Formation of 3-MCPD Esters in Palm Oil: Effect of Partial Acylglycerols

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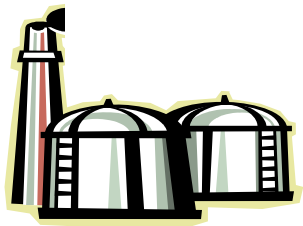
3-MCPD esters: knowledge gaps

crop

crude oil



refining process

refined oil

- raw material quality?
- precursors?

- processing conditions?
- post-treatment?

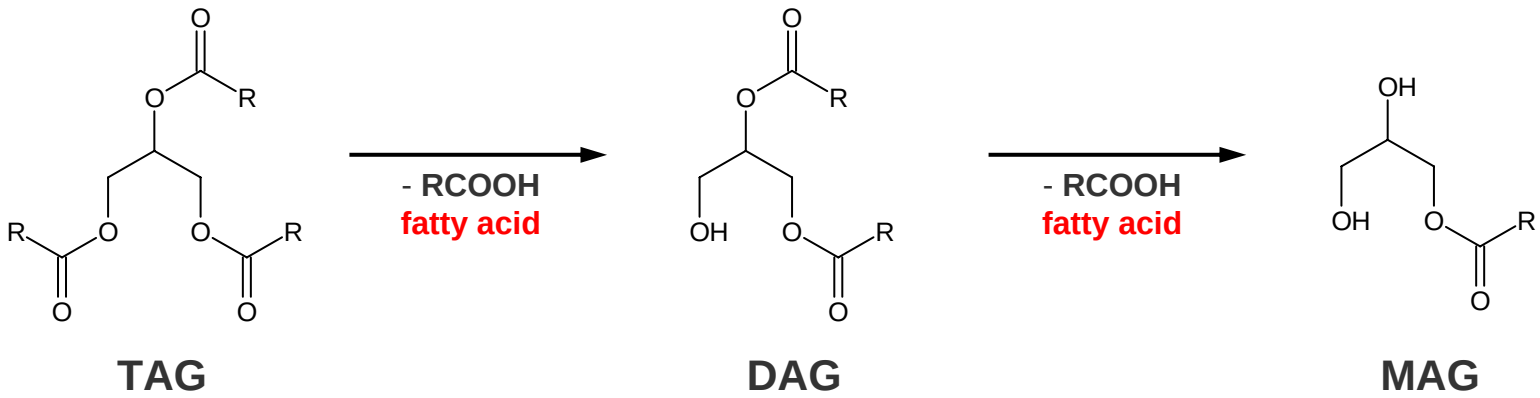
effective mitigation strategy?

Occurrence of 3-MCPD esters in oils/fats

- Crude vegetable oils/fats: usually trace levels
- Refined fats/oils: almost always present (typically 0.3–6 mg/kg)
- Levels in various oils differ, a rough “classification”:
  - lower: rapeseed, soybean
  - medium: sunflower, olive, maize, grapeseed
  - higher: palm, recently: walnut, hazelnut, fish (Kuhlmann 2010, EFL)
- Large variation even within single type of oil, possibly given by:
  - (analytical methodology)
  - processing (refining) conditions
  - **minor components (precursors)**

Oil/fat hydrolysis

- (Enzymic) **hydrolytical reactions** of triacylglycerols:



TAG **DAG** **MAG**

- **Crude oil quality**: free fatty acid content (% FFA)
  - seed oils (RP, SF): very low FFA
  - trade limits (EU) for crude palm oil: 5%

Oil/fat hydrolysis (cont.)

- **Hydrolysis prevention**
  - fast processing after the harvest
  - enzyme inactivation

} positive cost implications

Receiving station
(fresh fruit bunches collection)

Sterilizer – oil mill
(fruit bunches sterilization)

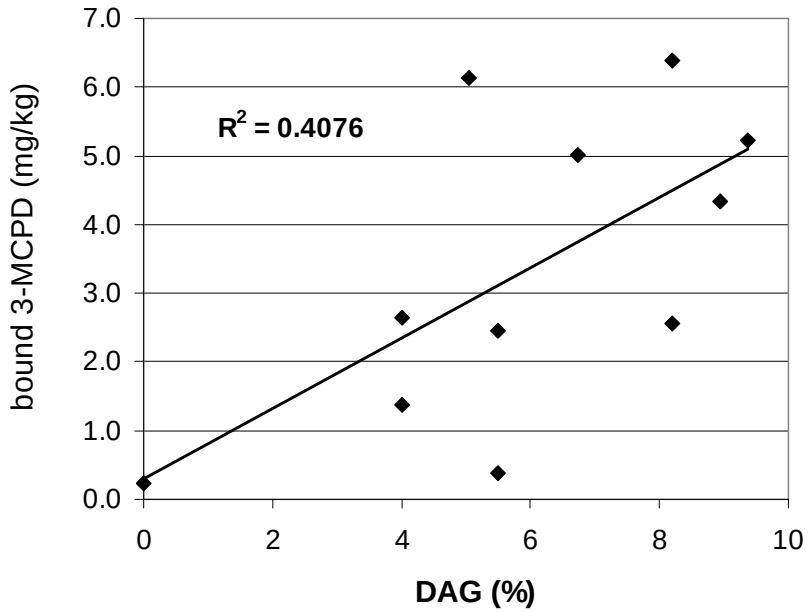
- **Fatty acids removed** by
  - chemical refining (neutralization)
  - physical refining (deodorization)

Formation of 3-MCPD/glycidyl esters affected by:

	Refining conditions (deodorization)	**Crude oil quality** (degree of hydrolysis)
3-MCPD esters	▫ no clear dependency on deodorization temperature shown	**???**
Glycidyl esters	▫ increased levels found at deod. temp. >220 °C ▫ progressive increase at higher temp.	▫ positive correlation with DAG levels established ▫ e.g. extremely high levels found in diglyceride-based oil (DAG ~80%)

Partial acylglycerols v. 3-MCPD esters

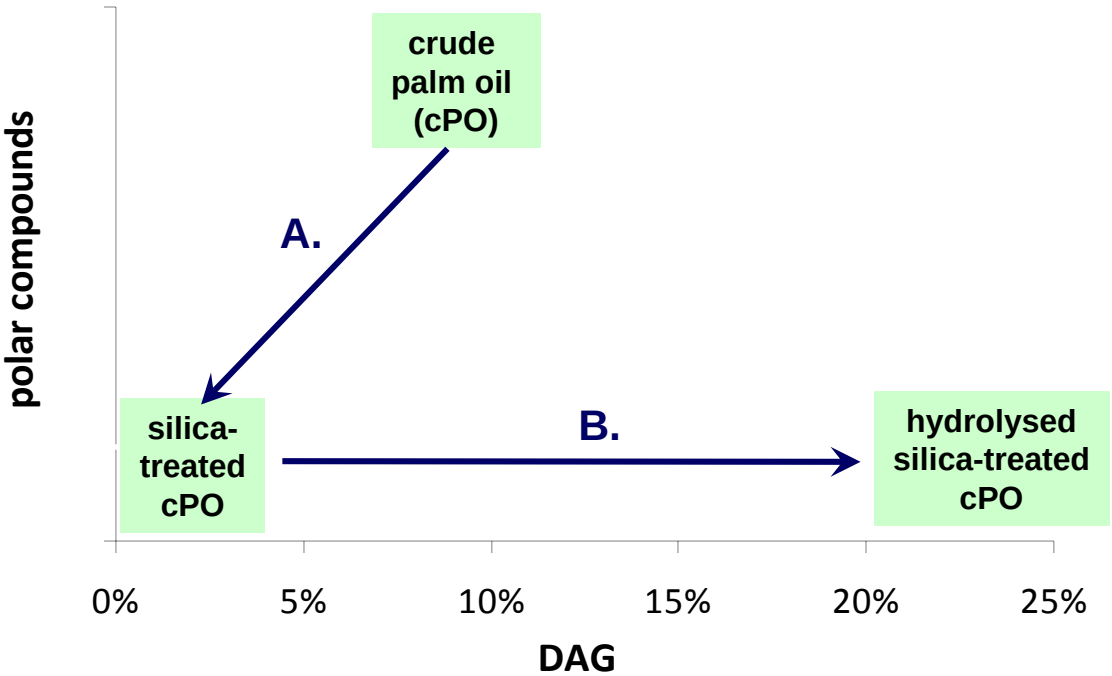
- a strong correlation between DAG and 3-MCPD esters formed not shown yet
- an example: Hrncirik, EFL 2009



- warning! - results of different studies may be affected by analytical methodology used (specificity towards 3-MCPD esters)

Experimental setup

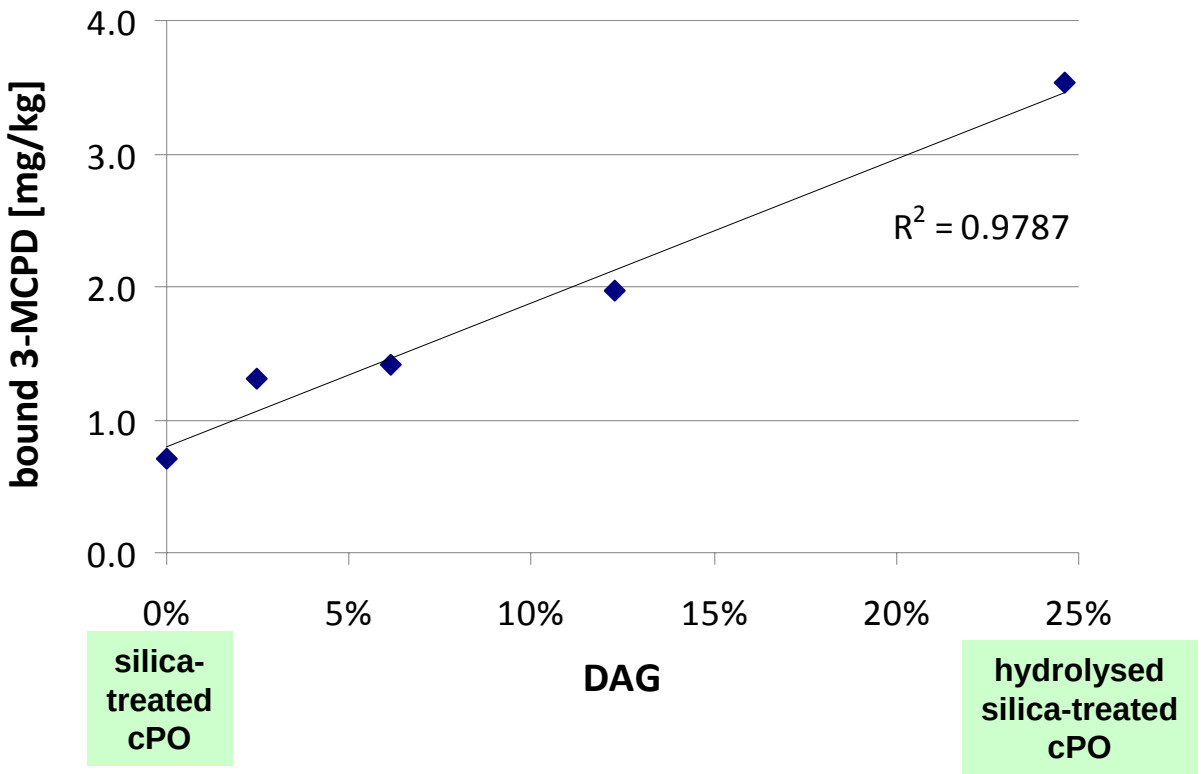
- Two techniques used for modification of crude PO composition:
  - **A. purification on SiO_2 column**: polar compounds (incl. DAG/MAG) removal
  - **B. enzymic hydrolysis**: TAG → DAG (→ MAG)



- Different blends prepared, processed
- Analysis of 3-MCPD esters: acid transesterification, PBA derivat., GC/MS
  - according Hrncirik, Zelinkova, Ermacora (2011), *Eur. J. Lipid Sci. Technol*. **113**

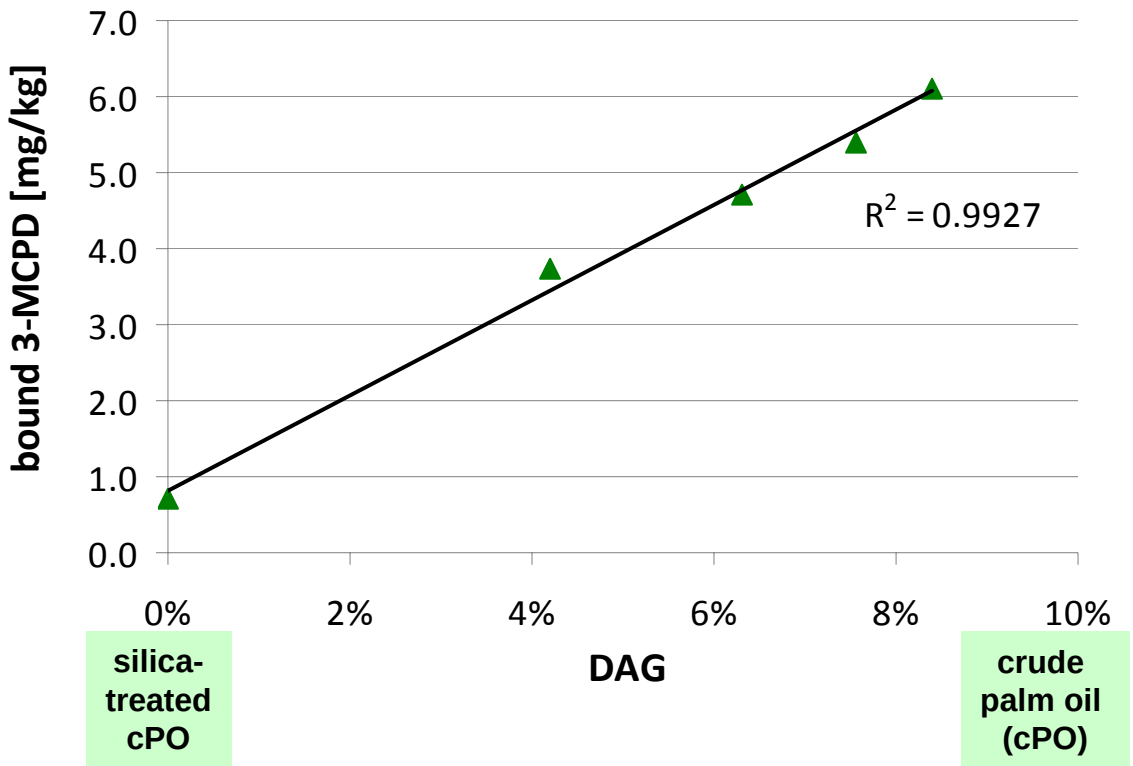
Experiment 1

Combination: silica-treated cPO ↔ hydrolysed silica-treated cPO



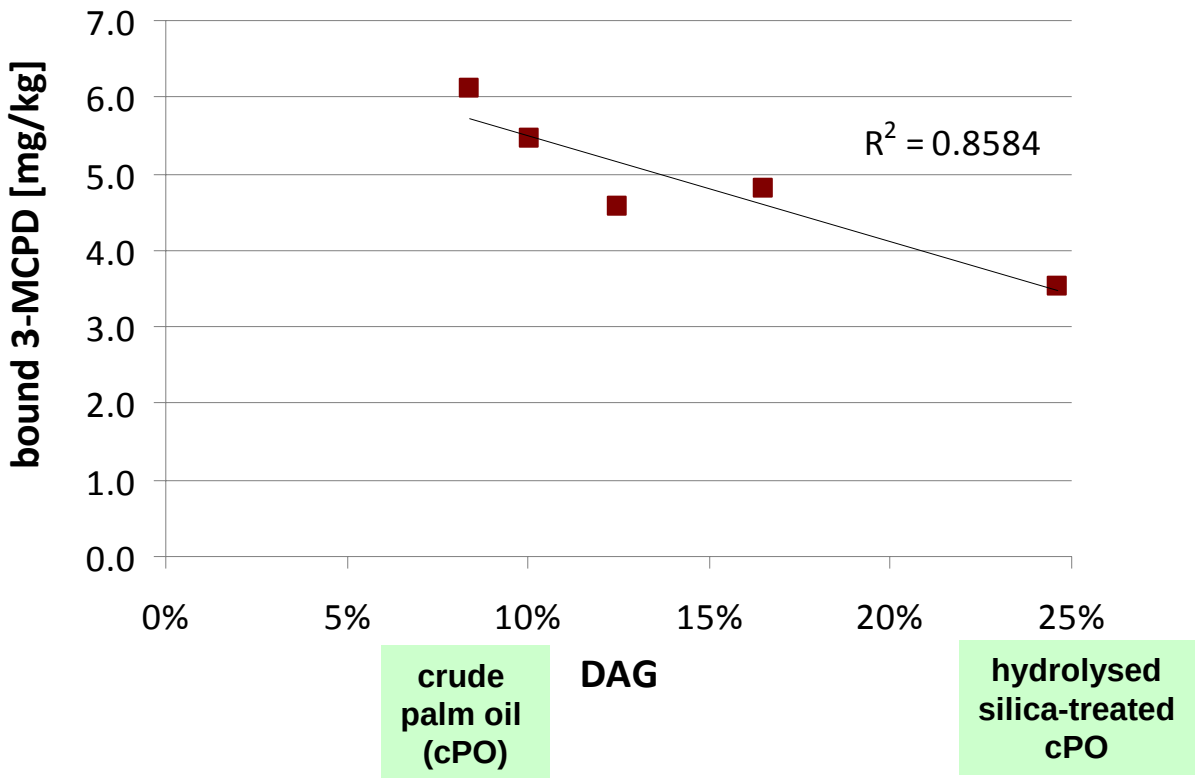
Experiment 2

Combination: silica-treated cPO ↔ crude PO

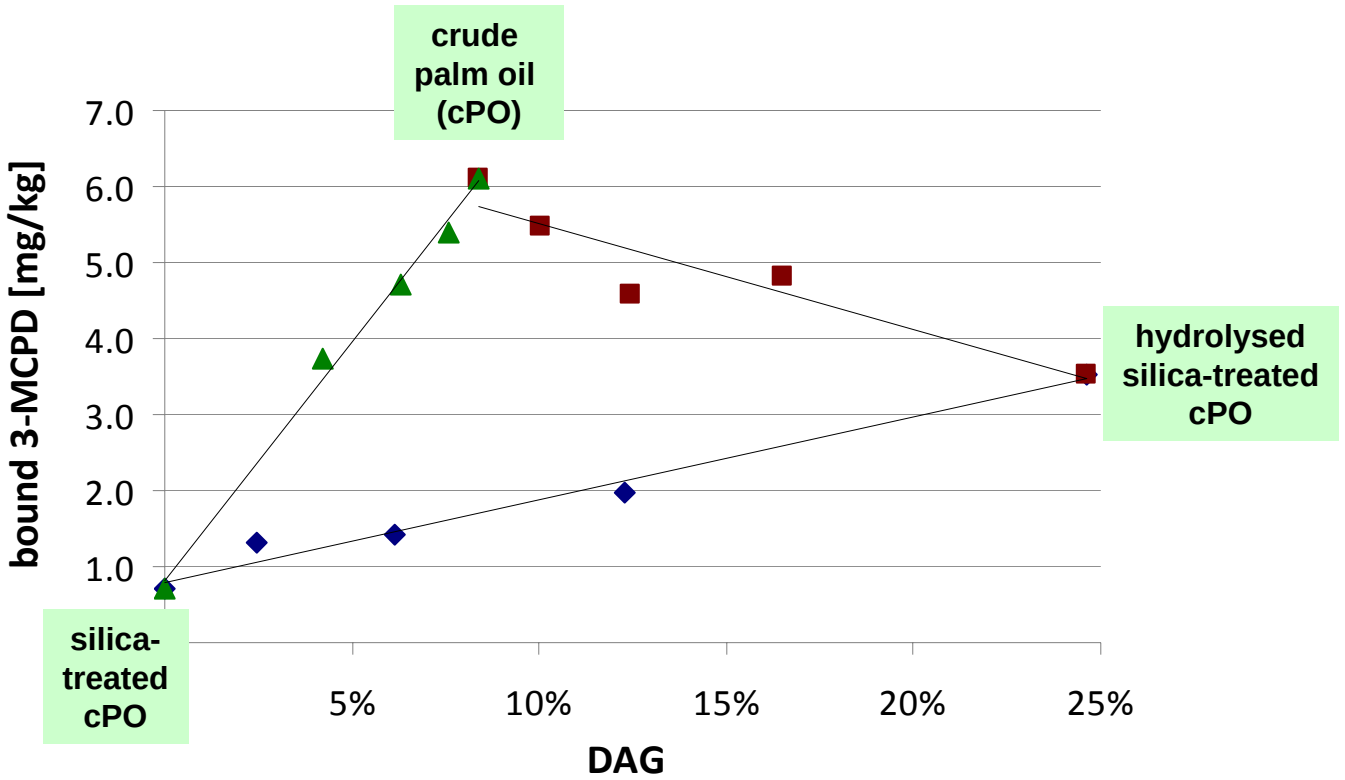


Experiment 3

Combination: crude PO ↔ hydrolysed silica-treated cPO



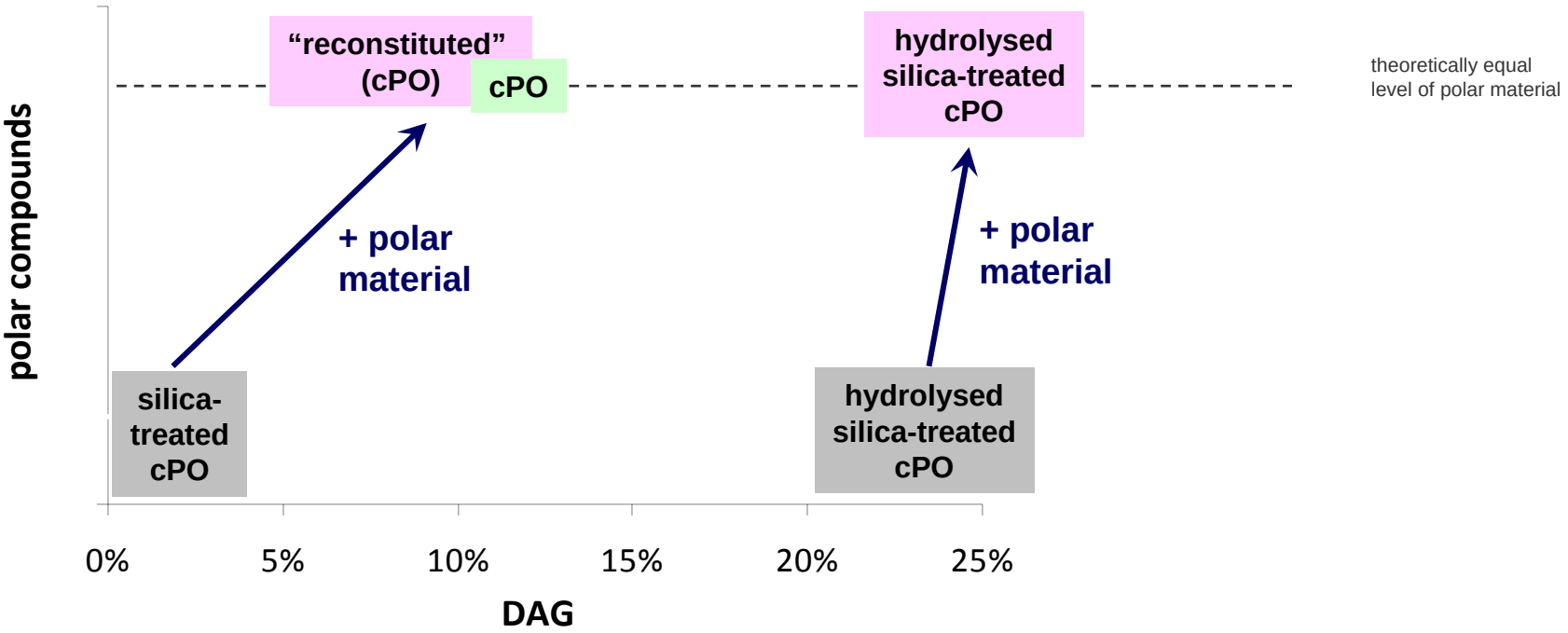
Summary: Experiment 1-3



- relatively limited effect of partial acylglycerols
- major impact of polar material present in crude PO

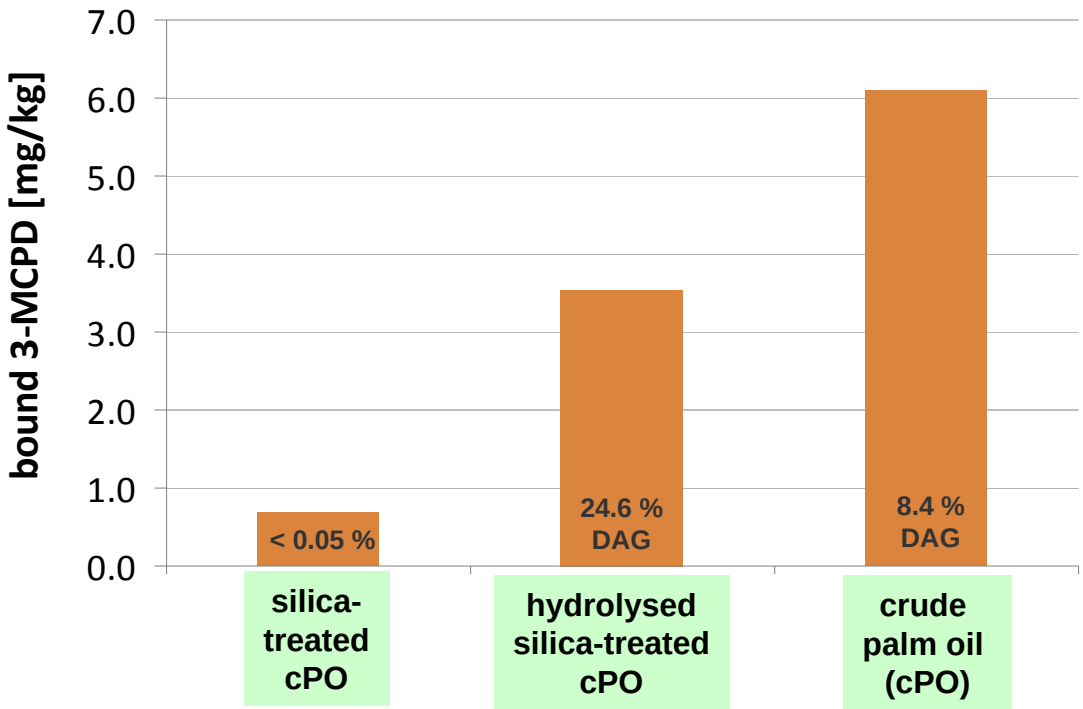
Experiment 4

- Polar material (isolated from cPO) eluted from SiO_2 column
- Re-introduced to silica-treated samples



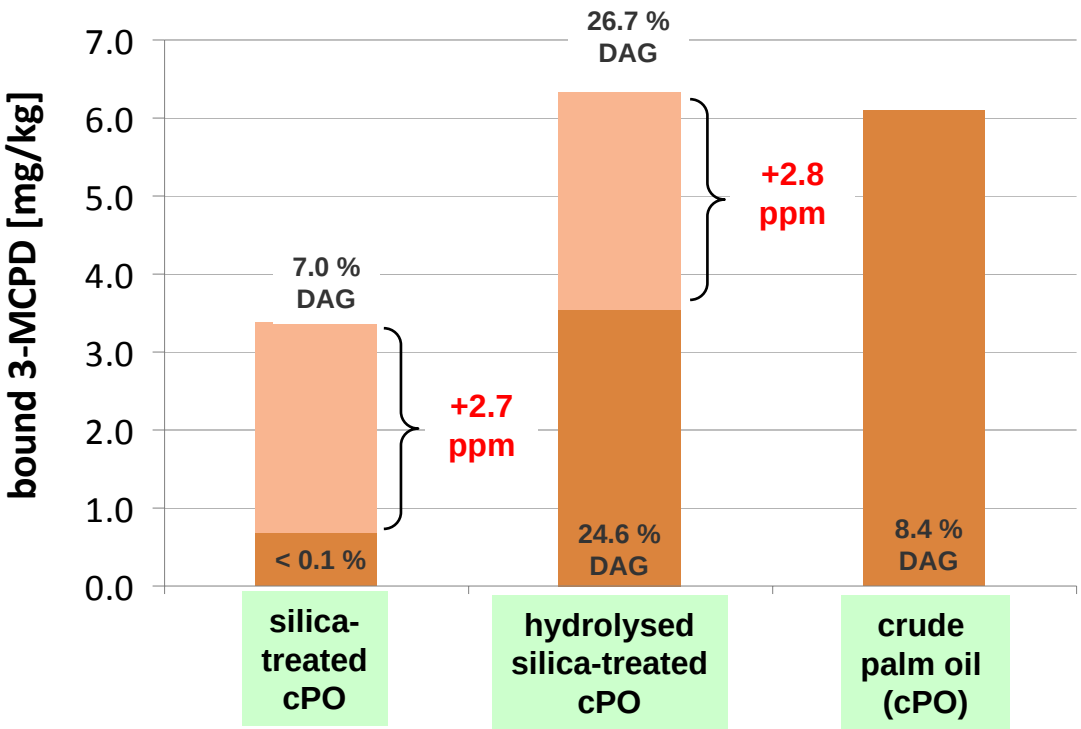
Experiment 4

- 3-MCPD levels in original materials after processing (Experiments 1-3)



Experiment 4

- the addition of isolated polar material into the matrix led to substantial increase of 3-MCPD esters (after processing)
- the increase was consistent; independent of DAG level



Summary: major findings

- purification on SiO_2 greatly reduces the level of precursors of 3-MCPD esters in crude palm oil
- partial acylglycerols seem to be involved in the formation of 3-MCPD esters, but they are not the critical factor determining the final levels
- the quality (= the degree of hydrolysis) of the crude palm oil does not seem to be critical for the formation of 3-MCPD esters
- the critical precursors can be (partly) recovered from SiO_2 column
- the structure/mechanism still remains to be elucidated