DECOMPOSITION OF CHLOROFLUOROCARBONS IN THE GLIDING ARC REACTOR

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Abstract

The aim of this work is decomposition of dichlorodifluoromethane (freon R12, CCl₂F₂) in a steam–nitrigen plasma-generating arc reactor at a bench scale. The freons decomposition grade depended on specific energy provided to the freon (kJ per mol of freon) and was determined for the steam/freon molar ratio of 9.3, 16.5 and 30. The grade of CCl₂F₂ decomposition increased with increasing of the specific energy. The highest decomposition grade 63% was achieved for the steam/freon mixture of 9.3 mol/mol. Carbon dioxide and monoxide, hydrogen and oxygen were the main gaseous products of the process. Neither chloride nor fluorine nor their other organic compounds were found in the reaction product. They were converted into respective hydrohalogenic acids.

1. Introduction

Chlorofluorocarbons are organic compounds composed of carbon, fluorine and chlorine. Chlorofluorocarbons (CFC’s) are called freons, it is a trade name. Freons were developed in the early 1930s and used in a variety of industrial, commercial and household applications. These substances are non-toxic, non-flammable and non-reactive. When released into the atmosphere, freons undergo photochemical reactions. UV radiation breaks the carbon–chlorine bonds and free chlorine takes part in ozone-depleting reactions. Each chlorine atom introduced into the stratosphere destroys thousands ozone molecules [1,2]. Various technologies were developed for decomposition of chlorofluorocarbons: catalytic oxidation, adsorption and thermal decomposition. However, these methods are problematic because of formation of toxic exhaust gases and deactivation or poisoning of the catalyst [3,4].

We are proposing destructive conversion of freons in a particular type of electrical discharge: gliding arc where non-thermal plasma is generated. In this discharge the electrons have high temperature but the temperature of heavy particles (atoms, radicals and molecules) is 10 to 100 times lower. The gliding arc reactor is very effective in decomposing hazardous gases and vapours like H₂S [5-7], CH₃SH and mercaptans [8], SO₂ [9], VOC’s [10,11], NOₓ [12] and CFC’s [13]. The process of chlorofluorocarbons destruction was formerly carried out in other plasma reactors generating electrical discharge: corona discharge [14,15] and corona discharge assisted catalysis [16], spark discharge and pulse high current discharge [17] and glow discharge [18].

Experimental

Fig. 1 shows a schematic of the experimental set-up. The set-up included a gas supply system, plasma reactor as well as units for sampling and sample analysis, power measurement system and electrical power supply unit. The flow rates of gases were controlled by a mass flow meter. Water was supplied into the vaporizer. The stream of gases (mixture of freon and nitrogen) and the steam was introduced into the plasma reactor between the electrodes where electrical discharge was generated. The plasma reactor consisted of a quartz tube comprising
six radially diverging electrodes. The distance between two opposite electrodes was 8 mm. The electrodes were connected to a high voltage source and supplied with 50 Hz mains. Unreacted freon, carrier gas (nitrogen) and gaseous products (CO, CO₂, H₂, O₂) were analysed using three gas chromatographs equipped with a thermal conductivity detector. Neither chlorine nor fluorine nor their organic compounds (other than initial one) were found in the gaseous product of the reaction. They were transformed into respective hydrohalogenic acids. Summary molar concentration of fluoride and chloride was determined by acidimetric titration with potassium hydrate (1 mol/dm³). The process of decomposition of dichlorodifluorocarbons was studied at the steam/freon mole ratio 9.3, 16.5 and 30.

Fig. 1. The experimental set-up

2. Results and discussion

The decomposition grade of the freon depended on the specific energy provided to the freon (350 – 1700 kJ/mol CCl₂F₂). The decomposition grade of CCl₂F₂ increased with increasing the specific energy. The relationships between the decomposition grade and the specific of energy provided to the freon are shown in Fig 2. The highest decomposition grades were achieved for the steam/freon mixture of 9.3 mol/mol. Therefore small addition of steam is more advantageous then a large one. When a large amount of steam was added a lot of supplying energy into reactor was consumed to dissociate rather water (not freon). Composition of output gases and concentration of the hydrohalogenic acids changed depending on the specific energy provided to the freon and an amount of steam (Fig. 3 – 4; Tab. 1)
Fig. 2. The influence of amount steam and specific energy provided to the CCl₃F on the Freon decomposition grade

Fig. 3. Composition of output gases for steam/Freon mixture 9.3 mol/mol

Fig. 4. Composition of output gases for steam/Freon mixture 16.5 mol/mol
Fig. 5. Composition of output gases for steam/freon mixture 30.0 mol/mol

Tab. 1. Concentration of the hydrohalogenic acids

<table>
<thead>
<tr>
<th>Flow rate of R12, l(n)/h</th>
<th>Flow rate of steam, l(n)/h</th>
<th>Specific energy, kJ/mol R12</th>
<th>Overall decomposition of R12, %</th>
<th>[H'], mol/l</th>
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<td>13</td>
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</table>

3. Conclusions

Our tests show clearly a feasibility of freons (and generally CFC) destruction AND upgrading process via steam reforming with a full recovery of HF and HCl as well as the synthesis gas using a very simple GlidArc reactor producing non-equilibrium and catalytic plasma at relatively high power and high throughput. Our tests were successful and the destruction rates were already close to industrial demand, especially as concerns the freon conversion into HF and HCl. There is no consumption of argon or other noble gas as the plasma forming gas for other plasma techniques. There are no problems with plasma stability as, by definition, the GlidArc discharges must be UNSTABLE. Projections for greater power and flow are possible, up to an industrial level.

The use of steam-supported plasma offers the coupled advantages of a convenient source of oxygen, which combines with carbon to reduce a tendency for sooting, and of hydrogen, which provides a thermodynamically preferred path for the removal of bounded fluorine and chlorine as HF or HCl being easily removed from the exhaust as concentrated acids. Another product, the synthesis gas, can be used for further fuel synthesis via the Fischer-Tropsch route.
GliDArc reactors can be easily integrated to many processes, can reach an industrial size at a multi-electrodes mounting (a large GliDArc pilot at more than 100 m\(^3\)(n)h is under testing in Alberta, Canada), can process fluids containing poisons, liquids or solids, can directly produce very reactive medium allowing efficient gas processing. GliDArcs are inexpensive, powerful and easily controllable. High energy consuming and/or troublesome classical processes can therefore be substituted by this quite cold and catalytic plasma assisted process at low energy expense, especially for not-too-much diluted freons CFCs. Otherwise, a pre-concentration of pollutants will be desirable.

Reference