Ethyl formate — where are we up to?

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Abstract

Ethyl formate is a fumigant that has been used for many years on dried fruit and has several properties that appear to make it a useful rapid fumigant for grains and similar durable commodities. It has particular advantages associated with its existing registration on a food (dried fruit): rapid breakdown to low-toxicity compounds; and a natural occurrence in a wide range of plant material. Early stages of current research at the CSIRO Stored Grain Research Laboratory are concentrated on gaining information that can be used to develop uses that match the material's properties with the needs of industry. This is being done through quantifying exposure conditions required for a high level of insect control and investigating the compound's rate of breakdown and formation of residues over a range of conditions.

Laboratory studies so far have confirmed that kill can be very rapid and breakdown in the presence of grain is normally fast. Rapid action and high sorption/breakdown are valuable attributes but they also create problems. Time is not available for the gas to distribute far from its point of application and there is no latitude to allow for insects to develop from a less susceptible to a more susceptible age during exposure.

Continuing studies are aimed at determining the concentration profile required to kill all stages of major pest insects and determining the rate of sorption/breakdown under a range of conditions. Studies to date indicate that the amount applied rather than the time retained is critical to obtaining a high level of kill. This in turn implies that it is a material well suited to use in unsealed structures, as gas retention for a number of days is not required.

Field trials have investigated use under a range of relatively unsealed conditions on bulk wheat, oats, field peas, and canola. Limited but successful trials on disinfestation of equipment and facilities also show promise.

Introduction

There are only two fumigants widely available for use on grain and similar commodities. These are methyl bromide and phosphine. The problems of methyl bromide and ozone depletion are well documented elsewhere. Phosphine is relied upon for a large amount of stored-product pest control in Australia, and much of the rest of the world. It continues to be an effective treatment but there is an increased (but in Australia still small) number of reports of strains that are significantly resistant to specific types of phosphine treatment (Collins et al., these proceedings). Unless some alternative to the excessive reliance on phosphine is developed, it is probable that in time this material will not be able to continue its crucial role.

The need to find replacements for methyl bromide and alternatives to relieve the selection pressure for phosphine resistance has led to the revaluation of materials that have been shown to have potential for fumigation in the past. Ethyl formate (EtF) is a material in this class. It is a liquid at normal ambient temperatures, has a boiling point of 54°C, and vaporises readily at normal grain temperatures. The vapour has previously been shown to be toxic to stored product insects by Muthu et al. (1984), who also discuss the literature on history of research and use of (EtF) back to 1927.

The current paper concerns research after Muthu et al. (1984). It aims to show the current status of research and the direction that EtF use may take. It does not attempt to present the details of the research; this will be done through individual papers at this conference and subsequently elsewhere.

Post-1984 research

The paper of Muthu et al. (1984) showed that EtF had many of the properties required of a fumigant and demonstrated its efficacy in a range of conditions. The largest potential problem with the material was that of flammability. Dosages around 400 g m^{-3} were required for insect control, but the lower explosive limit (LEL) is about 85 g m^{-3}. Muthu et al. (1984) claim that if proper precautions are taken this does not create a significant risk. The work by Muthu et al. is important as it can be used as part of the preliminary stages in taking a candidate fumigant from potential to commercial use (Table 1).

Dried fruit

In Australia, interest in EtF was renewed through its use as a disinfestant of dried fruit. Hilton and Banks (1997) conducted a series of insect mortality and sorption studies aimed at verifying and, if possible, improving the use of EtF applied to dried fruit during packing for insect control. They conclude that EtF was not only a good fumigant of dried fruit but also that it had some potential as a fumigant of durable commodities. Research on EtF use on dried fruit has continued and a recent trial fumigation has shown that its use as a fumigant of dried fruit in shipping containers shows promise (R. Reuss and C. Tarr, unpublished observations).

Grains and similar commodities

Considerable work has now been carried out in investigating the potential use of EtF on durable commodities. This can be summarised as three groups of interrelated activities: effects on insects; interactions with commodities; and field trials.

Insects

A range of test exposures to insects, plus the literature data, have been used to characterise immature *Sitophilus oryzae* as one of the most tolerant species/stages to EtF (Damcevski and Annis, these proceedings). Studies with this species have been used as a benchmark on which to compare species. The full results of these studies are given elsewhere. However, important findings to date include that an application rate of around 80 g m^{-3} is efficacious for most species tested but marginal for immature *S. oryzae*. More importantly, the application rate is a better indicator of efficacy than estimated, as opposed to measured $C \times t$ products (*Ct*). On the basis of laboratory exposures this seems to be a function of very rapid insect

Table 1. An overview of the steps used at the CSIRO Stored Grain Research Laboratory (SGRL) to take a new fumigant from an idea to routine use. Additional but important steps apply to commercial partners and regulatory bodies; these run simultaneously with those undertaken by SGRL. The status of work on ethyl formate is indicated by as follows: **major steps are in bold type**; *essentially completed actions are in italics*; work in progress is in normal text; and work yet to be started is in brackets ().

• **First-stage screening**
– *An informed, good idea based on literature and chemical characteristics*[a]
– *Is it toxic enough to insects?* [a]
– Does it stay around long enough? Sorption and reaction[a]
• *If passes the above, take time to review risks more thoroughly*[a]
• **Second-stage screening**
– *Identify target species/stage*
– *Determine gross effects on grain e.g. germination*
– *Develop analytical methods — dosage, commodity, and environment levels*
– *Develop interim application method*
– Screen sorption/residues[a]
– (Interaction with important materials)
• If passes, start formal risks analysis
• **Systematic detail**
– *Determine dosage requirements for target species/stage — time, concentration, and temperature*
– Systematic sorption and residue analysis in primary commodities
– Determine a provisional 'label dose'
• *Begin commercialisation*
• **Proving use**
– *First stage field trials with end user/commercial quality assessment*
– Proving the provisional 'label dose' by challenging over diverse conditions in laboratory
• **Commercialising activities**
– (Major field trials — efficacy, residues, work-space and environmental monitoring)
– (Information and laboratory support towards registration — efficacy, residues, environmental monitoring)
• **Supporting activities**
– Developing new application methods to meet changing industry needs
– (Developing new label rates to meet changing pest parameters — resistance and new species)
– Responding to changes in the regulatory environment

[a] Started or completed pre-1984 work (Muthu et al. 1984).

kill and rapid breakdown of EtF on cereal commodities (Damcevski and Annis, 1998). This means that the concentration is changing quickly and a large proportion of insect death has occurred before any meaningful *Ct* can be assessed, also that a substantial portion of *Ct* is accumulated after insects have died.

Commodity

A method has been developed to determine natural and residual levels of EtF in a range of granular and non-granular commodities (Desmarchelier et al. 1999; Vu and Ren, in press). Natural background levels have been estimated over a range of commodities: wheat, barley, oats, canola, rice, faba beans, cottonseed, and chickpeas (Desmarchelier et al. 1998, 1999; Vu and Ren, in press). Field trials and laboratory investigations have shown that wheat, oats, barley, canola, paddy rice, and rice products can be aired easily to a stage at which the levels of residual EtF are indistinguishable from natural levels (Desmarchelier et al. 1998; Reuss et al., these proceedings). End-user assessment was made of wheat (milling and baking) and barley (malting and brewing) treated in field trial conditions. No effects of use of the material were detected.

Field studies

Field trials with ethyl formate to date have been mainly opportunistic rather than part of a planned program. They have included successful disinfestation of plant and machinery, disinfestation of sampling systems (Allen, these proceedings), and surface disinfestation of grain. Closely monitored small-scale field trials (~50 t) have been carried out on dried fruit, wheat, barley, canola, and oats. All trials have been satisfactory in that no problems were found in terms of application method, operator safety, insect control, commodity damage, ventilation, or residues at outloading.

Application methods

Three methods of application have been investigated; each has its advantages and disadvantages. Each method appears to be possible at the small experimental trial level. Their scale-up and conversion to robust commercial procedures should not be too difficult but have not yet been attempted. The three potential application methods are described below.

- Direct admixture with grain during grain movement. In this method an ethyl formate and water mixture is sprayed directly onto grain as it enters storage. This requires grain movement; it gives good distribution and is best suited to prophylactic treatments or rapid disinfestation of infested grain. The results of research so far suggest that a high degree of sealing is not required for this type of application.
- Volatilisation with recirculation. In this method, a measured amount of pure EtF is applied to a sealed system and allowed to mix freely by natural or forced-air movement. Owing to the flammability of EtF this method requires careful planning and operation to ensure sources of ignition are not present during the application procedure.
- Direct application in water. Aqueous EtF is sprayed directly onto the commodity requiring surface disinfestation. This is the least tried method and more experimentation is required before its range of applicability can be established.

Conclusions

All research to date has been encouraging for the future of ethyl formate as a useful disinfestant in the grain industry. However, the research is limited and many gaps exist. Further studies in the laboratory and in the field are required before the true range of applicability can be determined. On the limited information obtained so far the following conservative conclusions are possible:

- a commercial partnership is essential to progress the use of ethyl formate;
- few problems are foreseen as regards acceptability by commodity end users;
- there is a high probability of some commercial use; and
- there is promise of considerable commercial use.

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