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Refining of palm oil: A review on palm oil refining process, 3-MCPD esters in refined palm oil, and possible reduction tactics for 3-MCPD esters

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■ **Abstract :** Palm oil is one of the basic edible vegetable oil which is used in almost every food processing industries. The palm oil is derived from the oil palm. Globally, About 80% fractions of oil palm are used for edible purposes. Therefore for the healthy life, the quality of palm oil should be good. The process of palm oil manufacturing is same as other vegetable oil manufacturing. As other vegetable oil, in palm oil manufacturing involves four major steps which are neutralization, degumming, bleaching and deodorization. These four steps were jointly known as refining process. 3-MCPD is a process contaminant forms during high heat processing mainly in the deodorization process. The recent studies shows that 3-MCPD is carcinogenic and genotoxic in nature. This review work mainly focuses on the hazards of 3-MCPD and possible routes to reduce its level to tolerable limits.

■ **Key words :** 3-MCPD, Bleaching, Degumming, Deodorization, Palm oil, Refining

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The palm oil is derived from the oil palm, *Elaeis guineensis.* Oil is the basic fraction of oil palm which gives commercial value to this crop. Palm oil can be archieved both from mesocarp of fruit and kernel of nuts. The oil obtained from mesocarp of fruit is known as palm oil whereas the oil obtained from kernel of nuts is known as palm kernel oil. Palm oil constitutes unsaturated (Oleic acid) and saturated (Palmitic acid) fatty acids (Noor *et al.*, 2017). About 80% of products formed from palm oil are used as edible intension (Basiron, 2007). Food products processed using palm oil have long shelf life than the food products processed from other vegetable oils because palm oil contains higher amounts of unsaturated fatty acids such as oleic acid which is responsible for oxidative stability. Both palm oil and palm kernel oil are rich source of saturated fatty acids esterified with glycerol, around 50% and 80%, respectively (Mukherjee and Mitra, 2009). Palm kernel oil is also acquired from oil palm and having very different chemical composition, physical properties and applications than palm oil. Palm oil is generally used in some food applications, such as cooking oil, shortening, and margarine (Ho and Chow, 2000).

To become tolerable for human consumption, most edible oils should be purified (Gibon *et al.*, 2007 and Gibon *et al.*, 2009). Due to the high requirement of palm oil, it is necessary to refine the oil to get quality product to meet healthy life. Crude palm oil may contain phosphatides, colour compounds, peroxides and other contaminants which affect the human health when consumed. The refining process is one of the basic and most convenient process to remove such types of contaminants from oil. Production of vegetable oil comprises of various manufacturing steps, among these, refining is the most crucial step (Khan, 2015). Crude palm oil is usually refined and fractioned into liquid palm olein and solid palm stearin (Clemens *et al.*, 2017).

Crude palm oil is refined to eliminate the unacceptable substances before consumption. Minor components including oxidation products, free fatty acids, phospholipids, pigments, trace metals and other impurities are discharged during refining (Ramli *et al*., 2011). Most of the edible oils are refined in two ways physically and chemically. Chemical refining is also called as alkali refining in which the degummed palm oil is treated with alkali (mainly sodium hydroxide) prior to bleaching. This process is called as neutralization. Chemical refining of palm oil involves four major steps degumming, neutralization, bleaching and deodorization. Whereas physical refining of palm oil comprises three steps degumming, bleaching and deodorization. The many edible oils were processed by removing unwanted components which can affect taste, appearance, shelf stability, and safety and consumer acceptance. Both acceptable as well as unacceptable chemical changes will occur in oil during the refining process because of high temperature.

3-monochloropropane 1,2-diol is process adulterant forms during high temperature processing mostly, during deodorization. Recent studies reported that 3-MCPD is carcinogenic and genotoxic in nature. 3-MCPD consumption may results in formation of tumours in various organs; kidney is the main target organ.

Refining of palm oil :

As palm oil is derived from fruits of oil palm, palm oil is produced at oil mill by pressing, striping, sterilization and clarification. The crude palm oil is extracted from oil palm by series of unit operations like pressing, crushing etc which will results in the formation of free fatty acids (FFA), phosphatides, pigments, sterols, traces of pesticides, hydrocarbons, etc. Such components may affect the quality of finished product as well as productivity and yield of processing. To eliminate such unwanted components and make finished product suitable for human consumption, crude palm oil must be refined. As earlier discussed, there are two methods of refining of palm oil which are physical and chemical refining. Physical refining involves three main steps degumming, bleaching and deodorization while chemical refining involves one additional step *i.e.* neutralization.

Degumming :

Degumming is the initial step of the refining process which decreases the amount of phospholipids (Matthäus, 2012). Phospholipids are responsible for the disintegration of oil which results in low grade finished product. Phospholipids are responsible for white precipitation in oil which causes difficulties during hydrogenation. Oxidation reaction in oil tends to the formation of dark-colored compounds from phospholipids during storage and processing. A degumming process is necessary in physical refining of oils but it is elective in chemical refining process. It comprises the treatment of crude oil, with water, salts, enzymes, caustic soda, or dilute acids to remove phosphatides, waxes, pro-oxidants, and other impurities (O'Brien, 2004). The degumming process transforms phosphatides to gums. These gums are insoluble in oil and can be separated from oil by filtration, centrifugation or settling.

The crude oil can be degummed to discharge impurities by different types of degumming methods which are water degumming, acid degumming, dry degumming and enzymatic degumming. Water degumming is the simplest process among other degumming processes in which the hydratable phosphatides are removed by mixing water in crude oil. In acid degumming, the crude oil is treated with phosphoric acid or citric acid at the temperature of about 80°C-95°C and then 2-5% water is mixed to it. In dry degumming, crude palm oil is mixed with 0.05-0.1% concentrated phosphoric acid and heated at the temperature of about 80-110°C. Similarily, an enzyme for example phospholipase is used in enzymatic degumming.

Neutralization :

Neutralization is the chemical refining process frequently employed to lower free fatty acids from the degummed oil in the form of soap. The main byproduct of chemical refining is called as soapstock, which is a mixture of fatty acid soaps, salts, phospholipids, impurities and entrained neutral oil (De Greyt, 2013). In neutralization, the oil mass from degumming process is neutralized with alkali or caustic soda mainly sodium hydroxide (NaOH), potassium hydroxide (KOH), sodium bicarbonate ($NaHCO_3$) and sodium carbonate (Na_2CO_3) for elimination of free fatty acids in the form of soapstock. This soap solution is then separated from neutralized oil by gravity settling. And the residues of alkali are removed by washing the oil with hot water. The reaction takes place in neutralization is as follows:

$$\text{R-COOH + NaOH} \quad \text{ì} \quad \text{R-COONa + H}_2\text{O}$$

Bleaching :

Bleaching is the process in which the degummed oil or neutralized oil is treated with bleaching earth under the vacuum and heat to remove trace metal complexes, pigments, phosphatides and other impurities by absorptive effect of bleaching earth or clay. Compounds such as phospholipids, colorants, soaps, contaminants etc are expelled out to obtain acceptable characteristics in edible oils during bleaching (Silva *et al*., 2013). In the purification, discoloration, and stabilization of vegetable oils, the bleaching step is a key step (Okolo and Adejumo, 2014). Bleaching is a process where the degummed oil or neutralized oil is heated to high temperature (85-110°C) with bleaching clay under vacuum (720-760mmHg). The equipment where bleaching is to be done is called as bleacher. In bleaching various different types of bleaching clays or earths are used such as acid activated bleaching earth, fuller's earth, activated charcoal etc.

Deodorization :

Deodorization is a vacuum stripped and steam distillation method operated at high temperature (220°C-260°C), during which odiferous components and free fatty acids are removed to obtain odourless oil. It is important to consider that during the deodorization, there are some possibilities of occurrence of some other reactions such as thermal decomposition of triglycerides into free fatty acids, formation of trans isomers and loss of tocopherols and sterols (Angel *et al.*, 2011). The bleached oil may contain minute quantities of odiferous compounds and residues of chemicals from neutralization process. This bleached oil is deodorized in a distillation column called as deodorizer to eliminate odour and free fatty acids from oil. The deodorizer is kept under high vacuum (720-760 mmHg) and bleached oil is heated at temperature of about 220°C -260°C and the steam is injected in deodorizer. During deodorization, free fatty acids are discharged as refining waste from upper section of deodorizer. The deodorized oil is then cooled and the filtered to obtain sparkling oil.

3-MCPD Ester :

Many edible oils are industrially processed by removing components which can negatively impact appearance, taste, shelf stability, safety and consumer acceptance (MacMahon *et al.*, 2013). Both acceptable as well as unacceptable chemical changes appear in oil during the refining process because of high temperature. 3-MCPD and glycidyl esters are process contaminants formed during heat induced reactions, especially during deodorization. Recent studies show that when fat containing and salt containing foods are processed at high temperature, in the presence of chlorine, there will be the chances to form 3-MCPD (OEHHA, 2009). 3-monochloropropane-1,2-diol (3-MCPD) is a member of a group of chloropropanols. 3-MCPD belongs to the chloropropanol compounds which comprises of major 5 substances: 2-monochloropropane-1,3-diol (2-MCPD), 2,3-dichloropropan-1-ol (2,3-DCP), 1,3-dichloropropan-2-ol (1,3-DCP), 3-monochloropropan-1-ol, and 3-chloropropane-1,2-diol (3-MCPD) (Lee and Khor, 2015). The structure of 3-MCPD consist of three carbon atoms with a chloride compound and two alcohol compounds. It is a colorless liquid but having tendency to turn straw-yellow and is soluble in water, alcohol, diethyl ether, and acetone (IARC, 2013). The molecular formula of 3-MCPD is $C_3H_7ClO_2$.

Palm oil and fat are the richest source of 3-MCPD and the amount is four to six times higher than the amounts in normal fat margarine (EFSA, 2016). Since 1980, 3-MCPD esters have been studied as food-processing contaminants and are found in various food types and food ingredients, particularly in refined edible oils (Cheng *et al.*, 2017). Worldwide, the existence of 3-MCPD in refined vegetable oils has become a new safety issue. In animal studies, unbound 3-MCPD is found to be carcinogenic which induces infertility and glitch of certain organs (Zulkurnain *et al.*, 2013). Consumption of 3-MCPD for a short period may cause tumours in various organs; kidney is the main target organ. The level of chloride, level of acylglycerols, pH, temperature and time are the main factors responsible for the formation of 3-MCPD esters (Kuntom *et al.*, 2013). The formation routes of 3-MCPD can be divided into three groups: the first pathway is the acid hydrolysis, which is the reaction of hydrochloric acid with residual vegetable oil; the second route is the heat processing; and third route is the processing of oil in presence of chlorine (Jedrkiewicz *et al.*, 2015).

Reduction tactics :

As we earlier discussed about the contamination of palm oil with 3-MCPD, there is a great demand to remove this contaminant from oil. There are many possible mitigation procedures have been used for reduction of 3-MCPD. These include dealing with crude palm oil quality; and refined palm oil quality, and some modifications in refining process.

Considering several researchers' suggestions, there is one major component (di-acylglycerol) which is plenty reactive to form 3-MCPD (Lin *et al.*, 2015). Degumming and bleaching are the most vital steps in refining, as in which lessen the amount of di-acylglycerols. Free fatty acids also plays a considerable role in formation of 3-MCPD. Lower the levels of free fatty acids, lower will be the level of 3-MCPD. Deodorization is one of the process which is responsible for the effective reduction in free fatty acids. Another compound which is responsible for formation of 3-MCPD is chlorine. Chlorine is the main precursor for formation of 3-MCPD. In order for MCPD esters to be formed, chlorides or compounds containing chlorine must be present in the system (Ibrahim *et al.*, 2015). The chlorine or chloride containing compounds may be unconditionally added externally in the oil. Chlorine is soluble in water. Therefore, there is a possibility to displace chlorine from oil when the oil is washed with water before degumming and neutralization process. Washing of oils with water before refining has a beneficial effect on level of 3-MCPD.

In the research carried out on reduction of 3-MCPD by us, we found substantial reduction in 3-MCPD if refining process is modified. Use of less concentration of acid (about 0.02%) during degumming may decreases 3-MCPD level in palm oil. Phosphoric acid is seems to be more effective in reduction of 3-MCPD than citric acid. The use neutral bleaching earth instead of acid activated bleaching earth is a potential tool to reduce 3-MCPD. But neutral bleaching earth may impart negative effect on final color of the finished product. Bulk density of neutral bleaching earth is lesser than the acid activated bleaching earth because there is availability of larger surface area to bind contaminants on it in neutral bleaching earth. The efficient reduction in 3-MCPD will also seen if the bleaching earth is used in the concentration of 2.5%. Vacuum facilitates the removal of undesirable components by evaporation, which helps in reduction of temperature in refining process and contributes effective reduction of 3-MCPD. Deodorization is most crucial step for formation of 3-MCPD. Because the oil is processed at high temperature (220°C -260°C) during deodorization. The main aim of deodorization is to remove odour as well as FFA from oil. Removal of free fatty acids during neutralization and bleaching results in a reduction in deodorization temperature. Reduced temperature of deodorizer results in lower level of 3-MCPD.

Conclusion :

Palm oil is one of the basic edible vegetable oil which is used in almost every food processing industries. The palm oil is extracted from the oil palm. Globally, About 80% fractions of oil palm are used for edible purposes. Palm oil is extracted from oil palm fruit in oil mill by following different unit operations like pressing, cooking, clarification etc. These operations may impart negative effect on crude palm oil quality. Hence to meet consumer acceptability, the crude palm oil must be purified. 3-MCPD is process contaminant occurred when oil is held at higher temperatures relatively for long time. It is a carcinogenic compound found in most of the vegetable oils. 3-MCPD can be reduced by applying some modifications in refining process and also by maintaining the quality of raw material used in refining process. From the study conducted by us, it is concluded that when the crude palm oil is degummed at temperature of 85°C with 0.02% phosphoric acid then bleached at temperature of 90-100°C with 2.5% of neutral bleaching earth under the vacuum and then deodorized at 250°C for period of 1 hour, there is significant reduction in the level of 3-MCPD.

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