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Measurement of Ethylene Gas Prior to and During Transport

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1.0 Introduction

Ethylene gas is a natural plant hormone, which is known to modify plant development and to promote ripening in very small amounts. Because of the very low concentration at which it is effective, and the consequent difficulty in detecting its presence, it is not generally measured within the transport chain and has often been implicated in poor outturns of produce.

The objectives were to measure ethylene gas in ambient air and cargoes prior to and during transportation from the Southern Hemisphere to Europe. A further objective was to examine the application of ethylene removal techniques.

The presence of ethylene gas can have both detrimental and beneficial effects on fresh fruits. Detrimental effects include flesh softening of some fruit, initiation of ripening of stored preclimateric fruit. Other problems are russet spotting of lettuce, bitterness in carrots, toughening of asparagus, yellowing of squash and cucumber, flower abscission and closure, leaf abscission and chlorosis.

Beneficial effects include faster and more even ripening of fruit when ethylene is applied to fruit before the natural ripening process has commenced. Treatment with ethylene can also be used to degreen citrus and to initiate sprouting of some flowers and bulbs.

Natural sources of ethylene are ripening or damaged fruit. The production of ethylene varies widely; apples are one of the more prolific producers. Sensitivity to ethylene generally is in inverse proportion to its rate of production.

Ethylene removal is not necessarily beneficial to all produce, some generate little and appear to be relatively insensitive under normal conditions. For example Bartlett pears stored under controlled atmosphere with ethylene scrubbing tend to ripen unevenly when removed from store.

The banning of the anti-scald treatment dpa may provide an incentive for ethylene scrubbing. It has been found that scald which develops after several months storage can be prevented in a low carbon dioxide and low ethylene environment.

2.0 Ethylene Measurement

The measurement of ethylene in the laboratory can be simply carried out using a basic gas chromatograph fitted with a flame ionisation detector. In the commercial environment is not generally carried out except in the largest fruit stores which possess a gas chromatograph. Occasional testing is carried out with air samples taken and sent for analysis. The problem that then occurs is knowing how much has been lost and having confidence in a sample that may have travelled several hundred miles. One fruit exporter uses metal toothpaste tubes which they claim are ideal for this purpose.

During sea transport measurement of ethylene by any method other than detector tubes is impractical and is not normally carried out. The tubes are filled with molybdate-palladium reagent and the most sensitive will indicate 0.5 - 10 μl/litre ethylene concentration. Ventilation requirements are estimated using the concentration of carbon dioxide as a measurable tracer which it is hoped relates to the ethylene concentration.

Ethylene can be measured successfully in the field using portable gas chromatographs fitted with a photoionization detector (PID), which are readily available but still somewhat expensive. The particular model used in this study, a Photovac 10S50 utilises air as a carrier gas and can be run from internal batteries for several hours. It is capable of detecting and measuring ethylene to a concentration below 0.01 ul/litre.

Other less expensive equipment is also available which uses a PID detector connected to a pump. Whilst such equipment is very sensitive it is unable to discriminate between ethylene and other hydrocarbons.

3.0 Ethylene Removal

Four methods of ethylene removal were examined and details are given below.

3.1 Ventilation with Air

Forced ventilation with air is the method which is most commonly used to remove ethylene in conventional and container transport. Land stores do not usually have a fresh air ventilation system but rely upon frequent door openings.

A disadvantage of ventilation is that ambient air has to be cooled and dehumidified which consumes refrigeration power and hence energy. Further because ambient air contains a lot of water, frequent defrosting of the evaporator coils is required. Prior to and during a defrost cycle temperature control and distribution in a cargo is inferior. Ventilation with outside air has the requirement that such air is uncontaminated with ethylene from other sources such as pollution from internal combustion engines.

3.2 Chemical

Techniques for the chemical removal of ethylene gas have been commercially available for many years. Ethylene is oxidised using potassium permanganate suspended on an aluminium oxide bed.

Over the years chemical removal of ethylene has been tried on many trial shipments with reportedly good results. However, despite this there has been a reluctance of packers to spend even the small amount for the remover. Chemical removal systems are only in general usage for shipping mixed cargoes of fruit and vegetables to isolated oil exploration sites or remote areas such as the Falkland Islands.

The disadvantage of using chemical scrubbers is that they need to be replaced for every journey and that the quantity required depends on the ethylene production. It has also been shown by Blanpied, Bartsch and Turk, 1985, /4/ in a 200 tonne Empire apple store that removal efficiency decreased quickly. After 12 days the efficiency had decreased to 25% and necessitates regular replacement which is not practical during shipment. The reduction in efficiency is more related to absorption of water rather than the permanganate becoming consumed.

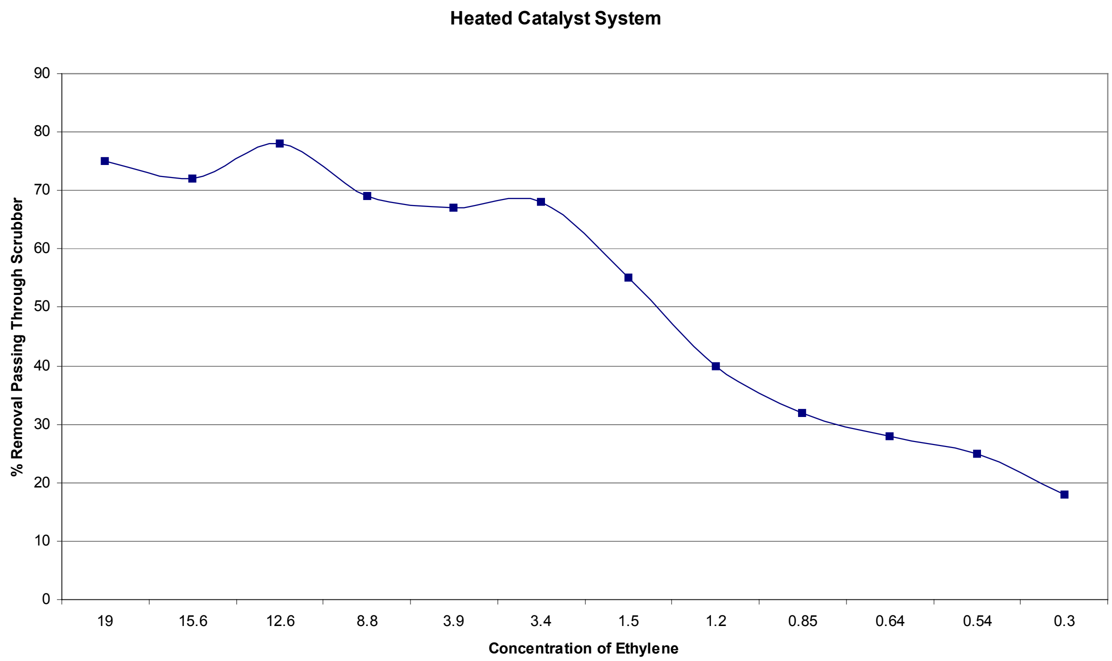
3.3 Catalytic Scrubber

In this system ethylene is oxidised catalytically over a platinum catalyst heated to approximately 250^{o}C. The claimed advantage of the system is that units are easy to install and operate and they maintain a constant low ethylene concentration because the conversion efficiency of the machine stays at 90 - 98%.

The disadvantage of the system is that the catalyst bed is very expensive and is only warrantied by the manufacture for 2 - 3 years. Further the scrubber even with an efficient heat exchanger puts a significant heat load on the refrigeration system which results in some dehumidification and additional energy use.

Measurements on a manufacturers production unit showed the conversion efficiency to be reduced significantly at lower ethylene concentration which severely effect the economics of the system.

Figure 1 Efficiency of Heated Catalyst System



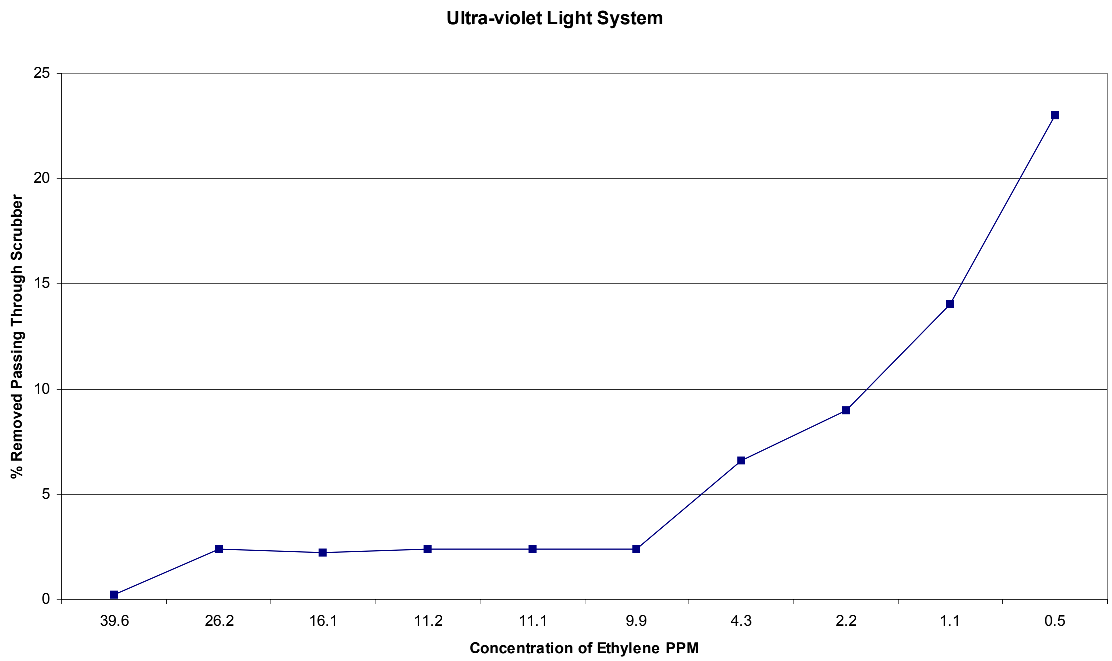
As can be seen from figure 1 the efficiency of removal of ethylene falls with reducing concentration. This causes problems in sizing a unit for a given task. The manufacturer insisted that the conversion efficiency should be at least 90% and claimed the problem was due an interaction with the insulating material. A modified unit was not tested.

3.4 Ultra Violet Light

It has been shown by A.J Scott and K.J Shorter/3/ that ethylene can be removed by the use of Germicidal lamps. The lamps emit ultra violet radiation at 184 and 254nm though the active wavelength appears at 184nm. The ultra violet radiation appears to be responsible for the degradation of ethylene and not the ozone which is also produced as a by-product. The ozone can be removed either by a UV lamp emitting at 254nm, rusty steel wool or a propriety filter.

Such a unit was constructed and installed in a refrigerated integral shipping container. The efficiency was measured by comparing the ethylene going in to that coming out. Figure 2 below shows the variation of efficiency at different concentrations of ethylene gas.

Figure 2 Efficiency of Ultra Violet System

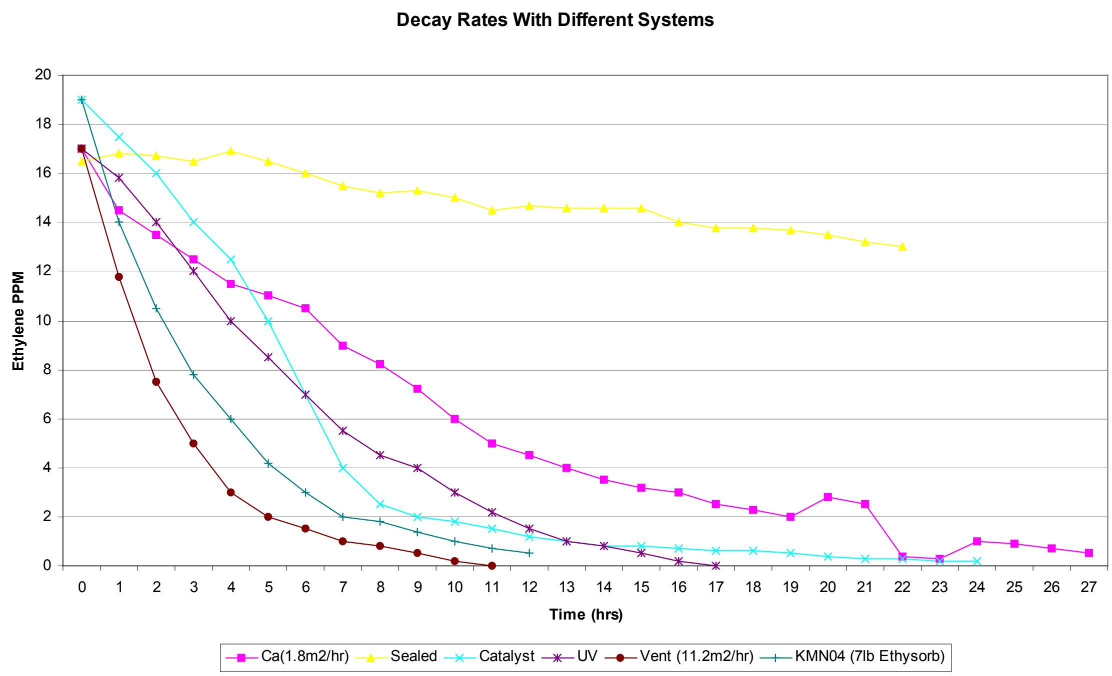


The apparent increase in efficiency at lower concentrations of ethylene shown above in figure 2 is probably due to the unit being effectively overwhelmed. Later results showed a much lower efficiency at low concentrations of ethylene.

4.0 Appraisal of Ethylene Removal Systems

Each of the ethylene removal systems was installed in a 20' integral refrigerated container of 35 M^3 and the time taken to remove ethylene monitored. The results are shown below in figure 3.

Figure 3 A Comparison of Ethylene Removal Systems.



* The catalytic system used in this test was designed for a 300 tonne store, in the above a correction for a 12 tonnes store has been made.

5.0 Ethylene Measurements in the Commercial Environment

The next two sections summerise the results of a number of trials in commercial environments. Indicative results are presented, but precise details cannot be given of all results because of commercial considerations. In particular, exact locations and ships names cannot be specified.

5.1 Ambient Measurements

Ambient levels in the environment were measured at pack houses, container terminals and ports in Australia, New Zealand and elsewhere to determine the level of ethylene contamination of air.

Table 1-Measured Ethylene Concentrations in Ambient Air

Sample Locations	**Ethylene Concentration**			
	Range	**Mean**	**Samples Analysed**	**Sources**
Australian Terminals	0 – 0.015	0.006	23	Pollution
New Zealand Terminals	0 – 0.026	0.004	19	Pollution
New Zealand Fruit Terminals	0.002 – 0.038	0.010	20	Pollution
Belgium Fruit Terminals	0.003 – 0.015	0.010	12	Pollution
Pacific Ocean	0 – 0.009	-	20	Pollution
Atlantic Ocean	0 – 0.010	-	17	Pollution
Flushing	0 – 0.190	-	4	Pollution

Table 1 shows ambient levels of ethylene were rarely found to exceed 0.01 ul/litre except near heavy industry where a level of 0.2 μl/litre was detected.

5.2 Measurements in Store Prior to Transport

Ethylene levels were monitored in and around kiwi fruit stores prior to shipment, and in controlled atmosphere apple and pear stores.

Table 2 Measured Ethylene Concentrations in Fruit Stores

Sample Locations	Ethylene Concentration			
	Range	Mean	Samples Analysed	Sources
Ambient New Zealand	0 – 0.010	-	26	Pollution
Ambient Australia	0 – 0.010	-	22	Pollution
Kiwi Fruit Pack House	0 – 0.070	-	51	Forklifts
Kiwi Fruit Stores	0.005 – 0.055	0.015	55	Fruit
Air Apple Stores	1 – 30	24	4	Fruit
Air Pear Stores	2 – 25	15	5	Fruit
CA Pear Store	11 - 118	22	22	Fruit
CA Apple Store	27 – 243	71	11	Fruit

Table 2 shows in kiwi fruit stores ethylene levels were found to be below 0.03 ul/litre except where internal combustion engines were operating nearby. Controlled atmosphere apple and pear stores were found to have levels, up to 250 ul/litre.

6.0 Measurements during Transport

6.1 Ethylene Levels at Loading

When fruit is loaded onto a ship, initially full refrigeration with no air freshening is applied to get the cargo to carriage temperature as soon as is possible. Measurements were also taken during loading of kiwi fruit and apples during the initial heat removal phase and with air freshening applied. Kiwi fruit is a low ethylene producer but extremely sensitive, apples are less sensitive but high producers.

6.2 Kiwi Fruit

In the holds of a ship recently loaded with New Zealand Kiwifruit, ethylene gas concentrations were found to be low, between 0.001-0.008 ul/litre.

In another shipment ethylene gas concentration was monitored immediately after loading and was found to be between 0.015-0.038 μl/litre. The results were higher than might be expected, this was due to the high level of air pollution found during the measurements caused by still air and several ships on the berth.

6.3 Apples

Ethylene measurements were taken in recently loaded apple decks with the refrigeration running but without any air freshening, the apple pulp temperature was between 2.5 - 5.0 °C. Ethylene gas concentration was found to be between 5.0 - 15.0 ul/litre. 72 hours later, with the ventilation system running at full speed (4.5 air changes/hr), ethylene gas was again measured. At the ventilation outlets it was found to be 0.5 ul/litre and inside the holds 0.5 - 1.7 ul/litre.

6.4 Ethylene Levels in Mixed Cargoes

Ethylene concentration was monitored in a container ship with a mixed fruit cargo and ethylene migration examined.

It was shown that a problem can exist in mixed shipments on refrigerated container ships where levels were detected of 50 μl/litre emanating from apples which were contaminating other supposedly isolated areas.

Ethylene concentrations measured in the chilled cargo refrigerated spaces were considerably higher than expected. The ethylene was being produced from the cargo of apples and pears. Other cargoes carried were grapes.

Ethylene gas seemed to be moving around quite freely in supposedly isolated areas of the ship. It was measured in each of the taint compartments and found to be at the levels shown in table 3.

Table 3 Ethylene levels found in refrigerated container ship

Location	**C_2H_4 μl/litre**	**Containers**
Port	47	26 Pears
Centre	46	36 Apples
Starboard	10	26 Pears
Port	42	11 Pears, 13 Grapes
Centre	55	36 Apples
Starboard	10	18 Grapes, 8 Pears
In the next hold carrying frozen cargo, ethylene had penetrated and was found to be 0.5ul/litre.		

7.0 Measurements of Ethylene Removal Systems.

7.1 Ventilation

A shipment of kiwi fruit was monitored using fresh air to remove ethylene gas and carbon dioxide. The ventilation was adjusted to maintain the carbon dioxide concentration at 0.5%. The ethylene concentration was monitored and is shown below in figure 4.

Figure 4 Removal of Ethylene by Ventilation

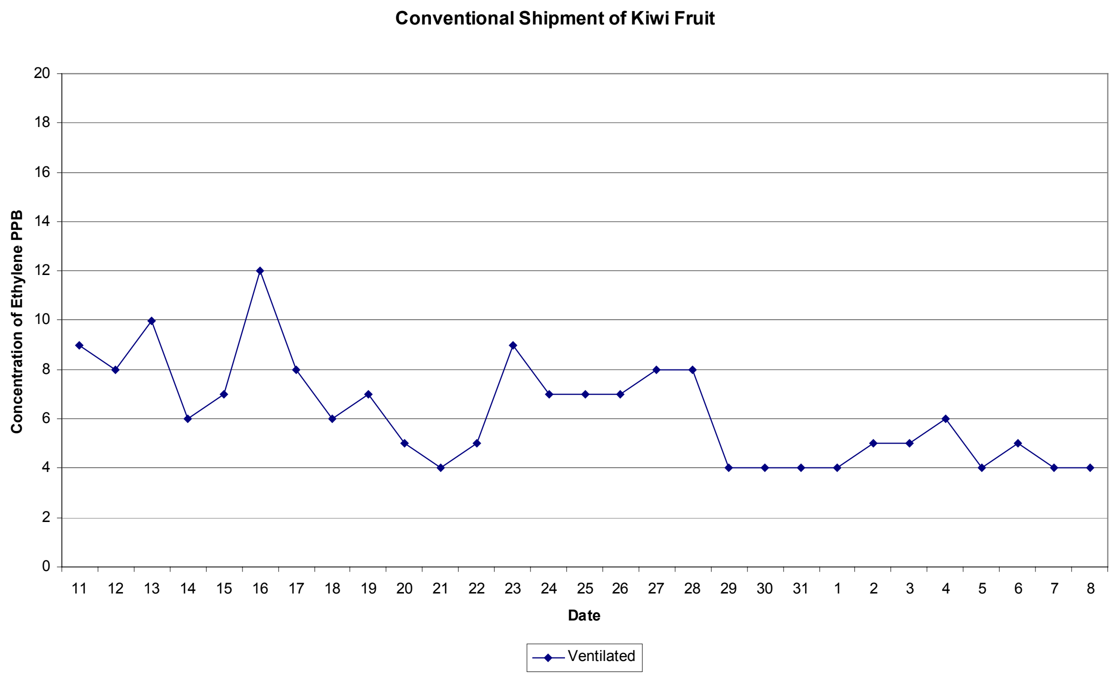


Figure 4 shows the ethylene to have been maintained at satisfactory levels well below 0.030 μl/litre. Ventilating with air also produced a high level of relative humidity of around 93%.

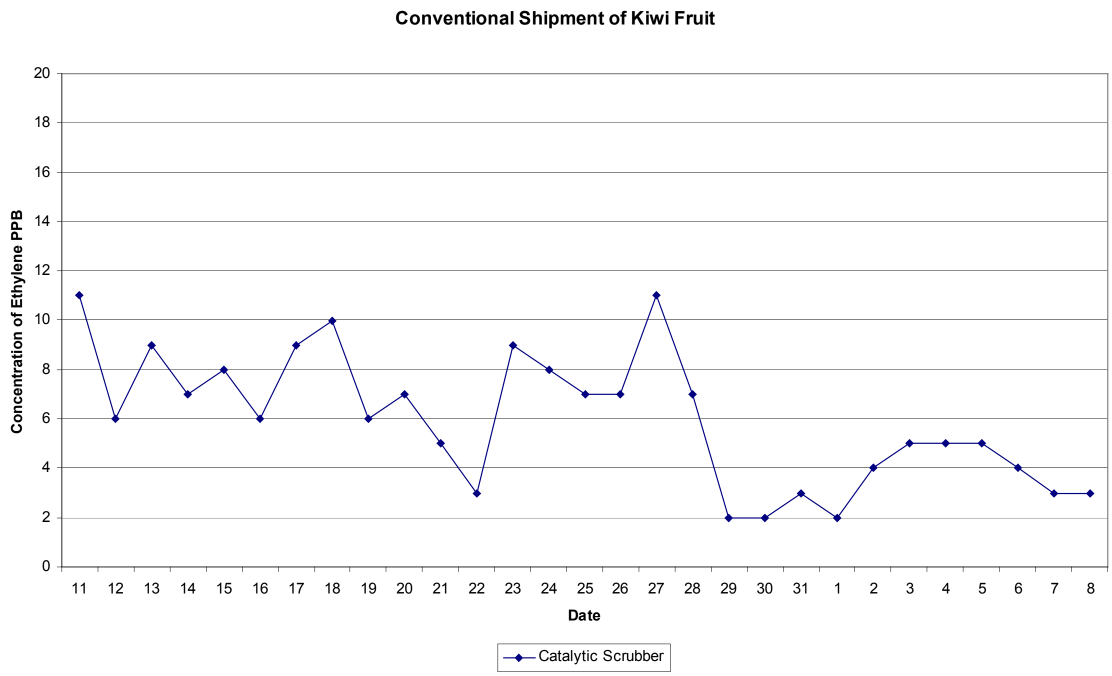
7.2 Catalytic Removal

A shipment of kiwi fruit with one of the cargo holds fitted with a heated bed catalytic ethylene remover was monitored during a voyage from New Zealand to Antwerp. The aim was to allow the carbon dioxide level to rise but not the ethylene concentration. It was expected that this would result in firmer fruit at outturn.

Unfortunately due to leakage of carbon dioxide into an adjacent hold the carbon dioxide level only reached around 1.7%. Despite this the experiment showed that it is possible to obtain firmer kiwifruit by scrubbing ethylene and maintaining elevated levels of carbon dioxide. Figure 5 shows the ethylene concentration which does not rise above 0.012 μl/litre.

Ethylene removal using a catalytic scrubber was moderately successful but the removal efficiency was found to be lower than anticipated from the manufacturers specification.

Figure 5 Ethylene concentrations in Ships Hold



More severe problems with regard dehumidification due to the extra heat load on the refrigeration plant and the degradation of Cfc's leaking from refrigeration equipment were discovered which damaged the scrubber.

The relative humidity was found to be 10% lower in the holds fitted with the ethylene scrubber than those ventilated with air. During the voyage it was hoped that an energy saving could be demonstrated because it was not necessary to cool and dehumidify ventilation air. However, it was necessary to install three unit in the refrigerated compartment which contained 750 tonnes of fruit, which resulted in twice as much power being consumed. Power saving could only be achieved by using a larger unit which would be more efficient with the savings of scale.

7.3 Ultra Violet Removal

An ultra violet ethylene remover was installed in a fruit store in Australia. Outside the store there was a remarkable amount of rubbish scattered around, this included bins of fruit, empty boxes and half filled bins of rotting kiwi fruit. Rotting fruit are a significant source of ethylene. Amongst this, apples were being taken from controlled atmosphere store and packed into cartons.

One cold room had been leased to a kiwi fruit packer and was partially filled with Kiwi fruit trays and pallets. The high level of ethylene in the store emitted from the apples and pears was thought to constitute a hazard to the kiwi fruit and so the operators had installed an ethylene scrubber. Kiwi fruit are said to be affected at levels above 0.030 ul/litre of ethylene.

In fact two scrubbers were present, a prototype and a production model which it was hoped would be maintaining the ethylene at a suitable level. Ethylene gas level was found to be around 0.086 ul/litre in the store and 0.080 ul/litre in the outlet air stream from the scrubber. This represents a conversion efficiency of only around 7%. The manufacturer of this particular unit states that the scrubber efficiency drops off quite markedly for very low ethylene gas levels. Therefore, as there is a large source of the gas nearby leaking into the store from the apples, pears and rotting fruit, the scrubber was struggling to reach the very low ethylene concentration necessary for kiwi fruit.

8.0 Conclusions

It was determined that under conditions of normal refrigerated air storage ethylene can be removed by ventilating with ambient air which is seldom sufficiently polluted to cause any injury even to very sensitive products. Highest concentrations were found in busy streets and while sailing past large chemical works at Flushing.

Generally ethylene was found not to be a problem for shipments where the cargo was all the same. However, high levels were found in mixed cargoes, which could lead to product deterioration.

High ethylene levels were measured in controlled atmosphere stores and in such cases a method of removal would be of benefit. Two methods were evaluated, a heated bed catalyst and an ultra violet system and their efficiencies and effectiveness were determined.

The heated bed was found to lose efficiency at low concentrations and a problem was found when operating in stores with CFC direct expansion. The load it placed on refrigeration plant also caused dehumidification. The ultra violet system used little energy and did not contribute greatly to the heat load on the refrigeration plant. However, its efficiency was found overall to be low.

Overall it was concluded that ventilation with air is still the best method for the removal of ethylene gas.

9.0 Major References

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