Thermal steam plasma decomposition of organochlorine compounds

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Abstract. For the almost complete processing of organochlorine compounds are required a high temperature, hydrogen to produce hydrogen chloride and a high degree of mixing. Reforming chlorobenzene by steam and carbon dioxide in the presence of methane using a three-phase AC plasma torch was carried out. Soot composition was analyzed by energy dispersive X-ray analysis. The yield of soot was 0.84% wt. of raw materials, the content of chlorine in the soot was 2.08% by wt.

1. Introduction
The world has accumulated a large amount of chlorine-containing organic waste. Some of them cannot be processed by traditional incineration [1]. One of promising methods for the processing of these materials may be plasma thermal processing, where an electric arc plasma torch can be successfully used as plasma source. Nowadays plasma generating installations using electric arc can be divided into two categories: direct current (DC) and alternating-current (AC) plasma torches. The most widely used are DC devices, overview of the various modern models is presented in [2], AC systems designed for industrial applications are presented in [3]. A variety of gases can be used in plasma torches as the plasma forming medium, of particular interest are devices that operate on the steam [4-7], there are some plants in which the electric arc is in contact with liquid water [8].

There are a number of plasma methods for processing chlororganic substances using nonequilibrium plasma: DBD [9], corona discharge [10], glow discharge [11], etc. It is typically considered the interaction of chlorine-containing substances with the thermal plasma of air [12] or inert gases [13]. In this case the active oxygen concentration is not high, but it is possible to significantly increase the temperature due to the exothermic reaction. Thus chemical bond C-Cl must break and new stable chemical compound forms (for example, HCl). This process is possible only with an excess of hydrogen, which is not enough in aromatic compounds. In this case, thermal steam plasma may be used:
Usage of steam instead of air gives several advantages:

1. No nitrogen involved in the reaction and consequently no risk of formation of toxic nitrogen compounds.
2. The volume of the waste gases is 2-3 times lower than at air plasma processes that reduces the cost of the gas cleaning.
3. Steam is highly effective agent which prevents the formation of soot reaction.

If the original compound contains an insufficient amount of hydrogen for binding chlorine, additional quantity of hydrogen may be produced in the high temperature zone by reaction of steam with methane. The required hydrogen may be produced by thermal steam and carbon dioxide plasma reforming of methane [14]:

$$C_xH_yO_zCl_n + (x - z)H_2O = xCO + \frac{y+2x-z-n}{2}H_2 + nHCl \quad (1)$$

$$C_xH_yO_zCl_n + \frac{4x-z+n-y}{2}H_2 = (x - z)CH_4 + zCO + nHCl \quad (2)$$

The specific energy consumption is about 37.5 MJ/kg of converted methane.

The article deals with the processing of organochlorine substances by the example of the decomposition of chlorobenzene using an AC plasma torch operating on a mixture of steam, carbon dioxide and methane.

2. Experimental installation

The investigation was carried out on a laboratory facility shown in Fig. 1. Main part of facility was AC plasma torch tested on a mixture of steam, methane and carbon dioxide [15]. It is a plasma torch with rod electrodes and vortex stabilization of the electric arc and plasma-forming mediums two inputs (the electrode zone and the arc zone). Carbon dioxide (shielding gas) and methane (for power control) were fed in the electrode zone and vapor of organic substance, steam were fed in the arc zone.

Chlorobenzene, the simplest aromatic compound, was chosen as an organic matter. When heated, chlorobenzene easily forms soot, so its decomposition is a major challenge.

Sampling of the reaction products was carried out at the points S1 and S2. The composition of the product gas was determined by mass spectrometry Cirrus 300. Sampling of soot was carried out by gravimetric analysis (ISO 9096) using quartz filter. Soot was investigated by X-ray diffractometer, Fourier transform infrared spectrometer and scanning electron microscope.
3. Results and discussion
Flow rates of plasma forming mediums were the following: CH$_4$ - 0.3 g/s, H$_2$O - 2.9 g/s, CO$_2$ - 2.9 g/s, C$_6$H$_5$Cl - 4.0 g/s. Power of plasma torch increased with increasing flow rate of chlorobenzene (from 92 to 106 kW – Fig. 2). This is due to the energy consumption at the steam reforming and the increase in heat capacity and thermal conductivity (for account of hydrogen formation).

![Fig. 2. Power of plasma torch versus mass flow rate of chlorobenzene.](image)

The average temperature in the plasma reactor was 1250°C. Due to the produced gas vortex inside the reactor components are uniformly mixed. The sampling of the product gas and the soot was carried out for 10 minutes. The composition of the dry product gas is shown in Table 1.

| Substance | CH$_4$ | H$_2$ | CO$_2$ | CO | HCl |
|-----------|--------|--------|--------|----|-----|
| Concentration, mol % | 0.04 | 45.05 | 3.13 | 45.51 | 6.27 |

The main products of the reaction are hydrogen and carbon monoxide, while other chlorine-containing compounds, except for hydrogen chloride, were not detected. This indicates the complete decomposition of chlorobenzene. The produced product gas can be purified from hydrogen chloride and used to produce thermal and electrical energy, as well as for the synthesis of organic substances.

Energy dispersive X-ray analysis showed (Table 2) that the sample of filter with soot contains carbon, chlorine and products of erosion of electrodes and the plasma torch case (made of stainless steel).

IR-spectroscopy confirmed the presence of chlorine-containing compounds (Fig. 3). The peaks in the spectrogram correspond to C-Cl, O-H, C-O, Cl-O the chemical bonds. This indicates the formation of complex solid chlorine-containing organic substances. Despite the heated filter is used, soot contains water and, possibly, phenolic compounds.
Fig. 3. IR-spectrum of soot with quartz filter.

Table 2 Composition of soot with quartz filter material

| Chemical element | Concentration, % wt. |
|------------------|---------------------|
| C                | 43.39               |
| O                | 28.88               |
| Na               | 0.30                |
| Al               | 0.58                |
| Si               | 16.71               |
| S                | 0.18                |
| Cl               | 1.31                |
| K                | 0.13                |
| Cr               | 0.59                |
| Mn               | 0.35                |
| Fe               | 4.84                |
| Ni               | 0.30                |
| Cu               | 2.44                |

XRD-ray analysis confirmed that the soot is predominantly in an amorphous state. The peaks on the XRD pattern correspond to Al₂O₃ cell (Fig. 4).

Fig. 4. XRD pattern of soot with quartz filter.

When calculated on the dry product gas soot yield was 1.31% mass. of raw materials, and the chlorine content in the soot - 1.61 wt.%.

The feed residence time in the plasma reactor is 0.1 s, which is not enough for the complete conversion of chlorobenzene. Furthermore, so as stoichiometric ratios were selected, local unevenness of components mixing is very likely possible. Thus soot formation reaction becomes more likely.
Probably, for the decomposition of chlorine-containing soot it is require a longer residence time and a
greater excess of steam.

4. Conclusion

The simplest chlorine-containing aromatic compound (chlorobenzene) was selected for the
investigation. The result revealed that the high temperature (above 1250 °C) does not provide
complete decomposition of chlorobenzene to hydrogen chloride. Sooting is explained small excess
oxidant, competing reaction of steam with methane, and small residence times. Further research
should focus on determination of process conditions with minimal soot formation.

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