td>
<td></td>
</tr>
</tbody>
</table>

**B. Fatty acids with nonconjugated trans-double bonds**

<table>
<thead>
<tr>
<th>Abbreviated designation</th>
<th>Structure</th>
<th>Common name</th>
<th>Melting point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>18:1 (11)</td>
<td>CH₃·CH₂·CH·CH·CH·CH₂·CH·H·COOH</td>
<td>Elaidic acid</td>
<td>46</td>
</tr>
<tr>
<td>18:2 (11, 12)</td>
<td>CH₃·CH₂·CH·CH·CH·CH·H·COOH</td>
<td>Linolealaidic acid</td>
<td>28</td>
</tr>
</tbody>
</table>

**C. Fatty acids with conjugated double bonds**

<table>
<thead>
<tr>
<th>Abbreviated designation</th>
<th>Structure</th>
<th>Common name</th>
<th>Melting point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>18:3 (9, 11, 13)</td>
<td>CH₃·CH₂·CH·CH·CH·CH·CH·CH·CH·CH₂·CH·H·COOH</td>
<td>α-Eleostearic acid</td>
<td>48</td>
</tr>
<tr>
<td>18:3 (11, 13)</td>
<td>CH₃·CH₂·CH·CH·CH·CH·H·COOH</td>
<td>β-Eleostearic acid</td>
<td>71.5</td>
</tr>
<tr>
<td>18:4 (9, 11, 13, 15)</td>
<td>CH₃·CH₂·CH·CH·CH·CH·CH·H·COOH</td>
<td>Palmitic acid</td>
<td>53</td>
</tr>
</tbody>
</table>

* Geometry of the double bond was not determined.

In oils originating from plants, linoleic and oleic acid are the most common fatty acids (Table 5). The more saturated the fatty acid, the higher the melting point. This is due to the fact that the unsaturated fatty acids, in contrast to saturated fatty acids, are bent. The bending of the molecule prevents normal crystal arrangements, which leads to a lower melting point (Belitz and Grosch, 1987). Table 6 shows the melting points of some saturated and some unsaturated compounds.
Table 5. Structure and proportion of the major fatty acids in plants (Belitz and Grosch, 1987)

<table>
<thead>
<tr>
<th>Abbreviated designation</th>
<th>Structure</th>
<th>Common name</th>
<th>Proportion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>14:0</td>
<td><img src="image1" alt="Structure" /></td>
<td>Myristic acid</td>
<td>2</td>
</tr>
<tr>
<td>16:0</td>
<td><img src="image2" alt="Structure" /></td>
<td>Palmitic acid</td>
<td>11</td>
</tr>
<tr>
<td>18:0</td>
<td><img src="image3" alt="Structure" /></td>
<td>Stearic acid</td>
<td>4</td>
</tr>
<tr>
<td>18:1 (9)</td>
<td><img src="image4" alt="Structure" /></td>
<td>Oleic acid</td>
<td>34</td>
</tr>
<tr>
<td>18:2 (9, 12)</td>
<td><img src="image5" alt="Structure" /></td>
<td>Linoleic acid</td>
<td>34</td>
</tr>
<tr>
<td>18:3 (9, 12, 15)</td>
<td><img src="image6" alt="Structure" /></td>
<td>Linolenic acid</td>
<td>5</td>
</tr>
</tbody>
</table>

a Numbering of carbon atoms starts with carboxyl group C as number 1.
b A percentage estimate based on world production of edible oils.

Table 6. The effect of number, configuration and double bond position on the melting points of fatty acids (Belitz and Grosch, 1987)

<table>
<thead>
<tr>
<th>Fatty acid</th>
<th>Melting point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>18:0 Stearic</td>
<td>69</td>
</tr>
<tr>
<td>18:1 (tr9) Elaidic</td>
<td>66</td>
</tr>
<tr>
<td>18:1 (c9) cis-2-Octadecenoic acid</td>
<td>51</td>
</tr>
<tr>
<td>18:1 (9) Oleic</td>
<td>12.4</td>
</tr>
<tr>
<td>18:2 (9, 12) Linoleic</td>
<td>-5</td>
</tr>
<tr>
<td>18:3 (tr9, tr12) Linolelaicidic</td>
<td>28</td>
</tr>
<tr>
<td>18:3 (9, 12, 15) α-Linolenic</td>
<td>-11</td>
</tr>
<tr>
<td>20:0 Arachidic</td>
<td>75.4</td>
</tr>
<tr>
<td>20:4 (5, 8, 11, 14) Arachidonic</td>
<td>-49.5</td>
</tr>
</tbody>
</table>

2.2 Triacyl glycerols

Triacyl glycerols consist of three fatty acids esterified to a glycerol molecule (Figure 2).

Figure 2. Schematic drawing of a triacyl glycerol (Alberts et al., 1989)
They are the major constituents in fats and oils and make up the adipose tissue, acting as an energy storage pool. Depending on the type of fatty acids the triacyl glycerols contain, they have different melting points. More saturated and longer fatty acids give a higher melting point. Plants growing in a colder climate have a higher degree of unsaturated fatty acids to obtain the same physical properties as plants growing in warmer countries (Beliz and Grosch, 1987). The distribution of fatty acids in the fat molecule determines the consistency of the fat and triacyl glycerols with similar arrangement have similar melting and crystallization properties (Table 7).

### Table 7. Positional distribution of individual fatty acids in triacyl glycerols of some natural fats (Navar, 1985)

<table>
<thead>
<tr>
<th>Source of</th>
<th>Position</th>
<th>Fatty acid (mol %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4:0</td>
<td>6:0</td>
</tr>
<tr>
<td>Cow's milk</td>
<td>1</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>43</td>
</tr>
<tr>
<td>Coconut</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Cocoa butter</td>
<td>1</td>
<td>34</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>37</td>
</tr>
<tr>
<td>Corn</td>
<td>1</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>14</td>
</tr>
<tr>
<td>Soybean</td>
<td>1</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>13</td>
</tr>
<tr>
<td>Olive</td>
<td>1</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>17</td>
</tr>
<tr>
<td>Peanut</td>
<td>1</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>11</td>
</tr>
<tr>
<td>Beef (loin)</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>-</td>
</tr>
</tbody>
</table>
2.3 Phospholipids and glycolipids

Phospholipids and glycolipids are the major constituents of biological membranes (Figure 3).

a) \[
\begin{align*}
\text{CH}_2-\text{O} & \text{-CO-R} \\
\text{R}_2-\text{CO} & \text{-O-CH}_3 \\
\text{CH}_2-\text{O} & \text{-P} \text{-O-CH}_2\text{-CH}_2\text{-N} \text{-CH}_3 \\
& \text{CH}_2
\end{align*}
\]

b) \[
\begin{align*}
\text{HO} & \text{-CH}_3 \\
\text{HO} & \text{-CH}_2 \\
\text{HO} & \text{-OH}
\end{align*}
\]

Figure 3. Schematic drawing of a) the phospholipid phosphatidyl choline or lecithin, b) the glyceroglycolipid monogalactosyldiacyl glycerol and c) sphingosine (Bellizzi and Grosch, 1987)

The phosphatidyl derivates, which are one of the building blocks in phospholipids, consist of a glycerol molecule esterified to two fatty acids and to phosphoric acid. To the phosphoric acid, another molecule, for example an amino acid, is also esterified. The phosphatidyl derivates are named after the derivates of phosphatidic acid, such as phosphatidyl choline, in which the phosphate group is esterified to choline. Glyceroglycolipids consist of 1,2-diacyl glycerols with a mono-, di-, tri- or tetrasaccharide bond in the third position of glycerol. Galactose is the major sugar component in glycolipids. Sphingolipids contain sphingosine, an amino alcohol with a long unsaturated hydrocarbon chain (Figure 3), instead of glycerol. In sphingolipids a fatty acid is linked by an amide bond to the sphingosine, which has its primary HO group either esterified with phosphoric acid or bound to a mono-, di- or oligosaccharide.

Phospholipids and glycolipids have one hydrophobic and one hydrophilic moiety. This makes them surface-active. In aqueous media they form orderly structures, like micelles and planar double layers (Figure 4).
In this structure the hydrophobic parts cluster in the interior and the hydrophilic moieties are turned against the water. Biological membranes have the form of a double layer. Other hydrophobic molecules, like fat-soluble vitamins can be dissolved in the interior of the membranes. Oxygen is also easily dissolved in the membranes. This makes the oxygen easily accessible to the lipids, which may thus be oxidized.

2.4 Other lipids

There are also a large number of other lipids such as sterols, sterol esters, carotenoids, waxes and tocopherols. The total lipid composition differs a great deal between different foods, depending on the function of certain lipids (Table 8).

| Table 8. Composition of lipids in various foods (Beltz and Grosch, 1987) |
|--------------------------|---|---|---|---|
|                          | Milk | Soya | Wheat | Apple |
| **Total lipids**         | 3.6  | 23.0 | 1.3  | 0.033 |
| **Triacylglycerols**     | 94   | 88   | 41   | 5     |
| **Mono- and**            | 1.3  |     | 1    |       |
| **Diacylglycerols**      |     |     | 1    |       |
| **Sterols**              | <1   | 1    | 1    | 1.3   |
| **Sterol esters**        |     | 1    | 2    |       |
| **Phospholipids**        | 1.3  | 10   | 20   | 47    |
| **Glycolipids**          | 1.5  | 29   | 17   |       |
| **Sulfolipids**          | 1    | 1    | 1    |       |
| **Others**               | 0.54 | 7    | 1.5  |       |

*Total lipids as %, while lipid fractions are expressed as percent of the total lipids.
Waxes act as protection against water in animals and against dehydration in plants. Tocopherols are and carotenoids can be converted into vitamins (E and A, respectively). Tocopherols also act as antioxidants, α-tocopherol being the most active in living tissue and δ-tocopherol the most active in foodstuffs (Belitz and Grosch, 1987, Prokorny, 1987, Gottstein and Grosch, 1990). Cholesterol is a very important constituent of membranes and belongs to the sterol group. It acts as a stabiliser in the membranes (preventing the phospholipids from flip-flopping in the membranes) (Figure 5).

Figure 5. Cholesterol position in the cell membrane (Alberts et al., 1989)
3. Lipid oxidation

Lipids in foods (or in living tissue) are susceptible to oxidation. When lipids in food are oxidized, a rancid flavour (that is easily recognized) is formed. The flavour is due to formation of volatile compounds that developed from intermediate hydroperoxides. Hydroperoxide formation and decomposition is a radical chain reaction.

The radical chain reaction, and thereby the rancidity reaction, can be divided into three parts, initiation, propagation and termination. During the initiation, free radicals are produced and the reaction can be described as (Labuza, 1971):

\[ \text{Initiator} \rightarrow \text{Free radicals} \quad (\text{reaction rate} = R_r, \text{rate constant} = k_i) \]  \hspace{1cm} (2)

The free radicals formed during initiation react further during the propagation step:

\[ R^- + O_2 \rightarrow ROO^- \quad (\text{rate constant} = k_n) \]  \hspace{1cm} (3)

\[ ROO^- + RH \rightarrow ROOH + R^- \quad (\text{rate constant} = k_p) \]  \hspace{1cm} (4)

The termination steps can be expressed as:

\[ \begin{align*}
\text{ROO}^- + \text{ROO}^- & \rightarrow \quad \text{Non radical products,} \\
\text{ROO}^- + R^- & \rightarrow \quad \text{rate constants } k_n, k_p \text{ and } k_r \\
R^- + R^- & \rightarrow \\
\end{align*} \]  \hspace{1cm} (5-7)
Criteria typical of a free radical mechanism, are found in the fat oxidation reaction (Labuza, 1971):

1) The reaction rate is not a direct function of the number of double bonds, but increases drastically as the number is increased.

2) The calculated quantum yield is greater than one.

3) Small amounts of various compounds either accelerate (pro-oxidants) or inhibit (antioxidants) the reaction.

4) A very long induction period is obtained, when starting with a very pure material. The induction period is a period at the "beginning" of the oxidation reaction when no actual oxidation can be seen. During this period the oxidation rate is very low. When the induction period ends, a large increase in the oxidation rate is seen. This defines the end of the induction period.

5) The reaction has a moderately high activation energy.

The reason for the increased rate with more highly unsaturated fatty acids is the increased sensitivity towards hydrogen abstraction, created by the two double bonds surrounding a methyl group. They will weaken the bond between the carbon and a hydrogen on the interrupting methyl group and thereby facilitate hydrogen abstraction.

Lipid oxidation can be divided into three types, according to the mechanism of initiation: autoxidation, photooxidation and lipoxygenase oxidation (Hall, 1983).

3.1 Autoxidation

The actual initiation reaction of autoxidation has been the subject of some discussion
(Schaich, 1992, Pokorny, 1987, Chan, 1987a). In the absence of hydroperoxides and radicals formed from other reactions, there is no obvious way of initiating autoxidation. When hydroperoxides are present, they can be decomposed according to the following reactions (Chan, 1987a):

\[ \text{ROOH} + \text{Me}^{II} = \text{RO}^- + \text{OH}^- + \text{Me}^{III} \]  
\[ \text{ROOH} + \text{Me}^{III} = \text{ROO}^- + \text{H}^+ + \text{Me}^{II} \]

(8)  
(9)

where Me is a metal and the notions II and III stands for the reduced and the oxidized form of the metal, respectively. The radicals formed can then abstract a hydrogen from a fatty acid and a chain reaction is initiated. Me in the formula above could be a free metal ion or a metal ion bound to a protein complex, like haemoglobin or myoglobin. Metals often responsible for the catalysis of hydroperoxide decomposition are iron and copper (Prokorny, 1987).

If the hydroperoxide level is high, a bimolecular process (Reaction 10) could also be possible for the decomposition of hydroperoxides (Prokorny, 1987). The decomposition leads to formation of radicals, which can then initiate new reaction chains. This does not happen at the initial stage of autoxidation, when the hydroperoxide level is low.

\[ 2\text{ROOH} \rightarrow \text{RO}^- + \text{H}_2\text{O} + \text{ROO}^- \]  

(10)

What, then could initiate the autoxidation reaction when hydroperoxides are not present? There is a possibility that there may be a metal-catalysed decomposition of unsaturated fatty acids, at least in the case of polyunsaturated acids (Heaton and Uri, 1961, Schaich, 1992). If this reaction is important for initiation there must be inhibitors present to explain the induction period obtained. Another, more probable, explanation of the initiation could be the action of reduced forms of oxygen (Lingnert and Ekstrand, 1989, Belitz and Grosch, 1987). One form of oxygen that initiates lipid oxidation is the hydroxyl radical. Once formed, hydroxyl radicals will react with all kinds of compounds (Belitz and Grosch, 1987) and either produce other radicals that can react with the fatty acids or directly abstract a hydrogen molecule from the fatty acid. Another reduced form of oxygen that could possibly initiate
lipid oxidation is the superoxide anion, $O_2^-$. Lingnert and Ekstrand (1989) studied the effect of this anion on oxidation initiation. They found that the superoxide anion initiated the oxidation reaction in the absence of the enzyme superoxide dismutase, SOD. SOD catalyzes the dismutation of superoxide anions into hydrogen peroxide and oxygen. They also found that hydrogen peroxide itself did not initiate lipid peroxidation. In the presence of metals, hydrogen peroxide is transformed into hydroxyl radicals by the Fenton reaction, thus leading to initiation of oxidation reactions.

When a radical is formed from a fatty acid during autoxidation, a hydrogen bound to a carbon atom next to a carbon atom engaged in a double bond is abstracted. This is due to the weakening effect of the double bond on the hydrogen, and can be illustrated using oleic acid as an example (Figure 6):

![Chemical Reaction Diagram]

Figure 6. Autoxidation of oleic acid. Primary reaction products: I 11-Hydroperoxyoctadec-9-enoic acid, II 9-hydroperoxyoctadec-10-enoic acid, III 10-hydroperoxyoctadec-8-enoic acid, IV 8-hydroperoxyoctadec-9-enoic acid (Belitz and Grosch, 1987)
Table 9. Monohydroperoxides formed by autoxidation (\( {\text{^3}\text{O}_2} \)) and photooxidation (\( {\text{^1}\text{O}_2} \)) of unsaturated fatty acids (Belitz and Grosch, 1987)

<table>
<thead>
<tr>
<th>Fatty acid</th>
<th>Monohydroperoxide</th>
<th>Position of HOO-group</th>
<th>Proportion (%)</th>
<th>( {\text{^3}\text{O}_2} )</th>
<th>( {\text{^1}\text{O}_2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oleic acid</td>
<td></td>
<td>8</td>
<td>9</td>
<td>27</td>
<td>48</td>
</tr>
<tr>
<td></td>
<td></td>
<td>9</td>
<td>10</td>
<td>23</td>
<td>52</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10</td>
<td>8</td>
<td>23</td>
<td>52</td>
</tr>
<tr>
<td></td>
<td></td>
<td>11</td>
<td>9</td>
<td>27</td>
<td>48</td>
</tr>
<tr>
<td>Linoleic acid</td>
<td></td>
<td>8</td>
<td>9, 12</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>9</td>
<td>10, 12</td>
<td>46.5</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10</td>
<td>8, 12</td>
<td>0.5</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12</td>
<td>9, 13</td>
<td>0.5</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td></td>
<td>13</td>
<td>9, 11</td>
<td>49.5</td>
<td>34</td>
</tr>
<tr>
<td></td>
<td></td>
<td>14</td>
<td>9, 12</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Linolenic acid</td>
<td></td>
<td>9</td>
<td>10, 12, 15</td>
<td>31</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10</td>
<td>8, 12, 15</td>
<td>13</td>
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<td></td>
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<td>12</td>
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<td></td>
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</tr>
<tr>
<td></td>
<td></td>
<td>15</td>
<td>9, 12, 16</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>16</td>
<td>9, 12, 14</td>
<td>46</td>
<td>25</td>
</tr>
</tbody>
</table>

A resonance-stabilized radical is formed. This radical reacts with oxygen and the oxygen binds to either of the two carbon atoms that is not located in the middle of the three stabilized carbons. The possible reactions of oleic acid will produce four different hydroperoxides.

Six different hydroperoxides could be formed from linoleic acid (Table 9), although the yield of the 9- and the 13-hydroperoxides is much greater. This is due to the fact that the hydrogen bound to the 11th carbon atom, which is situated between the double bonds, is more easily abstracted (see above) (Figure 7).

Figure 7. Autoxidation of linoleic acid. Primary reaction products: I 13-hydroperoxyoctadecanoic acid, II 9-hydroperoxyoctadecanoic acid (Belitz and Grosch, 1987)
With abstraction of this hydrogen a five carbon stabilized radical is formed, which allows addition of oxygen to the 9th, 11th and the 13th carbon atom. When oxygen is added to the 9th or the 13th carbon atoms a conjugated double bond system is formed. This system is energetically more favourable than an interrupted system of double bonds, which is obtained if oxygen is added to the 11th carbon atom. Another possible hydrogen abstraction is the abstraction of the hydrogen bound to carbon atoms 8 or 14. These hydrogens are more firmly attached than the hydrogen on the 11th carbon atom and the abstraction only gives a three-carbon atom stabilized radical. The hydroperoxides obtained from such an abstraction are the 8, 10, 12, and 14-hydroperoxides, but they are only formed in smaller amounts due to the less energetically favoured abstraction. This is the reason why almost only the 9- and 13-hydroperoxides are formed. From linolenic acid a mixture of the 9, 12, 13 and 16-hydroperoxides are formed (Paquette, 1987a).

3.2 Photooxidation

Theoretically, there are two types of photooxidation (Belitz and Grosch, 1987). In type I photooxidation, a sensitizer takes up energy from light and then reacts directly with the fatty acid, generating substrate radicals. In type II photooxidation, the sensitizer, after taking up energy from light that converts the sensitizer into an excited state, transforms the energy to an oxygen molecule. The oxygen molecule, then gets excited into singlet oxygen. The singlet oxygen in turn reacts with an unsaturated substrate in a cyclo-addition reaction (Figure 8):

![Figure 8. The cyclo-addition reaction of singlet oxygen with an unsaturated compound (Belitz and Grosch, 1987)](image-url)
Chlorophyll is an example of a photooxidation sensitizer (Belitz and Grosch, 1987).

The hydroperoxides formed from photoinitiated oxidation differ from the ones obtained through autoxidation (see Table 9), as the oxygen is added directly to the double bond. Once the hydroperoxides are formed they decompose in the same way as in autoxidation, yielding radicals that react in the autoxidation pathway. This always gives a mixture of hydroperoxides obtained from the two initiation types and also a mixture of decomposition products.

3.3 Lipoxygenase-mediated oxidation

Lipoxygenase is an enzyme found in many plants and in erythrocytes and leucocytes (Belitz and Grosch, 1987). It oxidizes unsaturated fatty acids with an 1-cis,4-cis-pentadiene system. The active center of the enzyme is an iron atom bound to a porphyrin ring. There are at least two types of lipoxygenases, named L1 and L2, in plants (Belitz and Grosch, 1987). Lipoxygenase L1 oxidizes only free fatty acids with a high stereo and regioselectivity and gives rise to a hydroperoxide with a cis,trans-diene system. For linoleic acid some enzymes give rise to the 9-hydroperoxide and some to the 13-hydroperoxide (Table 10). Lipoxygenase L2 acts more like a catalyst of autoxidation with much less specificity for linoleic acid.

Table 10. Occurrence and properties of various lipoxygenases (Belitz and Grosch, 1987)

<table>
<thead>
<tr>
<th>Food</th>
<th>pH optimum</th>
<th>Peroxidase specificity*</th>
<th>4-LOOH (%)</th>
<th>12-LOOH (%)</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soybean, L-1</td>
<td>9.0</td>
<td>5</td>
<td>95</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Soybean, L-2</td>
<td>6.5</td>
<td>50</td>
<td>50</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>Peas, L-2</td>
<td>6.5</td>
<td>50</td>
<td>50</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>Peanut</td>
<td>6.0</td>
<td>0</td>
<td>100</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Potato</td>
<td>3.5</td>
<td>95</td>
<td>5</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Tomato</td>
<td>5.5</td>
<td>95</td>
<td>5</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Wheat</td>
<td>6.0</td>
<td>50</td>
<td>10</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Cucumber</td>
<td>5.5</td>
<td>75</td>
<td>35</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Apple</td>
<td>6.0</td>
<td>10</td>
<td>99</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Strawberry</td>
<td>6.5</td>
<td>75</td>
<td>77</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Gooseberry</td>
<td>6.5</td>
<td>45</td>
<td>35</td>
<td>11</td>
<td></td>
</tr>
</tbody>
</table>

* Against linoleic acid; 9- or 13-LOOH, cf. Fig. 3.24a.
The L1 enzyme is activated by hydroperoxide and during activation Fe²⁺ is oxidized to Fe³⁺. During the oxidation, the fatty acid is bound to the enzyme and oxygen is attached to a double bond in the fatty acid, with iron acting as a catalyst without changing the oxidation number. In the end, the fatty acid is released now in the form of a hydroperoxide (Belitz and Grosch, 1987). The type II enzyme can react with esterified fatty acids and also releases radicals during the oxidation process, leading to autoxidation products (Belitz and Grosch, 1987).

3.4 Cyclization reactions

In a system of double bonds, the carbon atoms situated on the outside of the system are denoted outer carbon atoms and the carbons situated inside the system are denoted inner carbon atoms (Figure 9).

![Figure 9. Schematic drawing of a fatty acid. In this figure carbon atoms number 4 to 9 (calculated from the methyl end) are inner carbon atoms.](image)

When unsaturated peroxyl radicals are formed, with the oxygen bonded to the inner carbon atoms, cyclization can take place. By autoxidation of fatty acids, these peroxyl radicals can only be formed from fatty acids containing three or more double bonds and by photooxidation, from fatty acids with two or more double bonds. The cyclization reaction may produce, for instance, dioxans, diolefinic and hydroperoxy epoxides (Belitz and Grosch, 1987, Chan, 1987b). This makes the yield of inner hydroperoxides lower which can be seen in Table 9. The proportion of the 10 and 12-hydroperoxides from the photooxidation of linoleic acid is smaller than the proportions of the 9 and 13-hydroperoxides, although they should theoretically be obtained in the same yield (Paquette, 1987a).
3.5 Isomerization reaction

Isomerization is a free radical chain reaction, with the first stage being the reverse of the oxygenation step in equation 3 (Chen, 1987b). Once a peroxy radical is formed, the rearrangement reaction will continue in the absence of significant chain termination, as the reaction is essentially one of equilibration (Figure 10).

![Reaction Diagram]

Figure 10. Schematic drawing of isomerization of a disaturated compound (Beltz and Grosch, 1987)

The isomerization reaction can lead to a mixture of hydroperoxides, from initially one kind of hydroperoxide.

3.6 Decomposition of hydroperoxides

The hydroperoxides formed from the oxidation of lipids are fairly stable at 40°C in the absence of metal ions or metal-containing compounds (Grosch, 1987). They do, however, decompose at high temperatures and by metal catalysis. Hydroperoxides can also react further to form polymers under high temperature conditions, such as in frying oils (Paquette et al., 1985b).

The peroxy radical obtained from equation 8 reacts further by abstracting a hydrogen from another fatty acid, producing a hydroperoxide and a new radical (eq. 3). On the other hand,
the alkoxy radical obtained in equation 7 is further decomposed by metal catalysis in a reaction scheme following β-scission (Bell et al., 1951, Badings et al., 1959, Frankel et al., 1961 and Swoboda and Lea, 1963). These reactions give rise to more radicals and volatile compounds (Figure 11).

The β-scission can occur via two routes, either by scission of the carbon-carbon bond next to the oxygen-bearing carbon atom, away from the olefinic linkage (scission A), or by scission of the carbon-carbon bond between the oxygen-bearing atom and the double bond (scission B). Scission A, which is energetically more favourable (Ohloff, 1973) due to the formation of a resonance-stabilized oxoene or oxodiene, results in the formation of an unsaturated oxo compound and an alkyl radical. The alkyl radical can react further by abstracting a hydrogen atom from another fatty acid and, if this end is thought to be the methyl end, give rise to an alkane, or react with a hydroxy radical to produce an alcohol. The B scission will yield a saturated oxy-compound and an 1-olefin radical. This radical can react
further with a RH compound to produce (if thought to be the methyl end) an alkene or combine with a hydroxy radical to give an 1-enol which will tautomerize to the corresponding oxo-compound.

Hexanal, which is a fairly common volatile compound to study in order to follow the lipid oxidation (Hall et al., 1985, Koelsch et al., 1991), can be formed through oxidation of linoleic acid by scission according to route B from the 13-hydroperoxide. It can also be formed from the 9-hydroperoxide by scission A to 2,4-decadienal, which, in turn, is further oxidized by route A to hexanal (Chan et al., 1976). If the scission along route B is prohibited (Ohloff, 1973), hexanal could be formed from the 13-hydroperoxide first by isomerization of the hydroperoxide into the 9-hydroperoxide and thereafter by scission along route A to yield 2,4-decadienal (Chan et al., 1976), which decomposes further into hexanal.

Heterolytic cleavage of the hydroperoxides can take place in aqueous systems (Ohloff, 1973) (Figure 12).

Figure 12. Proton-catalysed cleavage of linoleic acid 13-hydroperoxide (Ohloff, 1973)
The cleavage is initiated by protonation of the hydroperoxide group. From the 13-hydroperoxide of linoleic acid, the formation of hexanal in aqueous solutions can be explained by this mechanism.

The oxidation course can be divided into two stages, unimolecular and bimolecular stage (Labuza, 1971). The notion is derived from the different stages of hydroperoxide decomposition. In the beginning of the oxidation process when the oxidation rate is rather low, the decomposition of hydroperoxides takes place through a metal-catalysed reaction (see above). This is a unimolecular reaction where the metal ion catalyses the decomposition of a certain hydroperoxide molecule. In the bimolecular stage, as previously mentioned, two hydroperoxide molecules can be decomposed according to:

\[ 2 \text{ROOH} \rightarrow \text{RO}^- + \text{H}_2\text{O} + \text{ROO}^- \]  

(10)

This is an exothermic reaction and the reaction is not metal-catalysed. For this reaction to occur, the concentration of hydroperoxides has to be rather high. At the beginning of the bimolecular decomposition stage, the food product is usually so spoiled, by unimolecular decomposition of hydroperoxides into volatile compounds, that eating it is out of the question.

3.7 Influence of oxygen

The composition of the low molecular weight products formed at moderate temperatures (below 80°C) and in the presence of air is different from that obtained by anaerobic pyrolysis (thermal decomposition) of monohydroperoxides. In particular, the proportion of unsaturated compounds tends to be smaller in the presence of oxygen (Grosch, 1987). In the absence of oxygen, 2,4-decadienal was found to be favoured as a decomposition product from the 9-hydroperoxide of linoleic acid, but was also formed from the 13-hydroperoxide (through isomerization of the 13-hydroperoxide to the 9-hydroperoxide). In the presence of oxygen, the reactions of the 9-hydroperoxide was found to lead to an increase in the formation of
hexanal and disappearance of 2,4-decadienal (Grosch, 1981). The rearrangements (isomerization) of the monohydroperoxides, which occurs under anaerobic conditions (Chan et al. 1976), could not be detected due to the lack of 2,4-decadienal. Schieberle and Grosch (1981) have shown that the oxidative cleavage of 2,4-decadienal proceeds through unstable peroxides (Figure 13).

The cleavage leads to the formation of hexanal, 2-octenal and other volatiles (Matthews et al., 1971). The extent of oxidation is also influenced by the amount of oxygen present. This will be discussed in chapter five.

![Figure 13. Autoxidation of 2,4-decadienal at 38°C (Schieberle and Grosch, 1981)](image)

### 3.8 Anti- and prooxidants

Antioxidants are compounds that inhibit or retard the oxidation reaction. There are two types of antioxidants, preventive and real antioxidants (Pokorny, 1987). The preventive antioxidants could be (Pokorny, 1987):
- compounds that break down hydroperoxides into stable compounds
- compounds that react with the double bonds in the lipids to make them less susceptible to reaction
- compounds that take care of the energy from singlet oxygen and converts it into the triplet form
- compounds that deactivate metals.

Real antioxidants react with the radicals formed in the oxidation reaction and convert them into less reactive compounds. The energy from the radical is taken care of by the antioxidant, which is then converted into a stable radical. The antioxidant radical can react further with another oxidation radical or another compound to give stable products or be rearranged into a stable product.

Prooxidants are compounds that initiate or accelerate the oxidation reaction. They may be, for instance, metals (initiate oxidation) or sensitizers (produce singlet oxygen).
4. Solubility and diffusion of oxygen in food

A critical factor for the oxidation reaction to occur is the availability of oxygen. In a packed food product, the oxygen content in the headspace (if there is a headspace) is usually much greater than the oxygen content in the product itself. This is due to the low solubility of oxygen in food compared to the possible oxygen concentration in the gas phase (in air about 21%). Baron and Lubbecke (1981) measured the oxygen content in the headspace and in the liquid phase of non-alcoholic drinks. They found that the headspace oxygen made a large contribution to the total amount of oxygen available, especially in small bottles. The oxygen solubility in water at 20°C is 9.2 ppm, which corresponds to 9.2 μg/g water (Dahl, 1991). In a sealed gas-tight container with air in the headspace, the gas phase contains about 30 times more oxygen (in units of weight per volume) than the water phase at 20°C. This can be illustrated with Figure 14.

![Diagram of oxygen content in bottles](image)

**Figure 14.** Proportional amounts of oxygen in bottles (total volume 57 ml) filled to various levels with air-saturated water and with air in the headspace (Dahl, 1994)

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The solubility of oxygen in fat is higher than in water. Soybean oil dissolves about 55μg oxygen/g oil. This reduces the importance of the headspace oxygen, compared with the water case (Heiss and Robinson, 1975). To be able to keep the oxygen availability as low as possible, it is of the greatest importance to keep the headspace volume as small as possible. For porous products, like powder products, where the porosity of the product makes the headspace rather large, it is of great importance to keep the oxygen concentration as low as possible (Heiss and Robinson, 1975). This is because exclusion of the headspace above the product will not lead to a large decrease in oxygen availability, as much oxygen is held inside the particle pores.

Final control of the $O_2$ content in aseptically packed UHT-milk would be most readily achieved by controlling the volume filled into a container to leave an appropriate headspace. Zadow (1973) studied the relationship between the level of dissolved oxygen in water and UHT-milk and the headspace volume of a sealed container. He derived equations for the solubility, which, in the case when filling and storage take place at the same temperature, could be expressed as follows:

$$pO_2 = \frac{WGB \cdot 2442 (C-D)A}{EW \cdot 2886 AK_e}$$  \hspace{1cm} (11)

where: $pO_2$ = oxygen partial pressure of the liquid after equilibrium (mm Hg)

W = mass of liquid filled into the container (g)
G = filling temperature (K)
B = oxygen partial pressure of the filled liquid at G K (mm Hg)
C = atmospheric pressure (mm Hg)
D = water vapour pressure at G K (mm Hg)
A = headspace volume at G K (ml)
E = storage temperature (K)
$K_e$ = Henry's law constant for $O_2$ at E K for the filled liquid
Zadow found a linear relationship between the calculated and the experimental values for water:

\[
pO_2(\text{expt}) = 1.054 \times pO_2(\text{calc}) - 7.49
\]

with a correlation factor of 0.998. For UHT-milk the equations did not fit as well. This was explained by the use of K-factors for water, which meant that no allowance was made in the calculation for the presence of about 13% of milk solids and that an oxygen-consuming reaction (oxidation) could take place in the milk.

Usually the oxygen that dissolves into a liquid will lead to oxidation in all parts of the product (Heiss and Robinson, 1975). In compact foods, like highly viscous products (for example margarine, chocolate and mayonnaise), the situation is different. When the oxygen diffusion is slower than the oxygen consumption, the rate-limiting effect of the oxygen diffusion will produce an oxidized region near the surface (Schrader et al. 1980). Reaction products from this region will slowly diffuse into the rest of the product and lead to off-flavour and off-taste (Heiss and Robinson, 1975). In a thin slice of butter with diffusion from two sides, the oxygen concentration, according to the author's computer simulations, will look as follows (Figure 15):

![Diagram](image)

Figure 15. The oxygen concentration profile in a slice of butter, with oxygen diffusion from two sides, a thickness of 3.5 cm and a diffusion coefficient of \(0.22 \times 10^{-6} \text{ cm}^2/\text{s}\) (Heiss and Robinson, 1975)
It should be considered that the butter is saturated with oxygen at the beginning. During the oxidation reaction this oxygen is consumed and the diffusion starts to be rate-limiting.

In experiments made to examine the shelf-life of tomato ketchup inside a plastic bottle (composite of polypropylene and ethylene vinyl alcohol), Burgess et al. (1990) measured the oxygen diffusion rate through the bottle and the oxygen consumption rate of the ketchup. They found that in ketchup stored in beakers, only the surface directly exposed to the air showed colour changes. Further down in the ketchup there was an increasing redness. They therefore assumed that all oxygen reaching the ketchup through the bottle wall, was reacted in the ketchup close to the bottle wall.

Marcuse and Fredriksson (1968) explained their low reaction rates obtained in oil emulsions, at low oxygen concentrations, with the rate-limiting effect of diffusion.

Reinelt et al. (1979) examined the influence of the oxygen diffusion on the oxidative reaction in packaged foods. They set up a model for the simulation of the deterioration reaction and compared it with experimental results for mayonnaise. In a work from 1980, Schrader et al. continued the work of Reinelt et al. They developed a method to measure the oxygen concentration at different depths of a compact food and tested it on a CMC gel. The experimental values were compared with calculated values, obtained from a model developed from Reinelt et al. (1979). Experiments were also made on sunflower oil, soya oil, margarine and butter (See chapter 6.6 for more results and further explanations). The permeability and diffusion rates of oxygen, as well as the oxygen content, were measured in the products. (Table 11).

<table>
<thead>
<tr>
<th>Lebensmittel</th>
<th>$D \cdot 10^4$ cm$^2$ s$^{-1}$</th>
<th>$P \cdot 10^4$ cm$^{-3}$ s$^{-1}$ bar$^{-1}$</th>
<th>$\alpha$ cm$^{-1}$ bar$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Butter</td>
<td>0.129</td>
<td>0.415</td>
<td>0.298</td>
</tr>
<tr>
<td>Margarine „Rama“</td>
<td>0.235</td>
<td>0.455</td>
<td>0.182</td>
</tr>
<tr>
<td>SB-Margarine</td>
<td>0.232</td>
<td>0.393</td>
<td>0.156</td>
</tr>
<tr>
<td>Mayonnaise</td>
<td>0.234</td>
<td>0.460</td>
<td>0.161</td>
</tr>
<tr>
<td>Speiseöl</td>
<td>0.600</td>
<td>-</td>
<td>0.179</td>
</tr>
</tbody>
</table>
Verhey (1971) studied the penetration of air into different milk powders. The powders were dried using different methods and had different fat contents. They were stored in air for three months, during which time repeated measurements were made. Penetration curves for oxygen and nitrogen were obtained from the measurements. The penetration of air into the powder could be divided into three phases. In the first phase, air penetrated into vacuoles in the powder particles through micro-pores. This phase was succeeded by a phase with oxygen diffusion through the walls of the particles. Oxygen penetrated the walls faster than nitrogen, due to the higher solubility of oxygen in fat. This was concluded from the faster oxygen penetration with higher fat content. In the third phase, the oxygen concentration inside the vacuoles was the same as outside of the particles and diffusion of nitrogen begun. This ended when the concentration ratio between oxygen and nitrogen was the same in the vacuoles as outside the particles. The volumes of residual gas and oxygen were measured using a previously published method (Verhey and Lammers, 1970). Verhey found that the duration of the experiment (three months) was insufficient for any of the powders to reach equilibrium.

Quast and Karel (1971) examined the diffusion of oxygen in dry foods. They measured the steady-state transfer of oxygen through a porous bed of known cross-section and thickness and calculated the effective diffusivity from the equation:

\[ N = \left( A \right) \left( D_{\text{eff}} \right) \frac{\Delta P}{\Delta X} \times \frac{273}{T} \]  

(13)

Where:
- \( N \) = rate of oxygen transfer (cm\(^3\) O\(_2\) STP/s)
- \( A \) = cross-sectional area (cm\(^2\))
- \( D_{\text{eff}} \) = effective diffusivity at temperature \( T \) (cm\(^2\)/s)
- \( \Delta P \) = partial pressure differential through the bed of thickness \( \Delta X \) (atm)
- \( \Delta X \) = bed thickness (cm)
- \( T \) = temperature (K)

The oxygen partial pressure was measured with probes and the rate of oxygen transfer was calculated from the oxygen concentration in the lower chamber and the gas flow rate (Figure 16).
Quast and Karel determined the diffusion of oxygen in potato chips, fish meal and milk powder and compared it to the oxygen consumption rates of oxidation. They found that the oxygen diffusion was limiting the oxidation rate in chips at low oxygen levels (2%), but not at high levels (21%). For fish meal the oxygen consumption rate is very high and the diffusion of oxygen is rate-limiting even at atmospheric oxygen levels, if only the bed is deep enough. This would be the case if the bed was about 100 cm deep for the kind of fish-meal studied. In milk powder, the oxidation rate was found to be very low over a period of 100 days. This, together with the diffusion data led to the conclusion that oxygen diffusion was not likely to be rate-limiting in milk powder.

The most common cause of deterioration in anhydrous milk fat is oxidation (Evans et al., 1973). As the diffusion of oxygen in fat is low (Reinelt et al., 1979), it is of the greatest importance that the dissolved oxygen level initially present in the fat is low. This oxygen will be the only oxygen available for the oxidation reaction in the middle of the product. Evans et al. (1973) presented a method to measure the dissolved oxygen in anhydrous milk fat during manufacturing. They inserted a probe into a production line immediately prior to the packing point and performed the measurements using an amperometric method.
Radtke (1979) studied the oxygen consumption in coffee. She found that coffee saturated with air released about 60 μg oxygen/g coffee if it was held in a nitrogen atmosphere. The desorption of oxygen was rather fast and after 30 hours, no further release of oxygen could be detected. For coffee that had been protected as much as possible from oxygen during roasting, grounding and packaging, 15 μg oxygen/g coffee was desorbed. In further studies, Radtke (1985) developed methods to measure the oxygen content bound to roasted coffee. She analysed the amount bound to or entrapped in the coffee particles by dissolving the coffee in deoxygenated water. Analysis of the entrapped gas inside the particles (released by dissolving the coffee) showed that the oxygen concentration inside the particles was higher than 20.9%, although the content differed between different coffee blends. The oxygen content in different commercial coffee packs was calculated at pO₂ = 10mbar and was found to vary between 16 and 24 μg oxygen/g coffee.

Rajapakse et al. (1990) studied the diffusion of oxygen in apples, Asian pears and nectarines. They examined the oxygen content immediately beneath the skin and at the centre of the fruit. The test samples were withdrawn from the fruit with a syringe and the oxygen concentration was determined by gas chromatography. They also measured the oxygen concentration outside the fruit in small chambers glued to the fruit and found considerable resistance to diffusion through the skin of the fruits. Rajapakse and his co-workers detected a significant resistance to oxygen diffusion in the fruit flesh. In nectarine, the diffusion through the flesh was lower than through the skin, leading to large oxygen gradients across the cross-section of the fruit. These gradients can lead to different rates for oxygen consuming reactions, at different places in the fruit. In low-oxygen environments, this could lead to some detrimental effects on internal quality of the product, such as development of disorders, off-flavours and off-odours.
5. The influence of oxygen availability and oxygen concentration on lipid oxidation.

The oxygen accessible to packaged food can be divided into three parts (Figure 17): oxygen dissolved in the food, oxygen surrounding the food (for example in the headspace) and oxygen diffusing into the package through the wall and through pinholes in the package.

![Diagram of headspace and product](image)

Figure 17. Illustration of the oxygen accessible to packaged food. \(v_1\), \(v_2\) and \(v_3\) shows possible diffusion (Heiss and Robinsson, 1973)

Under conditions when the oxygen content is not limiting, one can initially make the assumption that all the reacted oxygen can be found in the hydroperoxides. This implies that very little hydroperoxide decomposition occurs in practice, as only a few ppm of the low-molecular peroxyde breakdown products are necessary for a food to be rancid (Labuza, 1971). By applying steady-state kinetics to reaction 2-7 (Chapter 3), i.e. assuming that the concentrations of \(R^-\) and \(ROO^-\) do not change with time and that termination through step 6 and 7 do not occur (high enough \(O_2\)-concentration), the oxidation rate can be explained by (Labuza, 1971):

\[
- \frac{d(O_2)}{dt} = - \frac{d(ROOH)}{dt} = \frac{k_p(R)^{1/2}}{(2k_p)^{1/2}} (RH) \tag{14}
\]

This reaction formula implies that most or all of the free radicals are in the form of peroxy radicals. When the partial pressure of oxygen is limiting, the rate equation solution is much more complicated. If it is assumed that:

\[
(k_p)^2 \cdot k_r \cdot k_{p^n} \tag{15}
\]
the solution becomes:

\[
- \frac{d(O_2)}{dt} - \frac{d([ROOH])}{dt} = \frac{k_r [R]^n}{(2k_i)^{1/2}} \frac{(R_H)}{(O_2)^{1/2}} = \frac{[O_2]}{(O_2)^{1/2}} \frac{[k_r][k_i]}{(k_p)^n k_o} (R_H)
\]

(16)

Equation 16 shows that if the second term in the denominator is small compared with the oxygen pressure, the equation will reduce into equation 14. If the initiation rate is constant and the concentration of substrate is high enough to be assumed to be constant, equation 16 can be manipulated to (equation 1):

\[
- \frac{d(O_2)}{dt} = \frac{pO_2}{k_1 pO_2 + k_2} - R_o
\]

where \(pO_2\)=oxygen partial pressure

\(k_1, k_2\)=constants

\(R_o\)=rate of oxidation

the expression can be rearranged into:

\[
\frac{1}{R_o} = (k_1 \cdot \frac{k_2}{pO_2})
\]

(17)

From equation 1 it can be seen that the rate of oxidation is proportional to the oxygen partial pressure at low oxygen pressures, where \(k_1 pO_2 < k_2\). With high oxygen partial pressures, when \(k_1 pO_2 > k_2\), the oxidation rate is not affected by the oxygen pressure, as was said before. The constants \(k_1\) and \(k_2\) are dependent on the surface area and temperature (Marcuse and Fredriksson, 1968), and the plot of equation 17 is a straight line. When the surface available to the oxygen atmosphere, divided by the total volume of oxidizable substrate increases, the constant \(k_1\) decreases and thereby, the effect of decreasing the oxygen partial pressure is reduced (Figure 18).
Figure 18. Effect of surface area and oxygen pressure on the relative rate of oxidation, $k_1 = 1/A$ and $k_2 = B/A$ (Karel 1960 in Labuza 1973)

This implies that a decrease in oxygen pressure for dehydrated foods will not be very effective, unless a major decrease is effected.

The oxygen consumption curve can be measured for different products with different oxygen pressures. A schematic curve is shown in Figure 19.

Figure 19. Schematic presentation of oxygen absorption during lipid peroxidation (Karel, 1974)
The curve shows both the actual oxygen uptake and the fate of the oxygen absorbed. The oxygen uptake curve varies a lot between different foods. This is due to many different factors like the fatty acid composition, other oxygen-consuming reactions, the presence of pro-oxidants, the antioxidant content, structure of the food, and water activity (Labuza, 1980, Lingnert, 1992). This makes it very hard to predict the oxygen sensitivity. Both the amount of oxygen consumed and the rate of oxygen consumption influence the shelf-life of the product. Some approximate values for the oxygen amount needed for a product to be rancid is given by Heiss (1984) in μg oxygen/g Food (Table 12):

When conducting experiments with food, two different approaches can be used. Either the oxidation changes can be studied at constant oxygen levels or the experiments can be performed within a sealed container with constantly decreasing oxygen concentration. A mixture of these two approaches can be seen in containers that are semipermeable to oxygen and able to resupply some of the oxygen used by the oxidation reaction.

**Table 12.** Oxygen amount needed for a product to become rancid at 20-25°C and with unlimited oxygen availability (Heiss, 1984)

<table>
<thead>
<tr>
<th>Product</th>
<th>μg oxygen/g food</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beer</td>
<td>1-4</td>
</tr>
<tr>
<td>Wine</td>
<td>3</td>
</tr>
<tr>
<td>UHT milk</td>
<td>1-8</td>
</tr>
<tr>
<td>Whole egg powder</td>
<td>35</td>
</tr>
<tr>
<td>Potato granules</td>
<td>10-40</td>
</tr>
<tr>
<td>Coca-Cola</td>
<td>40</td>
</tr>
<tr>
<td>Tomato ketchup</td>
<td>70</td>
</tr>
<tr>
<td>Emmentaler cheese</td>
<td>420</td>
</tr>
</tbody>
</table>
5.1 Oxidation changes with constant oxygen levels

Oxidation at constant oxygen pressure is not a natural situation, unless the oxidation is performed in air. Constant oxygen pressure in air is obtained with oxidation in a package without any protection against oxygen diffusion.

Experiments at constant oxygen levels are performed in order to study the rate and course of oxidation. This can be done by studying the total amount of oxygen consumed during a certain period, for a specified oxygen pressure, or by studying the rate of oxygen uptake at different oxygen pressures, at different extents of oxidation and at different stages of the oxidation process. The extent of the oxidation is a measurement of the total oxygen consumption (in µl STP/ g sample) prior to the experiment, while the stage of oxidation refers to the different periods in the oxidation reaction, for example the induction period and the bimolecular stage. These stages are not reached at the same extent of oxidation for all products.

A typical oxygen uptake curve is shown in Figure 20. It shows the oxygen uptake for potato chips at 37°C. The steep increase in oxygen uptake seen in the curve is related to the beginning of the bimolecular decomposition of hydroperoxides (Quast and Karel, 1972a).

![Figure 20. Oxygen uptake of potato chips at 37°C and pO₂=0.21 atm (Quast and Karel, 1972a)](image-url)
In Figure 21 the mean value of the oxygen uptake at different oxygen partial pressures is shown, for three different types of food.

Experiments performed at constant oxygen pressures are often made with the Warburg apparatus. It was invented by Warburg and has later been modified by several users. Originally the apparatus consisted of a flask connected to a manometer. Any change in the amount of gas inside the flask was directly read on the manometer as long as the temperature and the atmospheric pressure were constant (Dahl, 1989).

When experiments are conducted with constant oxygen levels the oxygen consumed has to be resupplied in some way. This can be done by adding the amount of oxygen consumed during a time interval (Herlitze et. al., 1973, Reinelt et. al., 1979). Another approach is to channel a gasstream of constant gascomposition through the measuring cell (Koelsch et. al., 1991).

Marcuse and Fredriksson (1968) studied the oxygen uptake in a model system of emulsions of fatty acids and esters. They used a modified Warburg apparatus that monitored continuously the oxygen uptake and resupplied the oxygen used. The uptake was studied at different constant oxygen gas concentrations, from 0.5% to 21% oxygen, at atmospheric pressure. Marcuse and Fredriksson found a decrease in the rate of oxygen consumption with
lowering of the oxygen pressure. The decrease was dependent on the various oxygen-dependent and non-oxygen-dependent reactions of the propagation. These reactions could vary with the temperature, substrate and pH, but not with light irradiation. They also found that the decrease in oxygen consumption at low oxygen pressures, could be a rate-limiting effect of slow oxygen diffusion. The degree of the limiting effect of oxygen on the oxidation rate in different foods is discussed in chapter four.

Herlitze et al. (1973a) investigated the oxygen-sensitivity of different products. They found that the sensory limit for consumption was reached at different extents of oxidation and different storage times, when the samples were examined under different oxygen partial pressures (Figure 22).

Figure 22. Oxygen consumption rate for tomato ketchup at different oxygen partial pressures. a=sensory limit for selling, b=colour limit for selling (Heiss, 1984)
With higher oxygen partial pressures, the food was considered inedible sooner than at a lower oxygen pressure. The amount of oxygen consumed when the product was regarded as rancid was smaller, on the other hand with lower oxygen pressures. This discrepancy in the amount of oxygen consumed could be due to the fact that different products are formed if the oxidation is limited by the oxygen availability, than if the oxygen content is not a limiting factor (Karel, 1974). Herlitze et al. (1973a) also found that the time to reach, and the total oxygen absorption when the sensory limit for consumption was reached, were dependent on the status of the product at the beginning of the storage, the temperature during storage, the oxygen permeability of the package, the oxygen availability and any heat treatment of the product when packaged. With these findings in mind, Heiss and Robinson (1975) discussed the important properties when packaging oxygen-sensitive food. They presented hypothetical curves for the total oxygen consumption when the sensory limit was reached after different storage times and treatment of a product (Figure 23, 24).

![Figure 23](image)

**Figure 23.** Oxygen consumption of a product with different treatment and storage conditions up to the sensory limit for selling. a) with and b) without storage prior to filling. The package in case 1 has a higher permeability to oxygen than in case 2 (Heiss and Robinson, 1973)

![Figure 24](image)

**Figure 24.** The role of the headspace volume for the oxygen consumption of a product up to the sensory limit for selling, a–c shows decreasing headspace volumes (Heiss and Robinson, 1973)
5.2 Oxidation changes with decreasing oxygen levels

When the content of oxygen dissolved in the food (in the case of a liquid food), or in the headspace in a packed food is measured, a decrease in oxygen concentration inside the package is usually seen. This is due to the consumption of oxygen by lipid oxidation or other oxidative reactions. A typical plot of the dissolved oxygen content against time is showed in Figure 25.

![Dissolved Oxygen Content vs Storage Time](image)

**Figure 25.** Changes in dissolved oxygen content of indirectly heated UHT processed milk stored in the dark at 20°C (Thomas *et al.*, 1975)

When oxygen is measured in an air-tight packaged food at low headspace oxygen concentrations, an increase in the oxygen content in the gas phase can sometimes be seen (Radtke, 1979; Villota, 1980). This phenomenon is more often seen in dry food, and is due to oxygen diffusing out of the product into the gas phase. In dry products the diffusion of oxygen out of the particles is rather slow and the oxidation process is often also slow. This can give a notable increase in the oxygen concentration during the first stages of the measurements.

To be able to follow the oxidation process with a decrease in the oxygen concentration inside the package, several samples normally has to be stored. This is because the oxygen level usually changes after opening of the container for oxidative measurements. This means that one container is needed for each measurement. To overcome this problem, a method for
inserting a probe into a food container was developed by Johnson et al. (1964). This method was also used by Quast and Karel (1971) when they studied the oxygen diffusion in some dry foods. A further development of the measuring method was published in 1972 (Quast and Karel, 1972a). The test chamber is shown in Figure 26 and consists of a container with a rubber seal on either side.

When the measurement is carried out, the oxygen probe is inserted from the left by pushing the rod to the right through the rubber seals. This technique allows calibration of the probe between measurements, which is of great importance if the measurements are conducted over a long period of time. One disadvantage of this technique is that special containers have to be used. There could also be a problem with leaking rubber seals. To be able to measure low oxygen levels, a probe with high sensitivity is needed and this could be hard to find.

When experiments are made at a low oxygen level, it is difficult to detect the small changes in oxygen levels that occur. The measurements can be carried out both in the liquid phase (if a liquid food is being studied) or in the gas phase. Dahl (1991) investigated the different methods available for detecting oxygen, both in the gas and the liquid phases. When oxygen is measured in the gas phase, a common way of detecting the oxygen is to use a solid state gas sensor, in which case a zirconium oxide cell is the one most commonly used. Another way to measure oxygen is by gas chromatography with a TCD detector. Dahl (1994) used a modified Zirconia type cell to measure low oxygen levels and was able to measure the oxygen concentration in the gas phase down to 10 ppm. Aschkenasy and Robe (1985) used an instrument with a Zirkonium detector to control oxygen levels in soup packets. With oxygen
levels in the headspace over 2%, the analyzer automatically gave off an alarm signal. Many different systems have been developed for measurement of oxygen inside packages. Krüger (1975) and Cook et al. (1985) used two different methods for analysis of gas in beverage headspace. Krüger collected the gas released from bottles opened under water. He reacted away the CO₂, measured the gas volume (O₂ and N₂), removed the oxygen by reaction with sodium ditionate and finally measured the residual N₂ volume. Cook’s group, on the other hand, punctured the containers and let the headspace gas in the package flow into an evacuated cell. The oxygen content was then measured by GC.

The most commonly used oxygen electrode for liquid measurements is a membrane-covered probe, originally developed by Clark (Dahl, 1991). These polarographic sensors measure the partial pressure of oxygen dissolved in the liquid. Recent developments of the Clark oxygen electrodes have led to measuring devices that are very small. Revsbech (1989) developed a microelectrode with a detection limit of 225μM O₂. Suzuki et al. (1992) and Suzuki (1993) presented an electrode with a measuring area of 0.2 x 2 mm. This electrode can also be rebuilt to a biosensor.

The oxygen electrodes usually give their readings as a percentage of saturation, calculated from the partial pressure of the oxygen dissolved in the liquid and the oxygen partial pressures of the calibration gases. To determine the solubility of oxygen in a liquid, a phase equilibrium technique was used by Dahl (1989). This technique is a further development of the multiple phase equilibration used by McAuliffe (1971) and is based on “extraction” of oxygen out of a liquid into nitrogen inside a closed system. The gas equilibration is repeated several times and after each equilibration the gas mixture is injected into a gas chromatograph and the oxygen is detected with a TCD detector.
6. The influence of oxygen availability on the rate and extent of oxidation in different foods.

In this chapter a closer look on the influence of oxygen on oxidative reactions in different groups of food will be taken. The chapter will deal with liquid products, dehydrated products, oils, fats and emulsions and products that do not belong to either of these groups.

6.1 Liquid products

The studies done on liquid products will be divided here into experiments made on fruit juices, milk products and other liquid products. The group of milk products will be further divided into UHT-processed milk and pasteurized or non-treated milk.

6.1.1 Fruit Juices

In fruit juices, the oxidation process studied is usually the ascorbic acid oxidation, but other oxidation processes are also studied. Starr and Francis (1968) studied the effect of ascorbic acid and oxygen on the relative stability of four anthocyanin pigments in cranberry juice. The oxygen amounts were 0, 0.3 or 2 ml oxygen in nitrogen in the headspace of the package. The total volume of the headspace was not, however, given. The loss of pigment was greater with both increasing levels of dissolved ascorbic acid and headspace oxygen. This was explained by a reaction sequence where ascorbic acid was oxidized to a radical, which, in turn, reacted with the pigment.

Trammel et al. (1986) studied the effect of the level of dissolved oxygen on taste, ascorbic acid loss and browning in single-strength orange juice. The juices had initial oxygen contents of 0.6, 1.8, 6.5 and 10.1 ppm, where 10.1 ppm corresponds to juice at 15°C that has been saturated with air. The juices were packaged in glass bottles with a headspace of 5 ml, which
gives a total amount of oxygen in the headspace of 0.1 mg. (No information is given about what oxygen amounts correspond to 1 ppm dissolved oxygen!) The results from the sensory evaluation did not show any extension of the shelf-life, with reduction of the initial dissolved oxygen concentration, but lowering of the oxygen level from 10.1 to 0.6 ppm improved the taste of the juice during the first two months of storage. The ascorbic acid loss and the browning was found to be reduced by decreasing of initial oxygen content.

Barron et al. (1993) studied the oxygen concentration and the ascorbic acid degradation in packed apple juices and compared the results with computer simulations. They found that the oxygen diffusion was rate-determining for ascorbic acid oxidation in juices and water. A good correlation was found between the experimental and simulated values of oxygen partial pressure at different depths in the juices. In the experiments, the apple juices were initially saturated with air. Throughout the experiments, diffusion from the air was allowed in one or two dimensions through the package, or with one side of the package open.

Solomon (1994) studied the effect of oxygen and fluorescent light on the quality of orange juice. In the experiments the orange juice was packaged in glass bottles closed with lids with different permeability to light or oxygen, or aseptically filled in cardboard packages. In orange juices packaged in glass bottles, Solomon found an increase in ascorbic acid degradation with increasing oxygen availability. With low levels of dissolved oxygen (less than 2 ppm), no light-induced ascorbic acid degradation was seen. In the experiments with the cardboard packages, stored under light or dark conditions, a significantly lower retention of ascorbic acid was seen compared with air-tight glass bottles (control) stored in the dark. The juice in the cardboard packages had an initial oxygen concentration of 6.2 mg/l and the control sample had a concentration of 3.1 mg/l. Ascorbic acid degradation was significantly correlated with the level of dissolved oxygen and the length of the storage time, but the effect of light was found to be insignificant.
6.1.2 UHT-treated milk

UHT stands for ultra high temperature. Basically, there are two different UHT processes, direct heating and indirect heating. In directly heated milk, steam is injected into the milk to heat it. During cooling of the milk the injected steam is evaporated. In indirect heating, the milk is heated in a heat exchanger with plates or tubes. After the heat treatment the milk can be degassed to lower the dissolved oxygen content. In indirectly heated milk, the oxygen concentration is about 8 ppm and in directly heated milk it is less than 1 ppm (Badings et al., 1980)

Many authors have examined the influence of oxygen availability on the quality of UHT-treated milk. The connection between oxygen content and milk quality is not as simple in this kind of milk. During heating of the milk, -SH groups from the milk proteins are released. They influence the milk flavour and give a "cabbage-like" or "cooked" taste (Zadow and Birthistle, 1973 and Thomas et al., 1975) at the beginning of the storage period. The sulphydryl group content rapidly decreases and the O₂ levels decline correspondingly during the first few days, as the flavour improves (Thomas et al., 1975). Zadow and Birthistle (1973) found that milk with an intermediate level of dissolved oxygen (pO₂) of 60-100 mm Hg, determined about 4 hours after production, had a better flavour during the whole storage perio than milk containing either a higher or a lower O₂ content. On the other hand, Thomas et al. (1975) found no effect of the initial O₂ content on acceptability after 2 weeks of storage. They found a higher acceptability for milk with a high (8.9 ppm) initial oxygen concentration during the first 8-13 days of storage, but after that the acceptability was independent of the initial O₂ content. The higher acceptability at the beginning of the storage period, with a higher initial oxygen content, was explained by a faster decrease in the -SH groups. With a low oxygen content (1.0 ppm) the "cabbage" taste remained for several weeks. Thomas et al. used air-tight bottles, filled to capacity, and stored the bottles at 20°C in the dark. Zadow and Birtwistle stored their milk in glass bottles with headspace volumes of 0, 5, 10, 15 and 150 ml of air in the dark at 2, 20 and 38°C. In their samples with 0-15 ml of headspace, a decrease in the dissolved oxygen content to a stable value was seen. For the sample with 150 ml of headspace, a very slow decrease in oxygen concentration was noted.
This decrease continued throughout the storage period of 77 days. When the samples were stored at low temperature, the influence of varying oxygen contents was very small. For the samples stored at 20°C, an initially low oxygen content resulted in poor flavour performance during the first few weeks of storage. On the other hand a high initial oxygen content resulted in a very good flavour performance during the first few weeks, but oxidized or rancid flavours developed after extended storage.

Lechner (1976) examined the ascorbic acid degradation in relation to the oxygen content in UHT milk. She studied both degassed and undegassed milk samples. The ascorbic acid content decreased linearly with the decrease in oxygen and after 13 days the ascorbic acid content had reached zero. During this time the oxygen content had decreased from 7.33 ppm to 2.82 ppm.

Jeon et al. (1978) examined the production of volatile flavour compounds in UHT-processed milk. The milk was packed in enamelled cans and stored for 5 months at 3, 22 or 35°C. Half of the milk was used in its original form and the other half was fortified with 200 mg of ascorbic acid per litre of milk before processing. There is no data on the ascorbic acid content of the untreated milk. In the non-fortified milk, the ascorbic acid was oxidized within a week when stored at 22 or 35°C and after 30 days when stored at 3°C. The fortified milk showed a decrease in ascorbic acid that levelled off at 170mg/l milk. To follow the whole oxidation process, the dissolved oxygen concentration was measured. In the control milk (no extra ascorbic acid), the oxygen concentration decreased to 1 ppm in 60 days at 35°C, to 2 ppm in 5 months at 22°C and to 4.5 ppm after 30 days and remained constant throughout the rest of the storage period at 3°C. The fortified milk showed a faster decrease in dissolved oxygen level and had 1 ppm oxygen left after 15 days at 22 or 35°C and after 5 months at 3°C. Most of the volatile components found in the stored samples were found to be present in the milk samples at the beginning of the storage period (with the exception of aliphatic aldehydes), although at a lower level. All the compounds present at the beginning of the experiments increased in amount during the storage period. The hexanal content increased during the whole storage period at 22°C in the control milk, but reached a maximum after 90 days at 35°C in the control milk. This was explained by no oxygen being present in the 35°C sample.
after 90 days. In fortified milk, a much smaller formation of hexanal was seen. This was again explained by the low availability of oxygen for the lipid oxidation reaction. The production of odd-numbered methyl ketones was found to be independent of the oxygen and ascorbic acid content, but dependent on temperature. Methyl ketones are not produced by lipid oxidation, but are known to be generated from β-keto alkanoic acid esters of glycerides, which constitute about 0.04% of butter fat (Parks et al. 1964). The formation of 1-butanol was also found to depend solely on the temperature and not on the dissolved oxygen concentration and ascorbic acid content. The contribution of the different volatile compounds to the flavour was also investigated. Hexanal and propanal were found to be the most important compounds for the development of a stale flavour. Pentanal and heptanal were found to be the second two most important compounds for the production of off-flavour. The fortified and the non-fortified samples, with different ascorbic acid content, leading to different oxygen content, showed no extreme differences in the profiles, when n-alkanals, methyl ketones, n-alkanals + methyl ketones and overall flavours at different oxygen levels were examined (Figure 27).

Badings et al. (1980) discussed the effect of the oxygen content on the quality and keeping properties of packaged milk. In the case of UHT milk, they concluded that the ascorbic acid and reducing compounds present in the milk are oxidized by the oxygen present. In the UHT milk the content of ascorbic acid was 15 to 20 ppm. Three to four ppm of oxygen is sufficient to oxidize this amount of ascorbic acid. This led to the conclusion that, in order to keep the ascorbic acid at a high level, the oxygen concentration had to be kept as low as 1 ppm and the containers had to be air-tight.

![Figure 27](image-url)
Gallusser and Bergner (1981) studied the oxygen uptake from the headspace and the consumption of dissolved oxygen in UHT-treated milk. The milk was directly heated and packed in containers with and without a headspace. The milk contained 3.5 or 0.3% fat and was packed in Tetra Briks or combiblocs. In the milk packed without a headspace, the oxygen content increased linearly from 0.5 ppm to about 1 ppm over a period of 90 days. In the milk with low fat content the greatest rise in oxygen content was seen. The increase in oxygen content was explained by diffusion through the walls of the package. In the milk samples packed with a headspace, a decrease in oxygen content from about 8 ppm to 3.5 ppm was first seen. After about 20 days, a levelling out in the oxygen consumption rate was seen and a relatively stable oxygen content was obtained. This was explained by diffusion of oxygen through the package walls and through pinholes in the package, with a simultaneous oxygen consumption by oxidation. When the curve showed a constant value the oxygen consumption was said to equal the rate of diffusion of oxygen into the package. Gallusser and Bergner also studied the consumption rate of oxygen in directly heated milk. They found the consumption to be 10 mg O₂/l milk over a storage time of 10 weeks in the milk packaged with a headspace consisting of air. In another article, Gallusser and Bergner (1981) examined the reactivation of phosphatase in UHT-treated milk with low oxygen content. During the heat treatment the phosphatase is denatured and the absence of the enzyme is used as an indicator of sufficient heat treatment. When free -SH groups are present in the milk, the enzyme can be reactivated during storage. In milk with high oxygen availability, a lesser degree of reactivation was seen than in milk with low oxygen availability. This was explained by the higher degree of oxidation of the free -SH groups in the milk with high oxygen availability.

Early and Hansen (1982) studied the influence of temperature on oxygen consumption in UHT milk, packaged in polyethylene/paper/polyethylene/aluminium/polyethylene-laminated Tetra Brik cartons, filled in a Tetra Brik aseptic filler. The initial oxygen content was 1.5 ppm and the storage temperatures were 24 or 40°C. In the samples stored at 40°C, a decrease in the oxygen content to 0.5 ppm was seen over the storage period of 24 weeks. On the contrary, an increase in the oxygen content to 7.0 ppm was seen in the samples stored at 24°C. The results were explained by diffusion of oxygen through the package. In the case
with the higher temperature, the oxidation rate was higher than the diffusion rate and the reverse applied at 24°C. They also followed the oxidation rate by measuring the production of n-alkanals. Their results showed a decrease in the amount of alkanals in contrast with earlier studies (Jeon et al., 1978, Kirk et al., 1968). This was explained by the low initial oxygen content together with the absence of oxidized flavour, which indicated that no autoxidation took place. The authors offered no explanation of the oxygen consumption during storage.

Schröder (1982, 1983) investigated the effect of oxygen availability on lipid oxidation in UHT milk. She studied the effect of oxygen availability in relation to the presence of light or copper. The oxygen requirement for the two cases differed, as did the characteristics of the off-flavour produced. Copper induced an off-flavour that was described as "cardboardy" and light-induced oxidized flavour was described as "painty". The light-induced oxidized flavour increased in intensity with increasing oxygen loss and could be prevented with an initial oxygen content of 6.6 mg/l or less, if further access to oxygen was denied. When more oxygen was supplied from the headspace or through an oxygen-permeable container, the oxidized flavour did develop. On the other hand, copper-induced oxidized flavour development was not associated with high oxygen uptake and moderate deoxygenation resulted in a greater flavour intensity than non-deoxygenation. Light-induced oxidation did not occur until the ascorbic acid initially present was consumed, whereas the copper-induced flavour developed with ascorbic acid still present. The differences found in the O₂ requirements for the development of copper-induced and light-induced oxidative flavour in whole milk and the different relationship to ascorbic acid oxidation were suspected to be due to the off-flavour production by two separate pathways.

Wadsworth and Bassette (1985) determined the role of dissolved oxygen as a contributor to flavour deterioration in UHT milk. They examined the stale flavour in the milk. In milks with high oxygen content (7-7.5 ppm) and unlimited access to oxygen through the lid, a stale flavour developed sooner and with greater intensity than in milks in capped bottles with lower (<4 ppm) oxygen content. They also measured the development of acetaldehyde, propanal, n-pentanal and n-hexanal. These products did not appear to be the principal contributors to
staling in sterile milks. Acid degree values and TBA values increased in the milk samples during storage, but did not parallel the development of a stale flavour. Wadsworth and Bassette therefore concluded that the products of lipid oxidation are not the major contributors to stale flavour.

The degradation of vitamin A in UHT-treated milk was examined by McCarthy et al. (1986). Two different milks were studied; one with a natural content of vitamin A and one fortified with vitamin A. The milk was aseptically filled in Tetra Brik cartons and stored at 23°C. The experiments showed rather large losses of vitamin A, larger than in other studies (Lembke et al., 1968, Ferretti et al., 1970). During the storage period of 14 weeks, the concentration was reduced to at least half the original level. The oxygen concentration in the milk first decreased during storage (up to 4 weeks) and then begun to increase. This was mirrored into loss of vitamin A, where a faster rate of loss was seen up to the fourth week. The increase in oxygen content in the milk, after the fourth week was explained by diffusion of oxygen through the package.

Sur and Joshi (1989) examined the oxygen content of UHT-treated milk samples stored in Tetra Pak polylaminated cartons at two different temperatures (22 and 37°C). They found a decrease in the oxygen concentration from 8.2 ppm to about 4.2 ppm over 35 days at 22°C. With the higher temperature (37°C) a somewhat larger decrease in the oxygen content was seen (8.2 to 4.0 ppm).

Loss of ascorbic acid, folacin, vitamin B12 and changes in the oxygen content of UHT milk were examined by Andersson and Öste (1992). The milk was indirectly treated and stored at different oxygen concentrations in two different experiments. In the first experiment, the package had a maximum diffusion rate of oxygen of 0.04 cm³/24 h at 25°C at normal atmospheric pressure and in the other experiment a maximum diffusion rate of 0.01 cm³/24 h. In the first experiment the oxygen content was 0.6, 3.9 or 5.4 ppm. After 18 weeks, at all three oxygen contents, all the ascorbic acid was oxidized. In the second experiment the oxygen content was 0.5, 2.1 or 3.3 ppm. A total loss of ascorbic acid was seen only in the sample with the highest oxygen concentration, although the decrease in ascorbic acid content
was large in the other samples too. It was found that the higher the oxygen content, the faster the total loss of ascorbic acid. During the first few weeks of storage, the oxygen content decreased in the samples. After about three weeks, the oxygen concentration was stable or increasing, depending on the packaging material used. The loss of folacin was found to be dependent on the initial oxygen concentration and the storage temperature. With more than 3.9 ppm oxygen after the UHT treatment, there was a total destruction of folacin already after 1 or 2 weeks of storage. In both experiments there was a loss of about 30% of the vitamin B12 during the UHT treatment. This loss was independent of the oxygen content in the milk. After 18 weeks of storage, no difference could be seen in vitamin B12 content between the samples with different oxygen levels.

6.1.3 Pasteurized or non-treated milk

Few investigations have been made on the effect of oxygen availability on lipid oxidation in pasteurized or non-treated milk. This is due to the short shelf-life of this kind of product, as a result of bacterial deterioration.

The most important factor for the deterioration of pasteurized products is recontamination of the milk after heat treatment (Becker et al., 1977). This group investigated the effect of oxygen availability, temperature and degree of recontamination of milk over a period of up to 26 days. The difference in shelf-life between the recontaminated and non-recontaminated milk, with unlimited access to oxygen was about 8 days (Figure 28).

There was also a big difference in oxygen consumption between the samples. The recontaminated sample used about ten times as much oxygen to reach the quality limit, which was reached 8 days sooner, as mentioned earlier. This is illustrated in Figure 29.
Figure 28. Quality changes in pasteurized milk stored at 5°C, measured by sensory analysis. o--o) non-recontaminated milk with unlimited access to oxygen, o-o) recontaminated milk, unlimited access to oxygen, x-x) recontaminated milk, limited access to oxygen, T) quality limit (Becker et al., 1977)

Figure 29. Oxygen consumption of pasteurized milk stored at 5°C. o--o) non-recontaminated milk, unlimited access to oxygen, o-o) recontaminated milk, unlimited access to oxygen, T) quality limit (Becker et al., 1977)
The time to reach the quality level also differed for recontaminated samples with different access to oxygen. At 5°C, the difference in shelf-life between the samples stored with and without access to oxygen, was 4 days. The oxygen was found to be consumed by the bacteria and a big difference in oxygen consumption was seen between samples recontaminated with different floras. If the flora contained large groups of anaerobic or facultative anaerobic bacteria the difference between samples stored with or without access to oxygen was smaller.

Shekar and Bhat (1983) examined the effect of the level of dissolved oxygen on the keeping quality of cow's milk and buffalo milk. The milk samples were either pasteurized before the experiments or used as they were. Four different levels of dissolved oxygen were studied for each kind of milk. The authors found that acidity developed faster in buffalo than in cow's milk. They also found a faster development of acidity in samples with higher oxygen levels, as well as in unpasteurized samples compared with pasteurized samples. The degree of oxidation was not studied in the samples. In other experiments, Shekar and Bhat (1984) studied the dissolved oxygen content in cow's milk and buffalo milk. They found a higher oxygen content in whole milk than in skimmed milk. The oxygen content in buffalo milk was higher than in cow's milk.

Allen and Joseph (1985) reviewed the deterioration of pasteurized milk with storage. They found many factors to be involved in the deterioration of the milk. The factors could be divided into:
- factors inherent in the milk itself, such as ascorbic acid content, free fatty acid levels and native metal content.
- external and processing factors, including handling, agitation, temperature, exposure to light and contamination by metals or microorganisms.

The dissolved oxygen level must also be considered. Milk in the udder contains very little oxygen (Ford, 1967, Guthrie, 1946). On leaving the udder it rapidly takes up oxygen from the air, with the greatest absorption during milking. The oxygen content in freshly pasteurized milk determined using an $O_2$ electrode was reported to be 9.0 mg/l at 20°C (Lechner, 1976), 8.11 g/ml at 25°C (Mrowetz and Thomasov, 1973) and 8.4 mg/l at 25°C (Allen and Joseph, 1983). The fate of the oxygen consumed is shown in Table 13.
Table 13. Oxygen consumption (mg/l) by pasteurized milk over 6 days in dark storage at 7°C in the absence of headspace. 0.78 mg/l of oxygen could not be accounted for. (Allen and Joseph, 1983)

<table>
<thead>
<tr>
<th>Total O₂ consumed</th>
<th>4.10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Consumed by</td>
<td></td>
</tr>
<tr>
<td>Bacteria</td>
<td>1.48</td>
</tr>
<tr>
<td>Ascorbate</td>
<td>1.41</td>
</tr>
<tr>
<td>Peroxidation</td>
<td>0.003</td>
</tr>
<tr>
<td>Oxidation of SH groups</td>
<td>0.14</td>
</tr>
<tr>
<td>Loss through septum</td>
<td>0.29</td>
</tr>
</tbody>
</table>

As can be seen from this table, most of the oxygen is consumed by bacteria and ascorbic acid oxidation.

6.1.4 Other liquid products

The autoxidation of ascorbic acid has also been studied in aqueous model systems. Capietti et al. (1977) used ascorbic acid oxidation to monitor the level of oxygen dissolved in an aqueous solution. They added known amounts of ascorbic acid and ascorbic acid dehydrogenase to water saturated with oxygen and made a calibration curve for a Clark-electrode. This curve was used for measuring the oxygen content and the amount of ascorbic acid in canned green peas.

Curda et al. (1979) measured the influence of oxygen on ascorbic acid oxidation in a model system. The samples were stored in air-tight glass jars with three different headspace volumes (100, 75 and 50 ml in a 125 ml jar). The headspace consisted of air and the samples were stored for up to 98 hours. They found good agreement between the oxygen decrease in the container and the oxidative destruction of ascorbic acid.

Eison-Perchonok and Downes (1982) studied the rate of ascorbic acid oxidation in a model system with a constant level of dissolved oxygen. The oxygen content was 10, 15 or 21% in an oxygen/nitrogen mixture that was bubbled through the solution. The rate constant was found to be of the first order with respect to ascorbic acid and oxygen.
Singh et al. (1976) and Mack et al. (1976) studied ascorbic acid oxidation and oxygen uptake in infant formula. The influences on the oxygen uptake of light intensity, storage temperature and initial dissolved oxygen level was measured. The dissolved oxygen levels were 1.0, 4.9 and 8.7 mg/l and the samples were stored in air-tight plexiglass boxes without head space. Mathematical computer-aided simulation was used to predict the ascorbic acid degradation and the findings were compared with experimental results. The degradation was found to be different under dark and light conditions, respectively. In the dark, the ascorbic acid degradation was independent of the dissolved oxygen level. Under light conditions, a dependence of the dissolved oxygen level was found and the oxidation rate increased with the light intensity up to a value of 1756 lux. Increasing the light intensity above this level did not increase the rate of oxidation. Mack et al. (1976) instead measured the oxygen consumption in the same infant formula. The oxygen consumption was found to be linear during the 24 hours of the experiment and the oxygen-consuming reaction was found to be ascorbic acid oxidation. The consumption showed a linear increase with increasing light intensity (between 0-4300 lux) and was also found to be dependent on the temperature. In the dark, the oxygen consumption was found to be independent of the initial dissolved oxygen concentration.

6.2 Dehydrated products

The control of the moisture content during the processing of food is an ancient method of preservation. Description of preservation by drying in the sun can be found in the Bible, in ancient Egyptian hieroglyphics, and in the journals of Marco Polo (Labuza, 1976). One way of expressing the water content is the water activity. Water activity ($a_w$) is described as the ratio of the vapour pressure of water in the food ($p_v$), divided by the vapour pressure of pure water at the same temperature ($p_{w0}$). Food with a water activity below 0.6 is stable to microbial growth and is classified as a dehydrated food (Labuza, 1980). The oxidation process shows a special dependence on the water activity (Figure 30), and is the only reaction that proceeds at a higher rate at very low water activity (below $a_w=0.3$) (Labuza, 1980). The large dependence of the oxidation process on the water activity makes it necessary to keep the water activity constant, in experiments where other factors, like oxygen dependence, are studied.
Figure 30. Overall effect of water activity on relative reaction rates. Upper curve is for lipid oxidation, lower for other reactions (Labuza, 1980)

6.2.1 Model systems

Teixeira et al. (1981) investigated the oxygen uptake and β-carotene decolouration in a dehydrated food model consisting of non-fat dried milk, microcrystalline cellulose and crystalline β-carotene. The oxygen content was measured both as headspace oxygen and entrapped oxygen. The oxygen levels studied were 1 and 2% oxygen in the headspace. To measure the entrapped oxygen, the sample was evacuated for 2-3 minutes and then dissolved in deaerated water. The entrapped and adsorbed oxygen was then released to the headspace and analysed. It was found that the rate constants for β-carotene decolouration were functions of the oxygen concentration in the headspace of the samples. An increase was seen with higher headspace concentration.

Kacyn et al. (1983) investigated the kinetics of the oxidation of dehydrated food at low oxygen pressures. The oxygen levels were 0.53, 1.05, 2.17, 5.49 or 10.69% in the headspace
and the model system consisted of methyl linoleate dispersed on either microcrystalline cellulose or on a non-fat milk powder. The oxygen contents where obtained by repeatedly evacuating the sample flasks and filling with the desired gas mixture. Bimolecular oxidation kinetics were found in both systems with the rate of oxidation being more rapid (with a factor of 5 to 6) in the cellulose system. The slower oxidation in the milk system appeared to be due to encapsulation of part of the lipid in the milk solids and the smaller internal surface area of the milk solids, compared with the cellulose support.

Koelsch et al. (1991) investigated hexanal formation via lipid oxidation as a function of the oxygen concentration. They studied a freeze-dried system composed of soybean oil, water, Tween 20 and microcrystalline cellulose at oxygen levels of 1.2, 4.5, 10.0 and 15.4 % oxygen in headspace nitrogen. Their system had a moisture content of 2g H₂O/100g solids, which is a moisture content that would increase the rate of lipid oxidation (Labuza, 1976). They measured the oxidation on-line by collecting the hexanal formed in the reaction on Tenax traps (Figure 31).

**Figure 31.** Schematic apparatus for maintaining a constant oxygen concentration with Tenax traps for continuous measurement of hexanal formation (Koelsch et al., 1991)
Koelsch et al. derived kinetic models for the formation of hexanal. During the monomolecular phase, with no limiting effect of the substrate availability, they found the hexanal formation to be:

\[ [H] = [H_0] \cdot \left( \frac{k_i}{3} \right) t^3 \]  \hspace{1cm} (18)

where: 
- \([H] = \) hexanal concentration (ppm)
- \([H_0] = \) initial hexanal concentration (ppm)
- \(k_i = \) rate constant (ppm/s)
- \(t = \) time (s)

where the rate constant \(k_i\) is dependent of the oxygen concentration as:

\[ \frac{2 \sqrt{k_k}}{\sqrt{k_1}} = \frac{1}{k_a} + \frac{1}{k_b [O_2]} \]  \hspace{1cm} (19)

where: 
- \([O_2] = \) oxygen concentration
- \(k_a, k_b, k_i = \) rate constants

Their experiments showed that their cubic model provided statistically comparable fits with the zero model of Hall et al. (1985). Koelsch et al. also derived a model for the bimolecular stage of the decomposition of hydroperoxides. They could not fit their experimental data to this model. Neither did the exponential model, proposed by Hall et al. (1985) correlate with their experimental values. Their experimental values showed that the induction period for the sample with the lowest oxygen value (1.2% oxygen in the headspace) was seven times longer than for the sample with the highest oxygen level (15.4% oxygen in the headspace).

Berends (1993) studied a freeze-dried model system consisting of linoleic acid dispersed on CMC. The influence of water activity and temperature on the oxidation rate was investigated at constant oxygen concentrations of 1.5 and 8%. The oxidation rate was measured as
hexanal headspace concentration. By using "first order kinetics" on the results at different oxygen concentrations and water activities, equations for the hexanal production were obtained. These equations were used to predict the time to produce a certain amount of hexanal from the oxidation reaction. This time could be used to predict the shelf-life of the product if the maximum allowed hexanal production for acceptability of the product is known. The author also found that the hexanal production at different temperatures could be calculated from the hexanal production at one temperature using the Arrhenius plot, for a fixed oxygen concentration.

6.2.2 Freeze-dried products

Toumy et al. (1969) studied the effect of low oxygen levels on the flavour, rehydration ratios and development of volatile compounds in freeze-dried combination foods. The oxygen levels in the experiments levelled between 1 and 21 % of oxygen in the headspace of the package, which were cans. They found a correlation between oxygen uptake and flavour and odour ratings, but not between oxygen uptake and rehydration ratios. The findings reinforced the recommendations made by the US armed forces to package freeze-dried food with a headspace concentration of oxygen below 2%.

Experiments on a freeze-dried product were also conducted by Simon et al. (1971). They predicted the storage stability of a freeze-dried shrimp product, packed in flexible films, by computer-aided calculations. From sensory evaluations, limits for oxygen consumption and colour changes were obtained. These values, together with oxygen consumption rates for the product, obtained by a Warburg apparatus and with oxygen permeability data of the polymers, were used to calculate the shelf-life for packed shrimp bars. Storage tests showed that the actual shelf-life was longer than predicted on the basis of the oxygen absorption. This was explained by the oxygen consumption varying with varying oxygen concentration in the headspace during the experiment.
Bishov et al. (1971) compared the taste, odour and colour ratings and oxygen absorption between freeze-dried products packaged in 0, 0.5, 1 and 2.2% oxygen in the headspace in cans. Zero oxygen atmosphere was obtained by packaging in 5% hydrogen in nitrogen atmosphere with a palladium catalyst. For oxygen-sensitive products like carrots and sweet potatoes, loss of quality was observed in packages with headspace containing as little as 0.5% oxygen within 1 month at 37°C. They did not find any significant difference in odour and flavour between samples stored at zero and 0.5% oxygen. Samples packaged in 1% oxygen became significantly poorer in odour than those at zero oxygen after 2 months. With regard to flavour, differences from the zero oxygen pack were significant after 2 months at 1% oxygen and after 2 weeks at 2% oxygen.

6.2.3 Milk powders

Many researchers have studied the effect of oxygen on spray-dried milk powders. Tamsma et al. (1970) compared the flavour and physical properties of foam spray-dried milk foamed with air and with nitrogen. They found no difference in taste between the two ways of drying. The ratings were done immediately after drying, and after 3 and 6 months of storage. Ibsen and Hansen (1988) and Ibsen (1989) found that the oxidative stability of whole milk powder, expressed by the TBA value, decreased when increasing concentrations of ozone were added to the drying air. The organoleptic quality was also negatively influenced.

Zimmerman et al. (1974) investigated scavenger pouches as packaging material for milk powder, cereals and citrus crystals. The pouches were made from a film of polyester/foil/iomer/catalyst/iomer, called Moraflex 7F. They investigated the residual gas levels of oxygen and hydrogen inside pouches packaged with milk powder at different temperatures (0, 45, 73 and 100°F) and relative humidities (20, 50 and 90% R.H.). The pouches were packaged with a gas mixture of 92% nitrogen and 8% hydrogen, leading to a residual oxygen concentration of 0.4-1.3% in the freshly packaged pouches. This level was lowered to less than 0.1% in 48 hours for most cases. The quality of the milk powder was tested with sensory analysis. No flavour changes could be detected during a 12-month period under any storage conditions tested.
Curda et al., (1979) measured the headspace oxygen content of hermetically closed food packages. The samples were stored with a headspace of 0.5 ml, containing air. During 45 days of storage of milk powder, 2 µg oxygen was absorbed. The authors found good agreement between oxygen consumption and the flavour and odour development in the powder.

Hall and Lingnert (1984) investigated the odour and flavour profiles of dried milk with addition of antioxidants and stored in air or nitrogen. Samples with added antioxidants or samples stored in nitrogen showed a slower loss of positive flavours and odours and a slower increase in off-flavours than unprotected samples. Hall et al., (1985) continued the work on milk powder, with investigations of the kinetics of the formation of volatile fat oxidation products and other volatile compounds. They developed a kinetic model for the formation of fat oxidation products. The model consisted of an initial linear phase and an exponential phase. The formation rates of oxidation products in the linear phase were, in most cases, found to be lower for samples stored in nitrogen than in air. Hall and Andersson (1985) used multiple linear regression to determine predictive equations to relate the intensity of the flavour properties in whole milk powder to the volatile compounds formed.

Iensen and Hansen (1988) studied the influence of the packaging material on the organoleptic quality of milk powder. There was no significant difference in the samples stored in tins and in samples stored in foils with a continuous metal layer. Samples stored in foils without a metal layer, and no barrier towards oxygen permeation, showed the fastest loss in flavour.

In recent years there has been an increasing focus on cholesterol oxidation products. Some of the cholesterol oxidation products have been implicated in a number of adverse biological effects including atherogenesis, cytotoxicity, carcinogenesis and inhibition of cholesterol synthesis (Kumar and Singhal, 1991). Whole milk powders contain about 0.1% cholesterol, which in the presence of oxygen, heat, light or radiation may undergo oxidation (Chan et al., 1993). This group studied the effect of spray-drying processes and packaging systems on the cholesterol and fat oxidation in whole milk powders. Lipid oxidation, including the generation of cholesterol oxidation products, was greatest in the samples processed with a high NOx level (8 ppm) in direct-fired driers. In powders packed with an oxygen absorber, no influence
of the drying process could be seen on the development of cholesterol oxidation products. Powders packed in polyethylene pouches showed a higher degree of lipid oxidation than powders stored in glass bottles. This was found to be due to oxygen leakage through the pouches.

6.2.4 Potato products

Potatoes are susceptible to lipid oxidation, even though they only contain 0.5% lipids (Lilja, 1985). This is due to the large amount of unsaturated triglycerides in the lipid fraction. Up to 75% of the potato lipid fraction may consist of linoleic and linolenic acid (Lilja 1985).

Quast and Karel (1972b) studied the influence of oxygen concentration, temperature, light intensity and relative humidity on potato chips. They found that the start of a rapid period of oxidation was reached at an extent of 1200 to 1500 μl O₂ STP/g. A rancid flavour had then already been detected. The rate of oxygen consumption at different relative humidities and different oxygen partial pressures is shown in Figures 32 and 33.

**Figure 32.** Rate of oxidation of potato chips at 37°C as a function of equilibrium relative humidity (Quast and Karel, 1972b)

**Figure 33.** Rate of oxidation of potato chips at 37°C as a function of the oxygen partial pressure (Quast and Karel, 1972b)
As can be seen from the Figures, the oxidation rate shows a very strong function of oxygen concentration when the concentration is low. Quast and Karel drew the conclusion from their experiments that packing of the potato chips with an oxygen concentration below 1% in an inert package would result in a very significant increase in the storage life of the chips. The package should also be designed to avoid light penetration.

Quast et al. (1972) developed a mathematical model for oxidation of potato chips, as a function of the oxygen pressure, extent of oxidation and relative humidity at equilibrium. The model looks as follows:

\[
R_A T E = \left( E X T \times \frac{P_1 \cdot P_2 \cdot E X T}{R H^{1/2}} \right) \cdot \frac{pO_2}{(P_3 \cdot P_4 \cdot pO_2)}
\]  

(20)

where: RATE = Rate of oxidation (μl O₂ STP/g hr)
EXT = Extent of oxidation (μl O₂ STP/g)
RH = Equilibrium relative humidity (%)
pO₂ = Oxygen partial pressure (atm)
P₁-₄ = constants

and was developed from 843 experimental values obtained from earlier experiments (Quast and Karel, 1971, 1972b). The constants in the model were obtained by linear regression of the experimental results. To test the model further experiments were carried out. The constants obtained from these experiments were similar to those from earlier experiments, but showed larger standard deviations.

Quast and Karel (1973) continued their development of a mathematical model for prediction of the shelf-life of potato chips. The influence of the oxygen and moisture permeability of the packaging material on the predicted values was investigated. The effect of the package size, bulk density and initial conditions inside the package was also simulated.
Herlitze et al. (1973) investigated the influence of different oxygen concentrations in the headspace on the oxidation in orange lemonade, potato chips and ketchup. They used oxygen concentrations of 20, 70, 100 and 150 torr and added the oxygen used after each measuring point. The measurements were made in a test cell. Their experiments did not show any lipid oxidation in potato chips, when the sensory test showed an unacceptable flavour and they could not find any connection between the oxygen consumption and the peroxide value.

Sapers et al. (1972, 1973, 1974, 1975) studied the flavour quality and stability of potato flakes. In the first experiments, the flavour changes and development of volatile components during storage were investigated. The samples were stored with and without antioxidants and in air or nitrogen (< 2% oxygen) in cans. The authors did not find any flavour changes for samples stored in nitrogen for 9 months. Samples stored with antioxidants in air had a slight hay-flavour after nine months of storage and samples stored without antioxidants in air showed a moderate hay-like flavour after six months of storage. This flavour was associated with autoxidation and the taste development was accompanied by production of aldehydes. The influence of the raw material and processing on the flavour quality was also investigated (Sapers et al., 1973). The experiments showed no influence of these factors if the samples were stored in nitrogen (<2% oxygen in the headspace). If the samples were stored in air, the presence of peel, defective raw material and high rate of process water turnover during the cooking and cooling decreased the stability of the potato flakes. Sapers et al. (1974) investigated the effects of drying conditions, moisture content and packaging. In all samples packed in air, the oxygen content greatly exceeded the amount needed for oxidative reaction and no significant differences between the headspace volume and oxidative deterioration could be seen. In final experiments on potato flakes (Sapers et al., 1975), the effects of antioxidants on the product quality were investigated. A combination of BHA/BHT added to a corn oil solution was found to be the best preservative, when the flakes were stored in air.

Lisberg and Chen (1973) studied dried potato granules packaged in nitrogen-filled cans or in air-filled foil-lined cartons. There was no difference in rehydration or non-enzymatic browning for samples packaged with or without access to oxygen. Rancidity developed in the potato granules in the cartons due to the presence of air.
In experiments on explosion-puffed potatoes (Konstance et al., 1978), the influence of packaging and the addition of antioxidants on autoxidation in the potatoes was studied. The development of hexanal in samples stored in nitrogen in cans was not found to be dependent on the storage temperature (-18°C and 23°C) and no difference in hexanal development or taste was found between samples stored in nitrogen in cans and in pouches with oxygen scavengers. The pouches, however, showed susceptibility to pinhole leakage.

Paik et al. 1994 investigated lipid oxidation in potato chips packaged in foil pouches laminated by orientated polypropene (20μm)/metallized polyester (12μm)/polyethylene (15μm)/ionomer (7μm). The samples were stored at 23 or 40°C in 90% RH and in 1.5 or 20% O₂. To follow the oxidation, the oxygen concentration in the headspace and the peroxide value were measured and the chips were sensorically evaluated. At 23°C the oxygen concentration in the package increased to 2% in the samples with low oxygen values, during a storage period of 150 days. In the samples with a high oxygen content the oxygen partial pressure remained unchanged. Chips stored at 40°C showed an increase in oxygen concentration from 1.5 to 17.5%. This was said to be due to the greater oxygen permeability of the package at higher temperatures. The oxidation rate also increased with increasing temperature, but the increase in oxygen permeability was much greater. The peroxide value only showed minor differences between samples stored at 1.5 or 20% oxygen at the same temperature, but there were differences between samples stored at 23 and 40°C. Sensory evaluations, however, showed a significant difference between samples stored in nitrogen-flushed packages (1.5% oxygen) and samples stored in air. The samples stored at low oxygen levels at 23°C were rated the best. Paik et al. also compared these experimental values with values calculated from the model of Quast et al. (1972). The constants in the mathematical model were taken from Quast et al. The comparison showed a smaller influence than, predicted from the model, from lowering of the oxygen partial pressure for the experimental values. This was explained by the use of a different type of frying oil, different frying conditions and character of the potato chips.
6.2.5 Other dehydrated products

In an early work by Sidwell et al. (1961) the influence of the moisture content, surface area, oxygen partial pressure and absorbability of other gases on the oxygen content in dehydrated foods was investigated. The oxygen content was measured as dissolved oxygen from food submerged in deoxygenated water. It was found to increase rapidly in the moisture region below the monomolecular layer value. In samples stored in a oxygen-helium atmosphere the oxygen content in the samples was higher than in samples stored in an oxygen-nitrous oxide atmosphere.

Quast and Karel (1971, 1972a,b) studied the effects of different environmental factors in dry foods. In the first experiments, Quast and Karel (1971) measured both the oxygen uptake in dry foods and the diffusion rates through the food. They found that the oxygen uptake in potato chips at 37 °C and at atmospheric oxygen pressure during the post-induction period was 176 ml O₂ STP/ g hr (STP=0°C, 1 atm). In fish meal the oxygen uptake under the same conditions was 24 ml O₂ STP/ g hr but without an induction period. The oxygen consumption in potato chips as a function of the oxygen partial pressure is shown in Figure 34.

![Figure 34. Rate of oxygen uptake of potato chips in the post-induction period at 50°C (Quast and Karel, 1971)](image-url)
Figure 35. Rate of oxygen uptake of fish meal at 23°C (Quast and Karel, 1971)

The corresponding value for fish meal is shown in Figure 35.

Radtke (1979) made experiments on roasted coffee. She investigated the effects of the oxygen concentration in the headspace on oxidative deterioration, measured by sensory analysis. The coffee was packed in 5, 3, 1, 0.5 or "0" % oxygen. The results showed that the oxygen consumption rate increased with increasing oxygen concentration in the headspace. After 3 to 4 weeks the samples with 0.5 and 1% oxygen had used up all their oxygen. Radtke found good agreement between oxygen availability and flavour scores. Samples stored at higher oxygen partial pressures showed a faster decrease in flavour scores. The temperature also influenced the ratings and a high temperature gave a faster loss of quality. Coffee packaged in 5% oxygen reached the sensory limit within 4 months, while samples packaged in 0.5% oxygen had not reached this limit in 2 months. There was no difference in sensory quality between samples packaged in 0.5% and 1% oxygen up to the 9th month of storage. By this time none of these products had reached the limit for sellability of the product. The experiments also showed that 10 μg oxygen/g coffee was bound to the coffee. This amount was released when the coffee was packed in nitrogen.
Villota et al. (1980) evaluated literature data on the storage stability of dehydrated food. They found in their review that even when the samples were stored in nitrogen, up to 2-5% of the headspace was oxygen. This is due to the ability of the product to bind oxygen, which slowly desorbs to the headspace. They found that the smaller the oxygen content, the longer the shelf-life of the product, and that freeze-dried products were more sensitive to oxygen because of their high porosity and thereby large surface area, which facilitates oxygen absorption and decreases the diffusion influence. Their article contains tables of the shelf-life of different products with respect to drying process, additional treatment and storage conditions.

Saguy et al. (1983) improved the method of Teixeira et al. (See section 6.2.1) for measuring entrapped and adsorbed gases in dehydrated foodstuffs. They also investigated different powders and divided them into type I and type II powder, according to their behaviour when evacuated. In type I powders the gas volume retained upon evacuation, remained constant after reaching a plateau, regardless of evacuation time. For type II powders, the evacuation time determined the retained gas content (Figure 36).

Milk powder, carrot base, and beet powder were found to be type I powders and instant potatoes and orange base powder were found to be type II. The evacuation time required to reach the plateau was 2-3 minutes in the experiments made on 4 grams of skimmed milk powder.

![Figure 36. Effect of evacuation time on the volume of entrapped/adsorbed gas retained by dehydrated fruit and vegetable powders. ■) instant potatoes, △) carrot base powder, ○) beet powder, ●) orange base powder (Saguy et al., 1983)](image-url)
6.3 Oils, fats and emulsions

The experiments of Marcuse and Fredriksson (1968) on lipid oxidation was one of the earliest in the field regarding low oxygen pressures at atmospheric total pressure. Most experiments conducted before 1968 used low total pressure to investigate the effect of low oxygen concentration on lipid oxidation. In their experiments, Marcuse and Fredriksson measured the oxygen consumption at 0.5, 1, 2.5 and 21% oxygen in nitrogen in the headspace of oil emulsions of linoleic and linolenic acid and linolenic acid ethyl ester in a closed container. The oxygen consumption was measured in a modified Warburg apparatus at constant oxygen pressure. They found a decrease in the oxygen consumption rate with lowering of the partial oxygen pressure, and this was found to be due to the varying influence of the non-oxygen-dependent and oxygen-dependent reactions of the propagation and on the varying rate-limiting effect of slow oxygen diffusion.

Marcuse and Fredriksson (1969) continued their work on oil emulsions, by investigating the effect of addition of inhibitory and retarding antioxidants to the emulsion. In the case with inhibitory antioxidants, where BHA, α-tocopherol and PG were investigated, no effect of lowering of the oxygen partial pressure was seen on the oxidation rate. When retarding antioxidants were used (glycine, alanine, histidine and tryptophane), lowering of the oxygen partial pressure led to a lowering of the oxidation rate. If both an amino acid and an inhibitory antioxidant were added to the emulsion, a synergistic effect was obtained. By lowering the oxygen partial pressure, both an increase in the induction period and a reduction of the oxidation rate after the end of the induction period was seen.

In later experiments, Marcuse and Fredriksson (1971) studied the effect of lowering of the oxygen partial pressure when metal salts were added to the reaction medium. They studied the effect on systems which contained additions of Fe³⁺, Fe²⁺, Cu²⁺ or Co²⁺ ions. In the case with Cu²⁺-ions, a lowering of the oxygen partial pressure could lead to inversion of the pro-oxidant behaviour of the ion into an antioxidative one. This was not seen with the other metal ions.
Curda et al. (1979) measured the oxygen consumption from the headspace and the sensory quality of mayonnaise. The samples were packaged in air-tight glass jars and stored at room temperature for 41 days. During this time the oxygen absorption was 1.88 mg O$_2$/100 g food. The sensory evaluations showed a decrease in quality but the product did not reach the sensory limit.

Min and Wen (1983) investigated the effects of 2.5, 4.5, 6.5 and 8.5 ppm dissolved free oxygen on the volatile compound formation and the disappearance of dissolved free oxygen in soybean oil during storage. The samples were stored at 55°C in air-tight 50 ml flasks without a headspace. The rate of oxygen disappearance in oil containing 8.5 ppm of oxygen was three times as fast as that in oil containing 2.5 ppm oxygen and the amount of compounds formed in oil containing the highest oxygen level was twice that in oil containing 2.5 ppm oxygen. Even though all the dissolved oxygen disappeared after almost 48 hours the formation of volatile compounds continued beyond this time.

Shekar and Bhat (1983) investigated the effect of the level of dissolved oxygen on the keeping quality of milk fat from cow and buffalo. They found the dissolved oxygen value of cow's and buffalo milk fat to be 5.25 and 5.53 ppm, respectively. The oxidative stability of the fats was investigated at three different values of dissolved oxygen (5.5, 2.8 and 0.75 ml O$_2$/100g fat for buffalo ghee and 5.3, 2.2 and 0.5 ml O$_2$/100g fat for milk ghee) and the rate of oxidation was followed by measuring the peroxide value. The authors found an increased rate of oxidation with increasing dissolved oxygen levels. The way of packaging the samples was not mentioned in the article.

Keogh and Higgins (1986) studied the effect of dissolved oxygen levels, fluorescent light, copper levels in the fat and efficiency of natural antioxidants (α-tocopherol, Ronoxan A-a mixture of α-tocopherol, ascorbyl palmitate and lecithin) and nitrogen on the oxidation of anhydrous milk fat. The oxidative changes were measured by determining the peroxide value, TBA value and by organoleptic evaluation. Samples were packed in cans with nitrogen or air in the headspace. The oxygen availability was found to influence the stability and it was concluded that the initially dissolved oxygen content (3.1 mg/kg) should not be allowed to
increase by exposure to air. Ronoxan A and nitrogen flushing reduced the rate of peroxide and TBA development in the fat compared to the control, during storage at 25°C. Keogh and Higgins could not find any correlation between chemical tests and oxidized flavour scores. They explained this with development of lactones and ketones produced by non-oxidative reactions, which influenced the flavour scores.

Brimberg (1991) investigated the kinetics of autoxidation of lipids. She linearized rate data from earlier measurements and found that in her models, the increase of oxygen increased the degree and rate of oxidation. Addition of hydroperoxides was also found to increase the oxidation rate in proportion to the amount added. In most of the data, the oxygen concentration was kept at a constant level and the oxygen consumption was measured. Brimberg (1993a,b) further developed her models for oxidation of fats and compared them with rate constants from the literature.

Dahl (1994) investigated the oxidation of a linoleic acid emulsion at different oxygen availability levels. The oxygen amounts were 0.11, 0.45, 3.4 and 12.5 mg. Ten ml of linoleic acid emulsion were used in the experiments. The oxidation was followed by measuring the conjugated diene formation by UV spectroscopy, the hexanal formation from the headspace and the oxygen concentration in the headspace and dissolved in the emulsion. They did not find any correlation between the initial oxygen availability and initial oxidation rate, but found a limiting effect of the oxygen availability on the extent of oxidation.

6.4 Meat Products

Labuza (1971) reviewed the kinetics of lipid oxidation. He also wrote about different product groups susceptibility to lipid oxidation. For beef he concluded that the adipose tissue lipids of beef are highly saturated and the lipids of the lean tissues, which constitute about 2 to 4% of the total fat, are more important in lipid oxidation. Close to 25% of the fatty acids in the phospholipids, which make up the lean tissue, have two or three double bonds and over 19% have four or more double bonds. Although it contains highly unsaturated fatty acids, raw beef
does not present a serious lipid oxidation problem as it is usually degraded by bacterial or enzymatic action. When beef is cooked and stored it becomes susceptible to lipid oxidation, as "denatured" hemoglobin is a better lipid oxidation catalyst than when bound to myoglobin. The enzymatic degradation is usually not as important in processed food. This leads to a greater influence of the lipid oxidation on the quality. The most important oxidation in beef is the oxidation of oxyhemoglobin and myoglobin to the brown pigment metmyoglobin. This oxidation can be limited by packaging in 2% oxygen.

Shicai (1983) investigated the storage stability of hamburgers in different packaging materials, with different oxygen permeability. The packages were PET/CCP, OPP/PVDC/CCP and OPP/Al/CPP, which had oxygen permeabilities of 84.0, 9.5 and 0 ml/m² and day respectively. The pouches were stored at 5, 15 and 30°C. Peroxide values, TBA values and the sensory quality were investigated after 25, 53, 90 and 140 days of storage. Pouches with the highest oxygen permeability were found to be unsuitable for packaging of hamburgers due to a rapid rise in the peroxide value in only 25 days. The pouches with low oxygen permeability showed very similar chemical and sensory results as the Al-laminated pouches, regardless of temperature and days of storage.

Yen et al. (1988) investigated the colour stability of vacuum-packed dry salami as a function of the oxygen transmission rate of the packaging films and light exposure. The films had oxygen transmission rates of 1, 11, 30, 72 and 90 cc O²/m² d at 23°C, 0% RH and 1 atm, and the salami was stored in light or in the dark at 5°C for 8 weeks. There are two different colour changes in meat during storage; one with regard to the lightness of the product and one to the red color of the product (Yen et al., 1988). The different oxygen transmission rates of the products did not influence the lightness of the product, but the difference in redness was significantly influenced. A higher oxygen transmission rate resulted in a larger colour change. In the samples stored in light the changes in redness were more pronounced than in samples stored in the dark, and after 8 weeks of storage the light factor was more important for colour changes than the oxygen permeability factor.
Kanner et al. (1988) investigated the dependence of oxygen and free metal ions on the muscle lipid peroxidation in minced turkey. The samples were either incubated in polyethylene bags before or after heating or packed in cans under vacuum and heated. After heating the products were chilled in iced water to 5°C within less than 30 min. The samples were stored at 4°C and TBARS and conjugated diene values were measured to follow the lipid oxidation. As long as the samples were stored under vacuum, TBARS and the conjugated diene values did not change much during 30 days of storage. If the cans were opened to the air for several days, the minced muscle started to peroxidize at a very rapid rate, independent of the previous storage time.

Lingnert (1992) investigated the effects of processing of the food on lipid oxidation. In processing of sausages, a lower hexanal production was obtained when the meat mincing was performed in CO₂ or under vacuum, compared with air. The hexanal content was lower at the beginning of the storage period and the production of hexanal was also lower during storage of sausage processed in CO₂ or under vacuum. This was explained by a lower oxygen content in the sausage.

Rödel et al. (1993) investigated the oxygen partial pressure in meat products. They used a needle electrode to measure inside the product at different depths. The electrode was 7 cm long and had a diameter of 0.35 mm and a detection limit of 0.05 mm Hg. In pork and finished meat products the oxygen partial pressure was found to be below the detection limit. The authors also measured the oxygen partial pressure in unheated sausage mixtures and found it to be different if the mix was kept in air or under vacuum.

Ahn et al. (1993) studied the effect of the oxygen availability on prooxidant catalysed lipid oxidation of cooked turkey patties. Breast meat was used to evaluate the effect of heme pigments and a meat mixture to evaluate the effect of NaCl and free ionic iron on the development of lipid oxidation. The samples were stored at 4°C for up to 7 days. The authors found that the effect of all the prooxidants tested was highly significant only when oxygen was freely accessible to the patties during storage.

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6.5 Fruit and fruit products

Harvey et al. (1986) investigated the effect of deaeration and storage temperature on the colour and flavour stability and ascorbic acid retention of aseptically packaged guava puree. The product was deaerated prior to heat processing and aseptical packaging. Deaeration was found not to benefit either the colour or flavour stability but did give a slightly better ascorbic acid retention when the samples were stored at 10°C. At higher storage temperatures no improvement in the above mentioned quality parameters could be seen. The results could be explained by only a slight decrease in the initial level of dissolved oxygen (from about 10.2 to 9.5% dissolved oxygen) for the deaerated samples compared with the non-deaerated samples, indicating insufficient deaeration.

Curda et al. (1979) investigated the oxygen content in the headspace of different products packed in hermetically closed containers. The experiments made on apricot jam showed an oxygen uptake of 27 μg from a headspace of 0.5 ml air during 41 days of storage. To measure the effect of the oxygen uptake on the quality of the product, sensory evaluations were performed. After 15 days the jam reached the sensory limit with regard to colour, after 22 days the limit for taste and after 29 days the limit for odour. The limits for taste and odour correspond to oxygen uptakes of 1.4 and 3.3 mg O2/100g jam, respectively.

6.6 Various foods - comparisons of results from a simulation program for shelf-life predictions and experimental values

In a number of articles in the seventies and the beginning of the eighties, German researchers investigated the effect of packaging and diffusion on oxygen sensitive products. They tried to calculate and predict the shelf-life of a number of products packaged in oxygen-permeable packages. To be able to make these calculations the oxygen sorption behaviour, the oxygen tolerance and the shelf-life have to be known by means of sensory analysis (Herlitze et al., 1973b). They concluded that:
- the oxygen sorption of the food is dependent on the oxygen partial pressure
- the oxygen consumption before the product becomes sensorically unacceptable is between 30 and 200 µg O₂/g food and is not constant, but depends on the oxygen partial pressure and the time.
- It is possible to calculate the shelf-life of a product or, conversely, calculate the allowed oxygen permeability of the package for a given shelf-life.

To be able to make these predictions the oxygen consumption of orange juice, tomato ketchup and potato chips were measured. After each measurement, in a measuring cell, the used oxygen was added again. This gave a relatively constant oxygen concentration in the headspace. The oxygen consumption measurements was made at partial pressures in the headspace of 150, 100, 70 and 20 torr. The results are shown in Figure 37.

![Figure 37](image)

Figure 37. Oxygen consumption and sensory limits for some foods stored at 25°C and at different oxygen partial pressures, O₆) orange juice, Tₖ) tomato ketchup, Kₖ) potato chips. a) sensory limit for sale according to taste, b) sensory limit for sale according to colour (Herlitze et al., 1973a)
As can be seen from the Figure, the consumption of oxygen was most rapid for orange juice, followed by tomato ketchup and potato chips. The orange juice also reached the sensory limit more quickly than the other products. To be able to calculate the shelf-life a differential equation was formulated:

\[
\frac{dpO_2}{dt} = \frac{DO_2 F RO_2 T}{V_H} (p_2O_2 - pO_2) - \frac{RO_2 T m_g}{V_H} v_2
\]  

(21)

where: \( pO_2 \) = oxygen partial pressure (Torr)
\( t \) = time (h or d)
\( DO_2 \) = oxygen permeability of the packaging material (cm²/mm² d at)
\( F \) = area of the packaging material (m²)
\( RO_2 \) = oxygen gas constant (KJ/Kg K)
\( T \) = temperature (K)
\( V_H \) = headspace volume (cm³)
\( p_2O_2 \) = oxygen partial pressure in the air (Torr)
\( m_g \) = sample mass (g)
\( v_2 \) = oxygen consumption rate of the product (μg/g h)

Equation (22) together with the equation:

\[ m_{s\text{ max}} = f(t) \]  

(22)

where: \( m_{s\text{ max}} \) = maximal oxygen uptake (μg/g).

was solved with the aid of a computer program.

Reinelt et al. (1979) discussed the calculation of the shelf life of high viscosity products. They measured the oxygen consumption of compact food in slices of different thicknesses. The oxygen partial pressure was 200 mbar and the oxygen was only allowed to diffuse into the sample slice from one side. Their results in the experiments on mayonnaise are shown in Figure 38 and 39.
Figure 38. Oxygen consumption for mayonnaise at different depths of a thin slice, $T=20\degree C$, $pO_2=200\text{mbar}$, storage in the dark (Reinelt et al., 1979).

Figure 39. Oxygen concentration at different depths of a thin slice of mayonnaise, $T=20\degree C$, $pO_2=200\text{mbar}$, storage in the dark, total thickness of the slice=26 mm (Reinelt et al., 1979).

To be able to calculate the predicted shelf-life of the product, Reinelt et al. also investigated the sensory quality at different oxygen consumption rates. The authors then put together a computer-aided calculation model, derived from the one earlier developed by Herlize et al. (1973), to calculate the oxygen consumption at different depths of the product and tested it against experimental values. The model showed good agreement with the experimental values. In the article, simulations of the influence of different factors, such as different diffusion rates, reaction rates, package permeability, oxygen availability and headspace volume, on the oxidative reactions are shown.
Schrader et al. (1980) developed a method to calculate the oxygen concentration and concentration of unreacted fatty acids in compact foods. They also developed a measuring device to be able to test the calculated values. The model values showed good agreement with the experiments. The permeability and diffusion constants for sunflower oil, soya oil, margarine and butter were also measured. From these values the oxygen concentration and concentration of linoleic acid in margarine were calculated. The calculations showed that only an outer layer of the margarine was affected by oxidative reactions.

Heiss (1977 and 1984) reviewed the findings from the German articles cited above.
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