Decomposition of CFC and Halon waste gases in normal-pressure plasma reactors *

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Abstract—The normal-pressure decomposition of CF_2Cl_2 and CF_2ClBr in air by non-equilibrium plasma was studied. The pressure of CF_2Cl_2 and CF_2ClBr was 2.67×10^3Pa, added the dry air to 1.01×10^5 Pa, discharged by corona or DBD, 11.5% of CF_2ClBr was decomposed by corona after 120s discharge, more than 85% of CF_2Cl_2 and 95% of CF_2ClBr were decomposed by DBD after 10s discharge respectively. The main products were CF_2O, Cl_2 and Br_2.

Keywords: decomposition, CFC, Halon, normal-pressure, plasma.

1 Introduction

Since the 1970's, the CFCs and Halons emitted by human have been widely thought as substances which may cause ozone depletion in stratosphere(Kerr, 1991). The CFCs and Halons are stable substances, and their lives are longer than decades years(Hammit, 1987). It is very difficult to decompose the CFCs and Halons waste gases with usual methods.

Non-equilibrium plasma method is known as an efficient way to treat pollutants which are difficult to dispose with usual methods. And there are lots of reports that scientists have successfully decomposed some pollutants by low-pressure non-equilibrium plasma (Arno, 1996; Breitbarth, 1997). There are several ways to engender the non-equilibrium plasma, but only corona and dielectric barrier discharges can engender the non-equilibrium plasma in high pressure. The corona discharge is the partial breakdown near electrodes under high-voltage electric field, and it can be realized at 10^5Pa. It was reported that CF_3Cl (CFC-13) was decomposed by corona discharge in 1.013×10^5 Pa and 48.5% of CF_3Cl was decomposed (Liu, 1997). The dielectric barrier discharge is usually operated at an elevated pressure of 0.1—10 bar and initiated in a gap between two electrodes, at least one of which is covered with dielectric (Xu, 1995; Eliasson, 1991). In this paper, the corona discharge and dielectric barrier discharge are utilized to decompose CF_2Cl_2(CFC-12) and CF_2ClBr(Halon, 1211) at total pressure of 1.01×10^5Pa.

2 Experimental section

The normal-pressure plasma apparatus are shown in Fig. 1. Fig. 1a shows the corona discharge reactor. The glass cell is 150 millimeters long and its inside diameter is 25 millimeters. There are two coiled electrodes made by ferro-tungsten alloy in the cell. One of the electrodes is linked with high-voltage alternating current power, the other is linked with ground. Fig.1b shows the dielectric barrier discharge reactor. The DBD reactor is composed with two coaxial hollow quartz tubes, the inside tube's diameter is 10 millimeters and the outside one is 20 millimeters, the thickness of the tubes are 1.2 millimeter. The electrodes are made by aluminum foil, and the

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quartz is used as dielectric. The electrodes are linked with high-voltage alternating current power whose voltage can be changed from 2.0—15kV. When the powers work, the non-equilibrium plasma is engendered in the reactors by the effect of the high-voltage alternating current electric field.

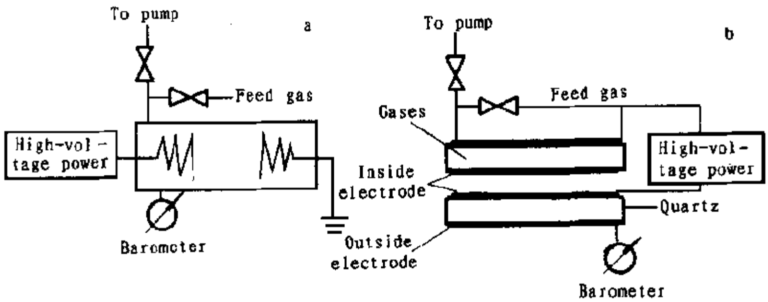

Fig. 1 The normal-pressure plasma apparatus
a. corona discharge reactor; b. DBD reactor

The mixture of CFC-12 or Halon 1211 gases and dry air was fed in the reactors, then switch on the high-voltage power, after certain seconds discharge, the products are analyzed by GC and FT-IR. The percent $\eta(\%)$ decomposition of waste gases can be attained by:

$$\eta(\%) = \frac{W_0 - W_D}{W_0} \times 100\%.$$

3 Results and discussion

3.1 The decomposition of CF_2ClBr by corona discharge

The mixture of CF_2ClBr and air is fed in the corona discharge reactor. The initial pressure of CF_2ClBr was kept as 2.67×10^3Pa, and the total pressure is changed from 5.33×10^3 Pa to 1.01×10^5Pa. After 120's corona discharge, the change of CF_2ClBr's decomposition efficiency in air with different total pressure is shown in Fig. 2.

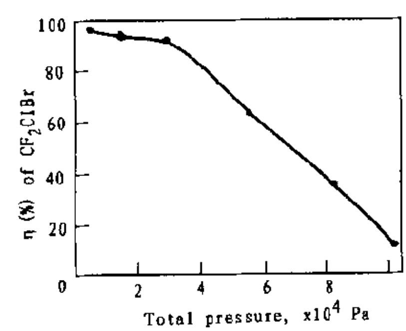

Fig. 2 The effect of total pressure on decomposition of CF_2ClBr with corona discharge in air

The decomposition efficiency of CF_2ClBr decreased when the total pressure increased. When the gases was corona discharged at 1 atm. (1.01×10^5Pa), only 11.5% of CF_2ClBr was decomposed.

3.2 The decomposition of CF_2Cl_2 by dielectric barrier discharge

In normal atmospheric pressure, the mixture of CFC-12 (or Halon-1211) and air can discharge stable and continuously in DBD reactor(Fig. 1b). The pressure of CF_2Cl_2 was 2.67×10^3 Pa, added air to 1 atm in the dielectric barrier discharge reactor, then linked the high-voltage middle-frequency power, the discharge occurred in the reactor. The change of decomposition efficiency with the discharge time is shown in Fig. 3.

In dielectric barrier discharge reactor, the CF_2Cl_2 can be decomposed very fast. When the time of discharge was longer than 30s, the CF_2Cl_2 was almost decomposed. Through analyzing the FT-IR figure(Fig. 4) of products after discharge 30 seconds, we inferred the main products of this plasma reaction are: CF_2O(1956.2 cm^{-1}, 1943.7 cm^{-1}, 1928.1 cm^{-1}, 1256.2 cm^{-1}, 1240.6 cm^{-1}, 1231.2 cm^{-1}, 975.0 cm^{-1}, 775.0 cm^{-1}), COClF(1875.0 cm^{-1}, 1862.5 cm^{-1}, 1101.4 cm^{-1}, 1093.7cm^{-1}) and CF_4(1281.2 cm^{-1}).

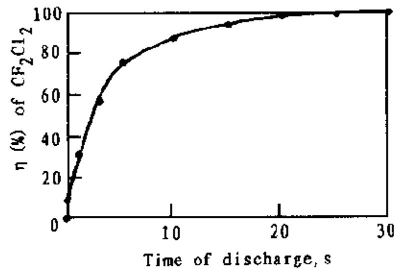

Fig. 3 The curve of decomposition efficiency of CF_2Cl_2 with discharge time

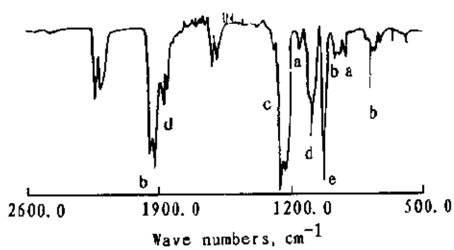

Fig. 4 The FT-IR figure of CF_2Cl_2 in air after discharge
a. CF_2Cl_2; b. CF_2O; C. CF_4; d. COClF; e. SiF_4

3.3 The decomposition of CF_2ClBr by dielectric barrier discharge

The experimental process was similar to 3.2, 2.67×10^3 Pa CF_2ClBr discharged with air in the DBD reactor. After 20s discharge, the CF_2ClBr was almost degraded, and the FT-IR figure of products is shown in Fig. 5. This reaction transformed the CF_2ClBr into CF_2O (1956.2 cm^{-1}, 1943.7 cm^{-1}, 1928.1 cm^{-1}, 1256.2 cm^{-1}, 1240.6 cm^{-1}, 1231.2 cm^{-1}, 975.0 cm^{-1}, 775.0 cm^{-1}) and a little CF_4(1281.2 cm^{-1}).

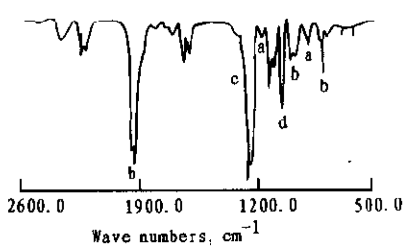

Fig.5 The FT-IR figure of CF_2ClBr in air after discharge
a. CF_2ClBr; b. CF_2O; c. CF_4; d. SiF_4

In non-equilibrium plasma, CFC-12 and Halon-1211 can react with oxygen in air and be transformed into other substances. There are so many high energy electrons which are accelerated by the high-voltage electric fields in plasma, these electrons can bomb the CFC-12 and Halon-1211 molecules in reactors, and product many radicals such as CF_2Cl, CF_2Br, CF_2, CCl_2F, Br, Cl, F etc. And in plasma, the O_2 molecules can be decomposed as active O radicals. The O_2 molecules and active O radicals can react with radicals produced by CFC-12 and Halon-1211 and eliminate them. This process made CFC and Halon waste gases mainly transform into CF_2O, Br_2 and Cl_2, and those substances can be absorbed with NaOH solution, finally transformed into NaF, CO_2, NaCl and NaBr.

Although the CFCs and Halons all can be decomposed in normal pressure by corona discharge and dielectric barrier discharge, but the efficiencies between these two methods are greatly different. The reaction of CFCs and Halons with oxygen in corona discharge is slower than in dielectric barrier discharge, and decomposition efficiency in dielectric barrier discharge is higher than in corona discharge. The difference above can be explained by analyzing the mechanism of these two kinds of discharge: in corona, the discharge is partial, only the area near the electrodes can discharge and product electrons. Although the area nearer the electrodes can discharge more violently and engender higher energy electrons, but most of area in reactor can not cause the breakdown and engender electrons; in the dielectric barrier discharge, although the discharge is comprised of a great deal of randomly distributed microdischarges both in time and in space, but in general, the discharge occur in entire space between the dielectric layers, the dielectric layers can make the discharge relatively stable and uniform, and avoid the spark discharge. In dielectric barrier discharge, the electrons are accelerated and limited in the space between two dielectric layers. So as this point, there is a higher electron density in dielectric barrier discharge, and lead to a higher collision possibility of CFCs(or Halons) with electrons, and product more active radicals to react with O_2 or O, make the CFCs and Halons decompose faster.

4 Conclusion

The mixture of CFCs (or Halons) and dry air can be discharged in corona reactor and in DBD reactor at 1.01×10^5Pa. In non-equilibrium plasma, the CFCs and Halons react with oxygen in air and are mainly transformed into CF_2O, Br_2 and Cl_2, and the products can be transformed easily into other non-toxic substances. At 1.01×10^5 Pa, the decomposition efficiency of CFCs and Halons by DBD is higher than by corona discharge. The non-equilibrium plasma engendered by dielectric barrier discharge can be one of the ideal methods to treat the CFCs and Halon waste gases.

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