3-MCPDE & GE

Tackling the formation of 3-MCPDEs and GEs in edible oils involves following good practices – during cultivation, harvest and transport of oil fruits and seeds, to refining and post-refining *Serena Lim*

Edible oils are produced from various commodities – including fruits, seeds, nuts and fish – and their refining at 200°C or higher can produce carcinogenic 3-monochloropropane-1,2-diol esters (3-MCPDEs) and glycidyl esters (GEs).

Humans are exposed to 3-MCPDEs and GEs from consuming refined oils or food products containing refined oils, such as infant formula, dietary supplements, fried potato products and fine bakery wares.

The occurrence of 3-MCPDEs and GEs in food oils was first reported in the mid-2000s and various regulations and recommendations have since been introduced, setting maximum limits for these process contaminants.

The EU set maximum levels for GEs in February 2018 (*see box, pg20*), while the European Food Safety Authority (EFSA) set a tolerable daily intake for 3-MCPDs in January 2018 of $2\mu g/kg$ body weight per day (0.002ppm/kg body weight).

The Codex Alimentarius Commission (CAC) is also expected to adopt a new Code of Practice (CoP) in July on how to prevent and reduce 3-MCPDE and GE formation in refined oils and foods made with refined oils.

The EFSA has found that palm oil and palm fats have the highest levels of 2-MCPD, 3-MCPD (including esters) and GEs among vegetable oils.

Formation factors

Most unrefined oils do not contain detectable levels of 3-MCPDE or GE but different types of unrefined oils have different capacities to form them during the deodorisation step of edible oil refining, according to the CAC draft CoP.

The processing conditions during refining also have an important effect on the 3-MCPDE and GE formation.

"For vegetable oils, factors that contribute to the capacity to form 3-MCPDE and GE during refining include climate, soil and growth conditions of source plants or trees, their genotype, and harvesting techniques. These factors all affect the levels of precursors of



Mitigation str

3-MCPDE and GE, such as acylglycerols and chlorine-containing compounds," the draft CoP says.

"3-MCPDE forms primarily from the reaction between chlorine containingcompounds and acylglycerols like triacylglycerols (TAGs), diacylglycerols (DAGs) and monoacylglycerols (MAGs). GE forms primarily from DAGs or MAGs."

Some chlorinated compounds are also precursors for 3-MCPDE formation. Oil-producing plants or trees absorb chloride ions (in the form of chlorinated compounds) during growth, from soil (including from fertilisers and pesticides) and from water. These chloride ions are converted into reactive chlorinated compounds, leading to the formation of 3-MCPDE during oil refining, the draft CoP says.

Oil fruits and seeds contain the enzyme lipase. Lipase activity increases when fruit matures, while the lipase activity in seeds remains stable. Lipase interacts with oil from mature fruits to rapidly degrade TAGs into free fatty acids (FFAs), DAGs, and MAGs. The effect of lipase in seeds that are appropriately stored is negligible.

Mitigation strategies

Because 3-MCPDEs and GEs are formed via different mechanisms, varying mitigation strategies are needed to control their formation.

"GE is generally easier to mitigate

than 3-MCPDE because its formation is directly associated with elevated temperatures, with formation beginning at about 200°C and becoming more significant at temperatures above 230°C," the draft CoP says.

GE is formed mainly from DAGs and does not require the presence of chlorinated compounds. Oils can be deodorised at temperatures below 230°C to avoid significant GE formation. However, it is not practical to decrease deodorisation temperatures below the threshold that would lead to 3-MCPDE formation (160-200°C), as that could affect the quality and safety of the oil.

The CoP says that although 3-MCPDE and GE are primarily produced during deodorisation, mitigation measures can be applied across the edible oil production chain, from agricultural practices (such as cultivation, harvesting, transporting and storing of oil fruits and seeds), to oil milling and refining (crude oil production and treatment, degumming/bleaching and deodorisation), as well as to post-refining measures (additional bleaching and deodorisation and the use of activated bleaching earth).

"Where possible, it may be best to remove precursors at the earlier stages of processing, to minimise the formation of 3-MCPDE and GE.

"In concert with mitigation of 3-MCPDE and GE, it is also important to consider

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the overall impacts on the quality of refined oils and oil-based products, including properties such as smell and taste, FFA profiles, stability attributes, levels of nutrients, and the removal of contaminants such as pesticides and mycotoxins."

Recommended practices

Producing edible vegetable oils involves several major steps: cultivating, harvesting, transporting and storing the fruits and seeds for further processing; palm oil milling where fruit is sterilised and crude oil is extracted; oilseed crushing where oilseeds are cleaned, ground, steamed and crude oil is extracted; and refining of the crude oils.

Producing edible fish oils involves harvesting the fish, steam cooking, dewatering/wet reduction (which involves pressing the liquor, separating the oil and water, and optionally, water washing the oil), and refining of the crude oils.

There are two main types of edible oil refining. Chemical refining consists of degumming (removal of phospholipids); neutralisation (addition of hydroxide solution to remove FFAs through formation of soaps); bleaching (using clays) to reduce colours and remove remaining soaps and gums, trace metals, and degradation products; and deodorisation (a steam-distillation process carried out at low pressures, 1.5-6.0 mbar, and elevated temperatures, 180-270°C) to remove FFA, colours, and volatile compounds, including certain contaminants.

Physical refining involves degumming, bleaching, and deodorisation (which occurs at higher temperatures than chemical refining), as it does not have a neutralisation step. While several factors influence the selection of physical refining, it is typically conducted on oils containing low levels of phospholipids.

Good agricultural practice

The CoP says that when it comes to palm oil and planting new trees, farmers should consider selecting plant varieties with low lipase activity in oil fruits, as low lipase activity is one factor that can reduce formation of FFAs and acylglycerol precursors.

"During cultivation of oil plants or trees, farmers should minimise the use of substances such as fertilisers, pesticides, and water that have excessive amounts of chlorine-containing compounds, in order to reduce chlorine uptake by the fruits and seeds. Non-chlorinated sulfate fertilisers could serve as an alternative to chlorine-containing fertilisers."

Farmers should also harvest oil palm fruits when they are at optimal ripeness, minimise handling of the fruits to reduce bruising and prevent formation of FFAs, and avoid using damaged or overripe fruits, which may be associated with higher 3-MCPDE and GE formation.

Oil palm fruits should also be taken to oil mills as soon as possible.

Oil milling and refining Crude oil production and treatment

The draft CoP says processors should consider storing oilseeds for milling at cool temperatures (below 25°C) and dry conditions (optimally under 7% moisture content) to help ensure low levels of lipase.

Once oil palm fruits are at the mill, processors should sterilise them immediately (preferably within less than two days of harvesting) at temperatures at or below 140°C to inactivate lipases (with temperatures varying depending on the sterilisation method). Fruits may be washed before sterilisation to remove chlorine precursors. For oilseeds, processors should clean, grind and heat to inactivate lipases.

"Processors should consider washing crude vegetable oil with chlorine-free water to remove chlorine-containing compounds. They should avoid using residual vegetable oil recovered from solvents or additional extractions, as this oil tends to have higher levels of precursors, such as DAGs and chlorinecontaining compounds."

Processors should also assess precursors in batches of crude vegetable oils or fish oils (such as DAGs, FFAs or chlorine-containing compounds) to adjust refining parameters and target appropriate mitigation strategies depending on the type of vegetable oil or fish oil being processed and processing conditions.

"Preferentially refining crude vegetable oil or fish oil with low concentrations of precursors can produce finished oils with lower levels of 3-MCPDE and GE."

Degumming

During the degumming stage, processors should use milder and less acidic conditions (either degumming with a low concentration of phosphoric, citric, or other acids or water degumming) to decrease 3-MCPDE in vegetable oils or fish oils. The concentration of acid depends on the quality of the crude vegetable oil or fish oil. Care should be taken to remove sufficient concentrations of phospholipids and acid to ensure quality.

Lowering the degumming temperature may help to reduce formation of 3-MCPDE precursors in vegetable oils. However, the degumming temperature will depend on numerous factors including the type of vegetable oil.

Neutralisation

Using chemical refining (neutralisation) as an alternative to physical refining can help remove precursors (such as chloride) and reduce FFAs, which may allow for lower deodorisation temperatures in vegetable oils or fish oils. However, chemical refining can lead to excessive oil loss (especially for palm oil due to higher FFA levels) and may have a greater environmental impact than physical refining.

Bleaching

Using greater amounts of bleaching clay may reduce formation of 3-MCPDE and GE in all vegetable oils and fish oils. However, bleaching clays that contain significant amounts of chlorine-containing compounds should be avoided.

The use of more pH-neutral clays reduces the acidity and potential to form 3-MCPDE in palm oil, some seed oils and fish oil.

Deodorisation

The draft CoP says processors should consider conducting deodorisation of vegetable oils and fish oils at reduced temperatures to decrease formation of GE. For example, it has been suggested

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 that deodorisation should be conducted at 190-230°C for vegetable oils and less than 190°C for fish oils. The temperature will vary depending on the residence time of the oil.

As an alternative to traditional deodorisation, processors can conduct dual deodorisation of vegetable oils and fish oils (2-stage deodorisation) to reduce the thermal load in oil and decrease formation of GE, with a smaller reduction in 3-MCPDE. This includes both a shorter deodorisation period at a higher temperature and a longer deodorisation period at a lower temperature.

"Consideration needs to be given to parameters such as temperature, vacuum pressure, time and variations in equipment design and capability. Also, additional post-processing may be required to reduce levels of GE."

Use of a stronger vacuum can help

evaporate volatile compounds due to the increased steam volume and rate of stripping, contributing to decreased deodorisation temperatures and reduced formation of GE, and to a lesser extent 3-MCPDE, in vegetable and fish oils.

Short-path distillation (in place of deodorisation) has been shown to reduce the thermal load and formation of esters in fish oil, contributing to lower amounts of 3-MCPDE and GE in comparison to conventional deodorisation.

Short-path distillation enables gentle removal of volatile compounds at relatively low temperatures. This is accomplished through reduced pressure, where the boiling point of the compound to be separated is lowered and there is increased efficiency due to the short distance between the evaporator and the condenser surface.

However, additional post-processing

EU considers 3-MCPDE provisions and GE changes

The EU enacted Regulation (EU) 2018/290 on 26 February 2018 to set maximum limits for **GEs** in vegetable oils and fats, and products containing them, in Section 4:

- **4.2.1** Vegetable oils and fats placed on the market for the final consumer (maximum 1,000 μ g/kg)
- **4.2.2** Vegetable oils and fats for the production of baby food and processed cereal-based food for infants and young children (maximum 500µg/kg)
- **4.2.3** Powder infant formula, follow-on formula and foods for special medical purposes (75µg/kg until 30 June 2019, then 50µg/kg from 1 July 2019)
- **4.2.4** Liquid infant formula, follow-on formula and foods for special medical purposes (10µg/kg until 30 June 2019, then 6µg/kg from 1 July 2019)

Additional GE provisions are currently under discussion in working groups with member state experts, according to Frans Verstraete of the European Commission Health and Consumers Directorate-General. They include adding fish oil and oils from other marine organisms to the scope of Sections 4.2.1 and 4.2.2 above; and adding young child formula to sections 4.2.2, 4.2.3 and 4.2.4.

Also under discussion are maximum levels for **3-MCPD and 3-MCPDEs**. There are two proposed levels for vegetable oils and fats and fish oils for the final consumer, or for use as food ingredients:

- 1,250µg/kg for unrefined oils, refined oils and fats from coconut, maize, rapeseed, olives (except olive pomace oil) sunflower, soyabean and palm kernel and mixtures of oils and fats from this category only.
- 2,500µg/kg for other refined vegetable oils (including live pomace oil), fish oil and oils of other marine organisms and mixtures of oils and fats from this category only.

For mixtures of oils and fats from the two different categories, the oils and fats used as ingredients must comply with the maximum level set for each oil and fat. If the quantitative composition of the mixture is not known, then the sum of 3-MCPDs and 3-MCPDEs should not exceed $2,500 \mu g/kg$.

- For vegetable oils and fats destined for baby food and processed cereal-based food for infants and young children and young child formulas, a level of 750µg/kg is being considered.
- For infant formula, follow-on formula and foods for special medical purposes intended for infants and young children (powder) and young child formula, the level proposed in $125 \mu g/kg.$
- For infant formula, follow-on formula and foods for special medical purposes intended for infants and young children (liquid) and young child formula, the level proposed is 15µg/kg.

using mild deodorisation is needed to address sensory considerations after short-path distillation

Post-refining treatment

Additional bleaching and deodorisation following initial bleaching and deodorisation has been shown to achieve lower levels of GE in refined palm oil. (The second deodorisation should occur at a lower temperature than the first deodorisation.)

Application of activated bleaching earth during post-refining has been shown to reduce GE in refined vegetable oils.

Use of short-path distillation (at <1mbar pressure and 120-270°C temperature) on bleached and deodorised vegetable oil can reduce acylglycerol components and levels of 3-MCPDE and GE.

Treatment of refined medium chain triacylglycerol (MCT) oil with fatty acids and a cation counterion, such as an alkali metal, as well as one or more bases, converts 3-MCPDE to MAGs, DAGs and TAGs, and GEs to DAGs.

Food products Oil selection

Selecting refined vegetable oils and fish oils with low levels of 3-MCPDE and GE (either through natural occurrence or through application of mitigation measures) results in lower levels of 3-MCPDE and GE in finished products containing these oils.

For example, variation in levels of 3-MCPDE and GE in infant formula has been observed and selection of oils low in 3-MCPDE and GE can result in infant formulas with lower 3-MCPDE and GE levels.

However, manufacturers also may have to consider quality or compositional factors. For example, for infant formula, refined oils are selected by manufacturers to ensure these products meet compositional criteria.

Processing modifications

Reducing the amount of refined vegetable oils and fish oils used in finished products may be an alternative to reduce the levels of 3-MCPDE and GE in the finished product. However, this could impact the organoleptic or nutritional qualities of the finished products. Use of refined vegetable oils themselves during frying does not contribute to formation of additional 3-MCPDE and GE, but the formation of additional 3-MCPDE during frying may result from the type of food that is fried, such as meat and fish products.

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