THERMODYNAMIC STUDY OF MERCURY CONTAINING WASTE BY PYROLYSIS

Yailen Busto, E.W. Palacios, F.M.G. Tack, L.M. Peralta, L.M. Ríos, M. Yera

Technological University of Israel, Research Department, Quito, Ecuador; Central University of Ecuador, Faculty of Odontology, Quito, Ecuador; Gent University, Bioengineering Science Faculty, Gent, Belgium; Central University of Las Villas, Faculty of Chemistry and Physics, Santa Clara, Cuba; Iberoamerican University of Ecuador, Research Department, Quito, Ecuador
yailenb09@gmail.com

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Introduction

The present communication aims to properly study the thermodynamic behaviour of mercury containing waste by thermal decomposition using pyrolysis. The proposed reaction mechanism considers both homogeneous and heterogeneous mercury reactions, the species of mercury present in the sludge matrix as well as the chemical-physical properties of the mercurial sludge. The thermodynamic parameters that best describe the model of mercury thermal decomposition in the solid waste are determined.

Methods

Sampling and chemical analysis

The mercurial sludge sample used for the experiment was collected from a filled niche, located around the chlor-alkali Cuban factory "ELQUIM". Sampling, sample preparation and chemical analysis has been described in previous publication (Busto et al., 2011).

Thermodynamic analysis

Thermodynamic analyses were performed using Mondeja's Methodology which is based on Kirchhoff's Equation. A scheme that involves 6 homogeneous and heterogeneous reactions (Busto et al., 2013) was proposed considering the chemical and physical composition of the sludge sample, the mercury fractionation study previously reported (Busto et al., 2012), in which the presence of $HgCl_2$, HgS and $HgSO_2$ in the sludge matrix was suggested and the mercury reactions reported by O' Neil et al. (2001).

Results

Chemical reaction mechanism

To describe the thermal decomposition of the mercurial sludge sample generated by a chlor-alkali Cuban plant, a scheme of six reactions was proposed (Busto et al., 2013). Once a reaction mechanism (reaction pattern) was built, considering also the Gibbs free energy values obtained for each proposed reaction, the kinetic model was adjusted in order to satisfy the experimental results. The proposed reaction mechanism used in this study is based on the thermal decomposition in the solid phase followed by several gas phase reactions. Thermal decomposition reactions in the solid phase were considered a fast processes influenced by the temperature but limited by the diffusion and particle size of the sludge sample L'vov (2001, 2008).

Thermodynamic analysis of the reaction scheme

The reaction mechanism was thermodynamically evaluated to verify the probability of occurrence of these reactions by considering the Gibbs free energy values (ΔG). Thermodynamic parameters were determined

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at the highest working temperature of the furnace (450 °C). Table 1 shows the thermodynamic parameters (ΔGj, ΔHj and Kej) calculated for each reaction using Mondeja's Methodology.

Table 1. Thermodynamic parameters (ΔG, ΔH, Ke) of the kinetic reaction mechanism

Reactions	$\Delta G_{450\,°C}$ (kJ mol^{-1})	$\Delta H_{450\,°C}$ (kJ mol^{-1})	$Ke_{450\,°C}$
R_1	$-3.06\cdot10^{2}$	$-3.65\cdot10^{2}$	147.83
R_2	4.81	$1.57\cdot10^{2}$	$9.23\cdot10^{-1}$
R_3	$-5.36\cdot10^{1}$	41.42	2.44
R_4	$-4.13\cdot10^{4}$	$-1.76\cdot10^{5}$	$2.32\cdot10^{298}$
R_5	-3.38	$2.35\cdot10^{2}$	1.06
R_6	$-2.2\cdot10^{2}$	$3.2\cdot10^{2}$	38.12

The analyzed reactions showed spontaneous behaviour where the variation of the Gibbs free energy ΔG ranged from -3.38 to $-4.13\cdot10^{4}$ kJ mol^{-1}. Reactions R_1 and R_4 are exothermic reactions due to their $\Delta H < 0$ while the other reactions have an endothermic behaviour. On the other hand, the equilibrium constant of each reaction Kej showed in all cases that the direct reactions are favored with $Ke > 1$, except for R_2 which exhibited a low Ke_2. The same behaviour of the R_2 obtained from this study has been previously reported L'vov (2008), where the inverse reaction (HgO formation) is favored. Due to the thermodynamic results obtained for reaction R_2 as well as its low significance on the kinetic model (corroborated by simulation), this reaction was not further considered. The high equilibrium constant value obtained for reaction R_4, where is highly favored the Hg, SO_2 and O_2 formation, is in line with previous results reported by Navarro et al. (2009). This reaction mechanism describes a complex mechanism of five heterogeneous (gas-solid phase and liquid-gas phase) and one homogeneous (gas phase) reactions. It has been assumed that R_1, R_3 and R_5 occur in parallel.

Conclusion

In the present research the thermodynamic behaviour of mercury containing waste by thermal decomposition using pyrolysis was studied and the reaction mechanism proposed. This mechanism considers both homogeneous and heterogeneous mercury reactions, the species of mercury present in the sludge matrix as well as the chemical-physical properties of the mercurial sludge. The thermodynamic parameters that best describe the model of mercury thermal decomposition in the solid waste were determined. This thermodynamic study can be applied in engineering calculations to dimension the installations and determine the optimal conditions to treat a mercury containing sludge.

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