

MICROWAVE PLASMA: POLLUTION REDUCER OR PRODUCER?

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ABSTRACT

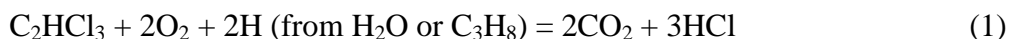
The purpose of this research program is to investigate the possibility of using a microwave plasma device to treat volatile organic compounds (namely trichloroethene) released from industrial cleaning processes. Very high destruction efficiencies can be achieved by using either conventional combustion or a microwave plasma. However, the microwave plasma alone is found to produce more unwanted by-products than conventional combustion, as well as being less energy efficient. Therefore, hydrogen (from fuel or water) must be added to the process in order to prevent production of much more harmful chemicals than the original solvent to be treated. A process combining fuel combustion and microwave plasma is proposed. Health and safety concerns are also raised.

The research reported in this paper was undertaken as part of a PhD study that commenced in March 2001 and is due to finish in September 2004. The work is carried out at IRIS and is jointly funded by the CRC for Intelligent Manufacturing Systems and Technology and IRIS.

INTRODUCTION

The potential for large financial penalties and poor public image resulting from environmental non-compliance has led to a trend of increasing expenditure on pollution abatement in developed countries. Volatile Organic Compounds (VOCs) are one of the groups of chemicals under scrutiny for their potential to adversely affect health and the environment. Many industrial cleaning processes require chlorinated hydrocarbon solvents (classed as VOCs) and so must comply with emission regulation.

The aim of this research is to investigate the possibility of treating one such solvent, trichloroethene (TCE), with a microwave-induced plasma. If viable, this would be a very attractive option: the capital costs of a microwave plasma unit are low; there are no electrodes required as in other plasma sources; the use of plasma would enable leaner burning than in a conventional flame. However, as the microwave plasma operates at a minimum “temperature” of 4000°C, the process would be more energy efficient if conventional gas burning could be incorporated into the process, using the plasma to speed up the degradation of unwanted combustion products. The addition of hydrogen from the alkane fuel would also enable the stoichiometry to be adjusted for the formation of the desired products, hydrogen chloride and carbon dioxide (1).



So one mole of water or a quarter of a mole of propane would provide enough hydrogen for the above stoichiometry. For TCE levels of up to 1% in air, the humidity from normal air would provide enough hydrogen. However, the typical concentration to be treated is 2% TCE

in air. Therefore, it is expected that additional hydrogen, in the form of either an alkane or water vapour, will be required to yield the desired products. For this project, we have chosen to use propane as the primary hydrogen source.

In order to verify the above reasoning, three different TCE destruction methods are being investigated: microwave plasma, propane combustion and microwave plasma with propane. The variable inputs into the system are: 0 – 6 % TCE in dry air, flow rates from 4 – 15 l/min and powers ranging from 2 – 4 kW. As explained above, the addition of propane is expected to have a similar effect to that of water (i.e. to provide hydrogen to the system), and this hypothesis is also under investigation. Chemical analysis is carried out using Gas Chromatography (GC) with electron capture detection (ECD). Identification of peaks is done by GC/MS (Mass Spectrometry). Incident and reflected power is logged on-line.

Chemical modelling is carried out using Chemkin [1]. This helps with experimental planning as well as understanding the experimental outcomes.

RESULTS

Propane Combustion

TCE destruction was very effective; four nines' destruction (i.e. 99.99%) was achieved for concentrations of 3% TCE and below, while higher concentrations were reduced by at least 99%. Chlorinated aliphatics and low levels of chlorinated aromatics were formed as expected. These experiments were carried out early in the experimental process, and the GC column used was not ideal. Therefore, results are qualitative only. These are due to be repeated. However, it is clear that since chlorinated aromatics pose a much higher risk to health [2] than TCE [3], gas burning of TCE would not be attractive.

It should be noted that some solids were formed in the copper chimney that the exhaust fumes pass through. We performed atomic absorption analysis on the solid and found that it was all or mostly metal chlorides resulting from the HCl and possibly other acids being formed attacking the metal surfaces.

Microwave Plasma

The plasma is very effective at destroying the TCE, efficiencies ranging from 1.5 to 4 nines destruction. However, the formation of environmentally undesired products seems to be higher than in the propane combustion.

The major product is a chlorinated aliphatic, probably C_2Cl_2 or CCl_3CClO , yet to be successfully identified. Figure 1 shows the formation of this compound with increasing initial TCE concentration for different flow rates at 2kW. The lower flow rates correspond to the highest plasma temperatures (about 6,000K). At 12 l/min, the minimum temperature without plasma extinction has been reached, and this corresponds to about 4,000°C. However, other factors, such as the residence time and the quench rate vary with the flow rate. The amount formed generally increases with TCE concentration. Up to 1% and above 4%, more of this product is formed in the higher flow rate experiments, except for the apparent anomaly at 12

l/min and 6% TCE. This could mean that the slightly lower temperatures in the plasma are more conducive to the formation of this compound. It could also be that the reactor is not large enough for the higher flow rates, or related to the quench rate. Note that the 4 l/min runs had a huge peak at 3%TCE. This is not yet explained. It could be an anomaly, but these points are based on averages so it should not be discounted prematurely. Figure 2 shows the variation of the same peak for 2% TCE and 10 l/min with different power inputs. The variation in residence time and quench rate should be negligible in this case, making a comparison between different temperatures, or more accurately enthalpies in the plasma, possible. There is some variation, but not enough to conclude that there is any trend. It seems factors other than the temperature are affecting the formation of this product, which may be a precursor to other, even less desirable by-products.

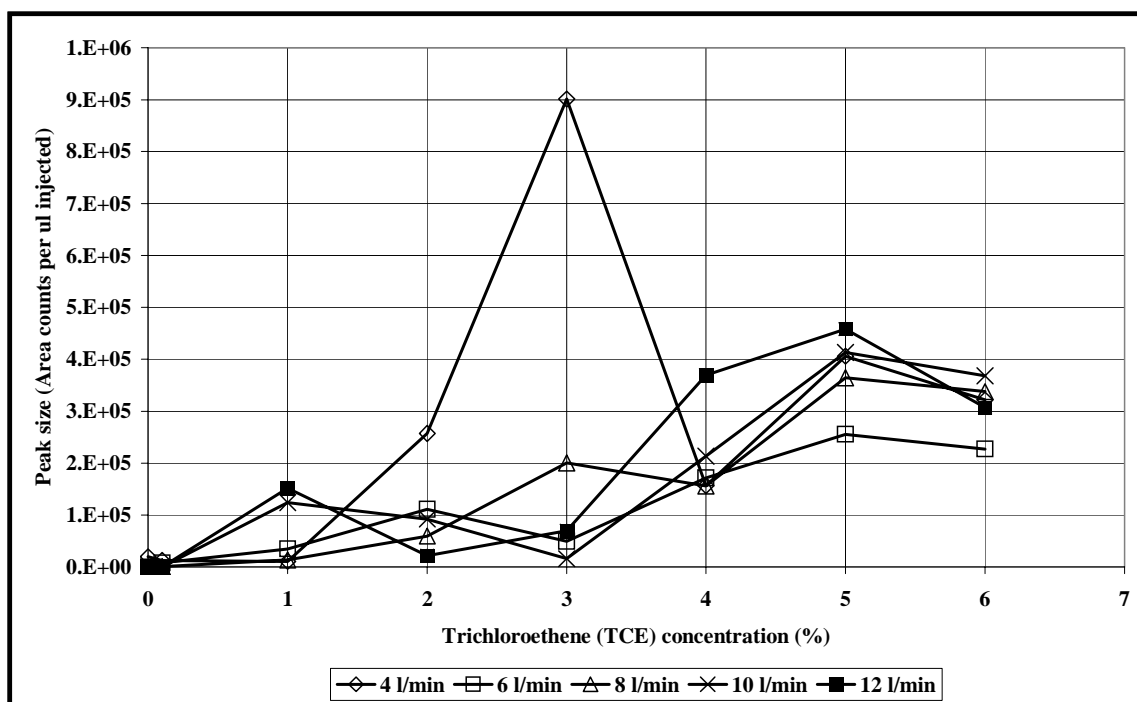


Figure 1: Area of the largest peak (elution time 4.7 minutes) against initial trichloroethene concentration

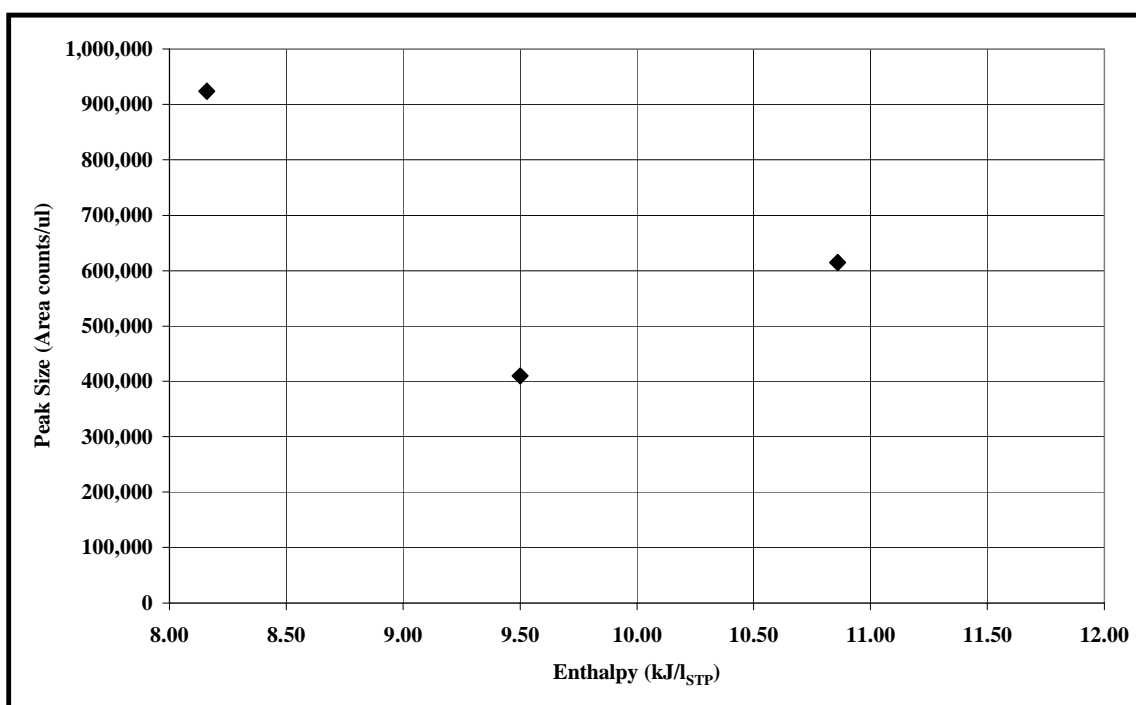
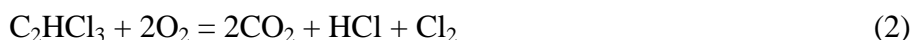


Figure 2: Area of the largest peak (elution time 4.7 minutes) against enthalpy in plasma

Since the plasma has no added fuel and is therefore leaner than the propane flame, aromatic formation was expected to be reduced in all experiments and absent at low TCE concentrations. It was hoped that the lack of hydrogen would result in the formation of chlorine gas, which could be scrubbed along with the HCl (2).



However, we have detected the presence of chlorinated aromatics in all runs containing TCE. The most persistent high-end peaks in the chromatograms are tetrachlorobenzene and a peak following that, either another tetrachlorobenzene isomer or chloronapthalene. Other chlorobenzenes, including hexachlorobenzene are formed.

Figure 3 shows the variation of the first tetrachlorobenzene peak with initial TCE concentration for varying flow rates. There is no obvious correlation between flow rate or TCE concentration and the amount of this tetrachlorobenzene isomer being formed in the gas phase. Strangely enough the 12 and 10 l/min runs peak significantly at 1 and 2 % respectively. Figure 4 shows the variation of the same peak for 2% TCE and 10 l/min with different power inputs. In this case, higher enthalpies in the plasma do seem to reduce the formation of this unwanted by-product significantly.

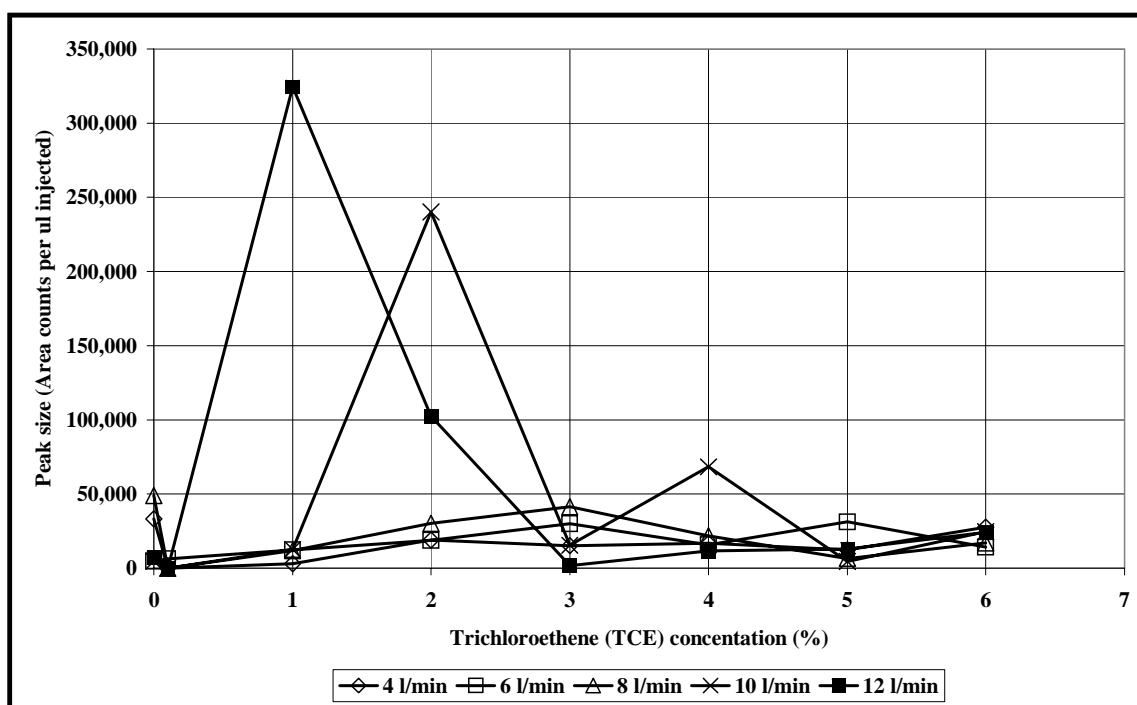


Figure 3: Area of the 16.3 minute peak (tetrachlorobenzene?) against initial trichloroethene concentration

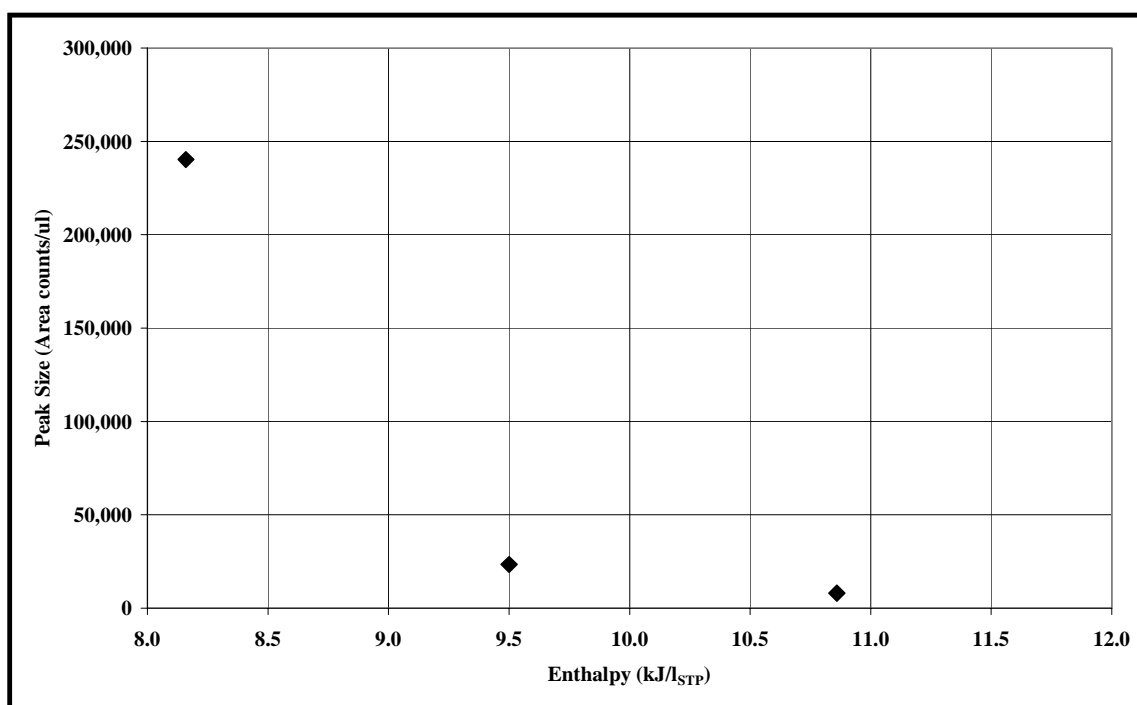


Figure 4: Area of the 16.3 minute peak against enthalpy

The most interesting outcome of the plasma experiments so far has been the formation of copious amounts of white solid inside the copper chimney. It starts melting and runs down the chimney and back into the plasma reactor at and above about 150°C. The mass being formed (about 50% by mass of TCE destroyed) cannot be accounted for by acid attack as in the propane experiments. Also, the chimney metal is not significantly corroded. We are currently getting this residue analysed by an independent laboratory.

The chlorinated aromatics (especially 1,2,4,5-tetrachlorobenzene and hexachlorobenzene) have low vapour pressures at the gas sampling temperatures (~300K). The detection of any of these compounds in the gas phase indicates that there is more condensing in the rig, chimney and gas sampling syringe. Therefore the formation of these compounds cannot be quantified from the gas phase analysis. If the analysis of the solid residue indicates the presence of 1,2,4,5-tetrachlorobenzene (melting point 140°C), this will be an astonishing finding and a sure indication that microwave plasmas should not be used for this purpose.

Microwave Plasma with Hydrogen from Propane or Water

It is hoped that the addition of hydrogen to the plasma will prevent the formation of the unwanted by-products, especially the chlorinated aromatics (see equation 1). These experiments will be done after a safety assessment when the nature of the chimney deposits is known.

MODELLING

Equilibrium modelling has shown that at plasma temperatures (4,000 – 6,000K) only simple molecules such as HCl, ClO, CO, etc. exist. It also shows that the most likely temperature range for formation of chlorinated aromatics is 600 – 700 K. This suggests that the variation in quench rate is more likely to be responsible for the variations in by-product formation than the other parameters such as plasma temperature.

It should also be noted that tetrachlorobenzene does not feature in our equilibrium calculations at all. Thermodynamic data available attaches the same properties to all three isomers of tetrachlorobenzene. However, the melting point of the symmetrical isomer, 1,2,4,5-tetrachlorobenzene, is 139°C, while the other two isomers melt at about 50°C. This makes 1,2,4,5-tetrachlorobenzene more stable than the data suggests and prevents tetrachlorobenzene from appearing in the equilibrium calculations. This work suggests that 1,2,4,5-tetrachlorobenzene plays a more important role than previously given credit for and is probably second only to hexachlorobenzene in terms of stability of chlorinated aromatics.

CONCLUSIONS

If microwave plasmas are to be adopted for the treatment of medium level pollution, quench rates and input concentrations must be well-understood and carefully controlled. Treatment of levels of TCE above 1% will require the addition of extra hydrogen (e.g. in the form of an alkane fuel) to augment that already supplied by ambient water vapour. At this stage it appears that the health and safety issues that may arise from non-ideal operation would be very serious and would possibly outweigh the benefits of reducing the amount of TCE released into the atmosphere.

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