ETHOXOFUME 1000 (EtO): methyl bromide alternative update

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Abstract

Ethylene oxide (C_2H_4O = EtO) is made from the oxidation of ethylene and over 15 million tonnes are produced annually. For over 80 years EtO has been used as a sterilant / fumigant. EtO is lethal to bacteria, viruses, moulds, insects and their eggs. Historically EtO was used in the fumigation of bulk grain. EtO is still widely used in "cold" sterilization of medical devices and instruments. With the precondition of destroying vented EtO at the completion of fumigation, EtO could be a niche methyl bromide (CH_3Br = MeBr) alternative. EtO is toxic by inhalation with an LD_{50} of 330 $mg.kg^{-1}$ EtO is classified as carcinogenic to humans by the International Agency for Research on Cancer (IARC). Occupational Limits: TLV-TWA (1 ppm); OEL (UK)-LTEL (5 ppm). EtO is a colourless, highly flammable gas (Lower Explosive Limit (LEL) = 3 vol% in air) which liquefies at 10.9°C. To reduce flammability EtO is mixed 12 vol% EtO in carbon dioxide (CO_2). Onsite mixing of EtO and Air is an option, however the EtO must be kept below 54 $g.m^{-3}$ (3 vol%) – higher doses of EtO would require on-site mixing with CO_2 or N_2. Quarantine fumigations using ETHOXOFUME 1000 are carried out using vacuum chambers to treat non-food import and export commodities. On completion of the fumigation the EtO/Air mixture can be exhausted using a high pressure fan and destroyed in a "burner" where it is converted to CO_2 and H_2O. The Ct product for the control of various species of insects show that EtO on a weight basis ($g.m^{-3}$) has better efficacy than MeBr. A conservative recommended dose rate of 48 $g.m^{-3}$ results in a concentration of 1.2 vol% for MeBr and 2.7 vol% for EtO (this is less than the LEL of 3 vol%).

Keywords: Ethylene oxide, Fumigant, Sterilant, Insecticide, Incineration

1. Introduction

With the Montreal Protocol listing of methyl bromide (MeBr), the search continues for alternative fumigants. The usage for MeBr is now restricted to Quarantine and Pre-Shipment (QPS) i.e. the fumigation of import and exports. In addition to QPS there are some Critical Use Exemptions (CUE) but these are now minimal. Pre - Montreal Protocol the usage of MeBr for stored product fumigations was in excess of 16,000 tonnes. The advantages of MeBr include low cost, short exposure time (hours not days), practically non-flammable and well documented efficacy. It has been difficult to find alternative fumigants to match these advantages.

There has been some effort evaluating existing volatile liquids and gases that could be considered as alternatives to MeBr. The barrier to introduce new chemicals is the high capital cost of chemical synthesis plant. Toxicology studies for new chemicals can also add significantly to pesticide registration costs.

With the exception of EtO most of the current fumigants cannot match MeBr on the critical issues of cost and efficacy. While gaseous phosphine (PH_3) is very attractive with regards to treatment costs, the PH_3 exposure time for bulk grain storage is at least 3x more than the 24 h required for MeBr.

EtO is a long term sterilant / fumigant however its current usage is the sterilisation of medical devices and quarantine fumigation. EtO is lethal to bacteria, viruses, moulds, insects and their eggs. Historically EtO was used in the fumigation of bulk grain. EtO is still widely used in the "cold" sterilization of medical devices and instruments. Current EtO treatments are carried out in vacuum chambers where the EtO is contained under vacuum and the aerated EtO is destroyed post treatment.

EtO is produced industrially by oxidation of ethylene with oxygen at ~250°C over a catalyst comprising metallic silver supported on alumina (>15 million tonnes of ethylene oxide is produced annually). EtO is the chief precursor to ethylene glycol (automotive coolant and antifreeze) and other high-volume

chemicals (surfactants, ethanolamine etc). EtO is manufactured in tonnage quantities in Australia and also imported in one tonne, stainless steel, pressurised drums.

EtO is toxic by inhalation with an LD_{50} of 330 $mg.kg^{-1}$. Laboratory animals exposed to ethylene oxide for their entire lives have had a higher incidence of liver cancer. EtO is classified as carcinogenic to humans by the International Agency for Research on Cancer (IARC). Occupational Exposure Limits: TLV-TWA (1 ppm); OEL (UK)-LTEL (5 ppm).

The US EPA Risk Management Decision (16 April 2008) stated "the benefits of continued use of EtO outweigh the associated occupational risks provided risk mitigation measures specified by the Agency were adopted". With preconditions of strict OH&S practices and destruction of vented EtO at the completion of fumigation, EtO could be a niche methyl bromide MeBr alternative.

EtO is a highly flammable gas (LEL=3% v/v in air) which liquefies at 10.9°C. Jones and Kennedy (1930) solved the EtO flammability issue by mixing 12 vol% EtO in CO_2. The internationally recognised non-flammable mixture is 9 vol% EtO in CO_2. The study of flammability of fumigants was published by Jones (1933) which detailed non-flammable fumigants including EtO (12 vol%), ethyl formate (14 vol%) and propylene oxide (8 vol%) in CO_2.

2. Materials and methods

Fumigation application options for EtO include EtO/CO_2 (existing commercial non-flammable mixture of 9% EtO in liquid CO_2), EtO/Vacuum (existing vacuum chambers are currently used for quarantine fumigations) and EtO/Air (potential application has precedents with the onsite mixing of PH_3/Air).

Fumigation application using EtO/CO_2 has the benefit of using a commercial non-flammable mixture of 9% EtO in liquid CO_2. Historically non-flammability was determined at 12% EtO and for decades the commercial non-flammable mixture was 10% EtO. Currently the internationally recognised non-flammable mixture is 9% EtO in liquid CO_2 (wt% & vol% are identical for EtO & CO_2 mixtures). The disadvantage of the non-flammable EtO/CO_2 is the number of industrial gas cylinders required to fumigate large grain storages.

Fumigation application using EtO/Vacuum also has the benefit of using proven existing technology and equipment. Fumigations using ETHOXOFUME 1000 (EtO), under specific directions by the Australian Quarantine Inspection Service (AQIS), are conducted at approved facilities. These EtO fumigations are carried out using vacuum chambers to treat non-food import and export commodities. AQIS Guideline: "Ethylene Oxide treatment code: T9020" - specifies an initial minimum vacuum of 50kPa, 1200

$g.m^{-3}$ EtO, 5 h exposure at 50°C. Most EtO documented fumigation quarantine schedules recommend a Ct less than 500 $g.h.m^{-3}$ however for snails in cargo the rate is increased a factor of 5 to ~2500 $g.h.m^{-3}$. The current AQIS recommended dosage of 1200 $g.m^{-3}$ for 5 h i.e. a Ct of 6000 $g.h.m^{-3}$ was reduced from 1500 $g.m^{-3}$ for 4 h after the recommendation of Ryan et al. (2004) on flammability issues. It is understood that the very high AQIS dose is required to ensure the effective fumigation of specially challenging commodities requiring fumigation especially coated (paint, resins, plastic) woods and other commodities. The additional sterilising properties of EtO are a bonus associated with using this sterilant/fumigant.

Disadvantage of vacuum application is the capital investment in vacuum chambers and associated equipment and the small capacity of chambers relative to grain storage.

Fumigation application using EtO/Air is not yet a proven technique. The onsite mixing of EtO and Air must be kept below the 3 vol% lower flammability limit. This could be achieved by the addition of EtO to recycled air from the space being fumigated and maintaining the EtO concentration less than 54 $g.m^{-3}$ (3 vol%). Although, higher EtO levels could be entertained, the oxygen level in the storage would need to be lowered – this option would require partial purging with onsite N_2 generation. Forced draught recirculation using high pressure fans has the benefits of achieving uniform distribution; allowing the addition of EtO to compensate for losses associated with leaks / sorption and extracting EtO to enable destruction on completion of fumigation. EtO is easily burnt by venting via an incinerator / thermal oxidiser / catalytic converter. On completion of the fumigation the EtO/Air mixture can be exhausted using the high pressure fan and destroyed in a "burner" where it is converted to CO_2 and H_2O. Other EtO capture and destruction options include converting to ethylene glycol by scrubbing with 5% aqueous sulphuric acid or adsorption onto activated carbon followed by subsequent destruction or burial.

EtO is a sterilant and has potential to sterilise imported grains (devitalisation of grain/exotic weed seeds and elimination of pathogens) and sterilise soil (microbes, insects, nematodes, weeds). High levels required for grain sterilisation would need to be conducted in modified atmospheres (lower oxygen with onsite generated N_2 to avoid flammability issues). While CO_2 is the preferred diluent for non-flammable mixtures, the transport cost of CO_2 to remote grain storage sites eliminates any benefit over on-site N_2 generation. The safe use in soil may be possible as the high EtO solubility in water allows "in-line" fumigation using water as the carrier. The reaction of EtO with water forming ethylene glycol should ensure minimal release of EtO to the atmosphere in soil fumigation applications.

3. Results

Reported Ct fumigant concentration x time product for the control of various species of insects (Monro, 1969) show EtO and MeBr have similar efficacy. While the Ct favours MeBr (M.Wt. = 94.94) this is more than equalised by the higher (2x) concentration achieved using ethylene oxide (M.Wt. = 44.05) e.g. a dose rate of 48 $g.m^{-3}$ results in a concentration of 1.2 vol% for MeBr and 2.7 vol% EtO.

The high concentration achieved by EtO neutralises any differences so the recommended dose rate for methyl bromide and ethylene oxide should be similar (it should be possible to use 30% lower EtO dose than MeBr). The recommended 48 $g.m^{-3}$ (2.7 vol% EtO) dose is attractive as it achieves an EtO level below the flammability level in air and this concentration should be efficacious for stored product insects in less than 24 h exposure time.

While ethylene oxide doesn't have ozone depletion issues, it is a known carcinogen and OH&S issues require significant more aeration than methyl bromide. As with existing sterilisation practice and registered label recommendations the aeration clearance level for ethylene oxide is the TLV i.e. 1 ppm.

Existing EtO sterilisation chambers are fitted with thermal oxidisers to ensure the EtO vented is less than 1 ppm. EtO readily burn to form CO_2 and H_2O. On-going testing is evaluating prototype toxic gases burning and pyrolysis in high temperature aggregate beds. While high temperature pyrolysis is shown to be effective with EtO, other issues include the development of portable equipment to service multiple locations and the need to accommodate large air dilution required to reach the 1 ppm TLV level.

4. Discussion

The sterilant / fumigant EtO, a known carcinogen, could have niche fumigation-sterilisation applications if the aerated gas post fumigation could be destroyed. EtO, a universally produced industrial chemical (>15 million tonne pa) has potential as a stored product fumigant.

Reported Ct product of fumigants for the control of various species of insects (Munro, 1969) show EtO and MeBr have similar efficacy (possible to use 30% lower dose using EtO vs. MeBr). Reported Ct product suggests 48 $g.m^{-3}$ as a maximum dose rate for stored product pests. Bond (Table 161984) gives Ct for eleven fumigants (including MeBr and EtO) for eight economic stored product pests.

EtO is toxic by inhalation with an LD_{50} of 330 $mg.kg^{-1}$. EtO is classified as carcinogenic to humans by the International Agency for Research on Cancer (IARC). Occupational Limits: TLV-TWA (1 ppm);

As the cost and efficacy is comparable to MeBr, the outstanding issue is the safe application of EtO and development of portable high temperature thermal oxidisers to destroy aerated EtO to ensure there is less than 1 ppm emitted.

This approach should satisfy the US EPA who sees benefits in the continued use of EtO provided risk mitigation measures are adopted

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