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Mitigation of 3-monochloropropane-1,2-diol and glycidol esters in refined palm oil via modified refining process

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- Recent scientific opinion on MCPDE and GE issues (2016 EFSA's report)
- Malaysian scenario: 3-MCPDE and GE in palm olein
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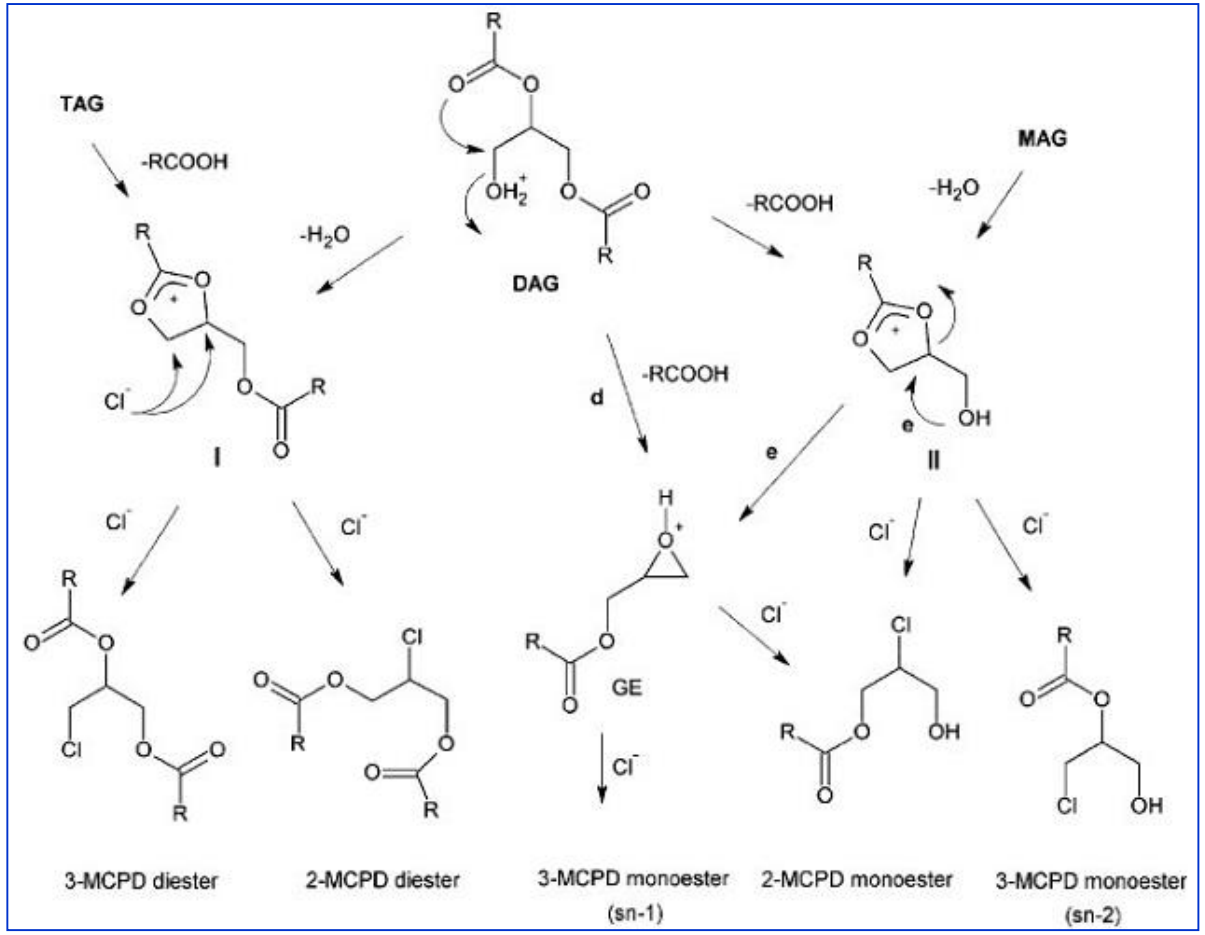
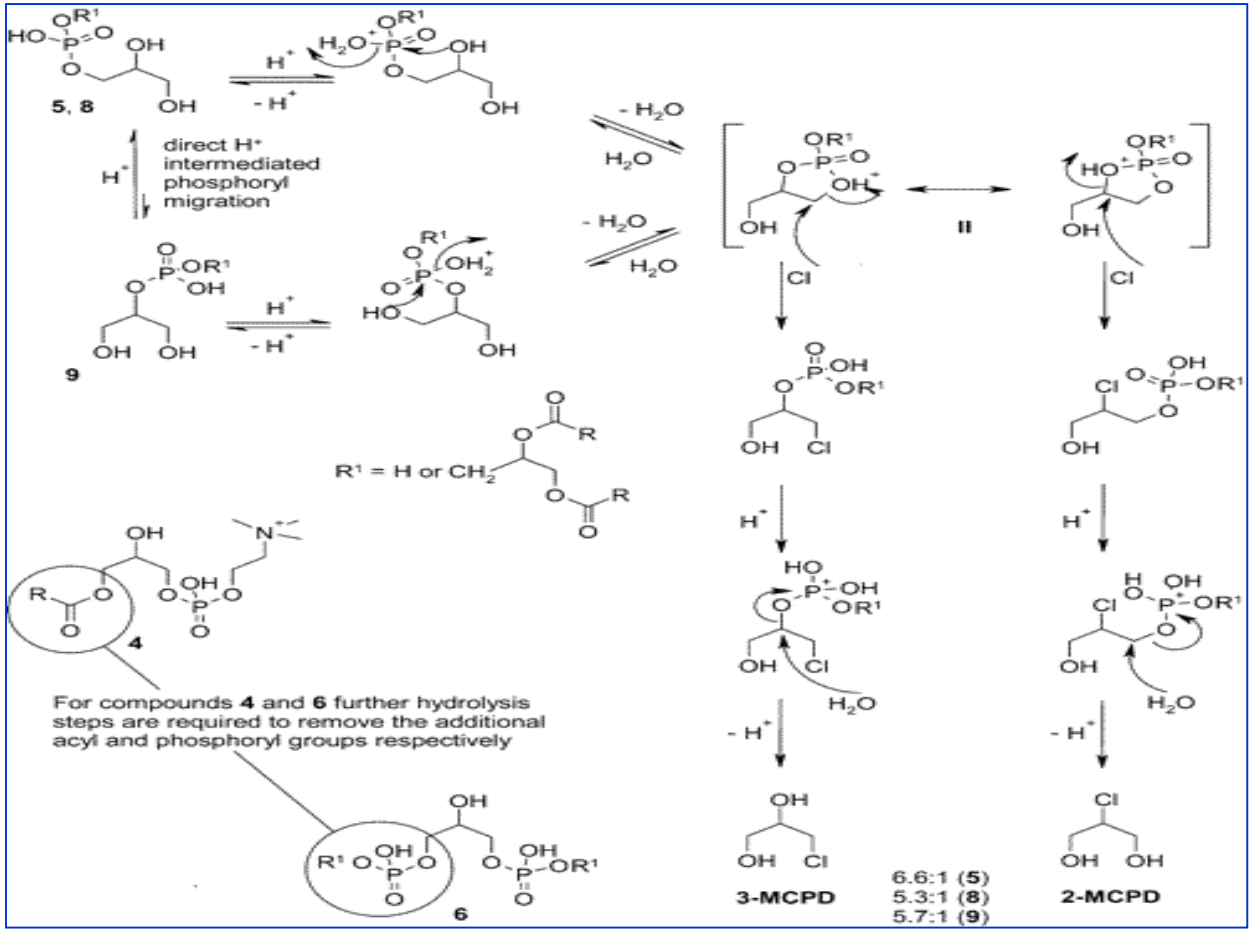
Introduction

- 3-monochloropropane-1,2-diol (MCPD)- and 2-Monochloropropane-1,3-diol (2-MCPD) and their esters and glycidyl esters are food contaminants found highest in refined vegetable oils.
- In refined vegetable oils, especially palm oil, these contaminant are formed during physical refining process.
- However, the exact mechanism of formation is still unclear.

Acyloxonium ion pathway vs. Glycerolphosphates pathway





EFSA Report

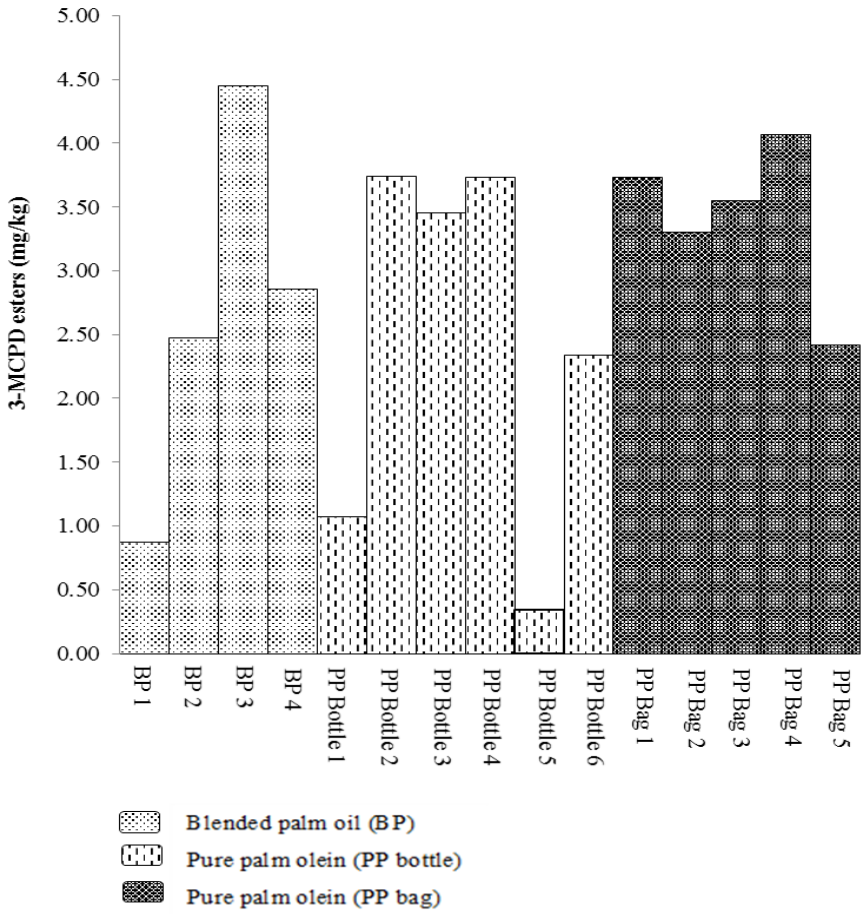
- According to the EFSA report "Risks for human health related to the presence of 3- and 2-monocholoropropanediol (MCPD), and their fatty acid esters, and glycidyl fatty acid esters in food", the panel on Contaminants in the Food Chain (CONTAM panel) has evaluated a total of 7,175 data.
- The report found that 3- and 2-MCPD and glycidyl esters are constantly highest in palm oil/fat while other vegetables oils containing substantially low levels of these process contaminants.
- Across the data, average content of these contaminants are:
  - **3-MCPDE : 2.91 ppm**
  - **2-MCPDE : 1.56 ppm**
  - **GE : 3.99 ppm**

Hazard characterization of MCPDE and GE

- The CONTAM panel suggested the tolerable daily intake (TDI) for 3-MCPD is 0.8 µg/kg body weight (bw) per day.
- For glycidol, the Panel selected a T25 value of 10.2 mg/kg bw per day for neoplastic effects in rats. *(T25 is the chronic daily dose in mg per kg bodyweight which will give 25% of the animals tumours at a specific tissue site)*
- However, no TDI could be established for 2-MCPD and its ester because of lacking of reliable data.

Level of MCPD esters in palm olein

3-MCPDE level in commercial RBD palm olein in Malaysia market

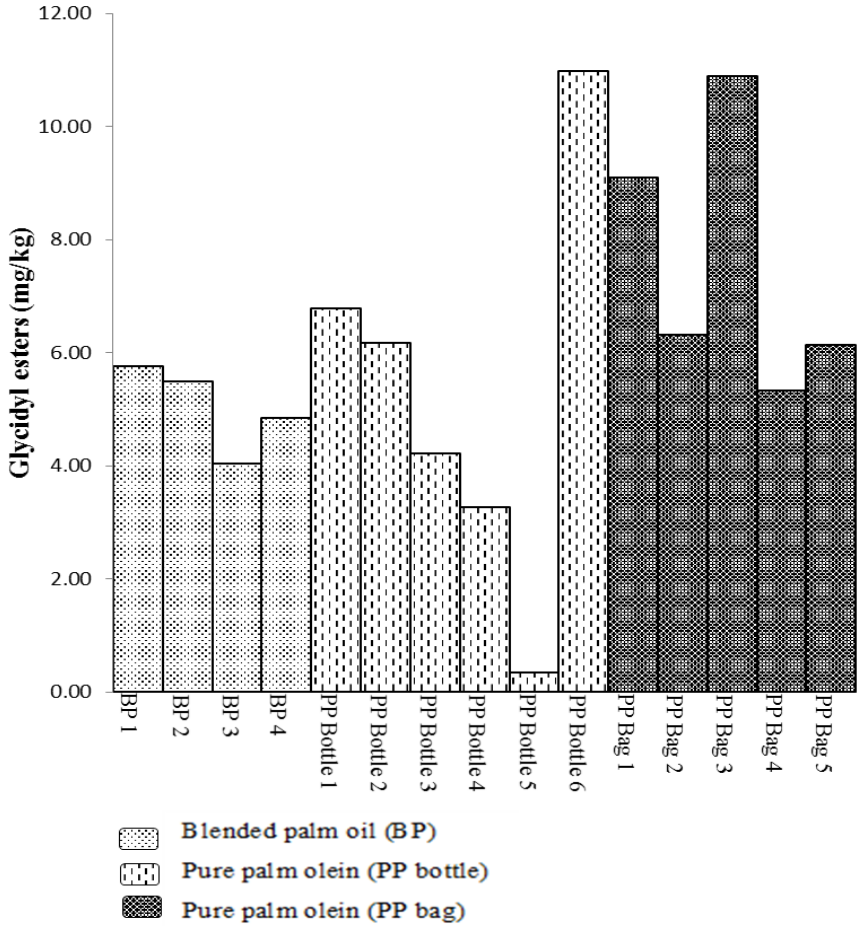


3-MCPDE levels:

0.34 – 4.45 mg/kg

Level of GE in palm olein

GE level in commercial RBD palm olein in Malaysia market

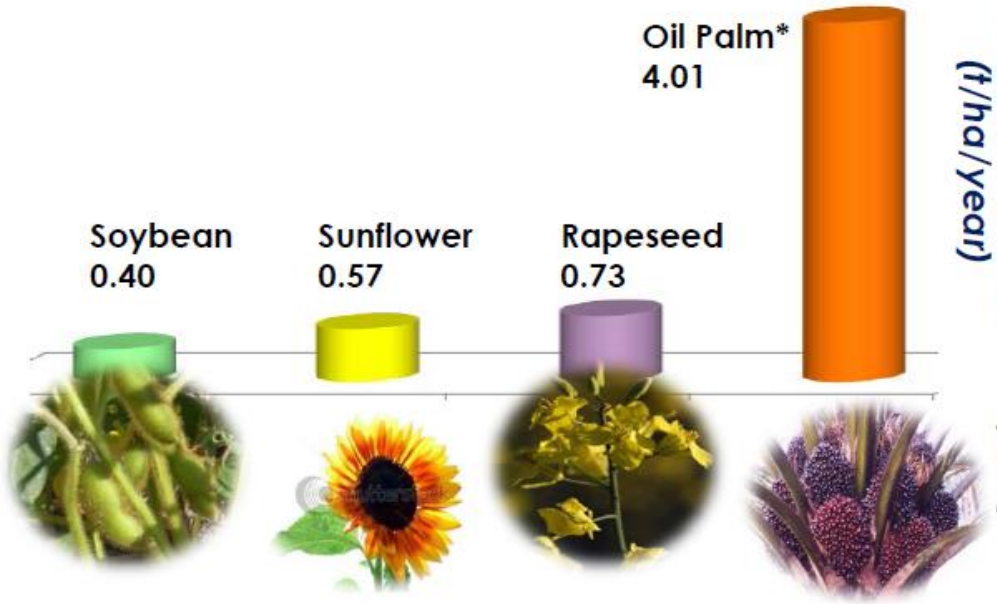


GE levels:

0.34 – 10.98 mg/kg

However, palm oil has its uniqueness and functional properties to the food industry

The Oil Palm – most productive oil crop

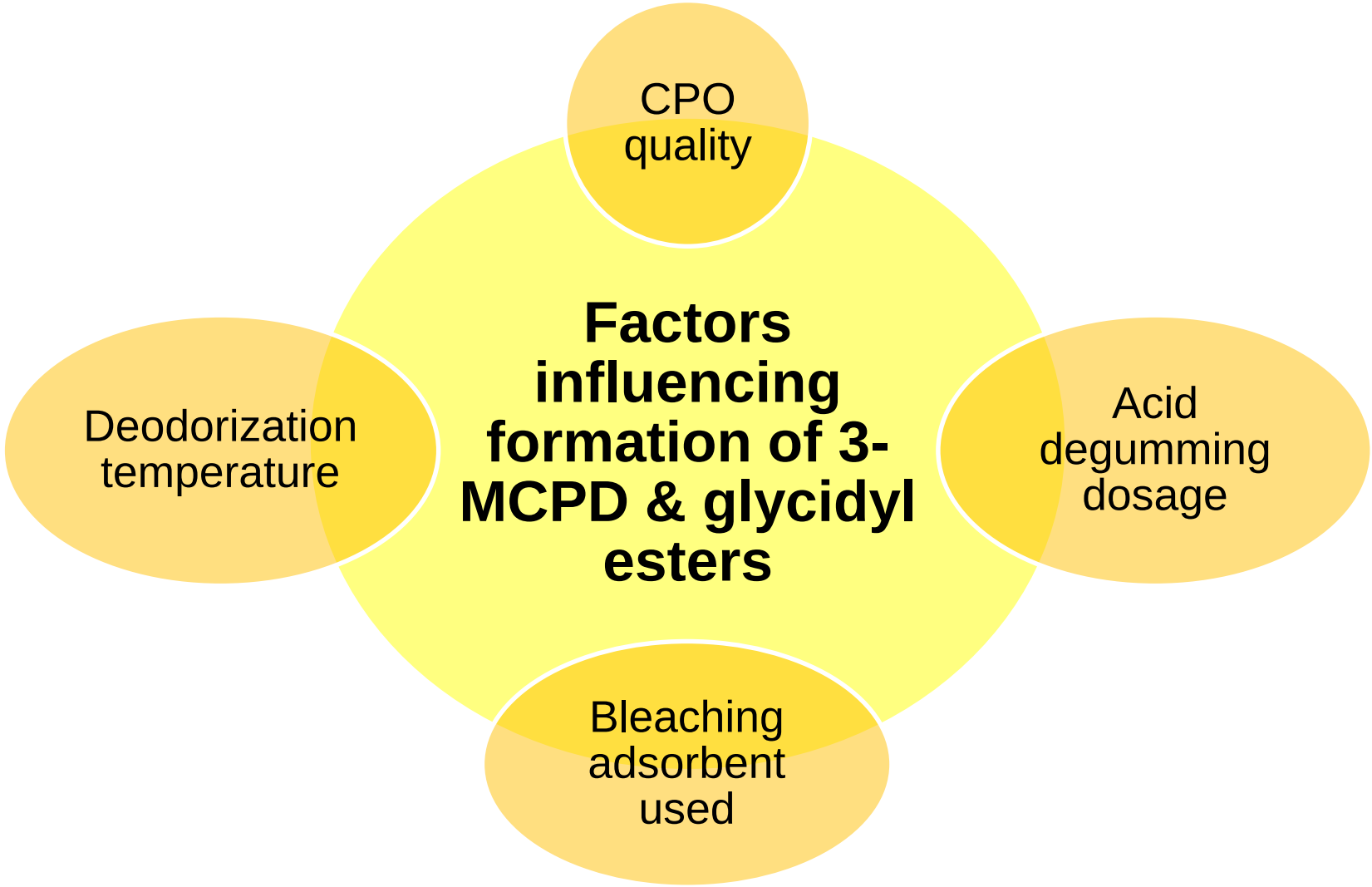


Source: Oil World Annual 2013
* Combined tonnage of palm oil and palm kernel oil

Oil Crops	Production (Mn T)	% of total production	Total area (Mn Ha)	% of total area
Oil palm*	59.39	42.3	14.8	8.3
Soybean	41.8	29.8	103.8	58.4
Rapeseed	24.4	17.4	33.3	18.7
Sunflower	14.8	10.5	25.9	14.6

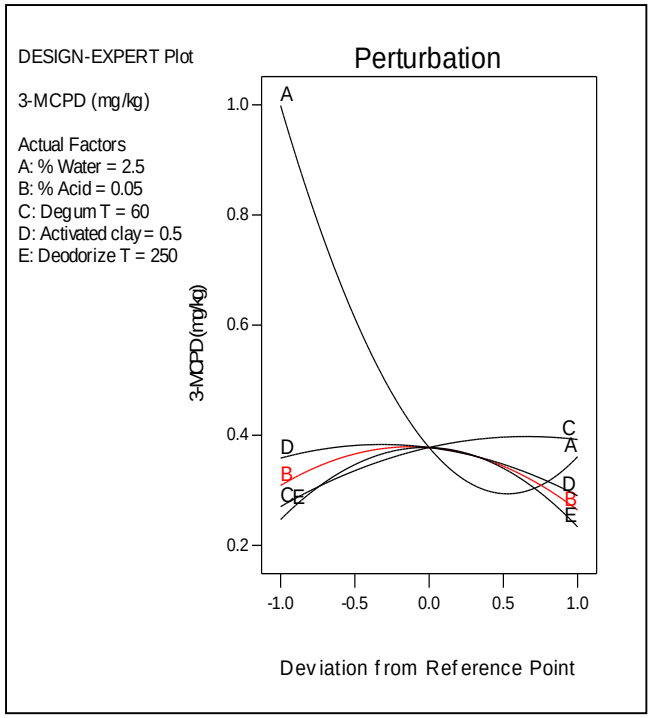
Refining process and the factors influencing formation of 3-MCPD & glycidyl esters

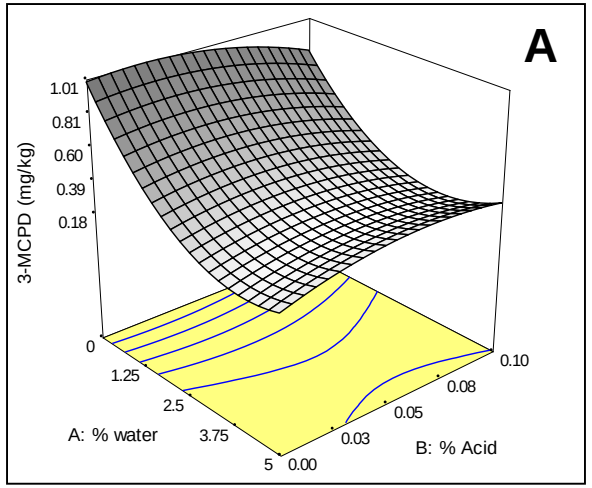
3-MCPD & glycidyl esters in palm oil

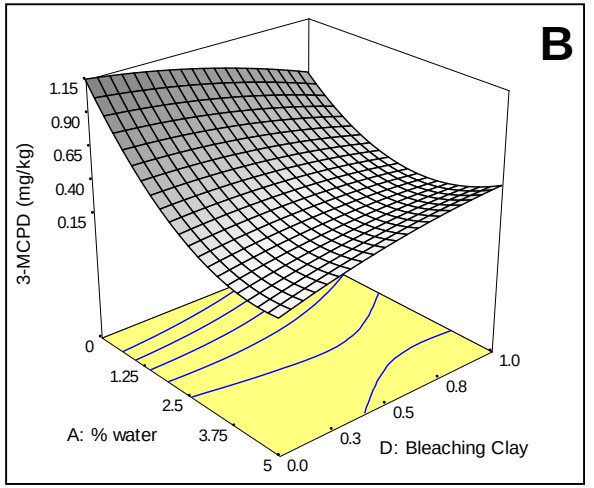


Reduction of 3-MCPD & glycidyl esters in palm oil

CPO	→	Washing	→	Degumming	→	Washing	→	Bleaching	→	Deodorization
		[50 ° C, 15 min]		[20 min, phosphoric acid 97%]		[50 ° C, 15 min, 1% water]		[90 ° C, 30 min, 1% Magnesol R60 & activated clay]		[90min]







Zulkurnian et al., Food Chem., 2012

Effects of degumming and bleaching on the reduction of ME and GE

Design of experiment: D-optimal design

16 experimental runs - 3 factorial and 4 center points

Process variables:

i) Phosphoric acid dosages (20%) (0 – 2.5 % w/w)

ii) Types of bleaching earths (1% w/w)

- Acid activated bleaching earth (acidic pH) (AAA)
- Acid activated bleaching earth (neutral pH) (AAN)
- Natural bleaching earth (NBE)

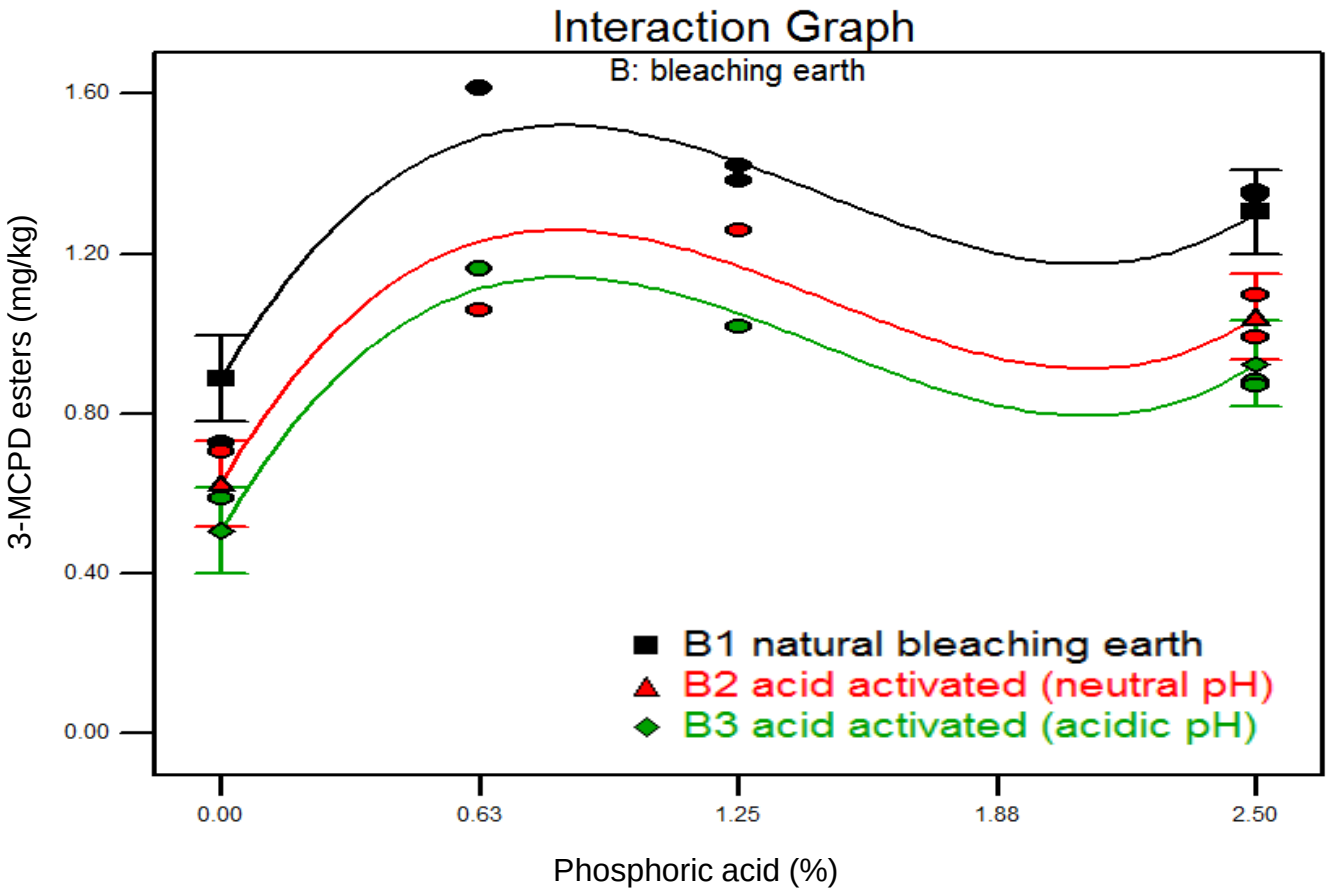
Response:

i) 3-MCPD ester

ii) Glycidyl esters

iii) Carotene

3-MCPD esters



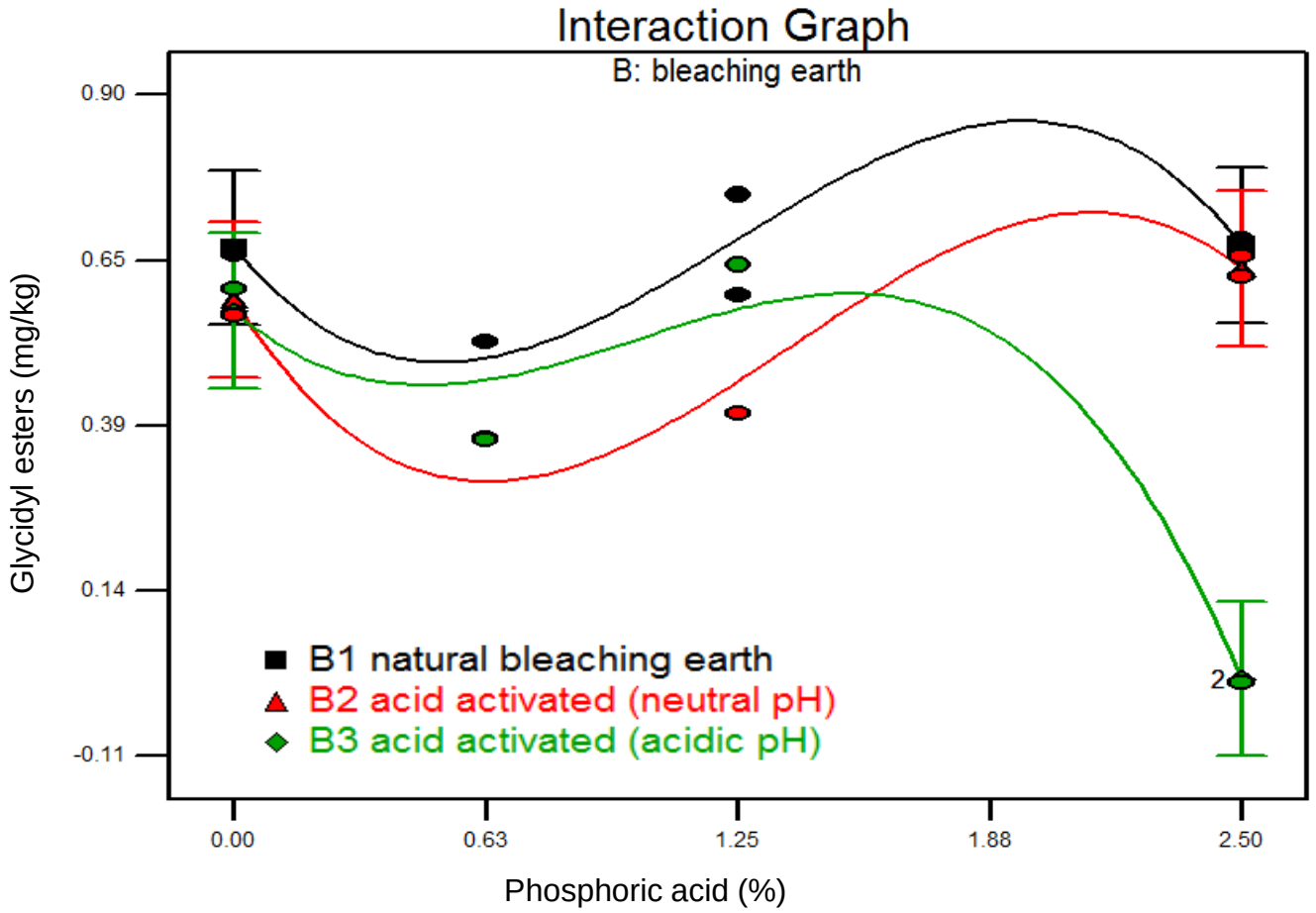
- AAA exerted a significant effect on ME reduction compared with NBE and AAN
- Precursors responsible for ME formation were removed from PO prior to deodorization
- Properties and the adsorption capacities of the bleaching earth were the predominant factors in ME removal rather than its acidity.

Table : Properties of three types of bleaching earths [a]

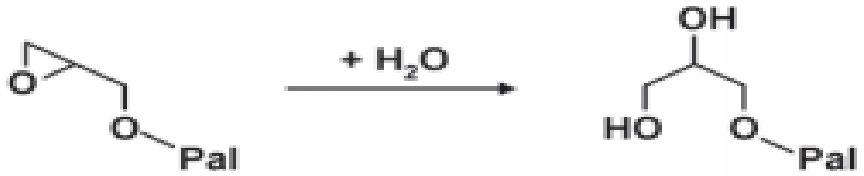
Types of bleaching earth	pH	Total Pore volume (cm^3/g)	Total Pore area (m^2/g)
Acid Activated (Acidic)	3.18 ± 0.01	0.380138	340.363
Acid Activated (Neutral)	7.27 ± 0.06	0.296388	177.953
Natural	8.61 ± 0.01	0.286729	120.564

[a] The total pore volume and area reported refers to pores with a diameter of 13.0 to 210.0 Å.

Glycidyl esters



- GE was largely removed when AAA + degumming process with high dosage phosphoric acid
- Possible mechanisms: Epoxide ring opening of GE to form glycerol monoester by a reaction with water under acidic conditions



Optimization of the physical refining process

Design of experiment: **Face-centered small central composite design**

29 experimental runs - 16 factorial, 8 axial and 5 center points

Process variables:

i) Phosphoric acid dosages (25%)
ii) Degumming temperature
iii) Bleaching earth dosage
iv) Deodorization temperature

Response:

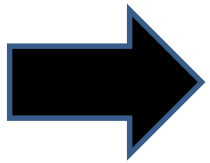
i) 3-MCPD ester
ii) Glycidyl esters
iii) FFA levels
iv) Colour

Factors	Symbol	Levels		
		-1	0	+1
Phosphoric acid dosage (%)	a	0	1.5	3
Degumming temperature (ºC)	T	50	70	90
Bleaching earth dosage (%)	b	1	2	3
Deodorization temperature (ºC)	T_d	240	250	260

Major outcomes from the modification of refining process

Optimized conditions

- 0.31% phosphoric acid dosage
- 50 °C degumming temperature
- 3% bleaching earth dosage
- 240 °C deodorization temperature



3-MCPD esters

- 1.10 mg/kg → 0.18 mg/kg
- Up to 90% reduction

Glycidyl esters

- 0.85 mg/kg → 0.17 mg/kg
- 80% reduction

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