Research Article

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Plasma recycling of chloroorganic wastes

Abstract: A high temperature of thermal plasma provides more efficient decomposition of the wastes in comparison to traditional combustion. Due to the high temperature and high density of energy in the plasma, the destruction rate is high, which determines a high efficiency waste decomposition. The main products of pyrolysis plasma chloroorganic compounds are pyrolysis gas and pyrolysis coke.

In order to reduce carbon soot, the steam supported reaction was used. Application of plasma at a temperature range from 1000 to 1750 K enabled destruction of the chloroorganic compounds with a very good yield. Several degradation products were received, which were analyzed. In the research electric arc plasma was used in the process of pyrolysis chloroorganic waste utilization. The reactor with a rotating arc was applied. Selected chloroorganic compounds were selected as the model: chloromethane (CH₃Cl), carbon tetrachloride (CCl₄), chlorobenzene (C₆H₅Cl) and dichlorobiphenyl (PCB-C₁₂H₈Cl₂). Based on the amount of the individual components, chloroorganic in the exhaust gases, and the amount introduced to the plasma decomposition, percentage yield was calculated.

Research results indicated that decomposition efficiency was more than 99,8% with the exception of CCl₄ pyrolysis, which in the exhaust had a content of 0.2% CCl₄.

Keywords: plasma, recycling, chloroorganic waste, pyrolysis

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1 Introduction

In recent years, research has been conducted on the industrial use of thermal plasma in waste utilization, especially the waste that contains harmful chemicals such as chloroorganic compounds (polychlorinated biphenyls PCBs) [1].

Decomposition of waste in the plasma guarantees a high speed of its destruction and a high degree of utilization. Compared to the normal combustion process it is faster and more effective.

The essence of the thermo-chemical neutralization and elimination of toxic substances is the use of a chloroorganic plasma zone for atomization, oxidation and conversion of the products to the simple inorganic compounds. Thermal plasma conversion of organic waste can be obtained by the inert gas plasma pyrolysis or gasification using air or water plasma. Both processes result in the formation of the mixture of combustible gases (H₂, CO, hydrocarbons), which can then be burned in chambers or gas turbines and chemically transformed to obtain hydrogen and synthetic fuels [2].

Pyrolysis is the process of thermochemical decomposition of carbon-rich organic material, which takes place at elevated temperatures without the little to no participation of oxygen. The composition and quantity of the pyrolysis products is dependent on the type of waste, the physicochemical properties and the process temperature.

The main products of pyrolysis plasma chloroorganic compounds are pyrolysis gas (CO, H₂, CO₂, lower gaseous hydrocarbons, hydrogen chloride) and pyrolysis coke (inorganic wastes in the form of molten slag) [3].

Various types of plasma reactors can be used for the destruction of chloroorganic wastes. The main goal of the research was the application of a plasma reactor ROTARC (rotating arc reactor) to destroy the liquid and gaseous or solid chloroorganic wastes. The objective was the testing of ROTARC with two different ways of feeding and mixing the toxic compounds with plasma to reach the most efficient way of their destruction. As the model, the following chloroorganic compounds were
selected: gaseous chloromethane (CH$_3$Cl), liquid carbon tetrachloride (CCl$_4$), liquid chlorobenzene (C$_6$H$_5$Cl) and solid PCB (C$_{12}$H$_8$Cl$_2$).

2 Experimental procedure

The plasma heater of the chemical reactor based on the rotating arc principle is shown in Fig. 1 [4]. The system mainly consists of ROTARC, a water cooled quartz tube reactor and the water cooled stainless steel quencher/scrubber. The ROTARC plasma device is composed of two coaxial water-cooled cylindrical electrodes with one end closed while the second end forms a plasma nozzle. The arc is ignited in the nozzle by a plasma gun and the arc is magnetically driven. On the top of the inner electrode a high pressure fluid injector is placed which produces a highly atomized conical spray. The ROTARC plasma device can be used in two working regimes: as a gas heater producing a hollow plasma torch or as a chemical reactor employing the rotating arc for thermal treatment of the gas medium. In the first case the atomized fluid is injected into the hollow plasma, in the second one the chemical medium is at first gasified and supplied as a working gas. Both methods can be used for the liquid waste (CCl$_4$, C$_6$H$_5$Cl). At first the chloroorganic compounds are gasified through an evaporation process and then delivered to the reactor as a gas. In the second method, the liquid waste is injected directly into the plasma. This method was also used for the solid waste PCB (C$_{12}$H$_8$Cl$_2$) which had to be previously dissolved in a proper solvent (cyclohexane). The gaseous CH$_3$Cl could be supplied directly from a container. The wet quencher/scrubber was designed for neutralizing acid gas (HCl), using a caustic solution. The samples of product gases (off gas) were sucked into the container for a later analysis. The chloroorganic destruction removal efficiency was measured by gas chromatograph (SRI), but the combustion gas analyzer (GA-4DT) estimated the content of CO and CO$_2$ in the off-gas. Also the pH of the drain water was controlled to estimate HCl and Cl$_2$. The ROTARC was operated at one (1) atmosphere with a nitrogen flow rate of 10 L min$^{-1}$.

3 Results and discussion

A major advantage of plasma processing is that the heat input may be accomplished in an atmosphere of any desired composition and reactivity. In practice there are only a few variations of chemical strategies available for thermal processing, i.e., pyrolysis and reaction with water. To optimize the conditions of the reaction, we have calculated the decomposition of chloroorganic wastes within the range of temperatures from 500 to 5000 K by using the CHEMSAGE [5] computer program based on the minimization of Gibbs’s free energy. Those calculations include the systems of pure compounds or their mixtures with water. The calculations of selected results are shown in Figs. 2-5.

Chloroorganic residues were added to the plasma reactor under a nitrogen atmosphere using two approaches: as a gas (CH$_3$Cl, and after the evaporation of CCl$_4$, C$_6$H$_5$Cl) and as a liquid (C$_{12}$H$_8$Cl$_2$) dissolved in cyclohexane. Pure compounds of the mixture with water were decomposed. Based on the amount of the individual components, the chloroorganic in the exhaust gases and the amount introduced to the plasma decomposition percentage yield was calculated.

A CHEMSAGE software was used for balance calculation. When entering input data for a non-ideal model, two important points must be considered. The first is the stoichiometric relationship between the independent system components in the Gibbs phase rule and the phase components resulting from the model. The second is the model equation for the integral molar Gibbs energy of the phase under consideration [5].
Figure 2: Pyrolytical decomposition and reaction with water of CH$_3$Cl.

Figure 3: Pyrolytical decomposition and reaction with water of CCl$_4$.

Figure 4: Pyrolytical decomposition and reaction with water of C$_6$H$_5$Cl.
Plasma recycling of chloroorganic wastes

\[ G_m = \sum_x G_i + RT \sum_x \ln x_i + \sum_{i<j} \sum_{\nu} L_{ij} (x_i - x_j) x_i x_j \]

where \( L \) are interaction coefficients.

It allowed the experimental selection of the optimal temperature distribution of chloroorganic substances. Too high temperatures led to the formation of harmful and more difficult to remove secondary products of recombinations such as Cl and O. Lower temperatures ranging from 1000 to 1750K enabled decomposition of chloroorganic compounds with very good yields above 99% for all compounds tested. A few simple degradation products were obtained which were analyzed using a gas chromatograph SRI and a exhaust gas analyzer (GA-4DT). Products such as HCl, H\(_2\) and small amounts of CH\(_4\) were noticed during the pyrolytical decomposition of CH\(_3\)Cl and C\(_6\)H\(_5\)Cl at temperatures between 1000 to 1500 K. During the pyrolytical decomposition CCl\(_4\) were obtained at temperatures ranging from 1000 to 1500K Cl\(_2\) carbon (soot) and undecomposed CCl\(_4\) to 0.2%. In the case of pyrolytical decomposition C\(_6\)H\(_8\)Cl\(_2\), compound such as HCl, H\(_2\) and carbon in the form of soot appear at temperatures of 1000 to 1500 K.

Chloroorganic compounds did not obtain carbon in the form of soot during the reactions with water at temperatures ranging from 1000 to 1750 K. The reaction of CH\(_3\)Cl and C\(_6\)H\(_8\)Cl\(_2\) with water obtained products such as HCl, H\(_2\), CO and CO\(_2\). In this case the reaction of CCl\(_4\) with water was prepared and HCl, CO\(_2\) trace amounts of CO and chlorine were obtained. C\(_6\)H\(_8\)Cl\(_2\) reacting with water formed products such as HCl, H\(_2\) and CO.

| Temperature [K] | 500 | 750 | 1000 | 1250 | 1500 | 1750 |
|----------------|-----|-----|------|------|------|------|
| PCB out / PCB in | 1.01% | 0.82% | 0.65% | 0.38% | 0.26% | 0.03% |
| CCl\(_4\) out / CCl\(_4\) in | 16.52% | 11.54% | 4.85% | 0.64% | 0.27% | 0.20% |
| CH\(_3\)Cl out / CH\(_3\)Cl in | 0.51% | 0.36% | 0.15% | 0.09% | 0.02% | 0.02% |
| C\(_6\)H\(_8\)Cl\(_2\) out / C\(_6\)H\(_8\)Cl\(_2\) in | 0.90% | 0.52% | 0.30% | 0.12% | 0.06% | 0.03% |


g_{_{\text{en}}}  = \sum_x G_i + RT \sum_x \ln x_i + \sum_{i<j} \sum_{\nu} L_{ij} (x_i - x_j) x_i x_j

4 Conclusions

To avoid the main disadvantages of chloroorganic processing resulting in the sooting and toxic Cl\(_2\) formation, the reaction with steam is the optimal way for their destruction. The lower the decomposition temperature
of chloroorganic compounds, the better it is in producing less harmful and difficult to remove secondary products.

In contrast to the calculation, soot appeared at temperatures below 2500 K. A high yield decomposition was observed at temperatures between 1000-1750 K. It amounted to over 99%.

In the experiment, CH\textsubscript{3}Cl decomposed preferably in the range between 500 – 1750 K (0.02% remaining).

The decomposition of CCl\textsubscript{4} (remaining 0.2%) was the most difficult.

References

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