Mild distillation for optimal oil quality

Frank Möllering

Twenty years ago, researchers at the University of Prague determined that heating edible oils above 225 °C for multiple hours during processing created toxins (http://dx.doi.org/10.1080/02652030600887628). Naturally occurring esters of 3-monochloropropanediol (3-MCPD), predominantly from a mixture of palmitic acid diesters with C18 fatty acids, such as stearic, oleic, linoleic acid, formed bound 3-MCPD in the refined oils. The compounds are known carcinogens and the industry began studying ways to avoid or reduce their production during refining.

- **Gentle refining can be performed while keeping process contamination (from pesticides, MOH, etc.) under control.**
- **Mild refining alone only achieves low reduction rates but has a positive effect on oil stability.**
- **Mild refining with short path distillation combines good stability with good contaminant reduction, while preventing any further process contamination.**
- **However, the process is not a cure-all and high-quality raw materials are still needed for best results. Oils heavily contaminated with MOH remain poor.**

The best approach is to avoid the steps that lead to the contaminant formation through optimal harvesting and rapid, optimised processing at the source. In this way, processors can achieve 3-MCPD levels less than 500 µg/kg. However, this strategy has the disadvantage of requiring food producers to be dependent on select suppliers. At Nutriswiss we have developed a way to ensure low 3-MCPD levels—particularly for infant formula applications—irrespective of the quality of the raw materials.

Beyond 3-MCPD we are focused on limiting the presence of other esters with genotoxic potential. The presence of these esters is technologically challenging in the typical refining of seed oils such as sunflower, soya or maize germ oil. In addition, contaminants such as pesticides from non-organic cultivation or polycyclic aromatic hydrocarbons (PAHs) can also be found in conventional or even organic oils.

SHORT PATH DISTILLATION: A KEY COMPONENT OF PROCESS CONTROL

To keep glycidol content as low as possible (under 50 µg/kg), processors can lower deodorization temperatures, but the downside is that then they cannot completely mitigate the presence of certain impurities. A reliable and sophisticated process to solve this problem is short path, or molecular, distillation (SPD). This processing step can be used to efficiently remove, or significantly reduce, contaminant levels from fats and oils. However, it is important that the product quality remains stable or is improved compared with conventional processes. Nutriswiss has done extensive tests to determine the ideal process parameters to achieve this goal.

At Nutriswiss AG, we used a continuous vacuum SPD process supplied by VTA, an equipment manufacturer based in Niederwinkling, Germany. The distiller is designed for heat sensitive products using low vacuum and short residence times. The SPD works using a scraper, or wiper, inside a cylindrical evaporator that distributes the oil in a turbulent, thin layer onto heated walls where distillation occurs.

An industrial SPD plant supplied by VTA Verfahrenstechnische Anlagen GmbH & Co. KG Source: Nutriswiss

Because the apparatus operates at a vacuum of up to 10^{-3} mbar, volatile components such as pesticides and free fatty acids, as well as tocopherols, can evaporate more easily under low thermal stress. These compounds are subsequently reliquefied and removed through a condenser located a few centimetres away, in the center of the cylinder. Meanwhile, the cleaned oil flows down the evaporator wall. The evaporation rate is normally about a few per cent; the temperature and pressure determined by the oil being processed and the substances being removed.

CUSTOMIZING THE REFINING STRATEGY

Depending on the quality of the starting oil—be it palm, coconut, or seed—Nutriswiss uses a combination of pretreatment, SPD, and mild deodorization. We select the process conditions for SPD in such a way that the natural beneficial ingredients of the oils, especially the tocopherols, are not reduced any more than with classical refining.

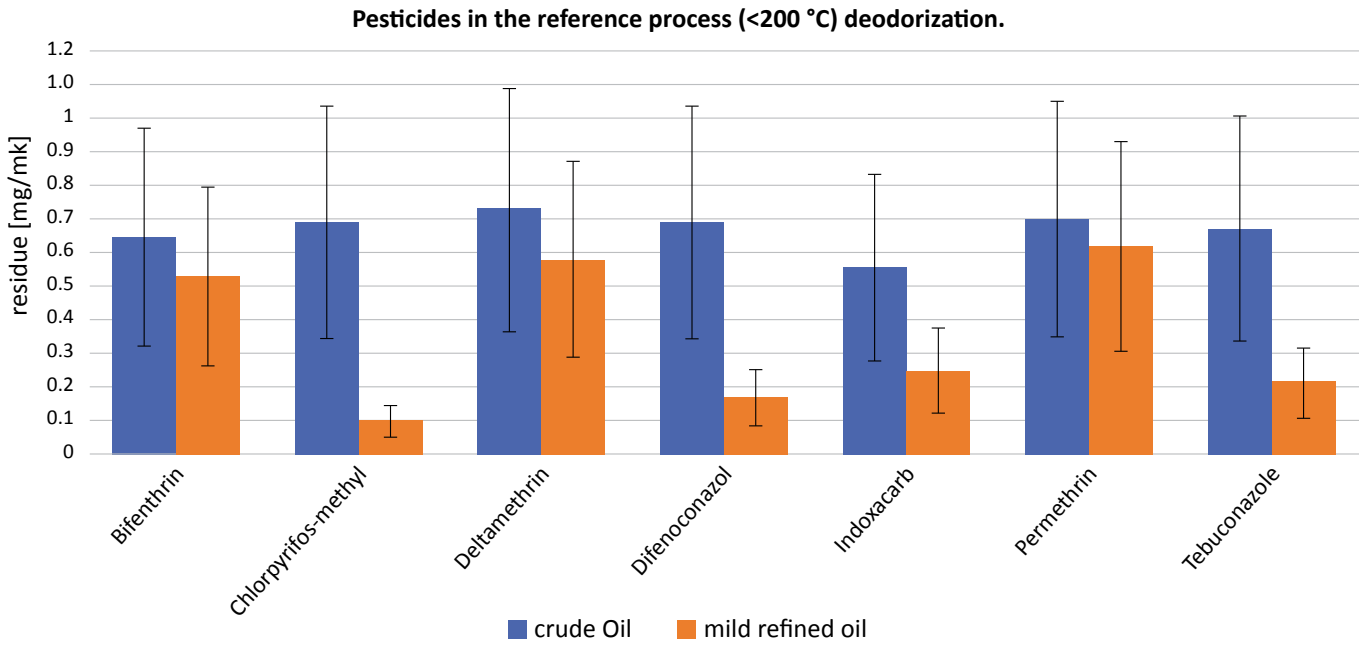
We have performed internal studies on optimizing the refining process so that the tocopherols in the base oil are largely retained or even increased. The explanation for this increase is the cleavage of dimeric bonds between tocopherol molecules, or ester bonds between tocopherols and other compounds. In addition, we found that with an appropriately pretreated seed oil and process parameters chosen to maintain a target tocopherol content comparable with physical refining, pesticides can be reduced by the following amounts:

compound	% reduction
anthraquinone	> 92
biphenyl	> 97
piperonyl butoxide	> 90
pirimiphos-methyl	> 80
folpet	> 93

The process also reduces heavy PAHs by approximately 95 percent, while eliminating activated carbon dosing. For comparison, the figure at the top of page 22 shows a comparison of a standard processing and mild refining process with deodorization temperatures less than 200 °C. For all the pesticides mentioned, the levels after SPD treatment were below the detection limit.

THE MOAH ISSUE: LEGISLATION, SOURCING, ANALYSIS, AND PROCESS

In 2022, an EU committee introduced limits for mineral oil aromatic hydrocarbons (MOAH). Owing to their chemical structure and lipophilic properties, MOAH accumulate and can be easily absorbed from machine lubricants exhaust gases, or tire abrasion. Tropical products such as coconut oil, palm oil or cocoa butter usually arrive in Europe by sea. By the time they arrive, the raw materials have already been pumped into tanks and ships several times. Open loading processes and contact



A graph indicating that pesticide levels are significantly lower after SPD treatment. Source: Nutriswiss

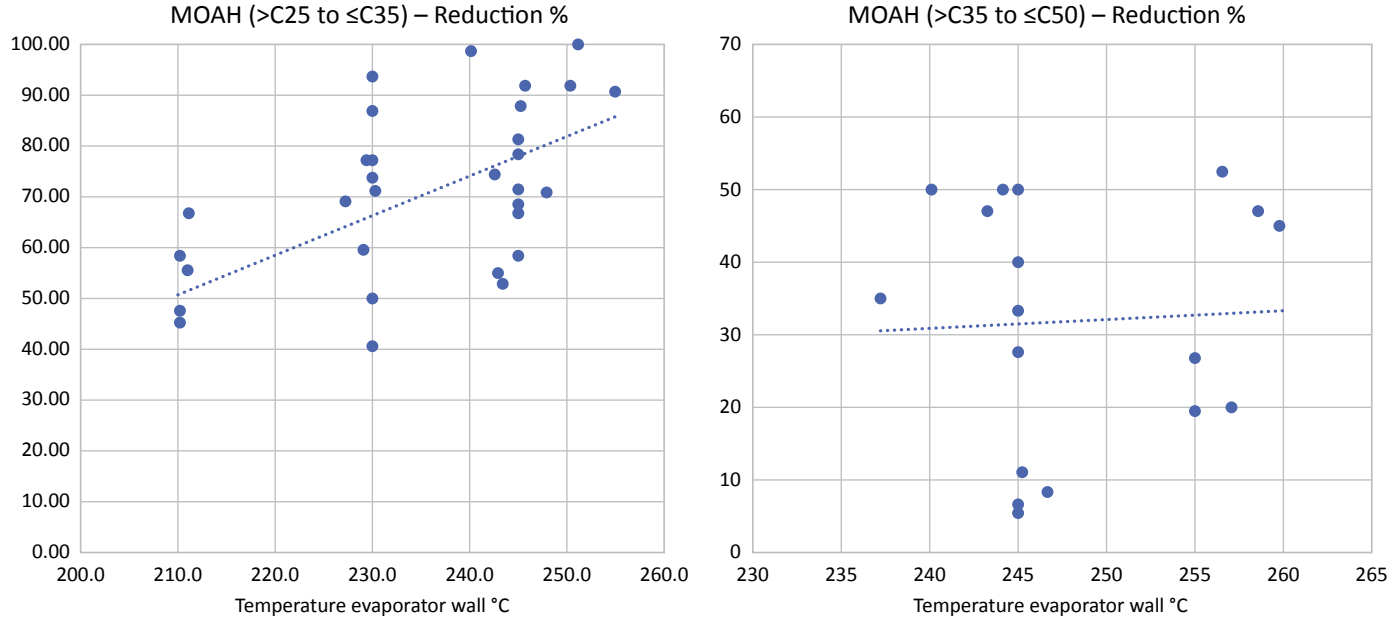
with pipes, ambient air, and other transported goods can also lead to the accumulation of harmful substances in the raw material.

Nutriswiss therefore relies on long-term contractual partners, the use of ISO-containers that comply with food-grade standards and its own controls for supply chain management. Before, during and after processing, a comprehensive key data profile is drawn up for each oil in our own or independent external laboratories. This clearly shows that the sourced material is significantly less contaminated on arrival at the factory than standard market goods, as reflected in measured MOAH values.

SHORT PATH DISTILLATION REDUCES HYDROCARBON CONTAMINATION

The EU's proposed limit of 2 mg/kg for oils and fats continues to be criticised by NGOs who argue the requirement should be less than 1 mg/kg (the detection limit) for MOAH. We found that by using the SPD process it is possible to effectively reduce both MOSH and MOAH while preserving tocopherols and avoiding 3-MCPD and glycidol formation.

However, the amount reduced depends on the distribution of the individual mineral oil hydrocarbon (MOH) fractions. For example, the MOAH fraction between C25 and C35 dropped by about 70 percent and the fraction from C35 to C50



Anticipated amounts that specific MOAH fractions can be lowered using SPD. Source: Nutriswiss.

The effects of SPD on storage stability.

	rbd palmstearin	Post refining rbd palm stearin incl. SPD	Post refining rbd palm stearin
3-MCPD [mg/kg]	1.02	0.68	1.13
glycidol [mg/kg]	0.39	0.04	0.02

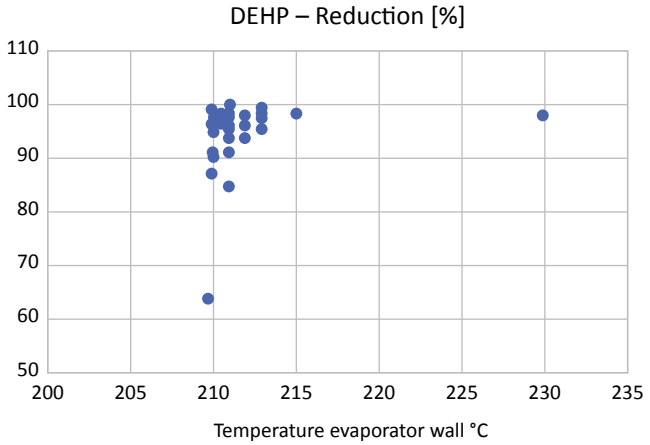
by approximately 30 percent. Therefore, we cannot generalize how much mineral oil is removed overall.

Mineral oils with three to seven aromatic rings are the main source of mutagenic concern, along with non-alkylated PAHs. In partnership with a leading German commercial laboratory, we examined how SPD could decrease these mineral oil components. We found that the MOAH components remaining in vegetable oils after SPD almost exclusively have only one or two rings. This phenomenon should be further investigated and substantiated in a future scientific study. Nutriswiss would be pleased to be a partner in such a project. Our studies also demonstrated the effect of refining on false positive results for MOAH caused by dehydrated phytosterols, which we resolved by a modified analysis.

As mentioned above, it is essential that attention is paid to the potential risk of contamination right from the source—during sowing, pesticide treatment, harvesting, transport, and storage through to pressing. We found that SPD processing was unable to convert oil heavily contaminated with MOSH and MOAH to a good quality raffinate. However, the process can transform an ordinary oil that is just outside the MOH guidelines for the German government's standard into an excellent product (https://tinyurl.com/3t8u46hz).

OTHER POSITIVE EFFECTS OF SPD

We also found that, although the use of mild refining steam temperatures less than 200 °C does not significantly reduce diethylhexyl-phthalate (DEHP), SPD does. In 2016, Aziz Tekin and his research team at Ankara University in Ankara, Turkey reported using SPD to lower DEHP in crude hazelnut oil by around 95 percent under typical processing parameters. Other plasticizer contaminants that can migrate into edible oils from plastic products, like DEHT ortho-phthalates, have been reduced effectively using SPD.



Resulting DEHP values after applying SPD with typical process parameters used for seed oils. Rates were reduced by around 95%. Source: Nutriswiss.

Another application is the post-refining of palm oil. The fractions manufacturers purchase are so-called RBD fats (refined, bleached and deodorised). In principle, these have a fixed 3-MCPD content; however, due to the effects of transport and storage on these fats, the refined quality is lost and they require post-refining. At Nutriswiss, we did an internal study to assess the influence of SPD on product stability after post-refining. Along with other positive effects, the SPD-treated variant proved more stable in the storage test in contrast to conventional post-refining.

MILD REFINING AND SPD

For the last 30 to 40 years, physical refining has ensured the removal of impurities and the reduction of free fatty acids. However, this type of refining introduces process contaminants such as 3-MCPD, glycidol, and trans fatty acids. Mild refining, with alkaline neutralization of free fatty acids and subsequent deodorisation at less than 200 °C, avoids the formation of these process contaminants and also results in a long shelf-life and better sensory properties.

Based on practical experience, at Nutriswiss we have been combining mild refining with SPD for several years to benefit from the advantages of both processes. We are currently working with a German university to test the effect on the quality of fatty acid oxidation products. However, initial results show that, in contrast to typical physical refining, combining mild refining with SPD does not result in any significant changes in oxidation products compared with mild refining alone. We are currently in the process of compiling our results into a publication.

The combination of mild refining and SPD results in a product of equivalent quality and potentially higher stability than that obtained from mild refining alone. In addition, the purity of such a product is significantly higher and can even exceed the results of typical physical refining with its high temperatures.

Frank Möllering has been head of research & development at Nutriswiss AG in Lyss, Switzerland, for 20 years. In addition to the typical tasks of product development, he and his development team have been investigating the advantages and possible applications of short path distillation (SPD) to refine fats and oils since commissioning a plant in 2020. He can be contacted at frank.moellering@nutriswiss.ch.