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THE LOW-TEMPERATURE PLASMA DESTRUCTION OF USED REFRIGERANTS

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Abstract. According to nowadays environmental policy, chemical compounds with chlorine and fluorine (i.e. CFC, halons) should be removed from every day usage in spite of their harmful impact on a protective ozone layer in the troposphere. The CFC's, HCFC's and other gases with chlorine or bromine stimulate the destruction of the ozone layer faster then natural processes. In the paper, the decomposition of HCFC-22 refrigerant in the low-temperature argon plasma jet is presented. A description of an experimental stand built at The Institute of Heat Engineering (The Warsaw University of Technology) is included. The construction of the stand and the working parameters of the destruction process are considered. The results of recent experiments and measurements are described. The data from spectral analysis of gaseous products of reaction are also added. In the conclusions of the paper the positive features of plasma technology usage in environmental applications are underlined.

Keywords: refrigerants, ozone depletion, plasma destruction.

1. Introduction

The ozone layer in the stratosphere protects life on earth from exposure to dangerous levels of ultraviolet light. It does so by filtering out harmful ultraviolet radiation from the sun. When CFC's, HCFC's and other ozone-degrading chemicals are emitted, they mix with the atmosphere and eventually rise to the stratosphere. There, the chlorine and the bromine catalyze the destruction of ozone. This destruction is occurring at a more rapid rate than ozone can be created through natural processes. The degradation of the ozone layer leads to higher levels of ultraviolet radiation reaching Earth's surface. This in turn has a bad influence on people's health and natural environment. Some refrigerants which are responsible for destruction of ozone are characterized by ODP (Ozone Depletion Potential) number (Tab. 1).

Table 1. ODP and GWP of some refrigerants

Symbol	Chemical formula	ODP	$GWP_{100years}$
Refrigerants			
CFC-11	$CFCl_3$	1,00	4000
CFC-12	CF_2Cl_2	1,00	8500
CFC-13	CF_3Cl	1,00	11700
CFC-113	$C_2F_3Cl_3$	1,07	5000
CFC-114	$C_2F_4Cl_2$	0,80	9300
HCFC-22	CHF_2Cl	0,06	1700
HCFC-123	CF_3CHCl_2	0,02	93
HCFC-124	$CHClFCF_3$	0,02	400
HCFC-141b	CH_3CFCl_2	0,11	1800
HCFC-142b	CH_3CF_2Cl	0,06	2310

That is why proper policy was taken into consideration in European Union. Now, the new Regulation 1005/2009 (16th September 2009) published in the Official Journal of the European Union on 31th, recasts the Regulation 2037/2000. The main modifications or additions compared to Regulation 2037/2000 relate primarily to:

- the prohibition to provide recycled HCFCs on a purely free or paying basis (Article 11-4). Recycled HCFCs "may only be used by the undertaking which carried out the recovery as part of maintenance or servicing or for which the recovery as part of maintenance or servicing was carried out".
- the obligation for undertakings and owners of equipment to keep a record on all movements of reclaimed, recycled and destroyed HCFCs. Undertakings using reclaimed or recycled HCFCs for maintenance or servicing shall keep a record of the undertakings that have supplied reclaimed HCFCs and of the source of recycled HCFCs (Article 11-7).

What is more, from 1st January 2010 the use of new HCFCs is banned.

Taking into consideration agreement dealt with exchange old refrigerants for new ones, there is increasing neediness of safe removal, storage and further utilization or destruction of used coolants. So the destruction and recycling of post-decomposition products seems to be very up-to-date subject for scientific examinations (Mollac *et al.* 2000).

The new technology for decomposition of volatile refrigerants is a plasma technology (Jurewicz *et al.* 1997;

Rusowicz *et al.* 2000; Ruciński *et al.* 2001). A volume of neutral gas (i.e. argon) is heated in electric arc to temperature of app. 10000 K, and then ionization occurs (McDowall *et al. 2004).* Such medium is used for decomposition of hazardous wastes into the single molecules. Considering of high-power density (2 ÷ 4 MW/m^3) there are very good conditions for HCFC-22 transformation into other products which could be semi-products for further purposes.

The described above physical phenomena are presented below.

2. Description of experimental stand

The experimental stand was built according to detailed project (Fig 1). The most important thing was to deliver energy with high enthalpy without destroying any part of the stand. So, the plasma generator and the system of cooling are the most important issues in the described processes.

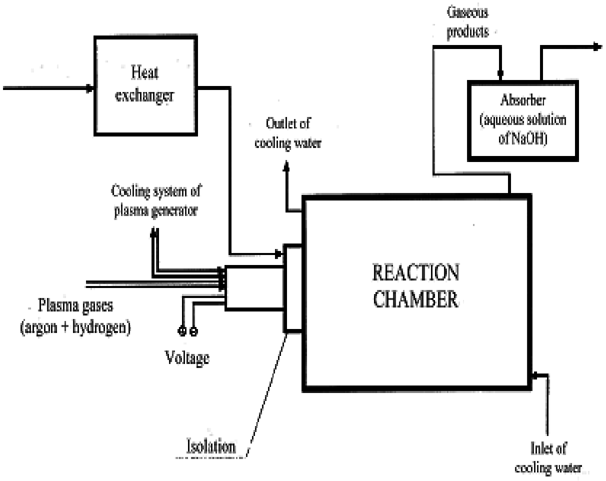

Fig 1. The general outline of the experimental stand

The experimental stand in detail consists of:

- control panel with gauges of: stream of plasmagenic gas and HCFC-22, electrical parameters (voltage: 20–50 V, current: 250–500 A), safety switches,
- plasma generator fed by argon neutral gas (0.5 dm^3/s, outflow diameter is 8 mm),
- DC generation system supplying power to plasma generator,
- cylindrical, stainless steel reaction chamber (volume about $0.1 \cdot 10^{-3}$ dm^3) with holes for outflow of exhausted gases coming from destruction,
- cooling system for plasma generator (0.33 dm^3/s of water flow) and reaction chamber

(water flow - 0.26 dm^3/s)

- vacuum pump for suction of products,
- alkaline solution for acid substances neutralization (which occurred while several last experiments were carried out).

Below the detailed scheme of the experimental stand is presented in Fig 2.

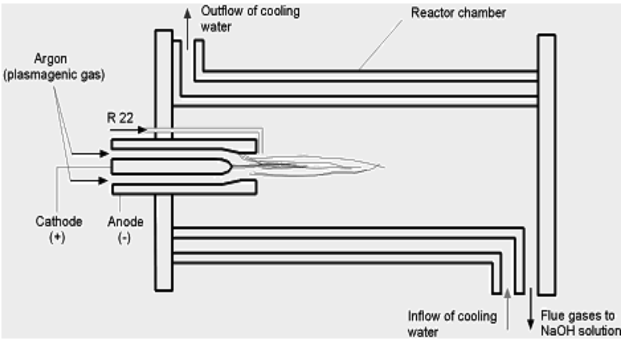

Fig 2. The general outline of the stand for decomposition of HCFC-22 in the free jet argon plasma

3. Experiments

Some stages of our experiments should be described before the presentation of final results of destruction process occurs.

Firstly, to make sure that waste gas will be decomposed in the volume of ionized argon, the refrigerant was put with argon into space between two electrodes (Ruciński *et al.* 2001; Cubas *et al.* 2005). The plasma generator was outside of the chamber and after an ignition of an electric arc in pure argon; the HCFC-22 was fed into the system. Both gases were mixed in a special cylindrical mixer. The stream of the HCFC-22 was minimized to reduce the possible impact of hazardous products occurred during an operation process on natural surroundings and health of people operating the stand. The plasma jet was not steady and continuous. Despite of this, the plasma jet changed its appearance and became orange. The cloud of black smoke (graphite powder) parallel with sharp, unpleasant smell reminding bitter almonds were noticed. After some time main jet divided into small ones and changed into beam of the jets directed differently.

The decision was made to introduce the waste gas separately from argon, by a thin pipe near the plasma jet outflow. This configuration was checked during further experiments.

The results observed were promising. The plasma jet was generated without any obstacles; HCFC-22 was introduced by pipe straightly into the hottest volume of the argon jet. The stream of HCFC-22 could change to 400 dm^3 per hour. The smoke and strong smell of acid gases occurred. So, there were signs of decomposition reactions taking place during the process. The second time the litmus papers were introduced and they get red after some time of presence in flue gases. The conclusion is: the strong acid products are observed during the decomposition.

According that observation, the review of the chemical literature and papers (Jurewicz *et al.* 1997) treating the plasma destruction of chemicals all over the scientific world specializing in this subject (Ya-Fen Wang *et al.* 1997; Zivota *et al.* 2000) was done. The object of interest was other's results and attempts of decomposition process of hazardous wastes.

The most important problem in destruction technology is a neutralization of the exhausted gases. The alkaline solution media were taken into consideration and then NaOH substance was chosen. Use of sodium alkaline was connected with necessary changes in experimental stand (Cubas *et al.* 2005).

The plasma generator with thin pipe mounted on the outflow of the plasma jet was closed in horizontal cylindrical reactor chamber. The chamber was cooled by water flowing through the inner space between two shells of chamber (made with stainless steel).

In the end of it a hole were drilled by which the flue gases flowed and after it were leaded outside of the chamber to NaOH solution.

Considering all danger circumstances the exact experiment was carried out. The flue gases were black (the graphite powder occurred) and after introducing them into alkaline solution, they were no longer acid.

The last stage was to find out what products of the experimental work. The solution was dried and grey powder obtained in such way was examined by means of X-ray spectroscopy (Bagla *et al.* 2000).

The flue gases were examined too.

4. Results and discussion

The powder was examined by means of X-ray diffraction phase analysis (Fig 3) thanks to Philips 1830 diffractometer working in Θ - 2Θ system equipped in the copper lamp Cu ($K_\alpha = 1{,}54\ \dot{A}$). It indicated the presence of NaOH, NaCl, NaF and NaCN in the products of low-temperature decomposition of HCFC-22 in free jet of argon plasma. Above these chemical compounds has possible explanation according to phenomena observed while the starting experiments were carried out. It has to be underlined that such products probably come from the acid flue gases. In the sodium alkaline solution they were neutralized and some salts created themselves. However, the products are rather dangerous because of NaCN salt, the results are promising.

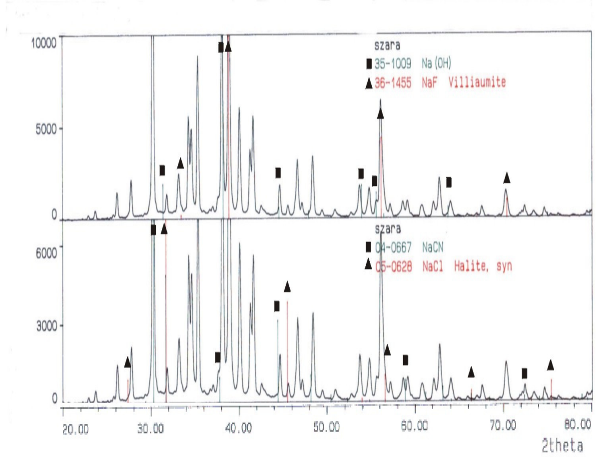

Fig 3. Diagram of X-ray diffraction pattern of powder from the experiment

The nitrogen should be eliminated from installation by ‘cleaning’ it with argon before the destruction process. It is very important because the nitryle group won’t be created there.

The flue gases are only argon and traces of other volatile products of destruction. The concentration of these is far below danger limits.

In addition, it is necessary to describe possible scenario when the conditions of the process change and some equipment failures could be observed. Then the undesirable products of destruction occur and immediate shut-down of the process is needed. In example, the entire break or the diminution of the inflow of the stream of hydrogen being w the component of the mixture of plasmagenic gases could take place. Then the benzenoids occurs in flue gases (Figs 4, 5).

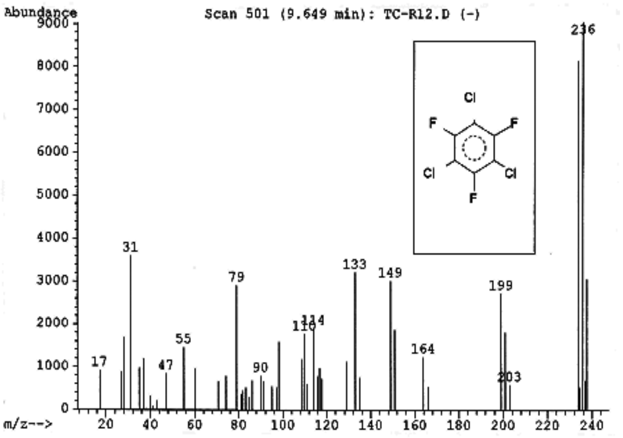

Fig 4. The absorption spectrum of the toxic products – the benzenoid is observed

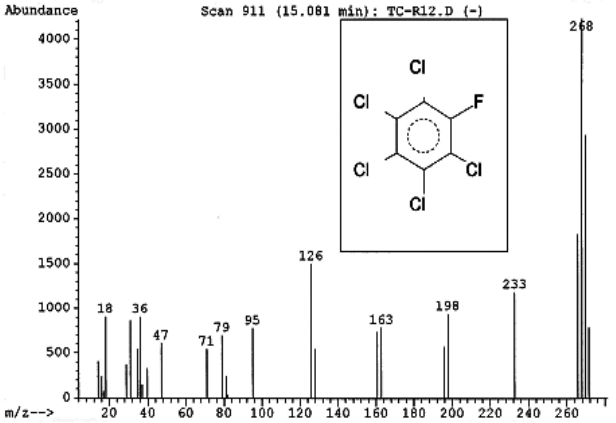

Fig 5. The absorption spectrum of the toxic products – the other benzenoid is observed

5. Conclusions

1. The paper mainly consists of description of decomposition of HCFC-22 (coolant replaced from refrigeration systems) in free jet of argon plasma. Many of problems were considered and way of avoiding them was underlined too. Stage after stage improvement of technology connected with complex chemical and physical conditions had been presented.
2. In addition the question could be asked about further usage of products of plasma destruction. So, the question is: how efficiently recycle the refrigerant compounds?

3. While, in spite of hazardous characteristics NaCN is used in gold mining as a inhibitor, NaF has many possible applications: in leather industry - for treatment of hides, in dental application - as active fluorocomponent in tooth pastes, in enamel, glass and ceramic production - as fluxing, dulling and etching agent, in production of welding agents - as component of welding rod coatings and welding powders, in aluminum-metallurgy - as molten bath component in aluminum refinement, production of soldering agents - as component for fluxing agents.
4. Possibility of NaCl recycling is well-known, while NaOH could be reused in next experiments.
5. The most important thing is that process will be developed thanks to working on phenomena occurred, while examination of stand will be carried out as well.

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