Eco-efficient electrical and innovative technology development for indoor air and gas exhaust treatment in industry

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Abstract

High indoor VOC levels can be found in various industrial sectors. A large fresh air ratio is often necessary in order to protect people who are exposed in these areas. This replacement air requires heating or cooling depending on the season, dehumidification and, in some cases, filtration to remove airborne bacteria, yeasts and molds. Furthermore, the standard technology for removal of VOCs is adsorption by active carbon filters which in turn have to be regenerated or incinerated. The overall energy consumption for air treatment can thus become very high. Important energy savings can be obtained if the indoor air is cleaned and partly recycled in the factory unit thanks to a strong reduction in the fresh air ratio. A cold plasma technology (non thermal plasma) has been shown in abundant past research to be effective in the removal and oxidation of VOCs. This technology is advantageous because the pollutants are decomposed rather than trapped. Up to now, commercial applications have been prevented by two major drawbacks: low energy efficiency of the process and production of by–products due to incomplete oxidation. The objectives of this work are to obtain a clear view of the ability of a cold plasma process to remove and oxidise different kinds of pollutants (ketones, alcohols), to investigate solutions to reduce electrical energy consumption of the process and to increase VOC removal performance. A combined plasma-catalysis reactor is a way to achieve better efficiency. These solutions will be investigated during the thesis and might promote cold plasma technology to BAT (Best Available Technology) label. Other applications that can be considered include exhaust gas treatment (odours and VOC's) and indoor air treatment in tertiary sectors.

Introduction

Emissions of Volatile Organic Compounds (VOC) is an important issue because of their implication in several health and environmental problems like human respiratory issues, formation of tropospheric ozone and destruction of stratospheric ozone (ozone layer). VOCs include more than 300 chemical species having varying chemical reactivity. They are volatile at ambient temperature and hence very difficult to control. They can be found in many industrial sectors as solvents, degreasers, cleaners or lubricants. The emission of VOCs has been subjected over the last twenty years to regulation by international or national protocols [1]. Problems of VOCs in air are not limited to industrial gas effluents but also concern indoor air quality in industry as well as in office buildings. In industry, many processes use VOC and pollutant concentrations in the ambient air can reach critical values for the health of people working in the area. To decrease pollutant concentration in the workplace, large amounts of fresh air need to be introduced by the ventilation system. The large air replacement ratio will induce high energy consumption to heat the fresh air and keep constant temperature in the building. In office buildings, the presence of VOC emitted by new furniture, paints, floors and cleaning and maintenance products can cause discomfort problems (sick-building syndrome). Studies show that level of the most common VOCs can be 5 to 10 times higher in indoor air than in outdoor environment [2]. This is particularly true in modern airtight buildings where average ventilation rates are lowered to save

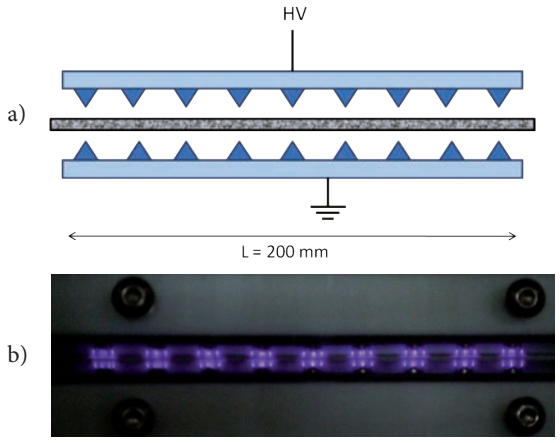


Figure 1. a) schematic diagram of the pin-to-pin reactor (side view) and b) photograph of discharges in air at atmospheric pressure. A small purple glowing region called a streamer develops near the tip of each pin.

energy. When the decision is made to replace air in polluted rooms, a large amount of energy needs to be spent to heat or cool the fresh air. A commonly used technology for VOC removal is absorption by activated carbon filters but this requires a large ventilation power to compensate the pressure drop induced by filters. Other methods like incineration, catalytic incineration, bio-filtration or condensation do not meet requirements for the treatment of air flow rates in the range of 100–10,000 m^3/h and low pollutant concentrations. Most of current available technology are large scale processes and need to be run continuously. The investment cost or operating cost is often very high and makes it unwieldy for small businesses or fragmented process. A VOC removal system would ideally be easily turned-on and off, support a changing pollutant concentration and have limited dimensions so as to be placed inside ventilation ductwork. A promising technology is the use of a non-thermal plasma to decompose VOCs. Electrical discharges have been applied to reduce NOx and SOx emissions in the industry [3][4] and have been proved to be efficient on VOC decomposition at laboratory scale air flow (few tens of L/h). Non-thermal plasma discharges have the advantage of producing reactive species with a high yield because a large portion of the electrical energy goes into the creation of oxidizing agents instead of heating the gas. Electrical discharges produce atomic oxygen and hydroxyl radicals that will react with pollutant molecules. This paper deals with the performance of non-thermal plasma for VOC removal. Three molecules will be studied: acetone, MEK (methylethylketone) and ethanol. Differences between molecules in term of removal efficiency will be discussed as well as the effect on the inlet concentration on the process. Next, the results of a plasma catalysis setup will be presented and the energy efficiency improvement of combining electrical discharge and catalysis will be investigated. Finally, an economical comparison with carbon filter is attempted and an example of possible system is given.

Background and Experimental setup

A plasma can be generated when energy is transferred to a gas by either electrical or thermal mechanisms up to the point when the gas molecules become ionized. Neutral gas molecules will emit electrons when their internal energy is above the ionization threshold. Plasma is then a mixture of free electrons, positive and negative ions and neutral species (atoms, radicals and excited species). This composition gives special behavior to the plasma like being affected by electric and magnetic fields and being chemically or physically reactive with surfaces. A non-thermal plasma has the characteristic of possessing very energetic electrons (high electron temperature) while other species of the background gas stay at lower energy (close to ambient temperature). Generation of non-thermal plasma then allows the creation of energetic electrons without significant heating of the gas. Electrons, through collisions with background molecules will create reactive species. In the case of ambient air, the most important species created are atomic oxygen O, hydroxyl radical OH, excited nitrogen N_2^* and ozone molecules O_3. These created species will then react with pollutant molecules. Different ways of producing non-thermal plasmas exist such as electron beam [5], corona discharge or dielectric barrier discharge [6]. In electrical discharge, plasma is created by the application of a high electric field (3–10 MV/m, i.e. 120–400 Td in terms of reduced field in air at atmospheric pressure) between two electrodes which lead to the breakdown of the gas. This work used a reactor with a dielectric layer placed between the electrodes preventing thermal arc creation and leading to the formation of filamentary discharges called streamers. Figure 1 shows a simplified schematic of the reactor and a photograph of the streamer discharge running. Each filament will act as a small chemical reactor where active species are created. The duration of a streamer is on the order of tens of nanoseconds with a peak current of a few tens of mA. The reactor had a pin-to-pin geometry with the dielectric (mica, 1 mm thickness) centered in the gap between opposing pin electrodes (based on EDF patent). The number of discharge sites in the reactor was fixed by the number of pins (18 in the case of these experiments).

Discharges are initiated more easily with a sharp pin due to the high local electric field close to the tip. The gap distance between electrodes was 3 mm and discharge initiation occurred around 11 kV. Gas flow was synthetic dry air at room temperature and flow rate between 1 and 4 L/min. VOC injection was made by a bubbler containing liquid pollutant fed by a small variable air flow allowing creation of an air flow with tuned concentration. The bubbler was maintained at 0 °C to avoid instability in the VOC injection due to a change of the ambient temperature. Residence time in the reactor was between 30 and 100 ms depending on the gas flow rate. Due to the presence of the dielectric barrier, the applied electrical power signal could be an alternative signal or a pulsed signal. The reactor was excited by positive voltage pulses up to 25 kV, 800 ns duration with voltage rise rate of 1 kV/ns. Frequency could be tuned from a few hertz to 2 kHz. Depending on the conditions of flow and voltage, total discharge current (sum of numerous unitary discharges) could attain a peak value of 20 A. Determination of electrical power deposited into the discharge was made by monitoring voltage and current. A Tektronix P6015A (75 MHz)

and a Tektronix CT-2 current transformer (200 MHz) were used for voltage and current measurement, repectively. Signals were recorded by a LeCroy WaveRunner 62 Xi digital oscilloscope (600 MHz – 10 GS/s). Discharge input power was calculated by the instantaneous voltage-current product method. A numerical program was used for treatment of data. Waveforms were averaged and the capacitive current was subtracted from the total current that was recorded (sum of capacitive and discharge current). Voltage and discharge current were then multiplied and the integral of the product over the duration of the pulse was made to find the energy per pulse. The average power corresponds to the product of the energy per pulse and the frequency. Chemical measurements were carried out with a Bruker Tensor 27 FTIR absorption spectrophotometer with a 20 cm path length gas cell. It allows the monitoring of the main discharge by-products such as CO, CO_2, ozone and the calculation of the target pollutant concentration. Additionally, time resolved CO_2 measurement has been performed by using a LI-COR LI840A infrared analyzer and ozone by a Perkin-Elmer UV/V absorption spectrophotometer.

Voc treatment by cold plasma

ENERGY EFFICIENCY EVALUATION

To determine the performance of the non-thermal (cold) plasma process on the removal of VOCs, several parameters can be used such as the target molecule removal efficiency (%), the energy cost or the energy yield (g(target pollutant)/kWh). All these parameters can be regarded as functions of the specific input energy (SIE) which corresponds to the energy deposited by unit volume of gas in the discharge. The SIE is expressed in Joule per liter ($J.L^{-1}$) and is calculated by the ratio of the power deposited in the discharge (in W) and the gas flow rate ($L.s^{-1}$). The specific input energy is widely use in the literature because it seems to a major factor which determines the performance of the process, and because it has a direct relation to the operating cost of the process. The conversion of VOC is evaluated through the removal efficiency (RE) that is the ratio of the converted VOC concentration over the initial pollutant concentration. Other parameters can be determined like the energy cost which corresponds to amount of energy needed to decompose one pollutant molecule. The energy cost is expressed in eV/molecule. The less the energy cost, the greater will be the efficiency of the process. These different parameters have non-linear trends and vary conversely indicating that there exists no universal parameter to characterize the efficiency of the discharge treatment.

TREATMENT OF ETHANOL, ACETONE AND MEK

The performances of the treatment of VOC by non-thermal plasma are strongly dependent on the considered pollutant molecule because of differing reaction rates with the active species created by the discharge. At a given energy density, production of reactive species such as atomic oxygen, hydroxyl radicals or excited nitrogen can be controlled by the energy deposition into the discharge and by the parameters of the flue gas (temperature, water vapor content). In these experiments, only the pollutant molecule is changed so the performances are only a function of the chemical kinetics between the pollutant and the reactive species. Figure 2 shows the removal efficiency of three pollutant molecules as a function of the energy density. The three target molecules chosen are ethanol (C_2H_6O), acetone (C_3H_6O) and methylethylketone (MEK, C_4H_8O).

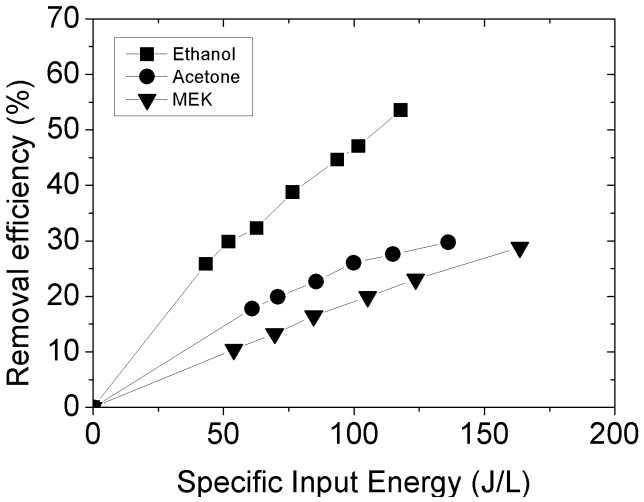


Figure 2. Removal efficiency of three VOCs versus the specific input energy (SIE). For a specific molecule at a given concentration, the SIE is the main factor. The flow rate is 2 L/min, and the inlet VOC concentration is 300 ppm.

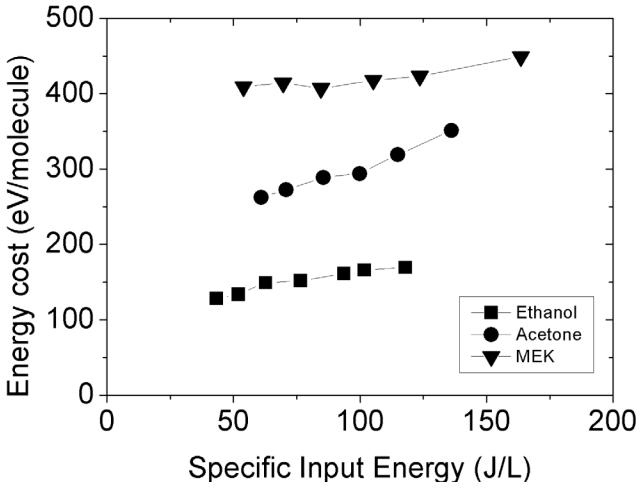


Figure 3. Energy cost versus energy density for three target pollutants. The higher the removal, the higher is the cost to destroy one molecule.

The energy deposited in discharge is increased by changing the voltage. The signal frequency is kept constant at 1400 Hz. At a given specific input energy (100 J/L) and VOC inlet concentration (300 ppm), the best removal was obtained for ethanol with almost 47 %. At the same SIE, acetone is harder to remove with 26 %. Finally, MEK is the most resistant VOC here investigated with only 19 % of removal. As expected the energy cost presented in Figure 3 is the inverse of the removal namely the easiest compound to remove will have the lowest energy cost. The energy cost is increasing with respect to the SIE (i.e. the removal efficiency) indicating that a compound becomes more and more costly to remove as the removal efficiency increases.

In theory a 100 % removal by plasma oxidation is even impossible. The limit value will be close to 99.9 %. The removal rate is calculated by the difference between the inlet concentration and outlet concentration of the target compound but doesn't mean that the removed pollutant has been completely oxidized into CO_2 and H_2O. To get information about the advancement level of oxidation, the CO_2 yield can be evaluated. The CO_2 yield is calculated as the ratio of the produced CO_2 over the number of carbon atoms removed. The CO_2 yield is sometimes also referred to as the CO_2 selectivity S_{CO_2}.

$$S_{CO_2} = \frac{[CO_2]}{([VOC]_{in} - [VOC]_{out}) \times \text{number of carbon atoms per VOC molecule}}$$

The CO_2 yield represents the amount of the CO_2 produced in lieu of the other carbon by-products like formic acid or formaldehyde and can be understood as the degree of advancement of the oxidation reaction. The best yield is obtained for MEK with 34 % at 100 J/L. Ethanol and acetone will have a selectivity of 17 and 13 % respectively for the same SIE. Analysis of the removal efficiency and the CO_2 yield shows that a compound can have good removal efficiency due to the fact that the molecule is only transformed into partially oxidized carbon by-products and not completely oxidized. By considering the results on the three target pollutants, the conclusion can be made that direct treatment of a high flow rate of air with VOC concentration in the hundreds of ppm (parts per million) is much too costly due to the low energy efficiency of the plasma process. Even for the easiest molecule to remove (ethanol), a removal efficiency of 80 % needs more than 500 J/L. For a flow rate of 1,000 m^3/h, which is quite low for an industrial effluent, the electrical power will be on the order of 138 kW. An electrical power supply able to deliver such a high power will be difficult and will critically the cost of the equipment and have an unacceptable operating cost. Research on improved methods such as the use of short length voltage pulses and changes in reactor or electrodes geometry have only given marginal improvements in the energy consumption. An increase of the residence time of the gas in the reactor has been shown to increase the removal efficiency. An increase of the residence time can be done by a reduction of the flow rate but this solution is unsuitable for direct effluent cleanup.

EFFECT OF THE POLLUTANT CONCENTRATION

The initial concentration of the pollutant will affect the efficiency of the conversion. The removal efficiency of ethanol as a function of the inlet concentration is plotted in Figure 4. At a given energy density, the removal efficiency decreases when the inlet concentration increases. This decrease is explained by the increasing quenching of reactive species such as O or OH by the byproducts of ethanol degradation, whose concentration increases with increasing inlet concentration.

Figure 5 shows the energy cost as a function of the inlet concentration. The energy cost decreases when the concentration increases. The decrease of the energy cost corresponds to an increase of the energy yield (mass of pollutant converted per kWh) and can be explained by the fact that a higher inlet concentration will increase the probability of reaction between ethanol molecules and reactive species.

Although higher inlet concentration brings better efficiency, the increase is insufficient to counter balance the increase of the concentration and leads to lower removal efficiency. The decrease of the energy cost can be explained by the increase of the reaction rate if one of the reactants (here the pollutant) is increased in initial concentration. Injection of VOC in the discharge is accompanied by a lower production of ozone. Oxidation of VOC will use atomic oxygen that therefore cannot be used in the ozone production reaction. Figure 6 shows the value of ozone non-formed (difference between ozone concentration with and without ethanol) in the discharge due to the presence of VOCs. This value is increasing with the inlet concentration of ethanol, confirming that a higher number of oxygen atoms participate in the oxidation of VOC rather than in ozone formation.

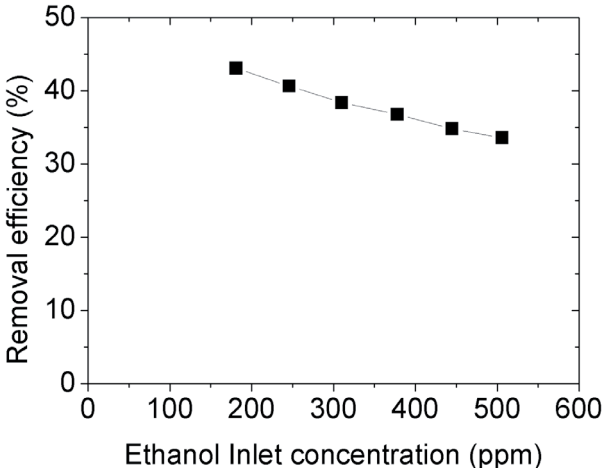


Figure 4. Removal efficiency of ethanol versus inlet concentration. Plasma at 78 J/L, air flow : 2 L/min. Increase of the concentration leads to a decrease of the performance on removal efficiency (in terms of percentage) whereas the total amount of removed ethanol increases.

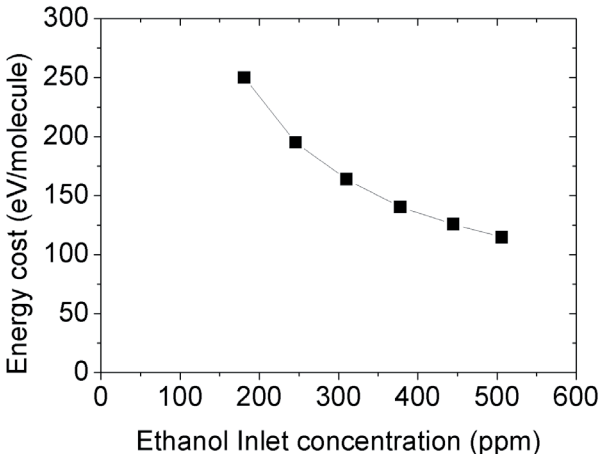


Figure 5. Energy cost of ethanol versus inlet concentration. Plasma at 78 J/L, air flow : 2 L/min. High inlet concentrations lead to a lower energy cost (better efficiency).

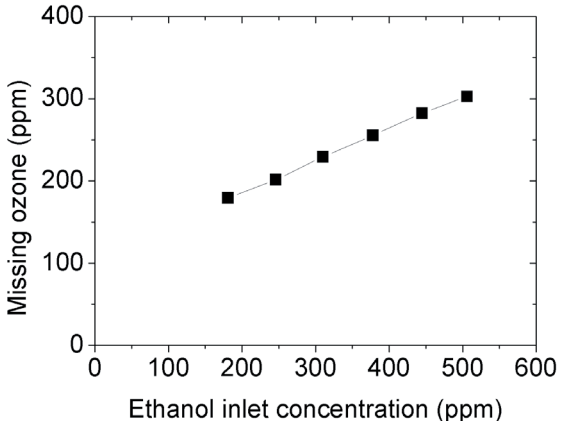


Figure 6. Loss of ozone formation versus ethanol inlet concentration.

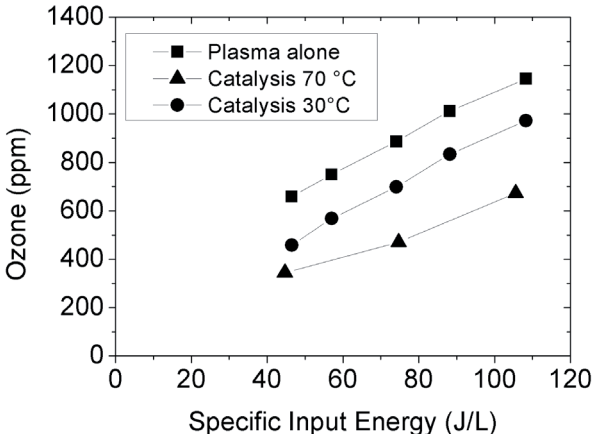


Figure 7. Ozone concentration versus energy density with and without catalyst at 30 °C and 70 °C. Air flow : 2 L/min. The presence of a catalyst will decrease the outlet ozone concentration. Heating of the catalyst enhances ozone destruction.

The total oxidation of VOC leads to the formation of CO_2 and H_2O. Monitoring of the CO_2 concentration can give an idea of the efficiency of the oxidation. The increase of the inlet concentration will lead to a decrease of the CO_2 selectivity from 16 % at 200 ppm to 14 % at 500 ppm.

Plasma and heterogeneous catalysis combination

To improve removal efficiency and reduce by-product formation, an electrical discharge reactor can be combined with other processes such as adsorbent filters or a catalyst reactor. Previous studies have shown that addition of a catalyst can be promising for the treatment of VOC [7] [8] although the effect on removal efficiency is difficult to interpret [9]. Various catalyst preparations can be used and the choice of the right materials is often difficult due to the changing results with respect to the target pollutant studied. In these experiments, a Pt/Pd type oxidation catalyst (1" diameter – 1" length cylindrical core cut out from a cordierite monolith honeycomb structure with a Al_2O_3 washcoat - including 10 % in weight of hydrocarbon adsorbent material and a 100 g/ft^3 precious metal Platinum / Palladium in a 4/1 ratio) was placed 40 cm downstream of the plasma reactor. In this configuration, most of active species (O atoms and OH radicals) can't reach the catalyst because of their very short lifetime and only ozone is long-living enough to have an influence on the catalysis surface. At room temperature, catalysis is inefficient in terms of conversion of VOC even if a portion of molecules can be adsorbed on the catalysis support. No CO_2 was detected when the catalysis was running at 30 °C demonstrating the non-active state of the catalyst. If ozone was injected in the gas flow then the catalytic reactions took place even at low temperature. The association of plasma and catalytic treatments can combine advantages of both methods and cancel defaults. The efficiency of the plasma can be improved and some of the by-products produced by the non complete oxidation of VOC can be oxidized further into CO_2 by the catalysis. The activation temperature of the catalysis can be lowered by the ozone produced in the discharge. Usually ozone doesn't react directly with most of VOCs in gas phase but this reaction is possible in the presence of catalytic material. Figure 7 (flow rate 2 L/min) shows the ozone concentration with and without catalysis. The ozone concentration was lowered by the passage through the catalyst. The decrease is about 20 % for a temperature of 30 °C and 47 % for a catalyst temperature of 70 °C.

Figure 8 shows the temporal evolution of the ethanol concentration during an experiment where a gas flow containing 320 ppm of ethanol was passing through the plasma-catalyst combination or only through the catalyst reactor kept at ambient temperature (22 °C). Experiments were carried out at energy density of 80 J/L and the catalyst was thermally regenerated between successive experiments. Regeneration of the catalyst (heating at 300 °C in clean air) allows desorption and oxidation of the adsorbed species. The monitoring of temporal evolution was necessary due to the adsorption of pollutant over the catalysis surface being time dependent. The removal of ethanol changes from 39 % to 73 % by adding plasma to the catalysis. At t = 65 min, plasma was turned on for the catalysis alone experiment to ensure that results were repeatable. The ozone decrease is accompanied by an increase of the CO_2, proving that there is a catalytic reaction induced by ozone over the surface.

Rough estimation of potential savings and process implementation

Many categories of industry use large volumes of solvents. Some processes generate large amount of VOC in the workplace environment that can lead to some health security issues. The industrial sectors which are facing these emissions are: printing, surface cleaning, vehicle coating and refinishing, coil winding wire coating, other coating (wooden surfaces, leather, metal, plastic, textile, fabric, film, paper), dry cleaning, wood impregnation, footwear manufacture, adhesive coating, manufacture of coating preparations, varnishes, inks, adhesives, rubber conversion, vegetable oil and animal fat extraction and vegetable oil refining, manufacture of pharmaceutical products. To decrease the level of VOC in the atmosphere, large amount of fresh air needs to be injected into the HVAC (Heating Ventila-

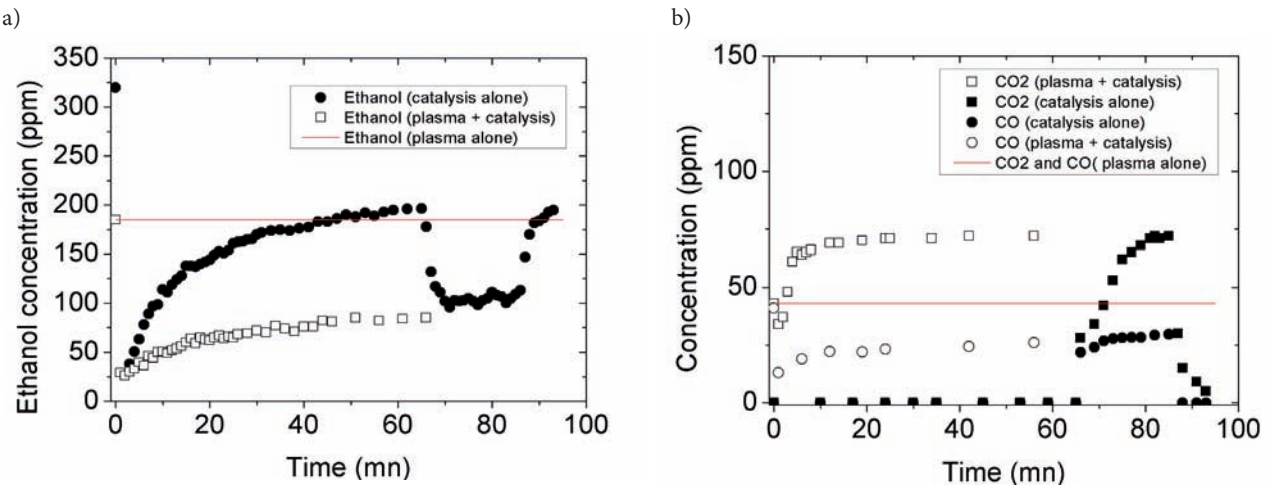


Figure 8. Temporal evolution of a) the ethanol concentration and b) CO and CO_2 concentrations for catalysis alone at ambient temperature and plasma-catalysis combination (plasma : 80 J/L, air flow : 2 L/min).

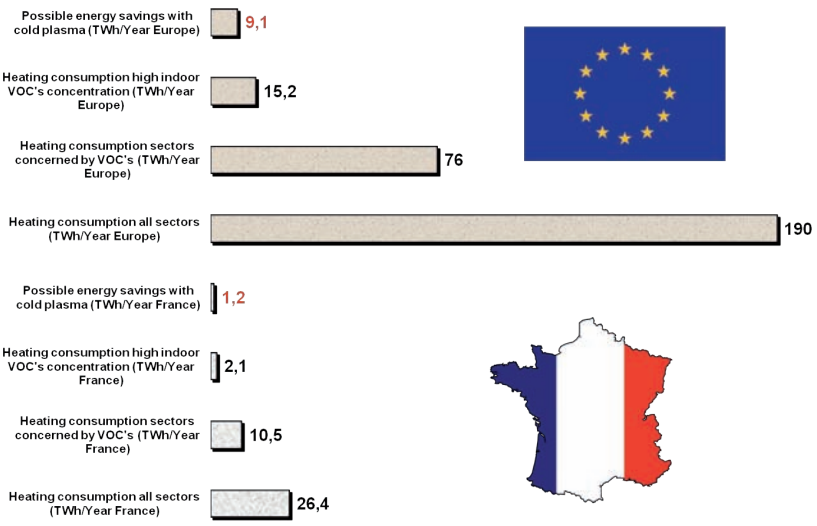


Figure 9. Primary energy consumption estimation for industrial building heating in France and in Europe.

tion Air Conditioning). Large fresh air replacement ratios will lead to an important energy consumption in heating or cooling processes. In France, the annual energy consumed for heating in industry is 26.4 TWh (data from [10]). Sectors concerned by VOCs represent 40 % of the total: 10.56 TWh but assuming that 20 % of the buildings are really concerned by high level concentration of VOCs (this ratio is based on energy savings expert's assumption) (> 10ppm) the heating energy is more like 2.1 TWh. The electrical energy consumption of ventilation is not included in the values. In Europe, the annual energy consumed for heating in industry is 190 TWh. Assuming the same ratio as for France, a 15.2 TWh heating energy is annually consumed by the buildings really concerned by high level concentration of VOCs. Figure 9 sum-up previous figures for France and Europe consumption in air heating.

According to the results obtained with an EDF software (OPTHUM) for a middle range building, it can be considered that it would be possible to reduce the heating energy by 60 % (concentrator + cold plasma). OpTHum simulates heating consumption in industrial buildings by using a thermal loss coefficient G (W/(m3.K)), building volume and HVAC air flow. OpTHum also simulates the energy consumption of air conditioning, humidification and drying. The calculation takes into account the outside temperature and humidity (every hour during a year) based on meteorological data. The town of Lyon was chosen for the source of meteorological data (representing average conditions in France). The software can compute global energy consumption for heating or cooling a building. Primary energy savings potential could then reach 1.2 TWh / year in France and 9.1 TWh/year in Europe. Combined with air-to-air heat exchanger options, 70 % of energy savings could be obtained. Figure 10 represents possible savings on heating with different systems. The electricity demand for ventilation is the same in the different configurations; only the difference between different fresh air ratios is evaluated. A more complete calculation including consumption of ventilation needs to be performed but has to be made especially for each case.

Figure 5 showed that VOC removal energy costs (eV/target molecule oxidized) decreases when the effluent VOC inlet

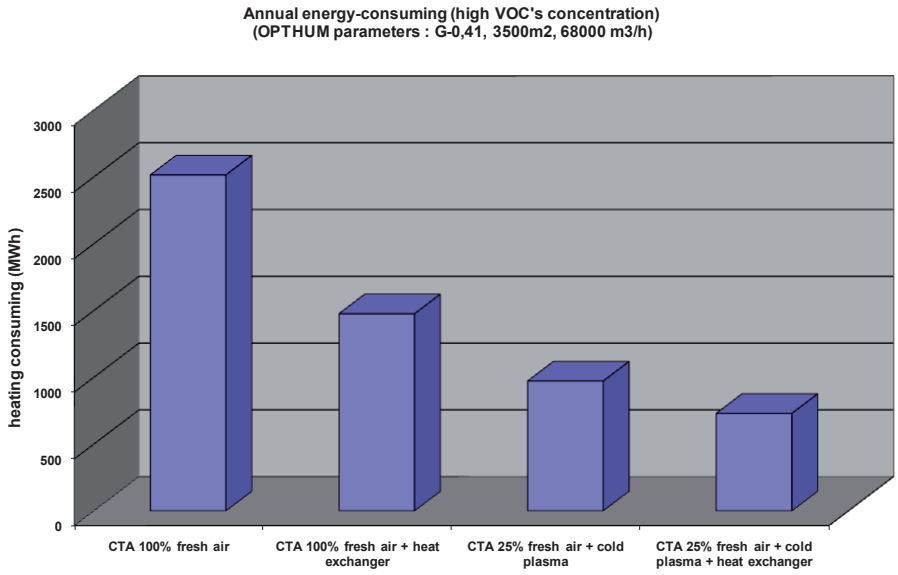


Figure 10. Results of energy spent for heating in an average industrial building and possible savings brought by implementation of cold plasma system.

concentration increases. On the other hand, removal efficiency increases with SIE (see Figure 2) whereas energy costs remain more or less constant, depending on the target molecule (Figure 3). To increase the SIE without increasing the total energy cost, one way is to reduce the treated flow rate (thus increasing the plasma residence time while keeping the discharge input power constant). This can be done by operating the plasma into a secondary air loop with lower flow rate. Concentration of the VOC will be higher due to the lower gas flow rate in the secondary loop into which the VOC will be desorbed either by gas heating by the plasma or auxiliary heating. To achieve correct removal efficiency without injecting high energy into the discharge, the system can be run in a closed loop that will increase the VOC residence time in the plasma. For the indoor air control application where the flow rates are high, one idea would then be to concentrate the pollutants inside a material. A second air treatment circuit will desorb the VOCs into a non-thermal plasma treatment to oxidize VOCs before exhausting. This technology is an innovative treatment. This concept has to be studied and tested experimentally, especially the part concerning desorption. The interest of a cold plasma treatment in the second circuit is that the air can re-circulate in the concentrator/desorber loop because it is not overheated (which would be the case of incineration). The air recirculation reduces cold plasma energy consumption for an equivalent VOC removal rate. Moreover, the thermal losses in the plasma process will enhance the concentrator desorption. The performance of the plasma process is strongly dependent on the targeted molecule. Some molecules that contain chlorine or fluorine atoms are very difficult to oxidize and partial oxidation can lead to the production of by-products more toxic than the initial molecule. The removal potential is then directly related to the type of pollutant and its concentration. Some industries such as microelectronics or pharmaceuticals release mostly chlorine and fluorine based molecules such as dichloromethane or chlorofluorocarbons (CFCs). In these cases the energy consumption to attain acceptable removal rates for cold plasma is so high that thermal oxidation is more appropriate.

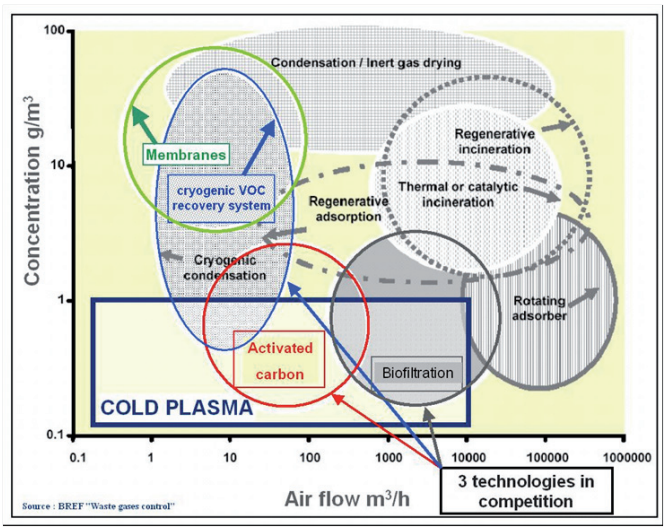


Figure 11. Range of application of different VOC removal techniques. The plasma process will be mostly in direct competition with activated carbon adsorbent filters (modified from [12]).

Plasma treatment of a gas will be more efficient for simple carbon-hydrogen chain compounds such as alcohol, ketones or aromatic compounds.

A VOC concentrator can effectively purify and concentrate a VOC loaded air stream exhausted from industrial factories. By being combined with a non-thermal plasma reactor or other solvent recovery equipment, both initial and operating costs of the entire VOC abatement system can be drastically reduced. An attempt to make a cost analysis comparison between carbon filter adsorption and non-thermal plasma has been made. Carbon filter technology was chosen for the comparison due to the fact that it is the standard technique for air streams of moderate flow rate (100–10,000m^3/h) contaminated with dilute concentrations of VOCs. The relative simplicity of use and the small footprint of carbon filter installations make it a good technique for comparison. Other removal techniques such as thermal in-

Table 1. Annual cost calculation for plasma reactor in a closed-loop system (extrapolation from experimental results and prototype costs).

Annual costs cold plasma + concentrator		
Purchased equipment costs	40 000 €	
Total Capital Investment	**60 000 €**	
Maintenance labor and materials.	2 000 €	/year
Annual filter replacement	1 000 €	/year
Annual electricity costs	1 700 €	/year
Total Annual Cost	**4 700 €**	**/year**

Table 2. Annual cost for carbon adsorbent filter in a single pass system (based on EPA documentation [11]).

Annual costs carbon adsorbent		
Purchased equipment costs	39 000 €	
Total Capital Investment	**62 000 €**	
Maintenance labor and materials.	4 340 €	/year
Annual carbon replacement	8 336 €	/year
Annual electricity costs	1 053 €	/year
Total Annual Cost	**13 729 €**	**/year**

cineration, catalytic incineration, cryogenic condensation, and scrubbing are not considered here due to their quite different range of application, size (biofiltering) or cost. The choice of a gas effluent cleanup technology will depend on many parameters among which the flow rate and pollutant concentration will be the most important. Figure 11 shows the usual range of application for different VOC removal technologies. Other considerations include the possibility of VOC recovery, humidity level of the gas or utilisation for single or multiple pollutant removal.

Tables 1 and 2 show examples of cost calculation for plasma – concentrator system and carbon filter systems. Cold plasma is an innovative technology but initial capital costs will be high: by extrapolation from the cost of a prototype, the capital cost of a system might be on the order of ten times that of its annual operating cost. Economies of scale, especially in the cost of the electrical power supply might reduce these values. The plasma calculation is made for a 1,500 m^3/h flow rate with 50 ppm toluene. Carbon adsorbent calculation was made for a 15,000 m^3/h flow rate and 5 ppm toluene concentration. In contrast to adsorption technology (activated carbon), the VOC's are treated in situ and annual costs are much less expensive. For example, with a similar investment, annual running costs with a plasma process should be 65 % lower than carbon adsorbent systems. Light maintenance labour and lack of consumable replacement parts is the main reason for the reduction in annual costs.

Comparing to thermal oxidation (not appropriate for low VOC concentration), there is no perpetual natural gas cost and consequently no dependence on the unreliable natural gas market. However that may be, cold plasma energy consumption would be negligible in regard of energy savings (Figure 10). This technology can be rapidly brought on or offline and the plasma power can be easily adjusted to the VOC emissions. An example of a cold plasma implementation in an air treatment circuit is given in Figure 12. A VOC adsorbent inserted in the main circuit can be desorbed in a second circuit (partial recirculation) with hot air provided by the cold plasma reactor. VOCs are oxidized in the plasma reactor with or without catalyst coupling. An exhaust duct (4) is necessary to evacuate by-products and to regulate the air temperature. A VOC measuring device adjusts the cold plasma power and the fresh air ratio in the rooftop. Of course, it is considered here that solutions for reducing the emissions "at the source" (better encapsulation, other formulations with less VOC …) can't eliminate all the diffuse VOC emissions.

Conclusion

By using electrical discharges, most of volatile organic compounds can be decomposed into CO, CO_2 and other carbon by-products. The decomposition ratio is strongly dependent of the target molecule and its reaction rate with atomic oxygen and hydroxyl radical that are the main oxidizing agents created in the discharge. The initial concentration of pollutant is another critical parameter. Removal percentage of the process is lowered if the concentration increases but leads to better efficiency. Ethanol was the easiest compound to decompose followed by acetone and MEK. A major concern is the energy efficiency of the process, a specific energy density of 100 J/L is needed to convert 47 % of ethanol in high concentrations conditions. Energy consumption is too high in the case of treatment of large air flow and is a strong disadvantage comparing to other market technologies like bio-filter or adsorbent carbon filters. A promising way to improve the energy efficiency is to combine the plasma discharge with a catalyst reactor. Preliminary results obtained at room temperature with a non-optimized catalyst show an increase of over 50 % of the removal rate of ethanol by adding a catalyst. The removal rate can be increased either by storage on the catalyst surface or by catalytic reactions initiated by the ozone over the catalyst surface. Measurement of CO_2 at the reactor outlet showed that the heterogeneous reaction of ozone with VOC occurs. Results on removal efficiency and energy cost by the plasma process alone lead to the conclusion

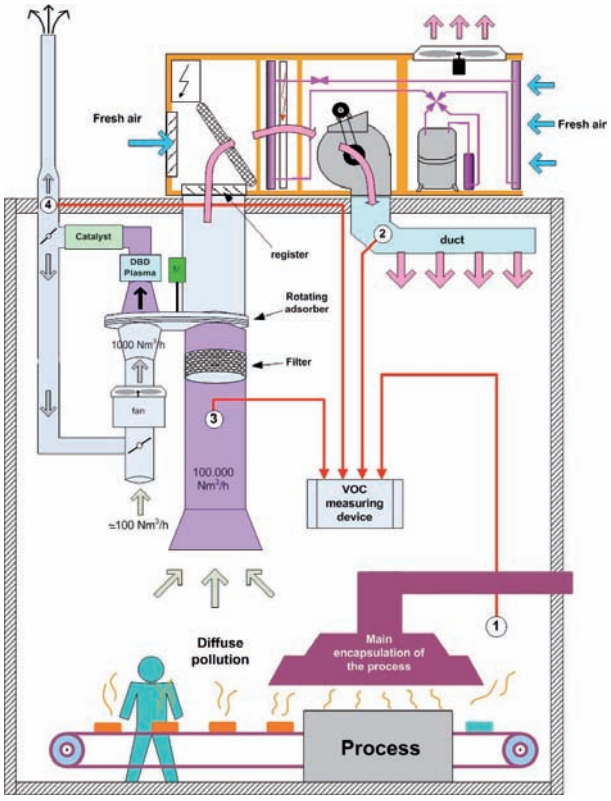


Figure 12. Schematic diagram of a possible system incorporating a concentrator device (rotating adsorber) with a secondary air loop including the plasma and catalyst reactors to remove VOC from ambient air in an industrial building.

that direct treatment of VOC is not yet economically viable due to low energy efficiency. Even though the addition of a catalyst can improve the performance of the process; improvement seems to come mostly from adsorption mechanisms and catalysis mechanisms are minor at ambient temperature. The main problem is that adsorption is time dependent and the performance of the system will quickly decrease when the catalyst is saturated. A plasma based system can be run economically if it is placed into the right environment: low gas flow rate, pollutant concentration in the hundreds of ppm range and long residence time. Use of a plasma reactor in a secondary closed-loop air circuit could meet these requirements. A closed-loop system is an interesting approach because plasma can be used as an oxidation reactor in conjunction with the absorber. Furthermore the increase of gas temperature induced by the plasma shall help for a better desorption. Analysis of potential savings shows that 1.2 and 9.1 TWh could be saved respectively in France and in Europe. According to preliminary market study, plasma could constitute a good alternative to the current process. By improving significantly the energy efficiency, plasma can be seen as a BAT for air treatment (electrical consumption, flexibility, ease of use, dynamics properties) as it already has been declared in the food industry [12]. Calculations and figures presented in this article need to be validated by a deeper market and cost analysis. Finally, only full scale experiments will be able to confirm promises of plasma technology and establish it as a mature pollution control solution.

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