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Remediation of Dichloromethane (CH$_2$Cl$_2$) Using Non-thermal, Atmospheric Pressure Plasma Generated in a Packed-Bed Reactor

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Ⓢ *Supporting Information*

ABSTRACT: This work describes the application of a non-thermal plasma generated in a dielectric barrier packed-bed plasma reactor for the remediation of dichloromethane (CH$_2$Cl$_2$, DCM). The overall aim of this investigation is to identify the role of key process parameters and chemical mechanisms on the removal efficiency of DCM in plasma. The influence of process parameters, such as oxygen concentration, concentration of initial volatile organic compounds (VOCs), energy density, plasma residence time, and background gas, on the removal efficiency of 500 ppm DCM was investigated. Results showed a maximum removal efficiency with the addition of 2−4% oxygen into a nitrogen plasma. It is thought that oxygen concentrations in excess of 4% decreased the decomposition of chlorinated VOCs as a result of ozone and nitrogen oxide formation. Increasing the residence time and the energy density resulted in increasing the removal efficiency of chlorinated VOCs in plasma. A chemical kinetic model has been developed on the basis of the proposed reaction scheme, and the calculation of end product concentrations are in general good agreement with the observed values. With the understanding of the effect of the key parameters, it has been possible to optimize the remediation process.
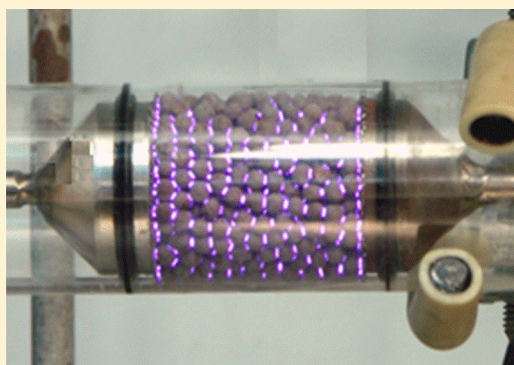
1. INTRODUCTION

Volatile organic compounds (VOCs) are a class of air pollutants that affect both the environment and human health.[1,2] Some VOCs are produced from natural sources, including emissions from plants and natural forest fires. The VOCs that are harmful for both the environment and human health are primarily released by man-made activities, such as from oil refineries, petrol storage and distribution, vehicle exhausts, solvent usage and manufacturing, surface coating and painting, and many other industrial processes.[1,3−5] Reducing the use of VOCs is the ideal approach, but "end-of-pipe" technologies are still necessary to remove or remediate. This work investigates the remediation of dichloromethane (CH$_2$Cl$_2$, DCM) as an example chlorinated VOC, using a packed-bed plasma reactor. DCM causes several health problems, such as headache, nausea, dullness, dizziness, pulmonary irritation, and effects on the central nervous system. Excessive exposure can cause abortion, affect the birth weight, and potentially cause cancer.[2,6]

There are several traditional ways to remove VOCs from waste gas streams, such as thermal oxidation, catalytic oxidation, and adsorption, but these techniques suffer from a variety of problems. Thermal oxidation has the problem of generating NO$_x$ and other harmful byproducts; catalytic oxidation suffers from catalyst deactivation and poisoning by lead, sulfur, and halogens as well as the disposal of contaminated used catalyst; and adsorption by materials, such

as activated carbon and zeolites, requires a batch operation and disposal of the adsorbing material. However, non-thermal plasmas generated at atmospheric pressure and room temperature provide several advantages for air pollution control. No heating is required for the non-thermal plasma process; it is generated at room temperature. The energy input into the reactor can also be rapidly varied and controlled depending upon load for increased energy efficiency compared to traditional thermal techniques. For example, atmospheric pressure plasmas have been shown to reduce diesel exhaust pollutants as well as several VOCs.[7−15]

Several studies have previously investigated the decomposition of DCM in plasma using different types of plasma reactors and operating conditions, for example, dielectric packed-bed,[16,17,19,21] pulsed corona,[22] electron beam,[22] and low-pressure radio-frequency (rf) plasma reactors[34] with differing background gases and oxygen levels. Fitzsimmons et al.[16] investigated the effect of the oxygen concentration on the removal efficiency of 500 ppm DCM in a non-thermal plasma generated in a packed-bed plasma reactor. They found a maximum DCM removal efficiency in nitrogen plasma with the addition of 2−3% oxygen. Despite these numerous studies, a
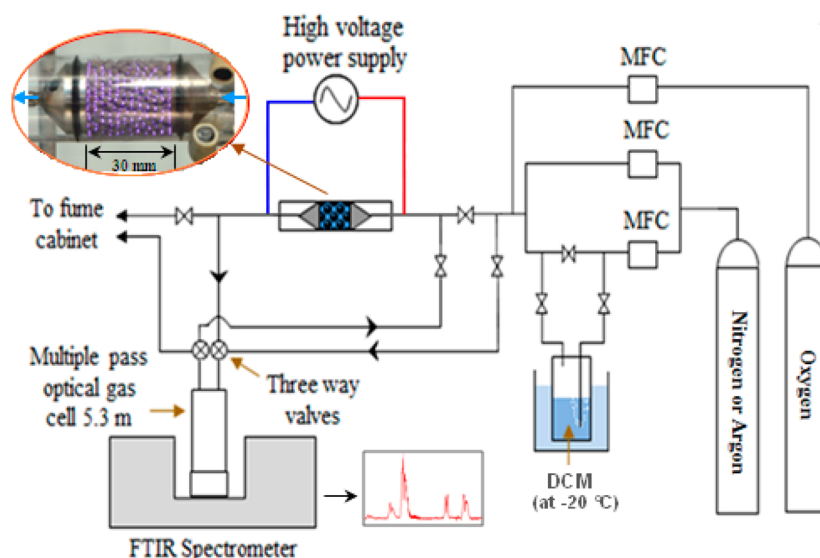
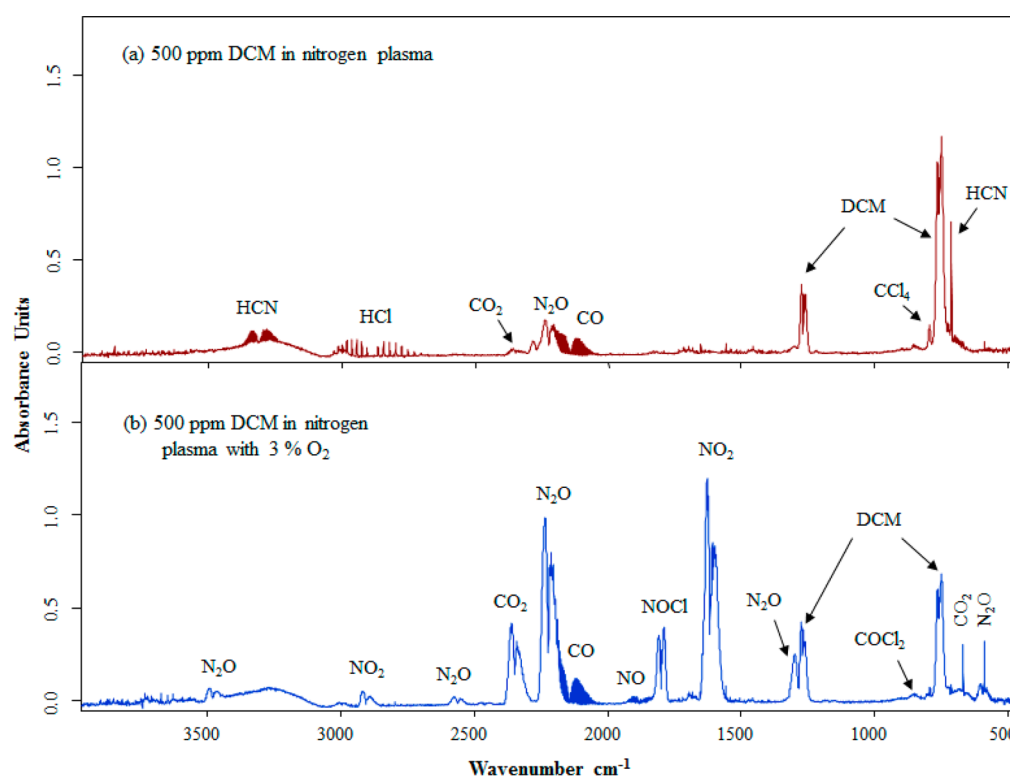**Figure 1.** Plasma inlet system that had been used to investigate the influence of a variety of parameters on the remediation of DCM.

Figure 2. FTIR spectra for 500 ppm DCM after plasma reactor in (a) nitrogen plasma without adding oxygen and (b) nitrogen plasma with adding 3% oxygen to the gas stream. A multiple pass optical gas cell with a 5.3 m path length, a total flow rate of 1 L min^{-1}, and an energy density of about 1000 J L^{-1} was used. Measurements were taken about 0.75 s downstream of the plasma reactor.

complete and clear understanding of the effect of different plasma parameters on the decomposition process for chlorinated VOCs is yet to be established. Most of the previously mentioned studies have found that adding oxygen to the gas stream resulted in either decreased removal efficiency of chlorinated VOCs or a maximum decomposition with small oxygen concentrations of about 3%. For environmental applications, it is more practical to use an air plasma rather than controlling oxygen concentrations to ~3%. It is also preferable to use atmospheric pressure rather than low-pressure reactors because of the reduced running costs.

The aim of this study is to identify the influence of key process parameters on the removal efficiency of DCM in non-thermal plasma generated in an atmospheric pressure packed-bed plasma reactor and to develop a kinetic model of the reaction scheme to further understand the chemical mechanism and to achieve maximum removal efficiency.[17]

2. EXPERIMENTAL SECTION

2.1. Experimental Setup. Figure 1 shows a schematic of the experimental arrangement. The atmospheric pressure plasma was generated using a packed-bed plasma reactor

consisting of a Pyrex glass tube about 20 cm long with an internal diameter of 31 mm. Two stainless-steel tubes ending with funnels and covered with stainless-steel meshes have been used as electrodes. Barium titanate beads, $BaTiO_3$, from CATAL International, Ltd., with a diameter of 1.4−2.8 mm, were used as the packed-bed dielectric filling material. The packed bed volume was about 24.9 cm^3, while the void volume was about 16 cm^3, allowing for a residence time of about 0.9 s with 1 L min^{-1} flow rate. Nitrogen or argon gas was passed through a bubbler containing liquid DCM (supplied by Sigma Aldrich with a purity of 99.6%). The flow rate of nitrogen and the temperature of the liquid DCM in the bubbler were controlled to obtain approximately 500 ppm DCM in the inlet gas stream of the reactor. Oxygen, with a concentration varying from 0 to 21%, was added to the gas stream, and the overall gas flow rate was set at 1 L min^{-1}. The gases were used as delivered and consisted of air (79% nitrogen and 21% oxygen), oxygen (99.99%), nitrogen (99.998%, oxygen-free), and argon (99.999%). A pulsed neon sign power supply (Hansen) providing a high voltage of about 14 kV (peak to peak) at a frequency of 20 kHz during each pulse and with a pulse repetition frequency of 100 Hz was used to generate the plasma. A 1000:1 (Tektronix TES TEC HVP 15HF) voltage probe and Pearson current monitor (model 411) have been used to characterize the supplied power.

The inlet gas stream and plasma reactor product stream were analyzed sequentially using a Fourier transform infrared (FTIR) spectrometer (Bruker Equinox 55, with a spectral resolution of 1 cm^{-1}) combined with a multiple pass optical gas cell with a 5.3 m path length and situated about 1.5 m away from the reactor, connected by a 4 mm inner diameter plastic tubing. Measurements commenced after about 15 min of initiating the plasma to ensure that a steady state was achieved. Most measurements were repeated at least 3 times, and an average result was reported. Examples of in-line FTIR spectra for DCM decomposition products with 0 and 3% of added oxygen are shown in Figure 2.

2.2. Calculation of Plasma Parameters. Concentrations of each species were determined by integrating the area under each absorbance band using Bruker's OPUS software and then comparing these to those obtained for equivalent integration limits from standard FTIR spectra in the Pacific Northwest National Laboratory (PNNL) database for 1 ppmv at atmospheric pressure, 1 m path length, 0.1 cm^{-1} resolution, and a temperature of 25 °C.[18] This approach is described in ref 17 and assumes a linear change in absorbance from 1 ppm of the standard to that obtained in the sample for low absorbance values. A 5% uncertainty in the concentration could be introduced by this approach.[17] Further uncertainties can be caused by variations in the temperature of the DCM bubbler, leading to an additional 6% error. These error bars are indicated on the figures. The concentrations of DCM entering ([DCM$_{in}$]) and leaving the reactor ([DCM$_{out}$]) were measured. The removal efficiency (η) of the DCM, the chlorine balance, and the carbon balance were calculated as follows:

$$\eta = \frac{([DCM_{in}] - [DCM_{out}]) \times 100}{[DCM_{in}]} \tag{1}$$

chlorine balance (%)

$$= \frac{([HCl] + 4[CCl_4] + 2[COCl_2] + 2[DCM_{out}]) \times 100}{2[DCM_{in}]} \tag{2}$$

carbon balance (%)

$$= \frac{([CO] + [CO_2] + [DCM_{out}]) \times 100}{[DCM_{in}]} \tag{3}$$

The energy density (J L^{-1}), which is the energy deposited in the gas per unit volume, was calculated by dividing the measured input energy per second (W) over the volumetric gas flow rate with a unit of L s^{-1}. The average power delivered to the plasma reactor is calculated by multiplying the time-dependent voltage and current and integrating over one pulse duration and then multiplying by the pulse repetition frequency, f (100 Hz)

$$P = f \int_0^T \sqrt{V(t)^2 I(t)^2} \, dt \tag{4}$$

where P is the deposited power measured in watts, $T \approx 0.01$ is the pulse duration in seconds, $V(t)$ is the voltage applied to the plasma reactor measured in volts, and $I(t)$ is the input current measured in amperes.

2.3. Kinetic Modeling. The chemical kinetics software, CHEMKIN II, was used to support the experimental work. The model used in this work was an adaptation of the reaction pathway originally reported by Wilman[19] and Fitzsimmons et al.[16,20] They developed a reaction scheme for the decomposition of DCM in a nitrogen−oxygen plasma. This model assumes a uniform processing of the gas in the plasma region. It also assumes the formation of active species during each half period of voltage with the formation of microdischarges. A fresh feed of the active species is added at each half cycle. The chemistry is initiated and progresses until the end of the pulse. For example, in a discharge with a frequency of 20 kHz and a plasma residence time of 0.9 s, there are 18 000 cycles. This means that there are 36 000 pulses for integration, with a 0.25 × 10^{-4} s time interval for each pulse. The concentration of the plasma end products was determined at the end of the process.

The rate equation and Arrhenius parameters used are given in the Supporting Information. Other input parameters were initial gas and active species concentrations, residence time, discharge frequency, pressure, and temperature. Active species concentrations were initially based on calculations of the electron energy distribution function for this type of reactor from ref 20. The initial atomic oxygen concentrations were adjusted slightly to give the best agreement with the observed product concentration. Table 1 shows the concentration of active species used in this work. The elements included in this model are C, H, O, N, and Cl. The number of species in this model is 77, and the number of chemical reactions is 224 reactions.

3. RESULTS AND DISCUSSION

3.1. Influence of the Oxygen Concentration on the Removal Efficiency of DCM and the Formation of Plasma End Products. These experiments have been carried out using the inlet system shown in Figure 1. A gas stream consisting of an initial concentration of approximately 500 ppm DCM in nitrogen was used. The oxygen concentration was

Table 1. Active Oxygen Concentration in ppm as a Function of Input Oxygen[a]

| O$_2$ (%)	O	O(^{1}D)	O$_2$($^1\Delta$)
1	0.0062	0.003	0.0008
2	0.0124	0.006	0.0016
3	0.0186	0.009	0.0024
5	0.0310	0.015	0.0040
10	0.0620	0.030	0.0080
15	0.0930	0.045	0.0120
21	0.1302	0.063	0.0168

[a]Other species, such as N, N*, N$_2$*, Cl, and CH$_2$Cl, are unaffected by the change in the concentration of added oxygen and have a value of 0.0098, 0.0096, 0.0286, 0.6×10^{-5}, and 0.6×10^{-5} ppm, respectively.

varied from 0 to 21% in a total gas flow rate of 1 L min^{-1} and an energy density of about 1000 J L^{-1}. Figure 3 shows the
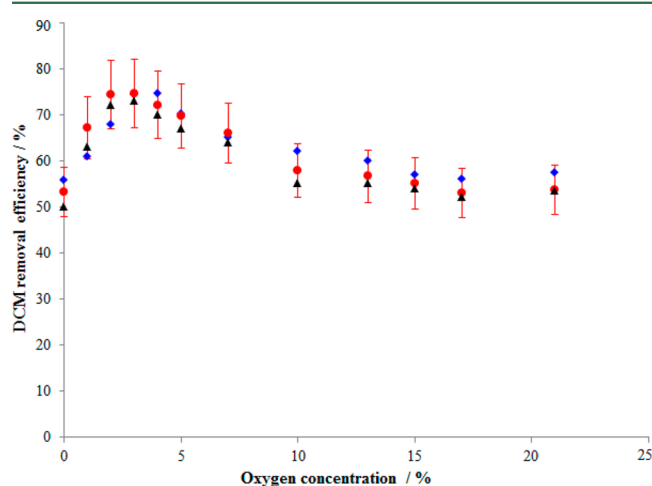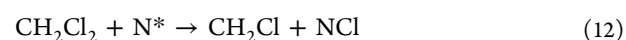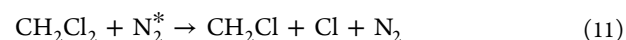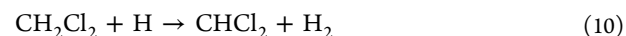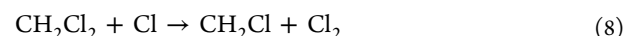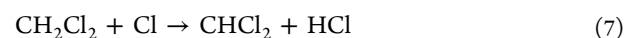

Figure 3. Removal efficiency of 500 ppm DCM in nitrogen non-thermal plasma as a function of oxygen concentrations in a packed-bed plasma reactor. A total flow rate of 1 L min^{-1} and an energy density of about 1000 J L^{-1} were used. Three measurements were made for each oxygen concentration indicated by the three different symbols.

influence of the oxygen concentration on the removal efficiency of DCM. Results show a maximum DCM decomposition with 2−4% of added oxygen to the gas stream. Beyond 4% resulted in decreasing the removal efficiency of DCM, which was in agreement with our earlier work in ref 21. In a pure nitrogen plasma, without the addition of oxygen, the decomposition of DCM is initiated as a result of electron impact with CH$_2$Cl$_2$ molecules in the gas stream. Electron impact decomposes CH$_2$Cl$_2$ and generates active chlorine and hydrogen atoms via the following reactions:[16,22,23]

$$e^- + CH_2Cl_2 \rightarrow CH_2Cl + Cl + e^- \tag{5}$$

$$e^- + CH_2Cl_2 \rightarrow CHCl_2 + H + e^- \tag{6}$$
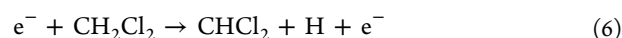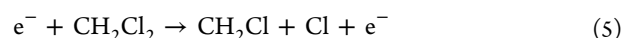
The contribution of the above reactions, however, is expected to be small because of the low concentration of DCM and electrons. In the case of using nitrogen as a carrier gas, energetic electrons in the plasma collide with nitrogen molecules, leading to the formation of active metastable nitrogen atoms and molecules. As a result of these initial reactions, active chlorine, hydrogen, and nitrogen atoms and molecules are formed. The decomposition of DCM proceeds

after that because of the reaction between DCM molecules and the formed active species in the plasma discharge.[16,22−24]

$$CH_2Cl_2 + Cl \rightarrow CHCl_2 + HCl \tag{7}$$

$$CH_2Cl_2 + Cl \rightarrow CH_2Cl + Cl_2 \tag{8}$$

$$CH_2Cl_2 + H \rightarrow CH_2Cl + HCl \tag{9}$$

$$CH_2Cl_2 + H \rightarrow CHCl_2 + H_2 \tag{10}$$

$$CH_2Cl_2 + N_2^* \rightarrow CH_2Cl + Cl + N_2 \tag{11}$$

$$CH_2Cl_2 + N^* \rightarrow CH_2Cl + NCl \tag{12}$$

Because of these reactions and further secondary reactions, end products, such as hydrogen chloride (HCl), carbon tetra-chloride (CCl$_4$), and hydrogen cyanide (HCN), were formed. These are listed in ref 17. The enhancement in the decomposition efficiency of DCM after adding oxygen to the gas stream is due to the participation of active oxygen atoms and molecules as well as OH radicals attacking DCM molecules. The addition of oxygen to the gas stream leads to the formation of the radicals O(^{3}P), O(^{1}D), and O$_2$($^1\Delta$) by electron impact.[23,25,26] The formation of these active oxygen radicals allows for faster DCM removal, mainly via the following reactions:[16,22−24,27]

$$CH_2Cl_2 + O(^1D) \rightarrow CH_2Cl + ClO \tag{13}$$

$$CH_2Cl_2 + O(^3P) \rightarrow CHCl_2 + OH \tag{14}$$
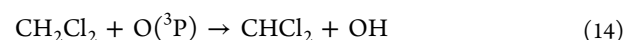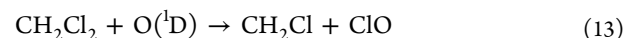
These reactions generate OH radicals, which, in turn, contribute to decomposing DCM via

$$CH_2Cl_2 + OH \rightarrow CHCl_2 + H_2O \tag{15}$$
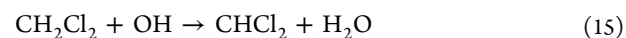
It is also possible that the above reactions involving O and OH could also take place because of the presence of residual water and oxygen in the system. Further reactions take place in the plasma, leading to the formation of plasma end products, such as carbon monoxide (CO) and carbon dioxide (CO$_2$). In nitrogen plasma, nitrogen oxides and nitrosyl chloride (NOCl) are also formed. Increasing the oxygen concentration by more than 4% resulted in decreasing the removal efficiency of DCM. Fitzsimmons et al.[16] found a similar relationship for DCM decomposition in the nitrogen−oxygen gas mixture. They showed that the reduction of DCM decomposition with an increasing oxygen concentration over 3% is due to the formation of NO$_x$ and ozone at higher oxygen concentrations. These consume oxygen and active nitrogen atoms and molecules, leading to less decomposition of DCM. Also, ozone has a low reaction rate with most VOCs compared to the rate with oxygen radicals.[28−30] Other studies have found similar results for the influence of the oxygen concentration on the decomposition of chlorinated hydrocarbons in plasma.[25,31]

Ozone as an end plasma product was not detected by Fitzsimmons et al. or in the current work. This does not mean that it has not been produced in the plasma. It could be consumed in the plasma between the pulses or decomposed after the plasma reactor and before the gas reaches the FTIR spectrometer. However, nitrogen oxides were formed with the addition of oxygen, and their concentration increased with an increasing oxygen concentration.

The main plasma end products for DCM decomposition in nitrogen plasma without oxygen addition were HCN, HCl, and CCl$_4$. Low concentrations of CO, CO$_2$, N$_2$O, and COCl$_2$ were

also detected, indicating the presence of oxygen in the system. This could be due to a small amount of water vapor in the inlet system as well as some impurities in the nitrogen and DCM gases; it also could be released from barium titanate as a result of either direct electron/ion impact or local heating near the contact points of the beads.[32] About 80% of the decomposed carbons were detected after the plasma reactor, mainly as HCN. The 20% of missing carbon is thought to be due to the formation of soot in the plasma reactor.[33] Soot deposition in the packed-bed region over the dielectric beads and the inner side of the glass tube was observed. Reactor components were cleaned regularly to remove soot deposition. Additionally, a pure oxygen plasma at 1 atm was also used for 15 min duration to oxidize and remove carbonated depositions at the end of each experiment for cleaning purposes. The main chlorine products detected after the plasma reactor were HCl, CCl_4, and $COCl_2$. About 60% of the decomposed chlorine was detected after the reactor. This is probably due to the formation of chlorine molecules (Cl_2), which are infrared (IR)-inactive.

With the addition of oxygen to the gas stream, the main plasma end products from DCM decomposition were CO, CO_2, NOCl, and small concentrations of $COCl_2$, in addition to nitrogen oxides also being formed. HCN, HCl, and CCl_4 were not detected after the addition of oxygen to the gas stream. This is due to the oxidation of these products by the reaction with active oxygen and OH radicals. Carbon balance calculations showed 45−50% missing carbon with the addition of 2−4% oxygen to the gas stream. This is probably due to the increased formation of soot with increasing the decomposition of DCM, which takes place at 2−4% added oxygen. The main chlorine component detected after the plasma reactor with the addition of oxygen is NOCl (a trace amount of $COCl_2$ was also detected). NOCl concentrations account for a small amount of the decomposed chlorine in the reactor, while the remaining chlorine is thought to form molecular chlorine.

The CO concentration in the exit gas appears to be independent of the added oxygen concentration in the range tested, although at a higher level than with no added oxygen (see Figure S1 of the Supporting Information). In contrast, the CO_2 concentration increases linearly with an increase in oxygen because of the oxidation of CO to CO_2 with higher percentages of oxygen. NOCl concentrations also increased steadily with increasing oxygen.

3.2. Influence of the Initial DCM Concentration. Figure 4 shows the results of these experiments carried out with a DCM range of 100−1000 ppm at a constant flow rate of 1 L min^{-1}. A linear decrease in the removal efficiency was observed with an increasing DCM concentration with both 0 and 3% added oxygen. Increasing the feed concentration of DCM requires a larger amount of active species in the plasma to carry on the decomposition process. A linear increase was observed in the HCN and HCl concentrations in plasma products when no oxygen was added, and likewise, the concentration of CO, CO_2, and NOCl also increased linearly with added DCM in the range used.

The energy cost increases linearly with increasing the initial concentrations of DCM. With 0% oxygen, it increases from about 950 to 1960 J/L for DCM concentrations of 100 and 1000 ppm, respectively. With 3% oxygen, it increases from 470 to 1250 J/L for DCM concentrations of 100 and 1000 ppm, respectively.

3.3. Influence of the Energy Density. Deposited power in the plasma was increased by increasing the input voltage
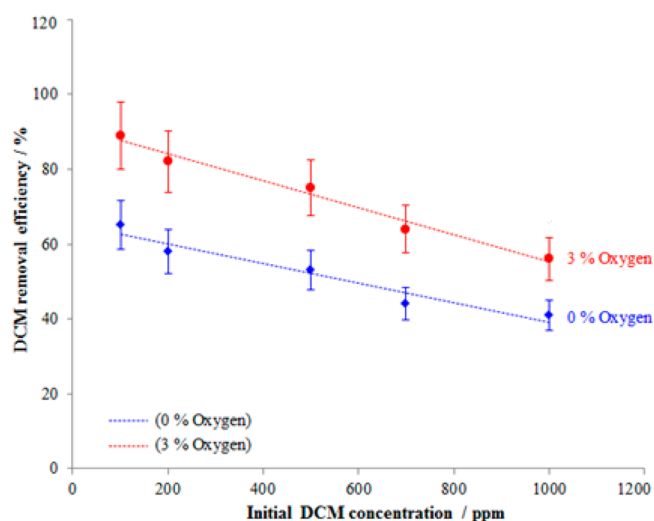
Figure 4. Removal efficiency of DCM as a function of the initial DCM concentration and two oxygen concentrations of 0 and 3% in a packed-bed plasma reactor. A total flow rate of 1 L min^{-1} and an energy density of about 1000 J L^{-1} were used.

using a variable transformer (Variac). As a result, the energy density in the plasma was increased from 0 to about 3000 J L^{-1} for an initial DCM concentration of 500 ppm with either 0 or 3% oxygen added at a total flow rate of 1 L min^{-1}. As seen in Figure 5, the removal efficiency of DCM increased linearly with
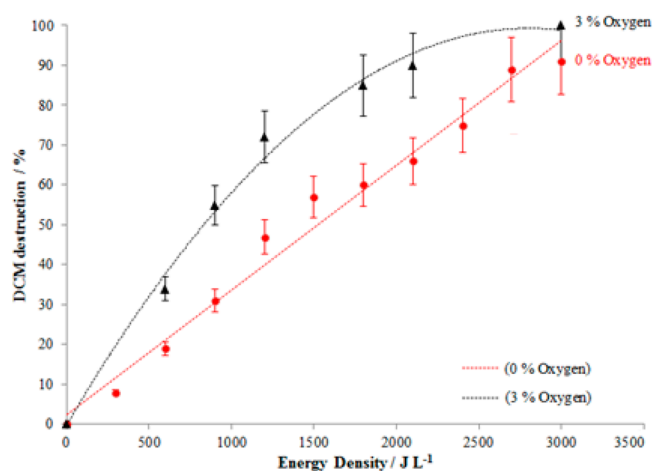
Figure 5. Removal efficiency of 500 ppm DCM in nitrogen non-thermal plasma as a function of the energy density and two oxygen concentrations of 0 and 3% in a packed-bed plasma reactor. A total flow rate of 1 L min^{-1} was used.

an increasing energy density in the case of nitrogen plasma without the addition of oxygen to the gas stream. Whereas the increase was nonlinear when 3% oxygen was added to the inlet stream, the percentage DCM decomposition was always greater for the same energy density, except toward 3000 J L^{-1}, where they appear to converge.

3.4. Influence of the Plasma Gas Residence Time. The residence time of the gas in the plasma region was controlled by changing the total flow rate of the gas stream entering the plasma reactor. Flow rates ranging between 0.5 and 2 L min^{-1} were used, giving residence times ranging between 1.95 and 0.49 s, respectively. Figure 6 shows the removal efficiency of 500 ppm DCM in nitrogen as a function of the residence time
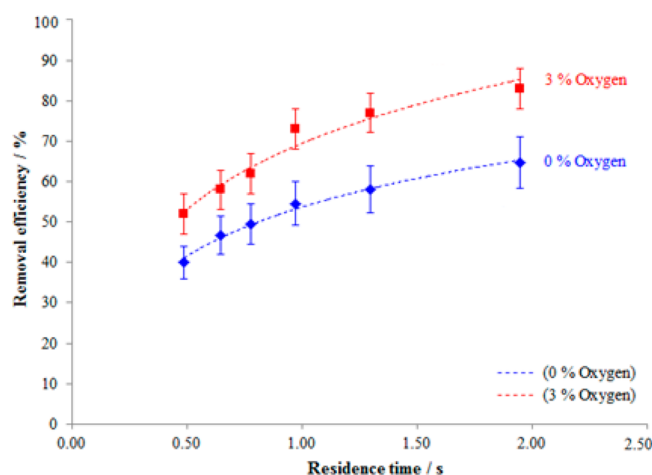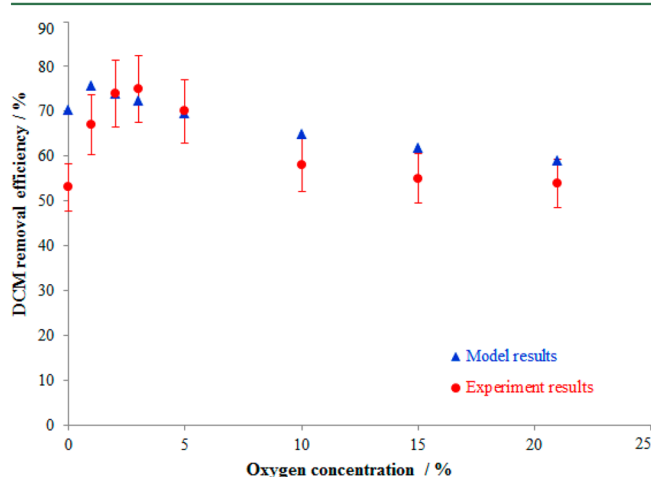
Figure 6. Removal efficiency of 500 ppm DCM in nitrogen non-thermal plasma as a function of the residence time of the gas in plasma. Two oxygen concentrations of 0 and 3% and a fixed energy density of about 1000 J L^{-1} were used.

and for no added oxygen and 3% added oxygen. A constant energy density of about 1000 J L^{-1} was used for each measurement. Results show that increasing the residence time of the gas in the plasma region resulted in increasing the removal efficiency of DCM in nitrogen plasma both with and without the addition of oxygen. Increasing the residence time of the gas components in the plasma region results in the formation of more active species per unit volume in the plasma. Results show that doubling the plasma residence time did not double the removal efficiency of DCM, as might have been expected. Further reactions, such as NO_x formation, may be enhanced, which do not necessarily contribute to DCM destruction.

3.5. Influence of the Background Gas on the Removal Efficiency of DCM. The influence of exchanging the background gas from nitrogen to argon was also investigated. With argon as the background gas and with no oxygen added, the main product species observed were HCl and CCl_4, with smaller concentrations of CO, CO_2, HCN, and $COCl_2$ (see Figure S2 of the Supporting Information). This was for a total flow rate of 1 L min^{-1} and an energy density of about 1000 J L^{-1}. With the addition of oxygen, the main end products were CO, CO_2, HCl, and $COCl_2$ (see Table S1 of the Supporting Information); however, now the removal efficiency of DCM increased continuously from about 70% with no oxygen to about 90% with the addition of 21% oxygen in contrast to the use of nitrogen, where a maximum of DCM destruction of about 73% was observed with around 2−4% additional oxygen (see Figure S3 of the Supporting Information). For argon, this was in agreement with the work carried out by Li et al.[34] The reason for this difference is probably due to the formation of nitrogen oxides in the case of nitrogen plasma formed from the main oxidizing agents O, OH, and O_3, whereas this route is not available in argon plasmas, and therefore, these species are free to participate in the oxidation and destruction of DCM. The formation of argon metastables may also play a key role in the enhanced decomposition. In contrast, Falkenstein et al.[25] observed a maximum decomposition for trichloroethylene in argon plasma with the addition of 0.3% oxygen. Further increases of the oxygen concentration reduced the removal efficiency of trichloroethylene.

3.6. Results of Kinetic Modeling. Figure 7 shows the experimental and modeling results of the decomposition of 500

Figure 7. Comparison of the simulation and experimental results for the removal efficiency of 500 ppm DCM in nitrogen plasma as a function of the oxygen concentration. A total flow rate of 1 L min^{-1} was used.

ppm DCM as a function of the oxygen concentration. A gas temperature of 75 °C, residence time of 0.9 s, and a total flow rate of 1 L min^{-1} were used. Simulation results show maximum DCM decomposition with the addition of 1% oxygen to the gas stream. Increasing the oxygen concentration in the simulation decreased the removal efficiency of DCM. These results are in a good agreement with the experimental results. Figure 8 shows
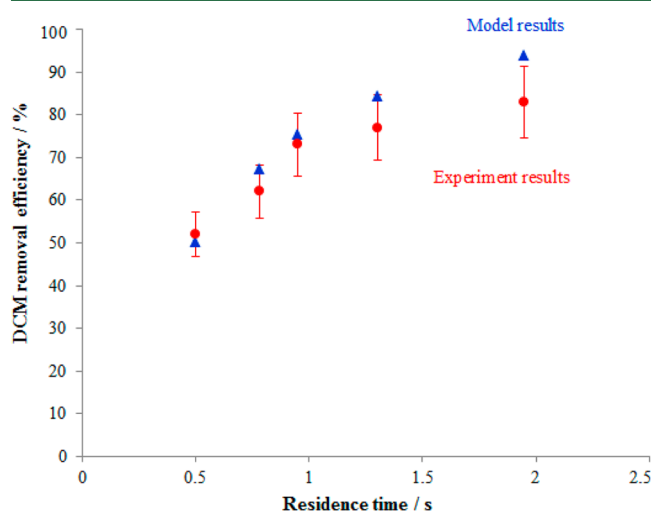
Figure 8. Comparison of the simulation and experimental results for the influence of the residence time on the removal efficiency of 500 ppm DCM in nitrogen and 3% oxygen gas mixture. A total flow rate of 1 L min^{-1} was used.

the experimental and modeling results for the influence of plasma residence time on the decomposition of DCM in a gas mixture of nitrogen and 3% oxygen. The residence time was varied between 0.49 and 1.95 s. Results show that the simulation results are in a good agreement with the experimental results. However, the model results for the concentration of the plasma end products, such as CO and CO_2, were not in an agreement with the experimental results

for both the oxidation concentration and residence time as process variables. This is most likely to be due to further oxidation of CO to CO_2 in the transport from the reactor to the measurement point. It has been observed previously when *in situ* CO measurements in a parallel plate dielectric barrier discharge (DBD) plasma reactor have been measured to be higher than CO measurements downstream.[35]

The model shows a sharp decrease in the HCl concentration with the addition of oxygen to the gas stream. However, the concentration does not drop down to zero as is the case with the experimental results. The NO_2 concentration predicted in the model was considerably less than experimental results. However, both the concentrations followed the same trend as a function of the oxygen content. The model predicts a high concentration of ozone. It was not possible to detect ozone as an end product of the experimental work because it is likely to react before it reaches the measurement volume of the FTIR spectrometer. However, it is believed to be formed in the plasma. As explained earlier, ozone could be consumed in the plasma between the pulses or decomposed after the plasma reactor before the gas reaches the FTIR spectrometer. Other end products, such as NO, N_2O, and NOCl, did not show a good agreement between the experimental and simulation results. More work is required to improve the simulation model, to obtain a better agreement for the formation of plasma end products with the experimental results.

In summary, it has been shown that there is an optimum 2−4% oxygen concentration for the removal of DCM in an atmospheric pressure non-thermal plasma generated in a packed-bed plasma reactor. Increasing the plasma energy density and decreasing the residence time also lead to higher efficiencies. Increasing the DCM concentration to above 500 ppm results in a decrease in efficiency. Although argon has been shown to be a better background gas than nitrogen for DCM removal, especially at higher oxygen concentrations, it is not practical in industrial applications. A kinetic model has been developed that accounts for the variation of DCM destruction as a function of the oxygen concentration and residence time but cannot yet fully account for the concentration of minor product species.

Further work is directed toward understanding the chemical reactions directly in the plasma region using *in situ* laser absorption spectroscopy with a parallel plate dielectric barrier plasma reactor. Further work is also focused on the effect of alkene additives, multi-stage packed-bed processes, and other types of chlorinated hydrocarbons.

In conclusion, atmospheric pressure non-thermal packed-bed plasma reactors are a promising technology for the remediation of VOCs in waste gas streams containing nitrogen and oxygen as long as the VOC loading is kept low.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Influence of the oxygen concentration on the formation of CO, CO_2, and NOCl as plasma end products for DCM decomposition in nitrogen non-thermal plasma (Figure S1), FTIR spectra for about 590 ppm DCM in argon plasma without adding oxygen to the gas stream (Figure S2), influence of the oxygen concentration on the formation of CO and CO_2 in nitrogen plasma (Figure S3), comparison of the simulation and experimental results for the influence of residence time on the formation of CO and CO_2 in nitrogen and 3% oxygen gas mixture (Figure S4), decomposition efficiency of 590 ppm

DCM and the concentrations of all species that exist in the plasma exhaust, in ppm, as a function of oxygen percentages in argon plasma (Table S1), and kinetic modeling. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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