

## Ethyl formate fumigation an overview update

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### Abstract

The historical fumigant ethyl formate [EF] is proving to be a methyl bromide alternative. EF effectiveness against dried fruit insects was published in 1925. Non-flammable mixture of EF (14.4 vol% EF) with carbon dioxide [CO<sub>2</sub>] was reported by Jones (1933). On-site mixing of EF liquid into a stream of CO<sub>2</sub> in export grain structures was trialed by Allen and Desmarchelier (2000). In addition to eliminating the flammability hazard, CO<sub>2</sub> has a synergistic effect with an optimal range of 5%-20%. Ryan and Bishop (2002) developed a commercial mixture of EF dissolved in liquid CO<sub>2</sub> which was compressed to 40 bar pressure in an industrial gas cylinder. EF is a highly flammable volatile liquid (b.pt.=54°C) which requires vaporization to minimize adsorption and achieve uniform distribution throughout the fumigation space. Pre- or post (on-site) EF/CO<sub>2</sub> mixture is converted to a gaseous mixture using a proprietary high pressure vaporiser. The EF/CO<sub>2</sub> gaseous mixture is accurately dispensed into the fumigation chambers by weighing. However, because the application rate of the EF/CO<sub>2</sub> mixture is between 75 and 420 g/m<sup>3</sup> fumigations need to be done in adequately tested gas-tight structures (De Lima et al., 1994) while vacuum chambers are generally satisfactory. The high velocity warm gaseous mixture can be connected to air amplifier/venturi device to improve mixing within the fumigation chamber. Since 1980 the successful use of EF to fumigate insects infesting stored cereals has been reported in India and Australia. Over the past 12 years ethyl formate has been found effective in controlling a variety of insects in citrus, grapes, strawberries, bananas and sweet corn in addition to stored cereals, pulses, dates and fodder crops.

Keyword: ethyl formate, CO<sub>2</sub> non-flammable mixtures, liquid fumigant vaporization, postharvest stored products, date fumigation

### 1. Introduction

The successful use of ethyl formate (EF) was reported in studies to control insect pests in dried fruits and in stored wheat (Neifert et al., 1925; Cotton and Roark, 1928; Roark and Cotton, 1929; Simmons and Fisher, 1954). Shepard et al. (1937) found EF more toxic than carbon disulphide to *Tribolium confusum* Duv and *Sitophilus granarius* L. Vincent et al. (1972) found that EF compared favorably to phosphine against insects infesting dates and other dried fruits. Muthu et al. (1984) conducted large scale tests on cereals, pulses, spices, dried fruits, nuts and dried tubers and recommended EF was a safe general fumigant for stored food. EF was recognized as an effective fumigant for control of insects in several commodities: cereals and pulses (Pruthi and Singh, 1945; CFTRI, 1979), clothing (Busvine and Vasuvat, 1966; David, 1943) and fresh fruit, vegetables and flowers (Aharoni and Stewart, 1980; Stewart and Aharoni, 1983; Stewart and Mon, 1984; Wang, 1982). EF was not found to adversely affect the quality or flavor of treated commodities. EF was also found to have fungicidal properties in cereals (Raghunathan et al,

1974; Deo and Gupta, 1986) without affecting viability or germination of the seeds. To minimize potential flammability in air Jones (1933) established the specific non-flammable mixture range of EF in CO<sub>2</sub> as 1:6 by volume to avoid dangerous explosions. An added benefit of CO<sub>2</sub> is that it accelerates the penetration of insecticides into insects' spiracles (Hazelhoff, 1928). Cotton and Young (1929) reported that CO<sub>2</sub> increased the toxicity of ethylene dichloride, ethylene oxide, carbon disulfide, and methyl chloroacetate to the confused flour beetle (*Tribolium confusum*) and the rice weevil (*Sitophilus oryzae* L.).

## 2. Materials and Methods

### 2.1. Dried fruit

Muthu et al. (1984) and found that EF had excellent potential as a replacement for methyl bromide in the treatment of durable commodities noting that the insects pests infesting dried fruits are generally the same as those found in cereal commodities. Hilton and Banks (1996) found that the rate of EF sorption in dried sultanas was independent of concentration but greatly increased with filling ratio and moisture content. Effective control for *Oryzaephilus surinamensis*, *O. mercator*, *Plodia interpunctella* and *Carpophilus hemipterus* was obtained in an 8-h fumigation at 541 g.h.m<sup>-3</sup>.

In the Middle East date infestation by nitidulid beetles (*Carpophilus*spp larvae) poses a serious contamination problem for which methyl bromide (MB) provided a solution. However, because of the phase out of MB an alternative is required. Effective treatment in Saudi Arabia using a commercial mixture of EF/CO<sub>2</sub>, [70g/m<sup>3</sup>/ 2.3% EF + 350g/m<sup>3</sup>/ 19% CO<sub>2</sub>] for 12h exposure result 100% disinfestation (proportion of insects found outside the feeding sites) and 100% mortality. Infestations of *Carpophilus*spp, in dates which is a serious contamination in the Middle East date industry for which fumigation using methyl bromide is the standard treatment in Israel were controlled using 2.3% EF / 19% CO<sub>2</sub> for 12 hours exposure (Finkelman et al., 2010).

### 2.2. Cereal grains

Allen and Desmarchelier (2000) conducted insect bioassay studies in desiccators at 25°C, using a dose of 70g/m<sup>3</sup> of EF with high (75%) and low (35%) humidity and with / without added 7% CO<sub>2</sub> for exposures of 30 minutes. They found that high humidity and addition of 7% CO<sub>2</sub> gave 100% mortality with *Lposcelis entomophilia* (psocids), *Oryzaephilus surinamensis* (sawtoothed grain beetle), *Rhyzopertha dominica* (lesser grain borer), *Sitophilus oryzae* (rice weevil) and *Tribolium castaneum* (red flour beetle). No control was achieved of *Trogoderma variabile* (warehouse beetle) at this exposure time. Damcevski and Annis, 2000 tested 90g/m<sup>3</sup> EF for 24 hours at 16, 24 and 29°C and found no survivors of *R. dominica* or *T. castaneum* adult or immature stages at 29, 24 and 16°C. However, while no *S. oryzae* adults survived, there were survivors of immature stages at all temperatures. After incubation for 14-21 days there was one adult at the 29°C and 305 adults from 16°C exposure compared to >2000 in the control. Wright et al. (2002) and Ren and Mahon (2003) evaluated EF as a liquid to find an alternative to dichlorvos and phosphine for wheat, sorghum and split faba bean in unsealed farm bins. They found that while residues in sorghum at 10°C persisted significantly longer than at 20°C all residues fell to natural levels without aeration, consistent with results from previous trials with EF on wheat.

Mahon et al. (2003) used a mixture of 26g/m<sup>3</sup> EF + 128g/m<sup>3</sup> CO<sub>2</sub> in a 260 m<sup>3</sup> semi-sealed seed store 30% loaded with seeds of barley, wheat and barley with an applied dose of 40kg Vapormate® (BOC Gases Ltd.). Mixed aged *Callosobruchus phaseoli*, *T. castaneum*,

*R. dominica*, *S. oryzae*, *Oryzaephillus spp.*, *Cryptolestes spp.* and psocids were all controlled. EF residues declined to natural levels and the treatment had no adverse effect on germination of the treated seeds. During fumigation the EF concentrations in the adjacent untreated stores and 1-3 m from the front door of the fumigated store ranged from 5 to 25ppm, far lower than the TLV (100 ppm). Haritos et al. (2006) evaluated EF as an alternative fumigant to methyl bromide (ozone-depleting) and phosphine (insect resistance) for stored grain. They found that combining 5 to 20% CO<sub>2</sub> with EF doses significantly enhanced efficacy against *S. oryzae*, *R. dominica* and *T. castaneum*. Mortality in 3h exposures of mixed stage cultures were 99.8% for *T. castaneum* and 95.1% for *S. oryzae* with applied EF doses of 111 & 185 mg.h litre<sup>-1</sup> respectively. They concluded that the combination of CO<sub>2</sub> with EF enhances the distribution and efficacy of the fumigant against stored grain insects. Haritos (Haritos, 2005 and Haritos et al., 2003) chose 50 tonne silos for efficacy studies in field trials. Insects were selected based on the frequency they were found in storages, the economic damage they caused and their known tolerance to insecticidal treatments. Phosphine resistant field strains of *Ryzopertha dominica*, *Tribolium castaneum* and *Sitophilus oryzae* in mixed stage cultures (eggs, larvae, pupae and adults) were exposed to EF+ CO<sub>2</sub> and showed that virtually 100% mortality across four trials at a range of temperatures (28-30°C) and moisture contents (10.7-11.7%). Based on these studies the recommended rate for the complete control of all stages of *R. dominica*, *T. castaneum* and Psocids (various species) was recommended as 70g/m<sup>3</sup> EF for 24 hour exposure. In large scale trials (Allen and Desmarchelier 2000) to disinfest empty silos of psocids, *Liposcelis spp.*, at Grain Export Terminals in Newcastle, NSW and Fisherman's Island, Queensland, EF was applied to the "partially-sealed" silos grain sampling system by on-site mixing and vaporizing the EF liquid in a stream of CO<sub>2</sub>. This gave 100% mortality of *Liposcelis spp.* and no residues of were detected in grain moving through the sampling path in equipment following treatment.

### 2.3. Strawberry fruit

EF was used in concentrations from 0.8 to 2.4% (24 - 72g/m<sup>3</sup>) to control western flower thrips and two-spotted spider mites in strawberry fruit (Simpson et al., 2004). EF effectively controlled western flower thrips but not two-spotted spider mite. None of the dosages affected strawberry fruit quality. However combined treatment of EF+ 10% CO<sub>2</sub> increased mite mortality significantly but did not result in complete control in the 1 hour exposure times tested.

### 2.4. Bananas

EF was successfully used in the disinfestation of bananas exported from the Philippines (Krishna et al., 2005). After several trials 80g/m<sup>3</sup> of EF + CO<sub>2</sub> (Vapormate®) equivalent to 2.6% EF and 24% CO<sub>2</sub> was found to control mites, mealybugs and soft scale. In laboratory and field trials these pests were eliminated when EF was applied into the plastic liner covering banana hands prior to chilling.

### 2.5. Grapes

Arthropods commonly infest table grapes in California. Simpson et al. (2007) successfully used EF in combination with CO<sub>2</sub> to control of all life stages of Western flower thrips, *Frankliniella occidentalis* (Pergande), Grape mealybug, *Pseudococcus maritimus* (Ehrhorn), Pacific spider mite, *tetranychus pacificus* (McGregor) and the omnivorous leafroller, *Platynota stultana* (Washington). The EF doses used ranged from 0.07% -3.48%, and the addition of 10% CO<sub>2</sub> achieved LC<sub>99</sub> in 1-2 hours exposure periods for all insects except spider mites. De Lima (2010a) used mixtures of EF + CO<sub>2</sub> for the control of light brown apple moth, *Epiphyas postvittana*

(Walker) in freshly harvested table grapes for export during the cool down process directly after harvest as well as during pre-chilling in the cold room to cover the major events in the table grape cool chain process. He used a range of conditions: CO<sub>2</sub> from 12 - 20%, temperatures from 10°C – 20°C, exposure times of 3-4 hours and EF concentrations of 30-52g/m<sup>3</sup> to achieve probit 9 level of control. De Lima (2010b) developed a quarantine treatment data package for registration of new label rates for use of Vapormate® in table grapes against light brown apple moth *Epiphyas postvittana* (Walker), redback spiders *Latrodectus hasselti*, long-tailed mealybugs *Pseudococcus longispinus* (Targioni-Tozzetti), two spotted spider mite *Tetranychus urticae* (Koch), plague thrips *Thrips imaginis* (Bagnall) and western flower thrips *Frankliniella occidentalis* (Pergande). Tests were carried out at 5, 10, 15, 20 and 25°C in the laboratory using pure technical grade product, and using commercial product Vapormate® (BOC Gases Ltd) in 20ft/6m (28m<sup>3</sup>) and 40ft/12m (68m<sup>3</sup>) ISO refrigerated shipping containers and in commercial licensed fumigation chambers. Successful quarantine treatments (probit 9) were achieved during the chilling process using doses from 16 to 52g/m<sup>3</sup> based on pest species, treatment temperature and exposure time. The studies showed that fumigation of Red Globe, Thompson Seedless and Crimson Seedless with EF+ CO<sub>2</sub> did not adversely affect fruit quality.

### 2.6. Citrus

Complete control of bean thrips in navel oranges was obtained by using EF (Mitcham 2011) in a simulation of a commercial fumigation in a 20 ft marine container using a concentration of 1% EF and exposing 6,000 bean thrips for 1 hour to give 100% mortality. Waxed citrus exposed to 2% EF dose was found in good condition even after 5 weeks of cold storage and simulated retail handling. De Lima (2011a) conducted laboratory and large scale trials to develop quarantine treatment data packages for registration of new label rates for citrus using Vapormate®. EF+ CO<sub>2</sub> mixtures were tested against Fuller's rose weevil *Asynonychus cervinus* (Boheman), light brown apple moth *Epiphyas postvittana* (Walker), longtail mealybug *Pseudococcus longispinus* (Targioni-Tozzetti), and citrus mealybug *Planococcus citri* (Risso). He achieved successful quarantine treatments using doses between 10 and 55g/m<sup>3</sup> ethyl formate + >10% CO<sub>2</sub> (60 – 330 g/m<sup>3</sup> Vapormate®) based on pest species, treatment temperature and exposure time in Navel oranges, Rio grapefruit and Imperial mandarins.

### 2.7. Sweet corn

To obtain fumigation treatments that do not damage produce while providing control in the shortest possible period over a range of temperatures that fit within the cool chain process, De Lima (2011b) developed new label rates for Vapormate® against several insect pests in sweet corn. The insects successfully controlled were: cotton bollworm or corn earworm, *Helicoverpa armigera*, native budworm or Australian bollworm, *H. punctigera*, two spotted spider mite *Tetranychus urticae*, plague thrips *Thrips imaginis*, western flower thrips *Frankliniella occidentalis*, green peach aphid *Myzus persicae* and corn aphid *Rhopalosiphum maidis*. Effective doses for 4 hour fumigation treatments were 30, 40 and 44 g/m<sup>3</sup> ethyl formate + >10% CO<sub>2</sub> at >21, >15 and >10°C respectively.

### 2.8. Baled hay

Insects infesting hay fodder exported to Japan were disinfested using laboratory and field research into EF+ CO<sub>2</sub> mixtures (De Lima, 2006). In fumigating 67 m<sup>3</sup> shipping containers filled with approximately 30 tonnes of compressed hay bales he applied Vapormate® (BOC Gases Ltd) at the rate of 720 g/m<sup>3</sup> (26% CO<sub>2</sub> + 120 g/m<sup>3</sup> EF) for 24 h in the winter temperature range of 8 to

19°C. All stages of *Sitophilus* spp. and *Tribolium castaneum* (>12,000 of each spp.) placed in vials in the hay bulk were killed. The final free gas concentration (58g/m<sup>3</sup> EF +8% CO<sub>2</sub>) was sufficient to provide longer term protection from re-infestation in transit.

### 2.9. Synergy of CO<sub>2</sub> and EF

The effect of CO<sub>2</sub> on EF efficacy was reported by Haritos et al. (2006) wherein EF at 12.5 g/m<sup>3</sup> and no added CO<sub>2</sub> resulted in 3, 82 and 91% mortality from 200 adult *T. castaneum*, *S. oryzae* and *R. dominica* respectively; but when combined with 5% CO<sub>2</sub> the mortality for each species increased to 99.5, 100 and 100% respectively. Adding 10 and 20% CO<sub>2</sub> to EF resulted in 100% mortality of all species, indicating that there was no antagonism at high CO<sub>2</sub> concentrations. No insect mortality was observed from exposure to 5, 10 and 20% CO<sub>2</sub> in the absence of EF. Potentiation of EF by CO<sub>2</sub> was found by De Lima (2006) to vary with species, with up to 27% increase in mortality for aphids, thrips, *T. castaneum*, and light brown apple moth in the presence of >10<15% CO<sub>2</sub>; while up to 22% increase in mortality was observed for red back spiders, two spotted spider mite, Fullers rose weevil, *Sitophilus* spp. and *Helicoverpa* spp. in the presence of >15% CO<sub>2</sub>. No mortality occurred in insects in 4 hour exposures to 20% CO<sub>2</sub>. Mealybugs were found to be so susceptible to EF gas alone that 6g/m<sup>3</sup>EF without added CO<sub>2</sub> was sufficient to give 100% mortality within an exposure period of 30 minutes at 10°C. In large scale trials using Vapormate® (De Lima 2006, 2010b, 2011a, 2011b) the accumulation of CO<sub>2</sub> in the free air space of the refrigerated 20 or 40 ft shipping container was always greater than 10% and often over 20% CO<sub>2</sub>. Depending on quantity of product applied the EF to CO<sub>2</sub> ratio in air was >1:8.4.

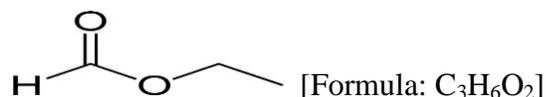
### 2.10. Pre-mix & on-site mixing of EF & CO<sub>2</sub>

The solvent-propellant properties of liquid CO<sub>2</sub> was the basis of a patent (Ryan et al., 1978) where active liquid constituents are dissolved in liquid CO<sub>2</sub> at high pressure (50 bar) and contained in an industrial high pressure gas cylinder fitted with a “dip” tube to enable withdrawal of the liquid mixture. Pre-mixing EF and CO<sub>2</sub> as liquids produces a non-flammable, self-propelled and ready to use mixture. On-site mixing, a common practice with liquid insecticides, also has benefits with fumigants. On-site mixing with CO<sub>2</sub> has advantages of choice selection of the active constituent and flexibility in the selection of the ratio of EF to CO<sub>2</sub> required to optimise efficacy. Carbon dioxide has a synergistic effect with other fumigants and reduces flammability. The general consensus on the optimal amount of CO<sub>2</sub> to improve efficacy is in the range of 5% - 20% (Ryan and Shore, 2010). In the early development of fumigant application methods, Jones (1933) noted the benefits of CO<sub>2</sub> to overcome flammability of potential fumigants including ethylene oxide (12.2% CO<sub>2</sub>), ethyl formate (14.4% CO<sub>2</sub>) and propylene oxide (8.3% CO<sub>2</sub>). The results of on-site mixing and vaporizing EF liquid into a stream of CO<sub>2</sub> in trials at Grain Export Terminals at Newcastle, NSW and Fisherman’s Island, QLD were reported by Allen and Desmarchelier (2000). These trials achieved 100% mortality of *Liposcelis* spp. (psocids: the target species) and left no residues on grain.

### 2.11. Summary of important chemical and physical properties

Ethyl formate is an ester formed when ethanol reacts with formic acid. Ethyl formate has the characteristic smell of rum and is partly responsible for the flavor of raspberries. It has the Generally Recognized As Safe [GRAS] status by the U.S. Food and Drug Administration.

Structure:



Synonyms: Ethyl methanoate; formic acid ethyl ester; ethyl formic ester; formic ether.

Identifiers: CAS No.: 109-94-4; RTECS No.: LQ8400000; DOT UN: 1190 26

DOT label: Flammable Liquid (highly flammable and poses a dangerous fire and explosion risk).

Molecular weight: 74.1; Boiling point: 54.3°C; Specific gravity (water = 1): 0.92 at 20°C

Vapor density: 2.6; Vapor pressure at 20°C: 194 mm Hg; Solubility: Soluble in water with some hydrolysis; miscible with alcohol, benzene, and ether; Reactivity: Unstable in heat or flame; readily hydrolyzes to the acid and the alcohol; Incompatibilities: reacts with nitrates, strong oxidizers, strong alkalis and strong acids; No Hazardous decomposition products reported; Flammability: assigned a flammability rating of 3 (severe fire hazard); Flash point: minus, -20°C (closed cup); Auto ignition temperature: 455°C; Flammable limits in air: 2.8% to 16.0%.

### 2.12. Occupational safety and health guidelines

According to the U.S Occupational Safety and Health Administration (OSHA), ethyl formate can irritate eyes, skin, mucous membranes, and the respiratory system of humans and other animals; it is also a central nervous system depressant. In industry, it is used as a solvent for cellulose nitrate, cellulose acetate, oils, and greases. It can be used as a substitute for acetone. The current exposure limit for ethyl formate is 100 ppm [300 mg/m<sup>3</sup>: OSHA PEL; NIOSH REL; ACGIH TLV]. There are risks to eyes, nasal irritation and narcosis in animals at high concentrations.

### 2.13. Natural occurrence of ethyl formate

EF and formic acid are present naturally in a variety of plant and animal products, such food grains, fruits, vegetables, beer, wine and spirits, tuna, meat, mussels, cheese and bread (Desmarchelier, 1999). In newly harvested wheat, barley, oats and canola natural levels of EF in stored crop varied from 0.5 to 2 mg/kg with commodity, temperature, moisture and period of storage ranging. The EF present in grains at harvest, increased during the first 4-5 months of storage, and then began to decline, particularly for grain temperatures higher than 20°C and moisture content higher than 9.5% (Ren and Desmarchelier, 2000). EF is used commercially in the manufacture of artificial Rum, as a flavor for lemonade and essences, as a fungicide and as an organic solvent (Merck Index, 1989).

### 2.14. Registered product

Registration of EF with the Australian Pesticide & Veterinary Medicines Authority (APVMA):

1. VAPORMATE® (APVMA Approval # 56186; BOC Gases: 16.7% EF/ 83.3% CO<sub>2</sub> w/w)
2. ERANOL® (APVMA Approval No. 51232 – ORICA: 98% EF w/w).
3. eMate® (APVMA Approval No. 64944 – VAPORFAZE: 98% EF w/w).

Note: ERANOL® and eMate® can be mixed on-site with CO<sub>2</sub> to dispense EF as a non-flammable gaseous mixture. In addition to eliminating flammability, the synergistic CO<sub>2</sub> enhances efficacy.

### 3. Conclusions

EF is a safe and effective alternative to methyl bromide for quarantine treatment of farm produce. Although EF is a natural product, it is toxic to insects and in its pure form it requires to be handled with care. It is much safer for human use than methyl bromide. In Australia its registration as a 98% pure product and as a mixture with CO<sub>2</sub> enables it to be used with more versatility for commercial applications in grain storage and in horticulture.

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