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From the Fundamentals to New Technologies
Long Beach, April 28,2012

Review on 3-MCPD and Glycidyl Esters in Vegetable Oils and Fats

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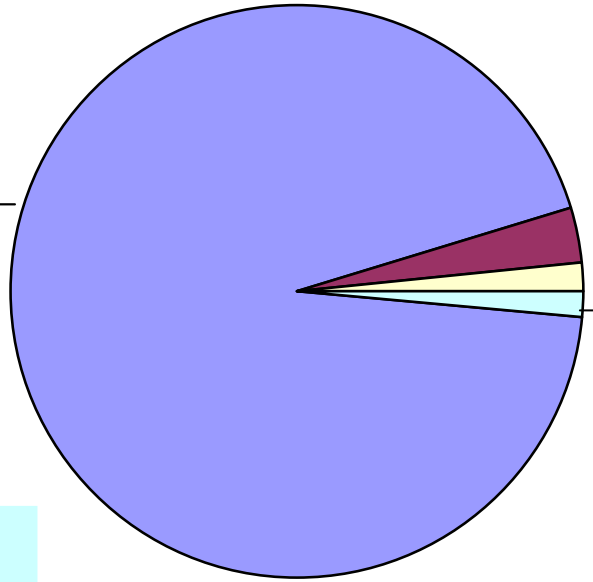
VEGETABLE OILS : GENERAL COMPOSITION

Acylglycerols (92-95%)
-Mainly Triacylglycerols
-Some Di- and Monoacylglycerols



FFA (0.3-5%)

Phospholipids (<3%)
-Hydratable PL
-Non-hydratable PL

Minor components (0.3-2%)
- Tocopherols, Sterols, Pigments,…
- Contaminants, Impurities,….

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VEGETABLE OILS : MINOR COMPONENTS

Valuable Minor Components

Tocopherols, Sterols,....

- Desired in the refined oil
- Good nutritional properties
- To be retained during refining

Side Reaction Products

Trans FA, polymers, (3-MCPD esters),...

- Formed during refining
- Bad nutritional properties
- Unwanted

MINOR COMPONENTS

Contaminants

Pesticides, PAH, Dioxins,...

- Present in crude oils
- Carcinogenic/Toxic
- To be removed during refining

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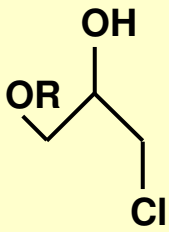
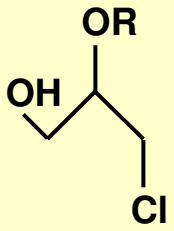
NEW CHALLENGE : 3-MCPD / GLYCIDOL ESTERS

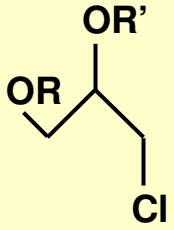
MCPD ESTERS



3-MCPD mono-*(sn1)* ester

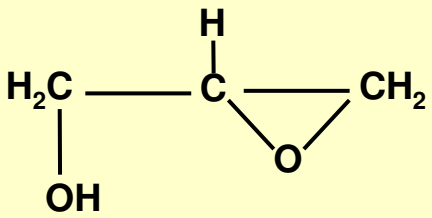


3-MCPD mono-*(sn2)* ester

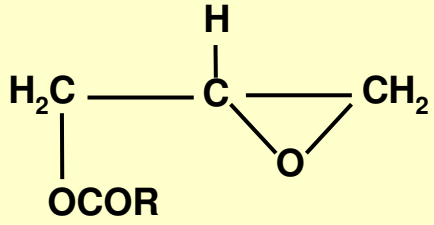


3-MCPD di-ester

GLYCIDOL ESTERS



Free glycidol



Glycidol-ester

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3-MCPD / GLYCIDYL ESTERS : Brief History

2007	Study of German BfR showing presence of significant levels of 3-MCPD esters in refined food oils
2008	EFSA agrees with statement of BfR that 3-MCPD esters are fully hydrolyzed to free MCPD during digestion
2009	ILSI workshop on 3-MPCD esters in food oils and fats AOCS Expert Panel initiative on method development New toxicological studies are initiated
2010-2011	Mechanisms of formation become more clear Mitigation strategies are developed Increasing demand for refined palm oil with low 3-MCPD/GE

TOXICITY OF 3-MCPD ESTERS

* 3-MCPD is a non-genotoxic **carcinogenic** compound

* Can cause **tumours** in various organs; kidney is main target organ

* Regulatory limit for free 3-MCPD in soy sauce and HVP : max. 20 ppb

* Toxicological risk evaluation of 3-MCPD **esters** based on assumption that all 3-MCPD esters are hydrolyzed to free 3-MCPD during digestion

* Actions of SCF and Joint FAO/WHO Expert Committee :

Lowest Observed Adversed Effect Level : 1.1 mg/kg body weight.day

Maximum Tolerable Intake : 2 mg/kg body weight.day

TOXICITY OF 3-MCPD ESTERS : RECENT STUDIES

* Barocelli et al. (2011) : 90 days toxicology study with rats

* Determination of toxicity of free 3-MCPD and 3-MCPD dipalmitate

Benchmark Dose Response Level ($BDML_{10}$)	
Free 3-MCPD :	2.5 mg/kg body weight.day
3-MCPD dipalmitate :	3.27 mg/kg body weight.day

* Earlier accepted TDI may be redefined

TOXICITY OF GLYCIDYL ESTERS

* Glycidol is considered a genotoxic **carcinogenic** compound

* Can damage DNA and can cause mutations and cancer

* Risk is evaluated by Margine of Exposure (MOE) value

  MOE = $BDML_{10}/EDI$

* **MOE > 10.000 for safe situation**

  MOE for adults : 3.050 – 12.000 low level of concern

  MOE for infants : < 1.000 may raise concern

  Source : Bakhiya et al. (2011)

TOXICITY OF 3-MCPD and GLYCIDYL ESTERS

* Current estimated levels of intake of 3-MCPD and Glycidyl esters (for adults) pose limited or now risk

* Some concern regarding presence of glycidyl esters in infant formulas

* Current advice of Toxicologists : LOWERING RESIDUAL LEVELS IN FOOD
  - Current TDI for 3-MCPD should never be exceeded
  - MOE for Glycidyl is > 10.000 in all cases

Source : Rietjens, Y. (2011)

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What is necessary to develop an efficient mitigation strategy ?

TARGET

MITIGATION STRATEGY

Current Refined Oil Specs :
< 2 ppm (standard)
< 1 ppm (infant food)

Accurate, user-friendly methods

- Should produce reliable results;
- Direct vs indirect methods;

Identificiation of critical edible oils

- Only a problem for palm oil ?

Precursors/mechanism of formation

- Identification of critical refining stages;
- How can precursors be reduced ?

3-MCPD and GLYCIDYL ESTERS IN FOOD OILS

MCPD ester and related compounds in various vegetable oils (source : FEDIOL, 2009)

OIL	N° Samples	Average content	Max. content
Rapeseed Oil	31	0.3 mg/kg	1.5 mg/kg
Sunflower Oil	49	1.0 mg/kg	5.7 mg/kg
Corn Oil	15	2.8 mg/kg	7.0 mg/kg
Palm Oil	**37**	**4.5 mg/kg**	**13 mg/kg**

* Results obtained with old DGF method C-III 18 (option A)
* Indirect method (transesterification of MCPD- and Glycidyl esters)
* Simultaneous determination of MCPD and glycidyl esters
* Highly criticized method giving no reliable results

3-MCPD and GLYCIDYL ESTERS IN FOOD OILS

MCPD ester and related compounds in various vegetable oils (Matthaus et al.,2011)

Oil	N° Samples	Average content (ppm)	Max. content (ppm)
Rapeseed Oil	10	1	1
Soybean Oil	11	0.5	0.6
Sunflower Oil	5	2	4
Corn Oil	4	7	9
Coconut Oil	3	7	7.5
Palm Oil	**70**	**6**	**14**

Results obtained with optimized DGF method C-VI (18)

* Very low levels in Refined Soybean Oil and Rapeseed/Canola Oil
* Highest levels found in Refined Palm Oil;
* Corn oil and coconut oil need careful monitoring (especially for GE);

3-MCPD and GLYCIDYL ESTERS IN FOOD OILS

Study of Haines et al. (2011 – JAOCS)

* Analysis of a large number of samples to validate their LC-TOFMS method
* MCPD mono-esters have not been found in refined food oils
* MCPD di-esters have only been found in refined palm oil
* Glycidyl esters were much broader detected in various food oils
* Suggestion that glycidyl ester formation is related to diglyceride content

→ - Palm Oil is the most critical oil
- All studies confirm need for accurate and user-friendly methods

ANALYSIS OF 3-MCPD AND GLYCIDYL ESTERS

INDIRECT METHODS

- Hydrolysis of all esters;
- No differentiation between individual (3-MCPD and glycidyl) esters;
- One figure is obtained;
- Less accurate, but more user-friendly
- Officially accepted (DGF)

DIRECT METHODS

- Individual quantification of each esters;
- Requires advances methods/equipment
- Required multiple standards;
- Not (always) user-friendly and accurate;

INDIRECT METHODS : DGF method C-VI (18)

- Replaces initial DGF method C-III (18) (Weisshaar et al. – 2008)
- Alkaline transesterification followed by GC-MS analysis
- Option A : Determination of 3-MCPD esters and glycidyl esters as free 3-MCPD
- Option B : Determination of 3-MCPD esters *alone* as free 3-MCPD
- Highly criticized (not accurate, not reproducible,….)
- Still most applied method for analysis of refined food oils

→ Alternative indirect method for 3-MCPD esters developed by Unilever (acidic transesterification)

DIRECT METHODS

Glycidyl ester analysis

- Method developed by KAO Corporatin (Masukawa, Y. et al, 2011)
- Combination of SPE and LC-MS
- Currently being tested in a collaborative study (coordinated by AOCS)

3- MCPD ester analysis

- Method developed by ADM (Haines et al, 2011)
- Based on LC-TOMS technique
- Very difficult to adopt requiring expensive and sensitive equipment
- Not suitable for routine QC analysis

3-MCPD ESTERS : PRECURSORS

CHLORINE DONORS

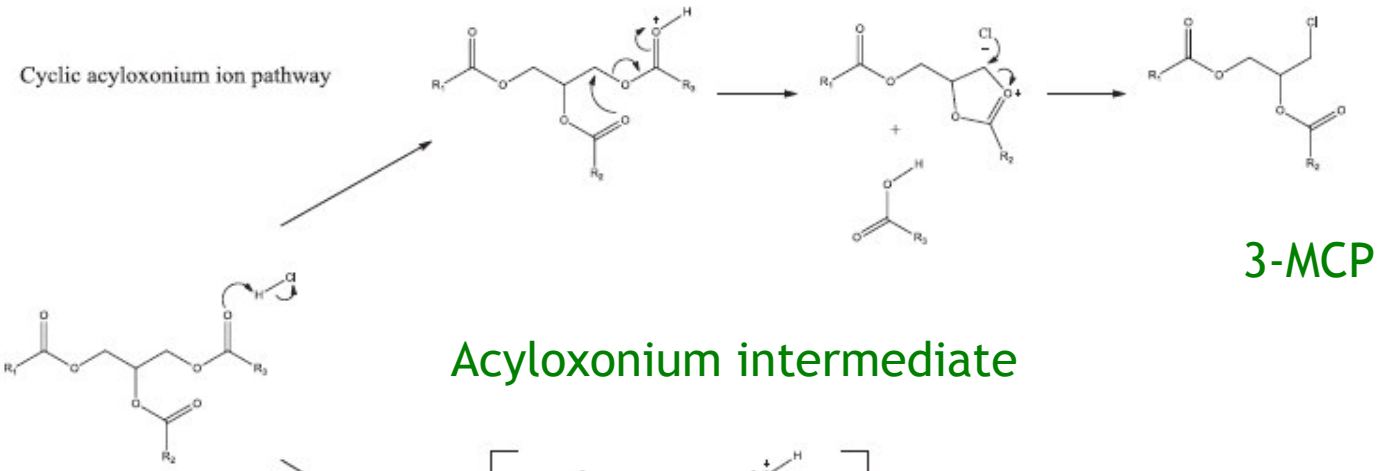
- Inorganic chlorine from fertilizers (KCl, NH_4Cl) and Flocculants in waste water treatment ($FeCl_3$)
- Organochlorines endogenously produced by oil palm
- Chlorine donors accumulate in palm fruits during oil palm growth
- Thermal degradation gives formation of reactive HCl

ACYLGLYCEROLS

- No straight correlation between MAG/DAG content and 3-MCPD esters
- TAG are main precursors

Ref : Nagy et al. (2011), food additives and contaminants,1-9

3-MCPD ESTERS : MECHANISM OF FORMATION

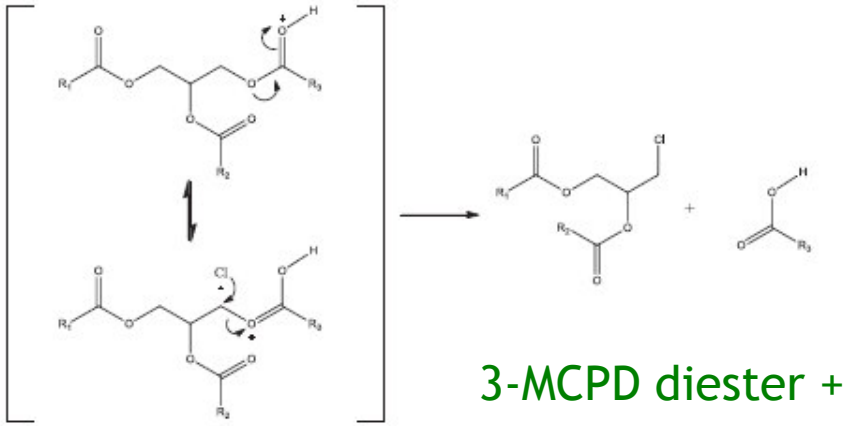


3-MCPD diester + FFA

Acyloxonium intermediate

Triglycerides
+ HCl

Acyloxonium ion pathway



3-MCPD diester + FFA

Ref : Destaillats et al. (2012), food additives and contaminants,29 (1),29-37

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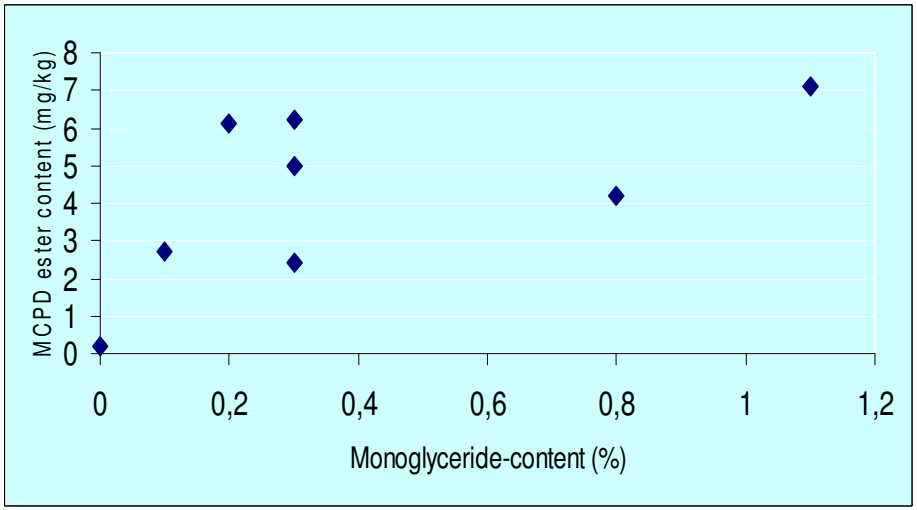
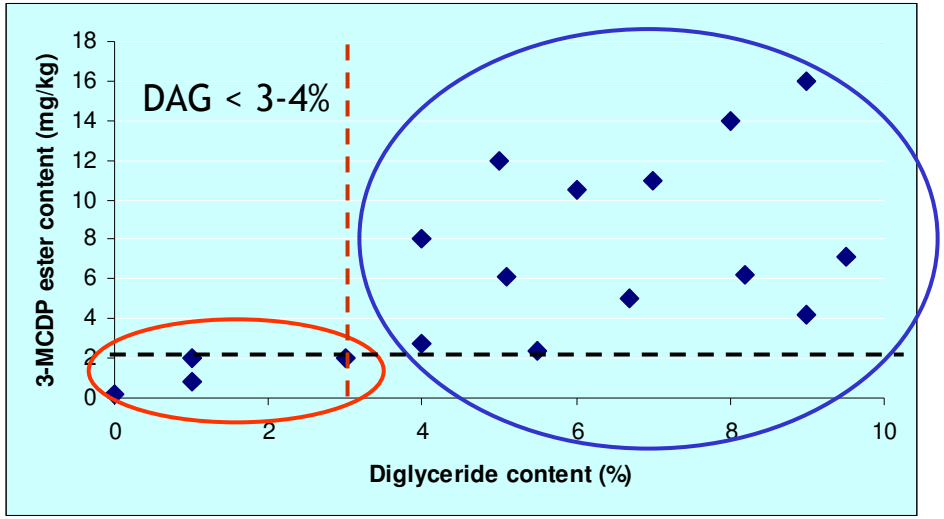
GLYCIDYL ESTERS : PRECURSORS



Palm Oil, deodorized at 260°C

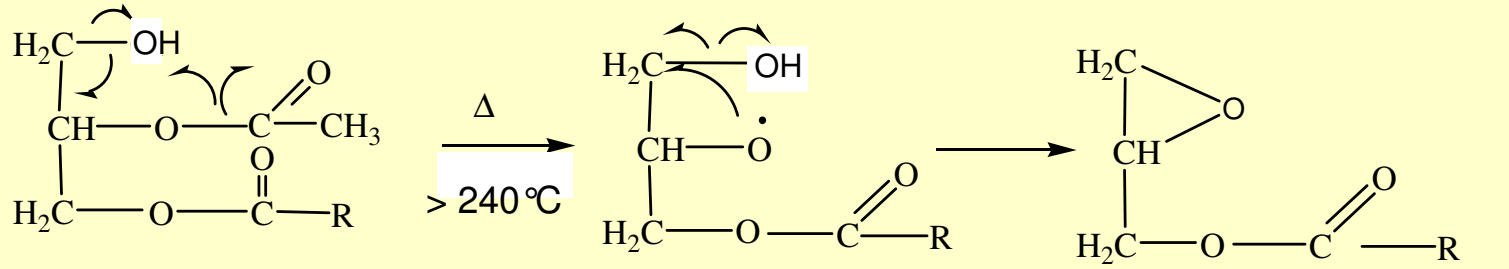


Palm Oil, deodorized at 260°C

* No apparent correlation between MAG and glycidyl ester formation
* Low DAG content will result in low 3-MCPD/glycidyl-ester content
* DAG-content : max. 3-4% (mostly > 5% in palm oils)

Reference:Karel Hrncirik (Unilever,2009) and Bertrand Matthaus (MRI, 2009)

GLYCIDYL ESTERS : MECHANISM OF FORMATION



DAG **Radicalar mechanism** **Glycidol-esters**

* Formation of glycidyl ester from DAG requires high temperature

* Glycidyl esters can also be formed from MCPD mono-esters
  - About 20% is converted, but MCPD mono-esters are nearly not present

* Oxopropyl esters can also be formed from DAG
  - Estimated 5-6 times less than glycidyl esters

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MITIGATION STRATEGIES

TARGET

Refined (palm) oil with Low content of 3-MCPD/GE esters

Standard spec : < 2 ppm
Infant formula : < 1 ppm

Reduction of critical precursors

- Upstream, preventive process on crude oil
- Removal of chlorides
- Reduction of partial glycerides

Removal of 3-MCPD/GE from refined oil

- Curative action on refined oil;
- (Multi-stage) enzymatic degradation
- Selective adsorption

Avoid/Minimize formation during refining

- Mainly aiming at palm oil refining process
- Should not affect other oil quality parameters

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REFINERS CHALLENGE

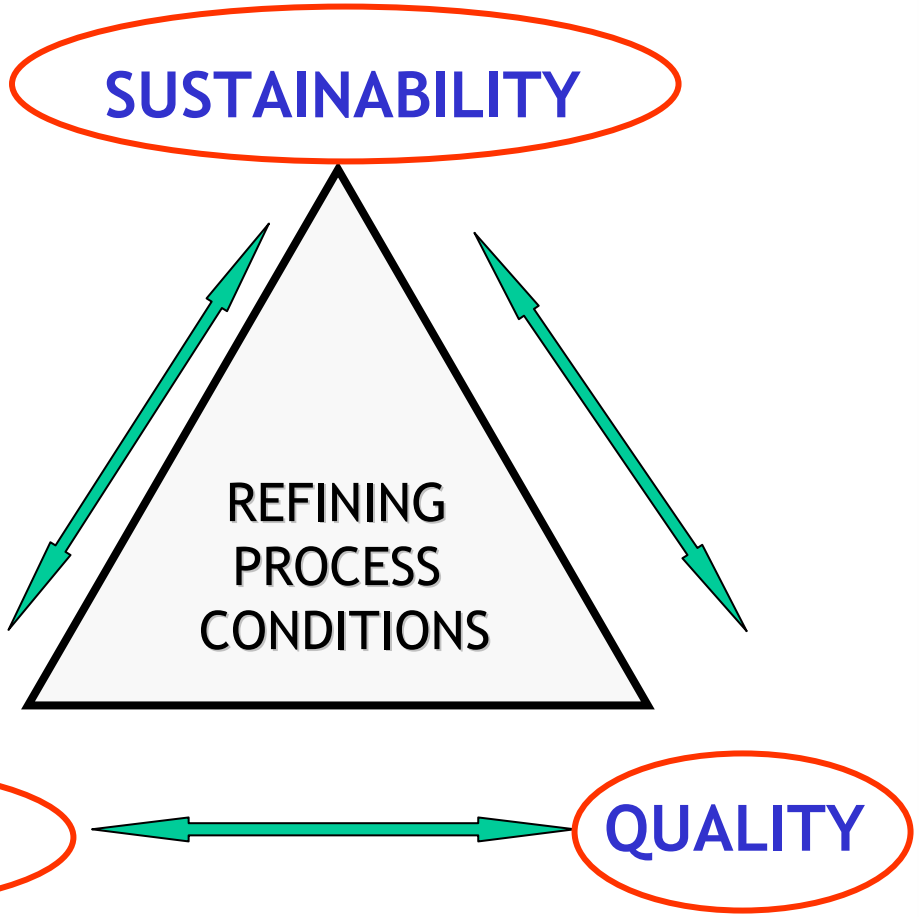
Adopting modified refining process that guarantees :

(1) Low 3-MCPD/Glycidyl esters (< 2 ppm)

(2) Excellent overall/nutritional quality

(3) Highest possible (cost-) efficiency

(4) Lowest possible side-streams



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PALM OIL REFINING

Crude Palm Oil

↓

DRY DEGUMMING

0.05-0.15% H_3PO_4 (85%)
70-90 °C, 1-15 min

→ - Wet degumming (washing)
- Other degumming acid

↓

BLEACHING

0.6-1.2% Activated Bleaching Earth
90-110 °C, 20-40 min, 30-100 mbar

→ - Natural bleaching earth
- Silica/activated carbon

↓

DEODORIZATION

250-270 °C, 45-90 min
2-4 mbar,0.6-1.2% stripping steam

→ - Lower temp./ longer time
- Chemical refining

↓

Refined Palm Oil

Effect of crude oil quality

CPO	DOBI	FFA (%)	DAG (%)	Activated Bleaching Earth (HCl)		Natural Bleaching Earth	
				MCPD (ppm)	GE (ppm)	MCPD (ppm)	GE (ppm)
Columbian			5.2	**2.3**	**3.0**	**1.1**	**3.6**
Malaysian 1			6.2	**9.6**	**3.8**	**2.7**	**4.6**
Malaysian 2	3.1	3.8	5.2	**9.7**	**3.5**	**2.1**	**4.0**

Bleaching with 1.5% activated or natural bleaching earth; Deodorization at 260°C during 1 hr at 3 mbar

* MCPD ester formation depends on crude oil quality and type of BE

  - *Determining factors in CPO are not clear (no test available yet)*
  - *More MCPD esters are formed with (HCl) activated BE*
  - *Effect more pronounced for crude PO with high level of MCPD precursors*

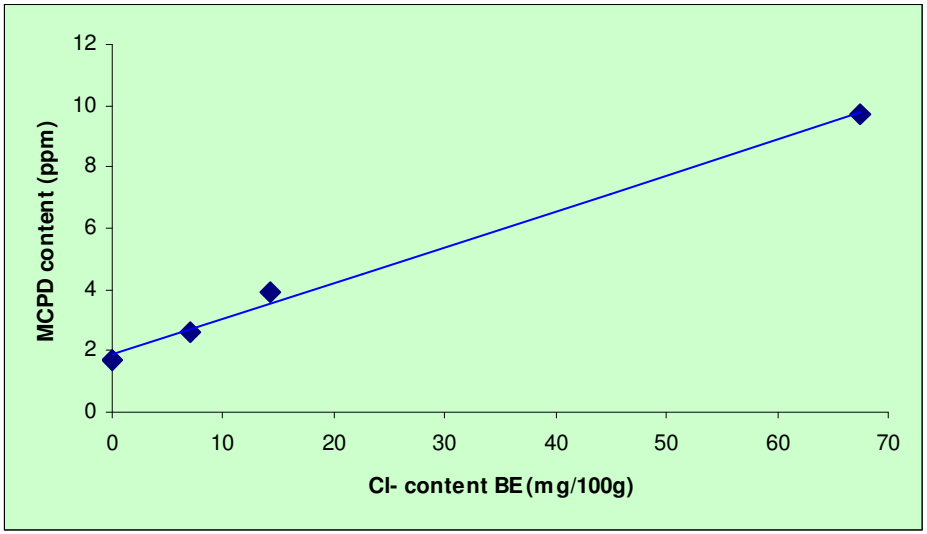
* GE ester formation not depending on crude oil quality and type of BE

Effect of bleaching earth

MCPD ester content in bleached & flash-heated palm oil

Bleaching earth	pH[1]	Cl- content (mg/100g)[2]	MCPD ester content (ppm)
Natural	7.7	0	1.7
Activated	3.65	7.1	2.6
Activated	3.10	14.2	3.9
Activated	3.26	67.5	9.7

[1]measured in 10% aqueous suspension; [2]measred in aqueous suspension
Palm oil bleached with 1.5% bleaching earth; flash heated to 220°C

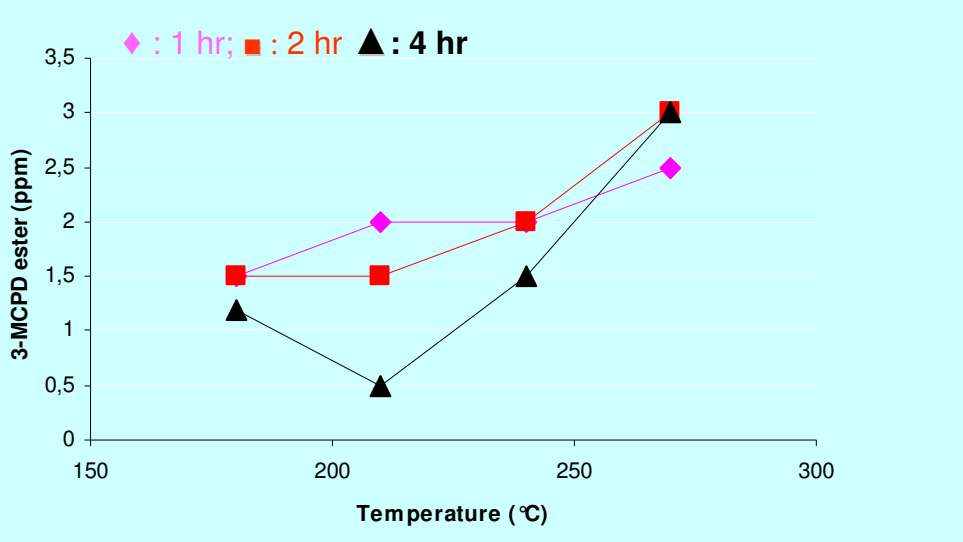


Higher MCPD ester content when Bleaching Earth contains more Chloride

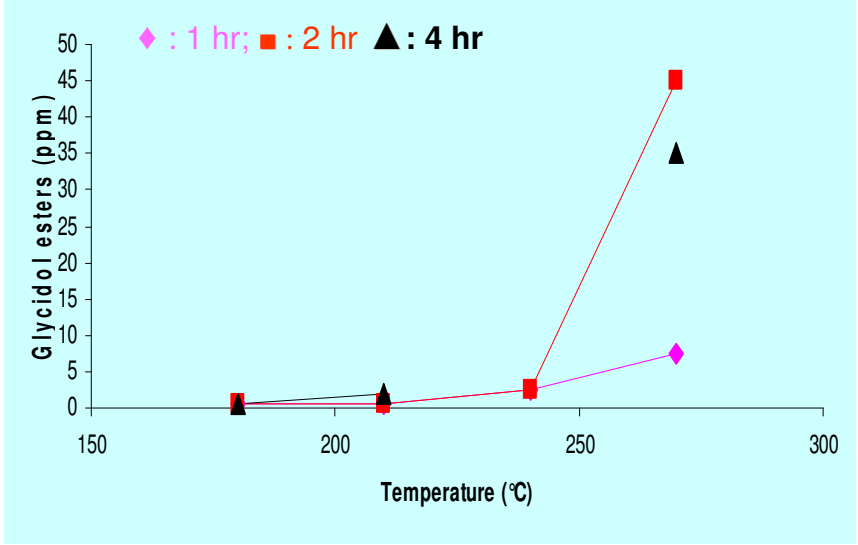
(at least for Crude PO with high(er) content of MCPD precursors)

Effect of (deodorization) temperature

3-MCPD esters



Glycidyl esters



- Temperature more important parameter than time
- At t > 240°C, mainly glycidol-esters are formed (exponential increase)
- 3-MCPD ester formation occurs already at 180°C

Source : Bertrand Matthaus (MRI, 2009)

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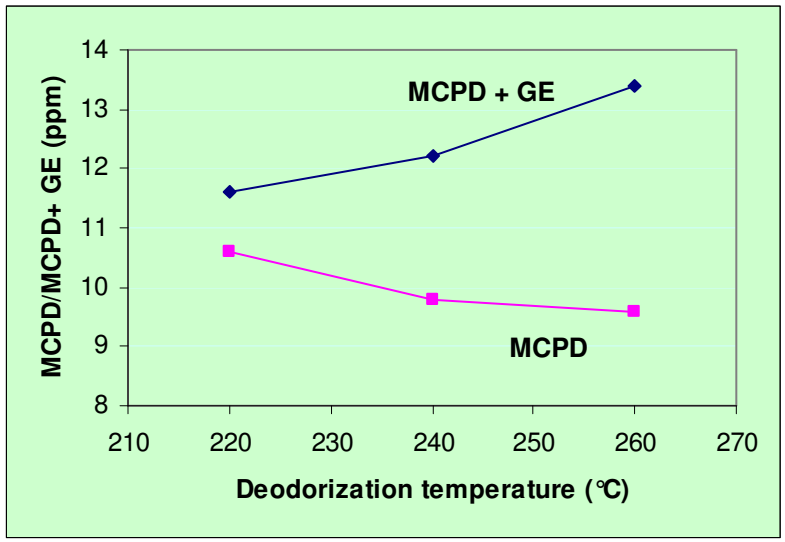
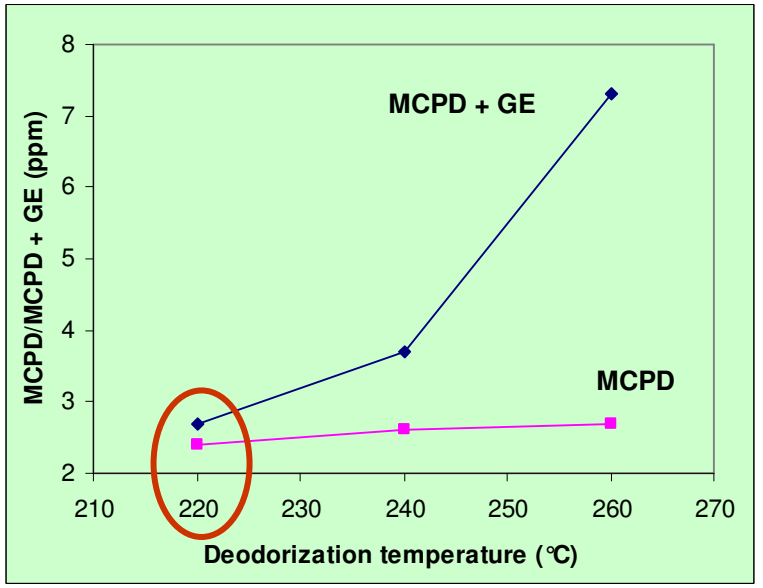
Physical Refining of Palm Oil

Feedstock : Malaysian palm oil (% FFA, 0.13% MAG, 6.2% DAG)
Bleaching : 1.5% bleaching earth/30 min/105°C
Deodorization : 60 minutes/ 3mbar/1% sparge steam

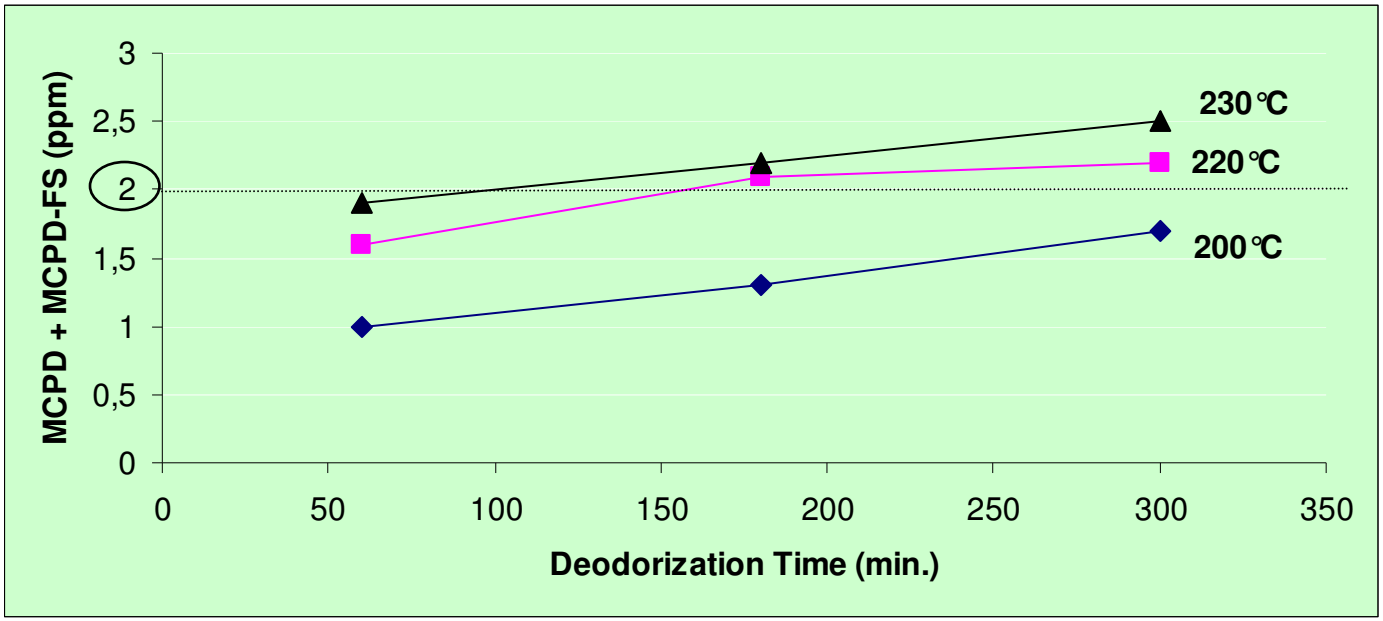
Activated Bleaching Earth (1.5%)



Natural Bleaching Earth (1.5%)



Chemical refining of palm oil



(chemical) refined PO with 3-MCPD/GE esters < 2 ppm can be obtained :

-Bleaching with natural bleaching earth;

-Long deodo time at T_{max} : 220-230°C for good heat bleaching and stability

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Summary

3-MCPD esters

-Chlorine precursors are present in CPO

-Can only be removed during CPO production (at palm oil mill)

-Formation promoted by use of HCl-activated bleaching earth

-Effective formation from TAG occurs already at 180°C

Glycidyl esters

- Can be present in various refined food oils

- Formed from MAG and DAG at high deodorization temperature (> 240°C)

-Formation not affected by type of bleaching earth

Conclusion

RBD palm oil with < 2 ppm 3-MCPD/GE ester can be produced, *if*

- Good quality CPO is used (low DAG-content, low Cl- precursors)
- Natural bleaching earth is used (for low 3-MCPD ester content)
- Deodorization is conducted at T < 230°C (for low GE content)

Alternative refining process for palm oil is required

-Chemical refining (drawback : soapstock as side stream)

-(Semi-) physical refining (challenge : low FFA, light color)