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Recovery of Metallic Materials from Printed Wiring Boards by Green Pyrolysis Process

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Currently, the main options for the treatment of electronic waste are involved in reuse, remanufacturing, and recycling, as well as incineration and land filling. Recycling of e-waste can be broadly divided into three major steps: (a) disassembly: selectively disassembly, targeting on singling out hazardous or valuable components for special treatment, is an indispensable process in recycling of e-waste; (b) upgrading: using mechanical processing and/or metallurgical processing to up-grade desirable materials content, i. e. preparing materials for refining process; (c) refining: in the last step, recovered materials are retreated or purified by using chemical (metallurgical) processing so as to be acceptable for their original usage.

To investigate an environmentally friendly process to recycle PWBs, the milled PWB powder samples with and without additives were pyrolyzed. Liquid, gas and solid products were achieved with different conversion fraction. PWB powders were pyrolyzed and in a thermo-gravimetric analysis, differential thermal analysis (TG/DTA) and exhausted gases were analyzed by mass spectrometer (MS). Analysis of the exhaust gases from the experiments using TG-DTA-MS showed that without $CaCO_3$ additives poisonous gases such as C_6H_6 and HBr were produced which were adequately controlled if $CaCO_3$ was added.

Keywords: WEEE, PWB, mechanical recycling, green pyrolysis, recovery of metals.

1. INTRODUCTION

Technological innovation and intense marketing is accelerating the update rate of electric and electronic equipment (EEE) and shorten the average lifespan. As a result, the amounts of wastes of electric and electronic equipment (WEEE) containing 3 % of printed wiring boards (PWB) are dramatically increasing. The UN Environment Program estimates that the world generates 20 – 50 million tones of WEEE each year and amounts are rising three times faster than other forms of municipal waste [1].

A significant amount of WEEE is still exported outside the EU (China, India) to maximize profits of recycling companies and scrap dealers, but on the other hand the used acid-baths for leaching process of precious metals is causing environmental pollution and serious health risks by released heavy metals and poisonous chemicals [2].

Disposal in landfill is the main method for treating non-metallic materials of PWBs, but it may cause secondary pollution and resource-wasting [3]. Therefore an integrated environmentally viable solution for recycling PWB is needed.

PWBs incorporated in the most electrical and electronic equipment contain valuable metals such as Cu, Ni, Au, Ag, Pd, Fe, Sn, and Pb. In order to employ a hydrometallurgical route for the recycling of valuable metals from PWBs, a mechanical pre-treatment step is needed allowing materials liberation and size reduction [4]. Electronic scrap from PWBs can be processed by mechanical methods like stamping, hammering, cutting or disintegrator milling [4 – 6].

Particle size, shape and degree of freedom play crucial role in material separation process [6 – 7]. Our previous studies have demonstrated that the medium particle size of the plastic component from a PWB after 4-stage disintegrator milling was near to 1 mm and after final milling the arithmetic mean diameter of the particle was 74 μm [5].

After milling the PWB powder was classified into fractions by sieving (– 0.125 mm; (0.125 – 0.315) mm; (0.315 – 0.63) mm; (0.63 – 1.25) mm; (1.25 – 2.5) mm; (2.5 – 5.6) mm and (5.6 – 11.2) mm) [5].

Magnetic separation of the ferrous metals showed sufficiently good results for larger fractions but for fractions with particle size less than 0.63 mm the separation is less effective because of the particles were adhering to each other [7].

Based on our earlier experimental results new inertial air-classifier was developed for separation of metallic and organic materials from PWB powders [7]. The best air separation results gave the milled PWB powder with particle size <2 mm. After the two times air separation the obtained powder had 80 % of metallic content.

The study of the chemical composition by energy dispersive X-ray microanalysis (EDS) of the PWB powder particles showed that in the plastic particles metallic grains or crystals are in the matrix and thus are not well separated by density separation or the air classification methods [5, 7].

For recovery of organic fraction of PWBs one of the options could be the design and preparation of new filler materials with higher density [8], good thermal resistance and dimensional stability in epoxy or phenol resin based compounds [2 – 3].

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Ferrous metals can be recovered by metallurgical methods. For separation and recovery of non-ferrous metals from milled material the pyrometallurgical or hydrometallurgical methods are applied [9 – 11].

Analysis of the exhaust gases from the experiments by using TG-DTA-MS (Thermo Gravimetric – Differential Thermal Analyzer – Mass Spectrometry) equipment showed that in pyrolysis of PWB powders without $CaCO_3$ additives the poisonous gases such as C_6H_6 and HBr were produced. Our experiments showed that the formation of poisonous gases was adequately controlled when $CaCO_3$ chemical powder was mixed with PWB before pyrolysis experiments.

The 50 gram scale pyrolysis experiments were performed using a high temperature tube furnace. The gas products, the liquid oil products and the solid products were collected and analyzed using GC-MS and ICP-MS equipment.

This inert gas controlled pyrolysis method provides a approach for the recovery of valuable metals from PWB and simultaneously control the emission of toxic gases.

The aim of the current study is to investigate the pyrolysis process of PWB powders and PWB powders + chemical additives in a small TG-DTA scales to control the formation of toxic gases like HBr and C_6H_6.

2. EXPERIMENTAL

The powders of Printed Wiring Boards (PWBs) with size of 100 µm – 500 µm were pyrolyzed in a TG/DTA-MS machine. Argon gas was used as carrier gas.

The evolved gases were measured using a MS. The initial mass, heating rate, carrier gas type and its flow rate, terminal temperature (T_m) and the holding time at T_m were varied in the experiments.

Pre-purging of gases was carried out for 60 min in order to keep the initial mass, temperature and atmosphere in a steady condition process.

After reaching T_m, samples were held there for some time, and then the system was naturally cooled down to room temperature.

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1. Pyrolysis of PWBs without Additives

TG, DTG and DTA curves showed that the sample temperature followed the heating procedure and no temperature jump as observed in the case of combustion. The DTA curves of pyrolysis are plotted in Fig. 1. DTA curve during pyrolysis was very complicated; the peak lasts at very long temperature range from 300 °C – 900 °C, which means that pyrolysis reaction occurred within a big temperature range.

Since the PWB is made of mixture of polymers, the degradation reaction for different polymers occurs at different temperature, thus the entire degradation lasts over a very long temperature range.

For current case, the pyrolysis reaction starts at ~330 °C no matter the conditions of gas flow rate and heating rate, with the following special features:

- with 10 °C /min heating rate, there is a small peak before ~250 °C with (50 – 75) ml/min, and a peak at ~700 °C with (100 – 150) ml/min gas flow rate;
- with 50ml/min gas flow rate, there is remarkable peak ~250 °C for (10 – 20) °C /min heating rate, and a peak at ~700 °C for 30 °C /min heating rate.

The TG and DTG curves with different flow rate and heating rate are also shown in Fig. 2. The final remaining mass fraction was somehow independent of gas flow rate, especially >100 ml/min.

To some extent, larger heating rate have accelerated the pyrolysis process. For TV PWB samples, with the same gas flow rate, the final mass fraction with heating rate of 10, 20 and 30 °C/min was 20 %, 22 % and 14 % respectively.

The degradation reactions still continued during the holding period at T_m and the period of temperature declining. The final remaining mass fraction depended on the holding time at the top temperature. Longer holding time degraded more PWBs.

The final mass fraction of PWBs by pyrolysis was 15 % – 25 % of the initial mass, far larger than the combustion process (~3 % – 13% for combustion process).

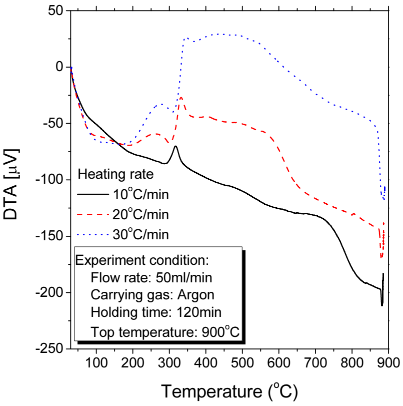

Fig. 1. DTA curves for the pyrolysis of TV PWB powders

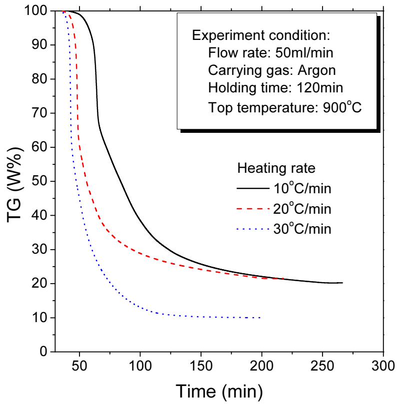

Fig. 2. TG and DTG curves of pyrolysis of TV PWB powders

3.2. Pyrolysis of PWBs with Additives

Pyrolysis experiments of PWB and "PWB+additives" were done using TG/DTA-MS machine. Additives were used to control toxic substances evolving from the pyrolysis process, and to enhance the pyrolysis reaction.

Samples were heated at 15 °C/min heating rate with 150 ml/min gas flow rate. The top temperature was 900 °C and the holding time was 2 hours. Five additive powders were used: $CaCO_3$, CaO, ZSM-5($Na_nAl_nSi_{96-n}O_{192}\cdot16H_2O$ $(0<n<27)$), Y-zeolite ($Na_xAl_YSi_ZO_m$) and Fe_2O_3. The additives were mixed with PWB powders with a mass ratio 5 : 1 (5 PWB : 1 additive).

Table 1 shows the composition of the remaining materials after pyrolysis. The pyrolysis of the pure PWB sample stopped at 77 min with a final mass fraction of ~36 %.

Table 1. The final mass fraction during pyrolysis experiments

	PWB	With additives				
		$CaCO_3$	CaO	ZSM-5	y-Zeolite	Fe_2O_3
Solid fraction, %	35.56	42.85	54.98	55.04	55.02	39.79
Fraction of residue subtracting additives, %	35.56	35.02	40.78	46.05	46.02	27.75

The pyrolysis of PWB+$CaCO_3$ samples stopped at 100 min with 43 % residue remained in the crucible. Since Bromine component in PWBs is ~6.5 % Br component in PWB materials, considering the decomposition of $CaCO_3$ and the reaction between $CaCO_3$ and HBr, there was ~35 % of residue after subtracting CaO and $CaBr_2$.

For the mixture of PWB+CaO, the final residue subtracting the additives and the inorganic products was ~41 %. For ZSM-5 + PWB and Y-zeolite + PWB mixtures, the residue fraction subtracting the additives and the inorganic products with these two additives was ~46 %.

Thus, ZSM-5 and Y-zeolite mainly acted as catalyst to accelerate the pyrolysis reaction but not as reactants. The pyrolysis of PWB+Fe_2O_3 stopped in 113 min with a ~28 % final residue fraction subtracting the additives and the inorganic products.

Thus, compared to other four additives, the effect of Fe_2O_3 on the pyrolysis of PWB was the best.

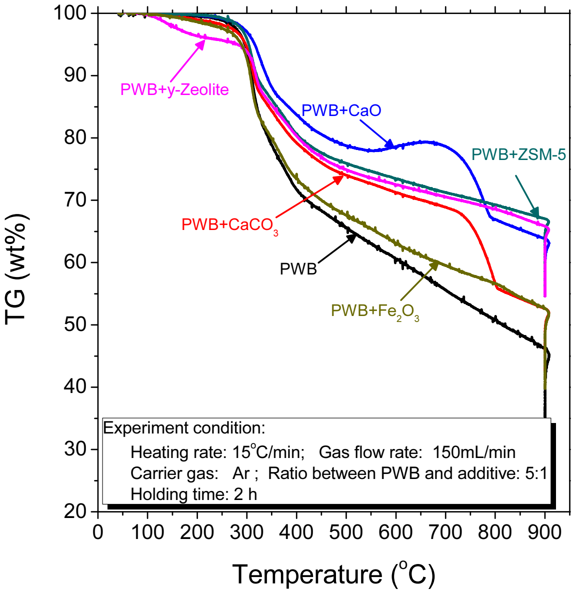

Fig. 3. TG curves for the pyrolysis of "PWB+ additives"

In Figs. 3 and 4 the mass loss fraction with temperature and time is described. The temperature reached the top temperature of 900 °C in 60 min.

DTA curves for different pyrolysis experiments are shown in Figs. 5 and 6. There were many peaks of endothermic and exothermic reactions during pyrolysis.

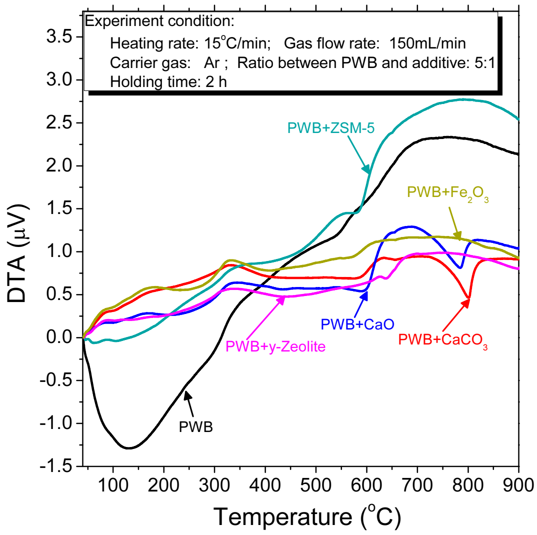

Fig. 4. DTA curves for the pyrolysis of "PWB + additives"

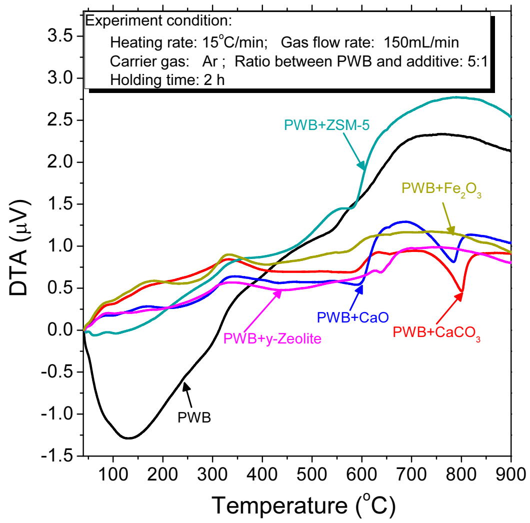

Fig. 5. DTA curves of pyrolysis of "PWB + additive"

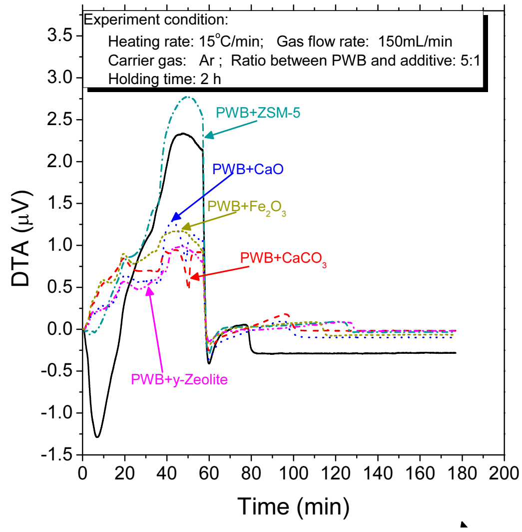

Fig. 6. DTA curves of pyrolysis of "PWB+additive"

For the pyrolysis of PWB + $CaCO_3$, signals of CH_4, CO, C_2H_6, C_3H_4, C_2H_3O, C_3H_6 or C_2H_2O, CO_2 or C_2H_4O, C_2H_5O, Cl_2, C_6H_6, H_2O and HCl were stronger than that of PWBs without additives, which means that $CaCO_3$ has a certain effect on enhancing the pyrolysis process. $CaCO_3$ could also control HBr emission.

CaO had a big effect on promoting the signal intensity of C_2H_2, CO, C_2H_6, HCl, C_3H_4. ZSM-5 could increase the peak of CH_4, HCl, C_3H_4, C_2H_3O, 1st peak CO_2 or C_2H_4O, C_2H_5O and C_6H_6, and lower the peak of HBr and H_2O signals.

Y-Zeolite could perform very well on producing CH_4, H_2O, C_2H_2, CO, HCl, C_3H_4, 1st peak C_2H_3O, 1st peak CO_2 or C_2H_4O, Cl_2 and C_6H_6, and lowers HBr.

Fe_2O_3 helps pyrolyze more PWB samples than other additives. MS signal from the pyrolysis of PWB+Fe_2O_3 had very strong intensity of CH_4, H_2O, C_2H_3O and 1st peak CO_2 or C_2H_4O. Fig. 6 shows that signal intensity of HCl, Cl_2, C_6H_6 and HBr could be controlled to a lower level by Fe_2O_3 than other additives.

MS signal peak intensities of exhausted gases C_6H_6 and HBr during the pyrolysis process are depicted in Fig. 7 and Fig. 8 respectively.

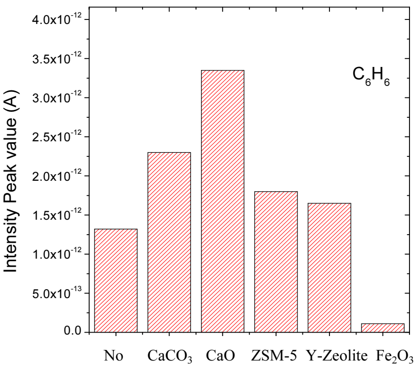

Fig. 7. MS signal of exhausted gas C_6H_6 during pyrolysis process

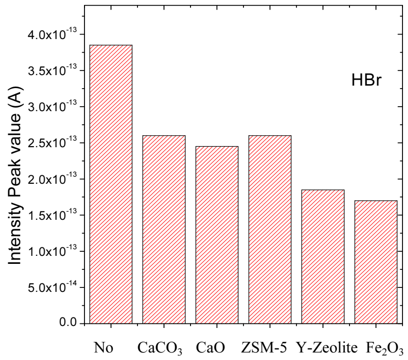

Fig. 8. MS signal of exhausted gases HBr during pyrolysis process

3.3. Kinetic Models for the Pyrolysis of PWBs

A thermogravimetric analysis (TGA) presents weight changes relative to the temperature. In the present study, kinetic models for the pyrolysis of PWB powders were developed.

The following symbols are used: apparent kinetic energy, E_a, (kJ/mol); pre-exponential factor, A (min^{-1}); reaction orders, n and m; gas constant, R (8.314 J/mol.K); absolute temperature, T (K); temperature at maximum conversion rate, T_m; time, t (min); degree of conversion, α; heating rate, β (°C/min), intergral kinetic model, $g(\alpha)$; and differential kinetic model, $f(\alpha)$.

The reaction rate in TGA studies can be defined as the variation of degree of conversion with time or temperature where the conversion (α) is calculated in terms of mass loss according to equation (1).

$$\alpha = \frac{W_0 - W_t}{W_0 - W_f}, \tag{1}$$

where W_0, W_t, W_f are the weights of sample at beginning, actual weight at each point of the curve and the final weight measured after a specific degradation process considered respectively.

Generally, the reaction rate ($d\alpha/dt$) of degradation is proportional to the concentration of the reactant as shown in equation (2):

$$\frac{d\alpha}{dt} = k(T)\cdot f(\alpha), \tag{2}$$

where $f(\alpha)$ is function of conversion and $k(T)$ is the rate constant (min^{-1}). Equation (2) expresses the rate of conversion ($d\alpha/dt$) at constant temperature (T) as functions of the reactant $f(\alpha)$ and the reaction rate constant (k) In case of polymer degradation, it is usual to assume that the rate of conversion is proportional to the concentration of the material which remains to react;

$$f(\alpha) = (1-\alpha)^n \ , \tag{3}$$

where n = reaction order. The function in equation (3) is used in polymer degradation kinetics where a solid material is decomposed to give gaseous reaction products.

Additionally, the temperature dependence of the rate constant, k (T) is by the Arrhenius expression:

$$k = Ae^{-Ea/RT}, \tag{4}$$

The combination of equations (2 – 4) gives the relationship in equation (5)

$$\frac{d\alpha}{dt} = A(1-\alpha)e^{-Ea/RT}, \tag{5}$$

The kinetic analysis methods used for thermal degradation of polymers base on equation 5 are summarized in the Table 2. Friedman's method is the most general derivative technique and is based on the inter comparison of rates of weight loss ($d\alpha/dt$) for a given conversion, α determined by using different linear heating rates β.

Table 2. Approaches to determine apparent activation energy for thermal degradation of PWBs

Method	Equation	x-axis	y-axis
Friedman	$\ln\left(\frac{d\alpha}{dt}\right) = \ln A + n\ln(1-\alpha) + m\ln(\alpha) - \left(\frac{E_a}{R}\right)\frac{1}{T}$	$\frac{1}{T}$	$\ln\left(\frac{d\alpha}{dt}\right)$
Flynn-Wall-Ozawa	$\Delta\ln(\beta) = -1.052\left(\frac{E_a}{R}\right)\Delta\left(\frac{1}{T}\right)$	$\frac{1}{T}$	$\Delta\ln(\beta)$
Kissinger	$\ln\left(\frac{\beta}{T_m^2}\right) = \left(\frac{AR}{E_a}\right) - \left(\frac{E_a}{R}\right)\frac{1}{T_m}$	$\frac{1}{T_m}$	$\ln\left(\frac{\beta}{T_m^2}\right)$
Coats and Redfern	$\ln\left(\frac{g(\alpha)}{T^2}\right) = \ln\left(\frac{AR}{\beta E_a}\right) - \left(\frac{E_a}{R}\right)\frac{1}{T}$	$\frac{1}{T}$	$\ln\left(\frac{g(\alpha)}{T^2}\right)$

Flynn-Wall-Ozawa (FWO) technique offers a simple way of determining activation energies directly from weight loses versus temperature data obtained at several linear heating rates [12, 13]. E_a can be obtained from a plot of $\ln(\beta)$ against $1/T$ for a fixed α. For a first order reaction, the Kissinger method is derived. It allows the determination of the E_a for the degradation process by plotting $\ln(\beta/T^2_m)$ versus $1/T_m$. T_m is the temperature corresponding to the maximum reaction rate i. e. DTG or DTA peak.

Coats and Redfern developed an integral method, which can be applied to TG/DTG data [14]. A plot of $g(\alpha)$ versus $1/T$ gives E_a and A from the slope and intercept of curve respectively. The model that gives the best linear fit is selected.

The different activation energies calculated using these methods are presented in Table 3. From the results of the apparent activation energies, it clear that the Kissinger method gave better linear correlations compared to other methods.

Table 3. Activation energy of PWBs pyrolysis determined by Friedman, FWO and Kissinger

Argon Flow Rate (ml/min)	E_a (kJ/mol)		
	Friedman	FWO	Kissinger
50	183	196	245
75	132	130	199
100	194	181	170
125	200	159	167
150	160	139	188

It is important to note that, the most consistent results were obtained for experiments with the highest argon purge gas flow rate (150 ml/min). The average activation energies for the lower conversion range ($\alpha = 0.1 - 0.4$) at different argon flow rate are presented in Table 3. Average values are also presented.

4. CONCLUSIONS

For small scale pyrolysis of PWB powders using TG-DTA-MS equipment, the reaction occurred within a big temperature range, and there were a few sub-peaks at 350 °C, 500 °C, and 700 °C respectively. The sub-peak temperature slightly increased with increasing gas flow rate.

Longer holding time degraded more PWB. The final mass fraction of PWB during pyrolysis was 15 % – 25 % of the initial mass. Larger heating rate accelerated the pyrolysis process, while the final mass fraction were the same no matter what heating rate was used.

The best pyrolysis conditions were: (15 – 20) °C/min heat rate, >100 ml/min gas flow rate, >900 °C top temperature, and long holding time. Fe_2O_3 is the most effective additive to help control HBr and C_6H_6 during the pyrolysis of PWB. MS signal from PWB+Fe_2O_3 experiment had very strong intensity of CH_4, H_2O, C_2H_3O and 1st peak CO_2 or C_2H_4O. Signal intensity of HCl, Cl_2, C_6H_6 and HBr were controlled at lower level than by other additives.

The average apparent activation energies obtained over the whole composition range from Friedman, FWO and Kissinger methods at 150 ml/min argon flow rate were 168, 166 and 188 kJ/mol respectively. This is in the range of expected values.

Acknowledgments

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