CONTROLLED ATMOSPHERES – A EUROPEAN PERSPECTIVE

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ABSTRACT

There have been many changes and developments in the technology of generation and application of controlled atmospheres (CA) since the resurgence of interest in their use for storage protection and shelf-life preservation in the 1970’s. Their capabilities are now backed-up by extensive temperature/CA concentration studies and by detailed fieldwork. However, despite the early promise, CAs are not widely used as a commercial alternative to prophylactic insecticide application and fumigation.

This paper discusses the important developments that have occurred in Europe in the stored commodity area. The loss of methyl bromide as a fumigant, poses a logistical and economic challenge for quality control and CAs offer one of the few alternatives for safe commodity storage. Consumer pressure for the removal of all toxic chemicals from the food chain is still the main driving force behind the largest potential change in the way stored commodities are protected. Reliance will have to be placed on cooling and drying strategies but with global warming and warmer longer summers for Europe, CAs may be required to cover the immediate post-harvest period before cooling becomes effective. CAs have also shown potential for use in combination with heat for certain commodity treatments where treatment time is critical.
CONTROLLED ATMOSPHERES

The Potential

In 2000, the Methyl Bromide Technical Options Committee (MBTOC) reported 12% of global methyl bromide (MB) production, approximately 9,000 tonnes, was used as a fumigant on durables including wood (Banks, 2002). Durables are commodities with a low moisture content that can be stored for long periods at normal temperatures without deterioration, if managed so that insects, mites, rodents and birds are excluded and fungal attack is prevented. These commodities include grains, oilseeds, dried fruits, nuts and cereal-based milled products. The 2005 phase out of MB in non-Article 5(1) (developed) countries (Anon, 2003), which includes Europe, is almost upon us. This change will bring extra costs and these may be substantial if MB cannot simply be replaced with another fumigant. There will certainly be problems adapting the new techniques to prevailing commercial and regulatory environments (Banks, 2002).

Many European supermarkets are requiring suppliers and farmers around the world to adopt IPM and environmental certification schemes. These supermarkets have established a set of standards on ‘Good Agricultural Practice’ in horticultural production called EUREP-GAP (FoodPlus, 2001). This requires growers to provide written justification of MB or other fumigants used and they have to demonstrate they have assessed the alternatives (Moeller, 2002). The agreement does not allow use of pesticides banned in the European Union (EU), therefore farmers outside the EU intending to supply EU supermarkets will be unable to use MB after it is phased out, if there are viable alternatives. Many former uses of MB in non Article 5(1) countries have already been replaced by phosphine for stored products. In most cases this tops the list of alternatives, which includes combinations of phosphine and CO₂, with raised temperatures and high or low pressures, controlled atmospheres (CAs), heating and vacuum-hermetic treatments (Bell, 1996a). While the limited choice of alternatives is strategically undesirable, at present the techniques available can achieve effective disinfestation of almost all stored products without recourse to MB (Anon, 2003). There are opportunities within Europe for CAs to replace MB and, through the dictates of the supermarkets, throughout the globe. In the present economic climate, while CAs may not be the first choice replacement for MB, they do offer some options for any given control situation.

Treatments with CAs based on CO₂ and nitrogen (N₂) offer an alternative to fumigation with toxic gases for insect pest control in stored products, but usually at an increased cost. They are effective in preventing the growth of fungal pests while under gas, but growth will restart once the CA is withdrawn. CAs do fulfil a specific niche where other fumigants are unacceptable such as in treating organic foods as
they leave no residues, nor do they affect the quality of the commodity (Navarro et al., 2002). A highly gas-tight structure is required for CAs to be economically feasible. Even so, CAs are limited by needing long exposure times for complete mortality (Navarro and Jay, 1987) but the times required may not be very much longer than those for phosphine fumigations (Navarro and Donahaye, 1990). If a rapid fumigation is required, a raised temperature should be considered (Navarro et al., 2002) as this will shorten lethal times (Adler, 1997; Rindner et al., 2001). In bulk products energy costs to heat the product before or after CA exposure may be high (Adler et al., 2000). There may be problems with quality damage but a safe window may be found between thresholds for control and damage.

Data on exposure times for control using CAs are available for many species and stages of stored product pests under particular sets of conditions (Annis, 1987; Bell and Armitage, 1992; Bell, 1996b). Most species are completely controlled by exposures ranging from 15 days with high CO₂ levels to 21 days with low O₂ at 25-29°C (Banks et al., 1991), though there are always exceptions and knowledge of the target pest is essential.

Methods for Generation

CAs, created by adding nitrogen (N₂) to an enclosure, or by adding atmospheres generated by the combustion of propane, require that there be a maximum of 1% O₂ for effective control, though 4% O₂ may be effective for population suppression (Conyers and Bell, 2007). For such low O₂ atmospheres to be achieved, the continuous application of the CA is required. Depending on the size of operation, CO₂ and N₂ can be transported to the site in cylinders, minitanks or in bulk, the only viable options in the absence of a local industrial source. N₂-based controlled atmospheres are in commercial use in Australia in an export grain terminal in bins originally designed and equipped for methyl bromide treatments (Cassells et al., 1994).

Three systems exist to provide N₂ on site. On-site generation of N₂-based atmospheres have made these CAs more competitive in price and convenience (Navarro and Donahaye, 1990; Banks et al., 1991; Bell et al., 1993; 1997). Alkane combustion units are suited to this requirement and systems capable of providing a low (<1%) O₂ atmosphere have been developed (Storey, 1980; Soderstrom et al., 1984; McGaughey and Akins, 1989; Bell et al., 1991).

The second system is known as pressure swing adsorption (PSA). In this process, compressed air is passed through a bed of molecular-sieve coke. The O₂ is separated due to its different rate of adsorption with the N₂ passing through the bed and into a holding tank. Two beds work alternately with one pressurised with incoming air while the other is returned to atmospheric pressure, releasing the more strongly
sorbed gases to waste. The O₂ content in the output gas depends upon size of plant and the airflow used. Some systems can reduce O₂ content to less than 0.3% at a flow rate of over 100 m³/h.

The third system is based on filtration of compressed air through membranes, which differentiate between O₂ and N₂. The semi-permeable membranes contain thousands of hollow membrane fibres capable of withstanding high pressures. Incoming air at 100-150 psi (7-10 bar) passes along the heated fibres and the gases are separated by their differential rates of diffusion. The O₂ permeates through the fibre walls, leaving N₂ whose purity is limited by flow rate and temperature. Output from plants can be scaled to meet local requirements by provision of larger capacity separators and hence a similar range of treatment capacities exists to that available for PSA. Both these latter systems have a high electrical power requirement.

Hermetic storage is another method of CA production. The O₂ can be reduced to 3-6% and CO₂ elevated to 12% (Varnava, 2002) combining the benefits of both types of CA. The time needed for O₂ depletion depends on moisture content (m.c.) and temperature of the commodity. A 67-m long “Silobag” with 12.5% m.c. wheat reduced the O₂ to an average of 10.4% and raised the CO₂ to 13.0% after 100 d whereas 16.4% m.c. wheat in a similar bag had an average O₂ of 5.6% and an average CO₂ of 22.8 after a similar length of time (Bartosik et al, 2003). However high moisture content increases the risk from mould and loss of germination and taste qualities.

A reduction in atmospheric pressure (760 mm Hg) is another way of generating a low O₂ CA. To control storage insects, the pressure must be reduced below 100 mm Hg (Navarro et al, 2002). Mortality of all life stages increased with increasing temperature with eggs as the most tolerant stage. Practical treatments of 2-5 days duration with 75 mm Hg at typical room temperature 22.5°C have been found effective against some pests (Hulasare et al, 2003).

There is no method for on-site CO₂ generation. Disinfestation using CO₂ at normal pressure can be achieved within a few days at elevated temperatures. Bagged or packaged commodities can be treated by CO₂ in chambers, gastight containers or in well-sealed stacks. Success of the treatment relies on the quality of the sheeting and the completeness of the seal of the between canopy sheet and ground sheet. A pressure test is conducted to check for gas tightness of the enclosure. Treatments with similar levels of CO₂ have been carried out in containerised cargo whilst in transit (Banks, 1988).

The time of exposure required for high CO₂ atmospheres can be reduced if the treatment is combined with pressure alterations. Application of CO₂ under high pressure (15-20 bar) can achieve good control with treatment times as short as 15-150
min, and efficacy can be further increased by a rapid decompression time (Riudavets et al., 2003). Effectiveness can be limited by the rate that gas penetrates into the commodity, and therefore the choice of product for treatment with this technique is important. Higher temperatures are beneficial and significantly shorter treatment times are achieved. In this combination, CO₂ acts more rapidly than MB, and therefore is an alternative for some export situations. Most stored products are disinfested in a few hours at pressures between 10 and 37 bar (Prozell and Reichmuth, 2001).

**EUROPE**

The main driving force in Europe for the use of CAs to control insects in stored products is as a replacement for MB. Different countries have shown different approaches for the replacement of MB. Some countries (Norway, Sweden, Denmark and for soil Holland and Germany) have banned using MB and to a certain extent this has helped find replacements but CAs have not been the first choice. This difference of approach across Europe is also seen in the registration for CAs. For some countries such as Germany, Holland and Israel, registration is required, while others like France and Italy have no regulation, with the UK taking the middle ground with registration for CO₂ but not for N₂ as the latter acts only by deprivation of O₂.

**Bulk commodities**

Until recently, for various technical reasons CO₂-based CAs were preferred to N₂-based ones for use on bulk grain. Recent developments in the on-site generation of N₂-based CAs have made these atmospheres more competitive in price and ease of application (Bell et al., 1993; 1997). Work in the UK has shown that grain stored in silos can be held under burner-generated atmosphere for several weeks at a cost of less than US$1/tonne of grain (Bell et al., 2001). Provision of a gas-proof sheet over the grain surface reduces by 90% the flow rate required to keep the O₂ at the required level (McGaughey and Akins, 1989). Further improvements can be made with sealing of the auger and all leakage sources around the base (Conyers et al., 1996; Bell et al., 1997). Burner gas CA can also be used for floor-stored grain with careful preparation and management (Conyers et al., 2001). The flow rate required to hold the O₂ at 1% in a plastic-sheet-lined box-shaped bulk (375 tonnes) was similar to a silo of similar capacity:

\[ 4.965 + (0.011 \times \text{tonne of bulk}) \text{ m}^3/\text{h} \]

even with a seal that was not as good as that for a silo (Bell et al., 2001). CAs from an exothermic generator have also been tested as a replacement for MB for disinfestation of dried figs for export in Turkey (Damarli et al., 1998). Complete mortality of *Ephesia cautella* (Walk.) was achieved in 10 tonne lots treated with <1% O₂ and 10-15% CO₂ at 25°C for 30 hours. A similar system was used to treat a
hotspot, which had been artificially induced with *Sitophilus granarius* (L.). The temperature of a hot spot, 38°C, allowed a burn gas treatment of the infested grain to be successfully completed in just two-weeks, with a reduction in temperature to 17°C by the end of the test (Conyers *et al*, 2003). Higher O<sub>2</sub> levels (~5%) have shown potential for insect population control with burn gas or N<sub>2</sub> for insects (Johnson *et al*, 2001) and mites (Conyers and Bell, 2007) and a maintenance CA treatment of 5% O<sub>2</sub> prevents reinfestation (Johnson *et al*, 2001).

In Germany, 5,239 metric tons of CO<sub>2</sub> and N<sub>2</sub> were sold for plant protection in 1998 (Anon, 1999) however grain and other food products would account for <5% of this. Concrete silos have been used for N<sub>2</sub> and CO<sub>2</sub> treatments (Adler *et al*, 2000). Depending on temperature and leakage, costs for effective treatment were between US$1.5/tonne for moderately leaky to $7.5/tonne for very leaky structures at 15°C with these costs reduced to US$1.38/tonne at 20°C. This does not include the cost of initial sealing but this can be spread over many years, as an effective seal with durable materials will last for some time. Flourmills have also been treated with a combination of CO<sub>2</sub> and heat at an estimated cost of US$5-7.5 per m<sup>3</sup> (Corinth and Reichmuth, 1995). This was not economical compared to MB fumigation with a range of US$2-3 per m<sup>3</sup>.

EcO<sub>2</sub> B.V. (formerly Ecogen) of Holland have developed a system for using CAs generated by burning propane or methane (natural gas) at a cost similar to MB. This system is in use commercially at the port of Rotterdam where 36 chambers, sited in various warehouses, have capacity for treatment of 80,000 tonnes of commodities a year. Additional capacity is under construction to allow treatment of freight containers. Treatments are also carried out in barges, bakeries, factories, warehouses, silos, vehicles and aircraft. There are computerised systems that control levels of O<sub>2</sub>, relative humidity and temperature. For buildings and silos mobile installations are used. Heat and low O<sub>2</sub> are being used as an MB replacement with 24-h treatments possible. The technique has been developed to treat wooden packaging material and pallets used for export and also for containers. With all these new developments the company is actively expanding in Holland and to Germany, Belgium, and the UK.

In Cyprus and Israel, hermetic storage is an important method for storage. There are five different structure types sealed hermetically in Cyprus with a total capacity of 85,000 tonnes, which is 30% of total storage capacity (Varnava, 2002). The latest of these are 12,000 tonne bunkers, which have a total treatment cost including labour, plastic sheet liner and maintenance of US $1.83/tonne. One-year storage losses were 0.32% and after 3 years they were only 0.96% (Varnava and Mouskos, 1997). This method protects against insects, rodents, and birds and allows access to international bulk grain markets (Varnava, 2002). In Israel, hermetic or sealed storage amounts to 20,000-60,000 metric tonnes which is at least 10% of annual grain consumption and comprises about 50% of the local grain storage capacity (Adler *et al*, 2000). CAs based on CO<sub>2</sub> are also used on several other commodities and in 1998, 330 metric tonnes of dates were treated. This CA is also used for treatment of wheat, seeds and herbs. 30-50 tonnes of CO<sub>2</sub> are used annually for treatment of grain in Italy (Adler *et
al, 2000). Burner gas has also been tried and the CA produced by this method was US$1-3/tonne more expensive than conventional fumigation (Contessi et al, 2001).

**Bagged and packaged commodities**

One of the most recent developments for this type of commodity has been the mobile plastic enclosure, 15 m³, with the top zipped to the bottom to form a gas tight seal (Navarro et al, 1988; Navarro and Donahaye, 1990; Navarro et al, 1994). This has been developed in Israel and is known as the ‘Volcani Cube™’ or ‘GrainPro Cocoon™’ (Navarro et al, 1999). It is very versatile and has been used with 60-80% CO₂ in crates on pallets. The gas is introduced in only 1 hour using high pressure. The quality of dates stored this way was unaffected and *Carpophilus* spp. were controlled (Navarro and Donahaye, 2000). These enclosures have also been used to hold a vacuum for 3-7 days at 22-75 mm Hg to disinfest cocoa beans (Finkelman et al, 2001; Navarro et al, 2001). All the target insects, *E. cautella* and *Tribolium castaneum* (Herbst) were killed, even using the minimum exposure time. The set up has also been used for hermetic storage with maize (Ferizli et al, 2001). The O₂ was reduced to 0.2% in 13 days and the CO₂ rose to 12% and these conditions remained stable for a further 50 days.

CO₂ under high pressure is in limited use in Germany to treat beverages and spices (Prozell and Reichmuth, 2001; Prozell et al, 1997). However this needs expensive chambers with a high investment cost of $100,000-500,000 but despite this there are commercial chambers in operation that are used for high value commodities like spices, herbs, cocoa, nuts and dried fruit (Adler et al, 2000).

In the UK there have been recent developments with burner gas CA, 0.5% O₂ and 13% CO₂ combined with heat. Bell and Conyers (2002) showed that three species of rice pests can be killed in 24h at 44°C; four pests of herbs and spices in less than 16h at 40°C; 6 pests of dried fruits and nuts at 38°C in less than 16h; and four pests of cocoa and coffee in less than 16h at 36°C. This treatment did not affect the product quality and this, combined with the speed of treatment, showed that it had the potential to replace MB quarantine and pre-shipment treatments.

**Artefacts**

Nitrogen and CO₂ are being increasingly used in the treatment of museum artefacts for quarantine and non-quarantine treatments (Gilberg, 1991; Reichmuth et al, 1992; Selwitz and Maekawa, 1998). The long treatment times for CA use can more easily be accommodated as a rapid treatment is not always necessary (Reichmuth, 2002). Many museums have access to chambers, but treatments can also be carried out in portable plastic enclosures, which are available for hire from Rentokil Initial plc in the UK for CO₂ treatments (Porck and Teygeler, 2000) and have been used
successfully for insect and mite control (Newton, 1990). Thermo Lignum® has developed another automated system, which uses heat and low O₂, in the UK. This utilises temperatures up to 36°C to produce more effective treatments of artefacts (Roux and Leary, 2001). In Holland, EcO₂ B.V. has also been using their automated burner gas technology the treatment of furniture and artefacts.

A new, portable, EU-financed, N₂ CA system has been developed in which the enclosure is custom-built around the artefact. The O₂ level is reduced by a series of atmosphere reductions by use of the compressor and by N₂ introductions from the CA generator (Akerlund and Bergh, 2001; Conyers, 2001). It is now in use in Sweden, Italy and Spain.

Insect control in furniture and artefacts in churches has been undertaken in Germany with CO₂ (Binker, 2001). Whole buildings have been covered in gas-tight sheeting and air-inflated balloons used to decrease the treatment void. Difficulties with sealing resulted in excessive use of the gas which was maintained at 70% through an automatic top-up system from a storage tank. About 1,000 tonnes in total were required to disinfect the largest church.

CONCLUSIONS

There has been some growth in the usage of CAs within Europe but it has been mainly in the more specialised areas of usage such as for high value commodities, and in museums. The development of the new plastic containers is unlikely to have a large impact in Europe as they are better used for small-scale applications found chiefly in Article 5(1) countries. Hermetic storage is still an important method in those countries that have traditionally relied on it and where the higher ambient temperatures are a benefit for this technique.

CAs have not replaced chemical fumigants for bulk treatments and until a ban on these substances comes into force due to environmental or consumer pressure, then it appears that this situation is unlikely to change. Even with the end of MB usage approaching, there is not much scope for change at present. With new fumigants, such as sulphuryl fluoride, being registered in several countries in Europe, the opportunities will lessen. It is perhaps with the powerful influence of the supermarkets, which affect the pest control strategies of suppliers so radically, that the future for increased CA usage may lie. CAs will nevertheless remain as a viable option for specialised sectors of stored product management for the foreseeable future.

REFERENCES


