

# Removing MCPDs and GEs from edible oil

**Bleaching earths alone cannot provide a complete solution to the formation of 3- and 2-MCPDs and GEs in edible oils. Preston Shanks explains how different oil types and their quality can affect the level of these potentially carcinogenic compounds and the role that heat- and acid-activated bleaching earths can play**

**T**he reduction of 3-MCPD esters and glycidic esters (GE) is a high priority for the oils and fats industry. On 26 February 2018, the EU enacted Regulation (EU) 2018/290, amending the earlier Regulation (EU) 1881/2006.

The amendment sets maximum limits for glycidyl fatty acid esters or GEs, with the level for edible oils and fats set at 1ppm (see *annex to regulation EC No 1881/2006*). It covers:

- Vegetable oils and fats placed on the market for the final consumer (maximum 1,000µg/kg)
- Vegetable oils and fats for the production of baby food and processed cereal-based food for infants and young children (maximum 500µg/kg)
- 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)
- 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)

In addition, the European Food Safety Authority (EFSA) published the “*Update of the risk assessment on 3-monochloropropane diol (3-MCPD) and its fatty acid esters*” in January 2018. In its scientific assessment, the EFSA set a tolerable daily intake (TDI) of 2µg/kg body weight per day (0.002ppm/kg body weight) for free 3-MCPD.

The EFSA found palm oil and palm fats to have the highest levels of 3-MCPD, 2-MCPD (including esters) and GEs. Roughly 6M tonnes of tropical

fats are refined across Europe, with 90% refined in the EU. Given the EFSA findings, it is likely to be a question of when, rather than if, the EU regulates 3- and 2-MCPDs as well. Palm oil is found to have 3-MCPD esters in its refined oil and the esters are also present in soft oils. Glycidol is considered a genotoxic carcinogenic compound and 3-MCPD is a non-genotoxic carcinogen.

To solve or comply with this issue of carcinogenic compounds, each step from the plantation to the final refined bleached deodorised (RBD) product must be considered. GEs are produced during the deodorising stage from partial glycerides, such as diacyl glycerides (DAG) at temperatures in excess of 230°C. Bleaching earth does not affect the production of GE but does remove it from RBD palm oil.

A post-deodorising bleaching step adds significant cost incurred by effectively double-refining the RBD oil. This route also means that during the required additional deodorisation step, GE may again form and would have to be monitored. Post-deodoriser bleaching with activated bleaching earth can also convert GEs to monoglyceride by acid catalysis (there is no reduction of 3-MCPD during this bleaching step).

The alternative is to deodorise at a lower temperature to prevent the production of GEs. However, this has concerns of free fatty acid (FFA) reduction, organoleptic quality and stability criteria. Adding additional refinery capacity would overcome any production bottleneck but at a cost.

Caustic refining remains an expensive choice with high refinery losses and greater environmental considerations of soap-stock treatment. As far as ▶



THE EU SET MAXIMUM LEVELS FOR GE CONTENT IN FOOD IN FEBRUARY AND IT IS LIKELY THAT IT WILL ALSO ENACT REGULATIONS FOR 3- AND 2-MCPDS, BASED ON FINDINGS BY THE EUROPEAN FOOD SAFETY AUTHORITY (HEADQUARTERS PICTURED ABOVE)

- ▶ GE is considered, a lower deodorising temperature is the preferred route. For 3-MCPD, the EU awaits the outcome of further assessments of 3-MCPD and its fatty acid esters.

### 3-MCPD precursors

The mitigation of 3-MCPD depends on several criteria, including production of crude palm oil (CPO) from the fruit bunches, the design of the refinery, the oil/fat in question, processing criteria and the type of bleaching earth used. All have their parts to play.

The chlorine precursors leading to the formation of 3-MCPD esters are reported as inorganic chlorine from water treatment, including ferric chloride, fertilisers, acid conditions that give rise to organochlorine compounds in the CPO, and hydrochloric acid (HCl)-activated bleaching earth containing chloride. A low partial glycerides content assists in mitigating 3-MCPD formation.

GEs may be formed from DAG during deodorising at high temperatures of more than 230°C. CPO typically has a DAG content greater than 5% within a range of 5-12%. Reports of no apparent correlation between mono acyl glycerides (monoglycerides) and 3-MCPD formation leave the DAG as a source of

3-MCPD formation during deodorising. A high FFA content will also increase levels of 3-MCPD esters during deodorisation.

GEs can also be formed from MCPD mono-esters but due to the almost total lack of this mono-ester compound and low conversion rates (approximately 20%) they are not discussed further. CPO with a low DAG content (max 4%) and low FFA (<1.5%) is desirable to assist in reduced 3-MCPD formation, but this level of DAG and FFA in the CPO is difficult to guarantee.

### Bleaching earth considerations

Acid activated bleaching earths have traditionally been the most effective products in the bleaching of edible oils and fats. Furthermore, acid activated calcium montmorillonite (bentonite) clay products have been dominant in this area.

Other natural activated bleaching earths (NABEs), such as attapulgite and sepiolite clays, are alternatives. They are not acid activated but may also be utilised in the bleaching process.

Acid activated clays are capable of bleaching the most challenging of oils but, during the 1980s, attapulgite/sepiolite heat activated clays were increasingly promoted. These clays were not acid

activated with mineral acid but were capable of heat activation, which increased the surface area.

Whilst effective on good quality oils, the heat activated NABE products were found to be less effective with the more challenging edible oil applications, especially in respect to colour removal in general and chlorophyll more specifically.

Acid activated clays provide a large surface area ranging from 160m<sup>2</sup>/g to more than 300m<sup>2</sup>/g. The large surface area accommodates acid sites and pores of varying sizes and volumes. These sites greatly contribute to the bleaching performance. The optimum pore sizes and volumes are more specifically located within a particle size distribution band, which is responsible for conducting the main bleaching process.

Natural clays have a more neutral pH with a much smaller surface area of around 60-160m<sup>2</sup>/g, along with reduced quantities of sites with optimum pore sizes and volumes. Although these natural clays exhibit reduced pore size, pore volumes and surface area, they have proved capable in bleaching a range of edible oils, notably in the physical refining of CPO to a colour specification, provided the CPO is of good quality.

With improvements seen in CPO production in recent decades and refineries adopting improved oil pre-treatment and refining techniques, natural bleaching earths are effective in bleaching good quality pre-treated edible oils and fats.

When considering 3-MCPD mitigation, natural activated clays can be useful due to their neutral pH and, although having a reduced surface area, can be adequate in terms of overall colour removal. Where CPO quality is lower than desired, acid activated earth remains the preferred choice as it is consistently more effective at the same or reduced dosage levels relative to natural bleaching clays.

Edible oil refineries processing a mixture of soft and tropical oils and fats prefer acid activated clays, due to their ability and flexibility to bleach a variety of oils and fats and, where the crude oil proves challenging due to higher levels of oxidative damage, FFA and trace metals.

For soft oils in general – and rapeseed oil containing chlorophyll – acid activated earths are also preferred due to their higher affinity for chlorophyll. There has been increased use of NABEs at refineries processing palm oil via the physical refining route, which requires CPO of good, consistent quality.

Some of these refineries also have a second bleaching earth silo for acid activated clay, used to achieve specification when the CPO is difficult to bleach with natural clay.

### Acid activation considerations

Acid activated bleaching earth has been the main bleaching earth utilised in refineries and is produced from high purity calcium montmorillonite clays. This clay is capable of activation to consistently high levels when using mineral acids, such as sulphuric or hydrochloric acid (HCl), in the activation process. The activated clay is subsequently water washed to remove salts and free acidity.

Acid activation increases the surface area with the aluminium and iron salts being substituted with hydrogen cations, increasing silicic acidity. It is these silicic acid sites that are responsible for bleaching the colour of edible oils and fats.

However, traditionally acid activated clay impacts ▶

- ▶ on 3-MCPD, especially when considering clays based on HCl activation that have both a residual chloride value and a relatively high free acidity (approximately 0.8%).

The acidity and chloride from HCl activated bleaching earth has been demonstrated to increase the 3-MCPD level. When palm oil is bleached with HCl activated clay, the MCPD ester content increases together with chloride levels. With chloride levels of 7.1mg/100g, the MCPD produced after heating the bleached palm oil to 220°C is 2.6ppm, which rises to 3.9ppm when the bleaching earth has a chloride content of 14.20mg/100g.

At a chloride dose of 67.5mg/100g, the MCPD content increases to 9.7ppm. When bleaching the same oil under the same conditions with natural bleaching earth containing zero chloride, the MCPD increases to just 1.7ppm.

Today, acid and heat activated clays are being considered with the aim of reducing 3-MCPD formation by acting to remove or reduce the chlorine precursors during the bleaching step, which lead to the formation of 3-MCPD during the deodorising process at temperatures above 180°C.

Natural raw clays are mixtures of different clay types. For example, attapulgite may contain calcium montmorillonite. This means the overall bleach effect and mitigation of 3-MCPD production will depend on the clay and degree and type of activation.

By successfully reducing the precursors during the bleaching step it may be possible to mitigate the formation of 3-MCPD to low ppm levels, with less than 1ppm being reported in RBD palm oil when using an activated clay with a low free acidity, large surface area, good pore size and pore volumes. The acidity displayed by this clay is pH 3-4, meaning it is acidic, but there is little buffer action.

This acidity, when expressed as free titratable acidity, is very low at 0.05-0.1% expressed as sulphuric acid. A clay with a pH of 3-4 may also have a much higher free acidity, for example 1.2% expressed as sulphuric acid. When selecting an acid activated clay type for 3-MCPD mitigation, the low free acidity value may be worth greater consideration over the actual pH value.

The nature of the raw clay to be activated has a great influence on the colour and oxidative stability of the RBD oil.

The bleaching earth has the challenge of removing the precursors leading to the formation of 3-MCPD whilst at the same time possessing

enough bleaching ability to reduce colour to the specification required in, for example, the RBD palm oil.

Bleaching with normal quantities of acid activated earth (typically 0.5%-1.5%) has been shown to have little effect on reducing 3-MCPD, but reports that larger amounts of acid activated bleaching earth reduced the 3-MCPD formation indicate that the bleaching earth is removing or reducing the 3-MCPD precursors in the bleaching step.

Selecting a bleaching earth that is acid activated, providing a large surface area for bleaching whilst at the same time being low in free acidity, will assist in chlorine precursor reduction during the bleaching process, leading to reduced 3-MCPD formation in the deodoriser.

NABE produced with no free acidity or acid activated earths with very low levels of free acidity are currently being investigated and may offer alternatives, with the potential of mitigating 3-MCPD production whilst offering good bleaching characteristics.

After bleaching with either NABE or acid activated bleaching earth with very low free acidity levels, the deodorising temperature could be operated at 220°C with little 3-MCPD formation or glycidic acid formation. Increasing the deodorising temperature from 180°C to 250°C accelerates 3-MCPD ester formation, starting at 1.4ppm at 180°C and increasing to 2.3ppm at 250°C. When temperatures greater than 240°C degrees are used, GE formation increases rapidly over a much shorter period.

Caustic refining (chemical refining) can produce low levels of 3-MCPD/GE esters and is a possibility but considerations of soap stock, higher neutral oil losses, effluent treatment and expensive equipment, such as centrifugal separators, make this choice unrealistic. NABE or sulphuric acid activated bleaching earth with low free acidity would still be a recommendation if the chemical refining method was chosen.

### Pre-treatment degumming

The removal of phospholipids when refining palm oil (CPO) is normally carried out by the addition of phosphoric acid at a concentration of 0.1-0.2%. This process is called dry degumming pre-treatment step or gum conditioning.

This pre-treatment places a high reliance on the acid activated bleaching earth to remove the

conditioned gums (phospholipids), but overall acid condition may result in the formation of 3-MCPD.

Reports of the organo-chlorine precursors being removed by water degumming is due to their partial water solubility and is another step to consider. Water degumming of CPO and bleaching with natural bleaching earth or acid activated bleaching earth with low free acidity offers the possibility of reduced 3-MCPD, with levels of 0.25ppm reported under laboratory conditions.

Care must be taken in consideration of complete removal of the phospholipids to ensure the RBD oil does not subsequently darken and develop poor taste and stability. Consideration of performing a water wash when the CPO is produced may offer more complete organo-chlorine removal and be preferable to water washing the CPO at the oil refinery after being transported over long distances.

### Conclusion

Bleaching earths alone cannot provide a complete solution to the problem of MCPD and GE formation. Considerations of CPO production and refinery operations all play their part. There is natural variation in CPO quality along with varied refinery designs, so as far as bleaching earth is concerned, each refinery's requirements will have to be individually assessed. Different oil types require different bleaching earth grades.

Bleaching earths can remove GEs but it is preferably to use low temperature deodorisation to limit its formation.

Bleaching earths cannot remove 3-MPCDs, which are formed by precursors present in the oil reacting in the deodoriser to produce the compound. However, bleaching earths can mitigate 3-MCPDs production by removing their precursors in the refinery bleaching step.

Recent discussions with a refinery using acid activated clay revealed GE produced at a level of 80µg/kg, conforming to current limits. The 3-MCPD level was 300µg/kg with no limits as yet being set. The RBD oil was produced for inclusion in baby food and although the GE and 3-MCPD levels were encouragingly low, the market sector is requesting levels lower than those obtained.

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*References: Bertrand Matthaus, Frank Pudel, Gabriele Schotz, Benoit Schilter, Claus Schurrz*