Natural preferences

Antioxidants play a vital role in preserving the quality of oils and fats products and extending their shelf life. While synthetic antioxidants are an effective solution, increased scientific and legal scrunity of them – along with consumer preferences – are leading to the growth of natural antioxidants *Ile Kauppila*

Oils and fats are susceptible to many different environmental and chemical effects that can affect the quality of the product. One of the most significant issues in oil production is oxidation and its prevention. When an oil product undergoes oxidation, its chemical properties change as it comes into contact with atmospheric chemicals, light, heat, and other factors.

"Oxidative rancidity plays an important role in the deterioration of fats and oils," says Kelly De Vadder, marketing manager of Kemin – an Iowa, USA-headquartered global ingredient manufacturer supplying speciality ingredients for human and animal health and nutrition, pet food, aquaculture, nutraceuticals, food technologies, crop technologies and textile industries.

"The most characteristic changes are the development of an unpleasant taste and smell, which become more obvious during the oxidation process. Additional changes in colour, viscosity, density and solubility also take place."

De Vadder explains that edible oils consist of approximately 96% triglycerides, composed of different fatty acids. Other compounds or groups of compounds, such as free fatty acids and phospholipids, are also present. Fatty acids are susceptible to oxidative processes resulting in a wide range of volatile and non-volatile degradation products.

"Therefore, one of the major challenges for the oil processing industry is to maintain the high quality of the product after processing," says De Vadder.

Antioxidants to the rescue

Antioxidants are chemicals that can be used to slow down the effects of oxidation. In edible oil production, they help in extending the shelf life and preserving the quality of oil and fat products. While there are other ways to reach similar effects, such as reducing the effects of sunlight by packaging oils in dark glass bottles, antioxidants play an essential part in maintaining the quality of edible oils and fats.

The chemistry of oxidation reactions is complex as it involves the effects of both heat and moisture in the final products.

Dipak Patil, from the Department of Chemistry at the Sardar Vallabhbhai Patel Arts and Science College, in a 2013 study '*Role of Antioxidants in Stability of Edible Oil*', divides fat deterioration into four main categories:

- **Hydrolysis** causes triacylglycerols in oils to form free fatty acids and glycerol, resulting in a "soapy" taste.
- **Rancidity** is an umbrella term used to cover a large number of unpalatable off-flavours generated through the auto-oxidation (or self-oxidation) of polyunsaturated fatty acids.
- **Reversion** is a type of flavour and odour degradation that is especially ▶

associated with unsaturated oils high in linoleic and/or omega-3 fatty acids, such as soyabean and fish oils.

- **Polymerisation** describes the cross-linking of unsaturated fats between two carbon atoms.

What these chemical processes have in common is that they are all chain reactions that have similar end results – the formation of so called free radicals in the oil product.

"Antioxidants interrupt these oxidation chain reactions in order to enhance the oxidative stability of the oil or fat," De Vadder says. Antioxidants present in the oil product give away their hydrogen atoms, which bond with the free radicals generated by oxidation, thus giving the product a longer shelf life and making it last longer during cooking processes, especially frying.

Classification of antioxidants

Antioxidants can be classified in several ways. Based on their mechanism of action, they can be divided between primary and secondary antioxidants. Primary antioxidants are free radical scavengers that delay the initiation stage or interrupt the propagation step of auto-oxidation, while secondary antioxidants slow down the rate of oxidation reactions that are already happening.

According to Mostafa Taghvaei and Seid Mahdi Jafari in a 2013 study '*Application and Stability of Natural Antioxidants in Edible Oils in Order to Substitute Synthetic Additives*', antioxidants can be further divided into two main groups – synthetic and natural antioxidants.

Synthetic antioxidants include chemicals such as butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), propyl gallate, and tertiary butylhydroquinone (TBHQ), out of which the latter is possibly the most widely used. These antioxidant products are, as their name implies, man-made through various chemical processes.

"These synthetic antioxidants are chemically synthesised petroleum-based products used primarily to retard lipid oxidation in order to preserve and stabilise the refined oils and fats within a food product," explains De Vadder. "On the other hand, natural antioxidants – such as tocopherols – are derived from a natural source. Most of the powerful natural antioxidants are found in plants."

Tocopherols are the most commonly found antioxidants in nature and they are also the most widely used antioxidants in edible oils. Other natural antioxidants include tocotrienols, squalene,

Essential oils and extracts from various plants, such as rosemary, are used to produce natural antioxidants

phytosterols, phospholipids, corn oil or rice bran oil-derived steryl ferrulates, and sesame oil lignans such as sesamol, sesamin and sesamolin.

Additionally, essential oils and other extracts from various plants – such as citrus peel, grape seed, green tea, olive, oregano, pomegranate, rosemary, sage and thyme – have in recent years been studied and brought into the marketplace. For instance, Kemin is the world's first and – at the time of writing – only SCS Global Services-certified producer of rosemary-based natural antioxidants for edible oils.

Markets prefer the natural

De Vadder tells *OFI* that, in recent years, there has been a push in the markets towards replacing synthetic antioxidants with natural free radical scavengers.

"Even though they are effective antioxidant solutions in edible oils, retailers and consumers would like to avoid synthetic antioxidants, such as TBHQ and BHA," she says.

The reasons for this market trend can most likely be found in increased scientific and legal scrutiny directed at synthetic antioxidants, in addition to consumers preferring natural products. Synthetic antioxidants are, as De Vadder says, efficient, but Taghvaei and Jafari note that despite rigorous safety tests and legal concentration limits in final food products, there are still doubts about their long-term health effects.

Some studies, as cited by the researchers, have found that BHT, for example, had adverse carcinogenic effects on the livers, kidneys and lungs of rats, while others have found that BHA and BHT are cytotoxic in rodents. However, they also point out that these effects were observed only at high concentrations that far exceed those permitted in human foods under any legislation. Nonetheless, the researchers conclude that it seems "logical" to replace synthetic antioxidants with natural ones if there is any doubt of their safety.

A natural challenge

But natural antioxidants are not perfect either. In a 2018 study titled '*Enhancing Oxidative Stability and Shelf Life of Frying Oils with Antioxidants*', Namal Senanayake points out that tocopherols exhibit the highest antioxidant activity when their concentration in the product is relatively low. At high concentrations they may even behave as pro-oxidants. Additionally, he states that the efficacy of natural tocopherols that have been added to oils during the frying process is debatable. However, when tocopherols are combined with the appropriate emulsifiers and speciality oils, they can be very effective in delaying the formation of total polar compounds (TPC) and di- and polymerised triglycerides (DPTG) and as such prolong the frying life of oils.

There is also the issue that only a

handful of natural antioxidants are available on the market. These include rosemary extract, mixed tocopherols, sage extract and green tea catechins.

The working mechanisms and effect of some natural antioxidants not yet on the market are not perfectly understood, and therefore more research is needed in the field. There is also the issue of money – while some natural antioxidants might be effective, they may not be economical to produce at mass scale. Taghvaei and Jafari state that this is especially the issue with some medicinal plants and their essential oils.

Furthermore, De Vadder adds that the production of antioxidants is not simple, and there are questions that must be answered before a producer can start up operations.

"Antioxidants come in all forms and shapes. They are not always directly applicable in a food system and, for this reason, customers often require tailor-made solutions to match their specific needs. These can range from changing liquid plant extracts to dry products (or vice versa), making oil soluble antioxidants water dispersible so that they can be applied to a water or a brine, or enable water soluble antioxidants to be applied into lipids.

"Furthermore, many antioxidants that work in synergy with each other are also insoluble with one other. To combine these water- and oil-soluble antioxidants in a physically stable blend, producers like Kemin must find the optimal ratio of specific emulsifiers that can hold these products together," explains De Vadder.

Legislation issues

Legislation can sometimes become an issue for antioxidant producers as well. As mentioned, the amount of synthetic antioxidants added into food products are strictly regulated. "Various regulatory organisations, including the US Food and Drug Administration (FDA), have placed tolerance limits on the amounts of synthetic antioxidants that can be added to fats and oils (typically below 200ppm)," wrote Senanayake.

Natural antioxidants are also subject to sometimes restrictive laws. For example, the 16 December 2008 Regulation (EC) No 1333/2008 of the European Parliament and of the Council on food additives requires all added antioxidants to be declared on food packaging by their category with either their name or E-number.

However, this requirement has caused confusion among producers due to the fact that some natural antioxidants

Although packaging oils in dark glass bottles can reduce the effects of sunlight on oil degradation, antioxidants also play an essential part in maintaining oil quality

can be used as either flavourings or antioxidants – or both. In an attempt to clarify the situation, the European Flavour Association (EFFA) released on a best practice guidance document on 31 May 2019 stating that what needed to be printed on the food label depended on the primary role of the additive.

More precisely, the EFFA stated that "if the primary intended use is to impart/modify the flavour of the food and the technological effect is secondary, then its use may be considered as 'not being intended for a technological function'. However, if the ingredient has been selectively extracted/enriched to obtain technologically active constituents and its main use is to deliver a technological function other than imparting/modifying the odour and/or taste in the final food, then it is considered an additive according to the Food Additive Regulation (EC) No 1333/2008." EFFA also made it the responsibility of the flavouring manufacturer to provide all the necessary information to enable the user of the additive to make the right labeling choices.

De Vadder says the statement has raised a lot of questions and that it requires clarification. "It is, however, clear that plant extracts should be reviewed on a case-by-case basis, taking in account all criteria of the food additive definition. Ingredients with multiple properties need to be assessed in their specific context of use."

Markets looking up

Still, De Vadder and Kemin are positive about the future. She says that the markets are looking up and demand for antioxidants – particularly natural ones – will continue to grow.

"This growth is driven by the growing demand of processed and convenience food. Furthermore, the industry is moving away from palm oil and replacing it with alternative vegetable oils. However, these oils are less saturated, which makes them more susceptible towards oxidation. In this case, antioxidants would be required to ensure the final product has a similar oxidative stability and shelf life."

Market research companies agree with Kemin's projection. According to Mordor Intelligence, key market players in the global food antioxidant sector – including Archer Daniels Midland Co, BASF, Barentz Group, Camlin Fine Sciences, Frutarom, EI Du Pont De Nemours and Co, Eastman Chemical Co, Kalsec, Kemin Industries, and Koninklijke DSM NV – can expect growth at CAGR 6% between 2019 and 2024.

North America and Europe are expected to grow the fastest due to easy availability of food and heavy government food subsidisation, especially in the USA. In Asia-Pacific, the major share of the market is held by Australia, China, India, and Singapore. Product development by the key companies in this region will trigger further market growth, Mordor Intelligence projects.

All in all, De Vadder concludes that antioxidants will continue to be needed and the industry is ready to tackle new challenges. "The effects of all processing steps on the quality of lipids in the final application are considerable. All these parameters influence the oxidative stability. Antioxidants need to be added to increase food lipid stability during and after processing. For sure, the future will evolve with new technologies, packaging solutions and ingredients to extend the shelf life," she says. ●

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