MOSTA
Malaysian Oil Scientists' & Technologists' Association

Glycidyl Ester Development: Holding Glycidyl Ester (GE) in Check

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Mitigating Process Contaminants during Palm Oil Refining: How to Prevent the Formation of GE and How to Eliminate GE Once Formed

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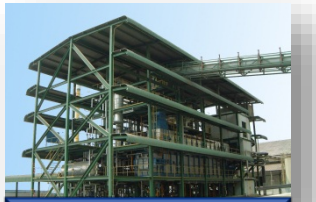
World Leading Specialist in Oils, Fats & Oleochemicals


Oilseeds


Preparation


Extraction


Animal Feed


Crude oil


Refining


Edible fats


Fatty acids
Fatty alcohols


Oleochemicals &
Biodiesel


Edible oil


Fat
Modifications

Biodiesel

Glycerine

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Global Coverage: Efficient Customer Service

Date of creation	Employees	Annual Turnover	Number of projects managed
1946	**1,200**	**500 M €**	**Over 25,000 plants/process sections**

Research & Development Centers	Worldwide Reputation and Presence
Belgium, Italy, France, United Kingdom	**21 Fully owned offices close to you**

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Innovation through R&D: Backbone of Leading Technology

U.K.

Belgium

France

Malaysia

Argentina

R&D centers

Pilot facilities

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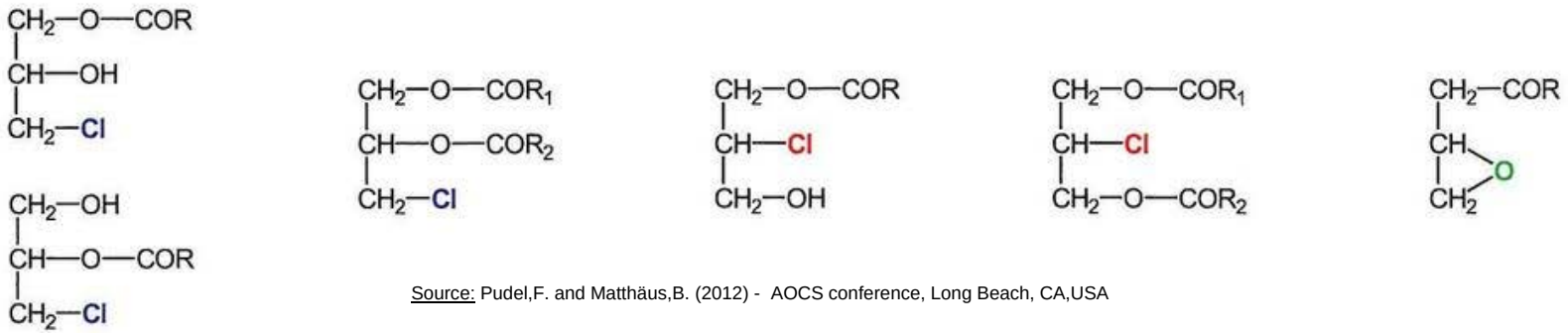
Challenge for Food Oils: 3-MCPD and Glycidyl Esters

3-MCPD		2-MCPD		Glycidyl esters
Monoesters	diesters	monoesters	diesters	



Source: Pudel,F. and Matthäus,B. (2012) - AOCS conference, Long Beach, CA,USA

* 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/GE in refined food oils
* Efficient mitigation strategies were developed and are industrially applied

Limits for GE and 3-MCPD

EU Regulatory Limits		
	3-MCPD	GE
Vegetable oils (incl. palm)	2.5	1.0
Vegetable oils (for use in infant food)	0.75	0.5

GE/3-MCPD esters are mainly issue for palm oil

Analysis of commercial oils (purchased in supermarket – 2016)

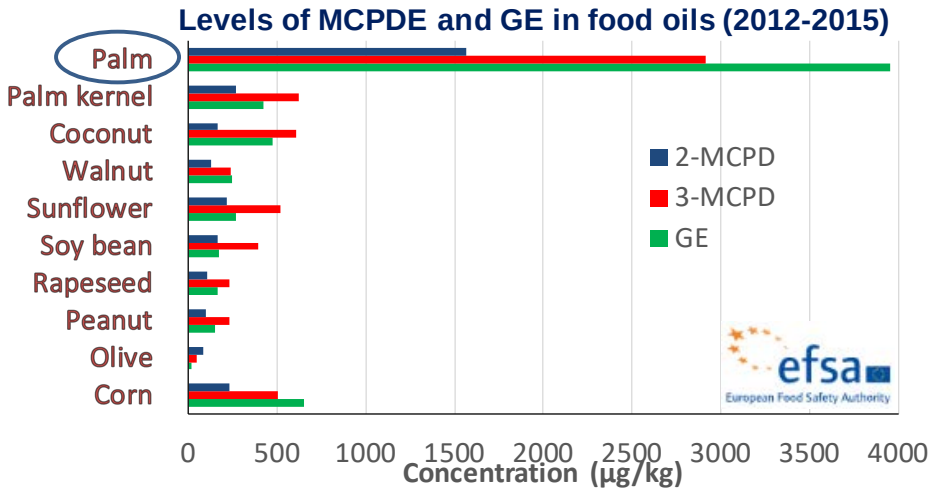
Oil	Glycidyl (ppm)	3-MCPD (ppm)	DAG (%)
Rapeseed	0.12	0.21	0.40
Sunflower	0.30	0.54	0.65
Coconut	0.25	0.54	N.A.
Corn	0.54	0.68	2.12
Soya	0.35	0.55	0.40
Palm	1.03-7.5	0.15-13.7	4-10

(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)

3-MCPD & GE: High Levels in Palm Oil



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

Highest levels of 3-MCPD esters and GE are found in palm oil

3-MCPD esters ≠ Glycidyl Esters

Mean Concentration (ppm) in 2015		
Oil	3-MCPD	GE
soybean	0.4	0.2
rapeseed	0.2	0.2
palm	3	4

Main precursors

3-MCPDE ← "Chlorine"

Main precursors

GE ← "DAG"

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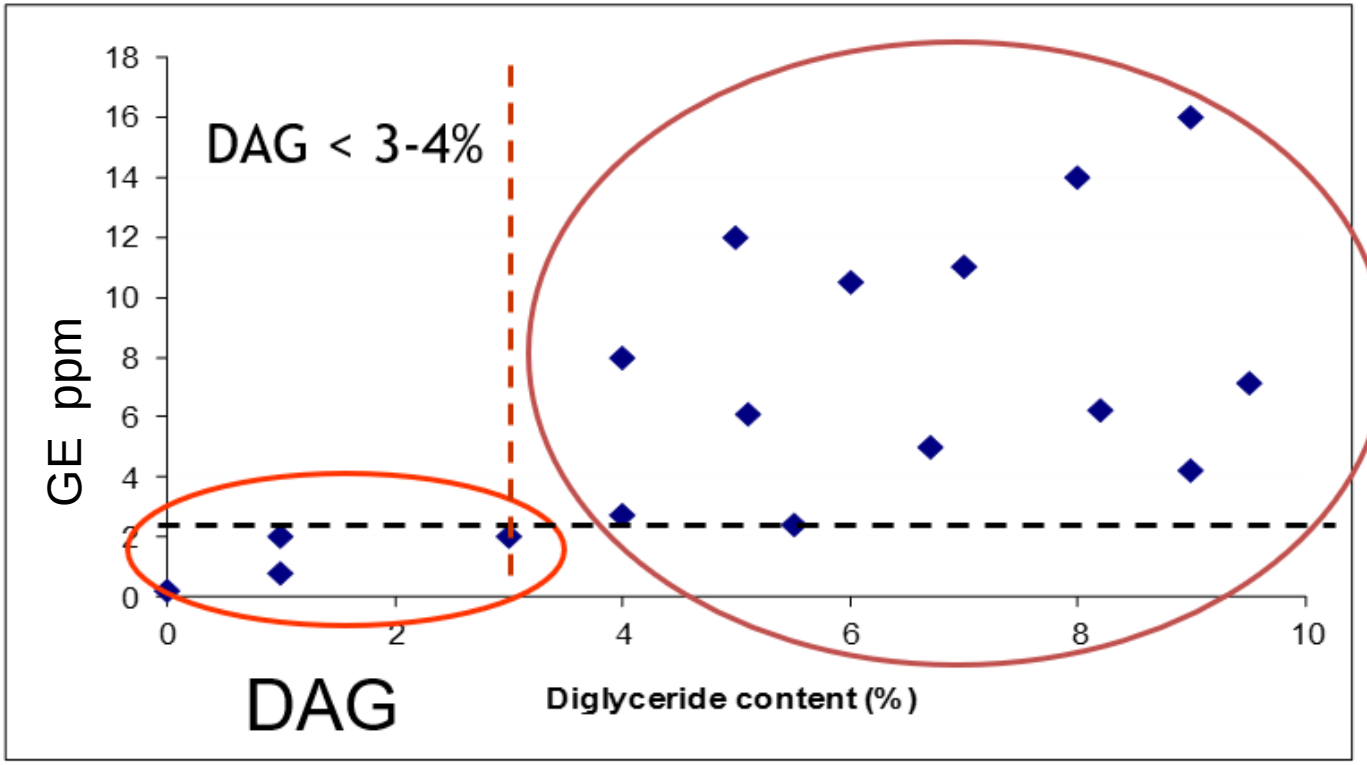
3-MCPD Esters ≠ Glycidyl Esters

	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 alkaline Not volatile	Conversion to MAG with strong acid (BE) Volatile

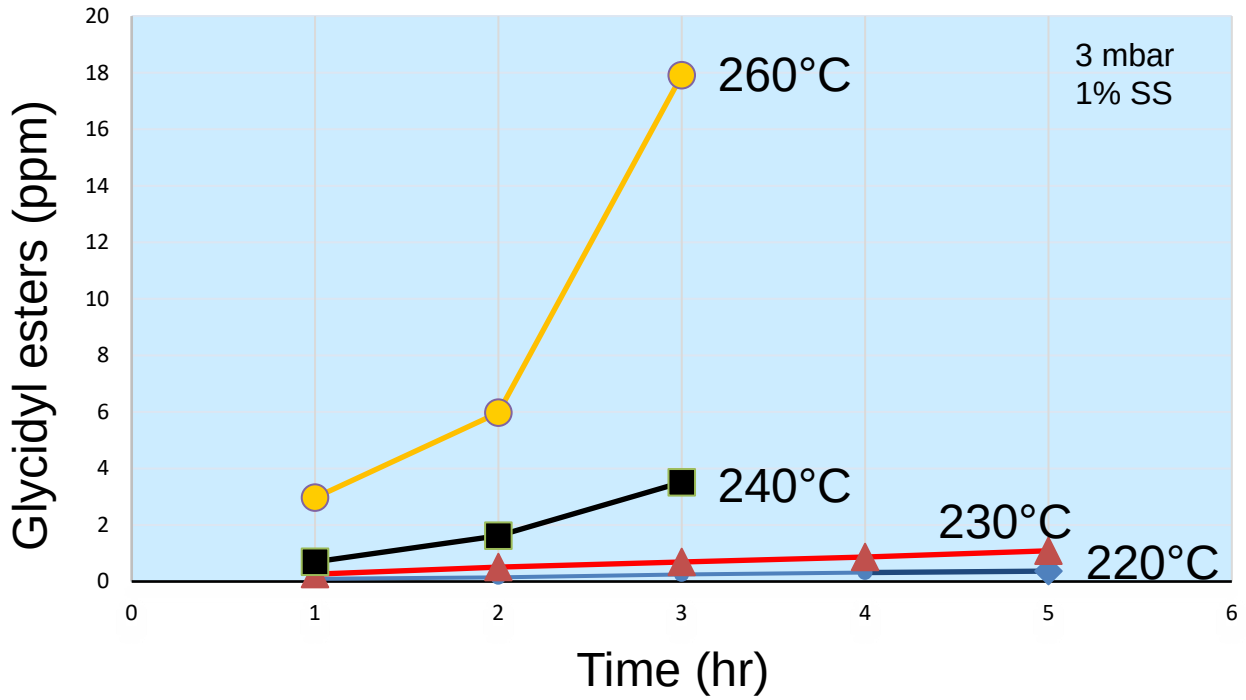
Different mitigation strategies for 3-MCPD esters and GE

Low DAG in CPO – Low GE



Palm Oil, deodorized at 260°C

GE Formation: Effect of Time and Temperature



Net GE formation at 260°C : ≈ 8 ppm/hr (= ≈ 0.13 ppm/min.)

Net GE formation at 220°C : ≈ < 0.1 ppm/hr

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

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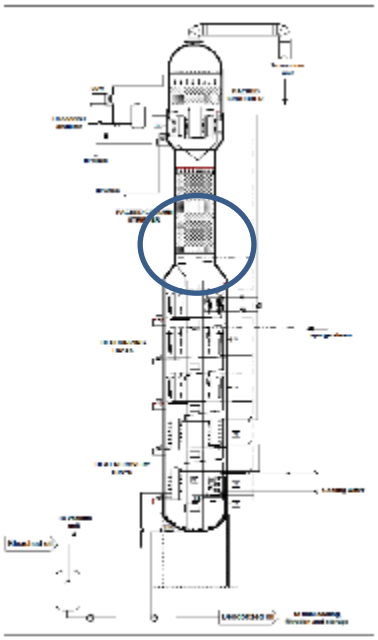
GE Formation: Effect of Packed FFA Stripping Column

10 min, 0.5% SS

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

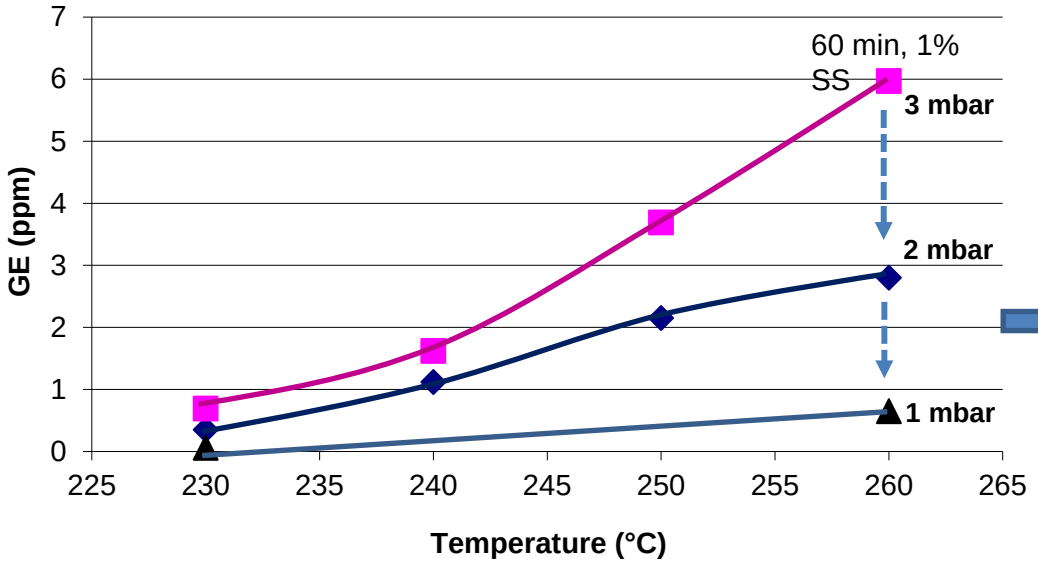


Short residence time at high(er) temperature gives:

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

→ **Dual temp high temp fast stripping / low temp mild deodorisation**

Can GE be Stripped During Deodorization ?



The lower the P, the higher the NO losses (MAG, DAG, Toco)

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

- Stripping will only be significant at higher temperature/lower pressure

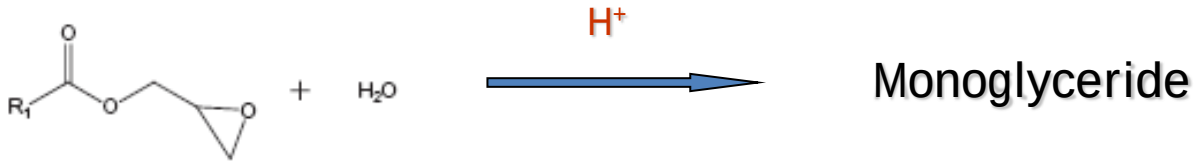
- Under 'normal' deodorizing conditions: formation > stripping

- Best strategy is therefore to limit formation (temp. < 240°C)

- Best compromise: strip at high T (250-260°C) , deodorise at low T (230-240°C)

Glycidyl Esters can be 'removed' 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 very efficient approach to get GE << 0.5 ppm in RBD Palm Oil (Fractions)

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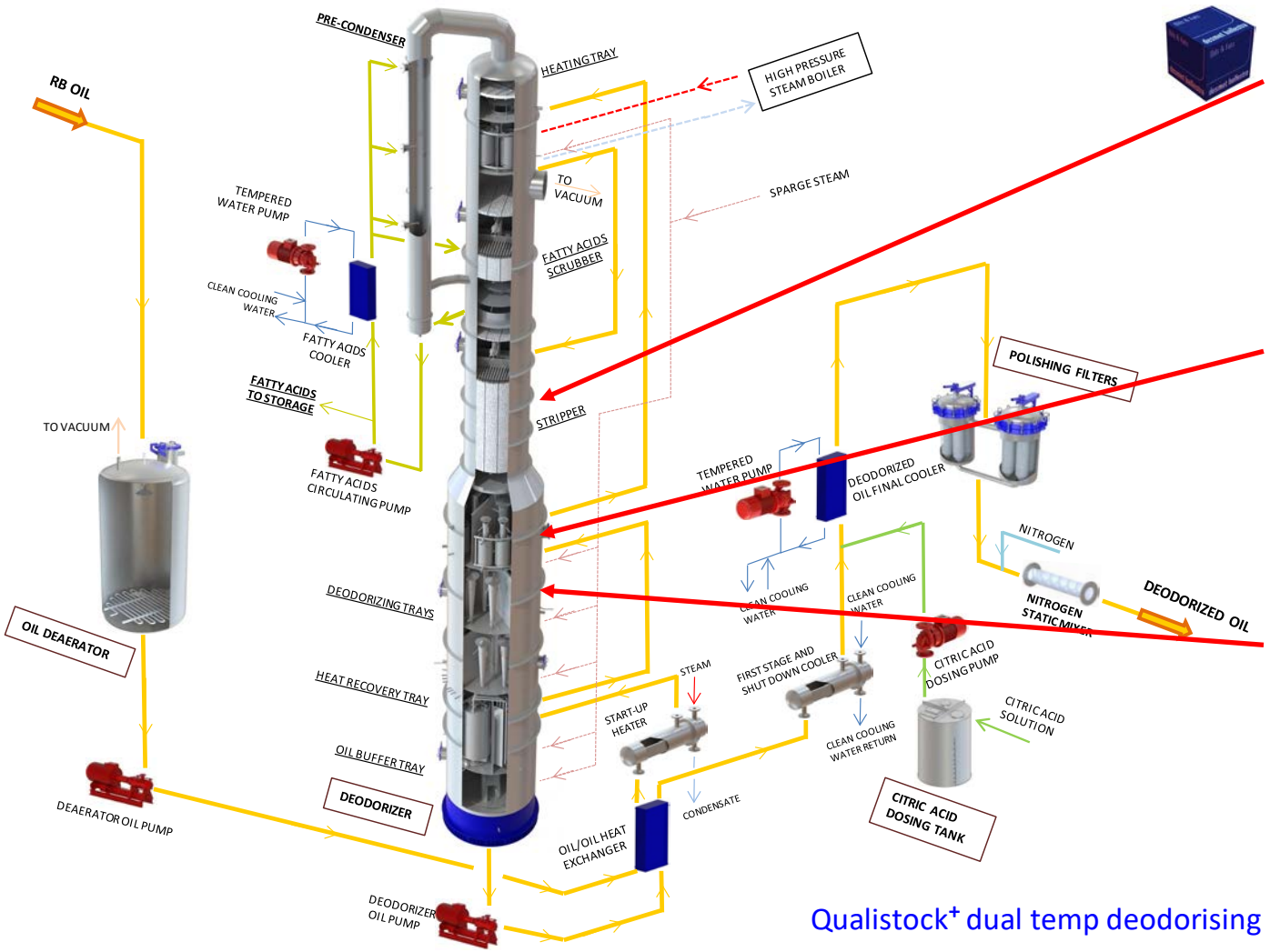
Current Strategies for GE Mitigation

GE Mitigation 1: Qualistock+™ Dual Temperature Deodorisation



Qualistock+ dual temp deodorising

Integrated Packed column stripper

- Short residence time
- High temperature FFA stripping

Dual Temp Deodorization

- Packed column stripper followed heat recovery to lower temperature

Tray type deodorizer

- Longer residence time
- Lower temperature
- Heat bleaching/ deodorization

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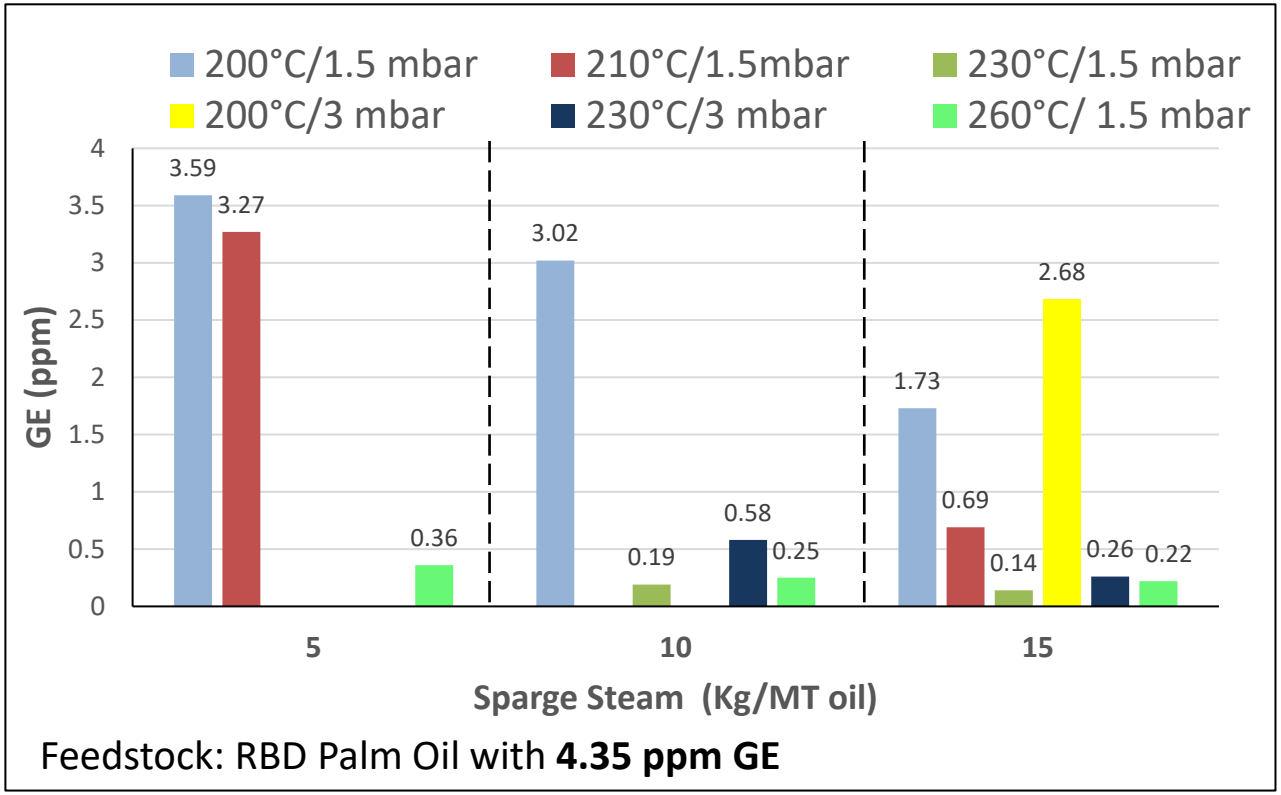
GE Mitigation 1: Qualistock+™ Dual Temperature Deodorisation

		Single Temperature	Dual Temperature
Temperature	**°C**	265	230 – 215
Sparging Steam	**%**	0.6	1.2
Deodorising Retention Time	**mins**	60	120
FFA	**%**	0.06	0.04
Colour	**R**	2.3	2.3
GE	**ppm**	**4.81**	**0.36**

Industrial Data

GE Mitigation 2: Stripping of GE from Refined Palm Oil



Feedstock: RBD Palm Oil with **4.35 ppm GE**

- ***Not enough GE Stripping at 200°C***
- ***More than 95% of the GE can be stripped when using proper stripping conditions***

Level of vacuum will have big impact on GE Stripping

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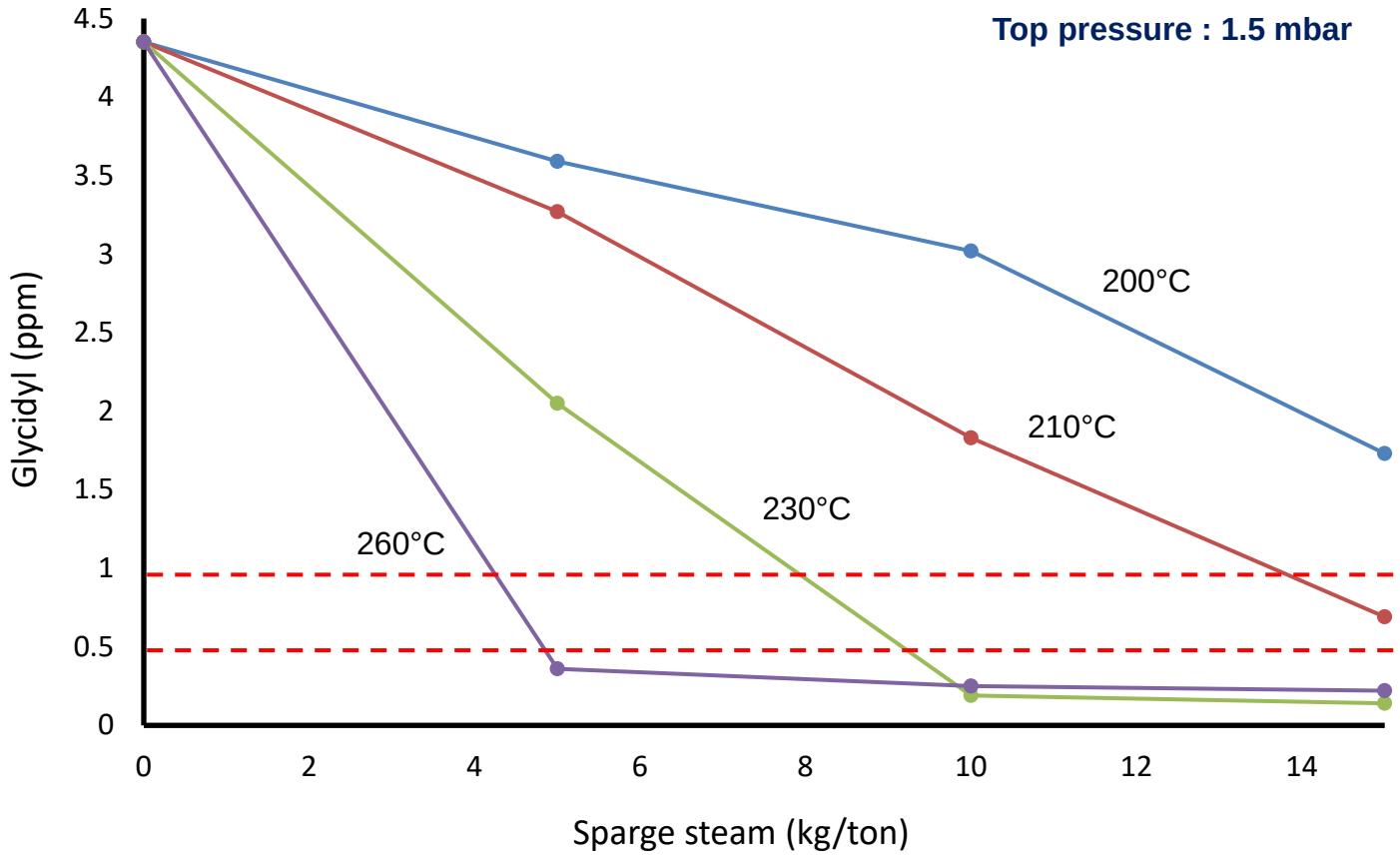
GE Mitigation 2: Post Stripping



GE Post-stripping will not only reduce GE, but will also create additional losses as other components will also be stripped (Toco, MAG, …)

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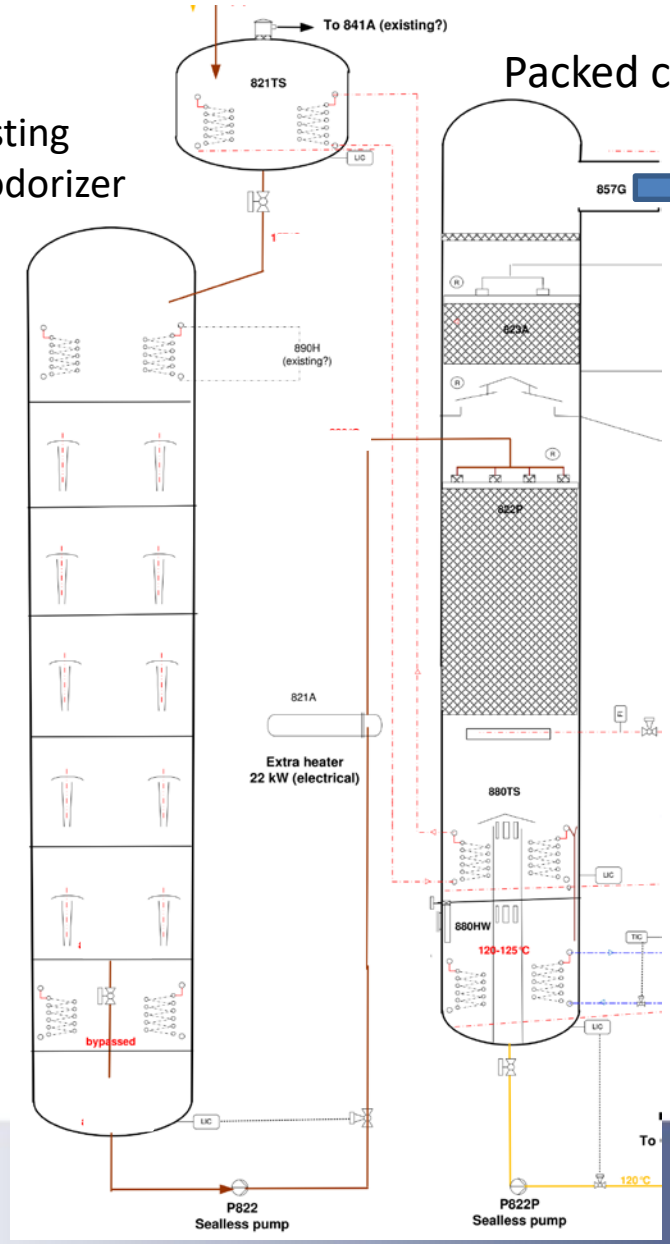
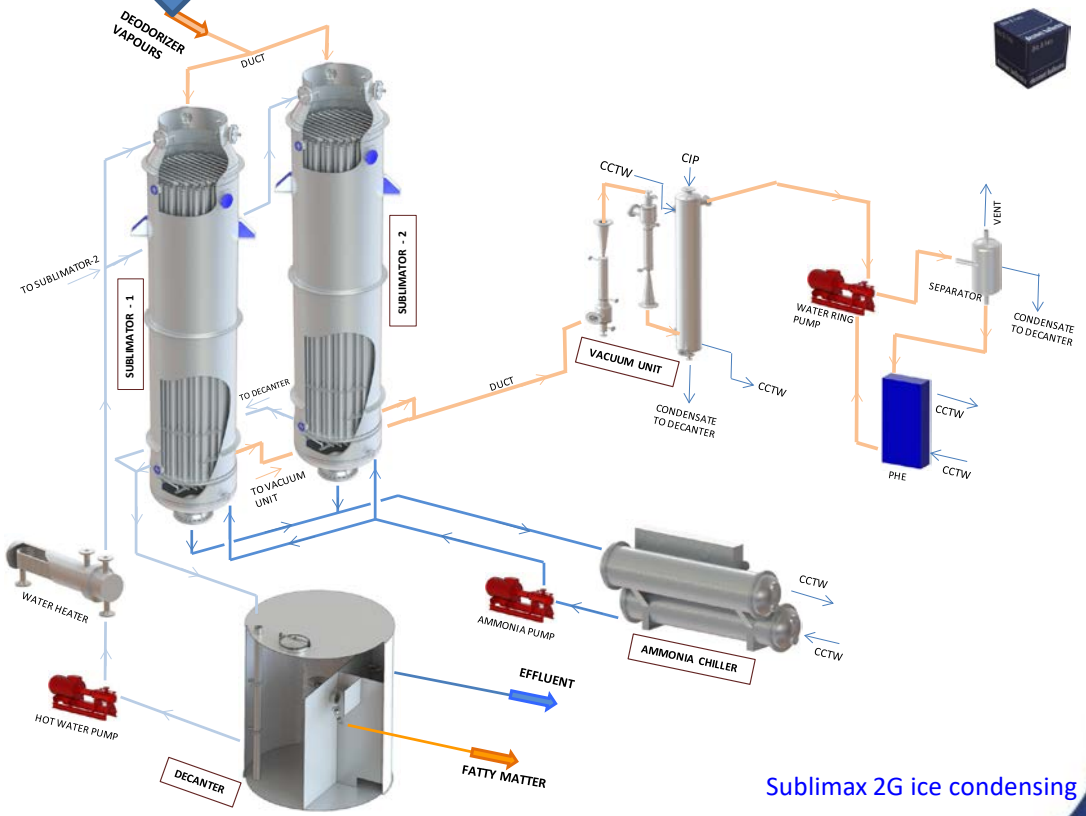
Stripping of GE from Refined Oil

Existing deodorizer



Packed column for GE post-stripping

Ice condensing for deep vacuum



Sublimax 2G ice condensing

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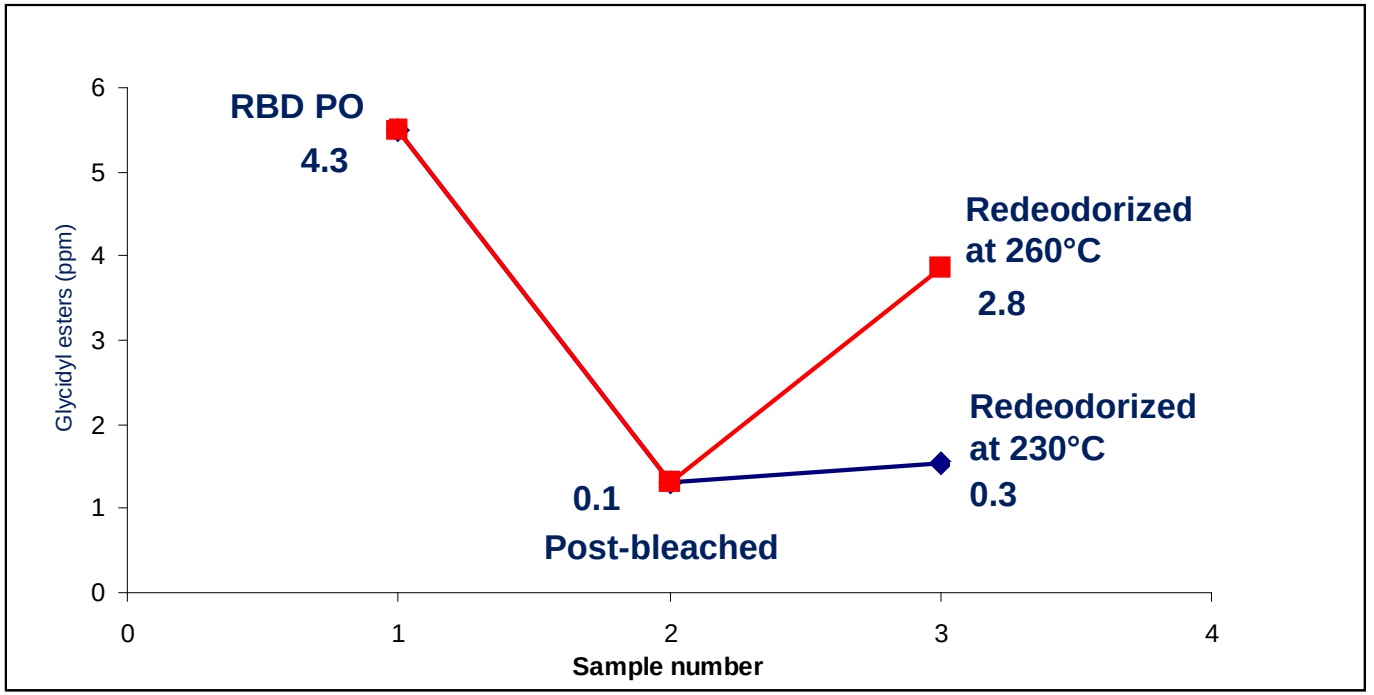
GE Mitigation 3: Mild Post Refining



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

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

Attention! GE may again be formed during post-deodorization

→ **low deodorization temperature required**

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GE Mitigation 3: Mild Post Refining

		RBDPO (Feed)	2nd Bleached PO	2nd Deodorised PO
Phosphoric Acid Dosage	**%**	-	0.05	-
Bleaching Earth	**%**	-	1 – 1.3*	-
Temperature	**°C**	-	105	210
Retention Time	**mins**	-	30	30
Sparging Steam	**%**	-	0.3	0.45
FFA	**%**	0.06 – 0.08	-	0.02 – 0.03
Colour	**R**	2.9	-	2.1 – 2.5
GE	**ppm**	**8**	**Not Detectable**	**0.15 - 0.40**

* BE dosage of 1.3% was mainly due to colour reasons. Required consumption for breaking down GE is lower.

Industrial Data

Desmet Ballestra Sublimax™ 2G

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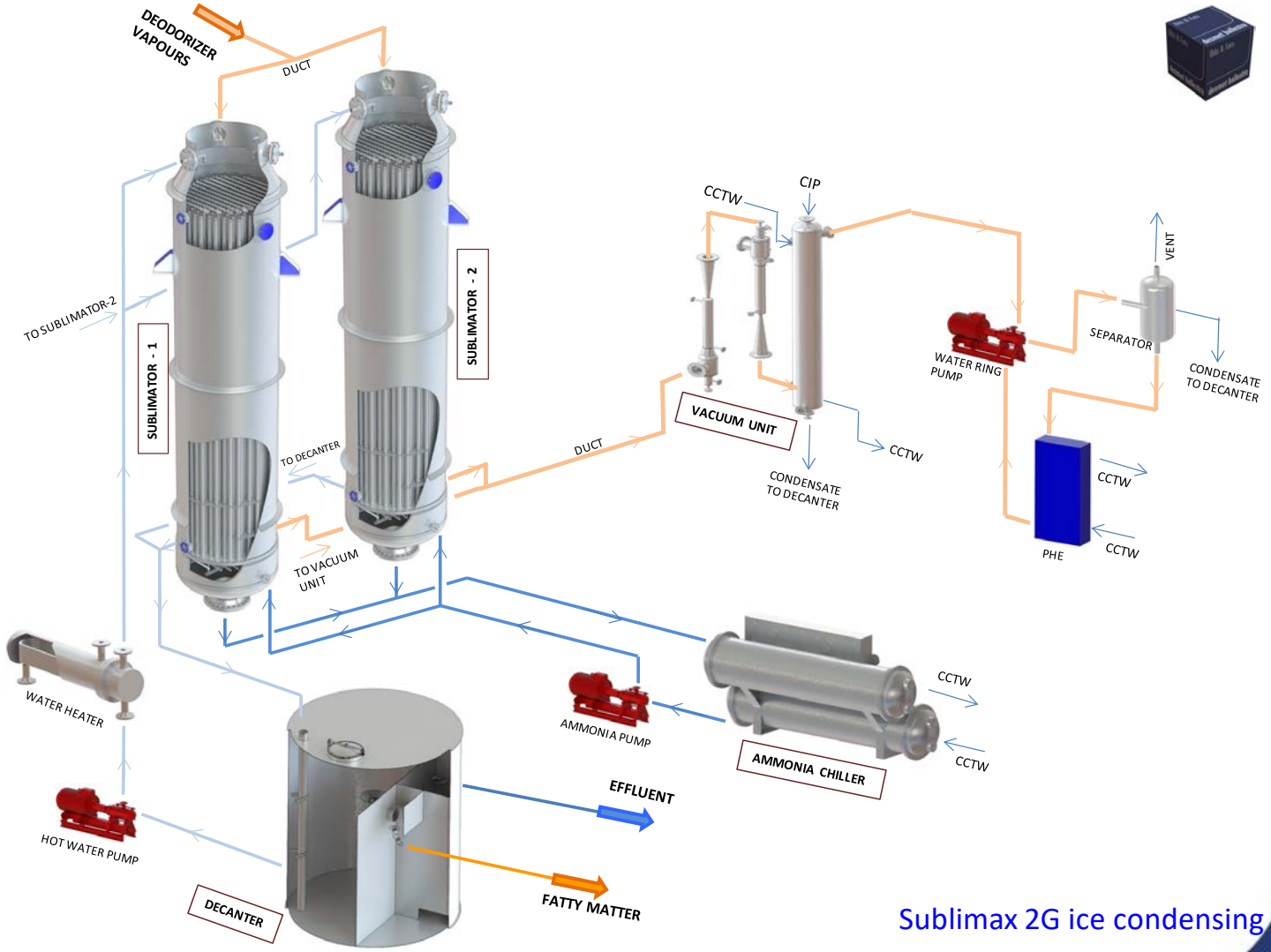
Desmet Ballestra Sublimax™ 2G



Sublimax 2G ice condensing

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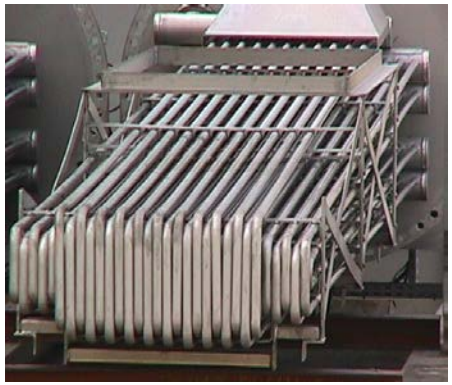
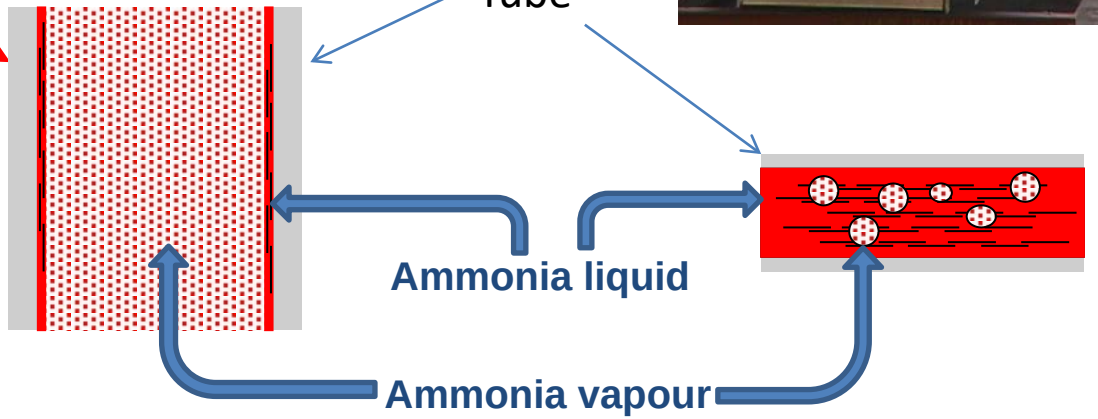
Desmet Ballestra Sublimax™ 2G

Sublimax: Vertical, with
Falling film ammonia evaporation

Classical: Horizontal, with
convective boiling liquid tubes





NH_3 mass: <100 kg

NH_3 mass: >>100 kg

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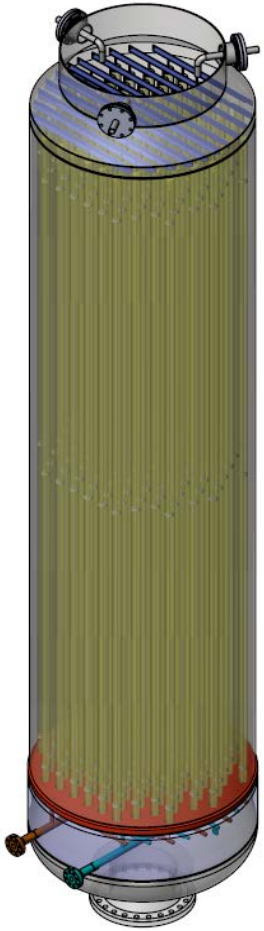
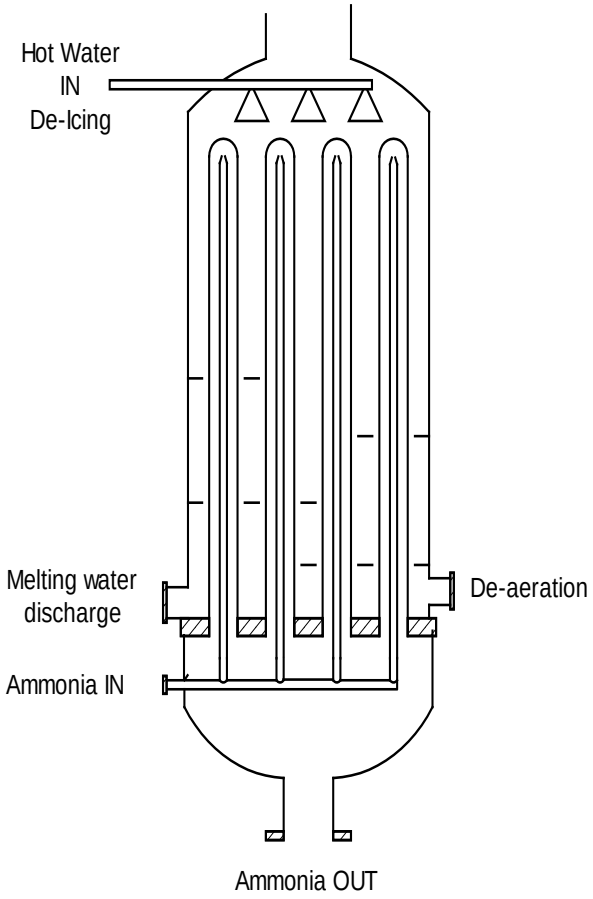
Desmet Ballestra Sublimax™ 2G





Main Advantages

- Effective heat transfer with falling film evaporation
- Low ammonia hold up in system
- Reduced heat loss during melting
- Reduced chiller peak load and electricity consumption
- Reduced motive steam and cooling water consumption for deaeration group
- Efficient cleaning with hot water spraying
- Self draining of refrigerant and melted ice
- Minimal welding joints
- Free vertical expansion of tubes

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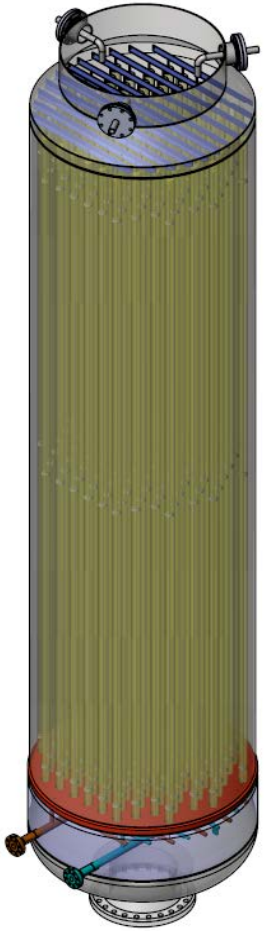
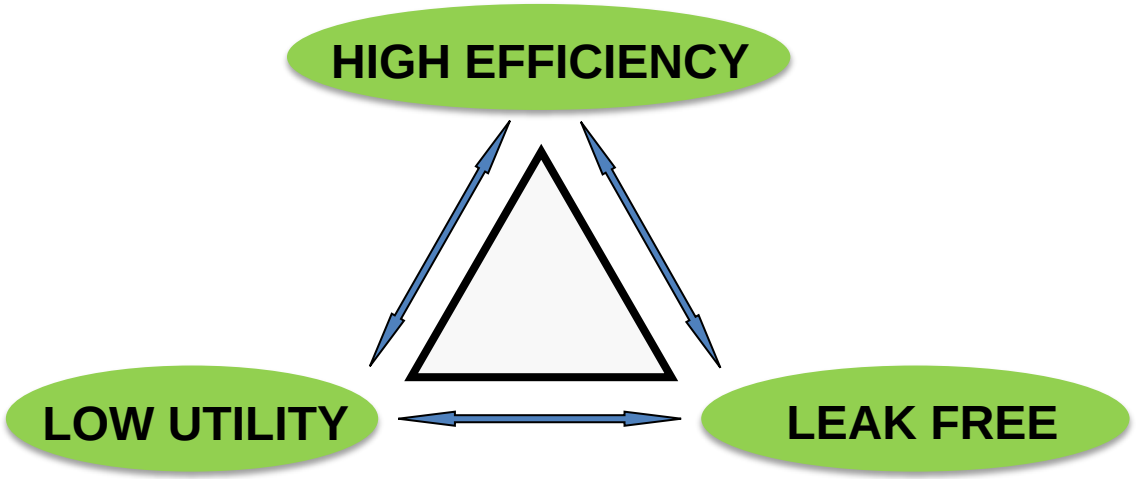
Desmet Ballestra Sublimax™ 2G



	Desmet Ballestra	Conventional
Suction Pressure (mbara)	2.0	2.0
Suction Temperature (°C)	8	8
Water Vapour (kg/h)	300	300
Air (kg/h)	8	8
FFA (kg/h)	5	5
Chiller Power (kW)	140	180
Steam Eq. for Melting (kg/h)	100	110
Motive Steam (kg/h)	133	180
Cooling Water (m3/h)	108	154

Desmet Ballestra Sublimax™ 2G

	Sublimax®	Horizontal
Freezing times	Long	Short
Energy consumption	Minimal, stable	Higher, with peaks
Drainage NH_3	Gravity	None
Ice removal tubes	Effective	Poor
Ammonia leakage risk	Negligible	Yes
Mass NH_3	Very low	High



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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

Technological Breakthrough with Continuous R&D

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Thank You for Your Attention

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