

Reaction Mechanism and Kinetics of the Mercury Solid Waste Pyrolysis: An Isoconversional Approach

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The present study focuses on the kinetic mechanism of mercury removal from contaminated solid waste generated by chlor-alkali plant using pyrolysis. The isoconversional method of kinetic analysis was used to calculate the kinetic parameters that best describe mercury thermal decomposition in the solid waste. A mechanism involving 6 heterogeneous and homogeneous reactions was proposed to represent the behaviour of mercury compounds in the solid matrix during thermal treatment. The proposed model was compared to nine models previously reported in literatures to elucidate the controlling reaction mechanism. Fitting each of these to the experimental data of thermal decomposition of the mercurial sludge sample, confirmed the hypothesis that not a single mechanism is ruling the process. The D1-diffusion mechanism could be considered the controlling step of the process at high retention times while at low thermal decomposition times (<15 min) the diffusion mechanism (D1) as well as the third order reaction mechanism (F3) could be controlling the process. Nevertheless, as a first depth-in to the knowledge of this polydisperse and multicomponent system (mercurial sludge), the diffusion mechanism (D1) can be considered the overall controlling stage as an increase of temperature smooths the progress of the chemical reactions involved.

1. Introduction

Mercury is a toxic, bio-accumulating trace metal whose emissions to the environment have increased significantly as a result of anthropogenic activities such as mining, chlor-alkali plants and fossil fuel combustion. It is released to the environment either naturally or through human activities in three forms such as elemental (Hg^0), oxidized (Hg^{2+}) and particulate (Hg^p) (Tauqeer et al., 2015).

A recent study developed by Lamborg et al. (2014) reported that anthropogenic perturbations to the global mercury cycle have led to an approximately 150 % increase in the amount of mercury in thermocline waters and have tripled the mercury content of surface waters compared to pre-anthropogenic conditions. Chlor-alkali industry represents one of the major concerns of mercury emissions due to the large amount of waste containing mercury generated by the process (Busto et al., 2015).

Cuba as a developing country still uses mercury cell technology to produce gaseous chlorine and caustic soda. It currently hosts more than 7,000 t of mercury contaminated wastes buried in concrete niches. Mercury wastes generated by the electrochemical Cuban plant were characterized as 'high mercury waste' (total Hg content exceeding 260 mg/kg) according to the US Land Disposal Restrictions (US EPA, 2008). According to US EPA (1997), thermal treatment represents the most suitable technology for 'high mercury wastes'. The potential of this approach to decontaminate the mercury containing wastes from the chlor-alkali industry in Cuba has been investigated by Busto et al. (2011).

Despite the fact that thermal treatment, specifically by retorting method, is a widely used technology to treat solid wastes highly contaminated with mercury (e.g. mercury wastes from the chlor-alkali process), almost all studies have focused so far mainly on achieving the best operating conditions at pilot and industrial scale that

increases the mercury removal efficiency of this treatment (Huang et al., 2011). In contrast, very few studies have been published on the kinetic reaction mechanism representing mercury behaviour during the thermal treatment (Taube et al., 2008).

Pyrolysis is the thermal degradation in the absence of oxygen (Manchantrarat and Jitkarnka, 2012). According to Oyedun et al. (2012), pyrolysis can be considered a thermo-chemical process is an efficient means with less emission to produce valuable products. However, the main researches have been focussed on energy conversion process more than a technique to recovery or reduce the heavy metal pollution.

The present communication aims to properly formulate a kinetic reaction mechanism that describes mercury removal by thermal decomposition using pyrolysis. The thermodynamic and kinetic parameters that best describe the kinetic model of mercury thermal decomposition in the solid waste are determined and the controlling reaction mechanism is investigated comparing the proposed model with nine previously reported in the literature.

2. Material and methods

2.1 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).

2.2 Thermal treatment set-up at bench scale

Thermal treatment was performed at the laboratory scale using a ceramic muffle furnace (L9/11/SKM/P330 Model, Nabertherm, Germany, Bremen) which has a temperature control accurate to ± 1 °C. The oven was located inside a fume cupboard (Model Potteau, Belgium) to avoid pollution with mercury vapours. The thermal decomposition of the sludge sample was studied in a flowing air atmosphere. For the kinetic study of mercury removal in the solid waste, total mercury content determinations for retorting temperatures of 250, 350 and 450 °C and for treatment times of 5, 10, 25, 30, 40, 50, 60, 90, 120 and 150 min were conducted.

2.3 Thermodynamic analysis

Thermodynamic analyses were performed using Mondeja's Methodology (Smith, 1991) which is based on Kirchhoff's Equation. This equation expresses the temperature dependence of the thermal quantities associated with a chemical reaction through the difference in heat capacities between the products and reactants taking into account their stoichiometric coefficients in the reaction equation (Aleksander, 1979). The reaction scheme of the mercury solid waste pyrolysis assumed for the analysis appears at Busto et al. (2013).

2.4 Kinetic analysis

For calculations, we considered that the Muffle furnace works as a "Perfect Mix Reactor". This was assumed since the internal temperature gradients in the oven were negligible due to the high temperature of the oven, its design characteristic and the high velocity of the gas (NLC, 2012). Since the thermal treatment was carried out at batch operation conditions, the kinetic parameters for each reaction were obtained by a non-steady state material balance of each species.

The kinetic study of mercury behavior (mercury content) at different thermal conditions was carried out using the Flynn, Wall and Ozawa (FWO) integral isoconversional method (Vyazovkin and Dollimore, 1996). This method yields the effective activation energy (E) and pre-exponential factor (A) which are the Arrhenius parameters for each given conversion (α). The general kinetic equation can be expressed as follow:

$$\frac{d\alpha}{dt} = A \cdot \exp\left(-\frac{E}{RT}\right) \cdot f(\alpha) \quad (1)$$

Where: t, R, T are the time (min), the universal gas constant (8.3144×10^{-3} kJ/mol·K) and the pyrolysis temperature respectively (°C) and α is the conversion of the species that contains mercury (dimensionless). It represents the fraction between the converted moles of mercury and the initial moles of mercury and can be calculated as follows:

$$\alpha = \frac{n_0 - n}{n_0} \quad (2)$$

Where: n_0 and n represent the initial and final moles for each reaction.

Moreover, from Eq(1) $f(\alpha)$ represents the mathematical function of α and can be determined adjusting the experimental data of mercury conversion with temperature. Besides, $d\alpha/dt$ is the variation of mercury conversion with the time and it can be calculated as follows:

$$\frac{d\alpha}{dt} = \frac{-1}{n_0} \frac{dn}{dt} \quad (3)$$

In order to calculate the values of the activation energy (E) for each reaction, Eq(1) was transformed into a logarithmic form, allowing to assess the E values from the slope of $\ln(d\alpha/dt)$ versus $1/T$ for each of the α values. Once the E value has been determined it is possible to find the kinetic model which best describes the measured data set. Additionally, a model-fitting analysis was performed to determine the most probable $f(\alpha)$ kinetic model consistent with the isoconversional kinetic results, following the methodology outlined by Vyazovkin and Wight (1997).

The general expression used to determine the kinetic rate for solid phase reactions was represented as follow:

$$R_{jfs} = k_j \cdot f(\alpha) \quad (4)$$

Where: R_{jfs} is the kinetic reaction rate of each reaction (thermal decomposition of mercury compounds in the solid phase expressed in min^{-1}) and k_j represents the kinetic constant (min^{-1}).

3. Results

3.1 Pyrolysis of mercury solid waste

Figure 1 shows the behavior of mercury in ashes of the sludge sample at different exposure times for three retorting temperatures (250, 350 and 450 °C). We observed that at lower temperatures the influence of the retorting time (until 30 min) is more pronounced than at higher temperatures. This phenomenon could be linked with a change in the controlling reaction mechanism during the thermal process. On the other hand, the behavior of mercury removal at 350 and 450 °C for the all-time series was well correlated.

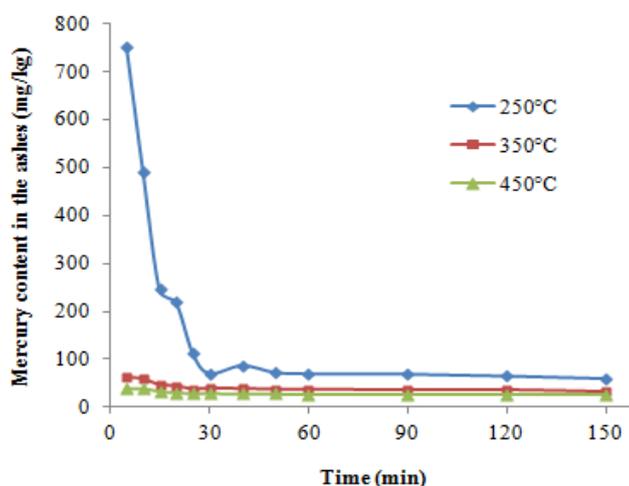


Figure 1: Behavior of mercury content in ashes with the pyrolysis time at three different temperatures

The efficiency of the thermal treatment in this type of mercury waste has been previously demonstrated. It was established that up to 300 °C the removal of mercury was below 50 %, while more than 90 % of the mercury was successfully removed after 60 min for treatment temperatures higher than 300 °C (Busto et al., 2011). In the present survey, the behavior of mercury removal followed the same pattern but the lowest values of mercury average content in the remaining ashes of 27 mg/kg (97.98 % of mercury removal) was obtained at higher temperature (450 °C) and exposition time (150 min).

3.2 Thermodynamic assessment of mercury solid waste pyrolysis

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 at the highest working temperature of the furnace (450 °C). Table 1 shows the thermodynamic parameters (ΔG , ΔH and K_e) calculated for each reaction using Mondeja's Methodology (Smith, 1991).

Table 1: Thermodynamic parameters (ΔG , ΔH , K_e) of the kinetic reaction mechanism

Reactions	$\Delta G_{450\text{ }^\circ\text{C}}$ (kJ mol ⁻¹)	$\Delta H_{450\text{ }^\circ\text{C}}$ (kJ mol ⁻¹)	$K_{e450\text{ }^\circ\text{C}}$
R ₁	-3.06×10^2	-3.65×10^2	147.83
R ₂	4.81	1.57×10^2	9.23×10^{-1}
R ₃	-5.36×10^1	41.42	2.44
R ₄	-4.13×10^4	-1.76×10^5	2.32×10^{298}
R ₅	-3.38	2.35×10^2	1.06
R ₆	-2.2×10^2	3.2×10^2	38.12

The analysed reactions showed spontaneous behavior where the variation of the Gibbs free energy ΔG ranged from -3.38 to -4.13×10^4 kJ mol⁻¹. Reactions R₁ and R₄ 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 K_e showed in all cases that the direct reactions are favoured with $K_e > 1$, except for R₂ which exhibited a low K_{e2} . The same behaviour of the R₂ obtained from this study has been previously reported L'vov (1999). Due to the thermodynamic results obtained for reaction R₂ 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 R₄ is in line with previous results reported by Navarro et al. (2009).

3.3 Kinetic model of mercury solid waste pyrolysis

The kinetic model of the reaction mechanism obtained to explain the thermal decomposition of mercurial sludge sample can be represented by the general function expressed by Eq(5).

$$f(\alpha) = (\alpha_f - \alpha)^{nr} \quad (5)$$

Where: α_f is the final conversion when the sludge is exhaust, and nr is the reaction order. In this expression, α is refers at the total mercury conversion in the solid matrix and nr is determine by the optimal adjustment of the kinetic model. It has been reported by Kafarov (1977) that Eq(1) is well suited for polydisperse systems and/or where a component is separated in different phases. On the other hand, it is very effective when there are changes in the diffusive stage that controls the process.

From the proposed reactions scheme, the prevalence of reactions containing HgS was observed as this mercury compound appears in the highest proportion in the sludge sample. Furthermore, the thermal decomposition of this sludge including gas-phase and solid-phase reactions allowed a best adjustment of the kinetic model. In Table 2 the kinetic parameters (α_f , k_j and nr) obtained experimentally for each retorting temperature are given.

As can be noticed from the results in the Table 3 at the retorting temperature of 250 °C, the kinetic model obtained by simulation did not result in a suitable adjustment with the experimental values. Contrarily, a very good fit of the experimental conversion with the empirical conversion values (simulated model) were achieved at 350 °C and 450 °C. This phenomenon could be linked with a change in the controlling reaction mechanism during the thermal process. The statistical comparison for two nonparametric tests is discussed below.

3.4 Statistical analysis

As a marked change was observed between the conversion behavior at 250 and 450 °C, the statistical analysis was done for these operating temperatures. The P values obtained at 250 °C from the Ranksum and Kruskalwallis statistical tests were 0.119 and 0.175 ($P > 0.05$) respectively. Equally, P values obtained at 450 °C from the Ranksum and Kruskalwallis statistical tests were 0.167 and 0.097 respectively; demonstrating that non-significant differences exist between experimental data and the proposal model.

Table 2: Kinetic parameters (α_f , k_j , nr) from adjusted kinetic model for each operating temperature

Kinetic parameters	250 °C	350 °C	450 °C
k_1 (min ⁻¹)	1.03×10^{-37}	2.08×10^{-29}	1.69×10^{-23}
k_2 (min ⁻¹)	5.15×10^{-10}	1.18×10^{-8}	1.62×10^{-8}
k_3 (min ⁻¹)	1.00×10^{-20}	1.00×10^{-14}	1.00×10^{-10}
k_4 (min ⁻¹)	2.83×10^{-2}	5.38×10^{-1}	5.73×10^{-1}
k_5 (min ⁻¹)	4.14×10^{-2}	7.98×10^{-2}	1.15×10^{-1}
k_6 (min ⁻¹)	4.00×10^{-20}	1.00×10^{-14}	1.93×10^{-2}
α_f (%)	9.75×10^1	9.76×10^1	9.79×10^1
nr	7.86×10^{-1}	1.03	1

Table 3: Comparison between maximum conversion values achieved by the experimental data and the simulated model

Time (min)	$\alpha_{250\text{ }^{\circ}\text{C}}$		$\alpha_{350\text{ }^{\circ}\text{C}}$		$\alpha_{450\text{ }^{\circ}\text{C}}$	
	Experiment (%)	Model (%)	Experiment (%)	Model (%)	Experiment (%)	Model (%)
15	81.4	61.6	96.5	97.56	97.40	97.95
30	94.7	72.4	97.1	97.57	97.80	97.96
60	94.7	85.1	97.2	97.57	97.91	97.96
90	94.8	91.2	97.3	97.57	97.92	97.96
120	95.1	94.1	97.3	97.57	97.93	97.96
150	95.5	95.48	97.56	97.57	97.96	97.96

4. Conclusions

In the present research a kinetic reaction mechanism which describes the mercury removal process by thermal decomposition of mercury solid waste generated by the Chlor-alkali process has been proposed. The experimental kinetic data was reasonably well represented by the simulated kinetic model. The effect of the retorting temperature was much stronger than the effect of the exposure time.

A comparison among 9 kinetic mechanisms of solid-state reactions well established on the literature (deceleratory behavior α -T curves) was carried out to elucidate the controlling reaction mechanism of the process. The application of these models - fitting method confirmed the idea that not a single mechanism is ruling the process. The D1-diffusion mechanism could be considered the controlling mechanism of the process at high retention times while at low thermal decomposition times (< 15 min) the diffusion mechanism (D1) as well as the third order reaction mechanism (F3) could be controlling the process. This behaviour was observed at low (250 °C) and high (450 °C) temperatures by a good fitting of the thermal decomposition data over the whole range of conversions.

References

- Aleksander M., 1979, Great Soviet Encyclopedia, 3th edition, Macmillan, New York, USA.
- Busto Y, Tack M.G.F., Peralta L.M., Cabrera X., Arteaga-Pérez L.E., 2013, An investigation on the modelling of kinetics of thermal decomposition of hazardous mercury wastes. *Journal of Hazardous Materials*, 260, 358-367.
- Busto Y., Cabrera X., Tack F.M.G., Verloo M.G., 2011, Potential of thermal treatment for decontamination of mercury containing wastes from Chlor-alkali industry. *Journal of Hazardous Materials*, 186, 114-118.
- Busto Y., Palacios E.W., Tack F.M.G., Peralta L.M., Cabrera X., Rios L.M., 2015, Behaviour of mercury from hazardous solid waste generated by chlor-alkali Cuban industry. *Remediation proposal at pilot scale*, *Chemical Engineering Transactions*, 45, 751-756, DOI: 10.3303/CET1545126
- Huang Y., Hseu Z., His H., 2011, Influences of thermal decontamination on mercury removal, soil properties, and repartitioning of coexisting heavy metals. *Chemosphere*, 84, 1244-1249.
- Kafarov V., 1977, *Cybernetic Methods in Chemistry and Chemical Engineering*. Ed. MIR. Moscow.
- L'vov B.V., 1999, Kinetics and mechanism of thermal decomposition of mercuric oxide. *Thermochimica Acta*, 333, 21-26.
- Lamborg C.H., Hammerschmidt C.R., Bowman K.L., Swarr G.J., Munson K.M., Ohnemus D.C., Lam P.J., Heimbürger L.E., Rijkenberg M.J.A., Saito M.A., 2014, A global ocean inventory of anthropogenic mercury based on water column measurements. *Nature*, 512, 65-68, DOI: 10.1038/nature13563, <www.nature.com/nature/journal/v512/n7512/abs/nature13563.html#supplementary-information>, accessed 05.03.2016
- Manchantrarat N. and Jitkarnka S., 2012, Impact of HY as an additive in Pd/HBETA catalyst on waste tire pyrolysis products, *Chemical Engineering Transactions*, 29, 733-738
- Navarro A., Cañadas I., Martínez D., Rodríguez J., Mendoza J.L., 2009, Application of solar thermal desorption to remediation of mercury-contaminated soils. *Solar Energy*, 83, 1405-1414.
- NLC (Nabertherm Laboratory Catalogue), 2012, *The Nabertherm Furnace World* <www.nabertherm.com>, accessed 10.03.2012.
- Oyedun A.O., Lam K.L., Gebreegziabher T., Lee H.K.M., Hui C.W., 2012, Kinetic modelling and analysis of waste bamboo pyrolysis, *Chemical Engineering Transactions*, 29, 697-702.
- Smith J.M., 1991, *Chemical Engineering Kinetics*, 6th edition, McGraw-Hill, Mexico.
- Taube F., Pommer L., Larson T., 2008, Soil remediation-mercury speciation in soil and vapour phase during thermal treatment. *Water Air and Soil Pollution*, 193, 155-163.

- Tauqeer A., Nazir S., Overgard K.I., Manca D., Mutaliba M.I.A., Khan E., 2015, Hazards of mercury—safety perspectives and measures, *Chemical Engineering Transactions*, 43, 2143-2148, DOI:10.3303/CET1543358.
- US EPA (United States Environmental Protection Agency), 1997, Office of Research and Development. Capsule Report, Aqueous Mercury Treatment. EPA-625-R-97-004, Washington, USA <www.epa.gov/ORD/NRMRL/pubs/625r97004/625r97004.pdf>, accessed 01.03.2012.
- US EPA (United States Environmental Protection Agency), 2008, Land Disposal Restrictions Regulations for Mercury-Containing Non-wastewaters. R 40 CFR Part 273, Washington, USA <www.epa.gov/epawaste/hazard/tsd/mercury/treatmnt.htm>, accessed 25.04.2013.
- Vyazovkin S.V., Dollimore D.J., 1996, Linear and nonlinear procedures in isoconversional computations of the activation energy of nonisothermal reactions in solids. *Journal of Chemical Information and Computational Sciences*, 36, 42-45.
- Vyazovkin S.V., Wight C.A., 1997, Isothermal and nonisothermal reaction kinetics in solids: In search of ways toward consensus. *The Journal of Physical Chemistry*, 101, 8279-8284.