

# CHAPTER 1 GENERAL INTRODUCTION

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Malaysian oil palm plantation

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## 1.1 MALAYSIAN OIL PALM PLANTATION

The oil palm tree (*Elaeis guineensis*) originates from West Africa where it grows in the wild and later was developed into an agricultural crop. In Malaysia, oil palm tree was introduced by the British in early 1870's just as an ornamental plant. By 1917, the first commercial planting took place in Tennamaran Estate in Selangor. The planting activities will then later lay the foundations for the current vast oil palm plantations and the oil palm industries in Malaysia. The cultivation of oil palm increased at a fast pace in early 1960's, under the government's agricultural diversification programme, which was introduced to reduce the country's economic dependence on rubber and tin. Later in the 1960's the government introduced land settlement schemes for planting oil palm as a mean to eradicate poverty for the landless farmers and smallholders. The oil palm plantations in Malaysia are largely based on the estate management system and smallholder scheme [1]. As of 2009, 4.69 million hectares of land in Malaysia are under oil palm cultivation; producing 25.48 million tonnes of crude palm oil and 3.07 million tonnes of crude palm kernel oil. For that reason, Malaysia is one of the largest producers and exporters of palm oil in the world, accounting for 11% of the world's oils and fats production and 27% of export trade of oils and fats [2].

Oil palm is a monoecious crop as it bears both male and female flowers on the same tree. Each tree produces compact bunches weighing between 10 and 25 kilograms with 1000 to 3000 fruitlets per bunch. Each fruitlet is almost spherical or elongated in shape. Generally, the fruitlet is dark purple, almost black and the colour turns to orange red when ripe. Each fruitlet consists of a hard kernel (seed) enclosed in a shell (endocarp) which is surrounded by a fleshy mesocarp. Palm trees may grow up to sixty

feet and more in height. The trunks of young and mature trees are wrapped in fronds which give them a rather rough appearance. The older trees have smoother trunks apart from the scars left by the fronds which have withered and fallen off. Oil palm tree will start bearing fruits after 30 months of field planting and will continue to be productive for the next 20 to 30 years, thus ensuring a consistent supply of oils. Each ripe bunch is commonly known as Fresh Fruit Bunch (FFB). In Malaysia, the oil palm trees planted are mainly the *tenera* variety, a hybrid between the *dura* and *pisifera*. The *tenera* variety yields about 4 to 5 tonnes of crude palm oil (CPO) per hectare per year and about 1 tonne of palm kernels. The oil palm is the most efficient oil-bearing crop in the world, requiring only 0.26 hectares of land to produce one tonne of oil while soybean, sunflower and rapeseed require 2.22, 2.00 and 1.52 hectares, respectively, to produce the same [1].

## **1.2 PALM OIL MATRICES**

The oil palm produces two types of oils. They are crude palm oil (CPO) from the fibrous mesocarp and crude palm kernel oil (CPKO) from the kernels. The various steps in extraction of CPO and CPKO are shown in Figure 1.1 and 1.2 respectively. Although both oils originate from the same fruit, palm oil is chemically and nutritionally different from palm kernel oil. It is one of the only two mesocarp oils available commercially, the other being olive oil. In conventional milling process, the FFB's are sterilised and the fruitlets stripped off. The loose fruitlets are then digested and pressed to extract the CPO. The kernels are separated from the fibrous mesocarp in the press cake and later cracked to obtain CPKO. Palm oil, being vegetable oils, is cholesterol-free. Having a naturally semi solid characteristic at room temperature with a specific origin melting point between 33 °C to 39 °C, it does not require hydrogenation for use as a food ingredient. CPO is deep orange red in colour due to the high content of natural

carotenes. Palm oil is rich source of carotenoids and vitamin E which confers natural stability against oxidative deterioration. Fractionation separates oil into liquid and solid fractions. Palm oil can be fractionated into liquid (olein) and solid (stearin) components. Palm oil has a balanced ratio of unsaturated and saturated fatty acids. It contains 40% oleic acid (monounsaturated fatty acid), 10% linoleic acid (polyunsaturated fatty acid), 45% palmitic acid and 5% stearic acid (saturated fatty acid). This composition results in an edible oil that is suitable for use in a variety of food applications.

Palm olein is the liquid fraction obtained by fractionation of palm oil after crystallization at controlled temperatures. In addition to finding uses as in the case of palm oil, palm olein is widely used as cooking oil. It is rich in monounsaturated fatty acid and antioxidant vitamins and is widely used as oil in diet in many parts of the world. This liquid fraction obtained from the refining of palm oil, is rich in oleic acid (42.7-43.9%), beta-carotene, and vitamin E (tocopherol and tocotrienols) [3]. Furthermore, production of monoacylglycerol from palm olein is an alternative that increases advantages and value added of palm olein [4]. Besides being marketed as liquid oil, it can be promoted for blending with other edible oils [5]. This is because its moderately low linoleic acid content is admirably suited for blending with oils with a high polyunsaturated fatty acid contents [6], prompting a nickname 'blending partner' for palm olein. For example, refined palm olein is blended with rice bran in Japan and it is blended with groundnut oil in Malaysia.

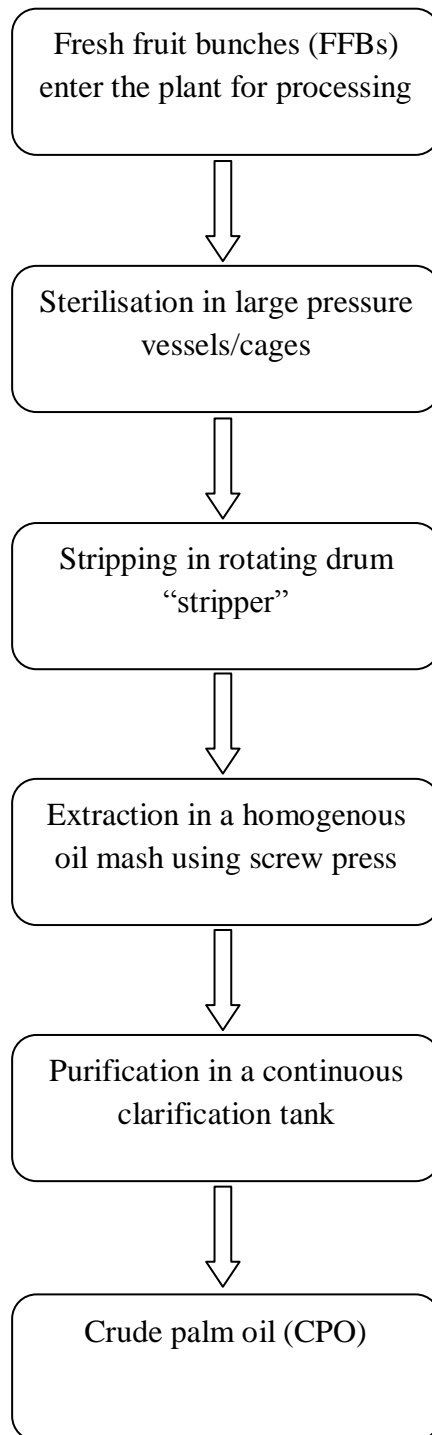


Figure 1.1: Crude palm oil processing flow chart.

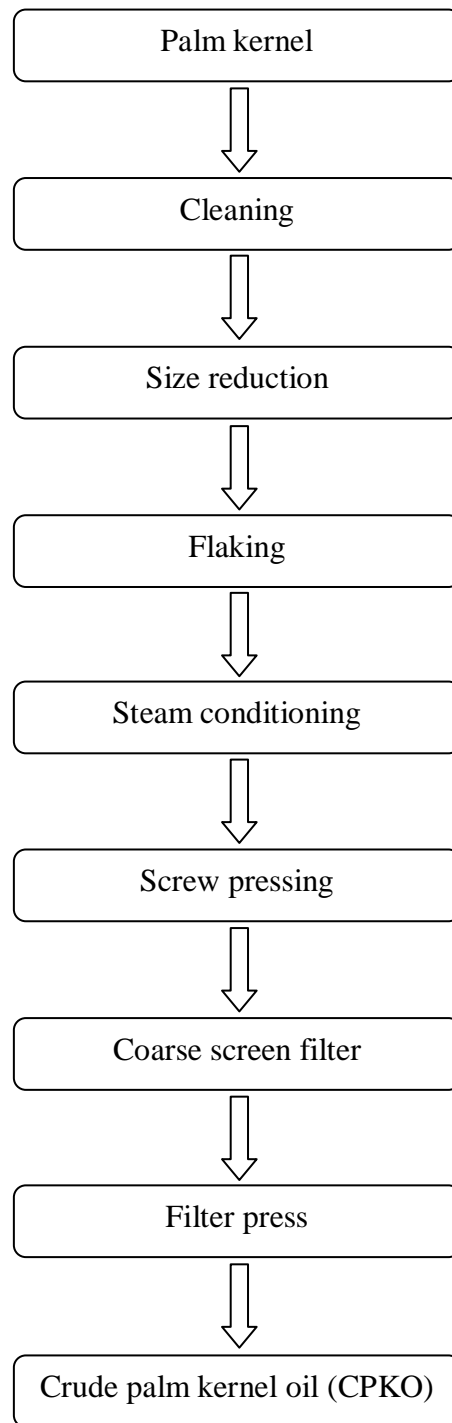


Figure 1.2: Crude palm kernel oil processing flow chart.

Palm stearin is the solid fraction obtained by controlled temperature fractionation of palm oil [7]. It is thus a co-product of palm olein. It is always traded at a discount to palm oil and palm olein, making it a cost effective ingredient in several applications. The physical characteristics of palm stearin differ significantly from those of palm olein. It contains 1-2% myristic acid, 47-74% palmitic acid, 4-6% stearic acid, 16-37% oleic acid, and 3-10% linoleic acid [8]. Palm stearin is a very useful source of fully natural hard fat component for products such as shortening and pastry and bakery margarines. The high melting fraction of palm stearin with melting point ranging from 45-55 °C is non-edible. However it could be appropriately blended and interesterified with liquid oils in order to modify the physical characteristics to meet the functional properties and the quality required for shortening [9].

Palm kernel oil is obtained from the kernel of the oil palm fruit. The oil composition is very different from that of the palm oil. It constitutes about 45% of the palm nut of the palm oil and on the wet basis, the kernel contains about 47-50% oil [10]. Palm kernel olein is the liquid component of palm kernel oil obtained from fractionation. It contains a high proportion of saturated fatty acids and is characterized by its high lauric acid content which ranges from 40-50% [11]. Palm kernel stearin is the more solid fraction of palm kernel oil obtained from fractionation. Native palm kernel oil is less suitable to be used in fat-based food products as compared to palm kernel stearin [12]. However, several studies have been conducted on blends of CPKO with other oils/fats in order to explore their potential uses in vanaspati [13], ice cream [14], margarine [15, 16, 17], and frying oil [18]. There is a growing trend to use palm kernel oil products as an ingredient in the production of non-hydrogenated trans-fat free margarine. Palm kernel stearin are called cocoa butter substitute and are mainly used as total replacement for cocoa butter in special recipes [19, 20]. In some instances,

particularly when hydrogenated, palm kernel stearin exhibits performance superior to that of cocoa butter. Apart from their excellent melting properties, hydrogenated palm kernel oil products generally have good resistance to fat bloom and show good resistance to oxidative stress [21].

### **1.3 PESTICIDE**

A pesticide is defined as any substance or mixture of substances intended for preventing, destroying, repelling or mitigating any pest [22]. A pesticide may be a chemical substance, biological agent (such as a virus or bacterium), antimicrobial, disinfectant or device used against any pest. Pests include insects, plant pathogens, weeds, molluscs, birds, mammals, fish, nematodes (roundworms), and microbes that destroy property, spread disease or are a vector for disease or cause a nuisance. Although there are benefits to the use of pesticides, there are also drawbacks, such as potential toxicity to humans and other animals. Food and Agriculture Organization (FAO) defined the term pesticide as *“any substance or mixture of substances intended for preventing, destroying or controlling any pest, including vectors of human or animal disease, unwanted species of plants or animals causing harm during or otherwise interfering with the production, processing, storage, transport or marketing of food, agricultural commodities, wood and wood products or animal feedstuffs, or substances which may be administered to animals for the control of insects, arachnids or other pests in or on their bodies. The term includes substances intended for use as a plant growth regulator, defoliant, desiccant or agent for thinning fruit or preventing the premature fall of fruit, and substances applied to crops either before or after harvest to protect the commodity from deterioration during storage and transport”* [23].



## **1.4 PESTICIDE CLASSIFICATION**

Pesticides can be classified by target organism, chemical structure, and physical state [24]. Pesticides can also be classed as inorganic, synthetic, or biological (biopesticides), although the distinction is sometimes quite blur. Some of the most common pesticides used today are fungicide, herbicide, and insecticide. On the other hand, many pesticides can also be grouped into chemical families. Prominent insecticide families include organochlorine, organophosphate, pyrethroid and carbamate.

### **1.4.1 FUNGICIDE**

Fungicides are chemical compounds or biological organisms used to kill or inhibit fungi or fungal spores. Fungi can cause serious damage in agriculture, resulting in critical losses of yield, quality and profit. Fungicides can either be contact, translaminar, or systemic. Contact fungicides are not taken up into the plant tissue and only protect the plant where the spray is deposited. Translaminar fungicides redistribute the fungicide from the upper sprayed leaf surface to the lower unsprayed surface. Systemic fungicides are taken up and redistributed through the xylem vessels to the upper parts of the plant and hence new leaf growth is protected for a short period.

### **1.4.2 HERBICIDE**

Herbicide, commonly known as a weed killer, is a substance used to kill unwanted plants. Selective herbicides kill specific targets while leaving the desired crop relatively unharmed. Some of these act by interfering with the growth of the weed and are often synthetic imitations of plant hormones. Herbicides used to clear waste ground, industrial sites, and railway embankments are non-selective and kill all plant material with which they come into contact.

### **1.4.3 INSECTICIDE**

An insecticide is a pesticide used against insects. Insecticides are used in agriculture, medicine, industry, and the household. The use of insecticides is believed to be one of the major factors behind the increase in agricultural productivity in the 20<sup>th</sup> century [25]. Most insecticides have potential to significantly alter ecosystems, in which many are toxic to humans while others could concentrate in the food chain. Systemic insecticides are incorporated by treated plants. Insects ingest the insecticides while feeding on the plants. Contact insecticides are toxic to insects brought into direct contact. Efficacy is often related to the quality of pesticide application, with small droplets often improving performance. Natural insecticides, such as nicotine, pyrethrum, and neem extracts are made by plants as defences against insects. Nicotine based insecticides have been barred in the U.S. since 2001 to prevent residues from contaminating foods [26]. Inorganic insecticides are manufactured with metals, while organic insecticides are synthetic chemicals which comprise the largest numbers of pesticides available for use today.

### **1.5 PESTICIDE RESIDUES**

A residue will result when a crop or food animal (commodity) or medium of the environment (air, water, soils, wildlife, etc.) is treated with a chemical, or exposed unintentionally to it by drift, in irrigation water, in feed, or by other means. The chemical will typically be detectable in the commodity or medium at the time of treatment or exposure, and also for some period of time afterward. The magnitude of the residue at any point in time will depend on the treatment or exposure level and on the rate at which the residue dissipates from the commodity. Dissipation rates are a function of the chemical's physical and chemical properties, and also of the environment in

which the chemical resides. For an example, an insecticide sprayed to protect some crops may dissipate by a number of processes, including:

1. Volatilization to the atmosphere (influenced by the insecticide's volatility or vapour pressure, temperature and wind movement).
2. Washing off by rainfall or overhead irrigation (a function of the chemical's water solubility).
3. Chemical degradation (influenced by molecular makeup of insecticide and by such factors as sunlight, moisture, and temperature).
4. Growth dilution (the chemical residue concentration will decrease as the crops become larger even without physical or chemical dissipation of residue from the crop).
5. Metabolism and/or excretion in the case of animals and some plants. The parent chemical may be converted to one or more degradation products that will then constitute the components of the remaining residue.

## **1.6 PESTS IN THE OIL PALM PLANTATION**

In oil palm plantation, yield can be severely affected by pests that compete against the palm for nutrients, infect, or damage the palm [27]. As a result, losses due to pests and efforts to control pests are major obstacles in the cultivation of oil palm. According to Wood *et al.* [28], a single bagworm outbreak caused leaf defoliation of 10-year-old palms and reduced the yield to 40-50 % over the next two years. Some of the pests and diseases that could be found in oil palm are listed in Table 1.1.

Table 1.1: Pests and diseases of the oil palm

Stage	Diseases, disorders, and pests
Nursery	Anthrachnose, leaf spot disease, aphids, cockchafers
Mature leaf	Crown disease, white stripe, patch yellow, leaf eating caterpillars, bagworms, nettle caterpillars
Stem and root	Ganoderma trunk rot/basal, stem rot, upper stem rot, termites
Bunch and fruit	Bunch and fruit rot, <i>Marasmius palmivorus</i> , bunch moth ( <i>Tirathaba rufivena</i> )
Young palms	Grasshoppers, rhinoceros beetles
Mature palms	Beetles, termites
Fruits	Rat ( <i>Ratticus tiomanicus</i> ), birds ( <i>Psittacula longicanda</i> , <i>Psittinus cynurus</i> , and <i>Loriculus galgulus</i> )

Source: Turner *et al.* [29].

### 1.6.1 WEEDS

The main problem in the oil palm plantation is weed that dominates during the immature stage in which the palm fronds are quite small. At this stage, the ground surrounding the oil palm is exposed to sunlight, assisting prolific growth of the weeds. Nonetheless, when the palm is matured, the close canopy prevents sunlight from reaching the ground, thus reducing weed growth. Furthermore, the shade provided by the palm canopy influences the nature of weed composition, and grass species tend to dominate as the oil palm gets bigger [30].

These noxious weeds can be grouped into shrubs, creepers, grasses, and ferns. The most prevalent shrubs are the *Eupatorium odouratum* and *Melastoma malabathricum*, found in most countries in the tropics. The plants have long been acknowledged as a major problem in Asia and can be eradicated mechanically, manually and by using herbicides. Creepers such as the *Mikania coradata* can cause yield depression in the palms. The most common ferns are *Gleichenia lineris*, *Lygodium spp.*, *Steochlaena palustris*, *Cyathea moluccana* and *Cyclosorus spp.* *Imperata cylinderca* is considered the most destructive grass. Palms that grow in areas where the weed is found are generally stunted and retarded in growth. Other grasses which are considered to be detrimental for the oil palm are *Pennisetum purpureu*, *Sorghum halapens*, *Brachiaria mutica*, *Chloris barbata* and *Ischaemum muticum* [31].

The effect of weeds on oil palm is difficult to quantify because of their long economic life (20-30 years) but they can affect the growth of crops or cause yield losses [32]. In Malaysia, attempts to assess crop losses caused by specific weed species have been made because they compete vigorously with crops for water, light, and nutrients [33]. For example, *Asystasia gangetica* was found to be competitive to oil palm and caused a yield depression of 13% [34]. A depression in oil palm yield ranging from 10-20% due to *Mikania micrantha* has also been reported [35, 36].

### **1.6.2 INSECTS**

Some of the major known pests of oil palm are grasshoppers, stick insects, bagworms, nettle and slug caterpillars, skippers, cutworm, leaf miner moths, bunch moths, rhinoceros beetles, black palm weevils, cockchafers, taro beetles, leaf miner beetles, leafhoppers, aphids, mealy bugs and scale insects. Damage by the oil palm leaf miner *C. lameensis* has been observed in all oil palm growing countries in Africa,

causing wide spread defoliation and result to considerable reduction in the yield of fresh fruit bunches (FFB) [37]. The oil palm leaf miner, *Coelaenomenodera lameensis*, formerly called *Coelaenomenodera minuta*, is endemic in West Africa [38, 39, 40]. It is the most important insect pest of the oil palm in West and Central Africa causing widespread defoliation and loss in yield of fresh fruit bunches [41].

In Malaysia the rhinoceros beetle, *Oryctes rhinoceros*, has emerged as major pest of oil palm since a prohibition on burning for clearance of old palms and organic matter was introduced in the 1990s. Rhinoceros beetle adults are particularly troublesome during establishment of young palms and damage is expected to increase with the current extensive replanting schemes in Malaysia, which provide an abundance of breeding sites for the pest as well as large numbers of susceptible young palms [42]. The infestation levels of *Oryctes rhinoceros* were investigated by Norman *et al.* in the oil palm trunk heaps at Sepang, Selangor, Malaysia [43]. A more recent study has suggested that in certain areas, *O. rhinoceros* can readily migrate to infest an area as soon as replanting is conducted, when there is an abundance of oil palm trunk chips [44].

The bagworm, *Metisa plana*, is caterpillars which feed on the oil palm leaflets, using small attached pieces of the leaflets as the outer casing for the caterpillar. It is an important pest of oil palms in Malaysia. Bagworm outbreaks are a recurring problem in some parts of Malaysia, especially in Southern Perak, Peninsular Malaysia. Infestations in smallholder plots are often left uncontrolled and over time, these populations can increase and can cause recurring outbreaks which can affect neighbouring plantations [45]. A moderate defoliation (10–13%) by bagworms can cause a yield decline of around 30–40% over 2 years [46].

### **1.6.3 DISEASES**

The main diseases which the oil palm is prone to are vascular wilt, basal stem rot, bud and spear rot, red ring disease, and sudden wilt. Of the five diseases mentioned, basal stem rot is the major disease in Malaysian oil palm plantation [27]. It is caused by several species of *Ganoderma*. Oil palm planted after coconut, especially on coastal marine clays, is susceptible to this disease. However, the disease also occurs on peat and inland soils. The species of *Ganoderma* that commonly found in Malaysia is *Ganoderma boninense*.

*Ganoderma* is a white rot fungus which causes economic loss of oil palm in various regions around the world including Southeast Asia [47]. Typically the fungus may attack already weakened oil palm as *Ganoderma* seldom seriously infects undamaged trees. A classic example is *Ganoderma adspersum*, which causes heart rot of beech and other broadleaved trees. The fungus is spread by spores and grows in the non-living tissues, which weakens the tree making it susceptible to wind damage [48].

### **1.7 PESTICIDE APPLICATION IN THE OIL PALM PLANTATION**

There are various pesticides applied in oil palm plantation in order to control pests and diseases. In Malaysia, the list of pesticides registered for use in oil palm is shown in Table 1.2. All pesticides are toxic and therefore should be applied according to the instructions on their labels since it can be fatal to humans and other organisms at high dosage.

### 1.7.1 HERBICIDES

Chemical weed control was recognized to be an economical practice in industrial plantations of oil palm trees and it can reduce reliance on manpower for hand weeding which can delay operations in time of scarcity, and increase weed infestation in the plantation [49]. Glyphosate and paraquat are by far the most widely used herbicides for weed control in plantation crops in the humid tropics [50]. Glyphosate is a broad-spectrum, nonselective and systemic herbicide that is formulated as an isopropylamine or trimethylsulfonium salt and used for postemergence control of annual and perennial weeds including *Imperata cylindrica* (Spear grass), *Panicum maximum* (Guinea grass), and *Cynodon dactylon* (Bermuda grass) [51]. Similarly, paraquat is a nonselective, postemergence herbicide but with fast contact action. Its limitation consists in the fact that it is not effective against perennial weeds [52].

Broad spectrum herbicide, paraquat, was used for more than 40 years, and was the only mostly used herbicide in Malaysian plantations. The use of this herbicide, however, has been halted since 2002 by the Government of Malaysia, for reasons of toxicity and hazards to humans, but was lifted in 2006 to allow for more comprehensive study. The prohibition of paraquat use left an open option to users for replacement such as glufosinate-ammonium and glyphosate [53]. All these herbicides are foliar applied, with paraquat activity being through contact [54], glufosinate-ammonium being partially systemic [55], and glyphosate being systemic [56]. A study by Wahyu *et al.* revealed that paraquat, glufosinate ammonium and glyphosate applied at recommended rates were effective in the control of the mixed weeds under young oil palms and caused no adverse effect on the ecological components of crops and soil microorganisms (bacteria and fungi) and left no detrimental level of residue in soil [57].



Table 1.2: List of pesticides registered for use in oil palm in Malaysia

Pesticide	Type	National MRL (mg kg <sup>-1</sup> )
Captan	Fungicide	10
Cyproconazole	Fungicide	0.1
Dithiocarbamates	Fungicide	1
Difenoconazole	Fungicide	0.1
2, 4-D	Herbicide	0.05
Ametryn	Herbicide	0.2
Cinosulfuron	Herbicide	0.1
Dicamba	Herbicide	0.1
Diuron	Herbicide	0.1
DSMA	Herbicide	0.1
Fluazifop-butyl	Herbicide	0.2
Fluroxypyr	Herbicide	0.1
Glufosinate ammonium	Herbicide	0.5
Glyphosate	Herbicide	0.1
Imazapyr	Herbicide	0.1
Imazethapyr	Herbicide	0.05
Metsulfuron methyl	Herbicide	0.02
MSMA	Herbicide	0.1
Paraquat	Herbicide	0.1
Sethoxydim	Herbicide	0.05
Triclopyr	Herbicide	0.1
Butocarboxim	Insecticide	2
Chlorpyrifos	Insecticide	0.5
Cypermethrin	Insecticide	0.5
Deltamethrin	Insecticide	0.2
Gamma HCH	Insecticide	2
Lambda cyhalothrin	Insecticide	0.1
Methamidophos	Insecticide	0.1
Methidathion	Insecticide	0.1
Monocrotophos	Insecticide	0.05
Acephate	Insecticide	0.5

Source: Food Act 1983 (Act 281) and Regulations. Schedule sixteenth [58]

### 1.7.2 INSECTICIDES

The used of insecticides in oil palm plantations is minimal as they are only applied when there is an insect attack. In Malaysia, the main insect problem in oil palm plantations is bagworm and rhinoceros beetle and a number of studies have been carried out to control this infestation. The insecticides applied for this purpose are

organophosphorus (OP) compounds which are applied through trunk injection. The use of OP compounds such as acephate, methamidophos, and monocrotophos is restricted to other crops [58]. They can only be applied on oil palm and coconut [27]. Besides OP compounds, synthetic pyrethroids such as cypermethrin,  $\lambda$ -cyhalothrin, and deltamethrin are also used to control *Oryctes* attack on immature palms. They are also stable compounds and are used against a wide variety of pests. According to Chung *et al.* [59], application of chemical insecticides such as carbofuran and cypermethrin has been widely used, but this method is costly and hazardous to non-target organisms.

### **1.7.3 FUNGICIDES**

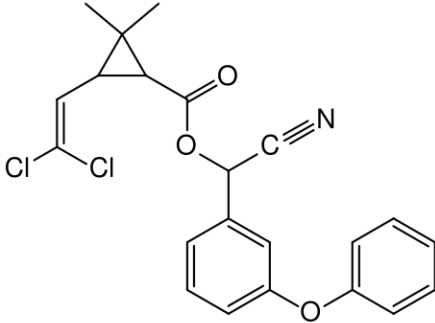
Fungicides are used to destroy or inhibit growth of fungi in oil palm plantations. Currently, pesticide regulations are in place today to ensure that fungicides control the disease without injuring the plant and leave no poisonous residue in edible oils. Some of the commonly used fungicides in oil palm plantations are benomyl, thiram, captan, and hexaconazole.

### **1.8 PESTICIDES SELECTED FOR PRESENT STUDY**

In this study, two types of synthetic pyrethroids were selected for method development and method validation in palm oil matrices and soil samples. The analytes of interest are cypermethrin (Table 1.3) and  $\lambda$ -cyhalothrin (Table 1.4). In oil palm plantations, cypermethrin and  $\lambda$ -cyhalothrin are commonly used to control bagworms (*Metisa plana*, *Pteroma pendula*, *Mahasena corbetti*), nettle caterpillars (*Darna trima*, *Setora nitens*, *Darna diducta*, *Setothosea asigna*), and rhinoceros beetles (*Oryctes rhinoceros*) [60].

### 1.8.1 CYPERMETHRIN

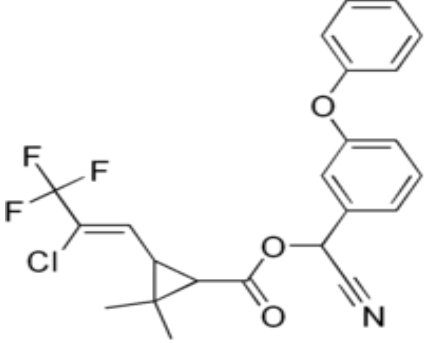
Table 1.3: Physical and chemical properties of cypermethrin

Common name	Cypermethrin
Structural formula	 <p>The chemical structure of Cypermethrin consists of a central cyclopropane ring with two methyl groups attached to one of its carbons. The other two carbons of the ring are part of a chain: one is bonded to a carbon atom that is double-bonded to a carbon atom with two chlorine atoms (2,2-dichlorovinyl group), and the other is bonded to a carbonyl group (C=O). The oxygen of the carbonyl group is part of an ester linkage to a chiral carbon atom. This chiral carbon is also bonded to a cyano group (C≡N) and a 3-phenoxybenzyl group (a benzene ring with an oxygen atom at the 3-position, which is further bonded to another benzene ring).</p>
Chemical name	(RS)- $\alpha$ -cyano-3 phenoxybenzyl (1RS)-cis,trans-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate
Chemical family	Pyrethroid
Molecular formula	$C_{22}H_{19}Cl_2NO_3$
Molecular weight	416.3
Physical form	Odourless crystals (pure), yellow-brown viscous semi-solid (technical, 93%)
Melting point	60-80 °C (technical)
Vapour pressure	0.51 nPa at 70 °C
Partition coefficient (o/w)	$4 \times 10^6$
Stability	Relatively stable in neutral and weakly acidic media, with optimum stability at pH 4. Hydrolyzed in alkaline media. Relatively stable to light. Thermally stable up to 220 °C
Solubility	In water at 20 °C, ca. 0.01 mg/L.
Mode of action	Non-systemic insecticide with contact and stomach action. Also exhibits anti-feeding action. Good residual activity on treated plants.
Phytotoxicity	Non-phytotoxic

Source: Kidd *et al.* [61]

### 1.8.2 λ-CYHALOTHRIN

Table 1.4: Physical and chemical properties of λ-cyhalothrin

Common name	λ-cyhalothrin
Structural formula	 <p>The chemical structure of λ-cyhalothrin consists of a central cyclopropane ring. One carbon of the ring is substituted with two methyl groups. The adjacent carbon is part of a propenyl chain that is substituted with a chlorine atom and three fluorine atoms. The third carbon of the propenyl chain is connected to a carbonyl group, which is further linked to a 3-phenoxybenzyl group. The 3-phenoxybenzyl group consists of a benzene ring with a phenoxy group at the 3-position and a benzyl group at the 1-position.</p>
Chemical name	α-cyano-3-phenoxybenzyl-3-(2-chloro-3,3,3-trifluoropropenyl)-2,2-dimethyl-2,2-dimethylcyclopropanecarboxylate.
Chemical family	Pyrethroid
Molecular formula	C <sub>23</sub> H <sub>19</sub> ClF <sub>3</sub> NO <sub>3</sub>
Molecular weight	449.9
Physical form	Colourless solid
Melting point	49.2 °C
Vapour pressure	200 nPa at 20 °C
Partition coefficient (o/w)	10 x 10 <sup>6</sup>
Stability	Stable to light. Stable on storage for more than 6 months at 15-25 °C.
Solubility	In water at pH 6.5 and 20 °C, 0.005 mg/L.
Mode of action	Non-systemic insecticide with contact and stomach action, and repellent properties. Gives rapid knockdown and long residual activity.
Phytotoxicity	Non-phytotoxic when used as directed.

Source: Kidd *et al.* [61]

## **1.9 EXTRACTION, CLEAN-UP, AND FRACTIONATION METHODS IN PESTICIDE ANALYSIS**

In the preparation of a sample for analysis, it is common practice to first extract the analyte away from the bulk of the matrix and then to remove potentially interfering co-extractives that will inevitably be present in the extract, by one or more clean-up steps. The strategy in choosing the proper extraction and clean-up conditions, and methods for subsequently fractionating samples into various subgroups of chemicals for separate determination, involve taking advantage of unique physical and chemical properties of the analyte. The main focus was to allow it to stand out from the bulk of substances that occur in the matrix that could interfere in the determination step by responding to the detection system employed. The analyte physical properties of most utility are polarity, which governs the solubility and chromatographic behaviour of the analyte; and volatility, which governs the vapour-condensed phase distribution of the analyte in such operations as co-distillation, headspace transfer, and gas chromatography.

### **1.9.1 EXTRACTION**

It is somewhat arbitrary to separate “extraction” from “clean-up” because many techniques do part or all of both virtually simultaneously. Supercritical fluid extraction (SFE), for example, can extract the analyte by crudely separate analytes into fractions by pressure, modifier, or flow programming, and some SFE instruments allow for selective trapping and elution of the SFE extractives using a solid-phase mini-column at the exit end of the SFE. But traditionally extraction has been done primarily with organic solvents that, once collected and concentrated, yield an extract which is cleaned up separately by one or more partition, chromatography, or chemical treatment techniques.

Physical properties really come into play in choosing the strategy for extraction. For extraction using solvents or supercritical fluids, conditions are chosen so that the polarity of the extractant matches the polarity of the analyte, hence the analytes will enter the solution but the bulk of the matrix remains undissolved. For solventless extractions that volatilize the analyte, conditions should be sufficient to promote efficient removal of analyte but not so harsh that the matrix decomposes and/or volatilizes as well. Strong solvents, acids or bases, high temperatures, and other extreme conditions should be avoided, because they may add significantly to the difficulty in the remainder of the procedure. Moreover, many pesticides are unstable in acid or base solution.

### **1.9.2 CLEAN-UP AND FRACTIONATION**

Clean-up refers to a step or series of steps in the analytical procedure in which the bulk of the potentially interfering co-extractives are removed, primarily by physical and/or chemical methods. For the analysis of one, or a few closely related analytes, the clean-up can be fairly drastic and tailored to the physicochemical properties of the analyte(s). For the analysis of multiple analyte residues, the clean-up step is generally softer and more universal, fractionating residues with somewhat differing physicochemical properties into polarity or volatility based classes for separate determination. All clean-up methods will represent a compromise between time and cost, on one hand, and the detection limit and/or breadth of analytes accommodated on the other hand [62, 63].

Specifically, then, it is the purpose of the clean-up to reduce the amount of these potential interferences to a sufficiently low level in order to permit determination of the pesticides of interest. The general strategy is to take advantage of physicochemical

property differences between the analytes and the background matrix as a basis for clean-up. Two types of clean-up procedures exist, either chemical or physical clean-up. Examples for physical clean-up are partition, precipitation, volatilization, and chromatography. Whereas, examples for chemical clean-up are partition, concentrated acids or alkalis, oxidation, and derivatization. Methods based on partitioning between immiscible solvents, and on chromatography tend to be the most commonly used for general pesticide clean-up, with the other methods serving for specialty clean-up for analytes of somewhat unusual properties or for difficult matrices.

### 1.9.2.1 NATURE OF POTENTIALLY INTERFERING CO-EXTRACTIVES

Recognition of the nature of potential co-extractives that may be present in food and other biological matrices is important in selecting the most appropriate clean-up procedures. Some major classes for foodstuffs are included in Table 1.5.

Table 1.5: Common interferences in pesticide residue analysis

Class	Types
Lipids	Waxes, fats, oils
Pigments	Chlorophylls, xanthophylls, anthocyanins
Amino acid derivatives	Proteins, peptides, alkaloids, amino acids
Carbohydrates	Sugars, starches, alcohols
Lignins	Phenols and phenolic derivatives
Terpenes	Monoterpenes, sesquiterpenes, diterpenes
Miscellaneous environmental contaminants	Most classes of organic compounds, minerals, sulphur, PCBs, phthalate esters, hydrocarbons

Source: Fong *et al.* [64]

### **1.9.2.1 (A) LIPIDS**

The class of chemicals designated as lipids includes waxes, fats, and oils. These are either hydrocarbons or esters containing a fatty acid and an alcohol portion. Esters in which the alcohol is glycerol constitute the classes of fats and oils. Waxes may include fatty esters, and also long-chain hydrocarbons such as exist in the surface cuticle of most leaves and fruits. Lipids occur in large amounts in crop and animal products. Butter, for example, is 81 % fat, and the remainder is water. Cheeses range to above 30 % fat and 61 % chicken eggs. Even some plant-derived foods, such as peanuts (49 %) and avocados (17 %) can contain high lipid levels. Lipids are soluble in many common organic solvents, therefore they may be present in the crude extract. Lipid esters are saponifiable with acids and bases, and degraded further with oxidizing acids. They tend not to be volatile, but their sheer bulk can still be problematic in gas chromatography because they tend to coat the column and injector ports, changing analyte chromatographic characteristics, and they may slowly degrade thermally into volatile products that survive to the detector.

### **1.9.2.1 (B) PIGMENTS**

Pigment includes a number of structurally unrelated coloured compounds, such as chlorophylls, xanthophylls, carotenoids, and anthocyanins. Pigments are soluble in some organic solvents, particularly the more polar ones, are destroyed by corrosive reagents, and are principal interferences in colorimetric and spectrophotometric determination steps.



### **1.9.2.1 (C) OTHER INTERFERENCES**

Peptides and amino acids contain nitrogen and often sulphur, and thus are potential interferences in determinations using N- or S-selective detection systems. Carbohydrates are colourless, non-volatile, and only sparingly soluble in organic solvents and thus give problems only with pesticides that possess low volatility and high water solubility characteristics. Lignins are somewhat similar, but with the caveat that they may degrade, hydrolytically or thermally, to phenols, which may interfere with analysis of phenolic metabolites of pesticides such as the carbamates and phenoxy acids. Certain vitamins, such as vitamin K, have physicochemical properties similar to those of many pesticides and drugs, and may thus interfere.

### **1.10 THESIS OBJECTIVES**

Oil palm farmers use a wide variety of pesticides including cypermethrin and  $\lambda$ -cyhalothrin to limit losses from pests especially insects in oil palm plantations. Due to this, an increase on the levels of pesticide residues found in oil palm products especially the oils could arise if good agricultural practice (GAP) in the use of pesticides in the plantations is not followed accordingly in order to authorize safe use of the chemicals under actual conditions necessary for effective and reliable pest control.

Pesticide residue method development in oil palm matrices have been recorded in the past for paraquat, glyphosate, glufosinate ammonium, metsulfuron methyl, methamidophos, monocrotophos, acephate, chlorpyrifos, deltamethrin, organochlorine, and hexaconazole. However, no cypermethrin and  $\lambda$ -cyhalothrin were considered. For that reason, in order to monitor the residue level of pesticides in palm oil matrices, good and reliable analytical method is needed for cypermethrin and  $\lambda$ -cyhalothrin.

Besides the oil matrices, the selected insecticides could also spread further from the application site and can contaminate the soils around the oil palm. Since soil is the principal reservoir of environmental pesticides and representing a source from which residues can be released to the atmosphere, groundwater, and living organisms, it is very important to monitor the chemicals in the soil too. Hence, reliable and effective analytical method is needed. Accordingly, the objectives of this study are:

- To develop a simple, cheap and efficient method of extraction and analysis for cypermethrin and  $\lambda$ -cyhalothrin residues in crude palm oil (CPO), crude palm kernel oil (CPKO), and soil samples.
- To apply the developed methods to CPO and soil samples from oil palm plantation in order to document the concentration status of the target pesticides via monitoring study.

## **1.11 THESIS OUTLINE**

**Chapter 1** describes the brief introduction regarding the oil palm plantation in Malaysia, palm oil matrices, pests and pesticides application in oil palm plantation.

**Chapter 2** describes the method development and method validation for determination of cypermethrin and  $\lambda$ -cyhalothrin in palm oil matrices. This chapter studies the development of efficient method of extraction and analysis based on low-temperature extraction using acetonitrile. Then, solid-phase extraction (SPE) and dispersive solid-phase extraction (d-SPE) were tested as clean-up procedures to obtain the best overall recoveries for cypermethrin and  $\lambda$ -cyhalothrin.

**Chapter 3** describes the method development and method validation for determination of cypermethrin and  $\lambda$ -cyhalothrin in soil samples. This chapter studies the optimization of the ultrasonic extraction procedure (USE) with regards to the solvent type, amount of solvent, and duration of sonication.

**Chapter 4** provides concluding discussion which considers the scenario of current analytical methodologies for pesticide residues in palm oil matrices and soil samples. This chapter will also discuss the recommendations for future research directions.