



Mitigation of 3-MCPD esters and related Compounds - Results from the FEI Research Project

Bertrand Matthäus¹, Anne Freudenstein¹, Frank Pudel², Peer Fehling²

¹Max Rubner-Institute, Federal Research Institute for Nutrition and Food; Schützenberg 12, 32756 Detmold; Germany

²Pilot Pflanzenöltechnologie Magdeburg; Berliner Chaussee 66; 39114 Magdeburg; Germany

Outline

- Research project applied at the Research Association of the German Food Industry (FEI)
- Effect of different refining steps on the formation of 3-MCPD esters and related compounds
- Influence of the raw material on the formation of 3-MCPD esters and related compound
- Summary

Research project for 3-MCPD esters

Research Association of the German Food Industry



Investigations on the formation of 3-monochloropropane-1,2-diol fatty acid esters (3-MCPD esters) in vegetable oils and development of minimization strategies



Max Rubner-Institut,
Münster (MRI)



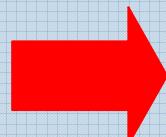
Pilot Pflanzenöl
Magdeburg (PPM)



Deutsche
Forschungsanstalt für
Lebensmittelchemie
(DFA)



Deutsches Institut für
Lebensmitteltechnik



Investigation of the technological possibilities to minimize 3-MCPD esters in fats and oils

Initial aim of the project

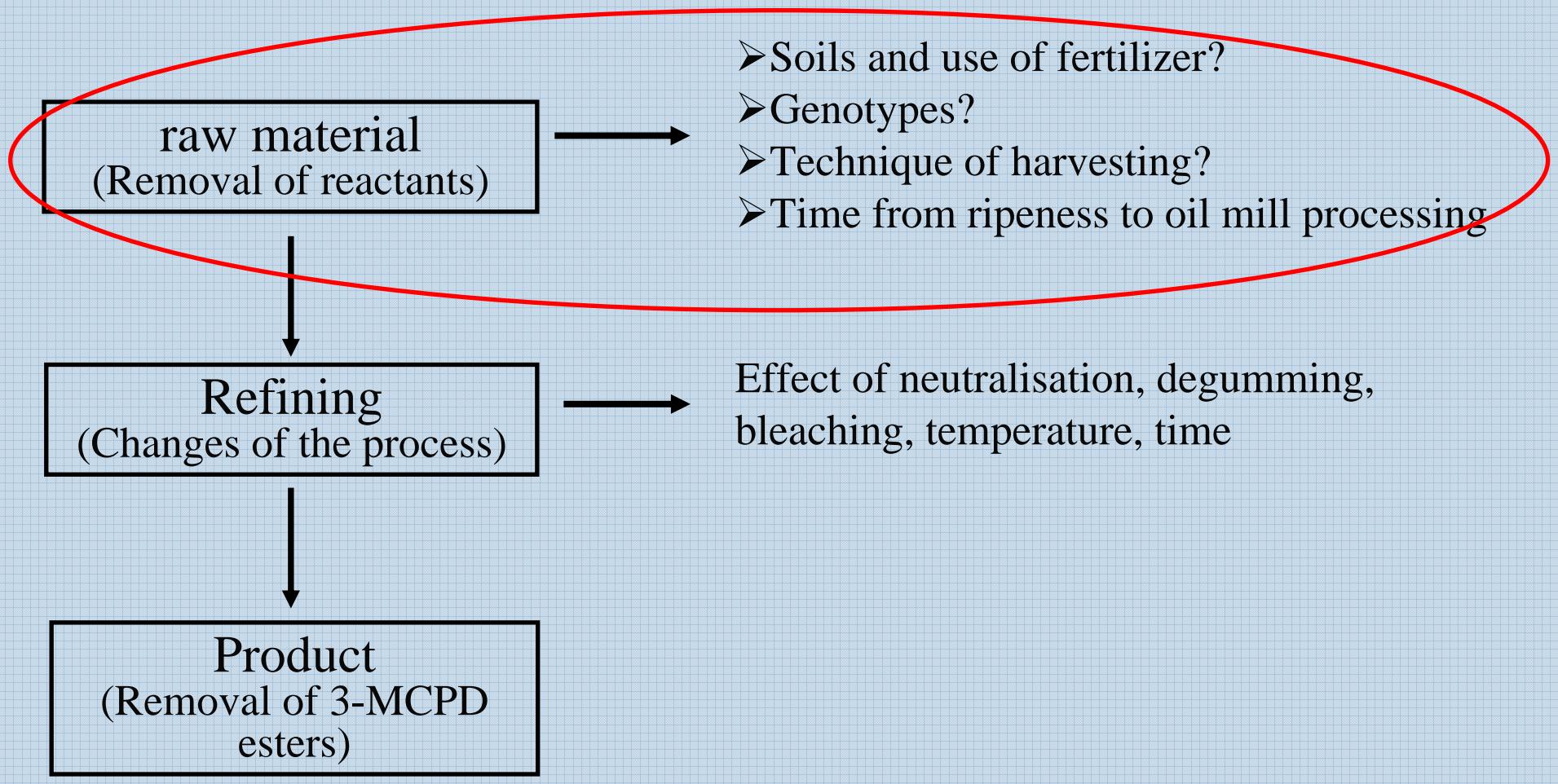
- **Systematical investigation** of correlations between the formation of 3-MCPD esters, process conditions and the composition of used raw and auxiliary materials
- **Recommendation for minimizing 3-MCPD-FE, without influencing the quality of the product**

Solution

- Investigation of relevant set screws
 - **Oil composition** (content of mono- und diacylglycerides, free fatty acids, chloride, etc.)
 - **Conditions during refining** (temperature, type and composition of used bleaching earths, composition of used chemicals – water, acids, basic solutions, auxiliary means, etc.)
 - **Conditions during hydrogenation and transesterification**
- Removal of 3-MCPD-FE from products
- Further development of analytical methods for free and bound 3-MCPD
- Model experiments for elucidation of the formation mechanism

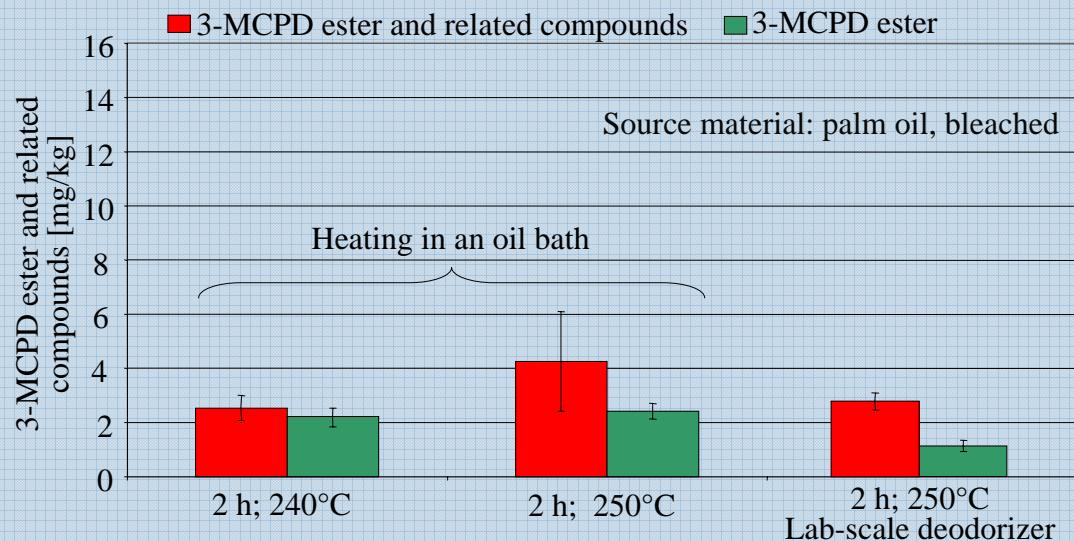


Changed focus of the project

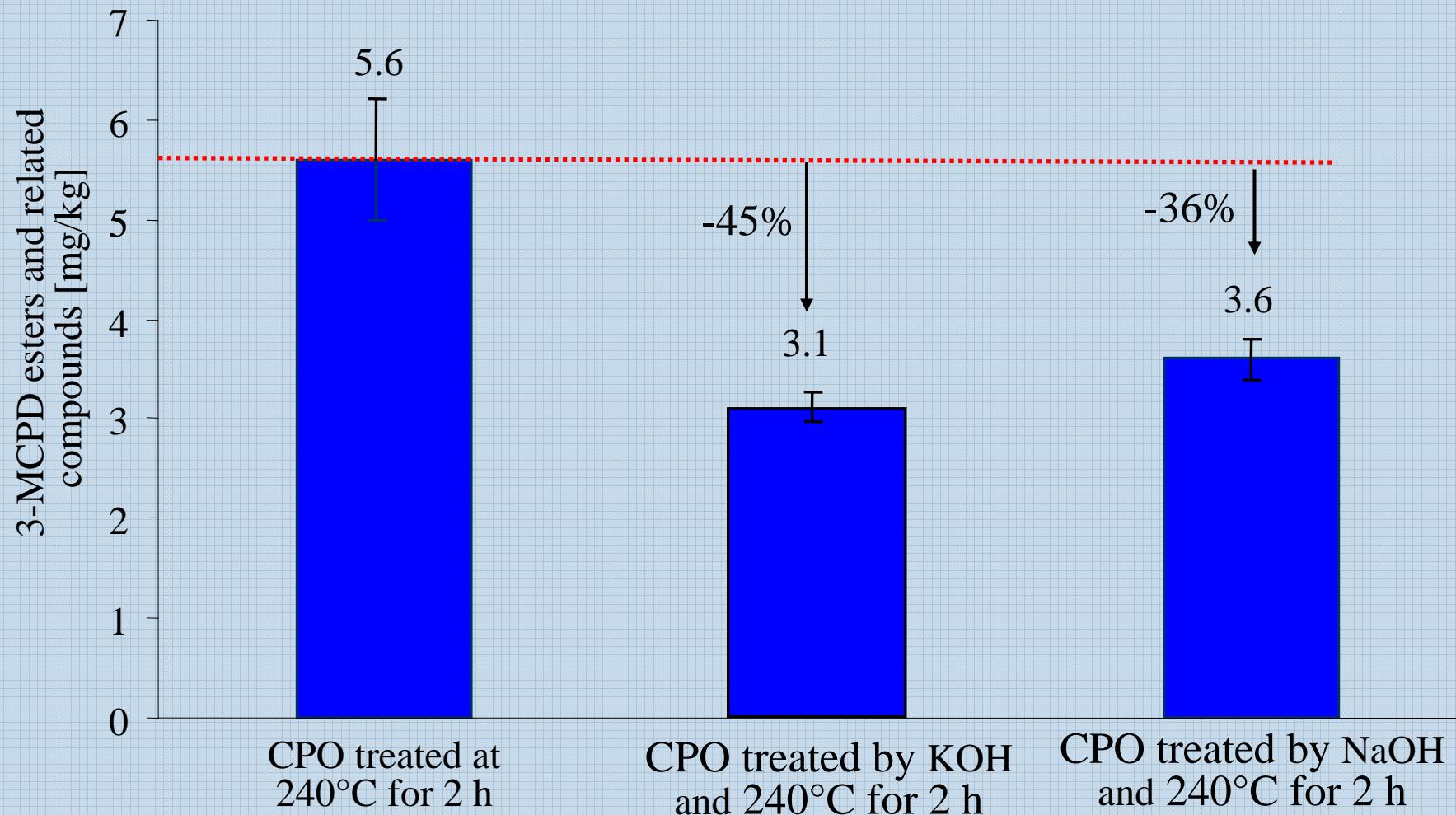


Methods

- The capability of the crude oils to form 3-MCPD esters and related compounds was evaluated by simulation of the deodorization step: Heating of 10 g crude oil at 240°C for 2 h in an oil bath → Measurement of 3-MCPD esters and related compounds
- 3-MCPD esters and related compounds were measured according to DGF method C-III 18 (09) (Part A); 3-MCPD esters were measured according to DGF method C-III 18 (09) (Part B)
- Measurement of inorganic chloride: Extraction of the sample by distilled water, centrifugation → ion chromatography

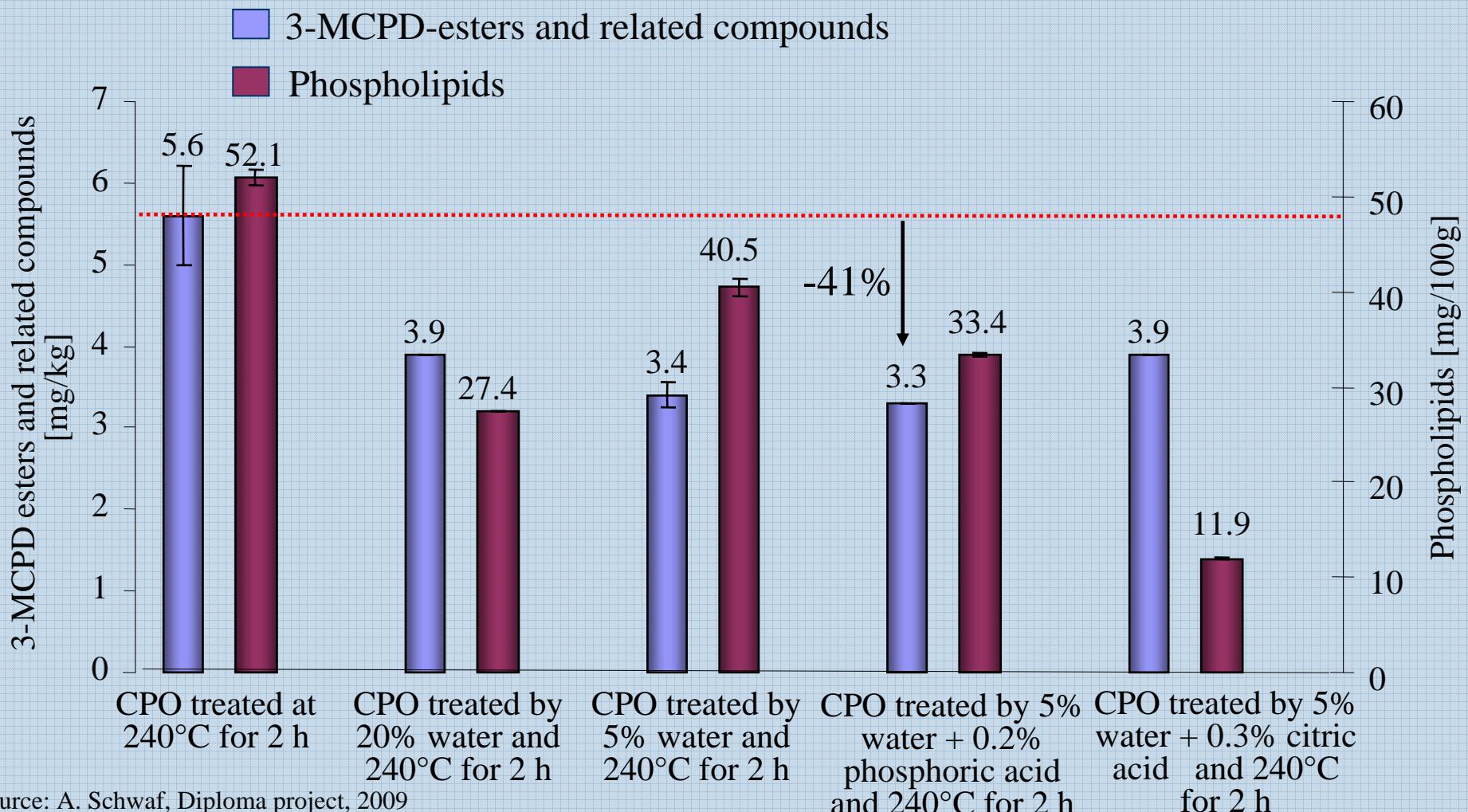


Influence of the neutralisation



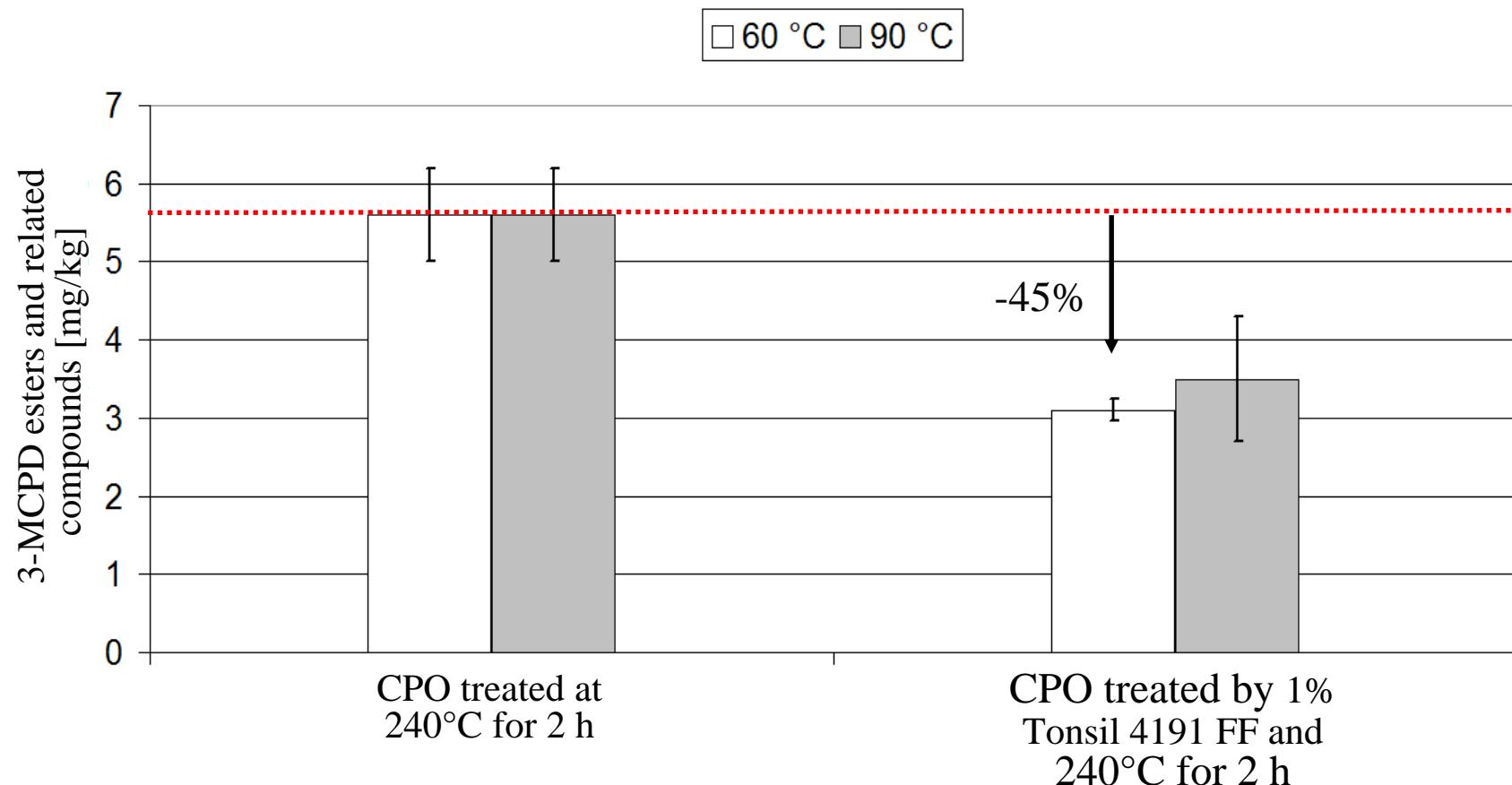
Source: A. Schwaf, Diploma project, 2009

Effect of degumming

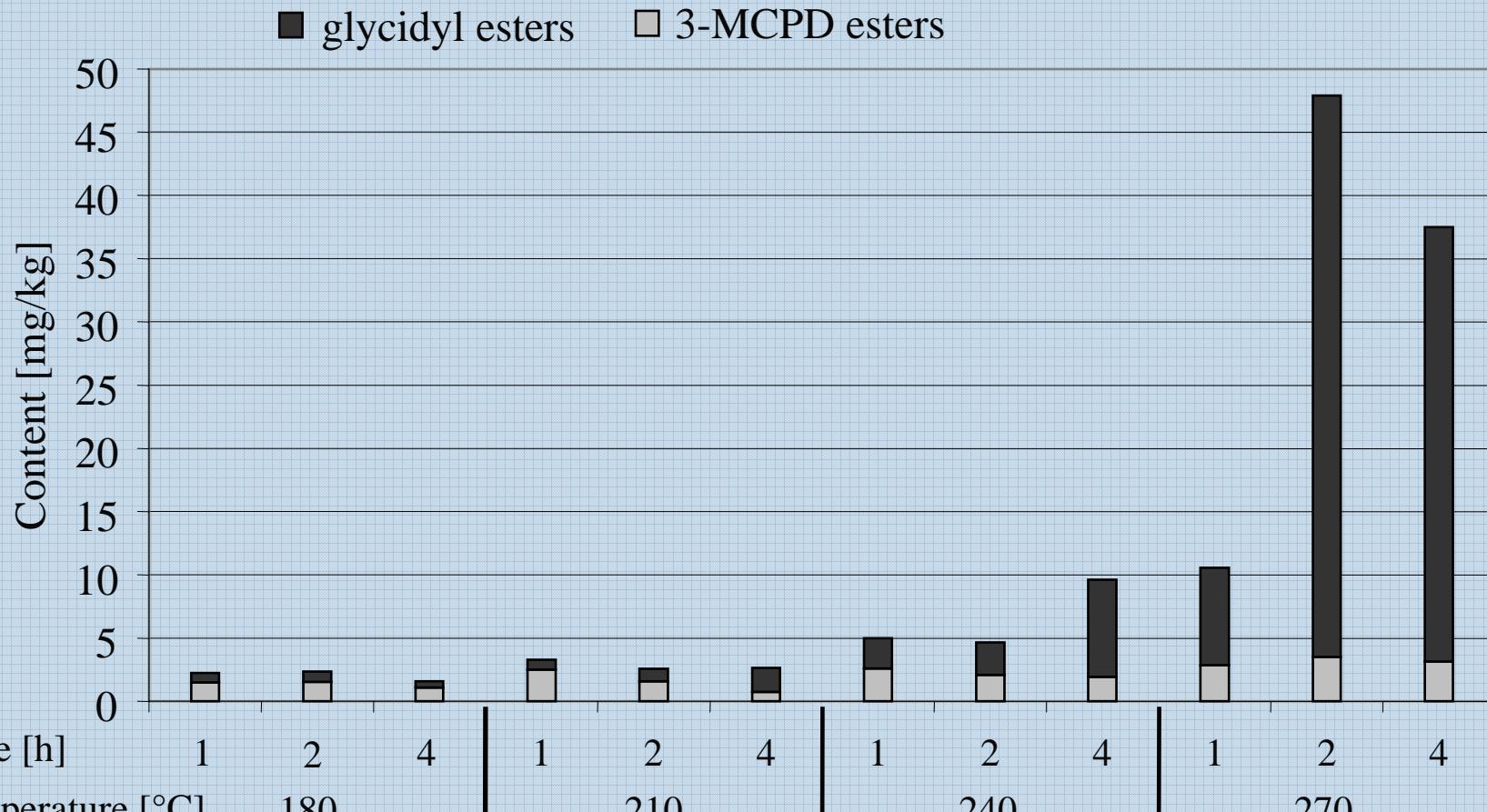


Source: A. Schwaf, Diploma project, 2009

Influence of bleaching on the potential of forming 3-MCPD esters and related compounds during deodorization



Influence of time and temperature during deodorisation on formation of 3-MCPD and glycidol esters

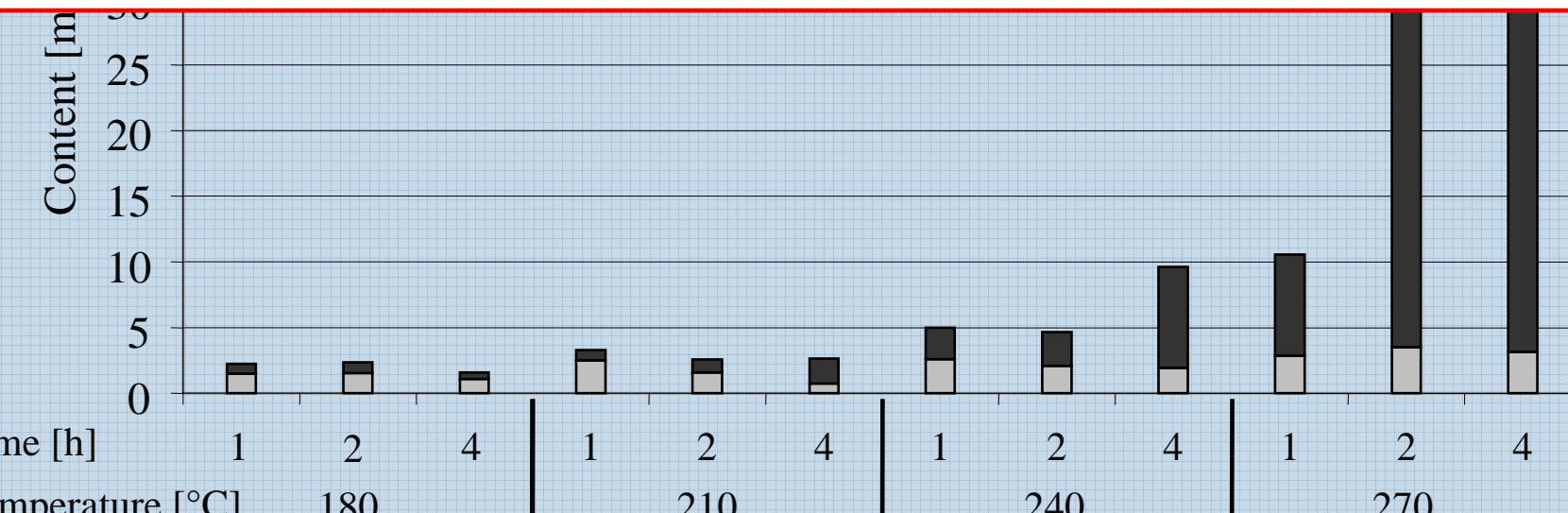


Influence of time and temperature during deodorisation on formation of 3-MCPD and glycidol esters

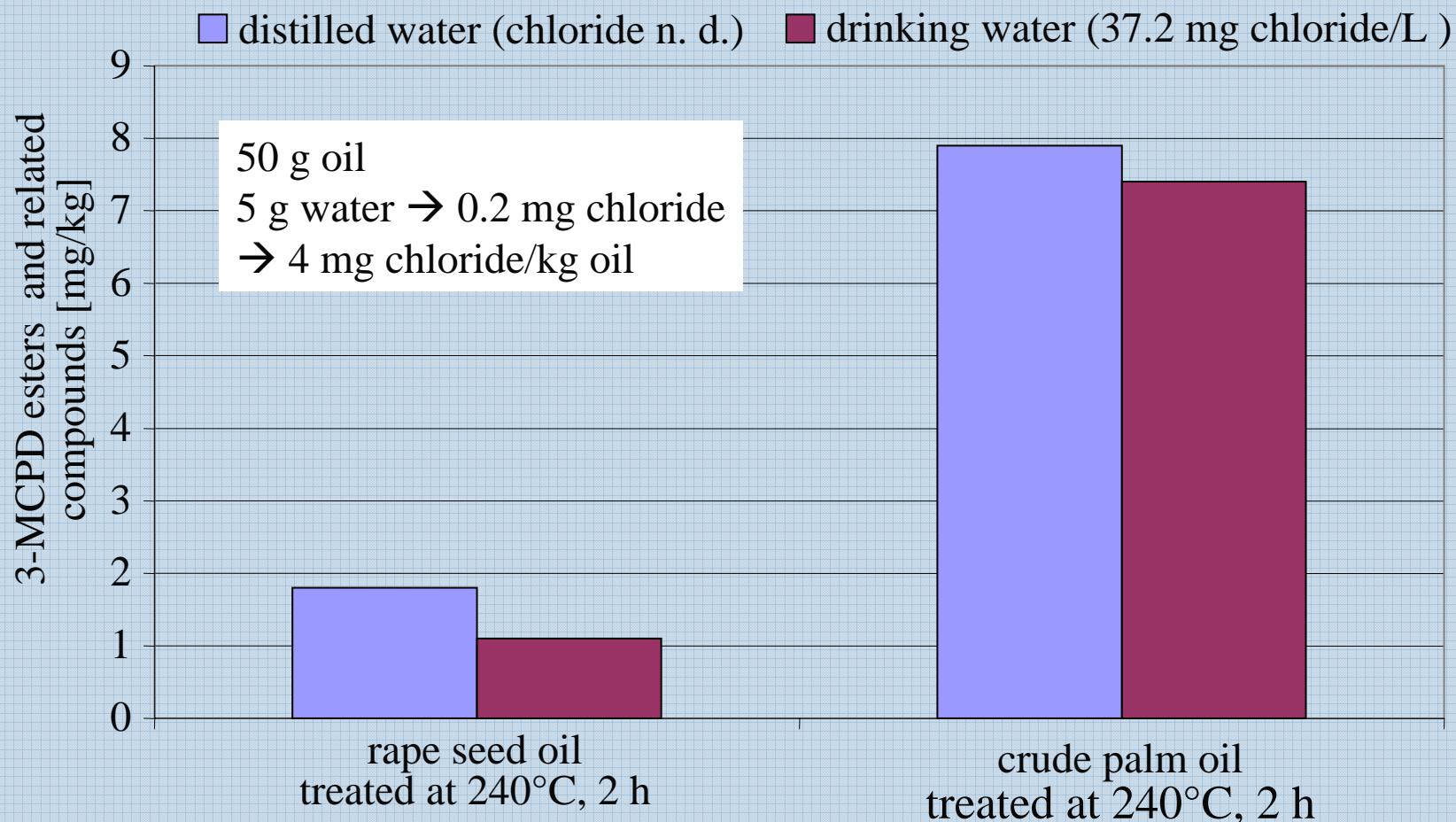
■ glycidyl esters □ 3-MCPD esters

50
45

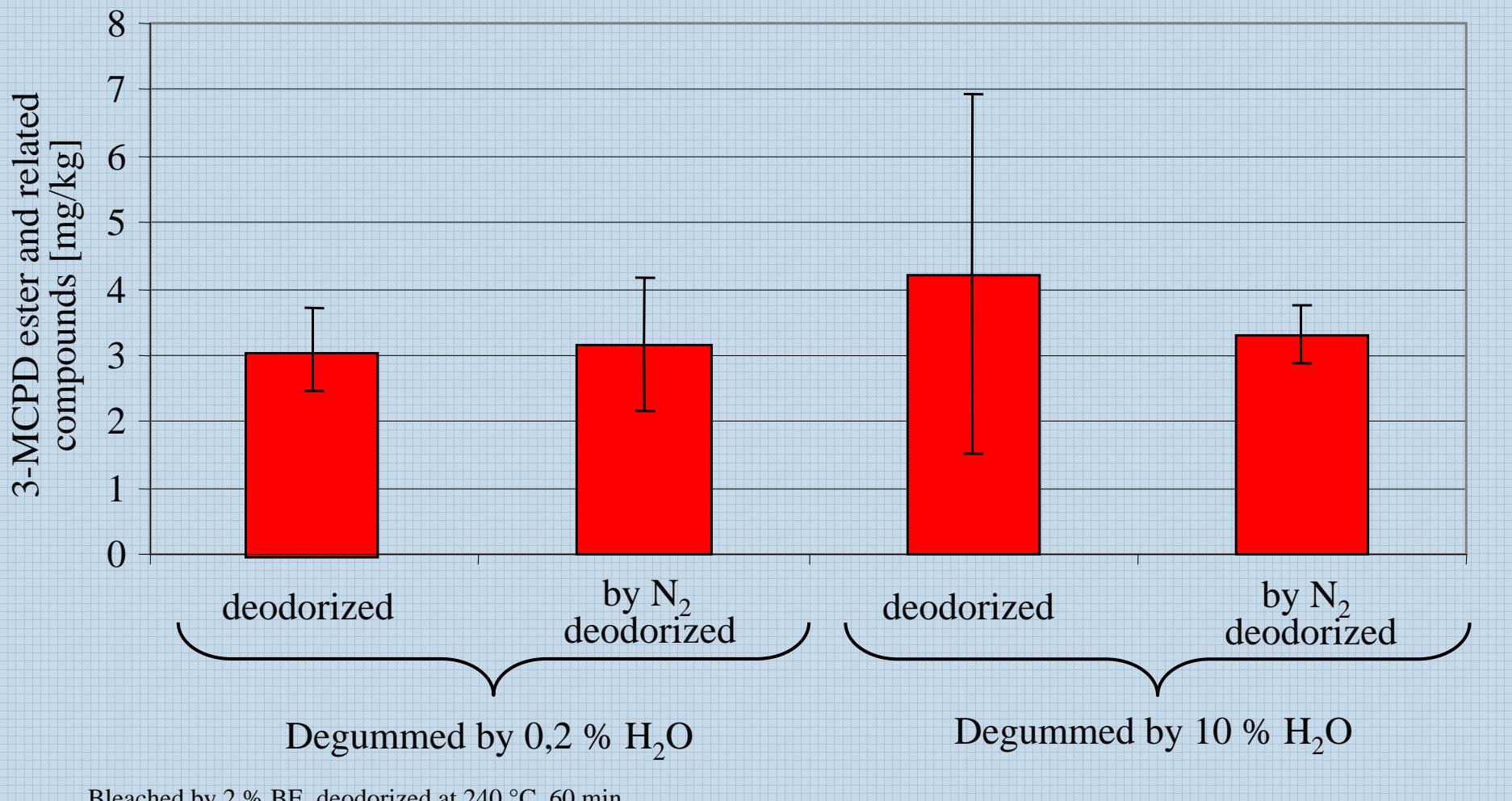
Refining at higher temperature results more in a glycidyl ester problem than in a 3-MCPD ester problem



Influence of the chloride content of water for the generation of the strip steam during deodorization



Deodorization with nitrogen in comparison to a deodorization with strip steam

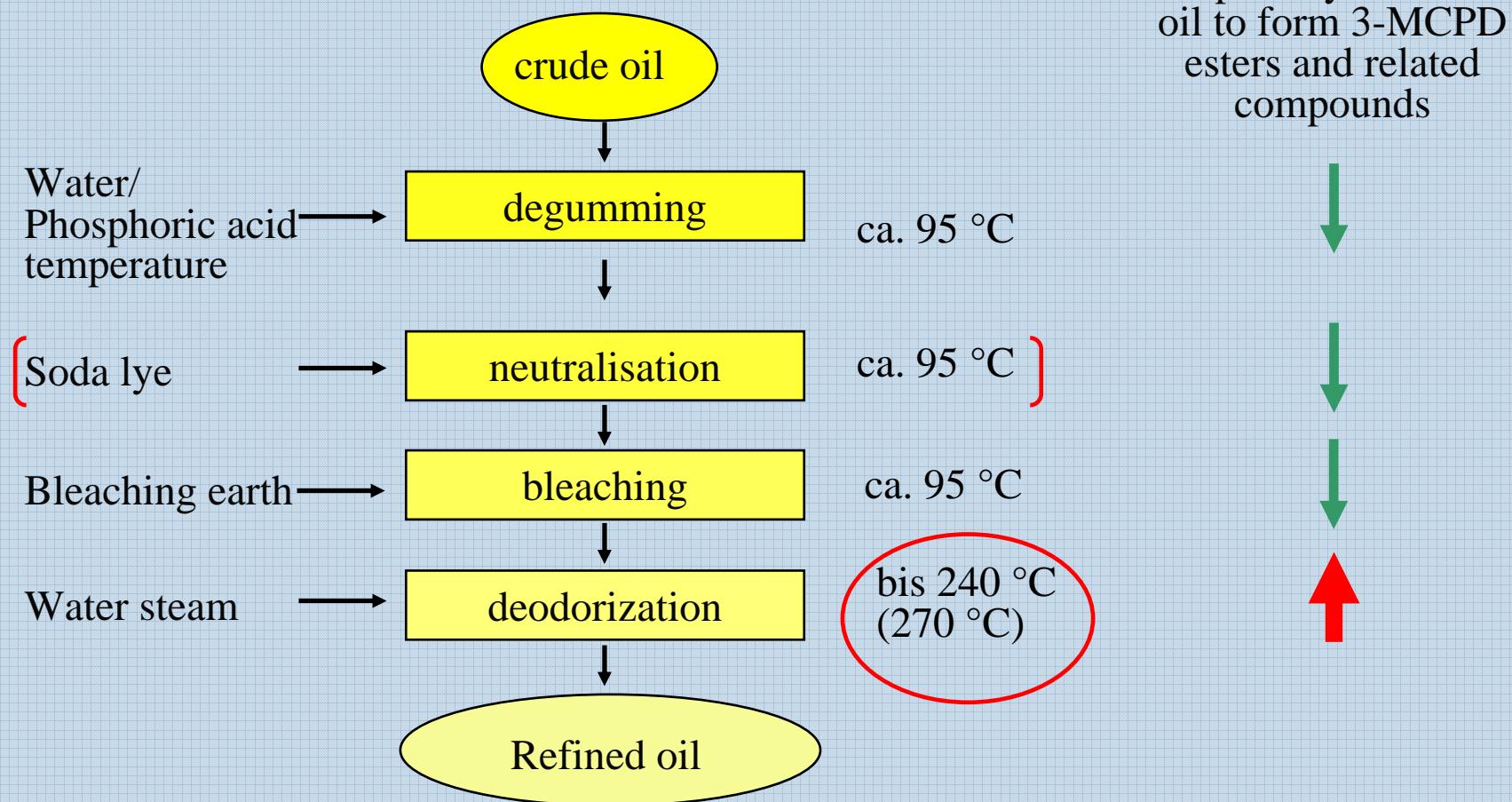


3-MCPD esters and related compounds in exhaust vapors of deodorization

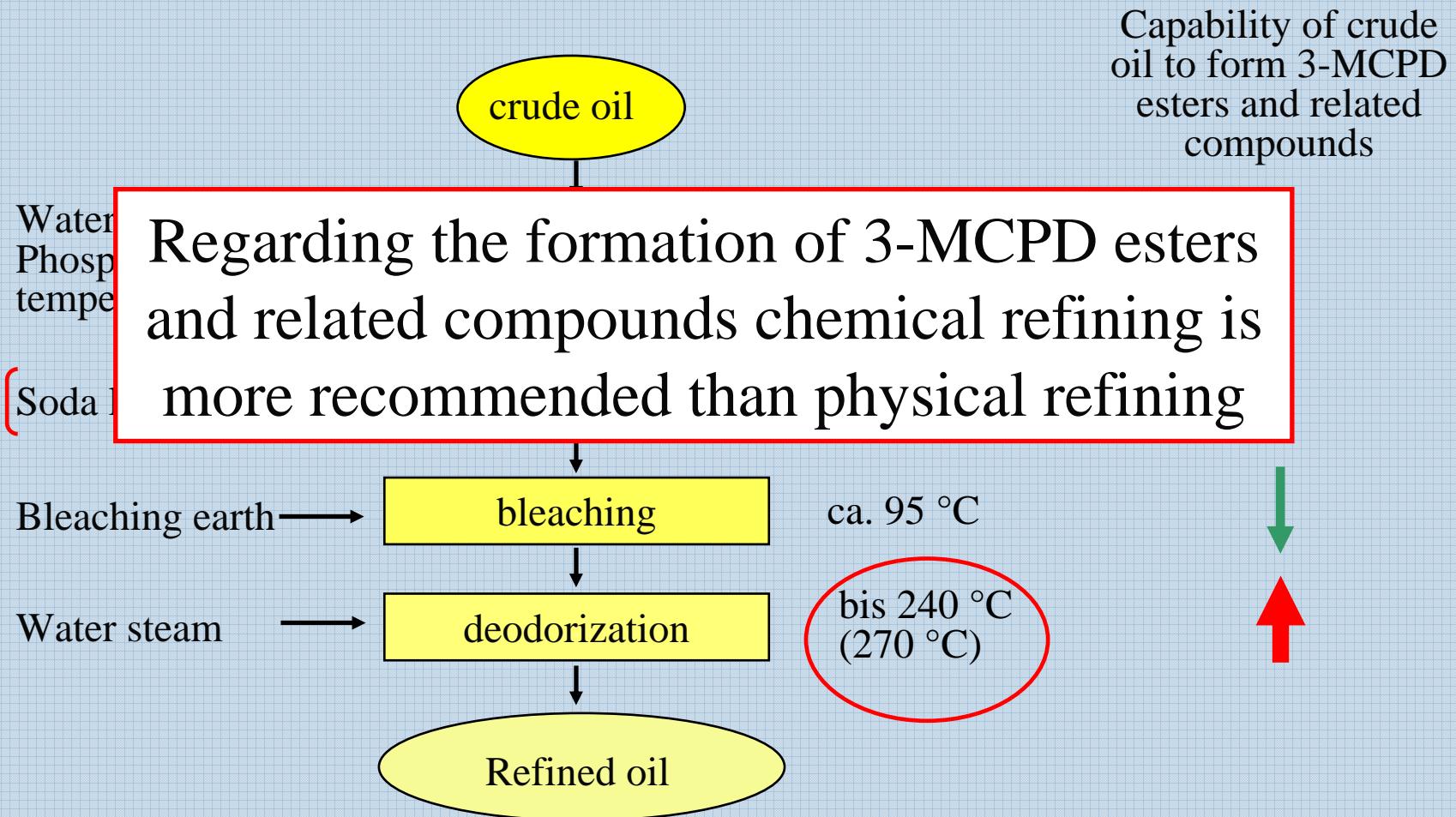
Sample number	Content of 3-MCPD esters and related compounds [mg/100 g Öl]	Content of 3-MCPD esters and related compounds in collected exhaust vapors [mg] = 3-MCPD esters from 100 g oil	Part of 3-MCPD esters and related compounds in exhaust vapors [%]
5511	0,4	0,010	2,8
5515	0,6	0,004	0,6
5515	0,3	0,013	4,2
5515	0,9	0,008	0,8

The content of 3-MCPD esters and related compounds found in exhaust vapors is only small

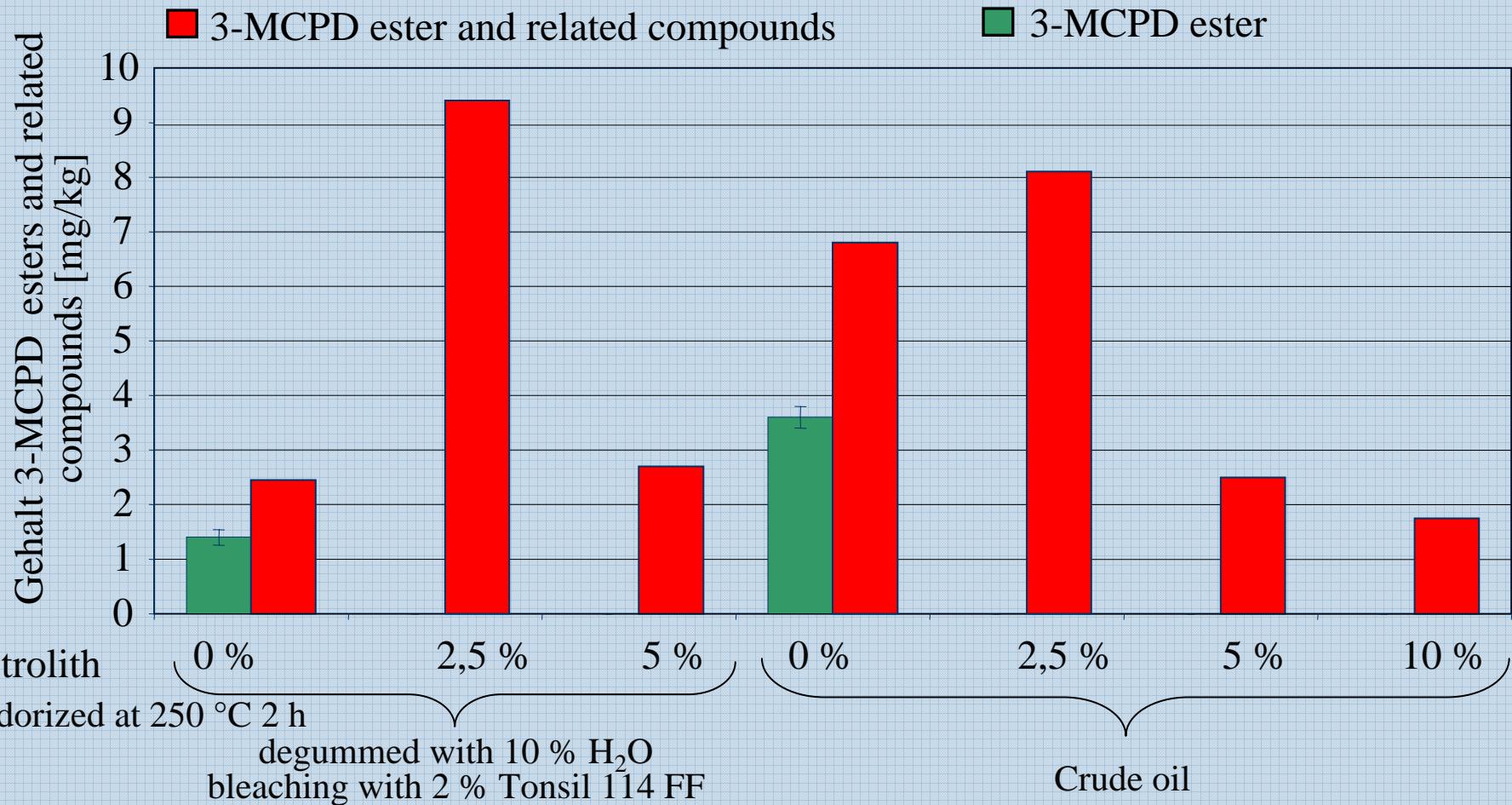
Impact of refining on the formation of 3-MCPD esters and related compounds



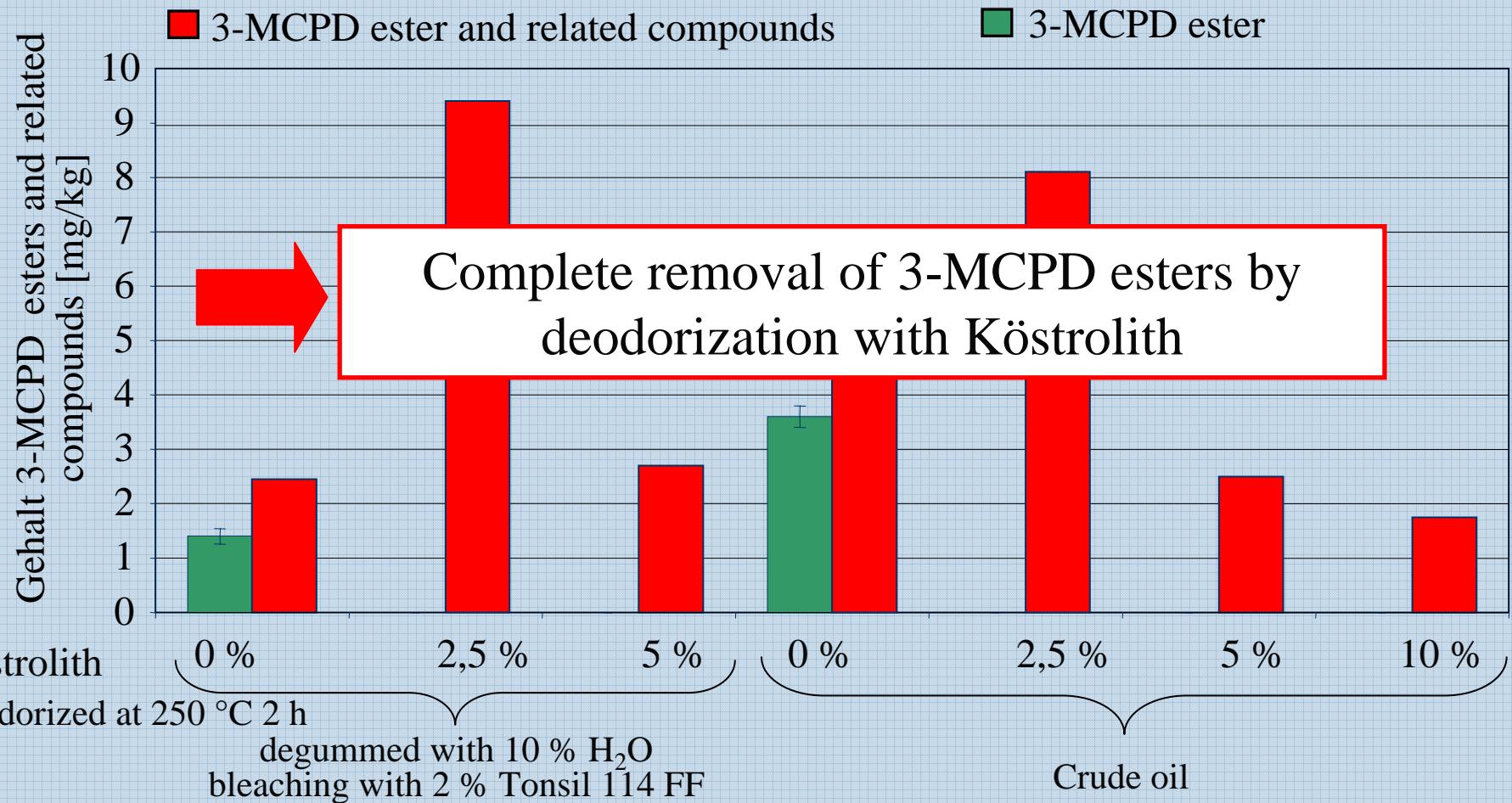
Impact of refining on the formation of 3-MCPD esters and related compounds



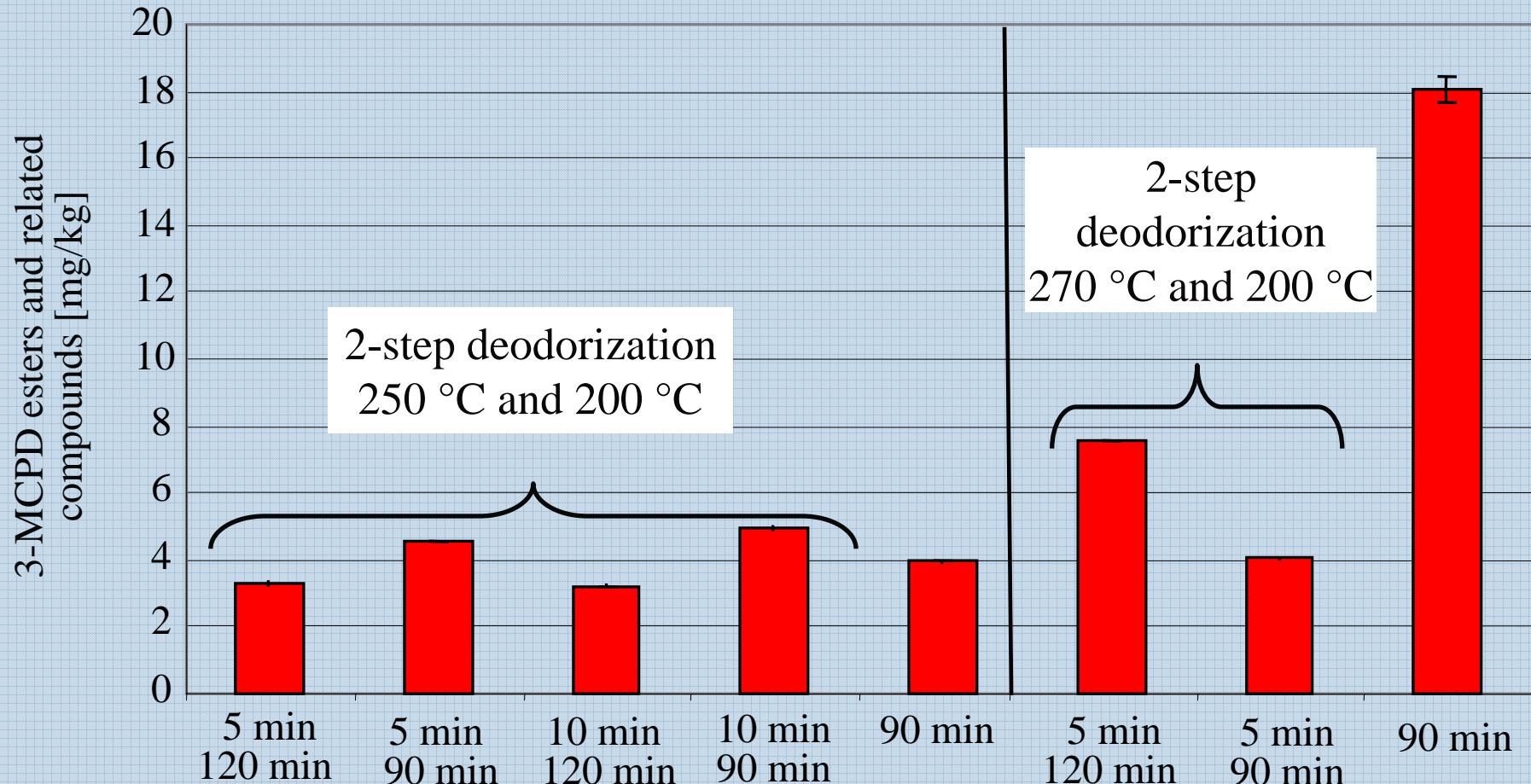
Influence of Köstrolith on the formation of 3-MCPD esters and related compounds during deodorization



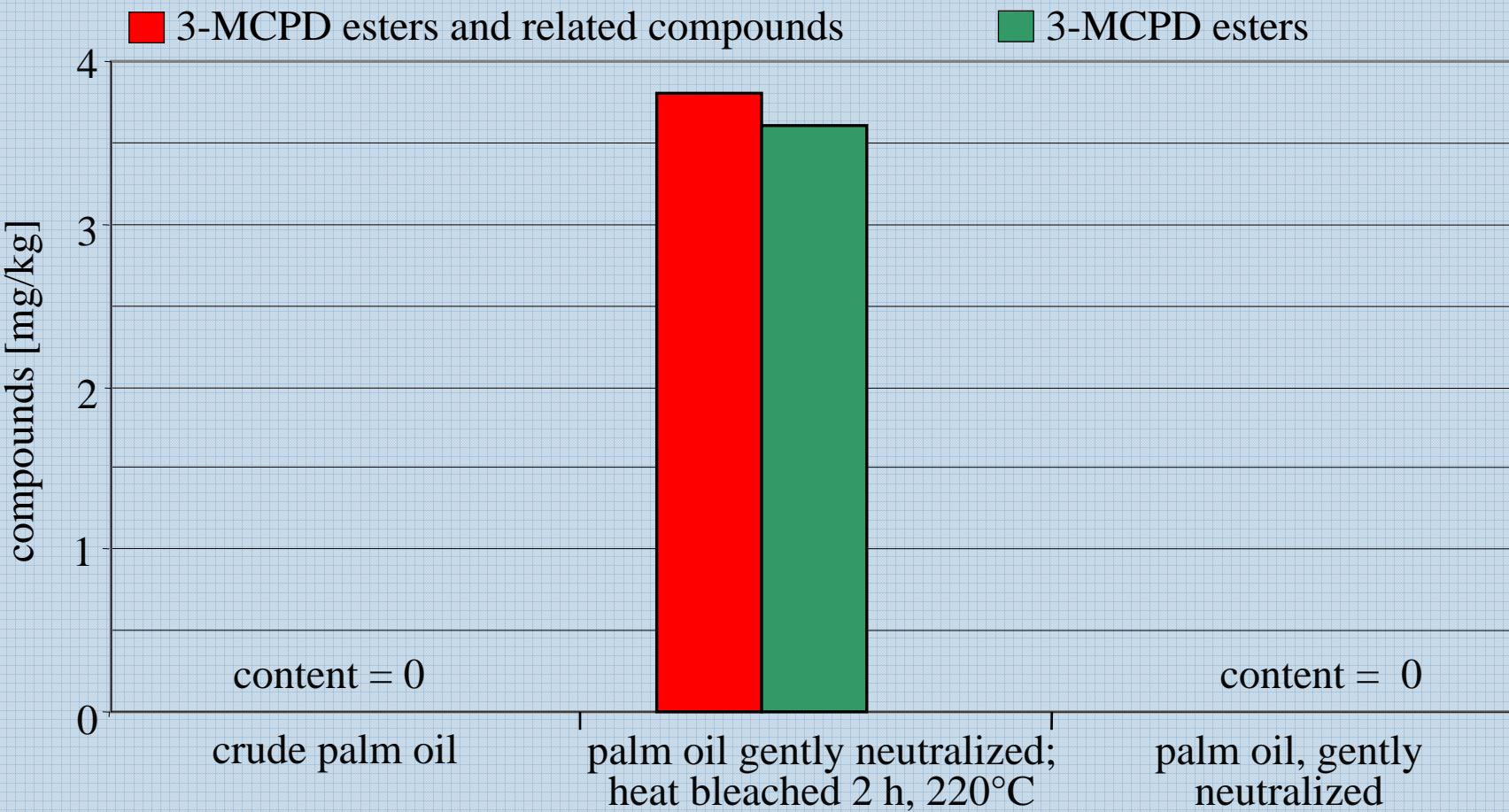
Influence of Köstrolith on the formation of 3-MCPD esters and related compounds during deodorization



Comparison of a conventional one-step deodorization with a two-step deodorization after bleaching (palm oil)



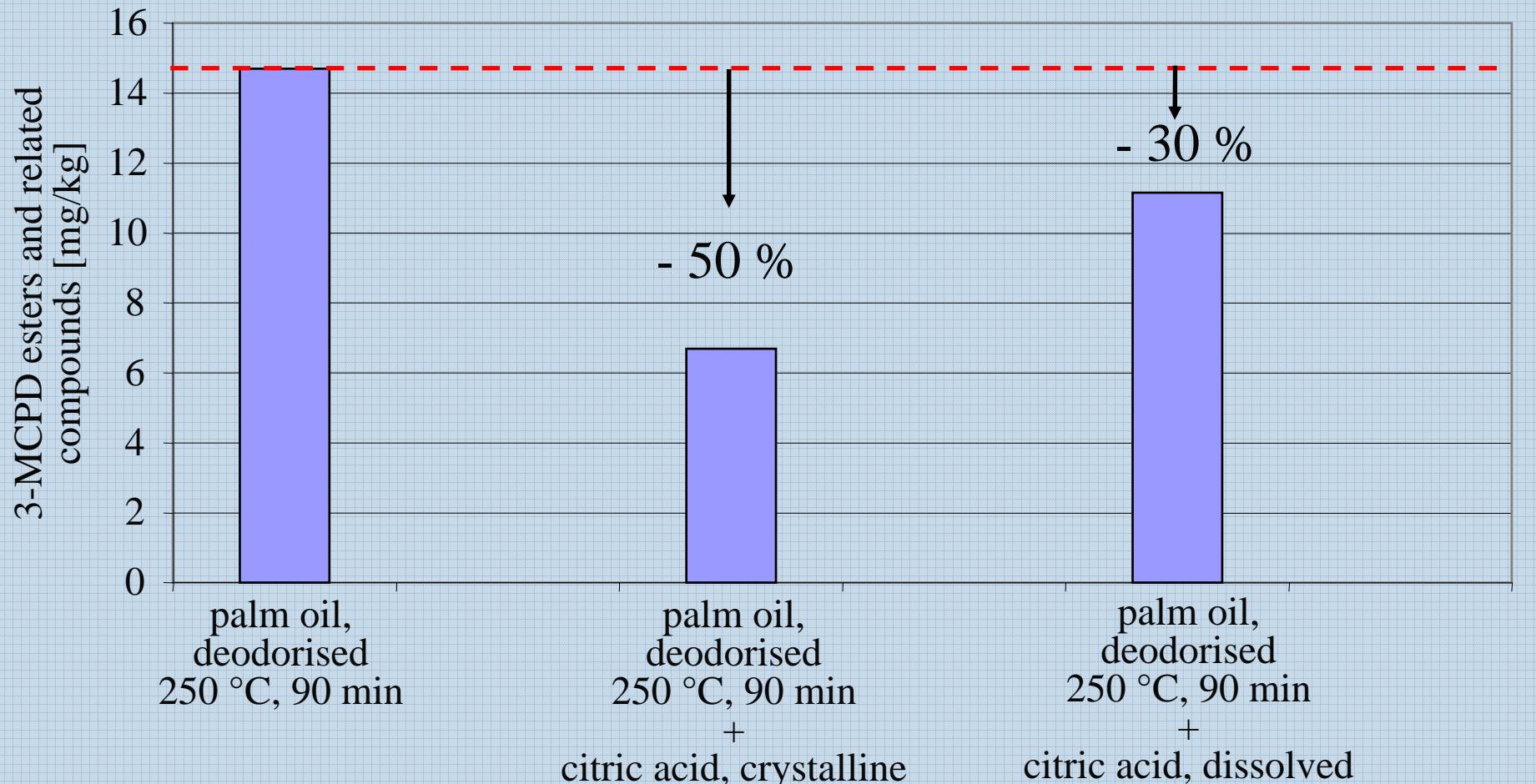
Red palm oil



Quality parameters of different palm oils

	Rancimat (120°C) [h]	Peroxide value [mmol O ₂]	Acid value	3-MCPD esters and related compounds [mg/kg]	Anisidine value
Palm oil, gently neutralized	13,2	0,8	0,4	0	6,1
Palm oil, industrial refined	8,4	2,2	0,7	5,8	8,4

Influence of citric acid during deodorisation



Importance of the raw material on the formation of 3-MCPD esters and related compounds

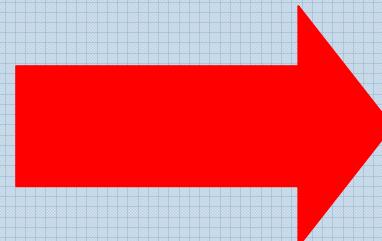
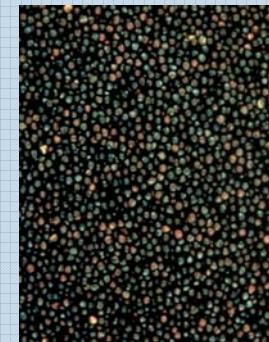


Fruits are

- not storable
- metabolic processes start on the tree if overripened or directly after harvest
- very susceptible against pressure and injuring



Endocarp
Mesocarp
Exocarp



Formation of

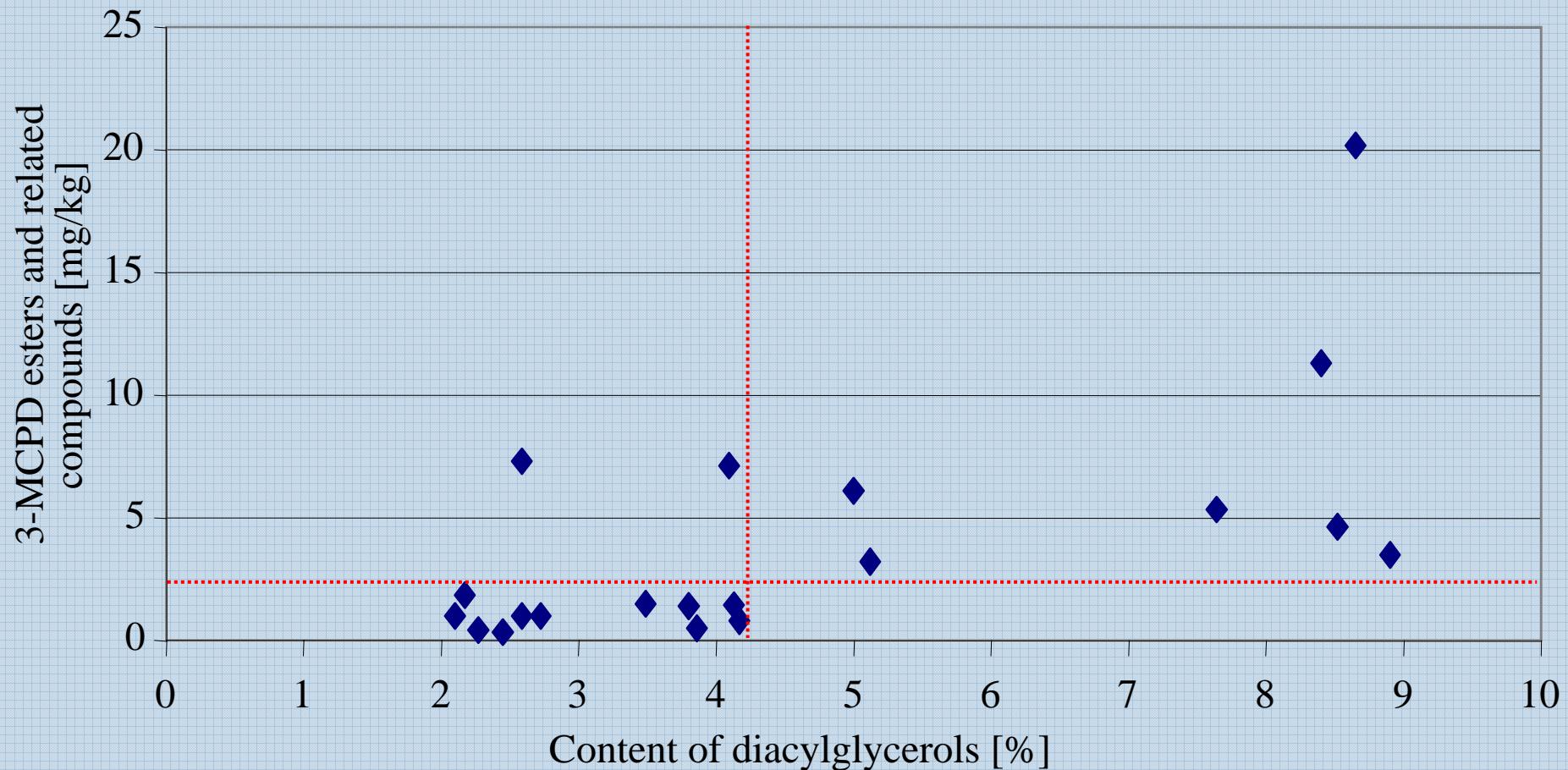
- Free fatty acids
- diacylglycerols



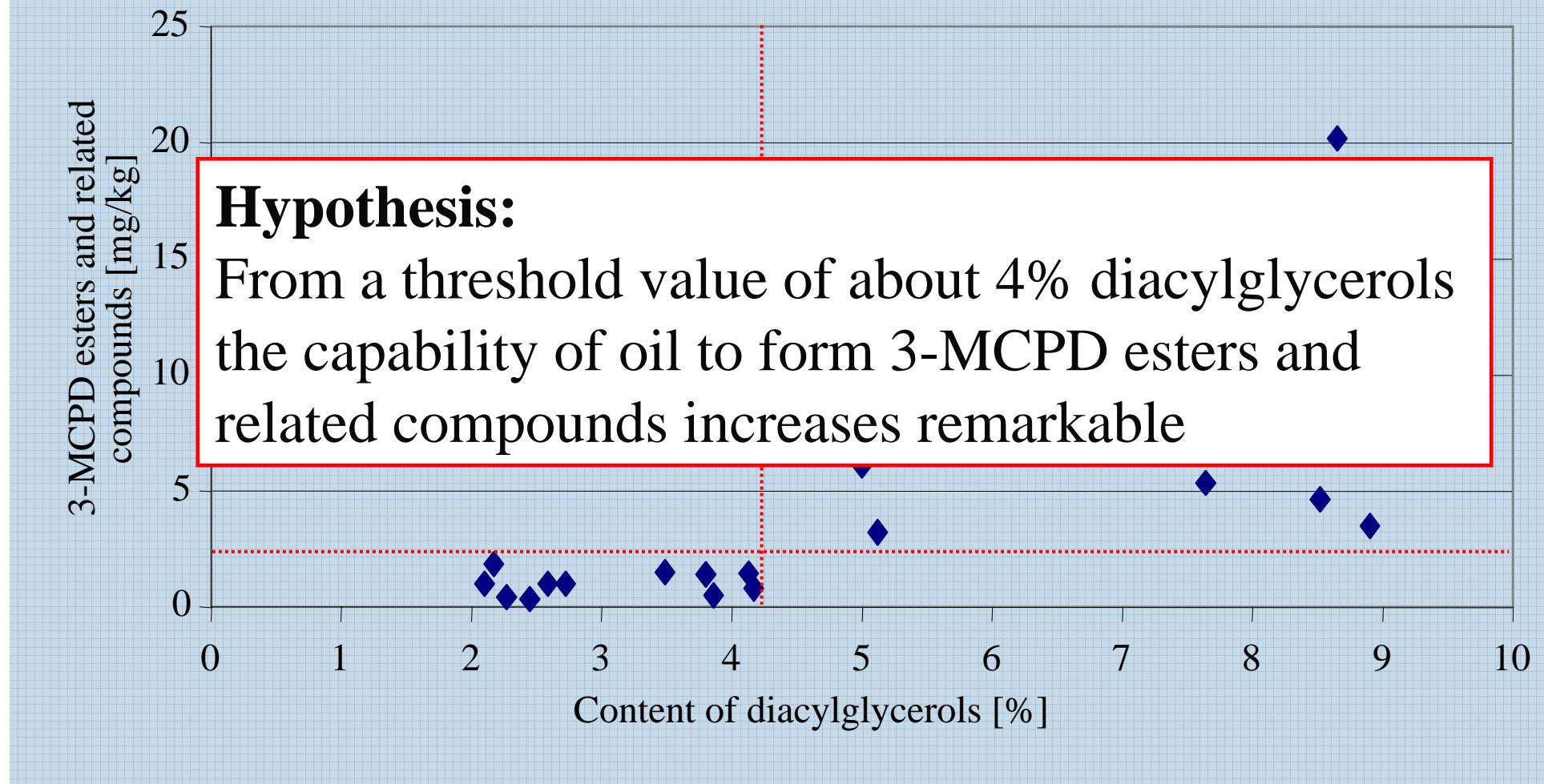
Precursors in the raw material

	Diglycerols (DAG)	Chloride	Remarks
soil / fertilizer / herbicides		✓	e. g. Paraquat
genotype	✓		no differences between different genotypes
climate / weather	✓		
harvest conditions	✓		increase of DAG in overripe fruits
Time between ripeness und processing	✓		increase of DAG with time

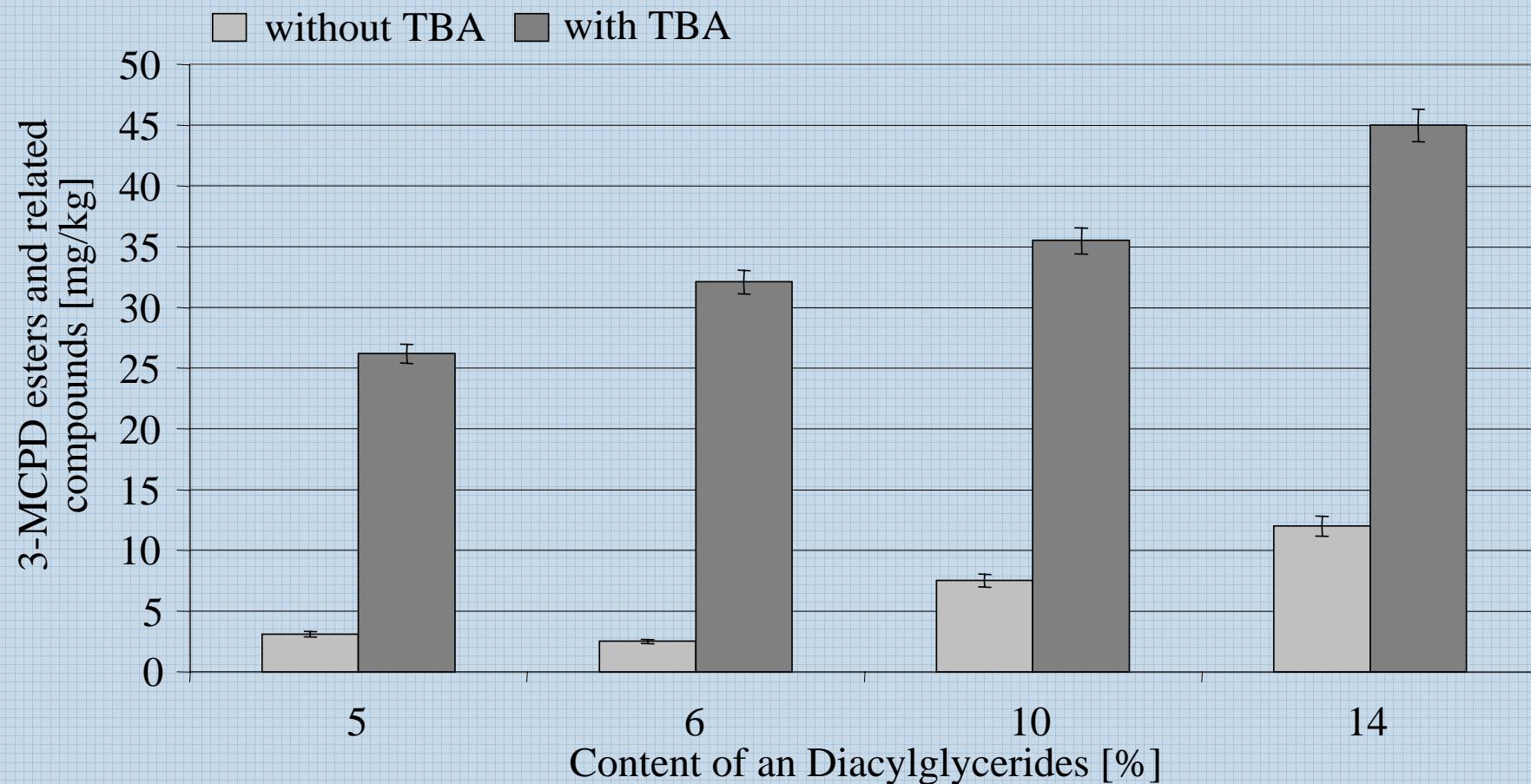
Correlation between content of diacylglycerols and capability to form 3-MCPD esters and related compounds



Correlation between content of diacylglycerols and capability to form 3-MCPD esters and related compounds

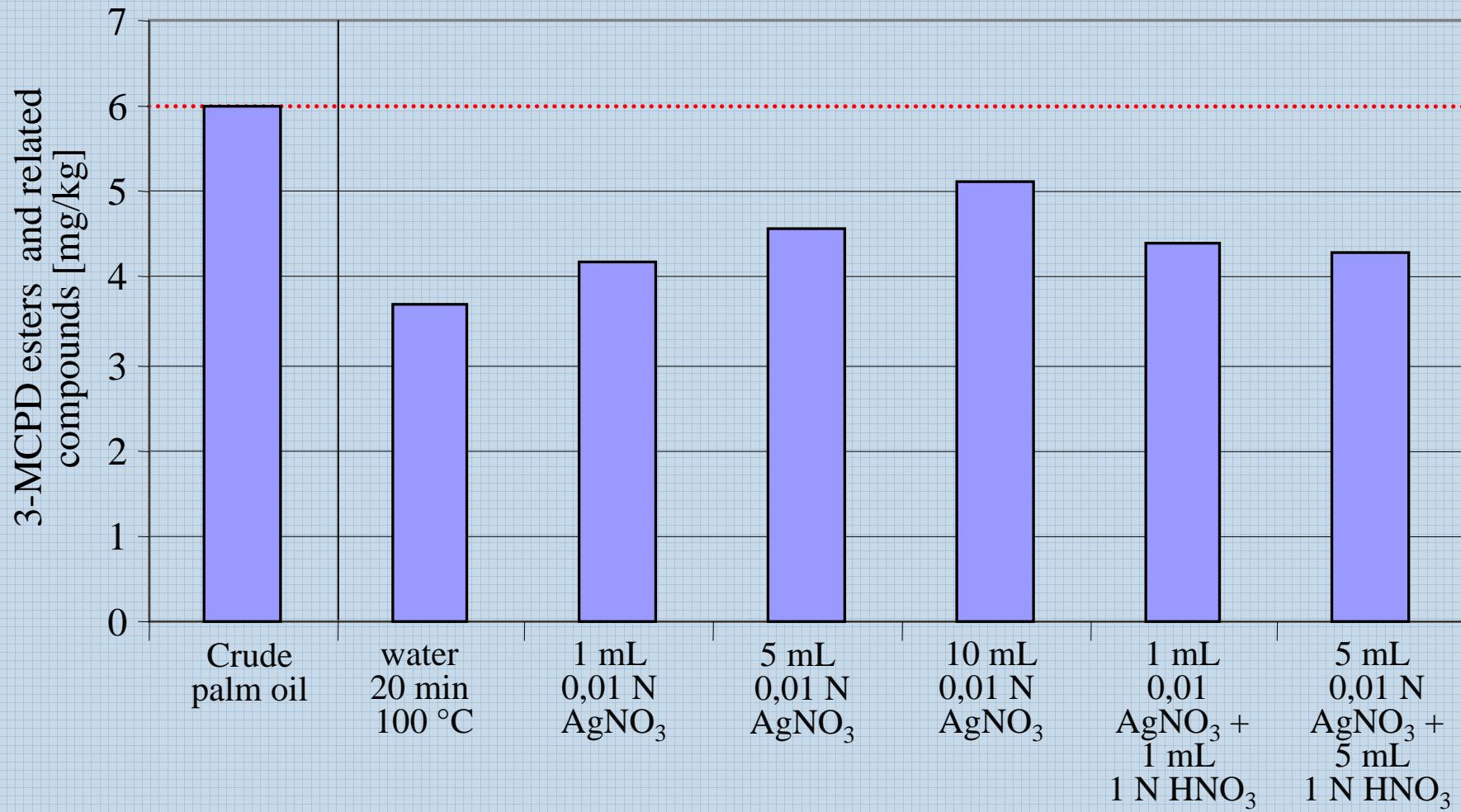


Influence of chloride on the formation of 3-MCPD esters and related compounds

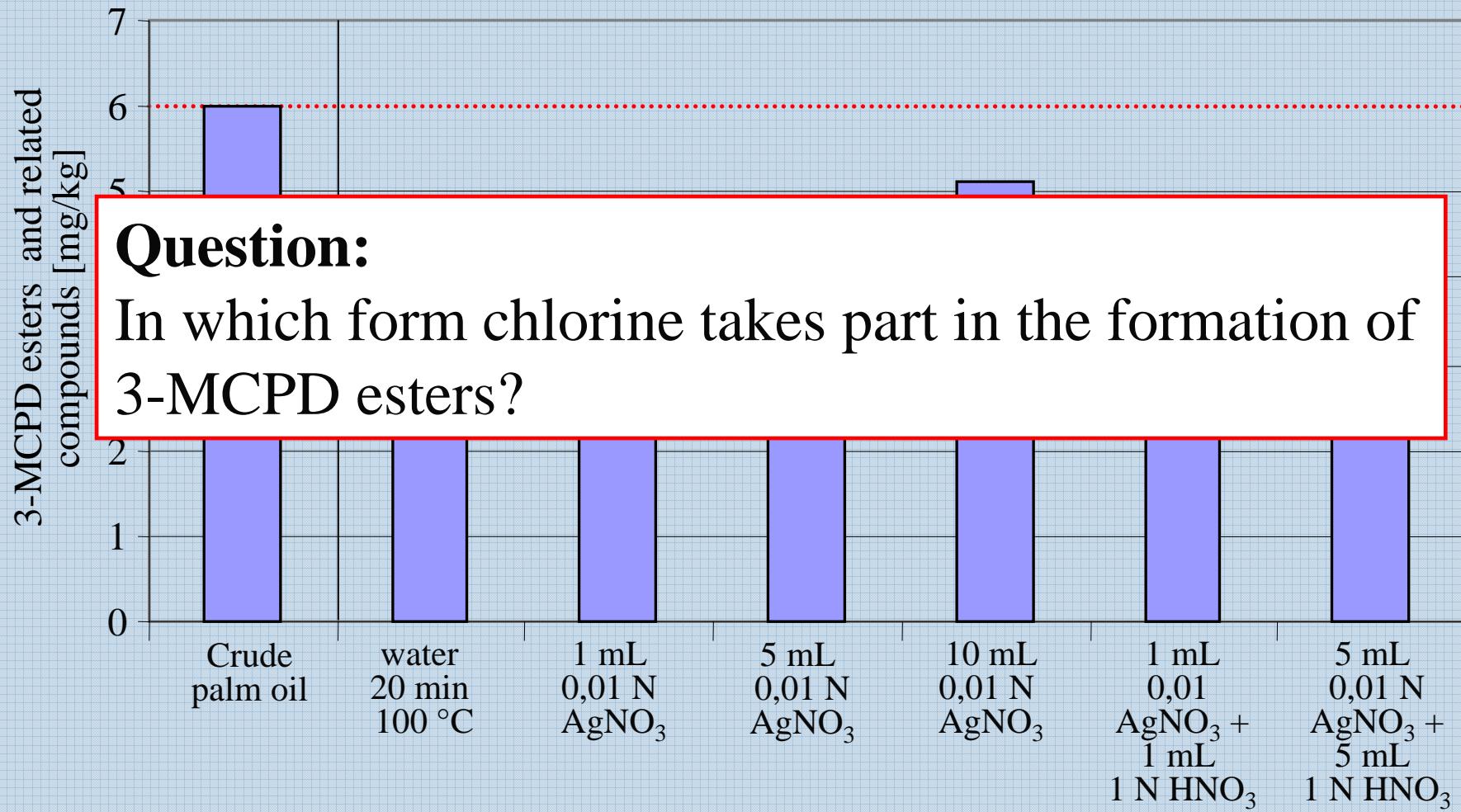


Source of chloride: Tetra-n-butylammoniumchloride

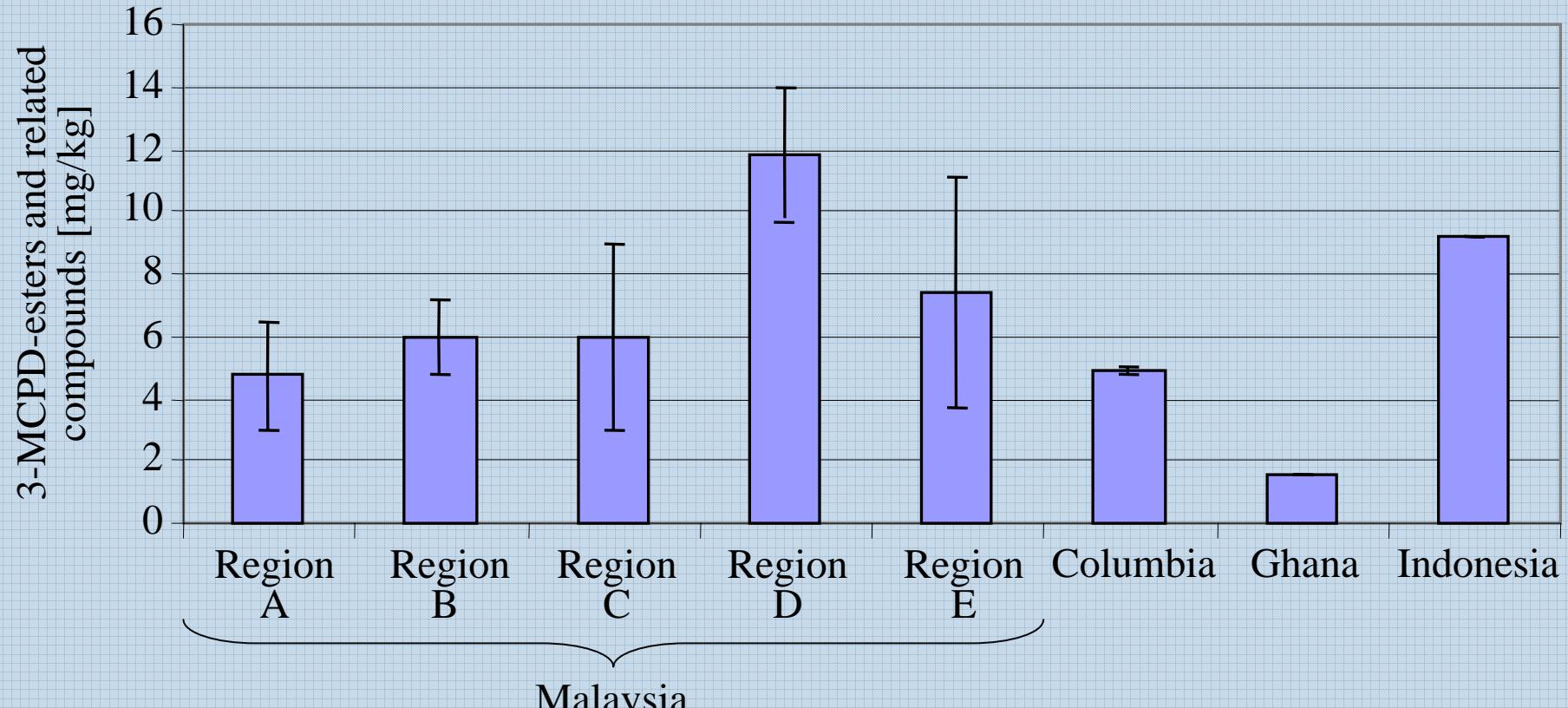
Influence of adding AgNO_3 on the capability to form 3-MCPD esters and related compounds



Influence of adding AgNO_3 on the capability to form 3-MCPD esters and related compounds



Capability of different palm oils to form 3-MCPD esters and related compounds



NS [mm/a]	2598	3144	4155	3675
Ø T [°C]	23.3 – 31.0	22.4 – 31.4	22.9 – 31.4	23.9 – 32.3

Capability of different palm oils to form 3-MCPD esters and related compounds

3-MCPD-esters and related
J. L. ...

Is the region responsible for different capabilities to form 3-MCPD esters and related compounds or other parameters influencing the capability?

Open questions are the effect of:

- Soils and use of fertilizer? → chloride content
 - Genotypes?
 - Technique of harvesting?
 - Time from harvest to oil mill processing?
- } Content of diacylglycerols

Malaysia

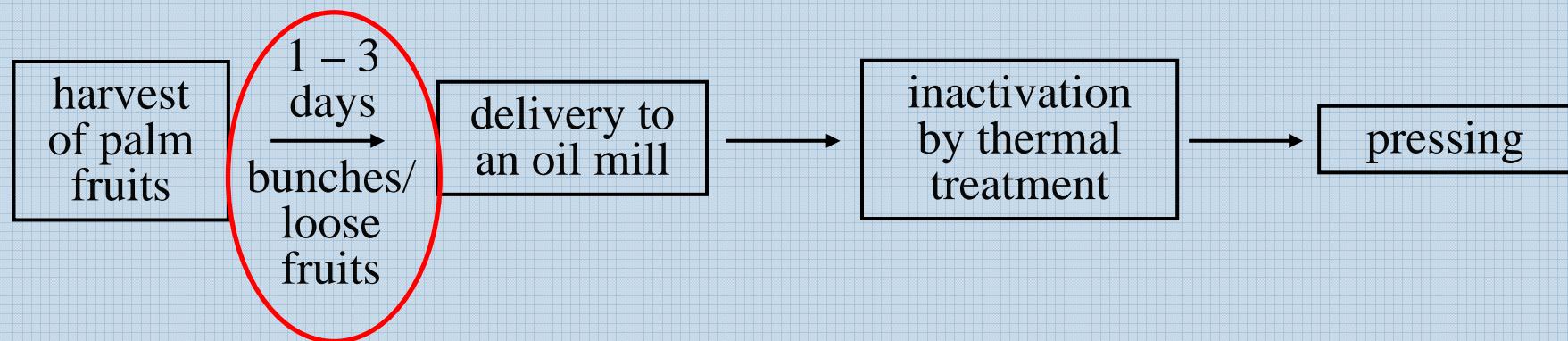
NS [mm/a]	2598	3144	4155	3675
Ø T [°C]	23.3 – 31.0	22.4 – 31.4	22.9 – 31.4	23.9 – 32.3

Effect of precursors on the formation of 3-MCPD esters and related compounds during refining

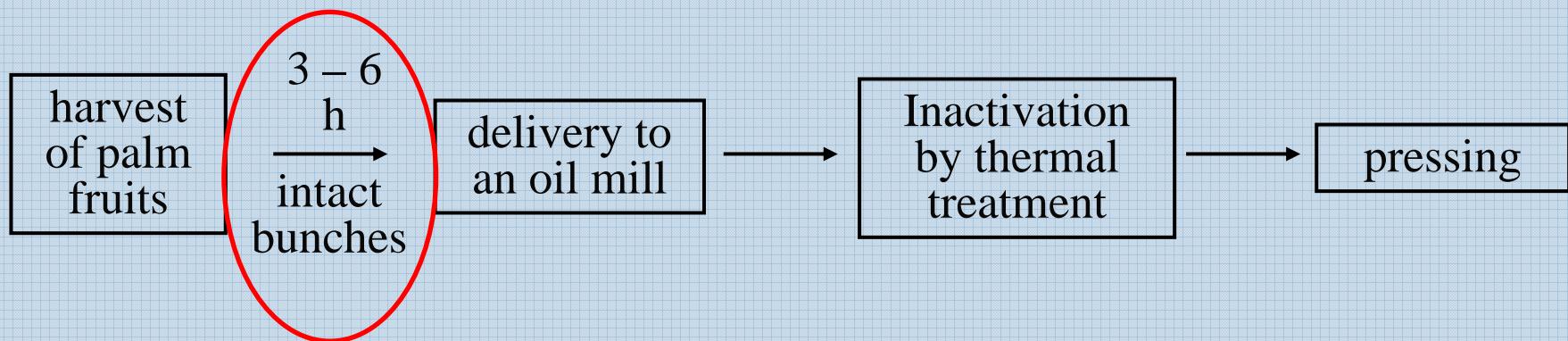
	Diacylglycerols	Chloride	Remarks
Addition of water / acid		✓	Introduces anorganic chloride into the process, but no effect
Addition of bleaching earths		✓	Reduces formation of 3-MCPD esters and related compounds
Acid-catalysed degradation of triacylglycerols	✓		
Washing step / degumming by water		✓	Results in lower amounts of 3-MCPD esters
Silver as reaction partner for chloride		✓	No effect

Processing of high-quality palm oil

Conventional palm oil

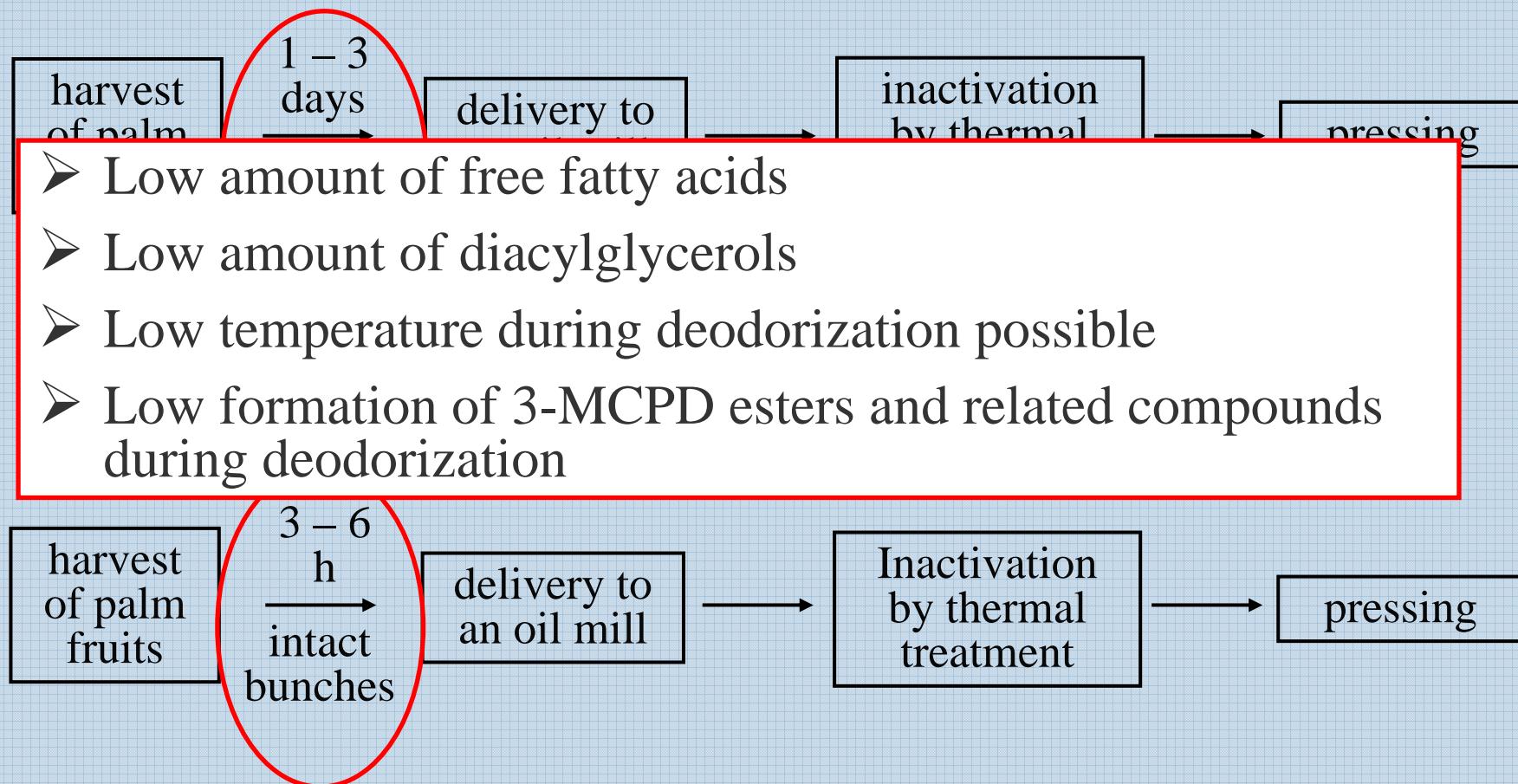


High-quality palm oil



Processing of high-quality palm oil

Conventional palm oil



- Low amount of free fatty acids
- Low amount of diacylglycerols
- Low temperature during deodorization possible
- Low formation of 3-MCPD esters and related compounds during deodorization

Summary

- **Initial situation:** High amounts of 3-MCPD-esters and related compounds in different vegetable oils
- FEI-Research project started in April 2009
- **Aim:** Recommendations for the definition of process conditions to minimize the formation of 3-MCPD-esters with simultaneous maintenance of product quality
- Focus of the project now not only on processing but also on the raw material
- Neutralisation, degumming and bleaching reduces the capability of palm oil to form 3-MCPD esters and related compound; high temperature during deodorization is most critical
- Chemical refining is recommended
- Water used of the generation of strip steam during deodorization has no effect on 3-MCPD ester formation
- Use of citric acid during deodorization drastically reduces the formation of 3-MCPD esters and related compounds
- **Hypothesis:** From a threshold value of about 4% diacylglycerols in the oil the capability for the formation of 3-MCPD esters and related compounds increases
- Chloride is necessary for the formation of the esters, but it is unclear in which form it reacts

Recommendations from the presented results

- Degumming, neutralization and bleaching reduce the potential of palm oil to form the esters
- Chemical refining instead of physical refining
- Introduction of a additional washing step before deodorization
- Temperature during deodorization as low as possible (eventually use of red palm oil)
- Two-step deodorization
- **Hypothesis:** Limit of about 4% diacylglycerols; higher contents before deodorization result in the formation of the esters
- Short time between harvest and inactivation of enzymes (few hours)
- Processing of high-quality raw material

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AiF-Project No.: BG 16004



Chr. Böhme, MRI

Dr. K. Vosmann, MRI

Petra Weitkamp, MRI

Andrea Schwaf, WWU Münster, MRI

N. Schumacher, FH Münster, MRI

The whole 3-MCPD ester research team of MPOB

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FORSCHUNGSKREIS
DER ERNÄHRUNGSDUSTRIE E.V.

Chr. Böhme, MDT

Dr. K.
Petra
Andrea

N. Schumacher, FH Munster, MRI

*Thank you very much for
your attention*

Getreide
Industrie e.V.

VIRKANDE ÖLZÄHLEN-
VIRARBEITENDEN INDUSTRIE
IN DEUTSCHLAND

The whole 3-MCPD ester research team of MPOB