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A summary of 2-, 3-MCPD esters and glycidyl ester occurrence during frying and baking processes

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ABSTRACT

Monochloropropanediol (MCPD) esters and glycidyl esters (GE) are the process contaminants found in frying and baking, except the refining process. The free form MCPD and glycidol are released from their parent esters via lipase hydrolysis while they are carcinogen and genotoxic carcinogen, respectively. MCPD esters and GE are formed endogenously during vegetable oil refining process. Then, their concentration were experimented during subsequent food processing methods, especially frying and baking. This review discussed the occurrence of 2-, 3-MCPD esters and GE during frying and baking processes. Process temperature, process duration, presence of precursors, and their combined effects are highly related to MCPD esters and GE formations. An elevated temperature and processing time can increase the formation of these contaminants until an optimum rate and then followed by the decomposition. Also, other factors such as the presence of chloride ions, moisture, and partial acylglycerol can further facilitate MCPD esters and/or GE formation.

Introduction

The presence of 3-chloropropane-1,2-diol (3-MCPD) and glycidol are widely found in refined vegetable oils in their respective ester form as the food process contaminants. An esterified form of 3-MCPD is known as 3-MCPD ester, while the esterified form of glycidol is known as glycidyl ester (GE). Besides, the chlorine ion can attach to one of the three carbon atoms within a glycerol backbone. A 3-MCPD ester has an isomer of 2-MCPD ester, in which the chlorine ion is attached at *sn*-2 position (F. Destaillats, Craft et al., 2012).

These compounds are potentially toxic to the human body due to the release of 3-MCPD and glycidol from their parent esters after ingestion into the gastrointestinal tract. Free form 3-MCPD can induce the tumours in rodent during animal studies (Bakhiya et al., 2011). Therefore, 3-MCPD is considered as carcinogen and it is reviewed as non-genotoxic by the European Scientific Committee on Food in 2001 (Knutsen et al., 2018). Meanwhile, glycidol is a genotoxic carcinogen and classified as a group 2 A by International Agency for Research on Cancer (IARC) as “probably carcinogen to human”. Before the year 2019, glycidol intake was recommended as ALARA (As Low As Reasonably Achievable) principle (Bakhiya et al., 2011; S. MacMahon, Begley and Diachenko, 2013).

To date, both of these compounds are suggested with the maximum limit in fats and oil-related products. The EU regulation sets the maximum level for GE at 1 ppm in vegetable oils and fats placed on the final consumer market or used as an ingredient in the food. Besides, the GE maximum level for vegetable oils and fats destined to produce baby food and processed cereal-based food is set at 0.5 ppm (Bonwick and Birch, 2019; Kok Ming Goh et al., 2021). The maximum level of a 3-MCPD ester is set by the European Commission to be 1.25 ppm for oils and fats from coconut, maise, rapeseed, sunflower, soybean and palm kernel oil and mixtures of oils and fats from this category. The European Commission also defined a 2.5 ppm 3-MCPD esters limit applied to other vegetable oils and fish oil and mixtures of oils and fats from this category and mixtures of oils and fats from the two categories mentioned above. The limit of 3-MCPD was only mentioned in hydrolysed vegetable protein and soy sauce at maximum limit at 20 μg/kg ((EU) 2020/1322, 2020; Stadler, 2015). 2-MCPD has insufficient toxicological data until now, and the potential hazard is considered equal to 3-MCPD (EFSA, 2016).

The formation of 2-,3-MCPD esters and GE is claimed to predominantly occur during the vegetable oil refining process (Hew et al., 2020;

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Zulkurnain et al., 2012). During the refining process, for example, palm oil refining, a high temperature is used at the deodorisation step. The deodorisation temperature used during palm oil refining process can achieve as high as 230 °C (Cheng et al., 2016; Nur Sulihatimarsyila et al., 2020; Artz et al., 2005; Ramli et al., 2011). At deodorisation step, a stream of water vapour is used to carry free fatty acid and odoriferous compounds under high temperature and low pressure (Véronique Gibon, De Greyt and Kellens, 2007). However, usage of high temperatures inevitability encourages the formation of MCPD esters and GE, especially when the precursors are in abundance. The precursors refer to chlorine ion, partial acylglycerol (e.g. mono- and di-acylglycerol) (Craft, Nagy, Sandoz, et al., 2012).

Subsequently, the refined vegetable oil is used during food thermal processing, mainly for frying and baking processes. Thermal processing of food which uses abusive temperatures is creating a favourable condition for the formation 2-, 3-MCPD esters and GE again. This present article summarises currently available data on the factors of forming 2-, 3-MCPD esters and GE during frying and baking processes.

The 2-, 3-MCPD esters and GE occurrences in different foodstuffs

The fundamental source of 2-, 3-MCPD esters and GE in our daily food system are mainly from refined vegetable oils (Andres et al., 2013). The use of refined vegetable oils in daily food processing (cooking) inevitability introduces the 2-, 3-MCPD esters and GE into various type of food matrices. These contaminants are mainly formed during the refining steps when chlorine ions (Colin G. Hamlet et al., 2011) are present, especially in a low pH and high-temperature condition (Li et al., 2016; Zhao et al., 2016). The contaminated vegetable oils are refined vegetable oils such as (but not limited to) palm oil, palm kernel oil, peanut oil, rapeseed oil, soya bean oil, corn oil, coconut oil, sunflower seed oil, walnut oil, and olive oil. As compared to unrefined vegetable oils, the content of 3-MCPD ester and GE can be elevated when the refining process uses a high temperature, especially during the deodorisation step (Freudenstein et al., 2013; Shimizu et al., 2012).

Besides, these contaminants occur in a wide range of foodstuffs. High-fat content products such as margarine, food emulsion, shortening, and special fats contain a high level of 2-, 3-MCPD esters and GE (Custodio-Mendoza et al., 2019; S. MacMahon et al., 2013) because they are the direct derived product from refined vegetable oils. Certainly, these contaminants are also subsequently found in various foodstuffs such as cereal products (including bakery, cereal, and biscuit), potatoes and snack foods, spreads, and fried food (including domestic frying processes).

The 3-MCPD esters contamination is also found in retail food, such as potato chips and french fries. This observation is expected because most of the products from this category use refined vegetable oil as the frying medium. In short, it is known that food with high fats content which undergone thermal processing can be highly associated with the occurrence of 2-, 3-MCPD esters and GE. Sometimes, 3-MCPD esters were also reported in non-thermal processed food such as cured fish, salami, and fresh dairy products. Robert et al. explained the possible formation of 3-MCPD esters at relatively low temperatures (40 °C) when a system is comprised of vegetable oils, water, sodium chloride and lipase (Robert et al., 2004). The report suggested that the formation of the 3-MCPD esters was via a lipase-catalysed lipolysis of triacylglycerol (TAG) and followed by nucleophilic attack of chloride anion.

Worth noting that 3-MCPD esters and GE in infant formula incur a high risk for infants and toddlers' consumption. The European Scientific Committee on Food has labelled 3-MCPD as a non-genotoxic carcinogen, and the Joint FAO/WHO Expert Committee on Food Additives (JECFA) has established a maximum tolerable daily intake (TDI) of 3-MCPD at 2 μg/kg body weight (Jedrkiewicz et al., 2015). A recent report by the European Food Safety Authority (EFSA) released an opinion that TDI of 3-MCPD at 0.8 μg/kg body weight daily (EFSA, 2016). A younger age group of humans, especially infants and toddlers, are low in body weight to tolerate the possible ingestion of 3-MCPD esters. Both 3-MCPD esters and GE are introduced to infant formula through the addition of refined vegetable oils (MacMahon and Beekman, 2019). Refined vegetable oils are added to the product as a mixture to yield a fatty acid composition similar to human milk (Innis, 2016). The choice of refined vegetable oils to formulate infant formula are palm olein, canola, coconut, sunflower, and soya bean oils (Nguyen and Fromberg, 2020). Surveillance research on baby formulas in the Brazilian market reported that the levels of 3-MCPD esters in baby foods varied from 0.062 mg/kg to 0.588 mg/kg in the whole product, while GE levels ranged from 0.032 to 0.213 mg/kg. Among these 33 infant formulas checked within the Brazilian market, there was no correlation between the oil content and the concentrations of contaminant (bound 3-MCPD) (Arisseto, Silva, et al., 2017). However, it is deduced that the chance of containing 3-MCPD esters in infant formula was high since palm oil and palm olein are used in formulating the fatty acid profile for infant formula. Palm origin oils are generally higher in the 3-MCPD esters and GE content.

It is noticeable that all the determined concentration of 2-MCPD esters is lower than the concentration of 3-MCPD esters. As a rule of thumb, the concentration of 2-MCPD esters should fall in the range of 40–80% of the concentration of the 3-MCPD ester (Kuhlmann, 2011). Table 1 shows the levels of 3-MCPD esters, 2 -MCPD esters, and GE in various foodstuffs reported. Vegetable oils are the popular sampling subject among scientists when detecting the esterified form of MCPD and glycidol, followed by food product for an infant (and toddlers), and some miscellaneous fatty food (including ready-to-eat bakery and fried food samples purchase from the market).

Factors affecting MCPD esters and GE formation during frying

Frying is one of the most widely used food processing methods. Frying is common in households, restaurants, and the food industries to produce crispy food. Frying changes the sensory and nutritional properties of fried food through complex interactions between food matrices and frying medium (Asokapandian et al., 2019). The fat is absorbed by fried food during the frying process. The degree of absorption is affected by the type of food, pretreatment, frying duration, frying temperature, frying medium, and their combined effects (Lumanlan et al., 2020; Mba et al., 2015). It is known that more than 90% of lipids in fried food are absorbed from the frying medium (Bansal et al., 2010; Choe and Min, 2007). The frying process involving high temperatures, which usually ranges from 120 to 180 °C (Oke et al., 2017). This frying temperature is similar to the temperatures used during deodorisation during the refining process. Therefore, numerous studies have checked the level of MCPD esters and GE during frying from various point of view (Aniolowska and Kita, 2016; Kalkan et al., 2020; Zhou et al., 2013). These following discussed factors encouraging the MCPD esters and GE formation is focusing on the most traditional frying method, including the deep-fat frying or immersion frying.

a. Frying medium

A refined vegetable oil is suitable for deep fat frying when it is oxidative stable, mild in flavour, high smoke point and low cost. Palm oil is one of the most stable refined vegetable oils used in deep fat frying (Asokapandian et al., 2019). The oil composition can greatly affect the properties to be served as a frying medium and the qualities of fried foods. MCPD esters and GE formation are also associated with the oil's composition. Most studies reported that the MCPD esters and GE formation mechanism are related to triacylglycerol (TAG) and partial acylglycerols, including the di- and mono-acylglycerols (Yao et al., 2019). Other minor compounds, such as chloride and phospholipids are involved in these proposed mechanisms too.

The percentage of di-acylglycerol (DAG) in palm oil falls between 6 and 10%. This figure is significantly higher than other vegetable oils which normally contain DAG content at 1–3% (Matthäus et al., 2011).

Table 1
Occurrence of 3-MCPD esters, 2-MCPD esters, and glycidyl esters in various foodstuffs.

Foodstuff	n	3-MCPD esters, μg/kg, mean, (min-max)	2-MCPD esters, μg/kg, mean, (min-max)	glycidyl esters, μg/kg, mean, (min-max)	Reference(s)
Baby food/infant formula	14	(62–588)	–	–	Zelinková et al. (2008)
	13	5.6 (3.7–65.0)	2.3 (1.3–29.0)	1.1 (0.6–31.2)	Nguyen & Fromberg (2020)
	70	108 (108–109)	44 (31–58)	87 (80–94)	EFSA (2016)
	40	150 (ND-600)	–	220 (ND-750)	(Adriana Pavesi Arisseto, Silva, et al., 2017)
	88	185 (0–316)	41 (0–52)	–	Wang et al. (2016)
	55	54 (3–119)	–	13 (1–50)	Spungen et al. (2018)
	5	(ND-138)	(ND-45)	(ND-56)	(K. M. Goh et al., 2019a,b)
Fish oil supplement	5	(1500–5500)	–	–	Jędrkiewicz et al. (2016)
Margarine	5	(1300–7300)	(630–1700)	–	Jędrkiewicz et al. (2016)
	5	(1355–3831)	(310–2082)	(1199–4899)	(K. M. Goh et al., 2019a,b)
	1	1766	732	3893	(Kok Ming Goh et al., 2019)
	170	408 (406–409)	159 (152–166)	361 (358–364)	EFSA (2016)
Refined vegetable fats and oil Palm oil/olein (RBD)	4	2670 (1490–5930)	–	–	Zulkurnain et al. (2012)
	501; 55; 498	2912	1565 (1563–1566)	3955 (3954–3955)	EFSA (2016)
		6200* (total MCPD)		18600	Haines et al. (2011)
	1	3749	1932	6610	(Kok Ming Goh et al., 2019)
	1	2584	1640	4848	(K. M. Goh et al., 2019a,b)
	324	(<250–5770)	–	–	(Abd. Razak et al., 2012)
	5	4140 (1400–8430)	–	6030 (1880–9530)	(S. MacMahon et al., 2013)
	≥20	3200 (1100–10000)	(200–5900)	3700 (300–18000)	Kuhlmann (2011)
Palm shortening	4	(ND-6200)*		(50–15500)	Haines et al. (2011)
Olive oil (general)	9	48 (48–49)	86 (85–88)	15 (0–31)	EFSA (2016)
Olive oil (refined)	5	56 (15–73)	–	48 (48–1100)	(S. MacMahon et al., 2013)
	5	(<300–2462)			Zelinkova et al. (2006)
Soya bean oil	≥20	200 (100–500)	(ND-100)	300 (100–600)	Kuhlmann (2011)
Olive oil (unrefined)	1	ND	ND	ND	(K. M. Goh et al., 2019a,b)
	5	5 (ND-25)	–	ND	(S. MacMahon et al., 2013)
	4	ND (<100-<300)	–	–	Zelinkova et al. (2006)
Peanut oil (refined)	1	656	537	656	(K. M. Goh et al., 2019a,b)
	3	49 (14–69)	–	49 (44–57)	(S. MacMahon et al., 2013)
	4	(100–900)	(100–400)	(400–1100)	Kuhlmann (2011)
Miscellaneous products Chocolate products	5	(122–1254)	(144–878)	(119–1166)	(K. M. Goh et al., 2019a,b)
Potato chips	3	(6–11)	–	–	Chung et al. (2008)
Prawn crackers	3	(25–33)	–	–	Bognár et al. (2020)
Breaded pork	1	93.6	–	–	
Breaded chicken liver	1	70.2	–	–	
French fries	8	57 (51–63)	23 (19–28)	41 (40–41)	EFSA (2016)
Bakery wares White bread	3	(8–13)	–	–	Chung et al. (2008)
Cereal bread	3	(11–13)	–	–	
Paper wrapper cake	3	(4–8)			
Egg tart	3	(8–14)	–	–	
Bread and bread rolls	75	29 (23–36)*	(14 (9.8–19)	51 (50–510)	EFSA (2016)

Notes: n = number of samples reported, ND = non detected (based on reported literature), "<" indicate the mentioned digits was below limit of detection or limit of quantification, * indicated a total MCPD esters was reported, "- "indicated particular data was not reported by cited reference(s).

Generally, a higher DAG content also reflected higher MCPD esters and GE in palm oil (Abd Razak et al., 2019; A. P. Arisseto, Marcolino and Vicente, 2014; S. MacMahon et al., 2013). According to a study by Matthaus et al. (2011) in the year 2011, oils with DAG higher than 4% showed a relatively high 3-MCPD esters concentration after 2 h of heating at 240 °C. This finding was in agreement with Yao et al., (2019) that heating of bleached soya bean oil spiked with different DAG concentrations. Both of these researches suggested that DAG is a precursor to form 3-MCPD esters during the stimulated frying system. Then, GE shares some of the common formation pathways with MCPD esters. GE can be formed by utilising acylglycerol, especially DAG and MAG, when heating under high temperature (Shimizu et al., 2012).

The study from Ben Hammouda et al. (2016) reported that MCPD esters and GE increased with the increase of refined palm oil (RPO) portion blended to refined olive pomace oil (ROPO). The 3-MCPD esters and GE in 100% ROPO were 1.10 mg/kg and 1.5 mg/kg, respectively. Then, 3-MCPD esters increased to 1.30 mg/kg, and GE increased to 4.00 mg/kg when 75% of RPO was used in the blended oil. The experiment was continued with french fries frying using these oil blends. After the frying, 3-MCPD esters and GE showed no significant difference ($p > 0.05$) between the blends. Xu et al., 2020 reported similar findings that frying did not elevate the 3-, 2-MCPD esters contamination when their initial concentrations were relatively low (<1 mg/kg) (Xu et al., 2020). In contrast, another study by Aniolowska & Kita in the year 2015 (Aniołowska and Kita, 2015) suggested that these contaminants may decompose during the frying process. This study used palm oil and rapeseed oil with initial contents of GE at 5.81 and 0.80 mg/kg, respectively. After the deep-fat frying of frozen french fries under the same frying parameters, the GE content was reduced to 1.27 mg/kg in palm oil and 0.42 mg/kg in rapeseed oil.

Besides, the olein fraction from a refined vegetable oil always contains higher MCPD esters and GE (Frédéric Destaillats, Craft, Dubois and Nagy, 2012; F. Destaillats et al., 2012a,b; Kyselka et al., 2018). The MCPD esters and GE tend to accumulate in the olein fraction instead of the stearin fraction due to natural selective co-crystallisation with TAG and similar polarity (V Gibon et al., 2018). Therefore, palm olein fraction is always associated with higher GE content than palm oil when undergone the same frying condition (Aniołowska and Kita, 2015).

However, palm oil is still one of the most suitable edible oils for frying, and it is favoured by the user due to its stability against oxidation. With all the efforts from food safety authorities and industries worldwide, the level of MCPD esters and GE in palm oil and related products are controlled in general (Abd Razak et al., 2019; Ramli et al., 2020).

b. Temperature

Processing temperature is a critical factor that affects the MCPD esters and GE concentrations in vegetable oils. To date, many published papers highlighted the effect of heating or frying temperature, either by simulation or actual frying (Aniołowska and Kita, 2016; Kalkan et al., 2020; Li et al., 2016; Shimizu, Weitkamp, Vosmann and Matthäus, 2013b; Yu Hua Wong et al., 2017a,b; Y. H. Wong et al., 2017a,b; Xu et al., 2020). In 2013, a heating simulation of diolein at 180, 200, 220, and 240 °C by Shimizu et al. (2013b) showed that the concentration of 3-MCPD esters was positively correlated to the heating temperature. It is worth mentioning that the concentration of the 3-MCPD esters in the 240 °C heating system was only slightly higher than in 220 °C. This data showed that the generation of 3-MCPD esters was slow down after the temperature had reached beyond 220 °C. The same correlation was reported by Li et al. (2016) in a simulating heating model system with different temperatures of 70, 100, 130, 160, 190, 220, and 250 °C. In this case, the concentration of the 3-MCPD esters decreased when the temperature went above 220 °C, suggesting decomposition had taken place. On the other hand, the increased heating temperature leads to the increasing of GE as well. Unlike 3-MCPD esters, GE formation accelerates rapidly when the temperature went beyond 240 °C (Matthäus and Pudel, 2013; Shimizu et al., 2013b).

Besides, the concentration of the 3-MCPD esters at 180 °C were generally higher than at 160 °C during the frying of potato chips (Y. H. Wong et al., 2017a,b) and chicken breast meat (Yu Hua Wong et al., 2017). Also, Ilko et al., 2011 reported that 3-MCPD esters (reported as bound 3-CPD, in μg/kg) concentration during the frying of potato chips was constantly higher in a frying temperature of 180 °C as compared to its pre-fried temperature at 158 °C (Ilko et al., 2011). The concentration of 3-MCPD esters can be reduced when the frying temperature continues to increase. GE did not behave the same as in simulation frying without food matrices. When frying using a food matrices system, GE concentrations were lowered in frying oil when frying temperature increased (Aniołowska and Kita, 2016; Yu Hua Wong et al., 2017a,b; Y. H. Wong et al., 2017a,b; Xu et al., 2020). Aniolowska and his group found that at 180 °C frying, GE concentration decreased two times faster than 165 °C. The rapid degradation of GE during high-temperature frying of food is due to the extended thermo-oxidative changes and attack of nucleophiles (from water and free fatty acids amines) to the reactive epoxy moiety on GE structure (Aniołowska & Kita, 2015, 2016; Xu et al., 2020).

Therefore, the formation and degradation of 3-MCPD esters and GE are happening simultaneously during the frying processes (Ermacora and Hrncirik, 2014). When the heating temperature went above a threshold temperature, the decomposition rate of 3-MCPD esters and GE is greater than formation.

c. Frying duration

During the common practice of deep-fat frying, the oils are heated continuously and repeatedly. This kind of frying practice indirectly exposes the frying medium to a long heating duration in total. The concentrations of MCPD esters and GE are affected by the total frying duration, including intermittent frying. In a heating model system using crude rapeseed oil by Li et al., (2016) (Li et al., 2016), the concentration of the 3-MCPD esters was positively correlated to the frying duration. However, when the frying time was prolonged, the concentration of 3-MCPD esters reduced drastically. In another study by the same group of researchers, 3-MCPD esters and GE concentrations reached a plateau heating; it was reported that 3-MCPD esters reached a plateau sooner than GE as the depletion of chlorine present in the system (Shimizu et al., 2013b).

Ben Hammouda et al., 2016 reported that, after 16 h frying of french fries, the concentration of 3-MCPD esters reduced significantly ($p < 0.05$). The same trend was observed in a few other studies during the frying of potato chips and chicken breast meat along with a total of 25 frying cycles (Yu Hua Wong et al., 2017; Y. H. Wong et al., 2017a,b; Xu et al., 2020). These data suggested that with prolonged frying with food matrices, the degradation rate of 3-MCPD esters were increased. In the case of GE changes during the frying of french fries (Aniołowska and Kita, 2015) and fish nuggets (Xu et al., 2020), the GE concentration decreased when the frying duration increased. In other frying studies using potato chips (Y. H. Wong et al., 2017a,b) and chicken breast meat (Yu Hua Wong et al., 2017) as the food matrices, the GE concentration increased slightly only after five repeated cycles. Therefore, GE is unstable during a prolonged frying duration.

d. Chlorine content

Sodium chloride is used in most of the domestic cooking applications, including frying. Chloride is a necessary precursor to form MCPD esters when it reacts with partial acylglycerol with heat (Bakhiya et al., 2011; Zhou et al., 2013). Both inorganic and organic chloride facilitates MCPD esters formation (Nagy et al., 2011). However, the affinity to form MCPD is varied when the chloride is derived from a different source (Freudenstein et al., 2013). Contrary, chloride content does not affect the GE concentration in a heating system (Shimizu, Weitkamp, Vosmann and Matthäus, 2013a). These findings from most researches are expected because chlorine is not found in a GE chemical structure.

In the frying studies conducted by Wong et al. (Yu Hua Wong et al., 2017; Y. H. Wong et al., 2017a,b), sodium chloride was introduced into the chicken breast meat and potato chips as seasoning before frying. The content of 3-MCPD esters was recorded higher when a higher concentration of sodium chloride was used.

e. Moisture content

Water promotes the hydrolysis of TAG into DAG and MAG during the frying process. The increase of DAG and MAG is leading to more significant MCPD esters and GE formation. Zhou et al. (2013) reported that 3-MCPD esters concentration notably increased when the water percentage increased to 10% in a frying model. In another frying model using soya bean oil (Svejkovska et al., 2006), the same trend was observed until 20% of water content. When the water content was more than 20%, the content of 3-MCPD esters started to decrease. The excess amount of moisture was not promoting 3-MCPD esters formation, yet, 3-MCPD esters decomposed upon an increase of moisture content up to 50%.

f. Components in food

Various foods are commonly processed by deep-fat frying. The food matrices can be complex, consisting of carbohydrates, protein, fats, and minor component such as micronutrients. During frying, food matrices can cause the degradation of the frying medium through a series of chemical reactions (Kalogianni et al., 2009). One good example is that the polymerisation products and polar compounds were significantly higher in the frying oil when food matrices were used (Kalogianni et al., 2009).

The food matrices also promote frying oil oxidation. Xu et al., (2020) reported that the oxidation indicators such as peroxide values and p-anisidine values were strongly correlated to 3-MCPD esters content (Xu et al., 2020). The increase of oxidation state in the frying system showed that the free radicals were generated and that encouraged the formation of the 3-MCPD esters. The transition metal such as iron in the chicken breast meat can be accumulated in frying oil and accelerate the frying oil degradation (Artz et al., 2005). Again, these degradations may further facilitate the formation of 3-MCPD esters and GE by providing them with the necessary precursors.

Moreover, moisture from the food matrices can transmit into the frying medium and causes the hydrolysis of TAG into partial acylglycerol. As a result of hydrolysis leading to partial acylglycerol formation, MCPD esters and GE contents increased. Therefore, the food with high moisture content seems to induce the MCPD esters and GE formation during frying processes.

Lastly, Arisseto, Marcolino, et al. (2017)) investigated the 3-MCPD esters content in various fried foods, including bananas, potatoes, cassava, onion, garlic, polenta, rice ball, and beef patty. They found that fried garlic and onion with the highest moisture loss and oil uptake contained the highest amount of the 3-MCPD esters. Food with higher oil-uptaking ability after the frying process may generally contain higher 3-MCPD esters concentration.

g. Frying mode

There are two main types of frying systems, which are batch frying and continuous frying. Batch frying is used in household and small-scale food processing manufacturers, while large-scale manufacturers prefer continuous frying for better production efficiency. In continuous frying, fresh oil is replenished consistently to control the total free fatty acid and partial acylglycerol in the frying oil. In a study by Tarmizi et al. (Ahmad Tarmizi and Ahmad, 2015), free fatty acid formed was two folds lower in continuous frying than batch frying.

In 2015, Dingel and co-researcher (Dingel and Matissek, 2015) investigated the changes of 3-MCPD esters and GE concentrations in a large scale continuous frying of potato chips. The results showed no significant changes in the 3-MCPD esters and GE concentrations during the given frying duration. To date, there is no comparison data between batch and continuous frying on their MCPD esters and/or GE formation. It is worth studying the effect of frying mode in controlled condition to understand MCPD esters and/or GE forming behavior.

Factors affecting MCPD esters and GE formation during baking

Baking is a thermal food process that covers a wide range of food products. The products processed by baking are normally cereal products, which are more often known as “bakery” products. Bakery products, especially pastry, bread, and cake, are popular foods among the consumers. This food provides specific organoleptic characteristics. The baking process can be extended to fish, meat, and pie products (Figoni, 2008). Scientists are interested in baking research dealing with culinary, sensorial, nutritional, chemical, microbial safety, and physical properties (such as rheological, texture, and porous structures of baked goods) (Flick et al., 2015).

The baking process causes a series of complex physicochemical changes among the core ingredients, which are fats, sugar, eggs, and flour (Conforti, 2006). Upon baking, numerous volatile compounds are formed within the system and contribute to baked flavour. These volatile compounds are simply the result of the Maillard reactions, which occur among the reducing sugar, amino acids, peptides, and protein (Matsakidou et al., 2010). Despite forming these desired compounds, the baking process can lead to the formation of potential mutagenic, carcinogenic, or cytotoxic compounds such as glycation end products (AGEs), low molecular mass browning product (<1 kDa), 5-hydroxymethylfurfural (HMF), and acrylamide (Nursten, 2002).

Baking processes involve fatty recipe and high temperature (at least 160 °C) can be a highly potential condition that is suitable for the MCPD esters and GE formation. Certainly, other intrinsic factors, such as the baking (processing) duration, presence of water (moisture content), salt, and addition of functional ingredients, are discussed in the literature. Worth noting that the number of reported studies regarding the baking process is relatively lesser than a frying process in the investigation of MCPD esters and GE formation. Besides, some of the studies are checking on the formation of free-form MCPD, especially 3-MCPD following the reported 3-MCPD contamination in the leavened dough system by Hamlet et al. (Colin G Hamlet, Sadd and Gray, 2004a). Hamlet demonstrated a series of testing on the high-pressure cooked leavened dough using different recipes consisted of white flour, salt, water, acetic acid, baking fat (triacylglycerols with palmitic, oleic, and linoleic acid fatty acids), flour improver, and yeast. This study showed that all the ingredients could affect the 3-MCPD content to different extend except acetic acid and bakery fat. The authors had deduced that the formation of 3-MCPD was derived from partial acylglycerol, especially a monoacylglycerol. From the proposed mechanism by Hamlet, a 3-MCPD mono-ester was formed and eventually hydrolysed into free 3-MCPD (Colin G Hamlet et al., 2004a; Colin G Hamlet, Sadd and Gray, 2004b). Although a cooked and leavened dough system was highly simulating a baking system, the research subject from Hamlet was free-form 3-MCPD, and the cooking apparatus was customised in a laboratory for the detection purpose.

Each reported and possible factors impose the formation of MCPD, MCPD esters and/or GE are discussed in further detail in the below sections.

a. Baking temperature

The process temperature during baking among available studies is between 160 and 220 °C. A study conducted on the biscuit baking system revealed that the formation of 3-MCPD and its esters were increased with an increasing baking temperature, especially at 200–220 °C. With a fixed baking time of 11 min, the increments of 3-MCPD and 2-MCPD were 3.2- and 2.6- fold, respectively. Worth noting that the reaction rate constant for 3-MCPD, 2-MCPD, and bound-MCPD (MCPD esters) were increased when the baking temperatures increased, based on the kinetic examination (Mogol et al., 2014).

In another study by Stauff et al. (2020), they suggested that free 3-MCPD, 2-MCPD, 3-MCPD ester, 2-MCPD ester, and GE were not endogenously formed during baking. The experiment was conducted using a carbon-13 labelled 3-MCPD ester spiked butter as the ingredient for a marketable browned biscuit. The baking temperatures used in this study were 140, 160, and 180 °C. Authors suggested that MCPD, MCPD esters and/or GE only formed up to the quantitation level when the baking duration was prolonged (between 24 and 72 min) at a fixed temperature. However, there were excessive surface browning of the biscuits, and therefore not suitable for the market purpose (Stauff et al., 2020). In short, when the biscuits were exposed to moderate baking temperatures, there was no endogenous formation of MCPD, MCPD esters and/or GE.

Goh et al., (2019) reported another study of baking the conventional cake using different parts of palm oil fraction. The author suggested that a high baking temperature (>160 °C) deteriorated the cake qualities in all types of shortening used, for instance, extra hardness and low springiness. Interestingly, the finding suggested that the increase in baking temperatures did not significantly increase 2-, 3-MCPD esters and GE concentrations. In contrast, a certain degree of 3-MCPD esters and GE decomposition was observed when the baking temperature elevated to 200 °C. Notably, the ratio between 2-MCPD ester to 3-MCPD esters was no longer in the range of 0.5–0.6, and it was increased to 0.72. The increases of this ratio suggesting 3-MCPD esters may undergo decomposition, or high baking temperature favour the formation of 2-MCPD esters. Besides, GE was drastically decomposed upon baking. At 160 °C baking temperature, GE content reduced by 70%. A higher reduction of GE to 5% (compared to original content) was observed when margarine and soft stearin were used as the shortening. In this case, supporting data showed an increase of potential precursors, such as diacylglycerol, was continuously formed. However, the MCPD esters and/or GE concentrations were not increased, indicating a higher decomposition rate instead of formation with the study baking condition and/or study (Kok Ming Goh et al., 2019).

An elevated baking temperature causes unnecessary thermal exposure to bakery wares, which directly deteriorate the organoleptic properties. Nevertheless, a model baking systems using higher temperature reveal a better understanding of MCPD esters and GE changing pattern within a designed recipe. Generally speaking, MCPD esters and GE are formed with the increase of temperature, but they can decompose when the excess temperature exposure is introduced. The formation and decomposition of MCPD esters and/or GE is most likely to occur simultaneously within a thermal system. The initial increment of MCPD esters and/or GE may exhibit proportional increment with temperature, but these contaminants' concentrations do not become a plateau when the heat is further increased. Eventually, the decomposition rate can surpass the formation rate. However, the decomposition is affected by a combination of extrinsic and intrinsic factors, especially a complex baking system like biscuit and cake. This explanation is agreed with the frying temperature experiments.

b. Baking duration

Stauff et al. discussed that GE was not formed during the long baking duration (72 min), although the baking temperature had risen to 180 °C. In most literature, it is described that the temperature for GE formation is 230 °C ((Craft, Nagy, Seefelder, et al., 2012); Frédéric Destaillats et al., 2012a,b). Conversely, 3-MCPD was formed after a long baking duration (72 min) at a fixed temperature (Stauff et al., 2020). Meanwhile, it was suggested that the kinetic effects of both baking duration and temperature were similar, which caused an increase of 3-MCPD (Mogol et al., 2014).

Baking duration and baking temperatures are two indispensable factors to process baked goods. However, baking temperature (thermal load) is considered a more important factor to form MCPD esters and GE than baking duration (exposure). In most cases, the baking duration is fixed during the baking process in the study of MCPD esters and GE formation evaluation with reasons. First, an increase of baking duration with the same thermal load causes unnecessary product weight loss, volume loss, high porosity, and extra hardness (Alifaki and Sakiyan, 2017). These quality changes are not desirable in the baking process. In other words, prolonged baking process time at lower thermal load sounds to reduce the possibility of MCPD esters and GE formation, but at the same time causing low qualities of finished products. Therefore, a baking recipe should be done within a suitable duration with other factors, such as thermal loading position (inside the oven), volume (of the recipe), heat transfer rate (equipment power), method of heat transfer (convection by oven) rate remained constant.

c. Choice of ingredients

The other factor affecting the concentrations of 2-, 3-MCPD esters, and GE during baking processing is the choice of ingredient. A cereal-based bakery good can consist of a wide range of ingredients, including functional additives. Variation in the recipe may further facilitate the formation of 2-, 3-MCPD esters and GE. The contents of these contaminants still can be affected by the factors (but not limited to) of chlorine content, high temperature, partial acylglycerol, pH, moistures, and/or ingredients substitution.

Fats or shortening as one of the major ingredients in baked goods can affect the content of 2-,3-MCPD esters and GE. Goh et al., (2019) tested the usage of margarine and several palm oil fractions, namely soft stearin, hard stearin, palm mid-fraction, and palm olein, for their application in a conventional baking recipe. The authors found that hard stearin and palm mid-fraction are naturally having a lower content of 2- and 3-MCPD esters. However, a baked cake should use softer fractions such as soft stearin and palm olein to achieve comparable qualities with the margarine recipe. This study indicated that the raw materials contaminant level could significantly affect the final concentration of 2- and 3-MCPD esters in the baked cake, excluding the baking temperature as an inducing factor. Contrary, GE degraded upon increased baking temperatures, yet the degradation was observed in all types of shortening used during the experiments (Kok Ming Goh et al., 2019).

In addition, several fat-rich cereal model systems were checked by Sadowaska-Rociek and his group in the year 2017. The findings showed that the 3-MCPD (free and bound) content was affected by the flour type. 3-MCPD esters were about 12–16 times higher than free 3-MCPD. Oat flour systems were reported to contain the highest 3-MCPD ester (1146 μg/kg), while the starch system showed the lowest 3-MCPD esters (924 μg/kg). Also, it was suggested that a lower pH and higher fat content were associated with higher 3-MCPD esters. Two possible reasons explained the observed data. First, a higher fat content provided reaction backbones (partial acylglycerol) to form 3-MCPD esters. Secondly, lower pH values provided an acidic condition can catalyse the reaction between lipids structure and chloride ions (Anna Sadowska-Rociek, Cieślik and Florkiewicz, 2017).

d. Sodium chloride in the recipe

Sodium chloride is the main source of chloride ions in most food. It was reported that the presence of salt increases the formation rate of MCPD esters (bound-MCPD) in biscuits during baking. Sodium chloride reacts with the partial acylglycerol present in the fatty portion of the baking recipe and forms MCPD esters. It was reported too that sodium chloride acts as a Lewis acid, which accelerates the sucrose hydrolysis (Fiore et al., 2012). Similarly, sodium chloride can facilitate the esters bond to be detached from acylglycerols, provide a glycerol backbone or empty site for chlorine ion to attach and form MCPD or MCPD esters. The very significant results reported by Mogol et al. found that removing salt from the baking recipe reduced the reaction rate constant of 2- and 3-MCPD by 85.4% and 57.5%, respectively (Mogol et al., 2014). Therefore, salt removal from the baking recipe is a logical approach to reduce the MCPD esters formation within an intended baking duration.

e. Moisture content

The effect of water on the MCPD esters and GE formation is significant, similar in the frying system. Moisture content in the baking system facilitates the formation of 3-MCPD when the heat is increasing with the presence of precursors, for instance, glycerol (Baer, de la Calle and Taylor, 2010; Calta et al., 2004). Water content in a baking (thermal) process can increase the formation of MCPD esters and GE by facilitating hydrolysis of triacylglycerol, altering the pH of the baking system, and promoting other potential reactions, for example, Maillard reactions. Contrary, excessive moisture content causes degradation of MCPD. Hamlet reviewed that MCPD generation was optimum at the range of 2–8% of water content at a given temperature compared to 45% water content (Colin G Hamlet et al., 2004a).

The importance of water content in the formation of 3-MCPD esters and GE was also explained by an experiment of replacing fats with inulin and pectin gels. The experiment showed that higher (>10%) inulin promoted the endogenous 3-MCPD esters formation, while pectin did not exhibit such properties. The observations suggested that inulin could not hold water molecules, allowing water to take part in forming the Maillard compounds, organic acids, and 3-MCPD esters. Sample with inulin as fats replacer also exhibit darker color and higher water loss upon baking. On the other hand, pectin showed stronger water-binding properties, which did not show accelerated Maillard and 3-MCPD esters formation. The authors also deduced that pectin caused a lower pH in the biscuit dough and caused a certain amount of GE decaying (A. Sadowska-Rociek and Cieslik, 2019). Since pectin trapped the water molecules, they cannot participate in the hydrolysis reactions to form 3-MCPD esters and GE.

f. Antioxidants in the fatty portion

An experiment involved the antioxidant fortification of the fatty portion can control 2-,3-MCPD esters, and GE formation during the baking process. The shortenings used were fortified by butylated hydroxyanisole (BHA), rosemary extract, and tocopherol at a single dosage and in the combination of BHA and rosemary extract or tocopherol. Results showed that rosemary was more effective than both tocopherol and BHA in generating lower 2-,3-MCPD esters, and GE when fortified at 200 mg/kg concertation into the fatty portion before the baking process. Effectiveness increased when a combined antioxidant was used. While BHA remained at 200 mg/kg, an increase in rosemary extract or tocopherol up to 800 and 1200 mg/kg was able to control the formation of 2-,3-MCPD esters, and GE. This phenomenon was explained by the antioxidant capability to reduce radical formation during baking (K. M. Goh et al., 2020). It was reviewed that a chlorine radical formed during the thermal process can attack a cyclic acyloxonium free radical to form MCPD (X. Zhang et al., 2013; Z. Zhang et al., 2015). Meanwhile, Goh et al. indicated that antioxidants stabilised the fats portion from oxidation, thus reduced the forming precursor such as partial acylglycerol, especially in the 1,2- esterified di-acylglycerol.

In short, the formation of MCPD esters and GE during temperature increment with precursors is illustrated in Fig. 1.

Conclusions and outlook of future research

The occurrence of 2-, 3-MCPD esters and GE in various food matrices is common by checking the reported literature. Their presence is found in various refined vegetable oils, as well as fried and baked products. There are several reasons for this phenomenon. First, MCPD esters and GE are formed endogenously during the refining process. Second, MCPD esters and GE are carried over from refined vegetable oils into food matrices. Third, further formation of MCPD esters and GE by high processing temperatures with potential precursors used during baking and frying processes. Else, MCPD esters and GE may be degraded when frying and baking temperature is too high.

MCPD esters and GE are formed during deodorisation step as a part of the refining process of vegetable oils to produce odourless edible oil. Both MCPD esters and GE formation are highly associated with high temperature used during the refining steps, with the presence of several vital precursors, such as chlorine and partial acylglycerols. The subsequent use of refined vegetable oils as frying medium or shortening in baking recipes causes the carry forward of 2-, 3-MCPD esters and GE into food matrices as contaminants.

Factors that significantly affects the MCPD esters are chlorine, moisture, and the presence of partial acylglycerol. For GE, the forming pathway and precursors are almost the same, except for the effects of chlorine ion. Processing temperature and duration are the two inseparable factors when frying or baking the food matrices. Both MCPD esters and GE appears to positively increase with processing temperatures and durations to reach a plateau concentration. Then, degradation or decomposition of these contaminations takes place when either process temperatures or duration is further increased.

MCPD esters and GE are dynamically changing their concentrations within frying or baking system, depending on their intrinsic (such as moisture content, presence of chlorine, and oil nature) and extrinsic factors (such as process temperature and duration).

Future study related to MCPD esters and GE formation during food processing should be extended to other thermal methods, for instance, grilling, smoking, and roasting. These are the domestic cooking methods which using uncontrolled temperature and cause the formation of harmful compounds such as polycyclic aromatic hydrocarbon. Yet, the effects of these cooking methods to the formation of MCPD esters and GE

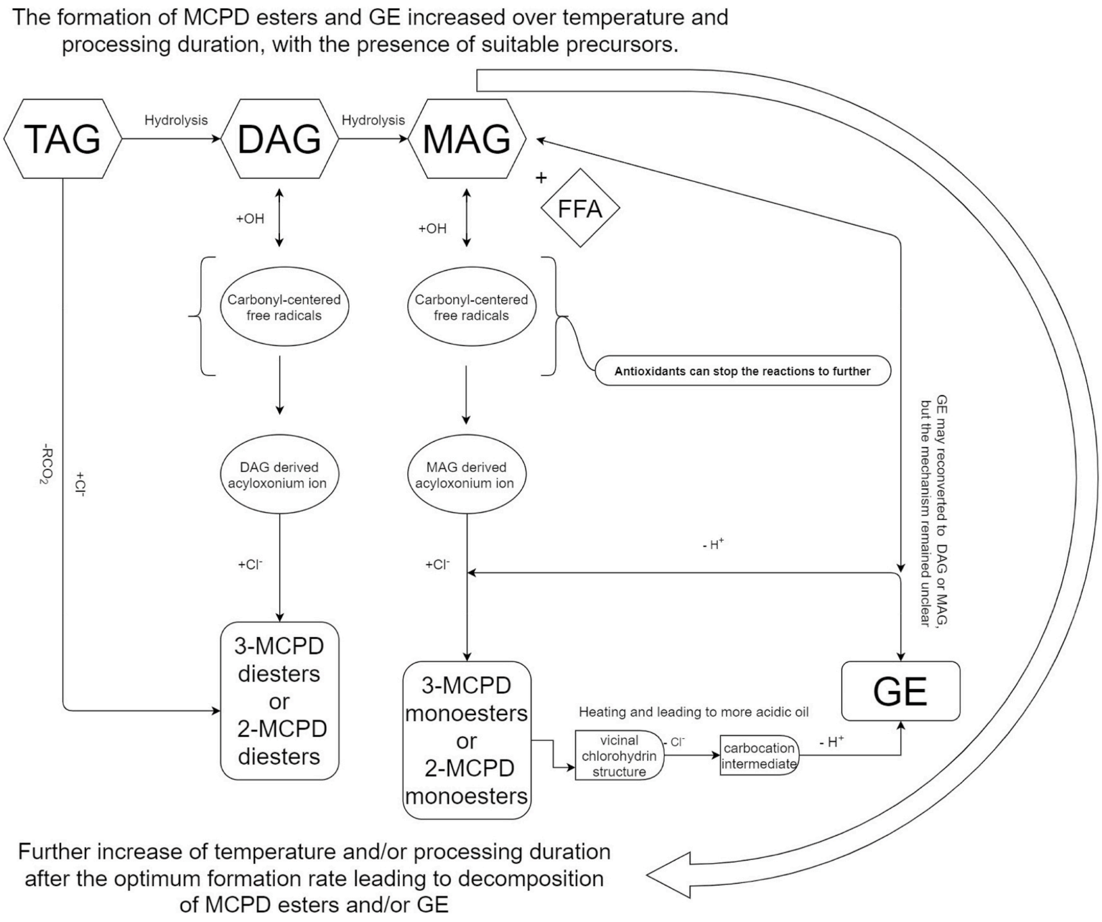

Fig. 1. The formation of MCPD esters and GE during temperature increment with precursors.

is not thoroughly checked.

In addition, the ability of microwave heating to create MCPD esters and GE within the system is remained unknown, although microwave normally serves as food reheating purpose only. It is known that electromagnetic wave causes temperature spiking in the food fatty portion very quickly and the potential to form MCPD esters and GE may be high. Lastly, air frying as a new emerging frying technique using minima or no additional oil for frying may still cause the MCPD esters and GE formation simply because a high temperature is unavoidable to create desirable food palatability characteristic. In short, research data from both simulated food thermal processing and surveillance study regarding MCPD esters and GE should be highly appreciated. We definitely need the input from researchers worldwide to fill the knowledge-gap regarding MCPD esters and GE formation in our food chain, because we are still on the pathway to fully understand their behavior during a food thermal processing.

CRediT authorship contribution statement

Kok Ming Goh: Conceptualization, Writing – original draft, Validation, Data curation, Funding acquisition. **Yu Hua Wong:** Writing – original draft, Resources. **Chin Ping Tan:** Writing – review & editing. **Kar Lin Nyam:** Writing – review & editing, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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