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Halogenated Wastes Safe Disposal: Polychlorinated biphenyls

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Abstract

The aim of this work is to have a review of some products where halogens are used in the manufacturing process along with the safe disposal methods of its wastes. Different halogenated compounds are introduced. The theoretical results are validated by comparing them with experimental results. Results show that incineration is a safe disposal method of polychlorinated Biphenyls (PCBs). The incineration of PCBs in rotary kiln is shown based on theoretical and experimental studies. Where energy and material balances are applied to rotary kiln incineration to derive the theoretical model. The results from the theoretical model is validated against experimental results. The disposal method by incineration for other halogenated compounds is presented. Different models representing the combustion of other halogenated components are analyzed. It is shown that incineration is the safe disposal method for halogenated compounds at temperatures around 1200 K to avoid the formation of toxic gas emissions like furan and dioxin. The theoretical results are comparable with the experimental data of the incineration process.

Keywords: Polychlorinated biphenyl; halogenated compounds; Incineration

Introduction

The halogens group in the periodic table consisting of five elements: fluorine (F), chlorine (Cl), bromine (Br), iodine (I), and astatine (At). In the modern IUPAC nomenclature, this group is known as group 17. Halogens react with metals to produce a wide range of salts, including calcium fluoride, sodium chloride, silver bromide and potassium iodide. They have many industrial applications such as in electrical equipment and brominated flame retardants [1]. Halogenated wastes come from Laboratory wastes containing various hazardous chemical reagents and reactants. They are often discharged from experiments, tests, or analyzing processes [2]. Famous halogenated components are Polychlorinated biphenyls (PCBs) which are a class of organic compounds. PCBs classified as persistent organic pollutants (POPs) that retard the biodegradation process and stayed for long time in the environment. PCBs contain 1 to 10 chlorine atoms attached to biphenyl and a general chemical formula of $C_{12}H_{10}$-xCl_x most PCBs were manufactured as cooling and insulating fluids for industrial transformers and capacitors stabilizing additives in flexible PVC coatings of electrical wiring and electronic components [3].

Studies show concentrations of polybrominateddiphenylethers (PBDEs) in the North American environment were increasing over the last twenty five years and are among the highest concentrations in the world [4] [5] [6] [7] as this product is banned in Europe and many countries in the world but it is still in use in north America.

For all of the above mentioned reasons, a need for safe disposal methods is investigated. One of the effective methods is thermal treatment. Incineration is one of the thermal treatment methods in waste management of halogenated wastes and substances, in which the wastes are combusted at high temperatures. Although, there are many other methods of remediation technologies [8] Such as chemical treatment, however, there are many risks incorporated with these methods. The risk of creating extremely toxic dibenzodioxins and dibenzofuransis high through partial oxidation particularly due to high thermodynamic stability of PCBs.

other risks are similar to other treatment methods are all degradation mechanisms are difficult to sustain. Intentional degradation as a treatment of unwanted PCBs generally requires high heat or catalysis. Environmental and metabolic degradation generally proceeds quite slowly relative to many other compounds.

In this work,the incineration mechanismof PCBs as the best safe disposal method will be presented as an example of halogenated compounds. Then the mechanism and model are validated against an experimental published data of similar chlorinated compounds.

Chemical equilibrium reaction of PCBs

Theoretical mechanism of the incineration of hazardous substances is difficult to anticipate as they have wide variations in the constituents. PCBs for example include the number of chlorine atoms varies from (1 to 10). A general stoichiometric relationship can be used to describe the structure of the feed stock to the incinerator [9] as the chemical structure of PCBs showed hydrogen and carbon as main component where chlorine atoms are added, and other chemicals formed minor composition in the structure or it can mix with the oils after use such as sulphur keeping in mind that the incineration process occurs not only for the pure oil but for its wastes:

$$C_mH_nO_pS_qN_xCl_y+v_{O2}O_2 \rightarrow mCO_2+\frac{n-y}{2}H_2O+qSO_2+\frac{x-a}{2}N_2+\alpha NO + yHCl \qquad 1$$

However, the following general expression and chemical reaction for PCBs incineration for this studyis considered as:

$$C_{12}H_{10-n}Cl_n + \frac{29-n}{2}O_2 \rightarrow 12CO_2 + (5-n)H_2O + n\,HCl \qquad 2$$

Where in the case of the heterogeneous combustion of carbon mono-oxide (CO) is assumed to be the main oxidation product of carbon. The total combustion to CO_2 takes place in the gas phase. Furthermore, waste compounds containing nitrogen are decomposed to give N_2 and NO according to the following equation [10]:

$$N_2 + O_2 \rightarrow 2NO \qquad 3$$

Which is used to evaluate α (in equation 1), which is the fraction of kiln temperature and excess oxygen. The resulting equations are solved simultaneously to get the required temperatures, flow rates, energy produced, and gas phase concentrations.

In previous work [3], studied the incineration process of PCBs wastes in a rotary kiln by a dynamic model consisted of a set of nonlinear equations comes from applying material and energy balances under unsteady state conditions. In another study [9] showed the model of PCBs incineration and validation. The dynamic model accounts for the variations in composition of PCBs (number of chlorine atoms) and the process conditions such as excess air, temperature, and pressure of operation. Then the equations are solved using MATLAB. Finally, the results are presented and discussed. Equation 4 which is derived by Bani-Hani et al [3] shows the energy change E with process parameters such as temperature T, mass M, time t, and heat capacities C_v.

$$\frac{dE_{tot}}{dt} = \frac{d}{dt}\left(M_s Cv_s\left(T_{gas} - T_{ref}\right)\right) + \frac{d}{dt}\left(M_{gas}\sum_i \frac{Mi}{\sum_i M_i}\int_{T_{ref}}^{T_{gas}} Cv_i(T)dT\right) \qquad 4$$

Model Validation

The incineration of PCBs requires high temperature to avoid the production of unwanted toxic byproducts such as furan and dioxin.

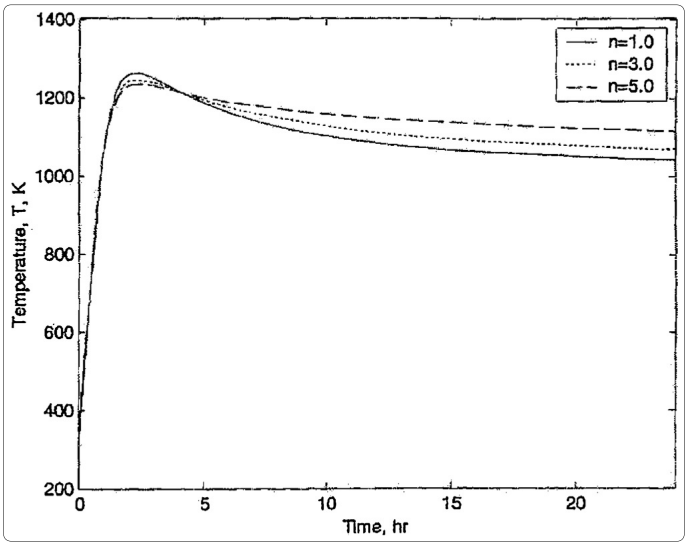

Figure 1. Temperature inside rotary kiln with different number of chlorine atoms and using 10% excess of air where n is the number of chlorine atoms

Previously published data [3] is shown in figure 1. Figure 1 shows an increase in the temperature of incineration with time till it reaches a steady state value. The temperature is higher for higher number of chlorine atoms, which is attributed to the need of more energy to break the bond of chlorine connected to the structure. It is shown in figure 1that the temperature is above 1000 K. The obtained results have been validated against published experimental data and found in good agreement.

The modeling of PCBs incineration is based mainly on experimental studies and pilot plants, on the other hand software or numerical solution needs some assumptions and approximations. Thus a comparison between theoretical results and experimental data is necessary. Figure 2 shows a comparison for some of chlorinated wastes incinerated in rotary kilns. The results obtained from the theoretical analysis are comparable to the published experimental data regarding the temperature of the combustion that reaches around 1200 K. the difference between the two results is attributed to variations in the component structure.

In their experimental work [11] investigated possible combustion mechanisms of chlorinated compounds such as dichloromethane (DCM) and chlorobenzene (MCB).

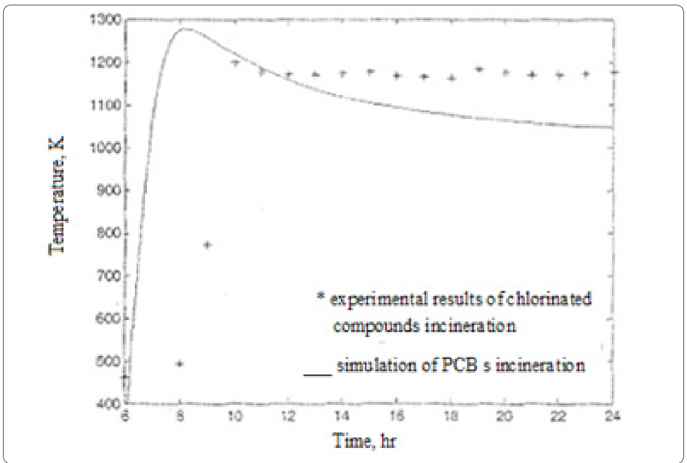

Figure 2. Temperature inside rotary kiln from the current model and compared with experiments

It is found that, to achieve a complete destruction of DCM and MCB, the temperature of combustion should be above 900°C (1173 K) and this is causing the degree of conversion of chlorine compounds very high(92-100%) [12]. Also adjusting the temperature to 300 °C, 600 °C, and 900 °C when investigating the formation of several chlorinated compound classes helps to estimate the effect of temperature on PVC combustion. The literature reviewed showed a comparable results with the model of PCBs combustion temperature which is 1200 K.

Conclusion

Incineration of halogenated wastes is a safe disposal method. However, the uncontrolled incineration of polyhalogentaed compounds is a main source of hazardous gas emissions. Thermal treatment of waste containing flame retarding products is a source of PBDEs to North American air. Results available in literature showed that the suitable temperature of incineration is about 1200 K to reduce emissions of polychlorinated dioxins and furans (PCDDs/Fs).

A temperature of 1200K is recommended to incinerate some halogenated compounds like PCBs. This temperature depends on the number of chlorine atoms and the amount of excess air. To control the air quality additional tools can used such as gas emissions control systems.

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