

EDIBLE FATS AND OILS IN THE NEW ZEALAND FOOD INDUSTRY

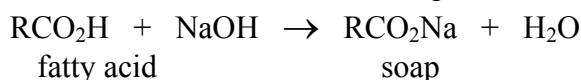
Non-dairy edible fats such as margarine and vegetable oils are an important source of food. They are extracted from plant or animal products. However, to bring them to the palatable condition needed for marketing them in New Zealand, significant processing is required. This is done in four steps, with two other steps included if necessary, depending on the required end product.

Step 1 - Extraction

Vegetable oils are extracted by heating the seeds of the relevant plant with solvents, pressure or both. Animal fats are extracted by heating up animal tissues and bones.

Step 2 - Refining

This involves chemically removing any free fatty acids found in the fat by reacting the fat with sodium hydroxide. This must be done quickly to prevent the sodium hydroxide reacting with the fat itself. These reactions produce soap and water:



Step 3 - Bleaching

Substances known as "adsorptive earths" are mixed with the oil or hot liquid fat. Any colours that are in the oils adsorb onto the earth and hence are removed from the oil.

Step 4 - Deodorising

The oil is heated under vacuum, and flavours are removed by distillation.

The oil may be fractionated (to change the relative proportions of different fats within the mixture) either at this point or before the initial refining. At this point it can also be chemically modified to change its physical properties such as hardness. It is then packaged ready for sale. At all stages of the process analyses are made to ensure that a high quality end-product is obtained.

The finished products made from edible fats and oils in New Zealand include various margarines, shortenings, vegetable oils and confectionery fats.

INTRODUCTION

Edible fats and oils are in common use in the home as butter, margarine, dripping and vegetable oils. The processing of butter is confined to the dairy industry, with the edible fats and oils industry in New Zealand being concerned with the manufacture of margarine, cooking fats and confectionery fats.

Edible fats and oils are an important part of New Zealand's food industry. Import statistics (**Table 1**) show the value of some of the main imports. These imports are supplemented by approximately 15,000 tonnes of tallow¹ with a value of about \$12 million.

¹Processed beef and mutton fat (see meat article).

Specialist edible oil manufacturers and many other food companies convert the raw materials to a wide range of food products. The main products of edible oil manufactures are described in a later section. Some other significant uses of edible oils include snack food frying, mayonnaise and dressings, and hardening (hydrogenation) followed by blending with butter oil for re-export.

Table 1 - Oil & Fat Import Statistics, 1995

| Oil or Fat | Tonnes | Value, NZ\$Million |
|--|---------------|---------------------------|
| Soya Bean Oil* | 21,000 | 24.6 |
| Palm Oil and its Fractions | 11,800 | 13.1 |
| Sunflower Oil | 8,050 | 8.9 |
| Canola/Rapeseed Oil | 4,900 | 6.0 |
| Coconut Oil* | 3,950 | 4.6 |
| Other (Corn/Maize oil, Peanut Oil, Palm Kernel Oil, etc) | 1,200 | 2.0 |
| Totals | 50,950 | 59.2 |

* Soya and coconut oils have technical uses in the soap, detergent and paint/coatings industries, so not all are used to make food.

Table 2 - The major fatty acids occurring in fats and oils

| Fatty acid | IUPAC name | Source |
|-------------------|---|---|
| lauric acid | Dodecanoic acid. | Major fatty acid of coconut and palm kernel oils. |
| palmitic acid | Hexadecanoic acid. | Major fatty acid of palm oil, ca. 25% in cottonseed oil, lard and tallow. |
| stearic acid | Octadecanoic acid. | Found in all oils and fats but in greater concentrations in solid fats. |
| oleic acid | <i>cis</i> -9-octadecaenoic acid | Major fatty acid of olive oil but occurs in all fats and oils. |
| linoleic acid | <i>cis,cis</i> -9,12-octadecadienoic acid | Major fatty acid of safflower, sunflower, soya bean and cottonseed oils. |

Fats and oils

Fats and oils comprise one of the three major classes of foods, the others being carbohydrates and proteins. Chemically they may be defined as esters of the three carbon trihydroxy alcohol, glycerol (propan-1,2,3-triol), and various monocarboxylic acids known as fatty acids. Since glycerol is a trihydroxy alcohol, monoacid, diacid and triacid esters are known.

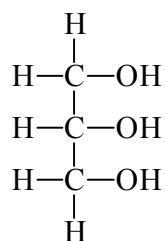
The majority of the fatty acids occurring in the more common edible fats and oils are straight chain compounds with an even number of carbon atoms, and they may be saturated, monounsaturated or polyunsaturated. An unsaturated acid of a given formula may have its double bond or bonds in various positions along the carbon chain giving rise to positional isomers. The carbon chains may be arranged *cis* or *trans* to the double bonds giving rise to geometric isomers. There are many types of fatty acids found in nature and these include hydroxy acids and branched chain acids. In edible fats and oils one encounters six major fatty acids which are listed in **Table 2**.

In industry one characterises oils and fats by their fatty acid composition as determined by gas liquid chromatography (GLC) which enables the food chemist to positively identify an oil as genuine or not. The GLC analyses of some common fats and oils are given in **Table 3**.

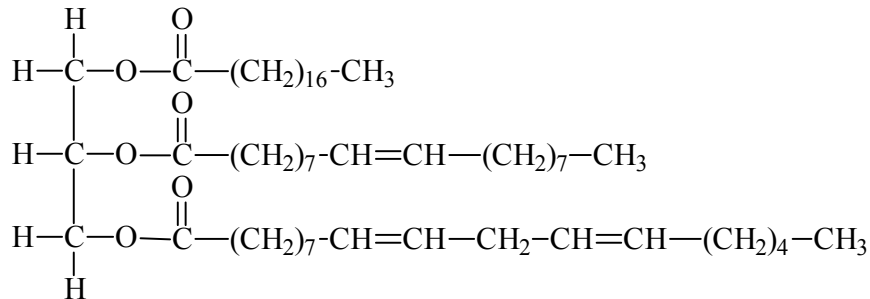
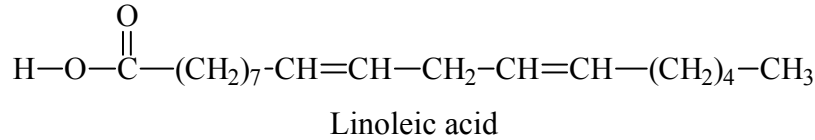
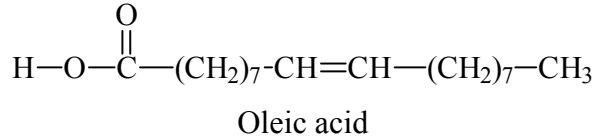
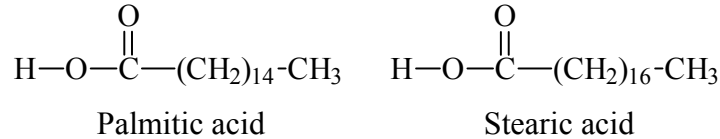
Table 3 - Fatty acid composition of some oils and fats by GLC

| | Lauric 12:0 | Myristic 14:0 | Palmitic 16:0 | Stearic 18:0 | Oleic 18:1 | Linoleic 18:2 | Linolenic 18:3 | Others |
|---------------------|----------------|------------------|------------------|-----------------|---------------|------------------|-------------------|--------|
| Tallow | — | 3 | 25 | 25 | 38 | 2 | 1 | 7 |
| Coconut oil | 47 | 16 | 8 | 3 | 6.2 | 2 | — | 17 |
| Sunflower | — | — | 6 | 5 | 18 | 68 | — | 3 |
| Corn oil (Maize) | — | — | 12 | 2 | 31 | 53 | 1 | 1 |
| Olive oil | — | — | 13 | 4 | 70 | 9 | 0.5 | 3.5 |
| Soyabean | — | — | 10 | 3 | 22 | 53 | 8 | 4 |

The bulk of the naturally occurring fats and oils are composed of the triacid esters known as triacylglycerols. The chemical structures of both glycerol, some of the fatty acids that attach to it to make fats and oils and an example of an oil are given below.



Glycerol



stearo-oleo-linolein (a triglyceride)

A commonly accepted convention is that if the triglycerides are solid at room temperature they are known as fats, and if liquid are oils. The physical nature of the fat or oil is determined by the character and siting of the fatty acid in the glyceride molecule. Fats are mixtures of solid and liquid glycerides, the distribution and concentration of these glycerides determine the physical properties such as melting point and crystallization behaviour.

Raw materials

The major raw materials used in New Zealand comprise tallow (beef and mutton fat) obtained from freezing works (see article) and vegetable oils imported from overseas. The vegetable oils include soyabean, sunflower, palm olein, palm stearine, coconut and other minor amounts of oils such as corn (maize), cottonseed and peanut oils. All these materials are used in different products for different applications and their processing involves several different chemical treatments.

THE REFINING AND MODIFICATION OF FATS AND OILS

When obtained in the crude state, oils and fats are mainly unpalatable, except for such fats as olive oil, lard and edible beef dripping. In Western society no one would find it pleasant consuming or cooking with crude vegetable oils such as sunflower, soyabean or maize oil. Crude oils contain unwanted impurities which must be removed to ultimately yield a bland or pleasant tasting stable product. The treatment involves a series of purifying steps, followed by modification into more useable products, and finally packaging.

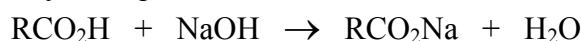
Step 1 - Extraction

Animal fats such as lard, beef and mutton tallow are obtained by cooking the tissues in large kettles either by dry heat or by steam, thereby removing the fat. Such processes are known as rendering. Essentially, tallow is obtained as a by-product of the meat processing industry by rendering trimmings, bones and other tissues such as caul and kidney fats which are not suitable for sale as direct meat products.

Coconut oil is obtained by hot pressing dry coconuts (copra). The extraction is carried out in screw presses known as expellers, which subject the copra to pressures up to 20 tons per square inch. The pressure squeezes the oil out of the flesh of the coconut, leaving behind a residue called "cake" which is milled and used as a meal supplement in cattle and poultry feed. Two newcomers to the New Zealand market are maize oil and canola oil, both products partly supplied by New Zealand grown material. Overseas, certain oils such as soyabean and cottonseed oil are obtained by extracting the seeds of these plants with solvents such as hexane.

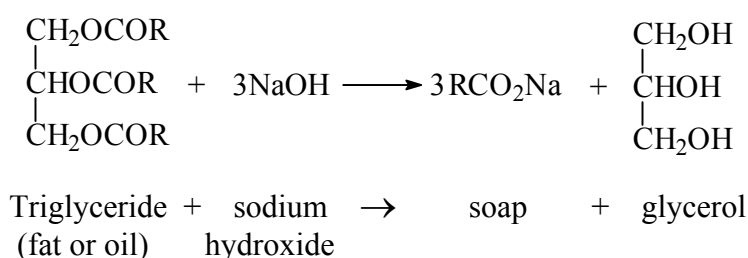
Step 2 - Refining

Refining usually refers to the removal of non-glyceride fatty materials by washing the oils with strong alkaline water solutions (sodium hydroxide solution). The major impurities in most crude oils are the free fatty acids. These react with sodium hydroxide (caustic soda) to form soap, as represented by the equation:



Soap is an ionic compound, consisting of solution cations and carboxylate anions. It dissolves in the water present and the solution is heavier than the oil (specific gravity² 0.9). The oil can be separated from the soap by gravity - that is, if we allow the mixture of oil and soap solution to stand, the oils (SG 0.9) will rise to the top, and the soap and water (SG 1.1) will sink to the bottom. If this is allowed to occur by standing, the time taken is lengthy and therefore, although this method is used, it has its obvious disadvantages. The process is carried out very rapidly by using centrifuges producing 5000 G. The short time of reaction occurring in modern continuous centrifugal processes also has the advantage of reducing losses of oil due to saponification³.

Saponification can be represented:



²Specific gravity is a measure of the density of a liquid. It is determined on an arbitrary scale, with water having a specific gravity of one (SG 1.0), thus liquids such as oil with a lower specific gravity are less dense than water and will float on water, whereas water will float on liquids with a specific gravity higher than one.

³This reaction is the chemical reaction carried out by the soapmaker.

This is an undesirable reaction for the oil and fat processor as it means the loss of valuable end-products.

Caustic refining removes other impurities such as pigments, protein residues and other unwanted fatty materials. These are removed by absorption on the soap. Note that after caustic refining any residual soap in the fat is removed by water-washing. The refiner carries out analyses on the finished oil to check whether all the free fatty acids and soap have been removed.

Certain modern methods of refining remove the free fatty acids by steam distillation under vacuum. This is known as physical refining and is the same process as deodorizing, which is discussed later.

Step 3- Bleaching

This is a very important step in oil and fat processing. In early days the process was thought to remove only coloured pigments, but more modern schools of thought consider the process to be much more than this. The process involves the removal of coloured materials and other impurities by adsorption with earths. The process would be better termed "adsorptive cleansing".

The most important adsorbent used in bleaching fats and oils is bleaching earth or clay. Natural bleaching earth consists mainly of hydrated aluminium silicates. These adsorbents are known as fullers' earths from their use in the "fulling" or scouring of wool. These are still used in the petroleum industry but have mainly been replaced in the oil and fats business by acid-activated earths. The raw materials for these adsorbents are bentonites or montmorillonite which have been treated with sulfuric or hydrochloric acid to yield very effective bleaching materials.

The bleaching process involves mixing 0.2 to 1.0 per cent of earth with the oil, heating to 100°C with stirring under vacuum for half an hour, and filtering off the spent earth in large plate and frame filter presses. The efficiency of the bleaching process is determined by measuring the reduction in colour of the fat or oil. This is carried out by colour measurements in a "Lovibond Comparitor" or a spectrophotometer. The theory behind the bleaching process is very complicated, but a simplification of the underlying principles is given by a consideration of the Freundlich equation.

$$\frac{X}{M} = KC^n$$

where X = amount of substance adsorbed

M = amount of adsorbent

C = amount of residual substance

and K and n are constants

The equation enables the laboratory chemist to calculate the amount of earth required to attain a required bleached colour, and also to compare the activity of different earths.

Step 4 - Deodorising

The final and crucial process in oil and fat treatment is deodorization. This is the removal of objectionable flavours and odours from the oil. This is achieved by a technique known as

steam distillation under reduced pressure. The theoretical considerations that apply to this operation are primarily Raoult's and Dalton's⁴ laws.

Steam distillation is often used in the organic chemistry laboratory to distill relatively non-volatile materials without decomposition. The same principles are used in deodorizing. Triglycerides have extremely low vapour pressures and are therefore non-volatile whereas aldehydes, ketones, alcohols and free fatty acids, which contribute to the flavours and odour of fats, are removed by steam distillation. Deodorization may be carried out in batch vessels with capacities of up to twenty or thirty tonnes or by a semi-continuous or continuous process.

The process is carried out by injecting high pressure steam into the fat at temperatures between 180-250°C with a vacuum of about 1kPa. This has the effect of removing odoriferous volatile compounds leaving the fat almost tasteless.

These are the basic processes for producing the finished oils and fats. These fats may then be modified either physically (such as by fractionation) or chemically (such as by hydrogenation).

Fractionation

The objective of fractional crystallisation of fats may be to eliminate from a fat or oil a fraction which is the cause of undesirable properties, or it may be to produce a new product with a narrower range of triglycerides and hence different properties.

In New Zealand butter oil is fractionated to provide the raw materials for a number of interesting products. Butter itself has limitations in application to uses such as spreading on bread, and for making baked goods such as puff pastry and croissants. Hard fractions of butterfat are good as ingredients for pastry or croissant baking, and can be combined with double fractionated soft fractions to make an acceptably spreadable refrigerated butter.

The process has two main steps: crystallisation, and filtering. The first is achieved by slowly cooling the butter oil in stirred tanks. Accurate control of cooling rate and agitation yields a "slurry" of high melting "stearine" crystals in a low-melting liquid "olein" which is easy to filter. A Florentine filter consists of a continuous stainless steel mesh belt onto which the slurry is poured. A partial vacuum under the belt draws the olein through where it is collected and pumped away. Movement of the belt carries the stearine to another location where the hard crystals are scraped off, remelted, and also pumped to storage tanks.

Fractionation is often carried out after the oil has been deodorised (**Step 3**), but sometimes it is done before the deodorising step (**Step 1**).

⁴Raoult's law states that above a mixture of solvents, $P_A = X_a P_A^o$, where P_A is the partial vapour pressure of the solvent, X_a is the mole fraction of the solvent in the solution and P_A^o is the vapour pressure of the pure solvent. Dalton's law states that when two or more ideal gases that do not react chemically are mixed together in a closed vessel, the pressure exerted by the mixture is the sum of the pressures each gas would exert if it alone occupied the volume at the same temperature.

Chemical modification

The main process used here is hydrogenation, which is used to harden oils, although other processes are also used.

Hydrogenation

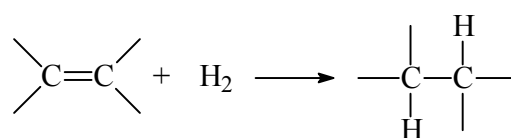
This is the process of adding hydrogen to a double bond in the molecule of a triglyceride. The reaction is carried out in the presence of a catalyst and results in an increase in the saturation of the molecule (i.e. a decrease in the number of multiple bonds) and a rise in the melting point.

The hydrogenation process can be taken to completion, in which case the product is a mixture of fully saturated glycerides and is wholly solid. This is carried out only in the case of coconut oil and with tallow to produce hard fats with special applications. More generally, hydrogenation is not taken to completion but to a pre-determined point where the required chemical and physical properties result. The reaction is controlled by the iodine value (see below) which is a measure of the degree of saturation of the fat.

Hydrogenation is usually carried out before bleaching (**Step 2**).

Increase in saturation

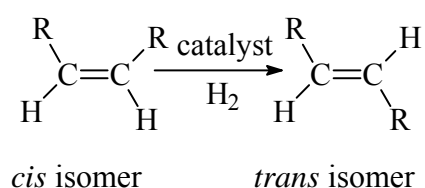
The reaction may be represented:



e.g. triolein + 3H₂ → tristearin

Isomerisation

During hydrogenation the unsaturated glycerides adsorb on the catalyst surface. Isomerization may occur, and the molecule may desorb without any addition of hydrogen. e.g.



The hydrogenation process is carried out in large vessels equipped with stirrers and cooling coils, the latter being essential as the reaction is exothermic. The catalysts used in the industry are usually reduced nickel catalysts supported on silica. Catalyst preparation is a highly skilled process and there are firms which specialise in the manufacture of these products.

Hydrogenation is used, for example, to convert coconut oil, which melts at 26°C, to more solid products which are used in biscuit fillings and ice-cream couvertures. Hydrogenation of a liquid oil can convert it to a solid fat which is used as an ingredient in polyunsaturated margarines. Hydrogenation increases the stability of oils by reducing the levels of

cis-unsaturated glycerides, by saturation and isomerization. The products of hydrogenation, the saturated glycerides and *trans* isomers are less prone to oxidation and polymerisation than the *cis*-polyunsaturated isomers.

Packaging

Due to the fact that fats and oils are complex mixtures and they exhibit the phenomenon of polymorphism (existing in several different crystalline forms) the solidification of fatty products presents several difficulties. The equipment for solidifying hot liquid fats is complex and diverse. Not only must the fat be solidified but it must also be produced in such a way that the texture is plastic. The most popular method for producing a glassy, plastic texture in fat is by means of a scraped-surface internal chilling machine. The most commonly used machine of this type is known as the "Votator". It is divided into chilling units and crystallizing and working units. The Votator is used to produce shortenings and table margarines and certain bakery margarines, but there are several other types of equipment used to produce margarines for specialized baking purposes.

PRODUCTS OF THE NEW ZEALAND EDIBLE OIL INDUSTRY

Bakery margarines

Especially formulated for the baking trade and used for cakes, short pastry and flaky pastry. These are based on tallow. Margarines are water-in-oil emulsions containing up to 16% water.

Table margarines (polyunsaturated)

These are prepared using suitable vegetable oils such as sunflower and soyabean. By blending hydrogenated fats and liquid oils a margarine is made which spreads straight from the refrigerator but does not melt sharply at room temperature. This margarine contains natural colouring, flavour, salt and skim milk.

Shortening

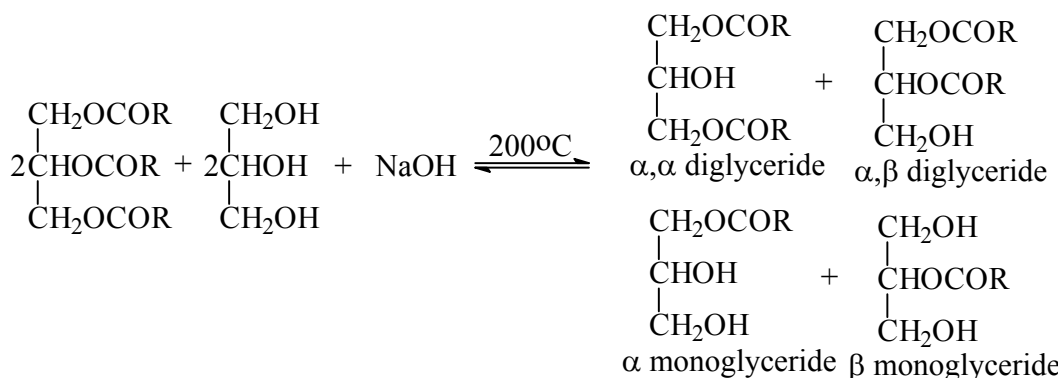
Dry fats usually well plasticized through a Votator so that they cream well. Used for mock cream, baking and frying.

Emulsified fats

Emulsifiers are compounds which affect the surface properties of fats. They are used especially in baking applications where they have a marked influence on the interaction of the fat with other food ingredients such as starch and protein. Emulsifiers are also used to stabilise water-in-oil emulsions such as margarine. In New Zealand the most common emulsifier used is known as GMS (glyceryl monostearate). This is prepared by transesterification in which hydrogenated stearine is reacted with glycerol and caustic soda, producing an equilibrium mixture of mono-, di- and triglycerides shown on the next page.

The reaction usually produces 35% monoglyceride, 5% diglyceride, 45% triglycerides and 12-15% of triglycerides. The catalyst is neutralised with citric acid.

GMS is effective as an antifoaming agent in the dairy industry and is excellent at maintaining bread in a fresh state after baking. There are many other emulsifiers used in the food industry but their chemistry and technology would require a separate chapter.



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Confectionery fats

These are based on hydrogenated coconut oils and are usually referred to by their melting points in degrees Fahrenheit.

Vegetable oils

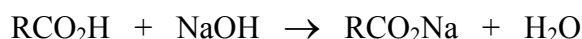
Sold as such for salad oils, frying, mayonnaise etc. A relatively recent addition to the New Zealand market is Canola oil from rapeseed grown in Otago.

THE ROLE OF THE LABORATORY

The primary role of the laboratory is quality control. The analytical methods below are used routinely to control the previously described processes and to maintain a constant check on product quality.

Free fatty acids (FFA)

All fat contains some free carboxylic acids, but these are removed by the refining process. The level of these free fatty acids is measured continuously to check the refining efficiency. The fat is mixed with alcohol (in which the carboxylic acids are soluble but the fat is insoluble) and the alcohol layer removed and titrated with sodium hydroxide. Carboxylic acids are weak acids so the resulting solution is alkaline at the end point because it contains the conjugate base of a weak acid. Therefore the indicator used is phenolphthalein ($pK_a = 9.6$), which changes colour at $\text{pH} > 8$. The reaction occurring is as follows:

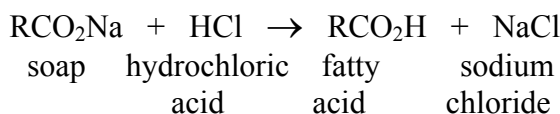


Soap test

Used to check whether all of the soap has been removed from the fat post-refining. Soap is titrated with hydrochloric acid using acetone as the solvent and bromophenol blue as the indicator.

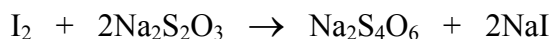
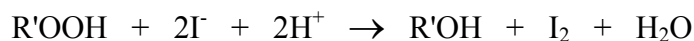
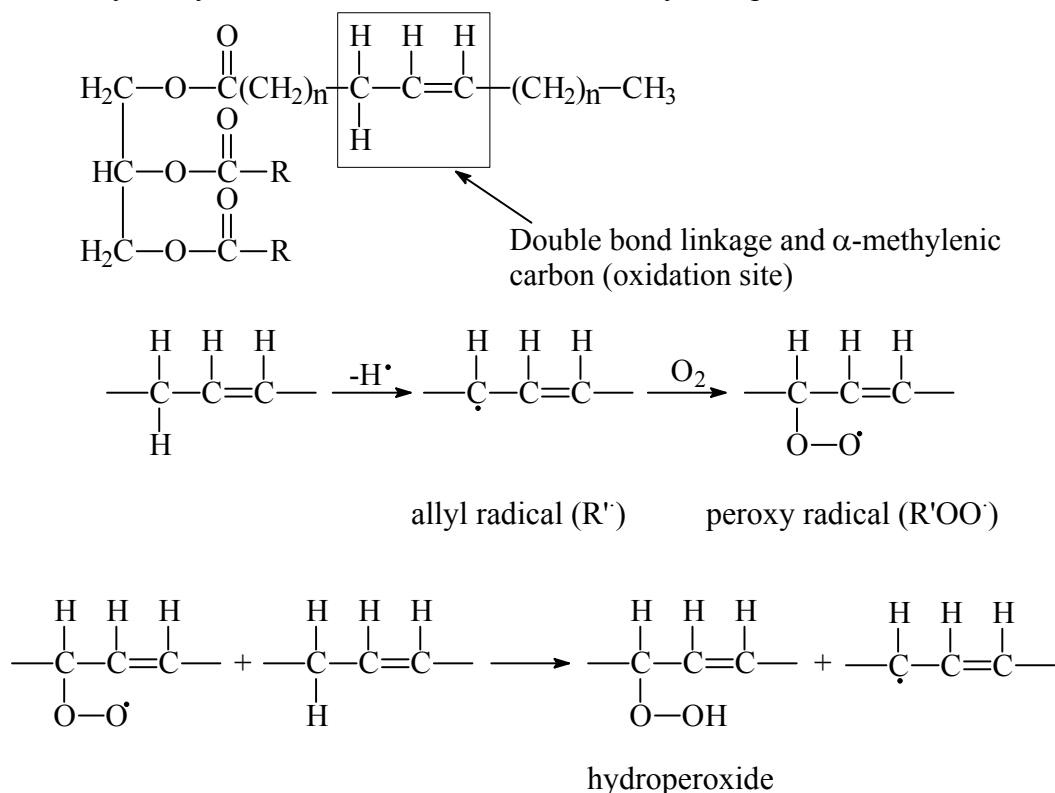
This reaction is effectively the reverse of the free fatty acid analysis. The soap test involves

titrating a weak base against a strong acid, so at the end point the solution contains a fatty acid and is acidic. Therefore, bromophenol blue ($pK_a = 4.2$), which changes colour in the pH range 3.0 -4.6, is selected as indicator.

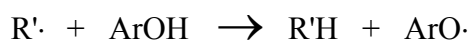


Peroxide value

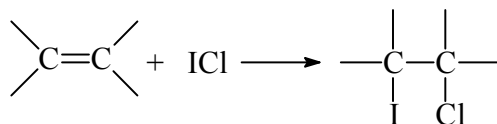
This is the analytical technique used to judge whether or not a fat is rancid. Oxidation is of particular significance in the edible oil and fat industry as it is the chief cause of flavour deterioration both in fats and in baked goods containing fat. One of the most common techniques for detection of the onset of rancidity depends on the reaction of oxidation products with iodide ions to produce iodine which is titrated with standard thiosulphate solution using starch as an indicator. Oxidation is a free radical reaction and is initiated by light and catalysed by transition metals. The reaction may be represented as follows:



Antioxidants such as substituted phenols delay the onset of rancidity in oils and fats by inhibiting or interrupting the free radical chain mechanism described above. They do this by transferring a hydrogen atom to the carbon-centred radical to give an unreactive phenoxy free radical:



This is the analytical technique used to monitor hydrogenation reactions. This test measures the number of double bonds in a fat, i.e. it is a measure of its degree of unsaturation. In practice, it is determined by the amount of halogen absorbed and is conventionally expressed as a weight of iodine absorbed per 100 parts by weight of fat. The method generally utilizes iodine monochloride⁵ as the addition reagent, the amount absorbed being calculated by titrating excess halogen with sodium thiosulphate.



Low resolution NMR of fats

As mentioned previously, fats are mixtures of solid and liquid glycerides and for the fat and oil processor to formulate blends of material for margarine and shortenings it is important to know the relative proportions of these solid and liquid components. Melting point determinations provide some data for this purpose but more precise data is obtained using the phenomenon of nuclear magnetic resonance spectroscopy (NMR). This technique makes use of the magnetic properties of hydrogen nuclei to investigate their environment in a sample. High resolution NMR is a means of investigating the chemical environment of the nuclei, and thus determining molecular structure. Broad-line NMR is concerned with the physical environment of the nuclei, and in particular with the arrangement and rates of motion of the nuclei. It will distinguish between protons in the liquid and solid state at a given temperature and it is this property which enables the technique to be of value to the fat processor.

ENVIRONMENTAL IMPLICATIONS

The edible oils and fats industry has a moderate to low impact compared to many others, but despite this many positive changes have been made in the last two decades. Many companies realise that their most severe impacts are often caused by inefficiency and waste of resources. It is in their financial interests to improve this situation, and also helps to market the company and its products to the public. We often have choice when selecting packaging, and environmental concerns are now very important in this process. Some examples of changes which have had a beneficial effect on the environment are shown in **Table 4**.

⁵Iodine monochloride (instead of iodine itself) is selected as reagent because the reaction occurring is an electrophilic addition. The iodine atom in the polar I-Cl molecule is more positive than the iodine atom in I₂, so the reaction proceeds faster. The addition reaction using I₂ itself takes place very slowly, and it is for this reason that the peroxide analysis mentioned earlier can be used. If the addition took place more quickly, the I₂ formed would add to the unsaturated fat and its concentration could not then be determined.

Table 4 - Environmental Impact Reduction in the Edible Oils and Fats Industry

| Before | After | Environmental Benefit |
|---|--|---|
| Heated fats stored in uninsulated tanks | Polyurethane foam or glass fibre insulation installed | Reduction in energy usage |
| Small, inefficient waste water treatment | Modern plants installed | Less spillage of oil and fat into sewers and waterways |
| Small batch process vessels | Larger semi-continuous process vessels | Reduction in energy usage |
| Dumping of spent nickel catalyst at public tips | Collection and sale of catalyst to recyclers | Removal of an avoidable environmental toxin from the dump |
| Direct cooling of malodorous process water using cooling towers | Indirect cooling of process water using heat exchangers linked to clean water cooling towers | Reduction of odour nuisance |
| Dumping of paper and cardboard waste | Collection and recycling | Slight reduction in environmental cost of paper production? |
| Most products sold in cartons, pails and drums | Many sold in bags, one tonne "pallecons", and in bulk tankers | Reduced packaging usage |
| Single use of water for cleaning plant & associated pipework | Recycled water for pre-rinsing steps | Reduction in water usage |
| Steam condensate overflowed to sewer while still hot | Condensate collected and used for heating and washing | Reduction in water and energy usage |

Written by Dr. L. Eyres (Abels Ltd.), updated by G. Webster (FoodChem Associates Ltd.).
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