**PROFESOR DR. DZOLKHIFLI OMAR**

# THE FUTURE OF **PESTICIDES TECHNOLOGY** IN **AGRICULTURE**

## *Maximum Target Kill with Minimum Collateral Damage*

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# Contents

## ABSTRACT

Pesticides are widely used in agricultural production and have an impact on human existence. They have been credited with increasing crop yields, protecting land and property, and even saving human lives. At the same time, pesticides are associated with some of the problems in agricultural production particularly those pertaining to pollution of the environment. The new paradigm in socio-environmental consciousness imposes on agricultural production to not only generate income but to be socially-responsible, sustainable and have minimum impact on the environment. In principle, sustainable agriculture espouses minimum use of pesticides, and only as a last resort. However in practice, this seldom happens and pesticide usage is deemed a necessary evil especially in areas of heavy pest infestation. There is therefore a cogent need to reconcile the necessity of pesticide application with the damage visited on the ecosystem. Towards this end, this lecture will present the options of effective pesticide application with respect to choice, formulation and delivery technology for maximum impact with minimum collateral damage.

Optimal dosage delivery that maximizes the biological effect on the target through the concept of controlled-release is one of the options to minimize the environmental impact of pesticides. Controlled-release of pesticides utilizes a depot system that continuously releases the active ingredient into the environment over a specified period of time. This would reduce the frequency of pesticide applications. Another novel approach to pest control is the use of biological pesticides or biopesticides. These are biorational (biologically rational) or ecorational substances that, when used for specific pests, have very limited or no effect on non-target organisms or the environment. The US Environmental Protection Agency defines them as any substances of natural origin that have a detrimental effect on specific target pests, possess a unique mode of action, and are non-toxic to man and the environment. They can either be living microbes and invertebrates, biochemicals derived from living organisms

or plant-incorporated protectants (eg transgenic Bt corn). The botanical insecticide, rotenone, extracted from the root of the tuba plant, *Derris elliptica* has been shown to perform similarly to the standard synthetic compound. Similarly, entomopathogenic fungi from the Hyphomycetes, which are naturally responsible for epizootics (disease epidemics) in insect pest populations, have good myco-insecticidal properties. Formulating the natural compound and the spores of entomopathogenic fungi for efficacy and ease of application in the field, minimizing handling hazards and accommodating the operational practices of Malaysian farmers, represents monumental challenges. The microemulsion of rotenone and water dispersible granulation of *Metarhizium* spores have been successfully formulated.

A major problem in the application of pesticides is that a large proportion of the pesticide does not reach the target, with spray efficiency, particularly with insecticides, estimated to be less than 1%. Research in finding a solution that would have far reaching commercial and environmental implications has been directed to the spray volume application rate, selection of an appropriate atomizer and equipment calibration. The final product would be a precision equipment, calibrated to deliver the recommended dosage of pesticide with an optimum spray droplet size and exact number of droplets per given area. This technology would vastly improve the efficiency of utilization of the active ingredients of the pesticide. The above development and research findings pave the way for the future not only in ensuring the most effective application of pesticides for crop protection, but also in enhancing food safety and protecting the ecosystem.

## INTRODUCTION

Pests account for about 30% of agriculture crop losses in the field and a further 10-12% in storage. The pests include insects, plant diseases, weeds, mites, rats and others. Various techniques could be employed to control these pests; for example by destroying them directly (mechanical control), utilizing temperature or humidity to reduce the survival of pests (physical control), modifying the agriculture ecosystem in ways that makes it no longer suitable for pests to live in (cultural control), controlling the entry and movement of the pests (legislation control), utilizing the natural enemies of the pests (biological control), manipulating the immunity of the crop against the pest (host-plant resistance) and using chemicals to suppress the pest population (chemical control). The most common method to control pests is chemical control by using pesticides. A pesticide is known as the chemical tool used to manage all kinds of pests by controlling, preventing, repelling, destroying or mitigating any pest (Ware, 1991). There are many types of pesticides including herbicides, insecticides, fungicides, miticides, rodenticides, biopesticides and disinfectants, antiseptics, sterilizers and sanitizers. The farmer's preference of using pesticides to control pests is due to pesticides being easy to obtain and use. They provide the result expected by the farmers and is probably the only tool available when there is an outbreak of the pest.

Recently introduced pesticides have undergone a development process to suit current requirements. They have become more environmental friendly, less toxic to humans, more specific to target and could be used as one of the tools in pest management. The amount applied has reduced drastically since 40 years ago when pesticides were applied in kilograms or litres of active ingredient per hectare. The present rate of pesticide application is in grams or millilitres per hectares. These new pesticides require more sophisticated technology for even and efficient application. In agriculture, the use of pesticides cannot be avoided as other alternatives have yet to give similar results in terms of cost effectiveness.

The growing awareness of disadvantages and environmental problems caused by pesticides and the need for sustainable agriculture production to conserve agriculture inputs require the research on pesticides to focus on reconciling the necessity of pesticide usage with the damage inflicted on the ecosystem. This lecture will present the options of effective pesticide application with respect to formulation and delivery technology for maximum impact with minimum collateral damage.

## PESTICIDES AND THEIR APPLICATION

Early use of pesticides was traced back to around 1000 B.C., but the earliest record of insecticides is related to the use of sulphur. Pliny the Elder (A.D. 23-79) recorded most of early insecticide use in his *Natural History*. A variety of materials such as extracts of pepper and tobacco, soapy water, salt solutions, fish oil and brine, among many others, were utilized for pest control. In early 1940, insecticides available included arsenicals, petroleum oils, nicotine, pyrethrum, rotenone, sulphur, hydrogen cyanide gas and cryolite. The Modern Era of Chemical control began with the discovery of the insecticidal properties of the synthetic organic insecticide, DDT.

World pesticides usage is valued at US30,424 million in 2006 with herbicides at US14,863 million, insecticides at US7,380 million, fungicides at US7,180 million and others at US1,060 million. The value of the pesticide market in Malaysia was at RM323 million in 2004 and the breakdown is given in Table 1.

**Table 1** The Malaysian Agrochemical Market (2000 to 2004) in RM Millions

| Pesticides | 2000 | 2001 | 2002 | 2003 | 2004 |
|---|---|---|---|---|---|
| Herbicides | 273 | 220 | 209 | 214 | 218 |
| Insecticides | 68 | 70 | 62 | 61 | 64 |
| Fungicides | 23 | 25 | 23 | 23 | 24 |
| Rodenticides | 14 | 11 | 13 | 14 | 17 |
| TOTAL | 378 | 326 | 307 | 312 | 323 |

The use of pesticides in agriculture has advantages and disadvantages. Pesticides that act on the nervous system are often hazardous to animals and humans. Up until September 2007, there were 96 active ingredients of insecticides registered in Malaysia of which about 68% act on the nervous system (Figure 1).

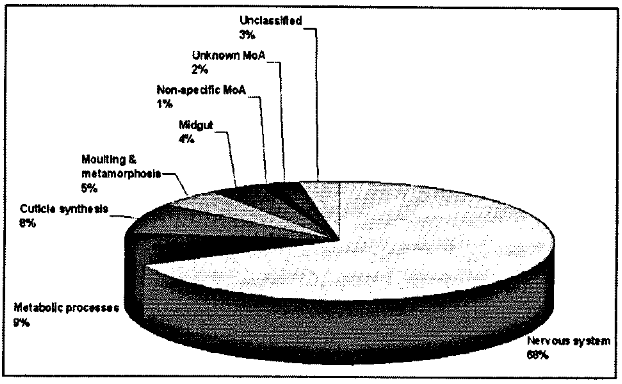
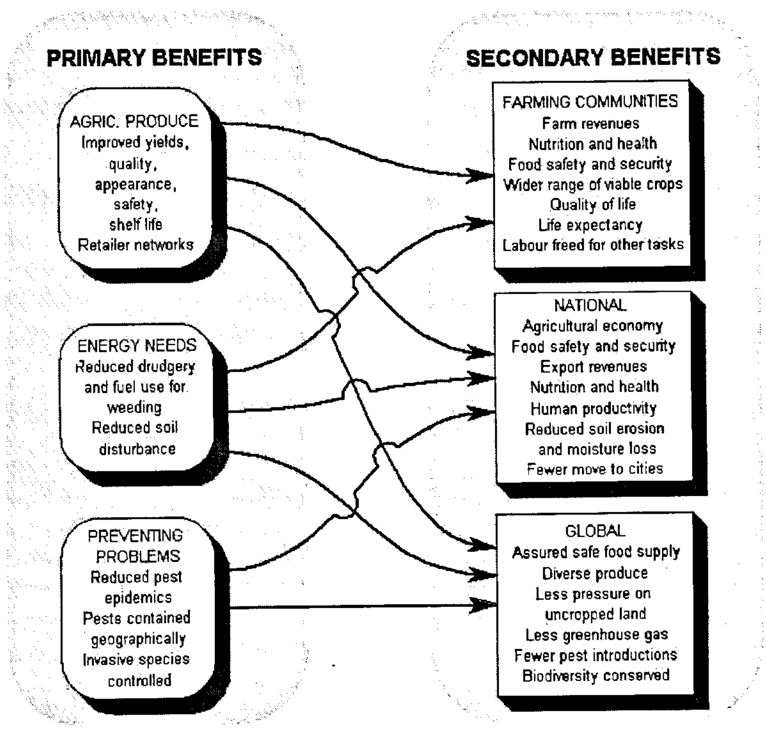



**Figure 1** Classification of registered insecticides in Malaysia according to site of action.

Some pesticides can cause nerve or liver damage, birth defects, cancer and more recently, even disrupt the endocrine system. In the environment, some pesticides are being associated with soil and water contamination that would have detrimental effects on some organisms. Pesticides can also cause problems when they are not used judiciously in agriculture, such as the resurgence of pests, emergence of secondary pests and the development of pest resistance toward pesticides. However, pesticides also provide benefits to mankind as summarized in Table 2.

**Table 2** The benefits of using pesticides




(Pesticide Resource Center)

As pesticides have both pros and cons in its usage, their use is being regulated. The Pesticides Act of 1974, the principle legislation for the control of pesticides in Malaysia, is implemented by the Pesticides Board which comprises various heads of government agencies, and is under the jurisdiction of the

Department of Agriculture. Apart from this there are other acts which govern other aspects such as health and safety.

All pesticides contain active ingredients and inert ingredients. The active ingredients are the substances that perform the desired effect of the pesticide while the inert ingredients are mixed with the active ingredients to create the final product. The preparation is known as pesticide formulation. The formulation is to improve storage, handling, effectiveness, safety and application. The formulation also plays a critical role in ensuring improved efficacy, more effective targeting and achieving significant reduction of environmental impacts. The pesticide could be formulated to be used as dry formulations such as dust, granules and bait or as liquid sprays. For liquid sprays, the common formulations for undiluted use are ultra-low volume (ULV) and fogging formulations while those for mixing and spraying with water, include soluble powder or liquid, wettable powder, emulsifiable or soluble concentrates, flowable liquids and water dispersible granules.

Pesticide application is very inefficient. Most of the pesticides in field applications fail to reach the target and only a minor proportion of pesticide is actually doing the job of controlling the pest. The process of pesticide application is very complex (Figure 2). It is expected that under these circumstances efficiency is low. Nevertheless options are available to improve the delivery of pesticides that would require some small changes in the normal practices of pesticide application i.e. through the formulation. Improved or better formulations could be designed to increase the performance of pesticides.

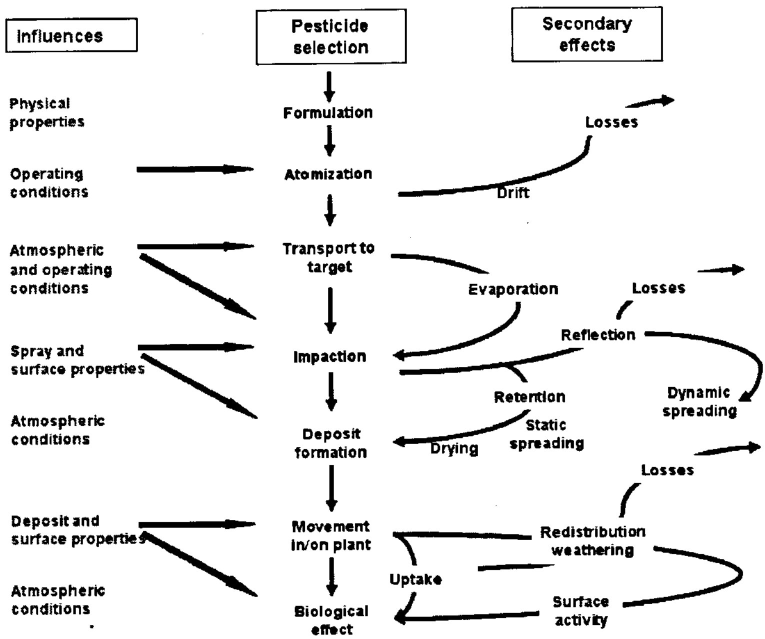



**Figure 2** Processes in the application of pesticide (Young, 1989)

## CONTROLLED-RELEASE FORMULATION OF PESTICIDES

Herbicides account for most of the pesticide use in the world. In Malaysia, almost two thirds of the pesticides used is herbicides. Some herbicide applications, particularly soil applied or incorporated herbicides, have a short span of effectiveness due to the quick release of the active ingredient with only a minor proportion actively controlling the pest while a major proportion of the active ingredient is wasted. This could lead to soil and water contamination. An effective approach to reduce environmental loss of herbicide and providing more efficient weed control is through the use of controlled-release formulations. Controlled-release formulation of pesticides is defined as depot systems which continuously release their toxic constituents into the environment over a specified period of time (Cardarelli, 1976). It is a combination of active ingredient and inert ingredients arranged to allow delivery of the active ingredient to the target at controlled rates over a specified period. The advantages include prolonged effective duration of non-persistent pesticides, lesser pesticide used for the same period of activity resulting in less waste and fewer applications, reduced losses due to environmental factors (such as evaporation, photolysis, leaching, run off and physical, chemical and biological degradation), reduced environmental contamination, reduced toxicity to non-target organisms, prolonged efficacy and greater safety to the user (Figure 3).

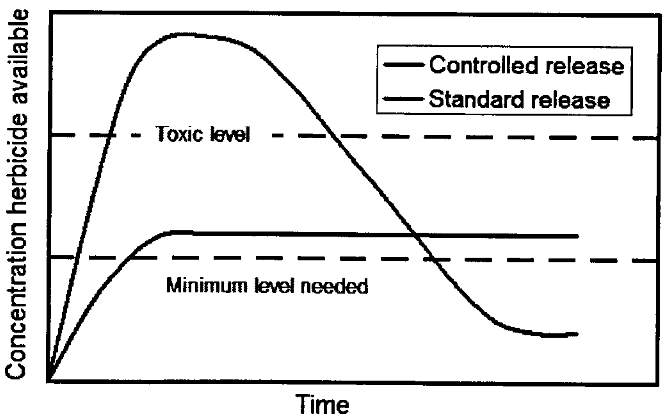



**Figure 3** Comparison of the efficiency of using controlled release (CF) and standard release formulation of pesticides.

A controlled-release system by encapsulation of the pesticide in polymers such as sodium alginate was commonly used (Connick, 1982; Hussain, 1992). Alginate was used as binder and kaolin or clay as the inert material. In direct seeded rice, the alginate controlled-release formulation of thiobencarb gave better yield as compared to the conventional granular formulation (Omar and Mohamad, 1994).

Controlled-release formulations (CRF) of diuron prepared using sodium alginate as a matrice and agricultural by-products {empty fruit bunch (EFB), sawdust (SAW) and paddy husk (PH)} as inert materials released diuron of the CRF to reach maximum level 20 days following placement in distilled water and maintained the same rate for up to 60 days. Evaluation of efficacy on the germination of *Paspalum conjugatum* and *Diodia ocimifolia* showed that the CRF provided significantly better control than the conventional formulation (CF) 2 months after treatment (Mazlan et al, 2000) (Figure 4).

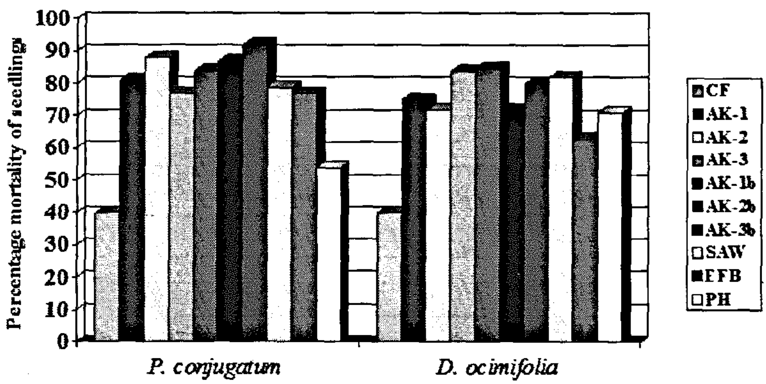



**Figure 4** Percentage mortality of *Paspalum conjugatum* and *Diodia ocimifolia* seedlings sown 2 months following application of controlled-release formulation and conventional formulation.

The use of alginate as the binder in the prepared controlled-release formulations failed to immediately release diuron at a concentration sufficient to kill the weed seedlings. The formulations required several days for the release of active ingredient to reach maximum levels. This allows some of weeds seedlings to survive as the dose may not be sufficient to kill the seedlings. Thus, the herbicide could not cause maximum impact on the weed seedlings. Furthermore, the alginate is expensive. The use of pectin (P1K1, P2K1) as an alternative to the alginate shows more immediate release of the active ingredient. The formulations also release more active ingredient within 24 hours as compared to the alginate CRF (AK1) (Figure 5). Pectin is easily available and cheaper than alginate.

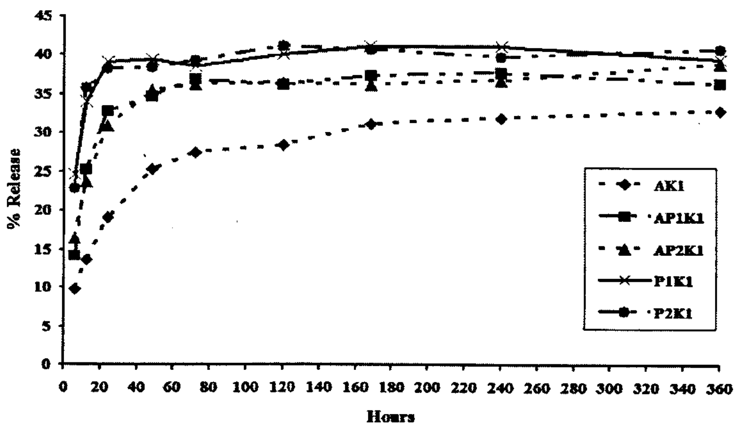



**Figure 5** Release rate of alachlor from alginate (AK1), alginate with pectin (AP1K1, AP2K1) and pectin (P1K1, P2K1) controlled-release formulations

Determination of the efficacy release rates of alachlor and diuron by bioassay technique using *Cucumis sativus* as bioindicators showed that pectin-kaolin CRFs (P1K1 and P2K1) and alginate:pectin-kaolin CRFs (AP1K1 and AP2K1) gave lower values for the lengths of shoot (Figure 6) and root (Figure 7) and the fresh weight of *C. sativus* compared to the alginate:kaolin CRFs (AK1). During initial treatment, the performance was similar to that of CF. This suggests that the addition of pectin improved the initial release of alachlor. Hence, its activity was shown early at the beginning of the treatment and the performance increased with time. Over a period of time all the CRFs performed significantly better at inhibiting elongation of shoot, root and fresh weight compared to CF.

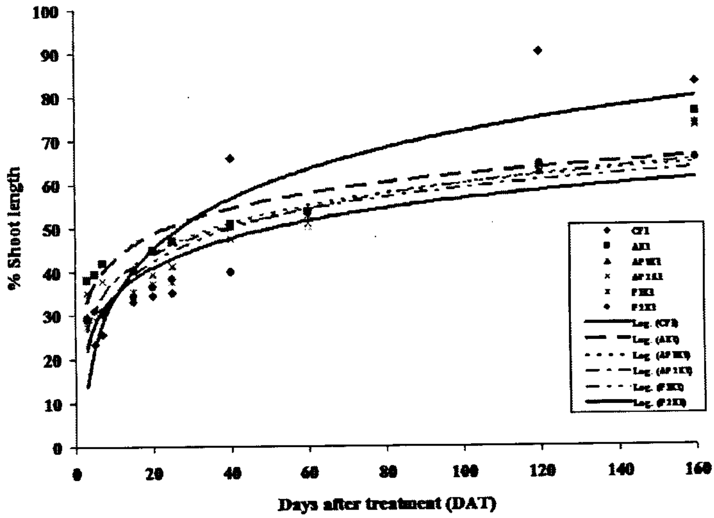



**Figure 6** Influence of time on the shoot length of *Cucumis sativus* exposed to various controlled-release formulations of alachlor recorded at 10 DAS

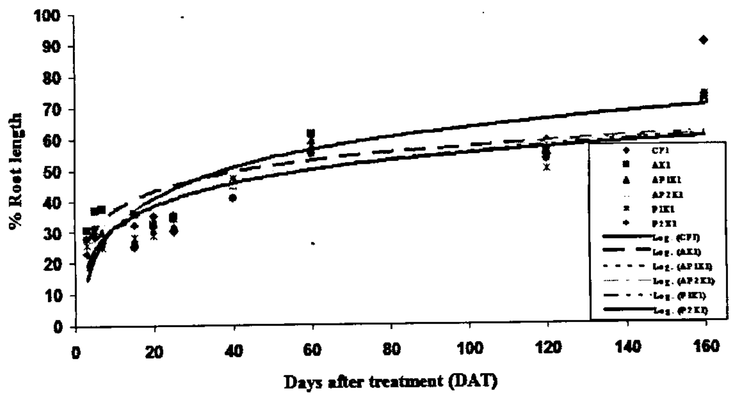



**Figure 7** Influence of time on the root length of *Cucumis sativus* exposed to various controlled-release formulations of alachlor recorded at 10 DAS

## MICROEMULSION FORMULATION OF PESTICIDES

The formulation of pesticides is a critical issue in ensuring improved efficacy, more effective targeting and for achieving significant reductions of environmental impact. Earlier water miscible formulations such as emulsifiable concentrate and wettable powder have certain disadvantages while newer formulations such as suspension concentrate, water dispersible granules and micro emulsion reduce hazards and use of solvent and have improved stability. The emusifiable concentrate formulation is one of the common formulations of pesticides in Malaysia. The formulation consists of an active ingredient and inert ingredients i.e. carrier, surfactant and other additives. These inert ingredients can have several different purposes including increasing the effectiveness of the active ingredients, making the pesticide easier to use or apply or allowing several active ingredients to combine into a solution. The growing awareness of environmental pollution and the stricter regulations require research on pesticides to focus not only on the environmental problems caused by the active ingredients (Krogh *et al.*, 2003) but also on reducing the use of inert ingredients especially those that are potentially toxic such as xylene, paraffins, solvent naphtha, toluene, phenol, acetonitrile and butoxy-2-propanol. These inert ingredients originates from mineral oil-derived commodities.

Emulsions are mixtures of two liquids that are immiscible, one of the two liquids being dispersed in the other in the form of droplets. The size of the droplets is usually larger than 0.1 μm, which gives emulsions a characteristic milky-white colour. Based on the particles/droplet size distribution, emulsion systems are divided into three types: (1) macroemulsion with particle size of the dispersed phase > 400nm (opaque); (2) microemulsions that are often transparent with particles < 100 nm; and (3) miniemulsions which may appear blue-white with intermediate particle size of 100 to 400 nm (Narayanan, 1996). The appearance of a dispersed system depends upon particle size distribution, of the dispersed phase, as described in Table 3.

**Table 3** Effect of particle size of dispersed phase on emulsion appearance

| Particle size | Appearance |
|---|---|
| Macroglobules | Two phases may be distinguished |
| > 1 μm | Milky-white emulsion |
| 1.0 – 0.1 μm | Blue-white emulsion, especially a thin layer |
| 0.1 – 0.05 μm | Gray semi-transparent, dries bright |
| 0.05 μm and smaller | Transparent, dries bright |

Source: Jones and Othmer (1979).

The emulsion requires the mixing of oil and emulsion. Surface active agents or surfactants such as emulsifiers are used to reduce the interfacial tension between water and oil and to stabilize oil/water and water/oil emulsions. However, the emulsions obtained are generally not stable thermodynamically and will degrade over time. A stable spray mixture is very important to attain an even distribution of active ingredient and spray droplet deposit on foliage. An approach to generating uniform dispersed phase domains is via microemulsions. Microemulsions are homogenous, transparent, isotropic, thermodynamically stable single dispersion of colloidals (5-50 nm) of water and oil stabilized by one or more surfactants (Binks *et al.* 2003). It is essential to choose suitable surfactants to formulate oil-in-water agrochemical microemulsion systems. In this case, the insoluble or hardly soluble organic agrochemicals are dispersed in micelles or oil/water microemulsions. By selectively using nonionic surfactants or a mixed surfactant, many agrochemical microemulsions can be formulated (Chen et al., 2000). There are three types of microemulsion: water-in-oil (W/O), oil-in-water (O/W) or bicontinuous systems in which water rich and oil rich domains are separated by surfactant rich sheets (Tenjarla, 1999).

The physical and chemical properties of spray solutions are very important as indicators of the solubility or compatibility of two different components. The presence of any two phases or immiscible components in a system immediately implies the existence of an interface (Myers, 1992). The work per unit area required to form new liquid/solid-air interface is the surface tension of the system. When it is created between liquid/solid-liquid, this energy is referred to as interfacial tension. It is usually reported in units of millinewtons per meter (mN/m) or dynes per centimeter (Myers, 1992). Mutually soluble materials have an interfacial tension of zero, while incompatible substances have a very high interfacial tension when mixed (approximately > 25 dynes/cm). If interfacial tension is less than zero, the interface between two immiscible liquids would tend to mix and cease to exist separately. If interfacial tension is above zero the interface tends to become as small as possible for a given volume of two phases (Volkov *et al.*, 1999). Even at low concentrations of surfactants in water, significant effects can be observed during interfaces with the solution. With increasing surfactant concentration, the experimentally measured decrease in surface tension becomes linear with the logarithm of the surfactant concentration. Finally, the linear decrease in surface tension stops and reaches a level known as the critical micelle concentration (CMC). At this stage surfactant molecules undergo cooperative self-association to form large surfactant aggregates (micelle) with the hydrophobic chains of the molecules residing in the interior of the aggregates and the hydrophilic head groups at the surface in contact with aqueous solutions. Thus, surface active agents are always perfectly correlated with materials that exhibit the characteristic of modifying interfacial interactions by way of enhanced adsorption at interfaces (Holland and Rubingh, 1992).

In surface chemistry, the contact angle is in the context of the wetting and spreading of liquid. There are two controversial descriptions on how the system can be described. In the case of a liquid which forms a uniform film ($\theta = 0^{\circ}$), the solid is assumed to be completely wet. If it is formed ($0^{\circ} < \theta < 180^{\circ}$), the system would be partially wetted and $\theta = 180^{\circ}$ would be non-wetting.

Alternatively, any system with $\theta < 30^{o}$ is defined as wetting. If ($30^{o} < \theta < 89^{o}$), the system would be partially wet and ($\theta > 90^{o}$) non-wetting (Myers, 1999). In order to measure the static contact angles, the condition of the system should be well controlled to attain the `true' angle and not a reflection of some contamination the solid surface or in the liquid phase of interest.

## DEVELOPMENT OF MICROEMULSION OF PESTICIDES

### Construction of Phase Diagram

The three-component phase diagram system is used to develop microemulsion systems (Murrell and Jenkins, 1994). A mixture of carrier (eg. methyl oleate) and surfactant at different ratios in the tube was titrated with distilled water. Each drop of distilled water added was weighed to calculate the percentage of methyl oleate, water and surfactant in the mixture. The solutions were agitated to confirm solubility. The phase change was noted by direct visual inspection of the samples based on the criteria of turbidity/transparency transition of a solution. The results obtained were used to plot a ternary phase diagram or three-component phase diagram (Figure 8), which consisted of carrier (methyl oleate), water and surfactant. Each of the three vertices is assigned with one particular component so that the vertex represents 100% of that component, while the opposite line is 0% of that component. The fraction of component water can therefore be indicated by lines parallel to the carrier-surfactant mixture and the phase boundaries between single-phase (isotropic) region and two-phase region can be assigned (Figure 9).

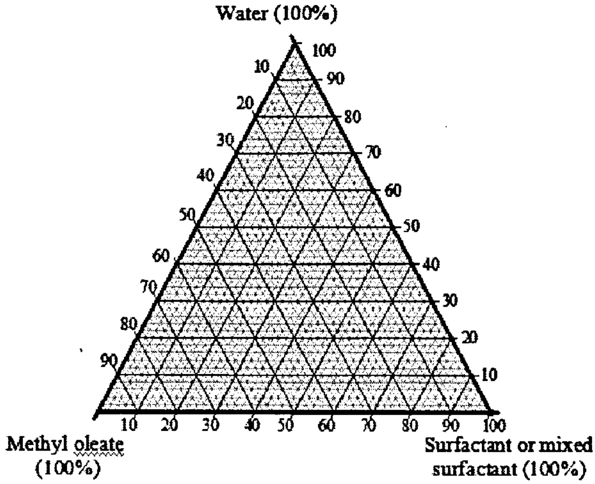



**Figure 8** Typical example three-component Phase Diagram

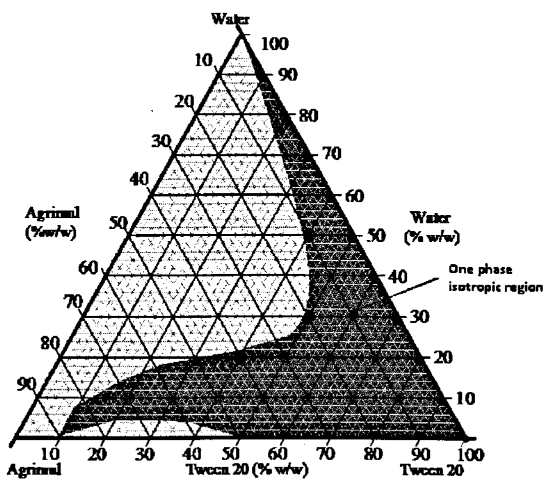



**Figure 9** Contracted phase diagram of Tween 20, Agrimul and water

## Oleochemicals as Carrier of the Active Ingredient in Microemulssions

There are several oleochemicals derived from palm oil such as methyl ester, fatty acid ester, fatty alcohol and alkyl polyglycoside that could be used as carrier and adjuvant in the microemulsion formulation of pesticides. They could be utilized either as a pre-mixture or tank mixture spray with herbicide, insecticide and fungicide (Henkel, 1995). They also have diverse functions and are used as surfactant, wetting agents, penetrant, spreader, sticker, stabilizer agents, activator etc.

Methyl oleote is one of the esterified seed oils derived from palm oil, from either the fats and oils route or fatty acids route, through the processes of transesterification or esterification. The beneficial effects of emulsified seed oils are reported mainly for selective herbicides controlling grass weeds in various broad-leaved crops (Schott *et al.,* 1991). This compound is classified in the methyl ester group which because of their diverse physical and chemical properties have a wide range of uses. One of the main uses of the liquid methyl ester is as a solvent in various pesticide formulations and as a replacement for mineral oil in crop oil concentrates. It has many advantages, for example its rapid biodegradability, low toxicity ($LD_{50}$>5000mg/kg), non irritating, low viscosity, mobile fluids and good solvency properties (Henkel, 1995). Although it is prevalent as a solvent, methyl oleate also has potential to serve as an activator adjuvant. It has been reported that esterified vegetable oils are often more effective than their current crude oils or than paraffinic petroleum oils (Manthey *et al.,* 1989). The study conducted by Omar *et al.* (1999), found that methyl oleate, a nonionic adjuvant derived from palm oil, has significantly stimulated deposition of spray droplets compared to other oleochemical type (S1) and organosilicone (PULSE) surfactants in Roundup® spray solutions.

### Sugar-Based Surfactants for Microemulsion

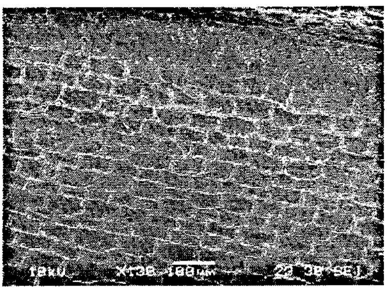
Sugar based surfactants such as alkyl glucosides, alkyl polyglucosides and glicolipids have recently been the object of numerous studies. In comparison with ionic and some nonionic amphiphiles, sugar based surfactants lower surface and interfacial tension more effectively and show a greater tolerance for electrolytes (Coppola *et al.*, 2002). Another important characteristic of these surfactants is that they are environmentally friendly, easily biodegradable, reasonably nontoxic and are produced from naturally occurring renewable resources such as fatty alcohols and glucose (Cognis, 2001) or starch and fat (Biermann *et al.*, 1993). They also display dermatological safety (eyes and skin), good wettability, good foam production and good cleaning ability.

## PERFORMANCE OF MICROEMULSION OF GLYPHOSATE

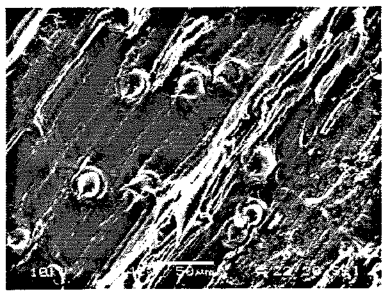
Leaf surfaces are the first barriers that pesticides must pass through before reaching the site of action. Many studies looked at the foliar cuticle which is a predominantly crystalline wax array embedded in a polymeric cuticle which overlays the epithelial leaf cell. The cuticle is a continuous non-living lipid layer covering all aerial surfaces of terrestrial higher plants composed of a lipid polymer and a mixture of extractable lipids (sometimes referred to epicuticular waxes), which serves primarily to protect the plant from dehydration (Baker, 1982; Holloway, 1982). At the same time the plant cuticle also acts as the principal barrier to spray deposition and the penetration of foliage-applied pesticides. The chemical compositions of both the polymeric and extractable lipids vary among species, among genotypes within species and among parts within plants. Most plant waxes are composed of a few major classes of aliphatic components including n-alkanes, wax ester, aldehydes, ketones, secondary alcohols, β-Diketones, fatty alcohols, fatty acids and triterpenoids (Eigenbrode and Espelie, 1995). The amount of cuticular wax varies between weed species (Table 4). The roughness of leaf surfaces also vary according to the species (Plate 1).

**Table 4** Cuticular wax of three important weeds species.

| Weed Species | Mean cuticular wax (μg/cm²) |
|---|---|
| *Diodia ocimifolia* | 14.21 (± 2.80) |
| *Asystasia gangetica* | 23.16 (± 1.67) |
| *Eleusine indica* | 45.63 (± 4.27) |



A *(Cyperus kylingia)*



B (*Pennisetum polystachion)*

**Plate 1** Smooth (A) and rough (B) of leaf surfaces

The hydrophobic nature of the wax often makes it a principal barrier to the penetration of foliage-applied herbicides. Water droplets spread poorly on leaf surfaces unless the surface tension of the spray solution is reduced to the critical surface tension of the leaf surface (McWhorther *et al.*, 1993). Adding adjuvant to the spray formulation increases the solid-vapor interfacial tension and hydrophiliszes the initially hydrophobic solid substrate just in front of the spreading droplet. This process causes the water droplet to spread over time (Starov *et al.*, 2000). In fact, another effect of adjuvants on leaf waxes is to alter diffusion of the pesticide and it is possible that this occurs either as alteration of the wax crystallinity, plasticisation of amorphous wax or changes in the wax-cutin matrix (Rodham, 2000). Baur *et al.*, (1999) illustrated that ethoxylated fatty alcohol surfactants and alkyl ethoxylate surfactants were shown to increase lipophilic pesticides mobility in plant cuticle, but may also reduce the partitioning from foliar deposit into the leaf cuticle by enhancing the solubility of the pesticide in the foliar deposit.

Studies were conducted on the effect of various preparations of glyphosate microemulsion formulation on the spread coefficient of spray droplets and their effectiveness on *Diodia ocimifolia, Asystasia gangetica* and *Eleusine indica.* The spread coefficient of some microemulsions was higher than that of the standard Roundup (Figure 10). This allows more glyphosate to penetrate and reach the site of action. The ME6 formulation showed a higher spread coefficient irrespective of the quantity of wax of the weeds. The formulation was also found to able to deliver glyphosate to the site of action faster than the standard Roundup as showed by the development and higher percentage of necrosis at 7 days after treatment (Figure 11).

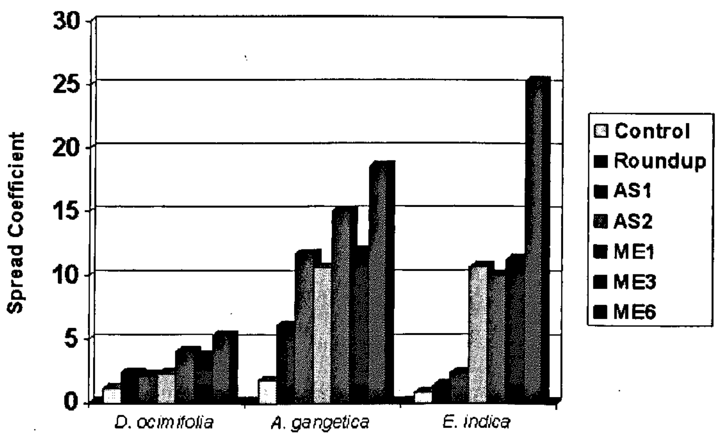



**Figure 10** Spread coefficient of various formulations of glyphosate applied to the middle leaf of *Diodia ocimifolia, Asystasia gangetica, Eleusine indica*

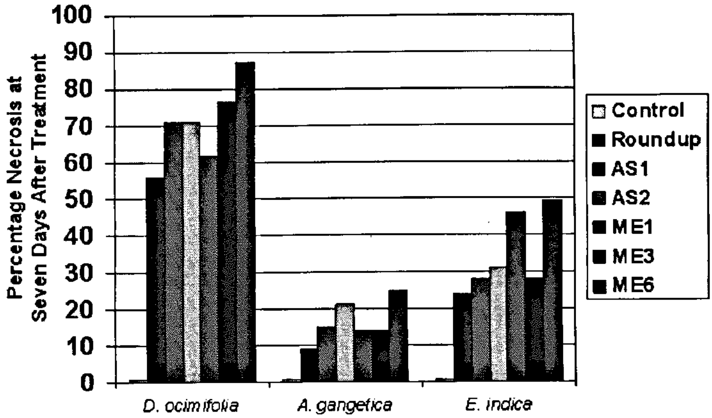



**Figure 11** Percentage necrosis of *Diodia ocimifolia, Asystasia gangetica, Eleusine indica* seven days after treatment with various formulations of glyphosate

## MICROEMULSION FORMULATION OF BOTANICAL PESTICIDES

New pesticides introduced into the market are generally very specific in their activities. The conventional organic insecticides such as organochlorine, organophosphate, carbamate and synthetic pyrethroid affect insect nervous systems. The insecticides introduced in the late eighties and early nineties such as chitin insect inhibitor, juvinile hormone mimics and ecdysone agonist affect developmental processes in insects. They are intended to cause an effect on insects alone. The recent insecticides introduced are either inhibiting or enhancing the activity of specific biochemical sites such as the uncoupler of the electron transport chain in respiration systems, nicotinyl acetyl choline receptors and salivary glands of sucking insects. Some are derived through fermentation of fungi such as spinosyn and bacteria such as avermectin and they are considered bio-based insecticides. These compounds are generally safe and environmental-friendly. The trend is almost similar with fungicides and herbicides. Nevertheless, resistance is likely to develop with the compounds having a very specific sites of action coupled with relatively simple chemical structures.

Botanical pesticide is compound derived from plant materials. Most works conducted in this area are on botanical insecticides. These botanical insecticides are sometimes referred to as natural insecticides. They are normally used by farmers in the form of crude extract of plant material in water and applied directly to the crop. The compounds are generally unstable and short-lived. Recent interest in organic farming has stimulated interest in botanical insecticides as the compounds to meet the criteria set for organic farming. Works conducted included on the formulation to increase effectiveness of the active ingredient, storage and ease of application. The common botanical insecticides used are azadiracthin and rotenone. Azadirachtin is derived from the seeds of the neem tree while rotenone is from the roots of *Derris eliptica*.

Rotenone, is known for its rapid action, fast degradation and relatively low plant and mammalian toxicity. Being a natural product, it is environmental-friendly and could be the best alternative to conventional synthetic chemical insecticides. To strengthen its claim as a biobased insecticide, rotetone should be formulated using biobased materials. Microemulsions have shown to be effective in delivering the active ingredient in herbicide formulations.

The microemulsion formulations of rotenone were prepared using oil palm-based methly ester as the carrier in the formulation. Rotenone in the form of Concentrated Liquid Crude Extract was incorporated into the selected microemulsion formulations obtained from the ternary phase diagram systems. The compounds used in the construction of the ternary phase diagrams were palm-based methyl ester, surfactant and water.

The surface tension of the formulations measured was lower than that of water while particle sizes determined were less than 100 nm (Table 5). These would give greater spray deposition on the target surface and enhance active ingredient distribution and penetration into the leaf cuticle.

**Table 5** Surface tension and particle size of various microemulsion formulations of rotenone

| Formulation | Surface tension (mN/m) | Particle size (nm) |
|---|---|---|
| Ag. BL7001/Ag. PG 8107U/water | 26.8 | 85.24 ± 0.84 |
| Ag. BL 7001/Ag. 9116/water | 26.4 | 226.56 ± 39.32 |
| Ag. BL 7001/Tween20/water | 22.7 | 24.85 ± 0.50 |
| Ag. BL 7002/Ag. PG 8107U/water | 27.3 | 45.48 ± 5.66 |
| Ag. BL7002/Tween20/water | 22.8 | 62.17 ± 0.38 |
| Edenor ME/Tween20/water | 26.9 | 98.06 ± 1.73 |

The toxicity of the selected rotenone microemulsion formulations, in comparison with rotenone commercial emulsifiable concentrate formulations (Saphyr 6.6 EC), against *Plutella xylostella*, when evaluated in the laboratory using 2nd instar larvae of the diamondback moth, showed comparable $LC_{50}$ values.

## WATER DISPERSIBLE GRANULES FORMULATION OF MYCO-INSECTICIDES

Entomopathogenic fungi, especially those from the Hyphomycetes, are responsible for epizootics that often regulate insect pest populations. Their spores have demonstrated good myco-insecticidal activities making them potentials for bioproduct development. Nevertheless, the success of biopesticides in the field ultimately depends on the right choice of isolates and the manner they are formulated. The formulation should not only maintain virulence and infectivity of the spores but also have similar physio-chemical properties of a conventional pesticide. Water-dispersible granule (WG) formulation of spores confers less handling hazards, accommodates the operational practices of farmers and is compatible with the inherent high humidity in Malaysia.

Spores from selected isolate of *Metarhizium anisopliae* obtained form mass-cultured (Figure 12) were used as active ingredient and tested for their sensitivity towards ingredients commonly used for WG formulation such as dispersants, wetters, fillers and binders.

Concentration of the ingredients was determined using ternary phase diagrams and WG formulation containing spores of *Metarhizium anisopliae*, was successfully formulated with high spore viability of 85% (Figure 13).

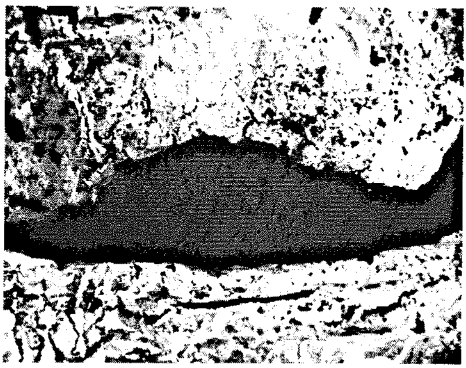


**Figure 12** Spores of *Metarhizium anisopliae*

**Figure 13** Water dispersible granules of *Metarhizium anisopliae*

## IMPROVING PESTICIDE APPLICATION TECHNIQUES

The application of pesticide is to distribute active ingredients in such a way that a major proportion of it will reach the intended target. The effectiveness of spraying will depend on the coverage which could be described as the number of droplets per square centimetre.

A basic guide for acceptable and effective droplets per $cm^2$ is as follows:

| Pesticide | No. of droplets/$cm^2$ |
|---|---|
| Systemic herbicides | 5 – 10 |
| Contact herbicides | 30 – 40 |
| Insecticides and systemic fungicides | 20 – 30 |
| Contact fungicides | 50 – 70 |

These general guidelines cannot be applied without consideration of other important factors such as spray droplet size, nature of the target, mode of action of pesticide etc. The following is the general guide for spray droplet size based on the target.

| Target | Droplet Size (μm) |
|---|---|
| Flying insects | 10 – 50 |
| Insects on foliage | 30 – 50 |
| Foliage | 70 – 150 |
| Herbicide where drift is to be avoided | 250 – 400 |

The efficacy of a chemical, following spraying, depends also on many factors such as leaf surfaces, spray retention, contact angle of droplet, concentration and susceptibility to the chemical. Small droplets give better coverage than large droplets.

Dosage in almost all cases is stated on the product recommendations label, which the manufacturer has developed after carrying out many tests, and should be conformed to. The dosage is commonly given as the amount of chemical for a given amount of carrier such as water. The rate does not specify how much should be applied per hectare. The applicator either applies too little or too much. Dose specified as the amount of active ingredient per hectare would be more accurate and the applicator can decide on the amount of carrier to be used to distribute the toxicant.

Different stages of a pest will vary the requirements for an effective dose to achieve control. Systemic compounds are translocated in plants so coverage errors are less important. Translaminar formulations would be desirable for pests located on the underside of foliage.

Timing is an extremely important aspect of the spray programme. It should take into account not only environmental and meteorological conditions but also the stage of development of the target pest or weed. In the case of insecticides, the stem borer and many other similar pests are only vulnerable for a few hours and, if not controlled, become difficult targets to reach as they are then inside the plant stem. Some pests are almost impossible to control but when the crop is treated at the right time, the results would be positive. Herbicides applied at the wrong time could cause yield losses. This can be due to spraying at a very sensitive crop development stage or because the weeds have developed to a stage when control with a particular chemical is no longer possible. The best chemical, equipment and application technology will be ineffective if used at the wrong time. Timing of the correct product application with correct coverage is essential for effective economic and biological control of a pest infestation situation.

Hence, many aspects of the pesticide application programme need to be considered in relation to the biology of the pest and the growth of the crop. Three very important parameters are coverage, dosage with choice of product and timing.

Hydraulic nozzles fitted to the knapsack sprayer are the most widely used atomizers to break spray liquid into droplets in the tropics. The hydraulic nozzle also measures the volume of spray liquid applied and determines the spray pattern. Currently, there are various types and designs of hydraulic nozzle that can cater to a majority of the needs of pesticide application. In general, the spray droplets produced by the hydraulic nozzles can be classified according to the spray droplet spectra namely very fine, fine, medium, coarse and very coarse. The type of nozzle influences the size of spray droplets (Table 6). One spray droplet spectrum may be more suitable than another depending on the target pests and environmental factors. For example, a fine droplet spectrum is recommended for insect control while coarse droplets should be used for weed control to minimise spray drift.

**Table 6** Effect of nozzle type on droplet size at 40 PSI and 0.5 GPM

| Nozzle Type | Volume Median Diameter (µm) |
|---|---|
| Hollow Cone | 360 |
| Extended Range Flat Fan | 460 |
| Standard Flat Fan | 470 |
| Full Cone | 680 |

Spraying Systems Co., 1990

The spray droplets in herbicide applications could also influence the effectiveness of herbicides. When the performance of three different Lurmark® fan nozzles were compared using paraquat on *Mikania micrantha*, necrosis was observed to be significantly higher when sprayed with 223 and 446 µm droplets compared to 662 µm droplets (Table 7). As such, good coverage is required for contact herbicide to function effectively. Small droplets give more droplets per cm$^2$ at similar spray volumes per hectare.

**Table 7** Necrosis of *Mikania micrantha* following spraying with paraquat*.

| Nozzle specification | VMD (µm) | Necrosis (%)** |
|---|---|---|
| 02-F110 (Orange) | 223 | 44 a |
| 05-F110 (Yellow) | 446 | 48 a |
| 08-F110 (Green) | 662 | 27 b |

*spray volume at 200 L/ha
**Means within column followed by the same letter are not significantly different at P = 0.05

The hydraulic nozzle is known to produce a wide spectrum of spray droplet sizes. The spectrum of spray droplets could be estimated based on the volume median diameter (VMD) and number median diameter (NMD) ratio. The larger the ratio the wider the range of spectrums of spray droplets produced by the nozzle. A study was conducted to determine the spray drift of two similar fan nozzles, one of which was designed as a drift guard nozzle. The spraying was carried out for 1 minute using a CP15 knapsack sprayer at a distance of 50 cm above ground. A wind speed of 8.8 km/h was generated by a table fan and spray drift was detected by placing water sensitive papers at various distances from the point of spraying. The number of droplets from the conventional fan nozzle (Lurmark® E-02 110) was found to be greater and further compared with the drift guard fan nozzle (Lurmark® SD-02 110) (Table 8). The drift guard nozzle produced bigger droplets and a narrower spectrum and thus the proportion of small droplets was lower than that for the conventional nozzle. This contributes to the lower spray drift.

**Table 8** Distance travelled by spray droplets from the conventional and drift guard nozzle.

| Nozzle | Spray droplet size | | | No. of droplets/cm² at various distances (m) | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | VMD (µm) | NMD (µm) | VMD/NMD ratio | 3 | 4 | 5 | 6 | 7 | 8 |
| Lurmark E-02 110 | 174 | 49 | 3.6 | 138 | 111 | 64 | 39 | 17 | 7 |
| Lurmark SD-02 110 | 234 | 124 | 1.9 | 102 | 92 | 42 | 24 | 12 | 0 |

Selection of atomizer plays important role on the delivery, improving the effectiveness and minimizing the environmental contamination of pesticides.

## CONCLUSION

As pesticides are going to play a major role in pest control, effort must be made to ensure that the chemicals are used only when necessary. Emphasis should be made on judicious application through pesticide labels. The dosage should be stated and directed in such a way that farmers will apply the correct amounts. Selection of pesticides must depend not only on its effectiveness on the target insect, but also on the effects on beneficial and non target organisms, environment and safety of spray operator and public. Newer insecticides introduced are mostly of biological origin and are normally biodegradable, safe and non- persistent. Selection of spray characteristics and sprayer to effectively deliver the active ingredient to the target will result in an increase in efficiency of utilization of the active ingredient. More studies are required to formulate simple, effective and acceptable pest management programmes. Coordinated efforts and sharing of information will lead to better planning of chemical control using pesticides.

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## BIOGRAPHY

**Dzolkhifli Omar** obtained a Diploma in Agriculture in 1974 from Universiti Pertanian Malaysia. He then earned his B.S. degree in 1977 from Louisiana State University and M.S. from Purdue University, USA in 1980. He joined UPM as a lecturer in 1981 and continued his studies at the Imperial College of Science and Technology, University of London in 1985 and obtained his PhD in 1988. His field of study is Entomology, specializing in Insect Toxicology and Pesticide Application Technology. He was promoted to Associate Professor in 1993 and Professor in 2003.

He was appointed the Head of the Plant Protection in 1997 and held the post until 2001. He was then appointed as the Coordinator of Post Graduate Students in 2003 where he was very much involved in restructuring graduate programs for the Faculty of Agriculture in line with the restructuring of the post graduate program in the University. In 2004, he was appointed as Deputy Dean (Research and Post Graduate Studies) and currently he still holds this post.

As a lecturer in the Department of Plant Protection, Faculty of Agriculture, Universiti Putra Malaysia (UPM), he is active in teaching, research, advisory services and administrative duties. In teaching, other than in his area of Entomology which he teaches at both undergraduate and graduate levels, he also lectures in the areas of Weed Science, Plant Pathology and basic cources in a agriculture. Currently, he is the Chairman of the Supervisory Committee for 8 post graduate students and to date he has supervised 5 PhD and more than 20 Masters' students and 60 undergraduate students.

In the research arena, he has been awarded research grants from various institutions, local as well as international. His research is mainly in the area of pesticides and their application techniques, which includes both basic and applied research. His capability and potential as a researcher has been recognised internationally whereby he was awarded the Research Contract by IAEA in 1989 and 1993, and Research Project by FOA/IAEA in 1989, to conduct research on the use of nuclear techniques to control the pest. Locally, he managed to secure 5 research grants from IRPA (since 1990) and recently from the Science Fund (MOSTI), FRGS (MOHE) and MPOB. He has published 45 articles in refereed journal/monograph, more than 150 articles in conference proceedings/technical reports/newsletters and is also editor and co-editor of 7 proceedings.

He served as Chairman/member of Panel of Evaluation of UPM for IRPA, Science Fund, FRGS and RUGS in the Agro sector. He is also member of panel of evaluation of Scence Fund at the national level. Currently he is serving as a resource person of Taninet.

In recognition of his expertise and research capabilities on pesticide, he is routinely sought by the private sectors to conduct trials on products to be introduced in Malaysia. He has been appointed to conduct consultancy works for multinational companies such as Du Pont, DowAgroScience, Sumitomo, Bayer, Syngenta and Phillip Morris as well as local companies such as Crop Protection, Zeenex and Agricultural Chemical Malaysia, Diversa Tech. and Biotech Heritage.

His nationwide reputation has also been acknowledged whereby he has been invited to be a member on various committees in several government agencies. He deliver talks organised by the Malaysia Agricultural Chemical Association (MACA), currentlys known as Malaysian Crop Care & Public Health Association (CCPH), and the Pest Control Association of Malaysia (PCAM) and other agricultural corporations.

In the international front, he has been involved in setting up minimum standard specifications for lever operated knapsack sprayers, initiated by IRRI and funded by ADB in 1992. This serves as the basis for an Asian regional implementation program to provide solutions for effective pesticide application using small sprayers. He was also appointed as site coordinator and resource person, by UNIDO, to organise the 2nd International Course on Pesticide Application Technology in 1996.

Active in all facets of agriculture, he was the Honourable Secretary of the 8th Malaysian Plant Protection Society Executive Council and Vice President of the 14th Council and is currently Life Member of the association. He is also a member of the Entomological Society of Malaysia (ENTOMA).

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