Steam, methane and carbon dioxide thermal plasma interaction with perhalocarbons

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Abstract. Many perhalogenated hydrocarbons (including carbon tetrafluoride and carbon tetrachloride) are limited in production, because they have negative impact on the environment. A number of plasma technologies for perhalogenated hydrocarbons processing is proposed in addition to chemical methods. Usage of thermal plasma of methane and steam may be effective for the processing of these materials into carbon monoxide and certain hydrogen halide. The first stage of the investigation shows that hydrogen chloride is the only chlorine-containing compound during carbon tetrachloride processing.

1. Introduction
Chlorinated organic compounds are widely used in industry as intermediates and end products, such as solvents, electric liquids, monomers for the production of plastics, etc. At the moment, the accumulated reserves of high-boiling mixtures of organochlorine compounds require environmentally safe disposal because chlorinated hydrocarbons are the main polluters of groundwater and are actively accumulate in the tissues of living organisms.

In particular, carbon tetrachloride (CCl₄) is one of the most dangerous of all chlorinated hydrocarbon which has a damage effect on the environment and human [1 - 3].

One method of treatment of hazardous organic compounds is incineration. Methods of conventional high-temperature destruction or oxidation of carbon tetrachloride are well studied [4 - 8]. However, the conditions of organic substances combustion cannot ensure their complete destruction and in the exhaust gases may be present dangerous products of chemical underfiring, such as phosgene, dibenzofuran, dioxins, aromatic hydrocarbons (primarily fused aromatics), and other thermally stable products. A number of plasma methods are proposed in addition to chemical ones: microwave plasma, electric arc plasma, non-equilibrium plasma of corona and barrier discharges. Most of the investigations are carried out under oxidizing conditions [9 - 10], which inevitably lead to the formation of toxic gases as reaction products such as phosgene.
A universal plasma heater based on the principle of a rotating arc is described [11]. Almost all organochlorines are decomposed at temperature of 1000-1750 K (with efficiency of > 99.8 %). Under pyrolysis of CCl₄ and C₁₂H₃Cl₂ soot was formed, which is unacceptable, since soot is deposited on the electrodes and insulators. The most favorable conditions were found with the addition of H₂O to decompose chlorinated waste. In this case, no soot, no toxic gas Cl₂ were formed.

The team of scientists of the Physics Department of the Spanish University of Cordoba considered the use of microwave plasma to decompose CCl₄ and C₂H₃Cl₃ [12]. A number of byproducts C₂HCl₃, CCl₄, and C₂Cl₄ generated during destruction under optimal conditions are within the range of ppb. Other by-products found in the outgoing gases (CO₂, N₂O and NO) may be captured by suitable filters.

It was found that CCl₄ conversion increases from 85% to 90% with an increase in steam consumption on a laboratory installation with gliding arcs using steam and air [13]. Experiments on chlorinated organic compounds decomposition were carried out at the discharge power of 600 VA and flowrate of 200 l/h. The main products of methyl chloride decomposition were molecular chlorine (Cl₂), trichloromethane (CHCl₃) and HCl. In addition, processing of carbon tetrachloride was investigated to obtain chlorinated polymer [14] via a double dielectric barrier discharge reactor. Methane was fed in the reaction to provide a source of hydrogen and carbon for the reaction with CCl₄ and its decomposition products. At temperature of 117 °C and applied voltage of 16 kV, the conversion of CH₄ and CCl₄ was 19.1% and 30.6% respectively, while at 157 °C and voltage of 18 kV its was 37% and 44.5%.

The paper presents a method for decomposition of perhalogenated hydrocarbons by the AC plasma torch operating on mixture of steam, methane and carbon dioxide for plasma reforming of methane [15].

Usage of steam as plasma forming gas instead of air offers several advantages:

- Nitrogen is excluded from the reaction and consequently there is no risk of formation of toxic nitrogen compounds.
- The volume of exhaust gases is 2-3 times lower than with air plasma, which reduces the cost of gas treatment.
- Steam is a high-performance agent preventing soot formation.
- If the initial material contains insufficient amount of hydrogen for chlorine fixation, additional amount of hydrogen produced by reaction of steam with methane can be fed into the high temperature zone.

2. Thermodynamic computation of decomposition of halogenated organic compounds

AC plasma torch with power 120 kW and thermal efficiency of no less than 90% was considered at simulation of carbon tetrachloride and carbon tetrafluoride decomposition [16]. Flowrates of plasma-forming substances: CO₂ is 2.9 g/s, H₂O is 2.9 g/s, CH₄ is variable. Stoichiometric reaction of carbon tetrachloride and carbon tetrafluoride with steam, carbon dioxide and methane for hydrogen production, needed for complete chlorine fixation into hydrogen chloride was accepted as initial conditions:

\[ \text{CCl}_4 + 1.049 \text{H}_2\text{O} + 0.427 \text{CO}_2 + 0.476 \text{CH}_4 = 1.903 \text{CO} + 4 \text{HCl} \]  

(1)

Process parameters computation was performed using software ChemicalWorkbench 3.5. Computation conditions: temperature 1500 K (at this temperature methane is completely decomposed under the action of steam [15]), pressure 101325 Pa. Stream 1: H₂O is 41.61% mass, CO₂ is 41.61% mass, CH₄ is 16.78% mass. Stream 2: carbon tetrachloride or carbon tetrafluoride. Composition of the product mixture as a function of Stream 1 for tetrachloromethane and tetrafluoromethane is presented in figures 1 and 2.

As can be seen if flow rate of steam, carbon dioxide and methane mixture is more than 0.3 kg/kg of carbon tetrachloride and 0.5 kg/kg of carbon tetrafluoride the products have no solid phase (graphite) and the only halogen-containing compound is certain hydrogen halide.
3. Experimental part
Experimental study of carbon tetrachloride decomposition was conducted on the laboratory installation, which schematic is shown in figure 3 using three-phase AC plasma torch (figure 4). This is a high-voltage plasma torch with rod electrodes installed in the individual cylindrical channels. The plasma forming gas (or gas mixture) can be supplied into the near electrode region and into discharge channels.
Figure 3. Schematic diagram of the experimental installation. T1, T2 and T3 – thermocouples, P – pressure gauge, S – sampling point.

Figure 4. Three-phase AC plasma torch.

More detailed description of the plasma torch, power supply and systems of electrical parameters measurement is presented in [16]. Liquid carbon tetrachloride is fed into the evaporator-superheater where it is evaporated and heated to temperature of about 150 °C, after which its vapors are mixed with the preheated methane and steam. The resulting mixture is fed into discharge channels of the plasma torch. At the same time a part of the reaction components is fed as a protective gas (carbon dioxide and small amount of methane) into the near electrode region. This allows adjusting the plasma torch power by changing the arc voltage drop at constant electric current. Thermal plasma obtained from these mixtures is sent into the lined reactor where the final conversion of carbon tetrachloride takes place.

Selected product gas is cooled, and condensate is removed. The condensate is analyzed for the hydrogen chloride content, and the cooled product gas is analyzed for basic composition by mass spectrometer (Cirrus 300) and FTIR spectrometer (Nicolet 380).

4. Results and discussion

Experiment on destruction of carbon tetrachloride started from feeding of 0.8 g/s of methane into the near electrode region, and 0.41 g/s of methane into discharge channels of the plasma torch. The total methane flow rate was 1.21 g/s. Plasma torch power was increased to ~100 kW. Then 2.44 g/s of CCl₄ vapors were fed. Model agent was supplied for about 15 minutes. Flow rates, rms voltage and power are presented in table 1. Composition dried reaction products from the sampling point S1 is presented in table 2.

Table 1. Parameters of plasma torch operation.

| Parameter                  | CO₂+H₂O   | CO₂+H₂O+CH₄ | CO₂+H₂O+CH₄+CCl₄ |
|----------------------------|-----------|-------------|------------------|
| Flow rate of CO₂/H₂O, g/s  | 2.9/2.9   | 2.9/2.9     | 2.9/2.9          |
| Flow rate of CH₄, g/s      | 0         | 1.21        | 1.21             |
| Flow rate of CCl₄, g/s     | 0         | 0           | 2.44             |
| rms voltage, V             | 1000      | 1215        | 1390             |
| Electric current, A        | 52.0      | 52.2        | 51.2             |
| Power, kW                  | 84.1      | 101.5       | 116.7            |
The average power of the plasma torch was ~117 kW and temperature in the reaction volume was ~1300-1400 °C. Thus, the specific energy consumption per 1 kg of decomposed CCl₄ in this experiment was ~13.3 kWh/kg. Available means of measurement did not detect the initial substance in the reaction product composition, therefore it can be assumed that the conversion was close to 100%. Furthermore, hydrogen chloride was the only chlorine-containing substance in the reaction products.

As far as the model substance flow rate in the experiment was less than stoichiometric, reaction products have significant amount of initial substances (CO₂, CH₄ and H₂O). It is impossible to avoid the presence of these components (except for methane) in the real process products, because such processes should be carried out with excess of an oxidant (steam).

5. Conclusion
On the whole the performed experiment confirmed the possibility of using a high-voltage three-phase AC plasma torch for processing of organochlorine compounds. Experimental results show that hydrogen chloride is the only chlorine-containing compound during carbon tetrachloride processing. Total content of H₂ + CO in product gas is about 45.5% vol.

Acknowledgements
The work is partially supported by the RFBR grant 15-08-05909-a.

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