Editor: Dr Matt Miller

Plant & Food RESEARCH
RANGAHAU AHUMĀRA KAI

www.plantandfood.com

Oxidation of food grade oils

What is oil oxidation?

Oil oxidation is an undesirable series of chemical reactions involving oxygen that degrades the quality of an oil. Oxidation eventually produces rancidity in oil, with accompanying off flavours and smells. All oil is in a state of oxidation - you cannot stop it completely - but there are ways to reduce it. Attempts should therefore be made to reduce oxidation at each stage of oil manufacture.

Oxidation is not one single reaction, but a complex series of reactions. When oil oxidises it produces a series of breakdown products in stages, starting with primary oxidation products (peroxides, dienes, free fatty acids), then secondary products (carbonyls, aldehydes, trienes) and finally tertiary products.

Oxidation progresses at different rates depending on factors such as temperature, light, availability of oxygen, and the presence of moisture and metals (such as iron). The type of oil also influences the rate of oxidation. Marine oils (including fish, mussel) are highly susceptible to oxidation due to the large number of polyunsaturated fatty acids (PUFA) they contain. These unsaturated fatty acids have reactive double bonds between their carbon atoms, whereas saturated fats have no double bonds so they oxidise more slowly.

How do we measure oxidation?

Measuring oxidation involves testing for the primary and secondary breakdown products. The most common test is peroxide value (PV). However, very rancid oils can have a reduced PV therefore the anisidine value (AV) and a Totox value are used to show the whole oxidation story (see Figure 1). Other measurements of oxidation are the acid value (free fatty acid FFA), thiobarbituric acid value (TBA) and iodine value (IV). Head space volatiles (smell) can also be tested using artificial nose technologies.

Peroxide value (PV)
Primary oxidation processes in oil mainly form hydroperoxides, which are measured by the PV. In general, the lower the PV, the better the quality of the oil. However PV decreases as secondary oxidation products appear (Figure 1). Most customers will require a PV of less than 10 in marine oils, but PV may need to be as low as 2, depending on the market.

The PV test is a good way to measure the amount of primary oxidation products in fresh oils. Oils with significant levels of peroxides may still be odourless if secondary oxidation has not begun. If oxidation is more advanced, the PV may be relatively low but the oil will be obviously rancid.

Anisidine value (AV)
The secondary stage of oxidation occurs when the hydroperoxides decompose to form carbonyls and other compounds, in particular aldehydes. These are what gives the oil a rancid smell, and they are measured by the AV. The lower the AV, the better the quality of the oil. Most customers will require an AV of less than 30 in marine oils but AV may need to be as low as 10, depending on the market.

The AV test is a good way to measure secondary oxidation products and should be used together with a primary test like PV.

Totox value
The Totox value is calculated by the formula AV + 2PV to indicate an oil's overall oxidation state. The lower the Totox value, the better the quality of oil.

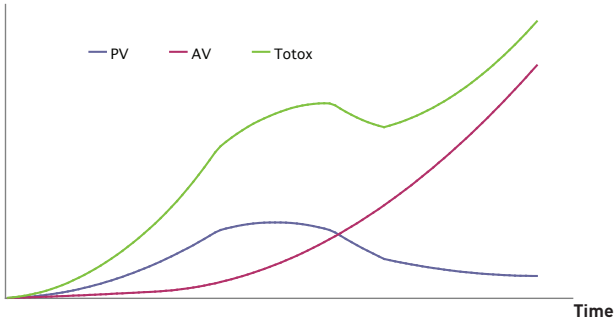

Figure 1 : The oxidation of oil over time as measured by peroxide value (PV), anisidine value (AV) and Totox value. Note: PV can decrease over time so AV and/or Totox calculation is needed to appreciate the whole oxidation story.

Acid value
The acid value (which is twice the free fatty acid (FFA) value) measures how many fatty acids (a component of oil) are cleaved from their parent molecules (triglycerides or phospholipids). Cleavage of a free fatty acid from a parent molecule shows hydrolytic breakdown and is often used in whole biological systems as an indication of stress. The test reveals enzymatic activity due to microorganisms in the raw material.

Thiobarbituric acid (TBA) value
The TBA value is a method to investigate secondary oxidative aldehyde products, usually in PUFA. The TBA test is unsuitable for complex food and biological systems. The test is not specific and can interact with other non-oil minor components (DNA, sugars).

Iodine value (IV)
The IV ("iodine adsorption value" or "iodine number" or "iodine index") measures the number of reactive double bonds present in an oil. A higher IV number indicates more double bonds in the sample and therefore that greater care will be needed to slow down oxidation. IV can range from 10 for coconut oil, 94-120 for rapeseed oil, and 117-143 for soybean oil, up to 185 for fish oil. IV is not a measure of quality but is an indicator of oil composition.

Preventing oxidation

Several different factors can be controlled to reduce the amount of oxidation that occurs in your oil. These include:

Temperature - the number one contributing factor of oxidation in oil. If possible reduce the temperature to the lowest possible throughout processing, shipping and manufacture.

Oxygen exposure (in the air) will be a catalyst for production of free radicals. To reduce oxidation, seal all containers with the smallest possible headspace, reduce the area of the oil in contact with air and/or cover the oil with an inert gas (like nitrogen) at all possible points.

Light (UV) can trigger the oxidative degenerative cascade. Reduce the exposure of the oil to direct light by using brown glass/plastic containers or black plastic bags.

Moisture in combination with these other factors can accelerate oxidation. If possible limit the amount of water in the oil to less than 0.2%.

Transition metals, in particular transition metals like iron and copper, can act as pro-oxidants. If possible, you may need to change equipment (e.g. no brass valves), limit time in contact with and/or remove transition metals from the oil to reduce oxidation.

Antioxidants (AOX) terminate the oxidation chain reactions and inhibit other oxidation reactions by being oxidised themselves. AOX do not stop oxidation, but do slow down the rate at which oxidation occurs.

There are many different ways AOX can reduce oxidation, so it is important to choose the right AOX for your application/product. AOX can be synthetic or extracted from natural plant sources. Common AOX are:

- Tocopherols (vitamin E)
- Carotenoids
  β-carotene
- Synthetic
  BHT- butylated hydroxytoluene
  BHA - butylated hydroxyanisole
  TBHQ - tert-Butylhydroquinone
  Propyl gallate
  Ethoxyquin
- Natural extracts
  Flavonoids
  Rosemary and spice extracts
  Tea catechins
  Seaweed
- Phospholipids
- Retinol (vitamin A)
- Preventive AOX
  Citric acid, phosphoric acid, ascorbic acid (vitamin C), ethylene diamine tetraacetic acid (EDTA), uric acid

FURTHER INFORMATION //

Dr Matt Miller
Plant & Food Research
300 Wakefield Quay
Port Nelson
Nelson 7010, New Zealand
tel: +64-3-539 1833
fax: +64-3-356 7049
millerm@crop.cri.nz