3-MCPD and GE: a new challenge

Certain processing techniques are now known to cause the occurrence of 3-MCPD, 2-MCPD and GE in edible oils and various strategies are being adopted to minimise their formation within the bleaching and deodorising process. Dr Marc Kellens and Dr Wim De Greyt write

The growing attention on the nutritional quality of food oils is one of the main drivers for new developments in the edible oil refining industry. Over the years, the refining process has continuously been improved to assure the production of high quality food oils with no or very low levels of contaminants (pesticides, polycyclic aromatic hydrocarbons, dioxins and PCB, for example) and minimum amounts of *trans* fatty acids (TFA). The production of low *trans* food fats was a big challenge for the oil processing industry as it required both a change of technology (from partial hydrogenation to interesterification and dry fractionation) and feedstock (from soft oils to palm oil fractions).

The occurrence of esters of 3-monochloropropane diol (3-MCPD) and 2-monochloropropane diol (2-MCPD) and glycidyl esters (GE) in food oils was first reported in the mid-2000s. Soon after, in 2007, the German Federal Institute for Risk Assessment (BfR) concluded that the oil processing industry had to search for alternative process techniques to reduce formation of these harmful process contaminants during oil refining. This call was taken seriously and initiated a lot of research projects in the academic world and the oils and fats industry. As a result, the mechanism of formation and toxicity for humans of 3-MCPD and GE is now better understood and critical refining stages are known. Validated analytical methods are also available and widely used for process control.

In May 2016, the European Food Safety Authority (EFSA) published its long expected scientific opinion on the risks for human health related to the presence of 3-MCPD/2-MCPD esters and GE in food. The report concludes that 3-MCPD esters and GE have the same toxicological profile as free 3-MCPD and glycidol and are therefore a potential health concern. GE are considered more harmful since some *in vivo* studies indicate that glycidol is a genotoxic compound. Not enough toxicological data is available to conclude about the toxicity of 2-MCPD.

Based on the available toxicological data, EFSA derived a tolerable daily intake (TDI) for 3-MCPD of 0.8 µg/kg body weight. This value is considerably lower than the earlier set TDI of 2.0 µg/kg body weight. The lower TDI value comes from a more conservative interpretation of the available toxicological data (lower uncertainty factor) and ensures a higher level of protection for consumers. No TDI is set for GE. Due to its genotoxic carcinogenic nature, its concentration in foods has to be minimised to the lowest achievable level.

Dietary surveys of different EU countries show that the mean exposure to 3-MCPD and GE is highest for younger groups of the population (infants, toddlers and young children). Health risk is highest for infants that only consume industrial infant formula, as their daily intake of 3-MCPD may be three times higher than the TDI. EFSA therefore highly recommends a significant reduction of 3-MCPD/GE in food products for infants.

Evaluation of the analytical data on the occurrence of 3-MCPD/GE in foods collected between 2009 and 2015 in 23 EU countries showed that food oils contributed most to the daily intake of these harmful contaminants. Mean 3-MCPD and GE values are highest in refined palm oil (fractions) and are five to 10 times higher than the mean values found in most other refined food oils (see *Table 1, below*). The data clearly shows that 3-MCPD/GE are mainly a challenge for palm oil processors and much less for refiners of other vegetable oils, who in their turn have to deal with TFA.

Formation of 3-MCPD and GE

In the past, edible oil processors have already implemented effective mitigation technologies. This has resulted in a substantial reduction of 3-MCPD and GE in refined food oils. From 2010 to 2015, levels of 3-MCPD and GE in refined palm oil decreased by 30% and 50% respectively. However, this reduction is still not enough. Members of FEDIOL, the federation representing the European vegetable oil industry, committed to reduce GE content to a maximum of 1ppm in all refined oil by September 2017. This is an ambitious goal, especially for palm oil, knowing that the average GE content in refined palm oil in 2015 was still around 4ppm. FEDIOL members also committed to continue reducing levels of 3-MCPD esters, but a concrete target value has not been set yet. In anticipation of eventual formal regulatory limits, producers of infant formula will impose very low levels of 3-MCPD (<1ppm) and GE (<0.5ppm) in food oils from 2018 onwards.

Mitigation strategies

3-MCPD esters and GE have different chemical and physical characteristics and do not have the same mechanism of formation. Hence, different mitigation strategies are required to achieve required low levels in refined food oils (see *Table 2, right*).

GE are mainly formed from diglycerides at high temperature (>230°C). This explains the high GE content in standard refined palm oil, as this oil typically has a high diacylglycerol (DAG) content (6-8%) and is deodorised at high temperature (260°C) for a longer time (approximately one hour). The same is true for TFA. Formation of GE can be minimised by reducing the heat load during deodorisation. In practice, deodorisation is best done at temperatures <240°C. A higher temperature (e.g. 250°C) for desired heat bleaching and more efficient FFA stripping is acceptable provided that the residence time is kept short. Dual temperature deodorisation (with a short residence time at a higher temperature followed by a longer residence time at a lower temperature) is industrially proven and implemented as mitigation technology to achieve a minimum amount of GE in the refined oil.

GE can also be removed from (refined) food oils. They have a similar volatility as monoglycerides (MAG) and can thus be stripped from the oil, but only at high temperature and deep vacuum (260°C and 1mbar). At a lower temperature and/or less deep vacuum, there will be more formation than stripping resulting in a net increase of the GE content in the refined oil. Hence, GE stripping requires quite extreme deodorising conditions, which will also result in the stripping of other volatile components such as MAG, tocopherols/tocotrienols and phytosterols. This will not only give higher oil losses but may also have a negative effect on the oxidative stability of the refined oil.

Another possibility to minimise GE formation is to reduce the DAG levels in palm oil. One interesting route to achieve this goal (2-3% DAG) is by enzymatic esterification of the FFA on the DAG ▸

TABLE 1: MEAN CONCENTRATION OF 2-MCPD, 3-MCPD AND GLYCIDYL ESTERS IN REFINED FOOD OILS

Mean concentration (ppm)			
Oil type	**3-MCPD**	**2-MCPD**	**GE**
Soyabean	0.4	0.2	0.2
Rapeseed	0.2	0.1	0.2
Sunflower	0.5	0.25	0.25
Palm	3	1.5	4
Objective		-	
2017[1]	-	-	1
2018[2]	<1	-	<0.5

[1] set by FEDIOL; [2] set by producers of infant foods

Source: EFSA report, May 2016

in crude or bleached palm oil. This will not only give lower GE levels but will also increase the overall yield during refining.

GE can also be degraded to MAG during post-bleaching with (non-HCl) activated bleaching earth. This gives very low GE levels (<0.5ppm) provided that post-deodorisation is done at a low temperature (maximum 230°C), (*see Figure 1, right*). Oil processors generally do not like such double refining, but so far it is the only industrial proven refining process for the production of palm oil fractions with <0.5ppm GE.

3-MCPD esters can be formed by reaction of triglycerides (TAG) with chlorine (precursors at temperatures >140°C. Hence, removing the chlorine precursors and/or avoiding acidic conditions during the refining process are the most effective mitigation strategies. This is, however, easier said than done. First of all, it is very complex to determine the amount and nature of chlorine precursors in crude palm oil (CPO) and in practice the 'potential' of a CPO for 3-MCPD ester formation is not known. Applying the same refining process on different CPO (from various plantations) can give significantly different 3-MCPD levels which is quite frustrating for both the technology provider and the oil refiner (*see Table 3, above*). Thoroughly washing the fresh palm fruit bunches (FFB) before CPO production, as well as washing the CPO before storage and refining, seems to be the most efficient processes for the removal of chlorine precursors (*see Figure 2, right*).

As 3-MCPD esters are already formed at quite low temperatures (140°C), it is not possible to control or minimise their formation during deodorisation. Bleaching is therefore the most critical refining stage for the mitigation of 3-MCPD esters. Selecting the proper grade of bleaching earth (natural or non-HCl activated) is very important. Physical refining of freshly washed CPO with use of natural bleaching earth can give 3-MCPD ester levels between 1-2ppm depending on the CPO quality and the efficiency of the washing process.

Chemical refining has shown to be a good process for low 3-MCPD esters but good CPO quality is still required to get <1ppm 3-MCPD. Although there's a growing demand for chemical refining lines for CPO, oil processors are still very reluctant to adopt chemical neutralisation on (high FFA) CPO as it gives high oil losses and a difficult to treat soapstock as a side stream. Current research focuses on the development of sustainable and economical mitigation technologies that consistently give RBD PO with 3-MCPD esters <1ppm. Chemical interesterification (CIE) is currently the only process that can remove/degrade 3-MCPD esters. CIE followed by post-bleaching with non-HCl activated bleaching earth (to degrade GE formed during CIE) and deodorisation at mild temperature (<220°C) is today the only industrial process that can give refined food oils with very low GE and 3-MCPD from standard quality (commodity) CPO.

TABLE 2: 3-MCPD ESTERS VS GLYCIDYL ESTER (GE)

3-MCPD ≠ Glycidyl Esters (GE)		
	3-MCPD	Glycidyl Esters (GE)
Toxicity	Carcinogenic (Non-genotoxic)	Carcinogenic (Genotoxic)
Precursors	Triglycerides, chlorine Acidic conditions	Diglycerides (DAG) Heat
Critical refining stage (for minimal formation)	Degumming, bleaching (starting at 140°C)	FFA stripping Deodorisation
Stability	Can only be degraded with strong alkaline Not volatile	Conversion to MAG with strong acid (ABE) Volatile
Different mitigation strategies for 3-MCPD esters and Glycidyl Esters (GE)		

TABLE 3: CPO QUALITY AND ORIGIN HAS IMPACT ON 3-MCPD ESTER FORMATION

CPO origin	DOBI*	FFA (%)	DAG (%)	Activated BE (HCl)	Natural bleaching earth
				3-MCPD (ppm)	3-MCPD (ppm)
Central America	1.6	3.0	5.2	2.3	1.1
South America	2.3	4.6	7.2	7.5	1.6
South East Asia- 1	2.7	4.2	6.1	8.1	1.7
South East Asia- 2	3.1	3.8	5.2	9.7	2.1
South East Asia- 3	1.6	5.1	6.2	9.6	2.7

* *deterioration of bleachability index*

FIGURE 1: EFFECT OF RE-REFINING ON GE FORMATION

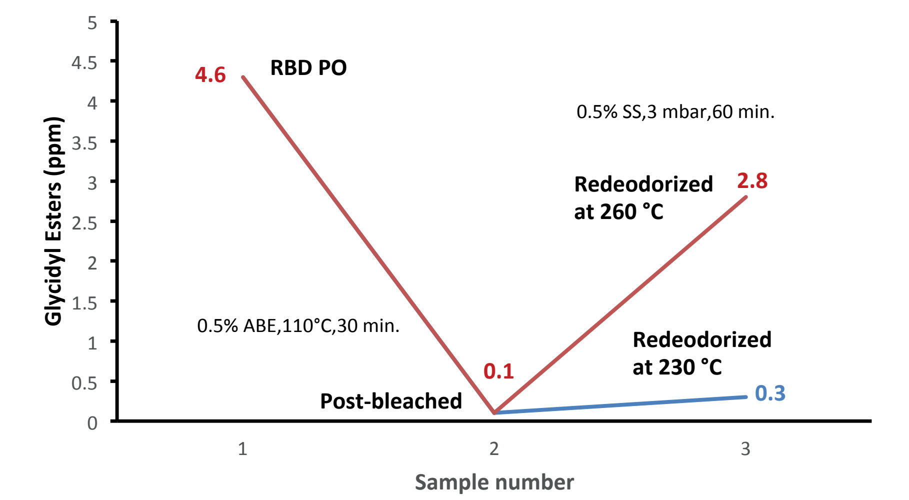

FIGURE 2: WASHING OF CPO – EFFECT ON ELEMENT CONTENT AND COLOUR

Parameter	CPO	Washed CPO
FFA (C16:0) %	3.67	3.53
P (ppm)	22.3	8.0
Fe (ppm)	20.3	2.68
Ca (ppm)	20.1	8.7
Mg (ppm)	12.3	1.7
K (ppm)	21.6	0.7
Na (ppm)	1.4	1.2

LEFT TO RIGHT: CPO, WASHED CPO, WASH WATER

Conclusion

The recent EFSA report has put 3-MCPD/GE on the agenda and brought an important new challenge to oil refiners. They will have to accelerate implementation of additional mitigation technologies to reduce 3-MCPD/GE levels further; especially in refined palm oil. With the active support of technology providers, it should be possible to properly address this issue and improve further the nutritional quality of food oils.

It is difficult to predict how far the consequences of the EFSA's recommendation to reduce 3-MCPD/GE in food oils will reach out to the global food oil processing industry, but as with *trans* fat issues in the past, when it smoulders in Europe, it may start a fire in the rest of the world. ●

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