Degradation of tetrafluoroethane using three-phase gliding arc plasma

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Abstract. The use of many chlorofluorocarbons (CFC’s) has negatively impacted the ozone layer. The Montreal Protocol was implemented, as a temporary solution for this problem by replacing CFC’s by hydrofluorocarbons (HFC’s). These kinds of gases have the propriety to be free of chlorine. However, in a next future, the Montreal Protocol also considers the replacement of HFC’s because they have a high global warming potential when they enter in contact with the atmosphere. One of the methods to remove those compounds is the gliding arc plasma because it presents some advantages. The inlet system works near the atmospheric pressure and can treat a continuous gas flow at low power with the possibility to convert a considerable volume of HFC’s [2-6].

1. Introduction

The three-phase gliding arc plasma is a self-oscillating discharge formed in three divergent electrodes. The discharge is initially developed at the shortest distance between the two electrodes having the biggest electric potential difference. After that, the arc diverges along these electrodes. The discharge length grows until a critical length, determined by the power supply. Beyond this point, the energy obtained by the electrical supply can no longer sustain the equilibrium phase of the gliding arc and the electrical conductivity in plasma channel decreases (when the arc length increases) until the extinction of the discharge. Then, a restrike appears, leading to a new periodic cycle [1,2].

This work presents an alternative to treat, in a safety way, the HFC’s. These gases are normally discarded by the refrigerant industry and their environmental impact has been amply measured. One of advantages to work with a three-phase gliding arc plasma is that the system works near to the atmospheric pressure and can treat a continuous gas flow at low power with the possibility to convert a considerable volume of HFC’s [2-6].

The study of the degradation includes an electrical analysis considering the efficiency of HFC’s conversion and gives preliminary parameters that will allow improving the system to be scaled in near future.

Results obtained in the present article, show that the gliding arc reactor proposed is effective to treat halogenated compounds, difficult to trait with conventional methods or non-thermal plasma [7].
2. Experimental setup
The experimental setup consists in a plasma reactor, a power supply, flow controllers and measurement systems and is schematically depicted in figure 1. The plasma reactor contains three copper electrodes (see figure 2) disposed inside of a cylindrical quartz tube of 56 mm ID and length of 410 mm. The power supply is composed by three phase high voltage transformer, a variable transformer controls the ignition discharge and three inductances stabilize the discharge plasma. The exhaust gases are directly connected to an alkaline scrubber system employed as a safety measure in case of acid gas were formed, following this system, there are two ports to sample and to vent residual gases. One of the ports is used for gas chromatography and the other one is for FTIR analysis.

The gases from the cylinders were controlled by three mass flow rate controllers (MKS, πMFC), in order to add water steam to the mixture, gases were bubbled in water and the mixture was then injected to the reactor. The discharges were formed at the closest points of the copper electrodes, having a very short contact time. Then they are spread by gliding axially along the electrodes by the gas force action. The arc disappeared at the end of the electrodes and a new discharge immediately is formed at the initial section. The copper electrodes were not cooled; as a result, the electrical energy was directly transferred to the treated gas mixture.

![Figure 1. HFC’s degradation system.](image1)

![Figure 2. (a) Triangular electrodes, (b) triangular electrodes with ceramic pieces.](image2)
3. Chemical background
The tetrafluoroethane was diluted in argon and air in a concentration of 20489 ppm in volume and a proportion given in table 1. The mixture of gases was bubbled to add water and injected to the reactor to be treated. The total flow rate applied to the reactor was 14.1 l.p.m.

| Gas     | Concentration |
|---------|---------------|
| R134-a  | 0.289 l.p.m.  |
| Ar      | 12.7 l.p.m.   |
| Air     | 1.1 l.p.m.    |

The mechanism of degradation developed inside of the reactor was described by two main reactions; the first reaction considers a mixture of tetrafluoroethane and water steam described in the reaction (1)

\[
\text{CH}_2\text{FCF}_3 + \text{H}_2\text{O} \rightarrow \text{CO} + \text{C} + 4\text{HF} \tag{1}
\]

When this reaction was developed in the degradation system, the reactor walls were covered with a carbon layer (see figure 3(a)) who worked like a conductor forcing to stop the degradation process.

The second mechanism of degradation (2) includes water steam and oxygen in the mixture of gases. It presents an enhancement, because the presence of oxygen from air avoids the carbon formation over the inner walls (see figure 3(b)). [4,6].

\[
\text{CH}_2\text{FCF}_3 + \text{H}_2\text{O} + \frac{1}{2}\text{O}_2 \rightarrow 2\text{CO} + 4\text{HF} \tag{2}
\]

One possibility to reduce the presence of CO is by oxidizing it with oxygen to reduce its negatives effects as is shown by reaction (3) [5, 6]

\[
\text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2 \tag{3}
\]

![Figure 3](image)

**Figure 3.** (a) Internal walls of the reactor covered of carbon, mechanism of degradation (1), (b) internal walls of the reactor carbon free mechanism of degradation (2).

4. Chemical analysis
To determinate the conversion factor of the system was necessary to determinate the initial and final concentration of tetrafluoroethane. The technique used to quantify was gas chromatography. The detector used was a FID (Flame Ionization Detector), a packed column of Porapak Q and Argon like a carrier gas was used in the analysis.
The detector has a temperature of 200° C and the oven has a temperature of 70° C isothermal, the carrier gas flow was 30ml min⁻¹.

The initial concentration of gas was 20489ppm and the final concentration was 1390 ppm, therefore the conversion rate obtained is around 93.21%. All the chemicals measures were verified three times.

The figure 4 is a chromatogram that shows the conversion of tetrafluoroethane before and after the plasma degradation.

![Chromatogram of tetrafluoroethane degradation](image)

**Figure 4.** Chromatogram of tetrafluoroethane degradation, employing fid detector, argon as carrier gas 30ml min⁻¹.

5. **Electrical analysis**

Voltages and currents were measured with an oscilloscope Tektronics MSO 2024, these signal can be observed in figure 5. It is worth to note that the value represents only one phase of the system, complementing it with other two electrical phases. The results here presented correspond to electrical signals during the tetrafluoroethane treatment with gliding plasma. These signals are not modified in a considerable way compared to these obtained when only argon is present in the reactor. This is because the very low HFC’s concentrations employed.

With the instantaneous voltage and current reported in figure 5, the corresponding instantaneous power is reported in figure 6 considering one and three phases, according with equation (4), the total RMS power can be calculated.

\[
\text{Three - phase power RMS} = \sqrt[3]{\frac{1}{T} \int_{0}^{T} [v(t) \times i(t)]^2 dt}
\]

(4)

From the RMS power values and the conversion of HFC’s the destruction efficiency can be obtained as follows:

\[
\text{Destruction efficiency} = \frac{\text{Converted HFC’s}}{\text{Supplied power}}
\]

(5)

The destruction efficiency was calculated in 33.36 l kW⁻¹ hr⁻¹.

Results obtained by [10] to treat the same molecule with another plasma technology (i.e. plasma torch with water) show efficiencies near to 100% at 0.16 kg/h of C2H2F4 mass yield rate. In this
work efficiencies of 93% at 0.074 kg/h were obtained, however the input energy in the system here proposed is low (around 519W). [7,9]

![Figure 5. (a) Plasma voltage discharge, (b) plasma current discharge.](image1)

![Figure 6. Instantaneous and RMS plasma power.](image2)

6. Conclusions
The degradation by three-phase gliding arc plasma is an effective way to reduce the gases that produce greenhouse effect like the tetrafluoroethane. The plasma reactor has a very high energy density media, the active species accelerate chemical reactions, besides the plasma reactor is compactness and has a low energetic cost.

This system can be used to detoxify other halogenated compounds [7-9]. Like a future work we will analyze the formation of species and radicals of NOx formed in the reactor by the presence of nitrogen and oxygen in the reactor and the improvement of HFC’s treatment efficiency at low power consumption.
Acknowledgments
The authors would like to thank CONACyT for the financial founds and for the scholarship 11557, as well as the LAP-ININ collaborators for the technical support and assistance during the experimental tests.

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