DGF Symposium on MCPD Esters and Glycidyl Esters, 20 – 21 June 2017, Berlin, Germany

STUDY OF 3-MCPD ESTERS AND GLYCIDYL ESTERS IN MALAYSIA

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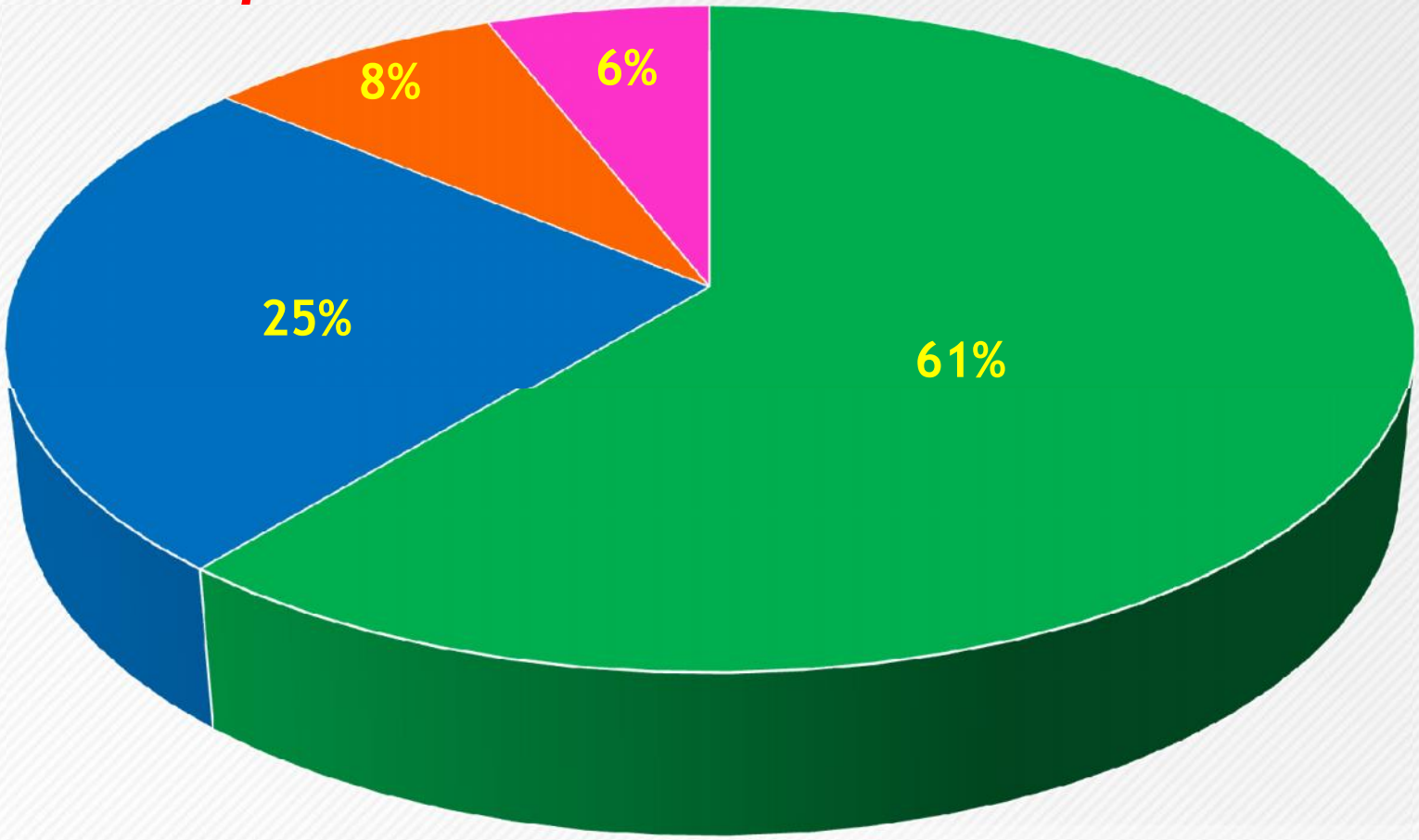
Presentation Outline

- Introduction
- Background
- Analytical Methods
- Surveys and Pilot Plant Trials
- Mitigation Measures
- Industrial Trials
- Malaysian Patents
- The Way Forward

Introduction to Palm Oil Industry in Malaysia

Export Value in 2016 : RM 67.58 Billion



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Major Export Destinations, 2016

Country	2016 (Million T)
India	2.83
EU	2.06
China	1.88
Pakistan	0.88
Turkey	0.66
Philippines	0.63
USA	0.59
Vietnam	0.56
Japan	0.46
Bangladesh	0.43

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Background of 3-MCPD and GE research in Malaysia

- **2009** – MPOB **started research works on 3-MCPD esters formation** in refined palm oil
- **2010** – **adopted** and established analysis of 3-MCPD esters using **BfR Method 008**
- **2010 to 2013** – carried out **surveys on commercial palm oil products** and **pilot plant trials** to mitigate the formation of 3-MCPD esters during refining of palm oil
- **2014** – **adopted** and established analyses of 3-MCPD esters and GE using **AOCS Method Cd 29a**
- **2016** - **identify technologies provider for mitigation** of 3-MCPD esters and GE at the mills and refineries
- **2017** – **mitigation study** on the formation of 3-MCPD esters and GE on **industrial scale**

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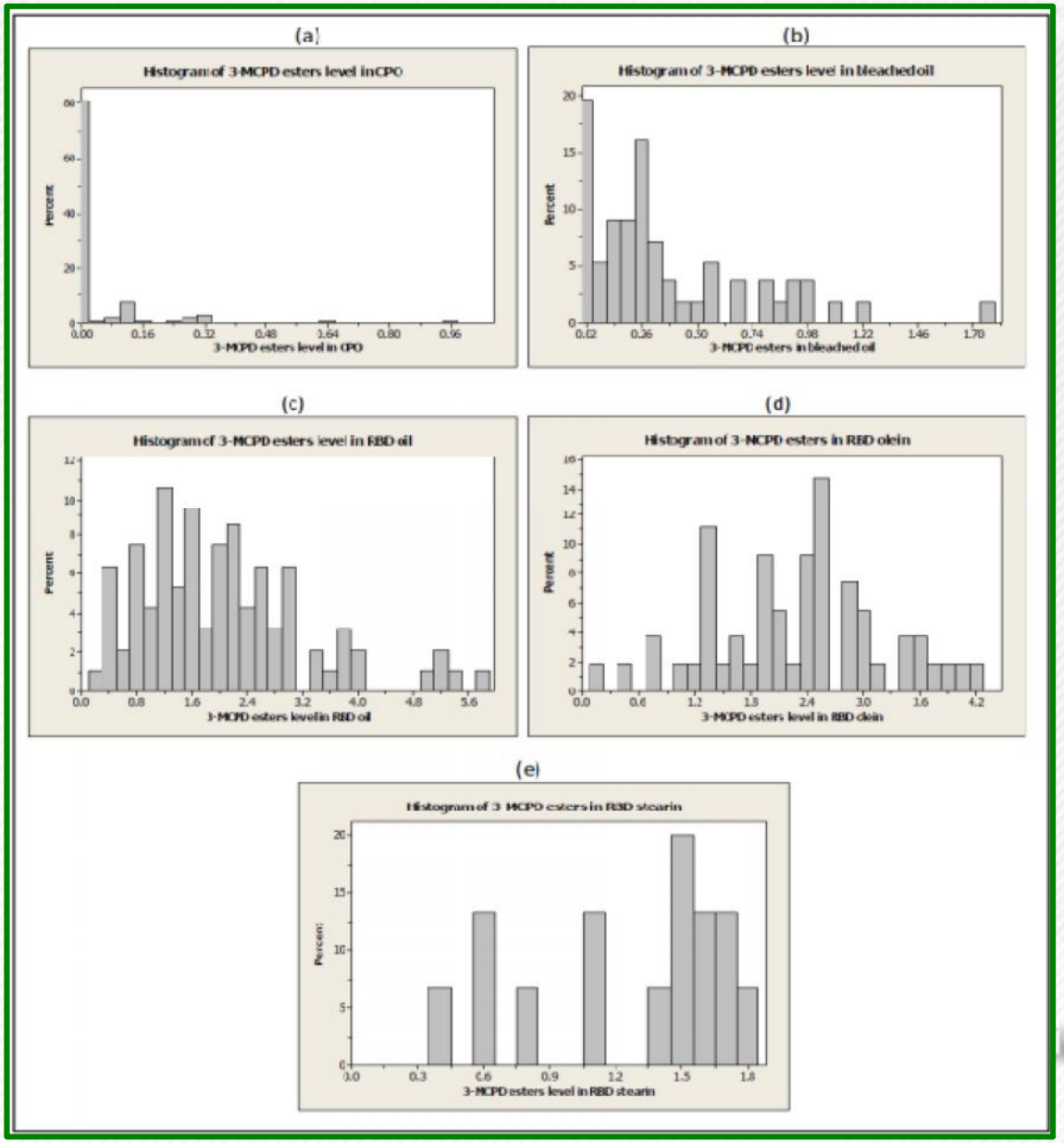
Analytical Methods

Method	Analyte	Description
DGF CIII 18 (09) B	Bound 3-MCPD esters	• Alkaline / H^+ and chloride • GC-MS • Indirect method
BfR 'Method 8'	Bound 3-MCPD esters	• Acidic transesterification • GC-MS • Indirect method
BfR 'Methods 9 and 10'	Bound 3-MCPD esters	• Alkaline / H^+ chloride free • GC-MS • Indirect method
AOCS Official Method: **(a) Cd 29a-13** (b) Cd 29b-13 (c) Cd 29c-13	Bound 2- and 3-MCPD esters and Glycidyl esters	• Acidic / Alkaline • GC-MS • Indirect method
ADM	Bound 3-MCPD esters and Glycidyl esters	• LC-MS/TOF • Direct method

Survey : 2010



CPO showed the lowest 3-MCPD ester values (< 0.25 to 0.9 mg/kg)

RBDPO showed the highest 3-MCPD ester values (< 0.25 to 5.8 mg/kg)

Graph shows percentage distribution of 3-MCPD esters in 324 samples of palm oil products in Malaysia

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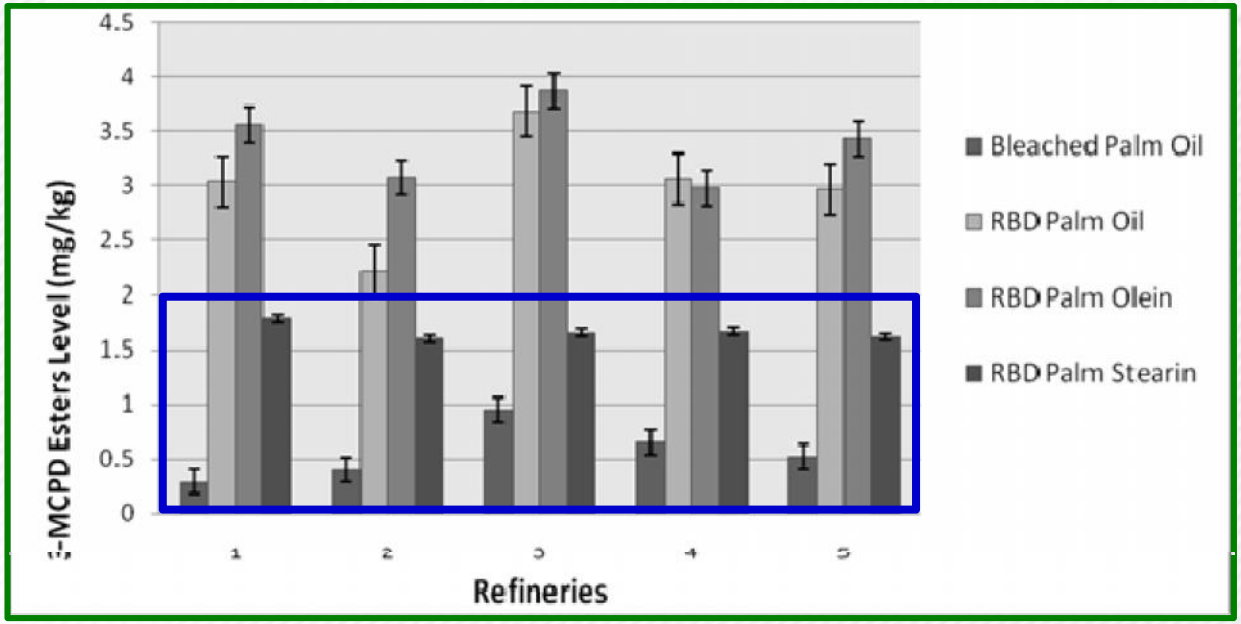
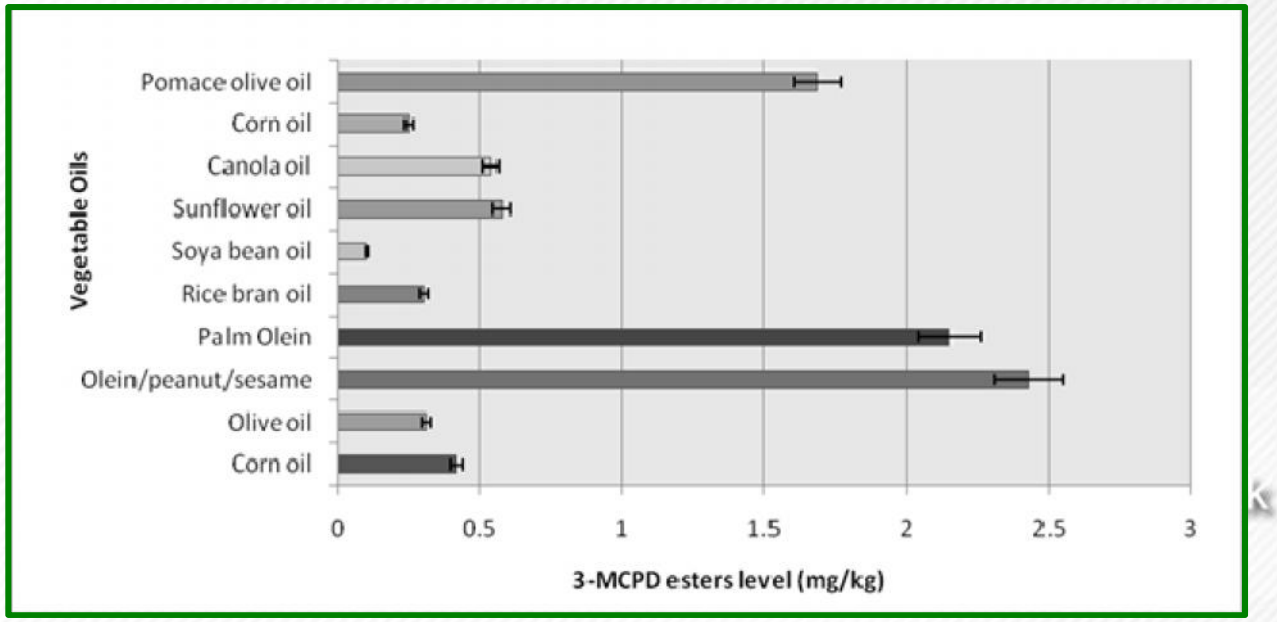
Survey : Palm oil products and commercial oils



3-MCPD esters in different type of palm oil products collected from 5 refineries



3-MCPD esters in commercial cooking oils in Malaysia

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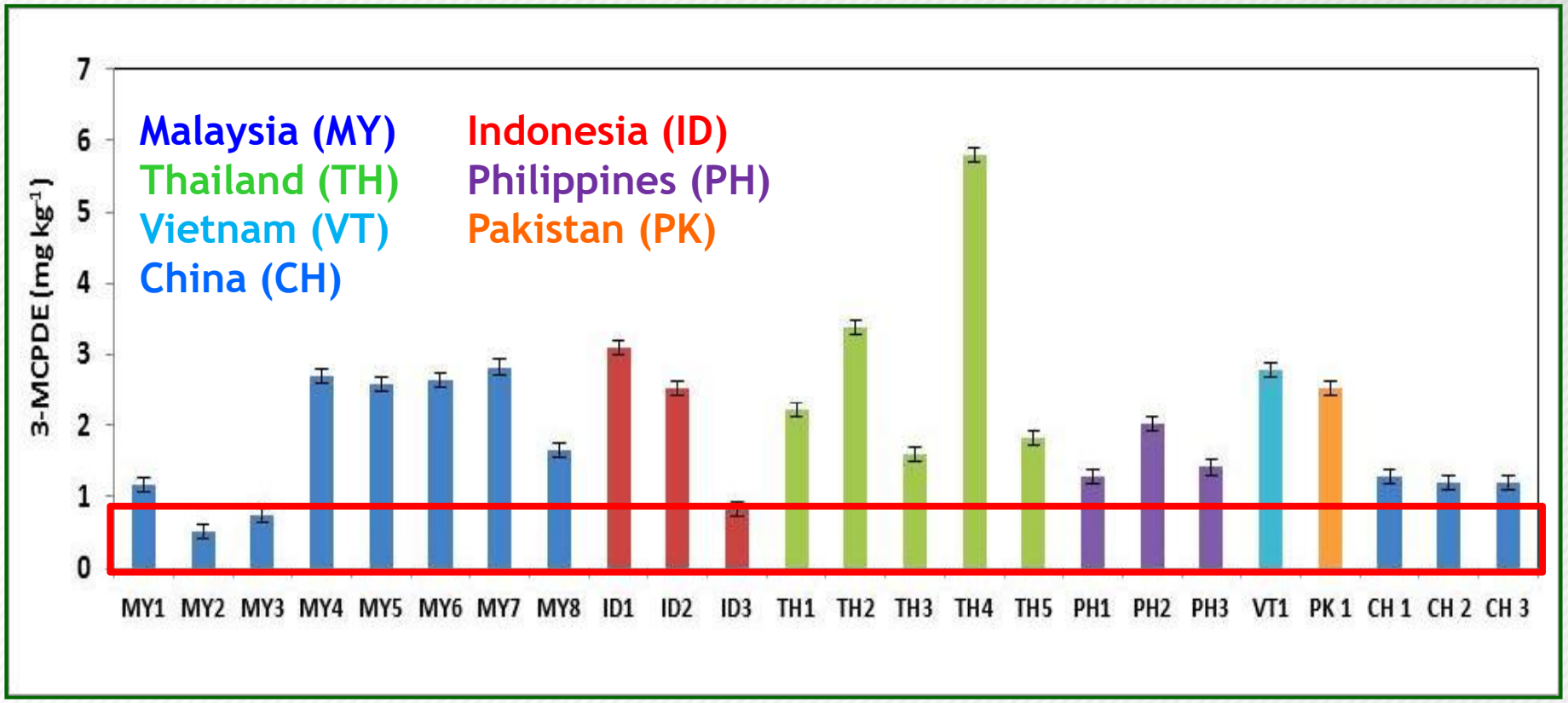
Survey : 2010 *vs* 2012

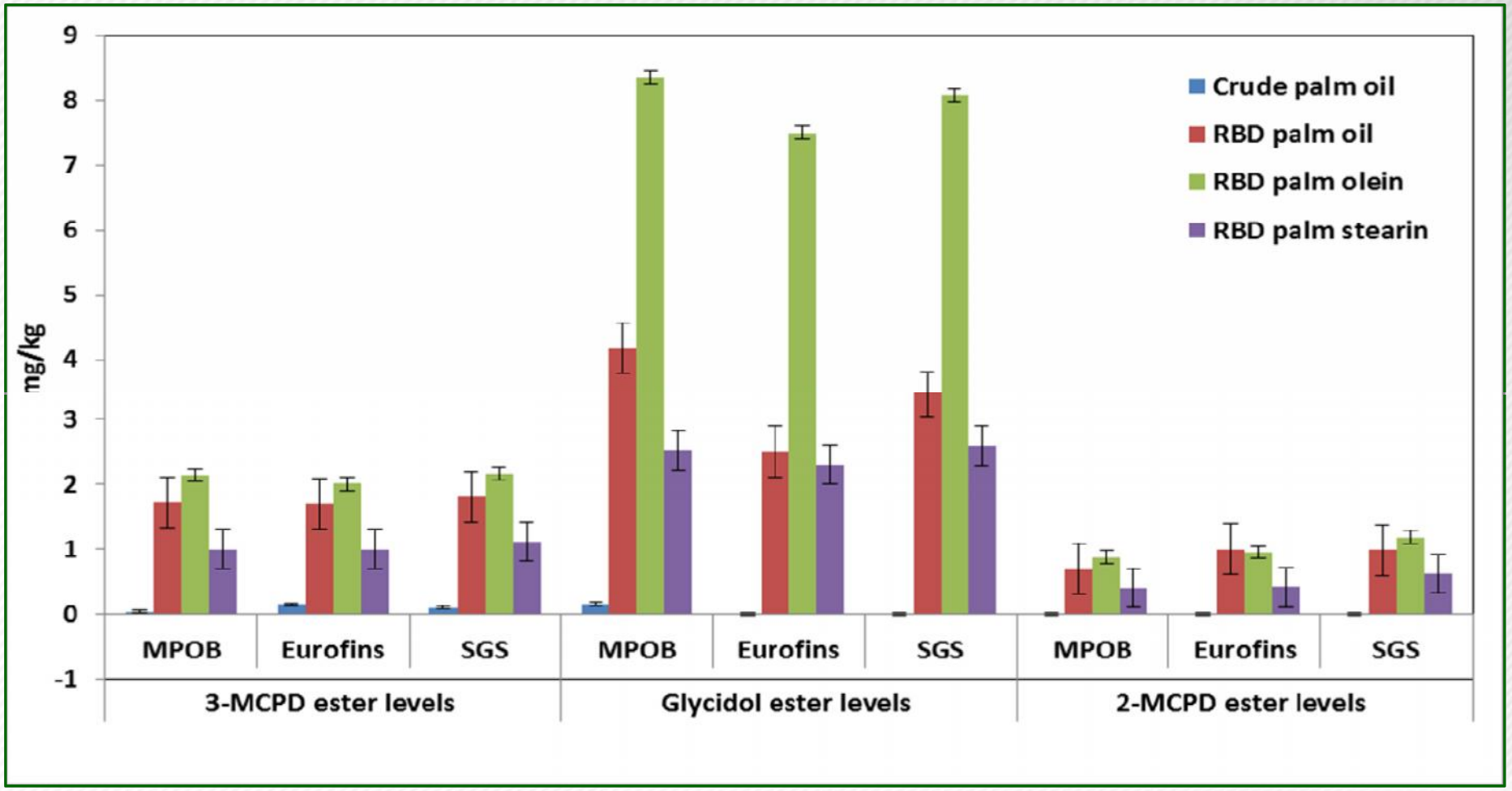
Type of sample	3-MCPD esters range (mg/kg)	
	2009	2012
Crude Palm Oil (*n* = 141)	< 0.25 - 0.9655	< 0.25 - 0.5
RBD Palm Oil (*n* = 115)	< 0.25 - 5.77	< 0.25 - 3.99
RBD Palm Olein (*n* = 50)	< 0.25 - 4.129	-
RBD Palm Stearin (*n* = 15)	0.354 - 1.787	-

Survey : 2014



Cooking oils (palm olein) from Asian countries

Cross-check analyses



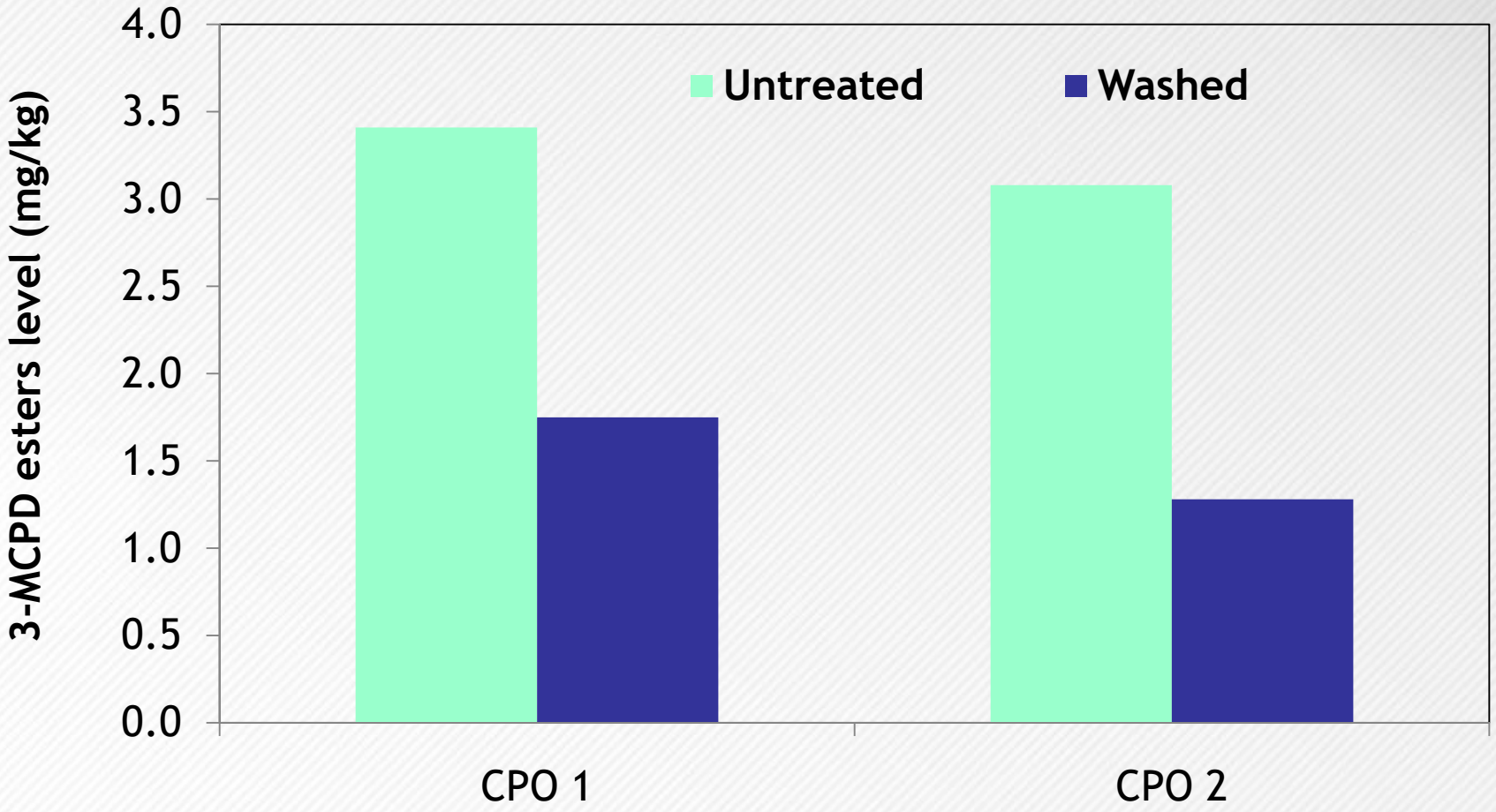
Total chlorine levels in palm oil products

Sample	Average value (ppm)	Range (ppm)
Crude palm oil	7.29 (± 5.9)	2.62 – 15.58
RBD palm oil	2.46 (± 0.9)	1.08 – 3.51
RBD palm olein	2.30 (± 1.1)	1.21 – 3.72
RBD palm stearin	1.89 (± 1.1)	0.15 – 3.10

Pilot plant trials

- Acid degumming followed by bleaching causes formation of 3-MCPD esters in bleached oils
- FFA and DAG are not directly correlated to the formation of 3-MCPD esters
- High deodorization temperature led to high formation of the esters

Effect of water washing



Washing of CPO can reduce the 3-MCPD esters formation by 50%

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Effect of FFA and DAG on 3-MCPD esters

Sample	FFA (%)	DAG (%)	3-MCPD esters (ppm)
CPO 1	0.4	3.5	1.62
CPO 2	58.0	7.9	< 0.25
CPO 3	2.8	3.9	0.69

FFA and DAG were not directly correlated with the 3-MCPD esters in heat treated CPO

Effect of FFA and DAG on 3-MCPD esters

Sample	FFA (%)	DAG (%)	3-MCPD esters (ppm)
CPO	3.5	6.1	4.76
E 3	7.8	13.7	4.02
E 6	6.7	12.2	3.44
E 9	6.5	21.6	3.21
E 12	7.8	22.4	2.48
E 24	7.1	25.5	2.48

Inconclusive correlation between DAG and 3-MCPD esters in enzymatically hydrolysed and heated CPO

Effect of DAG on 3-MCPD esters and GE

Sample	3-MCPD esters (ppm)	Glycidyl esters (ppm)
Pure CPO TAG (0.8% DAG)	Not Detected	Not Detected
TAG + 2% Polar (from column chromatography)	4.06	1.77
TAG + PP (2%)	2.34	4.68
TAG + PP (10%)	2.72	**15.86**
TAG + OO (2%)	1.41	2.52
TAG + OO (8%)	1.74	6.44

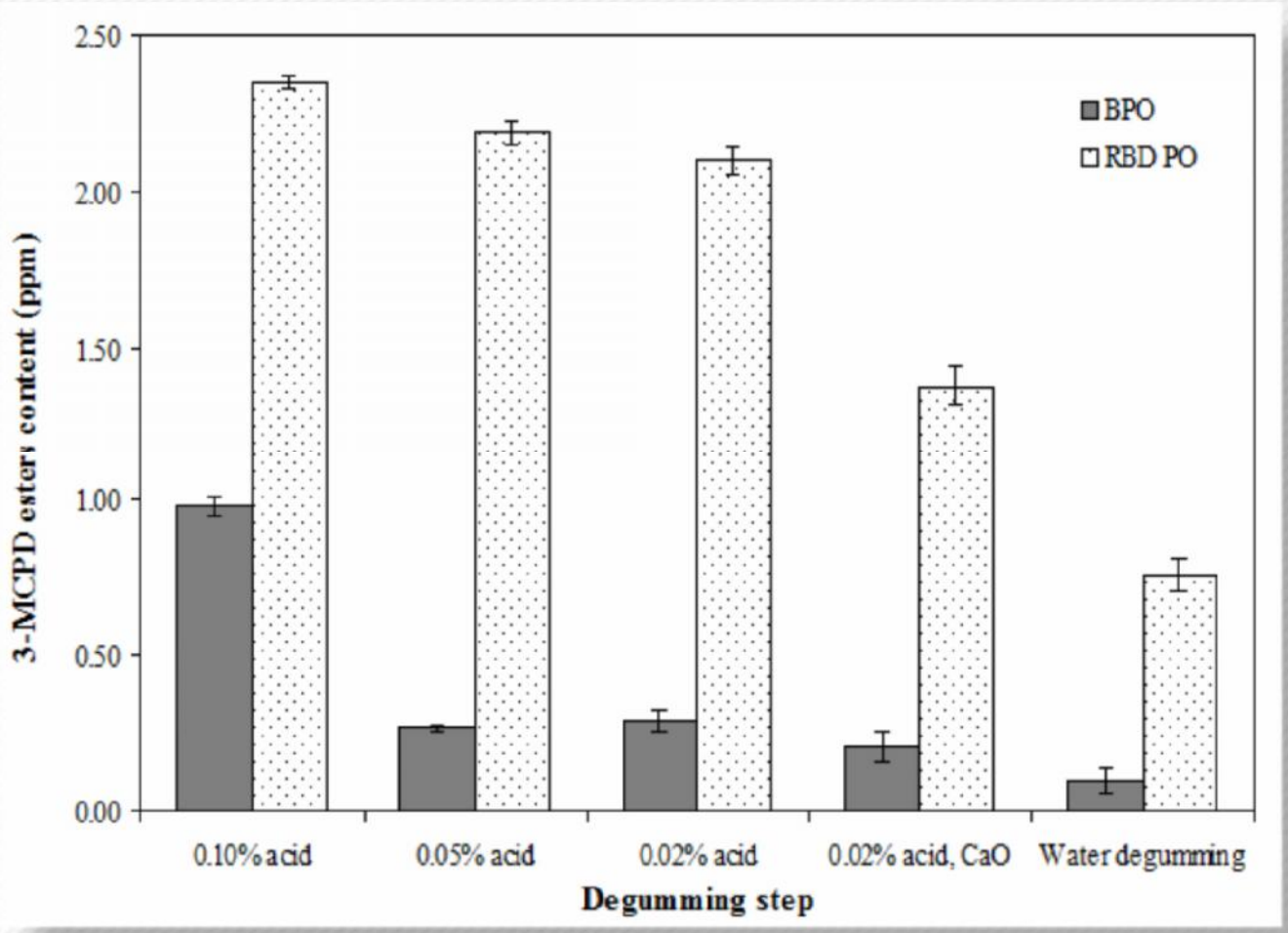
Direct correlation between DAG and GE in heated CPO added with pure DAG

PP = 1,3-dipalmitoylglycerol ; OO = 1,3-dioleoglycerol

Recommendations from pilot trials

- **Low FFA and DAG** levels in crude palm oil (CPO)
- **Rinse CPO** prior to refining
- Combine **acid degumming with water degumming**
- Use **bleaching clay with the lowest chlorine content**, while the **acidity (pH)** should be almost **neutral to alkaline**
- Reduce **deodorization temperature** from 260 °C to **230 °C**
- **Post refining** under mild conditions - **lowers GE** content

Effect of water degumming



Water degumming significantly lowered the 3-MCPD esters formation

Summary from pilot plant trials

Process	3-MCPD esters content (ppm)			
	Max	Min	Average	± SD
Standard				
Acid activated (*n* = 7)	3.89	2.18	2.82	0.57
Natural (*n* = 7)	2.67	1.60	2.21	0.37
Water Degumming				
Acid activated (*n* = 3)	1.50	0.49	0.91	0.52
Natural (*n* = 6)	0.76	0.25	**0.49**	0.22

Tackling the 3-MCPDE & GE issues in a nutshell

Oil Palm Supply Chain

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Current Status

In general :
3-MCPD ~3-4 ppm
GE ~ 6-8 ppm

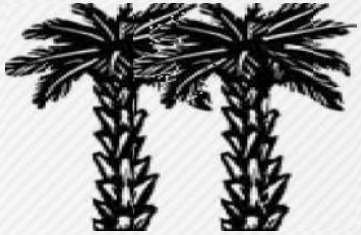
3-MCPDE and GE: Propose to reduce to the level accepted by all parties

3-MCPD

GE

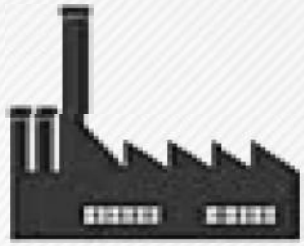
Mitigation Approaches

Plantations



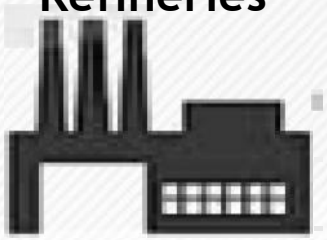
- Reduce chlorine in FFB by changing fertilizers used
- Reduce DAG in PO by ensuring milling within 24 hours

Mills



- Wash FFB to remove chlorine precursor
- FFB sterilization with steam without chlorine
- Wash fresh CPO with slightly alkaline water

Refineries



- Use natural bleaching earths
- Reduce deodorisation temperature to below 230 degrees Celcius at vacuum pressure of 1mbar

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Industrial trials

- In 2017, the **Malaysian Government** has **allocated a special research grant** to improve the quality and safety of the palm oil products – **focus on 3-MCPD esters and GE mitigation**
- **Identify technology providers** from within the industry as well as oversea
- **Collaboration** between technologies identified with selected milling and refinery partners
- **Dynamic monitoring** of 3-MCPD esters and GE during trials
- **Review outputs** from the trials and share best options with the whole industry for possible adoption
- **Preliminary data** – showed very **encouraging results**

Malaysian Patents

- **Sime Darby – Process of manufacturing crude palm oil fractions containing virtually no 3-MCPD esters**
  - Fractionation of CPO with low FFA (1.5%) and DAG (5.5%) contents
  - Deodorized under normal conditions to obtain 3-MCPD esters of < 0.5 ppm

- **Sime Darby – Process of refining CPO product**
  - Pre-treatment of CPO to remove gums, bleaching with earth and silica material
  - Deodorization not more than 240°C
  - To obtain product of < 1 ppm 3-MCPD esters

- **Loders Croklaan B.V.**
  - Treatment of crude oil with acid, bleaching with non-activated clay, deodorization at 180 - 255°C
  - To obtain product of < 2 ppm 3-MCPD esters
  - Possible steps include using enzymes or base in the process

Malaysian Patents

- **Loders Croklaan B.V. – Method for treatment of vegetable oil**
  - For removal of Glycidyl esters using acid activated clay and deodorization at lower temperature (< 200°C)
  - Reduction of 95% in Glycidyl esters content

- **University Putra Malaysia (UPM)**
  - Refining process of palm oil through water washing, centrifugation, acid degumming, followed by natural earth, silicate bleaching and deodorization at 260°C

- **Malaysian Palm Oil Board (MPOB) – Process of reducing 3-MCPD esters**
  - To reduce acidity and chloride contents in CPO during extraction process
  - Removal of chlorides during milling process enables refining to be carried out with less modification
  - Acidity due to vegetative materials during milling process has to be removed as much as possible
  - This process will be initiated during milling to study implementation at commercial scale

The Way Forward

- **Quality of CPO and refining process** will be the **key to mitigate** the formation of 3-MCPD esters and GE – **mandate for higher quality CPO**
- **Ensure palm oil products** produced in Malaysia **contain minimum levels** of 3-MCPD esters and GE – **comply with the importing countries**
- **By 2019** – will **establish Code of Practice** for the reduction of 3-MCPD esters and GE based on industrial trials carried out in 2017 and 2018
- Continuous advocacy plan and engagement with stakeholders

Acknowledgement

- Malaysian Government
- Director General of MPOB and MPOB's Top Management
- Director of Product Development & Advisory Services Division
- 3-MCPD esters Research Team

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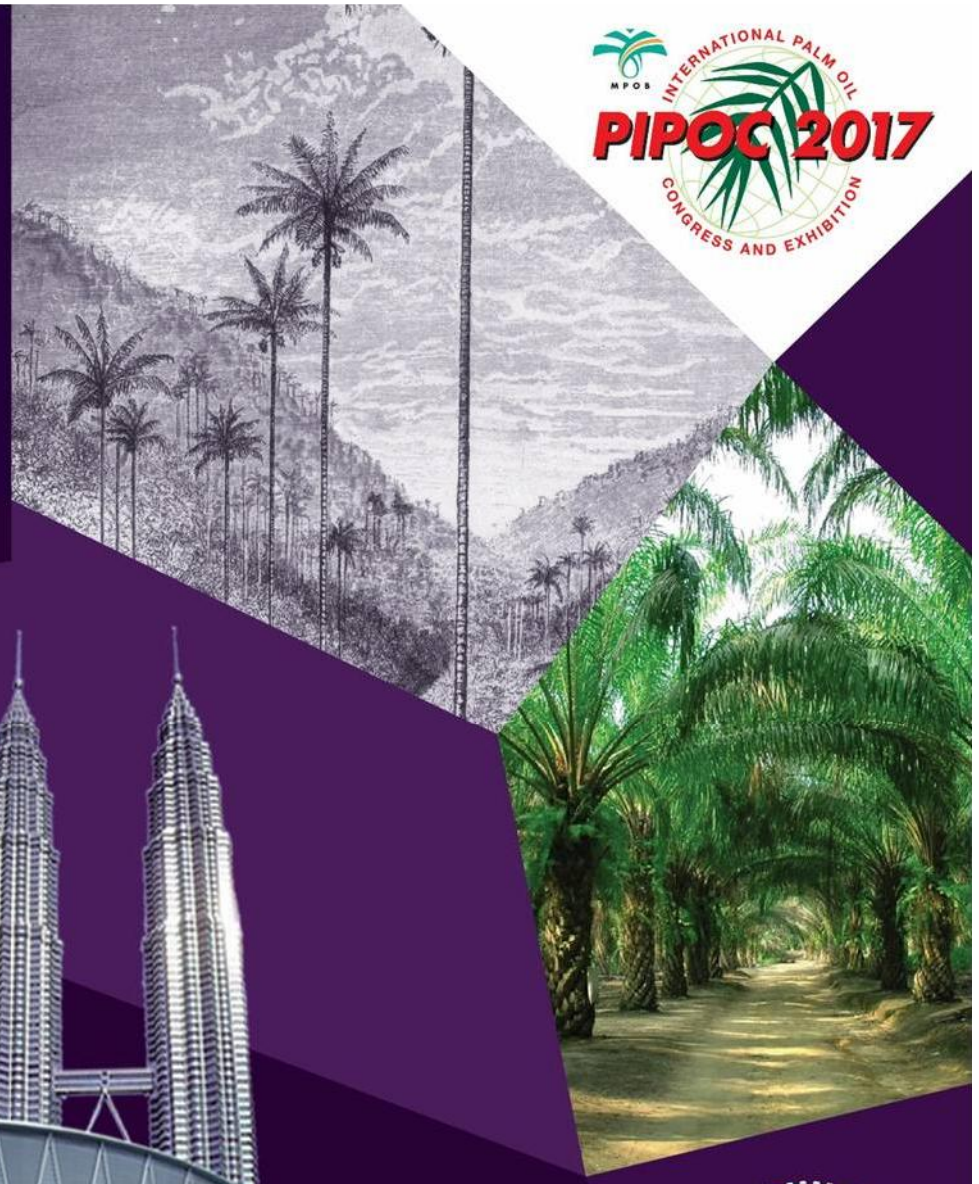
See you at PIPOC 2017

TREASURING THE PAST
CHARTING THE FUTURE



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