

Formation and Mitigation of 3-MCPD and Glycidyl Esters during Edible Oil Refining

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1. ABSTRACT

3-Monochloropropane-1,2-diol (3-MCPD) esters and glycidyl esters (GE) are process-induced contaminants formed primarily during the high-temperature refining of edible vegetable oils. Increasing regulatory scrutiny and toxicological concerns have made their control a critical challenge for the edible oil industry. This study examines the chemical pathways responsible for the formation of 3-MCPD and glycidyl esters during key refining stages, including degumming, bleaching, and deodorization. The influence of process variables such as temperature, residence time, chloride sources, diacylglycerol content, and the nature of bleaching earth is discussed. Analytical approaches used for the detection and quantification of these contaminants, including gas chromatography and liquid chromatography–mass spectrometry techniques, are briefly reviewed. Furthermore, practical mitigation strategies such as optimization of deodorization conditions, selection of low-chloride raw materials, modification of bleaching practices, and pre-treatment techniques for reducing precursor compounds are evaluated. The findings highlight that preventive process control is more effective than post-refining removal strategies. This paper provides a comprehensive overview of formation mechanisms and industrially feasible mitigation approaches, contributing to improved refining practices and enhanced food safety compliance.

KEYWORDS: 3-MCPD esters; Glycidyl esters; Edible oil refining; Deodorization; Process-induced contaminants; Mitigation strategies

2. INTRODUCTION

Edible vegetable oils are an essential component of the human diet and are widely used in household cooking as well as in food processing industries. To ensure consumer safety, stability, and sensory acceptability, crude oils undergo a series of refining steps including degumming, neutralization, bleaching, and deodorization. While refining improves oil quality by removing undesirable impurities, it may also lead to the formation of certain process-induced contaminants under specific processing conditions.

Among these contaminants, 3-monochloropropane-1,2-diol (3-MCPD) esters and glycidyl esters (GE) have emerged as compounds of significant concern in recent years. These esters are formed predominantly during high-temperature stages of oil refining and can be hydrolyzed in the human gastrointestinal tract to release free 3-MCPD and glycidol. Toxicological studies have associated these compounds with adverse health effects, including nephrotoxicity and potential carcinogenicity, leading to increased regulatory attention worldwide.

The formation of 3-MCPD esters is generally associated with the presence of chloride sources reacting with the glycerol backbone of acylglycerols under elevated temperatures. Glycidyl esters, on the other hand, are primarily formed from diacylglycerols through intramolecular rearrangement reactions at high deodorization temperatures. Factors such as oil composition, processing temperature, residence time, acidity of bleaching earth, and quality of process water play a critical role in determining the extent of contaminant formation.

In response to growing safety concerns, regulatory bodies such as the European Food Safety Authority and Codex Alimentarius have established maximum limits for 3-MCPD esters and glycidyl esters in edible oils. These regulations have prompted the edible oil industry to re-evaluate refining practices and implement effective mitigation strategies without compromising oil quality and processing efficiency.

The objective of this paper is to provide a comprehensive overview of the formation mechanisms of 3-MCPD and glycidyl esters during edible oil refining and to critically discuss practical mitigation approaches adopted at the industrial level. Emphasis is placed on preventive process control measures, optimization of refining parameters, and selection of suitable raw materials to minimize contaminant formation and ensure regulatory compliance.

3. CHEMISTRY & FORMATION MECHANISAM:

The formation of 3-monochloropropane-1,2-diol (3-MCPD) esters and glycidyl esters (GE) in edible oils is a consequence of complex chemical reactions occurring under high-temperature refining conditions. These reactions involve naturally occurring lipid components, such as mono-, di-, and triacylglycerols, as well as external factors introduced during processing, including chloride ions and acidic materials.

3.1 Formation Mechanism of 3-MCPD Esters

3-MCPD esters are formed through the reaction of acylglycerols with chloride ions in the presence of heat. Chloride sources may originate from crude oil, process water, degumming agents, or residual inorganic salts. Under elevated temperatures, especially during deodorization, the glycerol backbone of diacylglycerols (DAG) and monoacylglycerols (MAG) becomes susceptible to nucleophilic substitution by chloride ions, leading to the formation of chlorinated glycerol esters.

Acidic conditions further promote this reaction by increasing the reactivity of acylglycerol intermediates. The presence of acid-activated bleaching earths has been shown to enhance 3-MCPD ester formation by facilitating the release of chloride ions and catalysing esterification reactions. These esters remain bound to fatty acids within the oil matrix but can be hydrolysed during digestion to release free 3-MCPD.

3.2 Formation Mechanism of Glycidyl Esters

Glycidyl esters are formed primarily through thermal degradation and rearrangement of diacylglycerols at high temperatures, typically above 230°C. During deodorization, intramolecular elimination reactions occur in DAG molecules, resulting in the formation of an epoxide structure known as glycidol, which subsequently esterifies with fatty acids to form glycidyl esters.

Unlike 3-MCPD esters, the formation of glycidyl esters does not require the presence of chloride ions and is mainly driven by temperature, residence time, and the concentration of DAG in the oil. Oils with higher DAG content, such as palm oil, are therefore more susceptible to GE formation. Glycidyl esters are considered particularly concerning due to their ability to release glycidol, a genotoxic compound, upon hydrolysis.

3.3 Interrelationship between 3-MCPD and Glycidyl Esters

An important chemical relationship exists between glycidyl esters and 3-MCPD esters. Under acidic conditions and in the presence of chloride ions, glycidyl esters can be converted into 3-MCPD esters through ring-opening reactions of the epoxide group. This interconversion highlights the importance of controlling both chloride levels and acidity during refining, as mitigation strategies targeting one contaminant may inadvertently influence the formation of the other.

Overall, the chemistry underlying 3-MCPD and glycidyl ester formation emphasizes the critical role of refining conditions and raw material composition. Understanding these mechanisms is essential for developing effective preventive strategies to minimize contaminant formation during edible oil refining.

4. REFINING STAGES RESPONSIBLE FOR 3-MCPD & GLYCIDYL ESTER FORMATION:

The refining of edible oils consists of multiple sequential processing stages designed to remove impurities and improve oil stability and sensory quality. However, certain stages of refining create conditions that favor the formation of 3-MCPD esters and glycidyl esters. The extent of contaminant formation depends on the refining sequence, processing parameters, and characteristics of raw materials.

4.1 Degumming

Degumming is the initial refining step aimed at removing phospholipids and metal ions from crude oil using water, acids, or enzymatic treatments. Although degumming itself is conducted at relatively low temperatures, it may indirectly contribute to 3-MCPD ester formation by introducing chloride ions through process water, acid degumming agents, or residual salts. Improper water quality and high chloride content can increase the availability of precursors that promote 3-MCPD formation during subsequent high-temperature steps.

4.2 Neutralization (Alkali Refining)

Neutralization removes free fatty acids using alkali solutions and generates soapstock as a by-product. This stage generally poses a low direct risk for the formation of 3-MCPD and glycidyl esters due to moderate operating temperatures. However, incomplete removal of soaps and residual salts may increase chloride availability in later stages. Efficient washing and separation are therefore essential to minimize precursor accumulation.

4.3 Bleaching

Bleaching involves the adsorption of pigments, oxidation products, and trace contaminants using bleaching earths or activated carbon. This stage plays a significant role in 3-MCPD ester formation due to the use of acid-activated bleaching earths, which create acidic conditions favorable for chlorination reactions. High bleaching temperatures and extended contact time further enhance the reactivity of acylglycerols with chloride ions. In contrast, bleaching has a limited direct influence on glycidyl ester formation but can increase precursor availability for later deodorization.

4.4 Deodorization

Deodorization is the most critical refining stage with respect to the formation of both 3-MCPD esters and glycidyl esters. It is performed under high vacuum at temperatures typically ranging from 230°C to 260°C to remove volatile odor-causing compounds. These severe thermal conditions promote the breakdown of diacylglycerols and facilitate chemical reactions leading to contaminant formation.

Glycidyl esters are primarily formed during deodorization through thermal rearrangement reactions of diacylglycerols. Simultaneously, the presence of chloride ions and acidic residues can result in the formation of 3-MCPD esters. The duration of deodorization and peak operating temperature are critical factors influencing the concentration of these contaminants.

4.5 Influence of Oil Type

The susceptibility of oils to 3-MCPD and glycidyl ester formation varies significantly with oil composition. Oils with higher diacylglycerol content, such as palm oil and palm fractions, exhibit a greater tendency for glycidyl ester formation. Similarly, oils containing higher levels of naturally occurring or process-introduced chlorides are more prone to 3-MCPD ester formation.

Overall, while multiple refining stages contribute to precursor availability, deodorization remains the dominant stage responsible for the formation of 3-MCPD and glycidyl esters. Controlling upstream processing conditions is therefore essential for effective mitigation.

Accurate determination of 3-monochloropropane-1,2-diol (3-MCPD) esters and glycidyl esters in edible oils is essential for regulatory compliance and process optimization. Due to their occurrence at trace levels and their bound esterified form, specialized analytical methods are required for reliable detection and quantification.

5. ANALYTICAL METHODS:

5.1 Indirect Methods

Indirect analytical methods are the most widely adopted techniques for routine analysis of 3-MCPD and glycidyl esters. These methods involve the conversion of ester-bound contaminants into their free forms through hydrolysis or transesterification, followed by derivatization and instrumental analysis.

Gas chromatography coupled with mass spectrometry (GC–MS) is commonly used after derivatization of liberated 3-MCPD and glycidol. Standardized methods such as AOCS Official Method Cd 29a-13 are extensively applied in industrial and regulatory laboratories. Indirect methods offer high sensitivity and good reproducibility; however, they may be susceptible to analytical artifacts if reaction conditions are not carefully controlled.

5.2 Direct Methods

Direct methods aim to quantify intact 3-MCPD esters and glycidyl esters without prior chemical conversion. These techniques typically employ liquid chromatography coupled with tandem mass spectrometry (LC–MS/MS), allowing direct separation and identification of individual ester species.

Although direct methods provide more specific structural information and reduce the risk of artifact formation, they require sophisticated instrumentation, certified reference standards, and advanced technical expertise. As a result, their application is often limited to research laboratories and confirmatory analysis rather than routine quality control.

5.3 Method Performance and Challenges

Key performance parameters for analytical methods include sensitivity, selectivity, accuracy, and reproducibility. Matrix complexity, co-eluting lipid components, and variability in ester profiles across different oil types present significant analytical challenges. Sample preparation and cleanup procedures, such as solid-phase extraction, are therefore critical to ensure reliable results.

Inter-laboratory validation studies have demonstrated that indirect methods remain suitable for routine monitoring, while direct methods serve as valuable tools for method verification and research purposes. Selection of an appropriate analytical approach depends on laboratory capability, regulatory requirements, and the intended application of the data.

Overall, continuous improvement and harmonization of analytical methods are necessary to support effective monitoring and control of 3-MCPD and glycidyl esters in refined edible oils.

6. MITIGATION & CONTROL STRATEGIES:

Effective mitigation of 3-monochloropropane-1,2-diol (3-MCPD) esters and glycidyl esters requires a preventive approach targeting precursor reduction and process optimization rather than post-refining removal. Since these contaminants are formed during refining, control strategies must be integrated across multiple processing stages.

6.1 Control of Raw Materials and Precursors

The composition of crude oil significantly influences contaminant formation. Oils with high diacylglycerol (DAG) content are more susceptible to glycidyl ester formation during deodorization. Therefore, selection of high-quality crude oils and proper storage conditions to minimize hydrolytic degradation are critical. Reducing free fatty acids and DAG levels prior to high-temperature processing can substantially lower glycidyl ester formation.

Equally important is the control of chloride sources. Chlorides may originate from crude oil, processing water, or refining chemicals. The use of low-chloride water, careful selection of degumming acids, and minimization of salt contamination during handling and storage can significantly reduce the risk of 3-MCPD ester formation.

6.2 Optimization of Degumming and Neutralization

Degumming practices should be optimized to remove phospholipids and metal ions without introducing additional chloride ions. Enzymatic degumming has been shown to reduce precursor availability while minimizing the introduction of acidic or saline residues. During neutralization, efficient washing and separation of soapstock are essential to prevent carryover of salts into downstream processes.

6.3 Bleaching Optimization

Bleaching is a critical stage for controlling 3-MCPD ester formation. The use of neutral or low-acid bleaching earths is recommended to reduce acidic conditions that promote chlorination reactions. Optimization of bleaching temperature, contact time, and dosage of bleaching earth can further limit contaminant formation while maintaining effective impurity removal.

In some cases, blending different bleaching earths or incorporating adsorbents such as activated carbon has been shown to reduce precursor levels prior to deodorization.

6.4 Deodorization Process Control

Deodorization is the most influential stage in the formation of both 3-MCPD and glycidyl esters. Lowering deodorization temperatures and reducing residence time can significantly decrease contaminant formation. Multi-step or soft deodorization techniques, including pre-deodorization or short-path distillation, are effective strategies for minimizing thermal stress on the oil.

Precise control of vacuum conditions and steam quality also contributes to reduced formation of unwanted contaminants. Process optimization must balance contaminant reduction with oil quality, throughput, and energy efficiency.

6.5 Emerging and Advanced Mitigation Approaches

Advanced strategies such as enzymatic treatment, adsorption technologies, and precursor-specific removal techniques are being explored to further reduce contaminant levels. These approaches aim to target DAG or chloride precursors before high-temperature processing. While promising, their commercial adoption depends on cost, scalability, and regulatory acceptance.

Overall, mitigation of 3-MCPD and glycidyl esters is best achieved through an integrated refining strategy emphasizing raw material quality, optimized processing parameters, and preventive control measures. Continuous monitoring and process validation remain essential to ensure long-term compliance with evolving regulatory standards.

7. REGULATORY LIMITS & HEALTH CONCERN:

The presence of 3-monochloropropane-1,2-diol (3-MCPD) esters and glycidyl esters in edible oils has raised significant concerns due to their potential health risks and widespread dietary exposure. Upon ingestion, these esterified contaminants are partially hydrolyzed in the gastrointestinal tract, releasing free 3-MCPD and glycidol, compounds that have been associated with adverse toxicological effects.

Toxicological studies have identified 3-MCPD as a nephrotoxic compound with potential reproductive and developmental effects, while glycidol has been classified as a genotoxic and carcinogenic substance. As a result, international regulatory authorities have undertaken risk assessments to establish acceptable exposure limits and maximum permissible concentrations in food products.

The European Food Safety Authority (EFSA) has established a tolerable daily intake (TDI) for 3-MCPD and its fatty acid esters, while glycidyl esters are regulated using the margin of exposure approach due to the genotoxic nature of glycidol. Based on these assessments, the European Union has implemented maximum limits for glycidyl esters in edible oils and fats, as well as for 3-MCPD esters in vegetable oils and fats intended for human consumption.

Regulatory limits vary across regions, reflecting differences in dietary exposure, consumption patterns, and risk management approaches. In many countries, including India, regulatory frameworks are evolving in alignment with Codex Alimentarius recommendations and international standards. This has prompted edible oil manufacturers to adopt stricter quality control measures and implement mitigation strategies during refining to ensure compliance.

From an industry perspective, regulatory compliance not only ensures consumer safety but also supports market access and international trade. Continuous monitoring of contaminant levels, adherence to good manufacturing practices, and proactive engagement with evolving regulatory requirements are essential for sustainable edible oil production.

Overall, understanding the health implications and regulatory expectations associated with 3-MCPD and glycidyl esters reinforces the importance of preventive process control and highlights the need for ongoing research to further reduce consumer exposure.

8. CONCLUSION & FUTURE SCOPE:

The formation of 3-monochloropropane-1,2-diol (3-MCPD) esters and glycidyl esters during edible oil refining represents a significant technological and regulatory challenge for the edible oil industry. These contaminants are primarily generated under high-temperature processing conditions and are strongly influenced by raw material quality, precursor availability, and refining parameters. Among the various refining stages, deodorization has been identified as the most critical step contributing to their formation, while upstream processes such as degumming and bleaching play an important role in determining precursor levels.

This study highlights that effective mitigation of 3-MCPD and glycidyl esters is best achieved through preventive process control rather than post-refining removal. Optimization of deodorization temperature and residence time, careful selection of bleaching earths, control of chloride sources, and reduction of diacylglycerol content are key strategies for minimizing contaminant formation while maintaining oil quality. The integration of such measures into routine refining operations enables compliance with evolving regulatory standards and enhances consumer safety.

Future research should focus on the development of cost-effective and scalable technologies for precursor reduction, including enzymatic treatments and advanced adsorption techniques. Improved understanding of reaction kinetics and the interaction between refining parameters will further support the design of optimized refining processes. Additionally, harmonization of analytical methods and

generation of region-specific data will be essential for accurate risk assessment and regulatory decision-making.

In conclusion, continuous innovation, process optimization, and regulatory alignment are crucial for reducing the presence of 3-MCPD and glycidyl esters in edible oils. A collaborative approach involving industry, researchers, and regulatory authorities will play a vital role in ensuring the long-term safety and sustainability of edible oil production.

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