Experimental Study on Pyrolysis of Non-Metallic Materials Separated from Printed Circuit Board Waste via TGA and Analytical Vacuum Fast Pyrolysis of Non-Metallic Fraction of Printed Circuit Board Waste after Copper Separation

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Abstract: In just over half a century electronic equipment and products have revolutionized human lifestyle. At the product's end of life, e-waste, its components material and other materials have influenced and infiltrated environment in every part of globe. The hazardous effect of plastic materials and debris to biodiversity is well established, but mitigation and planning are often hampered by lack of quantitative data on waste accumulation patterns in landfill. Here we document a study on the pyrolysis of non-metallic material of printed circuit board, the basic elemental part of electronic waste. The non-metallic material is separated from printed circuit board waste during the copper separation processes and was found in powder form at average size up to 177 µm. The purpose of this study is to experimentally investigate the pyrolysis behavior of the non metallic material of printed circuit boards (PCB) waste fraction at a temperature range of 300 ◦C to 600 ◦C by means of the Thermogravimetric Analysis (TGA) and seek to find out the effective pyrolysis temperature that could be used in pyrolysis process in production scale. The experimental results reveal that the chemical composition of the PCB reflects that the main decomposition of PCBs occurs between 250 ◦C and 450 ◦C, and effectively decomposed at 403 ◦C. The pyrolysis of PCBs showed a varying production of aromatic compounds such as phenol, bromophenol, styrene, methylstyrene, and bisphenol A as well as non-aromatic compounds such as acetone and bromomethane, which are strongly related with the initial chemical composition of PCBs.

Keywords: Electronic waste, vacuum fast pyrolysis, printed circuit board waste, non-metallic fraction.

INTRODUCTION

Modern life increases the demand of using newer electrical and electronic equipment (EEE). Consumers discard large amount of EEE, while manufactures also produce large amount of new products at an alarming rate at the cost of environment. Printed circuit board, which form the basis of EEE industry, are technological waste that needs to be separated, recycled and disposed due to the diversity of materials and components [1]. Basic materials consisted in PCB can be classified into two categories which are metallic and nonmetallic. Metallic material is usually separated and recycled in a secondary material market because it has a higher value and can be recovered to form a new material [2]. Whereas the nonmetallic fraction or NMF is usually being discarded and sent for a conventional disposal treatment such as landfill and combustion or sometimes reused as filler [3]. In general, NMF is extremely difficult to separate and dispose because it contains variety of materials having mixed and diverse composition. Thermoset plastics (brominated epoxy resin), ceramic and glass reinforced fiber are basic elements in NMF and contain additive chemical substrates such as brominated flame retardant or BFR [4]. By incineration, it can generate toxic gases during heating process whilst landfilling causes heavy metal and other additives leach into groundwater [5]. These treatments are primitive but still widely used and cause secondary pollution, as well as the loss of material resources. This article presents a literature review and experimental study of using innovative pyrolysis method on NMF of PCB, showing their differences in terms of environmental impact and the appropriate waste disposal treatment for NMF of PCB material. This study is a historical review of publications related to the environmental problem derived from NMF of PCB, the effects and how they have been treated in the current waste disposal treatments. The article focuses on both the benchmark of the environmental impacts of the current treatments against the innovative pyrolysis waste disposal method and the development of a proper disposal technology for NMF of PCB. With the increasing demand of newer technology, there has been a rapid increase in the production of EEE that ends up generating e-waste and as a result greatly increasing the volume of the waste in landfills. This e-waste is difficult to dispose and close the loop of

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product lifecycle [6], as its material is diverse and complex. Thus, alternatives for the disposal of these materials in a way that does not harm the environment and generate secondary pollution is attracting the attention of many researchers from different fields [7]. According to Figure **1**, the population is continuously increasing, more waste is being generated, and there is also a social pressure of using environmentally friendly disposal system and technology to deal with the current problem of different types of materials [8]. Among EEE products, one of the main components to which an effective solution to reuse, recycle and recovery has not yet been found is the NMF of PCB after the PCB metal separation process [9]. One of the main difficulties pointed out by several researchers is the separation of components and materials [10], due to their diversity and complex mixture of materials. In order to recover the non-metallic materials of PCBs and to maximize the usage of each material, it is necessary to find a proper treatment to dispose it off effectively [11]. This is because the primitive waste disposal techniques such as landfilling and incineration are not designed to process modern life waste materials. However, it is necessary to totally separate them from each other to purify the waste material and increase the chance of having with less contamination [12], which is a complex process and it often makes the material unusable because of the temperature applied.

According to Figure **1**, the increment of the high demands for electrical and electronic equipment (EEE) and the waste that is being generated [13], are strongly linked to the population factors such as growth, density, distribution and demographics, as well as the manufacturing for high-technology for modern lifestyle [14].

MATERIALS AND METHODS

Sample Preparation

Since PCBs are basic component they are practically found in all EEE [15]. PCBs can be classified in many types according to their designs and various attributes for example, single layer boards; double-sided boards; multi-layer boards and rigid and flexible boards [16]. The standard IPC-2222 provides design information for different types of boards [17]. The design of electronic component forms the structure of a circuit that is required to make a complete functional EEE. The electronic components present in a board depend on its application and function [18], which may include semiconductors, transistors, diodes, capacitors, resisters, connectors and etc. [19]. Different parts or components also have a complex composition of materials and this lowers the recycling rate due to the difficulty in material separation. In general, the material present in PCBs can be categorized into four groups:

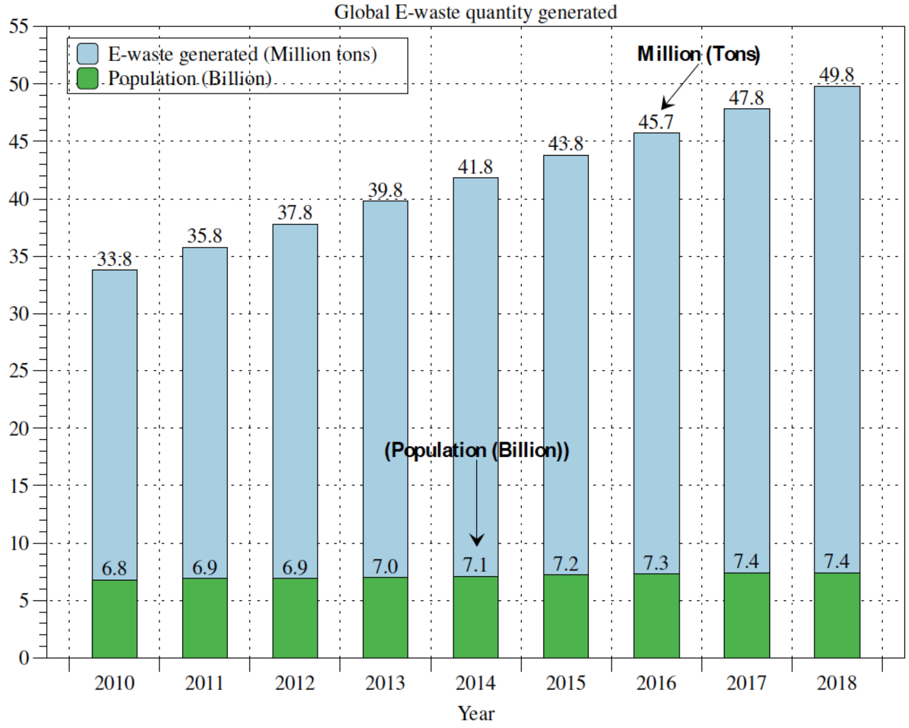


Figure 1: Population growth VS Waste Generated.

Metal (33%wt%), ceramics and glass (33%wt%), polymer (33%wt%), other material e.g. paper and liquid (1%wt%) as shown in Figure **2**.

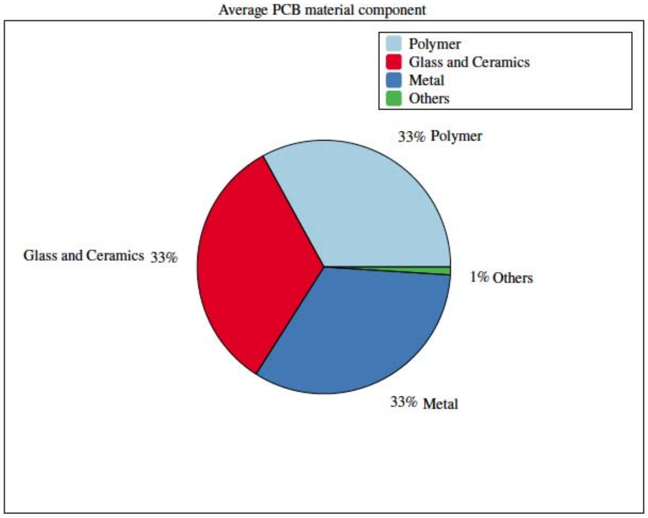


Figure 2: The average material composition of printed circuit board.

According to Figure **3** metal in PCB consist of base metal; for instance, copper, iron, aluminum, tantalum, gallium, gold, silver, chromium, lead, mercury. Polymer (plastic) is mainly brominated epoxy resin [20, 21]. Ceramics and glass are primarily silica and alumina. For waste of PCB without the mounting electronic components, the material composition comprises approximately 28%wt% of metal (mainly copper) and 72%wt% of non-metallic materials, which are polymer, glass and ceramics.

Non-metallic part of PCB is a matrix combination of three basic materials that are glass-reinforced fiber (GRF), ceramics and thermoset polymer (mainly brominated epoxy resin) as shown in Figure **4**. The thermoset plastic, especially brominated epoxy resin and other two materials as aforementioned details of NMF can be recovered if separate. Elemental composition of the non-metallic powder of PCB is shown in Figure **5**. Epoxy resin or thermoset plastic is not suited to be processed by normal heating environment after curing [11]. The thermoset material becomes hard after curing and permanently set as a solid, unable to be melted or reformed. The normal heating process will only lead material to combust atmosphere because oxygen being present [22].

In general, the non-metallic powder usually takes up to 70%wt% of the waste PCBs. Currently, following the harvesting of metal the remaining non-metal material (NMF is normally found in powder form) usually ends up in landfill or combustion process [23]. Therefore, not properly closing the loop of plastic material is not a sustainable way, neither is it an environmentally sound method of disposal of NMF waste from PCB material [16]. Landfills of waste PCBs or NMF will cause secondary pollutions because of heavy metal and brominated flame retardant (BFRs) leaching into the ground water

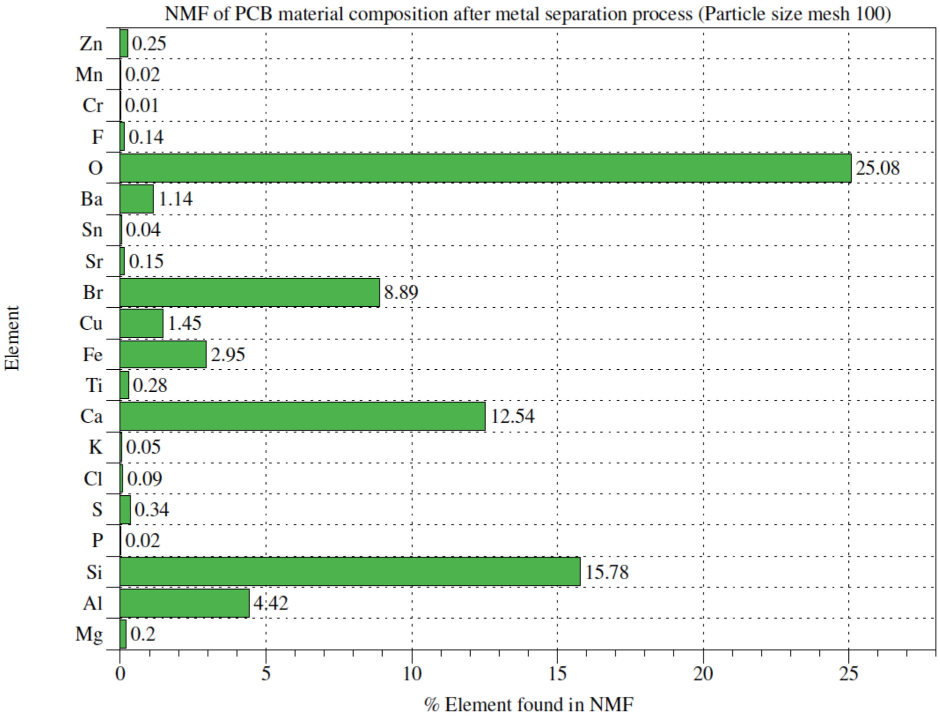


Figure 3: Elemental composition of Non-metallic material of PCB in powder form.

Figure 4: Non-metallic material of PCBs sample.

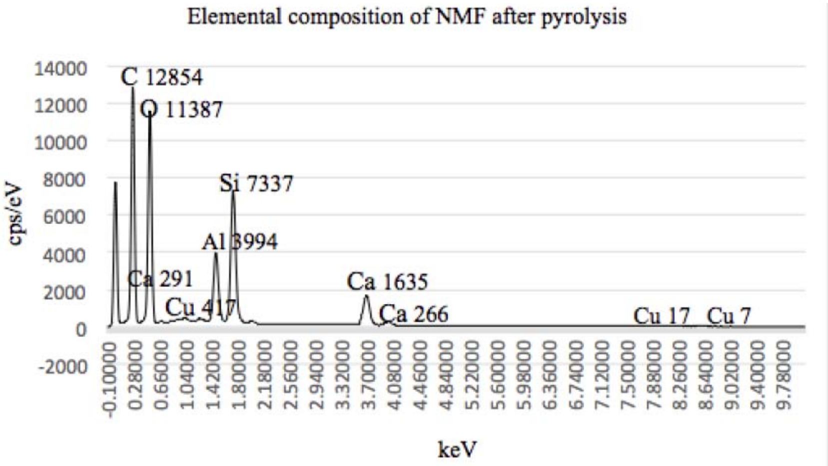


Figure 5: The material composition of non-metallic powder from waste PCB.

[24]. Disposal by combustion process will negatively impact the environment by generating toxic gases such as polybrominated dibenzodioxins and dibenzofurans (PBDD/FS). The only possibility of preventing combustion of the material while processing PCB powder is by processing the non-metallic powder under a controlled environment in a thermal process, without the presence of oxygen [18]. Therefore, pyrolysis is an environmentally friendly method that is suitable for the non-metallic powder [25].

Research on material recovery, resource re-utilization and safe disposal has shown significant intentions of a positive impact from an environmental protection perspective [26]. Most of NMF of waste PCBs can be captured by a three-stage separation process: reusable component disassembly, material preparation (size reduction) and separation via mechanical processing or chemical processing. Most of the PCBs are from the pneumatic separation process as show in Figure **6**.

In the past 10 years, there are a number of researches that have been done by using pyrolysis to recover waste PCBs, however little research has been focused on the use and quality of fuel oil [27]. Early studies of pyrolysis technology mainly focused upon: reactor development; identification of resulting products; condition and parameter settlement for fuel production process; rate of heating; other relevant variables.; and the mechanism investigation or kinetics modeling of the pyrolysis process [28]. These early studies were the genesis for the development of pyrolysis techniques used for removing organic compound in solid waste stream [29]. In experimental work, fuel oil was produced and optimized from

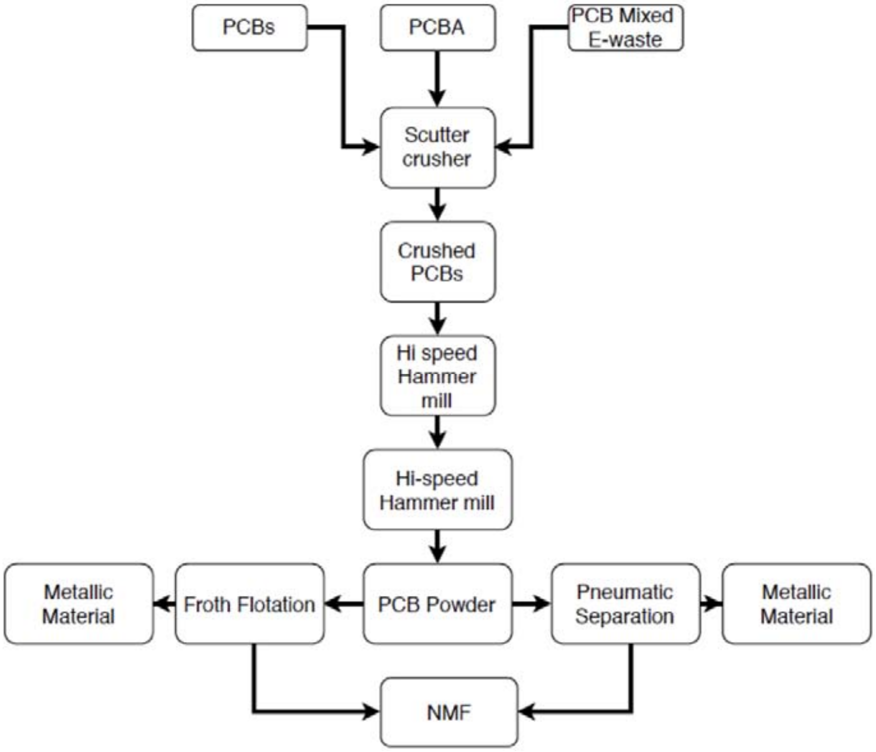


Figure 6: Flow chart the separation processing of non-metallic fraction.

applying pyrolysis method to the NMF of PCB waste. The fuel was tested and optimized to meet the fuel standard ASTMD396-15c Standard Specification for Fuel Oils and ASTM975-15c Standard Specification for Diesel Fuel Oils. The optimal conditions for preparing high quality fuel oil are recommended as a result of the findings of this study. This work researches technique for optimizing the fast vacuum pyrolysis technique to process the non-metallic powder, separated from e-waste PCB in order to produce and measure the output of quality liquefied combustible hydrocarbon based fuel [17]. Greater understanding of the kinetic parameters of thermal decomposition of non-metallic components of PCBs with varying parameters was achieved and recognized as innovative pyrolysis method. The vacuum fast pyrolysis experiments in this study was performed in a medium laboratory scale reactor.

Thermogravimetric Analysis and Differential Thermal Analysis (TGA/DTA)

For the thermal characterization of the sample, a Mettler Toledo thermogravimetric analyzer was used. Four different heating rates were chosen, namely: 12.5, 20, 30 and 40 ◦C/min. For each run 12 ± 0.2 mg of sample was used. The starting temperature was set at 28 ◦C and the temperature increased according to the specified heating rates under dynamic measurement. The temperature of 1000 ◦C was set as the final treatment temperature where the sample was treated isothermally for 10 min. However, the experiments were conducted using different heating rates to investigate the kinetic study as well as the partial of experiments were set to maintain at the max set targeted temperatures of 300, 400, 500 and 600 °C respectively to observe the differences. Thermogravimetric analysis (TGA) curve represents the percentage of mass loss of the sample in relation to its initial mass in the function of time. The NMF from waste PCB was individually pyrolyzed under a nitrogen environment at heating rates of 12.5, 20, 30 and 40 °C/ min. The TG curve of NMF from waste PCB (Powder), during pyrolysis at the heating rate of 12.5 °C /min is illustrated in Figure 4-1. The TG curves of NMF sample at the four heating rates (12.5, 20, 30 and 40 °C/min) are presented in Appendix A.

Mass loss of the NMF from waste PCB sample during pyrolysis can be observed in three main stages comprising dehydration, de-volatilization and solid decomposition as illustrated in Figure **7**. The first stage had a slight mass loss mainly caused by elimination of moisture and the initial stage of cracking process. In the second stage, de-volatilization was characterized by a step-up of mass loss, which represented the starting pyrolysis process. Most of the volatile components were released at high rates in the third

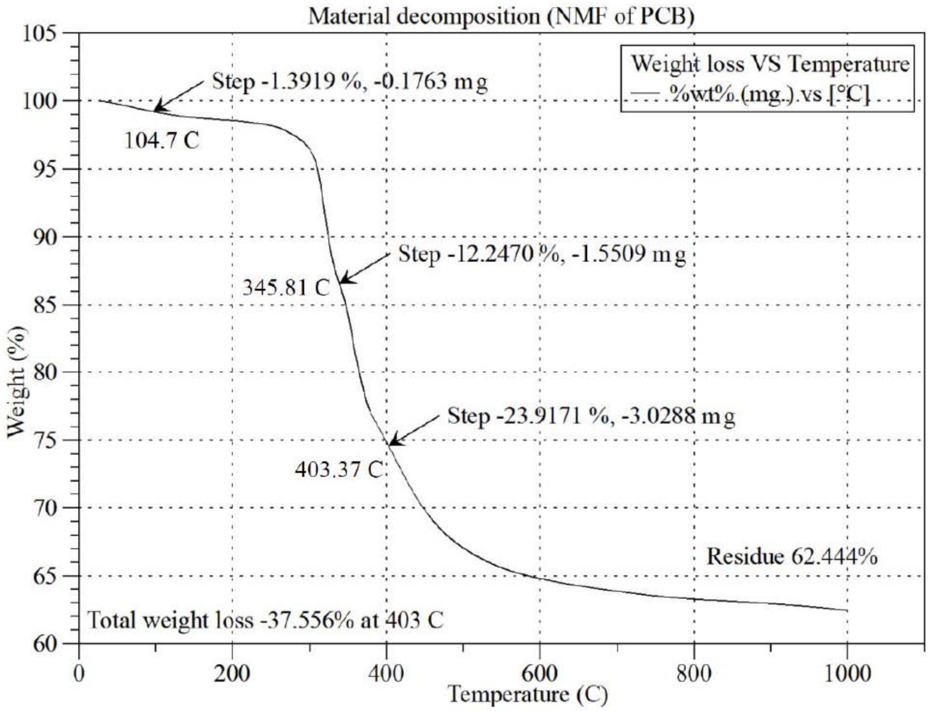


Figure 7: TG curves of the NM material from waste PCB under N_2 at 12.5 °C/ min.

stage; this resulted in the production of char during pyrolysis process. In the third stage, a significant mass loss continued as a result of decomposition of the solid residue. The maximum mass loss was observed at 403.37 which could be used to consider as an effective temperature for NMF from waste PCB.

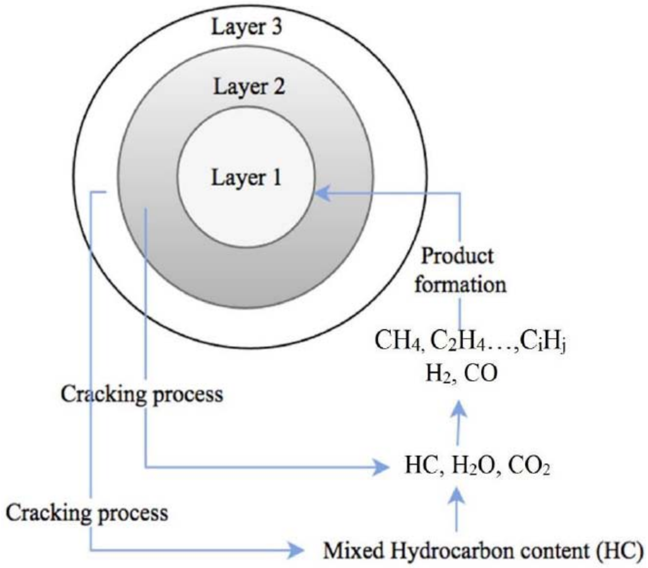


Figure 8: Three main stages from Pyrolysis of NMF particle.

Even though TG curve of NMF from waste PCB shows the three stages of mass loss, differences in thermochemical decomposition in related to processing time. The TGA was ended at 1000°C As shown in Figure **8**, in the first stage, the dehydration of the NMF from waste PCB occurred at temperatures of below 200 °C (104.7 °C) while the dehydration of material occurred at temperatures of below 400 °C (345.81 °C). Higher volatile matter of NMF from waste PCB resulted in lower de-volatilization temperatures. The de-volatilization of the NMF from waste PCB samples took place at temperatures in the range of 200– 400 °C and in the range of 400–600 °C, respectively. Mass loss and solid residue decomposition of NMF from waste PCB was small in the third stage. According to Figure **8**, NMF from waste PCB pyrolysis showed relative trends for the mass loss as a function of temperature, approximately over 37% mass loss at 403.7 °C. The loss in the mass of the NMF sample occurred at high temperatures, resulting in only 7% mass loss at over 400 °C. Significant differences in the amount of volatile matter released were found during pyrolysis. The percentage of cumulative mass loss of the NMF from waste PCB sample during pyrolysis at temperatures of 200, 300, 400, 500 and 600 °C was observed and averaged, as summarized in Table **1**.

A differential thermogravimetric (DTG) curve from differential thermal analysis (DTA), which is obtained as the first derivative of the TG curve, illustrates the rate of mass loss as a function of temperature in relation of time. The DTG curves of NMF from waste PCB during pyrolysis at the heating rate of 12.5 °C/ min

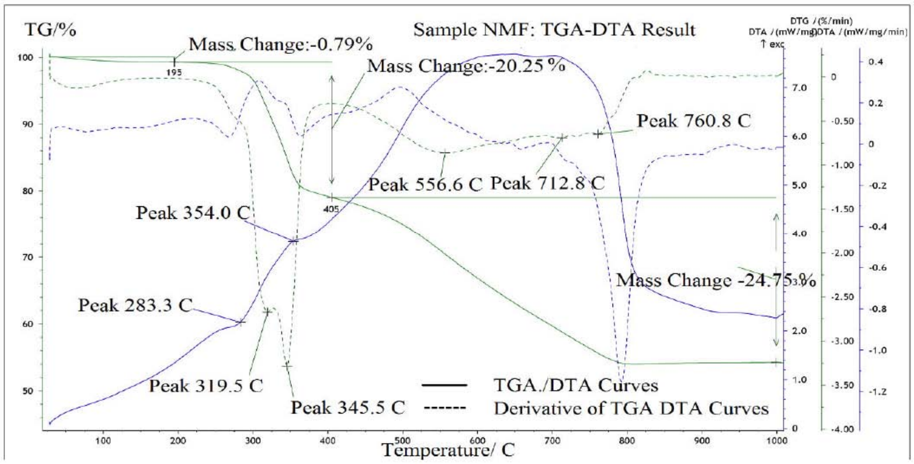


Figure 9: Differential thermal analysis of NMF from waste PCB.

Table 1: Cumulative Mass Loss of the NMF from Waste PCB Sample (Powder) during Pyrolysis in % of Initial Mass

Sample	200	300	400	500	600	**Remarks**
NMF	1.3919	13.638	37.556	44.327	48.242	

are presented in Figure 6–2. The DTG curves of the NMF powder from waste PCB sample at the four heating rates are presented in Appendix A.

The temperature at which the maximum rate of the sample mass loss occurs during the process, the maximum reactivity temperature, is identified as the peak in the DTG curve. The NMF from waste PCB demonstrated trends for maximum reactivity temperature, with the peak at 403 °C -405 °C. As indicated by the TG and DTG curves, these three stages manifested different features on the rate of mass loss, maximum reactivity temperature and end residue.

RESULTS AND DISCUSSION

The elemental analysis indicates that the non-metallic part of PCBs contain noble plastic based elements which would constitute the economical driving force for their recovery. The relatively high content of bromine compared with the low concentration of chlorine and low concentration in antimony indicates that the type of the flame retardant used for the manufacturing process of the examined PCBs are brominated flame retardants (BFRs). The low quantity of nitrogen in the sample indicates that the nitrogen containing compounds in the pyrolysis products such as aromatic amines would have low yields. The experiments have shown that materials with higher nitrogen content also produce relatively limited aromatic amines due to their retention in the solid residue.

Thermal Degradation Behavior

The initial mass of non-metallic material of PCBs contains epoxy thermoset plastic material roughly by half of its own weight which can be used to explain that because the presence of hydrocarbon content the initial material can be decomposed and changed into gas products. No mass change was observed from the beginning of the experiment until the temperature of approximately more than 120 ◦C -178 ◦C due to the presence of minimal moisture or water content in the sample. The higher mass loss rate occurs at temperatures 380 ◦C -390 ◦C and 403 ◦C -405 ◦C respectively as shown in Figures **9** and **10**. The mass derivative per Celsius indicates decomposition in two regions where different reactions are dominating, one at a temperature range between 380◦C -390 ◦C, followed by slower decomposition rate reactions at higher temperatures that it was selected for. Similar results have also been observed in other studies dealing with the decomposition of phenolic resins, where the decomposition, is completed in at least two different regions. Moreover, the decomposition curves shift to higher temperatures as the heating rate was increased. The decomposition occurs when the vapor pressure of the volatiles is greater than the ambient pressure. So, at higher heating rates the decomposition shifts to higher temperatures because the diffusion of the volatiles is inhibited at higher temperatures. The one step decomposition at a temperature range of 250–370 ◦C combined with the short length glass reinforced fiber GRF content in the material, indicates

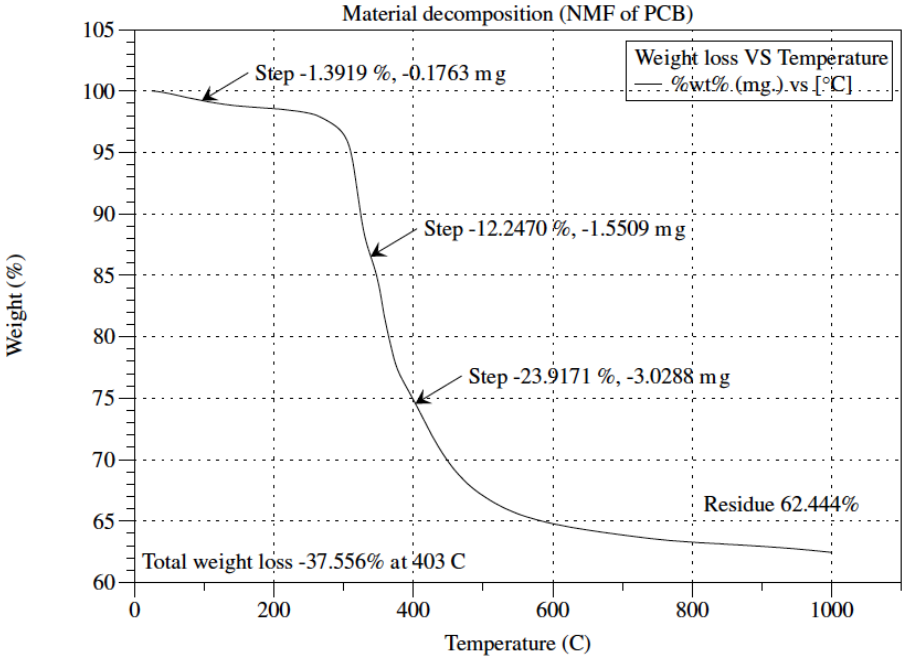


Figure 10: Average thermograph of TGA on initial testng of the sample material.

Table 2: Possible Products of Pyrolysis of Non-Metallic Material Separated from Printed Circuit Board Waste in Powder Form

Index	Group	Formable Compound	Formular
1	Hydrocarbon	Butane	C_4H_{10}
2	Hydrocarbon	Benzene	C_6H_6
3	Hydrocarbon	Toluene	C_7H_8
4	Hydrocarbon	Styrene	C_8H_8
5	Hydrocarbon	Methylstyrene	C_9H_{10}
6	Light compounds	Acetone	$(CH_3)_2CO$
7	Phenolic Compounds	Phenol	C_6H_6O
8	Phenolic Compounds	Phenol 2 Methyl	C_7H_8O
9	Phenolic Compounds	Phenol 2,6-dimethyle	$C_8H_{10}O$
10	Phenolic Compounds	Bisphenol A	$C_{15}H_{16}O_2$
11	Phenolic Compounds	*p*-cresol	C_7H_8O
12	Furans	Benzofurans	C_8H_6O
13	Furans	2-Methylbenzofurans	C_9H_8O
14	Furans	Dibenzofurans	$C_{12}H_8O$
15	Bromine Compound	Bromomethane	CH_3Br
16	Bromine Compound	Bromophenol	$C_{19}H_{10}Br_4O_5S$
17	Bromine Compound	Phenol 2,4- dibromo	$C_6H_4Br_2O$
18	Bromine Compound	Hydrogenbromide	HBr

that the plastics do not contain synergists of GRF in PCB meaning that there are at least 2 main materials which have different temperature properties. Brominated frame retardants with thermoset plastic have been examined in similar studies and their decomposition undergo a two-step decomposition. The pyrolysis gas is very rich in hydrocarbon such as CO, CO_2, H_2, CH_4 and in small part of O_2. The possible products of pyrolysis of NMF that can form hydrocarbon are shown in the Table **2** [9].

The temperature conditions were based on the TGA, since the decomposition characteristics of the sample were identified. Therefore, the examined temperature range varied between 400 ◦C and 900 ◦C. The products of vacuum fast pyrolysis for non metallic material of PCBs which were identified are summarized in Table **2** and their area percentages detected from the MSD are illustrated in figures as a function of temperature as well as their polynomial fitting to the experimental results. Thermal decomposition of brominated epoxy resins takes place by bond cleavage between the aromatic rings and the methylene bridges. The formed radicals undergo secondary transformations with hydrogen atoms, phenol, methylphenols, bis- and tris-phenols etc. and their methyl derivatives are being produced. Furthermore, studies of thermal decomposition of novolac resins which contain linear sequences in their structure usually produce isomers of bis (hydroxyphenyl) methane. These aromatics derive during the cyclisation reaction with the participation of hydroxyl or methyl groups in the ortho-position to methylene bridges. The presence of the bisphenol A in the pyrolysis products suggest that the initial fraction of the resin used for the manufacturing process of PCBs is the diglycidylether bisphenol A (DGEBA)-type epoxy resin. It is an easily made flame retardant which contain brominated bisphenol A segments in the polymer chain [18]. Moreover, this information can be extracted from manufacturer's specifications description of the product used for these experiments. Contrary to other studies where [8] amounts of bisphenol have been detected, low concentration of the aforementioned compound has been detected in this study. This can be explained by the difference in the initial material, which shows that the ash content is higher, [8] giving higher quantity of available volatile mass to react. On the other hand, the elemental analysis presented on that study is limited since the information of the bromine in not available in order to be compared with our investigation. The detection of bromophenol, dibromophenol and other similar in structure substances indicates the type of the flame retardant used for the manufacturing of the examined printed circuit boards. Furthermore, the detection of furans and dioxins on the products indicates that the flame-retardants used were polybrominated biphenyls (PBBs) or polybrominated diphenyl ethers (PBDEs), which are known from the hazardous products they produce during their decomposition at high temperatures [19]. According to [30], the production of the hydro bromic acid (HBr) in early stages of the pyrolysis process increase the production of a wide range of brominated aromatic species. A possible mechanism of the decomposition of brominated epoxy resin during the pyrolysis of PCBs is presented in Figure **3**. As the temperature increases the initial macromolecule chain of the resin cleavage formulates new lower molecular weight molecules. The higher energy bonds of Carbon and Oxygen in phenolic compounds [24], brakes at higher temperatures and other aromatic substances such as styrene, methylstyrene, benzene, and toluene are produced due to epoxy resin's decomposition. The experimental results showed that their quantity increases while temperature increase, which can also be explained through the decomposition of phenolic resin in higher temperatures, when more aromatic compounds are being produced due to the rearrangement of their molecular structure [31].

From the ultimate analysis, concentrations for the key elements C, H and O of NMF pyrolysis fuel at different temperatures were obviously comparable. This indicated that NMF pyrolysis fuel produced between temperature at 300 °C - 400 °C had relatively similar absolute elemental composition while in NMF pyrolysis fuel produced between temperature at 500 °C - 600 °C. also had the similar elemental composition. However, differences in the key elements were found that the NMF fuel produced between the temperature at 300 °C - 400 °C had produced lighter and better appearance liquid when comparing to NMF pyrolysis fuel produced between temperature at 500 °C - 600 °C. Both groups of fuel samples had a high percentage of carbon after thermochemical reaction during pyrolysis and a lower percentage of oxygen compared to the sample from higher temperature group (NMF pyrolysis fuel produced between temperature at 500 °C - 600 °C). The comparison of chemical compositions of the respective samples is illustrated in Figure **11**.

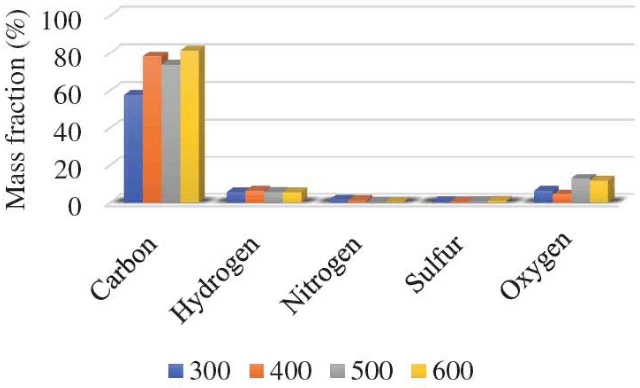


Figure 11: Elemental distribution of fuel samples.

It is evident from Figures **12** and **13** that the non-metallic powder after the process has become carbon black as solid residue. It shows varied surface area

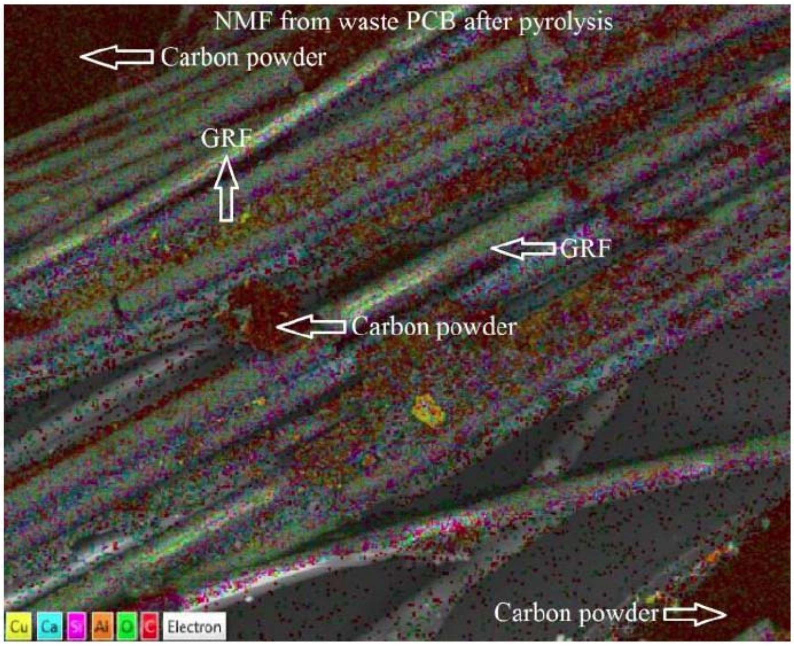
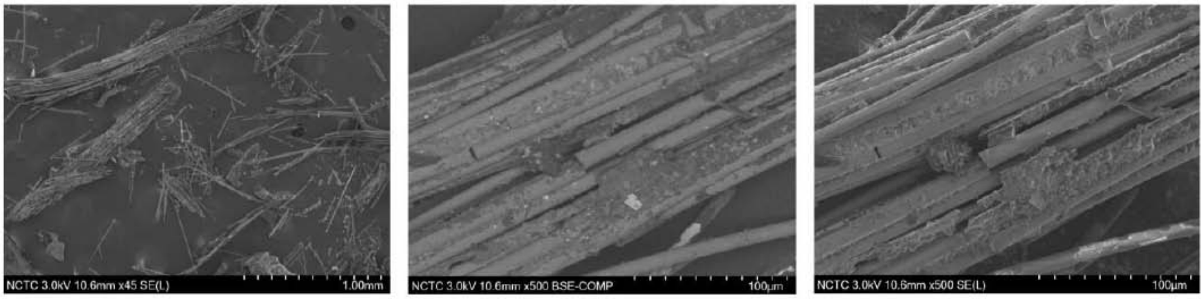


Figure 12: SEM image of solid residue from NMF pyrolysis after process.



Carbon Carbon Mode: BSE Carbon Mode: SE

Figure 13: SEM image of solid residue from NMF pyrolysis after process.

characteristics, flaky and tubular shape which indicates the characteristics of GRF. It is known that activation type (temperature, and heating rate during the process) greatly influence the surface area of chars generated from NMF pyrolysis.

During the decomposition of phenolic resins, debromination of the polymer fraction occurs mainly by the production of HBr as it is also stated in the literature. On the other hand, one part of the bromine reacts with available methyl radicals and forms bromomethane while the other part is still attached to aromatic phenolic rings, producing bromo-phenol. In this study the thermal decomposition of PCBs was investigated. The complexity of the sample was identified through the elemental analysis where various conventional metals such as copper and iron as well as noble metals were identified. The copper and nickel present in the PCBs may have influenced the reactions occurred during the pyrolysis of PCBs since both have catalytic effects for dioxins formation. However, minor area percentages of dioxins have been identified in this specific study. On the other hand, more investigation is needed in order to extract more reliable conclusions about the toxic substances generated from the pyrolysis of these materials. Furthermore, the low percentage of organic content indicates that for this specific examined fraction of PCBs waste, the energy recovery through pyrolysis cannot reach high yields. Thermogravimetric analysis has shown that thermal degradation of PCBs occurred in a two regions process, one between 250 ◦C and 370 ◦C, where the basic rapid decomposition occurred and the other at higher temperatures where a slow mass loss occurred. Using analytical pyrolysis several pyrolysis products were identified of which the most abundant was phenol, which indicates that the feedstock recycling of the monomer could be a valuable option for this process.

Moreover, other compounds were also identified such as more complex phenolic compounds, aromatic hydrocarbons, furans and bromine containing compounds. Through this experimental procedure, the possible reaction pathways were identified and were illustrated in Figures **3**, **6** and **13** accordingly:

- Thermal decomposition of the polymeric chain to form phenolic and bromophenolic species.
- Thermal decomposition of bisphenol A to from aromatic hydrocarbons.
- Dehydration of phenolic species to from benzofuranic structures.

The temperature conditions chosen for this experimental procedure (300 ◦C –600 ◦C) can succor to accomplish an overview of the pyrolysis products and the reactions occurring at different temperature windows. The low temperature conditions of the pyrolysis favor the production of phenol, brominated compounds, and bisphenol A, while higher temperature conditions favor the production of aromatic hydrocarbons. Therefore, the chosen temperature conditions can help us to yield the desirable products according to their preference. However, benzofuranic structures are also formed at high temperatures, indicating that high temperature conditions should be avoided

Carbon-Char Production

After dehydration, the devolatilization process yields several products which comprises flammable gases, volatile (steam oil) and char (carbon). Char yield is defined as the percentage by weight of a sample which remains as residue after pyrolysis. The amounts of char produced during TGA simulated as pyrolysis process at the temperatures of 300, 400, 500 and 600 °C are shown in Figure **14** with error bars of one standard deviation. Since all measurements are subject to some experimental uncertainties.

Figure **14** shows the SEM images of solid residue in the reactor after the pyrolysis of NMF powder. The micro graphical image in Figure **13** obtained from SEM of NMF material revealed the presence of large particles that appeared to be formed by several flaky particles that stacked together in the form of the material group of tubular agglomerates. The impurities were not supremely observed. The EDS analysis of NMF powder was conducted to ascertain the constitutions and changes in hydrocarbon content (ratio between C and H) due to the effect of thermal process, which are indicators of the hydrocarbon products and their qualities. In this study of the pyrolysis behavior and thermochemical reaction of the sample of NMF powder from waste PCB, four different heating rates comprising 12.5, 20, 30 and 40 °C/min were applied to the four temperatures 300, 403, 500 and 600 °C in order to investigate exothermic phenomenon of the thermal reactions as well as to determine the kinetic parameters of pyrolysis reaction. According to Figure **14** the NMF illustrated relatively similar trends of mass loss. However, higher heating rates during pyrolysis caused the shifts of the mass loss curves to higher temperatures. It can be seen that the de-volatilization stage (the second stage) was affected by the heating rates more than the dehydration stage and the solid decomposition stage (the first and third stages). The DTA/DTG curve of NMF powder at heating rates of 12.5, 20, 30 and 40 °C/min is shown in Figure **9**. The DTG curves of the NMF pyrolysis TGA under N_2 atmosphere the four set of maximum processing temperatures at 300, 403, 500, 600 respectively are presented here in Figure **15**.

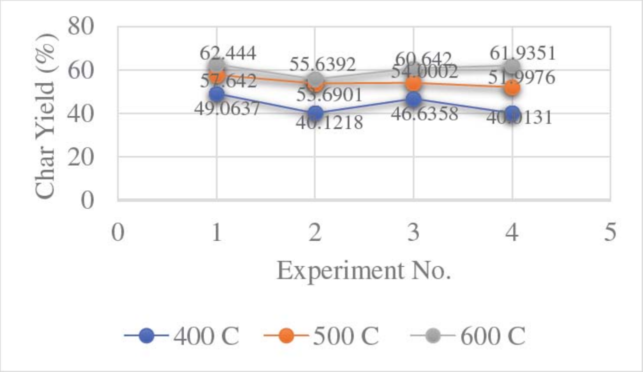
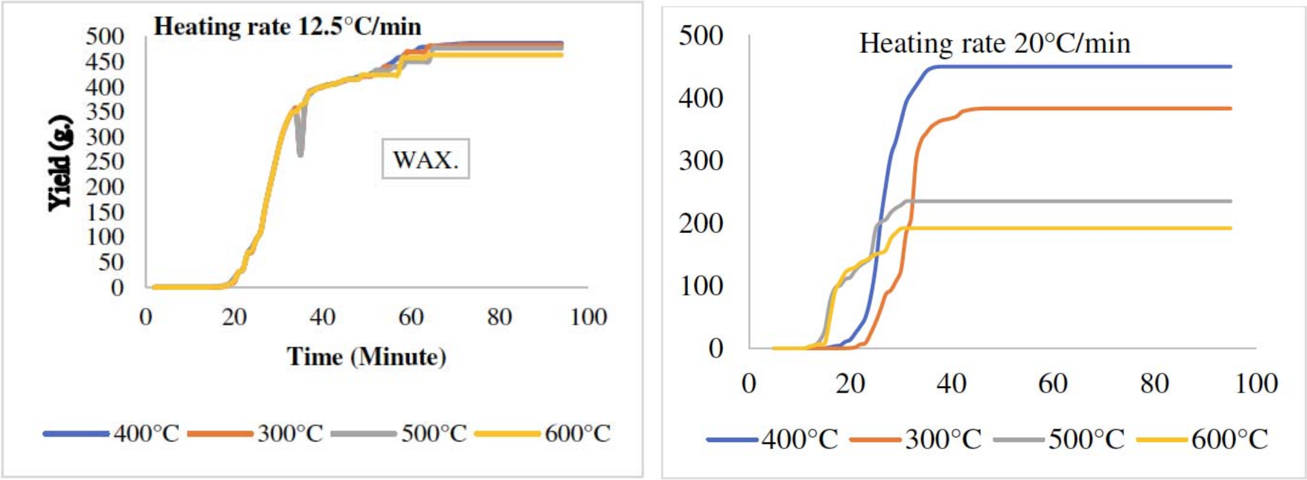


Figure 14: Char yield (Solid residiue) at 12.5 °C/ min.

The results from Figure **15b** revealed that the maximum reactivity temperature of NMF pyrolysis increased as the heating rate increased, ranging in the region of 350 to 405.7 °C. Based on the data derived from the DTG curves and TGA curve, the activation energy (E_a) and pre-exponential factor (A) of the thermochemical reactivity of the NMF sample during pyrolysis were determined using solid pyrolysis equation derived by Vachuska and Voboril. The average activation energy (E_{ave}) of the blends was also calculated from the mass fraction equation, Section 2.5 Kinetics model of NMF pyrolysis were described in thermal analysis details. Table **3** summarizes the thermo kinetic analysis of NMF from waste PCB.



a b

Figure 15: Wax product at this heating rate of 12.5.

Table 3: Thermo-Kinetic Analysis of the NMF during Pyrolysis Process

Sample	Fitting Equation	A(1/s)	Ea (kJ/mol)	E(average) (kJ/mol)
NMF from waste PCB	Y=21632X+21.13	$6.452x10^{10}$	174.6	174.6

According to Table **3**, under the set of same pyrolysis conditions, the activation energy (E_a) and pre-exponential factor (A) vary depending on each batch of NMF samples, processing time, reaction temperature and the heating rate. The activation energy was less than that in lower reaction temperature and heating rate, being 174.6 kJ/mol. It is noted that the activation energies of the NMF material, E_a, calculated from the DTG data with Vachuska and Voboril equation and the averaged value, E_{ave}, calculated from the mass fraction equation, were essentially equal. The plots of activation energy of NMF against reaction temperature and against their heating rates are presented with error bars equal to the standard error of the estimate in Figures **16** and 4.5. Uncertainty measures on slope and intercept of a least squares fit of activation energy of pyrolysis are summarized in Table **3**.

In the analysis of the kinetic parameters, the activation energy and pre-exponential factor during pyrolysis increased with the higher temperature and their increased heating rates. The plots of activation energy of NMF material against their processing temperatures and their heating rates also showed linear relationships (R^2 ~ 0.999). This also suggested that no significant degree of interaction between the temperatures and heating rates during pyrolysis. Thermal decomposition of pyrolysis of NMF from waste PCB appeared to take place independently as such pyrolysis behavior of the NMF can be predicted from that of the NMF samples at effective temperature and effective heating rate. The lack of synergy suggests that NMF can be processed with pyrolysis at targeted temperature as observed as well as the heating rate for use in pyrolysis energy conversion systems. The measurement of glass transition temperature, Tg, of the PCB scraps tested indicate that Tg is about 156 °C. Therefore, the temperature range was set above 200°C. and the selected temperature were 300 °C, 400 °C, 500 °C and 600 °C respectively. In order to check the effectiveness of temperature range for the NMF from waste PCB and to be decomposed, the results were examined at each targeted temperature respectively. Also, the effectiveness of the heating rate in relation to processing time were also examined in TGA and DTA before the actual process of pyrolysis experiment in this study. Through the tests, we determined that lower temperature for the reaction module could not achieve the goal very well, even in supercritical conditions. Figure 4.1 indicated the results. In part (a), NMF pyrolysis was producing less liquid when the temperature is above 200 °C at 300 °C and there is no significant effect when the temperature was below 200 °C; in part (b), The higher processing temperature causes the dark liquid. While in part (c) at 403 °C the liquid is light and achieved at maximum yield, NMF from PCB scraps were expanded to the

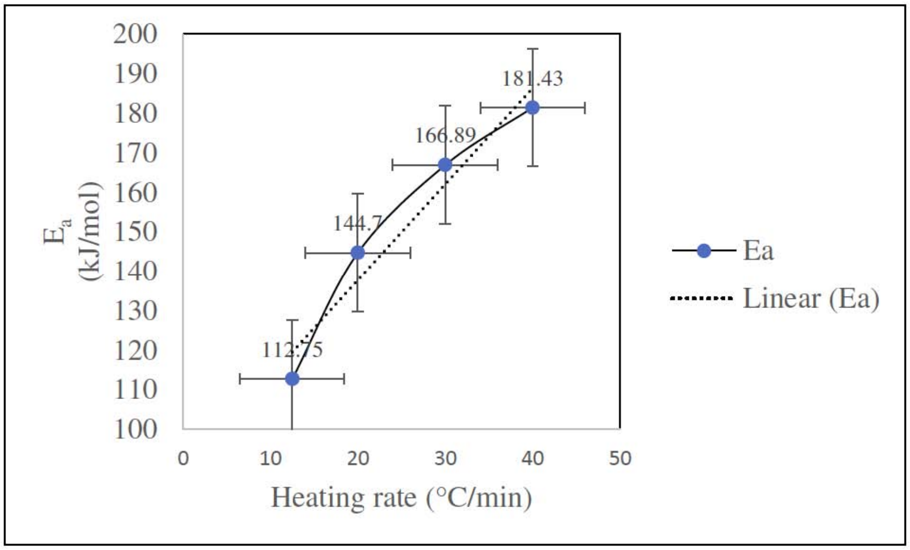


Figure 16: Activation Energy of NMF during pyrolysis against heating rates.

maximum level, and they can be easily decomposed at high temperature above 600 °C, according to the TGA and DTA results we can assume that the liquid will be darker than what we can produce from 600 °C. Therefore, we select the temperature at 403 °C for the initial study.

Figure 17: Liquid product from pyrolysis of NMF from scrap PCB.

CONCLUSIONS

Thermogravimetric analysis (TGA) was applied to investigate thermal decomposition during pyrolysis. Kinetic parameters during pyrolysis and combustion were determined through Vachuska and Voboril kinetic equation using the TGA results and pyrolysis of NMF results. Pyrolysis of the samples regardless of their type occurred in three stages comprising dehydration, de-volatilization and solid decomposition. The TGA results revealed that thermal decomposition profiles of both types of temperature ranges and heating rates (high (500 °C,600 °C)-low (300 °C,400 °C)) showed similarity, predominantly due to similar composition in particular the volatile content. However, temperature ranges and heating rates were found to have substantially different thermochemical behavior during pyrolysis and combustion in terms of mass loss, maximum yield, and appearance and end residue. Both types of temperature ranges and heating rates for the NMF samples had higher volatile components in higher temperature group and high heating rate than the group that process with lower temperature and lower heating rates; as a result, the stage of de-volatilisation played a larger part in the higher temperature ranges and heating rates than in the low temperature ranges and heating rates. During pyrolysis, trends of the mass loss and maximum reactivity temperature NMF were at 402 °C-406 °C, except slightly shifting to higher temperatures with lower heating rate at 20 °C/min. This implies that the low volatile content NMF had an effect on reducing the mass loss and increasing the maximum reactivity temperature. Moreover, yield production of the gas and liquid during pyrolysis corresponded to the sum of the results for the 403 °C at 20 °C/min. Measured TG data of pyrolysis indicated a linear relationship between yield and temperature and heating rate. Thermo kinetic analysis of the individual samples in each temperature and heating rate with a set of standard condition was carried out using the results from TGA. Activation energy (E_a) and pre-exponential factor (A) of the thermochemical reactivity of the NMF from waste PCB powder relationship between operating temperature and the heating rate during pyrolysis process were determined using Vachuska and Voboril.

Pyrolysis has been examined as an effective alternative of waste disposal treatment to the landfilling and incineration for solid waste disposal. The pyrolysis technology allows energy, material utilization and resource recovery. This research addresses the state of art of Non-Metallic Fraction (NMF) of PCB with pyrolysis method after the copper separation process with the aim of reducing the emission and increase the product quality at optimal conditions. The research has investigated regarding its technology and the developments, products quality and the environmental impacts to create an argument against the current waste disposal treatments which are not a proper solution for NMF of PCB. It can be concluded that the innovative pyrolysis process is an effective waste recovery especially for NMF in terms of maximizing material utilization. Based on this research information, the prospects of applying innovative pyrolysis technology to effectively dispose of NMF are evaluated and suggested that it is a proper waste disposal treatment. With the rapid development of technology in electronic industry and the frequent updating of all electrical and electronic equipment (EEE), the electronic waste (e-waste) has also rapidly increased in a short period of time. The current waste disposal treatments available for waste material are not coping with all the upcoming material in variety type of EEE product. As a typical e-waste, printed circuit board scraps (PCBs) are the basic component often found in the waste stream. PCBs are particularly problematic to recycle because of the complex mixed of materials. Non-metallic fractions (NMF) of PCBs are often found as leftover material after copper separation process. The main disadvantages of the NMF material are being challenged due to their diversity and complex mixed of materials such as brominated epoxy resin (thermoset polymer), glass reinforced fiber and ceramics. Therefore, it increases the difficulty of recycling or recovering it. The occurrence of dispose of waste NMF from PCBs recycling facilities by environmentally unfriendly, hazardous and primitive technologies has increased over the past years due to the limitation in a suitable technology for NMF. Massive amounts of dumping of NMF waste took place along with others primitive disposal treatment that did not aim to close the loop of the product. It is increasing and generating a secondary pollution for the planet. Open burning of waste NMF is also common for waste disposal. Dioxin and furans can be generated due to the combustion of BFR in the NMF. Pyrolysis as a new waste disposal method, a technology that not only can recover all valuable material but also deals with the organic matters in NMF. The differences of thermal property of each material consisted in NMF of PCB can totally separate each material in NMF. The thermoset polymer is a valuable resource and can be used to produce fuel. With the innovative design pyrolysis process, especially the NMF pyrolysis can ensure the lower emission and pollution when comparing to the current waste disposal method.

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