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Mitigation of 3-MCPD and Glycidyl Esters in Palm Oil

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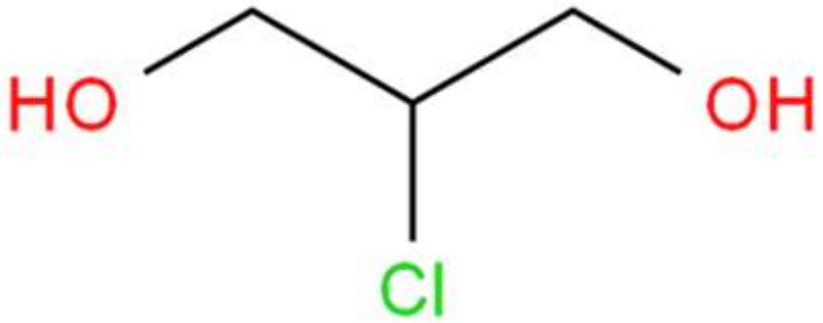
History & future

1960	• 3-MCPD raised attention as possible contraceptivum for males in the late 1960s
1970	• A decade later 3-MCPD was discovered as food contaminant
2000	• Occurrence of food-borne 2- & 3-MCPD & glycidyl esters in edible oils/ fats and fat-containing foods (2004-2011)
2013	• AOCS Official Methods (Cd 29a, b & c-13)
2017	• European Commission draft regulation on total 3-MCPD and ester-bound glycidol in 2016/2017
Future	• ???

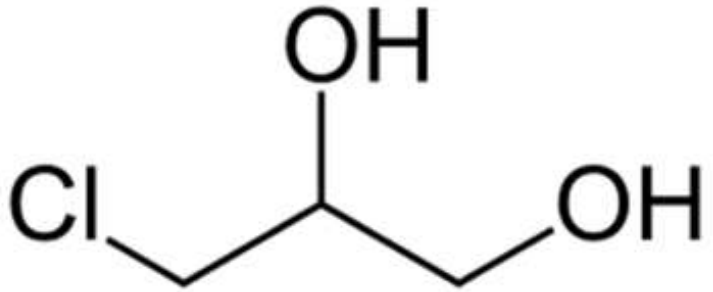
Introduction

- 3-monochloropropane-1,2-diol (**3-MCPD**)- and 2-monochloropropane-1,3-diol (**2-MCPD**) and their esters and **glycidyl** esters are food contaminant found highest in refined vegetable oils and fats.
- In refined vegetable oils, especially palm oil, these contaminant are formed during physical refinery process.

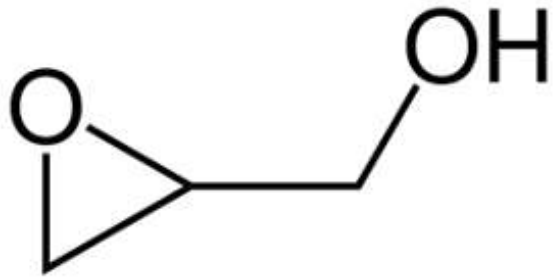
Chemical structures of “our beloved” contaminants



2-MCPD

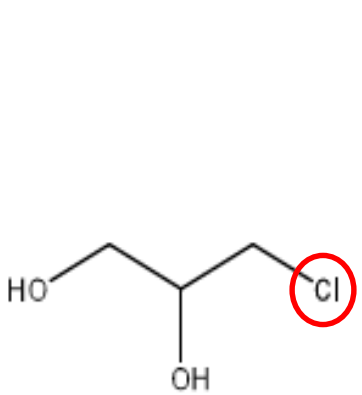


3-MCPD

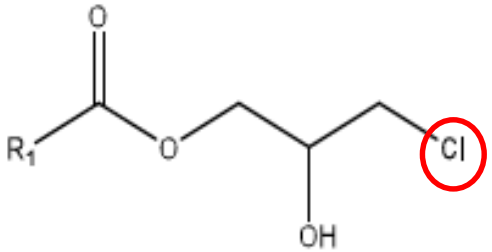


GLYCIDOL

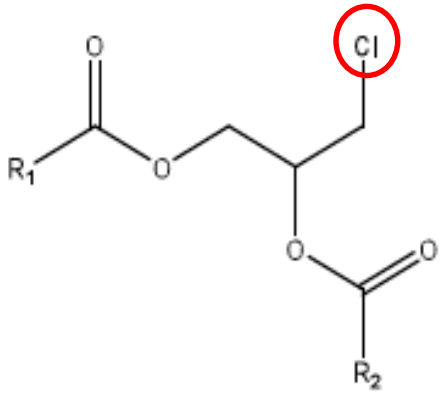
Free and bound 2-MCPD & 3-MCPD and glycidol



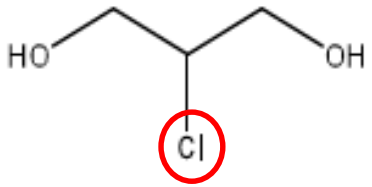
3-MCPD



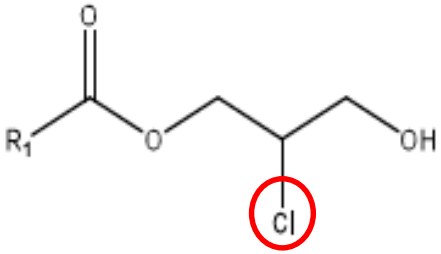
3-MCPD Monoesters



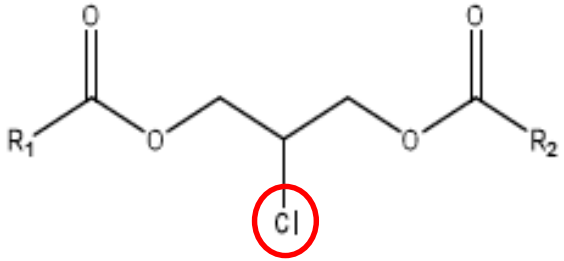
3-MCPD Diesters



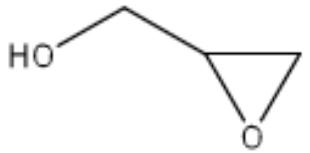
2-MCPD



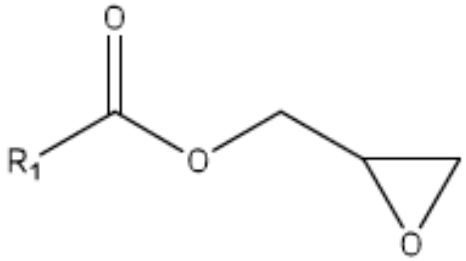
2-MCPD Monoesters



2-MCPD Diesters

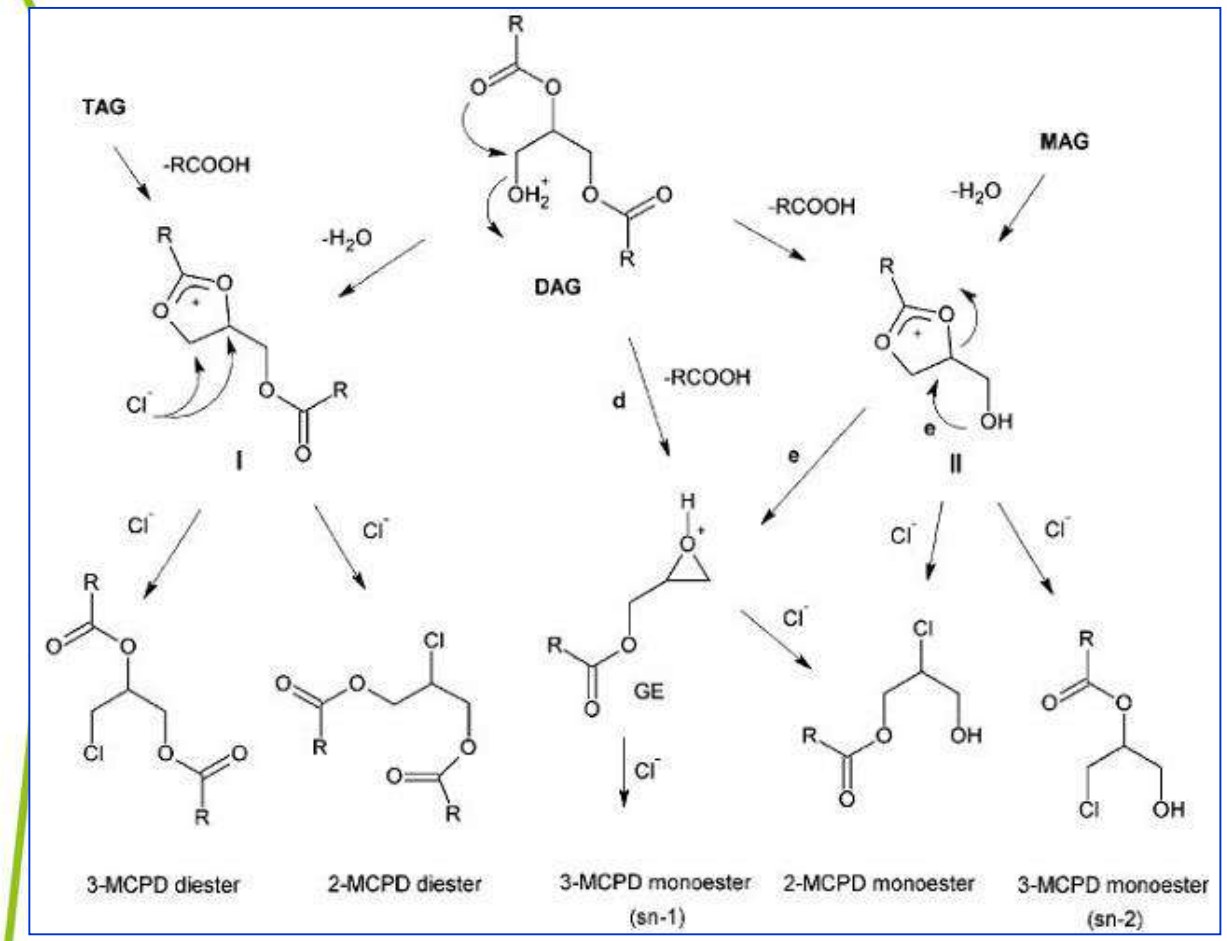


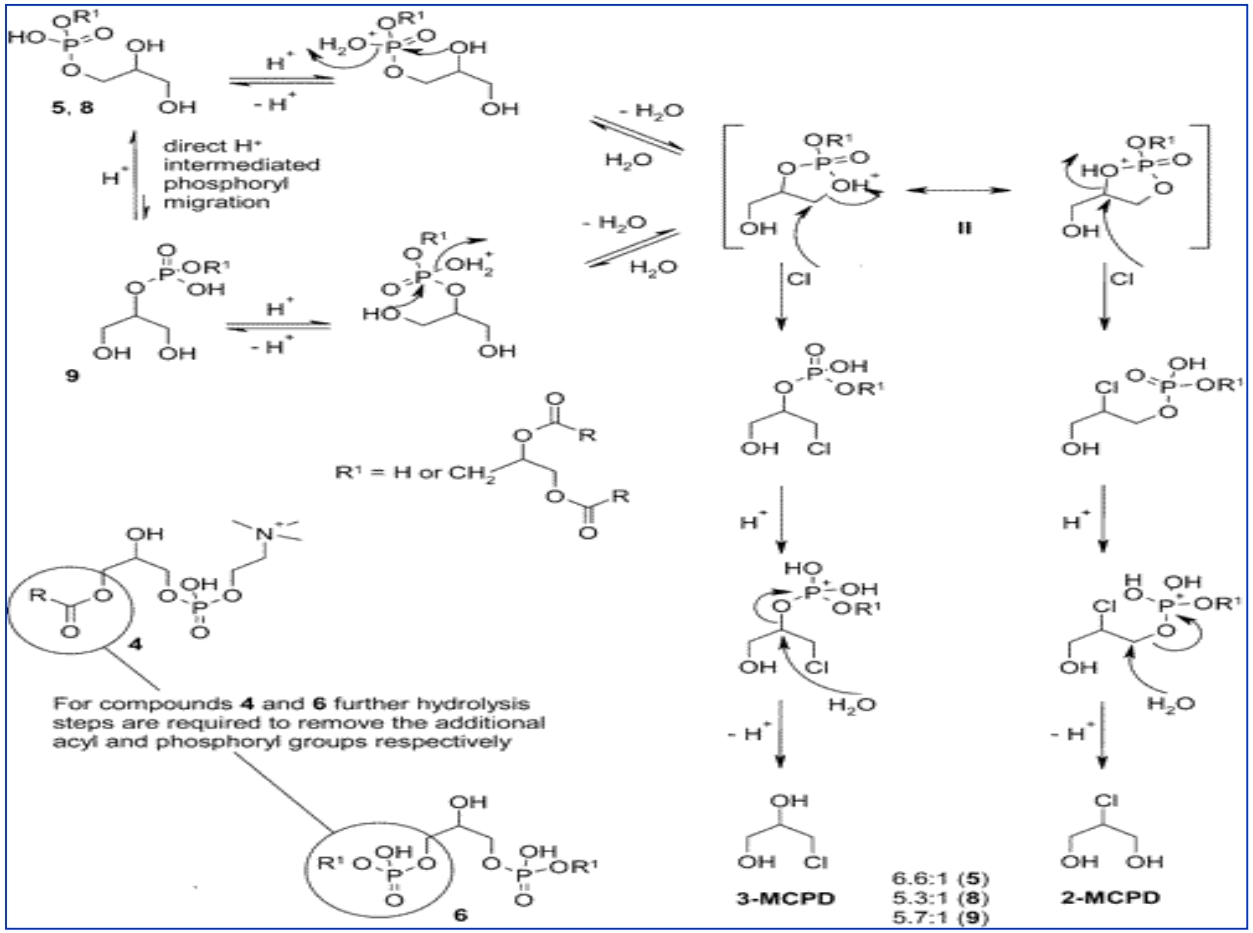
Glycidol



Glycidyl Esters (GE)

Acyloxonium ion pathway vs. glycerolphosphates pathway





Data reporting - “bound” and “esters”

- Accepted practice – Reporting of MCPD ester or glycidyl ester contents is related to the core components, not to the whole ester derivatives.

Description	Amount
Total 3-MCPD	1 mg/kg
Bound 3-MCPD	1 mg/kg
3-MCPD fatty acid esters expressed as 3-MCPD	1 mg/kg
3-MCPD esters	> 1 mg/kg

Data reporting - “bound” and “esters”

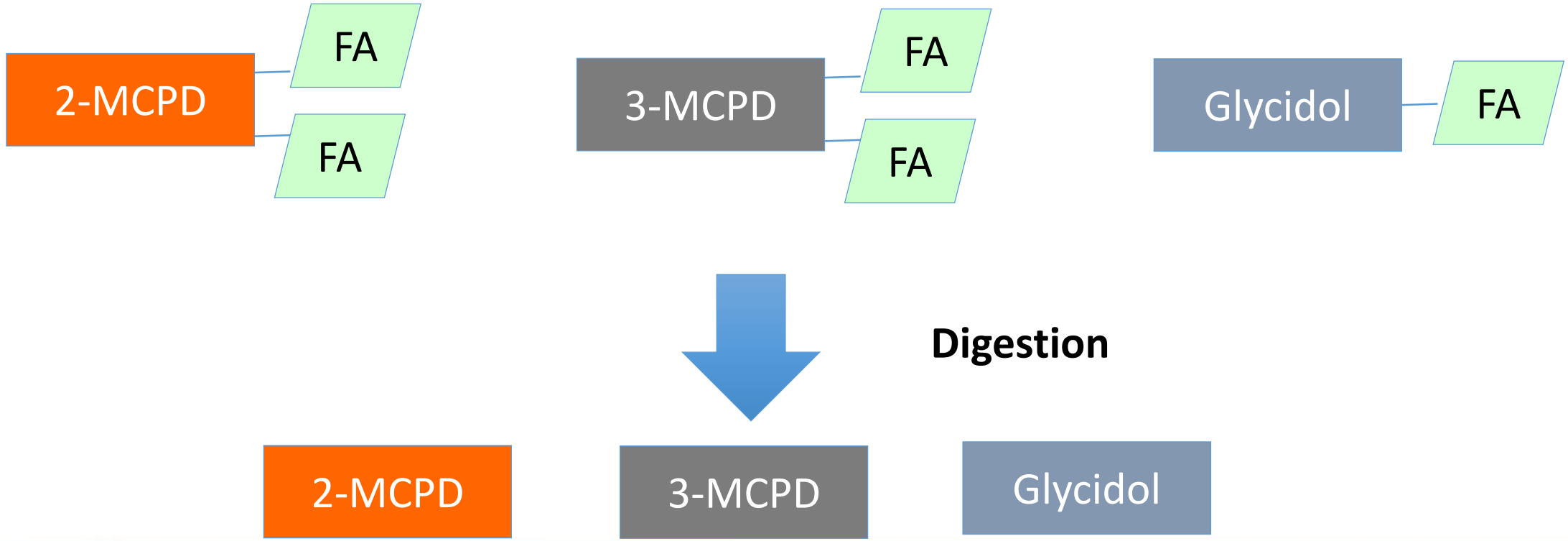
- Reporting the result of **1 mg/kg 3-MCPD** being present as the multiple fatty acid ester derivatives.
- The term **“bound”** is used to indicate that the core analyte is attached to another molecular shell as the free derivative.
- The terms **“2- or 3-MCPD esters” or “glycidyl esters”** should be used in the data reporting only when the entire molecules are quantified.

Hazard characterization of free 2-, 3-MCPD and glycidol

- Toxicity is related to **chlorine** or an **epoxy group** at the molecular backborne.
- **2-MCPD** – no official classification available.
- **3-MCPD** – non-genotoxin (2B: possibly carcinogenic to humans)
- **Glycidol**
  - genotoxic carcinogen (2A: probably carcinogenic to humans)
  - No TDI applies
  - Intake should be “as-low-as-reasonably-achievable”(ALARA)

Hazard characterization of bound 2-, 3-MCPD and glycidol

- What happens after intake???



Hazard characterization of bound 2-, 3-MCPD and glycidol

- j.efsa.2016.4426; EFSA Panel on Contaminants in the Food Chain (CONTAM)
- “Animal studies show extensive hydrolysis of esterified 3-MCPD and glycidol following oral administration……esterified and free forms were assumed to contribute equally to internal exposures.”

EFSA Report (2016)

- According to the EFSA report "Risks for human health related to the presence of 2- and 3-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 2- and 3-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:
  - **2-MCPD : 1.565 ppm**
  - **3-MCPD : 2.912 ppm**
  - **Glydicol : 3.995 ppm**

Regulation

Maximum Residue Limits (MRLs)			
Year	Legal regulation	Contaminant	MRL (mg/kg)
2001	EU 466/2001	Free 3-MCPD in soy sauce	0.02
2012	EU 232/2012	Free 3-MCPD in glycerol	0.10

Tolerable Daily Intake (TDI) 3-MCPD			
Year	Organization/source	Contaminant	TDI (µg/kg x bw x d)
1994	SCF, http://ec.europa.eu/food/fs/sc/scf/out91_en.pdf	Free 3-MCPD	2
2007	BfR, Opinion 047-2007	Bound 3-MCPD	2
5-2016	EFSA, j.efsa.2016.4426	Free & bound 3-MCPD	0.8
11-2016	JECFA, JEFCA/83/SC	Free & bound 3-MCPD	4

1st draft EC regulation

Sum of free-MCPD and 3-MCPD fatty acid esters, expressed as 3-MCPD	Maximum level (µg/kg)
Vegetable oils and fats intended for direct human consumption or use as an ingredient in food	2000 ****
Infant formula and follow-on formula (powder/ liquid) **[2019 proposal]**	125/15 **[50/6]** ****
****: *based on a TDI of 0.8 µg 3-MCPD/ kg x bw x d*	

Glycidyl fatty acid esters, expressed as glycidol	Maximum level (µg/kg)
Vegetable oils and fats intended for direct human consumption or use as an ingredient in food	1000
Infant formula and follow-on formula (powder/ liquid) **[2019 proposal]**	75/10 **[30/4]**

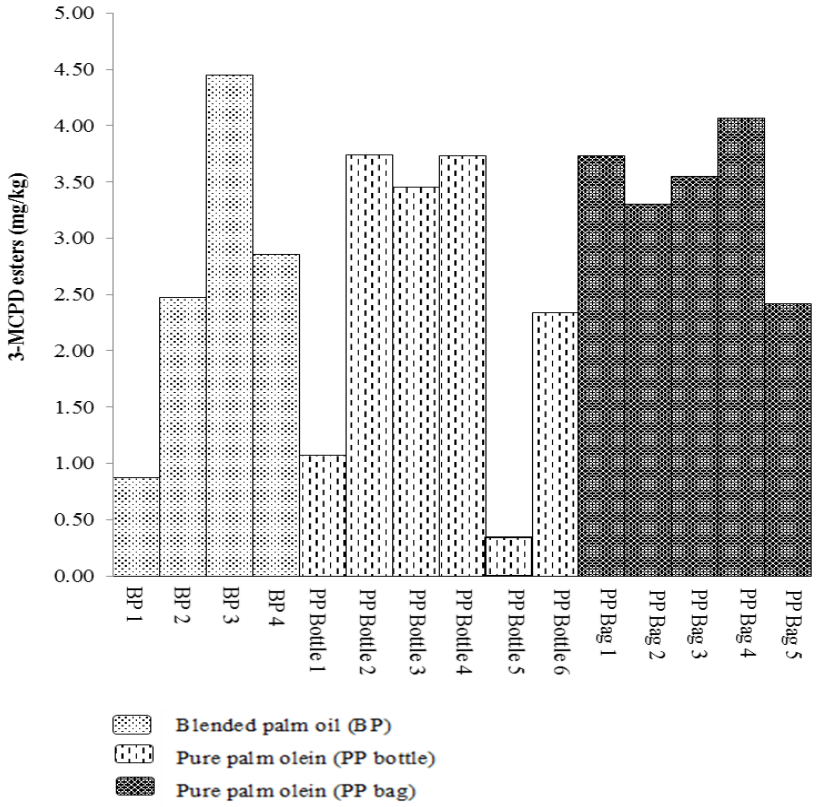
- **EC asked EFSA to review the calculation of TDI for 3-MCPD (ML might increase further).**
- **In subsequent regulation on glycidol might come into force firstly but 3-MCPD regulation later.**

Recent draft EC regulation for glycidol ester
(Ref. Ares(2017)41299615 – 22/08/2017)

4.2	Glycidyl fatty acid esters, expressed as glycidol	Maximum level (µg/kg)
4.2.1	Vegetable oils and fats placed on the market for the final consumer or for use as an ingredient in food with the exception of the foods referred to in the 4.2.2	1000
4.2.2	Vegetable oils and fats destined for the production of baby food and processed cereal-based food	500
4.2.3	Infant formula, follow-on formula and foods for special medical purposes intended for infants and young children (powder)	75 until 30.06.2019 50 as from 01.07.2019
4.2.4	Infant formula, follow-on formula and foods for special medical purposes intended for infants and young children (liquid)	10 until 30.06.2019 6 as from 01.07.2019

Level of 3-MCPD esters in palm olein

3-MCPD level in commercial RBD palm olein in the Malaysian market

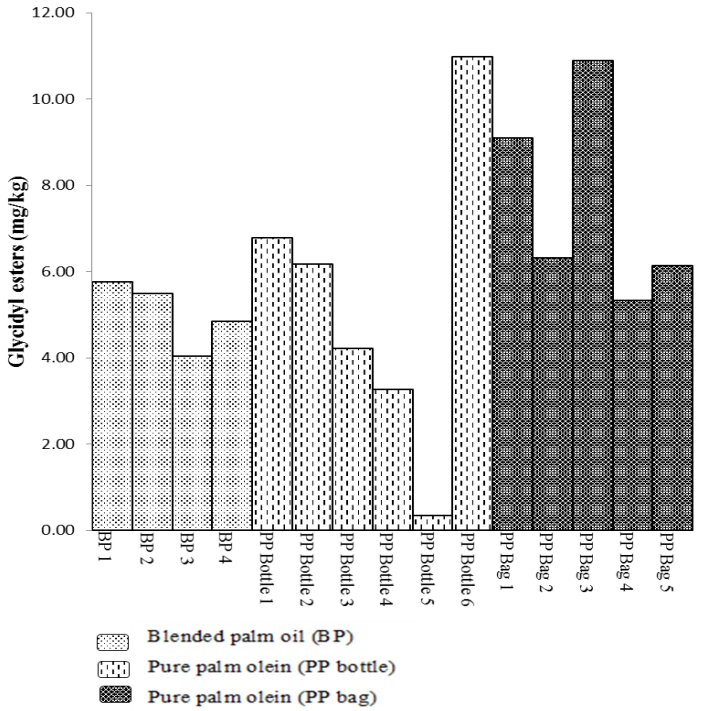


3-MCPD levels:

0.34 – 4.45 mg/kg

Level of GE in palm olein

Glycidol level in commercial RBD palm olein in the Malaysian market

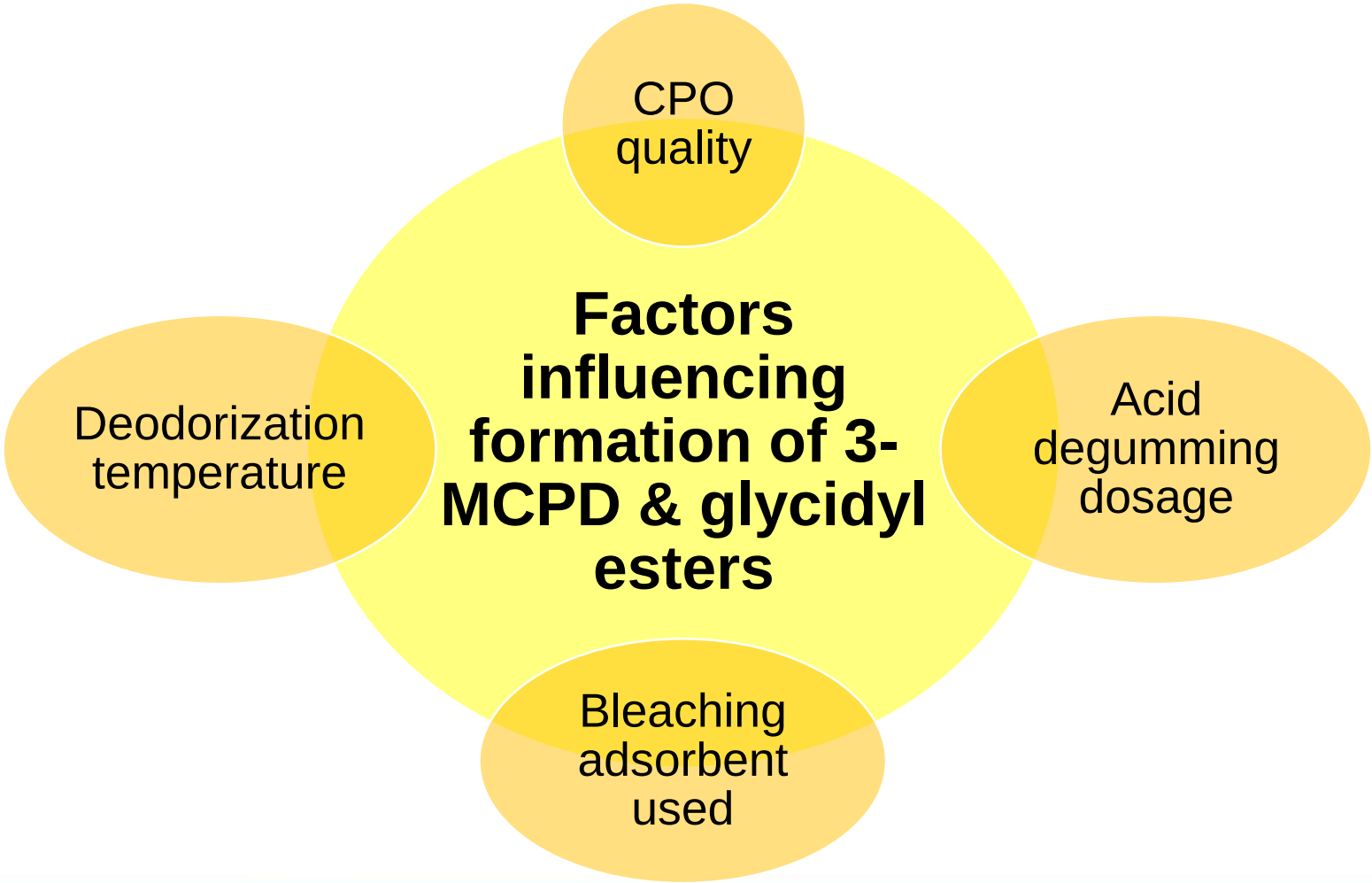


Glycidol levels:

0.34 – 10.98 mg/kg

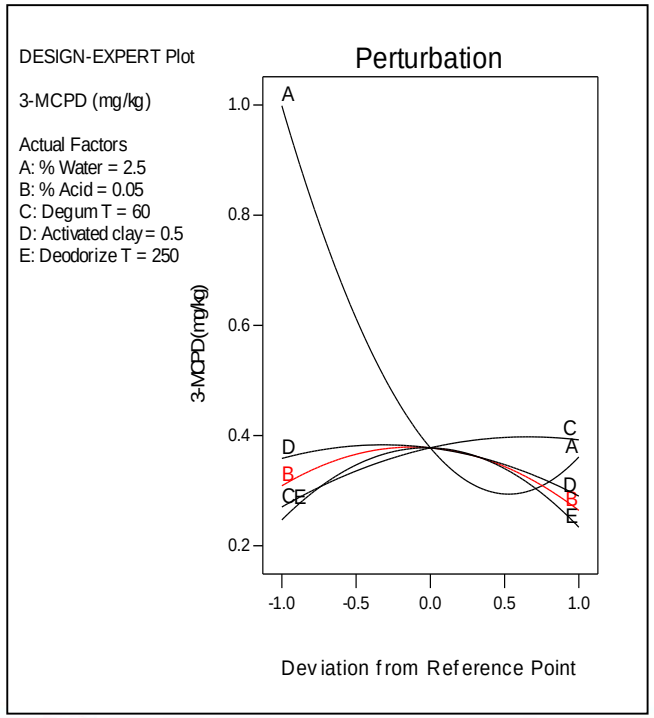
Refining process and the factors influencing formation of 3-MCPD & glycidyl esters

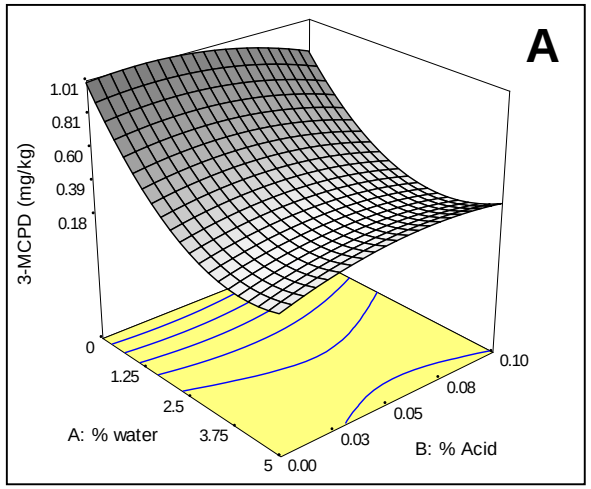
3-MCPD & glycidyl esters in palm oil

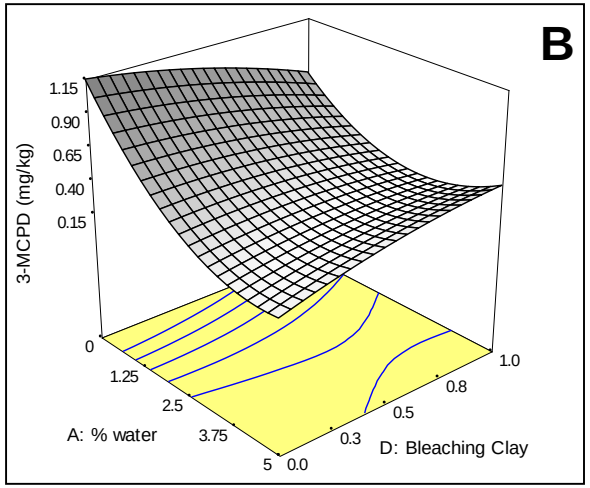


Reduction of 3-MCPD & glycidyl esters in palm oil

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

Objectives

1) To identify the precursors and factors affecting the formation of 3-MCPDE and GE in palm oil during the physical refining process.

2) To develop a mitigation solution for the physical refining process facilitating the production of RBD palm oil with reduced 3-MCPDE and GE levels and acceptable quality.

Influence of different crude palm oil (CPO) quality

Four different CPO qualities (Sime Darby Golden Jomalina Berhad)

- ✓ Premium Quality
- ✓ Superior Quality
- ✓ Standard Quality I (FFA: 3% max)
- ✓ Standard Quality II (FFA: 5% max)

Determination of quality for different CPO

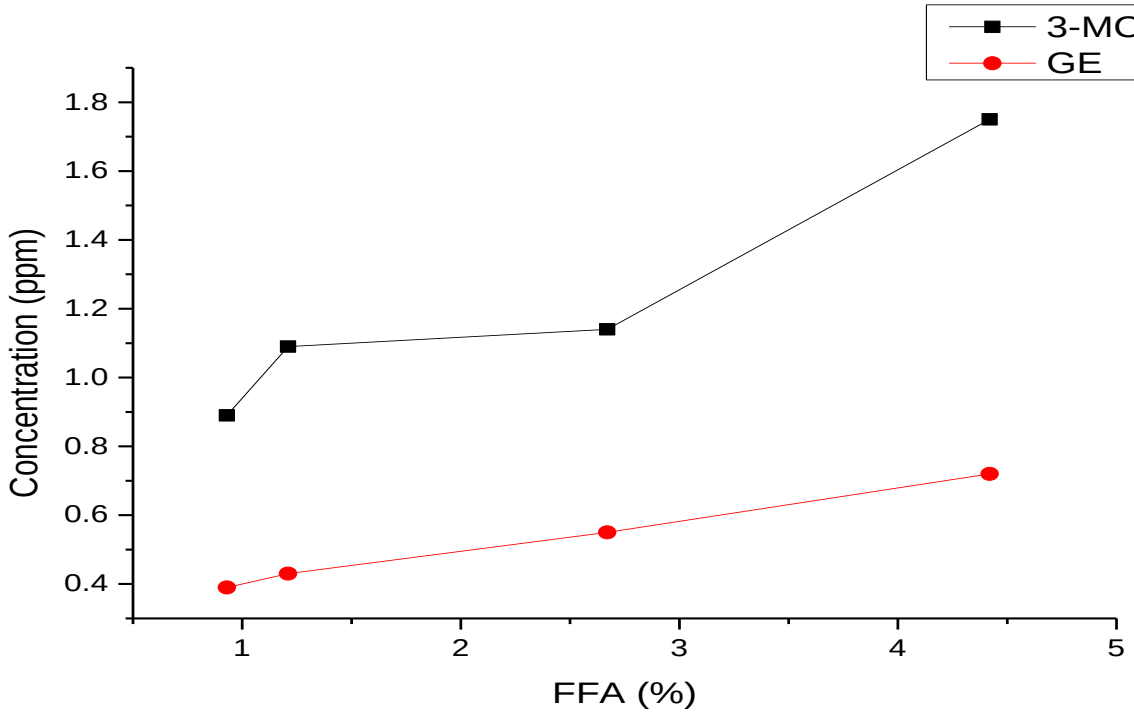
- ✓ Free fatty Acids (MPOB Test Method 2005)
- ✓ DOBI index (MPOB Test Method 2005)
- ✓ Carotene content (MPOB Test Method 2005)
- ✓ DAG and MAG content (AOCS Official method Ce 5b-89)

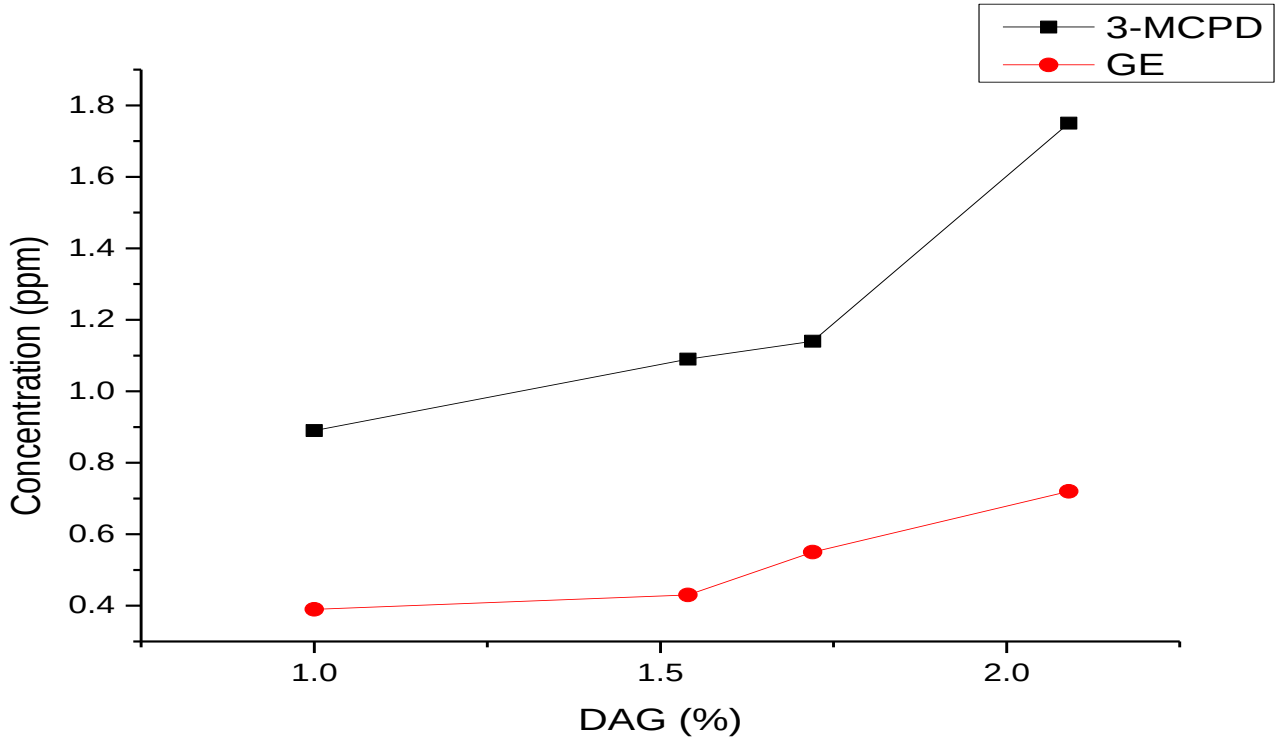
Results

Quality characteristic	Premium Quality (PQ)	Superior Quality (SQ)	Standard Quality I	Standard Quality II
3-MCPD esters of CPO [mg/kg]	< LOD	< LOD	< LOD	< LOQ
Glycidyl esters of CPO [mg/kg]	< LOD	< LOD	< LOD	< LOD
3-MCPD esters of RBD palm oil [mg/kg]	0.89 ± 0.02^{C}	1.09 ± 0.03^{B}	1.14 ± 0.02^{B}	1.75 ± 0.07^{A}
Glycidyl esters of RBD palm oil [mg/kg]	0.39 ± 0.03^{C}	0.43 ± 0.02^{C}	0.55 ± 0.03^{B}	0.72 ± 0.02^{A}
Free Fatty Acid (FFA) [%]	0.96 ± 0.03^{D}	1.21 ± 0.04^{C}	2.67 ± 0.01^{B}	4.42 ± 0.03^{A}
DOBI	3.67 ± 0.05^{A}	3.49 ± 0.08^{B}	3.24 ± 0.05^{C}	2.88 ± 0.04^{D}
β-carotene content [ppm]	586 ± 0.12^{C}	545 ± 0.24^{D}	649 ± 0.30^{A}	611 ± 0.22^{B}
Diacylglyceride (DAG)[%]	1.00 ± 0.16^{B}	1.54 ± 0.18^{AB}	1.72 ± 0.11^{A}	2.09 ± 0.15^{A}
Monoglyceride (MAG) [%]	0.0^{C}	0.0^{C}	0.06 ± 0.18^{B}	0.10 ± 0.14^{A}

[a] Standard deviations between batches are given in parentheses; results represent the means of two replicate trials. For each column, means with the same letter do not differ significantly at $p<0.05$.

Results


3-MCPD
GE
Concentration (ppm)
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
1
2
3
4
5
FFA (%)


3-MCPD
GE
Concentration (ppm)
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
1.0
1.5
2.0
DAG (%)

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:

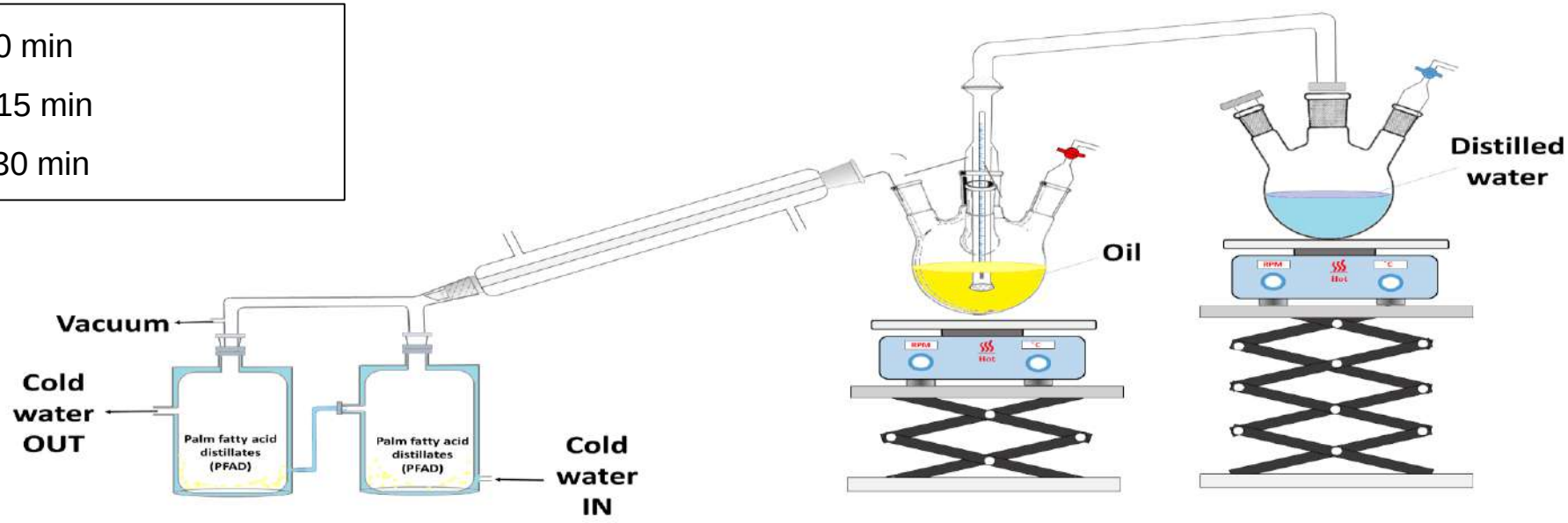
i) 3-MCPD ester

ii) Glycidyl esters

iii) Carotene

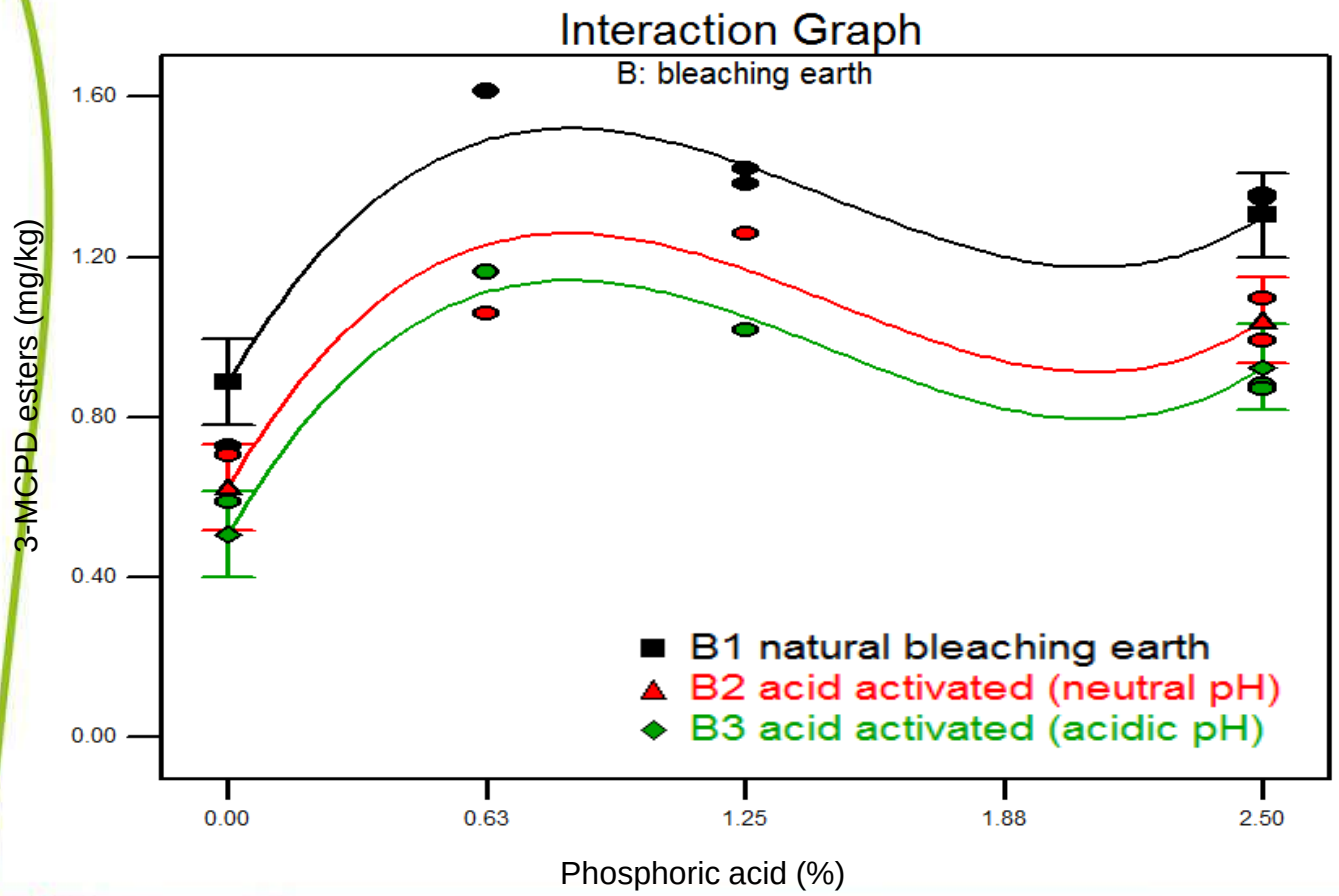
Laboratory physical refining unit with micro-scale deodorizer

Degumming	- 90°C for 10 min
Bleaching	- 105°C for 15 min
Deodorization	- 260°C for 30 min



Results

3-MCPD esters



- AAA exerts a significant effect on ME reduction compared with NBE and AAN
- Particular precursors that are responsible for ME formation are being adsorbed from BPO prior to deodorization
- Properties and the adsorption capacities of the bleaching earth are the predominant factors in ME removal rather than its acidity.

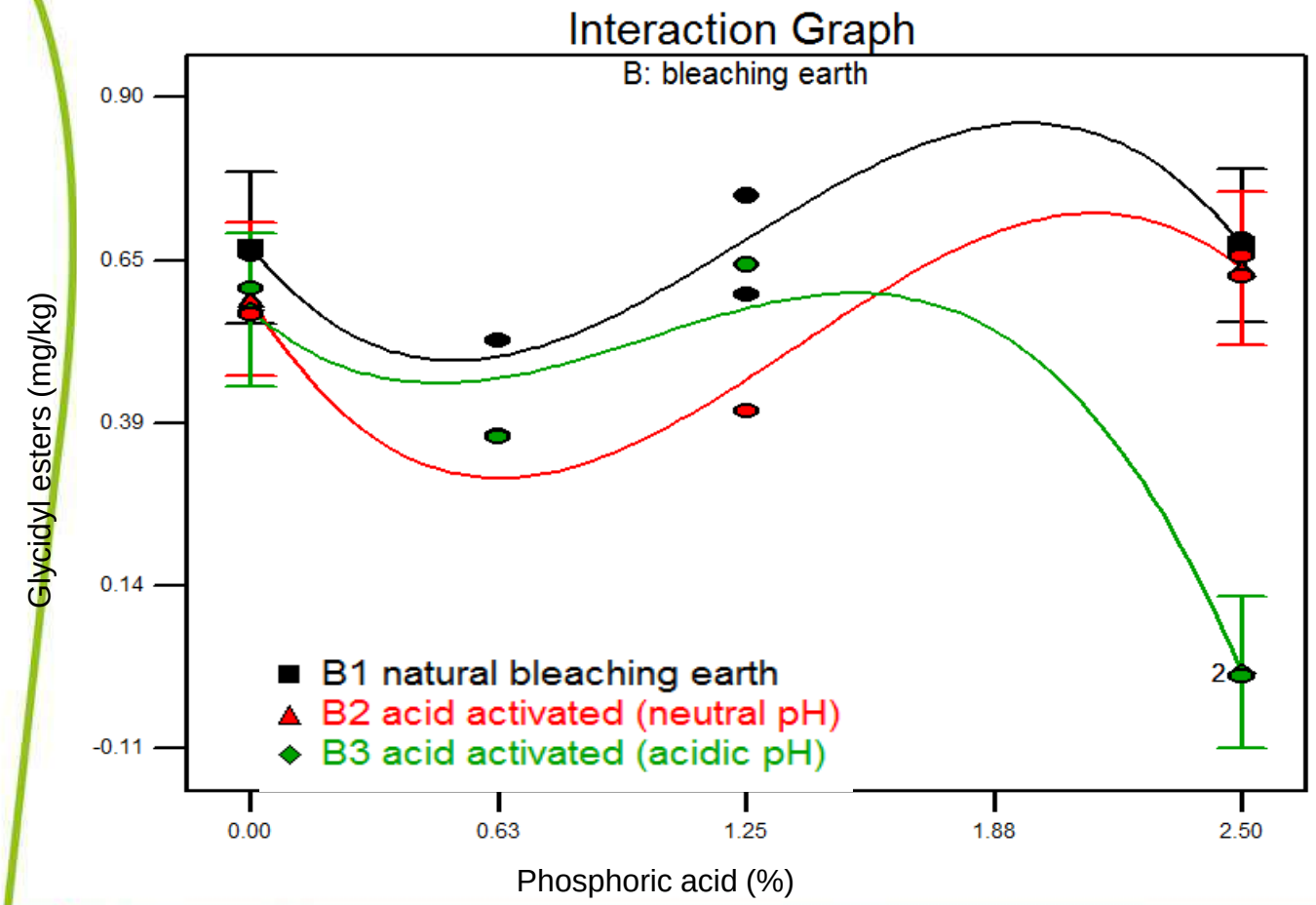
Table : Properties of three types of bleaching earths [a]

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

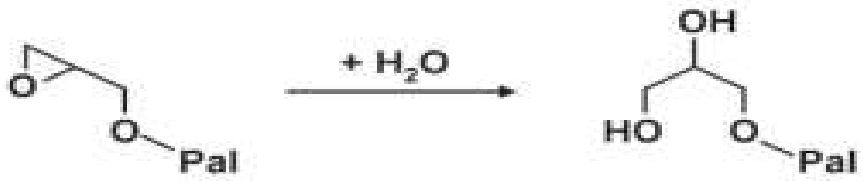
[a] The total pore volume and area reported refers to pores with a diameter of 13.0 to 210.0 Å.

Results

Glycidyl esters

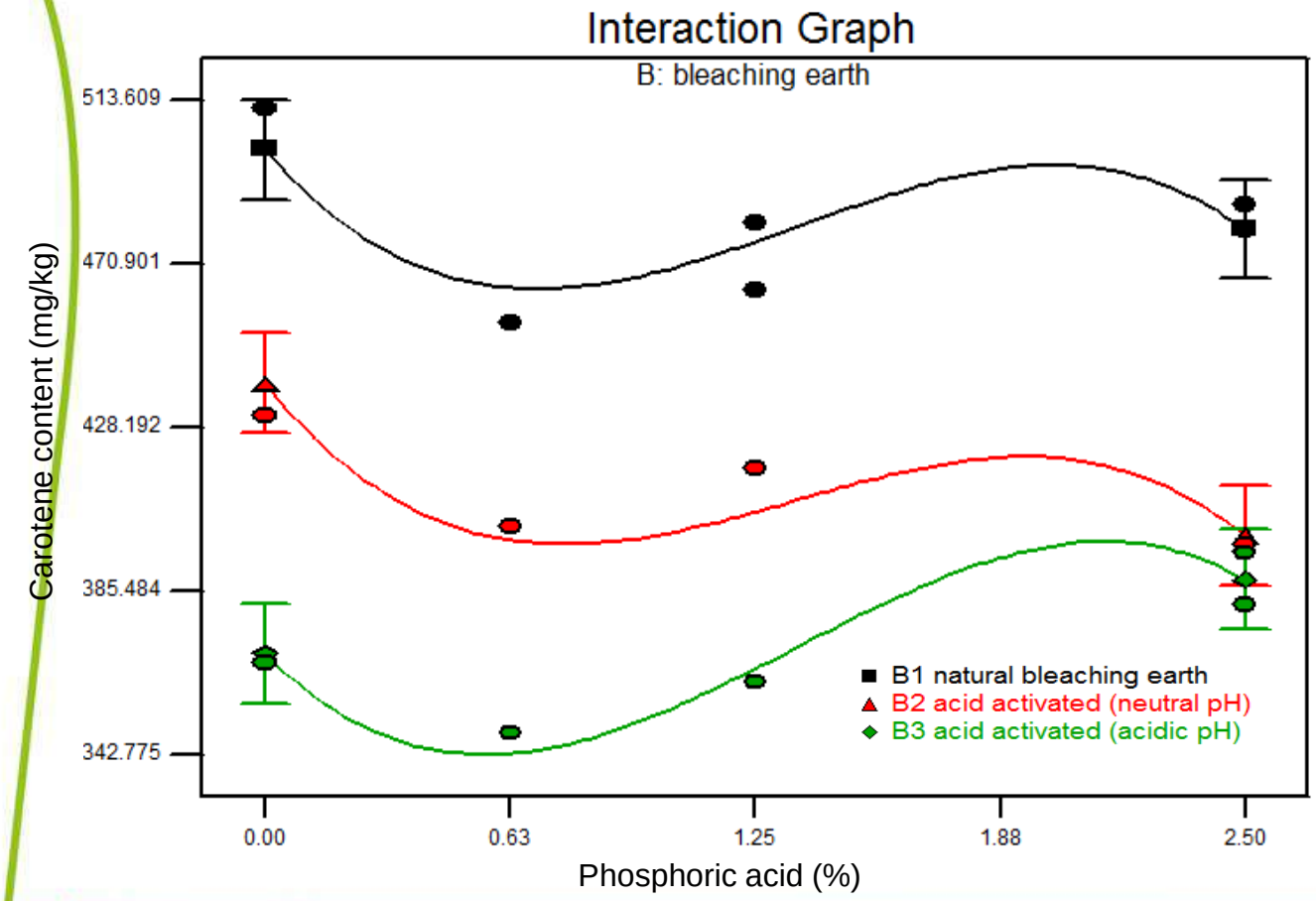


- GE was largely removed when AAA + degumming process with high dosage phosphoric acid
- Possible mechanisms: Epoxide ring opening of GE to form glycerol monoester by a reaction with water under acidic conditions



Results

Carotene content



- Carotenoid – oil soluble agents that will result in chlorination through reaction with acyloxonium ions (ILSI, 2009)
- AAA - removed most of the carotenes.
- NBE - retain most carotenes.

Optimization of the physical refining process that produces RBD palm oil with reduced levels of 3-MCPDE and GE

"The modification of palm oil refining may have an impact on the resulting overall quality of the final product…."

Response Surface Methodology (RSM)

1) Study the processing parameters that significantly affect each response and performs optimisation on the processing parameters that are found significant.

2) Identify suitable operating conditions to achieve lowest ME and GE with desirable product quality in the RBD palm oil.

Design

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

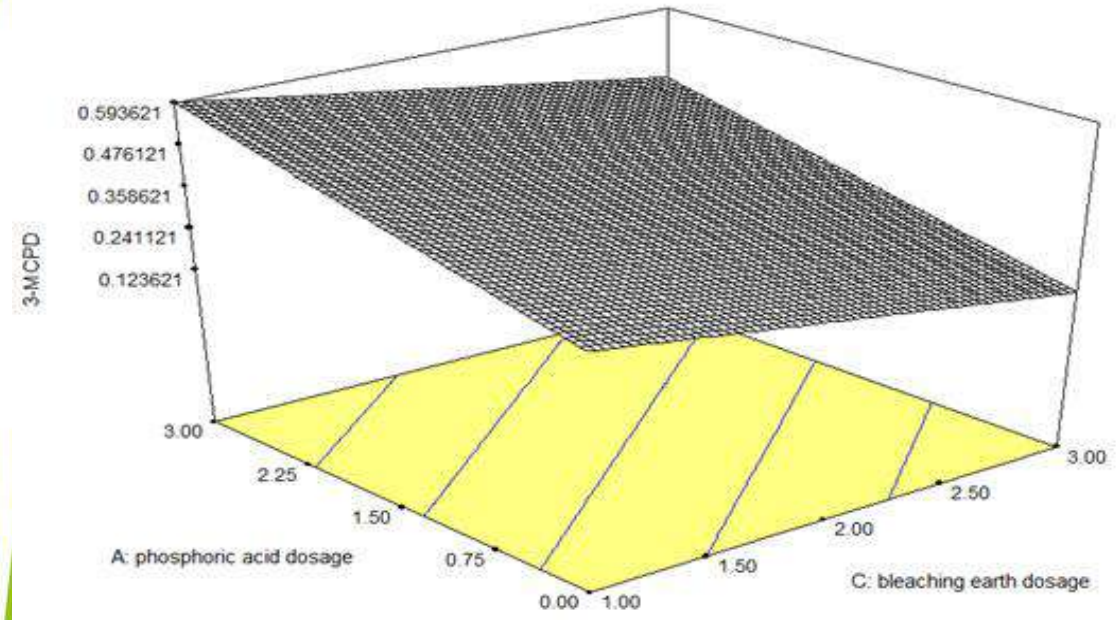
Factors	Symbol	Levels		
		-1	0	+1
Phosphoric acid dosage (%)	a	0	1.5	3
Degumming temperature (ºC)	T	50	70	90
Bleaching earth dosage (%)	b	1	2	3
Deodorization temperature (ºC)	T_d	240	250	260

Results

Table ANOVA, p-value, lack of fit test, F-test and the determination coefficient, R^2, of the three response variables of the final reduced model.

	3-MCPD esters (mg/kg, Y_1)	Glycidyl esters (mg/kg, Y_2)	Colour (ppm, Y_3)	FFA (%, Y_4)
Model	Linear	Quadratic	2FI	Quadratic
p-value	<0.0001	0.0008	< 0.0001	< 0.0001
F-value	15.83	6.40	122.96	19.12
R^2	0.5491	0.5935	0.9710	0.7612
Adjusted R^2	0.5145	0.5011	0.9631	0.7214
Lack of fit (*p*-value)	0.1632	0.0777	0.0749	0.1103
Lack of fit (*F*-value)	2.81	6.27	4.59	3.62

Results



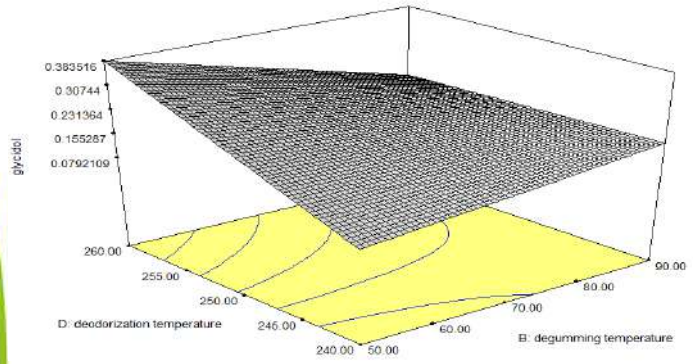
(a) Responses surface plots of 3-MCPD levels showing significant interactions between phosphoric acid dosage and bleaching earth dosage, with other factors held at center points.

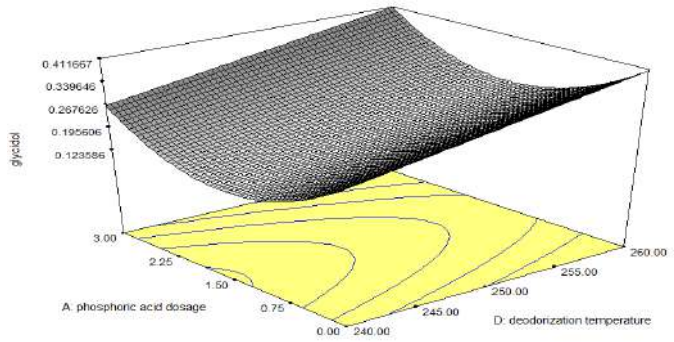
3-MCPD esters

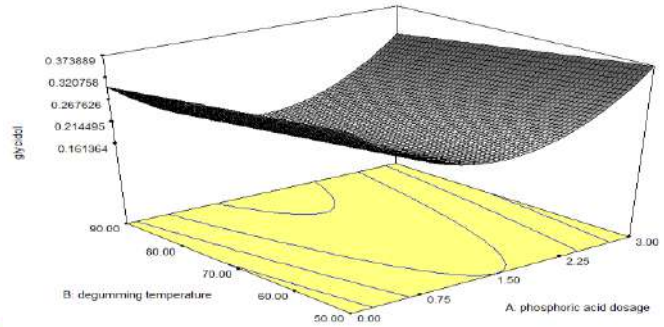
- Reduction of 3-MCPDE from 1.10 mg/kg to 0.10 – 0.79 mg/kg (reduction of 90%).
- ↓phosphoric acid dosage, ↓3-MCPDE.
- ↑bleaching earth dosage, ↓3-MCPDE.
- Degumming and deodorization temperature – no significant effect.

→ Deodorization temperature at 180-265ºC – insignificant impact on 3-MCPDE (Pudel et al., 2015)

Results



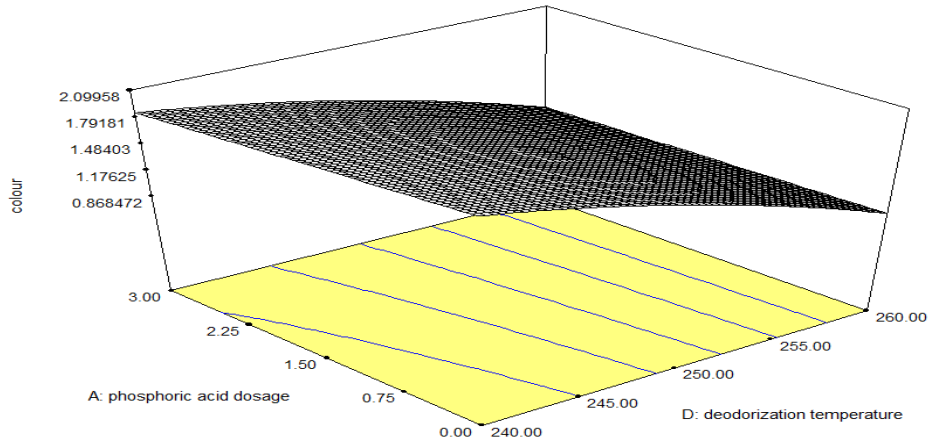


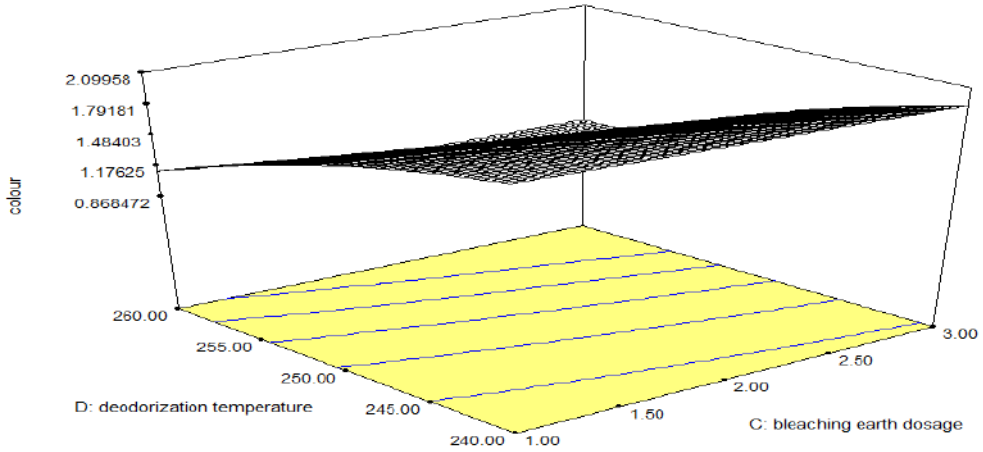


Glycidyl esters

- Reduction of GE from 0.85 mg/kg to LOQ – 0.64 mg/kg (reduction > 65%).
- ⇧deodorization temperature, ⇧GE.
- Deodorization temperature – crucial factor for GE formation.

Results

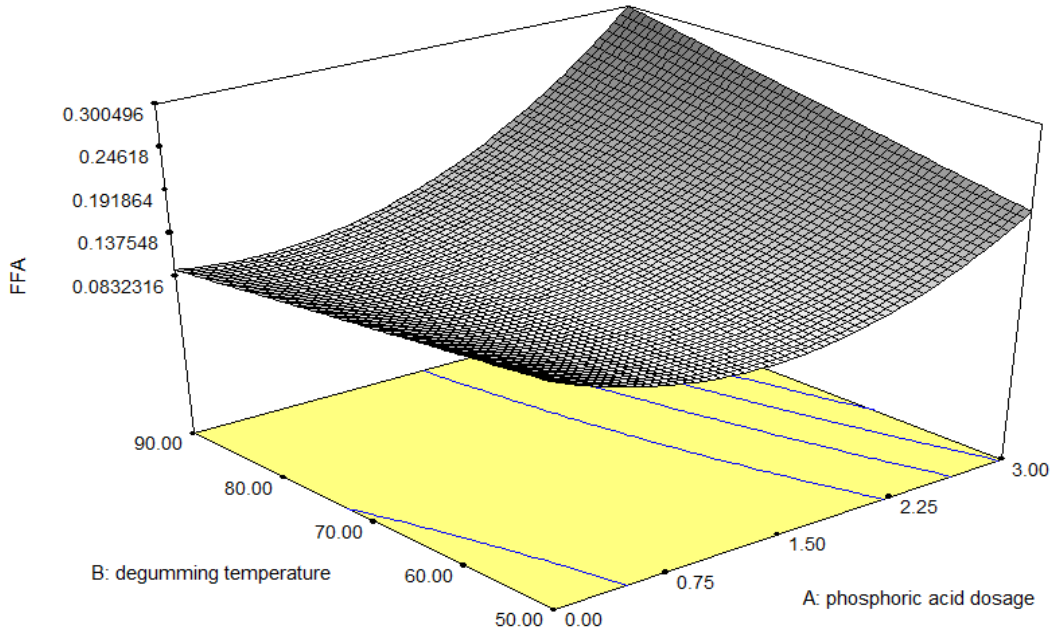




Colour

- RBD palm oil colours for all studies ≤ 2.2R.
- Deodorization temperature has greatest influence in colour reduction - carotenoid are thermally unstable.
- ↑phosphoric acid, ↓colour.
- ↑bleaching earth, ↓colour.

Results



Free fatty acids

- FFA content of RBD palm oil for all studies : 0.06 – 0.38 %.
- ⇧ phosphoric acid, ⇧FFA.

Results

Numerical optimization and validation of experimental model

Optimum conditions:

0.31%	phosphoric acid dosage
50ºC	degumming temperature
3%	bleaching earth dosage
240ºC	deodorization temperature

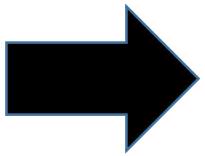
Observed and predicted values of the responses at optimum refining conditions (N=2).

	3-MCPD esters (mg/kg)	Glycidyl esters (mg/kg)	Colour (R)	FFA (%)
Experimental value	0.17 ± 0.01	0.17 ± 0.02	0.90 ± 0.14	0.10 ± 0.01
Predicted value	0.18	0.17	0.87	0.09
p-value	0.071	0.282	0.814	0.708

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

Summary

- From the survey taken by us (RBD palm olein), the levels of 3-MCPD and GE are generally more than 2 ppm.
- Levels of these contaminants exceeded the EFSA's mean values.
- Food regulatory agencies have been working hard to establish the limits for 3-MCPDE & GE in various oil/fat containing foods.

Summary

- Factors influencing formation of 3-MCPDE & GE are:
  - CPO quality
  - Acid degumming dosage
  - Bleaching adsorbent used
  - Deodorization temperature

- In optimized conditions, the content of 3-MCPDE and GE can be reduced at 90 and 80 %, respectively.

Summary

- We foresee with the suggested limits by the relevant authorities, palm oil industry have to modify the refining process of the palm oil-based products.

- Thus, there is also a need to improve current AOCS Official Method to further lower the detection limit of analysis in order to cater to the needs to quantify the presence of these contaminants at lower limit as compared to the suggested limit (GCMS to GCMS/MS?).

THANK YOU