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Pyrolysis kinetics of tetrabromobisphenol a (TBBPA) and electric arc furnace dust mixtures

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ABSTRACT

This work assesses the decomposition kinetics and the overall pyrolysis behavior of Tetrabromobisphynol A (TBBPA) mixed with Electric Arc Furnace Dust (EAFD) using experimental data from thermogravimetric analysis (TGA). Mixtures of both materials with varying EAFD:TBBPA ratios (1:1, 1:2, 1:3 and 1:4) were pyrolyzed in an inert atmosphere under dynamic heating conditions at different heating rates (5, 10, 30 and 50 °C/min). The pyrolysis of pure TBBPA proceeded through two decomposition steps: debromination and volatilization of debromination products. This is followed by char formation that also involves release of volatile organic matter. However, the pyrolysis of EAFD:TBBPA mixture proves to be more complex in nature due to the occurrence of parallel solid-liquid reactions that result in the release of HBr and other volatile organic compounds (VOC) coupled with bromination of metal oxides. Subsequent chemical events encompass evaporation of metal bromides and finally reduction of the remaining metal oxides, most notably iron oxide, into their metallic form by the char. Three models, namely, Kissinger, Flynn-Wall-Ozawa (FWO) and Kissinger-Akahira-Sunose (KAS), were deployed to derive kinetics parameters. Generally, it was found that the presence of EAFD has led to an increase in the apparent activation energy for the first stage of TBBPA decomposition due to the reduced evaporation of TBBPA.

1. Introduction

Electric arc furnace dust (EAFD) represents an environmentally hazardous material due to its high content of relatively easy leachable heavy metals. As thus, it also signifies an important secondary resource for metals such as Zn, Fe and Pb. For instance, the zinc content in EAFD varied between 4 and 37% [1]. Co-pyrolysis of EAFD with halogenated organic such as chlorides in PVC and bromides in brominated flame retardant materials (BFRs) has attracted great deal of research based on two compelling grounds: (i) recycling of bromide and chloride-containing materials, and (ii) extraction of metals from their oxides, present in EAFD, via pyrometallurgical [2–6] or pyro-hydrometallurgical routes [7–9]. Interest in studying the effect of metal oxides on thermal decomposition of TBBPA originates from their profound capacity to act as halogen absorbers or fixers. XRD measurements proved that part of bromine in TBBPA is converted into metal bromides and oxybromides [5,10,11]. Further reduction of metal oxides into metallic species accompanies enhancements in the yields of CO_2. The exact mechanism for the action of metal oxides is not well understood. A rise in concentrations of benzene suggests that metal oxides abstract a Br atom either from the original TBBPA or any other brominated species [7].

Detailed understanding of the interaction between the EAFD and PVC/BFRs is important in the pursuit to construct a recycling facility (for both categories of materials) at an industrial scale. This is especially more prevalent when investigating pyrolysis kinetics. Kinetic-related information is essential for process and equipment design where thermal decomposition takes place. Furthermore, elucidating kinetics parameters is essential for the prediction of thermal decomposition mechanisms halogen-laden materials and objects [12]. Al-Harahsheh et al. [13] studied the pyrolysis kinetics of EAFD-PVC mixtures. Despite of recent progress, literature reports no kinetics for pyrolysis of mixtures of EAFD and tetrabromobisphenol A (TBBPA). The latter constitutes the most widely deployed BFRs. Previous publications on the interaction between metal oxides/EAFD with TBBPA have reported mass loss profiles; bromine fixation efficiency and prominent interaction products [4–6,9,14–16]. The available kinetic models on

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decomposition of pure TBBPA are: single-step global apparent kinetics [17], a detailed model by Marongiu et al. [18], and correlational and simplified mechanistic model by Font et al. [12].

The most common method for treatment of BFRs-containing objects is pyrolytic incineration at temperatures exceeding melting points of BFRs. Pyrolysis kinetics of neat TBBPA samples were reported from different perspectives [12,18–21]. Marongiu et al. [18] suggested that TBBPA decomposition in the condensed medium involve loss of HBr, successive C-Br bond fission, followed by cross-linking condensation reaction and other reactions involving radicals and the parent TBBPA. Decomposition of TBBPA in the gas phase was shown to proceed in fundamentally different routes that mainly encompass cleavage of the isopropylidene linkage followed by fragmentation into brominated aromatic species [22]. Major pyrolytic products include HBr and brominated phenols. As a result, TBBPA decomposition causes major corrosion problems to the incinerator materials of construction and also pollute the environment. The major environmental burden of pyrolytic decomposition of TBBPA is the potential formation of polybrominated dibenzo-*p*-dioxins and furans (PBBD/Fs) via condensation of brominated phenols [21]. Several papers also considered the pyrolysis kinetics of printed circuit boards containing BFRs [23–28]. However, a limited number of papers have considered the pyrolysis kinetics of EAFD:TBBPA mixtures at varying ratios. To this end, the aim of this paper is to investigate the pyrolysis kinetics of EAFD:TBBPA mixtures. The underlying objective is to comprehend chemical phenomena dictating EAFD-assisted degradation of TBBPA.

2. Materials and methods

The chemical composition of EAFD used in the current work was reported in our previous work [13] following our method reported in [29]. The mineralogical composition of the collected EAFD sample was characterized by X-Ray diffraction analysis technique (XRD) employing a computer controlled Hiltonbrooks® XRD system with a Philips® PW 1050 diffractometer.

Table 1 shows the major elements present in the EAFD sample. Detailed composition is reported elsewhere [13]. The dust mainly contains Zn, Fe, Ca, Na, Pb, Si, K and Mn. The carbon content of the sample was analyzed by calorimetry and was found to be 2.63 ± 0.03% with 0.11 ± 0.01% being inorganic carbon.

The major crystalline phases present in the dust, as revealed by the XRD analysis, are: zincite (ZnO), franklinite ($ZnFe_2O_4$), magnetite (Fe_3O_4), halite (NaCl), sylvite (KCl), lead hydroxyl chloride (PbOHCl) and hematite (Fe_2O_3) [8].

Powdered 3,3′,5,5′-tetrabromobisphenol-A (TBBPA) of > 97% assay was obtained from Sigma-Aldrich. It was mixed with different proportions of EAFD collected from a Jordan Steel smelter located at Hashimia/Jordan (1:1, 1:2, 1:3, and 1:4 of EAFD: TBBPA designated as E-TBBPA1, E-TBBPA2, E-TBBPA3, and E-TBBPA4, respectively). To insure the good mixing the proper amounts of EAFD and TBBPA were dry mixed in ball mill with ceramic balls for 15 min.

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) analyses of the initial materials (EAFD, TBBPA) and their mixtures were performed using a TA-Q600 thermal analyzer. A representative 10 mg sample of the specified material was placed in a platinum pan and heated at different heating rates (5, 10, 30 and 50 °C/min.) under nitrogen at a flow rate of 50 ml/min.

3. Modelling of non-Isothermal kinetics

The rate of thermal decomposition of a solid material (dα/d*t*) can be expressed as the product of a temperature dependent specific reaction rate constant and a temperature independent function of the degree of conversion:

$$r_A = \frac{d\alpha}{dt} = k(T)g(\alpha) \tag{1}$$

where r_A is decomposition rate, *k* denotes the reaction rate constant, α signifies the extent of conversion and g(α) is a temperature independent function of conversion. The mathematical expression of the later relies on the proposed mechanism of decomposition. For polymer materials, g(α) is assumed to depend on the amount of unreacted polymer material, that is [30,31]:

$$g(\alpha) = (1-\alpha)^n \tag{2}$$

in which *n* represents the reaction order. The degree of conversion (α) is calculated from TGA data as a time dependent mass loss ratio according to

$$\alpha = \frac{W_o - W_t}{W_o - W_f}$$

where W_o, W_t and W_f are the initial mass of the sample, the actual mass at point in time during the degradation process and the final mass of the sample; respectively.

The temperature functionality of the reaction rate constant can be expressed based on the Arrhenius formula:

$$k(T) = Aexp\left(\frac{-E}{RT}\right) \tag{3}$$

where *E* represents the reaction activation energy, A is the pre-exponential factor, *R* is the universal gas constant and *T* is the absolute temperature (in K).

It follows that, the decomposition rate can be expressed as,

$$r_A = \frac{d\alpha}{dt} = Aexp\left(\frac{-E}{RT}\right)g(\alpha) \tag{4}$$

Assuming a constant heating rate at $\beta = dT/dt$, then Eq. (4) can be as arranged into;

$$\frac{d\alpha}{dT} = \frac{A}{\beta}g(\alpha)exp\left(\frac{-E}{RT}\right) \tag{5}$$

The integral form of Eq. (5) can be written as,

$$\int_0^\alpha \frac{d\alpha}{g(\alpha)} = \frac{A}{\beta}\int_{T_0}^{T} exp\left(\frac{-E}{RT}\right)dT \tag{6}$$

Based on the above analysis, different models have been proposed to calculate the activation energy and the pre-exponential factor using either the differential form (Eq. (5)) or the integral form (Eq. (6)) by measuring the mass loss (conversion) as a function of temperature at different heating rates (*β*). In this case, non-isothermal TGA data can be used to extract these kinetic parameters.

The Kissinger model utilizes the first derivative of the mass loss function $g(\alpha) = n(1-\alpha)^{n-1}$. At the maximum conversion point (α_{max}, T_{max}), the derivative of the mass loss function equals zero and hence the Kissinger model can be written as [32],

Table 1
Chemical composition of EAF dust (wt% – dry base) [13].

Zn	Fe	Ca	Na	Pb	Si	K	Mn	S	Mg	Al
25.91 ± 0.09	18.04 ± 0.31	3.98 ± 0.03	3.29 ± 0.03	3.15 ± 0.03	2.76 ± 0.08	1.84 ± 0.02	1.24 ± 0.01	0.78 ± 0.01	0.64	0.50 ± 0.00