3-MCPD esters formation in vegetable oil refining. Current state of knowledge

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Informationsveranstaltung 3-MCPD- und Glycidyl-Fettsäureester in Lebensmitteln von BLL und OVID
(Berlin, 25 January 2010)

BLL
Bund für Lebensmittelrecht und Lebensmittelkunde e.V.

OVID
VERBAND DER ÖLSAATEN-VERARBEITENDEN INDUSTRIE IN DEUTSCHLAND

Outline

1. Background info

2. Refining process

3. 3-MCPD formation during refining

3-MCPD esters in food (a brief history)

- 1978-1980: free 3-MCPD identified in vegetable protein hydrolysates (Velisek et al.)
  → free form monitored/regulated in **HVP / soy sauces**

more than 20 years later... an occurrence of 3-MCPD esters reported:

- 2004: in **fried food** (Svejkovska et al.)
- 2006: in **vegetable oils** (Zelinkova et al.)

- Nov 2007: BfR calls for reducing the levels in infant formulas, margarines and deep-frying fats

- Jan 2008: FEDIOL established "3-MCPD working group"
  - Study 2008: carried out, results presented at various occasions
  - Supporting other research activities
  - In contact with authorities and other industries

FEDIOL
The EU Oil & Proteinmeal Industry

Occurrence of 3-MCPD esters in edible oils

- **Crude oils:**
  - usually below LOQ
- **Refined oils:**
  - typically 0.5–6 mg/kg
- **Various oils differ in 3-MCPD ester content:**
  - low level: sunflower, rapeseed, soybean
  - medium level: maize, olive
  - higher level: palm
- **However, ...**
  - large variation even within single type of oil reported
  - uncertainty probably given by:
    - origin of the oil
    - processing conditions (bleaching/deodorization)
    - analytical methodology

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   G. v. Duijn "The Effect of the Refining Process Conditions on Contaminant Removal and Side Reaction Products Formation", Euro Fed Lipids, Graz 2009

3. 3-MCPD formation during refining

Minor components in crude oils – effect on quality

Minor component	Origin	Quality effect
Free Fatty Acids	Hydrolysis	Off-taste, smoke during frying
Peroxides	Oxidation	Off-taste
Phosphatides	From cell membranes	Burns at high temperature
Moisture	From oil crop, transport & storage	Components in free water
Dirt	Oil crop and harvest residues	Appearance
Taste & odour	From oil crop	Not matching with product taste
Metals	Soil, milling storage & transport	Catalyst for oxidation

Contaminants in crude oils – effect on health

Contaminant	Origin	Health effect
Heavy metals	Soil, milling storage & transport	Toxic
Poly Aromatic Hydrocarbons	Drying of oil crop	Carcinogenic, genotoxic
Pesticides above MRL	Crop protection chemicals	Toxic (ADI ≈ 100 x MRL)
Dioxins	Environmental polution	Highly toxic
Mycotoxins	Mould or fungus	Toxic
Mineral oil	Process, storage, transport	Toxicity depends on chain length
Residues previous cargoes	Overseas transport	Depends on component

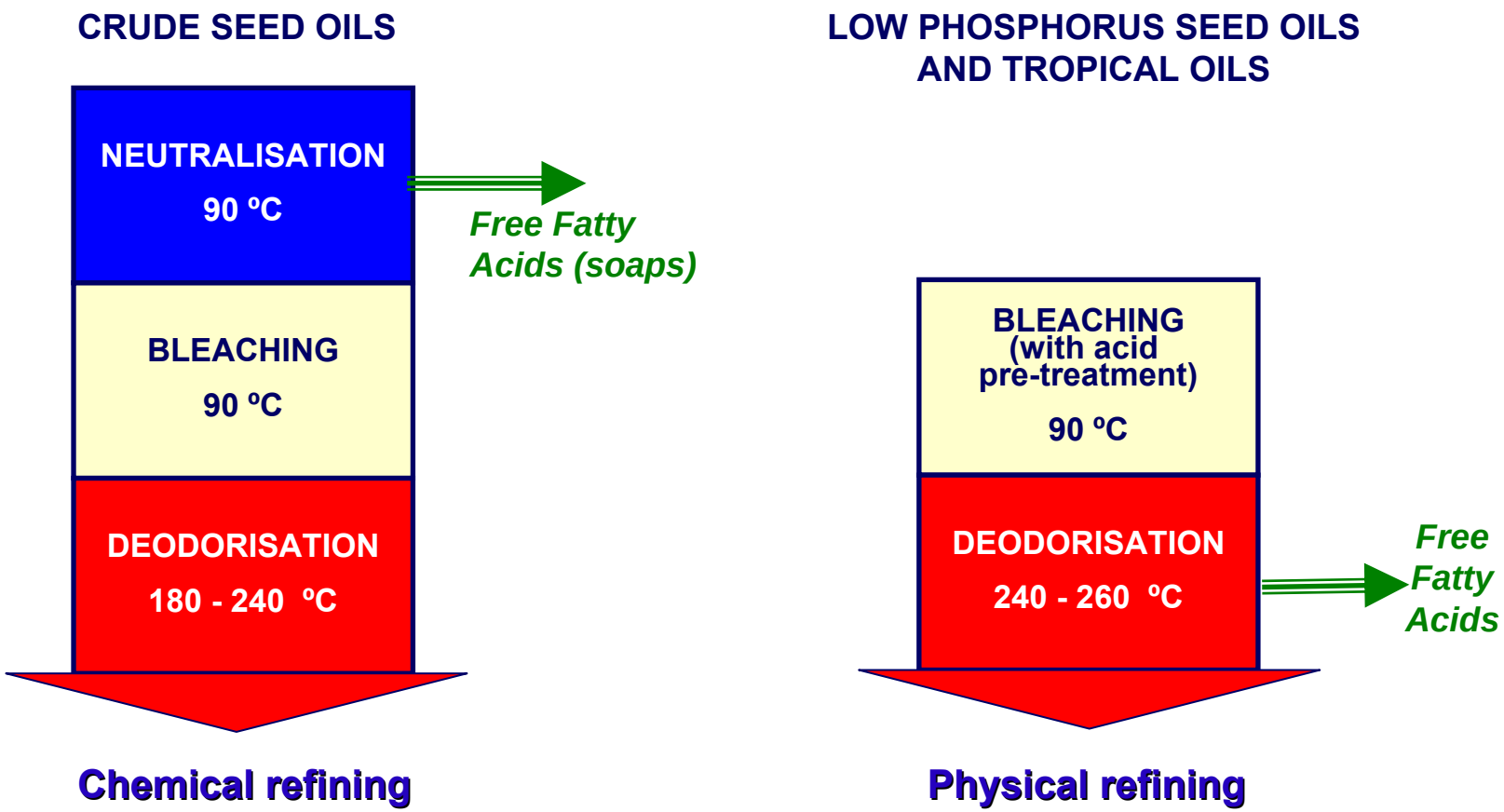
Crude Oil Risk Matrix*

	Pesticides	PAH	Mineral oil in edible oil imported in EU	Previous Cargoes in sea going vessels	Dioxins and PCB's	Aflatoxins	ZEN
EU LIMIT	**> MRL**	**BaP> 2 ppb**	**Fediol CoP**	**EC/4/2004**	**EC/1881/2006**	**EC/1881/2006**	**> 400 ppb**
Soybean oil							
Sunflower oil							
Rapeseed oil							
Corn oil							
Palm oil							
Palm kernel oil							
Coconut oil							
Groundnut oil							
Fish oil							
Linseed oil							
Cottonseed							
Grape seed							
Olive							

	Occurrence	Monitoring frequency:
high risk	Regularly (> once a year)	Every batch
medium risk	Occasionally (every 1-5 years)	Minimum once per quarter
low risk	Seldom (< once every 5 years)	Maximum once per quarter
regulated	Not applicable	Every batch (FEDIOL CoP)

* based on supply chain assessment and data of crude oil analysis (Unilever, 2001-2006)

Refining process



Refining link table – Impurities

Impurities	Free Fatty Acids	Peroxides	Phosphorus	Dirt	Metals	Taste	Colour
Crude oil reception							
Degumming							
Neutralization							
Bleaching							
Deodorization							

= *Chemical refining*

= *Physical refining*

= *Both chemical and physical*

Refining link table – Contaminants

Contaminants	Hydrocarbons < C20	PAH (BaP)	Pesticides	Aflatoxin B1	Zearalenone	Previous cargoes
Crude oil reception						
Degumming						
Neutralization					93%	
Bleaching					77%	
Deodorization						

= *Chemical refining*

= *Physical refining*

= *Both Chemical and Physical*

= *Must be on Fosfa/EU list*

Refining side reaction products – effect on health

Side reaction product	Origin	Health effect
Trans Fatty Acids	High temperature deodorization (>230°C)	Increases LDL and decreases HDL
3-MCPD esters	Deodorization	Related to toxicity of free 3-MCPD

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3. 3-MCPD formation during refining

K. Hrncirik: Formation of 3-MCPD esters during oil refining – experimental results, 3-MCPD-Esters in Lebensmitteln, Berlin, 2008

G. v. Duijn: Potential ways of reduction of 3-MCPD esters in vegetable oils, ILSI workshop, Brussels, 2009

K. Hrncirik: Investigation of the mechanism of the formation of 3-MCPD esters during oil refining, Euro Fed Lipids, Graz, 2009

Formation of 3-MCPD esters in oils/fats

- Reaction of Cl^- with lipid components

- Possibly affected by
  - conc. of (partial) glycerides (MAG, DAG, TAG)
  - conc. of chloride
  - temperature
  - time
  - pH value

  → conditions of refining process

Research objective

Formation of 3-MCPD esters during refining:

- Type of edible oil:
  - Fruit oils
  - Seed oils
- Quality of the crude oil:
  - Free fatty acids
  - MAG/DAG
  - Metals, minerals
  - Chlorides
- Refining process
  - Physical v. chemical
  - Deodorization
    - Temperature
    - Time

FEDIOL The EU Oil & Proteinmeal Industry **study 2008-2009**

FEDIOL study: Experimental design

Material used:
- one seed oil (rapeseed oil)
- one vegetable oil (palm oil)

Processes applied:
- chemical refining
- physical refining

Variable which may play a role:
- temperature (deodorisation)
- time (deodorisation)
- content of free fatty acids, mono-/diacylglycerols
- content of chlorides

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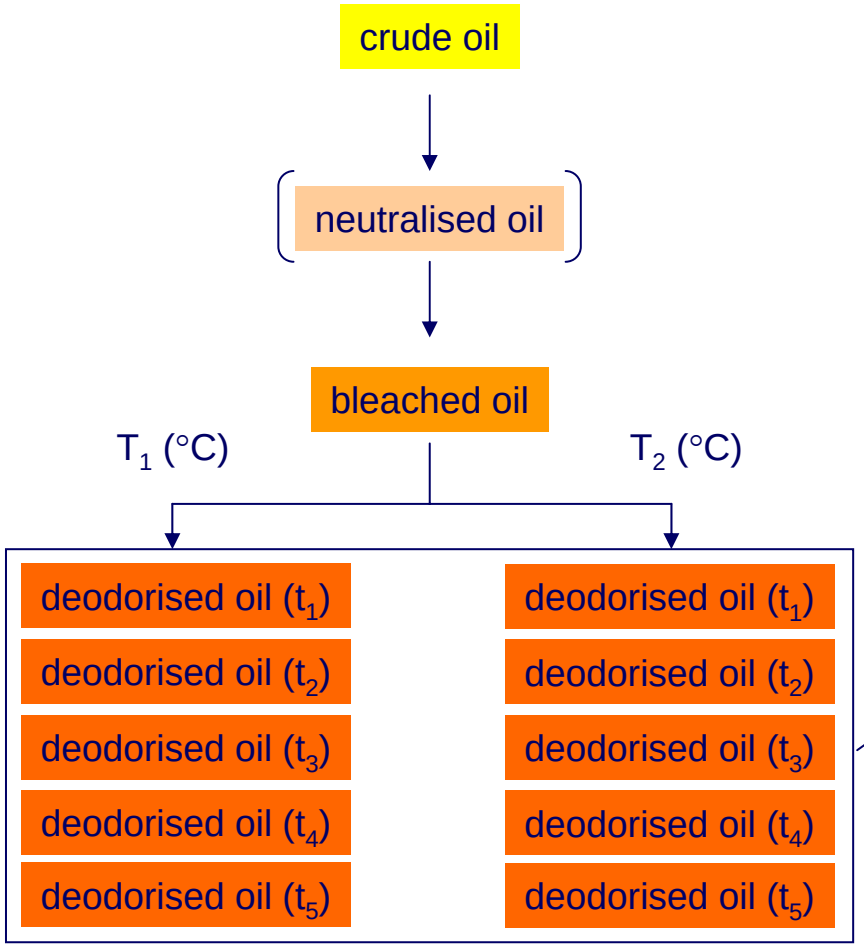
FEDIOL study: experimental concept



samples deodorized
on a pilot-plant scale (75 kg batch)

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FEDIOL study: major findings

- **3-MCPD esters formed:**
  → 20-30% during bleaching
  → 70-80% during deodorization

- **effect of pre-treatment (neutralization / bleaching v. 2-step bleaching):**
  → not conclusive

- **no simple relationship with FFA, partial glycerides, chlorides**

- **effect of deodorization time (1-5 hrs):**
  → no clear trends

- **effect of deodorization temperature (180 °C - 265 °C):**
  → results dependent on the analytical method used!

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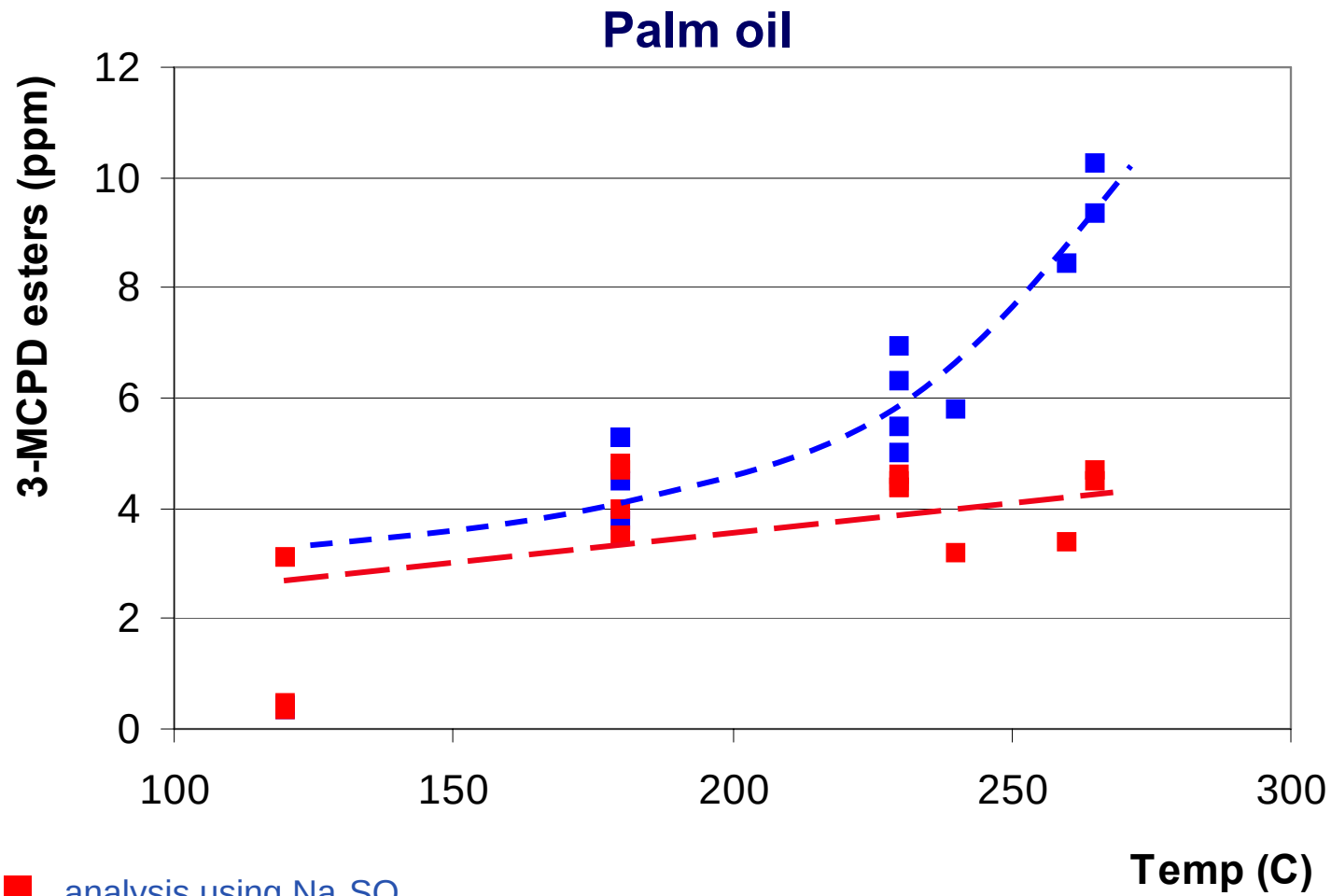
FEDIOL study: 3-MCPD ester formation during deodorization



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FEDIOL study: conclusions on 3-MCPD esters formation

- **obvious formation during the refining process**
  - **occurs both during bleaching and deodorization**
- **refining - freedom of operation limited**
  - **no quick win**
  - **more understanding required**
- **pronounced formation occurs only in some oils**
  - **large variation even within the same type of oil**
  - **discriminating (intrinsic) factor(s)?**
  - **FFA, MAG/DAG (oil quality)?**

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Research objective

Formation of 3-MCPD esters during refining:

- Type of edible oil:
  - Fruit oils
  - Seed oils
- Quality of the crude oil:
  - Free fatty acids
  - MAG/DAG
  - Metals, minerals
  - Chloride
- Refining process
  - Physical v. chemical
  - Deodorization
    - Temperature
    - Time

study 2009-2010

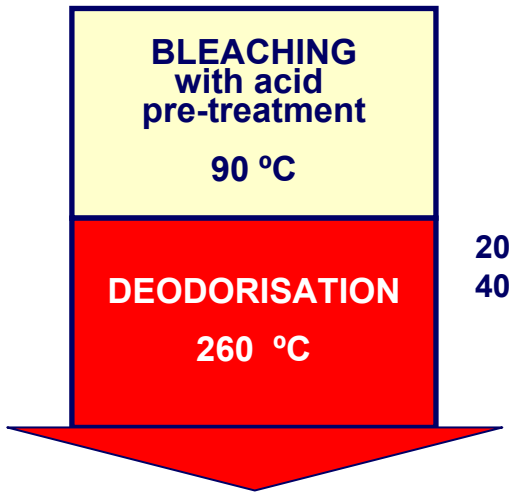
Experiment 1

Material:

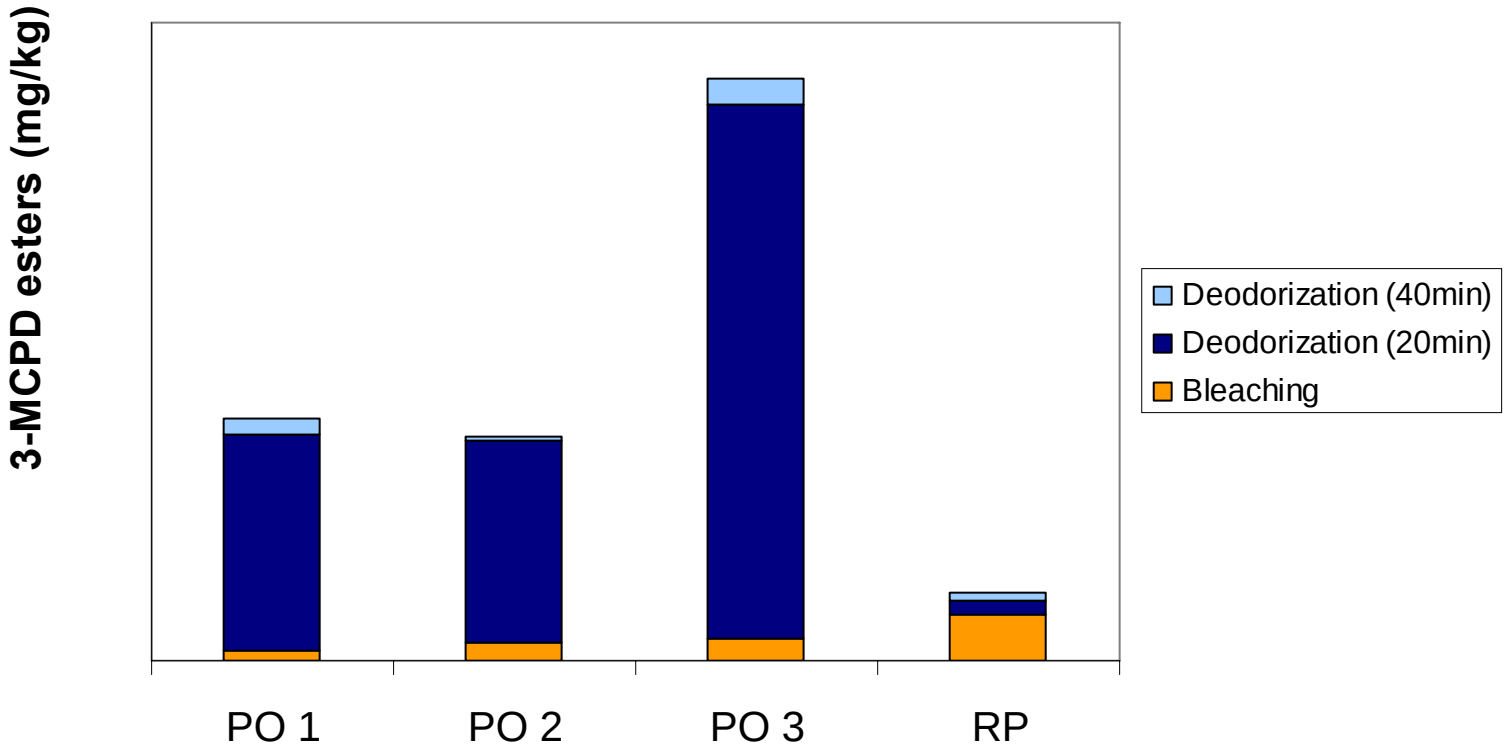
Oil type (crude)	FFA (%)	Mono-glycerides (%)	Di-glycerides (%)
Palm 1	1.4	0.1	4.0
Palm 2	4.6	0.3	5.5
Palm 3	6.8	0.3	8.2
Rapeseed	0.2	0.4	1.0

Processing:

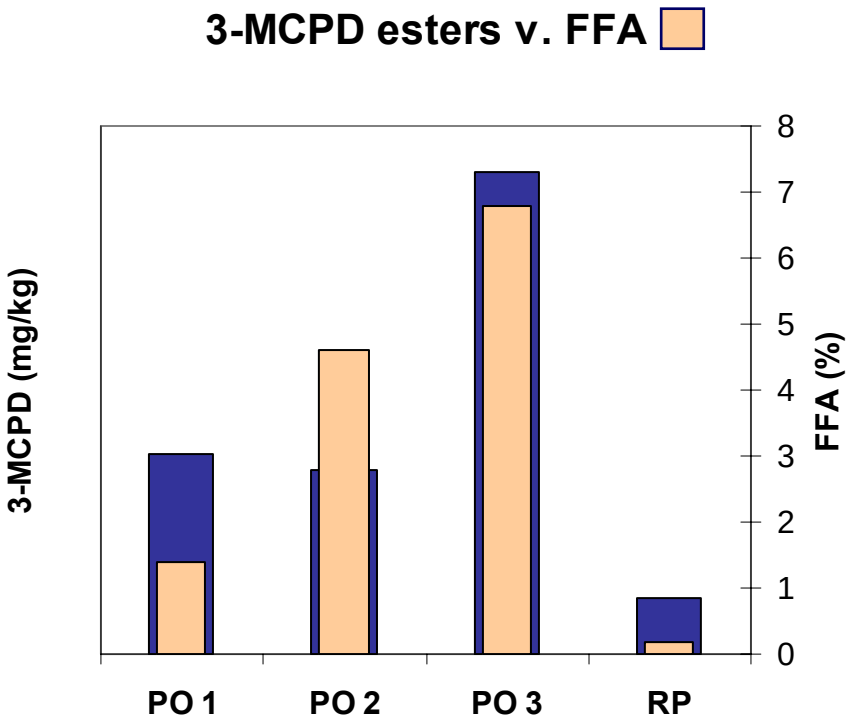
Physical refining

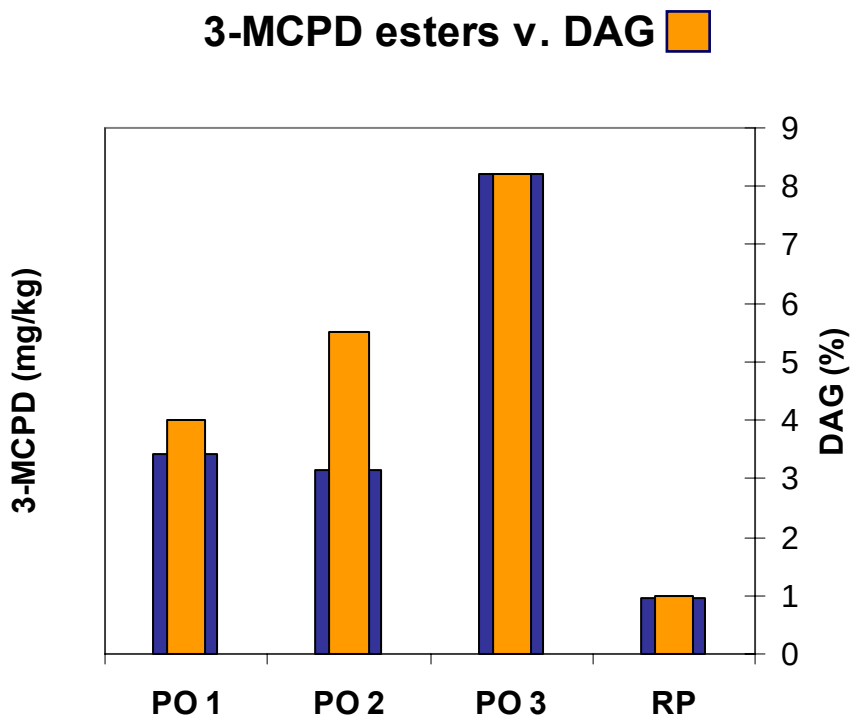


Experiment 1: formation during physical refining



Experiment 1: correlation with the oil quality





Experiment 2

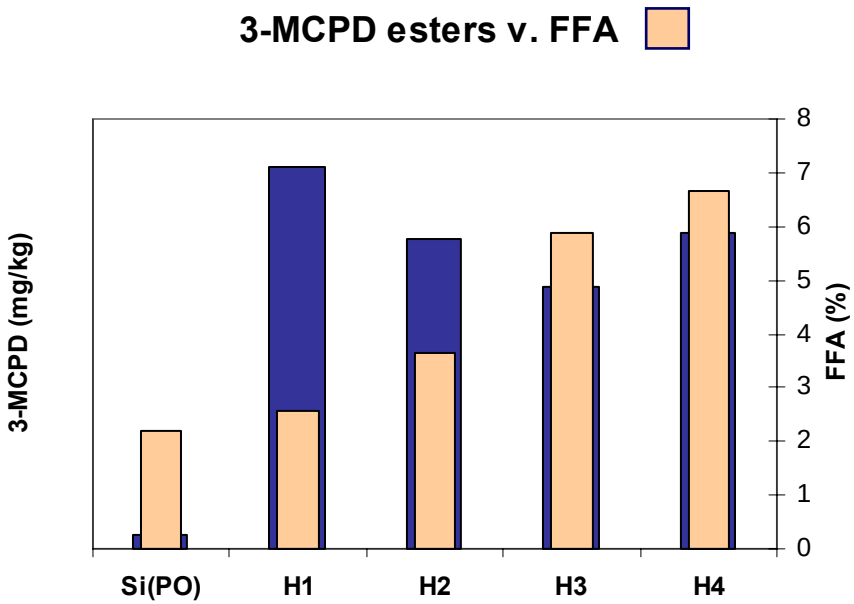
Material:

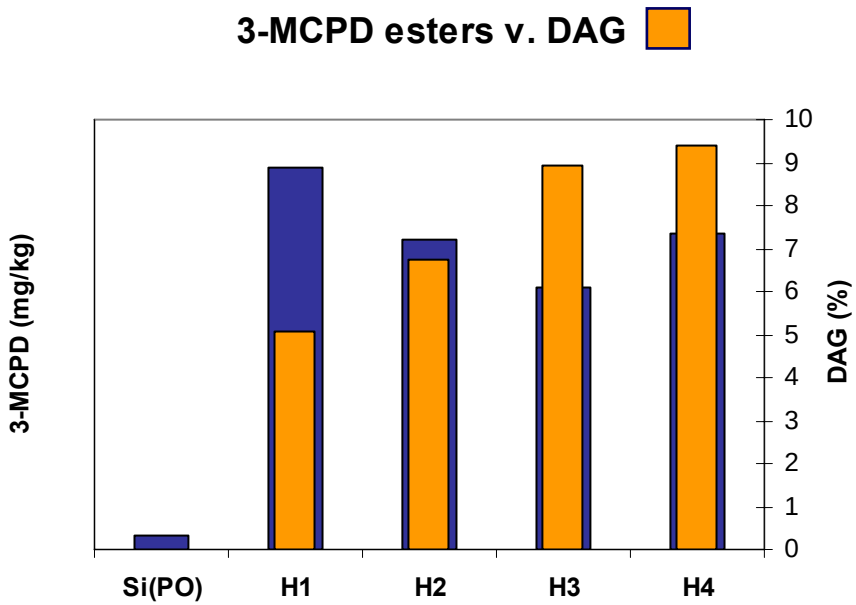
Oil type (crude)	FFA (%)	MAG (%)	DAG (%)
Silica treated PO	2.2	< 0.05	< 0.05
Blend 1	2.6	0.2	5.1
Blend 2 (low)	3.7	0.3	6.7
Blend 3 (medium)	5.9	0.8	9.0
Blend 4 (high)	6.7	1.1	9.4

MAG/DAG removed

Increased levels of FFA/MAG/DAG achieved by enzymic hydrolysis (50 ºC)

Experiment 2: correlation with the oil quality



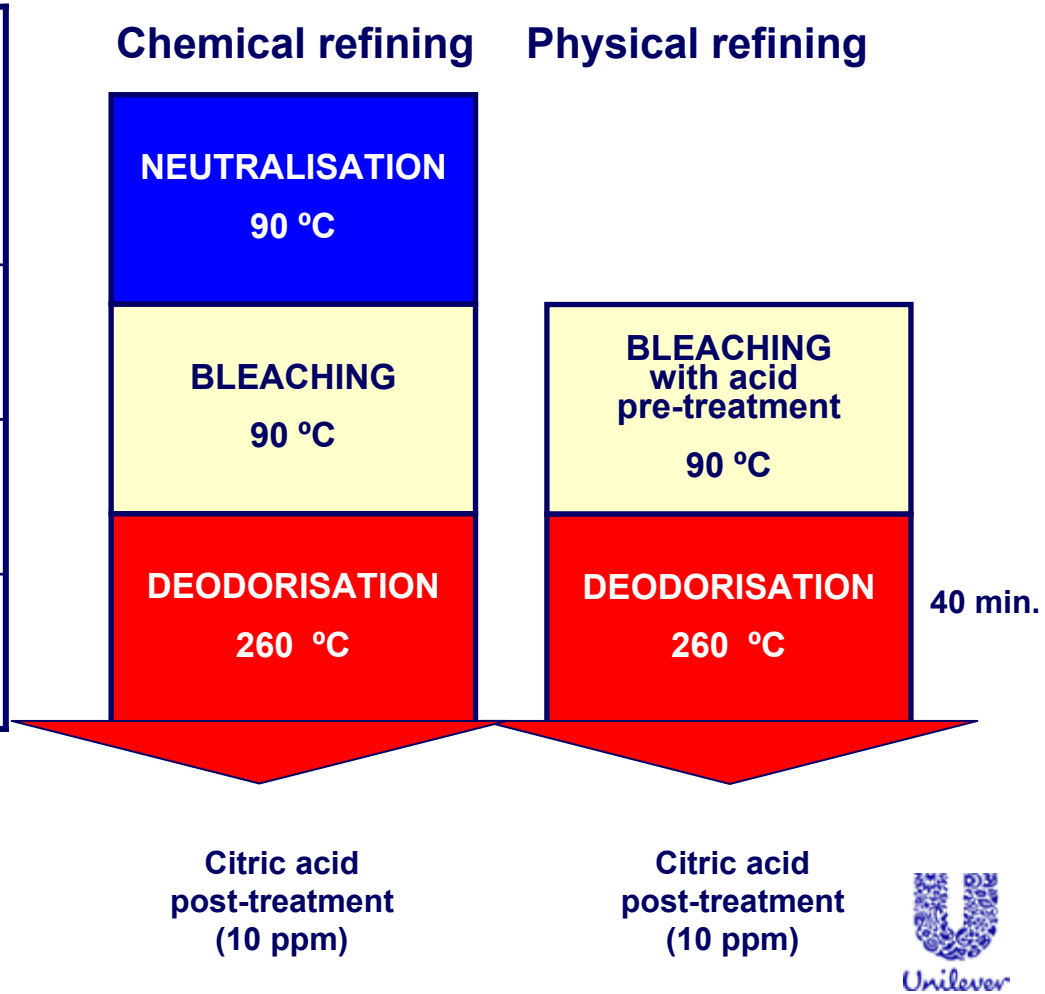


Experiment 3

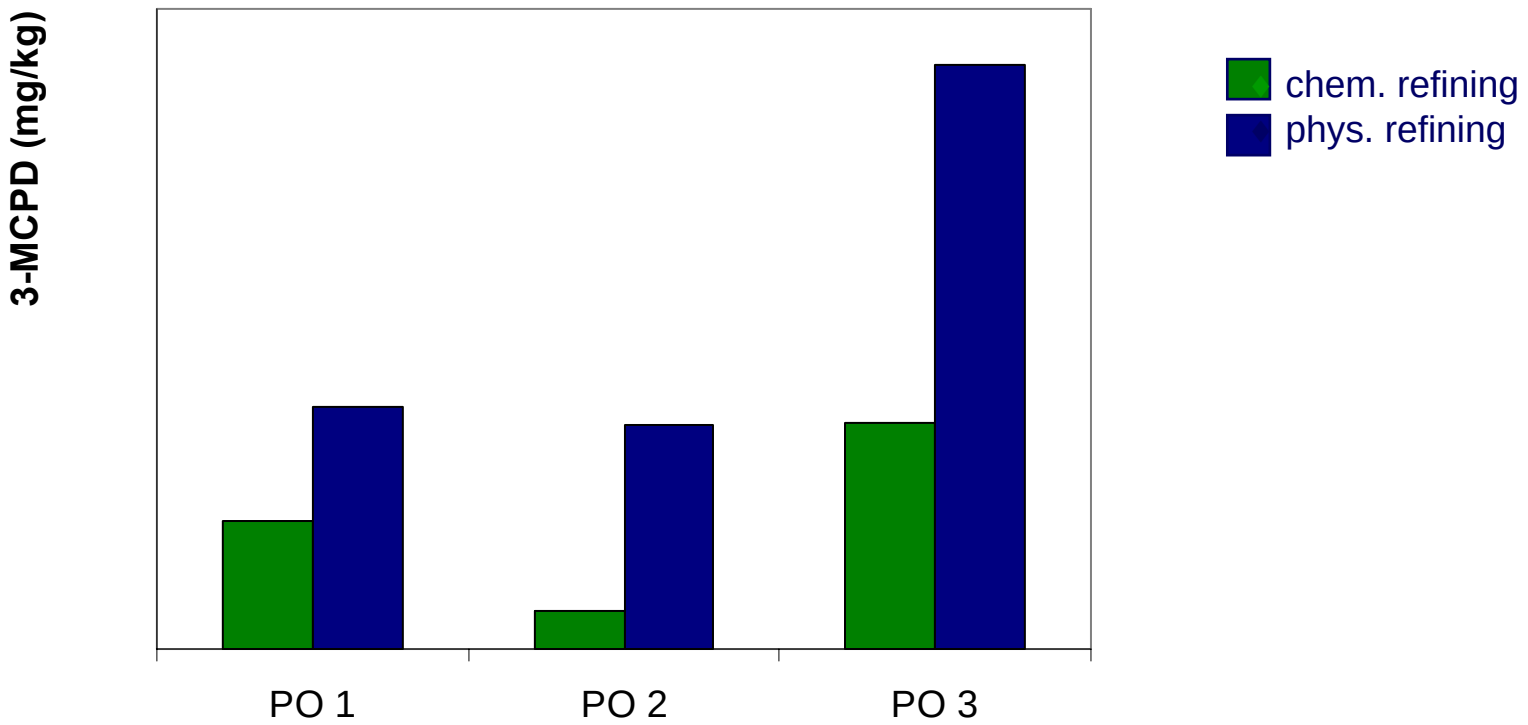
Material:

Oil type (crude)	FFA (%)	MAG (%)	DAG (%)
Palm 1	1.4	0.1	4.0
Palm 2	4.6	0.3	5.5
Palm 3	6.8	0.3	8.2

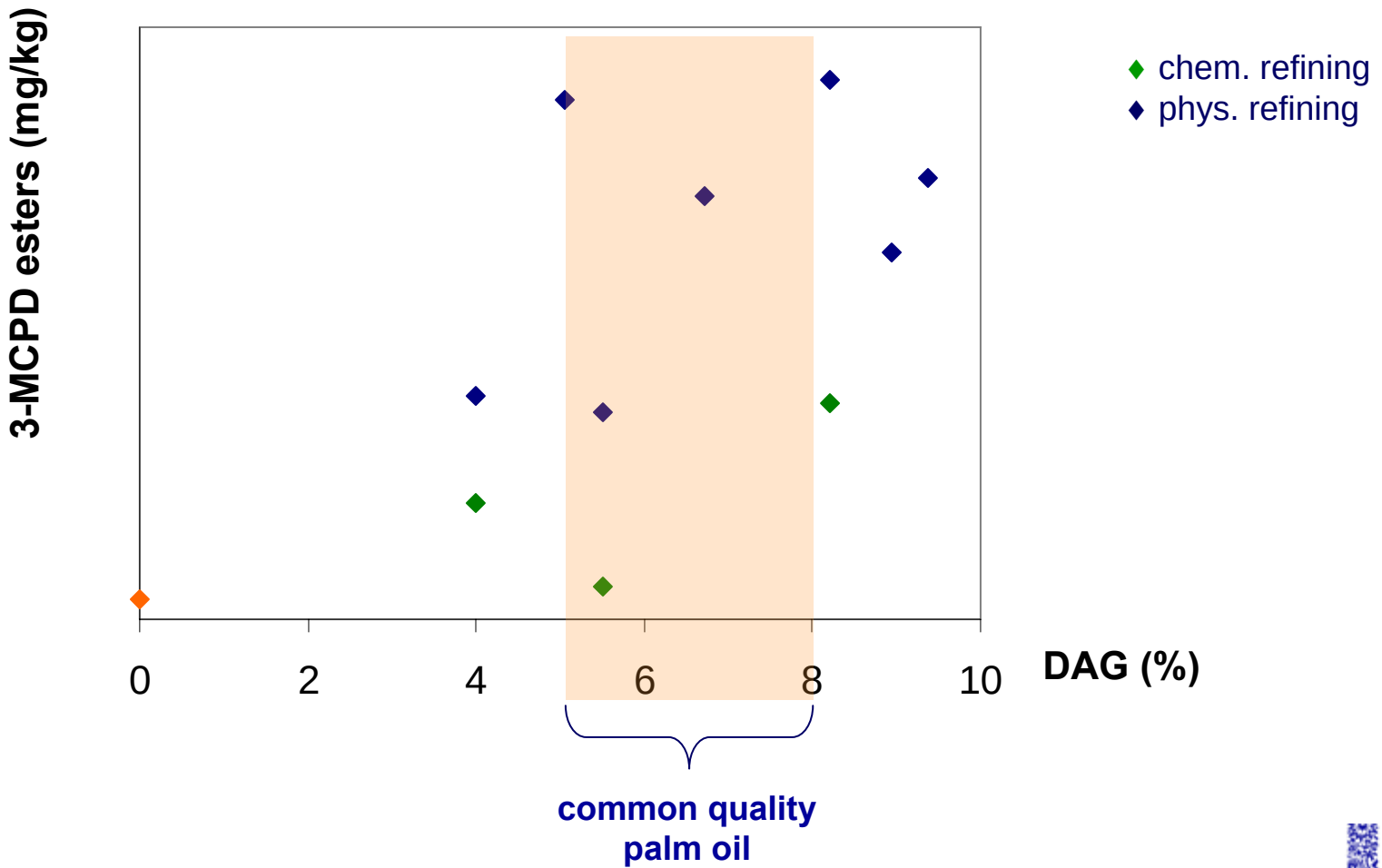
Processing:



Experiment 3: chemical v. physical refining



Summary: diglycerides v. 3-MCPD esters



Summary: major findings

Formation of 3-MCPD esters during refining:

- Type of edible oil:
  - Fruit oils
  - Seed oils

- Quality of the crude oil:
  - Free fatty acids
  - MAG/DAG
  - Chlorides

→ may play a role (inconclusive)
→ poor correlation between DAG/3-MCPD esters
→ MAG/DAG: not a limiting step

- Refining process
  - Physical v. chemical

→ chem.ref. (lab scale): ↓ levels of 3-MCPD esters
(costs?, environmental impact?)

  - Deodorization
    - Temperature
    - Time

→ formation accomplished within 20 min (260ºC)