2010

# Experimental study on thermal treatment of used printed wiring boards (PWBS)

Xiangjun Zuo

## Recommended Citation

Zuo, Xiangjun, "Experimental study on thermal treatment of used printed wiring boards (PWBS)" (2010). *Masters Theses*. 7358.
https://scholarsmine.mst.edu/masters_theses/7358

# EXPERIMENTAL STUDY ON THERMAL TREATMENT OF USED PRINTED WIRING BOARDS (PWBS)

by

XIANGJUN ZUO

A THESIS

Presented to the Faculty of the Graduate School of the

MISSOURI UNIVERSITY OF SCIENCE AND TECHNOLOGY

In Partial Fulfillment of the Requirements for the Degree

MASTER OF SCIENCE IN MATERIAL SCIENCE AND ENGINEERING

2010

Approved by:

Prof. Lifeng Zhang, Co-Advisor
Prof. Thomas Schuman, Co-advisor
Prof. Mark E. Schlesinger

# ABSTRACT

The availability of cheaper and better electronic products as a result of the rapid innovation in technology in past decades has driven the production of e-waste forward. Printed wiring board (PWB) is a component made of one or more layers of insulating material with electrical conductors. The existing processes of recycling PWBs use pyrometallurgical or hydrometallurgical methods, which generate atmospheric pollution. Green recycling has obvious benefits to decrease the amount of PWBs. Green recycling includes two features, 1) little or zero pollution of toxic gases and heavy metals, and 2) efficient (quick and economical) recycling.

The aim of this work is to investigate green thermal treatment of PWB wastes in laboratory scales. For small scale experiments, PWB powders were combusted and pyrolyzed using TG/DTA, and the emitted gases were measured using MS. The suitable combustion conditions: 15 $^{o}$C/min heating rate, >125 ml/min gas flow rate, above 600 $^{o}$C top temperature, and the holding time is not important for combustion process; The suitable pyrolysis conditions: 15-20 $^{o}$C/min, >100 ml/min gas flow rate, above 900 $^{o}$C top temperature, and longer holding time. In combustion experiments, $CaCO_3$, NaOH, $NaHCO_3$ and $Na_2CO_3$ were mixed with PWB powders with a mass ratio of 1:1 to control toxic gas emission like HBr. In pyrolysis experiments, additives such as $CaCO_3$, CaO, $Fe_2O_3$, ZSM-5, Y-Zeolite were mixed with PWB powders with mass ratio of 5:1 to control toxic gas emission and enhance the pyrolysis reaction. $CaCO_3$ was the best additive to efficiently control toxic emitted gas during the combustion process, and $Fe_2O_3$ was the best choice to control toxic emitted gas and enhance the reaction speed during pyrolysis experiment.

For large scale experiments, PWB samples were pyrolyzed to solid, liquid and gas products in a tube furnace. Liquid products were analyzed by FTIR. For pyrolysis of PWB without additives, averagely there were 47% solid products, 20% liquid products and 33% gas products. The yield (47%) of solid products in the tube furnace was far more than the yield (36%) in TG/DTA experiments. The results also showed that pyrolyzing smaller PWB powders produced more solid products.

Keywords: Printed Wire Boards (PWBs), Combustion, Pyrolysis, Green Recycling

# ACKNOWLEDGMENTS

This thesis grew out of a series of dialogues with my supervisor Dr. Lifeng Zhang. Through his socratic questioning, Lifeng brought me closer to the reality I had initially perceived, eventually enabling me to grasp its rich complexity. His capacity to combine critique with an immediate empathy and commitment towards workers and others engaged in struggle will always inspire me. Lifeng was at the centre of our friendships in laboratory of green process metallurgy & modeling, turning water into wine with his music, quick wit and incredible imagination. Amid the laughter and chapter drafts, Lifeng was always there to offer encouragement, at times embarrassed by his own extraordinary kindness.

I am very grateful for the support from National Science Foundation (NSF Grant No. CBET-0853458), Material Research Center and Intelligent Systems Center at Missouri University of Science and Technology.

I would thank my co-supervisor Dr. Thomas Schuman who gave me many suggestions for tube furnace experiments, and FTIR and GC-MS analysis.

I am also indebted to Dr. Huebner Wayne who is the chairman at MSE department. Wayne is very appreciated for his personal kindness and help towards my graduation.

For professional courtesy and for brownie points with my committee, I especially thank Dr. Thomas Schuman and Dr. Mark E. Schlesinger, for accepting to be the members of my committee.

I also want to thank Damoah, Lucas N. and my friends in my group. We have spent a wonderful time together.

Last but not least, I am forever grateful to my wife Rong Huang who gently offers counsel and unconditional support at each turn of the road. I also want to thank her for cooking very delicious food for me during the years that I have been working on this thesis, especially all the holidays that she accompanied me to do experiments and write thesis.

## TABLE OF CONTENTS

SECTION

# LIST OF ILLUSTRATIONS

# LIST OF TABLES

# 1. INTRODUCTION

## 1.1. BACKGROUNDS OF ELECTRONIC SCRAPS

Production and use of electrical and electronic equipment (EEE), such as TV sets, computers, mobile phones and many other daily-life items, have dramatically increased over past decades, while the lifespan of many products becomes shorter, as shown in Table 1.1 [1]. The rapid innovation in technology in past decades has resulted in availability of cheaper and better electronic products in the market. Thus the production of waste electrical and electronic equipment (WEEE) is also increasing, with estimates of 20-50 million tons per year being generated worldwide [2], and it is a problem that governments and policy makers have to handle [3-4]. WEEE is also called “E-wastes” or “E-scraps”. From the points of view of recycling and the valuable materials in the used EEE, “E-scrap” is more appropriate than “E-waste” since the used EEE are not real wastes to be dumped but had much benefit to recycle. Hence, in this thesis, the word “scrap” is used.

Table 1.1. Average Lifetime of Main Home Appliances in China [1]

| Products | TV set | Refrigerator | Washing machine | Air conditioner | Personal computer |
|---|---|---|---|---|---|
| Life time (years) | 8 | 9 | 9 | 10 | 5 in 1993 & 3.5 in 2003 |

In the US, it was estimated that over 315 million computers between 1997 and 2004 and 185 million computers between 2004 and 2007 would become obsolete [5]. In particular, the statistical data on January 2009 shows that every day Americans throw out more than 350,000 cell phones and 130,000 computers. E-scrap is the fastest-growing part of the U.S. garbage stream [6]. It is estimated that only 20% of the E-scrap generated within the US is currently collected and treated, with as much as 80% being unaccounted for [7].

E-scrap represents a complex mixture of two major material fractions: (i) metals (and alloys) and (ii) polymers. An example composition of PWB is as follows: 28% metals, 72% plastics (epoxy resins) [8], in details: C (22.5%) H (2.7%) O (5.4%) S (0.04%) Br (N6.5%)+ Pb, Zn, Sb, Ni, Cd, Ga, or As. Metals, particularly heavy metals, represent the quantitatively dominating fraction. .

In order to recover valuable materials and to avoid simple dumping, E-scrap can be processed mechanically and/or thermally. Thermal treatment of E-scrap has been recognized as presently one of the most effective and environmentally safe recycling methods concerning the recovery of precious metals, e.g., in smelter units, and of energy.

In industry, recycling of PWB scraps includes mechanical recycling that roughly separates different sections or parts (such as plastics, metals), and metallurgical recycling that recovers metals or high value materials from the products of mechanical recycling and controls the pollution through some exhaust gases treatment. Many mechanical recycling of E-scrap has been reported [9-10], thus it is not the focus of the current work. Hydrometallurical recycling of E-scraps has been extensively reviewed by Cui and Zhang [11].

Combustion or burning is a complex sequence of exothermic chemical reactions between a fuel(usually a hydrocarbon) and an oxidant accompanied by the production of heat or both heat and light in the form of either glow or flames, appearance of light flickering [12]. Combustion or incineration, as a method to dispose solid wastes and recover energy, has been accepted in industry. By incineration some environmentally hazardous organic substances are converted into less hazardous compounds. Disadvantages of incineration are the emission of substances escaping from fuel gas cleaning to air and the large amount of residues from gas cleaning and combustion.

Pyrolysis is the chemical decomposition of organic substances by heating. Pyrolysis, which occurs spontaneously at high temperatures, is a special case of thermolysis, and is most commonly used for organic materials [13]. Thermal decomposition, also called thermolysis, is defined as a chemical reaction in which a chemical substance breaks up into at least two chemical substances when heated. The reaction is usually endothermic as heat is required to break chemical bonds in the compound undergoing decomposition. The decomposition temperature of a substance is the temperature at which the substance breaks up into smaller substances or into its constituent atoms [14].

Pyrolysis has been recognized as an effective alternative resource recovery. Pyrolysis of wastes has been investigated in vacuum, molten salt, fluidized bed, rotary kiln, entrained, stationary and moving bed reactors. The main constituent in PWBs scraps is epoxy resin that is produced originally from crude oil and can be thermally cracked into fuels or petrochemicals. Thermal treatment of PWBs were reported using DC Arc Plasma furnace [15], fixed bed reactor [16]. PWBs scraps also represent a significant quantity of energy in terms of the energy consumed in processing petroleum. Recover part of this energy content in a form with the highest possible value, i.e., fuel oil, would be economically and environmentally attractive. However, there is a limited Br content in product oil and emissions.

Nevertheless, one of the most relevant drawbacks in dealing with thermal treatment of PWB scraps is the likely production of super-toxic halogenated dibenzodioxins and dibenzofurans from the bromine containing structures. During metallurgical recycling, the organic constituents are destroyed and toxic emissions are addressed via afterburners. Uncontrollable incineration of waste PWBs also produces potentially hazardous byproducts (including mainly dioxins, furans, polybrominated organic pollutants and polycyclic aromatic hydrocarbons) caused by burning BFR, epoxy resins and plastics.

The main drawback of the thermal treatment of E-scrap is the toxic products. Pollutants from PWB incineration include heavy metals, organic compounds, particulate and acid gas ($Br_2$, $Cl_2$, HBr, HCl, HCN, $NH_3$). The open burning of PWBs stripped of metal parts can produce toxic fumes and ashes containing polycyclic aromatic hydrocarbons and polychlorinated biphenyls [5], and induced emission of heavy metals as well [5, 17-18]. The volatile heavy metals are also a problem [19]. For the hydrometallurgical process, the leaching solution used in this process will enter into the environment like the water and air system. About 70% of the heavy metals (mercury and cadmium) in US landfills come from electronic wastes. Consumer electronics contribute 40% of the lead in landfills. These toxins can cause brain damage, allergic reactions and cancer. As an example, at Guiyu, China, many tons of E-scrap materials and process residues were dumped into workshops, yards, roadsides, open fields, irrigation canals, riverbanks, ponds, and rivers. It was reported that the blood lead levels of children in Guiyu ranged from 4.40 to 32.67 μg/dL with a mean of 15.3 μg/dL, exceeding the "elevated blood lead level" of 10 μg/dL in children [20]. PWBs incineration plants need contribute significantly to the annual emissions of cadmium and mercury. In addition, heavy metals not emitted into the atmosphere are transferred to slag and exhaust gas residues and can reenter the environment on disposal.

Green recycling includes two features 1) Little or zero pollution (toxic gases and heavy metals) and 2) Efficient (quick, economical and low energy consumption) for recycling. The ideal solution to PWB scraps is green recycling because 1) there is urgent need for recycling of E-scraps due to its big amount and quick increasing; 2) E-scraps, especially the plastic and polymer components are the new potential energy source and renewable materials by the conversion of waste plastics into fuel through pyrolysis; 3) there is a economic motivation for recycling since PWB contains lots of precious metals; and 4). toxic components, such as polycarbonate materials, bromine and chlorine, and heavy metals like lead, cadmium and mercury, have to be controlled during the recycling of E-scraps.

## 1.2. BRIEF INTRODUCTION OF THE CURRENT STUDY

The current work is to perform green thermal treatment of PWB wastes, and to find proper additives to 1) control the emission of toxic gases such as HBr and $C_6H_6$, and 2) speed up the thermal reactions, and to find the proper parameters for the combustion and pyrolysis process of PWBs, such as heating rate, gas flow rate, top temperature, and holding time at top temperature.

In this thesis, a brief literature review will be presented in the second chapter. The third is about the small scale combustion experiment of PWB powders in TG-DTA-MS furnaces. The fourth chapter will introduce the small scale pyrolysis experiments. Large scale pyrolysis experiments will be given in the fifth chapter. The last chapter will be the final conclusions of the current thesis.

# 2. LITERATURE REVIEW

## 2.1. LITERATURE REVIEW WORK IN PAST 10 YEARS

In the past 10 years, there have been many literature reviews on the recycling of E-scraps, as summarized in Table 2.1. The most extensive ones are those by Cui and Forssberg [10] on the mechanical recycling of E-scraps, and by Cui and Zhang [11] on the recovery of metals from E-scraps. However, the state of the art in the combustion and pyrolysis treatment for the plastics and polymers in E-scraps is still not well reviewed.

Table 2.1. Literature Reviews on the Recycling of E-scraps in Recent Years

| Authors | Article name and main purpose | Pages | Year | Ref. |
|---|---|---|---|---|
| Sum | Title: The recovery of metals from electronic scrap<br>Purpose: Overview pyromentallurgical and hydrometallurgical methods to recycle metals from E-scraps | 53-61 | 1991 | [21] |
| Menad et al. | Title: Combustion of Plastics Contained in Electric and Electronic Scrap<br>Purpose: Overview combustion methods to recycle plastics contained in electric and electronic scrap | 65-85 | 1998 | [22] |
| Gao et al. | Title: Printed circuit board recycling: a state-of-art survey<br>Purpose: Review the current situation in PWB recycling field as a reference and guideline for research and implementation. Both industrial applied methods and ongoing laboratory researches are summarized. | 234-241 | 2002 | [23] |
| Goosey et al. | Title: Recycling technologies for the treatment of end of life printed circuit boards (PCBs)<br>Purpose: Review technologies and processes to recycle materials from end of life PWBs. | 33-37 | 2003 | [24] |
| Cui and Forssberg | Title: Mechanical recycling of waste electric and electronic equipment: a review<br>Purpose: Review mechanical methods of recycling E-scrap. | 243-263 | 2003 | [10] |
| Levchik et al. | Title: Thermal decomposition, combustion and flame-retardancy of epoxy resins—a review of the recent literature<br>Purpose: Overview the recent literature on combustion and flame-retardancy of epoxy resins. | 1901-1929 | 2004 | [25] |
| Shuey et al. | Title: Review of pyrometallurgical treatment of electronic scrap<br>Purpose: A survey of pyrometallurgical processes of E-scrap. | 67-70 | 2004 | [26] |
| Kang et al. | Title: Electronic waste recycling : A review of U.S. infrastructure and technology options<br>Purpose: Various recycling technologies for the glass, plastics, and metals from E-scrap. | 368-400 | 2005 | [27] |
| Hilty | Title: Electronic waste—an emerging risk?<br>Purpose: Overview the development of electronic technology and the risk of E-scrap. | 431-435 | 2005 | [28] |

Table 2.1. (Continued) Literature Reviews on the Recycling of E-scraps in Recent Years

| Authors | Article name and main purpose | Pages | Year | Ref. |
|---|---|---|---|---|
| Wong et al. | Title: Export of toxic chemicals – A review of the case of uncontrolled electronic-waste recycling.<br>Purpose: Review the level of persistent organic pollutants such as PBDEs, PCDD/Fs, PAHs, polychlorinated biphenyls and heavy metals/metalloid concentrations of different environmental media at Guiyu, China, an intensive recycling site of E-scrap. | 131-140 | 2007 | [29] |
| Babu et al. | Title: Electrical and electronic waste: a global environmental problem<br>Purpose: Overview of E-scrap recycling, including the source, type of E-scrap, strategies and technologies to recover materials. | 307-318 | 2007 | [30] |
| Gupta | Title: E-waste recycling and health effects: A review<br>Purpose: Overview the effect of E-scrap recycling on environment and human healthy. | | 2007 | [31] |
| Susan | Title: Evaluating Electronic Waste Recycling Systems: The Influence of Physical Architecture on System Performance.<br>Purpose: Existing E-scrap systems operating in different countries are examined for correlations between the environmental and financial performance of existing systems with respect to both the context and the architectural options of those systems. | | 2008 | [32] |
| Huang et al. | Title: Recycling of waste printed circuit boards: A review of current technologies and treatment status in China.<br>Purpose: Current status of waste PWBs mechanical treatment in China technologies. | 339-408 | 2009 | [33] |
| Cui and Zhang | Title: Metallurgical recovery of metals from electronic waste: A review<br>Purpose: Recover precious metals from E-scraps by pyrometallurgical processing, hydrometallurgical processing, and biometallurgical processing. | 228-263 | 2008 | [11] |
| Guo et al. | Title: Recycling of non-metallic fractions from waste printed circuit boards: A review<br>Purpose: Recover non-metallic fractions from the PWBs using physical methods. Pyrolysis, gasification, supercritical fluid depolymerization and hydrogenolytic degradation were also slightly reviewed. | 567-590 | 2009 | [34] |
| Guo et al. | Title: Heavy metal contamination from electronic waste recycling at Guiyu, Southeastern China.<br>Purpose: The effect of E-scrap recycling activities at Guiyu, China on heavy metal pollution in the surrounding waterway system. | 1617-1626 | 2009 | [35] |
| Yu et al. | Title: Review and prospects of recycling methods for waste printed circuit boards.<br>Purpose: Comparing different technologies available for PWBs recycling and discovering the limitations of different recycling methods, ways to overcome these limitations, and potential combinations of these methods so as to realize more economically sound and environmentally friendly recycling of PWBs | 1-5 | 2009 | [36] |

## 2.2. MATERIALS COMPOSITION OF PWBS

PWB is a platform upon which microelectronic components such as semiconductor chips and capacitors are mounted. It is also called printed circuit board (PCB). However, since PCB also stand for a well-known toxic chemical Polychlorinated Biphenyls, PWB is used in this work. PWB is a component made of one or more layers of insulating material and electrical conductors. PWB can be either rigid, flexible, or a combination of both. It consists of three basic parts: a insulator substrate or laminate, conductive circuits printed on or inside the substrate, and mounted components. PWBs are estimated to be ~3wt% of the total electronic appliance and are the core components of many electronic systems installed in martial and demotic electronic appliances [37], as shown in Figure 2.1. PWBs consist ~72% of organic substance and ~28% of metals.

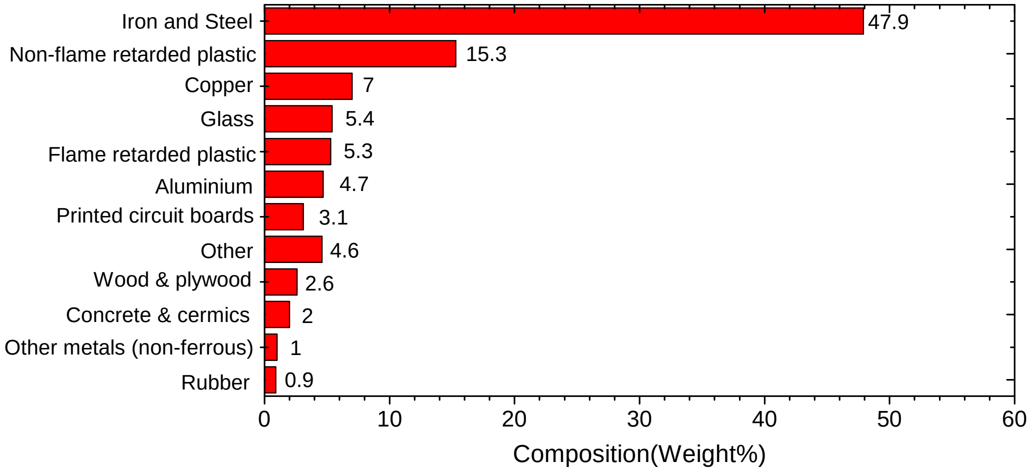


Figure 2.1. Material Composition of E-scraps [38]

Metals in PWBs include Cu, Al, Sn, etc. Depending on the different application and design of the PWB, various metals may be used in the manufacturing process, including precious metals such as copper, lead, silver, gold, platinum, and toxic metals such as mercury, cadmium, barium, gallium, cadmium, lead, bismuth, as shown in Table 2.2 [39]. These metals are from the electrical components and the solder used to attach them to the boards. Many of these metals have negative impacts on the environment and human health [37, 40-42]. The purity of precious metals in PWBs is more than 10 times higher than that of rich-content minerals [4, 43]. The main motivation to recycle the used PWBs is the value of the precious metals in them [11].

In all E-scraps, plastics and polymers account for approximately 15-20% in mass percentage [38]. However, in the PWBs, the organic substances are approximately 72%. The main composition of organic substances in PWBs is ethoxyline resin bromide or ethoxyline resin chlorinate. Many PWBs contain polymer films such as polyimides, polyethylene terephthalate, polyethylene naphthalate (less frequently), and glass fiber composites bonded with a thermoset resin. Typical density of a raw PWB is 2.15 g/cm$^3$ (an average value with no components) [44]. An example chemical structure of PWBs is shown in Figure 2.2.

Table 2.2. Main Elements within PWBs [39]

| Metal | wt% in PWB | Annual tonnage worldwide |
|---|---|---|
| Cu | 9.7 | 97,000 |
| Fe | 9.2 | 92,000 |
| Al | 5.8 | 58,000 |
| Pb | 2.24 | 22,400 |
| Sn | 2.15 | 21,500 |
| Zn | 1.16 | 11,600 |
| Ni | 0.69 | 6,900 |
| Sb | 0.35 | 3,500 |
| Cr | 0.24 | 2,400 |
| Ag | 0.06 | 600 |
| Cr | 0.052 | 520 |
| Au | 0.023 | 230 |
| Cd | 0.014 | 140 |
| Pd | 0.01 | 100 |
| Be | 0.003 | 30 |
| Hg | 0.0009 | 9 |
| Br | 6.5 | 65,000 |
| Cl | 0.24 | 2,400 |

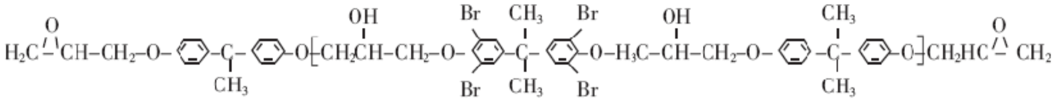


Figure 2.2. An Example Chemical Structure of PWBs [45]

Common resins include difunctional epoxy resins such as bisphenol A, multifunctional epoxy resins such as phenol and creosol based epoxy novolacs, BT epoxy blends, cyanate esters, and polyimides. The most commonly used substrate in PWBs is a glass fiber reinforced (fiberglass) epoxy resin with a copper foil bonded on to one or both sides [46]. The most common hardener forming the cross-linking required to create a thermoset plastic is dicyanodiamide. Sometimes diaminodiphenyl sulfone and diaminodiphenyl methane are also used [4]. Epoxy resins based on bisphenol A and diglycidyl ether of bisphenol A are high quality materials, and are widely used in advanced technological applications. The chemical structure of epoxy resin is shown in Figure 2.3.

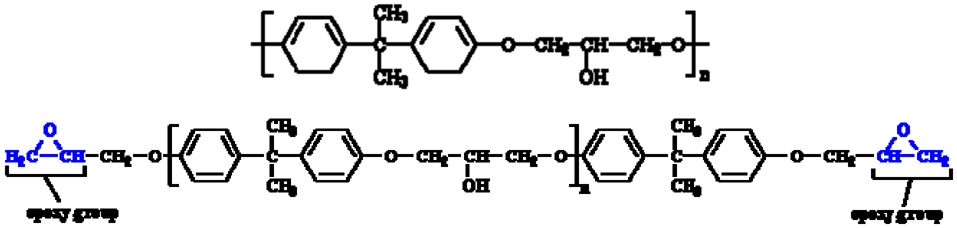


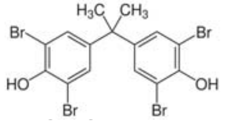
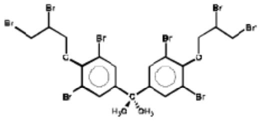
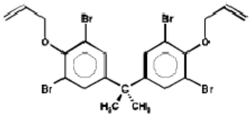
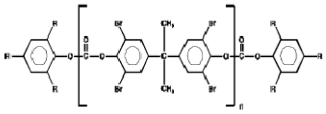
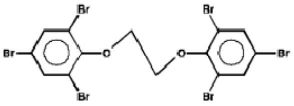
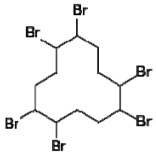
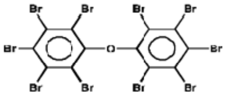
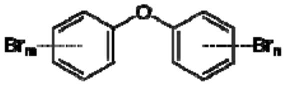
Figure 2.3. Chemical Structure of Epoxy Resin [47]

Flame retardant is one of the key parts of PWBs. Today, there are more than 175 chemicals classified as flame retardants. The four major groups are inorganic, halogenated organic, organophosphorus and nitrogen-based flame retardants [22, 48], which account for 50%, 25%, 20% and >5% of the annual production, respectively [48]. Brominated Flame Retardants (BFRs) are the major type of chemical flame retardants, and are very effective in plastics and textile applications [49]. Content of BFRs in different polymers are shown in Table 2.3.

The main toxic substances in PWBs are BFR such as TBBPA and PBDEs and heavy metals such as lead and mercury [39, 50]. Researchers have claimed that BFRs, cadmium, chloro-paraffins, chromium, copper, lead, mercury, nickel, PWBs, and silver compounds are the main toxic substances detected in PWBs [22, 51]. They can cause serious environmental problems if not properly disposed. The materials containing BFR are precursors for polybrominated dibenzo-p-dioxins and dibenzofurans (PBDD/Fs) [33, 52-53]. At the open burning sites in Ghana, some metals were present at concentrations over one hundred times typical background levels for soils, including lead, a highly toxic metal [2]. High levels of other toxic metals, including cadmium and antimony, were also present. Numerous classes of organic chemicals were also present in one or more of the samples, including many halogenated (chlorinated or brominated) chemicals.

The toxic effects of heavy metals on wildlife and humans are well known and consist of neurological problems, mental retardation, kidney damage, or even death [54]. Of many toxic heavy metals, lead is the most widely used in electronic devices for various purposes, resulting in a variety of health hazards due to environmental contamination. Lead enters biological systems via food, water, air, and soil. Children are particularly vulnerable to lead poisoning— more so than adults because they absorb more lead from their environments. The U.S. Centers for Disease Control and Prevention defined elevated blood lead levels as those ≥10 µg/dL in children ≤6 years of age [55].

Table 2.3. Content of BFRs in Different Polymers

| Polymer | Flame retardant | Structure | Bromine content (%) | Ref. |
|---|---|---|---|---|
| ABS | TBBPA |  | 8.6±0.4 | [56] |
| Polystyrene PS | TBBPA-bis-(2,3-dibromopropylether) |  | 3.2 | [56] |
| ABS/polycarbonate (ABS/PC) | TBBPA-bisallylether(TBBPA-ae) |  | 4.2 | [56] |
| ABS | TBBPA-carbonatoligomer (TBBPA-co); n=10,….,50 |  | 10.2 | [56] |
| ABS | 1,2-bis(Tribromophenoxy)-ethane (TBPE) |  | 10.6 | [57] |
| High-impact polystyrene (PS-HI) | Hexabromocyclododecane (HBCD) |  | 6.5 | [58] |
| SAPS-HI | Decabromodiphenylether (DECA) |  | 7.6 | [59] |
| PWBs | Polybrominated diphenyl ethers (PBDEs) |  | m+n=1, 2.., 10 | [60] |

In certain developing and transition countries these difficulties are amplified by a lack of regulations and/or lax enforcement in the recycling and disposal sector [1]. Combined with the existence of a very creative and low-income informal sector, the lack permits a profitable E-scrap recycling business thriving on uncontrolled and risky low-cost techniques (examples are shown in Figure 2.4 [1]). Most of the participants in this sector are not aware of environmental and health risks and either do not know better practices or have no access to investment capital to finance even profitable improvements or implement safety measures.

Figure 2.4. An Example of Low Quality Extraction of Copper from PWBs [1]

## 2.3. GENERAL COMBUSTION OF PWBS

Combustion is a gas phase reaction involving a fuel source and oxygen. As illustrated in Figure 2.5 [48], four steps involved in the combustion process are preheating, volatilization/decomposition, combustion and propagation. The second step is also called pyrolysis, and it is an endothermic reaction with the need of input heat. The decomposed liquid and combustible gases then react with the oxygen in the air—combustion process. The combustion is an exothermic process with no need of heat input to ignite.

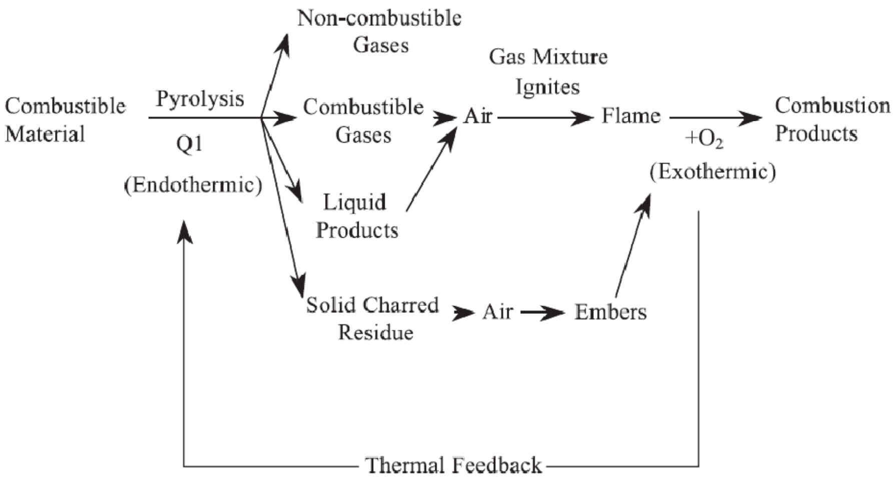


Figure 2.5. The Four Steps involved in the Combustion Process [48]

The products of combustion include not only $CO_2$ and $H_2O$, but also other gases and evaporated heavy metals. It was reported that, in best condition, copper was retained less than 5 min of residence in the incineration chamber of a fluidized bed incinerator.[61] In-house study on the open burning of (copper) cable wires showed extremely high levels of PCDDs and PBDDs and furans (PCDFs/PBDFs), resulting in 12,419 mg toxic equivalents per kilogram of waste input which were about three orders of magnitude higher than those for the open burning of household waste [54]. The open burning of computer casings and circuit boards stripped of metal parts can produce toxic fumes and ashes containing PAHs. Polychlorinated biphenyls (PCBs), which have been widely used as plasticizers, as coolants and lubricants in transformers and capacitors, and as hydraulic and heat exchange fluids, may also be present in the E-scrap stream [54].

Severe chemical contaminations were found in ash contaminated soil samples from open burning sites of e-scraps, as well as in sediment from a shallow lagoon, in Ghana [2]. Most samples contained numerous toxic and persistent organic chemical pollutants, as well as very high levels of many toxic metals, the majority of which are either known to be used in electronic devices, or are likely to be formed during the open burning of materials used in such devices. The nature and extent of chemical contamination found at these sites in Ghana [2] were similar to those previously reported for E-scrap open burning sites in China, India and Russia.

**2.3.1. Combustion for Energy Recovery.** Energy recovery is a key option for waste plastics, as their basic raw material, is derived from oil. Plastics have high energy potential. The heat value of plastics like PP and PET is even higher than the fuel, as shown in Figure 2.6 [22]. PS is similar to the fuel in heat value. Moreover, during the complete combustion of organic materials simple molecules such as $CO_2$, $H_2O$, $N_2$, $SO_2$ and hydrogen halide will form. The heat energy recovery from plastics has been studied for industries such as electric power making, iron making, and steam supplying. While in the past, there were much oppositions — justified by concerns around the poor environmental performance of old incinerators — today energy recovery is more widely required as an environmentally sound option.

Incinerating and combusting the plastic directly in order to utilize the heat energy released, and producing steam or electricity have received increased attention nowadays, since conventional energy sources are declining sharply. The use of incineration, together with the associated energy recovery, plays a complementary role for recycling and can reduce the amount of PWBs going to landfill by as much as 70%. Plastic contains as much energy as petroleum and natural gas, and much more energy than other types of garbage since plastics are made from fossil fuels. For instance, the PVC found in PWBs, cables and connectors holds in store 140kJ/mol and 290kJ/mol energy respectively, as shown in Table 2.4.

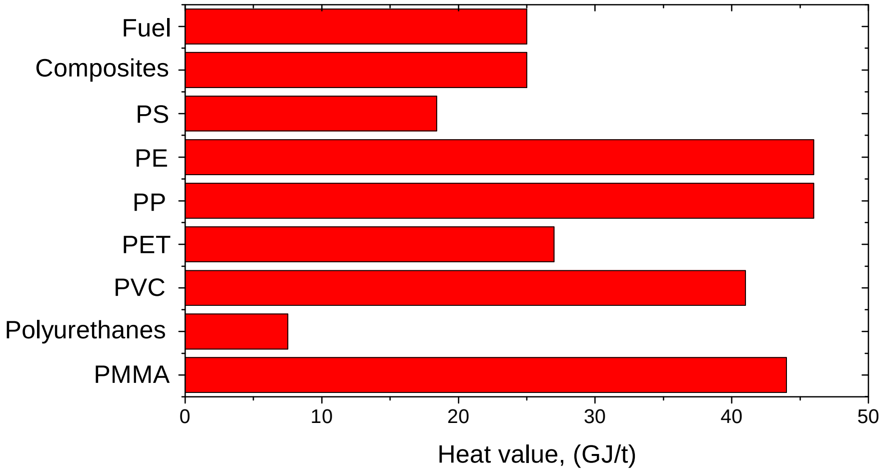


Figure 2.6. Heat Values of Fuel and Different Plastics [22]

Table 2.4. Kinetic Data of the Combustion of Plastics in E-scraps

| Type of resin | Decomposition temperature range (°C) | Maximum rate of decomposition temperature (°C) | Store energy (kJ/mol) | Ref. |
|---|---|---|---|---|
| PA 6 | 310-450 | 415 | 211 | [62] |
| PS | 320-415 | 355 | 172 | |
| PVC | 210-350(in PWBs) | 250-280(in PWBs) | 140 | |
| | 350-500(in cable and connectors) | 425(in cable and connectors) | 290 | |
| HDPE | 340-500 | 475 | 262 | |
| PP | 340-460 | 425 | 190 | |
| PET | 360-410 | 400 | 322.3-338.98 | [63] |
| Epoxy resins | 280-500 | 375 | 230.4 | [64] |
| TBBA | 180-270 | 250 | 179.1 | [65] |

Waste plastics are particularly interesting due to their high caloric value and the gate fee; hence the recycling industry is willing to invest in this field [66-68]. As an alternative to oil and pulverized coal, the injection of high caloric plastics into the tuyere zone in blast furnaces has been accomplished by several ironmaking companies, as shown in Table 2.5 [66-67, 69-70]. During the process, reducing gas ($CO+H_2$) rises through the raw materials in the furnace and reacts with the iron ore. Following the reduction reaction, the gas is recovered at the top of the furnace and reused as fuel. Waste plastics represent 5% of the fuel source, ~25 kg per ton of hot metal, out of a total fuel consumption of ~500 kg/thm. Recently, it was proposed that simultaneous injection of waste plastics with coal in innovative oxygen blast furnaces could provide up to 25% reduction of carbon emissions [71].

Table 2.5. Operational Practice of Injection of Waste Plastics in Industry [66-67, 69-70]

| Industry | Starting year |
|---|---|
| Stahlwerke Bremen GmbH, Arcelor Group, Bremen/Germany | 1995 |
| Keihin Works, NKK Corp., Kawasaki/Japan | 1996 |
| EKO Stahl GmbH, Arcelor Group, Eisenhüttenstadt | 1997 |

**2.3.2. Combustion/Incineration for Waste Treatment.** Incineration is the main industrial process to treat E-scraps. As an example, the Karlsruhe test incinerator TAMARA shown in Figure 2.7, is a mass combustor designed for a throughput of 150-300kg/h of preconditioned and a maximum flue gas volume flow of 1000Nm$^3$/h, mainly shredded wastes [72]. The maximum thermal capacity is approximately 0.5MW.

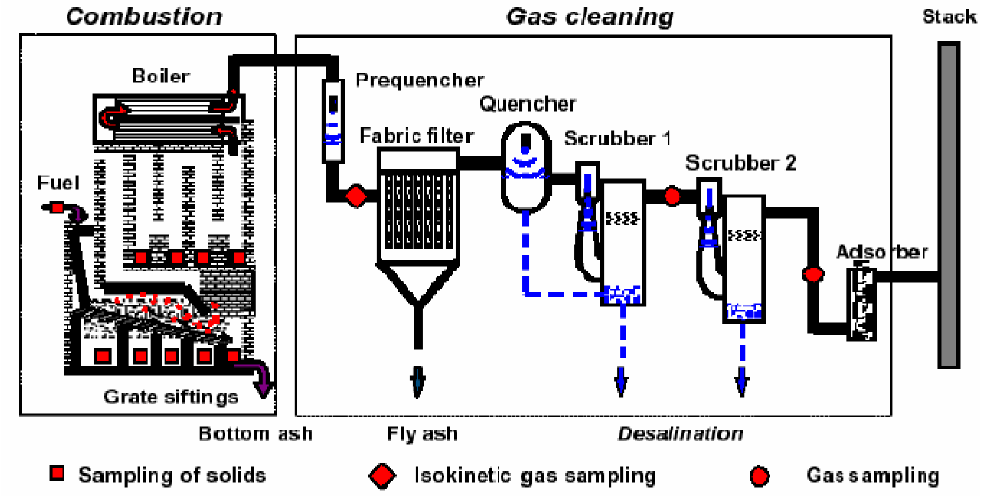


Figure 2.7. TAMARA Pilot Plant for Municipal Solid Waste Combustion [72]

Chen et al. [73] investigated the kinetics of thermal and oxidative decomposition of PWBs under various heating rates (5, 10, 15, 20, and 25 $^{o}$C/min) and oxygen concentrations (5, 10, and 15%) in the nitrogen-oxygen atmosphere by means of TG measurements. Zuo and Zhang [43] used TG/DTA-MS to combust PWBs samples at 10, 15, 20, 25 and 30 $^{o}$C/min heating rate under synthetic air (oxygen 20% and nitrogen 80%) with 50ml/min flow rate. Zheng et al. [74] adopted a novel fluidized bed to recycle glass fibers from nonmetal materials of waste PWBs. The thermoset resins in the nonmetal materials are decomposed in the temperature range from 400 $^{o}$C to 600 $^{o}$C. Sakai et al. [75] investigated the combustion behavior of BFRs in a rotary kiln furnace with a diameter of 170mm and a length of 860 mm, with a feed capacity of 0.5±1.0 kg/h.

## 2.4. PYROLYSIS OF PWBS

**2.4.1. Introduction of Pyrolysis.** The reuse of plastic wastes from the viewpoint of energy diversification has been paid much attention. As the thermal degradation products of polymers are distributed in a wide range of carbon numbers, the utility value of the products recovered is very low, hence, upgrading will be required for their efficient utilization. On the other hand, a selective recovery of useful fractions is possible in catalytic degradation and the product distribution is controlled more readily than the case of thermal degradation. Thus, the catalytic procedures are superior to thermal methods provided that the products are intended for resources [76].

Pyrolysis is one of the best methods for treating complex mixtures of waste polymers and to recover the material and energy content. The process consists of thermal decomposition at moderate temperatures in total absence or small amount of oxygen in which the structures of polymers break down into smaller intermediate products [77]. These can be used as fuel or raw materials for petrochemical industry while the additives to the polymer materials (e.g. metals, inorganic particulate fillers and reinforcements) remain in the residue.

Pyrolytic recovery of the organic materials contents seems to be an adequate way to utilize electronic waste. Because the majority of macromolecular organic substances decompose to volatile compounds at elevated temperatures, while metals, inorganic fillers and supports generally remain unchanged [78]. Pyrolysis of the organic flame retardants leads to volatile halogenated compounds that become components of pyrolysis gas and/or oil. Dehalogenation of the pyrolysis product of electronic scraps is essential to make it commercially acceptable. It would be obviously the most advantageous solution as pyrolysis and dehalogenation are carried out simultaneously.

Polymers such as PVC and ABS with flame retardant used in polymer materials contain heteroatoms such as chlorine, nitrogen, and bromine that remain as organic compounds in pyrolysis oils during thermal degradation and also produce acids or toxic gases such as HCl, HBr, HCN, $NH_3$ or polyhalogenated dibenzodioxins and dibenzofurans [77, 79], whose presence in pyrolysis oils from polymer waste is not desired. Therefore, the amounts of heteroatoms in pyrolysis oils have to be decreased as much as possible.

One possible method of recycling PWBs and recovering both the organic and non-organic parts is pyrolysis. The pyrolysis process, provided that the temperature is high enough, will melt the solder used to attach the electrical components to the PWBs [4]. The combination of the removal and recovery of the organic fraction of PWBs and the removal of the solder should enhance the separation of the metal components from the organic material. Although a significant amount of research into the pyrolysis of PWB wastes have been reported, most of the works have been carried out using analytical pyrolysis techniques or very small batch reactors [78, 80-83]. Also, most of the works for the pyrolysis of PWBs haves concentrated on the composition of the organic products, particularly the brominated organics.

Pyrolysis of organic materials contained in waste PWBs leads to the formation of gases, oils, and chars which can be used as chemical feedstock or fuels [4, 33]. Reported pyrolysis investigations are at experimental stage and have been carried out in vacuum, molten salt, fluidized bed, rotary kiln, entrained, stationary, and moving bed reactors [84]. Comparing to the incineration and combustion of PWBs, the pyrolysis process has several characteristics: [44, 62, 85] 1). Converting the organic solid substance into fuel gas, fuel oil and carbon-black as storage energy; 2) Emitting toxic substances such as sulfur, bromine and heavy metals in wastes; and 3) Keeping metals from being oxidized.

**2.4.2. Vacuum Pyrolysis of PWBs.** The vacuum pyrolysis method, with the sample being pyrolysed in a closed furnace with vacuum, has been used in recycling waste car tires.

The vacuum could help reduce the apparent activation energy of the PWBs pyrolysis, and increase the volatile of pyrolytic products and decrease the secondary pyrolytic reactions [86-87]. The vacuum is beneficial to raise the yield of liquid products. Results from the vacuum pyrolysis indicates a liquid oil yield of 20–36%, a gas yield of 2–35% and a solid yield of approximately 40-60% were obtained, as shown in Table 2.6.

Heating rate is a significant factor affecting the yield of products, as shown in Table 2.6. At a certain top temperature under a certain vacuum, the biggest yield of liquid products will be at about 15-20 $^{o}$C/min. At a lower heating rate the PWBs powders will reside at a certain temperature for a longer time so that the secondary pyrolysis reaction will take place. Some week oxygen-bridge bond and side-chain in benzene ring are easy to break to form free radical to decrease the oil yield and increase volatiles [88]. The terminal temperature can also greatly affect the yield of pyrolysis products. Generally, at same heating rate under same vacuum, lower terminal temperature will have a lower oil yield.

Table 2.6. The Yield of Oil/Gas from Different Vacuum Pyrolysis Experiments

| Yield of / product, wt%. | | Experimental conditions | | | Year | Ref. |
|---|---|---|---|---|---|---|
| oil | gas | | | | | |
| 25.33 | 8.76 | 10 °C/min, 30 min, 500 °C, Vacuum | | | 2006 | [86] |
| 21 | 2 | 10 °C/min, 30 min, Vacuum, 5 kPa | | 200 °C | 2008 | [89] |
| 31 | 2.5 | | | 300 °C | | |
| 36 | 2.5 | | | 400°C | | |
| 35 | 3 | | | 500 °C | | |
| 34.5 | 3 | | | 600 °C | | |
| 35 | 2.5 | | | 700 °C | | |
| 34.37 | 3.05 | 20 °C/min, 30 min, 400 °C | | Vacuum, 3 kPa | | |
| 34.67 | 2.25 | | | Vacuum, 10 kPa | | |
| 35.05 | 2.14 | | | Vacuum, 15 kPa | | |
| 34.36 | 2.24 | | | Vacuum, 20 kPa | | |
| 34.25 | 2.29 | | | Vacuum, 25 kPa | | |
| 34.05 | 2.34 | | | Vacuum, 30 kPa | | |
| 32.30 | - | 30 min, 400 °C Vacuum, 15 kPa | | 5 °C/min | | |
| 34.30 | - | | | 10 °C/min | | |
| 34.32 | - | | | 15 °C/min | | |
| 34.37 | - | | | 20 °C/min | | |
| 33.80 | - | | | 25 °C/min | | |
| 33.65 | - | | | 30 °C/min | | |
| 34.37 | 30.52 | 15-20 °C/min, 30 min | 300 °C | Vacuum, 5 kPa | 2009 | [90] |
| 35.05 | 34.92 | | 400 °C | Vacuum, 15 kPa | | |
| 34.05 | 34.78 | | 500 °C | Vacuum, 30 kPa | | |
| 26.32 | 34.38 | | 600 °C | Atmosphere | | |

Table 2.6 shows that the oil yield is 35% at the temperature of 400-550 °C and 20-30% at the temperature of 200-300 °C. With the increase of the terminal temperature the high molecular polymer like epoxy resin will be broken to some long bond compound so that more oil products will be obtained. However, if the terminal temperature is too high, secondary pyrolysis reaction of pyrolysis gases will happen to break the long bond to short bond, the amount of gaseous products will increase but not oil products [88-89].

Peng et al. [86] investigated the pyrolysis of waste PWBs in a bench-scale pyrolysis reactor under low vacuum and nitrogen. Experimental results showed that the apparent activation energy under vacuum became smaller than that in nitrogen, vacuum helped to increase the volatility of pyrolysis products, and weakened the secondary reaction, so the liquid yield under vacuum was increased at the expense of gas and solid yields. The increase of the degree of vacuum could help to obtain the liquid products. However, it does not mean that higher degree of vacuum has better value because too high vacuum degree does not only increase the asphalt fraction in liquid products but also decrease the commercial value of products. Wu et al. [89] investigated the pyrolysis of epoxy resin in waste PWBs in a pyrolysis oven. The PWB samples were heated to different terminal temperature (200-700 $^oC$) at different heating rate (5-30 $^oC$/min) for different holding time (10-150 min). The experimental results showed that the optimal condition was obtained as follows: pyrolysis terminal temperature at 400-550 $^oC$, heating rate of 15-20 $^oC$/ min, pressure of 15 kPa, holding time of 30min, as showed in Table 2.6. Hall et al. [91] recycled the organic compounds and metals from scrap PWBs by pyrolysing in a fixed bed at 800 $^oC$, and found that different gases release at different temperature from the mobile phone boards. Qiu et al. [90] pyrolysed waste PWBs in vacuum oven and investigated the products of liquid, solid and gas yield by FT-IR, GC-MS, and SEM. The results showed that the density and component of the liquid changes with different pressure. The oils mainly consist of phenol, substituted phenols, bisphenol-A and bromides of them, as showed in Table 2.6.

**2.4.3. Atmospheric Inert Pyrolysis of PWBs.** The waste PWBs can be pyrolysed in an inert gas (such as $N_2$, Ar, etc.) under atmospheric pressure, which mainly uses fixed bed as a reactor. The inert gas as a carrier could push the pyrolytic gas evolved from the pyrolysis process at a certain flow rate and prevent the secondary pyrolysis reaction from taking place. The yields of pyrolysis products (oil and gas) are listed in Table 2.7.

The main pyrolysis process takes place between 350-500 $^oC$. As temperature increases above 600, there is little change in the yield of products. The flow rate of nitrogen has a certain effect on the mass loss. Higher flow rate could take the pyrolysis gas away more quickly, thus the secondary reaction is hard to happen so the gas products decrease. The pyro-oil obtained during the pyrolysis process is a mixture of organic compounds (usually termed oils), and also contains some aqueous products. Water and hydrocarbons by-product could either be a product formed during the process (derived from the oxygen-containing functional groups, –COO–, OH–, –COOH–, etc.) or due to the original moisture in the samples, as shown in Tables 2.8 and 2.9 [92-93].

Table 2.7. Yield of oil/gas in Vacuum and Inert Atmosphere Pyrolysis Experiments

| Yield of product, wt%. | | Experimental condition | | Year | Ref. |
|---|---|---|---|---|---|
| oil | gas | | | | |
| 40.6 | 24.9 | 5°C/min, 30min, 540°C, Nitrogen, 100ml/min. Fixed-bed reactor | | 2000 | [19] |
| | 17-23/13-23 | 155°C/min, 30min, 1000°C, Nitrogen 100ml/min. | | 2003 | [94] |
| | 49/31(TBBA) | 10°C/min, 600°C, Nitrogen 60ml/min | | 2004 | [95] |
| 0 | 0.33 | 15°C/min, 30min, Nitrogen 200ml/min | 200°C | 2005, 2002 | [96-97] |
| 14.99 | 20.22 | | 300°C | | |
| 19.42 | 14.79 | | 400°C | | |
| 20.79 | 14.99 | | 600°C | | |
| 19.63 | 19.86 | | 800°C | | |
| 22.47 | 10.75 | 10°C/min, 30min, 500°C, Nitrogen | | 2006 | [86] |
| 22.7 | 4.7(Computer PWBs) | 10°C/min, 135min, 800°C, Nitrogen, Fixed-bed reactor | | 2007 | [4] |
| 28.5 | 6.5(Television PWBs) | | | | |
| 15.2 | 2.3(mobile phone PWBs) | | | | |
| 28.29 | 35.94 | 20°C/min, 900°C, Nitrogen, 10L/h-15L/h | | 2007 | [98] |
| 9.85±0.38 | 5.21±1.55 | 10°C/min, 30min, Nitrogen 200ml/min, A tubular oven, | 300°C | 2008 | [99] |
| 13.56±1.46 | 6.90±2.00 | | 400°C | | |
| 12.93±1.55 | 9.06±0.23 | | 500°C | | |
| 13.18±1.55 | 9.13±0.80 | | 600°C | | |
| 13.90±1.55 | 8.87±1.19 | | 700°C | | |
| 16.2±1.1 | 7.3±0.7 | 15°C/min, 30min, 500°C, Nitrogen 1000ml/min | | 2008 | [100] |
| 7.9, 14.4 | - | 10°C/min, Nitrogen, 0.19m/s, 0.48m/s, Fluidized bed reactors | 400°C | 2009 | [101] |
| 11.7, 15.2 | - | | 450°C | | |
| 15.1, 20.1 | - | | 500°C | | |
| 17.8, 23.5 | - | | 550°C | | |
| 18.1, 24.5 | - | | 600°C | | |
| 18 | 19 | 800°C, Nitrogen, 20min, Muffle furnace | | 2009 | [102] |

Table 2.8. Major Products in the Pyrolysis Oil Resulting from the Pyrolysis of PWBs

| The main products in the oil | Composition percentage, % | The main products in the oil | Composition percentage, % | Experimental information | Ref. |
|---|---|---|---|---|---|
| Phenol | 25.23/10.06/38.49 | *p*-Hydroxydiphenyl | 1.47/0.08/2.87 | 10$^{o}$C/min, 800$^{o}$C<br>Nitrogen<br>Sample:<br>computer<br>television<br>mobile phone<br>Quantify fraction of the pyr-olysis oil:<br>Computer 42.1%<br>Television 21.4%<br>Mobile phone 60.7% | [4] |
| 2-Methylphenol | 1.04/1.60/1.07 | Bisphenol A | 1.38/0.11/0.67 | | |
| 4-Methylphenol | 1.45/2.20/0.31 | Triphenyl phosphate | 0.92/4.25/0.09 | | |
| 2,6-Dimethylphenol | 0.27/0.50/0.15 | *o*-Cresyl phosphate | 0.55/0.00/0.00 | | |
| 2-Ethylphenol | 0.22/0.20/0.24 | *m*-Cresyl phosphate | 0.10/0.00/0.00 | | |
| 4-Ethylphenol | 0.47/0.26/0.61 | 2,4-Dibromophenol | 0.03/0.35/0.01 | | |
| 4-(1-Methylethyl) phenol | 8.61/1.26/16.11 | 2,6-Dibromophenol | 0.34/0.56/0.10 | | |
| TBBPA | 0.0006/0.0013/0.00 | | | | |
| Acetonitrile | 2.48 | 2H-1-benzopyran-3ol | 1.98 | 10$^{o}$C/min, 500$^{o}$C<br>Vacuum, 10 kPa<br>Nitrogen gas was pumped in the reactor for 20min. | [86] |
| Phenol | 46.37 | Dibromophenol | 0.93 | | |
| Methylphenol | 0.84 | Dibenzofurn | 0.63 | | |
| 2-bromophenol | 1.45 | p-hydroxybiphenyl | 4.06 | | |
| Ethylphenol | 0.58 | 1,3-dibromo-propanol | 0.78 | | |
| 4-(1-methylethyl) phenol | 12.73 | Bis(4-aminophenyl)-metylene | 0.21 | | |
| Isoquinoline | 0.11 | Biphenol A | 21.07 | | |
| Bromobiphenol A | 0.57 | 2,6-dibrom-4-(1,1-dimethylethyl)-phenol | 4.05 | | |
| Phenol | 1.0 | bromobisphenol A | 2.3 | 10$^{o}$C/min, 600$^{o}$C<br>Nitrogen, 60ml/min | [95] |
| 2-bromophenol | 2.0 | dibromobisphenol A (1) | 10.5 | | |
| 4-bromophenol | 3.3 | dibromobisphenol A (2) | 2.1 | | |
| 2,4-dibromophenol | 6.9 | tribromobisphenol A | 24.7 | | |
| 2,6-dibromophenol | 8.7 | Others | 6.6 | | |
| 2,4,6-tribromophenol | 8.1 | TBBA | 23.8 | | |
| Phenol | 49.4917 | 2,4-dimethylphenol | 6.3818 | Microwave 700W<br>The pyrolysis process was reacted in a microwave reactor | [103] |
| 2-Methylphenol | 13.2910 | 2,6-dimethylphenol | 1.4397 | | |
| Methylphenol | 13.7923 | Isopropylphenol | 5.2259 | | |
| 2,3-dimethylphenol | 3.3293 | | | | |

Table 2.9. Major Products in the Pyrolysis Gas Resulting from the Pyrolysis of PWBs

| The main products in the gas | Composition percentage, % | The main products in the gas | Composition percentage, % | Experimental condition | Ref. |
|---|---|---|---|---|---|
| $H_2$ | 4.6/3.2/5.7 | Propene | 2/1.1/2.7 | 10°C/min, 800°C<br>Nitrogen<br>Sample:<br>computer<br>television<br>mobile phone<br>Quantify fraction of the pyrolysis oil:<br>Computer 42.1%<br>Television 21.4%<br>Mobile phone 60.7% | [4] |
| CO | 27/21.8/36.1 | Propane | 1/1.6/0.4 | | |
| $CO_2$ | 51/51.5/45.8 | Butene | 0.8/1.8/1 | | |
| Methane | 10.3/14/6.4 | Butane | 0.5/1.2/0.2 | | |
| Ethene | 0.6/1.1/0.5 | Cl | 0/0/0.1 | | |
| Ethane | 1.9/2.7/0.6 | Br | 0.3/0.1/0.5 | | |
| $H_2$ | 38.52 | $C_1$–$C_4$ | 15.23 | 10°C/min, 500°C<br>Nitrogen/200<br>A tubular oven | [99] |
| CO | 7.23 | $O_2$ | 12.03 | | |
| $CO_2$ | 7.93 | $N_2$ | 9.50 | | |
| CH4 | 9.55 | | | | |

Pyrolysis oil obtained during the pyrolysis process under atmospheric inert condition is also a mixture of organic compounds (usually termed oils), and also contains some aqueous products. Similar results in the pyrolysis of different plastics have been reported [19, 92, 99, 104]. They all agree that water and hydrocarbons by-product could either be a product formed during the process (derived from the oxygen-containing functional groups, -COO-, OH-, -COOH-, etc.) or due to the original moisture in the samples [105].

Guan et al. [99] pyrolyzed the PWB sample (2.0 cm×2.0 cm) under nitrogen atmosphere, at 300, 400, 500, 600 and 700 °C in a tubular type oven. Peng et al. [106] also pyrolyzed PWBs under nitrogen atmosphere. Sun et al. [94] investigated the pyrolysis kinetics of PWB scraps under various conditions with TG. Sun et al. [97] also analyzed the pyrolysis products for different particle size of PWB powders (15 mm, 8 mm and 0.2 mm) at the same terminal temperature (600 °C). Li et al. [107] reported that the yield of products at higher heating rate was more than at lower heating rate because the organic substance could obtain a large quantity of heat in a short time as the higher heating rate was employed. Xiong et al. [108] investigated the characteristics of PWB pyrolysis and its kinetics using a tubular furnace and TGA. Guo et al. [109] pyrolysed waste polytet rafluoroet hylene (PTFE)-PWBs in a fixed bed at different heating rates (5, 10, 15, 20, 30, 50 $^{o}$C/min) under nitrogen atmosphere with flow rate of 50 ml/min. Guo et al. [110] also analyzed the composition of the pyrolysis oil products from the pryolysis of PWBs using GC-MS.

Hall et al. [4] used a fixed bed reactor to pyrolyze three types of PWBs (from computers, televisions and mobile phones) at 800 $^{o}$C. The pyrolysis products were analyzed using GC–FID, GC–TCD, GC–MS, GCECD, ICP–MS, and SEM–EDX. Wang et al. [101] used a fluidized bed reactor to pyrolyze scrap PWB particles under inert gas. Zhou et al. [111] studied the pyrolysis characteristic of waste phenolic-resin-based PWBs by TG and DSC. The composition of pyrolysis products were analyzed by pyrolysis gas charomatography mass spectrometry (Py-GC-MS).

# 3. SMALL SCALE COMBUSTION OF PWBS USING TG/DTA-MS

## 3.1. EXPERIMENTAL PROCEDURE

In the current study, PWBs from a used printer named HP C2121A and a used TV were studied and crushed to small particles with diameter of 100 - 500 µm, as shown in Figure 3.1. PWB powders was heated and decomposed in a thermo-gravimetric analysis and differential thermal analysis (TG/DTA) furnace. Synthetic air was used as the carrying gas to study the combustion. The evolved gases were measured using a mass spectrometer (MS).

The initial mass, heating rate, carrying 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 the room temperature.

Figure 3.1. PWB Scraps and Powders Used in the Current Study

## 3.2. COMBUSTION OF PWBS WITHOUT ADDITIVE

Eighteen combustion experiments without additive were performed by varying the air flow rate and the heating rate. The heating rates employed were 10, 15, 20, 25, 30°C/min and the gas flow rates were 50, 75, 100, 125 and 150ml/min, as shown in Table 3.1.

Table 3.1. Experimental Conditions of E-waste Combustion

| # | Initial Mass (mg) | Top Temperature | | Gas flow Rate (ml/min) | Heating rate, $^o$C/min |
|---|---|---|---|---|---|
| | | $^o$C | Holding time (min) | | |
| P7 | 15.1926 | 700 | 60 | 150 (air) | 30 |
| P8 | 12.7519 | 700 | 60 | 150(air) | 30 |
| P9 | 15.1905 | 700 | 60 | 100(air) | 30 |
| P10 | 14.1880 | 700 | 60 | 50(air) | 30 |
| P11 | 13.9977 | 800 | 60 | 50(air) | 30 |
| P12 | 10.5734 | 800 | 60 | 100(air) | 30 |
| P13 | 14.5545 | 800 | 60 | 150(air) | 30 |
| P14 | 12.3761 | 800 | 120 | 150(air) | 30 |
| P15 | 13.4736 | 900 | 60 | 150(air) | 30 |
| P16 | 13.2450 | 900 | 60 | 100(air) | 30 |
| P17 | 14.8798 | 900 | 60 | 50(air) | 30 |
| P18 | 12.9366 | 900 | 120 | 50(air) | 10 |
| P19 | 16.0073 | 900 | 120 | 50(air) | 15 |
| P20 | 15.8744 | 900 | 120 | 50(air) | 20 |
| P21 | 17.1034 | 900 | 120 | 50(air) | 25 |
| P22 | 13.3913 | 900 | 120 | 50(air) | 10 |
| P23 | 13.3244 | 900 | 120 | 50(air) | 20 |
| P24 | 14.468 | 900 | 120 | 50(air) | 30 |

**3.2.1 Effect of Gas Flow Rate.** Gas flow rate may have influenced on the conversion fraction and the products. In addition, the gas flow rate is an important parameter in the industrial scale applications. DTA curves for combustion experiments (TV PWBs) are shown Figure 3.2. Positive peaks in DTA curve meant exothermic reactions. The area of peaks means the energy released during combustion. With the maximum gas flow rate (150 ml/min), there was only one positive peak during the entire combustion process. While for other gas flow rate condition, there were two positive peaks and the first one was higher. The first exothermic reaction occurred at ~300-350 $^o$C, and the second one at ~350-450 $^o$C. The exothermic reaction was the reaction between samples and oxygen. Some organic substance in PWBs might be combusted in the air atmosphere at lower temperature. The initial sample mass rarely affected the combustion process. With gas flow rate increasing, the intensity of first peaks in experiments increased. With further increasing of the gas flow rate, the value of the second peak decreased, and finally disappeared. Possible reasons included:

- Too high gas flow rate might dilute the products, so the equipment could not detect it.

- Too much air provided abundant oxygen source that might combust all the materials at the first exothermic reaction (the first peak).

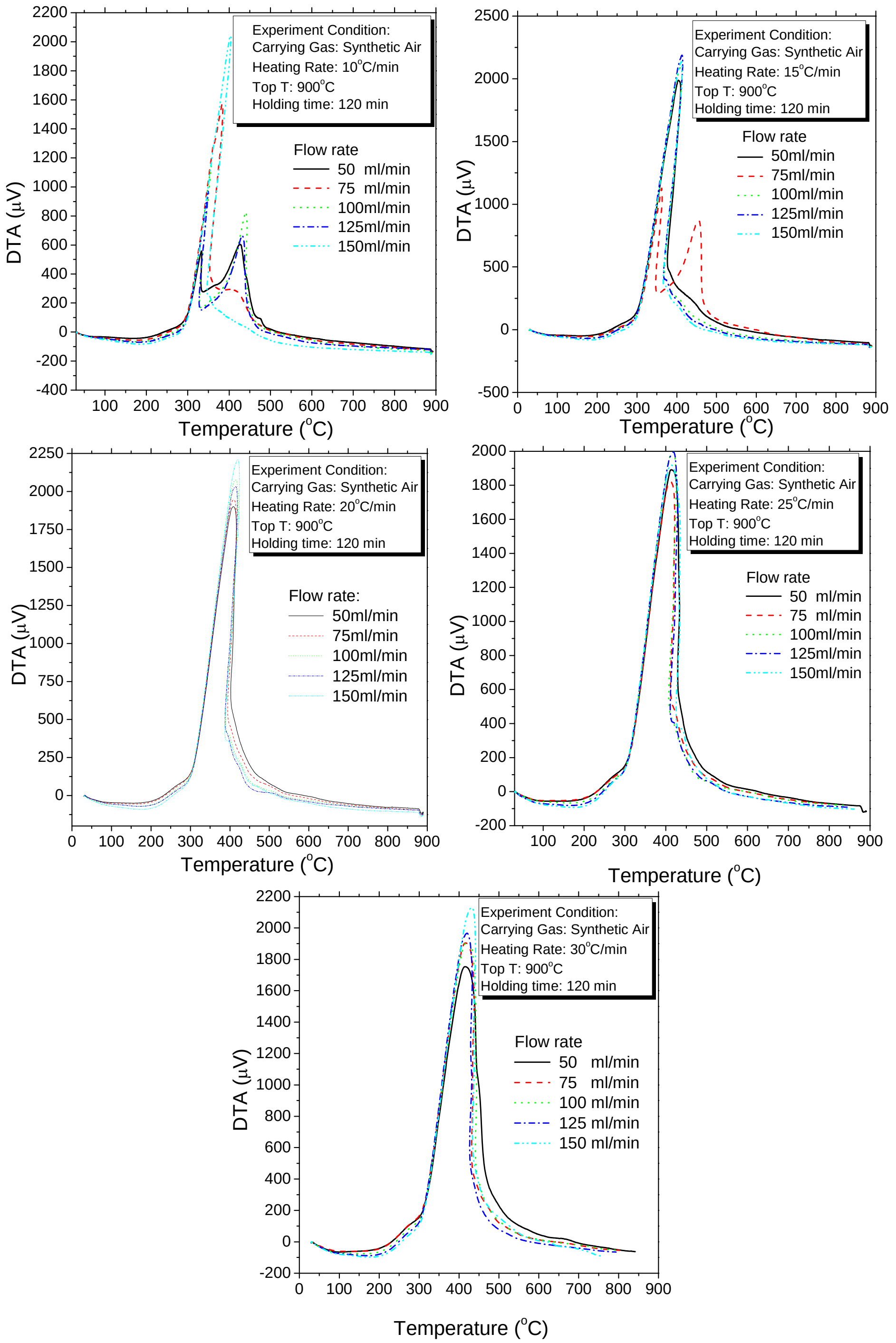


Figure 3.2. DTA Curves with Different Gas Flow Rates of 50-150 ml/min, 10-30 °C/min. (TV PWBs)

The DTA peak value as a function of air flow rate was shown in Figure 3.3. When there was only one peak in the DTA~T curve, the DTA peak value slightly increased with increasing air flow rate. With too low air flow rate, there might not be too much oxygen and some degradation reactions may occur before combustion. Large air flow rate meant more sources of oxygen, and thus more intensive combustion reaction. When there were two peaks in the DTA~T curve, the DTA peak value changed randomly with increasing air flow rate. As the air flow rate reached a certain critical value, the air flow rate had little effect on the combustion reaction.

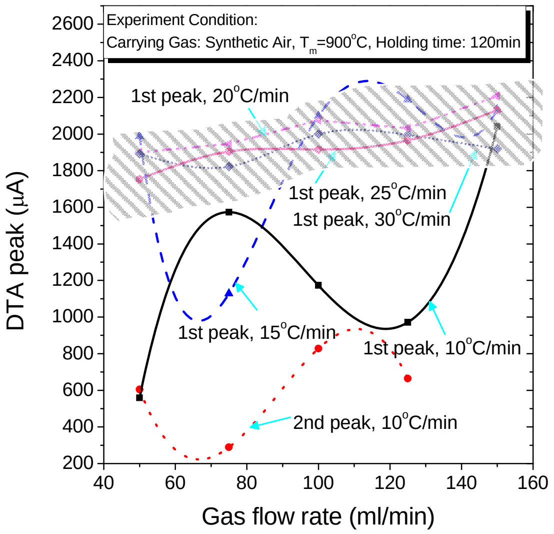


Figure 3.3. DTA Peaks with 10-30 °C/min Heating Rate and 50-150 ml/min Gas Flow Rate. (TV PWBs)

Due to the exothermic feature of the combustion reaction, there are temperature jumps in the T-time curve as shown in Figure 3.4. Different PWB sample have different temperature jump results. Under the condition of 50ml/min air flow rate and 30 °C/min heating rate, there are two jumps for printer PWBs, one at 310-420 °C, another at 330-520 °C, while there is one temperature jump for TV PWBs at 310-460 °C, as shown in Figure 3.4a. Figure 3.4b indicates that this temperature jump is independent of the air flow rate.

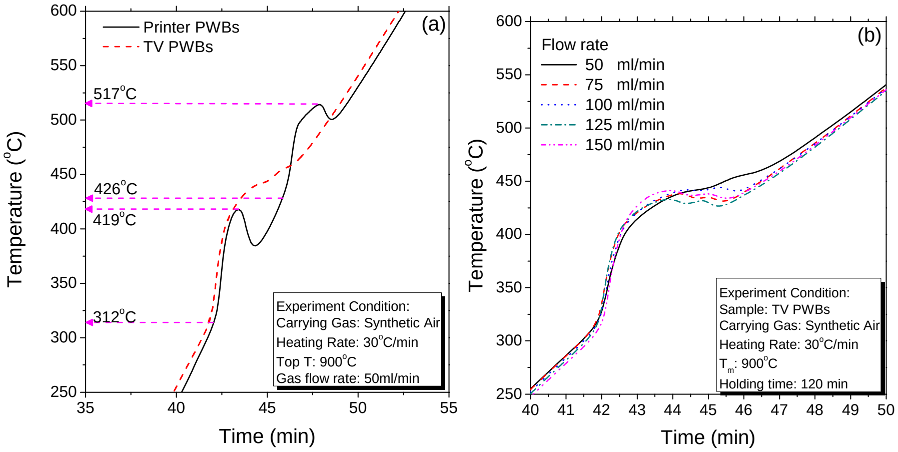


Figure 3.4. Sample Temperature *versus* Time (TV PWBs)

Figure 3.5 shows the mass loss (TG curve) in percentage and the derivative of the mass loss (DTG) of PWB samples. TG curves of TV PWBs indicated that the final remaining char was around ~13% of the original mass. The final remaining char is somehow independent of the gas flow rate and heating rate. DTG curves have two peaks in the experiments with 10 °C/min heating rate and one peak in the experiments with 25 °C/min heating rate. The signal intensity of DTG increases with the increase of gas flow rate. With 10 °C/min heating rate, the experiment with 150 ml/min gas flow rate has the maximum DTG signal intensity of 4,500 μg/min and the one with 50ml/min gas flow rate has the maximum signal intensity of 2,000 μg/min. TG curves of printer PWBs also indicated that the final remaining char of the combustion was around ~3% of the original mass, as shown in Figure 3.6. The difference of the final mass between TV PWBs and printer PWBs may be because of the difference of material compositions of these two PWBs. Figure 3.6 also indicates that the holding time at $T_m$ has little effect on the combustion process if the $T_m$ is larger than 600 °C. The curves DTG~T have three peaks, the second and third peaks decreases with increasing heat rate. The first peak is at 300-340 °C, the second peak is at 360-390 °C, and the third peak is at 420-450 °C.

With the same heating rate, the first DTG peak slightly increases with the increase of gas flow rate, as shown in Figure 3.7a. The second peak is independent of air flow rate (Figure 3.7b).

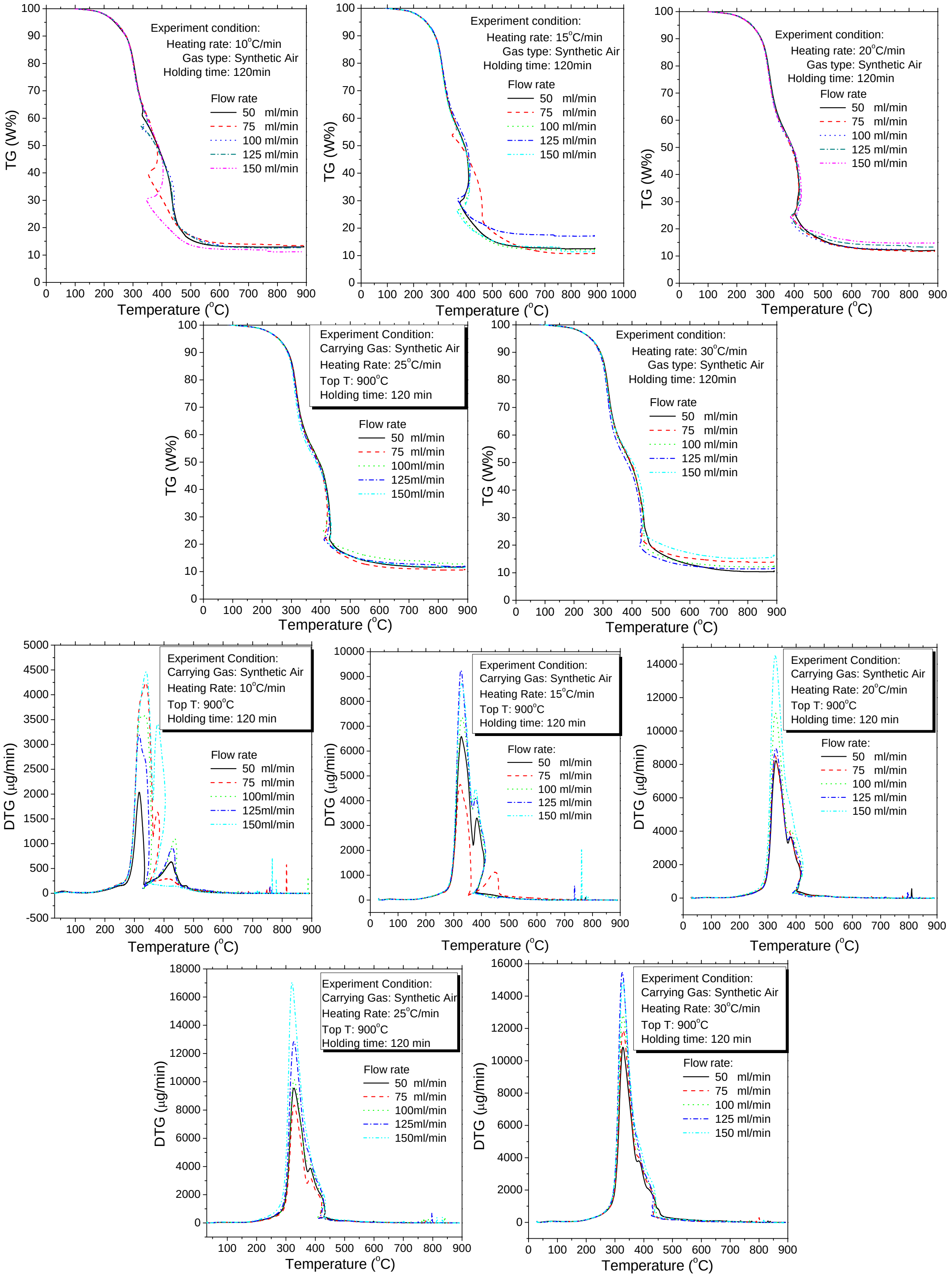


Figure 3.5. TG and DTG Curves for Experiments with Heating Rate of 10-30 °C/min and Different Gas Flow Rate (TV PWBs)

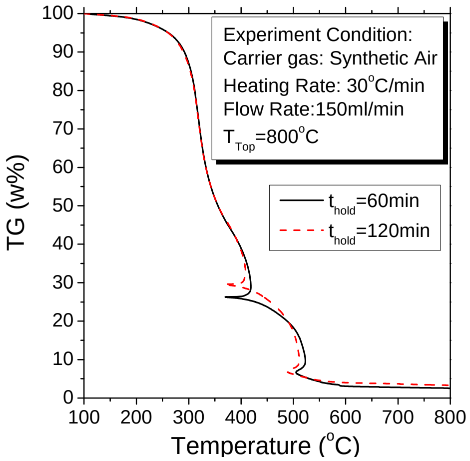


Figure 3.6. TG Curves for Experiments with Heating Rate of 30 °C/min and 150 ml/min Gas Flow Rate (Printer PWBs)

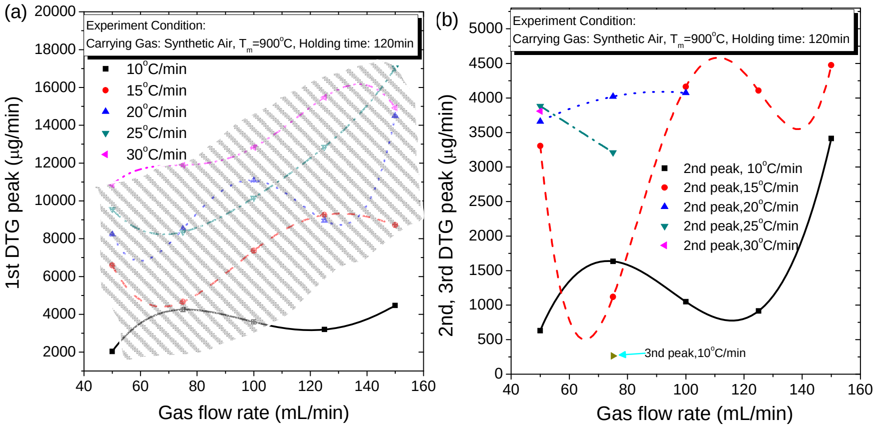


Figure 3.7. DTG Peaks with 50-150 ml/min Gas Flow Rate (TV PWBs)

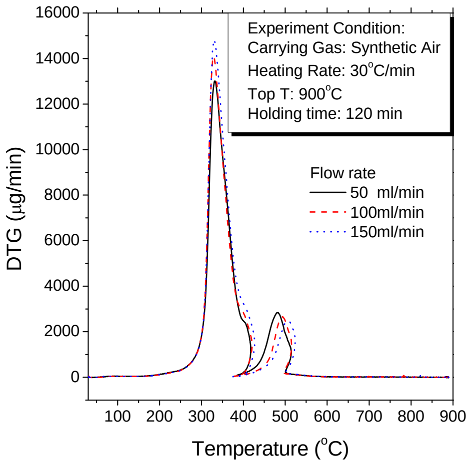


Figure 3.8. DTG Curves for Experiments with Heating Rate of 30 °C/min and Different Gas Flow Rate (Printer PWB)

Figure 3.8 shows again the combustion of TV PWBs and printer PWBs is slightly different. Compare to TV PWBs, the DTG curves of printer PWBs (Fig.3.8) have the flowing features:

- Gas flow rate has little effect on the combustion process;
- The second peak occurs at different time, so the two peaks are separated from each other, not like TV PWBs, the peaks are partially merged.

The mass loss can also be expressed by the conversion fraction, α, defined as:

$$\alpha = \frac{w_0 - w_t}{w_0 - w_f} \tag{3.1}$$

where $w_o$ is the initial mass, $w_t$ is the mass at $t$ time and $w_f$ is the final mass. The conversion fraction curves of the experiments with different heating rates and different gas flow rates, as shown in Figure 3.9.

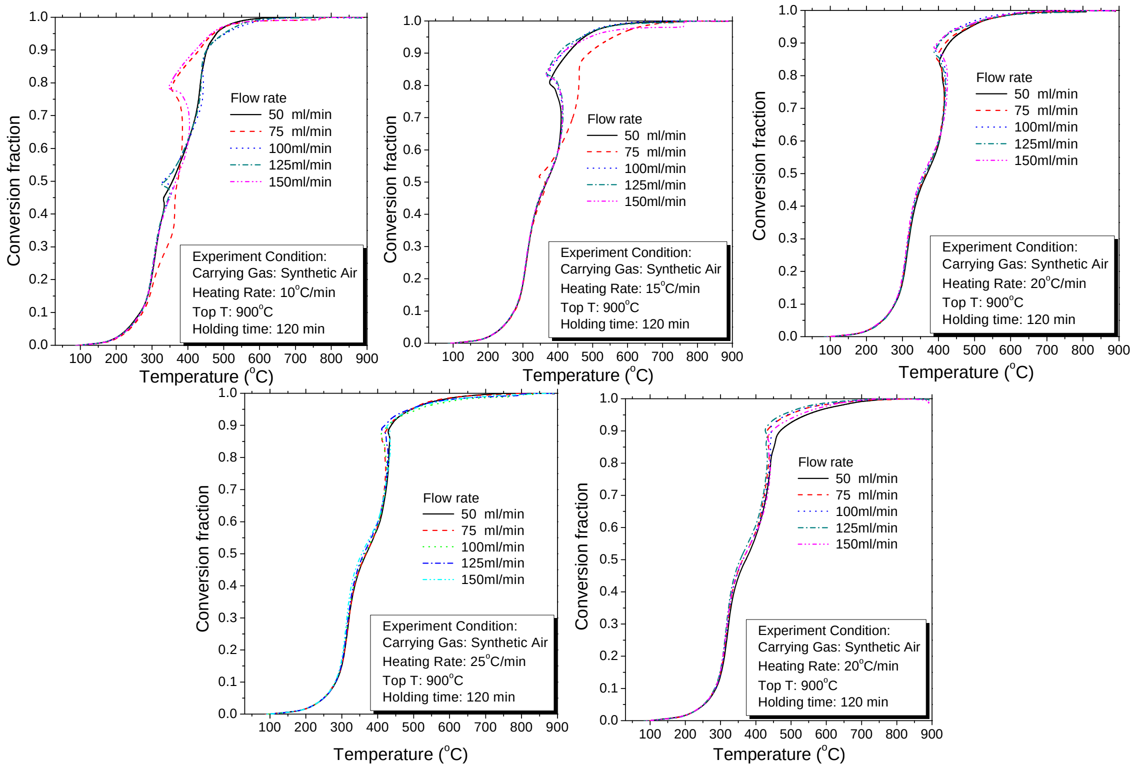


Figure 3.9. Conversion Fractions of the Experiment with Heating Rate of 25 °C/min and Different Gas Flow Rate (TV PWBs)

Figure 3.9 indicates that the conversion fraction is independent of air flow rate, especially when the heating rate is bigger than 15 °C/min. Most of the reactions during the combustion process and the main mass loss occur at 220-550 °C. For example, at 400 °C the conversion fraction is approximately 0.6 and at 550 °C the conversion fraction exceeds 0.96.

**3.2.2 Effect of Heating Rate.** The heating rate has great influence on the combustion process and the oxidization of metals. As shown in Figure 3.10, two abrupt temperature jumps were observed for the experiment with 10 °C/min heating rate, but only one jump for larger heating rate. Thus, the experiment with 10 °C/min heating rate has two obvious reaction peaks occurring at 300-350 °C and 390-445 °C respectively. For the first peak, both the peak start temperature and the range of temperature peak increase with the increase of heating rate.

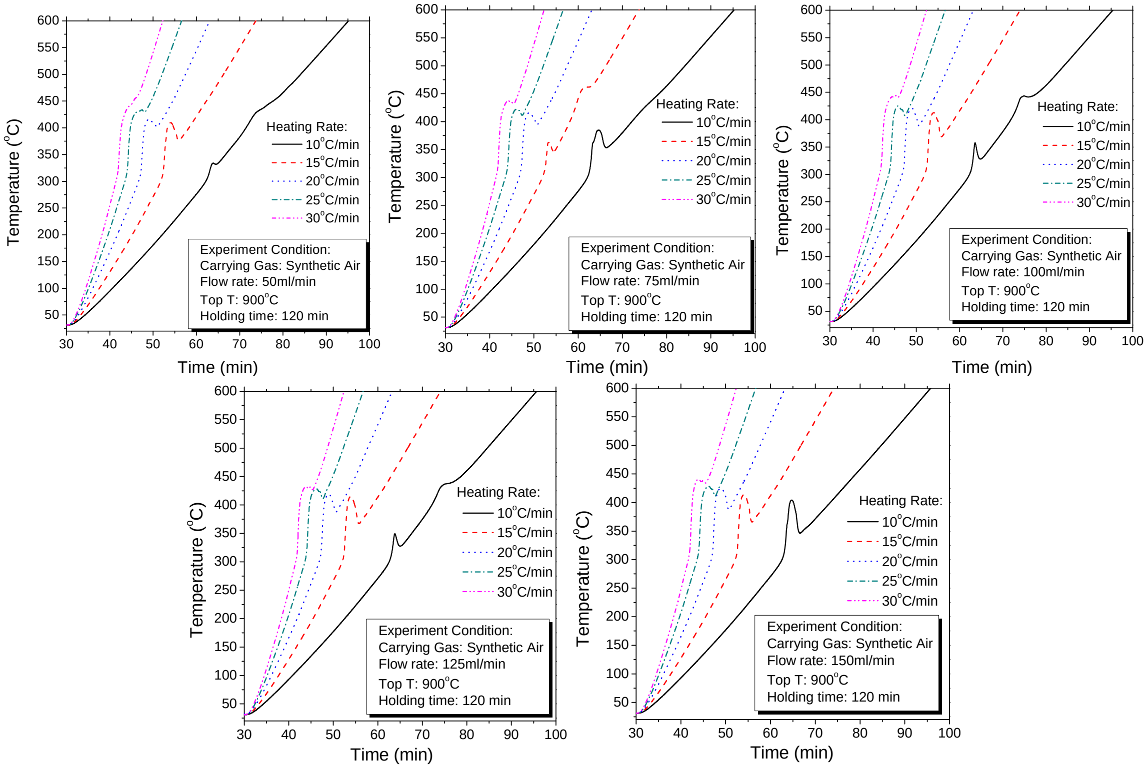


Figure 3.10. Sample Temperature *versus* Time (Different Heating Rate) (TV PWBs)

In addition, the peak scope becomes weak as the heating rate increases. As discussed above, with smaller heating rate (10 °C/min), the heat supply is not enough to start all the combustion reactions, so at ~300 °C, some reaction may occur first, and then when temperature increases to ~390 °C, other combustion occurs**.** The temperature jumps varying with heating rate are drawn in Figure 3.11a. The temperature jump increases with increasing heating rate, reaches the maximum heat value at 15 °C/min, and then decreases with further increases of the heating rate. The heat emitted during the combustion process is proportional to $\Delta T \times \Delta t$, which is shown in Figure 3.11b. In the industrial scale, larger heat emission is needed to propagate the combustion reaction. From the figure, it is concluded that the best heating rate should be approximate 15 °C/min.

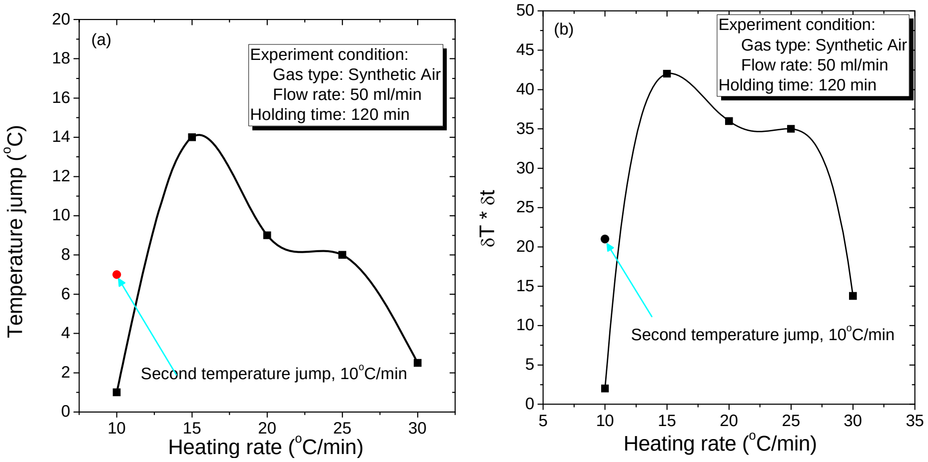


Figure 3.11. Temperature Jump Varying with Heating Rate (TV PWBs)

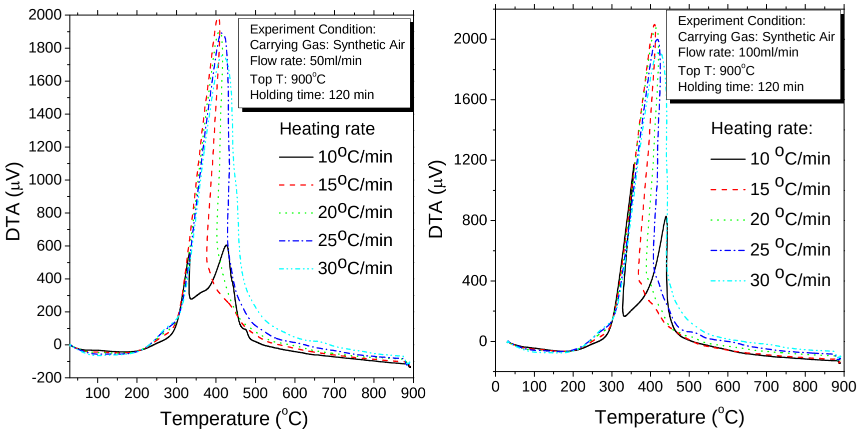


Figure 3.12. DTA Curves with Different Heating Rate of 10-30°C/min, Gas Flow Rate of 50 and 100 ml/min. (TV PWBs)

The DTA curves with different heating rate and gas flow rate are shown in Fig.3.2 and Figure 3.12. Two peaks of DTA are only observed in the experiment with 10°C/min heating rate. For experiments with only one single peak, the range of the DTA peak gradually shortens with the decrease of the heating rate. Unlike experiments with varying gas flow rate, the top peak signal intensity of DTA depends a little on the heating rate. Fig. 3.2 and 3.12 show that if the heating rate is over 15 °C/min, there will be only one peak. One peak implies one main combustion reaction. So the heating rate should not be less than 15 °C/min for the industrial combustion process. There will be only one peak if 125 ml/min gas is used no matter the value of the heating rate. In the industrial combustion process, complicated reactions should be avoided since complicated toxic gases may be generated. Thus, the reasonable gas flow rate should not be <125 ml/min.

The peaks value of the DTA curves varying with heating rate are shown in Figure 3.13. The DTA peaks increase with increasing in heating rate and reaches a constant value at 15°C/min. Since large heating rate impacts negatively on the mechanical and thermal properties of furnace materials, 15°C/min is enough and is the best for the industrial combustion process. Wu [89] has reported that the biggest product yield could be obtained at 15-20°C/ min heating rate during pyrolysis of PWBs.

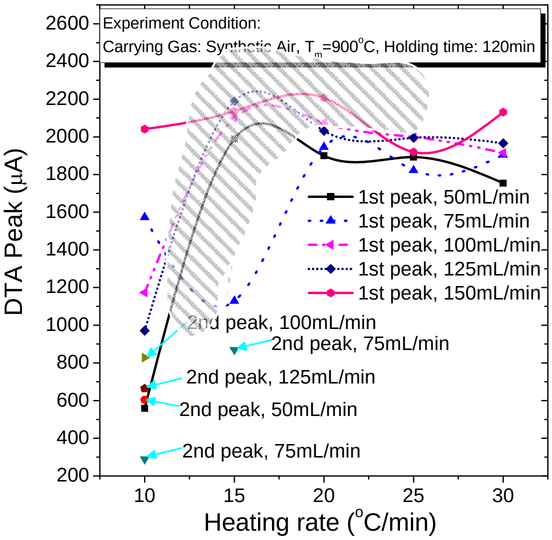


Figure 3.13. DTA Peak Varying with Heating Rate (TV PWBs)

For the experiment with 10 °C/min heating rate and 50 ml/min gas flow rate, five stages were observed from TG/DTG curves during the combustion process (as shown in Figure 3.14):

- First stage (30-300 °C): no reaction occurs in this period, but the moisture and weak coating materials were removed. Thus there was a little mass loss.

- Second stage (300-350 °C): the first reaction period. Sample temperature was far higher than heating procedure. Some organic substances reacted with oxygen strongly releasing a big heat. This period was only 2-3 min. Then the sample temperature dropped back to the normal temperature procedure quickly.
- The third stage (350-390 °C): No new reactions in this period, and with small mass loss.

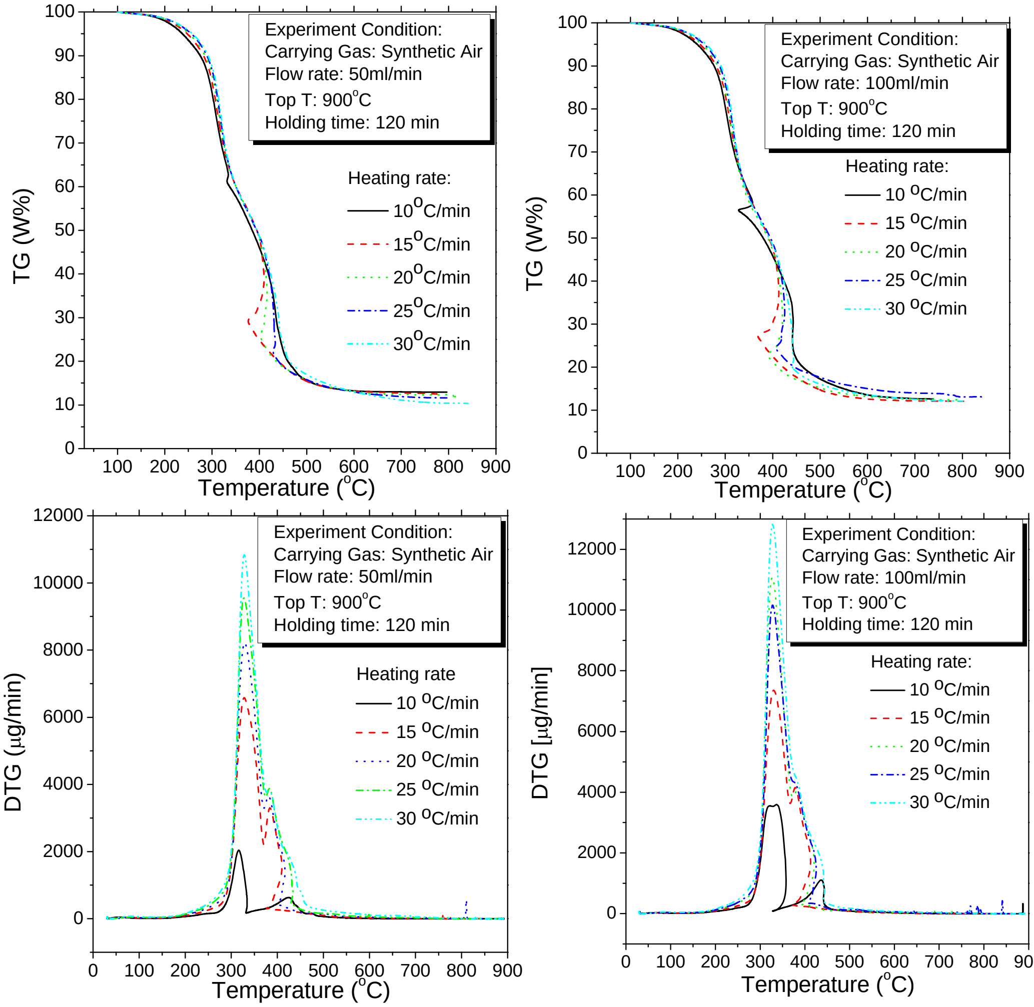


Figure 3.14. TG and DTG Curves for Experiments with 50 and100 ml/min Gas Flow Rate, and Different Heating Rate.(TV PWBs)

- The fourth stage (390-450 °C): The second exothermic reaction occurred here, and lasted ~1min. Sample temperature was far higher than heating procedure. Some organic substances reacted with oxygen strongly to release big heat.

- The fifth stage (>450 $^{o}$C): The sample temperature rose up continuously according to the heating set procedure and reach the terminal temperature (900 $^{o}$C), and held there for 120 min. No further reaction occurred at this stage.

For the experiment with 25 $^{o}$C/min heating rate and 50 ml/min gas flow rate, only one peak occurs on the DTA curve, three stages could be observed from TG/DTG curves during the combustion process:

- First stage (30-300 $^{o}$C): This stage is similar to the first stage of experiments with the heating rate of 10 $^{o}$C/min.
- Second stage (300-450 $^{o}$C): The main reactions occurred at this temperature range.
- Third stage (>450 $^{o}$C): No big change in this period.

The conversion fraction curves of combustion PWBs with different heating rates are plotted in Figure 3.15. There is little difference at after the temperature reaches at 600 $^{o}$C, and the conversion fraction can be over 97%. So 600 $^{o}$C is high enough for the combustion of PWB powders.

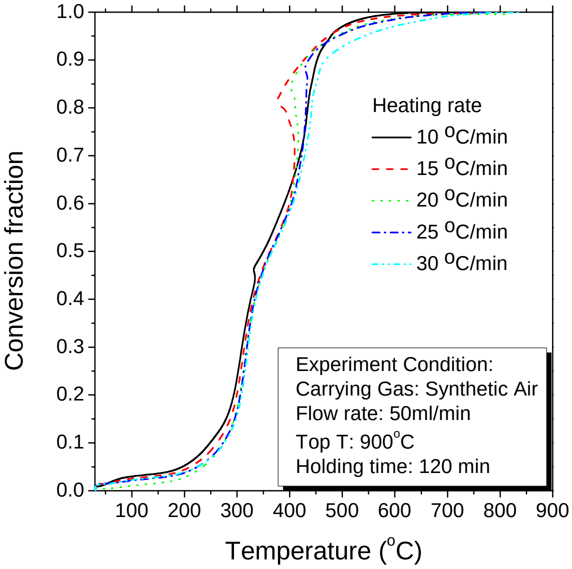


Figure 3.15. Conversion Fractions of the Experiment with Gas Flow Rate of 50 ml/min and Different Heating Rate. (TV PWBs)

**3.2.3. Emitted Gases Analysis.** The exhausted gases during combustion process were detected using MS machine. CO, $CO_2$, $H_2O$, $CH_4$, $C_2H_2$, $C_2H_2O$, $C_2H_3O$, $C_2H_4O$, $C_2H_5O$, $C_3H_5O$, $C_6H_6$, HBr were found during PWBs combustion, and the intensity increases with increasing heating rate. CO, $CO_2$, $H_2O$, $CH_4$, $C_2H_5O$, $C_6H_6$ and HBr gas signals varying with the temperature are plotted in Figure 3.16. For some gases, there were several peaks, which corresponded to the reaction temperature. The main MS signal peaks occur at 300-500 $^oC$ for combustion process, which corresponds to the DTA and DTG curves shown in Fig. 3.2 and 3.4. For low heating rate, the MS signal peaks are very narrow. This is because the temperature rises more slowly as a lower heating rate is adopted and the reaction speed may be faster than the rising temperature.

As shown in Fig.3.16, the MS signal peaks were over a big temperature range: 300-900 $^oC$, which implied that different reactions occurred at different temperature and different products were obtained since the PWB consisted of different organic materials. The temperatures of different evolved gases are listed in Table 3.2. For the combustion process, $CO_2$ and CO reached maximum at 350-400 $^oC$, which implies the main combustion reaction was at 350-400 $^oC$, corresponding to the DTA curves. For combustion, all gases ($CO_2$, $H_2O$, $CH_4$, $C_2H_5O$, $C_6H_6$ and HBr) had peaks at 300 $^oC$, which implied that at 300 $^oC$ the oxidization reaction occurred.

It should be noticed that $C_6H_6$ and HBr gas was detected, while Br element is one of the main composition of the BFRs in the PWB. Since HBr is toxic to human beings, in order to environmentally recycle PWBs, suitable methods should be developed to prevent HBr from being released into the air.

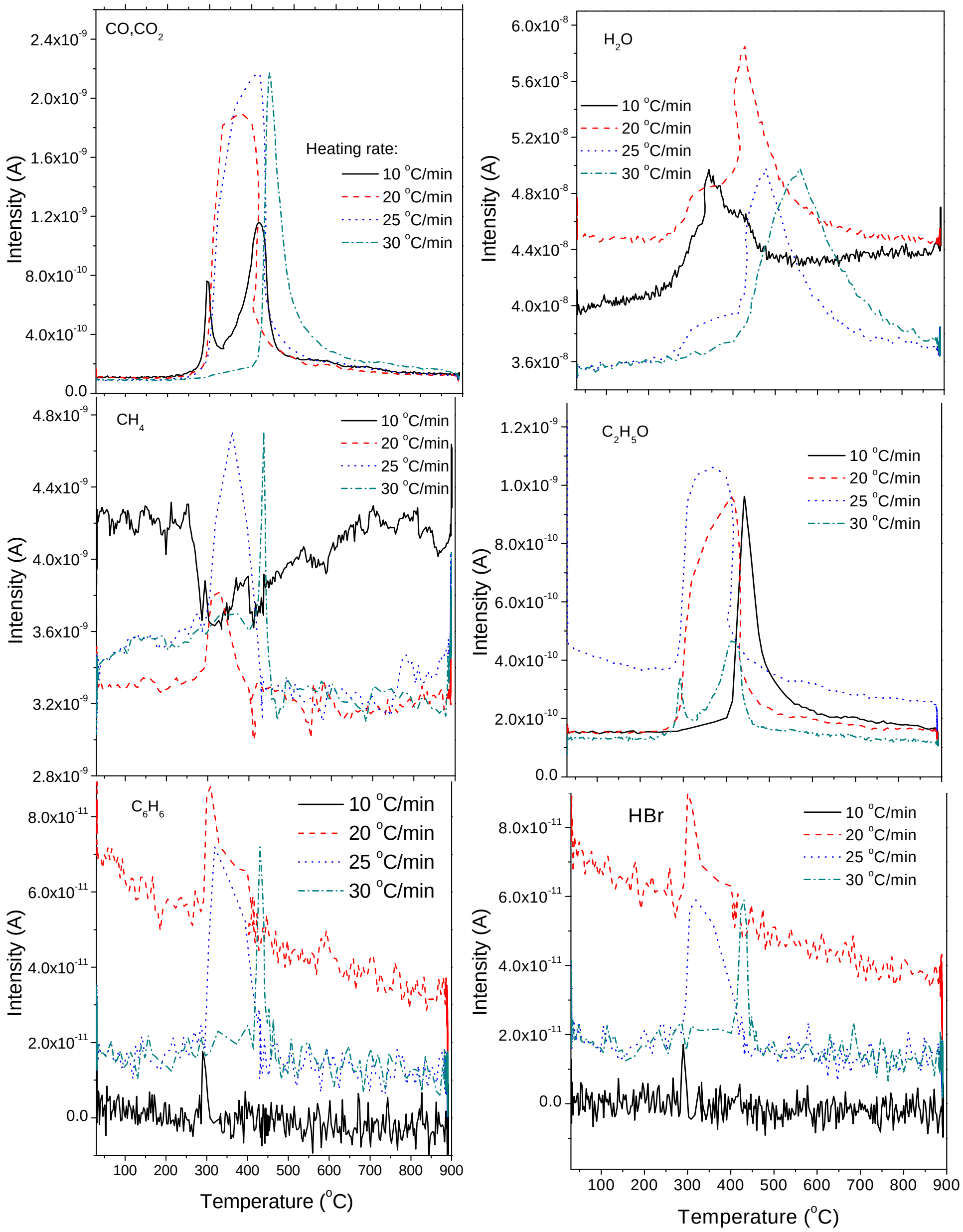


Figure 3.16 Exhausted Gases during Combustion Process (TV PWBs)

Table 3.2. The Evolved Gases at Different Temperature

| Experimental condition | Combustion | |
|---|---|---|
| | $T_{peak}$, °C | Gas type |
| 10°C/min, 50ml/min | 290 | $CO$-$CO_2$, $C_2H_2$, $C_2H_2O$, $C_2H_3O$, $CO_2$-$C_2H_4O$, $C_2H_5O$, $C_6H_6$, HBr |
| | 294 | $C_3H_4O$ |
| | | 346 |
| | 413-416 | $CO$-$CO_2$, $C_2H_2O$, $C_2H_5O$, $CO_2$-$C_2H_4O$ |
| | 420 | $C_2H_3O$ |
| 20°C/min, 50ml/min | 310 | $C_2H_2$, $C_6H_6$, $C_2H_2O$, |
| | 330, 331 | $CH_3$, $C_3H_4O$ |
| | 374 | $CO$-$CO_2$, $C_2H_3O$, $CO_2$-$C_2H_4O$, $C_2H_5O$, |
| | 427 | $H_2O$ |
| 25°C/min, 50ml/min | 360 | $CH_3$ |
| | 410-412 | $C_3H_4O$, $C_2H_5O$, |
| | 420 | $CO_2$-$C_2H_4O$, $C_2H_3O$ |
| | 440 | $CO$-$CO_2$ |
| | 478 | $H_2O$ |
| 30°C/min, 50ml/min | 431, 432 | $C_2H_2$, $Cl_2$, $C_3H_4O$, $C_6H_6$, HBr |
| | 436 | $CH_3$ |
| | 440 | $CO$-$CO_2$, $C_2H_3O$ |
| | 444 | $CO_2$-$C_2H_4O$ |
| | 468 | $C_2H_2O$ |
| | 482 | $C_2H_5O$ |
| | 559 | $H_2O$ |

## 3.3. COMBUSTION OF PWBS WITH ADDITIVE

In this chapter, combustion experiments were performed to control the emission of toxic gas during the combustion of PWB powder by adding chemical additives.

**3.3.1. Experimental Procedure.** The TV PWB samples mixed with certain chemical powders were combusted in TG/DTA. Evolved gases were measured using MS.

The MS signal intensity of different evolved gases were compared with those no additives and the effect of chemical additives on the control of gas emission was discussed. The heating rate was 20 $^{o}$C/min and the top temperature ($T_m$) was set to 900 $^{o}$C , and the holding time at the top temperature was 120 min. Synthetic air was used as the carrier gas with flow rate of 50ml/min. Chemical reagents, $Na_2CO_3$, $NaHCO_3$, NaOH and $CaCO_3$, were used. The chemical properties of additive reagent were listed in Table 3.3. The weight ratio between PWB powders and additives was 1:1.

The measured sample temperatures are shown in Figure 3.17. The TG-DTG-DTA curves with different additive are shown in Figure 3.18 and 3.19. For combustion experiments without additive, the sample temperature curve had an obvious jump which implied exothermic reaction. However no temperature jump was found during PWB combustion with additive. When using $NaHCO_3$, there was a temperature decrease at 165-200 $^{o}$C which might be caused by the decomposition of $NaHCO_3$, by following reaction:

$$NaHCO_{3(s)} \xrightarrow{\text{decomposition}} Na_2CO_{3(s)} + CO_{2(g)} + H_2O_{(g)}$$

Table 3.3. The Chemical Properties of Additive Reagent [112-113]

| Additive | $CaCO_3$ | NaOH | $NaHCO_3$ | $NaCO_3$ | CaO |
|---|---|---|---|---|---|
| Decomposing Temperature ($^{o}$C) | 600-1000 | - | >100 | 858.1-1000 | - |
| Melting Point ($^{o}$C) | 825 | 318.4 | 270 | 858.1 | 2580 |

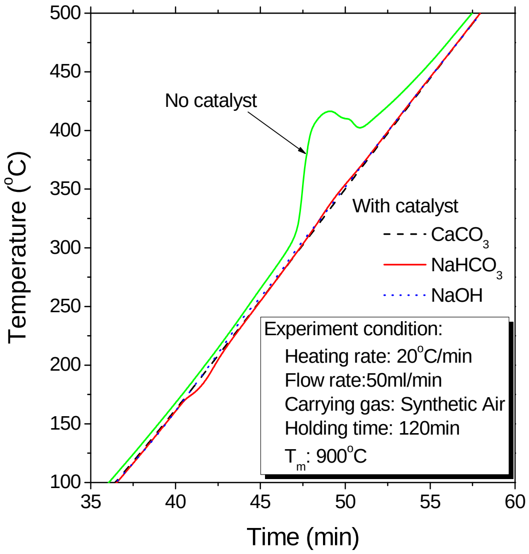
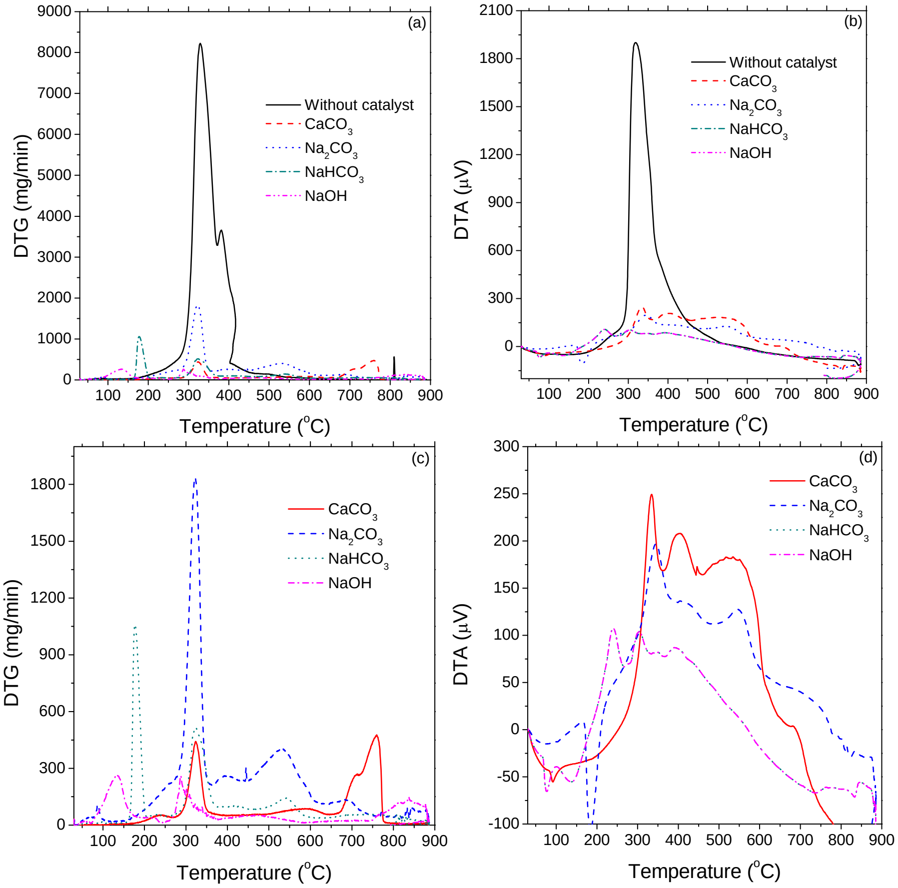


Figure 3.17. Temperature of PWB Powders with Additive during Combustion in TG-DTA Furnace



Experiment condition: Heating Rate 20°C/min; Air Flow Rate 50ml/min; T$_m$=900°C

Figure 3.18. TG, DTG and DTA Curves of PWBs Powders with Temperature.

**3.3.2. TG Analysis.** Mass loss shown in TG curves could be divided into two parts: 1). the mass loss between the room temperature and the terminal temperature ($T_m$) and 2). mass loss during the holding period at $T_m$. For the experiments without additives, no evolved gases could be absorbed, thus the mass loss (>85%) would be far larger than the experiments with chemical additives. The rapid mass loss could no longer be observed as the temperature rose to 900 $^oC$. However, for the experiments with additives, mass loss during holding period at the top temperature was observed.

Figure 3.19 showed profiles for pure chemical additives ($CaCO_3$, $NaHCO_3$, $NaCO_3$ and NaOH), pure PWBs and the mixture of PWBs and additives (1:1). The TG curves the pure PWBs exhibited four stages of mass loss, and ended with a stable residue at >700 $^oC$.

a) For pure $CaCO_3$ and PWBs, weight loss occurred at 500-700 $^oC$ and 150-300 $^oC$. The TG curve of PWBs+$CaCO_3$ is sandwiched between the pure $CaCO_3$ and PWBs, as shown in Figure 3.19(a). During 300-700 $^oC$, $CaCO_3$ has a little decomposition. The acidic exhaust gases mainly reacted with $CaCO_3$ to form $CO_2$ and calcium salts [114-115].

b) Since $NaHCO_3$ started to decompose at >100 $^oC$, there was a big mass loss at 100-170 $^oC$ (Fig. 3.19(b)). But little mass loss occurred at this temperature when only PWB sample was heated. Therefore, there was a big mass loss at 100-170 $^oC$ in TG curve of PWB+$NaHCO_3$ due to the decomposition of $NaHCO_3$. The decomposition products of $NaHCO_3$ were $Na_2CO_3$, $CO_2$ and $H_2O$. Therefore, the acidic gases could react either with $NaHCO_3$ and $Na_2CO_3$ that was generated from the decomposition of $NaHCO_3$.

c) For the decomposition of $Na_2CO_3$, Figure 3.19(c) shows that there was a small mass loss at 80$^oC$ which might be because the moisture was evaporated at this temperature. Over this temperature little change occurred. Mass loss of the mixture (PWB+$Na_2CO_3$) was mainly due to the degradation of PWB and the reaction between acidic exhaust gases and $NaCO_3$.

d) No mass change could be found as the pure NaOH was heated, as shown in Figure 3.19(d). The main mass loss of the mixture mainly stemmed from the degradation of PWB powders and the reaction between acidic exhaust gases and NaOH.

NaOH was hardly decomposed. Toxic gases like HBr, $H_2O$ and $CO_2$ could be also absorbed by NaOH. The emitted organic gases such as $CH_4$, $C_2H_2$ and $C_2H_6$ induced a little mass loss. However, since the holding time at $T_m$ was 120 min, $Na_2CO_3$ might stem from the reaction between NaOH and the decomposed $CO_2$ from the PWB organic materials, and the generated $Na_2CO_3$ might further be decomposed.

**3.3.3. DTG Analysis.** DTG curves could be plotted by differentiating the TG curves. As shown in Figure 3.19, the pure PWB sample presented the biggest DTG peak value. DTG peaks with $CaCO_3$ additive revealed two reactions: one at 250-350 °C and the other at 650-780 °C. An obvious peak could be observed at temperature range of 650-780 °C, which implied that some $CaCO_3$ decomposed reaction at this temperature.

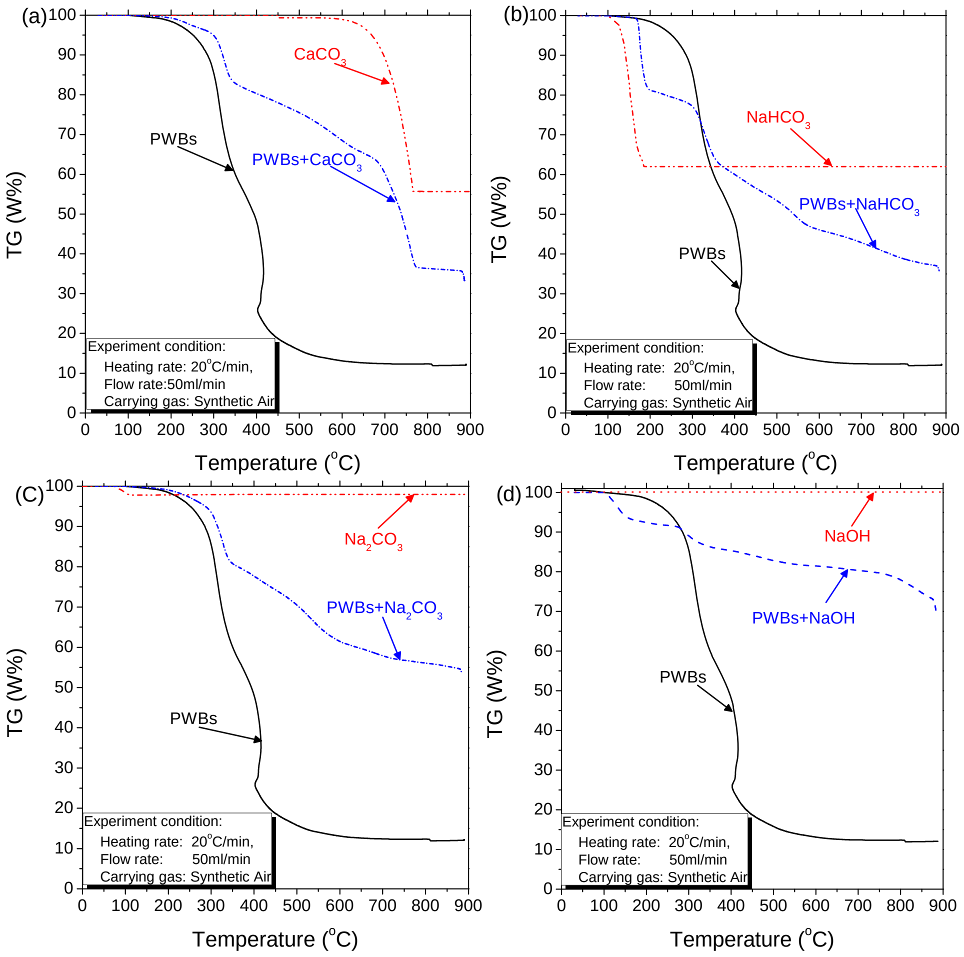


Figure 3.19. TG Curves of additives, PWB and PWBs+additives [116-118]

This reaction also could be also demonstrated by the $CO_2$ MS signal found in Figure 3.20. The first peak of DTG curves with $NaHCO_3$ occurred at approximately 150-200 °C, at which the $NaHCO_3$ reagent decomposed to $Na_2CO_3$ and $H_2O$ rather than the decomposition of PWBs powders. Figure 3.20 also shows that the experiment with $NaHCO_3$ additive has a peak occurring at the same temperature range.

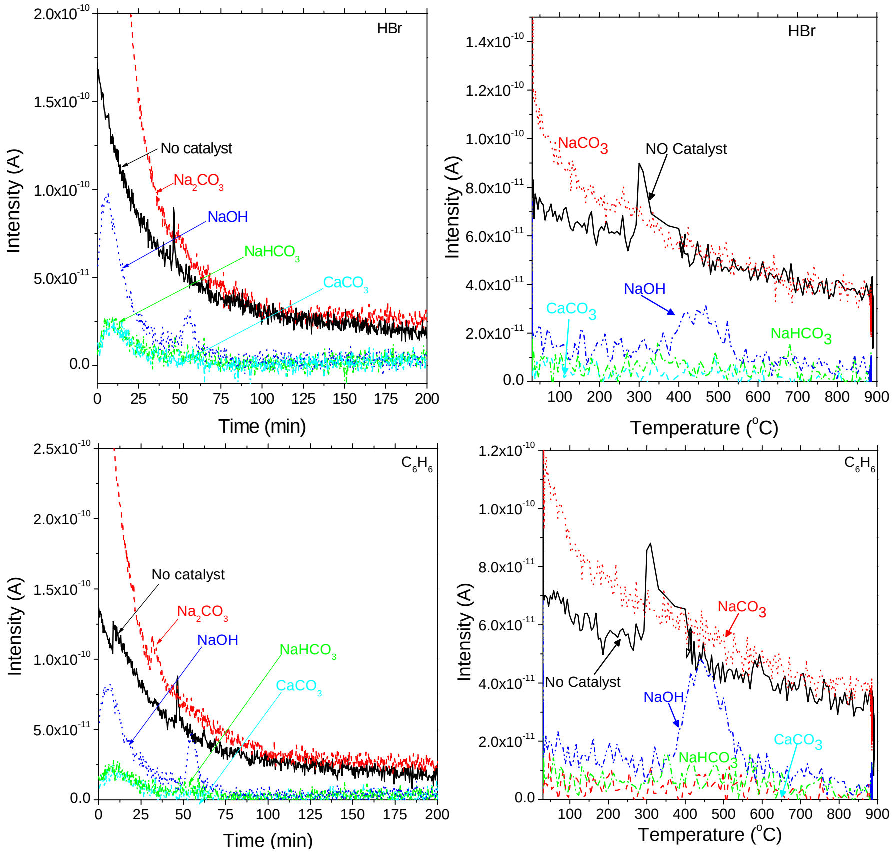


Figure 3.20. MS Signal of HBr and Benzene with Time and Temperature

**3.3.4. MS Analysis.** CO, $CO_2$, $H_2O$, $CH_4$, $C_2H_2$, $C_2H_2O$, $C_2H_3O$, $C_2H_4O$, $C_2H_5O$, $C_3H_5O$, $C_6H_6$ and HBr were found during PWB combustion. During PWBs combustion with the additives, there was no obvious temperature jump, as shown in Figure 18, which meant that there was no occurrence of strong exothermic reactions during combustion. In other word, the subsequent dehalogenation reactions were not exothermic.

The intensity of the emitted HBr and $C_6H_6$ gases during combustion was shown in Fig.3.20. In the experiments with additives, both HBr and benzene gases were hardly controlled by adding NaOH. The experimental results showed that the MS signal peaks were postponed to later time and temperature when using additives. For example, with no additives, the HBr MS signal peak occurred at time range of 40-45min and temperature range of 275-410 $^{o}$C. However, with NaOH additives, the MS signal peaks delayed to ~45-63 min and the temperature range of 375-550 $^{o}$C. As shown in Figure 3.21, as the $CaCO_3$ additive is adopted, the intensities of HBr and benzene MS signal peaks are close to zero. For the ability of controlling HBr and $C_6H_6$, the order should be $CaCO_3$>$Na_2CO_3$>$NaHCO_3$>NaOH. The MS signals of other evolved gases like CO, $CO_2$, $H_2O$, $CH_4$, $C_2H_2$, $C_2H_2O$, $C_2H_3O$, $C_2H_4O$, $C_2H_5O$ and $C_3H_5O$ were shown in Figure 3.22. The alkaline additives had a certain effect on inhibiting these acidic substances like $CO_2$ and some toxic gases. For the experiments with chemical additives some organic gases like $CH_3$, $C_2H_2$ and $C_2H_3O$ also had lower peak intensities than the experiment without additives, which implies that these additives can also act as catalyst to control the decomposition process to produce different organic gases.

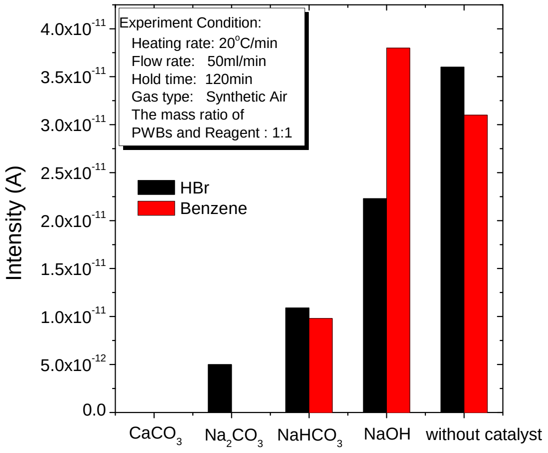


Figure 3.21. The MS Signal Peak Intensity of HBr and Benzene

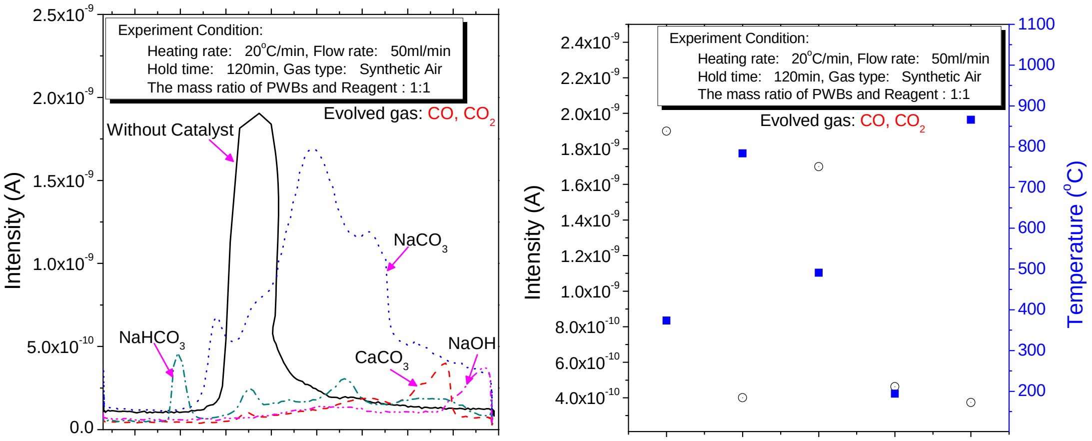


Figure 3.22. Other Evolved Gases MS Signal with Temperature

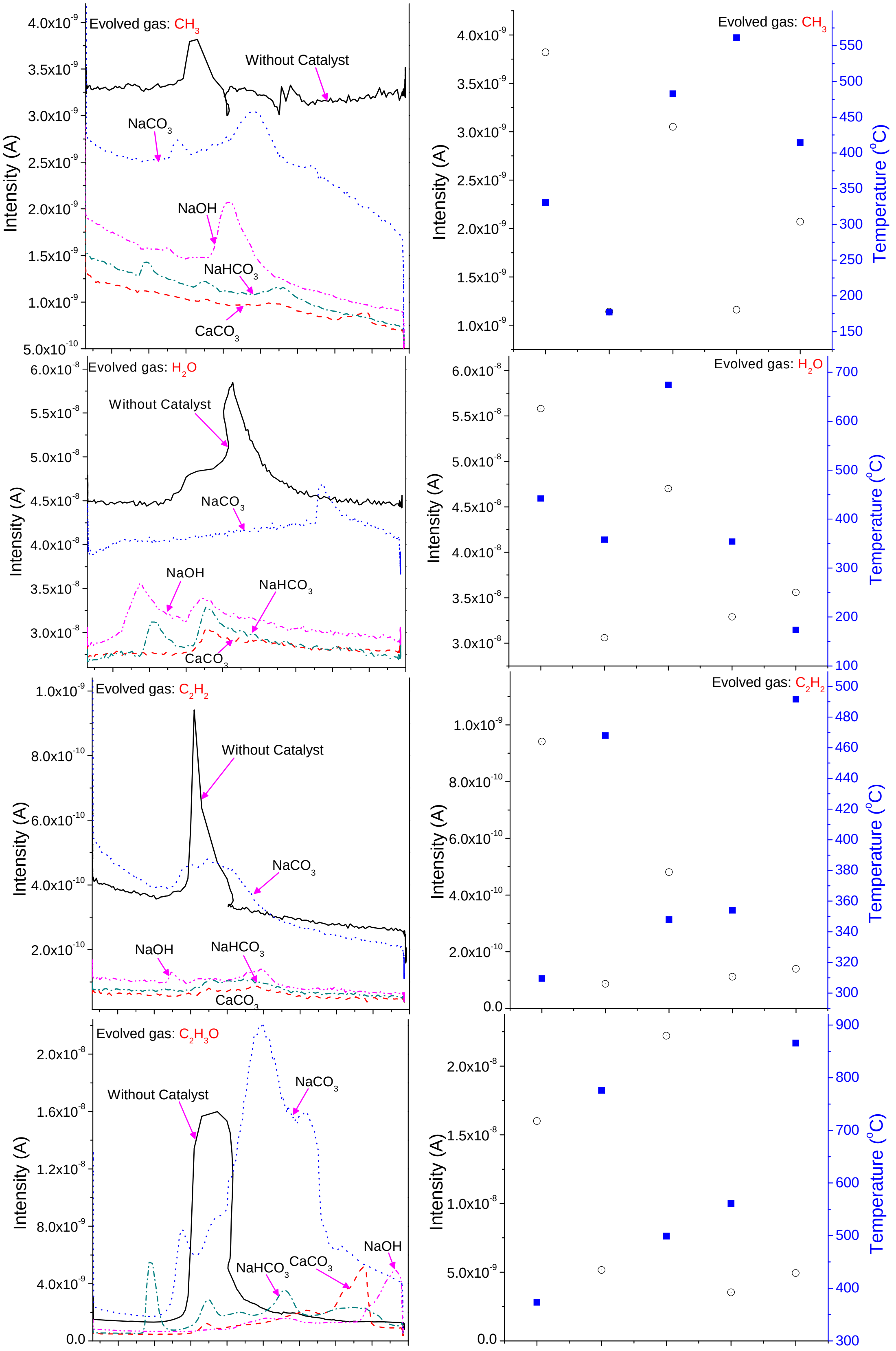


Figure 3.22. (Continued) Other Evolved Gases MS Signal with Temperature

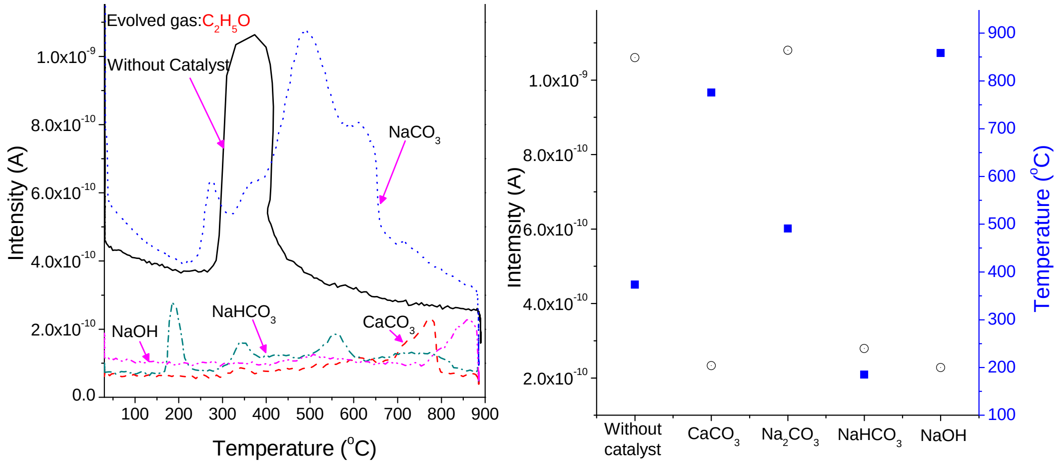


Figure 3.22. (Continued) Other Evolved Gases MS Signal with Temperature

### 3.3.5. Control HBr from the Gas Emission during the Combustion of PWBs.

During the combustion of PWB powders, HBr mainly released at 300-360 °C, accompanied by with the main chain scissions of epoxy and brominated epoxy backbones [115]. The chemical properties of additive, such as decomposition temperature and melting point are listed in Table 3.3.

Obviously, at a certain temperature, both PWB powders and additives would be heated and decomposed. $NaHCO_3$ could be decomposed as the temperature was higher than 100 °C and will react with HBr with the following reactions:

$$2NaHCO_{3(s)} = Na_2CO_{3(s)} + CO_{2(g)} + H_2O_{(g)}$$

$$2HBr_{(g)} + Na_2CO_{3(s)} = 2NaBr_{(s)} + CO_{2(g)} + H_2O_{(g)}$$

The thermodynamic equilibrium constant of the above reaction is:

$$K_{eq}(T) = \exp\left(\frac{-\Delta G^0(T)}{RT}\right) \tag{3.2}$$

$$\Delta G^0(T) = \sum\left(\Delta G^0_{\text{products}} - \Delta G^0_{\text{reactants}}\right) \tag{3.3}$$

where $K_{eq}$ is the thermodynamic equilibrium constant, $\Delta G^0$ is the Gibbs free energy change, $T$ is the Kelvin temperature, and $R$ is the gas constant.

$$K_{eq} = \frac{\alpha_{H_2O}\alpha_{NaBr}\alpha_{CO_2}}{\alpha_{Na_2CO_3}\alpha^2_{HBr}} \tag{3.4}$$

The melting point of NaBr is about 747 °C. Under this temperature, therefore, the concentration of HBr could be expressed:

$$\alpha_{\mathrm{HBr}} = \sqrt{\frac{\alpha_{\mathrm{CO_2}}\alpha_{\mathrm{H_2O}}}{K_{eq}}} \tag{3.5}$$

The above equation shows that the equilibrium concentration of HBr is dominated by the concentration of $CO_2$ and $H_2O$ in the emitted gas. Theoretically, if the concentration of $CO_2$ and $H_2O$ increases, HBr increases. However, $Na_2CO_3$ and NaOH had a certain catalytic effect on the thermal degradation of PWBs [98], the thermal degradation of PWBs is earlier than the decomposition of $Na_2CO_3$, as shown in Figure 3.22. It had a wider CO, $CO_2$ peak than the thermal degradation of PWBs without any additive. $NaHCO_3$, $Na_2CO_3$ and $CaCO_3$ were very efficient to control the emission of HBr compared to the case without additive, as shown in Fig.3.22. During the experiments, the additives and bromide products were melted to liquid which might corrode and destroy the crucible due to its strong basicity. In addition, MS results indicated that $NaHCO_3$ and $Na_2CO_3$ were not the best choice to remove the toxic gas like $C_6H_6$. Another important reason that $NaHCO_3$ and $Na_2CO_3$ are not suitable for the green recycling of PWBs in industrial scale is their higher price than $CaCO_3$. NaOH had effect on enhancing the thermal degradation of PWBs [98]. However, NaOH would be melted (as shown in Table 3.3) before the thermal degradation of PWBs. NaOH is more corrosive than $NaHCO_3$ and $Na_2CO_3$. In laboratory scale the $Al_2O_3$ and platinum crucibles would be corroded by NaOH.

In combustion process, the evolved HBr reacted with $CaCO_3$ to form $CaBr_2$, and released $CO_2$ and water vapor. The reaction between evolved HBr and $CaCO_3$ is:

$$2HBr_{(g)} + CaCO_{3(s)} = CaBr_{2(s)} + H_2O_{(g)} + CO_{2(g)}$$

The equilibrium constants calculated by FactSage software at different temperatures are calculated, as shown in Table 3.4.

Table 3.4. Chemical Equilibrium Constant for the Reaction of $CaCO_3$ and HBr

| Temperature, °C | 25 | 200 | 300 | 400 | 500 | 600 | 700 | 800 | 900 |
|---|---|---|---|---|---|---|---|---|---|
| $K_{eq}$, $\times 10^4$ | 20079 | 597 | 104 | 29.9 | 117 | 5.60 | 3.09 | 2.30 | 2.06 |

Thermal calculation shows that the equilibrium constant at 300-600°C is far larger than $2.55\times10^4$, which implies a complete reaction. The relationship between equilibrium constant and component concentration is given by:

$$K_{eq}=\frac{\alpha_{\mathrm{CO_2}}\alpha_{\mathrm{H_2O}}\alpha_{\mathrm{CaBr_2}}}{\alpha_{\mathrm{CaCO_3}}\alpha_{\mathrm{HBr}}^2} \tag{3.6}$$

In the reaction, because $CaBr_2$ and $CaCO_3$ are solid, $\alpha_{CaCO3}=\alpha_{CaO}\approx1$. Therefore, EQ.(3.6) could be simplified:

$$K_{eq}=\frac{\alpha_{\mathrm{CO_2}}\alpha_{\mathrm{H_2O}}}{\alpha_{\mathrm{HBr}}^2} \tag{3.7}$$

$$\alpha_{\mathrm{HBr}}=\sqrt{\frac{\alpha_{\mathrm{CO_2}}\alpha_{\mathrm{H_2O}}}{K_{eq}}} \tag{3.8}$$

Eq.(3.8) revealed that the equilibrium concentration of HBr is dominated by the concentration of $CO_2$ and $H_2O$. The organic compounds can be oxidized to produce $H_2O$ and $CO_2$ gas during combustion. In addition, huge amounts of heat will be released during the combustion process, thus the mixed sample would achieve a high temperature very quickly. $CaCO_3$ will be decomposed to produce much $CO_2$, so as to lower the equilibrium concentration of HBr.

## 3.4. CHAPTER SUMMARY

In this chapter, PWB materials from a used printer and TV were combusted in TG/DTA and the evolved gases were detected by MS. From the results as discussion above, it is concluded that:

a). Combustion process

- Heating in air atmosphere, there were two exothermic reactions. The first one occurred at 300-380 °C, and the second one occurred at 450-500 °C. Due to the release of big amount of heat during these two reactions, the sample temperature in these two temperature range abruptly jumped out the heating procedure, lasting 1-3 min.
- The gas flow rate and initial sample mass rarely affect the combustion process, only a little increase in temperature at the second peak resulting from increasing gas flow rate.

- The final remaining mass fraction during combustion was ~3% of the original mass for a printer PWBs and ~11-13% for a TV PWBs.
- Holding time at the top temperature had little effect on the combustion process.
- The suitable experimental conditions are 15 $^{o}$C/min heating rate, >125 ml/min gas flow rate, 600 $^{o}$C top temperature, and the holding time is not important for combustion.

b). Mass Spectrometry

- Due to the evolution of some toxic gases during PWB combustion, reasonable and advisable measurements should be adopted to control the emitted gases.
- As opposed to the combustion of PWB samples without additives, for PWB combustion with additive, there are no obvious exothermic reactions, indicating that dehalogenation reactions are not exothermic.
- The experiment without additive has the main mass loss during temperature ring and no obvious mass loss during the holding time at the top temperature period.
- The experiment with NaOH additive has smallest mass loss in the temperature rising period and biggest mass loss in the temperature holding time.
- The results showed that $CaCO_3$ and $NaHCO_3$ were very efficient to control the emission of HBr and benzene, lowering 80% compared to the case without additive. $Na_2CO_3$ can slightly control the emission of HBr gas but not for benzene gas mission, and NaOH has no obvious effect of the control of both gases.
- To some extent, some chemical additives can postpone the decompostion reaction to a later time and higher temperature, especially NaOH.
- Green combustion with suitable additives is an effective method to control the toxic gas emission during the combustion of PWBs. However, further investigations for the following related topics should be required:

  a) The detailed reactions during the combustion and pyrolysis of PWBs with and without additives and their activation energies;

  b) Behavior of heavy metals during combustion and pyrolysis;

  c) Other suitable additives;

  d) Industrial scale experimental design.

# 4. SMALL SCALE PYROLYSIS OF PWBS USING TG/DTA-MS

## 4.1. EXPERIMENTAL PROCEDURE

In the current study, PWBs from a printer named HP C2121A and a used TV were studied and crushed to small particles with diameter of 100-500 μm, as shown in Figure 3.1. Experiments of P25-P29, as shown in Table 4.1, have been done using the same TG/DTA-MS machine. Argon gas was used as carrier gas to investigate pyrolysis process. 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.

Pyrolysis experiments were conducted at certain heating rates (10, 20 and 30 °C/min) and certain argon gas flow rates (50, 75, 100, 125 and 150ml/min). PWBs samples were heated from room temperature to $T_m$=900 °C and then held at 900°C for 120 min. At the end of the holding period, TG/DTA still ran and the carrier gas (argon) was kept flowing until the reactor was cooled down to the room temperature. All experiments were carried out at atmospheric pressure.

Table 4.1. Experimental Conditions of E-waste Pyrolysis

| # | Initial Mass (mg) | Top Temperature | | Gas flow Rate (ml/min) | Heating rate °C/min |
|---|---|---|---|---|---|
| | | °C | Holding time (min) | | |
| P25 | 12.8722 | 800 | 60 | 150(Ar) | 30 |
| P26 | 13.6187 | 800 | 60 | 100(Ar) | 30 |
| P27 | 13.6097 | 800 | 180 | 50(Ar) | 30 |
| P28 | 13.3913 | 900 | 240 | 50(Ar) | 10 |
| P29 | 16.2128 | 900 | 240 | 50(Ar) | 30 |

## 4.2. PYROLYSIS OF PWBS WITHOUT ADDITIVE

**4.2.1. TG, DTG and DTA Analysis.** Since there is little combustion occurred due to the inert gas atmosphere, it was observed that the sample temperature followed the heating procedure exactly (as shown in Figure 4.1) and no temperature jump as observed in the case of combustion (Figure 3.4).

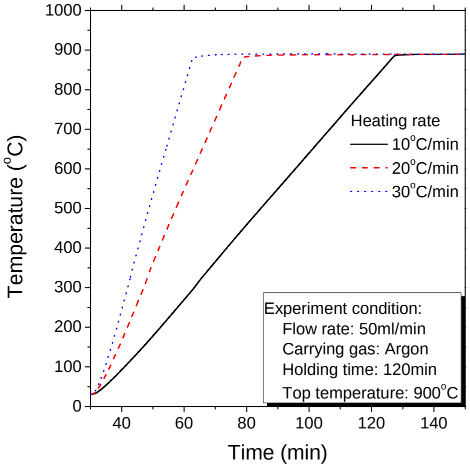


Figure 4.1. Temperature varying with time (TV PWBs)

The DTA curves of pyrolysis are plotted in Figure 4.2. DTA curve during pyrolysis was very complicated, the peak lasts very long temperature range from 300-900 $^{o}$C, which means that pyrolysis reaction occurred during a big temperature range. The possible reasons are:

- Since the PWB is made of mixture of polymers, the degradation reaction for different polymers occur at different temperature, thus the entire degradation lasts over a very long temperature range. For example, epoxy resin degrades at ~280 °C, while brominated flame retardant degrades above 390 °C [119-120].
- The pyrolysis reaction is slower than the combustion reaction and thus lasts longer time.

Some researchers have reported the pyrolysis temperature of PWBs to be ~300-600 $^{o}$C [86, 106]. For current the case, the pyrolysis reaction starts at ~330$^{o}$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 at ~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 a peak ~250 °C for 10-20 °C/min heating rate, and a peak at ~700 °C for 30 °C/min heating rate.

The sub-peak temperature slightly increased with increasing gas flow rate. For a certain heating rate, the experiments with lower gas flow rate have higher DTA signal intensity. With the same flow rate, the experiments with higher heating rate have higher DTA intensity.

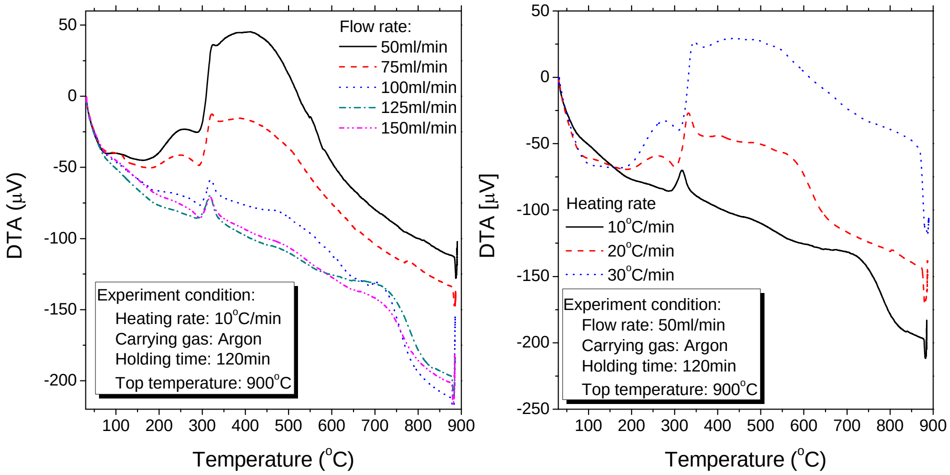


Figure 4.2. DTA Curves of Pyrolysis of PWB Samples (TV PWBs)

The TG and DTG curves with different flow rate and heating rate are shown in Figure 4.3. Compared to combustion process, there are the following characteristics for pyrolysis process:

- Since the speed of degradation (pyrolysis) reaction is generally slower than the combustion reaction, the temperature range for degradation reactions is far bigger than that in combustion reaction, as shown in Figure 4.2 and Figure 4.3.
- The final remaining mass fraction was somehow independent of gas flow rate, especially >100 ml/min. Figure 4.4 shows that most experiments present the same final remaining mass fraction except the two experiments with 50 and 75ml/min gas flow rates. Fig.4.3 shows the pyrolysis of a printer PWBs, indicating that the final mass fraction with 100 ml/min gas flow rate is much smaller than the

experiments with over 100 ml/min gas flow rate. Thus for PWB pyrolysis process, the argon flow rate should be >100 ml/min.

- To some extent, larger heating rate accelerated the pyrolysis process. The lower heating rate is the more successful the pyrolysis process is. Furthermore, the high heating rate requires stronger mechanical and thermal properties of lining refractory of the furnace. On the properties of the furnace for lime refractory, 15-20 $^{o}$C/min is the suitable heating rate for the pyrolysis process. For the printer PWB samples, the final mass fraction is the same no matter what heating rate was used, which probably depends on factors like the special organic composition and flame retardant used in PWBs. For example, with 50 ml/min gas flow rate, the final mass fraction was around 16%, as shown in Figure 4.4. However, for TV PWB samples, with the same gas flow rate, the final mass fraction with heating rate of 10, 20 and 30$^{o}$C/min is 20%, 22% and 14% respectively.
- The degradation reactions still continue during the holding period at $T_m$ and the period of temperature declining. The mass of PWB samples persists in decreasing during the entire pyrolysis process. The final remaining mass fraction depended on the holding time at the top temperature, which indicated again that the pyrolysis occurred over very long time, as shown in Fig.4.4. Longer holding time degraded more PWBs. Variation of conversion fractions with the temperature is shown in Figure 4.5, which supports this conclusion again. 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), and the holding time had little effect on the combustion process.

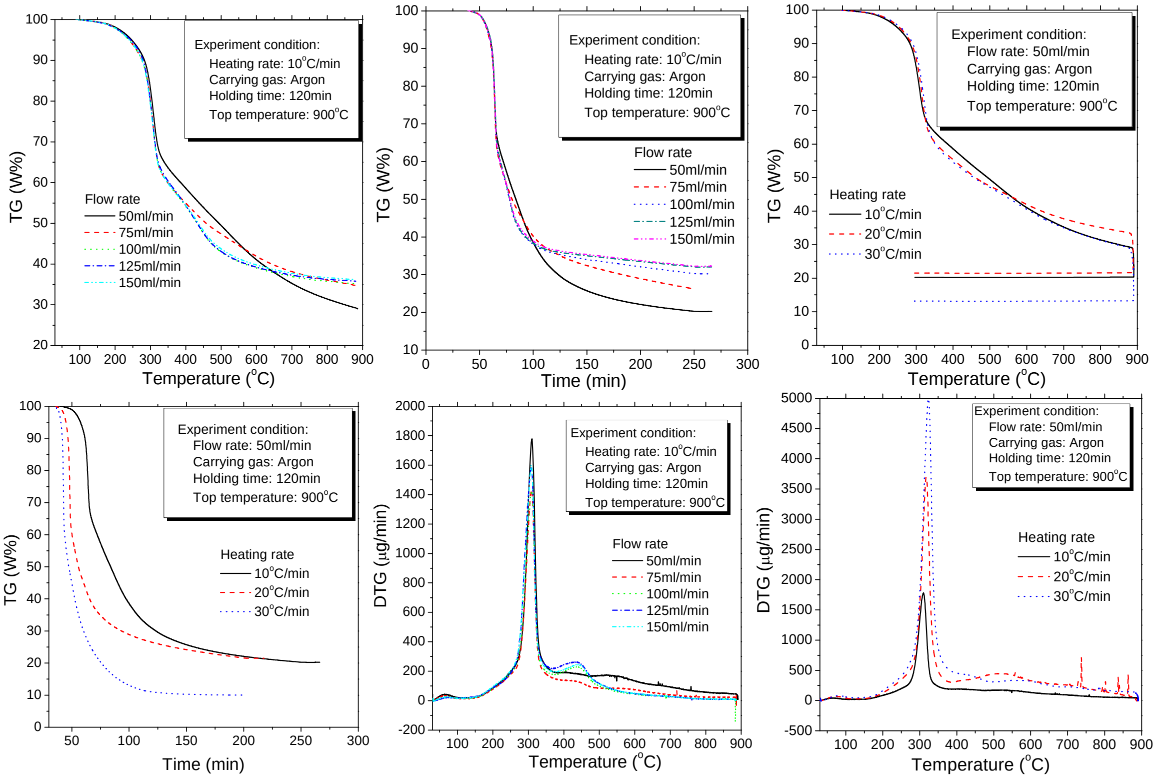


Figure 4.3. TG and DTG Curves of Pyrolysis of PWBs. (TV PWBs)

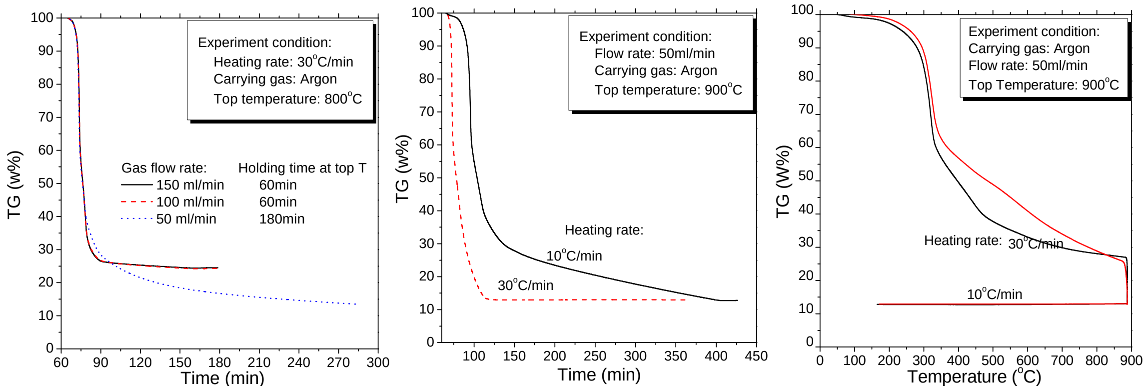


Figure 4.4. TG Curves for the Pyrolysis of PWBs (printer PWBs)

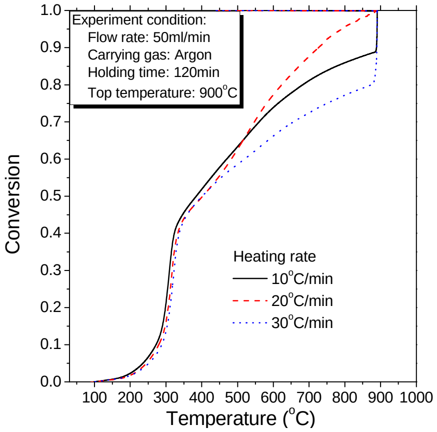


Figure 4.5. Conversion Fractions of the Experiment with Gas Flow Rate of 50ml/min and Different Heating Rate. (TV PWBs)

**4.2.2. Exhausted Gases Analysis.** The exhausted gases during pyrolysis process were detected using MS of CO, $CO_2$, $H_2O$, $CH_4$, $C_2H_2$, $C_2H_2O$, $C_2H_3O$, $C_2H_4O$, $C_2H_5O$, $C_3H_5O$, $C_6H_6$, HBr. The intensity increases with increasing heating rate.

CO, $CO_2$, $H_2O$, $CH_4$, $C_2H_5O$, $C_6H_6$ and HBr gas signals varying with temperature are plotted in Figure 4.6. For some gases, there were several peaks, which corresponded to the reaction temperature. The main MS signal peaks occurred at the temperature range of and 300-900 °C for pyrolysis process, which corresponded to the DTA and DTG curves shown above (Fig. 4.2 and 4.3). For low heating rate, MS signal peaks were very narrow. Because the temperature rises more slowly at a lower heating rate and the reaction velocity might be faster than the rise in temperature.

In pyrolysis process, degradation and decomposition reactions dominated the whole process, without oxidation reaction. As shown in Fig.4.6, MS signal peaks covered a big temperature range of 300-900 °C, which meant that the degradation reactions took place at different temperatures and yielded different pyrolytic products. The temperatures at which of different gases were emitted are listed in Table 4.2.

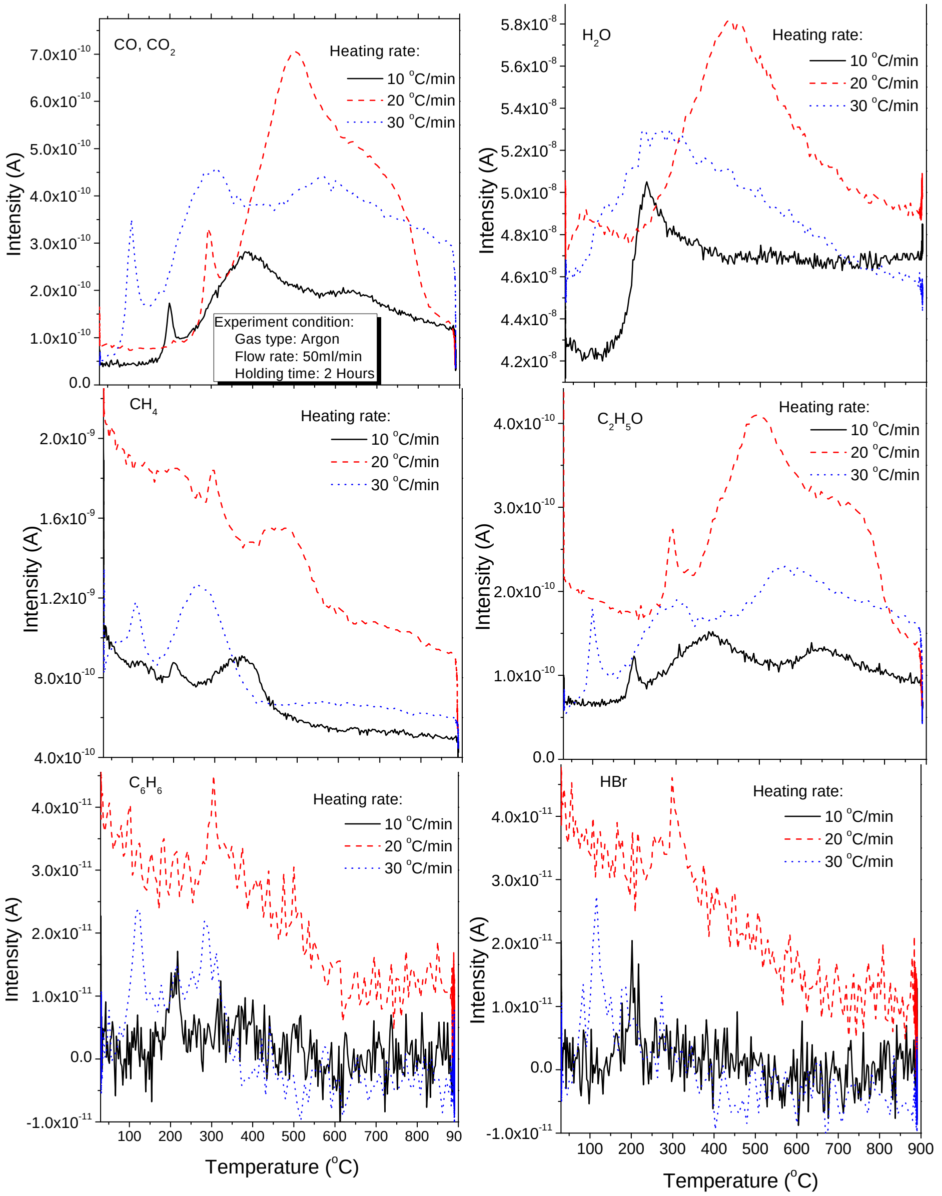


Figure 4.6 Exhausted Gases during Pyrolysis Process (TV PWBs)

It should be noticed that $C_6H_6$, and HBr gases were detected. HBr mainly came from the BFRs in PWB materials. Pyrolytic gases like $C_2H_2$, $C_2H_3O$ and $C_2H_4O$ in pyrolysis were also detected. Thus, in order to environmentally friendly recycle PWBs, suitable green methods should be developed to prevent HBr from being emitted into the air.

Table 4.2. The Evolved Gases at Different Temperature

| Experimental condition | Pyrolysis | |
|---|---|---|
| | $T_{peak}$, °C | Gas type |
| 10°C/min, 50ml/min | 200 | CO-$CO_2$, $CH_3$, $C_2H_2$, $C_2H_2O$, $C_2H_3O$, $CO_2$-$C_2H_4O$, $C_2H_5O$, |
| | 205 | HBr |
| | 215 | $H_2O$, $C_6H_6$ |
| | $H_2O$ | $C_3H_4O$ |
| | 290, 300 | $C_2H_2O$ |
| | 375 | $CH_3$ |
| | 380, 390 | CO-$CO_2$, $C_2H_5O$ |
| | 630 | $C_2H_3O$, $CO_2$-$C_2H_4O$ |
| | 650 | $C_2H_5O$ |
| 20°C/min, 50ml/min | 290 | CO-$CO_2$, $CO_2$-$C_2H_4O$, $C_2H_5O$, $Br_{2,}$ |
| | 295 | $CH_3$, $C_2H_3O$, |
| | 300 | $C_2H_2$, $C_3H_4O$, $C_6H_6$ |
| | 430 | $H_2O$ |
| | 455 | $CH_3$ |
| | 500 | CO-$CO_2$, $CO_2$-$C_2H_4O$, $C_2H_5O$ |
| | 505 | $C_2H_3O$ |
| 30°C/min, 50ml/min | 100 | $C_2H_3O$, $CO_2$-$C_2H_4O$, |
| | 105 | CO-$CO_2$, $CH_3$ |
| | 110 | $C_2H_2$, HBr |
| | 120 | $C_6H_6$ |
| | 150 | $C_3H_4O$ |
| | 200 | $C_2H_2O$, $C_2H_2$ |
| | 250 | $H_2O$, $CH_3$ |
| | 290 | $C_6H_6$, |
| | 300 | CO-$CO_2$, $C_2H_3O$, $C_2H_5O$, |
| | 305 | $CO_2$-$C_2H_4O$ |
| | 560 | $C_2H_3O$ |
| | 570, 575 | $CO_2$, $C_2H_4O$, CO-$CO_2$, $C_2H_5O$ |

## 4.3. PYROLYSIS OF PWBS WITH ADDITIVES

**4.3.1. Pyrolyzing the Mixture of PWB and Additive.** Pyrolysis experiments of PWB and “PWB+additives” have been done using TG/DTA-MS machine at the Material Research Center in Missouri S&T. These PWB powders are from Tallinn University of Technology, Estonia, that might include fine metal particles. Additives were used to control toxic substances evolving from the pyrolysis process, and to enhance the pyrolysis reaction.

Samples were heated at 15 $^{o}$C/min heating rate with 150 ml/min gas flow rate, as shown in Table 4.3. The additives were mixed with PWB powders with a mass ratio 5:1 (5 PWB+1 additive). Five different additives ($CaCO_3$, CaO, ZSM-5($Na_nAl_nSi_{96-n}O_{192}\bullet 16H_2O$ (0<n<27)), Y-zeolite ($Na_xAl_YSi_ZO_m$) and $Fe_2O_3$) were used. The temperature curve during the pyrolysis process is shown in Figure 4.7. The top temperature is 900 $^{o}$C in the current pyrolysis experiments.

Table 4.3. Pyrolysis of PWBs with Additive (PWB:additive=5:1)

| No. | PWB sample | Additives | | |
|---|---|---|---|---|
| | Weight, mg | Name | Weight, mg | Addition method |
| 1 | 20 | - | - | - |
| 2 | 20 | $CaCO_3$ | 4 | Mixed |
| 3 | 20 | CaO | 4 | Mixed |
| 4 | 20 | ZSM-5 | 4 | Mixed |
| 5 | 20 | Y-ZEOLI | 4 | Mixed |
| 6 | 20 | $Fe_2O_3$ | 4 | Mixed |

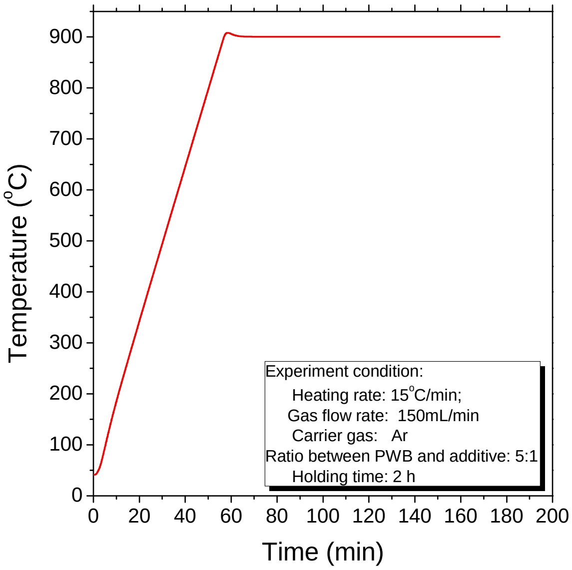


Figure 4.7. Temperature Curve of Pyrolysis Process

**4.3.2 TG and DTG Curves during Pyrolysis.** Figure 4.8 shows the variation of the mass loss fraction with temperature and time. The temperature reached the top temperature of 900 °C at 60 min. The pyrolysis of the pure PWB sample stopped at 77 min with a final mass fraction of ~36%, as shown in Table 4.4. It was reported that in general there is 6.5% Br component in PWB materials [39]. As the mixture of PWB and $CaCO_3$ was pyrolyzed, 43% residue remained in the crucible. Considering the decomposition of $CaCO_3$ at high temperature and the reaction between $CaCO_3$ and HBr, there was ~35% residue after subtracting CaO and $CaBr_2$. The pyrolysis of PWB+$CaCO_3$ samples stopped at 100min. The final residue subtracting the additives and the inorganic products is ~41% for PWB+CaO.

ZSM-5, Y-zeolite and $Fe_2O_3$ were also used during pyrolysis experiments. ZSM-5 and Y-zeolite were added during the pyrolytic experiment to enhance the reaction. The residue fraction subtracting the additives and the inorganic products with these two additives is ~46%. So, it is concluded that ZSM-5 and Y-zeolite mainly acts as catalyst to accelerate the pyrolysis reaction but not reactants. The pyrolysis of PWB+$Fe_2O_3$ stopped at 113min with a ~28% final residue fraction subtracting the additives and the inorganic products. So, compared to other four additives, the effect of $Fe_2O_3$ on the pyrolysis of PWB is the best.

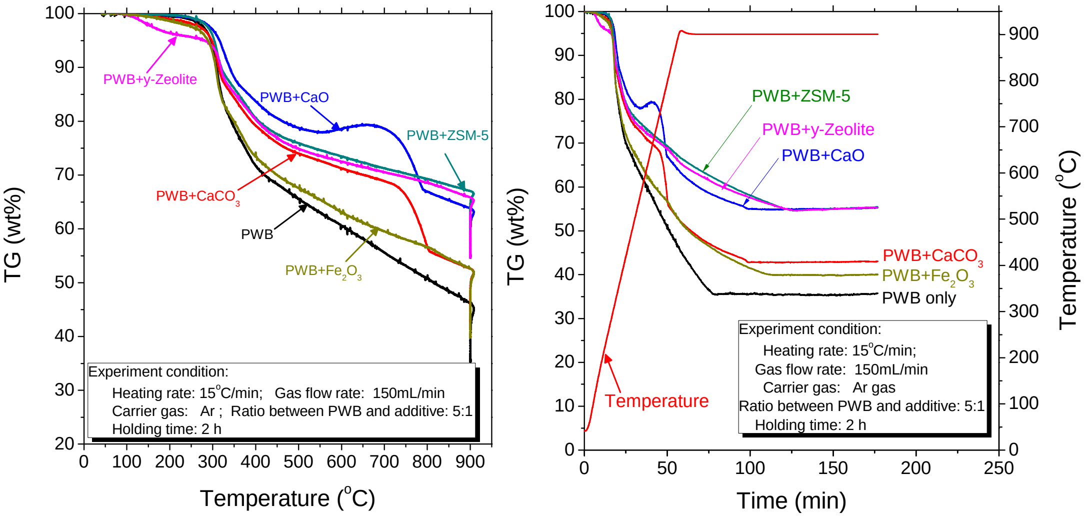


Figure 4.8. TG Curves for the Pyrolysis of PWB and "PWB+ Additives (mixed)"

DTA curves for different pyrolysis experiments are shown in Figure 4.9. There are many peaks which imply many endothermic and exothermic reactions during pyrolysis, which is much different from the combustion process.

Table 4.4. The Final Mass Fraction during Pyrolysis Experiment

| | 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 |

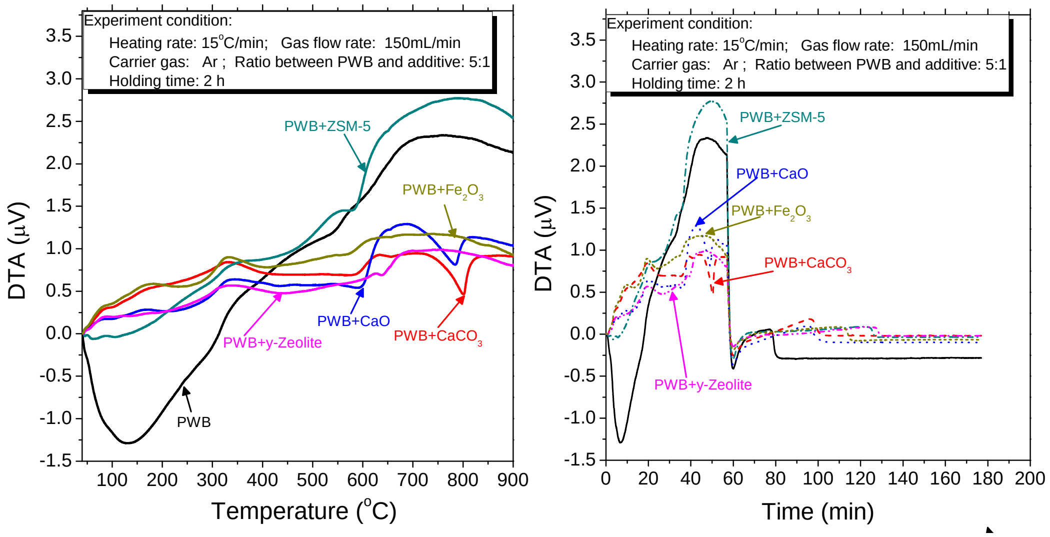


Figure 4.9. DTA Curves of Pyrolysis Experiment of PWB Sample and PWB+Additive(mixed)

**4.3.3 MS Signal of Exhaust Gases in Pyrolysis Experiment.** MS signals of CO, $CO_2$, $H_2O$, $CH_4$, $C_2H_2$, $C_2H_2O$, $C_2H_3O$, $C_2H_4O$, $C_2H_5O$, $C_3H_5O$, $C_6H_6$, HBr and signal peaks value were shown in Figure 4.10. Most of the gas signals have one peak except $C_2H_3O$, $CO_2$ or $C_2H_4O$ and $C_2H_5O$.

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 are stronger than the pyrolysis pf PWBs without additives, which means that $CaCO_3$ has certain effect on enhancing the pyrolysis process. $CaCO_3$ also could control HBr gas evolved from pyrolysis experiment effectively. CaO has big effect on promoting the signal intensity of $C_2H_2$, CO, $C_2H_6$, HCl, $C_3H_4$, 2nd peak of $C_2H_3O$, $Cl_2$ and $C_6H_6$, but not for $CH_4$, $H_2O$, 2nd peak $C_2H_3O$, 2nd peak $CO_2$ or $C_2H_4O$ and 2nd peak $C_2H_5O$. ZSM-5 could stimulate to produce $CH_4$, HCl, $C_3H_4$, $C_2H_3O$, 1st peak $CO_2$ or $C_2H_4O$, $C_2H_5O$ and $C_6H_6$, but lower 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 $C_6H_6$, specially for $CH_4$, $C_2H_3O$ and 1st peak $CO_2$ or $C_2H_4O$, however, and also lowers HBr. Fig. 4.8 and Table 4.4 show that $Fe_2O_3$ help pyrolyze more PWB samples than other additives. MS signal from the pyrolysis of PWB+$Fe_2O_3$ has 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 could be controlled to a lower level by $Fe_2O_3$ than other additives.

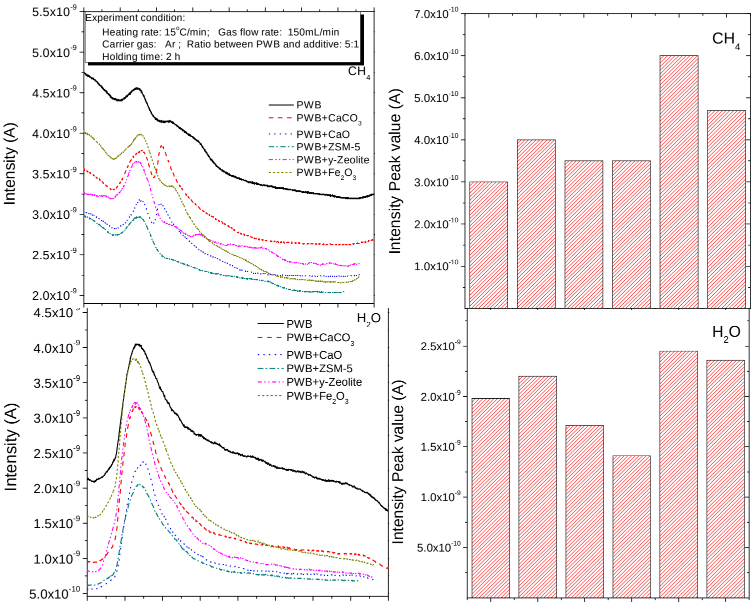


Figure 4.10. MS Signal Exhausted Gases during Pyrolysis Process

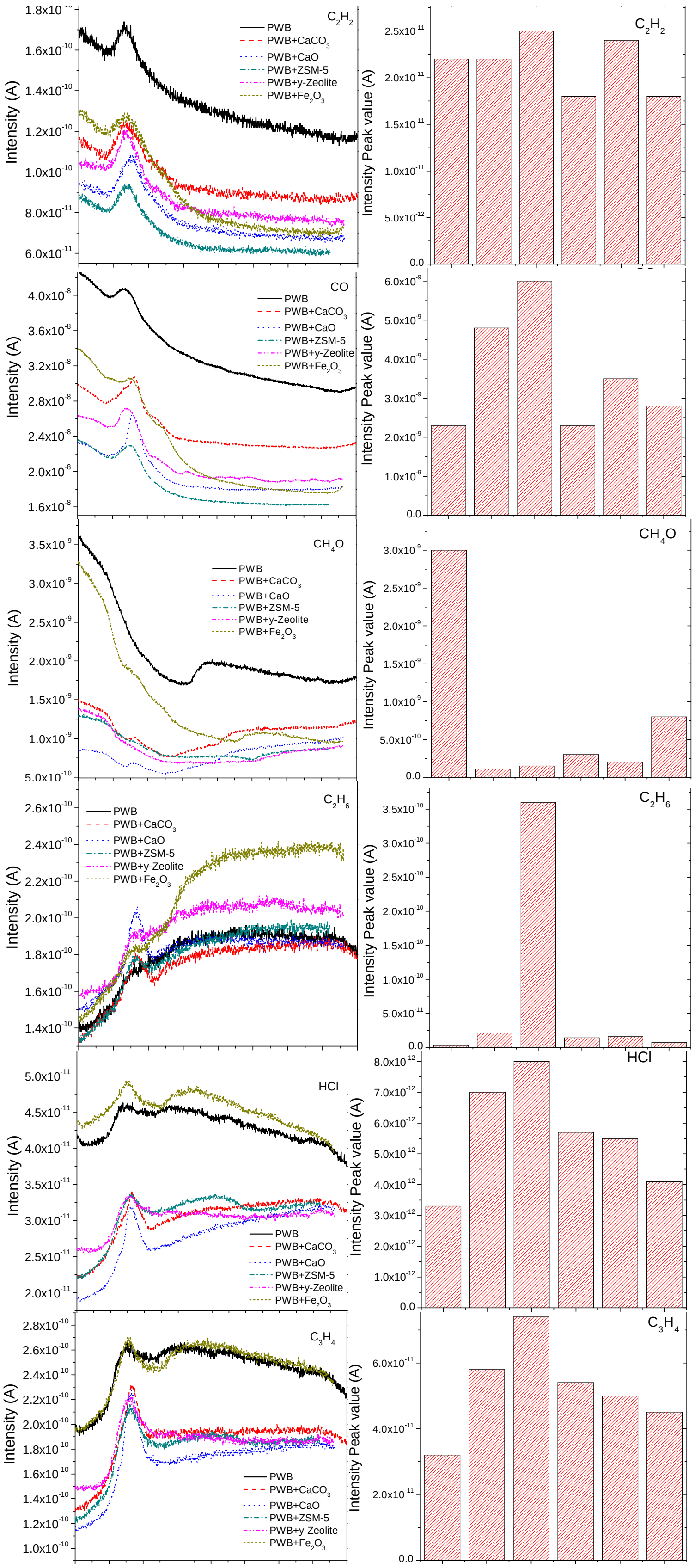


Figure 4.10. (Continued) MS Signal Exhausted Gases during Pyrolysis Process

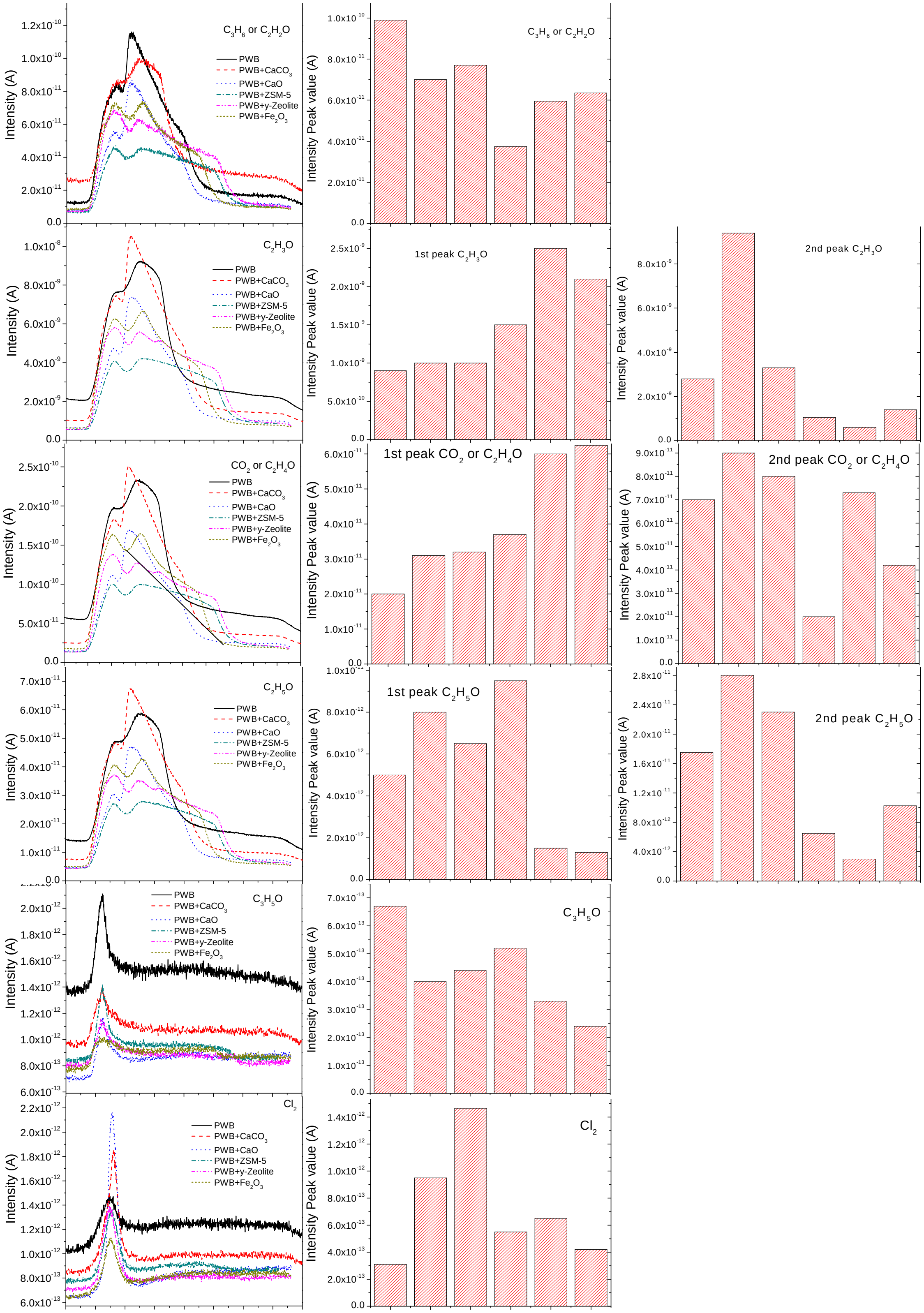


Figure 4.10. (Continued) MS Signal Exhausted Gases during Pyrolysis Process.

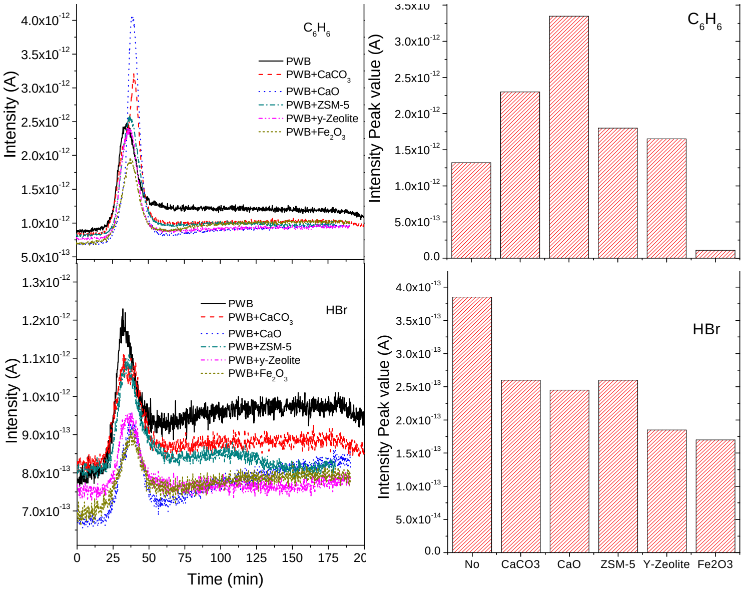


Figure 4.10. (Continued) MS Signal Exhausted Gases during Pyrolysis Process

## 4.4. CHAPTER SUMMARY

a). Pyrolysis process

- Running pyrolysis of PWB powders under argon gas, the sample temperature followed the heating procedure exactly and no temperature jump observed. The reaction occurred during a big temperature range, and there were a few sub-peaks at 350, 500, 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 would be the same no matter what heating rate was used.
- The suitable experimental conditions are 15-20 °C/min, >100 ml/min gas flow rate, >900 °C top temperature, and long holding time.

b). Effect of additives

$Fe_2O_3$ 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 has 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 could be controlled at a lower level by $Fe_2O_3$ than by other additives.

# 5. LARGE SCALE PYROLYSIS OF PWBs USING TUBE FURNACE

## 5.1. EXPERIMENTAL PROCEDURE

A tube furnace was used to investigate the pyrolysis of PWBs in a large scale. Figure 5.1 is the schematic of the experimental setup design. Figure 5.2 shows the picture of the real experiment equipment. Temperature is controlled via a feedback control using a thermocouple. The temperature controllers allow the operator to program the heating and cooling rates.

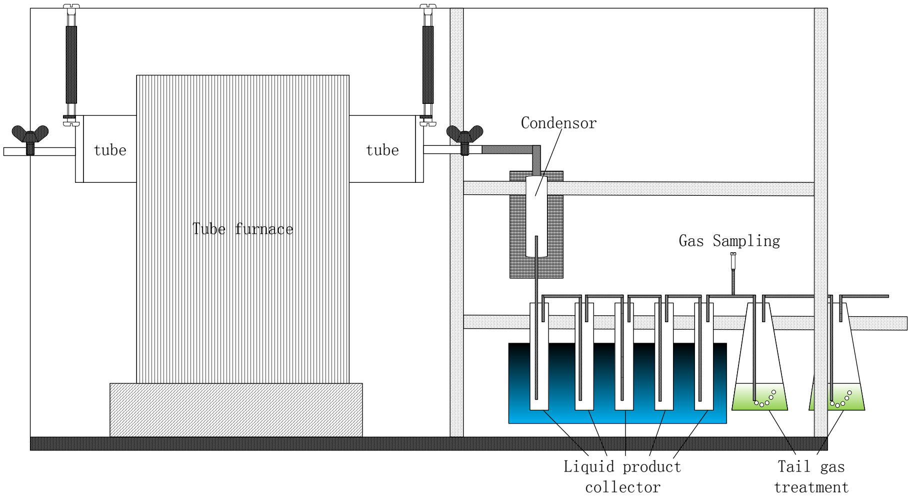


Figure 5.1. The Schematic of Pyrolysis Experiment Using Tube Furnace

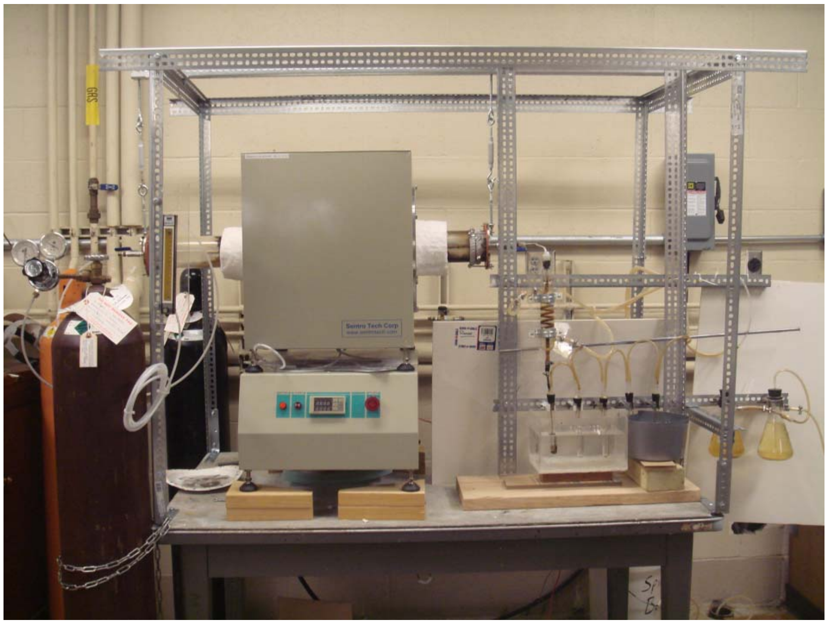


Figure 5.2. The Real Pyrolysis Experiment an Equipment Using Tube Furnace

Argon gas as a carrier was used to push out the gas emitted during the pyrolysis process at a certain flow rate and to prevent potential secondary pyrolysis reaction. The experimental procedure is as follows:

- Open the entrance cover of the tube furnace, then place the crucible containing the PWB sample to the middle of the tube, as shown in Figure 5.3. Close the entrance cover.
- Open the gas entrance and exit valves, and pump Ar gas into the pyrolysis system. Purging the tube furnace for 30 min before heating with a flow rate of 200 ml/min in order to make an inert atmosphere. The temperature varied according to the temperature procedure set-up. Temperature was recorded by a data logger, as shown in Figure 5.4.
- Turn on tube furnace to heat PWB sample to 900 °C at 15 °C/min heating rate with 200 ml/min gas flow rate. Hold at the top temperature for 120 min.
- Evolved gases from tube furnace were cooled down by an iced-water condenser. Liquid sample was collected in five glass tubes immersed in the ice bath. After the experiment, liquid samples were analyzed using Nicolet 670 Fourier Transform Infrared Spectrometer (FTIR), as shown in Figure 5.5.
- Turn off tube furnace.
- After tube furnace is cooled down to room temperature, take out solid products.

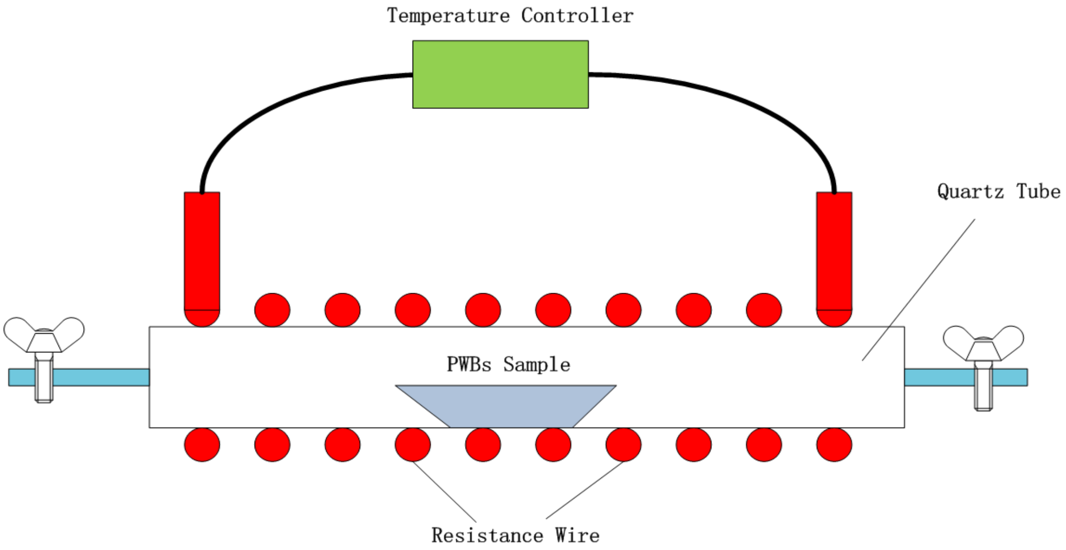


Figure 5.3. Samples in Crucibles Were Placed in the Middle of Tube

Figure 5.4. Temperature Data Logger

FTIR spectroscopy is a measurement technique for collecting infrared spectra. Instead of recording the amount of energy absorbed when the frequency of the infra-red light is varied (monochromator), the IR light is guided through an interferometer. After passing through the sample, the measured signal is the interferogram. Performing a Fourier transform on this signal data results in a spectrum identical to that from conventional (dispersive) infrared spectroscopy [121].

Figure 5.5. Nicolet 670 Fourier Transform Infrared Spectrometer (FTIR)

## 5.2. PYROLYSIS OF PWBS WITHOUT ADDITIVES

**5.2.1. Experiment Conditions.** Four regular pyrolysis experiments were performed. The experiment conditions are as follows: 50 g PWB unscreened powders; Carrier gas: Argon with 200 ml/min flow rate; 15 $^{o}$C /min heating rate; 900 $^{o}$C top temperature; 120min holding time at top temperature. The recorded temperature curve is shown in Figure 5.6.

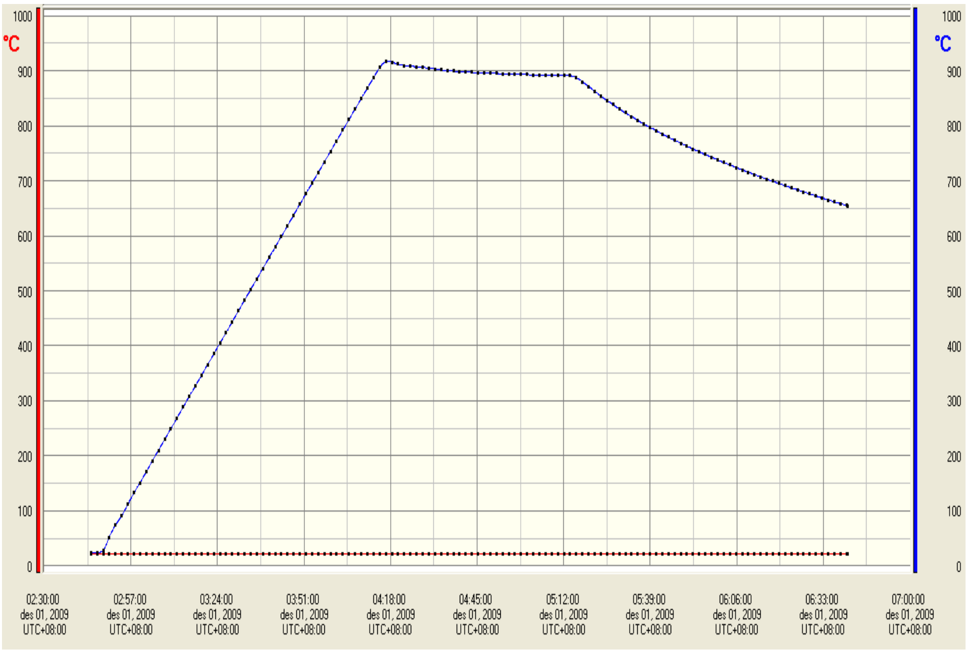


Figure 5.6. Recording Temperature Curve

**5.2.2. Pyrolytic Products.** Three types of products-solid product, liquid product and gas product-were produced during pyrolysis experiments, as shown in Figure 5.7. Solid products remained in the crucible after pyrolysis. The liquid products were collected by five glass tubes. Gas sample was taken at 300, 400 and 500$^{o}$C, respectively. Finally, the tail gas was treated by 5% NaOH solution, then released into the vent.

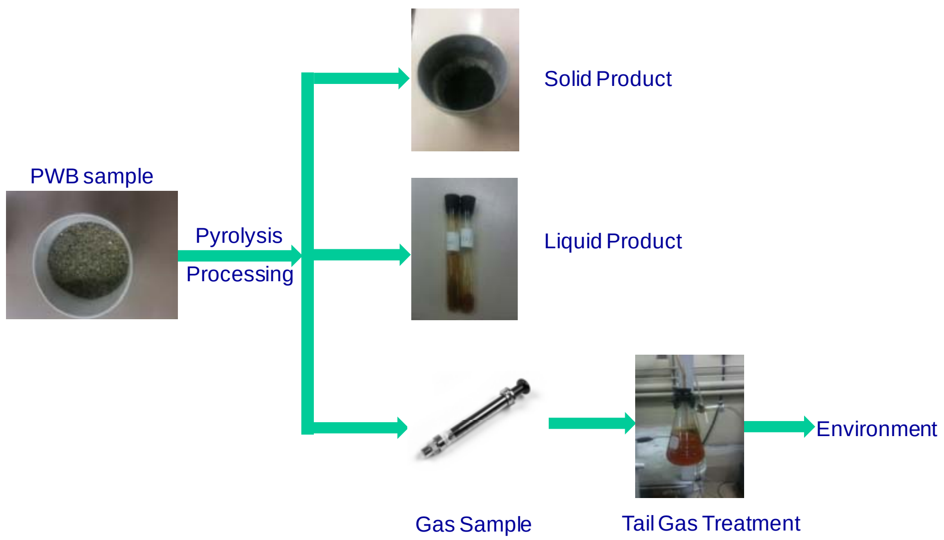


Figure 5.7. PWB Sample and Products

**5.2.2.1. Solid products.** Solid products mainly consist of glass-fiber, metals and carbon. The yield of solid and liquid products were estimated in each experiment by weighing the amount of each obtained, while the gas yields were determined by subtracting the yields of solid and liquid products from the initial mass of the PWB powders. After the pyrolysis experiment, the solid products were 22-30 g, as shown in Table 5.1. In average, the solid product produced without additives is ~24 g, and ~47% of the original mass. In other words, as 53% of PWBs were converted to liquid and gas products. As shown in Table 4.6, TG/DTA results showed that there is 36% residue remaining, which is far less than that in the current tube furnace experiments. Therefore, PWB samples in tube furnace might not be completely pyrolyzed.

Table 5.1. Solid, Liquid and Gas Products Produced in Pyrolysis Experiment

| Experiment | Heating rate, °C/min | Solid product | | Liquid product | | Gas product | |
|---|---|---|---|---|---|---|---|
| | | g | % | g | % | g | % |
| #1 | 10 | 23.7 | 47.4 | 7.3+2.4 | 19.4 | 16.6 | 33.2 |
| #2 | 10 | 23.3 | 46.6 | 8.2+2.4 | 21.2 | 16.1 | 33.2 |
| #3 | 5 | 25.2 | 50.4 | 7.05+2.4 | 18.9 | 15.35 | 30.7 |
| #4 | 15 | 22.5 | 45 | 8.0+2.4 | 20.8 | 17.1 | 34.2 |
| Mean | | 23.68 | 47.35 | 10.00 | 20.08 | 16.29 | 32.57 |

**5.2.2.2. Liquid products.** The pyrolysis oil obtained during PWB pyrolysis is a mixture of organic compounds (usually termed oils), and also contains some aqueous products. Similar results in the pyrolysis of different plastics were reported [92-93], indicating that water and hydrocarbons by-product could either be a product formed in the process (derived from the oxygen-containing functional groups, -COO-, OH-, -COOH-, etc.) or due to the original moisture in the samples.

As shown in Table 5.1, the current pyrolysis experiments produced 9.5-10.6 g of liquid products, averaging 20% of the original PWB mass. Liquid products could be fractionated using separating funnel, as shown in Figure 5.8. Ideally, three main products could be separated: heavy oil, water and light oil. Light oil is in the up layer, water is in the middle layer, and heavy oil and sediments are in the lower layer. It is difficult to separate the light oil using this method because it occupies the least volume and also its similar color to water.

Figure 5.8. Separating Funnel

FTIR analysis is sensitive to the composition change of the pyrolysis products. The collected oil from experiment #1 (Table 5.1) was analyzed using FTIR and the spectrum is shown in Figure 5.9. A few chemical functional groups could be found in pyrolytic heavy oil. The wide adsorption peak between 3600-3200 cm$^{-1}$ is caused by the stretching vibration of free O-H band. For alkane functional groups, several stretching vibration of alkane C-H band could be found at 3000-2850 cm$^{-1}$. Bending vibration of alkane C-H band could be found at 1465-1340 cm$^{-1}$, and the stretching of aliphatic C-H bond occurs below 3000 cm$^{-1}$. There is stretching vibration of olefin C-H at 3100-3010 cm$^{-1}$, stretching vibration of olefin C=C bond at 1675-1640 cm$^{-1}$, and bending vibration of olefin C-H bond at 675 cm$^{-1}$. A peak occurred at 2250-2100 cm$^{-1}$ stand for alkyne stretching vibration. Stretching vibration of C-H at aromatic ring may occur at 3100-3000 cm$^{-1}$. At 1600 cm$^{-1}$, 1580 cm$^{-1}$, 1500 cm$^{-1}$, 1450 cm$^{-1}$. There are four peaks with different density, which stand for aromatic compounds there. For alcohol and phenol functional groups, stretching vibration of C-O takes place at 1300-1000 $cm^{-1}$, and the out-of-plane bending of hydroxy O-H could be found at 769-659 $cm^{-1}$.

Figure 5.10 shows FTIR spectra of heavy oil from experiment of #2, #3 and #4 (Table 5.1) which had different heating rate. Comparing three FTIR spectrums from these three different experiments, it is difficult to find any difference among them. For #1 experiment, heavy oil, water and light oil could be separated from liquid products, and the FTIR spectrum is shown in Figure 5.11. FTIR spectrum shows much difference between the heavy liquid product and the light liquid product. For example, there are two strong absorption peaks at 1550-1400 $cm^{-1}$, and 1050-800 $cm^{-1}$ for the light liquid product, but not for the heavy liquid product. Around 1500 $cm^{-1}$ C=C stretching bond vibration for aromatic rings could be found. C-H bend vibration for alkenes is at 1050-800 $cm^{-1}$.

Consequently, the pyrolysis products from #2, #3 and #4 without additives mainly consist of aromatic compounds with phenol and substituted phenol, but few alkane chains.

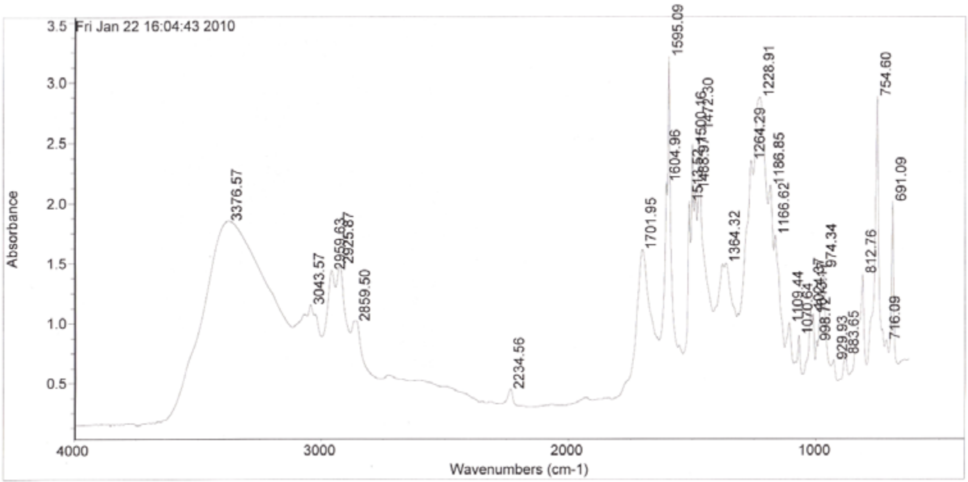


Figure 5.9. FTIR Spectra of Heavy Oil from Liquid Product (#1 Experiment).

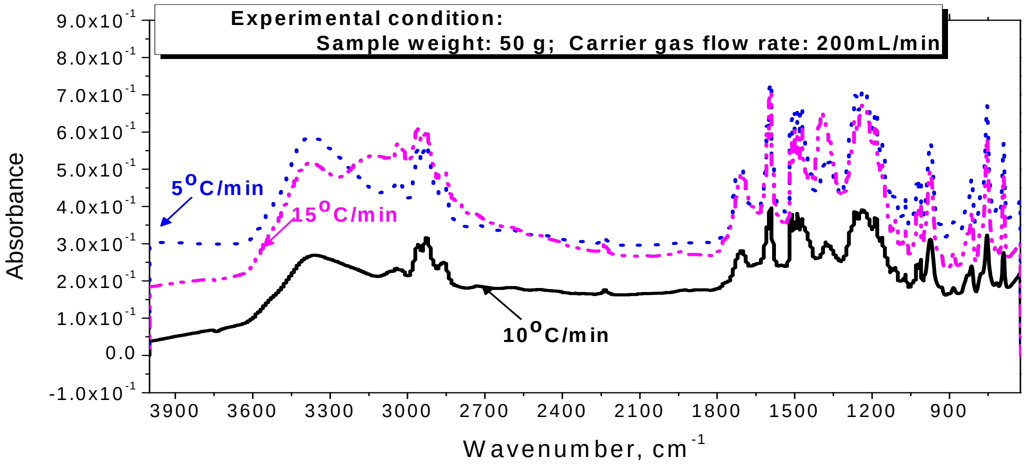


Figure 5.10. FTIR Spectra of Heavy Oil from Liquid Product (#2, #3 and #4Experiment)

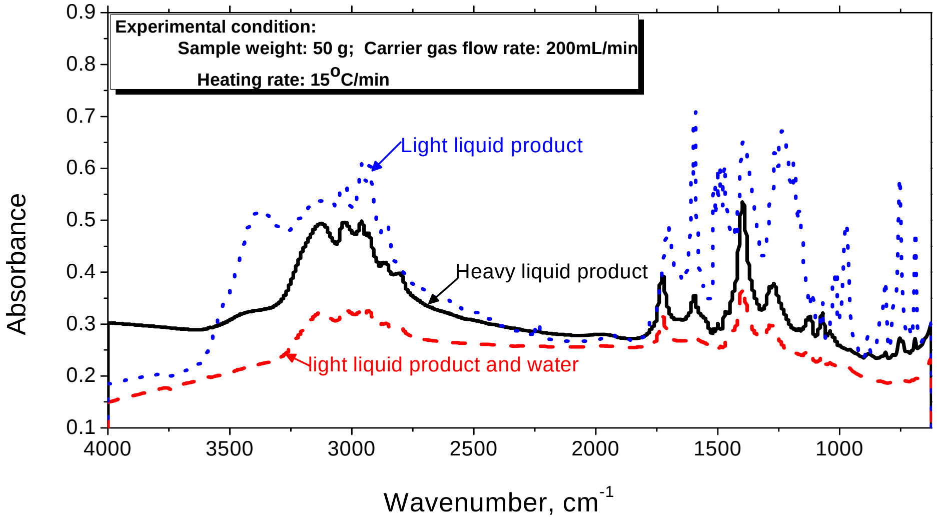


Figure 5.11. FTIR Spectra of Heavy Oil, Water and Light Liquid Product from Liquid Product (Experiment: #4)

## 5.3. PYROLYSIS OF PWBS WITH ADDITIVE

Additive $CaCO_3$ was added into PWB powders to control the toxic substance like HBr emitted during pyrolysis. The sample was converted to solid, liquid and gas products following the routing as shown in Fig. 5.7. Three experiments were performed in the current study.

**5.3.1. Experimental Procedure and Methods**. Experiment procedure of pyrolysis of “PWB+additives” is same as the pyrolysis of PWB only. Two methods of adding $CaCO_3$ were used:

- Mixed: PWB sample mixed with $CaCO_3$ sample in the ratio of 5:1. In the current study, 10 g $CaCO_3$ powder was used to mix with 50 g PWB powders.
- Mixed+UP: The same ratio was used in this method. However, 5 g $CaCO_3$ powder was used to mix with 50g PWB sample, and the other 5 g $CaCO_3$ powder was spread out as a layer on the mixed sample, as shown in Figure 5.12.

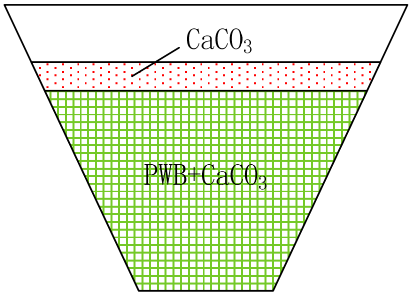


Figure 5.12. Mixed+Up Method

**5.3.2. Pyrolysis Products.** In PWB+additive experiments, solid product mainly consists of the pyrolysis residue (coke, tar, etc.) and decomposing products of $CaCO_3$ ($CaO$, $CaBr_2$).

Unscreened PWB powders were used for experiment #5. The experimental condition is the same as pyrolysis experiment without additive and the temperature procedure is shown in Figure 5.13. There were 32.35 g solid product, 9.76 g liquid product and 17.89 g gas products, as shown in Table 5.2. It is assumed that $CaCO_3$ had been decomposed in this experiment, thus the amount of $CO_2$ evolved from the decomposition of $CaCO_3$ could be calculated. Theoretically, decomposing 10 g additive $CaCO_3$ is able to produce 4.4 g $CO_2$ gas. Therefore, the actual gas products from the pyrolysis of PWB sample should be equal to the gas subtracting the $CO_2$ generated from the decomposition of $CaCO_3$ from the total gas products. Roughly, there were 26.75 g solid products, 9.76 g liquid products and 13.49 g gas products, and the yield was approximately 53.5%, 19.52% and 26.98% respectively. In Chapter 4, as shown in Table 4.6, the pyrolysis using TG/DTA-MS reported that the final mass of residue is 35% of the sample similar to experiment #5. The mass loses in TG/DTA is higher than that in tube furnace. So the pyrolysis of PWB in the tube furnace experiment is incomplete.

Screened PWB samples with size of 150-250 μm were used in experiments #6 and #7. For experiment #6, there were 40.58 g solid products, 6.46 g liquid products and 8.56 g gas products. After subtracting the weight of CaO and $CaBr_2$, there were 34.98 g (69.96%) solid products, 6.46 g (12.92%) liquid products and 8.56 g (17.12%) gas products. Obviously, the yield of solid products in screened PWB samples (#6 and #7) is bigger than, and the yield of liquid and gas products in this experiment is less than that in the unscreened samples (#5). The screened PWB powders contain more metal particles than unscreened samples.

Table 5.2. Solid, Liquid and Gas Products Produced in Pyrolysis Experiments with Additives

| Experiment | | Solid product | | Liquid product | | Gas product | |
|---|---|---|---|---|---|---|---|
| NO. | PWB Particles Size | g | % | g | % | g | % |
| #5 (b) | Unscreened | 32.35 | 53.91 | 7.36+2.4 | 16.1 | 17.89 | 29.82 |
| #5 (a) | | 26.75 | 53.5 | 9.76 | 19.52 | 13.49 | 26.98 |
| #6 (b) | 150-250 μm | 40.58 | 67.63 | 4.06+2.4 | 10.77 | 12.96 | 21.6 |
| #6 (a) | | 34.98 | 69.96 | 6.46 | 12.92 | 8.56 | 17.12 |
| #7 (b) | 150-250 μm | 40.31 | 67.18 | 5.7+2.4 | 13.5 | 11.59 | 21.23 |
| 7# (a) | | 34.71 | 69.42 | 8.1 | 16.2 | 7.19 | 14.38 |

Note: (a): After subtracting CaO or $CaBr_2$; (b): Before subtracting CaO or $CaBr_2$.

In experiment #7, the heating procedure is different from others, as shown in Figure 5.13. There were 40.31 g solid products, 8.1 g liquid products and 11.59 g gas products. In order to calculate the real yield of product, the weight of CaO and $CaBr_2$ should be subtracted. The real yield is 69.42%, 16.2% and 14.38% for solid, liquid and gas products respectively. Therefore, increasing holding time at 300, 400 and 500 $^{o}$C as shown in Figure 5.13 have little effect on improving the conversion fraction.

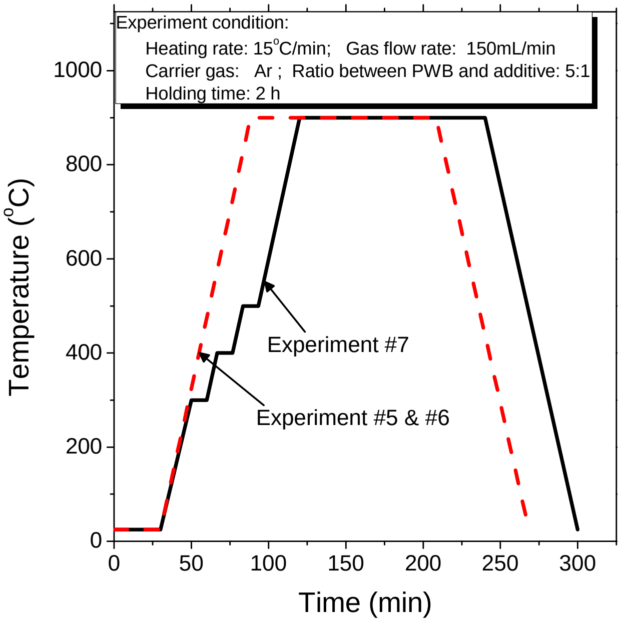


Figure 5.13. Recording Temperature Curve for #5, #6 and #7 Experiment

## 5.4 CHAPTER SUMMARY

PWB samples were pyrolyzed in a tube furnace. Three types of pyrolysis products (solid product, liquid product and gas product) were obtained. It is concluded that:

- As 50 g unscreened PWB samples were pyrolyzed in the tube furnace, in average, there were 23.68 g (47%) solid products, 10.00 g (20%) liquid products and 16.29 g (32%) gas products.
- The yield of solid products (47%) in tube furnace was far more than that (36%) in TG/DTA. PWB sample were not pyrolyzed completely in the tube furnace experiments.
- The pyrolysis liquid products mainly consist of aromatic compounds with phenol and substituted phenol, but few alkane chains.
- Addition of $CaCO_3$ into PWB powder is rarely beneficial to enhance the pyrolysis of PWB, but control the emission of the toxic gas like the toxic gas like HBr and $C_6H_6$.
- PWB powders with smaller particle size contain more metal during the pyrolysis process and thus have more solid products.

# 6. CONCLUSIONS

PWB materials from different electrical apparatus were combusted and pyrolyzed in TG/DTA furnaces and a tube furnace. The evolved gas products were detected by MS machine, and liquid products were analyzed by FTIR. The following conclusions are derived.

1. Combustion process in TG/DTA

During combustion process, there were two exothermic reactions. The first one occurred at 300-380 $^{o}$C, and the second one occurred at 450-500 $^{o}$C. Due to big amount of exhausted heat during these two reactions, the sample temperature in these two temperature range abruptly jumped out the heating procedure, lasting 1-3 minutes. The gas flow rate and initial sample mass rarely affect the combustion process, only a little increasing in temperature at the second peak with increasing gas flow rate. The final remaining mass fraction during combustion was ~3% of the original mass for a printer PWBs and ~11-13% for a TV PWBs. Holding time at the top temperature affected to a little extent the combustion process. The suitable combustion conditions are 15 $^{o}$C/min heating rat, >125 $^{o}$C/min gas flow rate, 600 $^{o}$C top temperature and the holding time is not important for combustion process.

The main emitted gases from the combustion of PWB powders are CO, $CO_2$, $H_2O$, $CH_4$, $C_3H_5O$, $C_6H_6$, HBr. The results showed that $CaCO_3$ and $Na_2CO_3$ were very efficient to control the emission of HBr and benzene, lowering 80% compared to the case without additives, $Na_2CO_3$ can control the emission of HBr gas but not for benzene, and NaOH has no any obvious effect on the control of both gases.

2. Pyrolysis process in TG/DTA

During pyrolysis process, the sample temperature followed the heating procedure exactly and had little temperature jump as in the combustion cases. The reaction occurred during a big temperature range, and there were a few sub-peaks at the big range peak, at 350 $^{o}$C, 500 $^{o}$C, and 700 $^{o}$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 by pyrolysis was 15-25% of the initial mass. Larger heating rate accelerated the pyrolysis process. While the final mass fraction would be the same no matter what heating rate was used. The suitable pyrolysis conditions are 15-20 $^{o}$C/min, >100 $^{o}$C/min gas flow rate, above 900 $^{o}$C temperature and longer holding time.

More emitted fuel gas like $C_2H_3O$, $C_2H_4O$ and $C_3H_5O$ could be produced during the pyrolysis of PWBs than the combustion process. $Fe_2O_3$ is the most effective additive to control HBr and $C_6H_6$ during the pyrolysis process. MS signal from PWB+$Fe_2O_3$ experiment has 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 could be controlled at a lower level by $Fe_2O_3$ than other additives.

3. Large scale pyrolysis process in the tube furnace

PWB samples were pyrolyzed in the tube furnace. Three types of pyrolysis products (solid product, liquid product and gas product) could be produced in the experiment. As 50g unscreened PWB samples were pyrolyzed in tube furnace, in average there were 23.68 g (47%) solid products, 10.00 g (20%) liquid products and 16.29 g (32%) gas products. The yield of solid products (47%) in tube furnace was far more than that of 36% in TG/DTA. The pyrolysis products mainly consist of aromatic compounds with phenol and substituted phenol, but few alkane chains. PWB powders with small size contain more metal particle than the unscreened sample, and thus pyrolysis experiment using small size PWB particles have more solid products.

# BIBLIOGRAPHY

1. Liu, X.B., M. Tanaka, and Y. Matsui, *Electrical and Electronic Waste Management in China: Progress and the Barriers to Overcome.* Waste Management and Research, 2006. **24**(1): p. 92-101.
2. *Chemical contamination at e-waste recycling and disposal sites in Accra and Korforidua, Ghana*. 2008. http://www.greenpeace.org/international/press/reports/chemical-contamination-at-e-wa,.
3. Balart, R., et al., *Kinetic Analysis of Thermal Degradation of Recycled Polycarbonate/Acrylonitrile-Butadiene-Styrene Mixtures From Waste Electric and Electronic Equipment.* Polymer Degradation and Stability, 2006. **91**(3): p. 527-534.
4. Hall, W.J. and P.T. Williams, *Separation and Recovery of Materials from Scrap Printed Circuit Boards.* Resources, Conservation and Recycling, 2007. **51**(3): p. 691-709.
5. Leung, A., Z.W. Cai, and M.H. Wong, *Environmental Contamination from Electronic Waste Recycling at Guiyu, Southeast China.* Journal of Material Cycles and Waste Management, 2006. **8**: p. 21-33.
6. Walsh, B., *Going Green E-waste Not.* TIME-Health & Science, 2009.
7. Huisman, J., et al., *2008 Review of Directive 2002/96 on Waste Electrical and Electronic Equipment (WEEE), Final Report*. 2007, United Nations University, AEA Technology, Gaiker, Regional Environmental Centre for Central and Eastern Europe, Delft University of Technology.
8. Motorola, *Material assay of the GSM 900 Handy PWB and GSM 900 BTS rack PWB*. 2005, Rapid Environ Assess Lab.
9. Zhang, L.F., et al., *Mechanical and Pyrometallurgical Recycling of Electronic Wastes*, in *2008 Global Symposium on Recycling, Waste Treatment and Clean Technology, REWAS(2008)*. October 12-15, 2008: Cancun, Mexico. p. 699-708.
10. Cui, J.R. and E. Forssberg, *Mechanical Recycling of Waste Electric and Electronic Equipment: A Review* Journal of Hazardous Materials, 2003. **99**(3): p. 243-263.

11. Cui, J.R. and L.F. Zhang, *Metallurgical Recovery of Metals from Electronic Waste: A Review.* Journal of Hazardous Materials, 2008. **158**: p. 228-256.
12. *Combustion.* http://en.wikipedia.org/wiki/Combustion.
13. *Pyrolysis.* http://en.wikipedia.org/wiki/Pyrolysis.
14. *Thermal decomposition.* http://en.wikipedia.org/wiki/Thermal_decomposition.
15. Jianjun, H., et al., *DC Arc plasma disposal of printed circuit board.* Plasma Science and Technology, 2004. **6**(4): p. 2423-2426.
16. Hall, W.J. and P.T. Williams, *Analysis of products from the pyrolysis of plastics recovered from the commercial scale recycling of waste electrical and electronic equipment.* Journal of Analytical and Applied Pyrolysis, 2007. **79**(1-2 SPEC ISS): p. 375-386.
17. Wobst, M., H. Wichmann, and M. Bahadir, *Influence of Heavy Metals on the Formation and the Distribution Behavior of PAH and PCDD/F during Simulated Fires* Chemosphere, 2003. **51**(2): p. 109-115.
18. Wichmann, H., et al., *Combustion Induced Transport of Heavy Metals in the Gas Phase—A Review.* Fresenius Environmental Bulletin, 2000. **9**: p. 72-125.
19. Chiena, Y., et al., *Fate of Bromine in Pyrolysis of Printed Circuit Board Wastes.* Chemosphere, 2000. **40**: p. 383-387.
20. Huo, X., et al., *Elevated Blood Lead Levels of Children in Guiyu, an Electronic Waste Recycling Town in China.* Environmental Health Perspectives, 2007. **115**(7): p. 1113–1117.
21. Sum, E.Y.L., *The Recovery of Metals from Electronic Scrap.* JOM, 1991. **9**(3): p. 53-61.
22. Menad, N., B. Bjorkman, and E.G. Allain, *Combustion of Plastics Contained in Electric and Electronic Scrap.* Resources, Conservation and Recycling, 1998. **24**: p. 65–85.
23. Gao, Z., J. Li, and H.C. Zhang, *Printed Circuit Board Recycling: A State-of-Art Survey.* Electronics and the Environment, 2002 IEEE International Symposium, 2002: p. 234-241.
24. Goosey, M. and R. Kellner, *Recycling Technologies for the Treatment of End of Life Printed Circuit Boards(PCBs).* Circuit World, 2003. **29**(3): p. 33-37.

25. Levchik, S.V. and E.D. Weil, *Thermal Decomposition, Combustion and Flame-Retardancy of Epoxy Resins—A Review of the Recent Literature.* Polymer International, 2004. **53**: p. 1901-1929.

26. Shuey, S.A. and T. P., *Review of Pyrometallurgical Treatment of Electronic Scrap.* Mining Engineering, 2004. **57**(4): p. 67-70.

27. Kang, H.Y. and J.M. Schoengung, *Electronic Waste Recycling : A Review of U.S. Infrastructure and Technology Options.* Resources, Conservation and Recycling, 2005. **45**(4): p. 368-400.

28. Hilty, L.M., *Electronic Waste—An Emerging Risk?* Environmental Impact Assessment Review, 2005. **25**(5): p. 431-435.

29. Wong, M.H., et al., *Export of Toxic Chemicals – A Review of the Case of Uncontrolled Electronic-Waste Recycling.* Environmental Pollution, 2007. **149**(2): p. 131-140.

30. Babu, B., A. Parande, and C. Basha, *Electrical and Electronic Waste: A Global Environmental Problem.* Waste Management & Research, 2007. **25**: p. 307-318.

31. Gupta, R.K., *E-waste recycling and health effects: A review*. 2007, Occupational Health and Safety.

32. Susan, F., *Evaluating Electronic Waste Recycling Systems: The Influence of Physical Architecture on System Performance*, in *Technology and Policy*. 2008, Massachusetts Institute of Technology: Cambridge, M.A.

33. Huang, K., J. Guo, and Z. Xu, *Recycling of Waste Printed Circuit Boards: A Review of Current Technologies and Treatment Status in China.* Journal of Hazardous Materials, 2009. **164**: p. 399-408.

34. Guo, J.Y., J. Guo, and Z.M. Xu, *Recycling of Non-metallic Fractions from Waste Printed Circuit Boards: A Review.* Journal of Hazardous Materials, 2009. **168**(2-3): p. 567-590.

35. Guo, Y., et al., *Heavy Metal Contamination from Electronic Waste Recycling at Guiyu, Southeastern China.* Journal of Environmental Quality, 2009. **38**(4): p. 1617-1626.

36. Yu, J.L., E. Williams, and M.T. Ju, *Review and Prospects of Recycling Methods for Waste Printed Circuit Boards*. 2009 IEEE International Symposium on Sustainable Systems and Technology, 2009: p. 1-5.

37. Bernardes, A., I. Bohlinger, and D. Rodriguez, *Recycling of Printed Circuit Boards by Melting with Oxidising/Reducing Top Blowing Process*, in *in Proc. Sessions and Symposia Sponsored by the Extraction and Processing Division, TMS Annual Meeting-EPD Congress*. 1997: Orlando, USA. p. 363-375.

38. Widmer, R., et al., *Global perspectives on e-waste*. Environmental Impact Assessment Review, 2005 **25**(5): p. 436-458.

39. Zuo, X.J. and L.F. Zhang, *Green Combustion of Waste Printed Circuit Boards*, in *TMS 2009 Annual Meeting*. February 15-19, 2009, EPD Congress: San Francisco, CA, USA. p. 1063-1068.

40. Oh, C.J. and S.O. Lee, *Selective Leaching of Valuable Metals from Waste Printed Circuit Boards*. Journal of Air & Waste Management Association, 2003. **53**: p. 897-902.

41. Yuan, C.Y., et al., *Experimental Studies on Cryogenic Recycling of Printed Circuit Board*. The International Journal of Advanced Manufacturing Technology, 2007. **34**(7-8): p. 657-666.

42. Barontini, F., et al., *Thermal Degradation and Decomposition Products of Electronic Boards Containing BFRs*. Industrial & Engineering Chemistry Research 2005. **44**(12): p. 4186-4199.

43. Zuo, X.J. and L.F. Zhang, *Recycling of Electronic Wastes: Degradation and Combustion*, in *TMS 2008 Annual Meeting & Exhibition*. March 9-13, 2008, Proceedings of sessions and symposia sponsored by the Extraction & Processing Division (EPD) of TMS, Edited by Stanley M. Howard: New Orleans, LA, USA. p. 491-496.

44. Pielichowski, K., J. Njuguna, and R.T. Limited, *Thermal degradation of polymeric materials* 2005, Shawbury, United Kingdom: Smithers Rapra Publishing.

45. Ye, C. and L. Wan, *Analyzing of the Gas Products by Pyrolysis Analysis Experiment of Wasted Print Circuit Boards.* China Resources Comprehensive Utilization, 2006. **6**: p. 7-9.
46. Jawitz, M.W., *Printed circuit board materials handbook.* 1997, New York: McGraw-Hill Professional.
47. *Epoxy Resins.* http://en.wikipedia.org/wiki/Epoxy_resin.
48. Alaee, M., et al., *An overview of commercially used brominated flame retardants, their applications, their use patterns in different countries/regions and possible modes of release.* Environment International, 2003. **29**(6): p. 683-689.
49. Zhu, L. and R.A. Hites, *Brominated flame retardants in tree bark from North America.* Environmental Science and Technology, 2006. **40**(12): p. 3711-3716.
50. Kimura, J., *Development of Recycling Technology of Wastes for Electronic Products and Components.* Zairyo to Kankyo/ Corrosion Engineering, 1995. **44**(9): p. 513.
51. Hedemalm, P., P. Carlsson, and V. Palm, *Waste from Electrical and Electronicproducts, A Survey of the Contents of Materials and Hazardous Substances in Electric and Electronic products.* In: The Nordic Council of Ministers, Report, 1995: p. 96.
52. Turnbull, A., *Industry Use of Brominated Flame Retardants in Electronic Equipment.* published in 2003 IEEE/ISEE Symposium proceedings, 2003.
53. Birnbaum, L.S. and S. D.F., *Brominated Flame Retardants: Cause for Concern?* Environmental Health Perspectives, 2004. **112**(1): p. 9-17.
54. Leung, A., Z.W. Cai, and M.H. Wong, *Environmental Contamination from Electronic Waste Recycling at Guiyu, Southeast China.* J. Mater. Cycles Waste Manag., 2006. **8**: p. 21-33.
55. Huo, X., et al., *Elevated Blood Lead Levels of Children in Guiyu, an Electronic Waste Recycling Town in China.* Environmental Health Perspectives, 2007. **115**(7): p. 1113-1117.
56. *Tetrabromobisphenol A (TBBPA).* http://www.sinoharvest.com/products/Tetrabromobisphenol.shtml.

57. *Bromine & Bromine Chemicals* http://www.solarischemtech.com/pro_bistribromophenoxyethane.asp.
58. *Hexabromocyclododecane.* http://en.wikipedia.org/wiki/Hexabromocyclododecane.
59. Altwaiq, A.M., M. Wolf, and E.R. Van, *Extraction of Brominated Flame Retardants from Polymeric Waste Material using Different Solvents and Supercritical Carbon Dioxide.* Analytica Chimica Acta, 2003. **491**(1): p. 111-123.
60. *Polybrominated diphenyl ethers.* http://en.wikipedia.org/wiki/Polybrominated_diphenyl_ethers.
61. Antonetti, P., et al., *Degradation products of the process of thermal recovery of copper from lamina scraps in lab-scale fluidized bed reactor.* Journal of Hazardous Materials, 2004. **108**(3): p. 199-206.
62. Buekens, A., *Feedstock Recycling and Pyrolysis of Waste Plastics: Converting Waste Plastics into Diesel and Other Fuels* ed. J. Scheirs and W. Kaminsky. 2006, University of Hamburg, Germany.
63. Saha, B. and A.K. Ghoshal, *Thermal Degradation Kinetics of Poly(ethylene terephthalate) from Waste Soft Drinks Bottles* Chemical Engineering Journal, 2005. **111**(1): p. 39-43.
64. Gao, M., W. Wu, and Y. Yan, *Thermal Degradation and Flame Retardancy of Epoxy Resins Containing Intumescent Flame Retardant.* Journal of Thermal Analysis and Calorimetry, 2009. **95**(2): p. 605-608.
65. Marsanich, K., et al., *Evaporation and Thermal Degradation of Tetrabromobisphenol A above the Melting Point.* Thermochimica Acta, 2004. **421**: p. 95-103.
66. Buchwalder, J., et al., *Results and Trends on the Injection of Plastics and ASR into the Blast Furnace.* ISIJ International, 2006. **46**(12): p. 1767-1770.
67. Asanuma, M., *Combustion and Gasification Behavior of Waste Plastics Injected into Raceway of Blast Furnace.* Ironmaking Conference Processing, 1998. **57**: p. 525-530.

68. McIlveen-Wright, D.R., et al., *A Comparison of Circulating Fluidised Bed Combustion and Gasification Power Plant Technologies for Processing Mixtures of Coal, Biomass and Plastic Waste.* Fuel Processing Technology, 2006. **87**(9): p. 793-801.

69. Lindenberg, H.-U., et al., *Plastic Recycling in Blast Furnaces (in German).* Stahl und Eisen, 1996. **116** (8): p. 89-93.

70. J. Buchwalder, J.H., W. Kaulbars and J. Lahr, *Proc., 6th Int.,Blast Furnace Conf.* Eisenhüttenstadt, 2001.

71. Sahajwalla, V., L. Hong, and N.S. Chaudhury, *Waste Plastics — A Resource for EAF Steelmaking*, in *AISTech2005-The Iron & Steel Technology Conference and Exposition*. 2005: Charlotte, N.C.

72. Fisher, M.M., et al., *Energy Recovery in Sustainable Recycling of Plastics from End-of-life Electrical and Electronic Products*, in *2005 IEEE International Symposium on Electronics & the Environment (2005 ISEE/SUMMIT).* May 16-19, 2005 New Orleans, LA, USA. p. 83-92.

73. Chen, K.S., et al., *Kinetics of Thermal and Oxidative Decomposition of Printed Circuit Boards.* Journal of Environmental Engineering, 1999(3): p. 277-283.

74. Zheng, Y., et al., *A Novel Approach to Recycling of Glass Fibers from Nonmetal Materials of Waste Printed Circuit Boards.* Journal of Hazardous Materials, 2009.

75. Sakai, S., et al., *Combustion of Brominated Fame Retardants and Behavior of Its Byproducts.* Chemosphere, 2001. **42**: p. 519-531.

76. Uemichi, Y., et al., *Product Distribution in Degradation of Polypropylene over Silica-Alimina and CaX Zeolite Catalysts* The Chemical Society of Japan, 1983. **56**(9): p. 2768-2773.

77. Brebu, M., et al., *Removal of nitrogen, bromine, and chlorine from PP/PE/PS/PVC/ABS-Br pyrolysis liquid products using Fe- And Ca-based catalysts.* Polymer Degradation and Stability, 2005. **87**(2): p. 225-230.

78. Blazso, M., Z. Czegeny, and C. Csoma, *Pyrolysis and debromination of flame retarded polymers of electronic scrap studied by analytical pyrolysis.* Journal of Analytical and Applied Pyrolysis, 2002. **64**(2): p. 249-261.

79. Brebu, M., et al., *The individual and cumulative effect of brominated flame retardant and polyvinylchloride (PVC) on thermal degradation of acrylonitrile-butadiene- styrene (ABS) copolymer.* Chemosphere, 2004. **56**(5): p. 433-440.

80. Bradna, P. and J. Zima, *Use of pyrolysis-gas chromatography/mass spectroscopy in the analysis of cured poly-functional epoxy resins.* Journal of Analytical and Applied Pyrolysis, 1991. **21**(1-2): p. 207.

81. Barontini, F., et al., *Thermal degradation and decomposition products of electronic boards containing BFRs.* Industrial and Engineering Chemistry Research, 2005. **44**(12): p. 4186-4199.

82. Luda, M.P., et al., *WEEE recycling: Pyrolysis of fire retardant model polymers.* Waste Management, 2005. **25**(2 SPEC. ISS.): p. 203-208.

83. Barontini, F. and V. Cozzani, *Formation of hydrogen bromide and organobrominated compounds in the thermal degradation of electronic boards.* Journal of Analytical and Applied Pyrolysis, 2006. **77**(1): p. 41-55.

84. Li, J., et al., *Printed Circuit Board Recycling: A State-of-the-Art Survey.* IEEE Transactions on Electronics Packaging Manufacturing, 2004. **27**(1): p. 33-42.

85. Madorsky, S.L. and S. Straus. *Thermal Degradation of Polymers at Temperatures up to 1200$^o$C.* in *High Temperature Resistance and Thermal Degradation of Polymers-comprising papers(with discussions) read ata a symposium organised by the Plastic and Polymer Group held on* 21st-23rd September, 1960. University of Landon, W.C.1.

86. Peng, S.H., L.Q. Chen, and G.G.M.Z. Cai, *Vacuum Pyrolysis of Waste Printed Circuit Boards.* Journal of Chemical Industry and Engineering(China), 2006. **57**(11): p. 196-202.

87. Gan, K., et al., *Pyrolysis Kinetics of Waste Print Circuit Board in Vacuum Condition.* Journal of South China University of Technology(Natural Science Edition) 2006. **34**(3): p. 21-22.

88. Zolezzi, M., et al., *Conventional and Fast Pyrolysis of Automobile Shredder Residues (ASR).* Waste Management, 2004. **24**: p. 691-699.

89. Wu, Q., K.Q. Qiu, and Z.H. Zhan, *Study on Vacuum Pyrolysis Discipliarian of Epoxy Resin contained in Waste Printed Circuit Boards.* Environmental Pollution & Control, 2008. **30**(12): p. 17-19.

90. Qiu, K.Q., W. Qian, and Z. Z.H., *The Analyses of Characteristics of Products from Waste Printed Circuit Boards by Vacuum Pyrolysis.* Journal of Functional Materials 2009. **40**(3): p. 515-518.

91. William, J.H. and P.T. Williams, *Separation and Recovery of Materials from Scrap Printed Circuit Boards.* Resources, Conservation and Recycling, 2007. **51**(3): p. 691-709.

92. Benallal, B., et al., *Characterization of Pyrolytic Light Naphtha from Vacuum Pyrolysis of Used Tyres Comparison with Petroleum Naphtha* Fuel, 1995. **74**(11): p. 1589-1594.

93. Mirmiran, S., H. Pakdel, and C. Roy, *Characterization of Used Tire Vacuum Pyrolysis Oil : Nitrogenous Compounds from the Naphtha Fraction.* Journal of Analytical and Applied Pyrolysis, 1992. **22**(3): p. 205-215.

94. Sun, L.S., et al., *Experimental Research on Pyrolysis Characteristics of Printed Circuit Board Wastes.* Journal of Chemical Industry and Engineering(China), 2003. **54**(3): p. 408-412.

95. Barontini, F., et al., *The Thermal Degradation Process of Tetrabromobisphenol A.* Industrial & Engineering Chemistry Research 2004. **43**(9): p. 1952-1961.

96. Duan, C., et al., *Research on the Gas from PyrolysisDuring Crushing of Discarded Printed Circuit Boards.* Journal of China University of Mining & Technology, 2005. **34**(6): p. 730-734.

97. Sun, L.S., et al., *Experimental Research on Pyrolysis of Printed Circuit Board Wastes and Analysis of Characteristics of Products.* Journal of Fuel Chemistry and Technology, 2002. **30**(3): p. 285-288.

98. Li, F., et al., *Experimental Study on the Effect of Eutectic Salts on Pyrolysis of Waste Printed Circuit Boards (PCB).* Journal of Fuel Chemistry and Technology, 2007. **35**(548-552).

99. Guan, J., Y.S. Li, and M.X. Lu, *Product Characterization of Waste Printed Circuit Board by Pyrolysis.* Journal of Analytical and Applied Pyrolysis, 2008. **83**: p. 185-189.

100. Marco, I., et al., *Pyrolysis of Electrical and Electronic Wastes.* Journal of Analytical and Applied Pyrolysis, 2008. **82**: p. 179-183.

101. Wang, M.H., et al., *Pyrolysis of Scrap Printed Circuit Boards Particles.* Journal of Fuel Chemistry and Technology, 2009. **37**(2): p. 238-243.

102. Wang, S.J., et al., *Catalytic Pyrolysis of Waste Printed Circuit Boards.* Journal of Wuhan University of Science and Technology, 2009. **32**(1): p. 90-93.

103. Tan, R.D., et al., *Products from Microwave Heating of Waste Printed circuit Boards.* Environmental Pollution & Control, 2007. **29**(8): p. 599-601.

104. Islam, M.R., M.S.H.K. Tushar, and H. Haniu, *Production of Liquid Fuels and Chemicals from Pyrolysis of Bangladeshi Bicycle/rickshaw Tire Wastes* Journal of Analytical and Applied Pyrolysis, 2008. **82**: p. 96-109.

105. Zhang, Y., et al., *Characterization of Pyrolysis of Waste Printed Circuit Boards by High-resolution Pyrolysis Gas Chromatography-mass Spectrometry.* Chinese Journal of Chromatography 2008. **26**(4): p. 519-522.

106. Peng, K., B. Xi, and Q. Yao, *An Experimental Research on Pyrolysis of Printed Circuit Board Backing.* Techniques and Equipment for Environmental Pollution Control 2004. **5**(5): p. 34-37.

107. Li, A.M., et al., *Characterization of Tar Produced from Phrolysis of Typical Hazardous Wastes.* Chongqing Environmental Science 2003. **25**(5): p. 21-23.

108. Xiong, Z.H., et al., *A Study on Pyrolysis and Kinetics of Printed Circuit Boards Wastes.* Techniques and Equipment for Environmental Pollution Control, 2006. **7**(10): p. 47-50.

109. Guo, X.J., et al., *Experimental Research on Pyrolysis of Polytetrafluoroethylene-printed circuit boards.* Journal Huazhong University of Science & Technology(Natural Science Edition), 2008. **36**(10): p. 121-124.

110. Guo, X.J., et al., *Analysis of Pyrolysis Oil from Waste Printed Circuit Boards.* Petrochemical Technology, 2008. **37**(7): p. 724-728.

111. Zhou, W.X., L.Q. Chen, and G.Q. Guang, *Pyrolysis Characteristic of waste Phenolic-Resin-Based Printed Circuit Boards.* Environmental Chemistry, 2009. **28**(1): p. 99-102.

112. *Gas Chromatography-Mass Spectrometry.* http://en.wikipedia.org/wiki/Gas_chromatography-mass_spectrometry.

113. Guiles, C., *Everything You Ever Wanted to Know About Laminates for Frequency Dependent Applications...But Were Afraid to Ask (Part I).* Arlon-Materials for Electronics, November 2008.

114. Zhou, W.X., et al., *Study on Copyrolysis and Dehalogenation of Waste Printed Circuit Boards and Calcium Carbonate.* Chinese Journal of Environmental Engineering, 2009. **3**(1): p. 169-174.

115. Peng, S., L. Chen, and M. Cai, *Forming and Scavenging of Hydrogen Bromide During Pyrolysis of Waste Printed Circuit Boards.* Journal of South China University of Technology (Natural Science Edition), 2006. **34**(10): p. 15-19.

116. Criado, J.M., J. Morales, and V. Rives, *Computer Kinetic Analysis of Simultaneously Obtained TG and DTG Curves.* Journal of Thermal Analysis and Calorimetry, 1978. **14**(3): p. 221-228.

117. Ni, X.M., et al., *A New Type of Fire Suppressant Powder of NaHCO3/Zeolite Nanocomposites with Core–Shell Structure* Fire Safety Journal, 2009. **44**(7): p. 968-975.

118. Soares, J.P., et al., *Thermal Behavior of Alginic Acid and Its Sodium Salt.* Ecletica Quimica, 2004. **29**(2): p. 57-63.

119. *Brominated flame retardant.* http://en.wikipedia.org/wiki/Brominated_flame_retardant.

120. *Epoxy resin* http://en.wikipedia.org/wiki/Epoxy_resin.

121. *Infrared Spectroscopy.* http://en.wikipedia.org/wiki/Fourier_transform_infrared_spectroscopy#FT-IR_method.

# ABBREVIATION LIST

| Full name | Initial |
|---|---|
| Printed wire boards | PWBs |
| Printed circuit boards | PCBs |
| Waste of electrical and electronic equipment | WEEE |
| Electronic waste | E-Waste |
| Electronic scrap | E-scrap |
| Thermo-gravimetric analysis | TG |
| Differential thermal analysis | DTA |
| Tetrabromobisphenol A | TBBA |
| Brominated flame retardant | BFR |
| Decarbophenyl oxide | DBDPO |
| Tetrabromophthaldiphenyl ethane | TBPME) |
| Brominated oligmer epoxy | BOE |
| Tribromophenoxy ethane | TBPE |
| Polybrominated Diphenyl Ethers | PBDE |
| Polybrominated dibenzo-p-dioxins | PBDD |
| Polybrominated dibenzofurans | PBDF |
| Polybrominated Biphenyls | PBB |
| Hexabromocyclododecane | HBCD |
| Polyamide 6 | PA 6 |
| Polystyrene | PS |
| Polyvinyl chloride | PVC |
| High-density polyethylene | HDPE |
| Polypropylene | PP |
| Polyethylene terephthalate | PET |
| Infrared spectroscopy | RAIR |
| High impact polystyrene | HIPS |
| Acrylonitrile–butadiene-styrene copolymer | ABS |
| Hexabromocylododecane | HBCDD |

| | |
|---|---|
| Tetrabromobisphenol A | TBBPA |
| Bromination of bisphenol A | BPA |
| Tribromoneopentylalcohol | TBNPA |
| Polycyclic aromatic hydrocarbons | PAHs |
| Polychlorinated dibenzo-p-dioxins | PCDDs |
| Gas chromatography-mass spectrometry | GC-MS |
| Fourier transform infrared | FTIR |
| Thermogracimentry | TG) |
| Thermogravimetry analysis | TGA |
| Polytetra fluoroethylene | (PTFE) |
| Differential scanning calorimetry | DSC |

# VITA

Mr. Xiangjun Zuo (April 22, 1980) is a master student at the Department of Materials Science and Engineering at Missouri University of Science and Technology (Missouri S&T) in the USA. He received his bachelor's and master's degree in Metallurgical Engineering at the College of Materials Science and Engineering, Chongqing University in China in July 2003 and June 2006 respectively. During 2003-2004, he worked as a engineer at the casting plant of the Southwest Aluminum Company (China), the biggest aluminum rolling product company in Asia. During October 2006-July 2008, he was a Ph.D. student at the Department of Materials Science and Engineering, Norwegian University of Science and Technology (Norway). He passed his master defense on March 26, 2010, and will receive his master degree at the Department of Materials Science and Engineering at Missouri University of Science and Technology (Missouri S&T) on May 2010. Xiangjun has extensive international research experience, including USA, Norway and China. Xiangjun has compound backgrounds in steelmaking, refining, (continuous) casting, recycling of steel, light metals and computational fluid dynamics application to metallurgical systems. Xiangjun has participated in 7 projects, 4 of them came from the industry. He published over 20 academic papers, and also attended several international conferences and made presentations there.