Crude Palm Oil De-Chlorination

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ABSTRACT

High concentrations of 3-monochloro-1,2-propanediol (3-MCPD) were found in refined, bleached and deodorised (RBD) palm oil recently, implying that the level in edible oil consumption will exceed the tolerable daily intake (TDI) of 0.8 μg kg⁻¹ body weight as determined by the European Food Safety Authority (EFSA) (2016). A study showed that the reaction prerequisites for ester formation are the presence of fatty acids and ionic-bound chlorine. Although fatty acids neutralisation is an effective oil purification method, various technologies have been introduced to address the de-chlorination issue in crude palm oil so that the MCPD ester content in palm oil meets the European and the American market requirements which are currently below 2 mg kg⁻¹, and a further reduction to 0.5 ppm has been proposed.

Keywords: crude palm oil washing, de-chlorination, glycidyl esters, MCPD

INTRODUCTION

In the refinery, crude palm oil (CPO) containing organic chloride compounds has been bleached using bleaching earth containing free hydrogen chloride. The carcinogenic 3-monochloro-1,2-propanediol (3-MCPD) found in refined, bleached and deodorised (RBD) palm oil is formed in proportional to the fatty acids content in the oil during the deodorisation step carried out at 180°C-260°C in vegetable oil refining. Neutralisation of free fatty acids in palm oil with potassium salts prior to deodorisation can suppress the formation of 3-MCPD esters (Šmidrkal et al., 2016).

Formation kinetic models have been developed indicating that monopalmitin models show a linear dependence between 3-MCPD ester formation and chloride ion concentration (Hamlet et al., 2014).

The formation mechanism is complex (Bund für Lebensmittelrecht und Lebensmittelmunde E V (BLL), 2016). A fatty acids-sodium chloride equilibrium is established with fatty acid salts and hydrogen chloride formation during deodorisation as shown in the reaction equation 1. Hydrogen chloride then reacts with acylglycerol as shown in Figure 1. Thus, the reaction prerequisites for 3-MCPD formation are the presence of fatty acids and ionic bound chlorine (Šmidrkal et al., 2016).

\[
R\text{O}H + Na\text{Cl} \rightarrow R\text{O}Na^+ + H\text{Cl}
\]

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DE-CHLORINATION FOR 3-MCPD MITIGATION

The CPO sent to the refinery contains less than 5% free fatty acids based on the Palm Oil Refiners’ Association of Malaysia (PORAM) specifications, but chlorine content has yet to be determined at the moment. A survey found that refined palm oil contains many organic chlorine compounds and inorganic chlorides such as calcium chloride (CaCl₂), magnesium chloride (MgCl₂), ferum (II) chloride (FeCl₂) and ferum (III) chloride (FeCl₃) (Yu, 2014). The fertiliser, muriate of potash, used in oil palm plantations and the coagulant used for water treatment in palm oil mills are believed to be the sources of chloride. An unofficial survey found that the chloride content in crude palm oil generally ranges from 7 ppm to 11 ppm.

3-MCPD ester formation can be reduced by washing crude palm oil with water or ethanol (Musfirah et al., 2013). Alfa Laval (2016) proposed three focal points in palm oil processing at which 3-MCPD formation may be mitigated, namely zero dilution oil clarification, crude palm oil washing, and oil neutralisation.

Caustic soda has been widely used to produce neutralised palm olein or neutralised palm oil. The water-soluble fatty acid salts formed via saponification encapsulates proteins and other impurities. The duly neutralised oil will then be washed, and the wash water is usually removed using a disc stack centrifuge. Finally, the purified oil is dried in a vacuum dryer (Alfa Laval, 2016).

Figure 1. MCPD ester formation reaction.
Zero dilution oil clarification eliminates chlorine contamination from the dilution water added into the press liquor in a conventional mill. Thus, the crude oil is mixed only with water present in the fresh fruit, adsorbed water during sterilisation and from live steam heating. Hot water may also be added at the oil gutter under the press to facilitate press liquor drainage. A three-phase decanter with a nozzle disc stack separator can be used for oil recovery. Typically, 20% of the process water can be saved and the gravity settling tank can be omitted (Alfa Laval, 2016).

Crude palm oil washing can be carried out after the clarification process to reduce further the chlorine content in the pure oil before vacuum drying. Various systems have been tried or are still on trial. Issues that need to be considered are oil loss due to emulsion, wash water quality and quantity, additional load on the wastewater treatment plant, and additional operational expenditure (OPEX) and capital expenditure (CAPEX) incurred.

The Earth’s crust contains an average of 0.055% chlorine. The common soluble inorganic chloride compounds in industrial water supply are CaCl₂, MgCl₂ and sodium chloride (NaCl). Chlorine has been used in potable water treatment since the early 1900s although undesirable chlorinated by-products, such as trihalomethane, are formed in the presence of humic and fulvic acids (Cantafio, 1994). Malaysia’s raw drinking water should contain less than 250 mg litre⁻¹ chlorides (Ministry of Health Malaysia, 2000), while the average free chlorine residual in tap water should be 0.75 mg litre⁻¹ but varies from 0.3 mg litre⁻¹ to 2.10 mg litre⁻¹. The taste and odour threshold concentrations are 5 mg litre⁻¹ and 2 mg litre⁻¹, respectively (Ong et al., 2007). Chlorine solubility at a temperature of 20°C and a pressure of 1 atm is 7.29 g litre⁻¹ in water as shown in the reaction equation 2 (Cantafio, 1994).

In alkaline conditions:

\[
\text{Cl}_2 + \text{H}_2\text{O} \leftrightarrow \text{HOCI} + \text{HCl} \quad (2)
\]
\[
\text{HOCI} \leftrightarrow \text{OCI}^- + \text{H}^+ \]

Medium-pressure UV de-chlorination is a proven technology involving photochemical reactions produced by UV light wavelengths between 180 nm and 400 nm. The peak wavelengths for free chlorine dissociation range from 180 nm to 200 nm, whereas the peak wavelengths for chloramines dissociation range from 245 nm to 365 nm. The UV dosage required depends on the total chlorine level, ratio of free versus combined chlorine, background organics level and concentration reduction target (McClean, 2007).

**DISCUSSION**

Vegetable oil and fat refiners are committed to reducing the level of glycidyl esters in all oils to 1 ppm (Fediol, 2016). In order to mitigate the issue of 3-MCPD ester in RBD palm oil, specifications for chlorine content in crude palm oil need to be established. In line with this, a rapid and simple method for determining chlorine content in oil is needed to support studies and surveys. A total halogens micro-coulometric combustion analyser has been introduced for this facility in the Trace Elemental Instruments laboratory. Samples are introduced into a furnace with an appropriate module for high temperature oxidation. The combustion gas with halide ions which is produced is fed into a sulphuric acid scrubber for rapid water and interference removal. The dried and clean gas is then led into a temperature-controlled titration cell with silver ions for the halide ion reaction. The halogen content in the sample is determined by the amount of charge used to regenerate the silver ions as shown in the reaction equation 3 (Trace Elemental Instruments, 2016). Table 1 shows the halogens content in different types of palm oil as determined by Metrohm Combustion IC.

**CONCLUSION**

A palm oil yield of 6 t⁻¹ ha yr⁻¹ can be achieved, which is the highest oil yield among the commercial oilseed crops. Unfortunately, a
recent survey found that the 3-MCPD level in RBD palm oil is the highest among the edible oils in the market. Studies show that the ester issue can be mitigated by neutralisation with potassium salts and de-chlorination of the crude palm oil prior to oil refining. Free fatty acids neutralisation and de-chlorination efforts need to be considered whether as a refining process modification or as a step integrated into palm oil milling.

REFERENCES


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The Inventor’s Dilemma

P. Kandiah*

A tricky issue that has long plagued inventors and researchers who invent potentially commercially useful products or processes is the dilemma as to whether to:

i) Seek patent rights for the invention,
ii) Keep the details of the invention confidential (or as a trade secret), or
iii) Publish the details of the invention and depend on copyright protection afforded by the Copyright Act. The publication could be in a peer reviewed journal, or as a paper presented at a conference proceeding.

So the question is, which path to take? That’s the dilemma. Let’s look at the various options available and the implications of each path to the inventor/researcher.

Where the research is undertaken in an academic institution or in a research institution, there is a culture of publishing the details of the invention in a peer reviewed journal or as a paper presented at a reputable conference. In fact, in many institutions, it is a policy or internal regulation, requiring all research output in the institution to be published as early as possible. Academics are still governed by the ‘publish or perish’ rule.

The publication, whether in a journal or in conference proceedings would nevertheless enjoy copyright protection, unless expressly disclaimed. But is copyright protection of the publication sufficient to protect the inventor’s interests or is it sufficient to prevent any other person from taking advantage of the invention disclosed in the publication by using the invention for commercial gain?

Copyright merely allows the owner (who could be the inventor, or the institution where the inventor is employed to do research) to prevent any others from substantial reproduction of the published works, but does not grant any right to prevent others from making use of the teachings or the details disclosed in the publication. For example, assume A publishes an article or a book entitled ‘The Art of Making Furniture’ where modern methods of making furniture are disclosed in detail. The publication (the book or the article) would enjoy copyright protection. What right does A have? Is copyright protection sufficient to protect A’s interests? If, say, a furniture manufacturer,
B, obtains a copy of the publication and follows the teachings in the publication to improve his manufacturing method or produce new types of furniture disclosed in the publication, there is nothing A can do to prevent B from using the teachings, or even to demand monetary compensation or royalty from B. A’s publication disclosing the details of his knowledge in making furniture will be deemed to be a donation to the public, allowing others to freely benefit from the creative or intellectual output. If A (or his employer) wanted to benefit financially from the creative efforts, then A (or his employer) has to claim proprietary rights to the invention by way of patent rights (on the assumption that the creative output is patentable).

Can copyright and patent rights be claimed for the invention? Or is a claim to copyright and a claim to patent mutually exclusive? Has it to be one or the other? The patent laws of all countries require that the features claimed in the patent should be novel as at the date of first filing of the patent application. So if the inventor has disclosed details of the invention to the public in any manner (e.g., by publishing details of the invention in a journal, on a website or even orally at a conference proceeding/seminar) prior to the filing of the patent application, the requirement of novelty is not met and a patent will not be granted, and if granted it can be invalidated for lacking in novelty. Even the inventor’s own publication (where the inventor is named as the author of the paper) is sufficient to destroy the novelty, and is no excuse. (Note: Some countries do excuse such prior publications by the inventor, provided the patent application is filed within a stipulated period (called the grace period).

It is advisable not to rely on the grace period as an excuse to publish the invention before filing the patent application. However, it is possible to file the patent application and thereafter, on the very next day, publish the details of the invention, although for strategic reasons it is not advisable to do so, especially if further research is still being carried out in the subject matter of the invention. The author has personal experience where a granted patent for a commercially important invention is being challenged by a competitor for lack of novelty citing the inventor’s own publication of the invention in his institution’s in-house publications and on the institution’s website.

Alternatively, can the inventor keep the invention confidential or as a trade secret instead of filing a patent or publishing the invention and claiming copyright? If the invention relates to a chemical product or a method of manufacture, details of which can be kept confidential within the four walls of the factory and which product or process cannot be reverse engineered within the four walls of the factory and which product or process cannot be reverse engineered by analysis of the product which is placed in the market, then it may be advantageous to keep the details of the product or process of manufacture as a trade secret. However in this modern age of availability of sophisticated analytical tools and techniques, I doubt if such a process or composition can be kept confidential and cannot be reverse engineered. Reverse engineering a product or process is lawful although it may not be morally acceptable or ethical. Further, once the trade secret is leaked, there is no way the secret can be put back into the bottle. It is also difficult to take legal action against anyone accused of using stolen trade secrets or of obtaining trade secrets unlawfully. If the inventor is désirous of commercialising his invention, then potential investors or licensees would demand to see patent rights and would not be favourable to obtaining a licence to use trade secrets.

In summary, it can be concluded that where an inventor is researching an area with potentially high commercial value, he is strongly advised to seek patent rights for the invention (assuming the results of the research meet the patentability criteria) rather than depend on copyright protection or trade secret.
Caution: This area of practice of intellectual property rights is complex and highly technical in nature. Inventors are strongly advised to seek professional advice from experienced practitioners in the field. This article is published purely for information and should not be construed as legal advice. Each case would depend on its own facts as to determine the best way to claim proprietary rights in order to commercialise the invention.

P. Kandiah is the Founder and Director of KASS International, an established intellectual property firm with offices in Malaysia, Singapore, Indonesia and Myanmar. Mr. Kandiah has vast experience in obtaining patents, trademarks and industrial design rights on a global scale, and also specializes in identifying patentable inventions, designing around patented technology, and advising on the commercialization of IP Rights, franchising and licensing strategies. For more information, visit www.kass.asia or drop an e-mail to kass@kass.asia