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Glycidyl Ester Mitigation during Rice Bran Oil Refining

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The Refiners' Challenge

Cost-efficient and sustainable production of high quality food oils

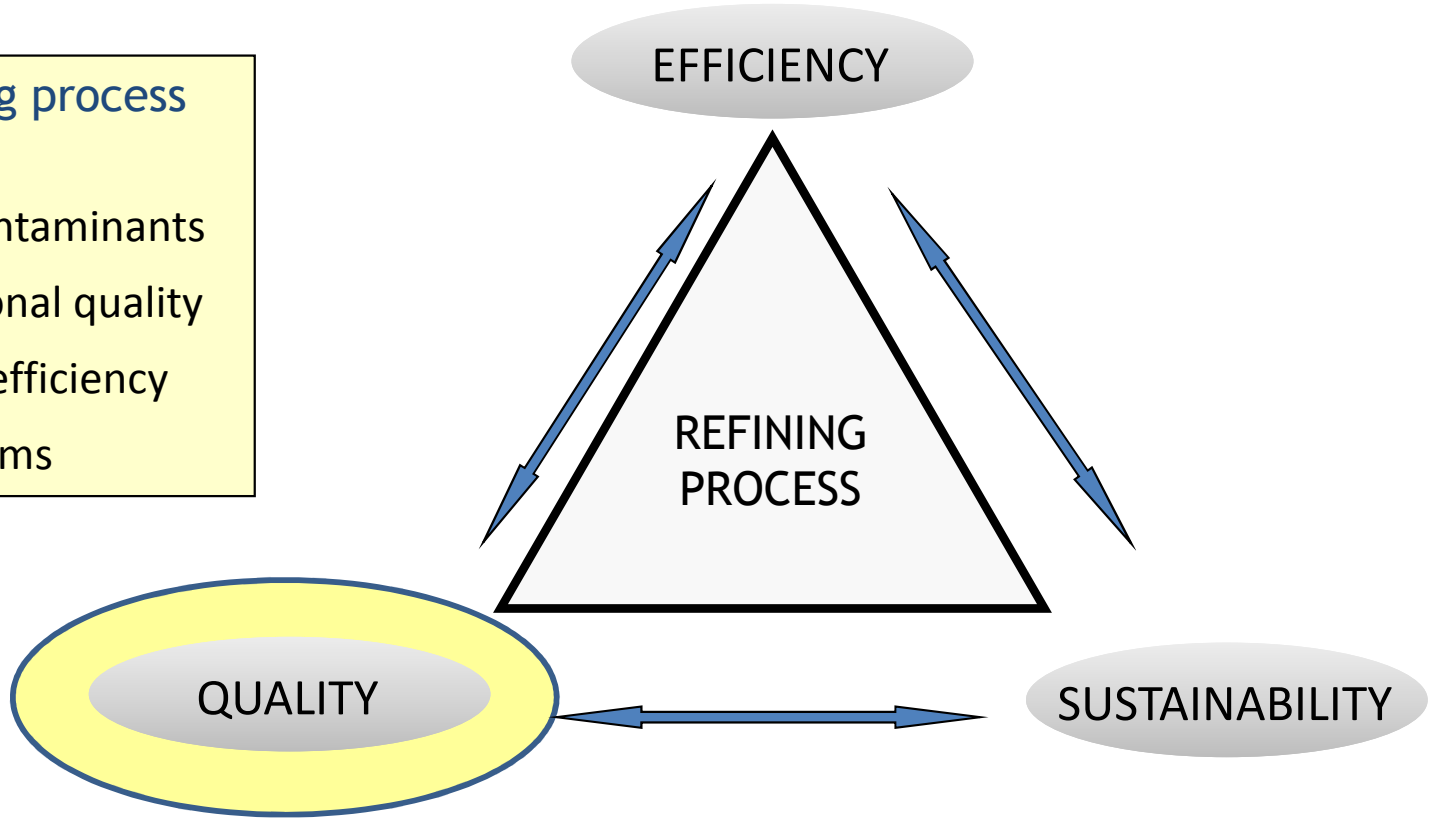
Adopting optimized refining process that guarantees :

(1) Low level/absence of contaminants

(2) Excellent overall/nutritional quality

(3) Highest possible (cost-) efficiency

(4) Least possible side-streams



Drivers for new developments in Edible Oil Processing

Refined Oil Quality : A broad Term

Organoleptic quality

Bland taste

No odor

Light & brilliant color

REFINING

Stability

Good cold stability

Good oxidative stability

Long shelf life

Nutritional quality

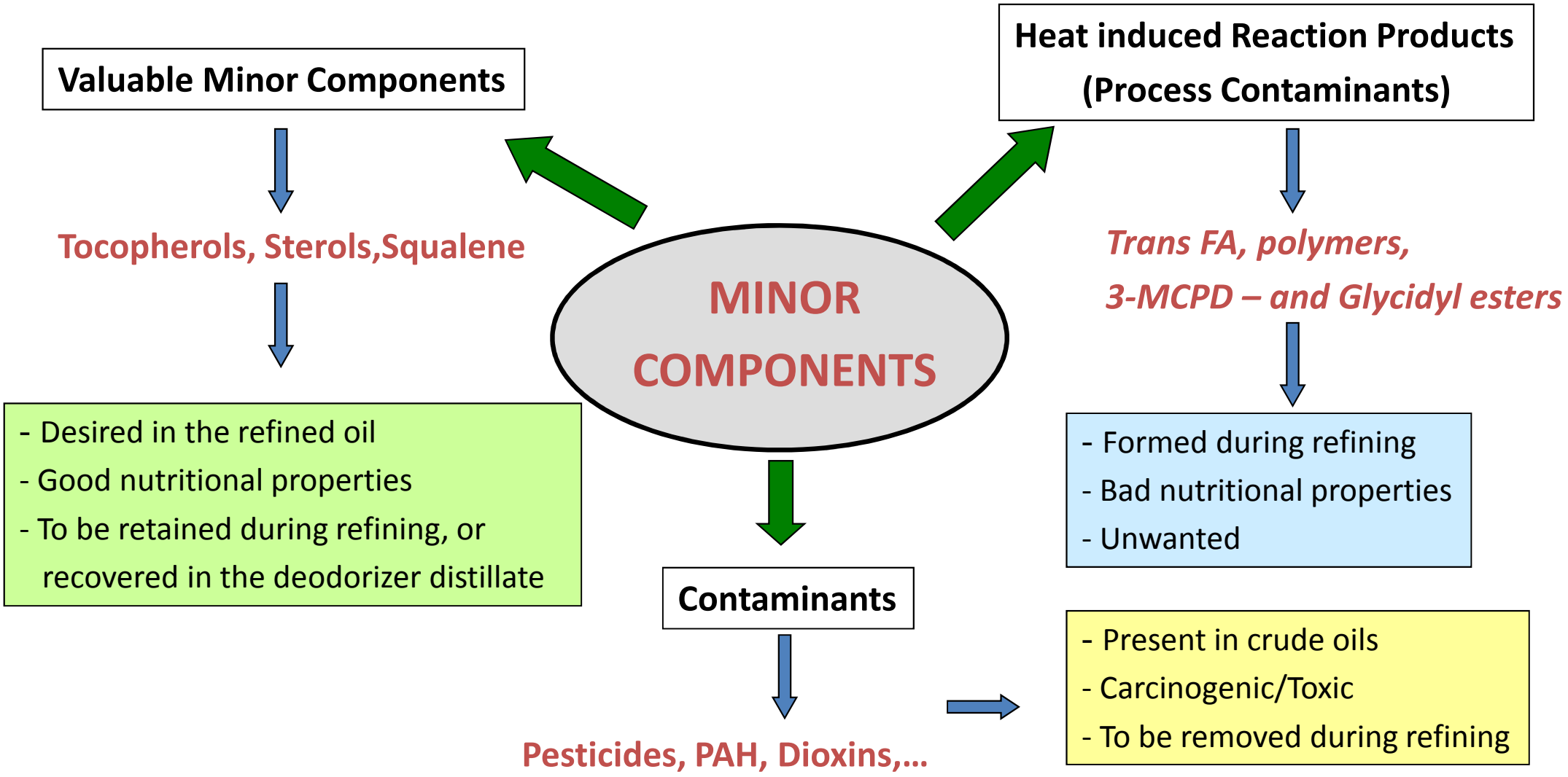
Low process contaminants (trans FA, GE, polymers,…)

Controlled tocopherols and phytosterols content

Low contaminants (PAH, pesticides, PCB, dioxins,...)

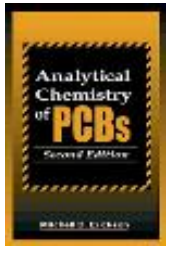
Safe for Consumption

Minor Components in Vegetable Oils



Contaminants in Vegetable Oils

Increasing attention for (process) contaminants in food oils

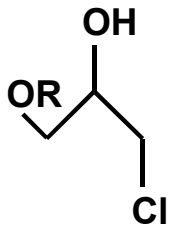
1990's	2000's	2010's	2020's
Trans FA, pesticides	Dioxins, PCB, PAH's	3 MCPD, glycidyl esters	Mineral Oil ? Phtalates
			
Soft Oils (soya, canola,...)	Fish Oils Coconut/PK Oil	Palm Oil (fractions)	

Increased concern about potential harmful nutritional effect

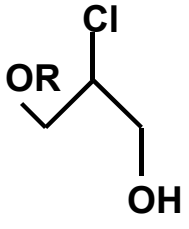
Improved analytical techniques for accurate and user-friendly analysis

New Challenge : 3-MCPD and Glycidyl Esters

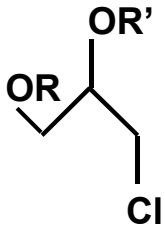
MCPD ESTERS



3-MCPD mono- ester

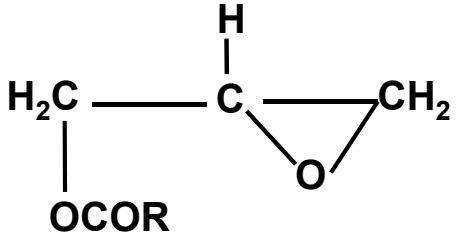


2-MCPD mono- ester



3-MCPD di-ester

GLYCIDYL ESTERS



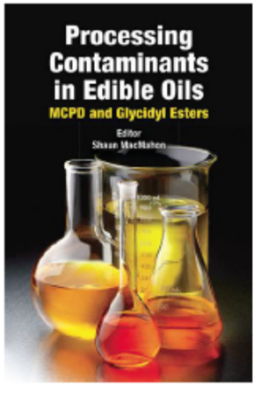
Glycidyl-ester

* Occurrence in food oils first reported mid of 2000's
* Were considered as potential harmful contaminant
* Oil processing industry was requested to reduce 3-MCPD and GE in refined food oils
* Call was taken serious and several R&D projects were initiated

What is known about 3-MCPD and Glycidyl Esters ?

- High research activity in the O&F industry during the past years
  * A lot of scientific literature has been published
  * Several patent applications have been filed (not all granted or applied)
- Established know-how
  * Official analytical methods are validated and published (AOCS);
  * Main precursors are known;
  * Mechanisms of formation are (mostly) understood;
  * Scientific opinion of EFSA about toxicity published in May 2016;

3-MCPD esters ≠ Glycidyl Esters



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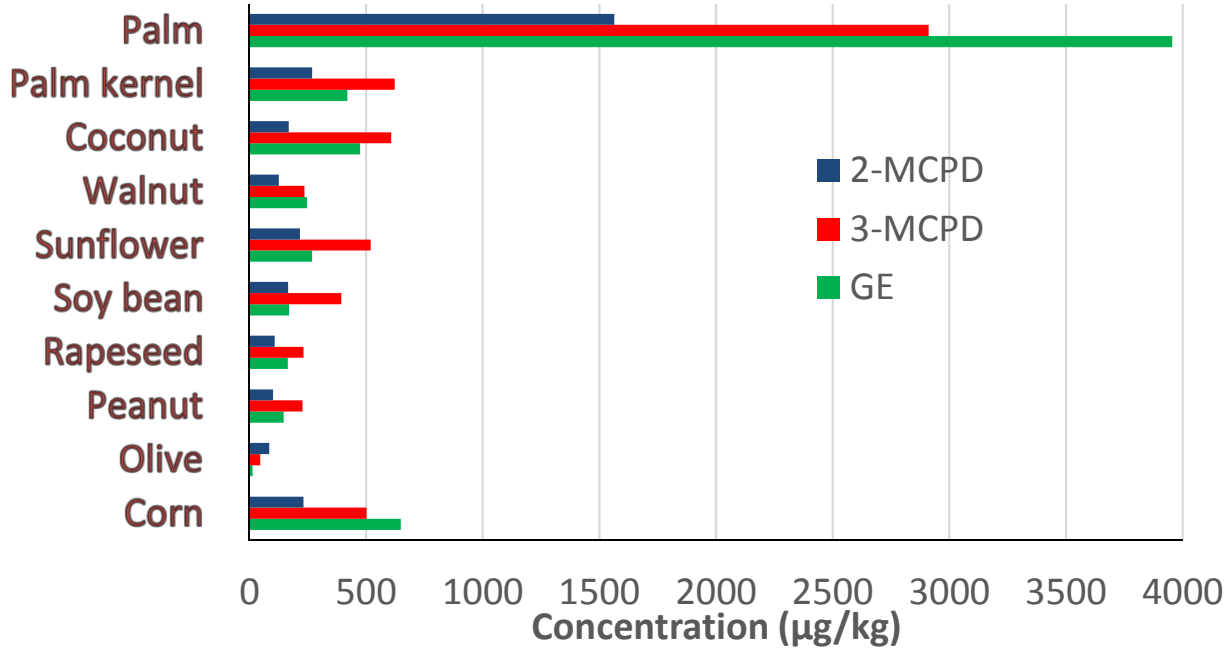
3-MCPD Esters ≠ Glycidyl Esters

	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 (BE) Volatile

Different mitigation strategies for 3-MCPD esters and GE

2,3-MCPD and GE in food oils (2012-2015)



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

Low levels for commodity soft oils. No published data on rice bran oil

Source: EFSA Scientific opinion. March 2016 doi:10.2903:j.efsa.2016.4426

EU Regulatory Measures for Glycidyl Esters

Ammendment to EC regulation 1881/2006

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

Foodstuffs ([1])		
4.1	**3-monochloropropanediol (3-MCPD)**	Maximum level (µg/kg)
4.1.1	Hydrolysed vegetable protein ([30])	20
4.1.2	Soy sauce ([30])	20
4.2	**Glycidyl fatty acid esters expressed as glycidol**	
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 4.2.2	1000 = 1 ppm
4.2.2.	Vegetable oils and fats destined for the production of baby food and processed cereal-based food ([3])	500 = 0.5 ppm
4.2.3	Infant formula, follow-on formula and foods for special medical purposes intended for infants and young children (powder) ([3,29])	75 until 30.06.2019 50 as from 1.07.2019
4.2.4	Infant formula, follow-on formula and foods for special medical purposes intended for infants and young children (liquid) ([3, 29])	10.0 until 30.06.2019 6.0 as from 1.07.2019 "

Max. levels expressed as free glycidyl

Following conclusion of EFSA that glycidyl is **carcinogenic and genotoxic**

New max. levels will be adopted **in 2018**

Current max. levels for GE are only valid for **vegetable oils**

No max. levels (yet) for :

- GE in animal fats/marine oils
- 3-MCPD in food oils

Regulatory and Market Situation for 3-MCPD

Tolerable Daily Intake (TDI) for 3-MCPD

3-MCPD is carcinogenic but non-genotoxic : TDI can be set

Source	TDI (µg/day.kg BW)
EFSA-2016	0.8
JECFA-2016	4.0
EFSA-2018[1]	2.0

[1]Revised opinion

No regulatory measures for 3-MCPD

Deeper evaluation of various TDI values is necessary

3-MCPD specs from infant food producers

Max. levels (ppm)	Palm Oil Fractions		Vegetable Oils	
	3-MCPD	GE	3-MCPD	GE
2017	3.0	1.0	1.5	1.0
2018	3.0	0.5	1.0	0.5
2019	No specs set yet	0.5	0.5	0.25
2020		0.5	0.35	0.1

3-MCPD specs for palm oil (fractions) were made less strict (supply issue)

Are GE/3-MCPD esters only an issue for palm oil?

Oil	Glycidyl (ppm)	3-MCPD (ppm)	Glycidyl +3-MCPD (ppm)	DAG %
Rapeseed	0.12	0.21	0.32	0.43
Sunflower	0.30	0.54	0.84	0.85
Coconut	0.25	0.54	0.79	N.A.
Corn	0.54	0.68	1.22	2.12
Palm	1.03-7.50	2.70-13.70	3.73-20.00	8.30

Analysis of commercial oils (supermarket) confirm that :

(1) Palm Oil is most sensitive oil for 3-MCPD/GE formation

(2) GE content in refined soft oils is generally very low (< 0.5 ppm)

(3) 3-MCPD content can also be high(er) in soft oils (quality dependent)

How sensitive is rice bran oil ?

Vegetable Oils : General Composition

Quality Parameter	Oil Type				
	Palm	Rice bran	Soya	Rapeseed	Sunflower
FFA (%)	**3-5**	**5-10**	< 1.0	0.5-2.0	0.5-2.0
DAG (%)	**6-8**	**6-9**	<2.0	<2.0	<2.0
PL[1] (%)	< 0.15	0.8-1.2	**1.5-3.0**	**0.5-1.5**	**0.5-1.3**
Tocopherols[2] (ppm)	600	1500	**1200**	700	700
Sterols (ppm)	300	> 1%	**4000**	**6000**	**4000**
FAC[3] (% rel. w/w)					
C16:0	42	20	8	4	6
C18:0	5	2	4	1	4
C18:1	41	40	28	60	28
C18:2	10	**33**	**53**	**20**	**61**
C18:3	<1	1.5	**9**	**7**	**1**

[1]PL = Phospholipids; [2]Tocotrienols in palm oil; [3]Fatty acid composition

Palm/Rice Bran Oil : high DAG (risk for GE formation)

Soy Oil : low DAG (less risk for GE formationa) but high PUFA (risk for trans formation)

GE/3-MCPD esters in refined rice bran oil?

Parameters	Commercial Refined Rice Bran Oil	
	Sample 1	Sample 2
FFA (% C18:1)[1]	0.054	0.061
Oryzanol (%)	0.25	0.57
Diglycerides (%)	**6.0**	**6.6**
3-MCPD[2] (ppm) Glycidyl[2] (ppm)	0.22 **1.22**	0.52 **1.70**
C18:2 (%) C18:3 (%) *Trans* FA (%)	32.5 1.3 0.45	32.0 1.2 0.70

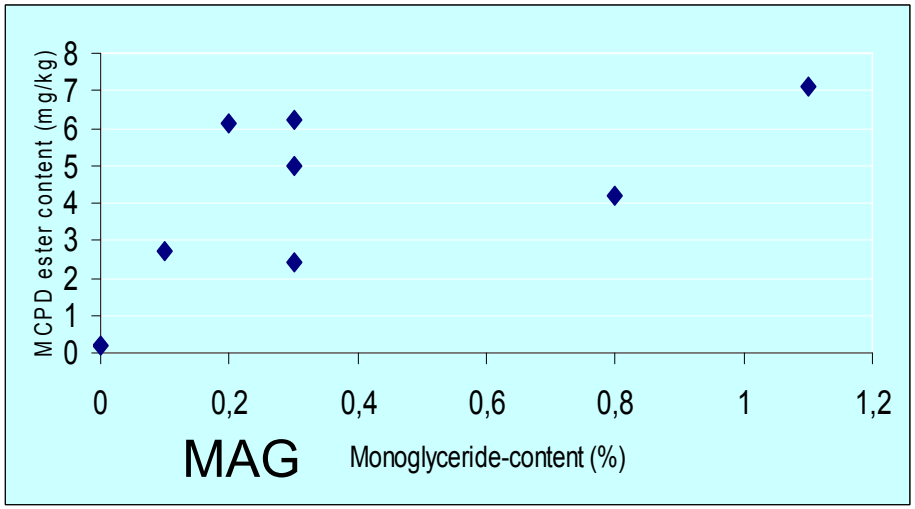
[1]against bromophenol blue as indicator; [2]AOCS Cd 29b-13 (indirect GC/MS method)

(1) Very low 3-MCPD content (< 0.5 ppm), meeting trade specs for infant food

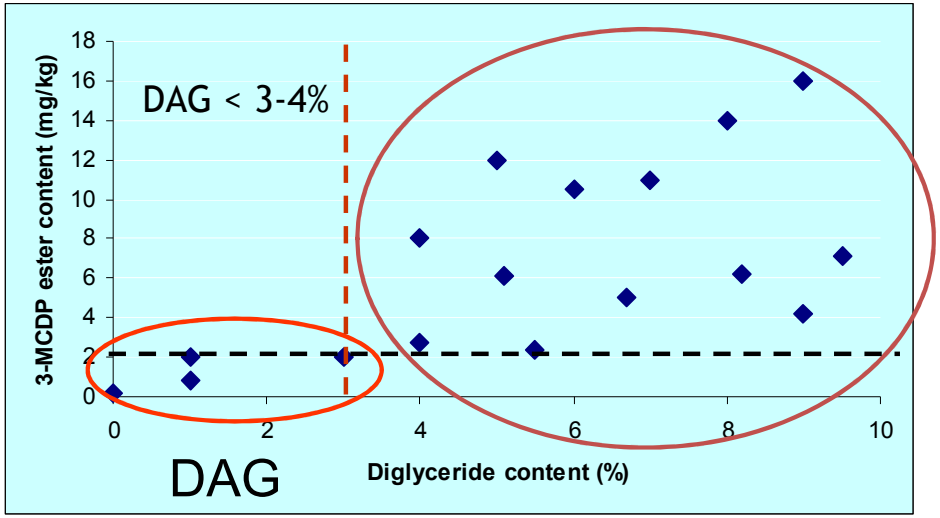
(2) Too high Glycidyl content (> 1 ppm), above max. EU spec

GE mitigation strategy is required for rice bran oil refining

Precursors for Glycidyl Ester Formation



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 glycidyl-ester content

* DAG-content < max. 3 % (typically 6-8% in palm oil)

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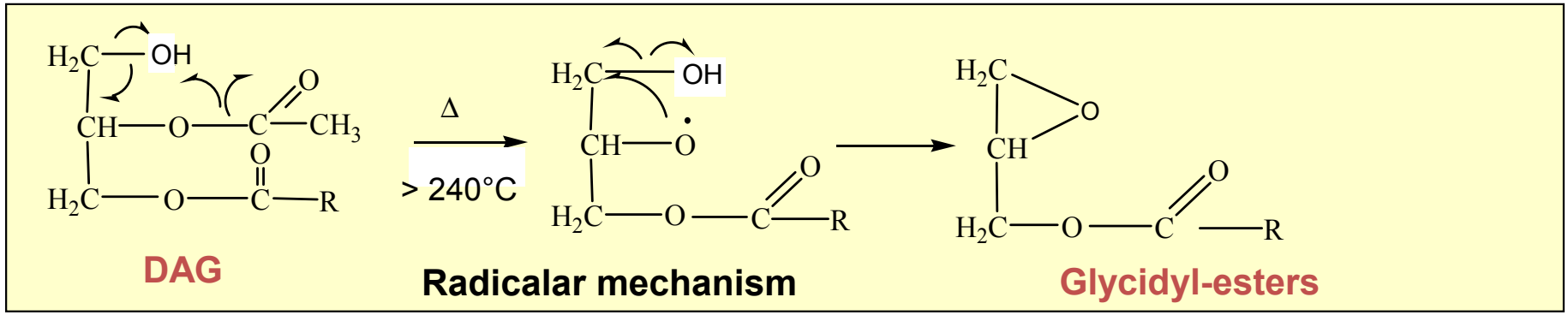
Glycidyl Ester Formation during Oil Refining



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

Palm oil and Rice Bran Oil are sensitive for glycidyl ester formation

- High DAG content (6-8%) for both oils
- Palm oil : high deodorization temperature (260°C)
- Rice bran oil : 235-240°C (chemical ref.) - > 240°C (physical ref.) during long time

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

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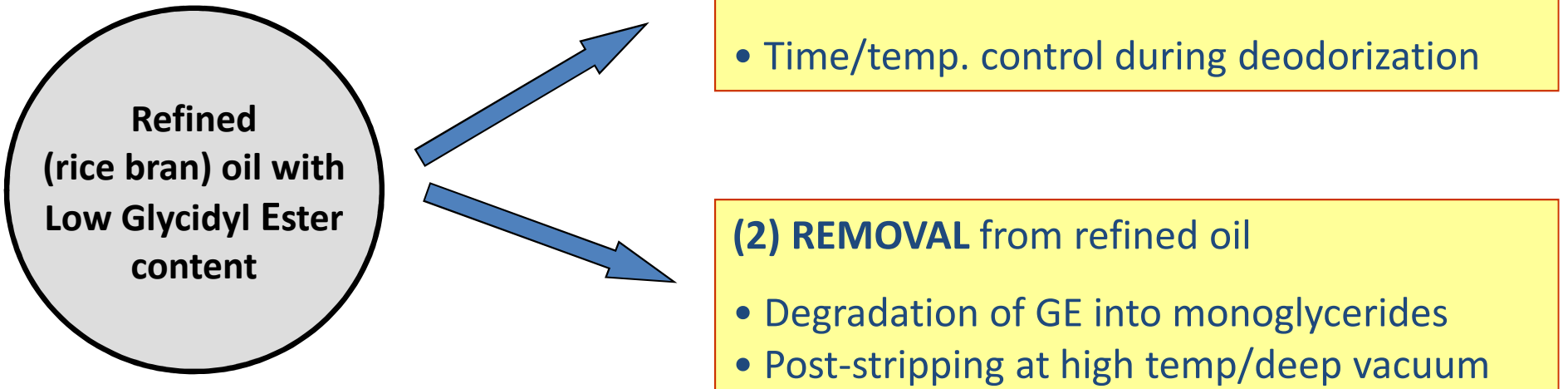
Mitigation of Glycidyl Esters during Rice Bran Oil Refining

TARGET



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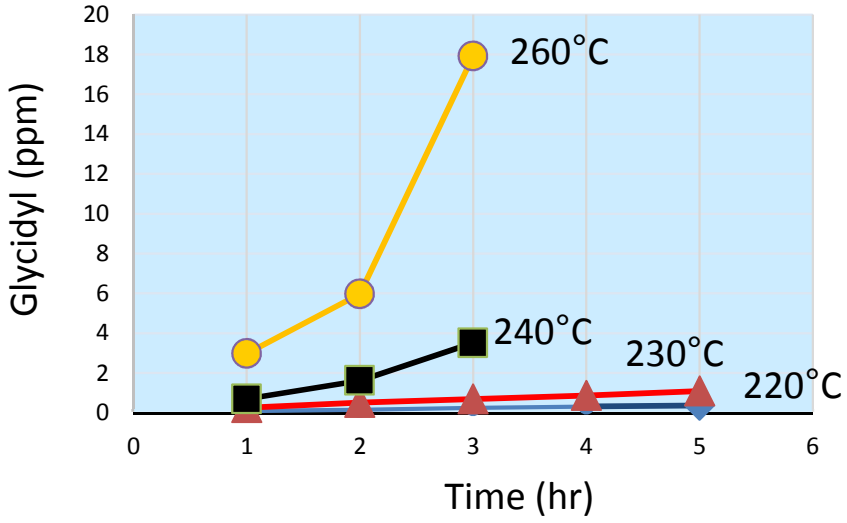
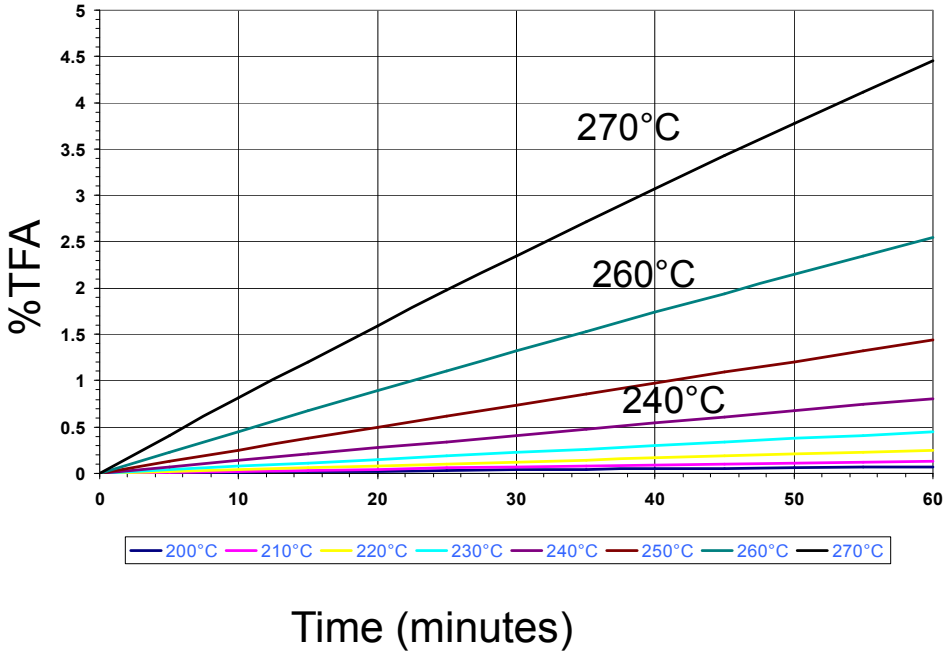
Minimize GE Formation during Refining

Glycidy Ester formation (palm) ⟷ ***Trans* formation (soy oil)**





Almost no GE formation at T < 230°C but very fast GE formation at T > 240°C

Time/temperature during deodorization is critical for low GE

Same approach as for the production of refined soft oils with low *trans* FA

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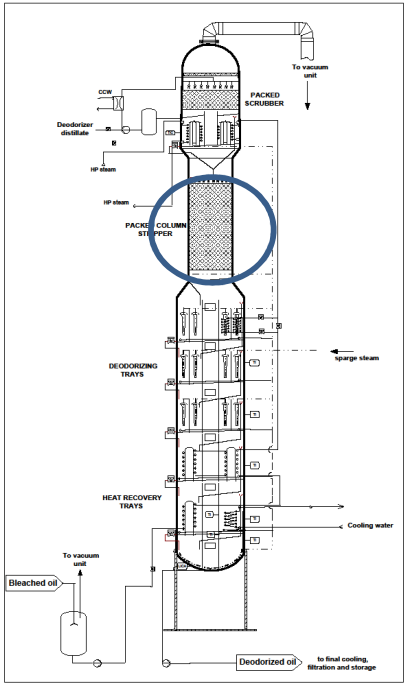
Packed Column Stripping of Bleached palm oil

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

No GE in bleached (palm) oil



Short residence time at high(er) temperature gives

- Almost no formation of GE during packed column stripping, even at T > 240°C
- Very efficient FFA stripping but only limited heat bleaching

→ Possible/Logical first stage of the deodorization process

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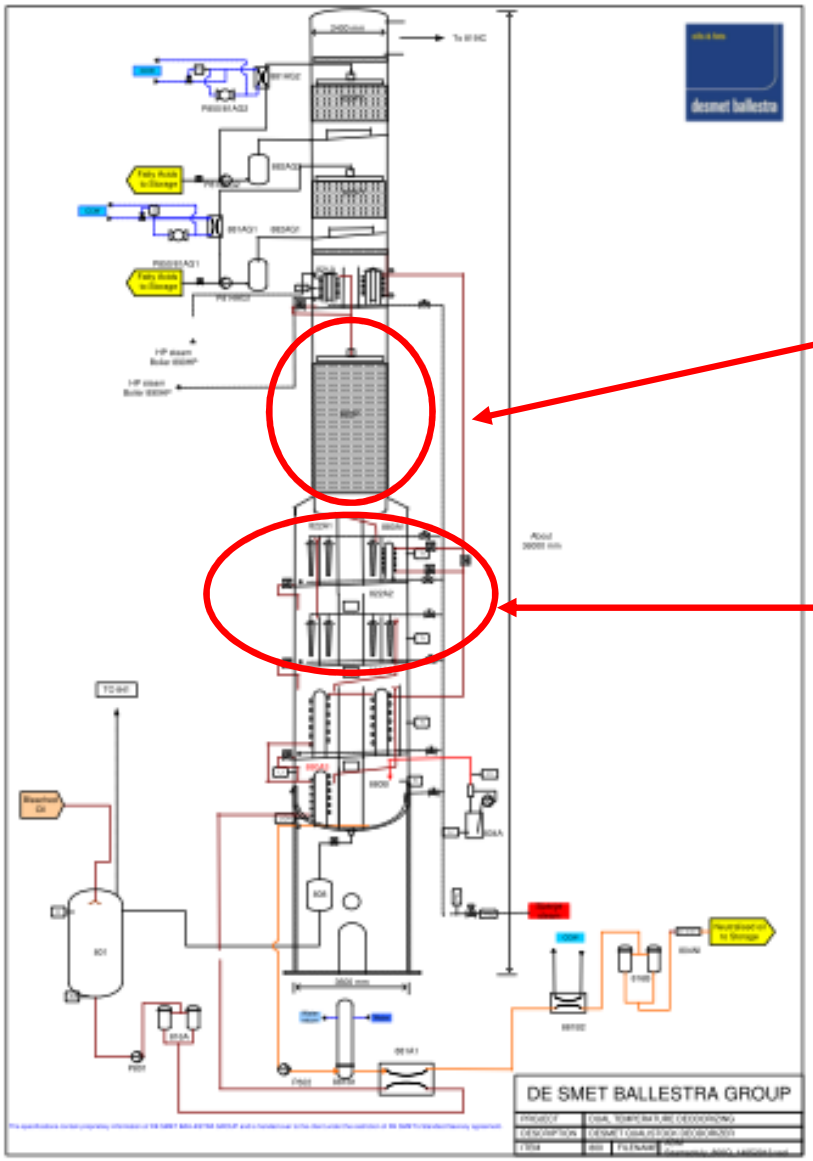
Dual Temperature Deodorization for low GE



Dual Temp Deodorization

- Packed column stripper followed by tray type deodorizer

Packed column stripper

- Short residence time
- High temperature (240-245°C)
- FFA stripping

Tray type deodorizer

- Longer residence time
- Lower temperature (220-225°C)
- Heat bleaching/deodorization

Deep vacuum (< 2 mbar)

- For GE stripping
- Closed loop with chilled water
- Ice condensing

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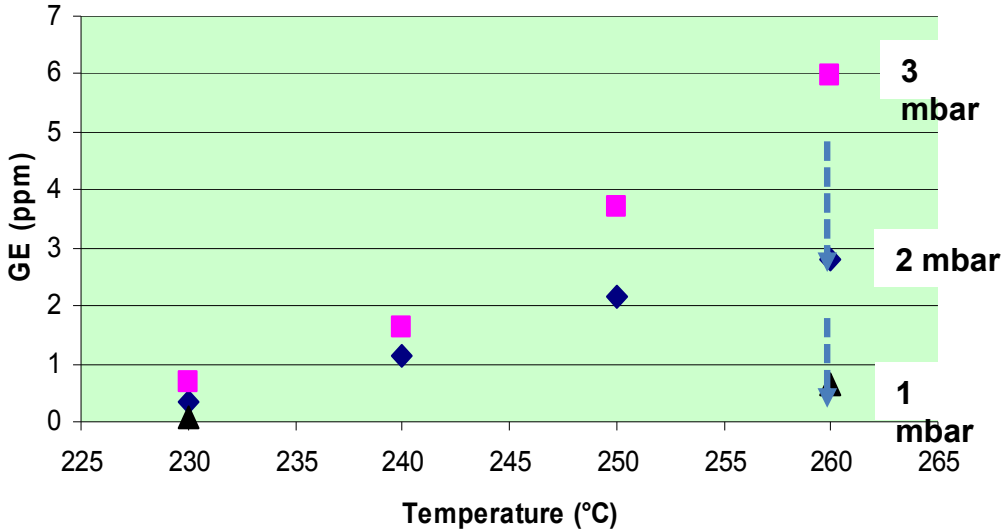
Glycidyl Esters can be stripped during Deodorization ?

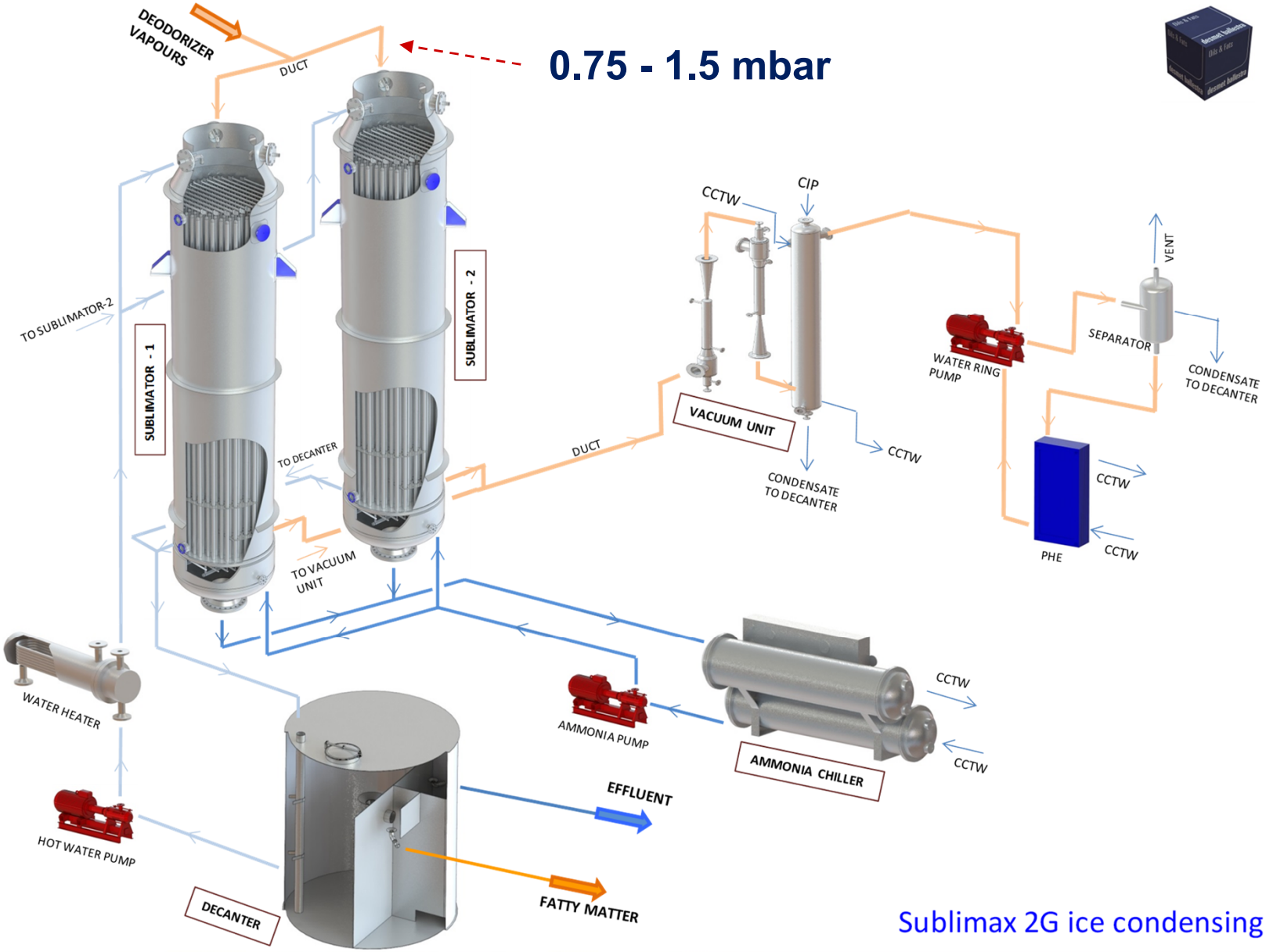


Lab Data

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

- Stripping requires lower pressure (deep vacuum)
- More GE are stripped at high temperature (but then also more GE are formed)
- Under 'normal' deodorizing conditions : formation > stripping
- Best strategy is therefore to **avoid first of all formation (temp. < 240°C)**

SUBLIMAX 2G Ice Condensing



Sublimax 2G ice condensing

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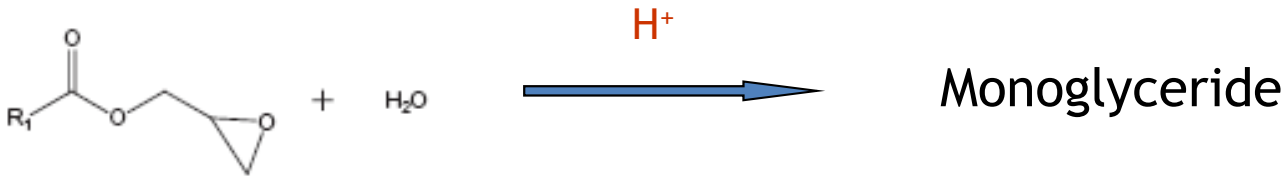
Removal of Glycidyl Esters from Refined Oil

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 efficient way to get GE < 0.5 ppm in RBD Palm Oil

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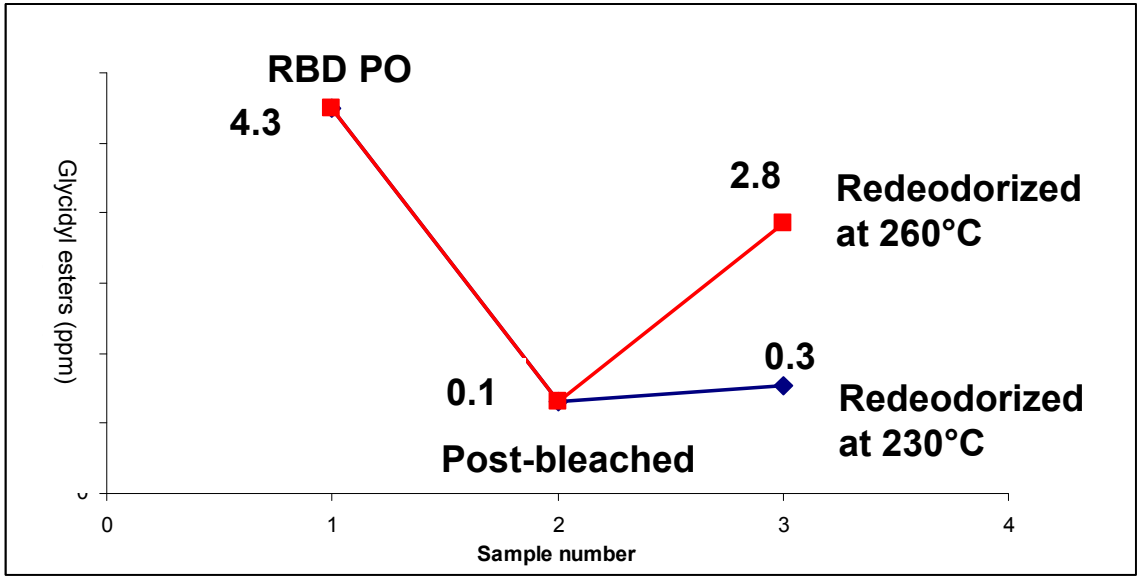
Removal of Glycidyl Esters from Refined Palm Oil



Lab Data

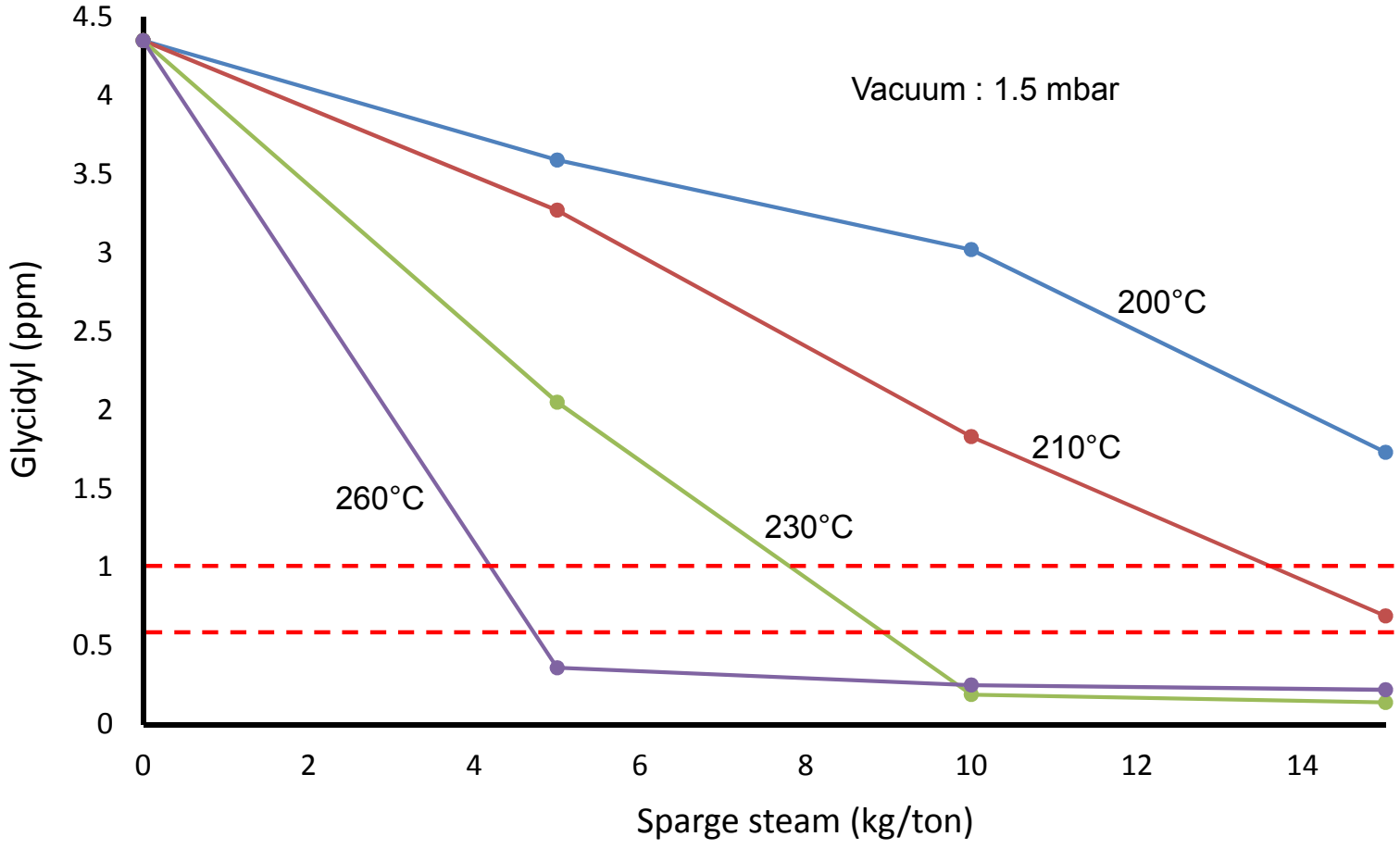
Post-bleaching : 0.5% Activated BE, 110°C, 30 min.

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

Glycidyl esters may again be formed during post-deodorization

→ *low deodorization temperature required*

Stripping of Glycidyl Esters from RBD (palm) oil



Glycidyl esters can be stripped from RBD oil, but also monoglycerides and tocopherols will be stripped

Mitigation of Glycidyl Esters during Rice Bran Oil Refining

What are the options ?

(1) Minimize formation of GE during deodorization

- (a) Standard deodorization (T < 240°C; time < 90 min)
- (b) Dual temp. deodorization/ normal vacuum (3 mbar)

GE < 1 ppm

- (c) Dual temp. deodorization/ deep vacuum (1.5 mbar)

GE < 0.5 ppm

(2) Remove GE from refined oil (= post-refining)

- (a) Post-bleaching (with ABE)+ mild post-deodorization
- (b) Post-stripping @ deep vacuum

GE < 0.5 ppm

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