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MARIUSZ JASIŃSKI, JERZY MIZERACZYK, DARIUSZ CZYLKOWSKI, ZENON ZAKRZEWSKI[1]

Decomposition of highly-concentrated chlorofluorocarbon CFC-11 using an atmospheric-pressure moderate-power microwave torch plasma

Results of the investigation of decomposition of chlorofluorocarbon CFC-11 (CCl_3F) in atmospheric-pressure flowing nitrogen or air using a moderate-power (several hundred Watts) microwave torch plasma (MTP) are presented. The gas flow rate and microwave power (2.45 GHz) delivered to the discharge were 2÷4 l/min. and 400 W, respectively. Concentrations of the CFC-11 in the flowing nitrogen or air were 50%. The results showed that the CFC-11 decomposition efficiency using the MTP was 100%. The removal yield (several hundreds g/h) and energy yield (almost 1 kg/kWh) are superior to those obtained by means of other methods and make the tested MTP highly attractive for the practical destruction of chlorofluorocarbons.

1. Introduction

Volatile organic compounds (VOCs), such as chlorofluorocarbons, hydrochlorofluorocarbons and hydrofluorocarbons, commonly called refrigerants, emitted to the atmosphere cause environmental problems, such as the depletion of the ozone layer, greenhouse effect etc. Therefore, efficient methods of destructing the stored refrigerants and those currently emitted to the atmosphere are in great demand. Conventional methods, e.g. adsorption, absorption, catalytic combustion proved not to be efficient enough [1]. To deal with the problem, thermal plasma processing [1-6] have been proposed as a method for the abatement of VOCs including refrigerants. However, thermal plasma techniques exhibit some serious drawbacks, which are high input power (from several kW up to hundreds kW), low energy efficiency and generation of NO_x if applied under air environments. Recently, non-thermal plasma techniques involving electron beam and electrical discharges have been tested as possible tools for efficient decomposition of VOCs including refrigerants into at least less harmful compounds [1, 7-9]. These techniques are

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becoming important due to their advantages such as low cost, high decomposition efficiency, small space volume requirements etc. However, the non-thermal plasma techniques are practically useful for the abatement of VOCs only with relatively low concentrations (< 1000 ppm) in the carrier gas.

Recently, we have proposed the use of the microwave torch plasmas (MTPs) operating at atmospheric pressure and low power (< 100 W) for destruction of highly-concentrated (several %) VOCs [10-13]. Obtained results showed that the abatement of VOCs using the low-power MTPs is highly efficient (VOCs decomposition efficiency is 100% in almost all cases tested) with relatively high energy yield (the mass of the decomposed VOC per 1 kWh is about 100 g/kWh). However, the VOCs removal yield (the mass of the decomposed VOC per hour is about 30 g/h) from a single microwave torch-reactor module is low for practical purposes. Although, the MTPs technique makes it possible to use the multi-module reactor system that increases the removal yield, in same cases the low-power (< 100 W) MTPs can be impractical.

In this paper we test the capability of an atmospheric-pressure MTPs operated at moderate power levels (several hundred Watts up to 1000 W) for abatement of highly- concentrated chlorofluorocarbons, using CFC-11 (CCl_3F) as an example. We expect that the moderate-power MTPs is more efficient in refrigerant abatement that the low-power MTPs.

2. Experimental set-up

The main parts of the experimental setup used in this investigation were a 2.45 GHz magnetron generator, microwave torch plasma (MTP) generator, plasma reactor, microwave power supplying and measuring system, gas supplying and flow control system, and Fourier Transform Infrared (FTIR) spectrophotometer for gas analysis. The experimental procedures were described in detail in [10, 11]. The essential design features of the MTP generator and reactor are shown in Fig. 1. The MTP generator is based on the TIAGO concept recently disclosed by Moisan et. al. [14]. The torch structure is built in a standard WR 430 rectangular waveguide. A conical nozzle is placed in a reduced-height section of the waveguide. It is attached, at the gas-inlet side, perpendicularly to the wide wall of the waveguide. It protrudes through a circular gap in the opposite wall. The microwave power, up to a few kW could be fed directly from a standard waveguide at one end of the torch structure while the opposite end is terminated with a movable plunger. The plasma is generated in the form of a 'plasma flame' at the end of the nozzle, which protrudes from the waveguide directly into a quartz plasma reactor. There is a cylindrical shielding grid inside the reactor, placed coaxially around the nozzle to improve the stability of the plasma flame. Therefore, in this torch-reactor configuration, the distribution of the electromagnetic field in the discharge region is determined not only by the shape and dimensions of the gap in the waveguide wall and the conical nozzle, but also by the influence of the shielding grid. The plasma torch was operated following the standard procedures.

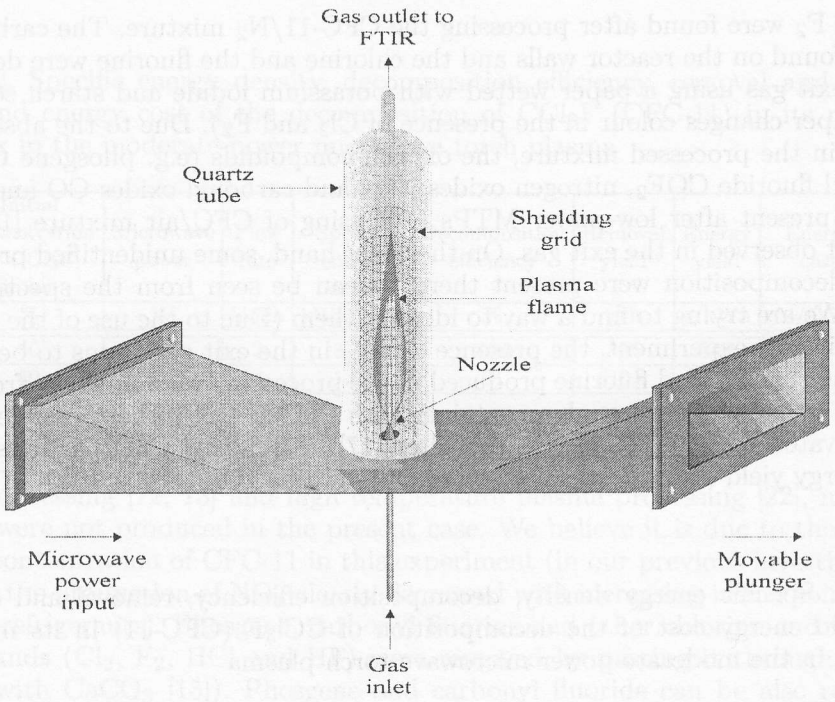

Fig. 1. Schematic of the moderate-power microwave torch plasma generator and plasma reactor for processing gas mixtures.

The processed gas [a mixture of the CFC-11 with nitrogen or synthetic air (80% $N_2 + 20\%$ O_2)] flowed at atmospheric pressure at a rate of $2 \div 4$ l/min. and exited through the nozzle at its conical tip to be ionized and form the 'plasma flame'. The gas flow rate was automatically set by a mass flow controller. Initial concentrations of CFC-11 in their mixtures with air or nitrogen were 50%. Compositions of the gas before and after the plasma processing were analysed using the FTIR spectrophotometer operating in the range of $4400 \div 1000$ cm^{-1}.

3. Results

In this chapter results of decomposition of chlorofluorocarbon CFC-11 in it mixtures with nitrogen or air using the moderate-power MPT system are presented.

3.1. Decomposition of CFC-11 in nitrogen plasma

The efficiency of the decomposition of CFC-11 was more than 80% at a nitrogen flow rate and microwave power delivered to the discharge equal to 2 l/min and 400 W, respectively (Tab. 1). Such by-products as carbon C, chlorine Cl_2 and

fluorine F_2 were found after processing the CFC-11/N_2 mixture. The carbon could be found on the reactor walls and the chlorine and the fluorine were detected in the exit gas using a paper wetted with potassium iodide and starch solution (this paper changes colour in the presence of Cl_2 and F_2). Due to the absence of the air in the processed mixture, the oxygen compounds (e.g. phosgene $COCl_2$, carbonyl fluoride COF_2, nitrogen oxides NOx and carbonyl oxides CO and CO_2, usually present after low-power MTPs processing of CFC/air mixture [12, 13]) were not observed in the exit gas. On the other hand, some unidentified products of the decomposition were present there, as can be seen from the spectrum in Fig. 2. We are trying to find a way to identify them (Due to the use of the quartz reactor in this experiment, the presence of SiF_6 in the exit gas seems to be possible). The chlorine and fluorine produced in the processing were removed from the exit gas by passing it through a container with $CaCO_3$ [15] (other possible filters are activated carbon [16, 17], zeolite filter [17] or fluidized CaO particles [18]). The energy yield of the decomposition of CFC-11 was about 690 g/kWh (Tab. 1).

Table 1. Specific energy density, decomposition efficiency, removal and energy yield and energy cost of the decomposition of CCl_3F (CFC-11) in its mixture with N_2 in the moderate-power microwave torch plasma

Initial concentration of CCl_3F in nitrogen	Microwave power	Flow rate	Specific energy density	Decomposition efficiency	Removal yield	Energy yield	Energy cost
%	W	l/min	kWh/Nm^3	%	g/h	g/kWh	eV/CCl_3F
50	400	2	3.33	82	275	687.5	7.5

The specific energy density (the energy delivered to 1 Nm^3 of the processed gas) was about 3.3 kWh/Nm^3. The removal yield was about 275 g/h. The energy and removal yields of the CFC-11 decomposition obtained in this experiment are superior to those when other plasma methods (e.g. gliding arc, corona discharge and low-power MTPs [12, 13, 19-21]) were employed for this purpose.

4. Decomposition of CFC-11 in air plasma

At the microwave power of 400 W delivered to the discharge, the decomposition efficiency of CFC-11 was about 90÷100%, depending on air flow rate (Tab. 2). The full decomposition of the CFC-11 was obtained at the lower air flow rate (2 l/min.).

The by-products of the CFC-11 decomposition were CO, CO_2, $COCl_2$, COF_2, Cl_2, F_2 and the unidentified compounds (peaks around 1000÷1200 cm^{-1} in the spectra presented in Fig. 3). Astonishingly, in contrast to both the low-power

Table 2. Specific energy density, decomposition efficiency, removal and energy yield and energy cost of the decomposition of CCl_3F (CFC-11) in its mixture with air in the moderate-power microwave torch plasma

Initial concentration of CCl_3F in air	Microwave power	Flow rate	Specific energy density	Decomposition efficiency	Removal yield	Energy yield	Energy cost
%	W	l/min	kWh/Nm^3	%	g/h	g/kWh	eV/CCl_3F
50	400	2	3.33	100	335	840	6.1
50	400	4	1.67	91	610.4	1526.7	3.4

MTP processing [12, 13] and high temperature plasma processing [22], nitrogen oxides were not produced in the present case. We believe it is due to the higher initial concentration of CFC-11 in this experiment (in our previous investigations [12, 13] the production of NO_x clearly decreased with increasing initial concentration of refrigerants). Phosgene, carbonyl fluorine and other chlorine and fluorine compounds (Cl_2, F_2, HCl and HF) were removed by passing it through a container with $CaCO_3$ [15]). Phosgene and carbonyl fluoride can be also removed from the exiting gas by passing it through a washing bottle filled with water, or recovered from the exiting gas by condensing it in a cooling system having the temperature below 9^oC and -83^oC, respectively.

Depending on the air flow rate, the energy yield of the decomposition of CFC-11 ranged from 840 to 1530 g/kWh, the specific energy density – $3.3 \div 1.7$ kWh/Nm^3 and the removal yield – $335 \div 610$ g/h, when processing CFC-11 in its mixtures with nitrogen.

5. Conclusions

The results of this investigation show that chlorofluorocarbon CFC-11 can be completely decomposed in the moderate-power microwave torch plasma. The other important merits are the relatively high removal (610 g/h) and energy yields (1530 g/kWh). Both results are much better than those when the low-power MTPs or other low-power plasma methods were employed. Also, the absence of NO_x as by-products in the processing of CFC-11 in its mixture with air is highly beneficial. This makes the moderate-power MTPs attractive as a practical means of refrigerant destruction.

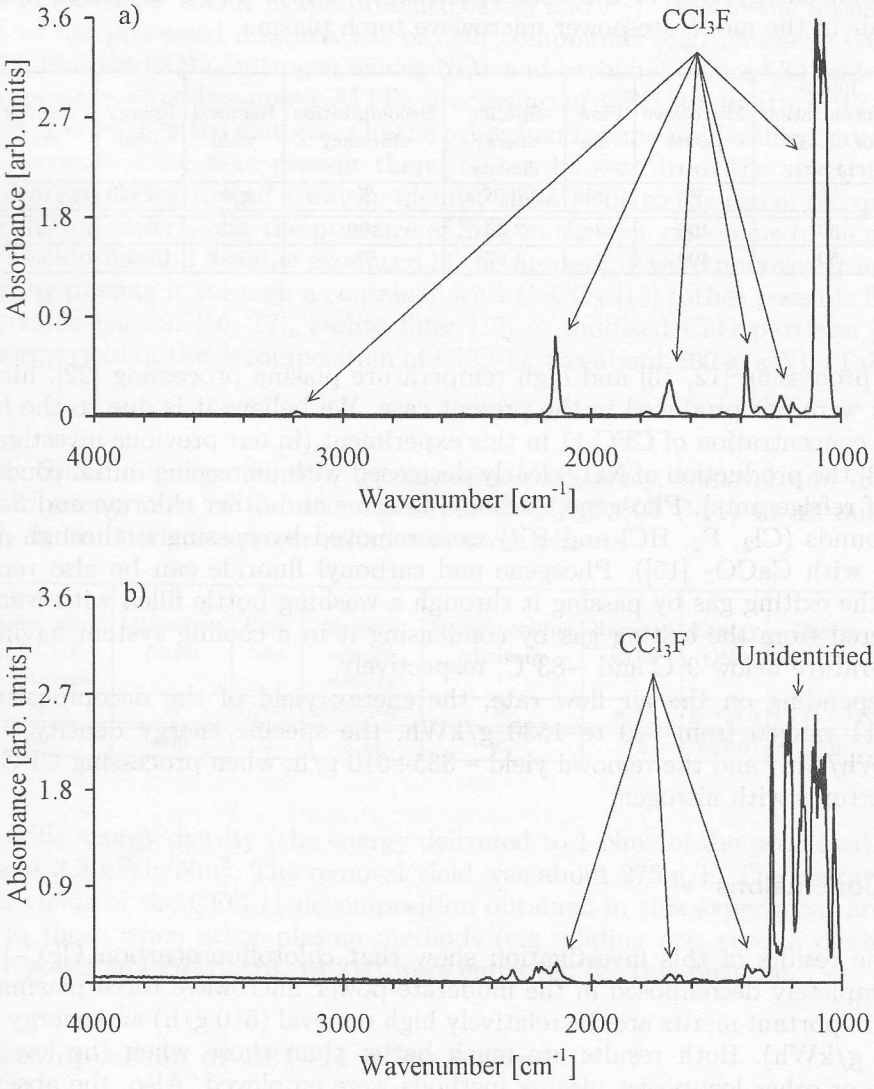

Fig. 2. FTIR spectra of N_2:CCl_3F (CFC-11, 50%) mixture before (a) and after (b) microwave torch plasma processing. Microwave power – 400 W, gas flow rate – 2 l/min.

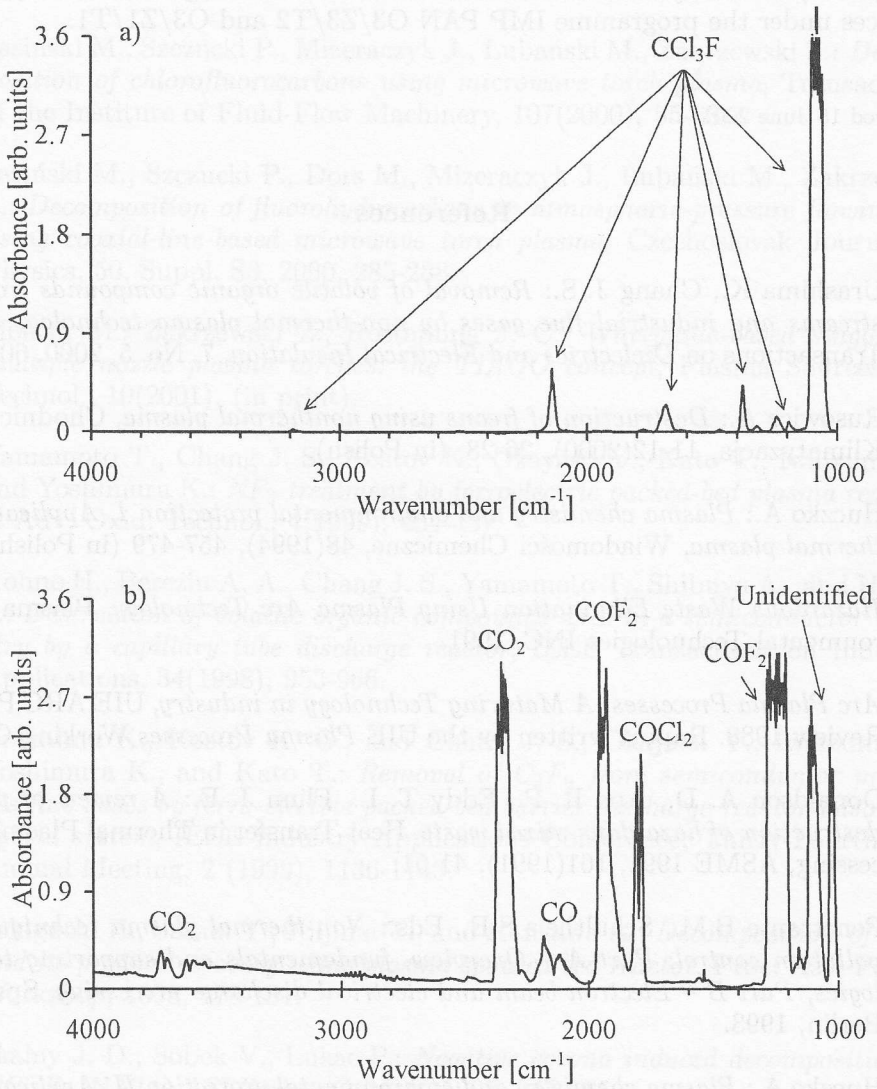

Fig. 3. FTIR spectra of air:CCl_3F (CFC-11, 50%) mixture before (a) and after (b) microwave torch plasma processing. Microwave power – 400 W, gas flow rate – 2 l/min.

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