Palm-based Methyl Esters as Carrier Solvents in Pesticide Formulations

Sumaiyah Megat Nabil Mohsin*; Ismail Ab Raman*; Zafarizal Aldrin Azizul Hasan* and Zainab Idris*

INTRODUCTION

A pesticide is a general term for any substance used for controlling pests, be it by deterring, incapacitating, killing or discouraging the pests. Pesticides can be classified according to their targeted pests, as shown in *Table 1*.

TABLE 1. PESTICIDE CLASSIFICATION AND THE TARGETED PESTS

Type of pesticide	Targeted pests
Insecticide	Insects
Herbicide	Weeds
Rodenticide	Rodents
Fungicide	Fungi
Acaricide	Arachnids of the order Acarina such as ticks and mites
Molluscicide	Molluscs
Bactericide	Bacteria
Avicide	Bird pests
Virucide	Virus
Algicide	Algae
Nematicide	Nematodes
Predacide	Vertebrate predators
Piscicide	Fish

Pesticide formulations typically consist of active ingredients responsible for the pesticidal effect and inert ingredients responsible for improving product performance, stability and usability. Examples of inert ingredients include carrier solvents, emulsifiers, stabilisers, fragrances and dyes. The majority of pesticides are in the form of dry and liquid formulations. Examples of the former include dusts, granules, pellets and wettable powders while examples of the latter are solutions, aerosols, suspension concentrates or emulsions.

Liquid formulations are usually the preferred form of pesticide. They are adaptable to a broad range of pesticide applicators, ranging from small target area applicators like portable sprayers and hydraulic sprayers, to large target area applicators such as low-volume ground sprayers, mist blowers and low-volume aircraft sprayers. In addition, liquid formulations are easier to handle, provide better pesticide distribution and have better homogeneity throughout the formulation. In particular, emulsions-in-water (EW) have been receiving increasing attention as noted by Seaman (1990) in his review of trends in the formulation of pesticides. In EW, the active ingredient along with a water-immiscible carrier solvent is dispersed as small spherical droplets in water through the assistance of a substance called an emulsifier. Emulsifiers are amphiphilic in nature and comprise a polar head group and a non-polar tail group. The emulsifiers position themselves by surrounding the carrier solvent droplets with their non-polar tails extending into the oil, and their polar head groups facing water, as illustrated in *Figure 1*. Emulsifiers

* Malaysian Palm Oil Board (MPOB),
6, Persiaran Institusi, Bandar Baru Bangi,
43000 Kajang, Selangor, Malaysia.
E-mail: sumaiyah@mpob.gov.my

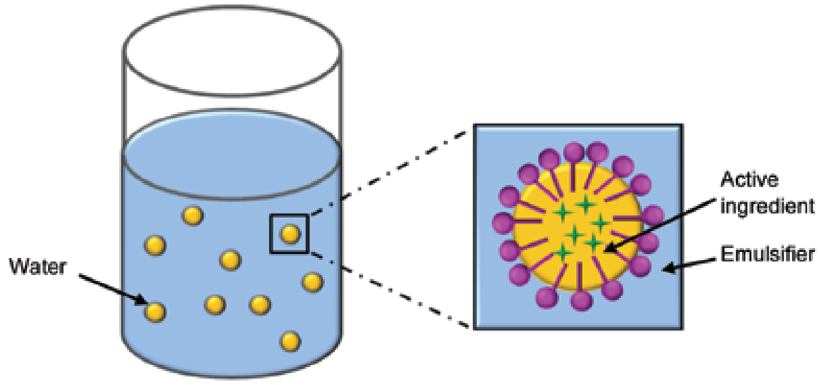


Figure 1. Emulsion-in-water.

keep the solvent droplets separated by causing them to be repelled from each other through an electrostatic and/or steric stabilisation mechanism. Thus, the carrier solvent droplets remain dispersed and a stable emulsion is obtained.

The use of pesticides that are produced using petroleum-based carrier solvents has garnered some concerns due to their toxicity to humans and non-target organisms, production of high volatile organic compounds (VOC) as well as fire and explosion risks. As the world's population continues to grow, the utilisation of pesticides is indispensable in keeping up with increasing food demand, and thus food production. Hence, there is a critical need to find alternative carrier solvents that can match the efficiency of petroleum-based carrier solvents without compromising the environment, public health or economic returns.

THE SHIFT TOWARDS GREENER SOLVENTS

Traditionally, petroleum based-solvents, such as gasoline, diesel fuel, xylene and trimethylbenzene, are used as carrier solvents (Chin *et al.*, 2012). However, the high volatility and low flash point of many petroleum-based solvents pose fire and explosion risks during transport, disposal and when in use. Additional costs are incurred in order to meet the requirements for special handling, storage and transportation of petroleum-based pesticides, all of which will be borne by the consumer. Moreover, the pesticides are often prone to causing off-target damage due to pesticide drift and volatility. The rapid depletion of fossil fuels, hazards to end-users and environmental pollution concerns due to excessive use of petrochemicals, in addition to the aforementioned issues of petroleum-based solvents, collectively motivate the agrochemical industry to move towards the use of 'greener solvents' in pesticide formulations.

Pioneering studies into the use of green solvents in pesticide formulations began with vegetable oils. Vegetable oils are triglycerides comprising glycerine and three associated fatty acid chains. They are biodegradable, non-flammable and pose substantially fewer health risks in comparison with petroleum-based solvents. Furthermore, it is well established that vegetable oils have a significantly lower vapour pressure than petroleum-based solvents. In spray-type applications, the use of carrier solvents with low vapour pressure prevents crystallisation of the solid active ingredient at the spray nozzle. Furthermore, the lower the vapour pressure, the less is their contribution towards emission of volatile organic compounds (VOC), thinning of the ozone layer and to photochemical smog (Roy *et al.*, 2007).

Unfortunately, vegetable oils have some unfavourable characteristics as carrier solvents. They are typically more viscous and thus have limited solvency for solid active ingredients when compared with to petroleum-based solvents (Hickey, 1987). Most pesticide emulsions are sold in concentrated form to be diluted according to the user's desired application. Thus, it is imperative for the carrier solvent to show a high solubility for the active ingredient in order to maximise loading. Viscosity of vegetable oils increases with fatty acid chain length and degree of saturation. Unsaturated oils have lower viscosity but are also prone to oxidation and film formation. Consequently, the film can trap active ingredients and prevent pesticidal activity. On the other hand, when active ingredients are dissolved in highly saturated vegetable oil, the droplets will be too viscous for good contact with the target, especially when applied under cold conditions (Beattie, 2002). Additionally, it was discovered that when vegetable oil is combined with surfactants, the resulting spray product does not exhibit good spreading, sticking and pest-penetrating properties (Miller and Westra, 1996).

FATTY ACID METHYL ESTERS AS CARRIER SOLVENTS

Researchers then turned their attention to a vegetable oil derivative that can approximate the properties and performance of petroleum-based solvents, namely, fatty acid methyl esters (FAME). FAME are similarly classified as 'green solvents' due to their biodegradability, low VOC production and non-toxicity to humans. Similar to vegetable oils, FAME have lower volatility and higher flash point than petroleum-based solvents. Formulations made with FAME have reduced fire and explosion risks, are not susceptible to composition loss due to vaporisation during storage, and require less storage and transportation cost unlike petroleum solvent-based formulations.

FAME can be derived from triglycerides and fatty acids contained in vegetable oils via either an acid- or alkali-catalysed reaction. *Figure* 2 illustrates general schemes for triglyceride transesterification and for fatty acid esterification.

Transesterification is a single-stage process in which vegetable oil is transformed into FAME with glycerol as a by-product, while esterification is a two-stage process which splits the vegetable oil into glycerine and its respective fatty acid, before being esterified into FAME (Turley *et al.*, 2004). Using transesterification processes, the large branched molecular structures of triglycerides are transformed into smaller straight-chained methyl ester molecules that are similar to fossil diesel components.

Nevertheless, some physical and chemical properties of FAME do differ greatly from their parent vegetable oils. Notably, FAME have viscosities that are closer to those of diesel, a traditional carrier solvent for pesticides. This reduction in viscosity leads to an increase in mobility and solvating power, making FAME more suitable as carrier solvents. A comparison of the physical and chemical properties of vegetable oil-based FAME and diesel fuel is given in *Table 2*.

Garst (1995) reported that methyl esters derived from plant oils impart good solvency property to various pesticide actives as shown in *Table 3*.

Hickey (1987) demonstrated that among the advantages of incorporating FAME in agricultural chemical applications are: (i) as a co-solvent, FAME can further lower viscosity and freeze point and improve solvency of the active ingredient; (ii) as a sole solvent or a co-solvent in a blended solvent system, FAME can provide good solvency, low viscosity and improved emulsifier solubility; and (iii) as a carrier in spraying insecticides, low viscosity FAME improve sprayability and reduce viscosity changes due to fluctuations in temperature.

TABLE 2. COMPARISON OF PHYSICAL AND CHEMICAL PROPERTIES OF VEGETABLE OIL-BASED FATTY ACID METHYL ESTER AND DIESEL FUEL

Solvent	[a]Kinematic viscosity ($mm^2 s^{-1}$)	[a]Flash point (°C)	[b]Vapour pressure (kPa)
Palm methyl ester	5.7 (37.8°C)	164	3.11 (70°C-100°C)
Soyabean methyl ester	4.5 (37.8°C)	178	12.30 (275°C -350°C)
Rapeseed methyl ester	4.2 (40°C)	-	4.69 (215°C -360°C)
Sunflower methyl ester	4.6 (37.8°C)	183	-
Diesel fuel	12-3.5 (40°C)	-	-

Note: [a] Fukuda *et al.* (2001); [b] Díaz *et al.* (2012).

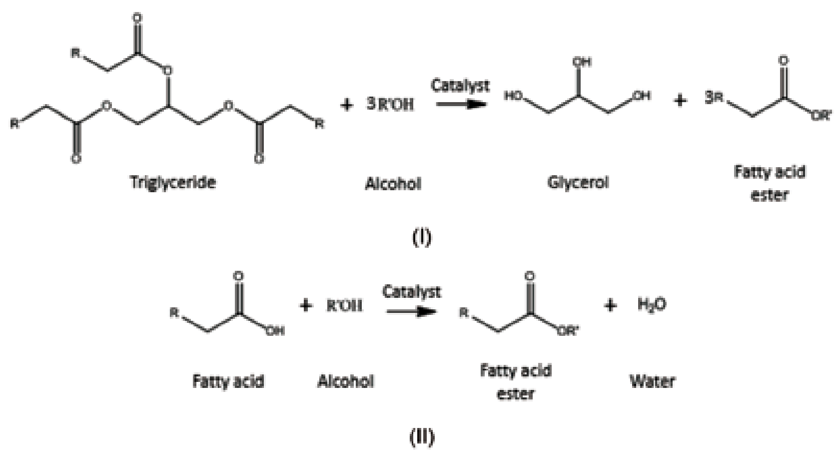


Figure 2. Schematic representation of (I) triglyceride transesterification and (II) fatty acid esterification.

Methyl esters from oils have been found to outperform their parent triglyceride oils and petroleum-based solvents in one class of pesticide application, *i.e.* foliar applications. For foliar applications, the efficacy of the pesticide formulations is dependent on four factors: (i) spread of the spray droplets on the leaf surface; (ii) retention of the spray droplets on the leaf; (iii) penetration of the spray droplets through the plant cuticle; and (iv) uptake of the spray

TABLE 3. PESTICIDE SOLUBILITY (wt %) AT 25°C

Pesticide active	Pesticide solubility (wt %)		
	Methyl caprylate/ caprate	Methyl laurate	Methyl canolate
Malathion	M	M	M
Permethrin	78	67	60
Chlorpyrifons	74	66	60
2,4-d-Isooctyl	M	M	M
Esters, dimethoate	12	4.2	2.7

Note: M - miscible in all proportion.
Source: Garst (1995).

droplets. These factors are difficult to achieve due to the morphological variations that exist among leaf surfaces. Leaf surfaces are covered with a plant cuticle, which is a lipophilic waxy layer covering the epidermis of leaves. The plant cuticle functions as an important barrier to inhibit the entry of environmental hazardous agents, pathogens and dusts, reduce the impact of insect pests, and to prevent excessive evaporation of water from the leaf. Some leaves are further covered with trichomes, which are fine hairs that prevent water droplets from reaching the epidermis. In comparison to triglyceride oils and petroleum-based solvents, methyl esters from oils have a greater ability to disrupt and dissolve waxes on the surface of trichomes and the leaf epidermis which leads to better spread, retention, penetration and uptake of methyl ester droplets (Manthey and Nalewaja, 1989; Mouloungui and Gauvrit, 1998; Xu *et al.*, 2011). McWhorter *et al.* (1993) reported that spray droplets of water and methylated seed oil spread more on johnsongrass leaf surfaces than droplets of water and petroleum oil. According to Western *et al.* (1998), methylated seed oils exhibit greater spray retention in comparison with petroleum oil adjuvants. In a study on yellow foxtail and large crabgrass, nicosulfuron absorption differed among the oil adjuvants, with methylated canola oil being the most effective, followed by vegetable oils, and petroleum mineral oil being the least effective (Nalewaja *et al.*, 1995).

PALM METHYL ESTER-BASED PESTICIDES

Several studies have been conducted on the use of palm methyl ester (PME) as carrier solvents in EW herbicides. PME-based glyphosate isopropylamine (IPA) EW nanoemulsion exhibited low spray deposition and high visible injury rate in creeping foxglove, slender button weed, buffalo grass weed and narrow-leaf weeds (*e.g. Eleusine indica*), indicating of a high uptake of glyphosate IPA (Jiang *et al.*, 2012; Lim *et al.,* 2013). Another study reported high biological efficacy of PME-based glyphosate IPA and triclopyr butoxyethylester (BEE) EW against a broad range of weed species, namely, a grassy weed (*Paspalum conjugatum*), a broad-leaved weed (*Asystasia gangetica*) and a woody weed (*Clidemia hirta*) (Ismail *et al.*, 2014). The authors further conducted a comparative study with commercial herbicides, Roundup® and Comet, and concluded that higher biological efficacy was brought about by the comparatively lower surface tension of PME, which enabled better spreading of and wetting by herbicide droplets on leaf surfaces.

In relation to insect control, PME was found to enhance the insecticidal effect of pyrethroid insecticide. Ismail *et al.* (2009) reported that a higher rate of rhinoceros beetle (*Oryctes rhinoceros*) control was achieved with 0.028% cypermethrin prepared in PME as opposed to 0.056% cypermethrin prepared in petroleum-based solvents. A factor governing the enhanced insecticidal activity by PME is their high permeability through the insect exoskeleton. The exoskeleton is protected by the insect`s epicuticle and a wax layer coating the epicuticle. Insecticide penetration into the exoskeleton as well as the membranes of target organs is necessary for insecticidal activity to ensue. Lipophilic FAME overcomes this barrier by adhering well to the exoskeleton, dissolving the epicuticular wax and carrying the insecticidal actives through to disrupt the internal protein organisation of the cuticle (Matsumura, 1985).

Additionally, a comparative study was conducted on the performance of PME as a carrier solvent for molluscicides (Massaguni *et al.*, 2016). Neem EW formulations were prepared in PME and two other vegetable oil-based carrier solvents, *viz.* refined, bleached and deodorised (RBD) palm olein and soyabean oil. Molluscicidal activity of the formulations was tested against the golden apple snail (GAS), and neem prepared in PME exhibited the lowest LC_{50} value. The authors postulated that the higher potency of the neem EW in PME may be attributed to the excellent wetting behaviour and good thermal stability of PME. Moreover, persistence analyses of the formulations on rice leaf surfaces showed that the longest half time (t1/2) was obtained with the PME carrier solvent, which indicates improved persistence of the highly biodegradable active due to the solvent.

COMPETITIVENESS OF FAME AS CARRIER SOLVENTS

Despite the technical advantages presented, there may be cost barriers to substituting petroleum-based solvents with vegetable oil-based FAME. Replacing carrier solvents in pesticide formulations requires an initial capital investment to optimise the new formulation, to conduct efficacy testing or field trials, and to modify machine operating procedures to adapt them to the new formulation. To balance the increase in production cost, pesticide manufacturers will then have no choice but to increase the price of the product.

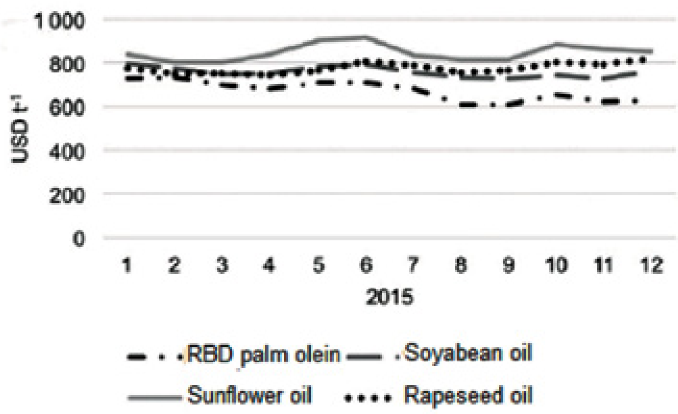
There being little difference in the physical and chemical properties of the vegetable oil-based FAME and petroleum-based solvents, factors affecting the comparative cost of the raw material will therefore have a bigger impact on the price competitiveness of the vegetable methyl ester-based pesticide. Rapeseed, soyabean, sunflower and palm oils are amongst the most produced, traded and consumed oils in the world market. They compete for the same market share as they have similar characteristics and similar applications. Monthly price trends of the four major vegetable oils in 2015 are shown in *Figure 3*.

Processed palm oil is represented by RBD palm olein which is closest in nature to the other major oils. It is clear that among the four major, the price of RBD palm olein, from which PME can be derived, is discounted by comparison.

Another source of PME is palm kernel oil. Palm kernel oil bears closer resemblance in characteristics and scope of application to coconut oil as they both contain high levels of lauric acid. As in the case of RBD palm olein, the price of palm kernel oil is lower than its main competitor. The monthly price trends of these two competing oils in 2015 are shown in *Figure 4*.

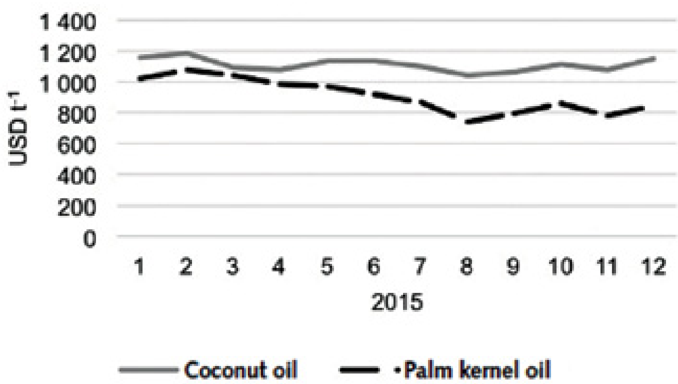
In addition to the cost, availability of the is also a key factor that needs to be taken into consideration in order to make the transition from petroleum-based solvents to vegetable oil-based FAME. Palm oil is a stable source of vegetable oil-based FAME as it is shown to surpass the production of other vegetable oils year after year (*Figure 5*).

Oil palm is the most efficient oilseed crop in the word. Palm oil alone ranks as the top vegetable oil in the world in terms of production. The production of palm oil and palm kernel oil in 2015/16 is forecast to grow to 61.72 and 7.28 million tonnes, respectively, accounting for 35% and 4% of the world's production of vegetable oils (USDA, 2016). High stability and availability



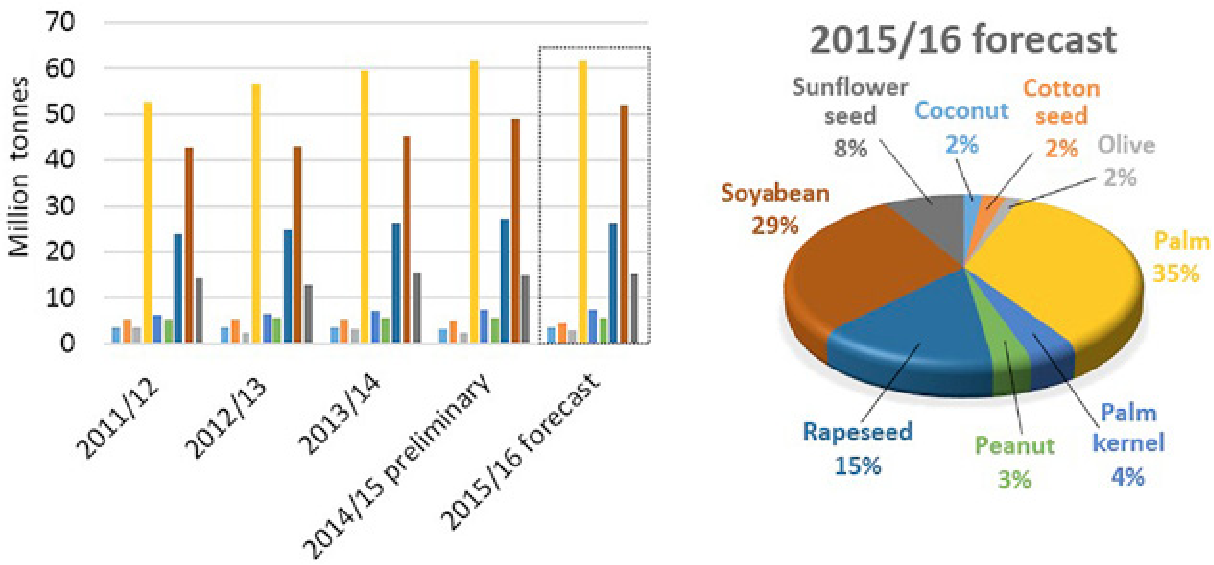
Source: *Oil World* (2015).

Figure 3. Monthly price trends of major vegetable oils in 2015.



Source: *Oil World* (2015).

Figure 4. Monthly price trends of coconut and palm kernel oils in 2015.



Source: USDA (2016).

Figure 5. World vegetable oils production (2011/12 to 2015/2016).

of the palm-derived oils can be attributed to high productivity of oil palm at an estimated 3.6 t of crude palm oil per hectare (Abdullah, 2016). The abundance of this source of oil warrants the liberal use of palm-derived oils in fields that are not limited to the food industry. Furthermore, this high availability can help reduce the cost of raw material and ensure price competitiveness amongst other vegetable methyl ester-based pesticides.

CONCLUSION

Carrier solvents play an important role in ensuring the efficient distribution and delivery of the active ingredients in pesticides. Petroleum-based solvents have many disadvantages such as low flash point, high volatility and toxicity. Vegetable oil-based FAME has the capacity to replace traditional petroleum-based solvents in pesticide formulations. Any hesitance related to cost in making the transition can be overcome by opting for the more cost-effective, stable and readily available PME. According to above findings, PME as carrier solvents appear to enhance pesticide efficacy, which may allow for a reduction in dosage or frequency of application, help to control adverse effects and reduce the cost spent on pesticides. Therefore, PME as a carrier solvent in pesticide formulations is a promising prospect for the agro-chemical industry.

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