Effect of Different Chlorine Sources on the Formation of 3-Monochloro-1,2-Propanediol and 2-Monochloro-1,3-Propanediol Fatty Acid Esters during Frying

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Abstract

Several studies indicated that chlorine salts provoke 3-monochloro-1,2-propanediol fatty acid esters (3-MCPD-FE) and 2-monochloro-1,3- propanediol fatty acid esters (2-MCPD-FE) formation in oils during frying. The amount of MCPD strongly depends on the type and the amount of chlorine salt. Food raw materials, additives themselves may contain several chlorine compounds, providing precursors for 2- and 3-MCPD-FE formation during frying. Then, the fat uptake can cause measurable concentrations in the fried food as well. This paper aims at screening chlorine compounds occurring in food industry. Influence of sodium chloride (NaCl), potassium chloride (KCl), calcium chloride ($CaCl_2$), ferric chloride ($FeCl_3$) and ammonium chloride (NH_4Cl) on the formation of MCPD-FE was investigated, mimicking frying conditions (175-180 °C, atmospheric pressure), applying high oleic sunflower oil as frying medium. 2-MCPD-FE and 3-MCPD-FE were determined by using an indirect method based on alkaline-catalyzed transesterification and GC-MS analysis. As expected, the reference sample without using any chlorine salt resulted only slight increase in 3-MCPD-FE concentration, and no increase in 2-MCPD-FE concentration. In case of the stable salts minor formation was observed. At as high as 3 % dosage of NaCl and KCl 1.6 and 2.4 mg/kg 3-MCPD-FE generated, respectively. Adding $CaCl_2$, NH_4Cl and $FeCl_3$ resulted in very strong MCPD-FE formation by both isomers (2- and 3-MCPD-FE) in this increasing order. 0.1 % $FeCl_3$ generated 70 mg/kg 2-MCPD-FE and 238 mg/kg 3-MCPD-FE by the end of 8-hour heating.

Keywords

3-MCPD-FE, 2-MCPD-FE, chlorine salts, frying, high oleic sunflower oil

1 Introduction

3-MCPD-FE (3-monochloro-1,2-propanediol fatty acid esters) and 2-MCPD-FE (2-monochloro-1,3-propanediol fatty acid esters) are food-borne contaminants, formed in fat containing food and food ingredients during high temperature thermal treatment. Free 3-MCPD was classified by International Agency for Research on Cancer (IARC) as possibly carcinogenic to humans – category 2B [1]. Tolerable Daily Intake (TDI) and Provisional Maximum Tolerable Daily Intake (PMTDI) values for free 3-MCPD have been defined [2, 3]. The current TDI by EFSA (European Food Safety Authority) is 2 µg/kg body weight/day [4]. The PMTDI determined by the Joint FAO/WHO Expert Committee on Food Additives (JECFA) is 4 µg/kg body weight/day since 2017 [5]. Although 3-MCPD occurs in ester bound with fatty acids, according to previous

studies 3-MCPD is released during digestion by enzymatic hydrolysis from their esters [6]. Currently, 2-MCPD and 2-MCPD-FE are not yet classified in terms of carcinogenicity. EFSA has identified a particular need for research on relevant long-term studies and on mechanisms of toxicity of 2-MCPD and their fatty acid esters because there is a limited amount of data available on their toxicity [7].

The presence of 3-MCPD was first reported in acid-hydrolyzed vegetable proteins [8], and currently, the level of free 3-MCPD is regulated only in acid-hydrolyzed vegetable protein and soy sauces, with maximum permitted level 0.02 mg/kg [9]. EFSA has decided to re-open the assessment of 3-MCPD, because of the divergences in opinions between the JECFA and the EFSA. The appropriate regulatory measures will be taken based on the outcome of the

assessment [10]. According to the literature data [11-13], 3-MCPD-FE occur in other foods beyond acid-hydrolyzed vegetable protein and soy sauces, for example in cooking oils, fried potatoes, in roasted and cooked meats, snacks, and practically all thermal-treated products that contain fat. During vegetable oil refining 3-MCPD-FE form in the step of deodorization conducted at high temperature (200-275 °C) [14-16].

In previous studies the formation of 3-MCPD-FE was reported during domestic cooking steps, as well [17-19]. Deep-fat frying is conducted typically at temperature between 150-180 °C. However a serial of complex reactions such as oxidation, hydrolysis, isomerization, and polymerization take place during this process, which result various reaction products. These compounds are present in both frying oil and fried food, as well [20]. Moreover this temperature fulfils the condition for 3-MCPD-FE formation, which starts at 140 °C [21]. Additionally the presence of chlorine-containing compounds and water is provided by their migration from the object fried in the oil, both of them affect the reaction [22, 23]. These chlorine sources are organic or inorganic, and they are in low concentration in food, but this level might be enough for formation of MCPD-FE.

For determination of MCPD-FE a number of analytical methods have been developed, they can be divided into two main groups: direct and indirect methods. With direct quantification methods, individual 2- and 3-MCPD esters are determined, and these methods are mainly based on liquid chromatography-mass spectrometry (LC-MS), and enlarged number of reference compounds and internal standards are required [24, 25]. Additionally the detection limits are higher for individual esters than for indirect method because latter is based on conversion of all of 2- or 3-MCPD-FE into free 2- or 3-MCPD which is than isolated, derivatised, chromatographically separated and quantified. The result is expressed as amount of 2- or 3-MCPD that can be released from 2- or 3-MCPD-FE. These methods require only a small number of analytical and internal standards.

The aim of current work was studying the formation of 3-MCPD-FE and its isomer 2-MCPD-FE during thermal treatment of high oleic sunflower oil (HOSO) in presence of different types of chlorine sources. Five different chlorine-containing salts were investigated: NaCl, KCl, $CaCl_2$, NH_4Cl and $FeCl_3$, which can occur in foods. Moreover, KCl and $CaCl_2$ are permitted as food additives in the European Union, E508 and E509, respectively [26]. The experiments were performed under laboratory conditions.

2 Materials and methods
2.1 Chemicals and solvents
Diethyl ether, ethyl acetate, n-hexane and HPLC-grade water were obtained from VWR (Debrecen, Hungary). Toluene, iso-hexane, sodium bromide, phenylboronic acid (PBA), and the four different chlorine containing salts (calcium chloride/$CaCl_2$, potassium chloride/KCl, ammonium chloride/NH_4Cl, and ferric chloride/$FeCl_3$) were obtained from Merck (Budapest, Hungary). Methanol, sodium hydroxide, and anhydrous sodium sulphate were purchased from Reanal Laborvegyszer (Budapest, Hungary). 1,2-Bis-palmitoyl-3-chloropropanediol-d_5 and 1,3-Bis-palmitoyl-2-chloropropanediol-d_5 internal standards were obtained from Chiron AS (Trondheim, Norway). All reagents and chemicals were of analytical grade. Sodium chloride/NaCl as table salt was purchased from the local market.

2.2 Samples
Refined high oleic sunflower oil (HOSO) was supplied by Bunge Limited (Bunge Zrt. Hungary).

2.3 Methods
For the thermal experiments 300 g of refined high oleic sunflower oil with 0.1 % (0.3 g by NH_4Cl and $FeCl_3$) or 3 % (9 g by NaCl, KCl and $CaCl_2$) chlorine compound in a 600 ml beaker was pre-heated in microwave-oven, then heated up to 180 °C on hot plate, magnetic stirring. The oil was kept gently stirred at 175-180 °C for 8 hours, sampled at T_0 (reaching 175 °C), 1, 2, 4, 6 and 8 hours. Two parallel experiments were conducted for each salt and for the reference without any added salt.

The quantity of 2-MCPD-FE and 3-MCPD-FE was determined by Official AOCS Cd 29b-13 Method [27]. This method is used for determination of 2- and 3-MCPD fatty acid esters and glycidol fatty acid esters in edible oils and fats (in this study we examined only 2- and 3-MCPD-FE). The method is based on alkaline-catalyzed ester cleavage, and derivatization of free diols with PBA. These derivatives are measured by GC/MS coupled system (Agilent 6890 coupled with 5973) in SIM (selected ion monitoring) mode. Deuterated internal standards were used for determination. Characteristic ions for derivatised MCPD-d_5 at m/z 150 and 201, for MCPD at 147 and 196; quantification was based on the ratio of m/z=201–m/z=196. SIM chromatogram of a sample is shown in Fig. 1. For 2- and 3-MCPD, the limit of detection was 0.03 mg/kg, and the limit of quantification was 0.1 mg/kg based on previous experiments (data are not shown).
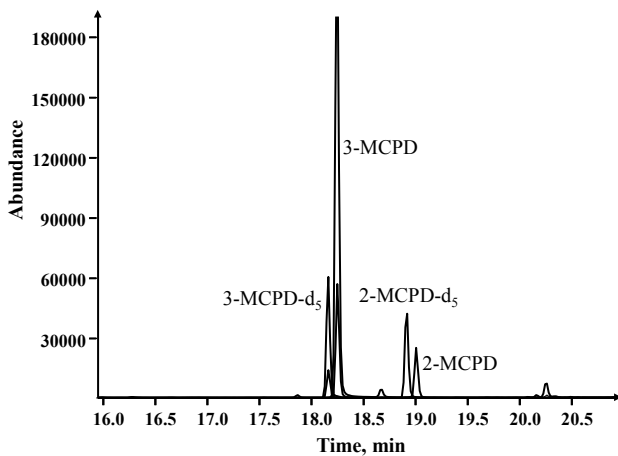
Fig. 1 SIM chromatogram (for derivatised 2- and 3-MCPD-d$_5$ m/z=150, 201; and for derivatised 2- and 3-MCPD m/z=147, 196) of a sample by GC/MS

3 Results

The results are expressed as mean of the two experiments for each applied salt and the reference without salt (Figs. 2-5). The raw material contained 2-MCPD-FE and 3-MCPD-FE under the limit of quantification (<LOQ = 0.1 mg/kg). During the thermal treatment of the refined high oleic sunflower oil without added chlorine salts, very small increase in 3-MCPD-FE content can be noticed, only a low level of 0.3 mg/kg was detected after 4-8 h of thermal treatment, as shown in Fig. 2. The concentration of 2-MCPD-FE did not reach the LOQ during the reaction time.

In presence of different chlorine salts 2-MCPD-FE and 3-MCPD-FE formed in different amounts depending on the salt type and heating time. Despite of the high dosage (3 %) of NaCl and KCl, these chlorine salts resulted the smallest increase in both MCPD-FE content. KCl provoked about 1.5-2 times higher 3-MCPD-FE level than the table salt. The dynamics of formation was also different. In case of potassium chloride the concentration of 3-MCPD-FE showed a maximum point during the thermal treatment at about 4 h. After this point the concentration decreased by about 10 % until the end of the process. With NaCl continuous increase until the end of the experiment was found. The rate of increase reduced between 6 and 8 h, showing that a maximum value could have been expected after 8 h. The level of 2-MCPD-FE did not reach the LOQ in the first 2 hours during the experiment with NaCl. At 4, 6 and 8 hour, the 2-MCPD-FE content generated by KCl was about 2.0-2.5 times higher than by NaCl. The dynamics of formation was the same for the two salts with continuous increase.

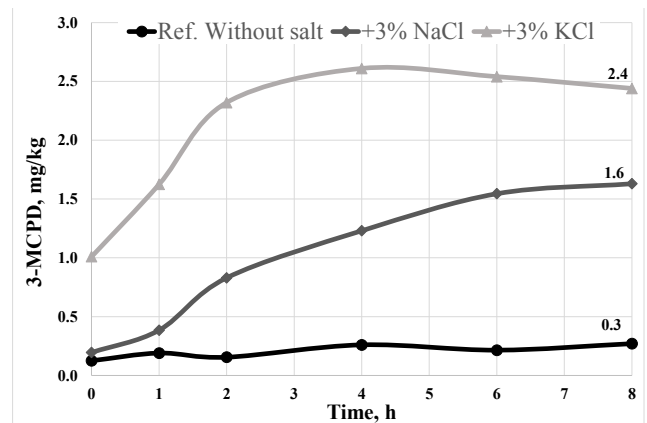Adding 3 % CaCl$_2$ generated 20-30 times higher increase in 2-MCPD-FE and 3-MCPD-FE content than NaCl.

Fig. 2 Formation of 3-MCPD esters during the thermal experiments with different salts (Reference test without salt; with 3 % NaCl; with 3 % KCl)
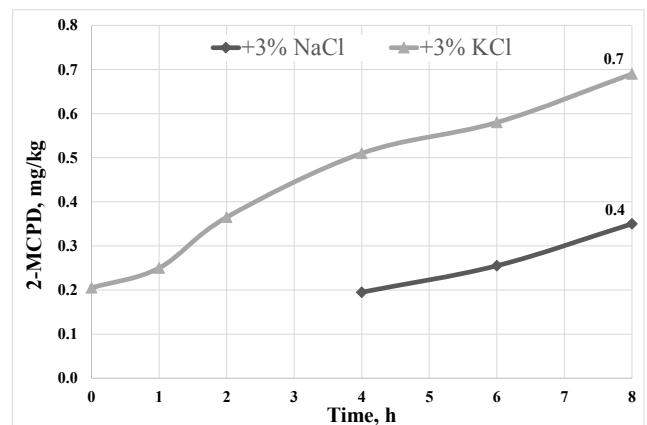

Fig. 3 Formation of 2-MCPD esters during the thermal experiments with different salts (with 3 % NaCl; with 3 % KCl)
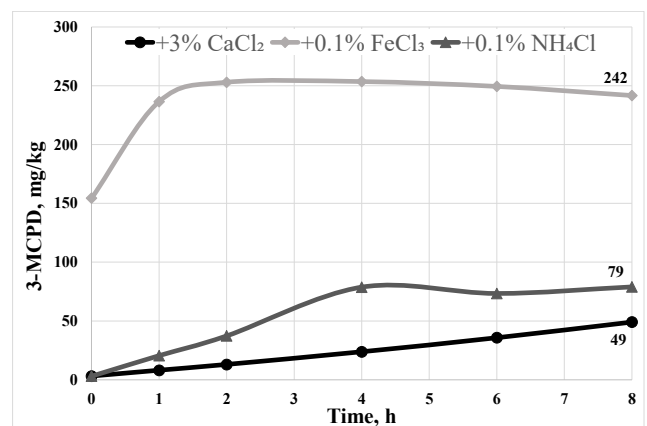

Fig. 4 Formation of 3-MCPD esters during the thermal experiments with different salts (with 3 % CaCl$_2$; with 0.1 % FeCl$_3$; with 0.1 % NH$_4$Cl)

After 8 hours about 9 mg/kg 2-MCPD-FE and about 50 mg/kg 3-MCPD-FE was measured, and the concentration of both increased steadily as in case of NaCl. Applying NH$_4$Cl (0.1 %) caused even 1.5-2.0 times higher 2- and 3-MCPD-FE concentration than the 3 % CaCl$_2$. After increasing to 79 mg/kg during 4 hours, the

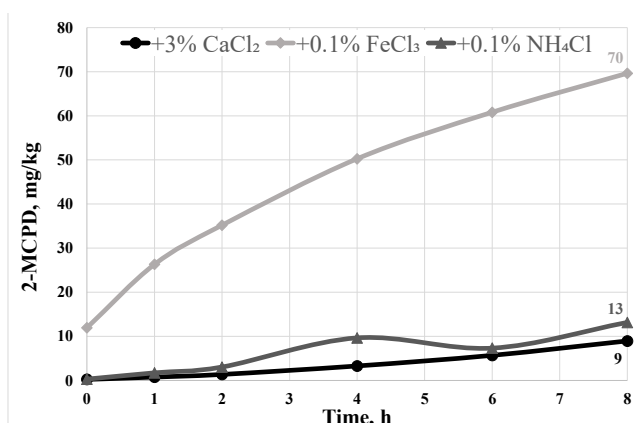**Fig. 5** Formation of 2-MCPD esters during the thermal experiments with different salts (with 3 % CaCl$_2$; with 0.1 % FeCl$_3$; with 0.1 % NH$_4$Cl)

Fig. 6 Ratio of 3/2-MCPD-FE during the thermal experiments with different salts (with 3 % NaCl, with 3 % KCl, with 3 % CaCl$_2$; with 0.1 % FeCl$_3$; with 0.1 % NH$_4$Cl)

3-MCPD-FE content stagnated in the remaining time of the test (4-8 h). The 2-MCPD-FE content showed increasing tendency till 13 mg/kg.

With 0.1 % FeCl$_3$, the level of MCPD-FE formation was substantially faster and higher than in the case of the other salts. FeCl$_3$ catalyzed 3-MCPD-FE formation, more than 100 mg/kg was observed already during the heat up period. The concentration reached about 250 mg/kg at 2 hours, and has stagnated for two more hours, and then slight decrease was noticed until the end of the treatment. The formation of 2-MCPD-FE showed different dynamics, the concentration increased steadily until the end of the experiment, reaching almost 70 mg/kg.

During the heating period to 175 °C, increase in 2- and 3-MCPD-FE content was already observed, especially in the case of KCl and FeCl$_3$, moreover 3-MCPD-FE content reached maximum value during the 8-hour heating by both salts. Generally, most of the contaminants formed during the first 2-4 hours of treatment in every experiment, as shown in Table 1.

The ratio of 3-MCPD-FE/2-MCPD-FE is presented on Fig. 6. Applying KCl and NH$_4$Cl in the first 1-2 hours the
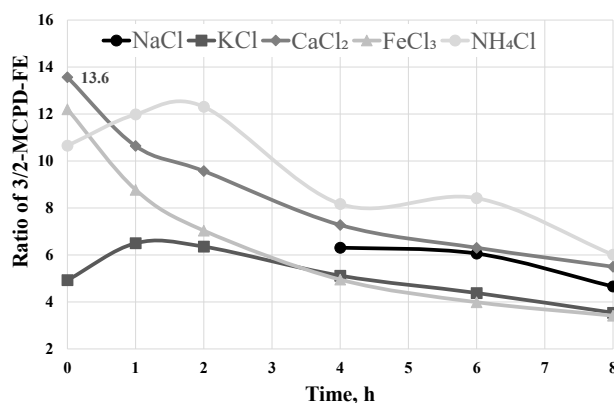
ratio increased, reached maximum (6 and 12 respectively) and then decreased during the rest of frying time. With FeCl$_3$ and CaCl$_2$ the ratio could already reach the maximum during the heat up period, therefore we found continuous reduction during frying. In case of NaCl the maximum ratio should fall between 2 and 4 hours, as at 2 hours no 2-MCPD-FE was detected yet, while at 4 hours the ratio already stagnated and then started decreasing. All in all, the maximum ratio was the highest and appeared the earliest with salts with the highest catalytic effect (FeCl$_3$, CaCl$_2$ and NH$_4$Cl).

4 Discussion

The presence of MCPD-FE, especially 3-MCPD-FE in vegetable oils during the refining process was examined exhaustively in previous studies [28, 29]. The formation of MCPD-FE was verified in fat containing food and food ingredients treated at high temperature as well [17-19]. Therefore the examination of frying process in presence of different chlorine sources is well-established. Moreover because of the fat uptake of the fried food, a clear carry-over of these contaminants can be assumed, which was proved before [30].

Table 1 2- MCPD-FE and 3-MCPD-FE content at T_0, and after 2-8h frying, in percentage of the value after 8 h treatment

	Ratio %									
	T_0		2h		4h		6h		8h	
	3-MCPD	2-MCPD	3-MCPD	2-MCPD	3-MCPD	2-MCPD	3-MCPD	2-MCPD	3-MCPD	2-MCPD
Without salt	46.3	-	57.4	-	96.3	-	79.6	-	100.0	-
+3 % NaCl	12.0	-	50.9	-	75.5	55.7	94.8	72.9	100.0	100.0
+3 % KCl	41.4	29.7	95.1	52.9	107.0	73.9	104.1	84.1	100.0	100.0
+3 % CaCl$_2$	6.4	2.6	26.5	15.2	48.5	36.7	72.9	63.5	100.0	100.0
+0.1 % FeCl$_3$	61.4	17.2	104.2	50.5	104.6	72.2	102.0	87.3	100.0	100.0
+0.1 % NH$_4$Cl	3.9	2.2	47.2	23.1	99.7	73.4	92.9	66.3	100.0	100.0

In our investigation even the most commonly used NaCl provoked measurable increase in 3-MCPD-FE level during 8-hour heating experiment. Other studies also reported the effect of NaCl on the formation of 3-MCPD-FE [22, 31]. Wong et al. [32, 33], showed in their studies the ability of NaCl for 3-MCPD-FE formation by soaking potato chips and chicken breast in different concentrations of NaCl solution prior to frying. They observed that higher concentration of NaCl in the soaking solution resulted higher concentration of 3-MCPD-FE in the oil. Calta et al. [23] concluded similarly in food processing simulation, as well. Wong et al. [33] also discovered that increasing the number of frying cycles caused partial decomposition (30-70 %) of 3-MCPD-FE, during frying of potato chips using 0, 1, 3 or 5 % NaCl solution for soaking; however, the 3-MCPD-FE content was higher in the raw material. Frying of chicken breast showed the opposite: increasing the number of frying cycles increased the 3-MCPD-FE content [32]. This observation proves the influence of the food matrices. In our study in case of 3 % NaCl, 3-MCPD-FE content did not achieved a decreasing phase, but with other salts stagnation or reduction was recognized.

Reduction of 3-MCPD-FE content was reported in deodorization studies as well. Ermacora and Hrncirik [34] noticed the thermal degradation of 3-MCPD-FE in model system simulating deodorization, at 180°C the degree of decline was 30 % after 24 h treatment. Similar results were obtained by Pudel et al. [35] with 4-6 hour long experiments at 200 and 240 °C. During frying experiments of Ben Hammouda et al. [36] 30-50 % degradation was observed after 16 h of thermal process.

As we described, all the examined salts caused increase in 3-MCPD-FE content of the oil, the level of change was very different depending on the type of the salt. In the study of Zhang et al. [37] NaCl, KCl and $FeCl_3$ promoted the formation of the contaminants from diglycerides at 240 °C, but $CaCl_2$ did not. At lower temperature (120 °C) only $FeCl_3$ showed catalytic effect. The same experiments with triglycerides were repeated by this research team, and the results showed that only $FeCl_3$ could form 3-MCPD-FE at 120 and 240 °C, NaCl, KCl and $CaCl_2$ could not [38]. They proved that Fe^{3+} promotes radical generation under the experimental conditions (high temperature and low moisture content), and the chlorine in $FeCl_3$ can immediately react with these radical intermediates to form 3-MCPD-FE. In the applied model reactions with analytical grade reagents the other examined chlorine salts did not support 3-MCPD-FE formation.

To the contrary, in our experiments we used real oil matrix, containing not only triglycerides, but also a numerous minor components, which might influence the catalytic effect of chlorine salts. Nevertheless, the strong catalytic effect of $FeCl_3$ was verified in both case, as in research of Kuhlmann [31] and Li et al. [39], as well.

The ratio of 3/2-MCPD was presented in some studies before, the value ranged from 1.7:1 to 5:1 [16, 40, 41]. Ermacora and Hrncirik [34] found that one of the degradation pathways for 3-MCPD-FE is the isomerization to 2-MCPD-FE. Similarly, Kuhlmann [40] explained the decrease of the ratio of 3/2-MCPD-FE with isomerization, while the overall MCPD-FE was increasing proportionally to the temperature increase in the deodorization experiments. Our results support the isomerization of 3-MCPD-FE to 2-MCPD-FE. The increase of 2-MCPD-FE content was steadily almost by all of the salts, while the concentration of 3-MCPD-FE stagnated or decreased during frying. It may be explained with the different availability of the carbon atoms on the glycerol backbone. The sn-2 position is less available for the chlorine than the sn-1 and sn-3, so in the first part of the thermal treatment the formation of 3-MCPD-FE is faster. However 2-MCPD where the chlorine is bonded to sn-2 carbon is more stable than 3-MCPD where the chlorine is in external position.

The formation of 3-MCPD-FE (and 2-MCPD-FE) at the beginning of the thermal treatment is one of our most important observations, and it is comparable with previous studies, not necessarily dealing with frying process. De Kock et al. [21] concluded similarly on 3-MCPD-FE formation during deodorization of vegetable oils (2-MCPD-FE was not examined).

5 Conclusion

Present investigation showed the effect of different chlorine salts on the formation of 3-MCPD-FE and 2-MCPD-FE at temperature of frying in high oleic sunflower oil. The 2-MCPD-FE content in the samples was always substantially lower than the 3-MCPD-FE content. Based on the results $FeCl_3$ and NH_4Cl expressed the strongest catalytic effect. The stable salts had magnitudes lower influence. Among these KCl caused significantly higher 3-MCPD-FE increase than NaCl. The results suggest that using of table salt itself does not cause health concerns in frying. From a practical point of view the real problem is the presence of $FeCl_3$ in the frying system. As proved in model system before, not only iron chloride but also other iron salts can catalyze the formation of MCPD-FE

if chlorine source is available in the system. It can be assumed that it works in the same way in real oil matrices. We concluded that in case of salts with stronger catalytic effect MCPD-FE noticeably increased already during the heat-up period, as well. The effect of short heating times (0-1h) and lower concentration (<0.1 %) of the most effective salt ($FeCl_3$) needs further study.

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