EXPERIMENTAL RESEARCH ON MICROWAVE INDUCED THERMAL DECOMPOSITION OF PRINTED CIRCUIT BOARD WASTES

Zhixiao Zhang
School of Mechanical Engineering, Hangzhou Dianzi University, Hangzhou 310018, China

Xintian Zhao
School of Mechanical Engineering, Hangzhou Dianzi University, Hangzhou 310018, China

Eilhann Kown
Department of Earth and Environmental Engineering [HKSM], Columbia University in the City of New York, USA

Marco J. Calstaldi
Department of Earth and Environmental Engineering [HKSM], Columbia University in the City of New York, USA

ABSTRACT

As a result of electronic industry development in China, significant amount of Printed Circuit Board (PCBs) wastes are generated. The thermal decomposition via combustion or pyrolysis/gasification is considered to be a feasible disposal way for PCBs. To understand the consequences of pyrolysis, gasification or combustion in WTE facilities, thermo-gravimetric analysis (TGA) has been carried to characterize the thermal decomposition mechanisms and extract the kinetic parameters in various atmospheres (N_2, CO_2 and air) to simulate different regions in WTE applications. TGA tests in N_2 atmosphere showed there was only one significant reaction in the low temperature range of 270~350°C, which was the decomposition of epoxy resin in PCBs. The behavior in CO_2 atmosphere was similar with that in N_2. However, the PCBs oxidation process in air atmosphere showed two thermal decomposition steps. One was the thermal decomposition similar to the volatilization in N_2 atmosphere and the second step showed oxidation behavior. Some pre-processing was investigated to explore possible benefits in WTE combustion. PCBs waste was pyrolyzed using a microwave tubular furnace. The liquid product were collected and then identified by means of gas chromatography–mass spectrometry (GC–MS). Most of the Br contained in PCBs was released into non-condensable gas in the form of HBr. The liquid product contained a large amount of phenolic compounds, bisphenol A and other aromatic compounds that can be used to produce related chemical products or used in WTE facilities. The experimental results including the thermal kinetic parameters and microwave induced pyrolysis indicate the complex mechanisms that take place during the pyrolysis of PCBs wastes.

1. INTRODUCTION

Print circuit boards (PCBs) are widely used in electronic products. The worldwide increasing rate of PCBs production is about 8.7% annually, and it is much higher in China, which is about 14.4%. The production of PCBs in China has been over 110 hundred million square meters and valued about $10.8 billion in 2005, which was more than 30% of the global PCBs production. Meanwhile, the cycle time of electronic products became shorter along with the innovation and upgrade of electronic products, which accelerate the replacement of electronic equipments. This results in large amount of PCB wastes from these electronic wastes. An increase about 4-8% by year of the PCB wastes was reported [1].

As an important type of electronic wastes, the component of PCBs is very complicated. PCB usually contains various metals, glass fiber, fire retardants and polymer materials. Mechanical recycling focused on the recovery of metals is the main current disposal method for PCBs. However, the toxic gases and dust emissions are generated during mechanical processing, for example in crushing and separation process [2]. Moreover, the glass fiber and polymers cannot be recycled after mechanical processing. Thus, thermal treatment of PCBs by pyrolysis, gasification or combustion is a more effective way to convert PCB wastes into energy and recover the metals simultaneously [3].

This work is concerned with the experimental research of thermal decomposition of PCBs. To understand the consequences of pyrolysis, gasification or combustion of PCBs in WTE facilities, the kinetic parameters of thermal decomposition of PCBs in different atmosphere were obtained. Furthermore, the microwave induced pyrolysis was performed in a bench scale microwave reactor. The effect of pyrolyzing

reaction conditions on thermal decomposition of PCBs and pyrolytic products were investigated.

2. EXPERIMENTAL

2.1 Materials

The PCB wastes used in this work was supplied by a local electronic laboratory. The PCB is composed of brominated epoxy resin on a supported glass fibers. The copper circuit was printed on the surface. The copper circuit was rasped off manually. Then the metal-free PCB was cut off to 5mm×5mm pieces, and then milled to powder with size between 140-180 mesh. In this work the metal-free PCB powder was used in thermo-gravimetric analysis. The cut off PCB pieces without milling was adopted in microwave induced pyrolysis experiments.

Table 1. Proximate and elemental analysis of PCB

Proximate Analysis /wt.%	
volatiles	23.26
fixed carbon	11.08
Ash	64.91
moisture	0.75
heat value (kJ/kg)	10592
Elemental Analysis /wt.%	
C	24.51
H	2.55
N	0.39
S	0.55
O	6.84
Br	6.43

The proximate and elemental analysis of PCB samples were carried out by a 5E-MACⅢ proximate analyzer and a LECO-CHNS932 elemental analyzer. The results are presented in Table 1. The bromine content of PCB samples was analyzed also, as shown in Table 1.

2.2 Thermo-gravimetric experiment

Thermo-gravimetric experiments were carried out in different atmosphere using a Thermo Electron SDT Q600 TGA system. Heating rates between 5℃/min to 30℃/min from ambient temperature to 900℃ were used in this work. A constant gas flow at 120mL/min of nitrogen, carbon dioxide or air was performed to simulate the pyrolysis, gasification or incineration process. About 8mg of PCB powder was used for each test.

In order to demonstrate the thermal decomposition mechanism of PCB sample, the overall reaction rate equation for the degree of conversion α can be expressed as:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \cdot \exp\left(-\frac{E}{RT}\right) f(\alpha)$$

where T is the reaction temperature(K), β is the heating rate (K/min), A is pre-exponential factor (1/min), E is activation energy (kJ/mol), R is the universal gas constant, $f(\alpha)$ is the kinetic mechanism function.

2.3 Pyrolysis experiments in microwave reactor

A laboratory-scale fixed bed tubular microwave reactor was used to perform the microwave induced pyrolysis experiments. The most popular microwave frequency for heating, 2450Hz, was used for this reactor. The microwave reactor was made of a horizontal placed quartz tube (35mm OD) and a microwave furnace with the capability of operating temperature up to 1000℃ and continuous microwave power output from 0-700W. The temperature of the samples was measured by a K type thermocouple contacted with the PCB sample. Nitrogen was used as the carrier gas at a constant flow of 200mL/min. The overall experimental scheme is presented in Figure 1.
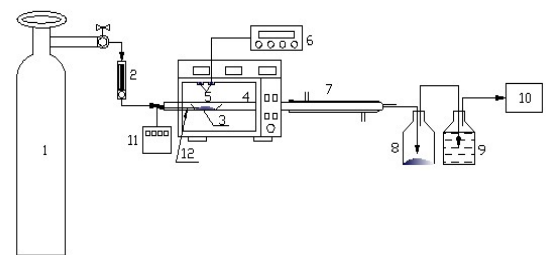
1.N$_2$ 2.Flow meter 3.Quartz carrier 4.Quartz tube 5.IR detector
6.Temperature control 7.Condensor 8.Liquid product 9.Washbottle
10.Gas 11.Temperature meter 12.Thermocouple
Figure 1. Illustration of microwave pyrolysis experiment system

SiC was used as the heating assistant in microwave furnace. A certain quantity of SiC powder was placed at the bottom of the quartz carrier and the cut off PCB sample was placed on the SiC layer. Then the quartz carrier was put in the quartz tube reactor. About 10g PCB sample and 20g SiC powder were used for each test. The pyrolysis experiments were carried out at a microwave power output of 350W, 500W, 600W, respectively, and held 20mins for each run. The volatile products were discharged from the microwave reactor and sent to the condensation and washing system. The liquid pyrolytic product and non-condensable gas were collected respectively. The condensed product on the tube and connection parts was washed out by acetone and collected together with the liquid product. Solid product was gathered when the test finished and the quartz tube was cooled enough.

The proximate and elemental analysis of solid product was carried out using a 5E-MACⅢ proximate analyzer and a LECO-CHNS932 elemental analyzer. The solid product was analyzed using JEOL JSM-6460 SEM/EDS to investigate the detailed surface characteristics and other elements contained.

The components in liquid pyrolytic product were analyzed by Agilent HP6890/HP5793A GC-MS system using a HP-5 column (length 30m, outer diameter 0.25mm, phase thickness 0.25μm). The column was firstly heated to 70℃ and held 3min, then increased to 270℃ at a rate of 20℃/min and held 10-20 min at 270℃. Helium was used as the carrier gas.
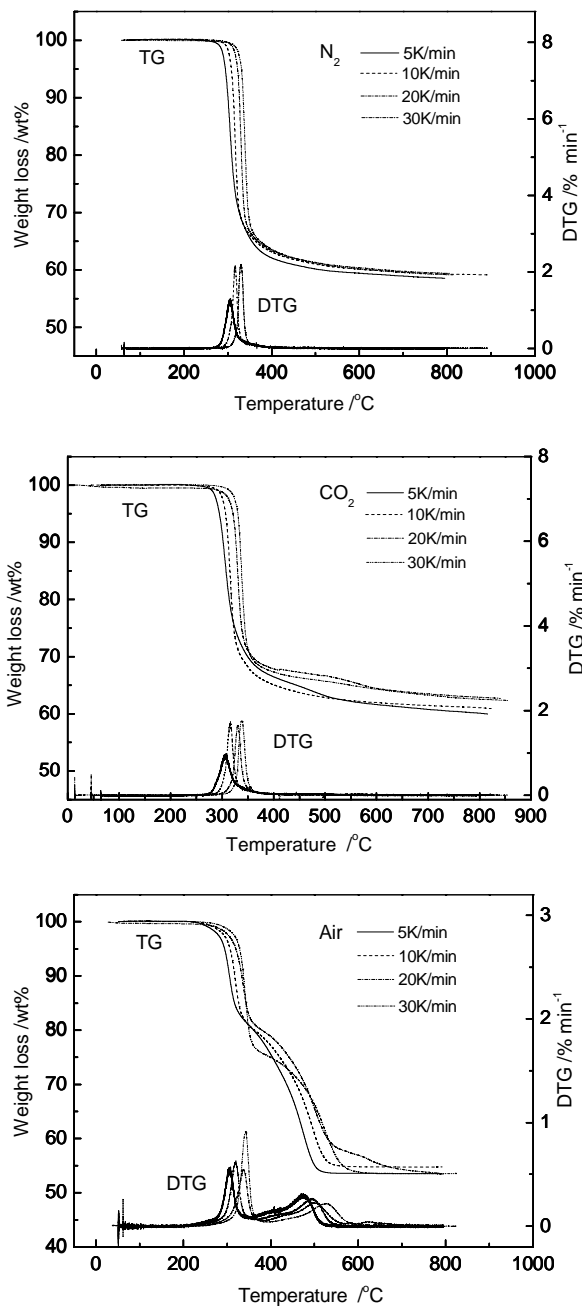
3. RESULTS AND DISCUSSION

3.1 TG-DTG analysis

Figure 2. TG and DTG curves in N_2, CO_2 and air atmosphere

The TGA analysis of brominated epoxy resin based PCB samples in various atmospheres (N_2, CO_2, air) and heating rates (5, 10, 20, 30 ℃/min) were carried out in order to simulate the atmosphere for pyrolysis, gasification or combustion. The TG and DTG curves were presented in Figure 2.

TGA worked in N_2 atmosphere showed that there was just one peak in the temperature range of 270~350℃, which was related to one significant reaction stage. This reaction stage was identified as the decomposition and volatilization of brominated epoxy resin. About 35% of the total mass was decomposed in this stage and another 4% of the PCB samples was further decomposed till the end of reaction at about 560-645℃. Similar to the decomposition behavior in N_2, just one peak appeared in the DTG curve in CO_2 atmosphere in the range of 260-390℃ with about 33% weight loss. The residue mass in CO_2 atmosphere was about 62% that was slightly lower than that in N_2. It is considered that the Boudouard reaction between carbon and CO_2 takes place in a relatively higher temperature range of 700-1200℃. The TGA experiments in this work were up to 900℃, which might restrain the further reaction and the weight loss. However, the PCB oxidation process showed two thermal decomposition steps from the TG and DTG curves in air atmosphere. The first step was similar to the decomposition and volatilization in N_2 and CO_2 atmosphere and the second step showed oxidation behavior. The initial reaction temperature T_i in air atmosphere was slightly lower than that in N_2 and CO_2 atmosphere, as shown in Table 2. The borders of the reaction stages moved to higher temperature when increasing the heating rate. However the initial reaction temperature just slightly changed under different atmosphere. In addition, the total weight loss in a certain atmosphere was similar at various heating rate. Therefore, WTE facilities with big heating rate should be effective to achieve higher efficiency when it is used to deal with the PCB wastes, such as the microwave reactor used in this work.

Table 2. Reaction characteristics of PCB using TGA

Carrier Gas	β /K.min^{-1}	T_i /K	T_f /K	T_{1max} /K	T_{2max} /K	W_f/W_0
N_2	5	264	561	305	—	58.6
	10	279	603	316	—	59.1
	20	292	632	329	—	59.4
	30	304	645	338	—	59.1
CO_2	5	256	565	306	—	60.0
	10	267	501	315	—	60.9
	20	275	591	331	—	62.7
	30	281	607	338	—	62.3
Air	5	235	516	305	472	53.5
	10	241	551	319	494	54.7
	20	255	664	337	499	53.6
	30	268	612	342	527	53.5

The kinetic mechanism parameters including activation energy and pre-exponential factor were determined using Flynn-Wall-Ozawa method. The kinetic mechanism function was verified using Coats-Redfern integral method [4]. The calculation results were presented in Table 3. The results indicate that the thermal decomposition of PCB in various atmosphere exhibits different mechanisms. The thermal decomposition at low temperature range for the there atmospheres adopted is similar.

It follows the stochastic coring and afterward growing mechanism. However, the oxidation reaction in air atmosphere at high temperature range is governed by diffusion mechanism.

Table 3. Kinetic parameters for PCB decomposition

Carrier Gas	E /kJ.mol-1	A /min-1	$f(\alpha)$
N_2	154.76	3.84×10^{11}	$5/2(1-a)[-\ln(1-a)]^{3/5}$
CO_2	156.85	6.31×10^{10}	$2(1-a)[-\ln(1-a)]^{1/2}$
Air	142.99	6.87×10^9	$4/3(1-\alpha)[-\ln(1-\alpha)]^{1/4}$
	165.04	4.46×10^7	$3/2[(1-\alpha)^{-1/3}-1]^{-1}$

3.2 Microwave induced pyrolysis

The microwave induced pyrolysis experiments were performed at different microwave power output using the experimental system shown in Fig. 1. The temperature profiles during the experiments were given in Figure 3. It can be seen that the PCB samples was rapidly heated up in the initial 1-2min. When using 350W microwave power, the temperature of PCB samples was heated to about 325℃ in 1min, and then kept rising to about 440℃ and 490℃ after 10min and 20min respectively. Increasing the microwave power accelerated the heating rate to a great extent. As shown by the temperature profile at 500W or 600W microwave power, the temperature of PCB samples reached up to 500℃ in the initial 1min, then dropped off suddenly to about 350-400℃ due to the decomposition of PCB samples. After this time, the temperature increased continuously.
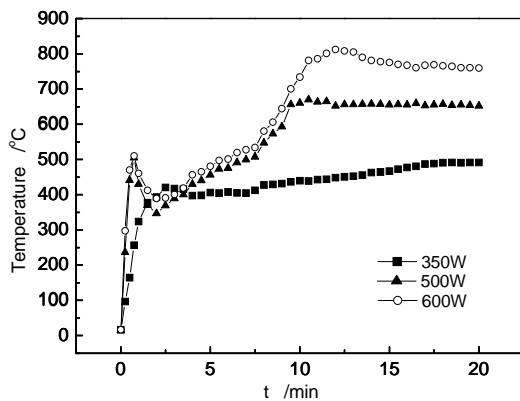

Figure 3. Temperature profile at different microwave power

Figure 4 shows the balance of pyrolysis products yield from the microwave induced pyrolysis of PCB. It can be seen that the pyrolysis was incomplete when using 350W microwave power since the solid yield (71.3 wt.%) was higher than the yield at 500W and 600W. Product balance at 500W and 600W were similar. The solid product about 66.5-68% indicates that the pyrolysis reaction was executed completely compared with the proximate analysis of PCB samples in Table 1.
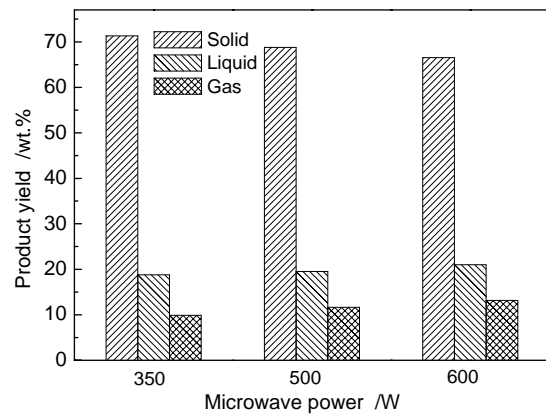

Figure 4. Pyrolysis products yield from microwave reactor

3.3 Characteristic of solid product

Table 4 shows the elemental and proximate analysis of solid product. The drop of volatile content with the simultaneous increasing of ash content in solid product validates the complete pyrolysis reaction at higher microwave power. The solid residue mainly consists of glass fiber, carbon and other inorganic metallic oxide of Ca, Si, Mg, Al, etc.

The SEM images of solid residues at microwave power of 350, 500 and 600W are shown in Figure 5. The surface of solid residue gets smoother at higher microwave power. The structure of galss fiber in PCB is clearly visible after the complete pyrolysis of epoxy resin, such as Fig. 5 (c) and (d). Therefore, the glass fiber and metals can be easily recovered from the solid residue with the energy and resource recovery at the same time during pyrolysis process of PCBs.

Table 4. Elemental and proximate analysis of solid product

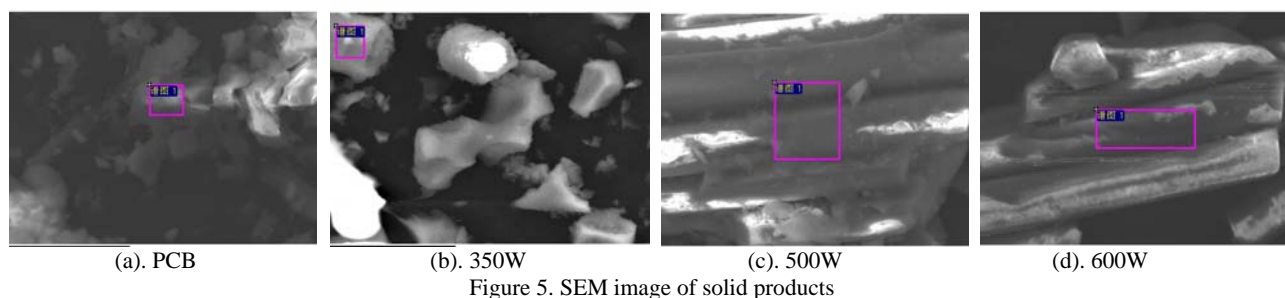| Microwave power /W	Elemental analysis /wt.%						Proximate analysis /wt.%			
	C_{ad}	H_{ad}	N_{ad}	S_{ad}	O_{ad}	M_{ad}	A_{ad}	V_{ad}	FC_{ad}	$Q_{b,ad/kJ.kg-1}$
350W	11.32	0.74	0.35	—	1.76	0.35	85.48	6.05	8.12	4924
500W	9.01	0.29	0.36	—	0.63	0.27	89.44	1.64	8.65	3632
600W(1:2)	9.01	0.26	0.31	—	0.67	0.14	89.61	1.25	9.00	4070

| (a). PCB | (b). 350W | (c). 500W | (d). 600W |

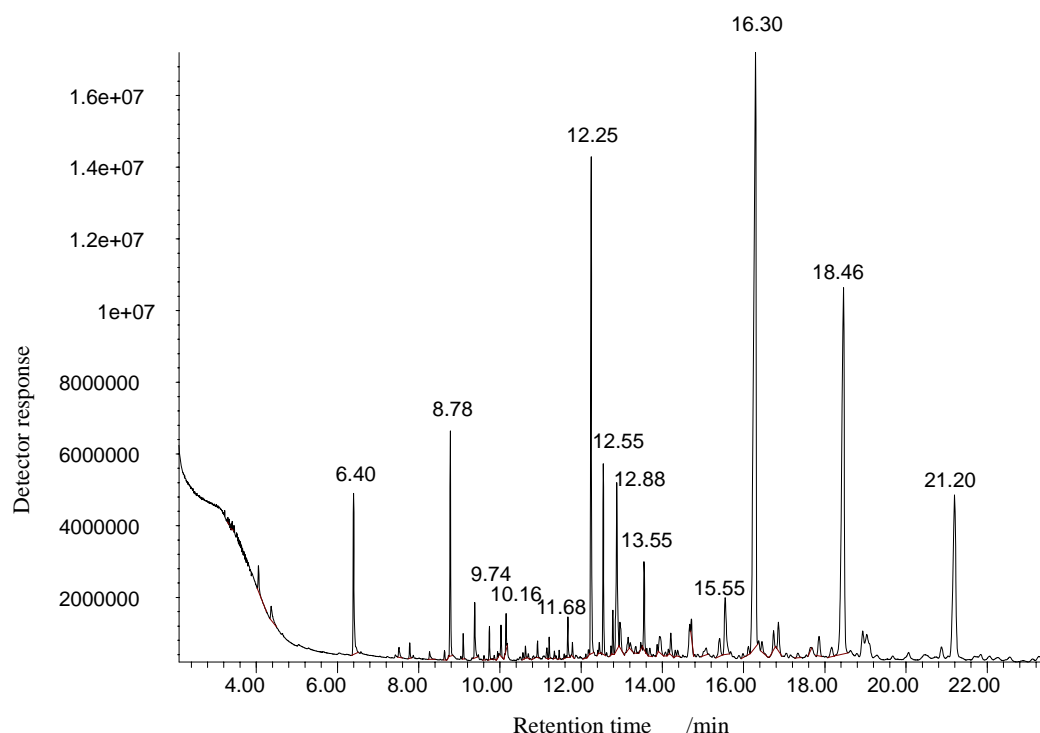Figure 5. SEM image of solid products

Figure 6. The total ion gas chromatogram of liquid product at 600W microwave power

3.4 GC-MS analysis of liquid product

The liquid product obtained from the PCB pyrolysis was analyzed with GC-MS. Figure 6 shows the gas chromatogram of liquid product at 600W microwave power. A list of the main peaks is presented in Table 5.

The liquid product consists of complicated organic substance. It is a mixture of brominated and nonbrominated compounds. More than eighty kinds of compounds were detected by GC-MS. Microwave induced fast pyrolysis of PCB samples leads to many kinds of phenolic, benzene and other aromatic compounds in the liquid pyrolysis product, such as phenol, 4-ethylphenol, naphthalene, 3-isopropylphenol, 1,2,4,5-tetramethylbenzene, p-phenylphenol, 1-(o-tolyloxy)benzene and 4,4'-(1-methylethylidene)bisphenol, namely bisphenol A[5], etc. Especially there are a large quantity of phenolic compounds and

bisphenol A, which are the main products of epoxy resin decompsition. As shown in Figure 7, the content of phenolic compounds decreased when using higher microwave power and related pyrolysis temperature. The complete pyrolysis reaction at higher microwave power leads to the further decomposition of bisphenol A based epoxy resin, and then leads to a increasing of bispeonol A in liquid product.

Due to the brominated fire retardants used in PCBs, a certain kinds of brominated compounds were detected in liquid product as well, such as 2-bromophenol, 4-Bromophenetole, 2,4-dibromophenol, 1-(3-bromo-4-hydroxyphenyl)ethanone, 4,5-dibromo-9-chloroacridine, 4-bromo-2,6-dimethylbenzenamine, (3,5-dibromophenyl)trimethylsilane, etc. The content of brominated compounds and the percentage of bromine in liquid product both decrease with the microwave power. The residual bromine in liquid product is just about 9-

5

14% of the total bromine in PCB. This is considered that most of the bromine contained in PCBs is converted and evaporated as hydrogen bromide during the pyrolysis process [6]. Therefore, the further bromine removal processing should be necessary when the liquid and gas products from PCBs pyrolysis are used in WTE facilities.

Table 5. GC-MS peaks of liquid product at 600W microwave power

| Retention time /min	Compound	Content /wt.%
4.06	(E)-hex-3-en-2-one	0.56%
4.37	2-methylpyridine	0.53%
6.40	phenol	3.21%
7.52	4-Bromophenetole	0.25%
7.78	(E)-N-(1-phenylethylidene)methanamine	0.24%
8.27	4-ethylphenol	0.2%
8.64	naphthalene	0.16%
8.78	3-isopropylphenol	3.39%
9.1	isoquinoline	0.4%
9.39	1,2,4,5-tetramethylbenzene	0.98%
9.74	1-(3-bromo-4-hydroxyphenyl)ethanone	0.49%
9.94	2,3-dihydro-3,4,7-trimethylinden-1-one	0.07%
10.03	3,4-dihydro-2H-chromen-3-ol	0.45%
10.16	2,4-dibromophenol	0.44%
10.57	2,4-dimethylquinoline	0.11%
10.93	2,3-dihydro-5,6-dimethyl-1H-pyrrolo[3,2,1-ij]quinoline	0.25%
11.59	9H-fluorene	0.07%
11.68	5-tert-butylbenzo[d][1,3]dioxol-2-one	0.61%
12.25	p-phenylphenol	8.43%
12.55	N-ethyl-N-tosyletheanamine	2.81%
12.78	4-(1-phenylethyl)phenol	0.68%
12.88	1-(o-tolyloxy)benzene	4.04%
12.96	2-benzylphenol	0.70%
13.16	4-(2-phenylpropan-2-yl)phenol	0.31%
13.55	1-benzyl-4-methoxybenzene	1.67%
13.70	2-(1-phenylethyl)phenol	0.21%
13.88	2-hydroxy fluorene	0.16%
14.21	2-(but-3-en-2-yl)-6-methoxynaphthalene	0.55%
14.72	2-(2-p-tolylpropan-2-yl)phenol	0.32%
15.55	hydroxymethyldiphenylsilane	2.19%
16.30	4,4'-(1-methylethylidene)bisphenol A	27.97%
18.46	(dodecahydro-3,7,10a-trimethyl-3-vinyl-1H-benzo[f]chromen-7-yl)methanol	18.76%
18.94	2,3-dihydro-3-(4-hydroxyphenyl)-3-methyl-1H-inden-5-ol	0.53%
21.20	4,5-dibromo-9-chloroacridine	8.75%
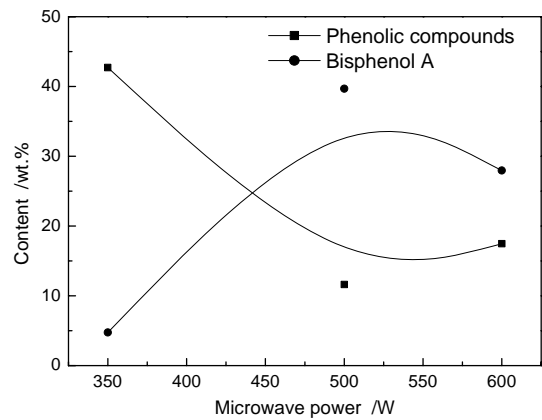
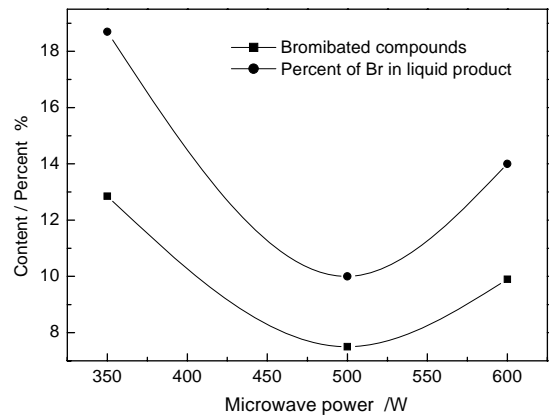Figure 7. Phenolic compounds and bisphenol A in liquid product

Figure 8. Borimated compounds and Br in liquid product

4. CONCLUSION

The kinetic mechanisms and parameters of thermal decomposition of PCB wastes were analyzed using TGA. This is valuable for understanding the consequences of pyrolysis, gasifying or combustion of PCB wastes in WTE facilities. The microwave induced pyrolysis of PCB wastes was further performed. Microwave induced pyrolysis proved to be suitable for the fast pyrolysis of PCB waste. Glass fiber and metals can be easily recovered from the solid pyrolysis product. The liquid product contains a large amount of phenolic compounds and bisphenol A, which make it to be a potential resource for related chemical products or used in WTE facilities. In order to minimize the pollution emission during the pyrolysis process and the after-utilization of pyrolysis products, brominated compounds should be removed and the debromination process should be further investigated.

REFERENCES

[1] J. Wang, I. Xu. Environment Implications of PCB Manufacturing in China [C]. IEEE International Symposium on Electronics and the Environment, 2004 ,USA: 156- 158.

[2] J. Cui, E. Forssberg. Mechanical recycling of waste electric and electronic equipment: a review[J]. Journal of Hazardous Materials, 2003, B99 :243–263

[3] G. Grause, M Furusawa, A. Okuwaki, et al. Pyrolysis of tetrabromobisphenol-A containing paper laminated printed circuit boards[J]. Chemosphere, 2008, 71: 872–878

[4] R. Zu, Q. Shi. Thermal analysis kinetics[A]. Science Press, 2001, Beijing

[5] M. Blazso, Z. Czegeny, C. Csoma. Pyrolysis and debromination of flame retarded polymers of electronic scrap studied by analytical pyrolysis[J]. Journal of Analytical and Applied Pyrolysis, 2002, 64:249–261

[6] Y. Chien, H. Wang, K Lin, et al. Fate of bromine in pyrolysis of printed circuit board wastes. Chemosphere, 2000, 40: 383-387