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DESTRUCTION OF HIGHLY-CONCENTRATED GASEOUS POLLUTANTS USING ATMOSPHERIC-PRESSURE MICROWAVE TORCH DISCHARGES

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A b s t r a c t. Results of the study of destruction of volatile organic compounds (VOCs) including Freons in their mixtures with the synthetic air or nitrogen in microwave torch discharges (MTDs) at atmospheric pressure are presented. Two types of the MTD, i.e. a low-power (~100 W) MTD and moderate-power (several hundred watts) MTD were applied for destruction of several VOCs, including Freons. The gas flow rate and microwave power (2.45 GHz) delivered to the discharges were in the range of 1÷3 l/min. and 80÷400 W, respectively. Concentrations of the processed gaseous pollutants were up to 75 %. The results show that the destruction efficiency of gaseous pollutants is up to 100 % with the removal rate of several hundred g/h and energy efficiency of about 1 kg/kWh. It was found that the microwave torch plasmas fully decomposed the pollutants at relatively low energy cost. This suggests that the MTDs are the useful tool for destruction of highly-concentrated gaseous pollutants.

K e y w o r d s: microwave discharge, VOC, plasma torch, Freons.

INTRODUCTION

Gaseous pollutants emitted to atmosphere cause environmental problems, such as the depletion of the ozone layer, the greenhouse effect etc. Efficient methods for removing the gaseous pollutants that are stored (i.e. Freons) or emitted by industry (i.e. VOCs) are strongly required. Conventional methods, e.g., adsorption, absorption, catalytic combustion seem not to be efficient enough [1]. Recently non-thermal plasma methods involving electron beam and electrical discharge are proving their potential for efficient removal of VOCs [1, 2].

Results of the study of destruction of VOCs: methane CH_4, toluene $C_6H_5CH_3$, carbon tetrachloride CCl_4, chloroform $CHCl_3$, chlorofluorocarbons: CFC-11 (CCl_3F) and CFC-12 (CCl_2F_2), hydrochlorofluorocarbon HCFC-22 ($CHClF_2$), hydrofluorocarbon HFC-134a ($C_2H_2F_4$) and fluorocarbon CFC-116 (C_2F_6) in their mixtures with the synthetic air or nitrogen in microwave torch discharges (MTDs) at atmospheric pressure are presented in this paper. Air or N_2 were used as a carrier gas to dilute and transport the gaseous pollutants to the MTDs. Concentrations of

the processed gaseous pollutants were relatively high, i.e. from a few up to a few tens percent. Two types of the MTD, i.e. the low-power (~100 W) MTD and the moderate-power (200-400 W) MTD were applied for destruction of VOCs, including Freons. The low-power MTD was applied for initial concentrations of gaseous pollutants (in air or nitrogen) of several per cent. The moderate-power MTD was applied for initial concentrations of gaseous pollutants (in nitrogen) from 10 up to 75 %.

EXPERIMENTAL SETUP

The main parts of the experimental setups used in this investigation were a 2.45 GHz microwave generator (magnetron), MTD generator, plasma reactor, microwave supplying and measuring system, gas supplying system and Fourier Transform Infrared (FTIR) spectrophotometer for gas analysis (Figs. 1 and 2). Two types of the MTD generators were tested: the low-power MTD generator (Fig. 1) and moderate-power MTD generator (Fig. 2). In both microwave plasma torches, the operating gas flowed through the inner duct of the coaxial line section of the torch system and exited through an outlet (a kind of nozzle) ending it. The gas flow rate was automatically controlled by a mass flow controller (Hastings Instruments). In the torch, the plasma was sustained at the tip terminating the inner conductor of a coaxial-line duct. The inner conductor protruded slightly beyond the end of the outer conductor. The plasma was generated in the form of a "plasma flame" above the nozzle

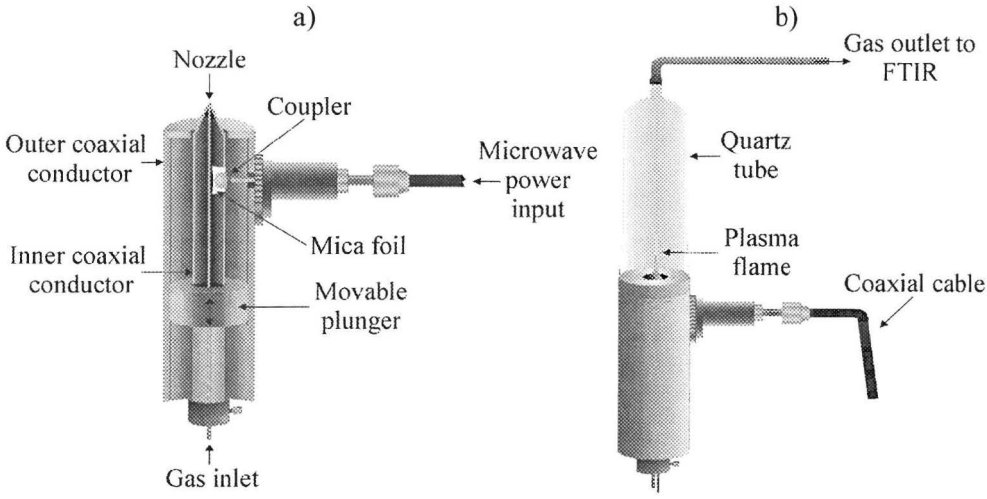

Fig. 1. Schematics of the low-power MTD generator (a) and plasma reactor (b) for processing gas mixtures.

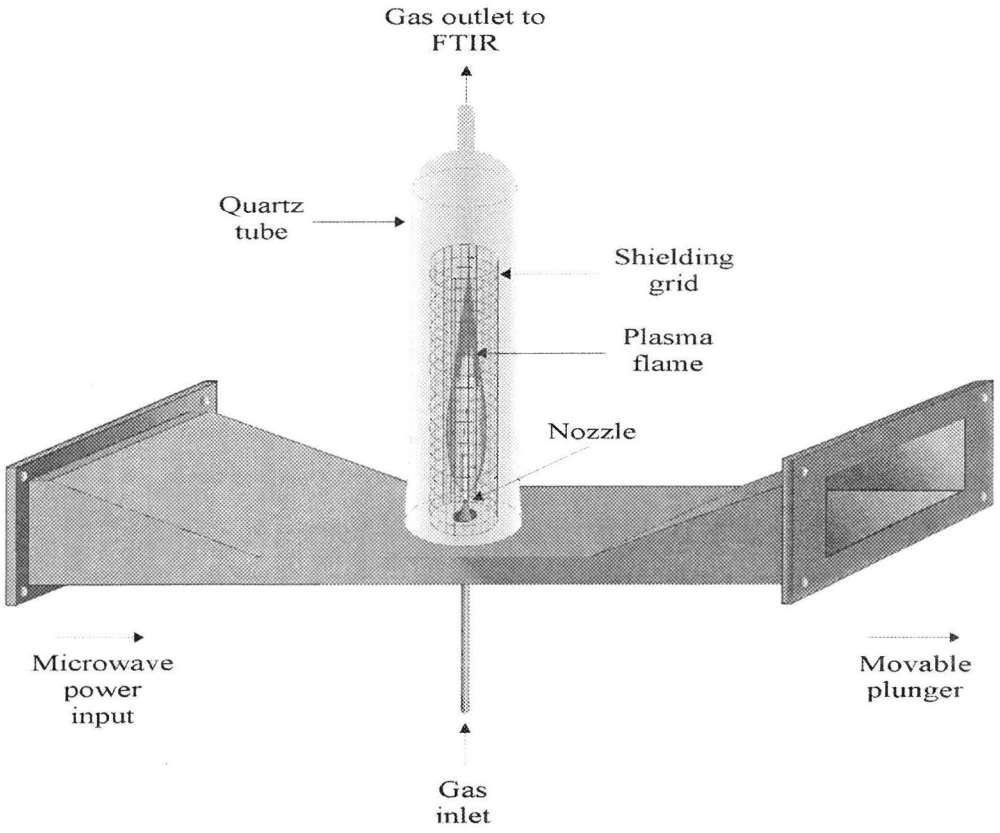

Fig. 2. Schematics of the moderate-power MTD generator and plasma reactor for processing gas mixtures.

within a quartz reactor. The microwave power was supplied to the MTD from a 2.45 GHz magnetron. Composition of the gas mixtures before and after the plasma processing was determined using a FTIR spectrophotometer operating in the range of 4000÷1000 cm^{-1}.

Low-power MTD

The experimental setup with the low-power MTD generator is shown in Fig. 1. Microwave power of about 70÷100 W was supplied to the torch system from a 2.45 GHz magnetron generator via a standard 50 Ω coaxial cable with the use of a coupler (microwave antenna). There was a mica foil between the coupler and the inner coaxial conductor. The mica foil improved the microwave coupling by increasing the capacity between the coupler and inner coaxial conductor. The

movable plunger enabled minimizing the reflecting power. The operating gas was a mixture of VOCs (including Freons) with the synthetic air or nitrogen. The gas flow rate ranged from 1÷2 l/min. Initial concentrations of gaseous pollutants in their mixtures with the air or nitrogen were up to 18 %.

Moderate-power MTD

The experimental setup with the moderate-power MTD generator is shown in Fig. 2. In this case the microwave power of about 200÷400 W was supplied to the MTD from a 2.45 GHz magnetron via a rectangular waveguide. A conical nozzle is placed in a reduced-height section of the waveguide. The movable plunger enabled minimizing the reflecting power. There is a cylindrical metal grid inside the reactor, placed coaxially around the nozzle to protect the personnel and instrumentation from the electromagnetic radiation. We found that the presence of this grid improves the stability of the plasma flame. The moderate-power MTD generator was used for processing Freons (CCl_3F and C_2F_6) diluted in the nitrogen. The gas flow rate ranged from 1÷3 l/min. Initial concentrations of CCl_3F and C_2F_6 in their mixtures with the nitrogen were up to 50% and 75%, respectively.

RESULTS

Application of the low-power MTD

In this chapter the results of destruction of VOCs [CH_4, $C_6H_5CH_3$, CCl_4 and $CHCl_3$] in their mixtures with the air and Freons [CFC-11 (CCl_3F), CFC-12 (CCl_2F_2), HCFC-22 ($CHClF_2$), HFC-134a ($C_2H_2F_4$) and mixtures of several Freons (CFC-12:HCFC-22:HFC-134a)] in their mixtures with the air or nitrogen using the low-power MTD are presented.

Generally, the low-power MTD (microwave power – 90 W, gas flow rate – 1 l/min.) in air decomposed CH_4(up to 6%), $C_6H_5CH_3$(up to 5%), CCl_4(up to 13%) and $CHCl_3$(up to 18%) completely. When the mixture of air: CH_4 was processed, CH_4 was fully decomposed into CO_2 and water vapour. However, due to the presence of O_2 in the carrier gas the destruction of CH_4 was accompanied with production of NO and NO_2. The same products and N_2O_4 were detected in the case of processing another ''pure'' hydrocarbon $C_6H_5CH_3$. When the mixture of air:CCl_4 was processed, CCl_4 was fully decomposed into CO_2, CO, H_2O and $COCl_2$. The same end products, and additionally HCl, were found in the case of $CHCl_3$ destruction in the mixture of air:$CHCl_3$. In both cases, CCl_4 and $CHCl_3$, nitrogen oxides were produced during the processing, similarly as in the processing of ''pure'' hydrocarbons. It should be noticed that the plasma processing of chlorinated hydrocarbons, like CCl_4 or $CHCl_3$, gives also Cl_2 [detected using a

paper wetted with potassium iodide and starch solution (this paper changes colour in the presence of Cl_2)].

The specific energy density, i.e. an energy delivered to 1 Nm^3 of the processed gas was 1.5 kWh/Nm^3. The highest removal rate, i.e. a mass of the pollutant destructed in an hour was from 2.4 g/h (CH_4, 6%) up to 49.4 g/h (CCl_4, 13%). The highest energy efficiency, i.e. a mass of the pollutant destructed using an energy of 1 kWh was from 28.2 g/kWh (CH_4, 6%) up to 555.6 g/kWh (CCl_4, 13%). These results are comparable with those when other plasma methods (e.g. corona discharge, gliding arc discharge) were employed for VOCs destruction [3-13]. However, in case of the other plasma methods the initial concentrations of VOCs were lower than in our experiment and the VOCs were not decomposed completely.

The low-power MTD was also used for destruction of either pure Freons (CFC-11, CFC-12, HCFC-22, HFC-134a) in the air or mixtures of several Freons (CFC-12:HCFC-22:HFC-134a) in the nitrogen. Concentrations of the Freons in the working gas were up to 8 %. The volume ratios of CFC-12:HCFC-22:HFC-134a in the tested mixtures were either 70:24:6 or 18:73:9. The Freon destruction efficiency was about 50÷100 %, depending on kind of Freons (CFC-11, CFC-12, HCFC-22, HFC-134a in air or mixtures of several Freons in nitrogen), Freon concentration (2-8 %), gas flow rate (1-2 l/min.) and microwave power (80-100 W) delivered to the discharge. The efficiency of 100 % was obtained for lower concentrations of Freons (2 %) at microwave power of 100 W and gas flow rate of 1 l/min. The direct products of CFC-11 (CCl_3F) destruction in air were CO_2 and phosgene $COCl_2$. The same products, and CO and carbonyl fluoride COF_2 were found in the exit gas when Freons CFC-12 (CCl_2F_2) and HCFC-22 ($CHClF_2$) were processed. The direct products of HFC-134a ($C_2H_2F_4$) destruction were CO, CO_2 and COF_2. During the air plasma processing of Freons, nitrogen oxides were produced due to the presence of the air. Using a paper wetted with potassium iodide and starch solution, Cl_2 and F_2 (which cannot be observed by FTIR) were found in the exit gas. The direct products of destruction of mixtures of Freons, CFC-12, HCFC-22 and HFC-134a in nitrogen were C, Cl_2 and F_2.

Phosgene, carbonyl fluorine and other chlorine and fluorine compounds (including Cl_2 and F_2) can be removed by passing the exit gas through the fluidized CaO particles [14], activated carbon [15, 16], zeolite filter [16] or $CaCO_3$ [17].

The specific energy density was in the range of 0.7-1.7 kWh/Nm^3. The highest removal rate was from 15 g/h (HCFC-22, 8%) up to 26 g/h (CFC-11, 8%). The highest energy efficiency was from 154 g/kWh (HCFC-22, 8%) up to 260 g/kWh (CFC-11, 8%). These results (and these when the destruction efficiency was 100 %) are superior to those when low-temperature plasma methods (e.g. corona

discharge, barrier discharge, surface discharge, silent discharge) were employed for Freon destruction [18-22].

Application of the moderate-power MTD

In this chapter the usefulness of the moderate-power MTD for destruction of Freons [CFC-11 (CCl_3F) and CFC-116 (C_2F_6)] in their mixtures with the nitrogen are presented. Initial concentrations of CCl_3F and C_2F_6 in their mixtures with the nitrogen were up to 50 % and 75%, respectively. The Freon destruction efficiency was about 60÷100 %, depending on kind of Freon (CFC-11 or CFC-116 in nitrogen), Freon concentration (10-75 %), gas flow rate (1-3 $lmin^{-1}$) and microwave power (200-400 W) delivered to the discharge. The efficiency of 100 % was obtained in all cases for lower concentrations of Freons (10-25 %). When Freon initial concentrations were 50 % the destruction efficiency of 100 % was obtained at microwave power of 300 W and gas flow rate of 1 $lmin^{-1}$. The direct products of both Freons destruction were CF_4, CF_3CN and some unidentified product (or products). Also carbon C, chlorine Cl_2 and fluorine F_2 were found in the by-products.

The specific energy density was in the range of 1.7-6.7 $kWhNm^{-3}$. The highest removal rate was 310 gh^{-1} for CFC-11 (50 %, 400 W, 3 $lmin^{-1}$) and 276 gh^{-1} for CFC-116 (50 %, 400 W, 2 $lmin^{-1}$). The highest energy efficiency was about 1000 g/kWh for CFC-11 (50 %, 200 W, 2 $lmin^{-1}$) and 700 g/kWh for CFC-116 (50 %, 400 W, 2 $lmin^{-1}$). These results (and these when the destruction efficiency was 100 %) are superior to those when other plasma methods (e.g. low-power MTD, plasmatron, gliding arc discharge) were employed for Freon destruction [23, 24].

CONCLUSIONS

The results of this investigation show that the several gaseous pollutants (VOCs, icluding Freons) can be completely decomposed in the microwave torch discharges. Unfortunately, the destruction of the several gaseous pollutants by the microwave plasma torch in air is accompanied with the production of harmful or toxic products (e.g., NO_x, $COCl_2$), which can be removed however, from the exiting gas using relatively easy methods.

The energy efficiency of the destruction of the several gaseous pollutants by the microwave torch discharges is similar or better than those when other plasma methods were employed.

This implies that the MTDs can be a useful tool for the destruction of highly-concentrated gaseous pollutants in air or nitrogen at atmospheric pressure.

Recently, in order to increase the removal rate of the destruction of gaseous pollutants we introduced a compact multi-discharge system. It is a fully waveguide-based system which by increasing the number of nozzles (the number of torches) can be a useful tool for the destruction of stored freons.

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DESTRUKCJA SZKODLIWYCH GAZÓW O DUŻYM STĘŻENIU ZA POMOCĄ WYŁADOWANIA MIKROFALOWEGO TYPU ''TORCH'' POD CIŚNIENIEM ATMOSFERYCZNYM

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S t r e s z c z e n i e . Prezentowane są rezultaty badań nad rozkładem lotnych związków organicznych (VOCs), włączając freony i ich mieszaniny z syntetycznym powietrzem lub azotem w wyładowaniach mikrofalowych. Wykorzystano dwa typy reaktorów o niskiej (~100 W) i średniej mocy (kilkaset watów) przy przepływie gazu 1÷3 l/min, odpowiednio. Koncentracja przetworzonych zanieczyszczeń gazowych wynosiła do 75 %. Uzyskano rozkład zanieczyszczeń gazowych do 100 % z szybkością kilkuset g/h i względnie wysoką efektywnością energetyczną 1 kg/kWh, co wskazuje na wyładowania typu "torch" jako na użyteczne narzędzie do rozkładu zanieczyszczeń gazowych o wysokim stężeniu.

S ł o w a k l u c z o w e : wyładowanie mikrofalowe, VOC, plazma „torch", freony.