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Glycerol-Based Process Contaminants in Palm Oil

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Abstract

Palm oil is one of the common used vegetable oil in food industry throughout the the world. This tropical palm fruit is reddish in color because of rich beta-carotene content. There are two types of palm oils that can be produced from the palm fruit. First type is palm oil, and it is produced from the pulp of the palm fruit. Second type is palm kernel oil and it is produced from the kernel part of the fruit. Palm oil exposed to high temperatures may have changes in its lipid matrix which leads to the formation of 3-monochloropropane-1,2-diol (3-MCPD) esters, additionally 2-monochloropropane-1,3-diol (2-MCPD) and glycidyl fatty acid esters. According to International Agency for Research on Cancer, 3-MCPD is a substances that have a possibility to cause cancer. European Food Safety Authority also has evaluated the risks of those substances for public health recently and stated that those substances are especially formed during the refining process of vegetable oils at high temperatures such as 200°C. There are two methods using for determining the esters of palm oil. First one is direct method based on LC-MS/MS which offers higher specificity and very low LOD/LOQ for each single 3-MCPD fatty acid esters, on the other hand it requires all set of standard materials for determination. The second method is indirect method including hydrolysis and derivatization of the analyte and determination step with GC-MS. In the scope of this study, 3- and 2- MCPD, their fatty acid esters, and glycidyl fatty acid esters occurrence during processes of palm oil, its regulation, its adverse effects on human health, and analytical methods for determining those type of esters are reviewed.

Keywords: Palm oil, Glycerol-based process contaminants, Analytical methods, Regulation, Health effects

INTRODUCTION

Palm fruit comprises a kernel enclosed in a shell called endocarp surrounded by pulp called mesocarp (Corley&Tinker, 2007). The color of the palm fruit is orange-red based on the higher content of the carotene. Palm oil is extracted from the ripened mesocarp of the fruits of palm oil tree (Elaeis guineensis). Crude palm oil and palm kernel oil are two different types of oils that can be obtained from the mesocarp and kernel of the palm, respectively. These oils are highly saturated in fatty acids. Their percentage is between 50% and 80% and they are esterified with glycerol. Palm oil exposed to high temperatures may have changes in its lipid matrix which leads to the formation of 3-monochloropropane-1,2-diol (3-MCPD) esters, additionally 2-monochloropropane-1,3-diol (2-MCPD) and glycidyl fatty acid esters.

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risks of those substances for public health recently and stated that those substances are especially formed during the refining process of vegetable oils at high temperatures such as 200°C. In the scope of this study, 3- and 2- MCPD, their fatty acid esters, and glycidyl fatty acid esters occurrence during processes of palm oil, its regulation, its adverse effects on human health, and analytical methods for determining those type of esters are reviewed.

Composition of Palm Oil

Palm oil and palm kernel oil includes higher amount of saturated fatty acids. Palm oil has semi solid state at ambient temperature and contains some various saturated and unsaturated fats in forms of palmitate (44%, saturated), oleate (39%, monounsaturated), linoleate (10% polyunsaturated), stearate (5% saturated), myristate (1%, saturated), linolenate (0.3% polyunsaturated) and glyceryl laurate (0.1% saturated) (Cottrell, 1991).

One tablespoon of processed palm oil is 120 calories and contains13.6 grams of fat, 2.17 mg of vitamin E and 1.1 mg vitamin K. Fresh red palm oil also contains higher amount of beta carotene.

Red colored palm oil is obtained in a process in which 80% of the original carotenoids level remain. Therefore, it can evaluated as natural source of carotenoids which enhances functionality of immune system and improves cardiovascular health. Carotenoids have antioxidant properties, therefore they preserve cells and tissues from the detrimental effect of free radicals.

Palm Oil Production: From Plantation To Final Use

After harvesting, the palm fruit is transported to the mills and sterilized with steam to inactivate enzymes and microorganisms (Gunstone, 2011). The fresh fruit bunches of the fruit needs to be processed within 48 hours. The palm fruit can produces two significant types of vegetable oils known as palm oil and palm-kernel oil. Another product is palm kernel cake which is used for livestock feed.

Processing and Refining

When the mesocarp is fully ripened palm fruits contains about 56–70% edible oil. This oil can be extracted by using different methods and these methods are classified by four pathways according to their degree of complexity. The basic operations used in the palm oil processing are fruit sterilization, fruit loosening/stripping, digestion, oil extraction and clarification.

Fruit sterilization denotes heat providing and moisture absorption. The goal of the process is to inactivate the lipolytic enzymes found in the mesocarp (Owolarafe et al., 2002; Poku, 2002).

There are two defined refining process for crude palm oil; physical refining and chemical refining. Physical refining includes degumming, bleaching, and deodorizing process where refined bleached deodorized palm oil (RBD) and palm fatty acid distillates are formed.

Two fractions can be obtained from RBD as palm stearin and palm olein. Chemical refining includes alkali neutralization, bleaching, deodorizing, neutralization and fractionation steps. At the end of the process palm stearin and palm olein are occurred (Ogan et al., 2015).

By-Products

Oil by-products including the empty fruit bunches, palm oil mill effluent, sterilizer condensate, palm fiber and palm shell are main byproducts that formed during the processing steps of palm. These by-products are used organic fertilizer in palm oil areas and also in the manufacture of soaps, animal feed while palm fiber and shell are used as fuel (Yusoff, 2006).

They are also widely used in the manufacturing of candles, cosmetics, toiletries and pharmaceutical products. Moreover, they are used in oleochemical industries and also used as a raw material in production of Vitamin E as well as production of animal feed (Tan, 2006).

Esters of Palm Oil

3-MCPD is known as a viscous liquid, it occurs as a racemic mixture of its enantiomers, (S)-(+) and (R)-(-) 3-MCPD (Velisek, 2002; Hamlet et al., 2004). Each enantiomer of 3-MCPD shows different toxicological properties. The (S)-enantiomer exhibits antifertility activity, while the supplementary (R)-enantiomer has a harmful effect on kidneys and 3- MCPD also showed genotoxicity in vitro (Lynch et al., 1998; Velisek et al., 2002).

3-Monochloropropane-1, 2-diol (3-MCPD) and other derivatived chloropropanols like 2-monochloro-propane-1,3-diol (2-MCPD) have been known as process contaminants occurred in thermally processed food products like bakery products, liquid seasoning as well as in refined oils. Besides, 3-MCPD is formed in the presence of sodium chloride that is naturally present in the food or added to the food (Hamlet et al., 2002; Hamlet et al., 2004; Franke et al., 2009; Baer et al., 2010). The amount of 3-MCPD increased at high temperatures between 100–230^{o}C and it could be reached its highest value at 230^{o}C. It is reported that the concentration 3-MCPD in unrefined oils and fats is in trace levels, and the main problem with 3-MCPD is related to the refining process for oils and fats (Pudel et al., 2011). Degumming with water, neutralization with potassium hydroxide and bleaching before deodorization can be rated among the useful techniques and methods to reduce and minimize the formation capacity of the palm oil in terms of 3-MCPD and glycidyl esters (Ramli et al., 2011). The lowest amount of 3-MCPD is generated in biscuits as they had a low salt content and their water content was below the optimum level (Calta et al., 2004).

For minimizing the 3-MCPD ester formation in edible fats and oils, acid dosage should be reduced based on the crude oil qualities. Otherwise acid degumming process should be substituted with other process. Besides, neutralization of the acidity prior to deodorization was shown, effective in reducing the formation of 3-MCPD esters (Weißhaar, 2008). In addition to processing conditions, growing conditions including regional, climatic, fruit cultivation, fertilization, and harvesting should be considered. In the future studies and researches, minimizing 3-MCPD esters will be influenced by the results of toxicological studies.

As a summary, in order to decrease esters and relevant compounds there exists three ways; removing of critical reactants from the raw material, changing of the refining process or removing of formed 3-MCPD esters and relevant compounds from the refined product (Henderson & Osborne, 2000).

Analytical Methods to Determine Esters of Palm Oil

To determine the esters of palm oil requires some sophisticated techniques including high pressure liquid chromatography (HPLC), gas chromatography equipped with mass spectrophotometric detector (GC-MS), and solid phase micro extraction (SPME). There are two methods using for determining the esters of palm oil. First one is direct method based on

LC-MS/MS which offers higher specificity and very low LOD/LOQ for each single 3-MCPD fatty acid esters, on the other hand it requires all set of standard materials for determination. The second method is indirect method including hydrolysis and derivatization of the analyte and determination step with GC-MS. Indirect method have an increased robustness, involve hydrolysis and derivatization. Also, it might induce chemical modifications of the analyte (Henderson&Osborne, 2000;Vicente et al., 2015). Recently, there is a promising new method has been released based on QuEChERS method (quick, easy, cheap, effective, rugged, and safe). The method includes direct analysis of the extract and it does not need derivatization and determination is based on gas chromatography–triple quadruple mass spectrometry (Genauldi et al., 2017).

Effects of Palm Oil and Their Esters on Health

Even though palm oil contains higher amount of saturated fatty acids, its preferential esterification at the sn-1 and sn-3 carbon of triglycerides decreases their absorption and metabolic effects. It is reported that there is no experimental data that enables to understand the relation between palm oil consumption and cancer, therefore it is reported if the limit set for saturated fatty acids intake is kept below %10 of total energy in the daily diet then adverse effects can be prevented (Marangoni et al., 2017). Regarding 3- MCPD, its occurrence in the consumed food attract attention of scientist due to its possible toxicological properties. According to International Agency for Research on Cancer, 3-MCPD is a substances that have a possibility to cause cancer. It is reported that the main target organ for 3-MCPD toxicity is the kidney, with chronic oral exposure resulting in nephropathy, tubular hyperplasia and adenomas (JECFA, 2002). On the other hand, there is a few data to determine the exposure of 3-MCPD to consumers, therefore it is recommended to get more analyses of 3- MCPD in foods (Boon and Biesebeek, 2016).

Regulations about Palm Oil and Their Esters

According to the Regulation (EU) No 1169/2011 on the provision of food information to consumers entered into application on 13 December 2014, specific information on the vegetable origin of refined oils and fats should be given on the food packaging. Therefore, food producers should indicate the specific type of vegetable fat and oil they used which includes palm oil. For free 3-MCPD in soy sauces and hydrolysed soy protein in the commission regulation (EC) 1881/2006 a limit of maximal 20 mg/kg exists and the Scientific Committee on Food (SCF) of the European Commission as well as the Joint FAO/WHO Expert Committee on Food Additives (JECFA) defined a tolerable day intake (TDI) of 2 mg free 3-MCPD per kg body weight.

Provisions for methods of sampling and analysis for the official control of 3-MCPD are laid down in Commission Regulation (EC) No 333/2007.

CONCLUSION

Palm oil isn't only used in food sector, but also used in cosmetics, pharmaceutical products, among others. Palm oil exposed to high temperatures may have changes in its lipid matrix which leads to the formation of 3-monochloropropane-1,2-diol (3-MCPD) esters, additionally 2-monochloropropane-1,3-diol (2-MCPD) and glycidyl fatty acid esters. Eventhough, 3-MCPD is declared as a substances that have a possibility to cause cancer. On the other hand, there is a few data to determine the exposure of 3-MCPD to consumers, therefore it is recommended to get more analyses of 3- MCPD in foods. Formation of 3-MCPD in foods can be minimized if the process conditions are optimized and raw material with higher quality can be obtained.

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