



Project Report

An investigation into the effects of CIPC use on the processing quality of stored potatoes

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in collaboration with *Sutton Bridge Experimental Unit*

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Preface

Poor or variable processing quality is a major source of losses within the UK potato processing supply chain and unacceptable fry colour remains the single most important cause for rejection of crops by processors. Poor control of CIPC application can result in the deterioration of processing quality resulting in downgrading of crops of good processing quality and the potential rejection of borderline crops. It has been suggested that through avoiding the CIPC fogging related reduction in processing quality in stored crops, potential savings could be made in the region of £10-30 per tonne. As over 1.5 million tonnes of potatoes are stored for processing into fried potato products each year, this is likely to result in significant savings for the GB industry.

This report covers a three-year BPC project undertaken by the University of Glasgow in collaboration with the BPC's Sutton Bridge Experimental Unit. The study has examined the thermal fogging process used in CIPC application and its effect on processing quality, focusing on the influence of ethylene produced during the combustion process. The study has investigated potential means of preserving processing quality or minimising the effect of CIPC application. These included: ventilation following fogging, use of alternative fogger fuels, reducing the number of CIPC fog applications, and removing ethylene and CO₂ from store atmospheres. The report identifies potential modifications to CIPC fogging practices that may be used to reduce fry colour deterioration in stored crops.

Dr Ewen Brierley, British Potato Council

Executive Summary

The provision of crops of a light fry colour, from store, is of the utmost importance to processors. Poor fry colour leads to rejection of crops on a quality basis. The application of Chlorpropham (CIPC) sprout suppressant, as a thermal fog is associated with a deterioration in fry colour. The BPC funded project at the University of Glasgow and its collaborator Sutton Bridge Experimental Unit investigates the effects of CIPC use on the processing quality of stored potatoes.

CIPC is the only sprout suppressant available for medium and long-term storage for processing in Britain. In the UK the majority of CIPC treatments are conducted as thermal fog applications. This is considered to be the most practical means of achieving successful sprout control.

The introduction of a hot fog into potato stores has a disruptive influence. It can physiologically alter the potatoes by creating a stressful environment. Tuber respiration rate increases and so the crop will age. Experimental trials conducted as part of this project have shown that it is the fogging process itself that is responsible for the decrease in crop quality following application, not the CIPC formulation applied.

Studies revealed that both carbon dioxide and ethylene were produced naturally by crop and from the combustion of petrol used to generate thermal fogs. Initially the fry colour problems were linked with carbon dioxide in combustion gases and from increased respiration. However carbon dioxide output from thermal fogger machines was less significant than expected. The levels were consistently lower than concentrations shown to have a deleterious effect in previous BPC funded work.

Ethylene is present in thermal fogs as a by-product of burning the hydrocarbon fuel used to generate the fog. The concentration of ethylene produced is associated with the running conditions of the fogger machine i.e. burner temperature, type and volume of fuel used etc. The ethylene created in a standard CIPC thermal-fog application is sufficient to induce a physiological response in tubers. Exposure of crop to ethylene affects respiration, dormancy period, sprout morphology, reducing sugar concentration and hence fry colour. The extent of the outcome depends on exposure time and concentration.

Following assessment of the fogging situation, various means of reducing the impact of CIPC application on fry colour were evaluated. Different approaches were undertaken and included both attempting to control and remove the contaminants present in thermal fogs.

By ventilating stores earlier than the recommended twenty-four hour period after treatment a vast improvement in fry colour was observed. In doing this the exposure time of crop to contaminants was greatly reduced. In the experimental work the stores were ventilated eight hours after treatment. This allowed adequate time for the effective

fraction of the thermal fog to settle. Currently ventilating stores earlier than the stated twenty-four hour period is not in accordance with the formulation labels' recommended procedure. However data from this project is being used to support the case for changes to label recommendations put to formulation manufacturers.

Generating less contamination when fogging was a further successful strategy for minimising the impact on fry colour. To do this 'cleaner' simpler fuels were used to create the thermal fogs. A clear improvement was seen when the CIPC treatment was carried out using methanol fuel. This 'bio-fuel' is renewable, however is considerably more expensive than petrol (the current standard) when fuel consumption and cost per unit volume are considered. LPG (liquefied petroleum gas) was another fuel studied. The distinction in quality between crop treated using petrol fuel and that treated with LPG was marginal. Improved fry colours were expected using LPG. This outcome was a consequence of an inefficient burner system in the fogger machine that had been adapted to burn LPG. The resulting fry colours are related to the excess of fuel consumed – more than would be the case if the burner had been fully optimised. The LPG system is continuing to be manipulated to obtain maximum efficiency, and is very much an option worth developing. Compared with petrol, LPG is cheap and clean, and is likely to offer improved fry colour and improved economy.

The impact of repeated fog applications throughout a season was investigated. By reducing the total number of fog applications fry colour was allowed to recover to a greater extent and was more predictable over the course of the storage period. By altering the rate of CIPC application, ensuring the same overall tailored dose was delivered in a season, the total number of treatments required was cut down. Less fogging means less frequent fog contamination in store. This work is experimental and is not covered by current label recommendations. The methodology has to be tested on a wider scale but it is a promising move toward resolving fry colour concerns.

Preliminary trials looking at reducing/removing fog contamination in stores have indicated the following. For an absorbent/scrubbing system to be physically and economically effective it would have to (i) be dynamic (forced air exchange with the store atmosphere), (ii) employ an affordable material with a high affinity for a specific range of compounds. Those materials tested so far have shown some improvement in crop quality. For optimum results the absorbent had to be regenerated frequently, introducing an additional complication. Continued research would be beneficial in this area.

The best improvements in fry colour post-fogging would be achieved by avoiding hydrocarbon fuels to generate thermal fogs. There are machines in the developmental stages that will do this, however the integration of such equipment into routine commercial procedure is still some way off. Therefore in the intervening period modifications to fogging practices such as those discussed are the best means of minimizing the detrimental impact that CIPC use has on the processing quality of stored potatoes.

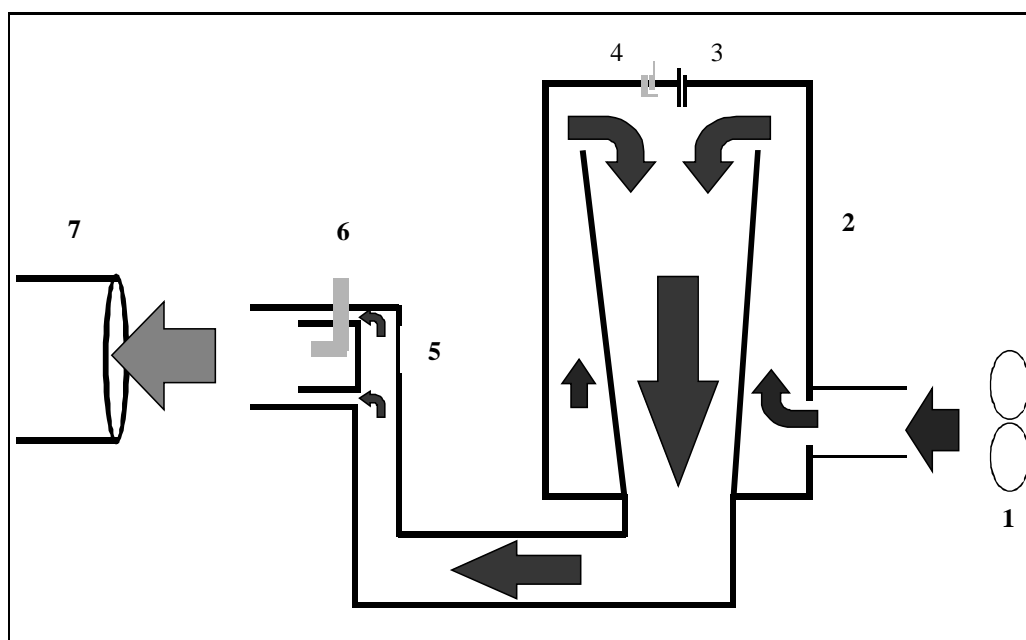
The Thermal Fogging Process

Investigation of representative commercial fogging machines

Thermal Fogging Machines

The schematic diagram below illustrates in elementary terms how thermal fogs are created using these machines. The CIPC formulation is taken up into the machine where the thermal fog is generated. Then fog is carried into the store by a flexible ducting pipe. The outlet of this pipe is positioned in store for optimum application. In addition to what is depicted below, there is a control panel, where the running conditions can be managed and monitored throughout application.

FIGURE 1. SCHEMATIC DIAGRAM OF A THERMAL FOGGING MACHINE



- | | |
|----------------------------------|-------------------------------------|
| 1. Blower pulling in ambient air | 5. Hot air stream into fog-head |
| 2. Combustion chamber | 6. CIPC formulation delivery nozzle |
| 3. Fuel injection nozzle | 7. Application pipe to store |
| 4. Ignition | |

The blower pulls in ambient, delivering this to the combustion chamber at a controlled rate. The fuel is injected into the air-stream and ignited. Most commercial operators use lead replacement fuel. The rate of fuel delivery is controlled by an electric pump and is adjusted using the pressure relief valve. Changes to the rate of fuel delivery are used to adjust burner temperature.

Burning petrol releases the energy that heats the cold air stream. Burning hydrocarbon fuels produces combustion gases mainly carbon dioxide and water vapour. As no mechanical system is 100% efficient there will be some unburned fuel, products of

incomplete combustion and also by-products of combustion i.e. contamination. This includes a wide range of contaminants (e.g. Benzene and poly aromatic hydrocarbons). The compound ethylene has been identified as a component of thermal fogs. Ethylene is suspected of causing deterioration in potato processing quality.

The hot air (ie exhaust gases) is directed into the fog-head where the CIPC formulation is delivered at a specified rate. The formulation is vaporized in the elevated temperature, creating the thermal fog. The fog is introduced to the store via metal ducting of particular diameter and length. Adjustments to the diameter/length are made to ensure the fog maintains speed and to maintain the temperature of the ducting to reduce condensation of fog and aid distribution inside the store.

Comparison of the main machines used commercially indicated that there are only slight differences in carbon dioxide and ethylene production. A small effect of burner temperature was noted (increasing ethylene yield at higher burner temperature). In terms of physiological response of tubers, such differences are not regarded as significant. Therefore further investigation of the running conditions was concentrated on one machine type (Unifog).

Fuel consumption and related energy production was studied. This included lead replacement petrol and alternative options, methanol and propane (LPG). The flow rate and the temperature of the fog was also studied. Crop storage trials were also carried out to determine the effect on processing quality.

Fuel consumption

The fuel consumption was measured over a fifteen-minute period that started when the application temperature had been reached. Only the fuel used to create combustion gases used in fogging was measured. The burner temperatures used are representative of the range in use for methanol-based CIPC formulations.

TABLE 1. VOLUME OF PETROL CONSUMED IN A FIFTEEN-MINUTE PERIOD (ML)

Date	Unifog	Burner temperature (degrees C)		
		engine only	400	500
Jul-00	B	880	2420	3120
Apr-01	A	700	2475	3100
Apr-01	B	800	2700	3575
Jun-02	A	830	1550	2170

TABLE 2. VOLUME OF METHANOL CONSUMED IN A FIFTEEN-MINUTE PERIOD (ML)

Date	Unifog	Burner temperature (degrees C)	
		400	500
Jun-02	A	5270	6000

The fuel consumption measured for LPG was not a true reflection of the amount of propane required for application. Hence, it was not included here. Investigations found

that the burner was very inefficient and so fuel consumption was higher than it would have been if the system were fully optimised. Further developmental work is underway to improve the LPG burner system.

More fuel is consumed at higher burner temperatures. A substantially greater volume of methanol was required to sustain the heat output required, than with petrol.

Energy production

The energy produced by the petrol combusted under a given set of application conditions can be calculated using thermodynamic principles. This energy is equal to reaching and maintaining the required burner temperature (plus any losses).

The assumptions in this model are that each unit of fuel consumed is combusted at 100% efficiency and will release its full energy potential. The exact efficiency of fuel combustion in the fogger system is unknown (but will not be 100%). Under operating conditions it is not expected to vary widely between fuel sources (the LPG burner is still being improved).

TABLE 3. ENERGY PRODUCED BY COMBUSTION OF PETROL (BASED ON AN AVERAGE VALUE OF PETROL CONSUMPTION AT EACH BURNER TEMPERATURE)

<i>Burner temperature</i>	<i>Energy released in 15 minutes (MJ)</i>
400°C	86.3374
500°C	111.3384

The volume of fuel required to release this known amount of energy can be resolved for different fuel types. By studying the chemical properties of these selected fuels it is possible to speculate on the volume of fuel required in each case.

TABLE 4. VOLUME OF FUEL REQUIRED TO ACHIEVE AND SUSTAIN BURNER TEMPERATURE FOR A 15-MINUTE PERIOD

<i>Burner temperature</i>	<i>Petrol (ml) *</i>	<i>Methanol (ml)</i>	<i>Propane (ml)</i>
400°C	2504	4745	3143
500°C	3229	6120	3923

*Measured value based on overall mean for fuel consumption assessed in different seasons of year

NB. Gas (propane) volumes are normally expressed as m³. To get m³ divide Litres by 1000.

Theoretically the volume of methanol required for generation of a thermal fog is much greater than that of petrol. The measured value at 400°C is greater than the theoretical, indicating the efficiency of the burner at this temperature is lower than at 500°C. The volumes of methanol fuel (theoretical and measured) at 500°C are very close.

Reliable figures for LPG consumption are not yet available. More LPG is expected to be required for application than petrol.

Thermal fog flow rate, volume into store and temperature

The flow rate of the fog entering the store and its temperature are key features that are likely to influence the effect of the fog on the potatoes.

Flow rate is a function of:

- The speed as it leaves the pipe (metres/sec)
- The diameter of the exit port of the pipe.

The equipment used to measure the speed is limited to use in temperatures below 80°C. Therefore the speed could not be measured at real application temperatures. The range calculated only includes the flow-rate as a result of air pulled in by the blower and the petrol combusted to run the engine (~60°C). The actual flow-rate would be faster as there would be more combustion gases from burning more fuel.

The flow-rate of air from the blower was measured and found to be in the approximate range 700-800m³/hour. When all the combustion gases are included the value is expected to increase to nearer 1200m³ (*H.J. Duncan, personal communication*).

The typical application time for a 2000 tonne store (based on use of a methanol CIPC formulation) is one hour. Thus the estimate of the volume of gas entering a 2000 tonne store per application is 1200m³.

In a representative full 2000 tonne box store, the total air (free & between potatoes) is roughly 75% that of the entire store volume*. Using this estimate of flow-rate (1200m³), a sizeable proportion (~20%) of air within the store is displaced within a relatively short time.

The temperature of the fog had not dropped as much as previously anticipated by the time it left the end of the ducting pipe. Originally the temperature of fogs applied at 400-500°C was thought to drop to roughly 100°C before entering the store. Measurements taken of hot air and combustion gases at a burner temperature of 400-500°C, were over 200°C at the end of the pipe. There should be a cooling effect of the CIPC formulation on the fog, but this might not be sufficient to cool the flow to below 100°C.

* Information on store dimensions from earlier trials by GU

Crop storage trials to determine the effect of thermal fogging on processing quality

First trial

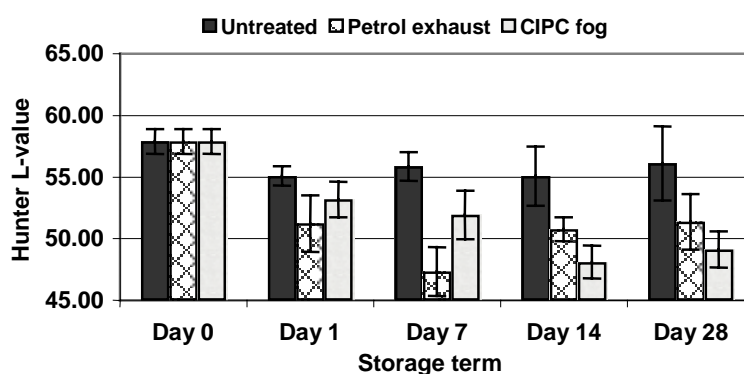
Trials were designed around a series of methanol-based CIPC treatments (MSS CIPC 50M), with varying levels of contamination. The aim was to investigate the impact of the thermal fogging process in causing deterioration in fry colour. The trials were conducted with previously treated cultivar Saturna crop in 12 tonne stores at SBEU held at 10°C and 95% relative humidity. The fry colour of the crop was assessed prior to treatments and 1, 7, 14 and 28 days after treatments. Assessments were conducted as per BPC standard operating procedure. The trials were conducted late in the storage season hence the relatively low baseline fry colour of the crop (evident in day 0 samples). The graphs display the Hunter L-value, which is a measure of brightness of the crisps. The higher the L-value, the better the quality of the fried sample. The value plotted is the mean of each treatment. Error bars show plus and minus one standard deviation. The treatments are outlined in the table below (*Table5.*).

TABLE 5. DETAILS OF TREATMENTS INCLUDED IN THE FIRST TRIAL

Treatments compared		
Untreated	Exhaust only	CIPC fog

The treatments in the first trial included Untreated (control), Exhaust only and conventional CIPC fog. All stores were ventilated 24 hours after treatment. In terms of carbon dioxide and ethylene production both the CIPC and exhaust only treatments create the same potential problem.

FIGURE 2. THE EFFECT OF THERMAL FOGGING ON FRY COLOUR DURING STORAGE



The results demonstrate that:

- Both the exhaust only and CIPC fog treatments have a detrimental effect on fry colour.
- Exhaust only seems to be more harmful initially.

- In both cases some recovery in fry colour occurs.
- At day 28 the fry colour of both these treatments is similar and significantly darker than the untreated samples.

These results show that it is the application process that is responsible for the decline in processing quality not the active ingredient (CIPC) itself.

Second trial

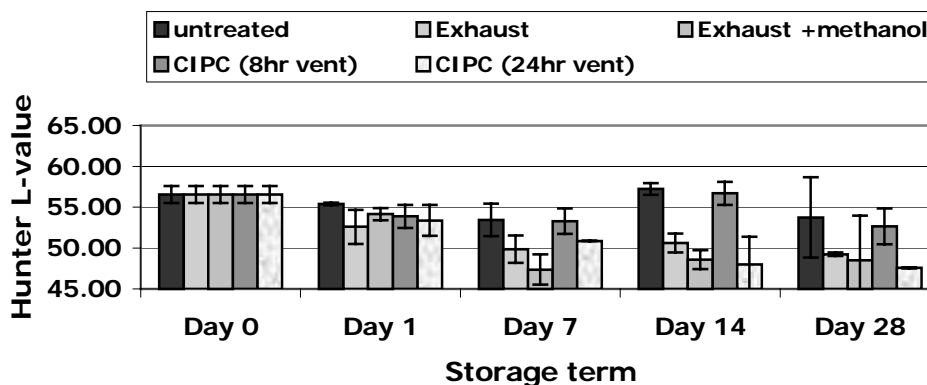
There were five treatments in the second trial studying the fogging process on a step-by-step basis. The treatments are detailed in the *Table 6*. Unless otherwise stated the stores were ventilated 24 hours after treatment.

TABLE 6. DETAILS OF TREATMENTS INCLUDED IN THE SECOND TRIAL

Treatments compared				
Untreated	Exhaust	Exhaust + methanol	CIPC fog (8 hour vent)	CIPC fog

Carbon dioxide was introduced to stores in comparable concentrations at each stage of the process. Concentrations, prior to ventilation were generally 0.3-0.4% (excluding untreated, 0.0%). Ethylene was detected in all treated stores (Concentration range 1-5ppm). The error bars on day 28 are large, however the trends remain the same.

FIGURE 3. THE EFFECT INDIVIDUAL COMPONENTS OF THE THERMAL FOGGING PROCESS ON FRY COLOUR DURING STORAGE.



- Investigating these stages separately showed the root cause of fry colour problems is burning hydrocarbon fuel (petrol) and exhausting it into store.
- Exhaust only was initially more harmful to fry colour
- Early ventilation of stores, after CIPC application, improves fry colour

The graph illustrates that exposure of crop to combustion products has a negative impact on fry colour. The longer this exposures time the more damaging the effect. Investigation of the combustion of petrol brought about the suggestion that ethylene

could be produced in levels physiologically significant to tubers. Using the fuel data and the temperature and pressure information, chemical equations were used to predict the amount of ethylene produced. These estimated concentrations of ethylene were all within the range of measured values (accounting for dilution with air in the store). Thus, the ethylene identified in stores following fogging is largely a result of combustion of hydrocarbon fuel. Experimental work to date has shown that ethylene contamination of CIPC fogs is widespread. Levels of contamination under UK conditions have been typically lower (0.2-10ppm) than those reported in North America (10-60ppm, Wang and Pritchard, 1997)

Third trial

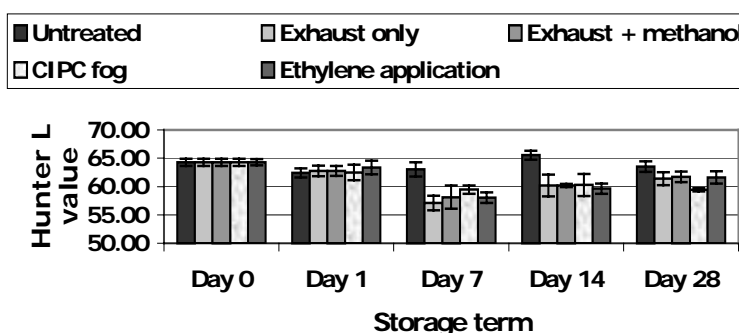
A trial was conducted to establish the effect of ethylene on potato tubers in storage under conditions of short-term exposure. Each stage of the fog generation process was tested for effect on fry colour. These treatments were compared to the effect of applying a standard concentration of gaseous ethylene (ethylene spike) to crop in storage. Ethylene was applied using a catalytic generator. The five treatments are detailed in Table 7. All stores were ventilated 24 hours after treatment.

TABLE 7. DETAILS OF TREATMENTS INCLUDED IN THE TRIAL

Treatments compared				
Untreated	Exhaust	Exhaust + methanol	CIPC fog	Ethylene spike (~5-10ppm)

Ethylene was detected in all stores that were treated by the fogger or ethylene generator. The starting material for the ethylene generator was ethanol. This was delivered to the catalyst at a rate sufficient to give a concentration of 5-10ppm in the store head-space.

FIGURE 4. THE EFFECT OF THERMAL FOGGING COMPARED TO THE EFFECT OF ETHYLENE EXPOSURE ON FRY COLOUR



Each stage of the fogging process caused a decline in fry colour as they all involve combustion products of petrol. The graph demonstrates that crop exposed to ethylene (including that from the generator) suffers a decrease in quality in the same way. All except the untreated samples are subject to the darkening of fry colour that is synonymous with CIPC thermal fog application. While the ethylene spike treatment demonstrates that ethylene is important in causing deterioration in fry colour, other compounds may also be involved.

Ethylene in Potato Stores

Introduction

Ethylene has been detected in appreciable amounts in store atmospheres post CIPC thermal-fog application. Both data from this project and previous literature has shown that it is central to the deterioration in processing quality of potatoes following fogging (*Wang & Pritchard, 1997*).

Ethylene is one of the simplest organic molecules with biological activity. It is a plant hormone that regulates many aspects of plant growth, development and senescence (*Abeles et al., 1992*). It is produced naturally in all higher plants in essentially all tissues. The production of ethylene varies with type of tissue and stage of development. It is important for physiological regulation of plants and, in particular, senescence and post-harvest physiology of fruits and vegetables.

Potato tubers are very sensitive to ethylene and their response to changing levels depends on exposure time, concentration, cultivar sensitivity, atmospheric composition and temperature (*Loughheed, 1987*). An increased ethylene level stimulates respiration, accelerates senescence and alters sprouting (*Saltveit, 1999*).

Ethylene is produced predominantly in the peripheral layers of the tuber, where cell division occurs. The rate of production increases with the advance of growth of sprouts (*Okazawa, 1973*). Any physiological or mechanical stress will cause an increase in production of this natural plant hormone in response (*McGlasson, 1969*). During certain stages of development and by a number of biotic and abiotic stresses both ethylene synthesis and sensitivity are enhanced.

External ethylene is considered a stress to potatoes. The threshold observed for phytotoxic effects of ethylene under laboratory conditions is $12\mu\text{g}/\text{m}^3$ (*Tonneijck et al., 2000*). Harvested vegetables may be unintentionally exposed to biologically active levels of ethylene and both endogenous and exogenous sources of ethylene contribute to its biological activity (*Saltveit, 1999*). Therefore exposure to external ethylene (e.g. generated by power plants, heavy traffic and from LPG powered forklift trucks used to load potato stores when used in a confined space) can induce increased internal ethylene production.

The initiation of sprouting in potato tubers is accompanied by a variety of biochemical changes. These are usually reflected in fluctuations in hormonal concentrations, respiration rate and the onset of nucleic acid synthesis and cell division and enlargement. *Rylski et al, 1974*, found that both short-term and long-term (8, 24 hour & 40 days) exposure to ethylene gave rise to a substantial increase in respiration rate, which peaked in every case twenty-four hours after treatment started. Sprouting appeared only to be stimulated by eight hour and twenty-four hour exposure. Long-term exposure to ethylene completely inhibited sprouting for the duration of treatment, but after ethylene application was discontinued sprouting ensued at an identical rate to that in the tubers that

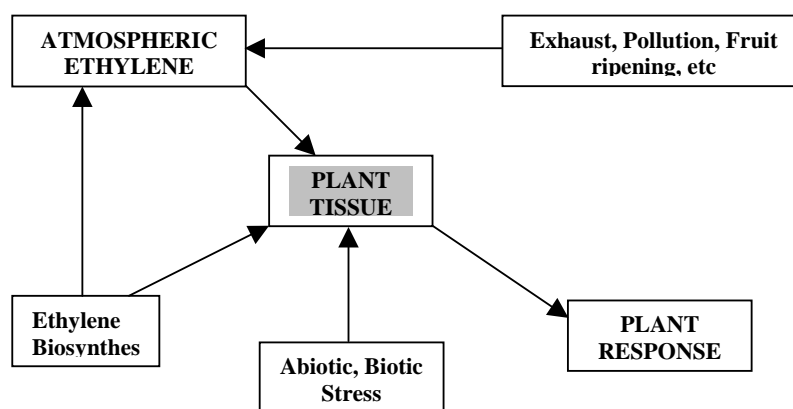
received brief exposure to the gas. However sprout morphology was different. Long-term ethylene exposure had inhibited elongation of sprouts. *Rylski et al* concluded that both short and long-term exposure shortens the duration of rest but only long-term exposure inhibits bud elongation. This change in sprout morphology is common to tubers that have been previously exposed to ethylene for a considerable time (*Prange et al, 1998*). The same smaller, more widespread rosette like sprouts resulted from removing tubers from continued ethylene exposure in previous GU trials. Although for the duration of ethylene exposure sprouting was inhibited.

This loss of apical dominance is related to the auxin concentration (a plant hormone that is involved in the control of many aspects of plant behaviour including the suppression of lateral buds). Numerous processes are controlled by ethylene in a close interaction with auxin, and often it is impossible to differentiate between ethylene and auxin effects. Although auxin is known to stimulate the production of ethylene at high concentrations, it is unclear if it is a requirement of ethylene stimulation. It is possible that auxin and ethylene interaction could result from regulation of sensitivity and transport rather than synthesis. Thus, auxin production rate could have different effects on ethylene sensitivity in specific tissues and at particular stages of development (*Smalle & Van Der Straeten, 1997*).

From this work the researchers concluded that ethylene treatments have a profound impact on vegetative development. They deduced that endogenous ethylene plays a less critical role in comparison to other plant hormones such as auxin or gibberellins. Earlier work (*Alam et al., 1994*) found that exogenous ethylene also released bud dormancy, but from protein profiles suggested it was by an indirect means. By accelerating or enhancing the action of other hormones. Nevertheless, it is vital in the control of plant response to environmental stresses.

Reducing sugar concentration is increased and hence fry colour darkens as a result of ethylene exposure (*Prange et al, 1998*). This has been shown in the experimental work within this project. Combustion gases, such as those created in the standard procedure for generation of a thermal fog are a known source of ethylene. Some important interactions between the plant and its environment that outline how ethylene affects plants are illustrated (*Fig 5.*) (*Salveit, 1999*).

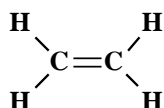
FIGURE 5. INTERACTIONS BETWEEN THE PLANT AND ITS ENVIRONMENT



The mechanism by which ethylene is synthesized in plant tissue from methionine is a three-step process: L-methionine → S-adenosyl-L-methionine (AdoMet) → 1-aminocyclopropane-1-carboxylic acid (ACC) → ethylene. There are two enzymes unique to this pathway ACC synthase and ACC oxidase. They catalyze the conversion of AdoMet to ACC and ACC to ethylene, respectively (*Mathooko, 1996, 7*).

Ethylene is a simple two carbon gaseous compound (*Fig 6.*) that will move freely in air and can absorb easily onto available sites.

FIGURE 6. THE STRUCTURE OF ETHYLENE



It is effective at very low levels, however the concentrations produced from stored tubers are too low for active sprout inhibition (*Rylski et al, 1974; Burton and Meigh, 1971*).

The synthesis and action of ethylene involves complicated metabolic processes, which require oxygen and are sensitive to elevated carbon dioxide. Endogenous sensitivity to ethylene alters during plant development, as does the rate of synthesis and loss by diffusion from the plant (*Saltveit, 1999*).

In a plant system the last step in ethylene production is oxidative and therefore requires sufficient oxygen levels within the skin of the tubers. Oxygen penetrating the skin may be restricted by the 'barrier' nature of the skin. Most of the available oxygen is consumed in respiration within the peripheral layers, so the rate of ethylene production is naturally low. If oxygen concentrations were to become lower than atmospheric levels then availability would be a limiting factor in ethylene production (*Personal communication, C Pidgeon, September 2001*). This is the basis for a lot of the controlled atmosphere systems in use in the fruit and vegetable post-harvest industry.

Over the years there has been a lot of literature published relating to the regulatory effect of carbon dioxide on ethylene biosynthesis in fruit and vegetables (*Burg & Burg, 1965; Ables, 1973; Lougheed, 1987; Chevery et al., 1988; Mathooko, 1996, 9*). There are various hypotheses put forward to explain its mode of action, however no final conclusive material. It is generally considered that carbon dioxide regulates ethylene biosynthesis, in part, by counteracting ethylene action via the regulation of ACC synthase and in some instances ACC oxidase.

Exogenous ethylene is known to have an autocatalytic effect on ethylene production. This stimulatory effect can be reduced by the presence of high concentrations of carbon dioxide (2-20%) (*Chevery et al, 1988; Mathooko, 1996, 7*).

Unfortunately carbon dioxide in potato stores in levels above 3% will induce a darkening of fry colour through increasing reducing sugar concentration (*Mazza and Siemens, 1990; Briddon and Jina, BPC project summary, 1999*).

Natural levels of ethylene production by potatoes in storage

Experimental work conducted as part of this project has found that the level of natural ethylene production is in the approximate range 0.2-2.0 nanolitres/litre. This internally produced ethylene is in the region of one thousand times less than levels measured in potatoes stores post fogging (0.2-10 μ l/L).

It is difficult to give an exact value as the levels discussed are very minute amounts. The sensitivity of the method of analysis fluctuated between days, presumably depending upon ambient conditions of sample collection and desorption. For this reason a calibration line was produced for each sample day, to account for daily variability.

The production of ethylene was increased most by elevating the storage temperature from the standard 10°C. The effect was not distinguishable at 25°C, but at 40°C production rate had in most cases roughly doubled.

Under conditions of elevated carbon dioxide (~1.5-2%), ethylene production rate was not significantly different to that in normal atmospheric conditions.

Application of exogenous ethylene (2ppm) did in some cases generate increased ethylene production, however the effect was not consistent between replicates of the same treatment. Therefore it is not conclusive that exposure to an external concentration of 2ppm ethylene will yield increased synthesis of hormonal ethylene.

It is important to bear in mind the likely sources of environmental stress tubers may be subjected to while in storage. These include short-term exposure to slightly higher carbon dioxide concentrations than normal following fogging, warm fog entering stores during sprout suppression treatment and the presence of residual ethylene from the fogging process.

The effect of exposure to ethylene with varying concentration and exposure time

The persistence of ethylene in store atmospheres is surprising considering its ability to move freely in air and its readiness to absorb onto suitable materials. Semi-commercial trials at SBEU have shown that it persists in store until ventilation following fog treatment. The current standard period left after fog application before ventilation is twenty-four hours.

Small-scale experiments at GU have found that even low concentrations of ethylene (0.5ppm, 1ppm) can remain present in store atmospheres for up to twenty-four hours. In a representative 'leaky' store (considered to be the normal) where some unintentional exchange with ambient air is expected the concentration of ethylene in store will reduce noticeably faster via dispersion into the fresh air.

A trial was conducted involving exposing potatoes in storage to a range of ethylene concentrations (0.5, 1, 5, 10 & 20ppm). This was carried out for samples in containers that received deliberate ventilation eight hours after application and in separate containers, samples that received deliberate ventilation twenty-four hours after application.

Potatoes were stored at 10°C for 28 days. All storage containers were kept in the same temperature controlled room, therefore ambient conditions were the same for each treatment.

Exposure to lower concentrations within this range (0.5-5ppm) had a greater impact on fry colour, most often producing the darkest crisps.

The negative effect of each ethylene treatment on fry colour was more pronounced when storage containers were not deliberately ventilated until twenty-four hours after treatment, compared to samples ventilated eight hours after treatment.

Respiration rates were high initially in samples from all treatments including the control (no ethylene exposure). As the containers and crop were left to settle in experimental conditions three days prior to application, this is not thought to be the response of tubers to movement and handling. Instead it may be the case that the control samples also displayed this high respiration rate as a result of exposure to trace amounts of ethylene that could potentially have been present in the outer storage facility and would be exchanging with air in all containers. The ethylene concentration in all other treatments was much higher than trace amounts. If this is the case there would have been a peak ethylene level in the outer storage atmosphere (even though at very low concentrations) on the day of ethylene applications. It is the earlier samples collected on the day following application that display this characteristically higher rate of respiration.

After a week of storage the respiration rate decreased in samples from all treatments. In containers ventilated eight hours after application the control consistently had a lower respiration rate than all samples exposed to ethylene. The pattern is less clear when crop was not ventilated for twenty-four hours after exposure was initiated.

In short exposure to ethylene, even trace quantities can increase respiration rate rather quickly. Although the effect does not appear to be very long-term when ethylene concentration is very low.

In conclusion potatoes exposed to ethylene will manifest this metabolic stress as a reduction in processing quality through darkening fry colours and increased respiration. The outcome is largely dependant on the concentration of exogenous ethylene, the exposure time and the gaseous composition of the store atmosphere.

Removing ethylene from stores is the best way to avoid these problems, but if elimination is not possible, dilution by ventilation can minimize its effects (*Saltveit, 1999*).

Summary of the effects of thermal-fog application of CIPC on fry colour

Investigation of methods of control

Experiment 1: Ventilation Times

The objective was to determine the effect of timing of ventilation post-application on processing quality. Components such as ethylene can remain in store air for up to twenty-four hours. Therefore by ventilating stores earlier than the standard twenty-four hours after application the exposure time can be reduced.

Materials & Methods

Experimental work was first conducted in May 2001 at SBEU using Cv. Saturna stored at 10°C and 95% relative humidity. CIPC (50% w/v in methanol) was applied using a Unifog at a rate of 0.5l per store (12 tonne capacity) and 0.18l per 4.38 tonne storage container. Samples were transferred to an untreated store 8 or 24 hours after treatment, emulating ventilation. In May all replication of treatments were performed in 12 tonne stores. The untreated is used as the control.

This experiment was repeated in November 2001 under identical conditions, except that the control was treated with a CIPC dust formulation instead of being left untreated. This dust treatment was necessary because the new crop had not previously been treated with any sprout suppressant. The (1% active ingredient) CIPC dust was used at a dose rate of 2g/Kg. Each treatment was applied to crop in a 12 tonne store and the duplicate treatment to crop in a 4.38 tonne storage container.

The baseline quality of the tubers (Cv. Saturna) was higher in November because the crop was fresh. The storage time of the trial was extended from 28 days to 42 days to allow any recovery in fry colour to be followed through. All chemical treatments were carried out in duplicate. In May three and in November four replicate samples were collected from each store per sampling occasion. The samples consisted of 10Kg trays containing approximately 30 tubers. Samples, including untreated material were assessed 0, 1, 7, 14, 28, 35* and 42* days after application. Assessment was made of a) weight of crisps with an unacceptable fry colour and b) the colour (Hunter Lab) of samples after removal of defects. The Hunter L-value assigned to each sample is a measure of the brightness and is determined instrumentally based on the reflection of light. The higher the L-value, the lighter the samples' fry colour. The percent fry defects are the fraction of the crisp sample removed because 50% or more of the surface area of an individual crisp is below acceptable colour (namely L-value 49).

* Only in the case of the repeat experiment in November 2001

Headspace concentrations of Carbon dioxide were measured using a landfill gas meter with a limit of detection of 0.1% CO₂. Headspace ethylene concentrations were determined with the use of a Gastec hand held pump and selective colorimetric detector tubes (semi-quantitative method). Assessments were made prior to ventilation of stores following treatment application. This method of assessment of ethylene is acceptable for the purpose of this trial, albeit only semi-quantitative. Originally samples were to be collected on a transportable medium and forwarded to GU for analysis by the fully quantitative method of Gas-Chromatography (GC). Maintaining sample integrity between collection and analysis proved problematic.

Results

The fry colour results presented are the mean values of each treatment. Error bars display the mean value plus and minus one standard deviation.

May 2001

FIGURE 7. THE EFFECT OF EARLY VENTILATION ON FRY COLOUR DURING STORAGE

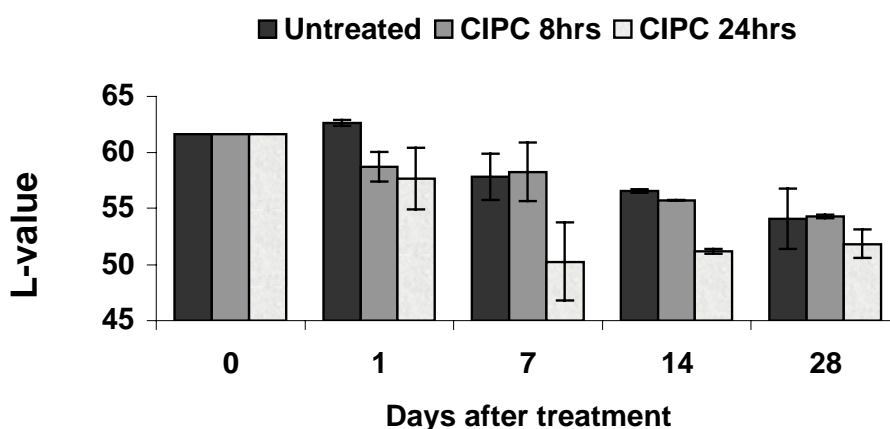
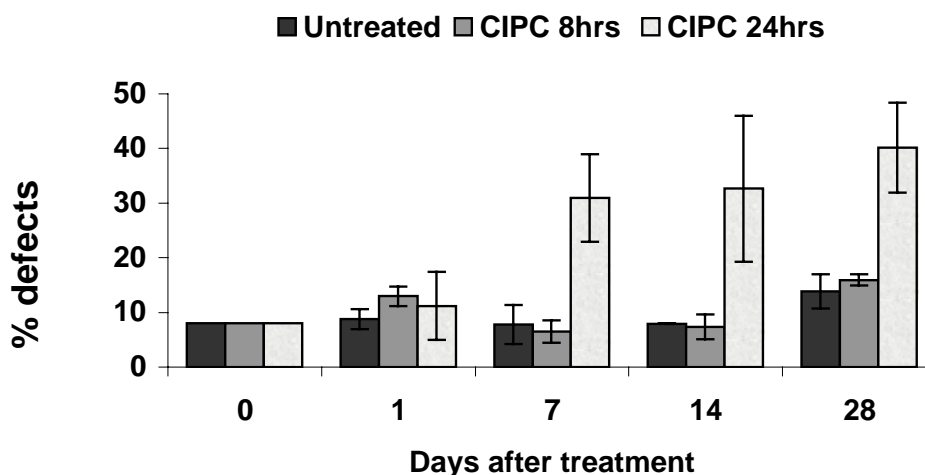


FIGURE 8. THE EFFECT OF EARLY VENTILATION ON DEFECTS DURING STORAGE



The level of CO₂ in the untreated stores atmospheres was below the limit of detection for the duration of the sampling time. In all stores that received fog treatment CO₂ was found in concentrations ranging from 0.3 or 0.4% at eight hours to 0.4 or 0.5% at twenty-four hours post application. Similarly with C₂H₄, levels were below the limit of detection in all untreated stores, however in every store that had been fogged C₂H₄ was identified. The concentrations were largely in the 1 to 5ppm range, though one sample extended into the 5 to 10ppm bracket. C₂H₄ was present in fogged stores for the entire period prior to ventilation.

From the fry colour results it is clear that

- Both CIPC treatments initially resulted in deterioration in fry colour compared with untreated material.
- During the period 7-28 days after treatment there was little difference in fry colour of untreated samples and those transferred 8 hours after fogging.
- Fry colour and weight of defects of samples transferred after 24 hours remained poor for the duration of the study.

November 2001

In this trial the crop was in storage for forty-two days after application of CIPC. All treatments involved the application of CIPC. The treatment used as a control for comparison with fog treatments and ventilation times was CIPC dust. The use of a sprout suppressant chemical was essential for all crop to ensure a fair comparison of crop quality. CO₂ levels were relatively low, but could be detected in each fogged store following application. The common, and maximum, concentration reached was 0.2% at eight hours post application. The levels remained at between 0.1 and 0.2% for the full twenty-four hours or until ventilation. Again C₂H₄ was present in stores as a result of thermal-fog application, ranging between 1 to 10ppm. On this occasion the concentration dropped slightly during the twenty-four hour period but the compound lingered in the store air until ventilation was allowed. The decline was significant yet still the quantity remaining in the stores had considerable implications in terms of effect on fry colour.

FIGURE 9. THE EFFECT OF EARLY VENTILATION ON FRY COLOUR DURING STORAGE

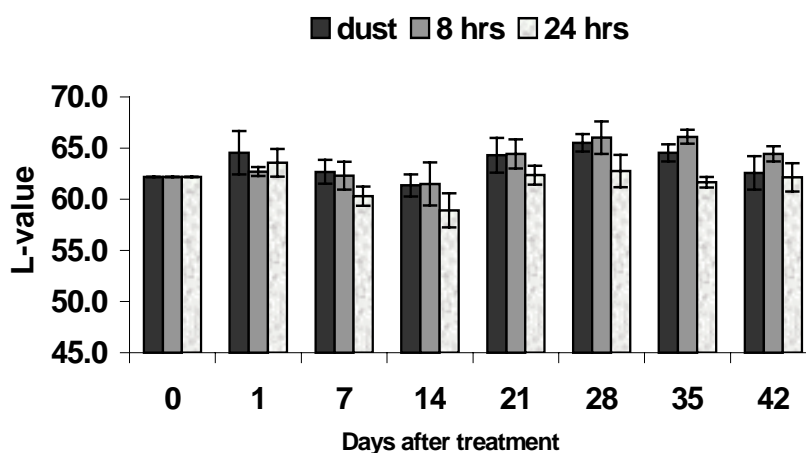
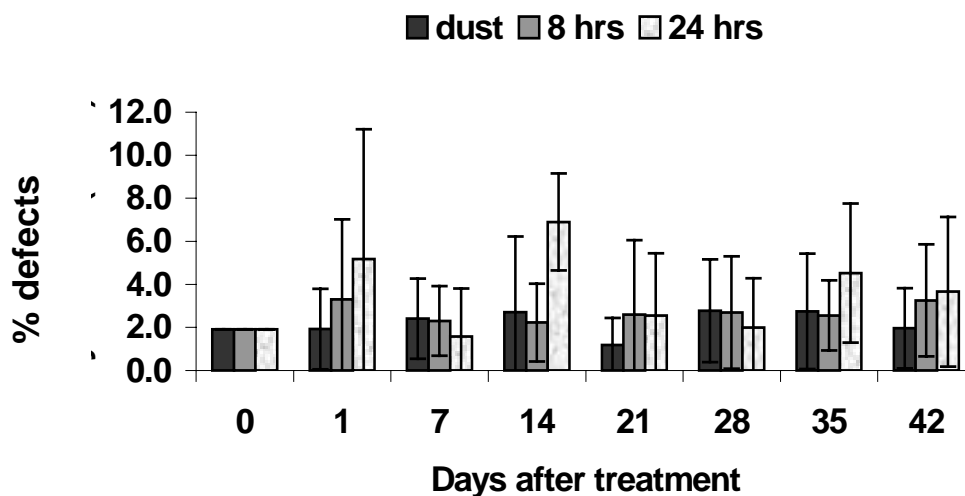


FIGURE 10. THE EFFECT OF EARLY VENTILATION ON DEFECTS DURING STORAGE



The results show that:

- Compared to dust, both CIPC fog treatments initially resulted in darker fry colours.
- Between 7-28 days after treatment the fry colour of dust treated samples and those transferred after 8 hours was very close. After this time the fry colour of the 8-hour samples became lighter than that of the dust treated samples.
- Repeatedly, the fry colour of samples transferred 24 hours after fogging was poorer than that of the 8-hour and dust treated samples.
- Overall the weight of defects was relatively low, but commonly samples transferred after 24 hours had the largest percent of fry defects.

Conclusions

The transfer of samples to an untreated store (emulating ventilation) 8 hours after conventional thermal-fog application of CIPC resulted in an improvement in processing quality of Cv. Saturna at 10°C, compared with samples transferred after 24 hours.

Reducing the exposure time of crops in store to contaminants present in the fog can successfully reduce the detrimental impact of thermal-fog application on processing quality.

Current CIPC formulation label recommendations state that stores should be left sealed for a twenty-four hour period after application of a CIPC thermal-fog (with the exception of 2 labels, which allow ventilation after a 12 hour period). Therefore in this experimental work the eight-hour ventilation was not in accordance with the recommended procedure. However this eight-hour period allowed adequate time for the effective fraction of the thermal fog to settle.

The period of time required for the fog to settle had been previously determined for the stores in which the trials were conducted. The time required in individual stores would have to be determined, but is unlikely to be as long as twenty-four hours after application. Factors that must be considered are health & safety of operators, environmental fate and efficacy. Always read the label recommendation of the product in use. Further information regarding ventilation times can be found in the BPC 'Store Managers Guide' published in 2001.

Data from this project is being used to aide the case for updating CIPC label recommendations.

Early ventilation is a simple and effective method that limits the damage that CIPC treatment has on fry colour.

Experiment 2: Alternative Fuels

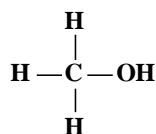
The objective was to determine the effect of using an alternative fuel source, to generate a CIPC thermal-fog, on processing quality. Other aspects that must also be considered are fuel consumption, cost and practicality.

Burning cleaner, simpler hydrocarbon fuels should produce a less polluted flow of combustion gases. The simpler the fuel's chemical structure (smaller carbon backbone) the less carbon dioxide and water vapour is generated per unit volume. This is also true of volatiles of a contaminant nature. Essentially, smaller ranges of contaminants in lower concentrations are produced from purer fuels.

On this basis methanol and liquefied petroleum gas (LPG) were investigated as potential options for reducing the impact that fogging has on fry colour. Currently the common fuel used to generate thermal-fogs is lead replacement petrol.

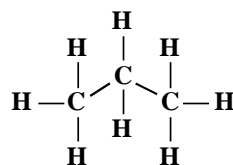
Methanol has the smallest structure of the three fuels. It is considered a bio-fuel as it is a renewable energy resource. It was available for experimental use promptly as the adaptations required to the existing fogging machines were straightforward.

FIGURE 11. THE CHEMICAL STRUCTURE OF METHANOL



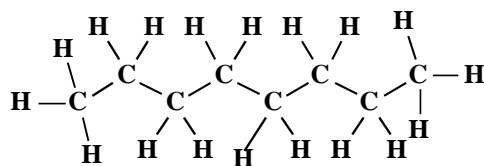
LPG is readily available and is at present used for many commercial purposes instead of petrol because it is both cheaper and cleaner to run. The more complicated process of adapting equipment to burn LPG meant that it was not ready for trials in May 2001, and after experimental trials in November 2001 still requires further work to optimize the system.

FIGURE 12. THE CHEMICAL STRUCTURE OF LPG (PROPANE)



The structure shown below is the nearest pure hydrocarbon structure to petrol. In reality, petrol is a very mixed and variable fraction of the distillation process and is a well-known source of pollutants.

FIGURE 13. ILLUSTRATION OF THE CHEMICAL STRUCTURE OF PETROL (OCTANE)



Materials & Methods

All practical trials were carried out at SBEU using Cv. Saturna stored at 10°C and 95% relative humidity. CIPC (50% w/v in methanol) was applied using a Unifog at a rate of 0.5l per store (12 tonne capacity) and 0.18l per 4.38 tonne storage container. Samples were transferred to an untreated store 24 hours after treatment, emulating ventilation.

The experiment was first conducted in May 2001. Untreated crop was used as the control and compared with crop treated using a petrol-fuelled fog (the usual fuel) and crop treated using a methanol-fuelled fog. All other conditions of application were identical. In May 2001 all treatments were conducted in 12 tonne stores.

Based on the findings from the trial in May and further developments in suitable fuel types the experiment was repeated in November 2001 with modifications to treatments. The treatments compared for their effect on processing quality were a petrol-fuelled fog (used in this case as the control), a methanol-fuelled fog and an LPG-fuelled fog. Where possible all other conditions of the application process were identical. Each treatment was applied to crop in a 12 tonne store and the duplicate treatment to crop in a 4.38 tonne storage container.

The baseline quality of the tubers (Cv. Saturna) was higher in the second trial because the crop was fresh as it was the start of the storage season.

In May three and in November four replicate samples were collected from each store per sampling occasion. Each sample was a 10Kg tray containing approximately 30 tubers. The fry colour of samples, including untreated material was assessed 0, 1, 7, 14 and 28 days after application.

Results were obtained for fry colour, fry defects and headspace concentrations of carbon dioxide and ethylene prior to the ventilation of stores.

Results

The fry colour results presented are the mean values of each treatment. Error bars display the mean value plus and minus one standard deviation.

May 2001

FIGURE 14. THE EFFECT OF THE USE OF METHANOL FUEL FOR CIPC APPLICATION ON FRY COLOUR DURING STORAGE

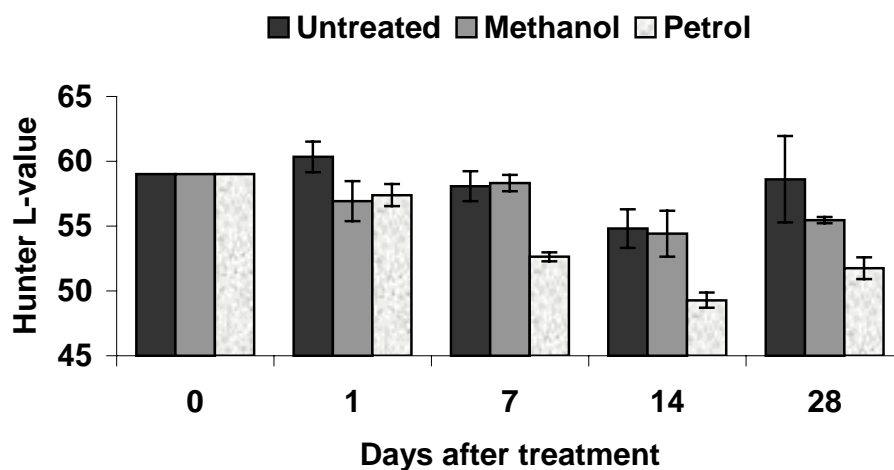
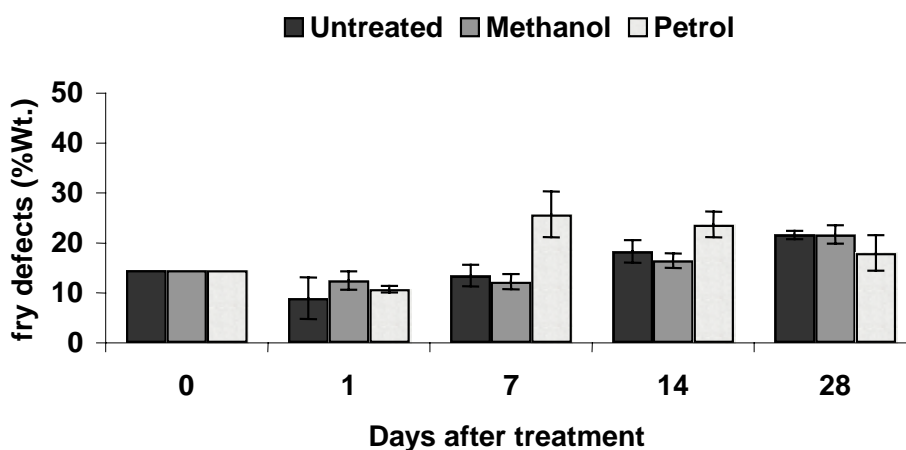


FIGURE 15. THE EFFECT OF THE USE OF METHANOL FUEL FOR CIPC APPLICATION ON FRY DEFECTS DURING STORAGE



CO₂ concentrations in stores treated with petrol fuelled-fog were between 0.1 and 0.2% at both the sampling times (eight and twenty-four hours post-application). In those stores treated with methanol fuelled-fog CO₂ was between 0.1 and 0.3% on both sampling occasions.

C₂H₄ was detected in stores treated with petrol fuelled-fog for the full twenty-four hour period prior to ventilation, in the range 1 to 5ppm. Methanol fuelled-fog caused diffuse

unquantifiable readings. The methanol propellant interfered with the colorimetric reagents.

It is apparent from the fry colour results that:

- On day one, CIPC applied using conventional petrol and methanol propellants initially resulted in a deterioration in fry colour compared to untreated samples.
- Between seven and twenty-eight days after application, the methanol-fogged samples have similar fry colours to that of the untreated.
- The processing quality of the petrol-fogged samples was relatively poor 7-28 days after application.
- The weight of fry defects was increased using petrol propellant seven and fourteen days after application.

The effects of all treatments appear to lessen slightly toward day twenty-eight. This is significant as the withholding period ('harvest interval') for CIPC treated crops is currently 21 or 28 days, depending on CIPC formulation.

November 2001

In this experiment the CIPC treatments compared for their effect on fry colour were petrol fuelled-fog (the control), methanol-fuelled fog and LPG fuelled-fog. CO₂ was below the limit of detection in all stores following fogging for the duration of sampling. C₂H₄ was identified in stores fogged using LPG and petrol. The levels were in the range 1 to 5ppm at eight hour post-application in each store. In the LPG treated stores the concentration dropped to between 0.2 to 1ppm within the twenty-four hour period preceding ventilation. Whereas in the stores treated with petrol-fuelled fog the concentration remained in the range 1 to 5ppm until ventilation. Again using methanol as a propellant for thermal fog caused interferences with the Gastec colorimetric system.

FIGURE 16. THE EFFECT OF THE USE OF AN ALTERNATIVE FUEL FOR CIPC APPLICATION ON FRY COLOUR DURING STORAGE

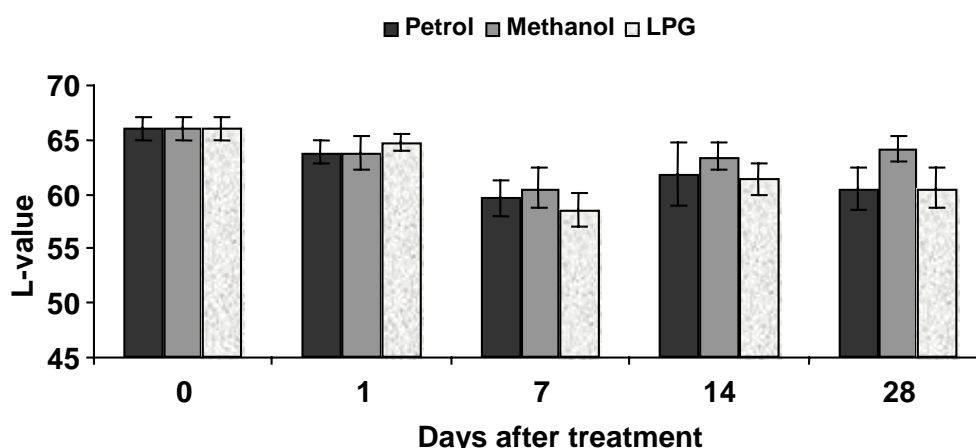
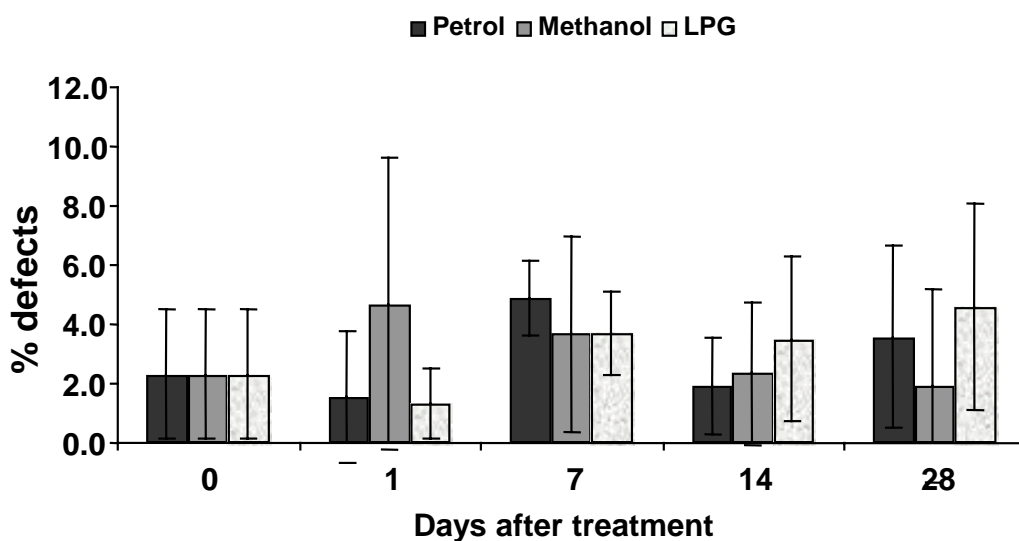


FIGURE 17. THE EFFECT OF THE USE OF AN ALTERNATIVE FUEL FOR CIPC APPLICATION ON FRY COLOUR DURING STORAGE



- CIPC applied using conventional petrol, methanol and LPG propellants initially resulted in a deterioration in fry colour.
- Methanol fuel was less detrimental to processing quality than LPG or petrol.
- The difference in effect on fry colour between CIPC applied using LPG and petrol was only slight.

Conclusions

Conventional CIPC application using combustion of petrol as a propellant resulted in a significant deterioration in fry colour and an increase in the weight of fry defects.

Producing a less polluted flow of combustion gases reduces the exposure of crop to contamination. Adopting different fuels can alter the extent of contamination produced on burning. Even with the use of cleaner fuels, relying on hydrocarbon combustion to generate the hot air stream required will produce an impure fog. However the degree of contamination will principally depend on the fuel type. This is evident from the poor fry colour exhibited by all samples collected one day after the CIPC thermal-fog was applied.

The impact on processing quality can be reduced by using a cleaner fuel than petrol.

The fry colours obtained when using methanol as a propellant were an improvement on the samples treated with the current industry standard. This was expected as methanol has the smallest chemical structure of the fuels tested therefore it can only form a comparatively limited range of compounds*. Thus, the smallest range of volatiles (of a contaminant nature) are introduced to the stores atmosphere.

* when combustion of the fuel is incomplete.

Improved fry colours were anticipated when LPG was used as a propellant for fogging. However the distinction between petrol and LPG was marginal. This was the first attempt at using LPG generated fog in crop trials with this equipment. In these circumstances it did not prove any more detrimental than petrol. The unexpected LPG results are due to an inefficient burner system, which meant fuel consumption was artificially high. This greater volume of fuel produced more combustion gases and contamination than would be the case if the system had been fully optimised.

Further development of an LPG fogging system is underway and forthcoming trials should determine the true effect of an LPG propellant.

Fuel consumption was measured for each fuel type with a Unifog machine under typical application conditions. A table of properties associated with the fuels was produced (see *Table 8*). These factors have to be weighted against each other to determine how practical the fuel is for use as a CIPC thermal-fog propellant.

TABLE 8. FUEL PROPERTIES

Fuel properties	Methanol	LPG	Petrol
Carbon dioxide, water vapour & contaminant production	Low	Intermediate	High
Fuel consumption compared with petrol	High	High	Standard
Relative cost per unit volume	High	Low	Standard

Although the improvement in fry colour is significant with a methanol propellant it would be an expensive option. The fuel consumption is high when compared to petrol. Methanol is more expensive to buy and a greater volume of fuel would have to be carried by the applicators. A license to carry and use alcohol for industrial purposes would be required and staff training to attain the license. The potential saving through increased crop acceptability has to be balanced against the envisaged cost of a CIPC application.

Compared with petrol, LPG is cheaper and cleaner to run and could mean improved fry colours at an affordable price. The fuel consumption should be low and the cost of fuel relatively cheap. It is presently used for many industrial and domestic purposes and so is readily available and adaptable.

The LPG system needs further development to increase the efficiency of the burner and work toward this is underway. When the LPG fogging machines are ready for commercial use, it is likely that the operator will be required to become CORGI registered for health and safety reasons.

Experiment 3: Dose Rates

The objective was to compare the effect of applying CIPC at different application rates on processing quality.

The application of CIPC as a thermal fog is considered a stress to potatoes in storage. The result of creating a stressful storage environment is the darkening of fry colour and potentially offsetting the effectiveness of the sprout suppressant action. By altering the dose rate of CIPC treatments, the number of applications required could be reduced. Cutting back the number of treatments would decrease the frequency of contamination from fogging entering stores. Hence not creating stressful conditions in stores as often. The efficacy of sprout control would have to be determined to ensure the benefit gained in quality is not at the cost of limiting sprout control. It is regarded that sprout control would not be limited by this procedure and may in fact be enhanced, however this issue has not been investigated as part of the experiment.

Materials & Methods

Experimental work was conducted at SBEU starting in January 2002 and continued until May 2002. The crop used was Cv. Saturna. It was held in 12 tonne stores at 10°C and 95% relative humidity. CIPC (50% w/v in methanol) was applied using a Swingfog machine. The treatments were as follows:

- **Half rate:** 0.25 l per application. Four applications conducted at 0, 4, 8 and 12 weeks of storage.
- **Full rate:** 0.50 l per application. Two applications conducted at 0 and 8 weeks of storage.
- **Double rate:** 1.00 l per application. One application conducted at week 0 of storage.

The time taken to apply was different for each treatment. It took twice as long to apply the double rate as it did to apply the full rate, and correspondingly it took half the time to apply the half rate. Consequently the stores received differing amounts of combustion products and contamination from the fogging process.

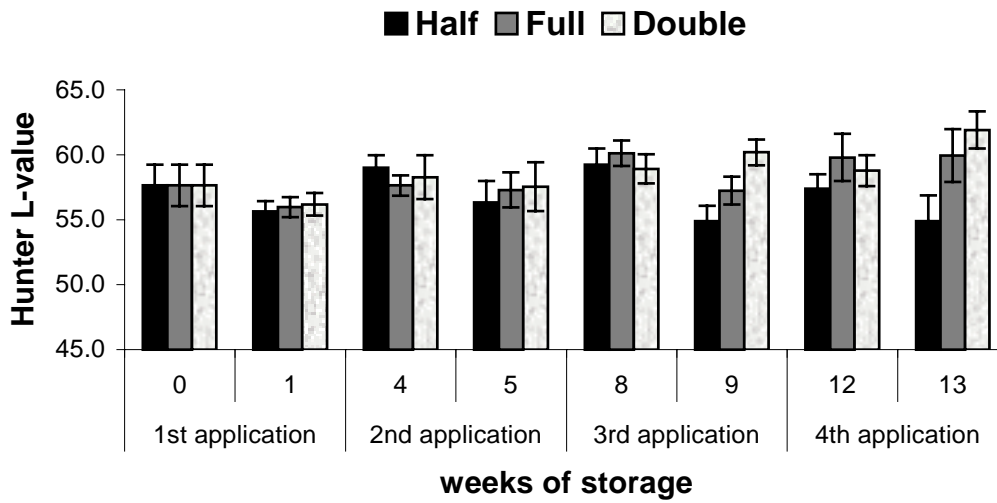
On each sampling occasion four replicate samples were collected from each store and assessed for quality. The samples consisted of 10Kg trays containing approximately 30 tubers. The fry colour of samples from each treatment regime was assessed prior to all four application dates and seven days following all four of the applications. Therefore quality was evaluated at 0, 1, 4, 5, 8, 9, 12 and 13 weeks of storage.

Results were obtained for fry colour, fry defects and headspace concentrations of CO₂ and C₂H₄ prior to ventilation.

Results

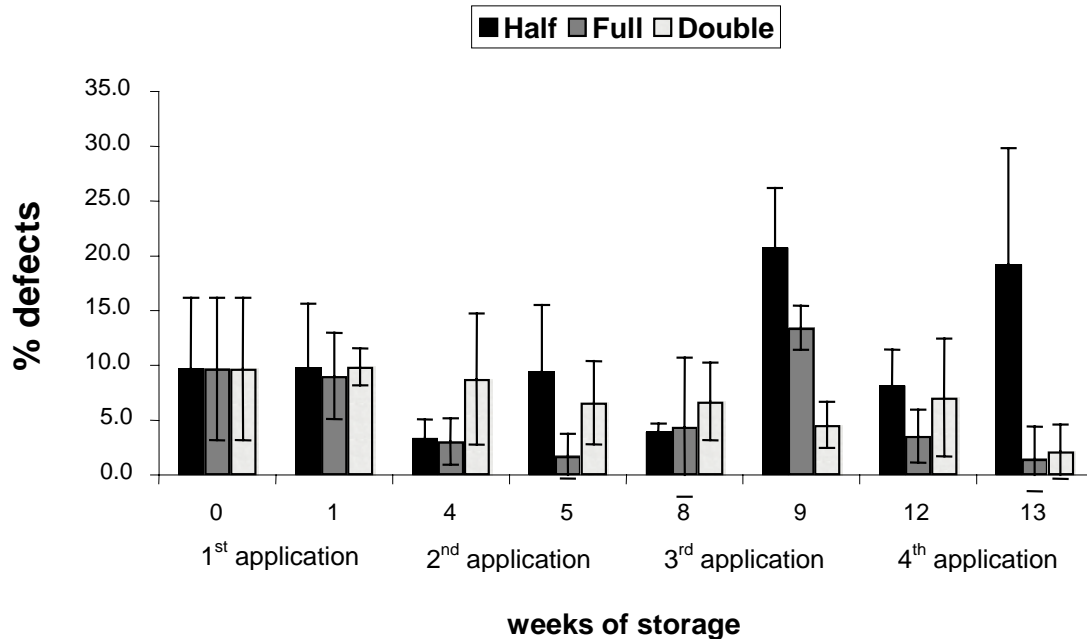
The fry colour results presented are the mean values of each treatment. Error bars display the mean value plus and minus one standard deviation.

FIGURE 18. THE EFFECT OF CIPC DOSE RATE ON FRY COLOUR DURING STORAGE



- All fog treatments resulted in an initial deterioration in fry colour.
- For the duration of the trial the samples with the darkest fry colour were those treated most frequently (half rate CIPC).
- Generally the samples with the lightest fry colours throughout, were those only fogged once (double rate CIPC) at the start of the 13-week period.

FIGURE 19. THE EFFECT OF CIPC DOSE RATE ON FRY DEFECTS DURING STORAGE



- After an initial increase, the % fry defects remained low in samples treated with the double dose of CIPC.

- In samples treated with the full rate, fry defects increased after both applications, however steadily declined between 1-4 weeks following fogging.
- The % fry defects rose after each fog application in samples treated with a half dose. The effect became increasingly pronounced with successive applications.

The effect of individual treatments is more apparent from the graphs overleaf. Each variable is presented separately in a graph of fry colour (Hunter L-value) against the storage time in weeks. Error bars have not been included, instead only the mean values are shown to demonstrate the pattern of fry colour results following treatments. From the half dose graph it is clear that each fog application causes a drop in quality. The repeated fogging means that after thirteen weeks of storage the crop is only in the lower end of the acceptable colour range for the commercial market (L value 58>). With the samples fogged at full rate there is a similar pattern, however a longer period between applications does allow the fry colour to recover to some extent. Samples fogged on a single occasion at the double rate at the beginning of the storage period gave the best quality.

FIGURE 20. THE EFFECT OF A HALF DOSE OF CIPC APPLIED PER TREATMENT ON FRY COLOUR DURING STORAGE

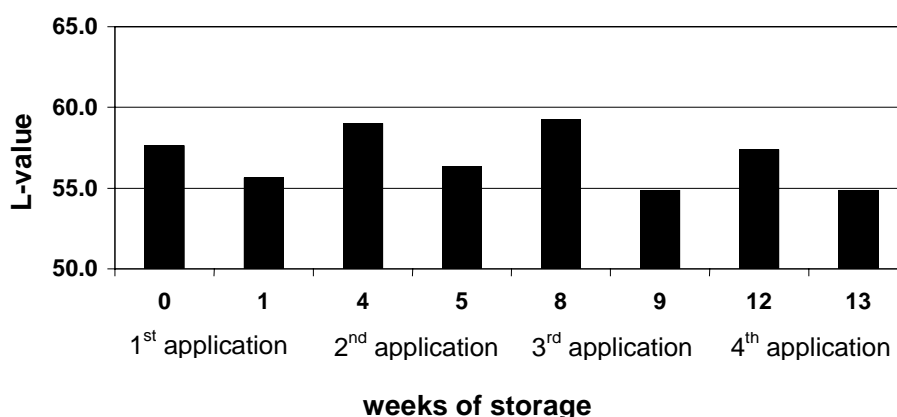


FIGURE 21. THE EFFECT OF A FULL DOSE OF CIPC APPLIED PER TREATMENT ON FRY COLOUR DURING STORAGE

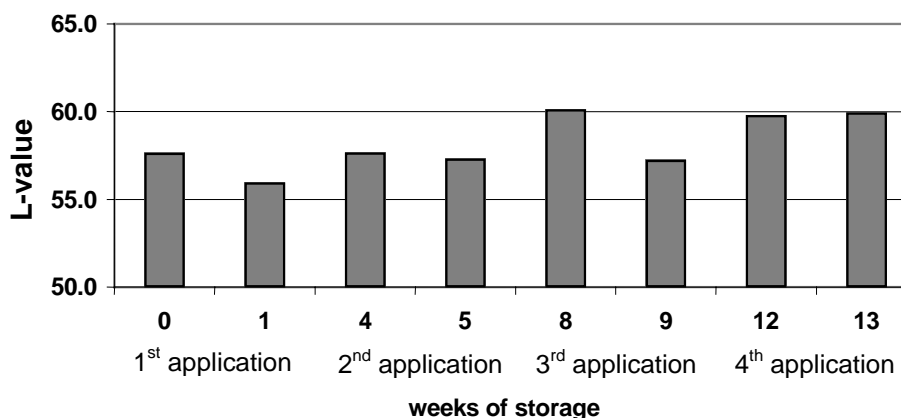
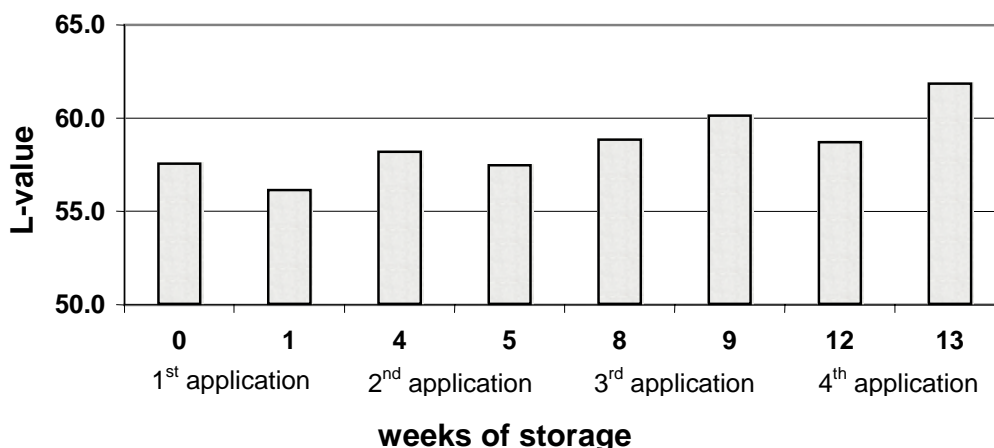
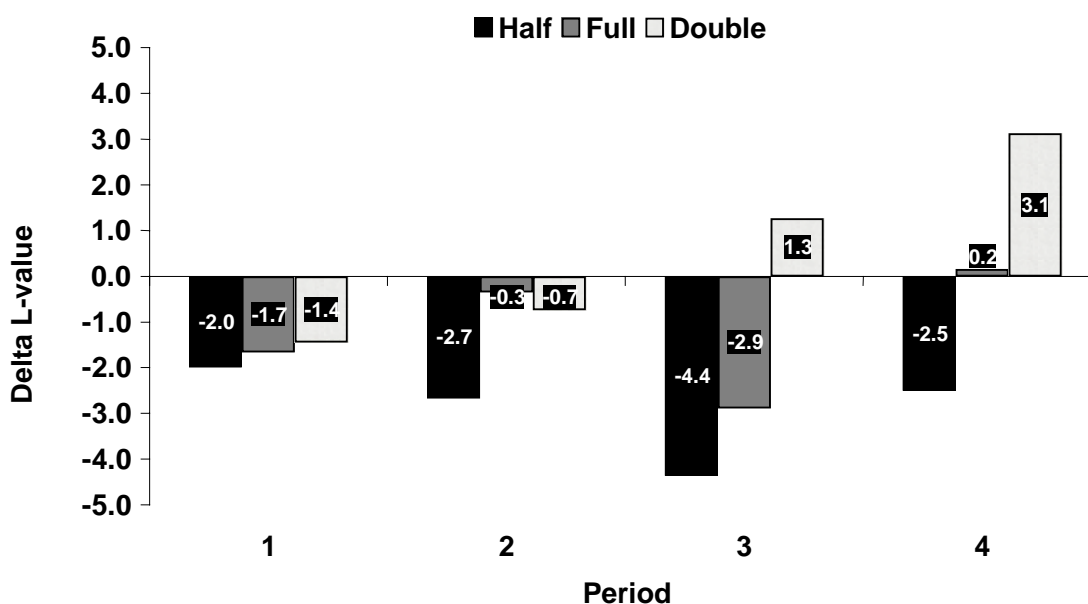


FIGURE 22. THE EFFECT OF A DOUBLE DOSE OF CIPC APPLIED PER TREATMENT ON FRY COLOUR DURING STORAGE



The Graph below is a plot of the difference between the L-value pre-application and seven days post-application. This information is included for every application period and variable. There are four application times (weeks 0, 4, 8 and 12) therefore four application periods and three variables. The half dose was applied on all four occasions. The full dose on two (weeks 0 and 4) and the double dose only once (week 0). This graph is perhaps the best illustration of the difference between treatments in terms of effect on fry colour both from individual and consecutive CIPC applications.

FIGURE 23. THE DIFFERENCE IN L-VALUE PRE-APPLICATION AND SEVEN DAYS POST-APPLICATION



High L-values are desired; therefore any increase in L-value displayed in the graph is a positive change. In contrast a negative number on the graph indicates that fry colour has darkened in the seven-day period since the previous sample was collected.

The week following fog applications fry colour of samples had declined with every dose of CIPC. It was anticipated that the initial decline would be greater in samples that had been fogged for a longer time (double dose>full dose>half dose). However this was not the case.

Crop fogged most often endured the greatest stress. This was reflected in the large negative changes in fry colour of samples treated at half dose.

The frequency of fogging appears to be a more dominant factor in influencing crop quality than the duration of the fog application itself.

The time taken to apply each dose did alter the overall amount of C₂H₄ detected in stores after treatment. The store treated with the double-dose, had the highest concentration at approximately 30ppm. The level determined in stores after full-dose application was within the range 10-30ppm on both sampling occasions. Correspondingly, in stores that received four half-dose treatments the C₂H₄ concentration was within the range 1-5ppm in each instance.

In these circumstances, where recurrent exposure is involved, the simple presence of C₂H₄ appears more significant than its abundance.

Conclusions

Having examined the disruptive influence that CIPC thermal-fog application can have in potato stores, it is obvious that it creates a stressful environment for the tubers. The unfavourable situation created is deemed to be the end result of a number of features. Probable contributing factors are (i) The heat of the fog as it enters the store (ii) The rate of fog flow into the store and its ensuing course and principally (iii) The products of burning a hydrocarbon fuel to generate the fog (lead replacement petrol).

Regardless of dose there is a detrimental impact on fry colour from every fog treatment. This negative effect re-occurs with each subsequent application. It appears that the degree to which quality is affected may augment with an increasing number of fog applications.

Recurrent applications could counteract the sprout suppressant activity of the CIPC. All applications conducted as part of this experiment have introduced ethylene to the potato stores in appreciable amounts. It is known that short-term exposure can stimulate dormancy break (see *Ethylene in Potato Stores*, p16-25). The exposure occurs when fog is allowed to settle after application before stores are ventilated. The fact that exposure to ethylene is intermittent could potentially be concentrating this counter effect. It would not render CIPC ineffective but it is an additional hindrance that is best avoided.

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A sufficient time interval before re-treatment can allow the quality of the potatoes to recover to some extent from the stress caused. Tailoring the CIPC dose per treatment, and thus reducing the total number of applications necessary, can achieve this.

The efficacy of CIPC in these experimental circumstances was not determined, though sprout control remained adequate.

SUMMARY OF THE EFFECTS OF THERMAL-FOG APPLICATION OF CIPC ON FRY COLOUR

Investigation of methods of removal

Experiment 4: Modifying Store Atmospheres

It has been shown that thermal fogging generates volatiles that have a negative influence on potatoes in storage. Even in the short time before ventilation, the exposure of tubers to these compounds can critically increase the reducing sugar content of the crop, hence causing the darker fry colour of crisps when processed.

The objective was to identify a means of removing the contaminants present in thermal fogs. The intention is that once a store is fogged, the crop inside would not be exposed to as many harmful by-products as with the existing process.

Preliminary investigations of adsorbent and scrubbing substances revealed that certain factors were crucial for a successful system. Before the optimal set of conditions could be resolved the adsorbent has to be tailored to the practical application required. The most appropriate substance depends on the compounds of interest, the matrix and treatment conditions. Including required contact time, dosing system, regeneration and safety measures.

As this is a meticulous process, requirements were curtailed from all typical by-products of combustion to ethylene specifically. Its influence has been examined thoroughly. This allowed for quantifiable and reproducible application of ethylene as a standard treatment to be conducted. It was applied in precise amounts at regular intervals to the headspace of all storage containers in equal concentrations.

The substances originally tested for efficiency of adsorption were Silver Nitrate (Johnson Matthey Chemicals Limited), Washed Bone Charcoal (Brimac 20:60 mesh) and Activated Carbon (Norit PK 1-3, lab no. NC15983). All three substances proved ineffective in a static system. Silver Nitrate and Washed Bone Charcoal were unsuccessful when shaken intermittently within an ethylene-spiked atmosphere. The action of the Activated Carbon was improved by use in the shaking arrangement. The adsorptive action of the Activated Carbon was further improved by integrating a second carbon trap (Carbosieve SIII 60:80 mesh, Supelco 10293) within a dynamic set up. For this reason a dual Activated Carbon trap in a dynamic assembly was the ethylene scrubber in the main experiment carried out.

Activated Carbon is a carbonaceous adsorbent with a high internal porosity, and hence a large internal surface area. It consists mainly of elementary carbon in a graphite like structure. It can be produced by heat treatments (activation) of raw materials such as wood, coal and peat. The internal pore structure created during activation provides the exceptional adsorptive properties.

These carbon materials used have a high affinity for a range of compounds, specifically carbon-based molecules and in particular those of low molecular weight. This makes them ideal for the purposes of the trial although they can be costly. The advantage in using carbon material is that it can be regenerated and therefore used time and time again. Another method of modifying the store atmosphere was creating elevated carbon dioxide levels in an attempt to inhibit the behaviour of ethylene. A further tactic undertaken was to use an ethylene trap in conjunction with a carbon dioxide trap to try to remove both from the store air. This was done to rule out any potentially synergistic effect of these compounds on the crop quality. The crop quality was quantified by measuring the reducing sugar concentration of tuber samples.

Materials & Methods

Experimental work was conducted at GU in 2 l and 5 l storage containers, each holding 2kg of Cv. Saturna that had been treated with CIPC earlier in the season. The crop temperature was maintained as close to 10°C as possible at all times, however minor fluctuations did occur. These fluctuations are reflected in the reducing sugar data. However, all samples were subject to these small changes and so any resultant trend is common to all treatments.

Each treatment was replicated three times, twice in the 2 l containers and once in a 5 l container. The smaller storage tanks were considered to be representative of typical store conditions. They were relatively closed systems yet some exchange with ambient air was expected. They are referred to as leaky stores. The larger storage tanks were totally closed systems allowing no exchange with ambient air other than when deliberately ventilated (sealed stores). All storage containers were ventilated frequently at suitable times arranged around treatment applications and sample times. The oxygen and carbon dioxide levels (from respiration) were never allowed to become restrictive. The containers were kept in a storeroom in which the temperature was controlled. Therefore any mixing with ambient air and ventilation was still within a controlled situation.

Ethylene applications were conducted using standard cylinders of pressurised gas (Scotty Gas) of two concentrations. The 100ppm gas was used at flow rates of 25ml/min and 10.5ml/min to create concentrations in containers of 10ppm and 4.2ppm respectively. A cylinder of 10ppm was used at a flow rate of 25ml/min to create a concentration of 3ppm. The treatments were applied on days 0 (4.2ppm), 7 (10ppm), 14 (3ppm) and 28 (3ppm) of storage.

Carbon dioxide was applied from a standard pressurised cylinder of 10% CO₂ in air (BOC gas). A flow rate of 25ml/min was used to create a 2% concentration in three specific containers. Following application of the C₂H₄ and/or CO₂, the air inside the containers was circulated through the appropriate trap. The entire volume of each container (2 l or 5 l) was passed over the trap at a flow rate of 20ml/min using a peristaltic pump and pvc tubing.

The traps used were;

1. **To remove C₂H₄ only:** A headspace bottle with 1g activated carbon with a glass wool plug and a silanized glass tube packed with a 2cm bed of carbosieve SIII resin with glass wool plugs.
2. **Elevated CO₂:** Applied from cylinder to achieve a 2% concentration in container. Circulated only through the pvc tubing.
3. **To remove C₂H₄ and CO₂:** As above to remove C₂H₄, following these traps was a CO₂ trap. It was a test tube with a side arm, rubber bung and inlet tube through the bung. It contained 20ml 2M NaOH, through which the container air was bubbled.
4. **Control:** circulated through the pvc tubing only.

The concentration of C₂H₄ remaining in store air 24-hours after treatment was determined to assess the % loss. 2.5ml disposable plastic syringes with 25G 1.5inch needles (luer lock) were used for collection. The syringes were plugged with a PTFE coated silicon bung until 2ml was injected into the GC for analysis approximately 2 minutes after collection.

The conditions of GC analysis using a PYE Unicam PU4500 and Spectra physics SP4290 integrator were:

Column: Haysep D 100/120 mesh (polydivinylbenzene)
Oven temp: 50°C
Injector temp: 200°C
Detector temp: 250°C
Injection volume: variable (10µL to 2000µL)

The GC was calibrated with standards of ethylene gas from pressurised cylinders. All injections were gas phase.

10ml and 25ml of store air was taken from the 2 l and 5 l containers respectively for measurement of CO₂ from respiration. These samples were collected 24-hours after treatment. The store air was bubbled through 2ml of 1M NaOH in small vials. The vials were then closed until analysed by colorimetric titration. Immediately prior to titration, 2ml of 1M BaCl and 3 drops of phenolphthalein pH indicator were added. The solutions were then titrated with 0.1M HCl. The titre volume was then used to calculate the amount of CO₂ trapped in solution, based on relationship the 1ml 0.1M HCl≡2.2mg CO₂.

Reducing sugar concentration was measured the day before each application, one day after and six days after the last C₂H₄ treatment. Two random tubers were collected from containers on every occasion. The weight removed was recorded and all associated results adjusted accordingly. Both tubers were washed, peeled, chopped finely and a representative sub-sample of approximately 25g was extracted by homogenising with 60ml methanol. The extracts were filtered through Whatman no.1 paper and made to 100ml in a volumetric flask. Dilutions in water were prepared as necessary for analysis.

Fructose (free and derived from sucrose) was determined by the Roe method (*J.H. Roe, 1934; Jarvis et al, 1974*). Fructose solely derived from Sucrose was measured by the Lelair-Roe method (*Cardini et al, 1955; Jarvis et al, 1974*) and Glucose plus Fructose was determined using the Somogyi-Nelson method (*Methods in carbohydrate chemistry, Whistler Wolfrom, volume 1*). All colorimetric analysis was performed using a Hitachi V-1100 Spectrophotometer.

From this information the amount of total reducing sugars commonly used as a gauge for processing quality, was calculated (total Fructose plus Glucose). The lower the reducing sugar concentration the higher the quality of the sample. The air inside the containers was refreshed regularly by removing the lids and allowing exchange with the room air for at least one hour.

Results

The most significant results gained from the trial are the reducing sugar concentrations. They are presented separately for the 2 l and 5 l containers to demonstrate the difference in efficiency of methods of modifying store atmospheres under entirely sealed and normal (slightly leaky) conditions.

The effect of intermittent ethylene exposure on reducing sugar concentration was more pronounced in the leaky containers. The extent of air exchange with ambient was dependant on the environmental conditions. The response of the modifications conducted is slightly different, to what it was in the sealed containers, as the underlying impact of ethylene is greater. This is clear from the control treatment, where ethylene was applied, but no effort was made to remove or reduce its concentration.

The graphs overleaf are the mean results of the reducing sugar concentrations of the samples stored in the 2 l tanks. An * indicates the sample was taken on the day following ethylene/carbon dioxide application and circulation.

FIGURE 24. THE EFFECT OF ETHYLENE PRESENCE IN STORE ATMOSPHERES ON REDUCING SUGAR CONCENTRATION IN A LEAKY ENVIRONMENT (CONTROL)

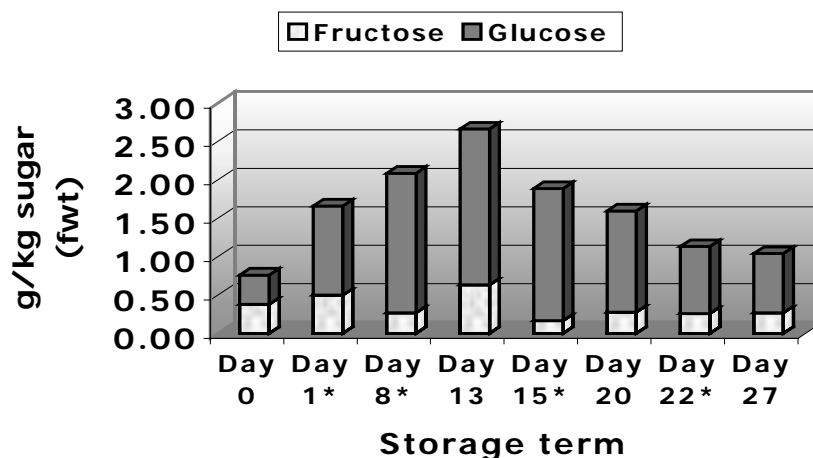


FIGURE 25. THE EFFECT OF REMOVING ETHYLENE FROM THE STORE ATMOSPHERE ON REDUCING SUGAR CONCENTRATION IN A LEAKY ENVIRONMENT

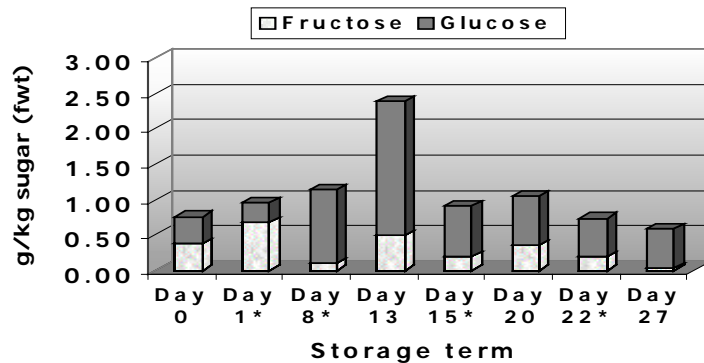


FIGURE 26. THE EFFECT OF ELEVATING CARBON DIOXIDE LEVELS IN THE STORE ATMOSPHERE ON REDUCING SUGAR CONCENTRATION IN A LEAKY ENVIRONMENT

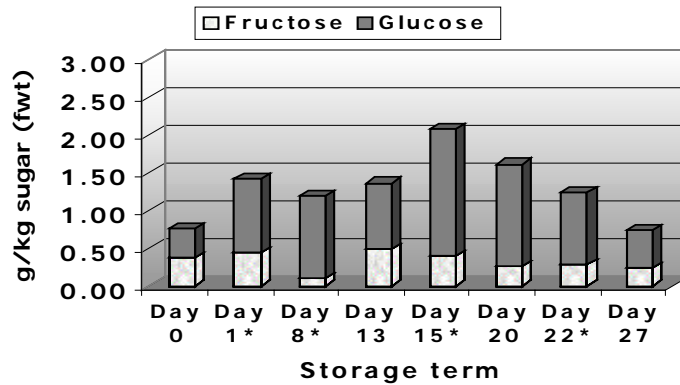
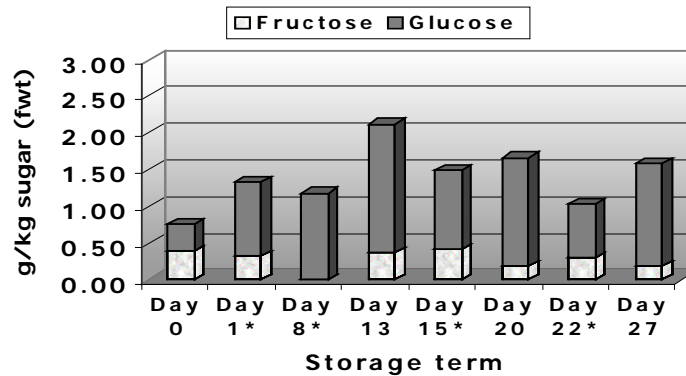


FIGURE 27. THE EFFECT OF REMOVING ETHYLENE AND CARBON DIOXIDE FROM THE STORE ATMOSPHERE ON REDUCING SUGAR CONCENTRATION IN A LEAKY ENVIRONMENT



The fructose concentration was consistently lower than glucose in all samples from all treatments. There was no definitive ratio of fructose to glucose concentration, however in general both of these sugars show the same trends. There were occasional exceptions when one of the extract aliquots generated a nonsensical value that had to be discounted.

The control treatment shows quite clearly the detrimental effect of C₂H₄ exposure on the reducing sugar concentration. This is most pronounced on Day 13, where the result of prolonged exposure is evident, by the elevated value.

In this slightly leaky storage situation, removing only C₂H₄ from the atmosphere was the best treatment for improving crop quality. Overall the reducing sugar concentrations were quite low throughout the duration of the trial, with the exception of Day 13.

Creating elevated levels of CO₂ had some beneficial action. It appears that this treatment delayed the effect of C₂H₄ exposure and lessened the impact when compared to the control. The maximum reducing sugar concentration was reached on Day 15. This was the poorest treatment for removal of C₂H₄ (*Table 9*) from stores. However it did have some advantage by way of inhibiting the effects of C₂H₄ on reducing sugar concentration.

Removing both C₂H₄ and CO₂ had a similar outcome to that of elevating CO₂, but the improvement in reducing sugar content was slightly less. The immediate effect is apparent, but this improvement is not as long lived as when only C₂H₄ is removed. This can be seen on sample days 20 and 27 where levels have increased since the previous sampling occasion.

This increased concentration on Day 13 was common to three of the treatments (Control, Removing C₂H₄ and Removing both C₂H₄ and CO₂). It is believed to be the result of prolonged exposure to C₂H₄. The percentage loss of C₂H₄ from each container (*Table 6*) showed that on Day 8 local ambient conditions did not encourage sufficient air exchange to remove all residual C₂H₄. Consequently small amounts remained present in the storage containers for a longer period than after of the other C₂H₄ applications.

The table (*Table 9*) overleaf details the percentage loss of C₂H₄ from storage containers due to circulation and trapping. This was assessed after circulation and prior to collection of tubers for sugar samples.

No trap or treatment used was 100% efficient at removing C₂H₄. On most occasions 100% loss was recorded from the smaller containers, however this is largely due to exchange with ambient air.

TABLE 9. % LOSS OF ETHYLENE FROM STORE ATMOSPHERES

Treatment	% loss of ethylene in the twenty-four hours after application							
	2 Litre storage containers				5 Litre storage containers			
	Day 1	Day 8	Day 15	Day 22	Day 1	Day 8	Day 15	Day 22
Removing ethylene	100.0	98.4	100.0	100.0	83.3	72.6	77.7	87.3
Elevated carbon dioxide	100.0	96.5	96.0	98.4	51.2	49.5	58.7	68.0
Removing ethylene & carbon dioxide	100.0	97.1	100.0	100.0	73.1	76.0	77.3	82.0
Control	100.0	98.6	100.0	100.0	64.3	58.3	72.0	78.0

The system designed specifically to remove C₂H₄ was the most effective trap under both sets of conditions. Removing both C₂H₄ and CO₂ had some success but C₂H₄ traps were

not as effective when coupled with CO₂ traps. In both instances the control lost more C₂H₄ from store than those containers treated with elevated CO₂. Elevated CO₂ was not a method of C₂H₄ removal, but was a reasonably successful method of countering the effects of C₂H₄ exposure on reducing sugar concentration. This system was effective in the leaky containers, but appeared to be limited in the sealed containers. It is possible that in these sealed containers the levels of CO₂ (from respiration) are themselves affecting the reducing sugar concentration. For this treatment to be beneficial adequate ventilation is essential.

Both sets of results in the above table have the same pattern, but the improvements in quality are greater in the smaller leaky stores. This is because a) the effect of C₂H₄ exposure was more significant and b) the efficiency of the trapping systems was greater in a leaky environment. From the respiration rates below (*Table 10*) it seems that the applied CO₂ was no longer present when the measurement was taken. Indicating it was not held in the store for long, before escaping. Even though its presence is transitory it has a notable effect on sugar levels. The most steady respiration rate is that of the control samples, where the storage atmosphere is not altered (only circulated). This suggests the other treatments could be having a disruptive influence, causing the respiration rates to fluctuate, in some cases greatly.

TABLE 10. RESPIRATION RATES

Treatment	Respiration rate (mg carbon dioxide/kilogram/hour)							
	2 Litre storage containers				5 Litre storage containers			
	Day 1	Day 8	Day 15	Day 22	Day 1	Day 8	Day 15	Day 22
Removing ethylene	11.49	30.83	19.30	37.81	50.88	28.82	14.44	26.56
Elevated carbon dioxide	15.46	21.99	19.68	32.65	20.32	7.60	13.85	28.93
Removing ethylene & carbon dioxide	6.29	25.09	16.85	29.54	27.96	21.11	17.47	44.62
Control	20.35	20.62	21.31	22.06	35.60	33.08	16.60	37.19

FIGURE 29. THE EFFECT OF REMOVING ETHYLENE FROM THE STORE ATMOSPHERE ON REDUCING SUGAR CONCENTRATION IN A SEALED ENVIRONMENT

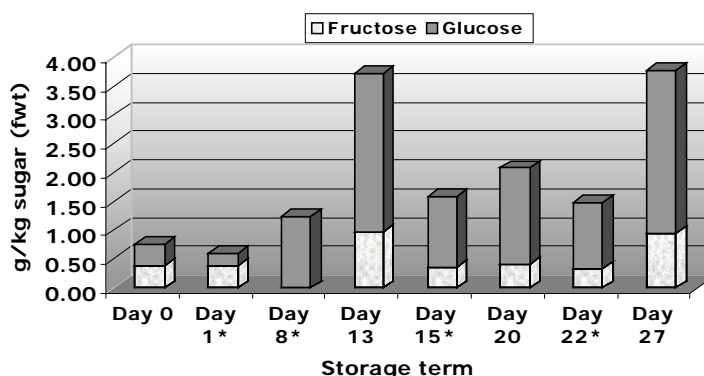


FIGURE 28. THE EFFECT OF ETHYLENE PRESENCE IN STORE ATMOSPHERES ON REDUCING SUGAR CONCENTRATION IN A SEALED ENVIRONMENT (CONTROL)

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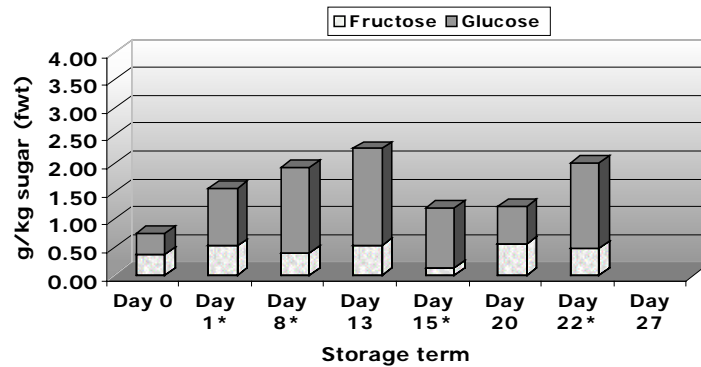
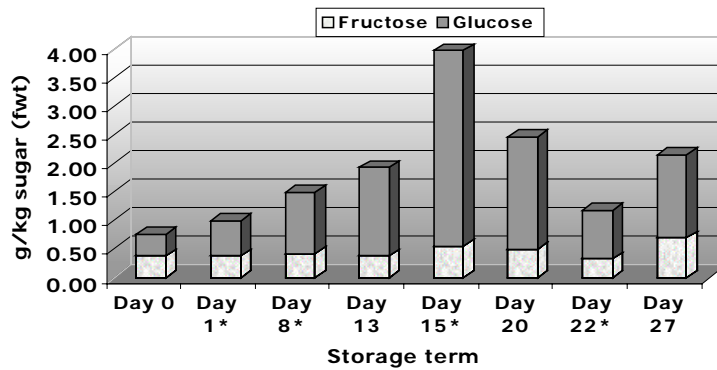
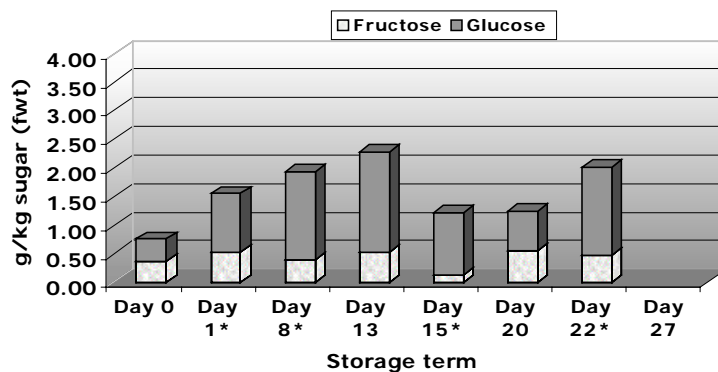


FIGURE 30. THE EFFECT OF ELEVATING CARBON DIOXIDE LEVELS IN THE STORE ATMOSPHERE ON REDUCING SUGAR CONCENTRATION IN A SEALED ENVIRONMENT



Again the control samples display the negative effect of C₂H₄ exposure on reducing sugar concentration. The trends in concentration over time are similar to the control samples in the leaky stores. However in the second half of the storage term the reducing sugar concentrations are lower in these sealed containers. The impact of C₂H₄ exposure is reduced in an environment where exchange with ambient air is limited (excepting intentional ventilation).

FIGURE 31. THE EFFECT OF REMOVING ETHYLENE AND CARBON DIOXIDE FROM THE STORE ATMOSPHERE ON REDUCING SUGAR CONCENTRATION IN A SEALED ENVIRONMENT



The effectiveness of the various methods is influenced by the extent of gas exchange with ambient air. Therefore the outcome is different in this situation. The removal of C₂H₄ from the store atmosphere is not as beneficial. The same general pattern of results was observed (With the exception of day 27), but the levels here were on most occasions slightly higher.

Elevated CO₂ levels were not as advantageous in the sealed atmosphere. Again the trend is comparable to the equivalent treatment in the leaky containers, but the reducing sugar values are generally higher. The glucose content was more sensitive to changes in the ambient CO₂ levels than fructose.

On a number of occasions the methods of removal/inhibition seem to be more detrimental than the exposure to C₂H₄ itself. This is most evident when removing C₂H₄ alone and elevating CO₂ levels.

The result of removing both C₂H₄ and CO₂ under these conditions was not clear. The pattern seems somewhat erratic, however it was most similar to the control graph. The reducing sugar levels are lower than that of the control on only two occasions. Implying this treatment also has a disruptive influence, but to a lesser extent.

Comparing all results to the control proved that none of the treatments were useful in a sealed environment. Even combining two partly successful treatments (determined from the leaky stores results) has no extra advantage if the conditions of use are not appropriate.

Overall, the reducing sugar concentrations resulting from the three methods employed in the sealed containers found that the most effective in maintaining crop quality was removing both C₂H₄ and CO₂. When odd values such as Day 13 (prolonged exposure) and Day 27 are excluded, the treatment of removing C₂H₄ could provide crop with a lower reducing sugar content. This illustrates the extent to which ambient conditions can influence the storage environment and any procedures undertaken.

The leaky containers, which undergo some unintentional exchange with ambient air, most resemble real potato storage facilities.

Conclusions

Exposure to ethylene gives rise to an increase in reducing sugar concentration and lowers the processing quality of potato tubers. The impact on reducing sugar levels is greater in a normal leaky storage facility, where some exchange with ambient air is expected.

Creating elevated levels of carbon dioxide (~1.5%) in the store could help to inhibit the effect of ethylene on the reducing sugar levels. Extreme care would have to be taken to ensure adequate ventilation was available. Any sizable increase in carbon dioxide (through respiration) above the applied dose could nullify the desired effect and cause sugars to increase as a result.

Removing ethylene from the store atmosphere, by means of an adsorbent material can be beneficial in preserving crop quality.

Those adsorbent systems tested (Activated Charcoal and Carbosieve SIII resin) were not 100% successful in scrubbing ethylene from the storage atmosphere. The efficacy was heavily dependant upon the local environmental conditions. The traps were much more effective in a leaky situation (even with the greater impact of ethylene exposure) than in a closed system without any exchange with ambient air.

The gas balance and most likely the oxygen availability seem to be important in the performance of the removing/inhibiting of ethylene action on the potatoes. The correct ambient conditions are imperative to the success of the adsorbent system.

Ideally the adsorbent system would be as close to 100% efficiency as possible. The adsorbents examined were highly sensitive to ethylene and are good options to involve in developing an improved system. The key feature that remains to be addressed is determining the simplest and most practical means of passing the store air over/through an adsorbent. The optimal operational procedure for doing this would also have to be assessed (including air flow-rate and regeneration-how and when).

Modifying store atmospheres is a practical option for minimizing the effect of standard thermal fog application of CIPC on the processing quality of stored potatoes. The benefit of the treatment in a large commercial potato store and any effect on CIPC efficacy has yet to be established.

A further option with potential in minimizing the effect on fry colour is the use of catalytic converters on fogging machines to reduce the production of harmful volatiles.

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