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# A new concept for controlling tiny-scale insect pest in green house – noval technology to apply liquid ethyl formate

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#### Abstract

As increased agricultural insecticide uses and trends in insecticide resistance, increased labor cost to apply insecticide and limited its application to fertility season in green house. There is a need of a safe, labor-saving and confined space application concept to manage control tiny-scale insect pest such as thrips and whitefly. Fumigation with ethyl formate (EF), which is considered as effective to various insect pest and safely use in quarantine treatment, was evaluated in the confined space (glass house) and semi-confined space (vinyl house). The new application technology for application of liquid EF could be the one of the key options for control of tiny flying insects in greenhouses that would save labor and operation costs. It could be connected to smartfarm technologies in the near future.

Keywords: Ethyl formate, Inert gas application, green houses, future smart-farm technology

#### 1. Introduction

Fumigants, like methyl bromide (MeBr) and phosphine, are widely used for guarantine and preshipment (QPS) fumigations and restriced use in preplant soil disinfestation because physically fumigants have less residues than solid/liquid active ingredients. Its use has advantages for better efficacies because it can penetrate into deep and easy in application even in tiny small space without additional labor work. This means that fumigants have a potential to replace liquid/solid pesticides in plant cultivation in case they are grown in sealed or semi-sealed enviroments. Even though we know the benefits, usage of fumigant in agricultural purpose especially in sealed system is limited because most fumigants are expensive to apply and normally higher toxic to mammals and human being in terms of acute inhalation toxicity. Ethyl formate (EF), a MeBr alternative which was re-evaluated and commercialized in recent years, is less toxic than other fumigants and has less risk on environments (Muthu et al, 1984). Use of EF on plant cultivation could solve the issue like emerging and increasing pesticide resistant insects (PSI) and residues on harvest. Moreover, in case of application in a sealed system, workers do not need to be exposed to pesticide solution directly which is hazardous and there will be decreased labor-cost. EF fumigation in greenhouse was considered as higher operation costs than pesticide and concerns of leaked out environments. In recent report, liquid EF (Fumate<sup>™</sup>) with inert gas application was cost-effective and safer protocols than formulated in gas cylinder to apply various imported and exported fruits (Kim et al, 2017, Yang et al, 2016, 2017a, 2017b). In the preliminary studies, efficacies of EF on tiny small insect pest in cucumber green house was reported by Kim et al (2016). In this research, we reported liquid EF with nitrogen applied in the confined space (glass house) and semi-confined space (vinyl house) model and was evaluated for the accumulative Ct product in two system and monitoring of ethyl formate level in spaces after fumigations and aerations for accessment of worker safety.

# 2. Materials and Methods

#### 2.1. Green houses

Two types of green houses were used, one was vinyl house (3.5m x 20.0m x 5.0m scales) and the other was glass house (8.0m x 5.0m x 24.0m), located at KNU site in Jinju, Korea.

### 2.2. Fumigation, gas sample collection and aeration

Ethyl formate (FumateTM, 99%) was supplied from Safefume Inc., Korea. Ethyl formate was vaporized with SFM-1 vaporizer system which fitted with an internal gas heater to heat inert gas (nitrogen or carbon dioxide) through the liquid ethyl formate and purge mixture into the greenhouse. For analyzing of EF concentration inside greenhouse, gas sampling lines were placed in green houses (6 locations in vinyl house (VH) and 12 locations in glass house (GH)). The gas samples in greenhouse were taken at timed interval by withdrawing the gas through an air pump into gas bag (SKC Tedlar bag, 1L). Prior to fumigation, the green houses were sealed and calculated dosages of ethyl formate (10 g m-3 for VH trials and 5 g m-3 for GH trials) were applied. For assessment of work safety in work environment, ambient air samples were collected from 4 locations (W, E, S and N) with jumbo syringe (1L, SGE); during during application (0-30 min), fumigation holding period (4-12 hours) and aeration (2 hours). The gas samples were stored in Tedlar gas bags until analysis.

# 2.3. A nalysis of collected gas sample.

The concentration of EF was determined using a Agilent Technology 7890N gas chromatography (GC) equipped with a flame ionization detector (FID) after isothermal separation on a 30 m × 0.32 mm I.D. HP-5 (0.25  $\mu$ m film) fused silica capillary column (Restek Co. Ltd.). The temperatures of the GC oven, injector and detector were 150, 200 and 200°C, respectively. Helium was used as the carrier gas at a rate of 2 mL/min. The peak areas were calibrated periodically using a standard.

#### 3. Results

# 3.1. Concentration of EF inside green house during fumigation

The concentration of EF was continuously decreased at both vinyl house (VH) and glass house (GH). However, the aspects of decrease in two trials were different. Concentration decreased rapidly at overnight in VH and at day time in GH. EF concentration in VH was higher than GH at both 4 and 12 hr trials. Although there were little difference in concentration of EF depending on location of samples, there was no signicant difference in tems of cumulative CT products. The cumulative CT products of EF were 17.53 and 22.67 g h m<sup>-3</sup> for overnight (12hr) and day time (4hr) application, respectively, in VH application. In GH trials, CT products of EF were lower than VH's, 4.53 and 2.62 g h m<sup>-3</sup> for overnight (12hr) and day time (4hr) application, respectively. (Fig. 1-Fig.4). Even though 2 times dose applied in VH, concentration of EF in VH is lower than expected. It could be different depending on sealing conditions, temperature when applied etc.

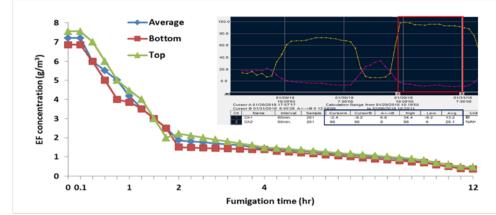


Fig. 1 Concentration of EF (g m<sup>-3</sup>) inside vinyl house for 12 hr fumigation.

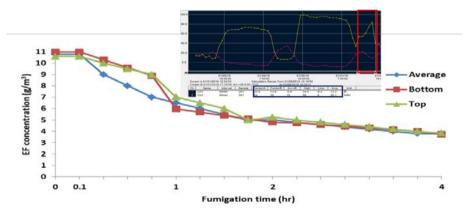


Fig. 2 Concentration of EF (g m<sup>-3</sup>) inside vinyl house 4 hr fumigation.

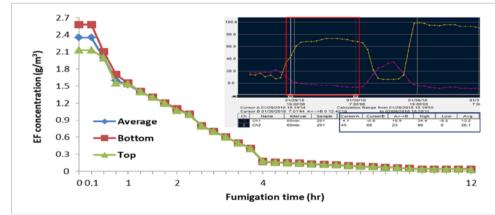


Fig. 3 Concentration of EF (g m<sup>-3</sup>) inside glass house for 12 hr fumigation.

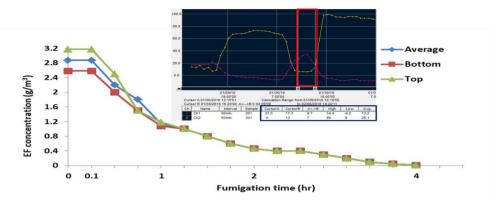


Fig. 4 Concentration of EF (g m<sup>-3</sup>) inside glass house for 4 hr fumigation.

3.2. Ethyl formate levels in the air samples outside green house during the EF application.

Ethyl formate levels from all ambient air samples were < 50 ppm in all trials during the 30 min application of EF (Tab. 1, 2).

Tab. 1. Ethyl formate levels surrounding vinyl house after 0 - 30 min of injection in 4 and 12 hr fumigation experiment.

Sampling	12 hr fumigation EF concentration (ppm)			4 hr fumigation EF concentration (ppm)				
time (min)	East	West	South	North	East	West	South	North
0	< 50	< 50	< 50	< 50	< 50	< 50	< 50	< 50
10	< 50	< 50	< 50	< 50	< 50	< 50	< 50	< 50
20	< 50	< 50	< 50	< 50	< 50	< 50	< 50	< 50
30	< 50	< 50	< 50	< 50	< 50	< 50	< 50	< 50

Tab. 2. Ethyl formate levels surrounding glass house after 0 - 30 min of injection in 4 and 12 hr fumigation
experiment.

Sampling			migation ration (ppm)				nigation ration (ppm)	
time (min)	East	West	South	North	East	West	South	North
0	< 5	< 5	< 5	< 5	20	20	20	20
10	< 5	< 5	< 5	< 5	20	40	20	< 5
20	< 5	< 5	< 5	< 5	7	< 5	< 5	< 5
30	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5

3.3. EFhyl formate levels inside green house during 2 hours of ventilation.

EF levels in the green house (GH) during 2 hours of ventialion were shown in Tab 3. As expected, EF levels in green house were continuously decreasing. After 30 min-ventilation, EF levels in GH was decreased to <10 ppm at both trials.

3.4. Carbon dioxide levels inside green house during the fumigation.

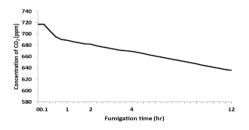
In case of 12hr-EF application in green house fumigation, liquid EF applied with inert gas (carbon doxoide) as carrier gas, it could be expect to help growing plants some crops depending on variety, concentration and exposure time of CO<sub>2</sub> etc. In this experiment, carbon doxoide (CO<sub>2</sub>) levels inside green house (GH) for 12hr fumigation was also monitored in Fig. 5 and 6. The levels of CO<sub>2</sub> was initially increased up to 700-800 ppm and decreased to 600-700 ppm at the end of fumigation.

	12 hr fumigation EF concentration (ppm)		4 hr fumigation EF concentration (ppm)		
	Entrance	Exit	Entrance	Exit	
0 min	< 10	< 10	1560	923	
5 min	< 10	< 10	966	873	
10 min	< 10	< 10	226	236	
15 min	< 10	< 10	130	122	
20 min	< 10	< 10	50	26	
30 min	< 10	< 10	< 10	< 10	
60 min	< 10	< 10	< 10	< 10	
120 min	< 10	< 10	< 10	< 10	

**Tab. 3** Ethyl formate levels in the vinyl house during 2 hours of ventialations after completion 4 and 12 hr fumigation experiment.

**Tab. 4** Ethyl formate levels in the glass house during 2 hours of ventialations after completion 4 and 12 hr fumigation experiment.

	12 hr fumigation EF concentration (ppm)		4 hr fumigation EF concentration (ppm)	
	Entrance	Exit	Entrance	Exit
0 min	< 10	< 10	90	90
5 min	< 10	< 10	15	18
10 min	< 10	< 10	15	< 5
15 min	< 10	< 10	< 5	< 5
20 min	< 10	< 10	< 5	< 5
30 min	< 10	< 10	< 5	< 5
60 min	< 10	< 10	< 5	< 5
120 min	< 10	< 10	< 5	< 5



820 800 Concentration of CO<sub>2</sub> (ppm) 780 760 740 720 700 680 660 00.1 12 1 2 nigation time (hr) Eu

**Fig. 5**  $CO_2$  level (ppm) in vinyl house during 12 hr fumigation (Mean  $CO_2$  level in the atmosphere is 400 ppm).

**Fig. 6** CO<sub>2</sub> (ppm) in glass house during 12 hr fumigation (Mean CO<sub>2</sub> level in the atmosphere is 400 ppm).

#### 4. Discussion

In this preliminary study on vinyl house, we found that liquid EF with inert gas (nitrogen or carbon dioxide) application, was cost-effective and labor-saving, which showed the promise for further reseaches. Because vinyl house application showed better sealed sytem than glass house system and EF levels during the application and ventilation after completion of fumigation was relatively safe in terms of current workplace safety guideline of EF (TLV-TWA, 100 ppm). The cumulative Ct products (>10 g h m<sup>-3</sup>) calculated in vinyl house both for 4 and 24 hr applications could be expected to be enough to control especially flying insect such as whitefly and thirps, which are hard to control with insecticides in green house system. However, for commercial use of EF in green house system, there is more researche required in terms of phytotoxic damages of different plants and their growing stages as well as fumigation conditions such as temperature and humidity in detail. Nevertheless, this newly emering liquid EF technology could provide a new concept to partly replace intergrated insecticide approach, which leads to build-up of resistance to insecticide and restricts application frequencies when crops are ready for markets.

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# Supporting quarantine and health & safety monitoring of fumigants and industrial chemicals in offshore transport containers with Gasmet Multicomponent FTIR gas detection technology

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Keywords: container, fumigation, Fourier Transform Infrared (FTIR), fumigant, library search tool

#### Abstract

Cargo containers and wooden packing materials are fumigated to control the spread of pests and microorganisms. However, fumigant gases are toxic and present a danger to human health even at low concentrations. Additionally, products shipped in containers may release VOCs from the solvents, coatings and glues used in manufacturing processes, and the concentrations of these vapors may be significant in the confined space of the container. Gas measurements are required in order to protect the health of any workers involved in opening these containers.

As potentially hazardous gases originate from a variety of different sources, the amount of gases that need to be monitored, in order to ensure a safe working environment, is very large. The Fourier Transform Infra-Red (FTIR) measurement principle allows simultaneous measurement of a large amount of inorganic and organic substances, regardless of their molecular weight. The portable Gasmet™ DX4040 Multicomponent FTIR Gas Analyzer records infrared spectra at 10 scans/second and is capable of sub-ppm detection. When used with a laptop computer and the pro version of Calcmet™ software, the DX4040 is capable of analyzing up to 50 components simultaneously with compensation for cross-interference effects.

A standard application has been developed for container measurements. The application consists of a gas library of 50 gases that has been configured to include all of the most important fumigants and other hazardous gases found in containers, along with a number of other commonly found gases for correction of cross-interference effects. A built-in QA/QC routine ensures reliable results and alerts the user of the possibility of unknown gases in the sample.

If the presence of unknown gases in the sample is suspected, these can be identified using the library search function available in the CalcmetTM software. Identification is undertaken by automatically finding matching spectra in the library of hundreds of different reference spectra measured by Gasmet for different compounds. Once the unknown compound has been identified, it can be added to the analysis for quantification. The measured sample spectra are not altered by the analysis and are saved so they can be re-analyzed at a later time if needed.

The Gasmet<sup>™</sup> DX4040 is battery powered, backpack sized designed for use in field conditions. The analyzer is portable, so there is no need for separate sampling and the sample can be collected and analyzed directly on site. Quick and easy sampling, coupled with fast, simultaneous analysis of all compounds makes for an