REMOVAL OF VOLATILE ORGANIC COMPOUNDS BY A HIGH PRESSURE MICROWAVE PLASMA TORCH [1]

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A helium microwave plasma torch was studied and optimised as a destruction system of volatile organic compounds. Attention was focused on trichloroethylene as a prototypical volatile organic compound, which is used technologically and which poses known health risks. The dependence of the destruction efficiency on the plasma conditions was obtained for different values of trichloroethylene concentrations. The results show a destruction and removal efficiency greater than 99.999%.

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1 Introduction

Volatile organic compounds (VOCs), such as carbon tetrachloride (CCl_4) or trichloroethylene (C_2HCl_3), are typical emission gases of semiconductors and paint industries. These gases must be removed from the clean rooms not only to increase the product yield, but also to protect human health. Specifically, trichloroethylene has shown evidence of being a carcinogen in animals and is suspected of being a human carcinogen and teratogenic agent [1].

Various technologies have been investigated for decomposing the VOCs: catalytic oxidation and combustion, thermal decomposition, carbon adsorption and condensation. However, these conventional methods seem to be inefficiently efficient in achiving the desired destruction efficiencies [2].

In the past fifteen years, non-thermal plasma technologies have been studied as a promising and an innovative approach to the problem of decomposing these volatile organic compounds [3]. Non-thermal plasmas (or, more correctly, non-equilibrium plasmas) are characterised by the fact that the electrons in the plasma have a higher energy than the ions and atoms or molecules, and this higher energy of the electrons can produce a sufficient number of reactive chemical radicals which cause the destruction of gaseous pollutants.

This work is focused on the study and optimisation of a destruction method of trichloroethylene (TCE). The system used to destroy TCE is an "axial injection torch" or TIA [4], which is a discharge source that produces a very stable high-pressure (atmospheric) plasma flame at

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2.45 GHz. This flame is a non-thermal plasma, which is characterized by electrons with kinetic energies much higher than those of the ions or molecules. Some modifications were made to obtain the maximum destruction percentage.

A wide range of concentration of TCE was studied, achieving destructions and removal efficiencies greater than 99.999% by using an applied microwave power from 300 to 1000 W. This range of power is typical also for conventional microwave ovens.

2 Experimental set-up

The plasma was produced by the axial injection torch (Torche à Injection Axiale or TIA). This device provides a free expanding microwave plasma that is comparatively stiff to impedance changes - caused by the introduction of samples - than other microwave plasmas [5]. This is an advantageous feature for the destruction of volatile organic compounds. The VOCs to be destroyed were introduced into the plasma by pre-mixing them with the carrier gas, helium, using a gas mixer.

In order to isolate and analyse the gases after the plasma destruction, a reaction chamber was designed and placed after the wave-guide [6]. Gas samples can be extracted from the chamber in order to be analysed by gas chromatography.

The three main parameters and their respective ranges of variation used in this work are: total flow (helium + TCE vapour) from 0.5 to 2.5 L/min; the TCE concentration in the gas from 100 to 60000 ppm, and the microwave power from 300 and 1000 W.

The highest concentrations of TCE were obtained by passing a controlled helium flow rate through a bubbler containing the volatile organic compound in order to carry VOC vapour with it. These concentrations were calibrated with the gas chromatograph.

After the plasma treatment, the gas mixture is passed through a $CaCO_3$ fluidised bed that absorbs the remaining VOCs and their discharge products [7]. Finally, the resulting gas is exhausted into a fume hood.

A schematic diagram of the experimental set-up is presented in Fig. 1.

Different diameters of the tip of the torch were used in order to increase the energy efficiency. A higher cross-section results in our ability to destroy a larger quantity of VOC per unit time.

3 Trichloroethylene analysis

Quantitative analysis of TCE was performed using an Agilent4890D gas chromatograph equipped with an electron capture detector (ECD) and a flame ionisation detector (FID). A calibration curve was generated in order to characterise the responses of these detectors to the analyte concentration. This calibration curve was carefully chosen to cover the wide range of concentration of the injected samples.

The trichloroethylene mass density was measured before and after entering the plasma in order to compute the corresponding destruction and removal efficiency percentage (%DRE) using its standard definition [8]:

$$\%DRE = \left(\frac{W_{in} - W_{out}}{W_{in}}\right) \times 100, \tag{1}$$

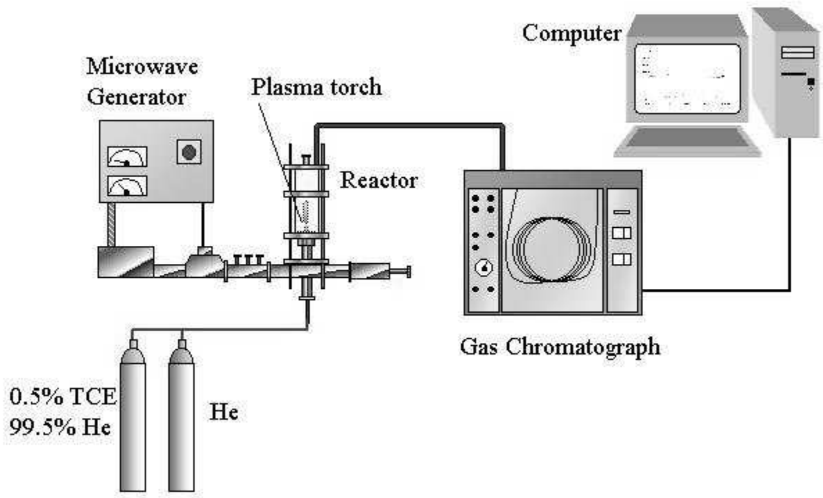

Fig. 1. Experimental set-up.

where W represents the weight of TCE in the reactor chamber and the in and out subscripts denote the quantity before and after being processed.

4 Results and discussion

The destruction of trichloroethylene depends on the plasma parameters, such as the electron density and the gas temperature. It is also very important to take into account the residence time of the TCE in the plasma, which is computed as a function of the plasma volume. This volume and the plasma parameters depend on the plasma conditions, i.e., the injected microwave power and the gas flow rate.

The destruction percentage was calculated for a wide range of parameters of the TIA, such as gas flow, applied microwave power, and concentration of TCE. Different diameters of the tip of the torch were also compared.

The main gas flow is a fundamental parameter for the operation of the TIA, because it maintains the adequate temperature for the proper operation of the torch. However, the gas flow greatly affects the destruction efficiency, because the residence time of the TCE in the plasma depends on the velocity of the gas as it exits the tip. Thus, it is important to obtain an optimum gas flow, which maintains a stable plasma in the reaction chamber and, at the same time, achieves high destruction percentages.

A fixed quantity of TCE was destroyed using different flows of He, between 0.5 and 2.5 L/min. We can prove that the efficiency of destruction decreases when the total flow increases. However, in this finding, there are two parameters that are playing the same role: when the gas flow increases, the residence time decreases, and the concentration of TCE also decreases (if a fixed mass of TCE is used). Both effects produce a decrease of %DRE, so it is necessary to study them separately.

4.1 Dependence of destruction efficiency on total flow

In order to study this dependence of %DRE on the total flow, we have to keep the concentration of TCE constant, which implies that the mass of TCE must be increased as the flow of helium increases.

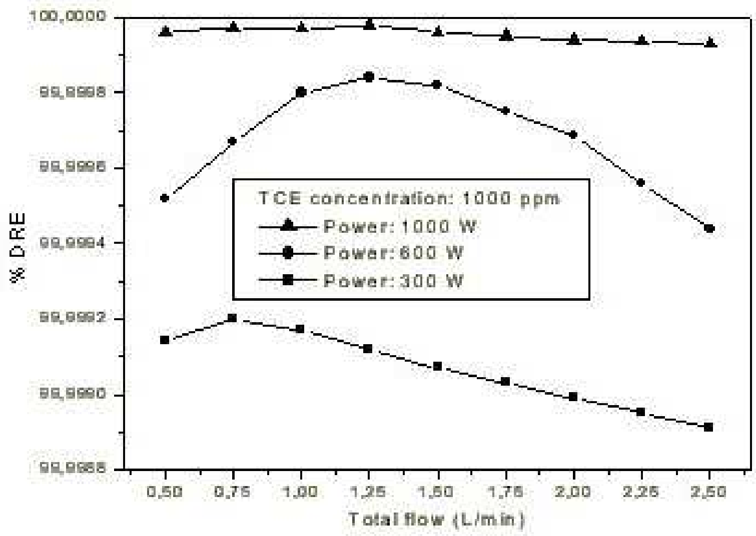

Fig. 2. Dependence of the %DRE on the gas flow for a mixed concentration of TCE and three different applied microwave powers.

Figure 2 shows the results of a study with 1000 ppm of TCE. The total flow was changed and the %DRE was measured for each value of the flow. Three values of applied microwave power were used in this study. We observe that a higher microwave power achieves an inreased destruction efficiencies. However, the effect of the applied microwave power will be discussed later.

It can be seen that there is an optimum gas flow value where the TCE destruction is maximum. At this point, the plasma has its highest efficiency to destroy a particular TCE concentration for a given value of the applied microwave power. The %DRE decreases at higher values of the helium flow. This is due to the decrease of the gas temperature in the plasma and to the reduction of the plasma volume, which implies lower residence times of the TCE in the plasma.

On the other hand, the lowest flow rates of helium do not achieve a good destruction percentage, because the TIA does not work properly when the total flows below 0.7 L/min.

4.2 Dependence of destruction efficiency on TCE concentration

Another important parameter to characterise the destruction capability of this set-up is the concentration of TCE in the gas mixture used to generate the plasma. We have observed that higher destruction percentages were obtained when higher TCE concentrations were used. This result implies that more TCE molecules are decomposed for a given energy and total flow when the TCE concentration increases.

Similar results have already been found by T. Yamamoto [9] and B.M. Penetrante [10] and these obseravtions suggest that secondary decomposition processes of TCE can be induced by fragments of ions and radicals that result from the initial decomposition of trichloroethylene. Thus, if the concentration is higher, this effect increases and the destruction efficiency improves.

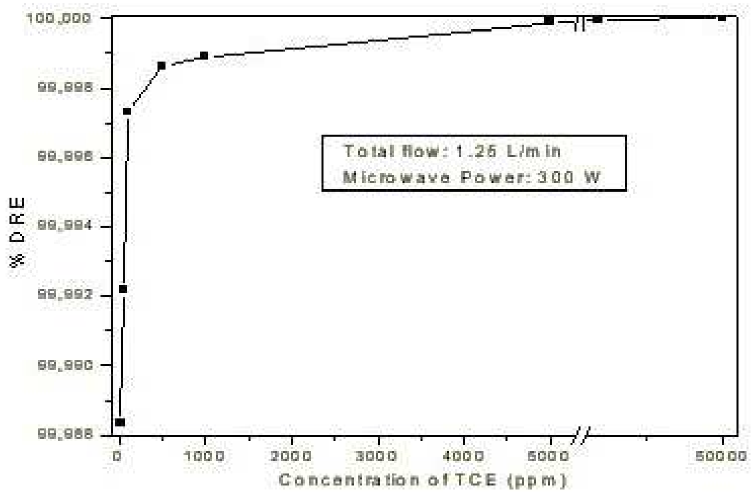

Fig. 3. Dependence of the %DRE on the TCE concentration in the plasma gas.

Our data also support that theory. Figure 3 shows the efficiency versus concentration of TCE using a fixed total flow (1.25 L/min) and a constant applied microwave power of 300 W.

Higher concentrations seem to be the best solution, because the energy efficiency is maximum. However, lower concentration are of importance in some applications such as the removal of air pollutants. In this case, a high destruction percentage can be obtained by increasing the applied microwave power or decreasing the total flow. Thus, it is possible to achieve optimum for the destruction of almost any quantity of TCE.

4.3 Dependence of destruction efficiency on applied microwave power

The energy of the plasma electrons increases when the microwave energy increases. Thus, the destruction capability improves when higher microwave powers are used, but the energy efficiency decreases.

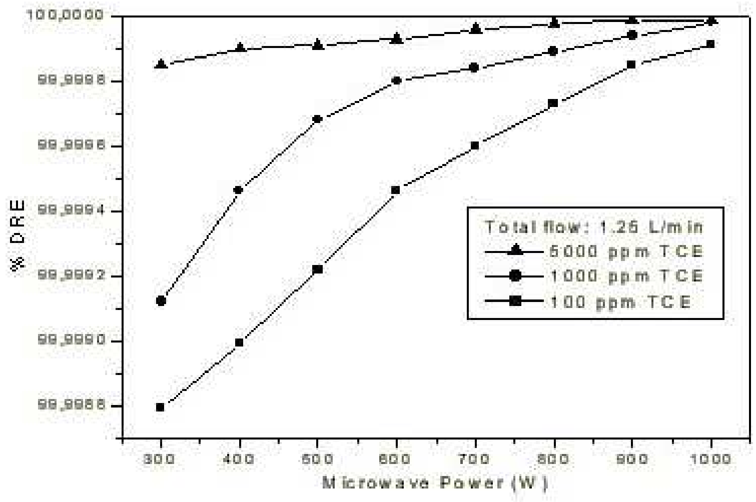

Fig. 4. Dependence of the %DRE on the applied microwave power for different TCE concentrations.

Figure 4 shows the dependence of the %DRE on the microwave power using a helium flow rate of 1.25 L/min and different applied microwave powers for three separate TCE concentrations. These results clearly show that the %DRE increases with the microwave power up to 900 W, where the destruction efficiency exceeds 99.999% for the highest concentrations. No significant further improvement of the %DRE was observed at even higher powers.

These results show that 99.99985 % of destruction is obtained with 1000 W at a concentration of 100 ppm. The same destruction percentage is obtained with 300 W at 5000 ppm. The conclusion is that we can use lower microwave power to destroy the same percentage of TCE if higher concentrations are introduced.

A study of destruction efficiency versus both the total flow and the applied microwave power was done in order to obtain a global view of the results. The %DRE was studied for a wide range of values of the total flow, the applied power and for several fixed concentrations of TCE in order to obtain the graph. A different graph was obtained for each concentration, as the volue of the TCE concentration is constant for all the points of each graph.

Figures 5 and 6 show a complete study for 1000 ppm of TCE. Figure 5 represents the results in the 3D graph and Fig. 6 illustrates a transversal view of this graph. We can observe the dependence of the efficiency on the total flow and the influence of the power on this dependence.

4.4 Effect of the cross-section of the tip of the plasma torch on the destruction efficiency

There are circumstances under which poor energy efficiencies were obtained as can be seen from the previous figures. With the present set-up, it is possible to improve the energy efficiency by changing the tip of the torch where the plasma is injected.

This is not surprising, as the destruction efficiency depends on the on the plasma volume and

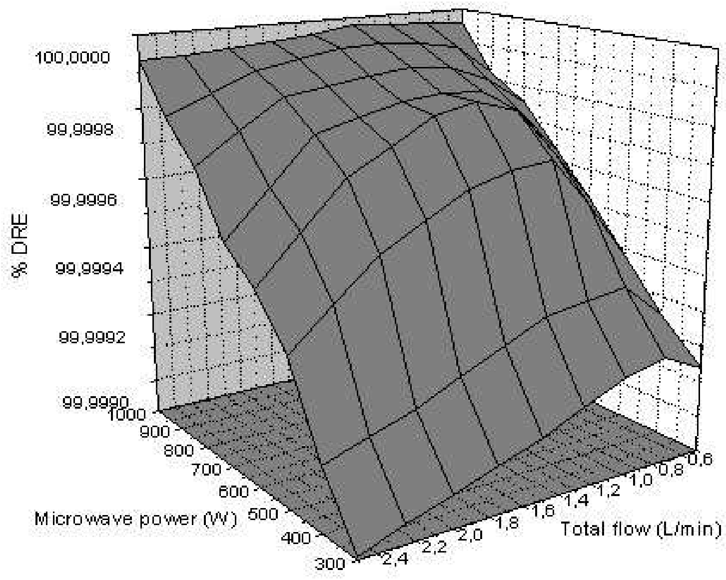

Fig. 5. 3D graph of the %DRE versus MW power and total flow.

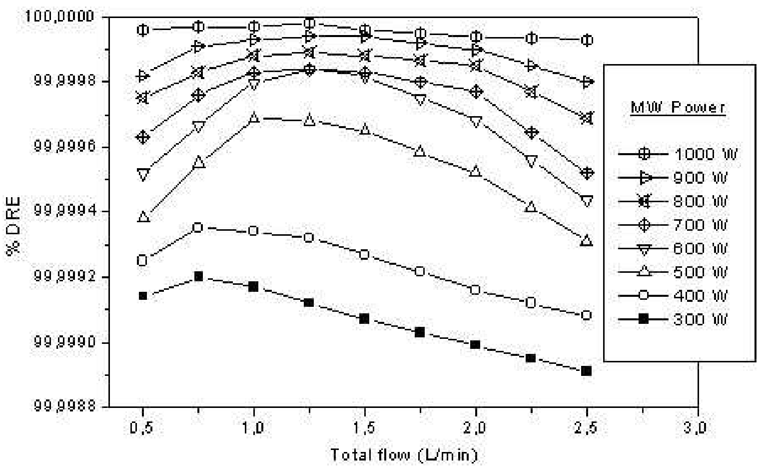

Fig. 6. Dependence of the %DRE on total flow for different powers.

residence time and these parameters depend directly on the velocity of the gas as it exits the tip. Thus, if we use a higher cross-section in the tip, we can achieve destruction of a larger quantity of TCE with the same destruction percentage, because a higher flow is necessary to maintain the same velocity of gas in the tip, if we maintain a fixed concentration of TCE in the gas.

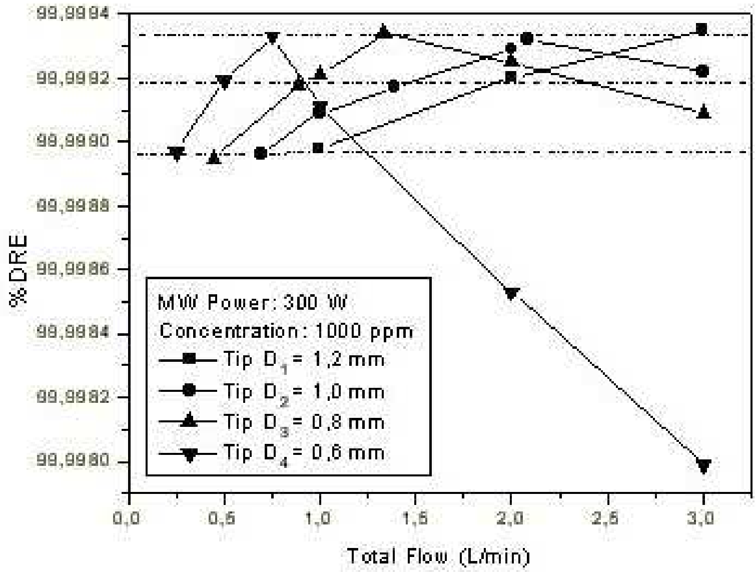

Fig. 7. Comparison of the destruction capabilities of four different tips of the TIA.

Figure 7 compares the results of experiments using 1000 ppm of TCE with four different internal diameters of the tips. The dash-dot lines link points with the same velocity of gas in the tip, and we observe that these points have the same destruction and removal efficiency. This demonstrates that the %DRE depends strongly on the velocity of the gas at the exit of the tip.

Energy efficiencies of more than 500 g/kWh were achieved in our apparatus with destruction and removal efficiencies up to 99.999%.

Hence, it is necessary to state that the results presented previously in Figs. 2-6 were obtained on a laboratory scale with a tip that had the smallest diameter. However, in an industrial processing facility, it would be interesting more appropriate to use bigger cross-sections.

5 Conclusions

This paper reports the effects of microwave power, gas flow rate, and TCE concentration on the decomposition efficiency of TCE by a microwave torch. The following observations are noteworthy:

- The TIA seems to be a promising device for VOC destruction yielding high percentage destruction efficiencies at comparatively low power expenditure.

- The TCE decomposition increases with microwave power.
- At fixed TCE concentrations and applied microwave powers, the decomposition efficiency decreases as the gas flow increases.
- The decomposition efficiency was slightly higher with higher TCE concentrations, which implies that more TCE molecules are decomposed for a given amount of energy when the TCE concentration is higher. This suggests that secondary decomposition processes of TCE can be induced by fragment ions and radicals from the initial decomposition of TCE [9,10].
- Energy efficiencies up to 500 g/kWh can be achieved using tips of the torch with higher cross-sections of the tip of the torch. The destruction efficiency depends on the velocity of the gas in the exit of the tip so that a larger quantity of TCE can be destroyed per minute when tips with higher cross-sections are used.
- The performance of the TIA can be optimised for a wide range of TCE concentrations.

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