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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 CO_2, 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 CO_2 and nitrogen (N_2) 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 CO_2 levels to 21 days with low O_2 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 (N_2) to an enclosure, or by adding atmospheres generated by the combustion of propane, require that there be a maximum of 1% O_2 for effective control, though 4% O_2 may be effective for population suppression (Conyers and Bell, 2007). For such low O_2 atmospheres to be achieved, the continuous application of the CA is required. Depending on the size of operation, CO_2 and N_2 can be transported to the site in cylinders, minitanks or in bulk, the only viable options in the absence of a local industrial source. N_2-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 N_2 on site. On-site generation of N_2-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%) O_2 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 O_2 is separated due to its different rate of adsorption with the N_2, 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 O_2 content in the output gas depends upon size of plant and the airflow used. Some systems can reduce O_2 content to less than 0.3% at a flow rate of over 100 m^3/h.

The third system is based on filtration of compressed air through membranes, which differentiate between O_2 and N_2. 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 O_2 permeates through the fibre walls, leaving N_2, 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 O_2 can be reduced to 3-6% and CO_2 elevated to 12% (Varnava, 2002) combining the benefits of both types of CA. The time needed for O_2 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 O_2 to an average of 10.4% and raised the CO_2 to 13.0% after 100 d whereas 16.4% m.c. wheat in a similar bag had an average O_2 of 5.6% and an average CO_2 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 O_2 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 22.5ºC have been found effective against some pests (Hulasare *et al*, 2003).

There is no method for on-site CO_2 generation. Disinfestation using CO_2 at normal pressure can be achieved within a few days at elevated temperatures. Bagged or packaged commodities can be treated by CO_2 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 CO_2 have been carried out in containerised cargo whilst in transit (Banks, 1988).

The time of exposure required for high CO_2 atmospheres can be reduced if the treatment is combined with pressure alterations. Application of CO_2 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, CO_2 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 CO_2 but not for N_2, as the latter acts only by deprivation of O_2.

Bulk commodities

Until recently, for various technical reasons CO_2-based CAs were preferred to N_2-based ones for use on bulk grain. Recent developments in the on-site generation of N_2-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 O_2 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 O_2 at 1% in a plastic-sheet-lined box-shaped bulk (375 tonnes) was similar to a silo of similar capacity:

$$4.965 + (0.011 \text{ x tonne of bulk}) \text{ m}^3/\text{h}$$

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 *Ephestia cautella* (Walk.) was achieved in 10 tonne lots treated with <1% O_2 and 10-15% CO_2 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, 38ºC, allowed a burner gas treatment of the infested grain to be successfully completed in just two-weeks, with a reduction in temperature to 17ºC by the end of the test (Conyers *et al*, 2003). Higher O_2 levels (~5%) have shown potential for insect population control with burner gas or N_2 for insects (Johnson *et al,* 2001) and mites (Conyers and Bell, 2007) and a maintenance CA treatment of 5% O_2 prevents reinfestation (Johnson *et al,* 2001).

In Germany, 5,239 metric tons of CO_2 and N_2 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_2 and CO_2 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 15ºC with these costs reduced to US$1-3.8/tonne at 20ºC. 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_2 and heat at an estimated cost of US$5-7.5 per m^3 (Corinth and Reichmuth, 1995). This was not economical compared to MB fumigation with a range of US$2-3 per m^3.

EcO_2 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_2, relative humidity and temperature. For buildings and silos mobile installations are used. Heat and low O_2 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_2 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_2 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 m^3, 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% CO_2 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 O_2 was reduced to 0.2% in 13 days and the CO_2 rose to 12% and these conditions remained stable for a further 50 days.

CO_2 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% O_2 and 13% CO_2, 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 CO_2 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 CO_2 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 36ºC to produce more effective treatments of artefacts (Roux and Leary, 2001). In Holland, EcO_2 B.V. has also been using their automated burner gas technology the treatment of furniture and artefacts.

A new, portable, EU-financed, N_2 CA system has been developed in which the enclosure is custom-built around the artefact. The O_2 level is reduced by a series of atmosphere reductions by use of the compressor and by N_2 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 CO_2 (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 disinfest 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.

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