

# Occurrence of 3-MCPD and glycidyl esters during potato chip production: effect of oil type, frying count and chlorine based textural enhancer usage

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In this study, potato chips were produced in a laboratory-scale with identical production flowsheet to the chips industry to investigate the effect of vegetable oil type and calcium chloride (CaCl<sub>2</sub>) content of blanching water on the formation of glycidyl esters (GE) and bound 3-MCPD during potato chip production. Various amounts of CaCl<sub>2</sub> (0%, 1%, and 2%) were used as blanching agent to enhance the textural properties as used in industry. Potato chips were fried using refined sunflower oil, refined canola oil, and refined palm olein in a small-scale industrial fryer. GE contents were 4.2 mg/kg, 5.78 mg/kg and 5.78 mg/kg and bound 3-MCPD contents were 1.2 mg/kg, 2.2 mg/kg and 3.0 mg/kg for potato chips fried in sunflower oil, canola oil, and palm olein, respectively. Also, the bound 3-MCPD content of the final product was increased as the amount of CaCl<sub>2</sub> in blanching water was increased. In general, bound 3-MCPD contents were increased gradually as the frying counts increased with the same batch of frying oil whereas GE contents fluctuated.

**Keywords:** Deep frying, Potato chip, Calcium chloride, Bound 3-MCPD, Glycidyl esters

## 1. INTRODUCTION

3-Monochloropropane-1,2-diol (3-MCPD) and glycidyl esters (GE) are well-known process contaminants of which esterified forms can exist in oils and fat products and free forms can be found in several processed foods [1, 2]. According to the formation pathway of the 3-MCPD, acyloxonium ions and GE are formed from monoglycerides (MAG) and diglycerides (DAG) because of high temperature applications. The presence of organic or inorganic chlorine ion causes the formation of 3-MCPD, which is a chloropropanol substance. Since GE pathway does not necessarily need chloride ions; they form in vegetable oils under elevated temperatures from precursors found in oils such as mono and diglycerides [2-5]. Due to reported carcinogenic effects of 3-MCPD, The European Commission Scientific Committee on Food recommended the tolerable daily intake (TDI) of 2 µg free 3-MCPD/kg body weight for 3-MCPD esters. EFSA Panel on the Contaminants in the Food Chain also determined GE as possible genotoxic carcinogenic assuming a complete hydrolysis of the esters to free glycidol following ingestion [6]. European Commission limited the maximum GE level to 1 mg/kg for vegetable oils and fats placed on the market and to 0.5 mg/kg for vegetable oils and fats destined for the production of baby foods [7].

Temperatures higher than 180°C causes bound 3-MCPD formation while temperatures above 230°C also accelerates GE formation in oils and fats. Different concentrations of GE and bound 3-MCPD's have been frequently reported in many studies for refined vegetable oils [2, 4, 8-11]. GE and bound

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3-MCPD formation mostly occur during the deodorisation step of vegetable oil refining. The temperature of deodorization, initial monoglyceride and diglyceride content of oil are found to be effective on GE and bound 3-MCPD formation [12]. Moreover, certain food preparation methods such as frying and cooking in high temperatures may cause the formation of these process contaminants that makes fried food products susceptible to GE and 3-MCPD existence at higher levels [13, 14].

Potato based fried foods and snacks are being consumed within a very wide age range and become a very important part of the dietary habit of society not only as a food product but also as a social element all over the world. During industrial fried potato chips production, potatoes are peeled, sliced into desired thickness, and blanched to deactivate pectolytic enzymes causing softening in fried products. During blanching, calcium salts, such as  $\text{CaCl}_2$ , are added to the blanching water to maintain better crispiness and improve the textural properties of potato chips. After blanching, excessive water on potato slices is eliminated and potato slices are fried in industrial fryers until water content is reduced under 5% [15]. Sunflower oil and palm olein are well-known frying oils used in the industrial-scale production of par-fried French fries and potato chips. Studies revealed that increasing chlorine content of the food products prior to thermal applications cause higher GE and bound 3-MCPD formation [16-18]. Moreover, duration of frying, type of frying oil, composition of food and processes applied to food prior to frying, also affects the GE and bound 3-MCPD formation [14]. EFSA declared "Potato chips" as one of the food groups to contain highest GE and bound 3-MCPD in the report [6].

The recent study focused on the determination of the effects of frying oil type and  $\text{CaCl}_2$  concentration of blanching water on GE and bound 3-MCPD formation during frying of potato chips. Also, five sequential potato chip frying runs were carried out with each frying oil and the effect of the frying count on GE and bound 3-MCPD content was investigated. This study also highlighted and triggered discussion on the recent situation of possible GE and bound 3-MCPD content of potato chips, which is a highly consumed snack food.

## 2. MATERIALS AND METHODS

### 2.1. MATERIALS

Potatoes (*Solanum tuberosum*), suitable for industrial potato chip production, were harvested from Torbalı, Izmir/Turkey and kindly donated from a local potato chip production company near Izmir/Turkey

and stored at  $+4 \pm 1^\circ\text{C}$  until frying operations.

Refined sunflower oil, refined canola oil, and refined palm olein were obtained from a local refining plant in original tin packages, stored at  $-26 \pm 2^\circ\text{C}$  until frying operations.  $\text{CaCl}_2$  with high purity ( $> 99\%$ ) was purchased from Merck, Germany. All reagents and standards were obtained at suitable purity degrees for analyses.

### 2.2. METHODS

#### 2.2.1. Production of Potato Chips

Potatoes were peeled using standard peeling knives and sliced into 1.5mm thickness with industrial slicer (Berkel, Italy). Potato slices, which are nearly 60 mm of diameter, were selected and used in frying operations to maintain uniformity in sample size. Selected potato slices were rinsed for 20 s with tap water as practiced in industry. After rinsing, the potato slices were blanched at  $75^\circ\text{C}$  for 5 min. The  $\text{CaCl}_2$  levels of blanching water was differed between 0%, 1% and 2% among trials to determine the effect of  $\text{CaCl}_2$  level on GE and bound 3-MCPD formation. Excessive blanching water on potato slices was eliminated before frying operations. Frying oil was kept heated at  $170^\circ\text{C}$  for 60 min before frying. Each frying operation consisted of 5 frying runs at  $170^\circ\text{C}$  temperature for 5 min and 350 g of blanched potato chips were fried at each frying run. Frying oil was kept at  $170^\circ\text{C}$  temperature for 30 min between successive frying runs. When a frying run was finished, the potato chips were taken from the fryer with a metal strainer and shaken to get the excess oil off the potato chips. Sampled potato chips were crushed and absorbed oil was extracted as sample for all chemical analyses with n-hexane for 70 mins using the Soxhlet extraction method [19]. When the extraction was finished, hexane was evaporated with a rotary evaporator under a gentle stream of nitrogen.

#### 2.2.2. Analysis Methods

Initial FFA contents of refined sunflower oil, refined canola oil, and refined palm olein were determined with AOCS Official Method Ca 5a-40. The FFA in oil samples was expressed as oleic acid percentage.

Total monoglyceride and diglyceride of oil samples were determined by capillary gas chromatography with AOCS Official Method Cd 11b-91. Monoglycerides and diglycerides are converted with bis(trimethylsilyl)trifluoroacetamide (BSTFA) and trimethylchlorosilane (TMCS) in pyridine into more volatile trimethylsilyl ether derivatives and determined by capillary gas chromatography.

Quantitative determination of bound 3-MCPD (esters) and GE (as bound glycidol) was done by using the DGF standard method C-VI 18 (10).

According to this method; 1,2-Bis-palmitoyl-3-chloropropanediol-d5 standard (TRC Inc, Canada) and sodium hydroxide (Merck) solution were added and the reaction stopped with addition of sodium chloride solution. Consequently, isohexane (Merck) extraction was applied to remove undesired nonpolar compounds. The sample was extracted with diethyl ether (Merck) ethyl acetate (Merck) mixture, derivatized by using phenylboronic acid (Sigma-Aldrich), dried under nitrogen gas and dissolved in isooctane (Merck) prior to GC-MS (Thermo Scientific, USA) injection. Same procedure was repeated by using sodium bromide solution instead of sodium chloride solution to avoid 3-MCPD formation from GE during analysis. The quantitative difference between two repeats was multiplied by the transformation factor and this value represented the GE content of the sample [20]. The detection limit was found as 0.05 mg/kg for bound 3-MCPD and 0.01 mg/kg for GE. The quantification limit was found as 0.15 mg/kg for bound 3-MCPD and 0.05 mg/kg for GE.

All combinations of frying trials with three different frying oils and three levels of  $\text{CaCl}_2$  concentration of blanching water including 0% of  $\text{CaCl}_2$  as control group were conducted in a full-factorial experimental design. Multivariate analysis of variance (MANOVA) was used to determine the effects of oil type,  $\text{CaCl}_2$  concentration of blanching water and frying counts (independent variables) on GE and bound 3-MCPD contents. One-way ANOVA was used for detailed statistical evaluation of each variable with Minitab 17.0 Statistical software. All frying trials were duplicated, and analyses were triplicated to ensure the robustness of statistical evaluation.

### 3. RESULTS AND DISCUSSION

#### 3.1. INITIAL COMPOSITIONS OF SUNFLOWER OIL, CANOLA OIL, AND PALM OLEIN.

Monoglyceride (MAG), diglyceride (DAG), GE and bound 3-MCPD contents of sunflower oil, canola oil, and palm olein were determined, and results are shown in Table I.

Palm olein is the liquid fraction, which is rich in stearic and oleic fatty acids, obtained by fraction-

ation of palm oil. Since palm olein is rich in saturated and monounsaturated fatty acids, has a better thermal oxidation resistance than many other vegetable oils. Due to its thermal oxidation resistance and suitability for cooking and frying, palm olein is being used in many applications in food industry.

Refining fruit oils such as olive oil, palm oil, and palm oil fractions end up with a high level of GE and bound 3-MCPD formation compared to seed oils [2]. This difference is due to the MAG and DAG contents since these compounds are known as precursors of GE and bound 3-MCPD [21]. Fruit oils such as palm oil and olive oil are more susceptible for hydrolysis reaction since fruit oils are exposed to water longer than seed oils. Therefore, the formation of MAG and DAG which are precursors of GE and bound 3-MCPD are generally higher in fruit oils [22]. As seen in Table I, palm olein had highest MAG and DAG, content among all frying oil samples in our study ( $5.9 \pm 0.3$  mg/kg and  $9.2 \pm 0.3$  mg/kg, respectively). As a result of this, palm olein has the highest initial amount of GE and bound 3-MCPD content, which are 0.44 mg/kg bound 3-MCPD and 10.46 mg/kg GE. This result agrees with a previous study documented that unrefined palm oil samples sold in grocery stores in the United States do not contain a detectable amount of GE and bound 3-MCPD, while refined palm oil samples obtained from various manufacturers contained between 1.51 - 7.23 mg/kg bound 3-MCPD and 0.33 - 10.52 mg/kg GE. Moreover, GE and bound 3-MCPD content of palm olein samples was reported as between 1.4 - 8.43 mg/kg and 1.88 - 9.59 mg/kg respectively [23].

Refined sunflower oil and refined canola oil are seed oils that known as less susceptible for GE and bound 3-MCPD occurrence in refining than fruit oils because of above-mentioned reasons. There was no detectable GE and bound 3-MCPD content in sunflower oil while 0.10 mg/kg bound 3-MCPD and 0.15 mg/kg GE were detected in refined canola oil.

#### 3.2. EFFECT OF $\text{CaCl}_2$ CONCENTRATION OF BLANCHING WATER AND FRYING RUNS ON GE AND BOUND 3-MCPD FORMATION

MANOVA was applied to determine the effects of the independent variables on GE and bound 3-MCPD formation during frying. According to the results of

**Table I** - Chemical composition of sunflower oil, canola oil and palm olein prior to potato chip productions.

	Monoglycerides (%)	Diglycerides (%)	GE (mg/kg)	Bound 3-MCPD (mg/kg)
Sunflower Oil	$3.5 \pm 0.1^b$	$3.1 \pm 0.1^a$	-	-
Canola Oil	$2.5 \pm 0.1^a$	$5.8 \pm 0.3^b$	$0.15 \pm 0.04^a$	$0.10 \pm 0.01^a$
Palm Olein	$5.9 \pm 0.3^c$	$9.2 \pm 0.3^c$	$10.46 \pm 0.15^b$	$0.44 \pm 0.03^b$

Values expressed as mean  $\pm$  standard deviation (two replicates) after statistical evaluation. The values in the same column followed by different superscripts (<sup>a,b,c</sup>) are significantly different ( $p < 0.05$ ).

**Table II** - GE and bound 3 MCPD levels in potato chips fried with sunflower oil, canola oil and palm olein with different CaCl<sub>2</sub> contents.

CaCl <sub>2</sub> Content of Blanching Water	Frying Run	Sunflower Oil		Canola Oil		Palm Olein	
		GE (mg/kg)	Bound 3-MCPD (mg/kg)	GE (mg/kg)	Bound 3-MCPD (mg/kg)	GE (mg/kg)	Bound 3-MCPD (mg/kg)
0% CaCl <sub>2</sub>	1	ND	ND	4.73 ± 0.01 <sup>x,c</sup>	0.2 ± 0.01 <sup>x,a</sup>	4.15 ± 0.03 <sup>x,c</sup>	0.6 ± 0.03 <sup>x,a</sup>
	2	ND	ND	0.52 ± 0.01 <sup>x,a</sup>	0.4 ± 0.01 <sup>x,b</sup>	12.15 ± 0.21 <sup>x,d</sup>	1.3 ± 0.03 <sup>x,b</sup>
	3	ND	0.2 ± 0.03 <sup>x,b</sup>	1.57 ± 0.03 <sup>x,b</sup>	0.7 ± 0.01 <sup>x,c</sup>	3.68 ± 0.04 <sup>x,b</sup>	1.5 ± 0.04 <sup>x,c</sup>
	4	ND	0.2 ± 0.03 <sup>x,b</sup>	6.31 ± 0.01 <sup>x,d</sup>	0.7 ± 0.01 <sup>x,c</sup>	4.20 ± 0.03 <sup>x,c</sup>	1.9 ± 0.04 <sup>x,c</sup>
	5	ND	0.1 ± 0.01 <sup>x,a</sup>	7.89 ± 0.04 <sup>x,e</sup>	0.7 ± 0.01 <sup>x,c</sup>	3.15 ± 0.07 <sup>x,a</sup>	2 ± 0.28 <sup>x,d</sup>
1% CaCl <sub>2</sub>	1	ND	ND	3.86 ± 0.01 <sup>x,d</sup>	0.2 ± 0.03 <sup>xy,a</sup>	6.83 ± 0.01 <sup>xy,a</sup>	2 ± 0.03 <sup>y,a</sup>
	2	ND	ND	1.57 ± 0.03 <sup>x,a</sup>	0.2 ± 0.03 <sup>xy,a</sup>	7.36 ± 0.08 <sup>xy,b</sup>	2 ± 0.07 <sup>y,a</sup>
	3	ND	ND	3.68 ± 0.03 <sup>x,c</sup>	0.6 ± 0.01 <sup>xy,ab</sup>	8.41 ± 0.01 <sup>xy,d</sup>	2 ± 0.04 <sup>y,a</sup>
	4	1.57 ± 0.03 <sup>y,a</sup>	0.3 ± 0.03 <sup>y,a</sup>	3.15 ± 0.04 <sup>x,b</sup>	0.8 ± 0.03 <sup>xy,b</sup>	7.36 ± 0.03 <sup>xy,b</sup>	2.3 ± 0.03 <sup>y,b</sup>
	5	1.57 ± 0.04 <sup>y,a</sup>	0.6 ± 0.03 <sup>y,b</sup>	6.83 ± 0.03 <sup>x,e</sup>	2.2 ± 0.28 <sup>xy,c</sup>	8.12 ± 0.04 <sup>xy,c</sup>	2.5 ± 0.04 <sup>y,c</sup>
2% CaCl <sub>2</sub>	1	3.68 ± 0.03 <sup>y,c</sup>	0.1 ± 0.03 <sup>y,a</sup>	5.26 ± 0.08 <sup>x,d</sup>	0.4 ± 0.01 <sup>y,a</sup>	11.00 ± 0.28 <sup>y,e</sup>	2.6 ± 0.07 <sup>z,b</sup>
	2	2.63 ± 0.03 <sup>y,b</sup>	0.3 ± 0.01 <sup>y,b</sup>	3.68 ± 0.04 <sup>x,c</sup>	1.1 ± 0.01 <sup>y,b</sup>	6.83 ± 0.03 <sup>y,b</sup>	2.4 ± 0.03 <sup>z,a</sup>
	3	1.05 ± 0.01 <sup>y,a</sup>	0.6 ± 0.03 <sup>y,c</sup>	1.73 ± 0.04 <sup>x,a</sup>	1.8 ± 0.01 <sup>y,c</sup>	9.99 ± 0.16 <sup>y,d</sup>	2.7 ± 0.03 <sup>z,a</sup>
	4	2.2 ± 0.01 <sup>y,b</sup>	1.1 ± 0.01 <sup>y,d</sup>	3.15 ± 0.04 <sup>x,b</sup>	1.9 ± 0.03 <sup>y,c</sup>	7.89 ± 0.06 <sup>y,c</sup>	2.6 ± 0.06 <sup>z,a</sup>
	5	4.2 ± 0.28 <sup>y,d</sup>	1.2 ± 0.04 <sup>y,e</sup>	5.78 ± 0.10 <sup>x,e</sup>	2.2 ± 0.07 <sup>y,d</sup>	5.78 ± 0.01 <sup>y,a</sup>	3.0 ± 0.01 <sup>z,c</sup>

ND: not detected. Superscripted <sup>x,y,z</sup> letters represents statistical differences in GE (mg/kg) and bound 3 MCPD (mg/kg) for different CaCl<sub>2</sub> contents for each column. Superscripted <sup>a,b,c</sup> letters shows statistical difference between frying runs for each CaCl<sub>2</sub> content.

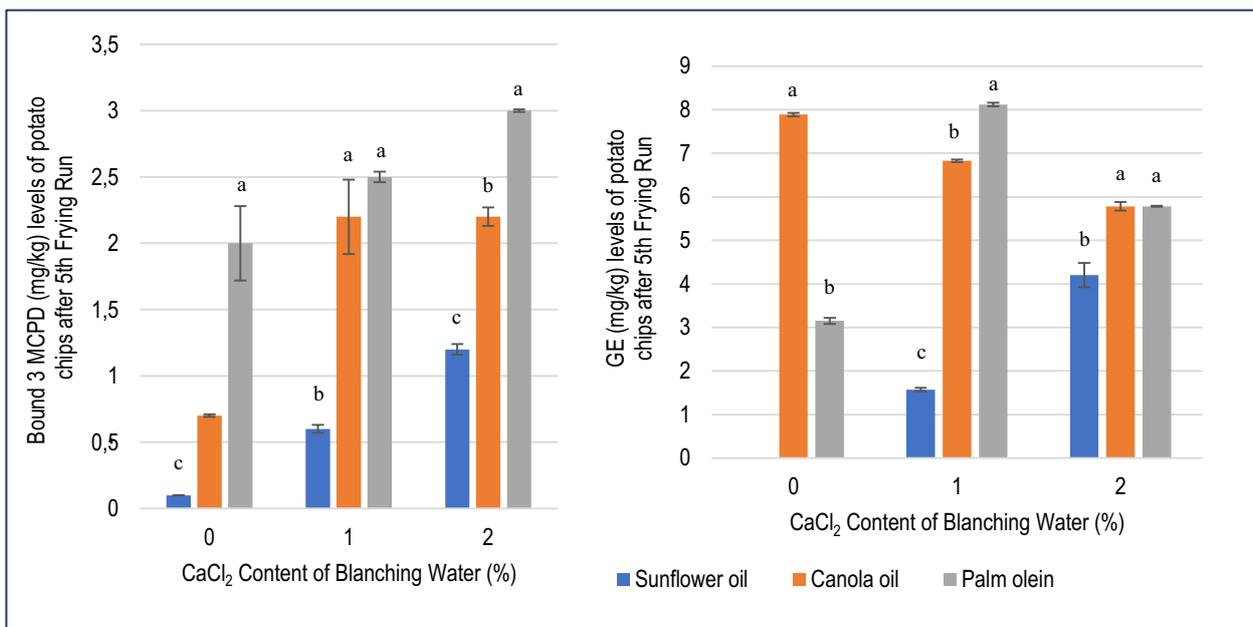
Wilk's and Lawley-Hotelling tests, the effect of oil type, CaCl<sub>2</sub> concentration of blanching water and frying counts were found to be effective on GE and bound 3-MCPD formation during production of potato chips ( $p < 0.001$ ). Since each independent variable was found to be effective, one-way ANOVA together with Tukey's post-hoc test was used for further statistical evaluations.

First, two columns of Table II show the results of GE and bound 3-MCPD content of potato chips fried in sunflower oil. Results showed that GE and bound 3-MCPD content reached up to 1.2 mg/kg and 4.2 mg/kg, respectively at potato chips blanched in 2% CaCl<sub>2</sub> and fried in sunflower oil after 5th frying run. In all potato chip samples fried with sunflower oil, bound 3-MCPD content significantly increased with the addition of CaCl<sub>2</sub> to the blanching water according to ANOVA. GE content of 1.57 mg/kg were detected in potato chips fried in sunflower oil that were blanched with 1% CaCl<sub>2</sub> after 4th and 5th frying run. For the potato chips, blanched in 2% of CaCl<sub>2</sub>, GE level decreased from 3.6 mg/kg to 1.05 mg/kg at first 3 frying runs and increased to 4.2 mg/kg level at 5th frying run. This fluctuation in GE content could be related to the formation pathway of 3-MCPD esters where the GE are mid-products of bound 3-MCPD and there is a possibility of conversion between GE and bound 3-MCPD. According to this formation pathway, GE can be formed from acyloxonium ions, acylglycerols and MCPD esters reversibly [3]. In a previous study, GE and bound 3-MCPD formation during industrial scale potato chips production was investigated and it was reported that potato chips fried in high oleic

sunflower oil were contained 0.4-0.6mg/kg of bound 3-MCPD and 0.1-0.4mg/kg of GE at the end of one-day production with the same batch of oil; supporting that frying is a considerable source for GE and bound 3-MCPD formation [13].

Canola oil had an initial 0.1 mg/kg bound 3-MCPD and 0.15 mg/kg GE content according to results stated in Table I. The bound 3-MCPD content of potato chips fried with canola oil varied between 0.2 mg/kg and 2.2 mg/kg. Although there is a statistical difference between 0% CaCl<sub>2</sub> content and 2% CaCl<sub>2</sub> content in bound 3-MCPD levels of potato chips fried with canola oil, bound 3-MCPD levels of potato chips blanched with 1% CaCl<sub>2</sub>, was not statistically different from other groups. In general, it can be followed from the results that increasing amount of CaCl<sub>2</sub> in blanching water, increases bound 3-MCPD formation during frying with refined canola oil. Frying count was also effective on bound 3-MCPD formation in potato chips fried with canola oil. For all CaCl<sub>2</sub> levels, bound 3-MCPD content was increased with frying runs. This showed that frying count, in other words, time of exposure to high temperature, was statistically important on bound 3-MCPD formation. GE contents were between 0.52 mg/kg and 7.89 mg/kg among all potato chips fried with canola oil. The change in GE correlated by neither CaCl<sub>2</sub> content of the blanching water nor frying counts for potato chips fried with canola oil.

According to our results, potato chips fried with palm olein has highest levels of GE and bound 3-MCPD content. Studies revealed that MAGs and DAGs are precursors of bound 3-MCPD and DAGs has superior potential for forming into 3-MCPD esters in



**Figure 1** - The difference of GE and bound 3-MCPD levels of potato chips after 5th frying run for sunflower oil, canola oil, and palm olein.

**Legend:**

a,b,c. Letters show statistical difference ( $P < 0.05$ ) between sunflower oil, canola oil and palm olein for each  $\text{CaCl}_2$  content (%) of blanching water. Error bars denotes standard deviations between measurements.

thermal treated model systems [24]. In our study, palm olein has highest MAG and DAG contents before frying operations (5.9% and 9.2% for MAGs and DAGs respectively). In a previous study it was indicated that bound 3-MCPD content of potato chips fried in palm oil was reached up to 0.26 mg/kg in and 1 mg/kg [18]. Likewise, in our study, we measured bound 3-MCPD content as 0.6 mg/kg after the first frying run with 0%  $\text{CaCl}_2$  concentration. GE and bound 3-MCPD content in potato chips were reached 11 mg/kg and 2.6 mg/kg respectively for the potato chips produced with 2%  $\text{CaCl}_2$  concentration and after first frying. As the frying runs proceeded, GE content was gradually decreased to 5.78 mg/kg at 5th frying run where GE content was not statistically changed with the frying counts. This may be associated with the formation pathway of 3-MCPD. However, similar tendency was not observed in any other frying oil or  $\text{CaCl}_2$  concentration in our study.

The bound 3-MCPD values have reached and exceeded 2 mg/kg when 1% or 2%  $\text{CaCl}_2$  was used in blanching water in fried potato samples fried with canola or palm olein. According to our results with all frying oils, in general, the chlorine concentration of frying medium was found to be a significant factor for GE and bound 3-MCPD content of fried potato products. Similarly, palm olein had an initial 3.02 mg/kg bound 3-MCPD content and increasing the NaCl concentration of the soaking water of potato chips causes an increase in GE and bound 3-MCPD formation in frying oil in a previous study [14].

Wong et al. reported that the 3-MCPD content of potato chips fried with palm oil were decreased after 3 days of consecutive frying [19]. This degradation behaviour of bound 3-MCPD, which was expressed in several studies, was not observed in our results since all frying operation was concluded in 3.5 hours with one batch of oil. Also, at every frying run, free chlorine ion, natural or originated from  $\text{CaCl}_2$ , was supplied with blanched potato slices, and consequently bound the 3-MCPD content of frying oil absorbed in potato chips was increased.

Deep fat frying is a simultaneous heat and mass transfer process. When the potato slices were immersed in hot oil, water vapor was formed due to high temperature, and it was transferred through the surface of the product due to pressure and concentration gradients. As a result, crust was formed, and pores were developed. Frying oil switch place with evaporating water and fills these pores [15].  $\text{CaCl}_2$  provides chlorine ion in its aqueous solutions, which was absorbed in potato slices during blanching operation of potato slices.

Absorbed frying oil was exposed to free chlorine ion of blanching water that was transferred by potato chips, and during the frying high temperature, GE and bound 3-MCPD formation occurred [19]. Our results showed that using  $\text{CaCl}_2$  in blanching water at potato chips production to maintain a hard-crusty structure increases the bound 3-MCPD formation during frying with sunflower oil, canola oil and palm olein unwillingly. Unlikely, the effect of  $\text{CaCl}_2$  concentration of blanching water on GE levels of

potato chips did not correlate since GE formation was not necessarily needs a free chlorine ion in presence. According to our results, lowest GE levels at every  $\text{CaCl}_2$  contents were measured in potato chips fried with sunflower oil likewise bound 3-MCPD contents. The fluctuation in GE levels as the frying runs proceeds might be due to conversion of GE to bound 3-MCPD when the oil was exposed to high temperatures in presence of chloride ions [25]. As stated before, since potato chips are generally salted and aromatised after the frying operation, the liberation of chlorine ion from NaCl and causing bound 3-MCPD or GE formation was not expected. During the industrial production of fried potato products, as so at fast food restaurants, same frying oil is continuously used for long intervals until the hydrolysis and oxidation levels reach the limit of disposal. Therefore, GE and bound 3-MCPD contents of potato chips collected after the 5th frying run for each oil type were used to discuss the effect of  $\text{CaCl}_2$  concentration on GE and bound 3-MCPD formation during prolonged usage of the frying oil (Fig. 1). Results showed that potato chips blanched with 0% of  $\text{CaCl}_2$  content, has the lowest amount of bound 3-MCPD. As the  $\text{CaCl}_2$  concentration increased, higher levels of 3-MCPD was detected in potato chips. According to Tukey's post-hoc test results, frying potato chips with sunflower oil causes lowest bound 3-MCPD formation for all  $\text{CaCl}_2$  concentrations where palm oil causes highest 3-MCPD formation as seen in Table II and Figure 1.

#### 4. CONCLUSION

3-MCPD is carcinogenic and GE is genotoxic carcinogenic process contaminants that are formed under high temperatures and presence of free chlorine ion in vegetable oils. Results showed that palm olein has a greater initial GE and bound 3-MCPD content than sunflower oil and canola oil. Potato chips fried using palm olein contained higher GE and bound 3-MCPD through all frying runs which possibly dependent on the initial content of MAGs and DAGs in palm olein which are known as precursors of GE and bound 3-MCPD.

Bound 3-MCPD was in the tendency to increase as frying runs proceeds in all  $\text{CaCl}_2$  contents and all oil types. The change in GE was not directly dependent on  $\text{CaCl}_2$  concentration for canola oil while increasing  $\text{CaCl}_2$  content of bleaching water caused an increase in GE for sunflower oil and palm olein. Prolonged uses of same frying oil also gradually increased the bound 3-MCPD formation in potato chips where GE contents were fluctuated as the frying runs were proceeded. The reported

degradation in 3-MCPD content was not observed in our study since every frying operation was continued approximately for 3.5 hours. Besides, further heat load to maintain a frying temperature for two or three days possibly cause the frying oil to reach waste limits due to oxidative stress. Moreover, because of the oil absorption of fried foods with consecutive frying, fresh frying oil needs to be added especially in industrial size fryers. Because of these reasons, it is not realistic using same batch frying oil in three-day period when industrial frying considered.

The most prominent finding of this study was the adjuvant effect of  $\text{CaCl}_2$  on bound 3-MCPD content in final products. Bound 3-MCPD formation accelerated with increasing  $\text{CaCl}_2$  concentration of blanching water. Therefore, using  $\text{CaCl}_2$  in blanching water to enhance the textural properties of potato chips cause an increase in 3-MCPD formation; that supports the need to investigate alternatives for improving texture during production of potato chips.

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#### BIBLIOGRAPHY

- [1] J. Velišek, J. Davidek, G. Janiček, Z. Svobodova, Z. Simicova, V. Kubelka, New Chlorine-Containing Organic Compounds in Protein Hydrolysates. *Journal of Agricultural and Food Chemistry*, 28(6), 1142-1144 (1980).
- [2] Z. Zelinková, B. Svejkovská, J. Velišek, M. Dolezal, J. Velišek, M. Doležal, Fatty acid esters of 3-chloropropane-1,2-diol in edible oils. *Food Additives and Contaminants*, 23 (12), 1290-1298 (2006).
- [3] C.G. Hamlet, L. Asuncion, J. Velisek, M. Dolezal, Z. Zelinkova, C. Crews, et al., Formation and occurrence of esters of 3-chloropropane-1,2-diol (3-CPD) in foods: What we know and what we assume. *European Journal of Lipid Science and Technology*, 113 (3), 279-303 (2011).
- [4] B.D. Craft, K. Nagy, W. Seefelder, M. Dubois, F. Destailats, Glycidyl esters in refined palm (*Elaeis guineensis*) oil and related fractions. Part II: Practical recommendations for effective mitigation. *Food Chemistry* 132, 73-79 (2012).

- [5] K. Hrnčirik, G. van Duijn, An initial study on the formation of 3-MCPD esters during oil refining. *European Journal of Lipid Science and Technology*, 113(3), 374-379 (2011).
- [6] EFSA CONTAM Panel, Scientific opinion on the risks for human health related to the presence of 3- and 2-monochloropropanediol (MCPD), and their fatty acid esters, and glycidyl fatty acid esters in food. *EFSA Journal* 14 (5:4426), 1-159 (2016).
- [7] European Commission, amending Regulation (EC) No 1881/2006 as regards maximum levels of glycidyl fatty acid esters in vegetable oils and fats, infant formula, follow-on formula and foods for special medical purposes intended for infants and young children. *Official Journal of the European Union* 55, 27-29 (2018).
- [8] J. Kuhlmann, Determination of bound 2,3-epoxy-1-propanol (glycidol) and bound monochloropropanediol (MCPD) in refined oils. *European Journal of Lipid Science and Technology* 113, 335-344 (2011).
- [9] K. Franke, U. Strijowski, G. Fleck, F. Pudel, Influence of chemical refining process and oil type on bound 3-chloro-1,2-propanediol contents in palm oil and rapeseed oil. *LWT - Food Science and Technology* 42, 1751-1754 (2009).
- [10] F. Pudel, P. Benecke, P. Fehling, A. Freudenstein, B. Matthäus, A. Schwaf, On the necessity of edible oil refining and possible sources of 3-MCPD and glycidyl esters. *European Journal of Lipid Science and Technology* 113(3), 368-373 (2011).
- [11] B.D. Craft, K. Nagy, Mitigation of MCPD-ester and glycidyl-ester levels during the production of refined palm oil. *Lipid Technology* 24(7), 155-157 (2012).
- [12] O. Özdikicierler, F. Yemişçioglu, A. Saygın Gümüşkesen, Effects of process parameters on 3-MCPD and glycidyl ester formation during steam distillation of olive oil and olive pomace oil. *European Food Research and Technology* 242, 805-813 (2016).
- [13] A. Dingel, R. Matissek, Esters of 3-monochloropropane-1,2-diol and glycidol: no formation by deep frying during large-scale production of potato crisps. *European Food Research and Technology* 241, 719-723 (2015).
- [14] Y.H. Wong, H. Muhamad, F. Abas, O.M. Lai, K.L. Nyam, C.P. Tan, Effects of temperature and NaCl on the formation of 3-MCPD esters and glycidyl esters in refined, bleached and deodorized palm olein during deep-fat frying of potato chips. *Food Chemistry* 219, 126-130 (2017).
- [15] S. Sahin, S.G. Sumnu, *Advances in Deep-Fat Frying of Foods*. CRC Press Taylor & Francis Group, Boca Raton.
- [16] X. Zhang, B. Gao, F. Qin, H. Shi, Y. Jiang, X. Xu, et al., Free Radical Mediated Formation of 3-Monochloropropanediol (3-MCPD) Fatty Acid Diesters. *Journal of Agricultural and Food Chemistry* 61(61), 2548-2555 (2013).
- [17] A. Ermacora, K. Hrnčirik, Influence of oil composition on the formation of fatty acid esters of 2-chloropropane-1,3-diol (2-MCPD) and 3-chloropropane-1,2-diol (3-MCPD) under conditions simulating oil refining. *Food Chemistry* 161, 383-389 (2014).
- [18] Z. Zelinkova, M. Dolezal, J. Velisek, 3-chloropropane-1,2-diol fatty acid esters in potato products. *Czech Journal of Food Sciences* 27, 421-424 (2009).
- [19] Y.H. Wong, K.M. Goh, K.L. Nyam, I.A. Nehdi, H.M. Sbihi, C.P. Tan, Effects of natural and synthetic antioxidants on changes in 3-MCPD esters and glycidyl ester in palm olein during deep-fat frying. *Food Control*, 96 (January 2018), 488-493 (2019).
- [20] DGF, DGF Standard Methods Section C – Fats C-VI 18 (10).
- [21] C. Li, L. Li, H. Jia, Y. Wang, M. Shen, S. Nie, et al., Formation and reduction of 3-monochloropropane-1,2-diol esters in peanut oil during physical refining. *Food Chemistry* 199, 605-611 (2016).
- [22] F. Shahidi, *Bailey's Industrial Oil and Fat Products*. 6. Edition John Wiley & Sons, Inc., New York.
- [23] S. MacMahon, T.H. Begley, G.W. Diachenko, Occurrence of 3-MCPD and glycidyl esters in edible oils in the United States. *Food Additives and Contaminants - Part A Chemistry, Analysis, Control, Exposure and Risk Assessment* 30(12), 2081-2092 (2013).
- [24] J. Šmidrkal, M. Tesařová, I. Hrádková, M. Berčíková, A. Adamčíková, V. Filip, Mechanism of formation of 3-chloropropane-1,2-diol (3-MCPD) esters under conditions of the vegetable oil refining. *Food Chemistry* 211, 124-129 (2016).
- [25] W. Cheng, G. Liu, L. Wang, Z. Liu, Glycidyl Fatty Acid Esters in Refined Edible Oils: A Review on Formation, Occurrence, Analysis and Elimination Methods. *Comprehensive Reviews in Food Science and Food Safety* 16, 263-281 (2017).