

# **PILOT SCALE SUPERCRITICAL FLUID CHROMATOGRAPHY : AN EXPERIENCE**

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**Malaysian Palm Oil Board**

# Presentation Outline

- **Development of separation to pilot scale**
- **Chemistry of palm phytonutrients**
- **Pilot scale SFC**
- **Conclusions**

# Development of Separation to Pilot Scale

- **Started in MPOB in 1992**
- **Method developed for the analyses of palm phytonutrients and glycerides**
- **Preparative scale study for the isolation and recovery of palm phytonutrients**
- **Problem encountered : chemistry of palm oil is complex**



# **Chemistry of Palm Oil and Phytonutrients**

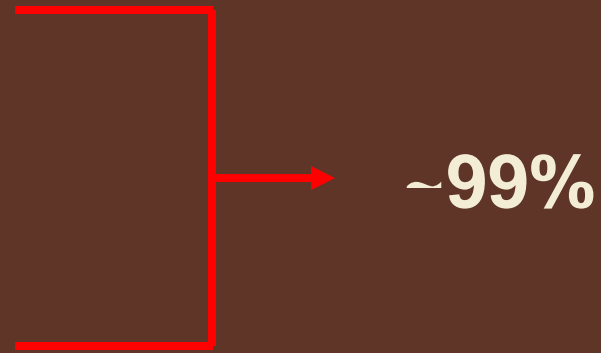
# Composition of Crude Palm Oil

Triglycerides

Diglycerides

Monoglycerides

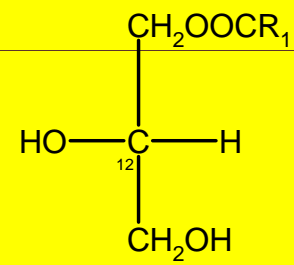
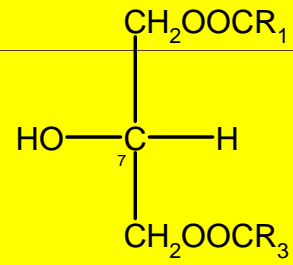
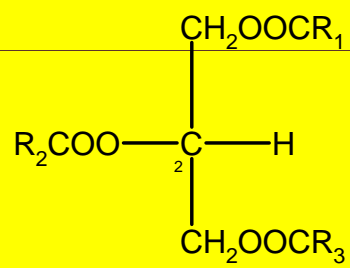
Free Fatty Acids



Minor components

(containing phytonutrients)





## Glycerides

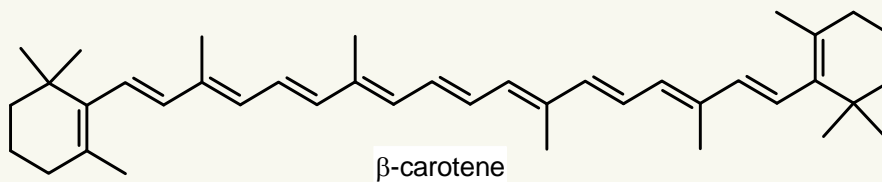
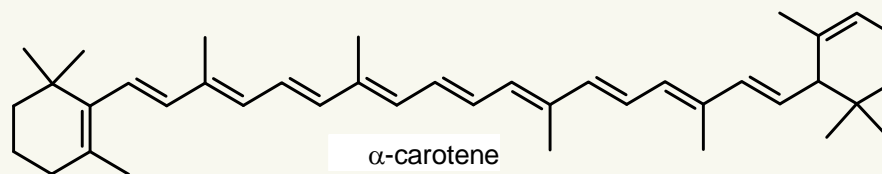
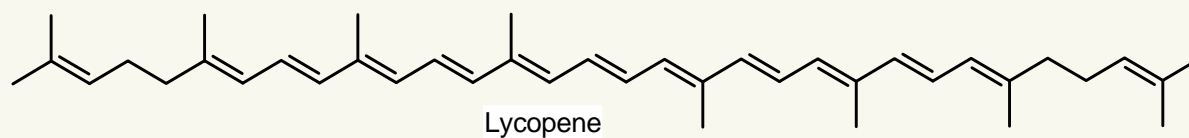
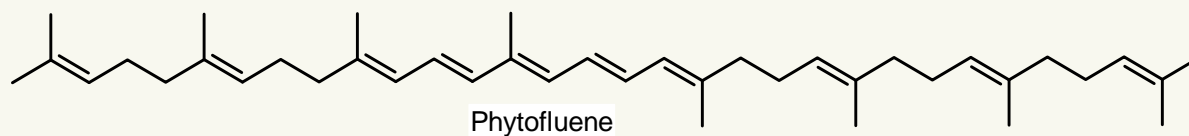
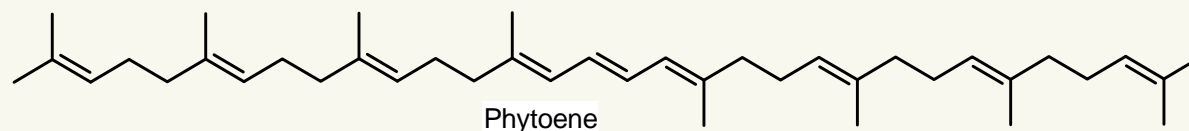
# Phytonutrients in Crude Palm Oil

Phytonutrients	Crude Palm Oil (ppm)
Tocols	600–1000
Carotenes	500–700
Phytosterols	300–620
Squalene	250–540
Coenzyme Q (Ubiquinones)	10–80
Lecithin (Phospholipids)	20–100

## Individual Carotenes Composition

Carotenes	Crude Palm Oil (%)
Phytoene	1.27
Phytofluene	0.06
$\beta$ -Carotene	56.02
$\alpha$ -Carotene	35.06
Cis- $\alpha$ -Carotene	2.49
$\zeta$ -Carotene	0.69
$\gamma$ -Carotene	0.83
$\delta$ -Carotene	0.33
Neurosporene	0.29
$\beta$ -Zeacarotene	0.74
$\alpha$ -Zeacarotene	0.23
Lycopene	1.30

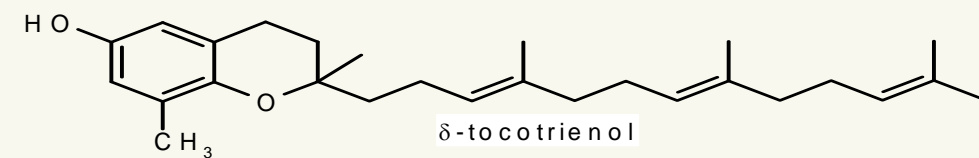
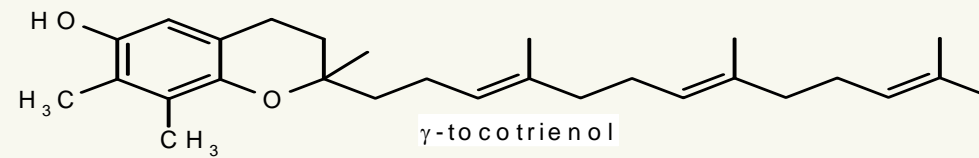
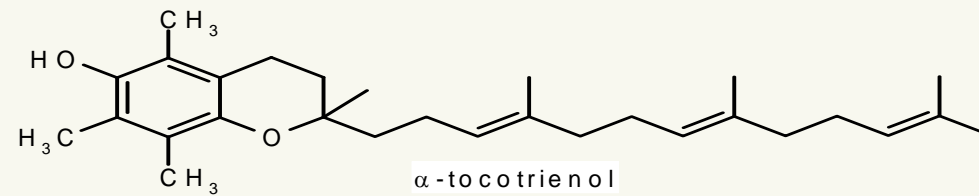
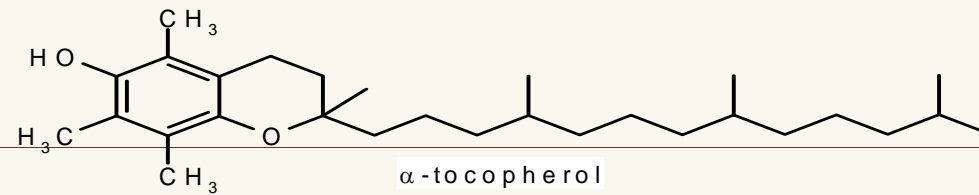
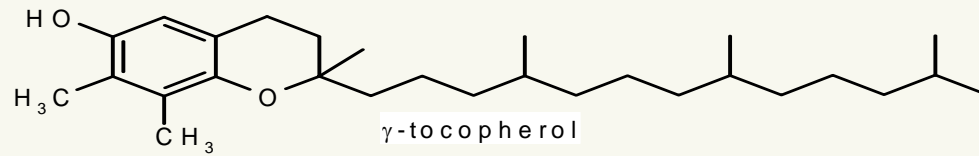
# Structures of Selected Palm Carotenes



## Individual Tocols Composition

Tocol	Crude Palm Oil (%)
$\alpha$ -tocopherol	22
$\alpha$ -tocotrienol	20
$\gamma$ -tocotrienol	46
$\delta$ -tocotrienol	12

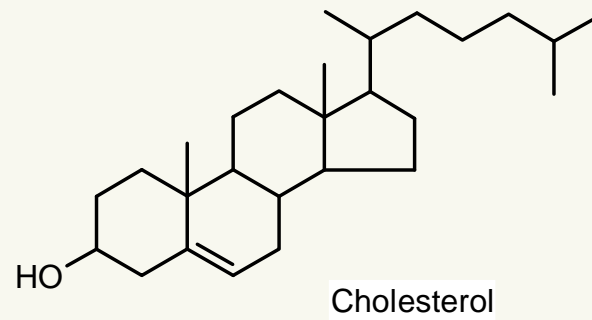
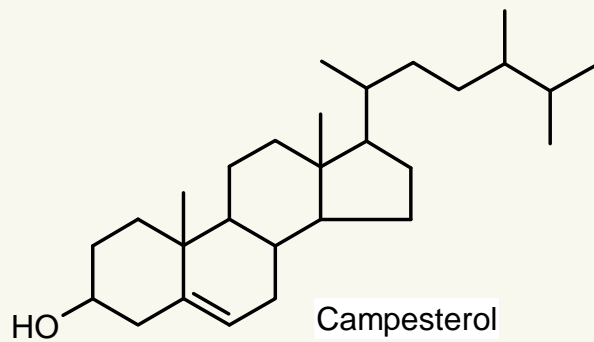
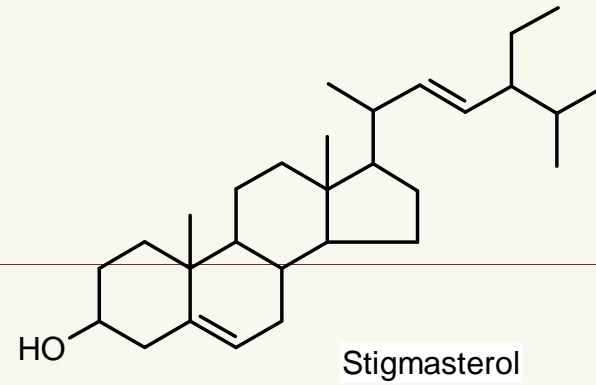
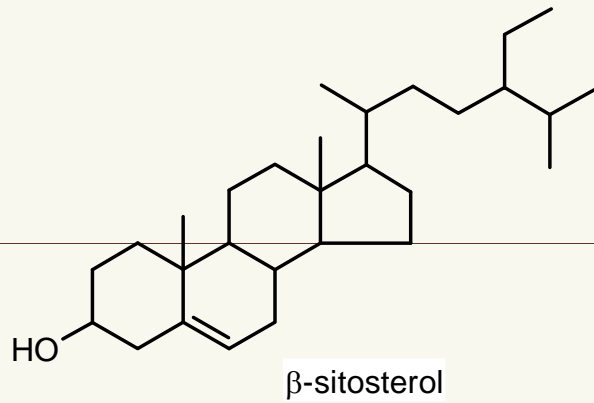
# Structures of Tocols



# Individual Sterols Composition

<b>Phytosterols</b>	<b>Crude Palm Oil (%)</b>
<b><math>\beta</math>-Sitosterol</b>	<b>60</b>
<b>Campesterol</b>	<b>13</b>
<b>Stigmasterol</b>	<b>24</b>
<b>Cholesterol</b>	<b>3</b>

# Structures of Palm Sterols



## **Separation involves :**

- **Separations of different classes of compounds. E.g. Hydrocarbon (squalene and carotenes), chromanols (tocols) and sterols**
- **Separation of structurally similar compounds e.g. individual tocols, individual carotenes and individual sterols**

# Values of Palm Phytonutrients

- Applications as nutraceuticals (health supplements), cosmetics, pharmaceuticals
- Fine chemicals
- Medical research



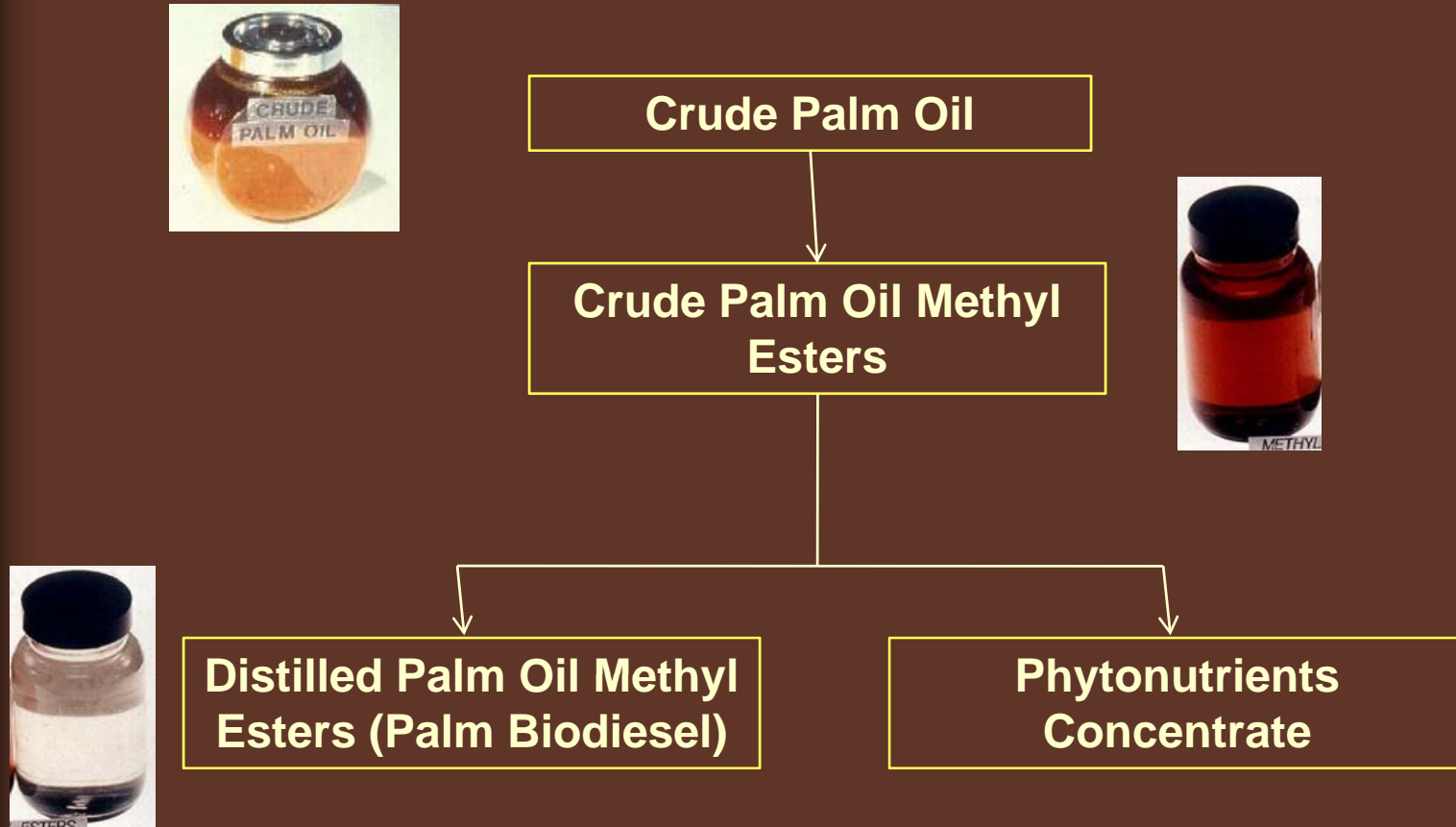
# Considerations for Pilot Scale SFC

- **Cost of equipments**
- **Chemistry of starting material**
- **Products – justify the cost of equipments?**
- **Safety – high pressure equipments**

## **Is it worth to isolate and recover the palm phytonutrients?**

- **Amount of palm phytonutrients is too small to be significant - complement the palm biodiesel production**
- **Value of high purity individual phytonutrients will be able to justify the capital investment**

# Complementing the Palm Biodiesel Production



Source :

Choo, Y.M, Ng, M.H and Mohd Basri, W. (2007). Supercritical Fluid Chromatography : Application in Oil Palm Industry. Paper presented at 1<sup>st</sup> International Conference on SFC, 24 – 25 September 2007, Pittsburgh, Pennsylvania, U.S.A.

# Value-Added Products

For every 1 tonne of palm methyl esters (palm biodiesel) burnt as fuel, we also burn away:

0.6 kg	Carotenes
0.8 kg	Tocols
0.5 kg	Phytosterols
0.4 kg	Squalene
0.05 kg	Coenzyme Q
0.06 kg	Phospholipids (lecithin)

# Value-Added Products

The values of the phytonutrients are:

<b>Carotenoids (30%)</b>	<b>US300/kg</b>
<b>Vitamin E (50%)</b>	<b>US500/kg</b>
<b>Phytosterols</b> <b>(Industrial Grade, as b-sitosterol)</b>	<b>US25/kg</b>
<b>Squalene (Nutraceutical Grade)</b>	<b>US33/kg</b>
<b>Coenzyme Q (Pharmaceutical Grade)</b>	<b>US2,800/kg</b>
<b>Phospholipids (Nutraceutical Grade)</b>	<b>US25/kg</b>

**Source :**

Choo, Y.M, Ng, M.H and Mohd Basri, W. (2007). Supercritical Fluid Chromatography : Application in Oil Palm Industry. Paper presented at 1<sup>st</sup> International Conference on SFC, 24 – 25 September 2007, Pittsburgh, Pennsylvania, U.S.A.

# Value-Added Products

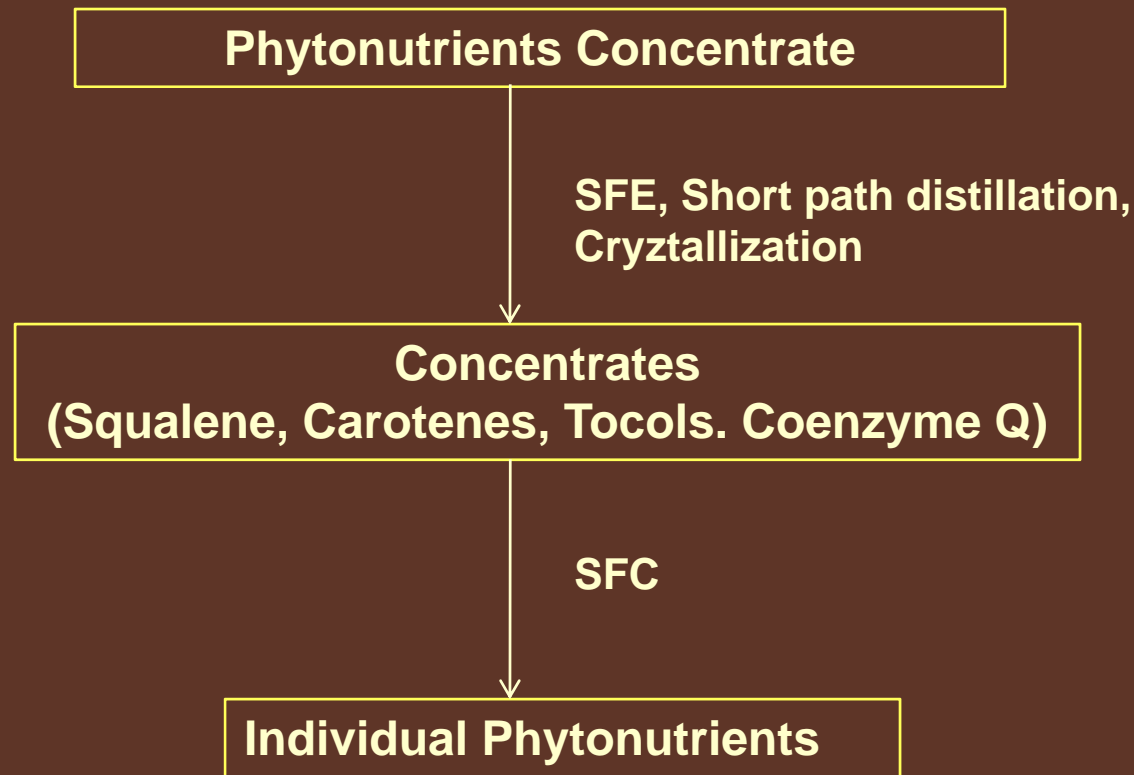
For every 1 tonne of methyl esters  
burnt as fuel, the value of  
phytonutrients burnt away is:

**~US 970/tonne  
(RM 3,686/tonne)**

**Source :**

Choo, Y.M, Ng, M.H and Mohd Basri, W. (2007). Supercritical Fluid Chromatography : Application in Oil Palm Industry. Paper presented at 1<sup>st</sup> International Conference on SFC, 24 – 25 September 2007, Pittsburgh, Pennsylvania, U.S.A.

# Purification before SFC



- ❖ High purity (>90%) of the following are to be produced:
  - individual carotene, e.g.  $\alpha$ - and  $\beta$ -carotenes, lycopene and phytoene
  - individual vitamin E isomers, e.g.  $\alpha$ - and  $\gamma$ -tocopherols,  $\alpha$ -,  $\gamma$ - and  $\delta$ -tocotrienols
  - $\beta$ -sitosterol

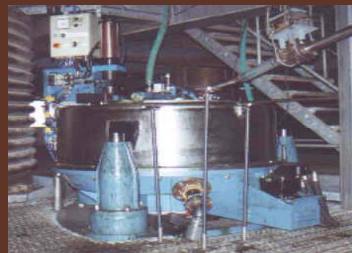
Source :

Choo, Y.M.; Ng, M.H.; Ma, A.N. and Yusof Basiron. A Method of Extracting and Isolating Minor Components from Vegetable Oil. Malaysian Patent Application No. PI20024432 (2002), European Patent Application No. 03257486.5, United States Patent No. 7161055

Choo, Y.M.; Ng, M.H.; Ma, A.N. and Yusof Basiron. A Method for the Isolation and Recovery of Individual Carotenes, Sterols and Coenzyme Q from Palm Oil. Malaysian Patent Application No. PI20040486 (2004)

# Pilot Scale Facilities in MPOB for the Production of Palm Phytonutrients

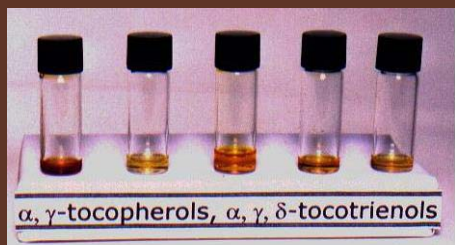
- Short path distillation
- Supercritical fluid extraction (SFE) (SC-CO<sub>2</sub>)
- Supercritical fluid chromatography (SFC) (SC-CO<sub>2</sub>)
- Crystallization



# Production of Individual Carotene, Tocols & Cholesterol-free Sterol



SFC



+



+



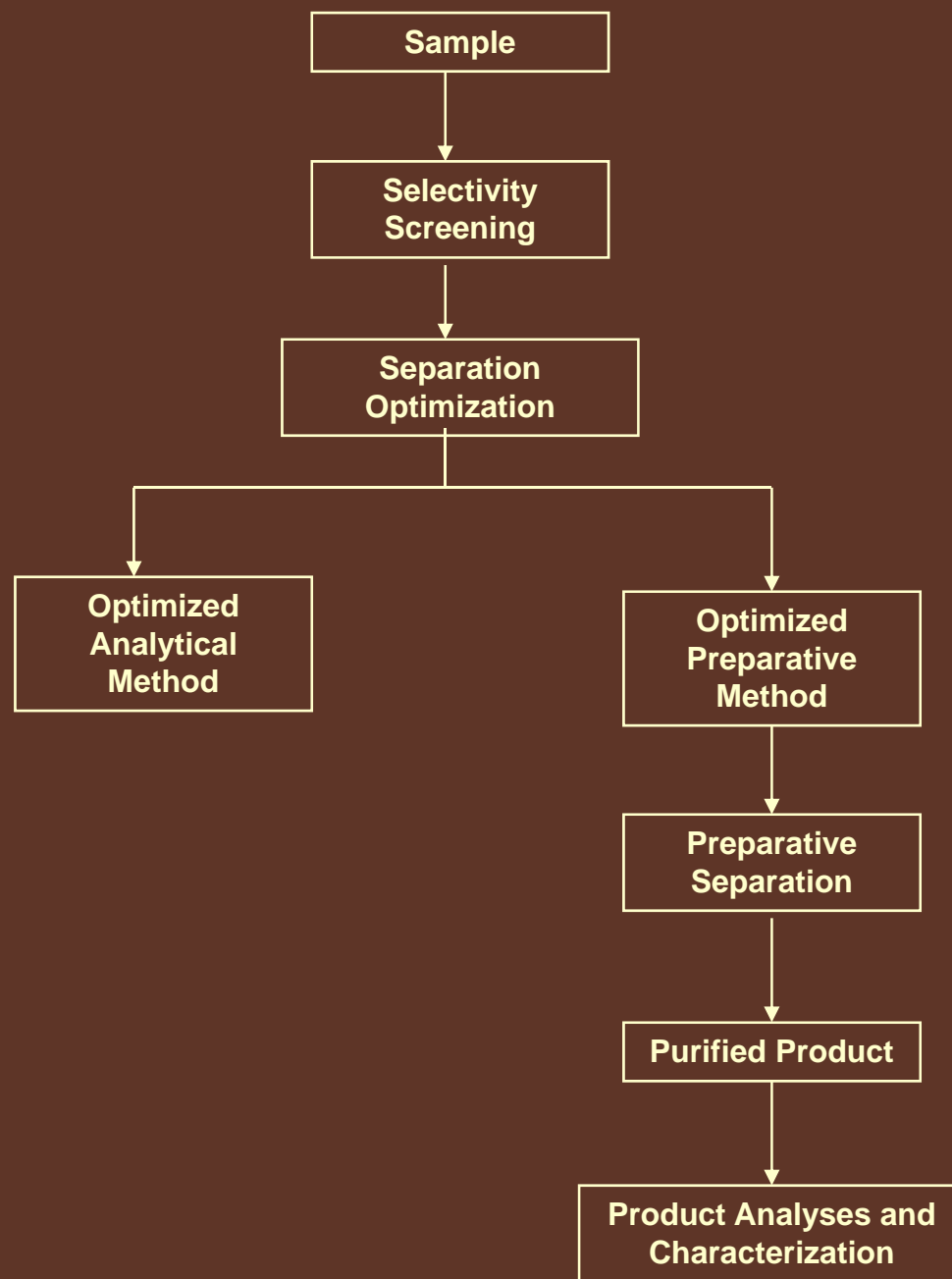
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# Disadvantages of Supercritical Fluids

- Physical chemistry of the fluids are very complex
- Recovery systems must be well engineered
- Capital costs for equipments are very high



# Optimized Separation

- **Compatible solvent system with feed material**
- **Maximized throughput**
- **Cost**

# Determination of Optimal Separation Parameters

- Temperature
- Modifier
- Flow rate
- Pressure

# Isolation Strategy

- **Compatibility of modifiers and solvents**
- **Solubility of desired product(s)**
- **Presence of undesirables**

# Confirmation Separation(s) Prior to Actual Run

- Changes in feed material
- Changes in separation
- Loading capacity
- Carry over
- Refinement in fraction collections

## Specification of SFC 600 System

- Manual and automated mode injection pump
- Column : 350mm I.D.
- Several stages collection
- CO<sub>2</sub> pump : 600kg/hr (max)
- Co-solvent pump : 40L/hr (max)
- CO<sub>2</sub> and co-solvent recycling system



## Receivers & Pumps

- **CO<sub>2</sub> receiver – eliminate the need for storage of gas cylinders**
- **Modifier receiver**
- **CO<sub>2</sub> pump : 600kg/hr (max)**
- **Modifier pump : 40L/hr (max)**



**Receiver**

# Column

- **Dynamic axial compression for large diameter, efficient and stable column**
- **Stationary phase of choice to be packed and repacked when necessary**
- **Determination of stationary phase needed (e.g. silica)**
- **Life time of column yet to be evaluated**



**Column**

## **Loading and injection of samples**

- **Dissolved in solvents**
- **Introduced as solution in organic solvent, and injected onto the column by loop valve**

# Problems

- Limited solubility of solutes in modifier
- Pilot scale SFC requires introduction of relatively large volumes
- Peak band broadening

## Possible Solution

- **Installation of packed pre-column and removal of solvents by passage of gas**
- **Solves the problem of different dissolving solvent and modifier**

# Separators

- **Several stages collections**
- **Fractions collected based on time**



**Separators and Flash Evaporators**



**Separators**

# Recycling Systems

- **CO<sub>2</sub> recycling system equipped with activated carbon filter to remove odour and impurities**
- **Parameters need to be optimised to ensure constant concentration of modifier in mobile phase after recycling**
- **High efficiency needed to minimize the consumption of CO<sub>2</sub> and modifier**



**Modifier Recycling**

# **Cost Considerations for Pilot Scale SFC**

**Con :**

- **High pressure devices**
- **Safety systems related to manipulation of high pressure compressible fluids**
- **Different temperature levels; many heating and cooling systems add to investment cost**

## **Cost Considerations for Pilot Scale SFC**

**Pro :**

- **Operating cost is much reduced**
- **Stationary phase is cheap and recycled**
- **No special column packing required**

# Conclusions

- **Palm based feed material need to be treated before loading into SFC**
- **Optimisation of separation conditions are important for good separation**
- **Safety is a major concern in pilot scale SFC due to the high pressure and heat exchangers**
- **Mobile phase recycling is needed to minimise operation cost**



THANK YOU