DESTRUCTION OF DIBENZOFURAN BY MICRO-WAVE/PLASMA

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Introduction

A lot of technologies have been developed to remove the pollutants, such as dioxin, emitted by waste incinerator gases. Some techniques consist in controlling the dioxin formation by the optimisation of combustion parameters or by improving the design of furnace structures. The others are to destroy or remove the dioxins after the incinerator, for instance, by adsorbing dioxins on activated charcoal. Numerous studies have been made on the dioxins since the PCDDs and PCDFs were discovered in waste incineration plants[1]; many of them concern the dioxin formation [eg 2 -7], whereas only a few deal with their destruction [eg 8-10].

In this paper, the feasibility of a process of dioxin abatement by micro-waves/plasma is presented. To investigate the dioxin destruction in plasma environment, we have chosen dibenzofuran (DBF) as a model molecule because DBF has the same structure and is more stable than PolyChlorinated Dibenzo-p-Dioxins and PolyChlorinated DibenzoFurans (PCDD/Fs). A possible reaction mechanism of dibenzofuran destruction in the micro-wave plasma of argon/oxygen is also explained from the experimental and literature results.

Material and Methods

The destruction of DBF is performed in a continuous reactor, made of a quartz tube of 2cm in diameter and of 30cm in length, which is placed in the resonant cavity of the experimental apparatus (Figures 1 & 2).

One of the difficulties of this study is that DBF is solid at ambient temperature and pressure. In order to feed the reactor with DBF, this species is previously dissolved in benzene. Benzene has been chosen because it is a good solvent to dissolve DBF. Besides, it is known to be an intermediary [8,9] or final product in DBF decomposition and it can also be a product formed during waste incineration. Thus, the presence of benzene will not change the reaction mechanism of DBF decomposition. The DBF concentration in the solvent benzene is 0.6% (mole/mole). The flowrate of the mixture benzene/DBF is regulated by a liquid mass flowmeter coupled with a vapour generation system (Figure 1) .

Two other gas mass flowmeters are used to monitor carrying gas argon and the dilution gas (Ar, O_2 or air), used for the plasma generation. The total gas reactant flowrate varies from 50 mL/min to 300 mL/min and the operating pressure of the reaction is between 15 torr and 20 torr before plasma starting.

A trap, cooled with liquid nitrogen, is connected at the exit of the reactor to accumulate the products of the reaction. The analysis of these products is realised by gas-chromatography. The used chromatograph, Agilent 6850, is equipped with a DB-5 capillary column (L=30m, d=0.25mm, e=0.50µm) and with a FID detector. The injected quantity of reaction products is 1 mL. The temperature program ranges from 40°C to 250°C. The possible remainders of reactants are identified with comparing their retention time to that of pure product. The gaseous products such as CO, CO_2 could not be analysed with this experimental set-up, they are vented by a vacuum pump.

The experimental apparatus used for plasma generation is from the SAIREM; this installation is represented in figure 2. It includes a magnetron of THOMSON CSF fed by a high voltage generator (type GMP 12 KTS). Its power can vary between 0 and 120W in a continuous manner. The magnetron plays the role of an oscillator having an exit frequency of 2450 MHz. The produced waves are emitted by an antenna and propagated in a standard rectangular wave guide (interior dimensions: 86.30 mm x 43.15mm) joined with magnetron. This guide is designed in brass. A wattmeter installed on the generator allows to measure the incident power Pi and reflected power Pr at each moment. The difference (Pi-Pr) is approximately the transmitted power from plasma. It should be noted that a little quantity of the transmitted power is actually transmitted to heat in the guide tube. A cooling water circulator protects the antenna from the returned microwave energy occurring in the case of loss of adaptability.

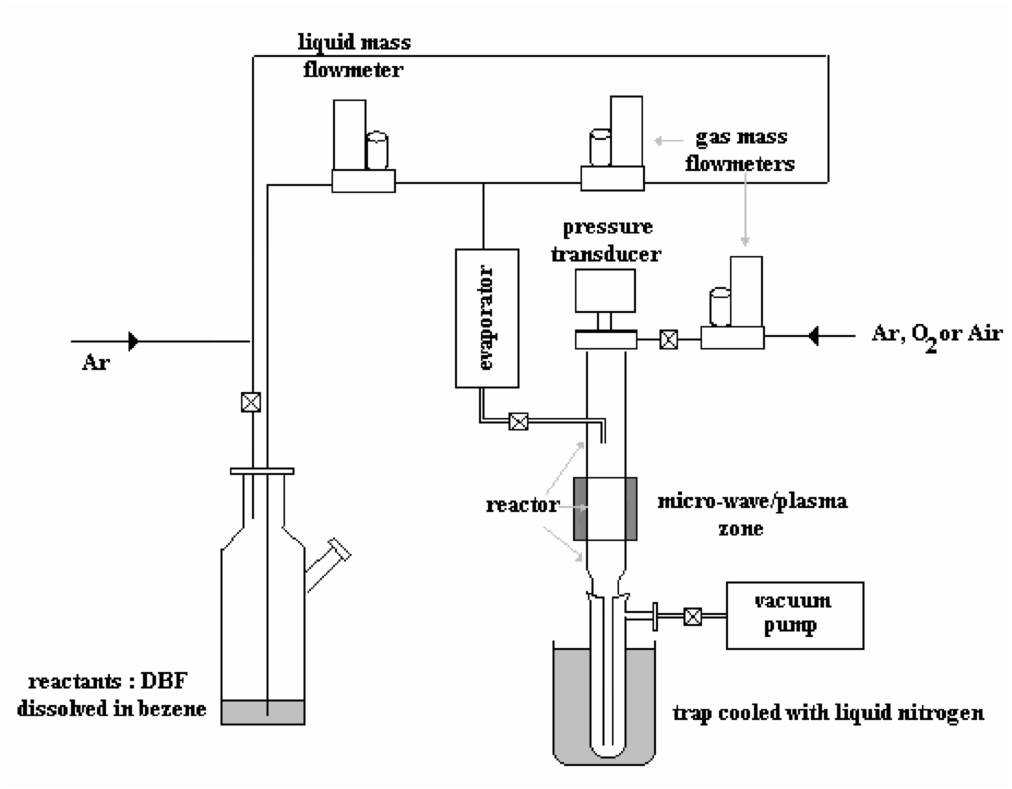

Figure 1: experimental set-up for dioxin abatement by micro-wave plasma

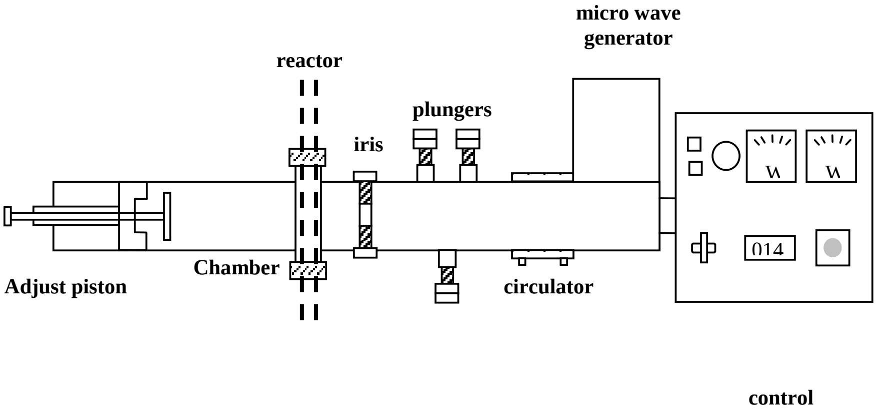

Figure 2: Scheme of generator and applicator of micro-waves

Results and Discussion

Three sets of experiments are performed, their results are reported in Table 1. In the first series (exp. 1-5), the reactor is fed by DBF/benzene and argon; the flowrate of argon is kept constant, whereas the incident power, P_{in}, is varying. In the second series, the flowrate of argon is varying and P_{in} is constant. Then in the third series (exp. 6-13), the incident power is kept constant, whereas the reaction mixture is added of a varying flowrate of oxygen.

No.	Total flowrate (mL/min)	pressure (torr)	P_{in} (W)	Ratio Ar/O_2	Benzene decomposition (%)	DBF decomposition (%)
1	200	19	500	-	99.96	100
2	200	18.8	400	-	99.92	100
3	200	17.9	300	-	99.68	100
4	200	18.8	200	-	100	100
5	200	18	150	-	99.91	100
6	100	12.8	400	-	99.43	100
7	150	15.2	400	-	99.68	100
8	250	19.7	400	-	99.76	100
9	300	22.4	400	-	99.45	100
10	100	11.0	400	1	97.18	100
11	150	12.0	400	0.5	97.79	100
12	200	14.8	400	0.33	99.34	100
13	250	16.8	400	0.25	99.59	100

Table 2 : operation conditions and destruction rate of reactants

The experiments 1 to 5 are performed in the plasma benzene/dibenzofuran/argon with an incident power equal or superior to 150 W. The gas-chromatography analysis of the products contained in the cooled trap shows that all the DBF and more than 99% of benzene are destroyed. These results are in good agreement with those of S. Shih et al.[11]. Indeed, they have studied the decomposition of benzene in radio-frequency plasma environments and they have found that the decomposition fraction of benzene could reach 99% when the incident power is more than 20W. In our case, the plasma could not remain stable with the reactants if the incident power is less than 150 W, consequently we have not realised the study in these conditions.

Another interesting point is that we have observed the formation of a black-carbon deposit on the wall of the reactor in our experimental conditions (i.e. lack of air or oxygen). Numerous researchers [eg 11-13] have reported that acetylene formed during the benzene decomposition by pyrolysis, oxidation, combustion or plasmas can explain the presence of black-carbon. Indeed, it could be possible to scheme[11, 12] the production of carbon-black by the following lumped reactions:

$C_6H_6 \rightarrow C_2H_2 + 4C + 2H_2$, where C are atoms of black-carbon

$2C_6H_6 \rightarrow C_{10}H_8 + C_2H_2 + H_2$

and $2C_6H_6 \rightarrow C_{10}H_8 + 2C + 4H_2$,

Nevertheless these reactions are lumped and do not explain the kinetics of black-carbon formation. In order to explain these reactions of deposition, a detailed mechanism describing polyaromatic species formation and pyrocarbon deposit, such as the one proposed by Ziegler et al.[14], could be exploited. Indeed this mechanism, initially proposed for propane pyrolysis, contains 608 elementary reactions involving 172 species, and describes the formation of gas phase species up to pyrene ($C_{16}H_{10}$).

The experiments 6 to 9 are realised in the plasma benzene/dibenzofuran/argon with a constant incident power equal or superior to 150 W ; the flowrate of argon, and so the pressure is varying. The experimental conclusions are the same that those of the previous experiments (i.e. 1-5).

The experiments from 10 to 13 are performed with a constant incident power; various quantities of oxygen are introduced in the system. The gas-chromatography analysis of the trapped products shows again that all the DBF and more than 97% of benzene are decomposed. In these experiments, compared to those in the plasma of benzene/dibenzofuran/argon, black-carbon deposit is not observed on the reactor wall. In these experiments, we can suppose that the final products of the decomposition are carbon dioxide, water and carbon monoxide. Indeed R Wörner et al.[9] have studied the thermal oxidation of dibenzofuran and they concluded that all the hydrocarbon products cannot form while the oxygen excess contained in the system represents more than 20% at 900 °C.

According to all the experimental results, we think that the decomposition mechanism of DBF in plasma can be described as a radicalar mechanism of pyrolysis (exp. 1-9) or an oxidation mechanism (exp. 10-13). In all these experiments (i.e with or without oxygen) we can suppose that the radicalar reactions of dibenzofuran decomposition begin either with the radical initiation by plasma or through a metathesis reaction with any radical R• also initiated in the plasma.

DBF + e^- → DBF• , where e^- is an electron generated in the plasma

DBF + R• → DBF• + R

Supposing that the decomposition of DBF in the plasma benzene/dibenzofuran/argon/oxygen follows a radicalar mechanism of oxidation, it can be then described, for instance, with the mechanism of Marquaire et al.[8] for thermal oxidation of DBF. In this mechanism the DBF oxidation is described in five steps : the formation of radicals DBF•, of PAHs, of benzofuran and its derivatives, of monoaromatic products (toluene, styrene,...) and finally the formation of aliphatic products (C_2H_2, C_2H_4,...), CO and CO_2.

In conclusion, a process of destruction of dibenzofuran in mixture with benzene by micro-wave/plasma is proposed in this paper. The experimental studies are performed in a benzene/dibenzofuran/argon plasma and in a benzene/dibenzofuran/argon/oxygene plasma. In each experiment, the destruction of DBF and benzene represents more than 97%. The experiments realised without oxygen in the plasma also produce a deposit of black carbon in the reactor. From our experimental results and literature reports, we deduce that the DBF decomposition can be described with a radicalar mechanism, such as the one proposed by Marquaire et al.[8]

The destruction of dibenzofuran by the micro-wave/plasma is an interesting technology in the dioxin abatement since it could be possible to apply it to the treatment of activated charcoal used in waste incinerators.

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