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Mitigating 3-MCPD- and Glycidyl Esters at the Refineries

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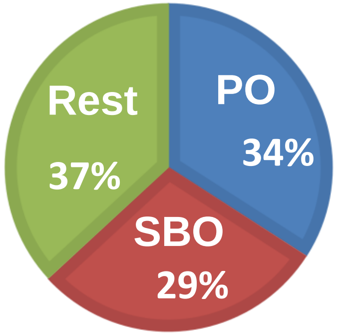
Edible Oil Refining

‘Purpose of refining of oils for edible uses is to remove undesirable components while maintaining the nutritional quality and stability of the refined oil’[1]

World VO production
180 Mio MT (2015/16)



Required refining capacity : > 500.000 TPD

Undesirable components

- FFA
- Phospholipids
- Traces of metals
- Pigments
- **Contaminants**

Quality requirements

- Good shelf life
- Bland odor & taste
- Good nutritional quality
- Safe (no contaminants)

[1]Source : FEDIOL Code of Practice on Oil Refining

Unwanted minor-components in Vegetable Oils

Contaminants

Seed/fruit processing
(pre- or post harvesting)

Pesticides, PAH,….

- Present in crude oils
- Remove during refining

Oil Processing (Heat)

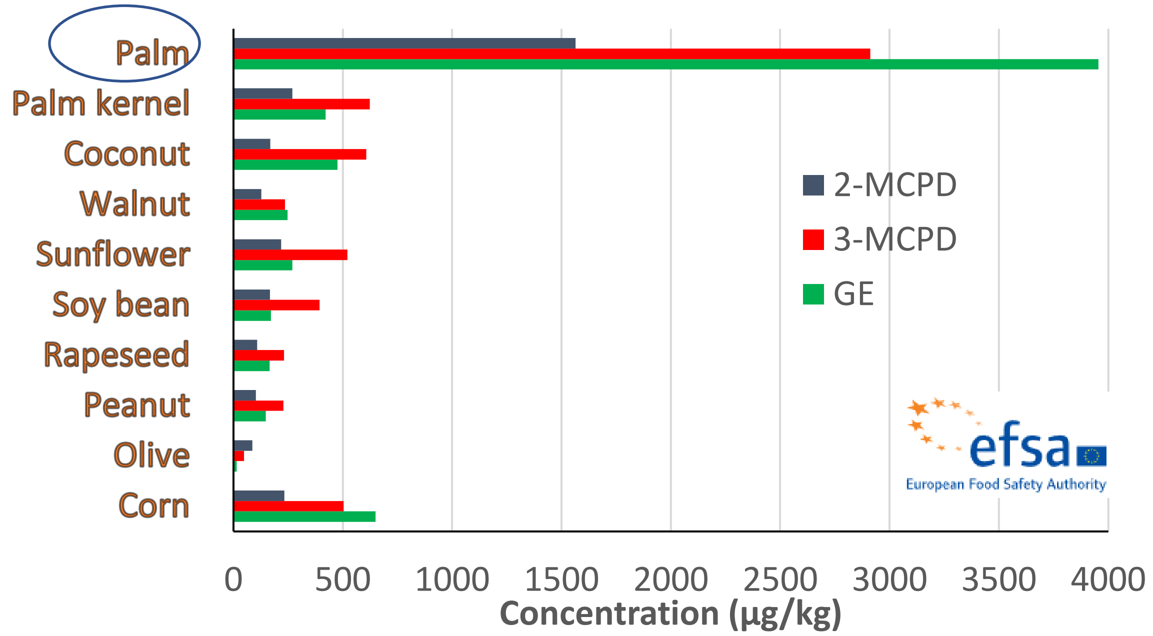
Trans FA, polymers,
3-MCPD - & Glycidyl esters

- Not present in crude oils
- Minimize/avoid formation during refining
- Post-refining removal

Environmental

Dioxins, PCB, mineral oil, ….

Levels of MCPD and GE in food oil



Mean Concentration (ppm)		
Oil	3-MCPD	GE
soybean	0.4	0.2
rapeseed	0.2	0.2
palm	3	4

Highest levels of MCPD esters and GE are found in palm oil

World PO production >60 Mio tons (34% of global VO)

Mitigating 3-MCPD /GE is mainly a PO challenge

Between 2010 – 2015

- 50% reduction of Glycidyl ester content
- 30% reduction of 3-MCPD ester content

Response of industry and authorities

10/4 EN Official Journal of the European Union 24.9.2020

ANNEX

In the Annex to Regulation (EC) No 1881/2006, Section 4 '3-monochloropropanediol (3-MCPD) and glycidyl fatty acid esters' is replaced by the following:

'Section 4: 3-monochloropropanediol (3-MCPD), 3-MCPD fatty acid esters and glycidyl fatty acid esters

	Foodstuffs (1)	Maximum level (µg/kg)
4.2	**Glycidyl fatty acid esters, expressed as glycidol**	
4.2.1.	Vegetable oils and fats, fish oils and oils from other marine organisms 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 4.2.2 and of virgin olive oils (*)	1 000 (***)
4.2.2.	Vegetable oils and fats, fish oils and oils from other marine organisms destined for the production of baby food and processed cereal-based food for infants and young children (3)	500 (***) (******)
4.2.3	Infant formula, follow-on formula and foods for special medical purposes intended for infants and young children (3) (29) and young-child formula (29) (**) (powder)	50 (***)
4.2.4	Infant formula, follow-on formula and foods for special medical purposes intended for infants and young children (3) (29) and young-child formula (29) (**) (liquid)	6,0 (***)

4.3	**Sum of 3-monochloropropanediol (3-MCPD) and 3-MCPD fatty acid esters, expressed as 3-MCPD** (****)	
4.3.1.	Vegetable oils and fats, fish oils and oils from other marine organisms placed on the market for the final consumer or for use as an ingredient in food falling within the following categories, with the exception of the foods referred to in 4.3.2 and of virgin olive oils (*):	
	— oils and fats from coconut, maize, rapeseed, sunflower, soybean, palm kernel and olive oils (composed of refined olive oil and virgin olive oil) (*) and mixtures of oils and fats with oils and fats only from this category,	1 250
	— other vegetable oils (including pomace olive oils (*)), fish oils and oils from other marine organisms and mixtures of oils and fats with oils and fats only from this category,	2 500
	— mixtures of oils and fats from the two abovementioned categories.	— (*****)
4.3.2.	Vegetable oils and fats, fish oils and oils from other marine organisms destined for the production of baby food and processed cereal-based food for infants and young children (3)	750 (******)
4.3.3	Infant formula, follow-on formula and foods for special medical purposes intended for infants and young children (3) (29) and young-child formula (29) (**) (powder)	125 (*******)

What is known about 3-MCPD and Glycidyl Esters ?

3-MCPD Esters ≠ Glycidyl Esters

	3-MCPD	GLYCIDYL (GE)
Toxicity	Carcinogenic (Non-genotoxic)	Carcinogenic (Genotoxic)
Precursors	Triglycerides, chlorine Acidic conditions	Diglycerides Heat
Mechanism of formation	Nucleophilic substitution (starting at 140°C)	Radicalar reaction (> 230°C)
Critical refining stage (for minimal formation)	Degumming - Bleaching (but formed during 1st stage of deodorization)	Deodorization
Stability	Can only be degraded with strong alcaline Not volatile	Conversion to MAG with strong acid (ABE) Volatile

Different mitigation strategies for 3-MCPD esters and GE

Mitigation of 3-MCPD Esters : a real Challenge

* Started initially as a 3-MCPD problem

* First focus of oil processing industry was on GE mitigation

- GE are more 'harmful' (genotoxic)
- Easier to implement : Less impact of CPO quality, GE removal possible

* EFSA scientific opinion is trigger for faster implementation of processes/technologies for 3-MCPD mitigation

- Lower TDI : 0.8 µg/kg BW.day
- Pressure from infant food producers and consumer organisations

Good understanding of the mechanism of formation and physico-chemical characteristics is basis for success

3-MCPD Esters : Mechanism of Formation

$$\text{Triglycerides + Chlorine precursors} \xrightarrow{H^+} \text{3-MCPD di-esters + FFA} \quad (1)$$

* Can be formed from triglycerides
  - Di-esters/Mono-esters : 85/15
  - Most 3-MCPD esters are NOT VOLATILE

* Reaction needs acidic conditions and chlorine precursors
  - Degradation of chlorine precursors in HCl (hypothesis from literature)

* Formation starts at 140°C
  - Most (if not all) 3-MCPD esters are formed during deodorization
  - But bleaching is critical process for 3-MCPD mitigation

Efficient removal of chlorine precursors and/or avoiding acidic conditions during refining is key for low 3-MCPD

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

Ways to minimize 3-MCPD esters in RBD Palm Oil

TARGET

Refined (palm) oil with Low 3-MCPD ester content

AVOID FORMATION

- Remove chlorine precursors from FFB or CPO
- Eliminate acidity (e.g. chemical refining)

MINIMIZE FORMATION during refining

- Optimized bleaching (type and amount of BE)

DEGRADATION of 3-MCPD esters in refined oil

- 3-MCPD esters are STABLE compounds
- Removal by selective adsorbents
- Stripping by Short Path Distillation
- Degradation possible during chemical IE

3-MCPD mitigation : Removal of Chlorine precursors

* Chlorine precursors

- Present in CPO at various concentrations → CPO QUALITY !!!!
- From various sources (fertilizers, soil, water) → PLANTATIONS
- Not possible to monitor CPO quality regarding 3-MCPD formation

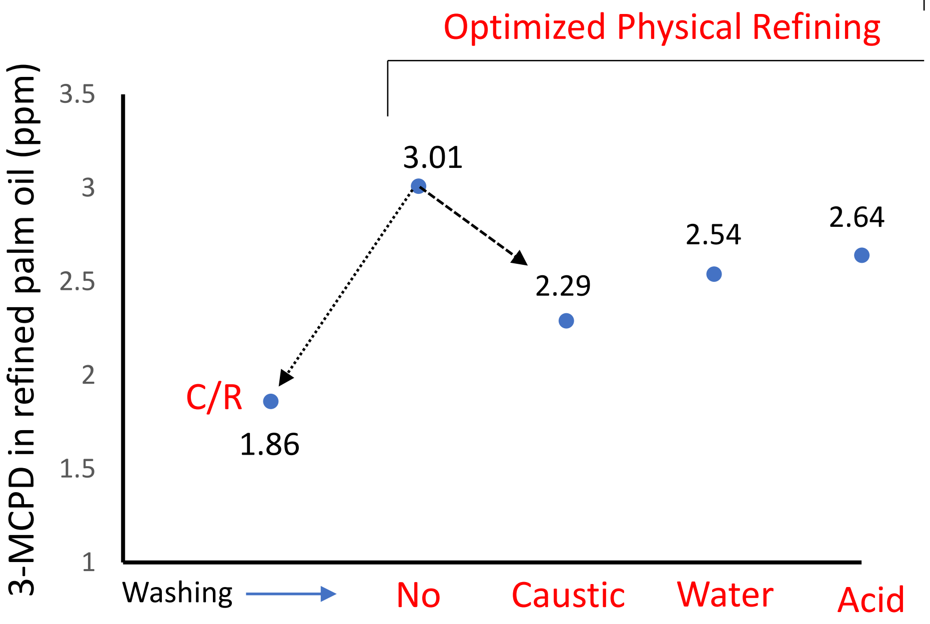
* Removal Chlorine precursors

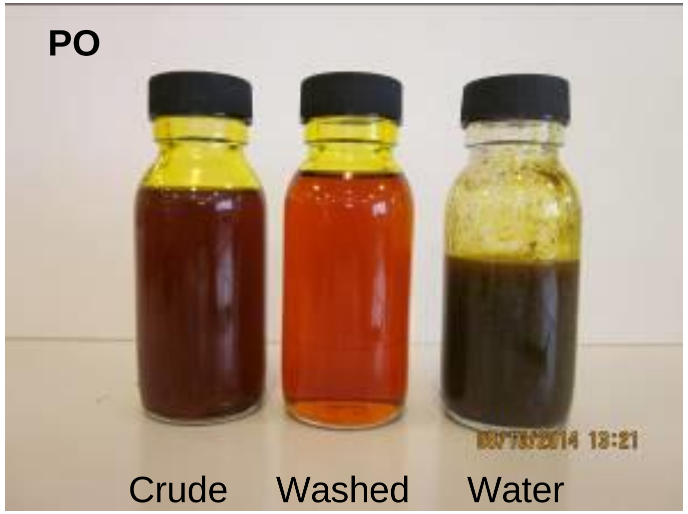
Decreasing Efficiency ↓

(1) WASHING of Fresh Fruit Bunches
(2) WASHING of *fresh* CPO
→ MILL

(3) WET DEGUMMING/washing of *stored* CPO
(4) ADSORPTION during *bleaching*
→ REFINERY

Effect of CPO washing on 3-MCPD ester formation





Parameter	CPO	Washed CPO
FFA (C16:0)	3.67	3.53
P (ppm)	22.3	8
Fe (ppm)	20.3	2.68
Ca (ppm)	20.1	8.7
Mg (ppm)	12.3	1.7
K (ppm)	21.6	0.7
Na (ppm)	1.4	1.2

* Positive effect of water washing (bad quality CPO)
* Most effect of 'caustic wash', but chem.refining is best
* More pronounced effect when applied on *fresh* CPO

3-MCPD mitigation : Neutralizing Acidity

* Origin

- Organic/mineral acids in CPO (feedstock origin, quality,….)
- Introduced during refining (degumming acid, activated bleaching earth)
- Formed during refining (HCl from degradation of chlorine precursors)

* Neutralizing acidity

(1) Chemical Refining → CURRENTLY THE BEST SOLUTION

(2) Choice of degumming acid : citric, phosphoric or no acid ?

(3) Natural Bleaching Earth : effect on standard quality parameters ?

(4) Neutralization of acidity formed during bleaching

CPO quality and type of bleaching earth

CPO	DOBI	FFA (%)	DAG (%)	Activated Bleaching Earth (HCl)	Natural Bleaching Earth
				MCPD (ppm)	MCPD (ppm)
Columbian	1.6	3	5.2	**2.3**	**1.1**
S.-E. Asian 1	2.7	4.2	6.1	**8.1**	**1.7**
South-American	2.3	4.6	7.2	**7.5**	**1.6**
S.-E. Asian 2	1.6	5.1	6.2	**9.6**	**2.7**
S.-E. Asian 3	3.1	3.8	5.2	**9.7**	**2.1**

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

- Crude palm oil quality
  * More important in physical refining ('less forgiving')
  * No quality parameter(s) to 'predict' 3-MCPD forming potential
  * Geographical/regional differences

- Type of bleaching earth
  * Natural bleaching gives less 3-MCPD
  * Effect is less for good quality CPO

3-MCPD mitigation : Post-Refining Options

* Stripping
  - Most 3-MCPD esters are *di-esters* with same, low volatility as DAG
  - Stripping is possible with SPD but gives very high oil losses (> 10%)

* Adsorption
  - Possible with specific adsorbents (e.g. Ca/Mg silicate)
  - Poor efficiency (low relative reduction, high amount of adsorbents)

* Degradation
  - under strong alkaline conditions, (eg. chemical interesterification)
  - risk to change physical and chemical properties of PO

Minimize Formation of 3-MCPD is the only realistic option

Chemical refining : Not the long term solution

Crude Palm Oil

↓

CHEMICAL NEUTRALISATION
90-95°C
0.02-0.05% H_3PO_4
NaOH (20-22% sol., 15-20% excess)

↓

WASHING
85-90°C; up to 10% wash water

BLEACHING
Natural bleaching earth

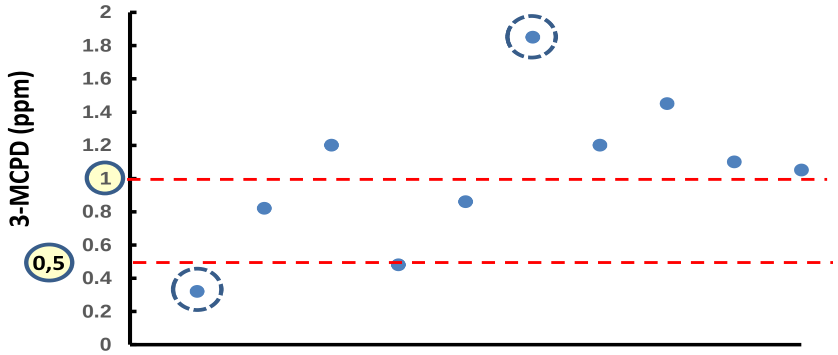
↓

LOW TEMP DEODORIZATION
200-220°C - up to 120 min

↓

Chemical Refined Palm Oil

3-MCPD Esters in Chemical Refined Palm Oil



Higher Operating Cost

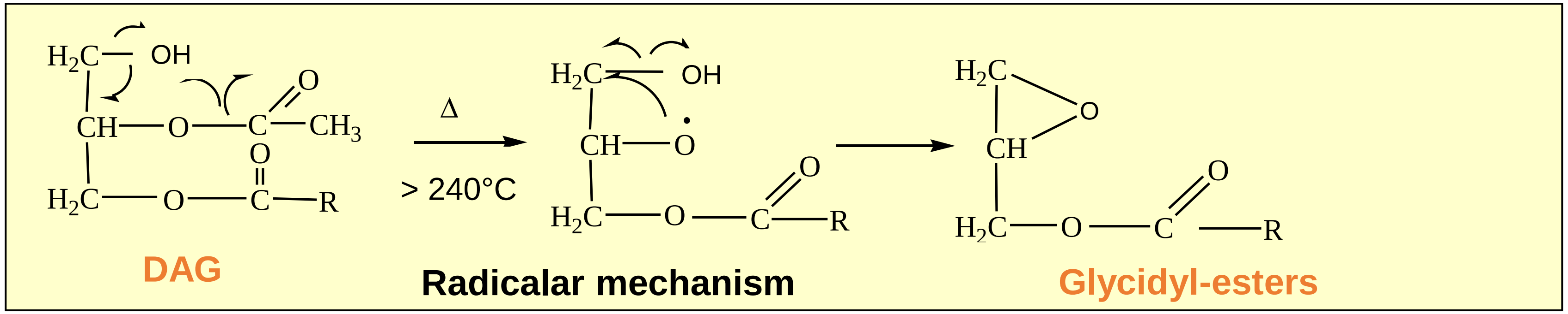
- Higher chemicals consumption
- Higher oil loss (acid oil vs PFAD)
- Soapstock splitting & WWT

↕

Gives Lowest 3-MCPD/GE

- Lower GE due to low deodo temp
- Lower 3-MCPD (NBE/'caustic')
- 3-MCPD < 0.5 ppm remains a big challenge (CPO quality !!!)

Glycidyl Ester Formation during oil refining



Formed from **diglycerides** at high temperature (T > 230°C)

Palm oil in particular is sensitive for glycidyl ester formation

- High DAG content (6-8%) and high deodorization temperature (260°C)

Almost **no glycidyl esters** in most other refined (soft) oils

- DAG typically < 2.5%
- Mostly chemical refining with deodorization at lower temperature

Ref : Destaillats et al. (2012), food chemistry,131,1391-1398

Ways to minimize Glycidyl Esters in Palm Oil

TARGET

Refined (palm) oil with Low Glycidyl Ester content

AVOID FORMATION

- Lowering DAG content in Crude PO (to < 3%)

MINIMIZE FORMATION

- Time/temperature control during deodo

REMOVAL from refined oil

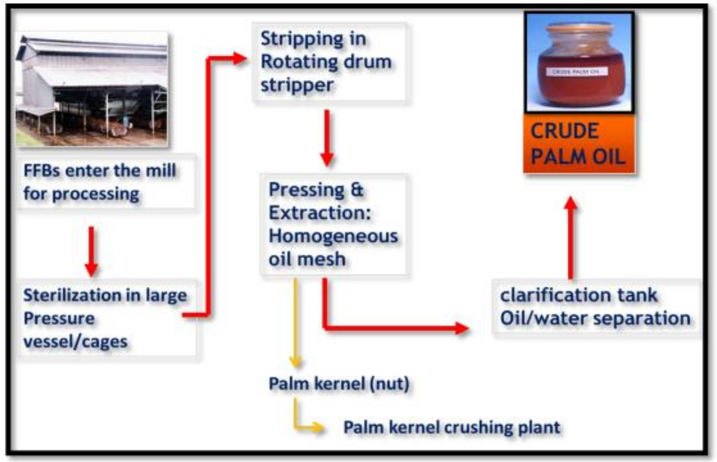
- Degradation of GE into monoglycerides
- Can be achieved during post-bleaching;
- Post-stripping at high temp/deep vacuum

Avoid Formation by Lowering Diglyceride Content

Production of CPO with lower DAG content

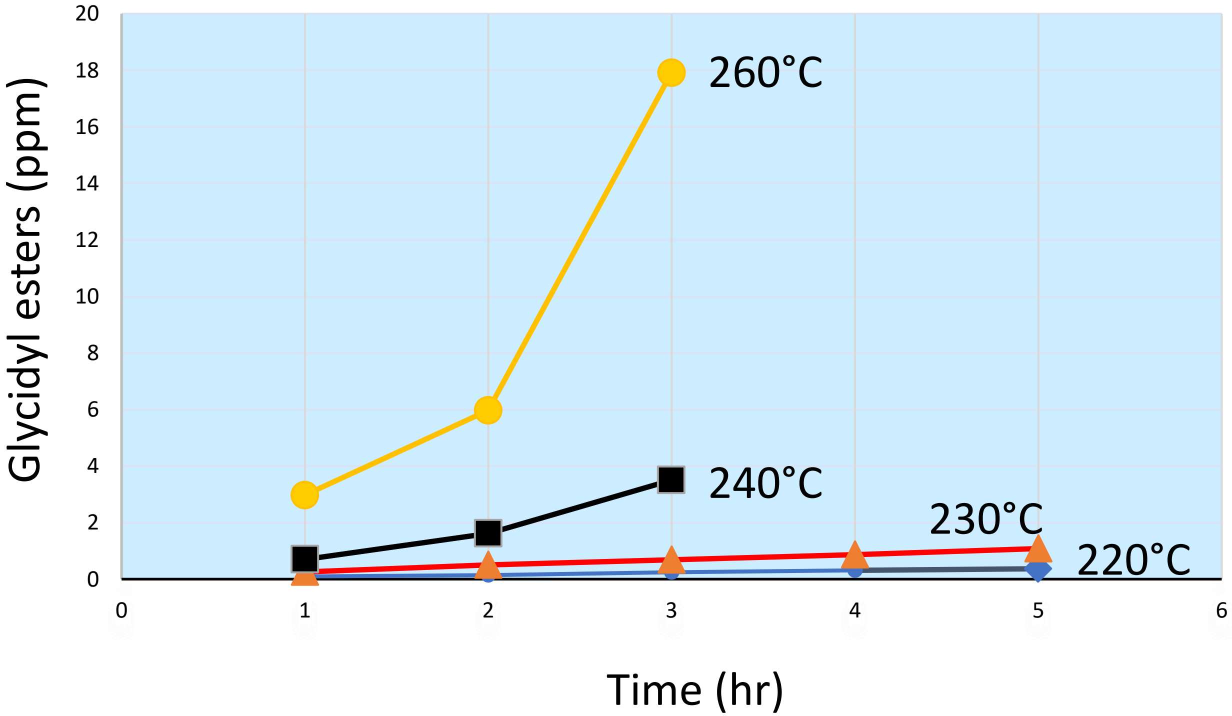
- Faster inactivation of endogenous lipase
- Requires change of harvesting practices
- Immediate treatment of oil palm fruit in the mill
- More difficult for smallholders & in rainy season

- Today's CPO quality standards under question:
  > Is there a need for a more stricter limit on some quality parameters like max. FFA, min. DOBI…?
  > How to practically implement higher CPO quality stds?
  > How much time needed to change the PO industry?



Palm oil milling process

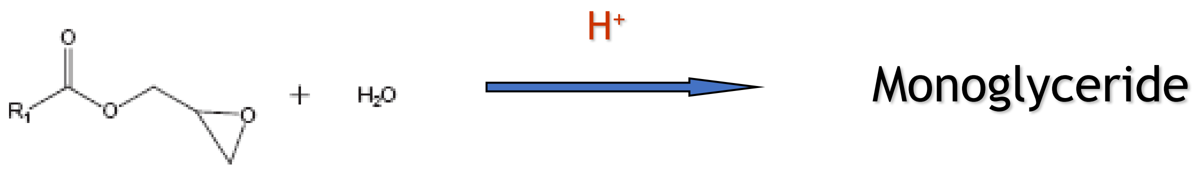
Minimize Formation : Effect of time and temperature



- Almost no formation of Glycidyl esters at T < 230°C
- Very fast formation at T > 240°C

Removal of Glycidyl Esters from Refined Oil

Acid catalysed conversion to monoglycerides

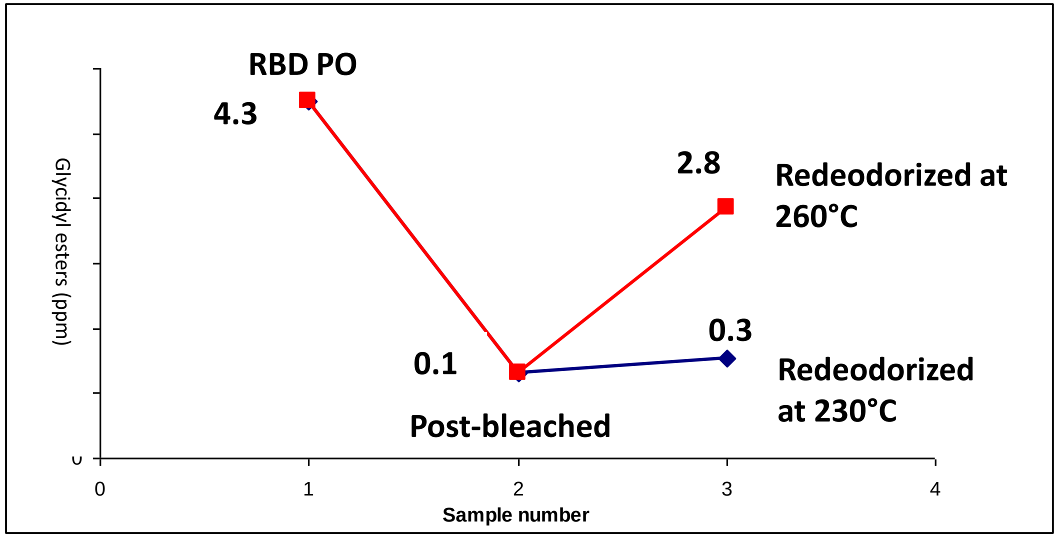


* To be applied on fully refined (deodorized) oil
* **Post-bleaching with acid activated BE** followed by mild deodorization

* **No effect on 3-MCPD esters**

Double refining with higher operating cost but most efficient way to get very low GE in RBD Palm Oil (< 0.5ppm)

Elimination of Glycidyl Esters from Refined Palm Oil



Lab Data

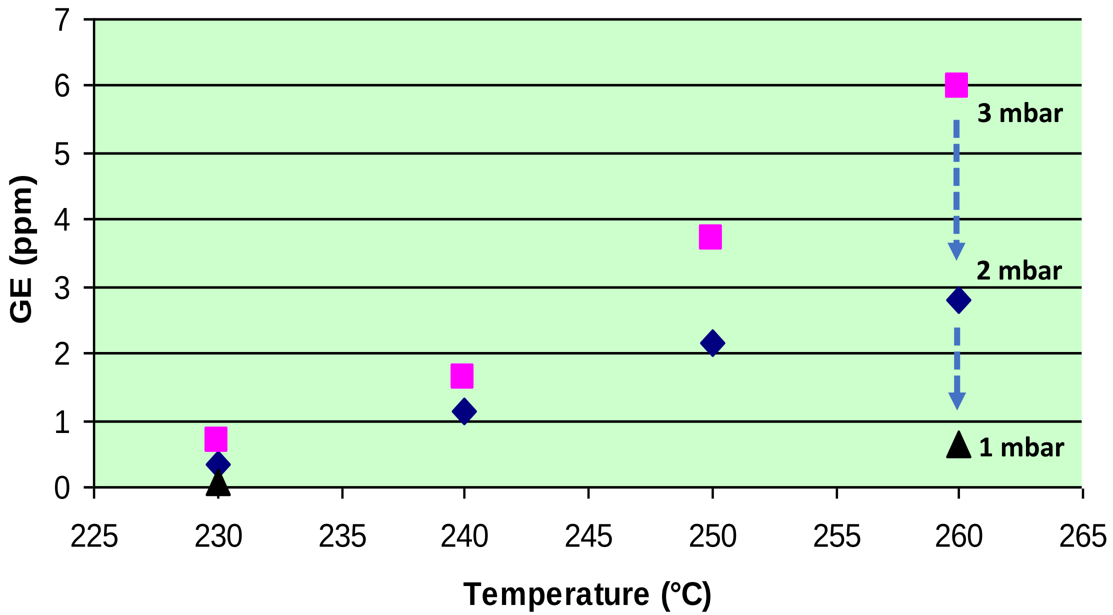
Post-bleaching : 0.5% Activated BE, 110°C, 30 min.

Post-deodo : 0.5% stripping steam, 3 mbar, 60 min.

Glycidyl esters may again be formed during post-deodorization

→ *low deodorization temperature required*

Can Glycidyl Esters be Stripped During Deodorization ?



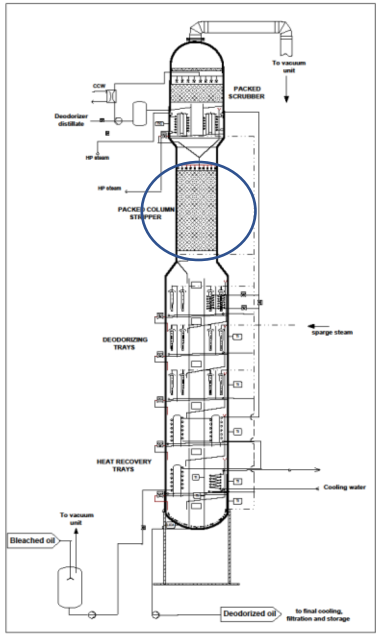
Lab Data

Glycidyl esters can be stripped from the oil, *but……*

- Stripping will only be significant at higher temperature/lower pressure
- Under 'normal' deodorizing conditions : formation > stripping
- Best strategy is therefore to **avoid formation (temp. < 240°C)**

Packed Column Stripping of Bleached palm oil

Temperature (°C)	GE (ppm)	Color (R – 5,25”)	FFA (% C16:0)
220	0.10	20	0.12
230	0.14	19	0,09
240	0.17	14	0,07
260	0.20	12	0,04



Short residence time at high(er) temperature gives

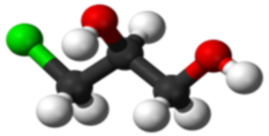
- Almost no formation of glycidyl esters, even at T > 240°C
- Very efficient FFA stripping but only limited heat bleaching

→ Possible/Logical first stage of the deodorization process

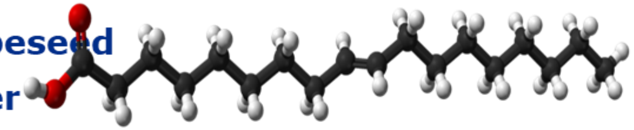
Dual Temperature Deodorisation for physical refining

- High temperature packed column stripping (240-250°C)
- Low temperature deodorization (220-230°C)

- **Prevent/limit formation of GE**
  - → **< 1 ppm GE standard spec**
  - → **< 0,5 ppm GE infant food**



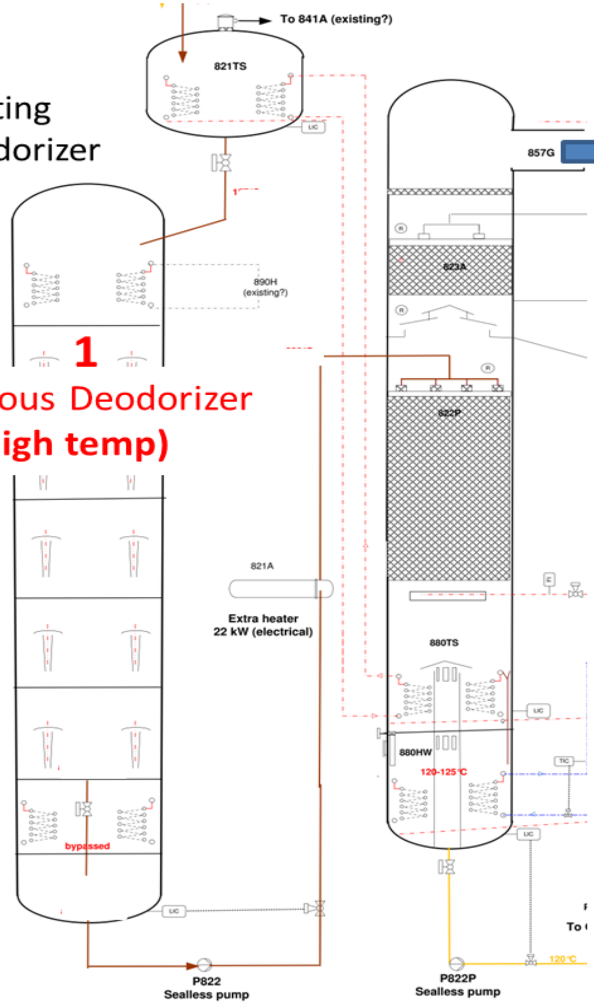
- **Prevent formation of *trans* FA (soft oils)**
  - → **max ~~1.0~~ 0.5% *trans* for soya/rapeseed**
  - → **max ~~0,5~~ 0.3% *trans* for sunflower**



⇨ **Lower heat load during deodorization to minimize formation of heat induced contaminants**

Single Temp Deodorizer + Packed Column Post-Stripper

Existing deodorizer



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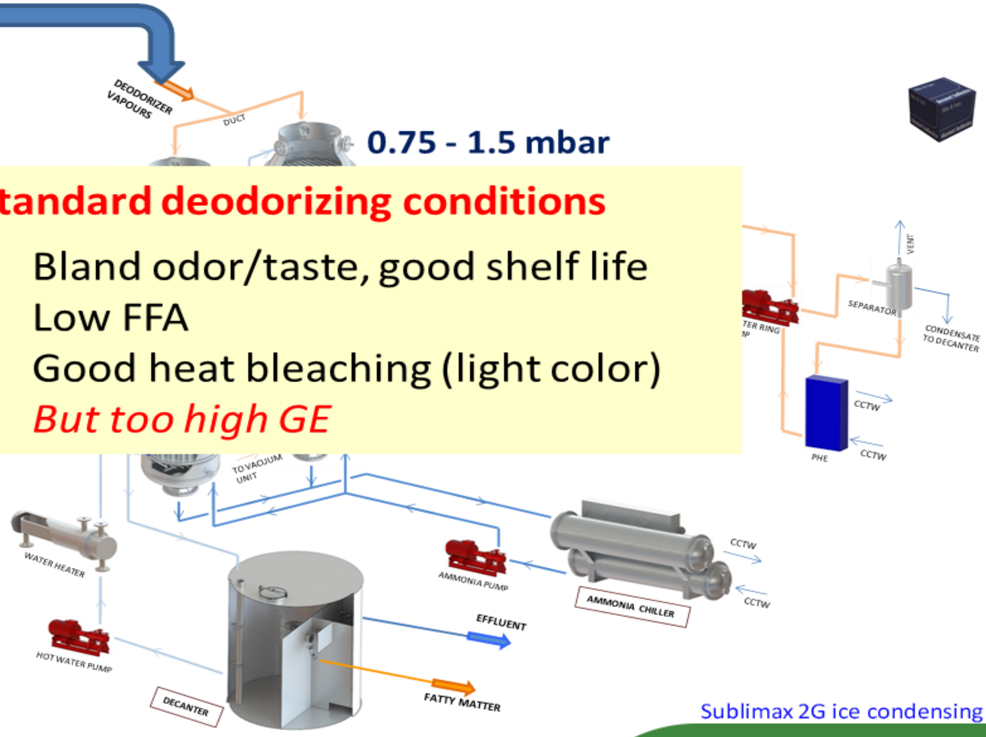
Continuous Deodorizer
(high temp)



Standard deodorizing conditions

- Bland odor/taste, good shelf life
- Low FFA
- Good heat bleaching (light color)
- *But too high GE*

Sublimax 2G ice condensing

Palm Oil Deodorization

	Single T	Dual T		Deodo + Post-stripper
Deodorizing conditions Temperature (°C) Time (min)	P/R 260 60	P/R 260-240 10-60	P/R 240-220 10-**120**	P/R 260-240 60-10
Color (R- 5 ¼" cell) Odor/taste	< 2.5 Bland	2.5 Bland	**4** Bland	**< 2.5** Bland
Glycidyl esters (ppm) Pesticides (ppb)	6-8 → N.D.	**2.4** → N.D.	**0.65** → N.D.	**< 0.5** N.D.

Standard deodorization + packed column stripping is best solution for Palm Oil

- ✓ **Very good standard quality, incl. light color**
- ✓ **Very low GE , possible to meet most strict EU specs (GE < 0.5 ppm)**

Easy to implement

Can also be designed as "add-on" (post-stripper) to existing deodorizers

Mitigation of Glycidyl Esters : Summary

Objective	Strategy	Process (Considerations)
GE : Max. 1 ppm **MINIMIZE FORMATION** **Only possible for oils with max. 7-8% DAG**	* Minimum formation * No stripping	**Chemical Refining** Deodorization @ T < 230°C Longer time for heat bleaching
	* Minimum formation * Some stripping	**Optimized Physical Refining** Dual temp deodo. (245°C - 220°C) Deep Vacuum < 2 mbar Heat bleaching remains challenge
GE : < 0.5 ppm **GE REMOVAL** **Post Refining** **No feedstock limitiation**	* GE Stripping Same volatility as MAG	**High temp. and deep vacuum** (260°C/1 mbar) Classical deodo technology of SPD Fast cooling required
	* Degradation in MAG (acid conditions)	**Degradation with Activated BE** Post-deodorization at low temp.

GE Mitigation processes are known and available for industrial implementation

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How to improve traditional palm oil physical refining ?

Crude Palm Oil

DRY DEGUMMING

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

BLEACHING

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

DEODORIZATION

250-265°C, 45-90 min
2-4 mbar,0.6-1.2% stripping steam

Refined Palm Oil

Alternative Options

3-MCPD

- Wet degumming (washing)
- Other degumming acid
- No acid at all > caustic

- Natural bleaching earth
- Silica/activated carbon
- **Combiclean process**

GE

- Lower temp / longer time
- Dual temp stripping/deodo

- Post refining

Optimized Physical Refining

Parameter	Crude Palm Oil	Standard PHYSICAL refining	Standard PHYSICAL refining	CHEMICAL refining	Optimized PHYSICAL refining
		Activated BE 1%	**Natural BE** 1%	Natural BE 1%	Natural BE 1%
FFA (% C16:0)	5.83	0.02	0.017	0.013	0.02
Color (Lovibond 5 ¼ ")	N.A.	1.8R/23Y	2.0R/24Y	2.3R/19Y	2.5R/32Y
Total chlorine (ppm)	5.0	N.A.	N.A.	N.A.	N.A.
3-MCPD (ppm)	-	**4.21** ↔	**1.25** ↔	**0.48** ↔	**1.18**
Glycidyl esters (ppm)		**3.12** ↔	**2.94** ↔	**0.48** ↔	**0.55**

Standard physical refining : 60 min/260°C/3mbar

Chemical refining : 120 min/225°C/3mbar

Optimized physical refining : 15 min/245°C followed by 45 min/230°C

3-MCPD esters : standard PR with ABE > standard PR with NBE = optimized PR > Chemical refining

Glycidyl esters : standard PR with ABE = standard PR with NBE > optimized PR = Chemical refining

Palm oil refining

Crude Oil

Caustic Neutralizing

wet physical for food

dry physical for nonfood / biodiesel

Next gen. chemical for infant formulation

Water Wash

Bleaching

Stripping/dedorisation

RBD Oil

improvements

Hydrodynamic cavitation

enzymes

Multistage bleaching

Selective adsorbents

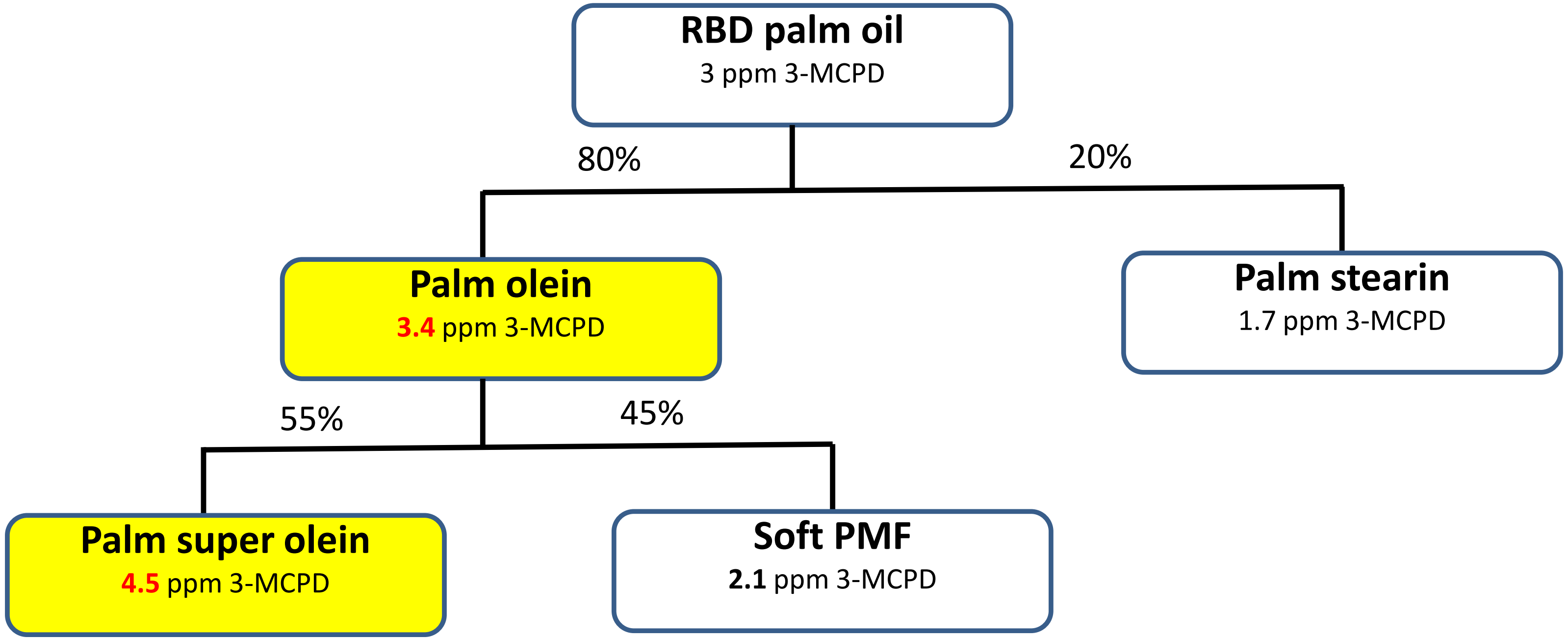
H-L Dual temperature

Low P ice condensing

Post purification

Dry Fractionation & 3-MCPD: even more challenging

Most RBDPO is fractionated & 3-MCPD limits will be applied also to PO fractions.



- Enrichment of 3-MCPD and GE in **palm olein fractions**
- Fully refined PO is most used as feedstock for dry fractionation
- RBD PO with < 1.3 ppm 3-MCPD is needed to get Palm super olein < 2 ppm 3-MCPD

Source : Hinrichsen (Olenex)- data presented at the DGF symposium (Berlin, April 21st-22nd, 2015

3-MCPD mitigation : Conclusion

* 3- MCPD mitigation is more complex :

(1) Part is out-of-refiners control (CPO /FFB washing at oil mill)

(2) Removal during post-refining is not (yet) possible

* 3-MCPD < 2 ppm is a realistic target for refined PO

(1) Starting from **good quality** CPO (regional/seasonal varieties)

(2) next gen. chemical refining (eg. Nano) or optimized physical refining

(3) More difficult for palm olein fractions (3-MCPD enrichment)

* 3-MCPD < 1 ppm remains big challenge for refined PO

(1) Chemical *or* Optimized Physical Refining of **very good quality** CPO

(2) Chemical Interesterification only when needed for final formulation

GE Mitigation : conclusion

* **GE < 1 ppm** is a realistic target for all refined food oils

(1) Can be achieved by 'standard' refining of soft oils with < 3% DAG

(2) Possible for CPO with < 8% DAG when applying :

* Low temperature deodorization (e.g. Chemical refining)
* Dual temperature deodorization (optimized physical refining)

* **GE < 0.5 ppm** is a challenge, but possible

(1) For soft oils with *low* or *dual* temperature deodorization

(2) For **most CPO** by a post-refining process

* Post-bleaching with ABE + low temp deodorization (costly)
* Post stripping at high temperature/deep vacuum (too costly)

Final Conclusion

No « **one fits all**” 3-MCPD/GE mitigation solution

Best solution will depend on

(1) Plant configuration : chemical or physical , new or existing plant

(2) Required specs : special vs commodity; individual or formulated fat (CIE)

(3) Technology development (efficiency – quality – sustainability)

New technical solutions (preventive and curative) are further explored and developed taking into account COST factor

→ final oil must remain affordable

Reference : De Greyt W. and Kellens M., 3-MCPD and GE : A new Challenge
Oils and Fats International , 32(7) - 2016

THANKS FOR YOUR ATTENTION!

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CPAL IV
CONGRESO PALMERO
GUATEMALA
2023

Transformando
EL ENTORNO

CALIFICA A NUESTRO CONFERENCISTA

PhD. León Espinosa