What are OLEOCHEMICALS?

Chemicals derived from natural oils/fats - could be of animal, marine or vegetable oil sources

Derived from breaking the oils/fats into corresponding constituents, *i.e.* fatty acids, glycerol, fatty esters, *etc.*

Normal process involves hydrolysis or transesterification
Global production oils and fats in 2011.
Palm Oil

Malaysia 2011:
Production of CPO = 18.9 mil tonnes
Production of CPKO = 2.14 mil tonnes
80 - 85% for food applications
15 - 20% for non-food applications
Palm Oil Chemistry

\[
\begin{align*}
\text{CH}_2\text{OCOR}_1 + \text{HCOCOR}_2 + \text{CH}_2\text{OCOR}_3 & \quad \text{3 H}_2\text{O} \\
\leftrightarrow & \\
\text{CH}_2\text{OH} + \text{R}_1\text{COOH} & + \text{R}_2\text{COOH} + \text{R}_3\text{COOH}
\end{align*}
\]

Triglyceride \quad Water \quad Glycerol \quad Fatty acids

\(R_1, R_2\) and \(R_3\) vary in chain length and degree of unsaturation
## Composition of Oleochemicals Depends on Starting Raw Materials

<table>
<thead>
<tr>
<th>R, R’, R”</th>
<th>Palm oil</th>
<th>Palm stearin</th>
<th>Tallow</th>
<th>Coconut oil</th>
<th>Palm kernel oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>C6</td>
<td></td>
<td></td>
<td></td>
<td>0.2</td>
<td>0.3</td>
</tr>
<tr>
<td>C8</td>
<td></td>
<td></td>
<td></td>
<td>8.0</td>
<td>4.4</td>
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<tr>
<td>C10</td>
<td></td>
<td></td>
<td></td>
<td>7.0</td>
<td>3.7</td>
</tr>
<tr>
<td>C12</td>
<td>0.23</td>
<td>0.3</td>
<td></td>
<td>48.2</td>
<td>48.3</td>
</tr>
<tr>
<td>C14</td>
<td>1.09</td>
<td>1.3</td>
<td>2.5</td>
<td>18.0</td>
<td>15.6</td>
</tr>
<tr>
<td>C16</td>
<td>44.02</td>
<td>55.0</td>
<td>26.6</td>
<td>8.5</td>
<td>7.8</td>
</tr>
<tr>
<td>C18</td>
<td>4.54</td>
<td>5.1</td>
<td>21.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C16:1</td>
<td>0.12</td>
<td></td>
<td></td>
<td>2.3</td>
<td>2.0</td>
</tr>
<tr>
<td>C18:1</td>
<td>39.15</td>
<td>29.5</td>
<td>42.8</td>
<td>5.7</td>
<td>15.1</td>
</tr>
<tr>
<td>C18:2</td>
<td>10.12</td>
<td>7.4</td>
<td>2.3</td>
<td>2.1</td>
<td>2.7</td>
</tr>
<tr>
<td>C18:3</td>
<td>0.37</td>
<td></td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>OTHERS</td>
<td>0.38</td>
<td>0.7</td>
<td>4.0</td>
<td>0.2</td>
<td></td>
</tr>
</tbody>
</table>
Basic Oleochemicals

**Basic:**
- Fatty acids
- Fatty methyl esters
- Fatty alcohols
- Fatty amines
- Glycerine

**Derivatives:** Basic oleochemicals subjected to further reactions
Production of Oleochemicals

1. Hydrolysis
   - PALM OIL / PALM KERNEL OIL

2. Transesterification
   - METHYL ESTERS

3. Hydrogenation
   - GLYCEROL
     - FATTY ACIDS
       - Amination
       - Hydrogenation
   - FATTY ALCOHOLS
     - Hydrogenation
     - Amination
   - FATTY AMINES
     - Amination
Oleochemicals Industry in Malaysia

- Started with one plant in 1980
- Currently in operation 17 plants - total production capacities 2.6 million tonnes.
- Major feedstock - processed PO, PS and PKO
Malaysian Oleochemicals: Export Volume and Value
Export Volume of Basic Oleochemicals

<table>
<thead>
<tr>
<th>Year</th>
<th>Fatty acid (x10^3 tonne)</th>
<th>Fatty alcohol (x10^3 tonne)</th>
<th>Methyl ester (x10^3 tonne)</th>
<th>Glycerine (x10^3 tonne)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2007</td>
<td>900</td>
<td>350</td>
<td>150</td>
<td>100</td>
</tr>
<tr>
<td>2008</td>
<td>800</td>
<td>300</td>
<td>100</td>
<td>80</td>
</tr>
<tr>
<td>2009</td>
<td>750</td>
<td>250</td>
<td>75</td>
<td>60</td>
</tr>
<tr>
<td>2010</td>
<td>700</td>
<td>200</td>
<td>60</td>
<td>50</td>
</tr>
<tr>
<td>2011</td>
<td>650</td>
<td>150</td>
<td>50</td>
<td>40</td>
</tr>
</tbody>
</table>
Major Export Destinations

- **European Union, 22.59%**
- **China, 14.49%**
- **Japan, 9.76%**
- **U.S.A., 8.52%**
- **India, 5.51%**
- **Rest of World, 39.11%**
Beyond Basic

- Consumer Products
- Formulation (Semi Finished)
- Derivatives (Intermediate Chemicals)
- Basic Oleochemicals
- Refined Oil
- Palm Fruit
Application of Oleochemicals

- Surfactant
- Washing and cleaning products
- Personal care products
Surfactant

- Surface active agent, a chemical that stabilises mixtures of oil and water by reducing the surface tension at the interface between the oil and water molecules

- Function - detergent, wetting agents, emulsifiers, conditioning agents, solubilisers.

- Hydrophillic head (charged molecules dissolves in water) and hydrophobic tail (long hydrocarbon chain derived from palm)
C12-C14 fatty acids for foams/lathers (from palm kernel oil)

C16-C18 fatty acids for cleaning purposes (from palm oil)
Soap

- Soap – is still the major application in the non-food sector
- 3 major methods of production
  - Saponification of oils/fats
  - Neutralization of fatty acids
  - Saponification of methyl ester
Soap from Oils and Fats (Saponification)

Mixture of fresh PO/PKO are boiled with excess alkali

Oils/fats converted to soap and soap lye.

Brine is added for better separation

The soap is dried, to produce soap.

The soap lye is processed to USP grade glycerin

\[
\begin{align*}
RCH_2COO-CH_2 \\
RCH_2COO-CH \\
RCH_2COO-CH_2
\end{align*}
\]

\[3 \text{NaOH}\]

\[3 \text{RCH}_2\text{COO}^- \text{Na}^+\]

\[+ \text{CH}_2\text{OHCHOHCH}_2\text{OH}\]

Soap + USP glycerin
Soap from Fatty Acids (Splitting)

In 80’s, oleochemicals industry developed in Malaysia

Fresh PO or PKO are split to fatty acids and sweet water

The fatty acids are either distilled, stripped or fractionated.

The sweet water is processed to USP grade glycerin

\[
\begin{align*}
\text{RCH}_2\text{COO-CH}_2 \\
\text{RCH}_2\text{COO-CH} \\
\text{RCH}_2\text{COO-CH}_2 \\
\downarrow \text{Steam} \\
3 \text{RCH}_2\text{COOH} + \text{CH}_2\text{OHCHOHCH}_2\text{OH} \\
\downarrow \\
\text{Fatty acids} \\
\text{USP glycerin}
\end{align*}
\]
Soap from Fatty Acids (Neutralisation)

Distilled, broad cut or fractionated fatty acids are neutralized to form soap.

\[
\text{RCH}_2\text{COOH} + \text{NaOH} \rightarrow \text{RCH}_2\text{COO}^- \text{Na}^+ \rightarrow \text{Soap}
\]
Soap

Quality of soap noodles produced in Malaysia

- PO  80, 75, 70, 60
- PKO  20, 25, 30, 40
- H₂O  9-12.5%
- TFM  79-83%
- FFA  1.3 - 7.0%
- GLY  0.4 - 0.6%
- Sesq. Present
- Titer 38-52°C
Soap Pilot Plant

1. AMALGAMATOR
2. ROLL MILL
3. PLODDER
4. PNEUMATIC PRESS MOULD
Specialty Soap

- Specialty soaps - contain special additives for specific functionality (1-5%)
- Process similar to toilet soaps
- Categories of additives:
  - emollients, humectant, moisturisers, occlusive agents, dermabrasive agents, medicaments, anti-irritants, etc.
Recently transparent soaps are very popular. Palm-based fatty acid was used to replace tallow. Process - neutralization of fatty acids. Can be used for decoration and skin care. Use as gifts.
## Typical Formulation of Transparent Bar Soap

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fatty acids</td>
<td>Surfactant</td>
</tr>
<tr>
<td>NaOH</td>
<td>Neutralizer</td>
</tr>
<tr>
<td>Glycerol</td>
<td>Humectant</td>
</tr>
<tr>
<td>Sugar</td>
<td>Humectant</td>
</tr>
<tr>
<td>Alcohol</td>
<td>Solvent</td>
</tr>
<tr>
<td>EDTA</td>
<td>Sequestering agent or chelating agent</td>
</tr>
<tr>
<td>Water</td>
<td>Filler</td>
</tr>
</tbody>
</table>
Process of Making Transparent Bar Soap at Lab Scale

1. Neutralization of fatty acids

2. Soap

3. Sugar, glycerol, alcohol, EDTA, water
Colour

Perfume
Mould
Performance Evaluation of Transparent Bar Soap

- Detergency test
- Foaming test
- Transparency value
- Hardness
- Ocular and dermal irritation test
Advantages of Palm-based Transparent Bar Soap

- Contains natural ingredient
- Low pH – closer to pH of skin
Fatty Alcohols

Most important market for fatty alcohols are mid-cut ($C_{12-14}$) and long chain ($C_{16-18}$)

- Derivatized - fatty alcohol ethoxylate (FAE), fatty alcohol ether sulphate (FAES), fatty alcohol sulphate (FAS).
Major application

→ surfactants for household detergents

For example dishwashing liquid, shampoo, shower bath, etc.
Methyl Ester Sulphonate (MES)

- MES is an anionic surfactant derived from oleochemicals. Therefore it is derived from renewable sources.
- It is used as active compound in cleaning products.
- It can be used to replace linear alkyl benzene sulphonate (LAS), the most commonly used petrochemical based surfactant in detergent products.
\[ \text{CH}_3-(\text{CH}_2)_n-\text{CH-CH}-\text{COOCH}_3 \]

\[ \text{SO}_3^- \text{ Na}^+ \]

(dissolves in water with the head group negatively charged = anionic surfactant)
MES Process

1. METHYL ESTER
2. Hydrogenation
3. SATURATED METHYL ESTER (IODINE VALUE < 0.5)
4. Sulphonation
5. Digestion
6. Bleaching
7. Neutralisation
8. Drying
9. Methyl Ester Sulphonate (MES)
# Methyl Ester Sulphonates (MES)

Saturated methyl ester as feedstock

## Properties of MES from Palm Stearin

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Guaranteed</th>
<th>MPOB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Active (%)</td>
<td>&gt;85</td>
<td>88.7 – 90.3</td>
</tr>
<tr>
<td>Disalt (%)</td>
<td>&lt;6</td>
<td>3.7 - 6.0</td>
</tr>
<tr>
<td>Volatile (%)</td>
<td>&lt;2.5</td>
<td>0.7 – 1.2</td>
</tr>
<tr>
<td>Methanol(%)</td>
<td>&lt;0.4</td>
<td>0.3 – 0.4</td>
</tr>
<tr>
<td>H₂O₂ (%)</td>
<td>&lt;0.1</td>
<td>0.02 – 0.1</td>
</tr>
<tr>
<td>Colour (Klett)</td>
<td>&lt;100</td>
<td>30 - 94</td>
</tr>
</tbody>
</table>
Performance of MES

- Good washing performance in hard water and without phosphate
- Good hard water tolerance
- Good synergy with soap as additive
- Good solubility
- Soft and no skin irritation
- Good biodegradability
MES produced by MPOB has been successfully formulated into powder and liquid detergent.

Formulations are usually kept as a trade secret by individual producers.
Fatty Amines

- Derivatives of Fatty acids and Fatty alcohol.
- Traditionally derived from reaction of fatty acids or fatty alcohols and ammonia or urea.
- Classified as Primary, Secondary, Tertiary amines and Quaternary Ammonium Compounds.
Examples of Fatty Amines
(chemical structures)

- **Primary Amines**
  - $\text{R-CH}_{2}\text{-NH}_{2}$
  - $\text{R-CH}_{2}\text{-CH}_{2}\text{-NH}_{2}$

- **Secondary Amines**
  - $\text{R-CH}_{2}\text{-CH}_{2}\text{-NH-CH}_{3}$

- **Tertiary Amines**
  - $\text{R-CH}_{2}\text{-CH}_{2}\text{-CH}_{2}\text{-NH-CH}_{3}$

Hydrocarbon feedstock = $\text{R}$

Ammonia = $\text{NH}_{2}$
Examples of Fatty Amines
(Quaternary Ammonium Compounds or Quats)

- Yellow: hydrocarbon source
- Cyan: hydrophilic positive amine
- Cyan: hydrophilic negative counter ion
- Preferred chemical structure:
  Esterquats-more environmentally acceptable

Traditional dialkyl quats

Quaternary triethanolamine ester or esterquats
Main Application of Fatty Amines

- Primary and secondary amines are used as precursor for tertiary amines.
- Largest application of fatty amines were in textile industries though some may go into specialized industries such as floatation ores, bactericides and additives in plastic.
- Awareness in environmental issues have changed the fatty amines industries significantly especially in household fabric care / softener.
Why we Need to Use Fabric Softener in First Place?

1. Softening and long lasting fragrance on cotton fabric: e.g towel.

2. Prevent accumulation of static charges on silk materials

3. Prevent excessive wrinkle on fabric after laundry
To reduce accumulation of cationic material that will retard the balance of ecosystem in the environment.
Fabric Softener from Palm Oil

Palm Oil Fruits

Palm Oil

Fabric Softener

Quaternary triethanolamine ester or esterquats

Fatty acid methyl ester or fatty acids
Cosmetic & Personal Care
Cosmetic and personal care are substances or preparation intended to be placed on the external part of human body with the aim to cleaning them, perfuming them, changing their appearance and protecting them or keeping them in good condition.
COSMETICS AND PERSONAL CARE

WHITE COSMETICS
- LOTION
- CREAM

COLOURED COSMETICS
- FOUNDATION
- LIPSTICK
- HAIR DYES
- BLUSHER
- EYE SHADOW

HAIR
- SHAMPOO
- CONDITIONER

SKIN
- SHOWER GEL
- SHOWER CREAM
- SHOWER FOAM
- SOAP
- FACIAL CLEANSER
- TONER
- MOISTURISER

FACE
- TOOTH PASTE
- MOUTH WASH

HYGIENE
- DEODORANT
- OTHERS
Emulsifier

- Emulsifier - a type of surfactant used to keep emulsion (immiscible fluids) well dispersed.

Hydrophillic head (water loving)

Lypophillic tail (oil loving)

O/W Emulsion
W/O Emulsion
Importance of Emulsifier
# Oleochemicals in CPC products

<table>
<thead>
<tr>
<th>Function</th>
<th>Class</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emollients</td>
<td>Fatty acids</td>
<td>Stearic acid</td>
</tr>
<tr>
<td></td>
<td>Fatty alcohols</td>
<td>Cetyl/Stearyl/Cetearyl alcohols</td>
</tr>
<tr>
<td></td>
<td>Esters</td>
<td>IPM, IPP</td>
</tr>
<tr>
<td></td>
<td>Triglycerides</td>
<td>PK glycerides, MCT</td>
</tr>
<tr>
<td>Humectant</td>
<td>Polyol</td>
<td>Glycerin</td>
</tr>
<tr>
<td>Surfactants/</td>
<td>Soaps</td>
<td>Stearates, Myristates (Na, TEA)</td>
</tr>
<tr>
<td>emulsifying agents</td>
<td>Esters</td>
<td>Glyceryl stearates, Sorbitan stearates</td>
</tr>
<tr>
<td></td>
<td>Ethers</td>
<td>Ceteareth-2, 12, Steareth-2, 21</td>
</tr>
<tr>
<td></td>
<td>Anionic surfactants</td>
<td>SLS, SLES</td>
</tr>
<tr>
<td>Thickener</td>
<td>Fatty alcohols</td>
<td>Cetyl/ Stearyl/Cetearyl alcohols</td>
</tr>
</tbody>
</table>
## Active Ingredients in Cosmetic Products

<table>
<thead>
<tr>
<th>Active ingredients</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sunscreen</td>
<td>3,4-Benzophenon, zinc oxide, titanium dioxide</td>
</tr>
<tr>
<td>Whitening agent</td>
<td>Arbutin, Kojic acid</td>
</tr>
<tr>
<td>Anti wrinkle</td>
<td>Vitamin A (carotenoids) and E (tocopherol and tocotrienol)</td>
</tr>
<tr>
<td>Anti inflammatory</td>
<td>Tea tree oil</td>
</tr>
<tr>
<td>Moisturising agent</td>
<td>Plant extract <em>eg.</em> cucumber extract</td>
</tr>
<tr>
<td>Anti acne</td>
<td>Tea tree oil</td>
</tr>
</tbody>
</table>
Colour cosmetic, for example compact powder, liquid foundation, lipstick, etc.
Leave on or wash off products with vitamin E. Example, lotion, cream, shampoo, conditioner, etc.
Glycerol

- Glycerol is a polyol obtained from either hydrolysis or transesterification – co-product of the fatty acid, fatty alcohol and biodiesel industries

- CH₂OHCHOHCH₂OH – mwt 92

- Non toxic, widely used in food, cosmetic and pharmaceutical industries
Glycerol .... Traditional Applications

- Many grades – pharmacopia > 99.5% medical & food uses
- Solvent/drugs carrier – cough mixture, antibiotics
- In food products as texture improver, *eg.* ice cream
- Transparency effect in soap
- Antifreeze – when add to water lowers melting point of water
Hygroscopic – useful as humectant in cosmetics, toothpaste, tobacco to prevent moisture loss on storage

Combine with other polyols to produce polyurethane

Convert to monoglyceride – as emulsifier for margarine, bakery products

Glycerol + HNO₃ → nitroglycerine an explosive
Recent Applications

- Epichorohydrin - building blocks for elastomer, resin, *etc.*
- Propylene glycol - as humectant in cosmetic, toothpastes, food, tobacco products, carrier for fragrance.
- Polyglycerol - converted to polyglycerol esters mainly used as emulsifiers in cosmetics and food.
Glycerol Derivatives

Polyglycerol from Crude Glycerine

A potential outlet for biodiesel glycerine
Polyol and Polyurethane

Polyol are compounds with multiple hydroxyl functional groups

\[ \text{H-O-R-O-H} \]

Reacted with isocyananates to make polyurethane

Two possible chemical processes
- Alkoxylation – polyether polyol
- Esterification – polyester polyol
Natural Polyol

- Derived from vegetable oils by several different techniques.

- Types of vegetables oil:
  - Castor oil, Soya bean oil, Canola oil,
  - Peanut oil and Palm oil

- Castor oil has been used since 1937 - the only natural occurring polyol

- Other are produced via chemical modifications
Formation of Polyurethane

ISOCYANATE + POLYOL → POLYURETHANE

GLYCEROL, DERIVATIVE OF TRIGLYCERIDES OR GLYCEROL
High Pressured PU Machine
Palm-based PU for Automotive Components

- PU products formulated palm-based polyol made from palm oil
Rigid PU
Ornamental products – Islamic motives

Ornamental products – contemporary motives
Thank you