Thermogravimetric analysis and kinetic study on large particles of printed circuit board wastes

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A B S T R A C T

Pyrolysis of large printed circuit board (PCB) waste particle was conducted on a specially designed laboratory-scale thermobalance (Macro-TG) with sample loading of 30 g under dynamic nitrogen atmosphere. The effects of heating rate (10, 15, 20 and 25 °C min⁻¹) and particle size (1 mm × 1 mm, 5 mm × 5 mm, 10 mm × 10 mm and 10 mm × 20 mm) were examined. To compare the different decomposition behavior of fine and large one, the thermal decomposition of PCB waste powder (approximately 5 mg) was also performed on a thermogravimetric analyzer (common TG) under various heating rates (10, 15, 20 and 40 °C min⁻¹) and particle size ranges (0.198–0.165 mm, 0.165–0.074 mm, 0.074–0.055 mm and 0.055–0.047 mm). Experimental results show that large particle has a pyrolysis reaction retardancy compared to fine one. The distributed activation energy model was used to study the pyrolysis kinetics. It was found that during pyrolysis process, values of frequency factor (k₀) changed with different activation energy (E) values. On common TG, the E values range from 156.95 to 319.37 kJ mol⁻¹ and k₀ values range from 2.67 × 10¹³ to 2.24 × 10¹⁰ s⁻¹. While, on Macro-TG, the range of E was 31.48–41.26 kJ mol⁻¹ and of the frequency factor was 19.80–202.67 s⁻¹.

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1. Introduction

The production of electric and electronic equipment is increasing worldwide. Both technological innovation and market expansion continue to accelerate the replacement of electric and electronic equipment and result in the generation of waste electric and electronic equipment in large scale. In China, by the year 2010, the number of obsolete larger household appliances (color TV sets, refrigerators, washing machines, air conditioners and personal computer) would be more than 160 million units (Li et al., 2006). Printed circuit board (PCB) is a major constituent of these obsolete and discarded electronic scraps and it accounts for approximately 30% of the total electronic scrap generated (Murugan et al., 2008). Due to the heterogeneous mix of organic material, metal and glass fiber, PCB waste is particularly problematic to recycle. However, the quantity of metals, especially copper, turns the PCB waste into an interesting raw material according to the economic point of view. In addition, PCB waste represents a significant quantity of energy in terms of the energy consumed in processing petroleum. To recover part of this energy content in a form with the highest possible value, i.e., fuel oils, would be economically and environmentally attractive. Moreover, the mandatory requirement of recycle and reuse of electronic scraps arising from PCB also drives the search of an environmentally safe manner to reuse and recycle PCB waste. Compared to landfill, incineration and other methods, pyrolysis can be considered as a viable technology to treat PCB waste. Since pyrolysis can lead organic substances to decompose to gases and liquids which can be used as chemical feedstock and usable fuels, while inorganic components (metals, fillers, glasses, etc.) generally remain unchanged (Blazsó et al., 2002; Marco et al., 2008). Simultaneously, the solder used to attach the electrical components to the printed circuit boards will melt. The combination of the removal and recovery of the organic fraction of printed circuit boards and the removal of the solder should aid the separation of the metal components from the organic material (William and Paul, 2007).

Thermogravimetric (TG) analysis is one of the techniques for studying the primary reaction in the decomposition of solids and has been widely used to study the thermal decomposition of PCB waste. The interpretation of the experimental data can provide information on the composition of the sample, order of reaction, number of different processes taking place in the reaction, and the corresponding kinetic constants. For an adequate design of a pyrolytic equipment, it is necessary to know the activation energy and the rate of the thermal decomposition of PCB waste which relies on kinetic studies of PCB waste under conditions of pyrolysis. In recent years, many researches into kinetic studies of PCB waste have been reported and most literatures available about kinetic studies have been conducted on commercial theromobalance equipments (named common TG) which take samples in the size of milligrams (Chen et al., 1999; Liou, 2004; Barontini and Cozzani, 2009).
Dates for the kinetic analysis of the PCB waste pyrolysis were generated using two different types of experimental setup: common TG apparatus and Macro-TG apparatus.

2.2. Apparatus and procedure

2.2.1. Common TG apparatus

Common TG analysis has been carried out in a WCT-1C thermobalance, consisting of a 1 mg precision microbalance and an alumina oven with graphite resistance of 0.1 °C precision, which allows continuous data registering. The temperature is controlled by a type-K chromel–alumel thermocouple wire placed about 1–2 mm below the platinum crucible. Each run, about 5 mg of PCB waste powder was placed in an alumina pan, and heated from room temperature to 800 °C at prefixed heating rate (10, 15, 20 and 40 °C min⁻¹) and then kept isothermal for 10 min. The data was recorded every 1 s by a data logging system, which provided listings of sample weight and temperature with time. The carrier gas (N₂) flow rate was maintained at 30 mL min⁻¹ for all TG experiments. The total analysis time was approximately 60 min. To verify the validity of the data, all experiments were performed two times.

2.2.2. Macro-TG apparatus

Thermogravimetric system built for pyrolysis studies of large PCB waste particle is shown schematically in Fig. 1. The main components of the system were a balance sensor which provided a means of measuring weight changes in all runs, a cylindrical stainless steel reactor with inlet for the carrier gas (N₂) and outlet for the volatiles and tars, a temperature controlled furnace and a computer to continuously record the weight and temperature for the entire reaction period.

The stainless steel reactor measured 375 mm in length by an internal diameter of 57 mm and was externally heated by a 2.5 kW temperature controlled furnace. The effective heating zone of the steelness reactor was about 265 mm. The sample basket was 25 mm in diameter and 90 mm in length, each run approximately 30 g of sample was placed in the sample basket. And then it was freely hung by a suspension wire from one end of the Level into the furnace tube. A type-K chromel–alumel thermocouple located directly above the sample basket was introduced to register the sample temperature during pyrolysis process. The Macro-TG reactor is capable of pyrolysing samples up to 800 °C at prefixed heating rate (in the range of 0–99 °C min⁻¹). Subsequently, approximately 30 g weights, with the bottom of which was slightly put on the electronic balance, was also suspended by a suspension wire and then connected to another end of the Level. The carrier gas was firstly introduced at a large rate of flow to purge residual impurities within the system, and then was established at 1.6 L min⁻¹. When the electronic balance output was stable, the furnace power was turn on for the pyrolysis to begin. As the sample began to decompose, the balance output would change. According to the Level law, the weight loss of the sample would be equal to the weight increase of the electronic balance output. Thus, the change in the mass of the sample would be known. Simultaneously, the mass-change to time and reaction temperature was recorded on a personal computer at sampling rates of 2 s. In order to ensure that the sampling technique employed was valid, a
separate blank run was conducted using an empty sample basket under each heating rate and this was used for baseline correction during pyrolysis of the sample. A problem encountered when constructing the Macro-TG was to eliminate the potential effect of gas convection on the experimental results caused by the gas flowing through the reactor. In order to solve this problem, a section of porous ceramic, which was put on the bottom of the reactor, was employed. As carrier gas was introduced to the reaction tube, it firstly passed through porous ceramic layer, and was preheated to reaction temperature due to the good regenerative heat of porous ceramic. In addition, the uniform distribution of through pores embedded in the ceramic enables the carrier gas distribution in homogeneous. By this means, buoyancy force and impact force of the carrier gas to the sample basket would be reduced to a lesser extent. Volatile products evolved during thermal degradation were transferred by the purge gas to the good regenerative heat of porous ceramic. In addition, the temperature of the furnace or the sample because of heat transfer limitations. While at the same time, higher heating rate may be required for the purge gas to reach equilibrium with the furnace power was turned off but the carrier gas was kept flowing until the reactor was cooled down to the room temperature. All experiments were carried out at atmospheric pressure.

3. Results and discussion

3.1. Common TG results

3.1.1. Effect of heating rate

Heat rate would be an important parameter in possible commercial applications because it would depend on the reactor used (Mastral et al., 2000). In this section, the PCB waste powder was not sieved to guarantee that the experimental data is in good agreement with the PCB waste characteristics. TG and DTG profiles obtained from the pyrolysis of PCB waste powder by different rates (10, 15, 20 and 40 °C min⁻¹) are shown in Fig. 2. Both TG (Fig. 2a) and DTG (Fig. 2b) curves shift to higher temperature at higher heating rates. Further, the initial reaction temperature (T₁), DTG peak temperature where the rate of weight loss is at a maximum (T₂) and final reaction temperature (T₃) all increased as the heating rates increased. Chen and Yeh (1996) found results similar to these. From Fig. 2 it also could be seen that T₁ varied in a temperature interval of 295–309 °C, T₂ max was about 316–341 °C and T₃ changed between 360 and 420 °C. The lowest values of these temperatures interval belong to the smallest heating value, and the upper limit of this range was determined for the biggest heating rate.

Heating rate could affect the pyrolysis of the sample from the following aspects: with an increase in heating rate, a larger instantaneous thermal energy is provided in the system and a longer time may be required for the purge gas to reach equilibrium with the temperature of the furnace or the sample because of heat transfer limitations. While at the same time, higher heating rate has a short reaction time (in the same temperature region), and therefore the temperature needed for the sample to decompose is also higher. This causes the maximum rate curve to shift to the right. This phenomenon was also observed by many researchers (Kumar et al., 2008; Liou, 2004; Wang et al., 2008).

3.1.2. Effect of particle size

In order to quantify the effect of particle size on reaction rate, the particle sizes of 0.198–0.165, 0.165–0.074, 0.074–0.055 and 0.055–0.047 mm were used. The TG and DTG profiles of different particle sizes at a heating rate of 20 °C min⁻¹ are compared in Fig. 3. It can be observed that particle size does not affect initial reaction temperature very much, and the values of T₁ were approximately 300 °C. As particle size decreased, peak temperature and final reaction temperature increased slightly. Peak temperatures were 327 °C for 0.198–0.165 mm, 327 °C for 0.165–0.074 mm, 330 °C for 0.074–0.055 mm and 334 °C for 0.055–0.047 mm. While, the final reaction temperatures were determined as 382, 363, 369.


Fig. 2. TG (a) and DTG (b) curves of PCB waste at different heating rates on common TG.
An increasing of evolved volatile matters and tars depends on the radius of the particle (Mermoud et al., 2006). The residence time of evolved volatile matters and tars depends on the radius of the particle inside a particle is different. Secondly, the residence time of evolved volatile matters and tars depends on the radius of the particle (Mermoud et al., 2006). An increasing in particle size causes temperature gradients inside the particle so that at a given time the core temperature is lower than that at the surface, which possibly gives rise to an increase in solids yield and a decrease in liquids and gases (Beaumont and Schwob, 1984).

Many researchers considered that particle size is an important variable which would affect the process rate. At first, due to heat transfer limitations, the heating rate at various position along a radius inside a particle is different. Secondly, the residence time of evolved volatile matters and tars depends on the radius of the particle (Mermoud et al., 2006). An increasing in particle size causes temperature gradients inside the particle so that at a given time the core temperature is lower than that at the surface, which possibly gives rise to an increase in solids yield and a decrease in liquids and gases (Beaumont and Schwob, 1984).

However, Chan et al. (1988) reported that particle size below 5 mm do not exert any influence on the process rate. Encinar et al. (1996) also found that particle size below 2 mm had no influence on the production of liquids and solids. One may therefore assume that inside the particles used in this study (with diameters up to 0.19 mm) there is no temperature gradient that leads to heat transfer limitations. The small difference obtained on TG curves probably due to the great heterogeneity of the sample composition. Chiang et al. (2007) and Liu (2004) considered that sample segregation take place during shredding and sieving process and fines products have a higher resin content than coarse particles. The presence of more resin in fine products makes them have higher temperature. Moreover, decreasing particle size resulted an increase in sample surface, which assisted the constituents in the PCB waste powder to interact with the pyrolysis medium to form volatile product. While at the same time, the carrier gas could reach every particle easily, and volatilization continues until relatively higher temperatures.

### 3.2. Macro-TG results

#### 3.2.1. Effect of heating rate

In this section, the particle size of sample used was 5 mm x 5 mm. Fig. 4a gives weight loss in relation to temperature (TG) during the pyrolysis of the sample. The experimental results (Fig. 4a) show the typical S-curves until the conversion reach values proximate to the unit. It can be also observed that TG curves are moved to the higher temperature when increasing the heating rate. DTG curves (Fig. 4b) of all the samples bear a resemblance during reaction and there is just one peak in each DTG curve. Low heating rate affected the shape of the curves in the favor of narrower and sharper, but increasing heating rate shifted the DTG peak to the right. Agrawal (1992) suggested that the values of $da/dt$ vs. $T$ obtained at different heating rates (Fig. 4b) can indicate whether the process can be described as a simple reaction. The width of the peak indicates the range of temperature for which the reaction takes place and an increase of this range indicates a decrease in the activation energy.

As can be seen, the initial reaction temperature $T_s$ moves from 337 to 383 °C when heating rate increasing from 10 to 25 °C min$^{-1}$. The peak temperature increases from 354 to 431 °C when heating rate varies from 10 to 25 °C min$^{-1}$. And the final reaction temperatures were determined as 373, 402, 446 and 463 °C for the heating rates of 10, 15, 20 and 25 °C min$^{-1}$, respectively. All of them increased as the heating rate increased. Additionally, it is found that at same heating rate, $T_s$, $T_{\text{max}}$ and $T_e$ all have a higher value than those obtained on common TG. Fig. 5 exhibits the TG results of common TG and Macro-TG at a heating rate of 20 °C min$^{-1}$. The
The phenomenon indicates that the large particle size has a pyrolysis reaction retardancy compared to fine one which may be caused by heat transfer limitation.

In our experiments, there may be three transport processes that may influence the global rate: (1) intraparticle transport which is affected by particle size; (2) particle-to-fluid transport which depend on carrier flow rate and particle size; and (3) intraparticle transport which depends upon the number of layers of particles in the sample basket (Encinar et al., 2000). Whenever the sample was heated on Macro-TG reactor, heat is first transferred to the particle surface by means of radiation and/or forced or natural convection, and then, heat is transferred inside the particle by conduction and through the pores by convection (Jalan and Srivastava, 1999). Large mass loading on Macro-TG reactor tends to deflect the measured temperature from the actual sample temperature and results in the reaction to take place inhomogeneously around the sample (Milosavljevic and Suuberg, 1995). Additionally, large particle size of the sample caused a significant temperature gradient increase between the surface and inner of the sample particles, and carrier gas can not easily diffuse into the sample. At first the light products from the surfaces of the sample particles were carried out by flow gas, and then would be that from the inner particle. This situation may result in reduction of conversion and retardancy of reaction.

3.2.2. Effect of particle size

For a gas–solid reaction system, reducing the sample size would be favor on the reaction to take place uniformly around the sample. Fig. 6a shows the TG profiles of PCB waste sample with different particle sizes (1 mm × 1 mm, 5 mm × 5 mm, 10 mm × 10 mm and 10 mm × 20 mm) at a constant heating rate of 20 °C min⁻¹. It can be observed that the curves obtained at 1 mm × 1 mm and 5 mm × 5 mm are very similar, and the same occurs with the curves at 10 mm × 10 mm and 10 mm × 20 mm. However, the mass loss profiles shift toward lower temperature at fine particle size. The corresponding DTG curves were shown in Fig. 6b. It can be seen from Fig. 6 that the initial reaction temperature is about 377–395 °C, the peak temperature is about 404–433 °C and the final reaction temperature is in the range of 446–481 °C. The phenomenon of pyrolysis reaction retardancy also exited when compared to fine powder. A possible reason for this may be that smaller particles are heating more uniformly and thus heat and mass transfer are easily facilitated which results in a higher mass loss (Katyal et al., 2003).

Additionally, in our experiments, for the same sample loading and for one sample basket, increasing the particle size will result in increasing the number of layers of particles in the sample basket which will affect intraparticle transport. Since a large number of volatile compounds are formed during thermal degradation of epoxy resin. In order to increase the rate of thermal decomposition, the gas volatiles should be removed as soon as possible. Owing to larger sample loading and an increase in the number of layers of particles, the carrier gas can not easily flow throughout the sample and this caused higher volatile residence time in the particles which may result in a greater possibility of secondary reaction.

4. Distributed activation energy model (DAEM)

4.1. Theoretical background

The so-called distributed activation energy model (DAEM) has been widely used to analyse complex reactions, such as pyrolysis of coals (Reynolds and Burnham, 1993). However, the previous methods used in this model were complex. Miura (1995) proposed a simple method for DAEM to investigate the kinetic parameters for the coal pyrolysis. This simplified method does not require a prior assumption and mathematical model fitting for obtaining the kinetic parameters. Only a set of experimental data obtained at three different heating profiles are required.

Where the model is applied to analysis PCB waste pyrolysis, change in the total volatiles, V, against time, t, is given by

\[ 1 - \frac{V}{V_e} = \int_0^\infty \exp \left( -k_E \int_0^t e^{-E/k} dt \right) f(E) dE \]  

(1)

where V is the total volatiles evolved by time t; V_e is the effective volatiles content of the pyrolysis sample; E is the activation energy;
The differences in the activation energies of many reactions; 

\[
\int_0^\infty f(E) dE = 1
\]  

(2)

For simplification, Eq. (1) can be rewritten as follows:

\[
1 - \frac{V}{V^*} = \int_0^\infty \phi(E, T) f(E) dE
\]

(3)

where, \( \phi(E, T) \) is equated to

\[
\phi(E, T) = \exp \left( - \frac{k_0}{a} \int_0^T e^{-E/kT} dT \right)
\]

(4)

and \( a = \frac{dT}{dt} \), the heating rates of pyrolysis.

By using a variable \( x = E/RT \) and employing an approximation \( p(x) = e^{-x^2} \), Eq. (4) can be simplified to

\[
\phi(E, T) = \exp \left( - \frac{k_0 RT^2}{aE} e^{-E/RT} \right)
\]

(5)

By further simplification by Miura (1995), the Arrhenius equation can be described as follows:

\[
\ln \left( \frac{a}{T^2} \right) = \ln \left( \frac{k_0 R}{E} \right) + 0.6075 - \frac{E}{R}
\]

(6)

Using Eq. (6), we can estimate both \( E \) and \( k_0 \) from the Arrhenius plot of \( \ln(a/T^2) \) vs. \( 1/T \) at the selected \( V/V^* \) values for different \( a \) values.

Different heating rates given different Arrhenius plots, therefore, theoretically, if two heating rates are used, a series of \( E \) values can be calculated from the slopes of the straight lines at different \( V/V^* \) levels. Considering the errors existing in experimental data, three different heating rates of 10, 15 and 20 °C min\(^{-1}\) were used in our study.

### 4.2 Kinetic analysis of PCB waste pyrolysis using DAEM

Fig. 7 show the relationships of \( V/V^* \) vs. \( T \) for PCB waste sample measured at \( a = 10, 15 \) and 20 °C min\(^{-1}\) on common TG and on Macro-TG, respectively. The Arrhenius plot of \( \ln(a/T^2) \) vs. \( 1/T \) was performed to obtained activation energy \( E \) at each selected of \( V/V^* \) and the results are shown in Fig. 8. Table 2 represents the calculated activation energy \( E \), frequency factor \( k_0 \) and correlation coefficients of least-squares analysis for a certain \( V/V^* \) value. According to Table 2, it is found that values of \( k_0 \) changed greatly with different \( E \) values. Kinetic analysis of PCB waste pyrolysis showed that the activation energy obtained was 156.95–319.37 kJ mol\(^{-1}\) with common TG and 31.48–41.26 kJ mol\(^{-1}\) with Macro TG. The difference in these activation energies is more than twice with common TG and less than 1.3 times with Macro-TG. It is can be considered that Macro-TG is more effective for recycling materials or wastes.

In present investigation, the activation energies obtained by DAEM for thermal decomposition on common TG may be divided into three groups over the whole range of conversion degree

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**Fig. 7.** \( V/V^* \) vs. \( T \) relationship measured at \( a = 10, 15 \) and 20 °C min\(^{-1}\) on common TG (a) and Macro-TG (b).

**Fig. 8.** Arrhenius plot of \( \ln(a/T^2) \) vs. \( 1/T \) at selected \( V/V^* \) values on common TG (a) and Macro-TG (b).
(V/V’ <0.25, 0.25–0.55, >0.55), which indicated that the degradation process of PCB waste is much more complex than a single component. The typical PCB waste mainly consists of epoxy resin, glass cloth filament, copper coils and metal (Sn, Pb, Fe, Ni, etc.). In general, liquefied epoxy resin is blended with brominated compounds (i.e., tetrabromobisphenol-A) to reduce the flammability of the boards. For crushed PCB waste, a perfect dissociation of the metals and the nonmetals can be achieved when its size is less than 0.6 mm (Li et al., 2007). Hence, thermolysis of PCB waste on common TG may consist of two competitive reactions: the thermal decomposition of brominated part and non-brominated part. These two steps may partially overlapped in continuous heating condition. So the V/V’ range from 0.25 to 0.55 corresponds to a transition from the first stage to the second one. However, the V values obtained on Macro-TG changed very little during pyrolysis process, which indicated that there was only one reaction occurred. This means that the decomposition of brominated part and non-brominated part entirely overlapped. From above observation, it can be concluded that an “individual pyrolysis effect” was indicated on common TG while a “group pyrolysis effect” was showed on Macro-TG for the inherently heterogeneity materials thermal decomposition.

It could also be observed from Table 2 that the activation energy on Macro-TG is significantly smaller than that on common TG at the same degree of conversion. The small activation energy for the pyrolysis reaction on the Macro-TG indicates that there may be significant mass and heat transfer effect during pyrolysis in the Macro-TG reactor. This phenomenon may be due to the fact that the thermal decomposition of resin is highly exothermic (Budrugeac, 1993). On common TG, since only approximately 5 mg sample was used, the mass transfer effect could be neglected. However, on the Macro-TG reactor larger amounts of sample loading will adversely release the reaction heat which could make the pyrolysis of the sample becoming easier and consequently the lower activation energy values were adequate to complete the pyrolysis process. Ferdous et al. (2002) also obtained the same conclusion when they studied the kinetic of lignin in a fixed-bed reactor.

### 5. Conclusions

The pyrolysis characteristic and kinetic behavior of fine and large PCB waste particle were studied on a common TG and a Macro-TG under nitrogen atmosphere. The effect of operating variable (i.e., particle size, heating rate) on the overall reaction rate is investigated. It is found that heating rate could not only affect the temperature at which the highest weight loss rate obtained, but also affect the maximum value of weight loss rate. TG curves obtained on Macro-TG are smoothly with one inflection point during reaction, and that there is just one peak in each DTG curve. The TG and DTG shapes are the same with those obtained on the common TG. But due to the large sample loading and large particle size used on Macro-TG, there exits significant difference between the decomposition behavior of fine and large PCB waste particle. Large particle has a pyrolysis reaction retardancy compared to fine one.

A distribution activation energy model was successfully applied for the kinetics of the pyrolysis of PCB waste sample. Results show that the values of frequency factor changed with different activation energies. Common TG experimental results indicated that the $E$ values of PCB waste pyrolysis range from 156.95 to 319.37 kJ mol$^{-1}$ and the $k_0$ values range from 2.67 to 10$^{13}$ to 2.24 to 10$^{17}$ s$^{-1}$. Macro TG results show that the range of activation energy was 31.48–41.26 kJ mol$^{-1}$ and of the frequency factor was 19.80–202.67 s$^{-1}$. The small activation energy for the pyrolysis reaction on Macro-TG indicates that there may be significant mass and heat transfer effect during pyrolysis. The variety of $E$ during pyrolysis process indicated that the degradation process of the PCB waste is much more complex than a single component, and a degradation mechanism, which consists of two reactions (degradation of brominated part and non-brominated part of PCB waste), is proposed as one possible way of thermal decomposition on common TG. However, on Macro-TG, these two steps maybe entirely overlapped, which would add the difficulty to control of toxic substances generated during pyrolysis process. These results would be useful in solving the disposal problems, and in developing pyrolysis systems for other inherently heterogeneous wastes.

### References


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