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### GENERATING USABLE AND SAFE CO<sub>2</sub> FOR ENRICHMENT OF GREENHOUSES FROM THE EXHAUST GAS OF A BIOMASS HEATING SYSTEM

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**ABSTRACT** CO<sub>2</sub> enrichment of greenhouses has been well proven to improve crop production whether it occurs from liquid CO<sub>2</sub> or combustion of fossil fuels. The main objective of this research is to demonstrate the use of a renewable fuel, biomass, to enrich a greenhouse with CO<sub>2</sub>. Biomass, in the form of wood chips or pellets, has received considerable interest as a sustainable and economically feasible alternative to heat greenhouses. Therefore, there is an opportunity to convert exhaust gases from a greenhouse wood heating system into a useful resource. Carbon dioxide can be extracted from flue gas via membrane separation which could prove to be an economical alternative to electrostatic precipitators. This technique has shown a lot of potential for large industries trying to reduce and isolate CO<sub>2</sub> emissions for sequestration and could be applicable to the greenhouse industry for enrichment. Additionally, some research has been done with wet scrubber using particular catalysts to obtain useful plant fertilizer. Sulphur (SO<sub>2</sub>) and Nitrogen (NO) emissions can be stripped out of flue gas to form ammonium sulphate as a by-product valuable to fertilizer markets. The potential of these techniques will be reviewed while experiments conducted at the Macdonald Campus of McGill University will begin in summer 2010.

**Keywords:** Exhaust gases, wood pellets, biomass, biogas, carbon dioxide, CO<sub>2</sub> reduction, CO<sub>2</sub> fertilization, air quality, natural gas, photosynthesis, scrubber, membranes, gasification.

**INTRODUCTION** A worldwide shift in policy is currently forcing most industries and governments to reduce greenhouse gases and alleviate their dependence on fossil fuels. The horticulture industry has not been spared of these changes. In northern climates, greenhouse operators must address this issue by balancing energy efficiency through structural or fuel saving techniques while keeping growing conditions optimal in order to compete with an international market. Specifically, heating requires improvements as it represents around a quarter of operational costs depending on the energy source (oil, gas, electricity, or biomass). Recent fluctuations of fossil fuel prices have increased the necessity to explore alternative systems and have allowed biomass heating to become an

economically viable option (Chau, Sowlati et al. 2009). Biomass has been recognised as a sustainable renewable fuel alternative that can also reduce greenhouse gas production (Petersen Raymer 2006). The combustion emissions from biomass are lower than from fossil fuels but still occur due to the natural thermo-chemical reaction of combustion. However, using waste exhaust gases from a heating system can be beneficial to greenhouse plants by providing a viable source of carbon dioxide (Hicklenton 1988). CO<sub>2</sub> enrichment is one of the commonly accepted techniques to enhance photosynthesis resulting in improved yields and income (Chalabi, Biro et al. 2002). Enrichment is commonly practiced with pure CO<sub>2</sub> in bulk or from combustion of hydrocarbon fuel (natural gas or propane). Usually, these fuels are employed in dedicated burners to provide CO<sub>2</sub> while a separate heating system provides most of the heat to the greenhouse (Hanan 1998). Enrichment from the exhaust of a natural gas or propane heating system has been proven feasible but using renewable energy could have further benefits. However, very little research has been performed on the feasibility of using CO<sub>2</sub> from a biomass heating system. The greenhouse gases emissions from these units are significantly lower on a life cycle basis when compared to fossil fuels and could be lowered further through enrichment and absorption by the crops in the greenhouse. While the overall system would not be considered carbon neutral throughout its complete life cycle, CO<sub>2</sub> enrichment from exhaust gases could still be referred as a mean to reduce carbon emissions directly at the source. Such an initiative could be part of carbon market and sequestration incentive. Furthermore, the use of biomass as the main fuel could improve the sustainability of greenhouse management.

Practically, CO<sub>2</sub> enrichment from exhaust gas of biomass boilers is still challenging and expensive considering the current practices and exhaust gas composition (Chau, Sowlati et al. 2009). However, recent technological development could help reduce cost and make this process a possibility. This paper provides an overview of different CO<sub>2</sub> enrichment benefits and practices from exhaust gas recovery. The usual composition of exhaust gases will be detailed to understand the various challenges in obtaining clean CO<sub>2</sub> from heating systems. Progressively, this review will concentrate on the potential of CO<sub>2</sub> enrichment from biomass flue gas. For that purpose, common techniques will be addressed, but the focus will remain on maturing technologies that may be applicable.

**CO<sub>2</sub> ENRICHMENT BENEFITS** Carbon dioxide is fixed and reduced into simple sugars during photosynthesis. The series of carbon-fixation reactions is called the Calvin cycle. However, CO<sub>2</sub> reaches this cycle through one of three metabolic pathways depending on the plant species (Graham, Graham et al. 2003). The C<sub>3</sub> pathway is used by the majority of plants on Earth such as common cereal grasses, soybeans and potatoes. The C<sub>4</sub> pathway is very efficient at fixing CO<sub>2</sub> and achieving higher net rates of photosynthesis which makes crops such as corn and sugarcane thriving. The CAM photosynthesis is common for plants growing in arid and desert conditions. The C<sub>3</sub> plants are the most common greenhouse crops, but they are less efficient at fixing CO<sub>2</sub> around ambient CO<sub>2</sub> levels. This reduced efficiency is due to photorespiration, which occurs in sunlight and is the consequence of the RuBisCO enzyme combining with oxygen instead of CO<sub>2</sub>. The plant releases some CO<sub>2</sub> during the day instead of O<sub>2</sub> and as much as half of the CO<sub>2</sub> fixed may be returned to the atmosphere (Graham, Graham et al. 2003). The main consequence of photorespiration for greenhouse operators is reduced biomass yield.

The more evolved metabolic mechanisms of C<sub>4</sub> and CAM plants reduces photorespiration problem directly. For C<sub>3</sub> plants, raising CO<sub>2</sub> concentrations in a greenhouse limits this process by reducing the binding affinity of RuBisCO in the plant to inadvertently absorb O<sub>2</sub> (Mortensen 1987). Consequently, yields are improved because of a higher photosynthetic rate, creating more carbohydrates which translate into increased biomass (Sánchez-Guerrero, Lorenzo et al. 2009). Yield increases are observed in various plants whether it is through larger total dry mass, bigger and more numerous fruits, larger leaves and flowers as well as earlier flowering time and reduced overall production time. High carbon-dioxide levels have also been reported to promote hormonal responses in terms of enhanced secondary compounds such as essential oils and antioxidants (Tisserat and Vaughn 2001). Benefits are widely accepted for general commercial greenhouse crops, including fruits, flowers and vegetables. Yields have been observed to increase from 21 to 61% in dry mass. Each crop responds differently and has an optimal enrichment CO<sub>2</sub> concentration level. On average, greenhouse crops benefit from concentrations between 700 and 900ppm (Wittwer and Robb 1964; Mortensen 1987; Willits and Peet 1989; Critten and Bailey 2002; Jaffrin, Bentounes et al. 2003; Tisserat, Vaughn et al. 2008; Sánchez-Guerrero, Lorenzo et al. 2009). These optimal levels can overcome the C<sub>3</sub> pathway inefficiency, but concentrations higher than 1500ppm can cause permanent damage to some plants. Moreover, injecting CO<sub>2</sub> into a greenhouse can counterbalance irradiance reductions. For instance, CO<sub>2</sub> enrichment can fully compensate for a 30% reduction in sunlight (Mortensen and Moe 1983). Higher CO<sub>2</sub> concentration decreases the leaves stomatal aperture leading to lower transpiration rates which correlates into enhanced water use efficiency (Leakey, Uribe-larrea et al. 2006). Since less water is necessary under enrichment conditions, nutrient uptake by the plant is increased (Sánchez-Guerrero, Lorenzo et al. 2009).

**COMMON PRACTICES FOR CO<sub>2</sub> ENRICHMENT** CO<sub>2</sub> enrichment is recommended from sunrise until sunset and the rate will depend mostly on crop type, crop age, CO<sub>2</sub> loss and ventilation rates (Mortensen 1987). Ventilation is the major parameter that has the most influence on CO<sub>2</sub> enrichment performance. In winter, since ventilation is reduced, CO<sub>2</sub> can reach a level close to depletion if not supplied, while in summer, during full ventilation, most of the CO<sub>2</sub> injected will be vented out. Economically, it is therefore preferable to reduce enrichment during high ventilation periods. One management strategy is to inject CO<sub>2</sub> only to prevent depletion, thus remaining at atmospheric levels (≈380ppm) while benefiting from some yield improvements and lower costs (Kläring, Hauschild et al. 2007). Other strategies involves maintaining concentration at atmospheric levels during ventilation period and enriching up to 800ppm when the greenhouse is kept closed (mornings and late afternoon of summer and most of winter) (Sánchez-Guerrero, Lorenzo et al. 2005). Passive cooling systems are also promising at reducing the necessity of frequent air exchanges and preventing substantial losses of CO<sub>2</sub>.

A common source of CO<sub>2</sub> is liquefied carbon dioxide from a pressurized tank and is a safe option to assure quality gas injection. (Wittwer and Robb 1964) Pure CO<sub>2</sub> facilitates control the desired concentrations but remains the most expensive source. (Hanan 1998) In comparison, fuel combustion is a cheaper alternative for both fixed and operational costs. (Hanan 1998) Propane is a popular fuel and consists of a mixture of 65% propane and 35% propylene. This later is phytotoxic following incomplete combustion.

(Hicklenton 1988) Depending on the access to the supply, natural gas for CO<sub>2</sub> enrichment only, is a safe, economical and popular alternative. (Hanan 1998)

**CO<sub>2</sub> ENRICHMENT FROM EXHAUST GASES** Exhaust gases taken from heating systems provide a “free” source of CO<sub>2</sub> for greenhouses. It can be considered free since it is a waste product of necessary heating but the method still requires investment for installation and maintenance (Hicklenton 1988). The technique bears some technical challenges but remains possible as long as optimal management strategies are followed, flue gas is cooled and toxic compounds are removed. Work by Chalabi et al (2002) have also confirmed significant economic benefit of CO<sub>2</sub> enrichment from exhaust gases over pure CO<sub>2</sub> (Chalabi, Biro et al. 2002).

**Optimal management strategies** Heating periods might not always coincide with CO<sub>2</sub> enrichment, requiring management strategies for optimal efficiency. Heating occur mostly at night (depending on climate) while CO<sub>2</sub> enrichment is required only during irradiance events typically during the daytime. A typical solution is to store the heat in a hot water or thermal fluid tank when producing CO<sub>2</sub> for the plants during the day. The hot fluid can then heat the greenhouse during the night via a forced air systems or radiation pipes (Chalabi, Biro et al. 2002). A second option, suggested for mild winter climates, is to enrich only in the mornings and late afternoon when solar greenhouse heating is at its lower levels. This morning/evening method proves to be useful since ventilation is typically not functioning during these time periods and increases enrichment efficiency (Sánchez-Guerrero, Lorenzo et al. 2005). It has been reported that injecting higher concentration of CO<sub>2</sub> than required, starting one hour before sunrise and for two subsequent hours, has produced similar results to continuous enrichment (Longuenesse 1990). In general, optimal enrichment procedures during the daytime will increase yields by 11% and this benefit increases to 24% when using heat storage strategies (Chalabi, Biro et al. 2002).

**Toxicity of main compounds** Theoretical combustion of hydrocarbons produces heat and emits Carbon dioxide and water vapour. However in practice, incomplete combustion generates compounds which can pollute the greenhouse atmosphere. If not treated, these can be detrimental to plant health as much as ultra-high CO<sub>2</sub> concentrations. The main compounds of interest produced during the combustion process are carbon monoxide (CO), nitrogen oxides (NO<sub>x</sub>), sulphur oxide (SO<sub>x</sub>), ethylene (C<sub>2</sub>H<sub>4</sub>), other VOCs, and fine particulates since they tend to be in higher concentrations in the exhaust gas of inefficient heating systems of greenhouses. (Hanan 1998)

Ethylene acts as a plant hormone which provokes early senescence (leaf death) in plants (Mortensen 1987). However, Hanan (1998) has concluded that ethylene can remain lower than the critical concentration of 50ppb as long as the flue gas CO does not exceed 50ppm (Hanan 1998). Still, even the best combustion systems using propane or natural gas might not avoid ethylene production but the concentration should remain low enough to be diluted and untraceable inside the greenhouse (Hicklenton 1988). Sulphur dioxide is produced only if sulphur is present in the fuel. For instance, SO<sub>2</sub> emissions were common when low quality kerosene was used, but are now significantly reduced with low-sulphur kerosene (less than 0.06% sulphur) (Mortensen 1987). Sulphur is found in biomass fuels but the resulting SO<sub>x</sub> emissions are generally considered minor combustion products (Van Loo and Koppejan 2008). For instance, wood pellets contain as low as

0.01% sulphur which makes SO<sub>x</sub> hardly measurable in stack (Todd October 6th 2008). Nonetheless, SO<sub>x</sub> should not be neglected since it remains one of the most important compounds for air pollution control (De Nevers 2000). Nitrogen oxides, whether in the form of NO or NO<sub>2</sub>, can be absorbed by plants and cause injuries such as chlorosis, necrosis or growth reduction (Mortensen 1987). NO<sub>x</sub> have been measured following enrichment using propane, kerosene, natural gas and biomass (Hicklenton 1988). It can reduce photosynthesis significantly at levels above 250ppb depending of the crop (Hanan 1998).

For injection of CO<sub>2</sub> in greenhouses, human health and safety have to be considered, and control measures must be applied. The source of the CO<sub>2</sub> can result in the production of hazardous compounds such as carbon monoxide which is very toxic for human and fine particulates which can cause respiratory problems. Compiled data from 2005 ASHREA are in Table 1. Indoor air quality standards for people are, for the most parts, stricter than the thresholds set for plants health. Therefore, respecting ASHREA standards should ensure clean greenhouse air quality for both workers and crops.

Table 1. ASHREA Standards to Indoor Environment

Compound		Concentration limit
Acrolein	C <sub>3</sub> H <sub>4</sub> O	0,02 ppm
Acetaldehyde	C <sub>2</sub> H <sub>4</sub> O	5,0 ppm
Formaldehyde	CH <sub>2</sub> O	0,1 ppm
Carbon Dioxide	CO <sub>2</sub>	3500 ppm
Carbon Monoxide	CO	11 ppm (8h)
		25 ppm (1h)
Nitrogen Dioxide	NO <sub>2</sub>	0,05 ppm
		0,25 ppm (1h)
Ozone	O <sub>3</sub>	0,12 ppm (1h)
Particulate		40 µg/m <sup>3</sup> (8h)
		100 µg/m <sup>3</sup> (1h)
Sulphur Dioxide	SO <sub>2</sub>	0,019 ppm
VOC		0,003 ppm

**Natural Gas and Other Hydrocarbons** Assuming proper combustion, natural gas is typically accepted by the industry to produce clean CO<sub>2</sub> from exhaust gas and is directly injected into the greenhouse (Chalabi, Biro et al. 2002). Chalibi et al (2002) reported that enrichment using natural gas typically increases fuel consumption by 25% from what is used for meeting the greenhouse heating requirements (Chalabi, Biro et al. 2002). However, this observed value could be reduced since it strongly depends on optimal enrichment strategies including system heat recovery efficiency. CO alarms are required inside the greenhouse since incomplete combustion of natural gas could be harmful, both for plants and humans. Water vapour can also be a concern and should be removed via condensers as it can cause fungus and mould growth within the glasshouse (Chau, Sowlati et al. 2009). Standard greenhouse practices dilute the exhaust gas with outside air which condense water vapour, decreases the flue gas temperature, and reduces harmful gas concentration to acceptable levels. The cool diluted gases are then distributed

throughout the greenhouse with standard circulation fans or perforated plastic tubes (Chalabi, Biro et al. 2002).

### **Unconventional Source**

Landfill Biogas Combustion of biogas, collected from a landfill, has been proven viable to supply both heating and CO<sub>2</sub> (Jaffrin, Bentounes et al. 2003). The extracted gas is directed into a combustion boiler which discharges the CO<sub>2</sub> inside a greenhouse once it is purified. Using biogas has its share of challenges considering it is a mixture of methane, carbon dioxide, residual oxygen and nitrogen along with hydrogen sulphide, various mercaptans, fat acids and more than 200 VOCs, all of which are below 100 ppm. However, since biogas is extracted from a heterogeneous landfill, its composition can vary. For instance, methane content can range between 23 to 54% depending on the conditions. The VOCs are predominantly destroyed once the gas is flared at over 900°C. Sulphuric acid is produced in the boiler from the reaction of SO<sub>2</sub> with water which increases corrosion. Rust appears in most exhaust gas recuperation system and can be avoided using stainless-steel equipment. A gas scrubber using a chemically reactive liquid purifies the gas from acid contaminants with periodic addition of NaOH or KOH to maintain pH above 8.0 (Jaffrin, Bentounes et al. 2003). To reduce risks of toxicity, the exhaust gas is cooled down and diluted up to 50 times with fresh air. Compounds such as CH<sub>4</sub>, CO<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>S, SO<sub>2</sub>, NO, NO<sub>2</sub>, C<sub>2</sub>H<sub>4</sub> and other VOCs are typically not detected at the exit of the scrubber after combustion (Jaffrin, Bentounes et al. 2003). However, Jaffrin et al (2003) reported that most toxic gases were found to be diluted and undetectable once injected in the greenhouse. Carbon monoxide, while detectable, was well below ASHRAE safety regulations (Jaffrin, Bentounes et al. 2003). Thereafter, they observed 30% yield increase in the supplemented greenhouse.

**BIOMASS HEATING SYSTEMS** Biomass resources such as wood residues, wood and grass pellets, agricultural residues or municipal solid waste can be appropriate fuels to provide both heat and CO<sub>2</sub> to a greenhouse. Biomass is acknowledged to be renewable by many governmental institutions and has proven to be profitable even compared to natural gas (Chau, Sowlati et al. 2009).

However, biomass combustion is not as clean as natural gas combustion. While it produces CO<sub>2</sub> and water vapour as well, it also leads to higher emissions of NO<sub>x</sub>, SO<sub>x</sub>, CO, and VOCs. Still, it must be reminded that the overall life-cycle greenhouse gas emissions of biomass compared to natural gas are much lower (Dones 2003). Therefore, more CO<sub>2</sub> is emitted at the stack of biomass boiler, but when considering resource extraction, transportation, transformation, use and disposal, and carbon fixation by trees, the carbon balance is better than with natural gas.

In terms of enrichment applications, combustion of dry and clean wood biomass can produce two times more useful CO<sub>2</sub> than natural gas for the same energy unit (Chau, Sowlati et al. 2009). Exact flue gas composition depends on furnace technology and efficiency. A well adjusted flow of oxygen should be pumped in the combustion chamber to limit VOCs and CO leakage. However, this process might cool down the exhaust gases prematurely to a point preventing conversion of CO into CO<sub>2</sub>. (Johansson, Leckner et al. 2004)

The greenhouse research center, “Centre d’information et de développement expérimental en sericulture” (CIDES), has performed an experiment using a corn stove as a fuel source to supply CO<sub>2</sub> to a greenhouse (Léveillé and Gendreau 1998). They reported that 1.7kg of CO<sub>2</sub> was produced from 1 kg of corn. For comparison, propane yields 3kg of CO<sub>2</sub> per 1 kg of fuel. The costs were approximated to be at 0.11CAN\$/kg for corn, 0.18CAN\$/kg for propane and 0.17CAN\$/kg of natural gas. These results reveal the potential of using biomass for CO<sub>2</sub> enrichment, but would need to be adjusted to the economic realities of the particular geographical location of application. Further consideration on the economics need to include the specific combustion efficiency of the system. The concentrations of the NO<sub>x</sub>, SO<sub>x</sub>, CO and ethylene were below toxicity levels while fine particulates were not listed in the report.

**Emission removal methods** Nowadays, VOC and CO emissions are limited by ensuring high temperature and proper oxygen injection in the combustion chamber (Jaffrin, Bentounes et al. 2003). The main undesirable emissions from biomass combustion are fine particulates which must meet local municipal regulations when vented outside. Therefore, when injecting biomass exhaust gas into a greenhouse, particulate levels must be lowered, as low as 40µg/m<sup>3</sup> according to ASHREA standards 2005, to respect workplace safety regulations. Reducing fine particulate concentration can be particularly costly. Scrubbers, cyclones and fabric filters are not always able to remove the fine particulate to the concentrations required. Electrostatic precipitators (ESP) are the only option to reduce the concentrations to acceptable levels. Unfortunately, an ESP can increase initial costs substantially and consequently decrease net present value of the whole system from 17 to 70%, making it only feasible for greenhouses larger than 7.5ha (Chau, Sowlati et al. 2009). Ultimately, a more affordable technique is required for fine particulates removal to practice safe and economical CO<sub>2</sub> enrichment from biomass. There are several methods to reduce undesirable emissions which can be categorised in two types (Devi, Ptasinski et al. 2003). The primary methods are modification and design choices made to the heating system itself while secondary methods are external to the heating system and can be added on.

Internal Modification The efficiency of biomass conversion into energy depends on the chosen thermo-chemical reaction as well as the system’s design. Internal modifications are important at reducing fuel consumption, pollution emissions and the costs of external modification. They may even alleviate the necessity of external modifications. Among the main thermo-chemical processes of biomass, combustion is the most well known and widely applied reaction for heating. Nonetheless, gasification is showing a lot of promises both in research and commercial applications (Devi, Ptasinski et al. 2003) (Murray 2010). Gasification converts biomass into a combustible gas mixture (syngas, comprised mostly of CO and H<sub>2</sub>) by combining low oxidation with high temperatures. At this level of oxidation, much less fine particulates will be emitted from the stack. By coupling a gasification chamber to a combustion chamber, the syngas is burned separately from the biomass fuel. With this design and an adequate level of air supply, fine particulates and undesirable gases can be reduced greatly. The energy efficiency for a gasification system is also higher than for combustion (Devi, Ptasinski et al. 2003). Net conversion efficiency for biomass combustion is reported to be at 20 to 40%. Gasification coupled with combustion can provide 40 to 50% net efficiencies (McKendry 2002). Consequently, gasification, along with a proper system design, could be a first step at facilitating CO<sub>2</sub> enrichment of greenhouses with biomass.

External Modification - Scrubbing systems Over the last decade, it has been observed that the adverse nitrogen oxides and sulphur oxides found in exhaust gases could be transformed into valuable by-products. Research suggested the conversion of NO<sub>x</sub> and SO<sub>x</sub> into nutrients for greenhouse plants fertilization, by mean of a scrubbing system with particular catalysts (Chou, Bruinius et al. 2005). The system exhaust gas originated from a heating system fuelled with biogas extracted from a landfill. Sulphur oxide is usually reduced from flue gas when scrubbed with aqueous ammonia to form ammonium sulphate as a by-product (Long, Xiao et al. 2004). The later is quite valuable for fertilizer markets as several million tons are produced each year in the United-States (Chou, Bruinius et al. 2005). It was found that NO and SO<sub>2</sub> could be simultaneously eliminated by adding cobalt (CO(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup>) and iodide (I<sup>-</sup>) ions, at an optimal molar concentration ratio, into the standard aqueous ammonia solution. The process resulted in the conversion of NO into nitrite and nitrate and the subsequent absorption and oxidation of SO<sub>2</sub> into sulphate. UV irradiation at 360nm was used to improve regeneration of cobalt(II) cations which helped maintain NO removal efficiency. The presence of SO<sub>2</sub> in the exhaust gas feed was essential for iodide ions regeneration. Conveniently, the process can be easily integrated in existing desulphurization scrubber (Long, Xiao et al. 2004).

The concept of waste, from municipal or industrial sources, is progressively being recognised as a resource. The same could be applied to exhaust gas. First, reducing emissions improves the overall efficiency of a process and second, the captured gases can become a useful resource. Further research is needed to assess the quality of fertilizers scrubbed from exhaust gas. These scrubbing systems could supply nutrients directly into the irrigation network of the greenhouse while the leftover gas, composed mainly of CO<sub>2</sub>, could be injected for enrichment. Future projects could demonstrate economical feasibility and overall sustainability of the method. Finally, a life-cycle analysis could compare these fertilizers with standard ones.

External Modification - Membrane separation of CO<sub>2</sub> Green and Maginnes (1978) developed a membrane based CO<sub>2</sub> system using an odorant free natural gas-fired turbine system for CO<sub>2</sub> enrichment. Exhaust gases exited the stack at around 450oC and contained about 2% CO<sub>2</sub>, 16 ppm NO<sub>x</sub> and no SO<sub>2</sub>. The exhaust was cooled to 82oC and directed between the two covering layers of polyethylene of the greenhouse. The nature of the polyethylene cover allowed high permeability of CO<sub>2</sub> but prevented diffusion of NO<sub>x</sub> which were at toxic levels. While providing heat to the greenhouse, it also supplied considerable concentrations of CO<sub>2</sub>, between 1500 to 6000ppm. In terms of yields, the greenhouse produced 15% more fruit than the non-enriched area (Maginnes and Green 1978). However, this particular application of polymer membranes did not reach a wide commercial adoption in the greenhouse industry. Most researches focus on membrane separation from fossil fuel combustion as a mean to store and sequester CO<sub>2</sub> (Yang, Xu et al. 2008). However, membranes could be applicable for CO<sub>2</sub> enrichment to reduce greenhouse gases at the source.

Membrane technologies are currently used for post-combustion capture of carbon dioxide (Zhao, Riensche et al. 2008). Compare to the conventional process of reversible solvent absorption, membranes are more energy efficient and much simpler for CO<sub>2</sub> capture (Scholes, Kentish et al. 2008). Yang et al, in their review of CO<sub>2</sub> separation and capture, had stated that the membrane process was the most promising technologies amongst all the others for its energy-saving, space-saving and ease for scale up (Yang, Xu et al.

2008). It is these exact characteristics that make membrane separation appealing for greenhouses application.

Two important characteristics serve to determine a membrane performance. First, the permeation rate ( $J_i$ ) represents the flux of a particular gas ( $i$ ) through the membrane. This rate depends on the permeability ( $P_i^*$ ), the area ( $A_m$ ) and the thickness ( $\delta$ ) of the membrane and is driven by the pressure differential ( $\Delta P$ ) between both sides (Scholes, Kentish et al. 2008). This pressure difference will constitute the majority of the cost associated with membrane separation. The following equation, assuming ideal gas, shows the relationship between these variables:

$$J_i \frac{P_i^*}{\delta} \cdot A_m \cdot \Delta P \quad (1) \text{ (Ho, Allinson et al. 2008)}$$

A greenhouse owner could purchase a particular membrane which would have known thickness ( $\delta$ ) and permeability ( $P_i^*$ ). With a plant base approach to CO<sub>2</sub> enrichment, the rate of CO<sub>2</sub> to be given during the day would be identified according to the crop.

The second important characteristic is the selectivity of the membrane and this will dictate the membrane's ability to allow diffusion of one gas and retain a different gas (Scholes, Kentish et al.). Most membranes have particularly high selectivity between two main gases such as CO<sub>2</sub>/N<sub>2</sub>, CO<sub>2</sub>/H<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> (Scholes, Kentish et al.). It was determined that a ratio higher than 200 for the two gases was required for membranes to be a viable process (Zhao, Riensche et al. 2008). There are various mechanisms that affect membrane separation including molecular sieving and solution-diffusion. Molecular sieving depends on the kinetic diameter of the molecules as well as the membrane pore sizes which will determine which gas can pass (Scholes, Kentish et al. 2008). Carbon dioxide has the benefit of having smaller kinetic diameter than most of the other compounds found in the flue gas. On the other hand, when membranes are non-porous, solution-diffusion is the main mechanism. Indeed, it is the solubility of a gas within the membrane and its diffusivity through the membrane structure that will determine the permeability and selectivity (Scholes, Kentish et al. 2008). The relationship between those two characteristics is important since a highly permeable membrane will usually have a lower selectivity (Scholes, Kentish et al. 2008). Most membranes are made of polymeric materials of different compositions to offer best cost-effective performance (Scholes, Kentish et al. 2008). It has been observed that the technology becomes competitive when flue gas CO<sub>2</sub> concentration is higher than 10%, depending on the application and the purity level desired (Carapellucci and Milazzo 2004).

Regardless of the material composition, membranes should have good thermal and chemical robustness along with good resistance to plasticisation and aging (Scholes, Kentish et al. 2008). Those properties combine with affordable manufacturing processes will ensure a cost-effective durability of the membrane. Although some material may offer the purest quality of CO<sub>2</sub>, the greenhouse industry has easy and affordable access to polyethylene and polycarbonate materials. Silicon membranes have also shown interesting diffusion properties in post-harvest storage of produce, an industry similar to the greenhouse industry. These particular materials, which are commercially available,

could offer interesting application possibilities for CO<sub>2</sub> separation from flue-gas (Stewart, Raghavan et al. 2005).

Issues to take into consideration are the accumulation of condensable vapour within the membrane matrix resulting in lower permeability and selectivity, as well as undesirable gases, such as CO, NH<sub>3</sub>, H<sub>2</sub>S, SO<sub>x</sub> and NO<sub>x</sub>, which can degrade the material prematurely (Scholes, Kentish et al. 2008). Fine particulates may also accumulate on the membrane and block membrane pores. Limited research had been performed on the effect of these gases on membranes and could become very beneficial when evaluating the feasibility of this technology for greenhouse CO<sub>2</sub> enrichment. Further research projects should develop this specific application of membrane separation technologies and assure affordability to greenhouse owners.

**CONCLUSION** Conclusion CO<sub>2</sub> enrichment is renowned as a profitable fertilizing method for greenhouse owners whether it is from pure CO<sub>2</sub> or from fossil fuel combustion. Biomass heating could serve as an alternative fuel to reduce greenhouse gases while CO<sub>2</sub> enrichment from the exhaust gas could help improving the overall carbon footprint. With current commercially proven technologies, biomass heating for CO<sub>2</sub> enrichment is a very expensive process since it requires electrostatic precipitators to remove fine particulates matter from the exhaust. By improving boiler efficiency, whether through combustion, gasification or a combination of both, little VOCs and particles would be produced. Current available scrubbers can alleviate NO<sub>x</sub> and SO<sub>x</sub>, but there is room to improve the technology to produce ammonium sulphate fertilizers that could be used directly in the greenhouse. Additionally, membrane separation techniques could be very efficient in preventing fine particles and undesirable gases to be diffused into the greenhouse while keeping a CO<sub>2</sub> enriched greenhouse safe for workers. It remains to be seen the final strategy will involve using a scrubbing, a membrane or both together. The membrane technology has the potential of being simpler to use and maintain for greenhouse owners who have direct access to materials such as polyethylene or polycarbonate. Further research need to be performed to optimize this CO<sub>2</sub> enrichment method from biomass fuels.

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