The reaction of chlorobenzene with plasma of H₂O, CO₂ and CH₄ obtained by an alternating-current plasma torch with a vortex stabilization

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Abstract. This paper presents the three-phase ac plasma torch with a vortex stabilization of the arc, and two inputs of plasma environments: the electrode zone and the arc zone. Shielding gas (carbon dioxide) is supplied in the electrode zone and steam, methane and vapor of chlorobenzene are fed in the arc zone. By means of it the life time of electrodes is increased significantly. Chlorobenzene is selected, as it is the simplest aromatic chlorine-containing substance. The chemical process flows in two pathways: the formation of synthesis gas and the formation of soot. The gaseous chlorine-containing compound was only hydrogen chloride, yield of soot was 0.98% by weight of the raw materials, and the chlorine content was 2.08 wt % by the soot.

1. Introduction
Established methods of chlorine-containing substances processing does not help to prevent the formation of dioxin-like compounds [1], as it is difficult to provide uniform heating to high temperatures and the required residence time. With the use of thermal plasma high temperature can be obtained for a wide range of gases and vapors. In this case, the most technologically simplest method is the use of air, however, the oxygen concentration therein is limited, and pure oxygen is dangerous. In the chemical industry steam is effectively used to reduce the sooting by the gasification reaction

$$C + H_2O = CO + H_2.$$  

Thus oxygen concentration is significantly increased, but the specific rate of endothermic gasification reduced. Kinetics study of thermal plasma waste destruction shows that the rate of disappearance of chlorobenzene with steam is four orders of magnitude less than that for oxygen [2]. These two factors are oppositely directed and it is required to establish optimal conditions for plasma destruction.
Papers on the plasma processing of tetrachloride and its derivatives are widely known [3–5], however, in most cases they are thermodynamically unstable and easily decomposed when heated. However, the most dangerous are the chlorinated aromatic substances, as its easy form soot when heated [6, 7]. As a result many researchers have used chlorobenzene for their tests. Chlorobenzene is the simplest aromatic organic compound with a boiling point of 131 °C containing chlorine. Thus different types of discharges have been investigated, for example, DBD with or without catalysts [8, 9]. Conversion of chlorobenzene was 80–85% at 310 specific input energy J/l and at initial concentration 500 ppm. Decomposition of chlorobenzene using glow discharge was investigated in the liquid phase [10]. The current, pH, volume and the concentration of iron salts were changed. By increasing the processing time of the solution from 40 to 240 minutes, the conversion increased from 40 to 95%.

The most prospective is the usage of thermal plasma. Thus, in comparison with the Ar plasma in the presence of oxygen yield of soot is less, however with increasing oxygen content the yield of soot is increased [11], and the higher input power reduced the ring number of the poly aromatic hydrocarbon molecules.

Alternating current and direct current plasma generators can be used on an industrial scale. Direct current plasma torches are more distributed, however expensive powerful rectifiers are required for large installations. Studies on ac plasma torches are limited, the review is presented in [12].

The IEE RAS has experience in the development of high-power plasma generators with a long service life and the use of thermal plasma generators for various plasma chemical applications [13–16]. With the use of high-voltage multi-gas plasma torches, experiments on plasma reforming of methane were carried. The plasma gas was mixture of steam, CO₂ and CH₄ [17], hydrogen and carbon monoxide, selectivities were 98%, and the methane conversion was 99%. Experiments on destruction of carbon tetrachloride were conducted [18]. The main aim of the article is to investigate the interaction of chlorobenzene with the plasma of H₂O, CO₂, CH₄ obtained by multi-gas ac plasma torch.

2. Experimental setup
The experimental study was conducted on the laboratory facility (figure 1) consisting of the ac plasma torch, plasma reactor, mass flow controllers, thermocouples and sampling system.

Alternating current plasma torch is a device with copper rod electrodes in three separate cylindrical electric-discharge channels containing two plasma-forming gas inputs. Carbon dioxide (shielding gas) and methane are introduced into the electrode zone. Using methane plasma torch power may be controlled. For example, for a mixture of methane, steam and carbon dioxide, the plasma torch power grows by an increase of the methane flow rate into the electrode zone (figure 2). As can be seen from the figure, it is possible to change the power of the plasma torch without changing the total flow rates of methane, steam and carbon dioxide [19].

During the experiment, steam, vapor of chlorobenzene and methane are fed into the arc zone. Total flow rates of plasmaforming media were as follows: CH₄—0.3 g/s, H₂O—2.9 g/s, CO₂—2.9 g/s, C₆H₅Cl—4.0 g/s. The ratios of raw material components are taken by the equations:

\[ C₆H₅Cl + 6H₂O = 6CO + 8H₂ + HCl, \]
\[ C₆H₅Cl + 6CO₂ = 12CO + 2H₂ + HCl, \]
\[ CH₄ + H₂O = CO + 3H₂, \]
\[ CH₄ + CO₂ = 2CO + 2H₂. \]

Excess oxidant (H₂O + CO₂) does not exceed 5%. Plasma reactor made of special refractory material and comprises two sampling points. One sampling point is used to analyze the product gas composition by mass-spectrometer, and the second sampling point is used to determine the amount of soot by gravimetric method (ISO 9096). The soot collected on the quartz microfiber
Figure 1. Scheme of the plasma laboratory facility: MFC—mass flow controller, S—sampling point, T—thermocouple, P—pressure meter.

Figure 2. The plasma torch power versus flow rate of methane into the electrode zone.

filter. The composition and properties of soot is determined by scanning electron microscopy, x-ray fluorescence spectroscopy, x-ray diffraction analysis, FTIR-spectroscopy and differential thermal analysis.

3. Results and discussion
During the experiment, the plasma torch power was about 106 kW, the composition of the product gas measured by the mass spectrometer was as follows: \( \text{CH}_4 \)—0.04 vol\%, \( \text{H}_2 \)—
45.05 vol%, CO₂—3.13 vol%, CO—45.51 vol%, HCl—6.27 vol%. The residence time of the reactants in a plasma reactor not exceed 0.1 s, the temperature in the reactor was about 1250 °C.

Due to the large flow rate of chlorobenzene soot is actively formed, its yield was 0.84 wt% of the raw material. Photomicrograph of soot and filter quartz is shown in figure 3, the soot composition (without material of filter) is shown in table 1. As can be seen, the soot contains erosion products of electrodes and plasma torch case (Fe, Ni, Cr and Cu).

This fact indicates the electric arc interact with a plasma torch case made of stainless steel. However, at the moment, it is impossible to say at what stage this happened. At the beginning of the operation of the plasma torch, the electric arc burns between the electrode and the plasma torch case but during normal operation arc rarely contacts the plasma torch case.

In the ir-spectrum of sample peaks correspond to bonds C–Cl, C–O, O–Cl (figure 4), the interpretation of the spectrum is shown in table 2. As can be seen from table 2, the sample contains complex chlorine- and oxygen-containing organic compounds, as well as metal oxides. This indicates the incomplete decomposition of chlorobenzene and there are two competing
Table 1. Composition of soot.

| Element | Composition (wt %) |
|---------|--------------------|
| C       | 68.87              |
| O       | 15.53              |
| Cl      | 2.08               |
| Cr      | 0.94               |
| Mn      | 0.56               |
| Fe      | 7.68               |
| Ni      | 0.48               |
| Cu      | 3.87               |

Table 2. Interpretation of sample spectrum.

| Wavenumber (cm\(^{-1}\)) | Type of bond                                                                 |
|---------------------------|------------------------------------------------------------------------------|
| 3441                      | v(O–H)                                                                        |
| 3334                      | v(O–H)                                                                        |
| 1628                      | δ(H–O–H)                                                                      |
|                            | v(C–O)                                                                        |
| 1100                      | v(C–O)                                                                        |
|                            | v(Cl–O)                                                                       |
|                            | v(CO\(_3\))                                                                  |
| 945                       | v(Si–O)                                                                       |
|                            | v(C–O)                                                                        |
|                            | δ(H–O–H)                                                                      |
| 801                       | v(Si–O)                                                                       |
|                            | v(Cl–C)                                                                       |
|                            | v(Cl–O)                                                                       |
|                            | δ(H–O–H)                                                                      |
| 559                       | v(C–Cl)                                                                       |
|                            | v(Fe–O) in α-Fe\(_2\)O\(_3\)                                                 |
|                            | δ(O–Si–O)                                                                     |
|                            | δ(O–Cl–O)                                                                     |
| 468                       | v(C–Cl)                                                                       |
|                            | v(Fe–O) in α-Fe\(_2\)O\(_3\)                                                 |
|                            | δ(O–Cl–O)                                                                     |

processes: the formation of hydrogen chloride and the formation of chlorine-containing soot. At the same time, a high temperature leads to the decomposition of light organochlorine compounds and they were not found in reaction products.

The x-ray diffraction pattern (figure 5) shows that soot is in the amorphous state. The peaks of diffraction pattern correspond to cell material (aluminum oxide).

The reason for the formation of only the amorphous phase is quenching of the sample from 1250 down to 15 °C.
As expected on curve of mass change (figure 6), there is a chemical reaction with a decrease in weight and heat release (combustion of soot). Self ignition temperature of soot is 404 °C.
Figure 6. Curves of differential thermal analysis of soot and filter material.

Obtained results indicate the high importance of decomposition parameters of chlorobenzene, such as the ratio of the reaction components, temperature, residence time. It is necessary to increase excess of steam and residence time, however, even in this case, the soot formation will occur. The temperature increase is not advisable, because it is considerably higher than the decomposition temperature of any organic matter under thermodynamic equilibrium conditions. Moreover, this fact is evidenced by the absence of liquid chlorine-containing organic substances in the reaction products. The rate of homogeneous reactions is much higher than the rate of heterogeneous reactions, suggesting that residence time is the most important factor.

4. Conclusion
The most hazardous chlorinated organic compounds are aromatic. At the same time to simplify the research it is possible to use chlorobenzene (simplest substances of this class). Chlorobenzene is disintegrated by thermal plasma of steam, carbon dioxide, methane. However, soot yield was 0.84 wt % of raw materials, which indicates about high soot formation. To reduce of soot formation it is require to increase flow rate of steam, which will increase the carbon gasification rate and refuse supply of methane. This hydrogenation reaction (hydrogen is formed by steam reforming) of chlorobenzene does not provide an adequate level of soot formation.

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