PALM OIL: GOING BEYOND BASIC OLEO CHEMICALS

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Dusit Thani Hotel
Manila, Philippines
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PRESENTATION OUTLINE

• Introduction
• What are the raw materials / feedstock?
• Properties / applications
• Surfactants – MES
• Biopolyols – Natural oil Polyols (NOP) in Polyurethanes
• Potential / Summary
THE UNIVERSE OF OLEOCHEMICALS
DOWNSTREAM ACTIVITIES

Profitability

High

Low

Less Consumption

More

Pharmaceutical

Cosmetics/Personal Care

Lubricant/Grease

Soap/Detergent

Basic Oleochemical
DRIVERS OF TODAY’S PRODUCTS

• Population growth
• Expanding middle class
• Increased focus on sustainability, environmental issues
• Built-up infrastructure

All fuels the development of a variety of end-users’ industries eg personal-care, detergents, other household products, building materials etc
WORLDWIDE SOURCES OF RAW MATERIALS FOR THE OLEOCHEMICALS

Source: www.apag.org/oleo/rm.htm
ADVATAGES OF RAW MATERIALS

- Interchangeable
- Many raw materials
- No such parallels exist in petrochemicals
- Natural are replenishable since they can be grown
- Supply assured
- Some are by-products of other industries
MAIN RAW MATERIALS

C16 - C18 Fatty acids

• Developed countries rely on soya, corn, sunflower, rapeseed, tallow and lard

C12 - C14 (lauric oils)

• All rely on SEA – Malaysia, Indonesia, Philippines
<table>
<thead>
<tr>
<th>R, R', R”</th>
<th>PO</th>
<th>PS</th>
<th>Tallow</th>
<th>CNO</th>
<th>PKO</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>
</tr>
<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>C16:1</td>
<td>0.12</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C18</td>
<td>4.54</td>
<td>5.1</td>
<td>21.8</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>2.3</td>
<td></td>
</tr>
<tr>
<td>OTHERS</td>
<td>0.38</td>
<td>0.7</td>
<td>4.0</td>
<td></td>
<td>0.2</td>
</tr>
</tbody>
</table>
Palm oil for non-food uses

- Palm oil rich in C16 and C18
  - Fractionated into palm olein and stearin
    - Palm olein – food
    - Palm stearin – nonfood / oleochemicals

- Palm Kernel Oil rich in C12 and C14
  - Fractionated into palm kernel olein and kernel stearin
    - Palm kernel stearin – food
    - Palm kernel olein – nonfood / oleochemicals
GLYCERIN

- Biodiesel Production
- Soap making
- Fat splitting

Used in - cosmetics, pharmaceuticals, polymers
THE UNIVERSE OF OLEOCHEMICALS
# Surfactant & Uses

<table>
<thead>
<tr>
<th>Types of Surfactants</th>
<th>Structure Examples</th>
<th>Main Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Anionics</strong></td>
<td>-ve FAS, FAES, Soap, LAS, AOS, SME</td>
<td>As active ingredients in cleaning products</td>
</tr>
<tr>
<td><strong>Cationics</strong></td>
<td>+ve Esterquats</td>
<td>As active ingredient in softening products</td>
</tr>
<tr>
<td><strong>Nonionics</strong></td>
<td>no charge FAE, MEE</td>
<td>As active ingredient in mild products</td>
</tr>
<tr>
<td><strong>Amphotericics</strong></td>
<td>+ve -ve Amine oxides</td>
<td>Foam booster etc.</td>
</tr>
</tbody>
</table>
TRADITIONAL FEEDSTOCK FOR PRODUCTION OF SURFACTANTS

**PETROCHEMICAL**

**LINEAR ALKYL BENZENE (LAB)**
**ALPHA OLEFIN (AO)**

Linear Alkyl Benzene Sulphonates (LAS)
- ‘workhorse’ of detergent industry
Alpha Olefin Sulphonates (AOS)
Alpha Olefin Ether Sulfates (AES)

**OLEOCHEMICAL**

**FATTY ALCOHOL**

Fatty Alcohol Sulfates (FAS)
Fatty Alcohol Ethoxylates (FAE) #
Fatty Alcohol Ether Sulfates (FAES)
MES VS FATTY ALCOHOL DERIVATIVES

Methyl Ester

Expensive Intermediate
Fatty Alcohol

High T high P
Hydrogenation

Sulfur trioxide
Sodium hydroxide

Fatty Alcohol Sulfates (FAS)

Methyl Ester

Mild hydrogenation

Saturated Methyl Ester

Sulfur trioxide
Hydrogen peroxide
Methanol
Sodium Hydroxide
Drying

Methyl Ester Sulphonates (MES)

Expensive Intermediate
Fatty Alcohol

Sulfur trioxide
Sodium hydroxide

Fatty Alcohol Sulfates (FAS)
# General Properties of Fatty Acids

<table>
<thead>
<tr>
<th>R, R’, R”</th>
<th>PS</th>
<th>PKO</th>
<th>General Properties/Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>C6</td>
<td>0.3</td>
<td></td>
<td>Irritants to eyes,</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Hydrotrropes, medium chain triglycerides (MCT)</td>
</tr>
<tr>
<td>C8</td>
<td>4.4</td>
<td></td>
<td>Good foaming power, good detergency</td>
</tr>
<tr>
<td>C10</td>
<td>3.7</td>
<td></td>
<td>Good detergency</td>
</tr>
<tr>
<td>C12</td>
<td>0.23</td>
<td>48.3</td>
<td>Good detergency</td>
</tr>
<tr>
<td>C14</td>
<td>1.09</td>
<td>15.6</td>
<td>Good detergency, Good lubricity, Poor oxidative stability (if unsaturated)</td>
</tr>
<tr>
<td>C16</td>
<td>44.02</td>
<td>7.8</td>
<td>Good solvent, sweet taste, moisturizing</td>
</tr>
<tr>
<td>C16:1</td>
<td>0.12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C18</td>
<td>4.54</td>
<td>2.0</td>
<td>Poor solubility</td>
</tr>
<tr>
<td>C18:1</td>
<td>39.15</td>
<td>15.1</td>
<td>Good detergency, Good lubricity</td>
</tr>
<tr>
<td>C18:2</td>
<td>10.12</td>
<td>2.7</td>
<td>Poor oxidative stability</td>
</tr>
<tr>
<td>C18:3</td>
<td>0.37</td>
<td></td>
<td></td>
</tr>
<tr>
<td>GLYCEROL</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
MES PROCESS

METHYL ESTER

Low Hydrogenation

SATURATED FATTY METHYL ESTER (IODINE VALUE < 0.5)

Sulfonation

Digestion

Bleaching

Neutralization

Drying

METHYL ESTER SULFONATES (MES) (>80% ACTIVE AND <6% DISALT)
### SUITABLE RAW MATERIALS FOR PRODUCTION OF MES BASED ON CHARACTERISTIC EVALUATED

<table>
<thead>
<tr>
<th>Weight (%)</th>
<th>Coconut C12-C14</th>
<th>Palm Kernel C8-C18</th>
<th>Palm Stearin C16-C18</th>
<th>Tallow C16-C18</th>
<th>Soya C18</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium methyl ester sulphonate (α-SME)</td>
<td>71.5</td>
<td>69.4</td>
<td>83</td>
<td>77.5</td>
<td>75.7</td>
</tr>
<tr>
<td>Disodium carboxy sulphonate (di-salt)</td>
<td>2.1</td>
<td>1.8</td>
<td>3.5</td>
<td>5.2</td>
<td>6.3</td>
</tr>
<tr>
<td>Methanol</td>
<td>0.48</td>
<td>0.60</td>
<td>0.07</td>
<td>0.00</td>
<td>0.03</td>
</tr>
<tr>
<td>Hydrogen peroxide</td>
<td>0.10</td>
<td>0.04</td>
<td>0.13</td>
<td>0.15</td>
<td>0.05</td>
</tr>
<tr>
<td>Water</td>
<td>14.0</td>
<td>15.2</td>
<td>2.3</td>
<td>2.9</td>
<td>1.4</td>
</tr>
<tr>
<td>Petroleum ether extractable</td>
<td>2.6</td>
<td>2.7</td>
<td>2.4</td>
<td>4.8</td>
<td>7.2</td>
</tr>
<tr>
<td>Sodium carboxylate (RCOONa)</td>
<td>0.2</td>
<td>0.2</td>
<td>0.3</td>
<td>0.3</td>
<td>0.5</td>
</tr>
<tr>
<td>Sodium sulphate</td>
<td>1.2</td>
<td>1.8</td>
<td>1.5</td>
<td>2.3</td>
<td>2.4</td>
</tr>
<tr>
<td>Sodium methyl sulphate (CH₃OSO₃Na)</td>
<td>8.0</td>
<td>8.4</td>
<td>7.2</td>
<td>7.7</td>
<td>2.5</td>
</tr>
<tr>
<td>10% pH</td>
<td>5.0</td>
<td>5.3</td>
<td>5.3</td>
<td>5.4</td>
<td>5.8</td>
</tr>
<tr>
<td>Klett colour, 5% active (α-SME+disalt)</td>
<td>30</td>
<td>310</td>
<td>45</td>
<td>180</td>
<td>410</td>
</tr>
</tbody>
</table>
HOW TO USE MES?

MES flakes were grounded and mixed with other dry materials & liquid additives.

- **Powder Detergent**
  - Density: 0.7-1 g/mL
  - Particle size: 230-1500 microns

- **Liquid Detergent**
  - pH: 8-9

MES flakes were dissolved (70-80°C) and blended with other solid and liquid materials (40-50°C).

- **Powder Pilot Plant (Marion Mixer)** with a capacity of 120 kg/hr detergent.
- **Liquid Pilot Plant** with two mixing tanks with a capacity of 50 liter and 120 liter.
DETERGENCY OF POWDER

Instrument: Spectrophotometer CM-3600d (whiteness), top loading
Condition: 50 ppm, 25°C, ratio wash liquor 1:18.5, dosage 0.8g/L
DETERGENCY OF LIQUID

Instrument: Spectrophotometer CM-3600d (whiteness), top loading
Condition: 50 ppm, 25°C, ratio wash liquor 1:18.5, dosage 1.62g/L
BIODEGRADATION OF MES VS LAS

% Biodegradability vs Days

- LAS
- MES
MES PERFORMANCE SUMMARY

- Good detergency especially in hard water and without phosphate
- Good tolerance to water hardness
- Good synergy with soap – as soap additive
- Good solubilizing power
- Mild and non-irritant to the skin
- Good biodegradation characteristics
**PERFORMANCES: MES VS OTHERS**

<table>
<thead>
<tr>
<th></th>
<th>LABS</th>
<th>SME</th>
<th>FAS</th>
<th>FAES</th>
<th>AOS</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>DETERGENCY(*)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>FOAMING(*)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>SOLUBILITY</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>SKIN COMPATIBILITY</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>SENSITIVITY TO H₂O-HARDNESS</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- Similar detergency power
- Similar foaming power
- Acceptable solution
- Better skin compatibility
- Lower sensitivity to water hardness

(*) Very similar, using optimum chain length selection

Source: Ballestra
**PALM BASED MES**

<table>
<thead>
<tr>
<th>Active</th>
<th>&gt; 85%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Disalt</td>
<td>&lt; 6%</td>
</tr>
<tr>
<td>Color</td>
<td>&lt; 100 Klett</td>
</tr>
</tbody>
</table>

**Detergency at Various Water Hardness**

- **MES 16/18**
- **AOS**
- **AS**
- **LAS**

**Effect of Disalt on Detergency**
### MES PRODUCTION COST

<table>
<thead>
<tr>
<th>Raw Materials</th>
<th>MES</th>
<th>LAS</th>
<th>Utilities &amp; Operating Costs</th>
<th>MES</th>
<th>LAS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfur</td>
<td>12.10</td>
<td>11.22</td>
<td>Electricity</td>
<td>21.35</td>
<td>18.36</td>
</tr>
<tr>
<td>M.E / L.A.B.</td>
<td>403.78</td>
<td>721.00</td>
<td>Steam</td>
<td>17.83</td>
<td>1.22</td>
</tr>
<tr>
<td>Sodium hydroxide</td>
<td>33.62</td>
<td>23.18</td>
<td>Cooling water</td>
<td>1.20</td>
<td>1.20</td>
</tr>
<tr>
<td>Methanol</td>
<td>15.36</td>
<td>-</td>
<td>Operating labor</td>
<td>12.00</td>
<td>12.00</td>
</tr>
<tr>
<td>Hydrogen peroxide</td>
<td>45.00</td>
<td>-</td>
<td>Maintenance</td>
<td>10.65</td>
<td>10.65</td>
</tr>
<tr>
<td>Sodium sulphate</td>
<td>2.00</td>
<td>-</td>
<td>General overhead</td>
<td>6.63</td>
<td>6.63</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>2.63</td>
<td>-</td>
<td>Tax and Insurance</td>
<td>1.96</td>
<td>0.88</td>
</tr>
</tbody>
</table>

**TOTAL COST OF MES**
$586.11/TONNE

**TOTAL COST OF LAS**
$806.29/TONNE

**SUMBER:** SOFW-Journal 130 6-2004

**China Price, 2006**
LAB $\to$ USD 1239.00/MT, LAS $\to$ USD 1004.47/MT
### Successful trials runs in China

1. 21-23 March 2005 – 28 tonnes
2. Nov/Dec 2005 - 1000 tonnes

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Randas</th>
<th>Ayanat</th>
<th>CHINA</th>
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</thead>
<tbody>
<tr>
<td>Alive(%)</td>
<td>&gt;85%</td>
<td>86.17</td>
<td></td>
</tr>
<tr>
<td>Salt(%)</td>
<td>&lt;5%</td>
<td>4.99</td>
<td></td>
</tr>
<tr>
<td>Color(5% Klett)</td>
<td>&lt;40</td>
<td>84</td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>5-8</td>
<td>55</td>
<td></td>
</tr>
<tr>
<td>Companies</td>
<td>Location</td>
<td>Capacity (tonnes/yr)</td>
<td></td>
</tr>
<tr>
<td>-----------------------------------------------</td>
<td>---------------------------</td>
<td>----------------------</td>
<td></td>
</tr>
<tr>
<td>Grundy</td>
<td>Kuantan, Pahang</td>
<td>24,000</td>
<td></td>
</tr>
<tr>
<td>Lion ECO Chemicals Sdn Bhd</td>
<td>Tanjung Langsat, Johor</td>
<td>25,000</td>
<td></td>
</tr>
<tr>
<td>KL Kepong Oleomas</td>
<td>Selangor</td>
<td>50,000</td>
<td></td>
</tr>
<tr>
<td>Guangzhou Keylink Chemical Co. (Lonkey-Sime Darby-Emery Oleochemicals)</td>
<td>China</td>
<td>40,000</td>
<td></td>
</tr>
<tr>
<td>Huish (upgraded from 54,000 tonnes/yr)</td>
<td>Utah</td>
<td>70,000</td>
<td></td>
</tr>
</tbody>
</table>
MES TECHNOLOGY PROVIDER

- Chemithon, USA
- Ballestra, Italy
- Stepan, USA
- Lion, Japan
THE UNIVERSE OF OLEOChemicals
POLYURETHANES

- Broad spectrum of properties and applications
- Solid to cellular
- Amorphous to crystalline
- Hydrophilic to hydrophobic
- Elastomeric to plastic
- Biodurable to biodegradable
• It is more diversified than man-made/natural polymer materials

• Can go into transportation, construction, furniture, electronic medical appliance etc

• **Key – versatile complex chemistry**

• Traditionally almost all chemicals from petroleum

But now, vegetable oils or NOPs from soya, castor and palm oils can be used effectively.
PU formulation
- Polyols – usually 2-3 types of polyols
- Isocyanate (TDI, MDI, PMDI)
- Blowing agent
- Additives
- Catalysts
- Cross-linkers
- Etc

MPOB polyol pilot plant
(1 tonne capacity)
## PALM-BASED POLYOLS

<table>
<thead>
<tr>
<th>Properties</th>
<th>POP PIONEER</th>
<th>POP PREMIER</th>
</tr>
</thead>
<tbody>
<tr>
<td>OHV, mg KOH/g sample</td>
<td>110–150</td>
<td>64–90</td>
</tr>
<tr>
<td>AV, mg KOH/g sample</td>
<td>&lt;1.0</td>
<td>&lt;1.0</td>
</tr>
<tr>
<td>Viscosity @ 25°C, cP</td>
<td>4800–7500</td>
<td>533–650</td>
</tr>
</tbody>
</table>
POLYOL

- Carpet underlay
- Flower foam
- Sandwich Panels
- Monier CoolBoard
- Refrigeration
- PU w Plywood
- Head Rest
- Coated fertilizer
- PU for furniture
- PU Sheets
PU products – rigid
– Factory trial at a local companies
PALM-BASED VISCOELASTIC FOAM (PB)

- Addition of 10 pphp of palm-based polyol – low resiliency, slow recovery
- Incorporation of 26% filler did improve mechanical properties of viscoelastic foam (e.g. tensile strength from 47 to 82 kPa)

<table>
<thead>
<tr>
<th></th>
<th>Resiliency</th>
<th>Wet comp. set</th>
<th>Dry comp. set</th>
</tr>
</thead>
<tbody>
<tr>
<td>PB</td>
<td>1.3%</td>
<td>2.6%</td>
<td>1.9%</td>
</tr>
<tr>
<td>Commerical</td>
<td>1.3%</td>
<td>2.6%</td>
<td>1.8%</td>
</tr>
</tbody>
</table>

Viscoelastic foam
Successfully produced with incorporation of POP Pioneer polyol from 5 to 15 pphp

<table>
<thead>
<tr>
<th></th>
<th>Resiliency, %</th>
<th>Impact Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Palm-based Seating Foam</td>
<td>~50</td>
<td>~3.4</td>
</tr>
<tr>
<td>Commercial Seating Foam</td>
<td>57</td>
<td>3.4</td>
</tr>
</tbody>
</table>
BIODEGRADATION STUDY

2 months Shake Flask Test:

Palm-based foams completely degraded in MN

Some of the petroleum-based foams were still in their original forms in MN

Palm-based foams deteriorated/fragmented in MS

No changes in petroleum-based foams in MS
**SURFACTANTS DEMAND OVERVIEW**

**SURFACTANT TYPES – %**
- Anionic: 56%
- Nonionic: 34%
- Cationic: 4%
- Amphoteric: 1%
- Others: 5%

**AREA OF USES – %**
- HH-Det: 49%
- I&I: 11%
- Text Aux: 7%
- Emul Poly: 5%
- Others: 18%
SURFACTANTS FORECAST TO 2030

2010 = 13.1 MIL TONNE
2030 = 29.87 MIL TONNE
SUSTAINABLE SURFACTANTS

CPO

Crude Glycerin

Crude ME

Minor comp.

Distilled ME

Saturated ME

New Uses

Anionic

Cationic

Nonionic

Winter Fuel
Polyurethane Production by Product Type

2010 NAFTA Total Production 2.85 Mtons*
2010 World Wide Total Production 13.65 Mtons (CAGR of 4.7%; 2011-16)

Global PU Market is dominated by DOW, BASF, Bayer, and Huntsman.

- 2011 BASF constructing 240,000 tonnes/year MDI in China.
- Huntsman plans to build a second 240,000/year MDI in Caojing, China.
- Bayer investing Ibil Euro to expand capacity MDI from 350ktpa to 1000 ktpa by 2015.
- Shandong Bluestar Dongda Chemical Co. investing $900 million to increase capacity polyether polyols from 160kt to 360kt.
SYNERGY: OLEO AND PETROCHEMICALS

Plant based / Animal Based
- Even numbered carbon chain
- Regarded natural

Petroleum based
- Branched and odd numbered carbon chain
- Regarded synthetic

Differences or absence of one characteristic in either one of the resources create an opportunity for synergism between both resources
Having the flexibility to use both NOPs and petrochemical polyols allows formulators to be creative – there are many raw materials eg EO is important in PU industry

PU are always formulated for specific performance and processing requirements. There is no single or specific polyol or isocyanate that can be used in all PU formulations.

NOPs can be used as partial or drop-in replacement in rigid and flexible formulations. Most applications require combination of polyols.

Understanding in structure - property relationship is necessary.
a value chain of basic oleochemicals, oleoderivatives and consumer/industrial end-products

Basic Oleochemicals
- Fatty acids
- Fatty alcohols
- Methyl Esters
- Glycerin

Oleo-derivatives
- Soap noodle
- Surfactants
- Dimeric Acids
- Azelaic Resins
- Bio Lubricants
- Glycerol Derivatives
- Esters
- Amines
- Metal Soap
- Agrochemicals
- Bio Polyols
- Fatty Alcohol Amide

End Products

20% of world capacity

2% of 20%
CONSUMERS’ DEMAND

- Safety, Health
- Environment Concern
- Renewable resources
- Non-Toxic
- Biodegradable
- Natural
- Green label
- Religious issues
Palm Oil: Perennial Crop

- Since 1875/ commercial planting 1917
- Life-long 25-30 yrs period
- Land need to be cleared once

Source: Oil World 2010
* Combined tonnage of palm oil and palm kernel oil

<table>
<thead>
<tr>
<th>Oil Crop</th>
<th>Production (million t)</th>
<th>% of total production</th>
<th>Total area (million ha)</th>
<th>% of total Area</th>
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<tr>
<td>Oil palm</td>
<td>52.30*</td>
<td>38.2</td>
<td>12.8</td>
<td>5.5</td>
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<td>Soya bean</td>
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HOLISTIC SUSTAINABLE DEVELOPMENT (SD) WITH EQUAL EMPHASIS ON THE 3PS

Source: Yusof et al, 2007
ACKNOWLEDGEMENT

- Zulina Abd Maurad, Process & Engineering Unit
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MPOB
THANK YOU

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