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ELECTROPLASMA-INDUCED DECOMPOSITION OF CHLORODIFLUOROMETHANE UNDER OXIDIZING CONDITIONS

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A b s t r a c t. Decomposition of chlorodifluoromethane (Freon R22, $CHClF_2$) was studied in non-equilibrium and low-temperature plasma conditions generated in a gliding discharge reactor. The process examined was run in the argon atmosphere with oxygen gas added as oxidant. The overall decomposition degree of the Freon and the composition of the outlet gases were studied in relation to oxygen concentration and to input reactor power. The maximum decomposition degree of the Freon (0.99) was attained in a gas mixture composed of the Freon (0.016 mol/mol), argon (0.441 mol/mol) and oxygen (0.543 mol/mol) at an input discharge power of 1.44 kW. Carbon dioxide, chlorine and fluorine were the main products of the process.

K e y w o r d s: chlorofluorocarbons, chlorodifluoromethane, plasma, decomposition.

INTRODUCTION

Chlorodifluoromethane ($CHClF_2$, R22) belongs to the group of fluorinated and/or chlorinated paraffin hydrocarbons (chlorofluorocarbons, CFCs) known as Freons. Freons were discovered in the 1920s and in as few as two years they were produced commercially. Freons are characterized by very specific physical and chemical properties. They are non-toxic, inflammable, non-corrosive, odorless, and chemically and thermally stable. Therefore, they found numerous commercial and industrial applications, primarily as cooling media, cleaning agents and solvents. Unfortunately, they proved to be very dangerous, because they deplete the ozone layer and give rise to the greenhouse effect. Therefore, in November 1992, the Montreal Protocol was revised to phase out CFCs by 1 January 1996. The present ban on the use of Freons in new refrigerating machines and air conditioners is the result of internationally concerted legislative actions. At the present moment, methods are looked for to destroy the existing large reserves of Freons efficiently and environmentally friendly. Thermal oxidation [1], biodegradation [2], and chemical [3, 4] and catalytic [5, 6] decomposition methods have been reported. One method is to decompose Freons in the plasma conditions generated by various types of electric discharges [7, 8].

The aim of this work is to study the decomposition of chlorodifluoromethane (R22, $CHClF_2$) in high-voltage gliding discharg generated in a plasma reactor at atmospheric pressure. The results of thermodynamic calculations [9] have indicated that the Freon should be decomposed in an oxidizing medium. Therefore, we proposed to use oxygen as the oxidizing medium. In the present study, the process was carried out in a gas mixture consisting of argon, $CHClF_2$ (Freon R22) and oxygen.

EXPERIMENTAL

Experimental setup

Figure 1 shows a scheme of the experimental setup. Its main part is a plasma reactor (Fig. 2) in which the gliding arc discharge was generated. The plasma reactor consists of a quartz tube comprising three knife-shaped working electrodes and an ignition electrode. The plasma reactor was supplied with a high-voltage alternating current (50 Hz). The reactant gases were introduced into the plasma reactor through a mixer followed by a nozzle. The unit supplying the gases included the gas cylinders of the carrier gas (Ar), of the oxidizing gas (O_2), and of Freon R22 ($CHClF_2$). The outlet gases were cooled and delivered to absorption vessels (four glass washers filled with a potassium iodide solution). Three glass burettes formed part of the sampling device. The flow rate of the outlet gases was measured by a gas flow meter.

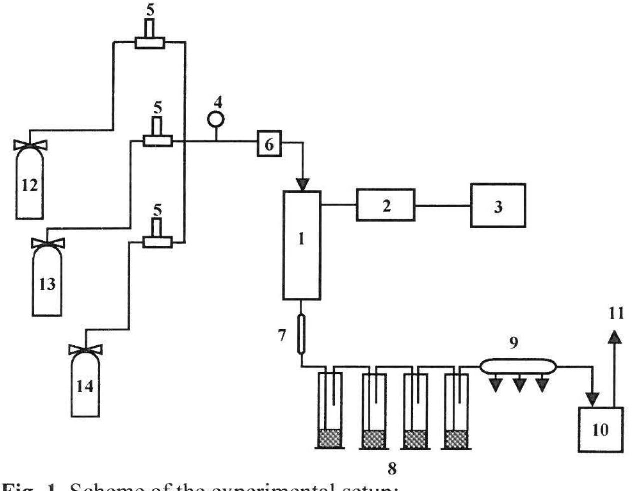

Fig. 1. Scheme of the experimental setup:
1 – plasma reactor, 2 – power supply unit, 3 – power measurement system, 4 – manometer, 5 – mass flow controllers, 6 – mixer, 7 – cooler, 8 – absorption units, 9 – gas sampler, 10 – gas measurement system, 11 – vent, 12, 13, 14 – reactant gases

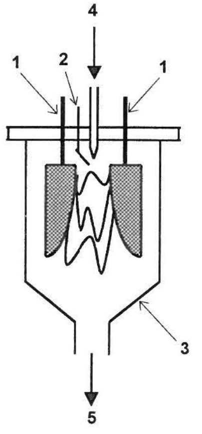

Fig. 2. Scheme of the plasma reactor:
1 – electrodes, 2 – ignition electrode, 3 – quartz tube, 4 – inlet, 5 – outlet

ANALYTICAL METHODS

Gas chromatography and iodometry were used for quantitative and qualitative determinations. The composition of the outlet gases was determined by gas chromatography with the aid of external standards. The analytical conditions are presented in Table 1. The amount of the gases absorbed (Cl_2 and F_2) was determined by iodometry. Aqueous potassium iodide was used as the absorbing solution. The iodometric data and the balance of chlorine and fluorine showed these gases to have been formed 60–80%.

Table 1. The gas chromatography conditions.

Chromatograph	HP 6890, Hewlett-Packard	GCHF, Chromatron
Detector	Flame ionization detector, FID	katharometer
Column	60/80 mesh Carbopack™ B/5% Fluorocol™, L = 4 m, ϕ = 3 mm	60/80 mesh Carboxen-1000, L = 2 m, ϕ = 4 mm
Carrier gas	He, 25 mL/min	Ar, 30 mL/min
Compounds determined	$CHClF_2$, $CHCl_2F$, CCl_2F_2, $CClF_3$, $C_2Cl_2F_4$, C_2ClF_5	CO_2, CO, CF_4

Process conditions

The process was run under well-established feeding conditions and at a constant voltage of the electrode. The total flow rate of the inlet gases was kept constant during the series of experimental runs (W_S = 64.4 mols/h). The concentration of $CHClF_2$ was kept constant in each experiment, too (0.016 mol/mol, 1 mol R22/h). The argon and oxygen concentrations were changed in the stream of the inlet gases (oxygen from 0 to 0.822 mol/mol; and argon from 0.985 to 0.163 mol/mol). The reactor power was changed from 0.75 kW for oxygen-free conditions (argon plasma only) to 1.55 kW for the maximum oxygen concentration used (0.822 mol/mol).

Process parameters

The overall Freon decomposition degree (U), equation 1, is defined in terms of the amount of the Freon introduced into the plasma reactor and decomposed so as to yield both the products containing chlorine and fluorine (other Freons) and ones containing no halogens (carbon oxides). The decomposition degrees of the Freon to carbon oxides (U_{CO_2}, U_{CO}) and to other Freons ($U_{C_nH_mCl_xF_y}$) were calculated by equations 2 – 4. The values required for the equations were evaluated from gas chromatography data. The degree of Freon decomposition to elementary carbon was calculated for oxygen-free conditions (argon plasma only) from the carbon balance expressed by equation 5. For an objective assessment of the decomposition process, the effective Freon decomposition degree (U_{ef}) was derived, equation 6. This degree is defined in terms of the amount of the Freon introduced into the reactor plasma and decomposed to yield only the products containing neither chlorine nor fluorine (simple products: CO_2, CO). In industry practice, the watt-hour efficiency determines practical application. Therefore, the overall and effective energy consumption (Z, Z_{ef}) was formulated (eqns. 7 and 8).

$$U = \frac{W_S[CHClF_2] - W_P[CHClF_2]}{W_S[CHClF_2]} \quad (1)$$

$$U_{CO_2} = \frac{W_P[CO_2]}{W_S[CHClF_2]} \quad (2)$$

$$U_{CO} = \frac{W_P[CO]}{W_S[CHClF_2]} \quad (3)$$

$$U_{C_nH_mCl_xF_y} = \frac{n \times W_P[C_nH_mCl_xF_y]}{W_S[CHClF_2]} \quad (4)$$

$$U_C = 1 - \sum U_{C_nH_mCl_xF_y} \quad (5)$$

$$U_{ef} = 1 - \sum U_{C_nH_mCl_xF_y} \quad (6)$$

$$Z = \frac{P}{W_S[CHClF_2] - W_P[CHClF_2]} \quad (7)$$

$$Z_{ef} = \frac{P}{W_S[CHClF_2] - \sum W_P[C_nH_mCl_xF_y]} \quad (8)$$

where subscripts S and P refer to the streams of reactants (inlet gases) and products (outlet gases), respectively; $W_S[CHClF_2]$, $W_P[CHClF_2]$ are the flow rates of $CHClF_2$ in the inlet and in the outlet gases, resp., [mol/h]; $W_P[CO_2]$, $W_P[CO]$ are the flow rates of carbon dioxide and carbon monoxide in the outlet gases, resp., [mol/h]; $W_P[C_nH_mCl_xF_y]$ is the flow rate of Freons formed in the decomposition process and of the undecomposed $CHClF_2$ in the outlet gases, [mol/h]; P is the input reactor power [kW].

RESULTS

The results of the present study are shown graphically in Figs 3–6. The degree of plasma-induced decomposition of Freon R22 is seen to be related to the composition of the inlet gas stream and to the input reactor power (Fig. 3). The decomposition process of Freon R22 carried out under oxygen-free conditions (argon plasma only) is a plasma pyrolysis that yields others Freons and elementary carbon. Five Freons ($CHCl_2F$, CCl_2F_2, $CClF_3$, $C_2Cl_2F_4$, C_2ClF_5) were determined in the outlet gases when this process was carried out in argon plasma without oxygen. The minimum overall and effective decomposition degrees were achieved in these conditions ($U = 0.81$ mol/mol and $U_{ef} = 0.35$ mol/mol). The overall and effective decomposition degrees increased as oxygen was added. Carbon dioxide was the main product of the decomposition in the oxidizing atmosphere. The concentration of CO_2 in the outlet gas increased as the oxygen concentration in the inlet gas was increased (Fig. 4). The concentrations of the resulting Freons in the outlet gases vary with oxygen concentration in the inlet gases (Fig.5). Two Freons (CCl_2F_2, $CClF_3$) were determined in the outlet gases when this process was carried out in the presence of oxygen. The effective energy consumption varied (1.15÷1.98 kWh/mol) over the examined range of oxygen concentrations (0÷0.822 mol/mol) and reactor powers (0.75÷1.55kW) (Fig.6). The effective energy consumption was maximum for decomposition of the Freon under argon plasma conditions. The overall energy consumption increased as the oxygen concentration was increased in the inlet gas (Fig. 6).

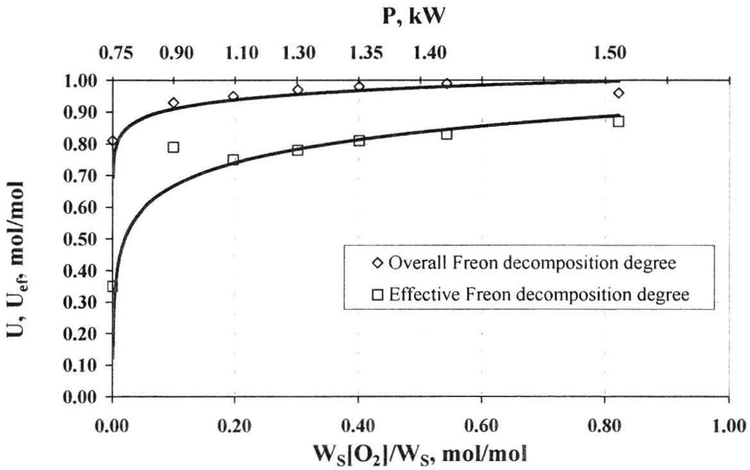

Fig. 3. The overall and the effective Freon decomposition degrees in relation to oxygen concentration in inlet gases and to input reactor power.

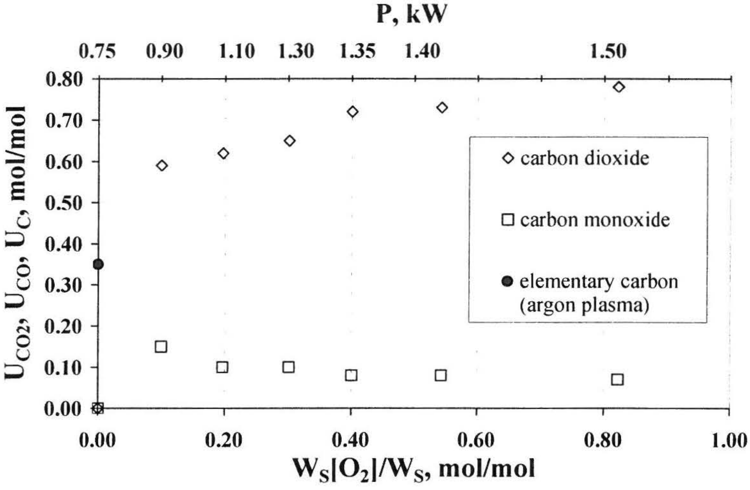

Fig. 4. The Freon decomposition degrees to CO_2, CO, and C in relation to oxygen concentration in inlet gases and to input reactor power.

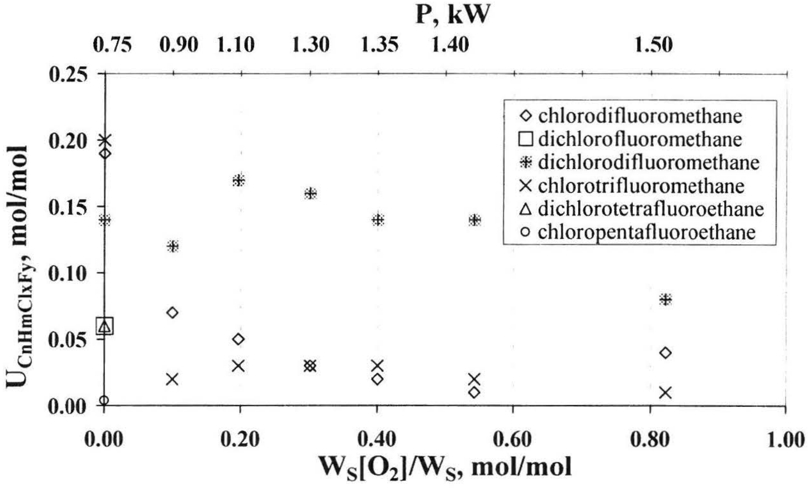

Fig. 5. The Freon decomposition degree to $C_nH_mCl_xF_y$ in relation to oxygen concentration in inlet gases and to input reactor power.

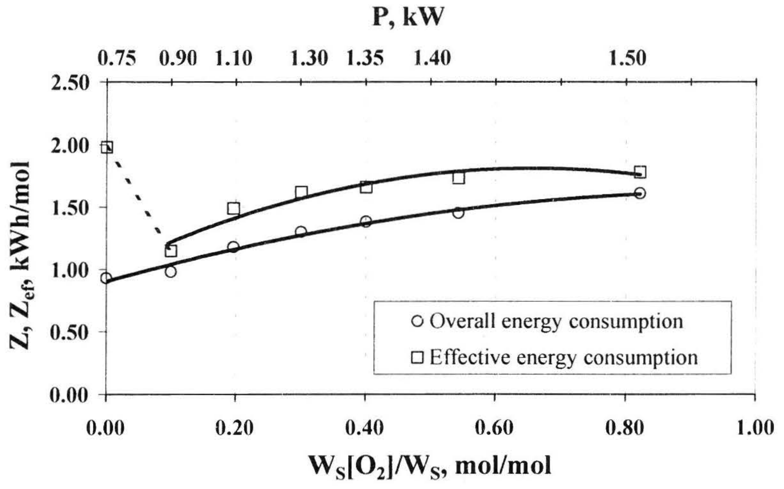

Fig. 6. The overall and effective energy consumption in relation to oxygen concentration in inlet gases and to input reactor power.

CONCLUSIONS

- The plasma-induced conversion of Freon R22 depends on the reactant gas composition and discharge power.
- The Freon R22 conversion degrees achieved were high. The maximum conversion degree was 0.99.
- The process should be carried out in the oxygen plasma only. In this case, the difference between the overall and effective Freon decomposition degrees has a minimum value.
- Elementary carbon was the main product of the decomposition run in oxygen-free conditions (argon plasma).
- $CHCl_2F$, CCl_2F_2, $CClF_3$, $C_2Cl_2F_4$, C_2ClF_5 were by-products of the decomposition run in oxygen-free conditions (argon plasma).
- Carbon dioxide was the main product of the decomposition run in the presence of oxygen.
- CCl_2F_2, $CClF_3$ and carbon monoxide were by-products of the decomposition run in the presence of oxygen.
- The reaction products were found to contain no Freon R14 (CF_4).
- The present process is favourable in that it avoids the possibility of formation of nitrogen oxides.

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ELEKTROPLAZMOWY ROZKŁAD CHLORODIFLUOROMETANU W ŚRODOWISKU UTLENIAJĄCYM

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S t r e s z c z e n i e. Badano rozkład chlorodifluorometanu (Freon R22, $CHClF_2$) w plazmie nierównowagowej generowanej w wyładowaniach poślizgowych w argonie z dodatkiem tlenu jako utleniacza. Badano wpływ stężenia tlenu i mocy wyładowania na stopień rozkładu freonu i skład gazów odlotowych. Maksymalny stopień rozkładu freonu (0.99) uzyskano dla mieszaniny freon (0.016 mol/mol), argon (0.441 mol/mol) i tlen (0.543 mol/mol) przy mocy wyładowania 1.44 kW. Głównymi produktami procesu był ditlenek węgla oraz nieorganiczne związki chloru i fluoru.

S ł o w a k l u c z o w e : chlorofluorowęglowodory, chlorodwufluorometam, rozkład.