

Pyrolysis Pre-treatment of PCBs: A Sustainable Solution to Convert Encapsulation into Marketable Product and Separation of Metallic Concentrate

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Abstract : Printed circuit boards (PCBs) are the essentially required component of all the electronic goods, containing variety of metals. PCBs are made up of several layers of epoxy resins, thin metallic sheets, etc. The metallic sheet encapsulated with resin hinders the hydrometallurgical metal dissolution process. The mechanical pre-treatment process is not feasible due to high energy consumption and non-availability of a compatible machine. Therefore, pyrolysis studies were conducted for the removal of capsulation of resin on metals presents in PCBs. Various experimental parameters were studied to optimize the pyrolysis process. The gas generated during the pyrolysis was condensed to get Low Density Oil (LDO). And the metal depleted poly-cracked carbon was converted to activated carbon and the metallic fractions processed for metal recovery using hydrometallurgy. The process has potential for commercialization after feasibility studies.

Keywords: PCBs, Recycling, Pre-treatment, Pyrolysis

1. INTRODUCTION :

In the modern era of advanced science and technology, electrical and electronic equipments (EEEs) such as household appliances, IT equipments, telecom and medical devices, etc. have become basic needs of our day to day life. And these needs of day to day life constrained the electrical and electronic industries for rapid technological improvement in the sophisticated electronic goods and their launch in the market as well as continuous replacement of the older ones. This has reduced the average life time of electronic goods, and lead in generation of large amount of electrical and electronic equipments (WEEEs) as waste [1,2]. Yearly global generation of WEEEs is 20-50 million tons per year which is multiple of three times quicker than other wastes [3]. All these EEEs possess an indispensable component called PCBs. However, improper recycling or disposal of these PCBs has significant adverse impact on the environment [4]. But the PCBs around 1-3% are the significant part of WEEEs [5], which contains variety of metals and materials viz. copper (Cu), nickel (Ni), aluminum (Al), iron (Fe), tin (Sn), lead (Pb), gold (Au), silver (Ag), palladium (Pd), platinum (Pt), glass fiber, epoxy resin, etc. [2] of economic importance.

The metallic world, in this era of metals and materials crises, where the high grade ores are continuously depleting, has concern about the significant need of WPCBs recycling as an alternative solution to fulfill the gap between demand and supply of metals [5]. WEEEs recycling in proper manner on zero waste concepts will

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not only decrease the environmental pollution but also conserve the natural resources. In order to enrich the metals value and removal of epoxy encapsulation from metals which hinders the hydrometallurgical leaching/dissolution, pre-treatment is essentially required.

In this connection various processes such as smelting [6], physical separation [7, 8] followed by crushing and grinding [2], stamp milling [9], shredding, hammer milling [10, 11], pyrolysis [12-15] have been reported or in practice for the pre-treatment of WPCBs, prior to hydrometallurgical metal extraction leaching/dissolution processes. About 90% and 65% of total metal recovery from PCBs of VC and 65% from PCBs of DVD by froth flotation and pneumatic separation [16], whereas about 83% Fe and Ni were separated as magnetic fraction, 92% Cu at guess of 700 which was decreased from 76 to 56% at guess of 3000 with little increase in grade of copper from 71.6 to 75.4% [17] was achieved using such physical separation processes. The common drawbacks of physical, mechanical and heat treatment/smelting processes are generation of gaseous pollutants, loss of yield during smelting [8, 18] production of harmful gases containing excess of dust which deteriorates the environment quality during mechanical processes such as crushing, grinding [2], expensive disposal of hazardous residue, and even after disposal flashback and leaching risk of landfills [19, 20] makes these processes unfavorable. Thus, in order to avoid such drawbacks, the pyrolysis process is prominent and effective in terms of environment, quantity and volume reduction, zero waste generation as well as complete conversion of whole WPCBs in to commercial products. Zhou et al., 2010 reported average recovery percentage 4.30, 27.73, 67.97 of gas, oil and residue, respectively from cellulose paper phenolic resin based WPCBs and 6.35, 21.45, 72.20, respectively from glass fiber epoxy resin based WPCBs [2].

As per the literature review, maximum pyrolysis investigations were performed in nitrogen or air atmosphere. But it is not favorable from environmental and product quality point of view, due to the reaction of organic materials with nitrogen and their loss in air environment. Hence, present investigation is focused on the development of improved pyrolysis process to make pyrolysis environmental, more sustainable, all products and byproducts commercial as well as to get more clean organic vapors by conducting the investigations in presence of argon and other environment. Present investigation will be helpful in large scale continuous run after feasibility studies.

2. EXPERIMENTAL

2.1. Material

Crushed PCBs of different sizes containing copper foil, epoxy resin and glass fibre as main material was used for the experimental purpose. Table 1 shows the particle size distribution of the sample used for experimental purpose.

Table 1. Size (BSS mesh) fractions of particles used in pyrolysis experiments

Size	+14	-14+32	-32+48	-48+65	-65+100	-100+150	-150+200	-200+250	-250+325	-325
Mass %	87.2	4.02	3.37	1.16	1.55	0.72	0.61	0.298	0.34	0.24

2.2. Methodology

Central processing unit (CPU) from WPCBs of personal computers was selected for the pyrolysis investigations. First, the WPCBs were segregated from CPU by dismantling and the parts of PCBs such as batteries, capacitors and others electronic devices were removed by thermal treatment and then clean PCBs free from component were obtained. Then it was cut into small fractions. The pot-type furnace possessing 14 cm depth, 9.5 cm of diameter, controller at the bottom to control temperature inside the pit at desire value and k-type thermocouple attached with display to measure the temperature was used for conducting the investigations. Glass reactors of different size were used to hold WPCBs material during pyrolysis operations. A condenser was attached with lid and vacuum pump. System pressure was measured with the help of bourdon gauge connected to the pump.

About 50 g of WPCBs sample was filled in the closed top glass reactor. The vacuum pump and furnace were switched on, and desired temperature was set to the controller. After the end of desired time period stopped and switched off and the reactor was taken back from the furnace to cool at room temperature. The reactor along with sample was weighed to record the mass before and after the investigation by which change in mass could be calculated. The oil collected through condenser was also weighed.

To conduct the pyrolysis investigations in argon atmosphere another glass reactor of 5.5 cm diameter and 6 cm of height was made. Argon was passed through a tower possessing sulphuric acid and bubbles obtained in tower during argon supply which served for measuring the rate of argon flow. The vapour obtained from the reactor was passed by a conduit attached with condenser which was open to the atmosphere from another side. However, in some experiments ice was used to condense the oil in condenser. For which condenser was immersed in a beaker filled with pack of ice.

Thermo gravimetric analysis (TGA) of WPCBs was conducted using TGA instrument Linseis STA PT 1600, Germany. In which WPCBs samples cut down in to suitable size using scutter-cutter was put in the crucible of instrument and heated on pre-determined heating rate of 1-10°C/minute. Heating was either in air or in argon stream. And in later investigations KOH solution was used in gas bubbler to record the gas flow rate as number of bubbles released/minute.

3. RESULTS AND DISCUSSION

3.1. Laboratory Scale Pyrolysis investigation

Pyrolysis investigations were conducted using 50 g of sample for each investigation in pot type furnace. The results obtained in these investigations would be more useful for large scale pyrolysis operations during WPCBs recycling in comparison of TGA. The liquid fraction obtained during pyrolysis was collected and characterized.

The mass loss in the sample was 12-16% when pyrolysis was carried out under vacuum at 300-400 °C. About 60% of the mass loss during pyrolysis could be recovered as oil in the condenser. About 10% of the total mass of the WPCB could be recovered as oil during pyrolysis. About 7-8% of the mass of the WPCBs were lost in that gas phase during pyrolysis. It should be noted that since 50% of the mass of the WPCBs is constituted by

ceramic materials, the actual recovery of oil was about 20% of the mass of the resin. The mass loss in the sample was about 14-17% when pyrolysis was carried out in argon stream at 300 °C, and 10.3% of the mass of the WPCBs could be recovered as oil under these conditions. More experiments have to be carried out to optimize the flow rate of argon for maximum recovery of oil during pyrolysis.

As discussed earlier, the base of the WPCBs is made up of epoxy resin and when this epoxy resin is subjected to pyrolysis, a sharp drop in the mass of the sample was observed at 400 °C, in the TGA.

3.2. Thermogravimetry Analysis (TGA)

Table 2 summarizes the results of TGA experiments. In all the experimental runs in TGA, the TGA profile consists of three segments: (a) an initial period, where the mass loss was very low, (b) a region where the mass of the sample dropped rapidly at a characteristic temperature and (c) another region where the change in mass with temperature was gradual. In some cases, there was an initial increase in the mass of the sample followed by a decrease in mass, with increasing pyrolysis time (and, therefore temperature). The initial increase in mass was due to the oxidation of metal on the WPCB. Since only some of the samples contained significant quantities of metal, the initial increase in mass on pyrolysis is exhibited only in these cases. The decrease in mass of the sample during pyrolysis was due to the release of volatile matter produced during the pyrolysis process.

Table 2. Pyrolysis in TGA

S.No.	Mass (mg)	Heating rate (°C/min)	Atmosphere	Flow rate (bubbles/min)	Mass loss (mg)	Mass loss (%)	Temperature (°C)
1	37.37	10	Air	ND	12.74	34.10	500
2	34.27	10	Air	ND	9.48	27.67	400
3	46.03	5	Air	ND	11.05	34.01	500
4	37.35	1	Air	ND	19.11	51.17	450
5	39.04	10	Argon	65	9.75	24.97	400
6	38.61	10	Argon	24-28	11.27	29.19	500
7	35.43	10	Argon	45-48	15.31	43.21	500
8	38.14	10	Argon	68	8.58	22.49	500
9	36.74	5	Argon	26	9.04	24.60	500
10	36.25	1	Argon	25-27	10.25	28.27	500

When the sample is heated in air, the volatile matter produced during heating would react with the oxygen in air. The temperature, at which sharp drop in the mass of the sample was done, denoted as the “pyrolysis-start” temperature T_s . Whenever a process is controlled by the kinetics of heat transfer in the system, the rate of the process decreases with increase in the heating rate. It can be inferred that on increasing the heating rate, the rate of reaction decreases and, therefore T_s , shifts to higher temperature and becomes constant at higher heating rates.

The total mass loss in the system decreases with increase in heating rate when the sample is heated in air. This decreases from about 50% mass loss at a heating rate of 1^oC/ minute to about 25% at a heating rate of 5^oC/ minute.

The temperature of the start of pyrolysis process, T_s , decreases with increase in flow rate of argon when pyrolysis is carried out in a flowing stream of argon, the heating rate remaining constant. This temperature increases subsequently on further increase in the flow rate of argon. The pyrolysis process can be represented by:



This shows that solid S_1 decomposes to produce a residual solid S_2 and a vapour species. When argon passes over the system, it sweeps the vapour away from the reaction site. This enhances the rate of forward reaction. At a constant temperature, the equilibrium constant for the reaction is given by

$$K_T = P_v \cdot a_{s_2} / a_{s_1} \quad (2)$$

Here, P_v is the partial pressure of the vapour phase and a_{s_1} and a_{s_2} represent the thermodynamic activities of the product solid phase and reactant solid phase, respectively. These activities are not influenced by the passage of argon and can be taken to be equal to unity. On the other hand, P_v decreases when the vapour phase is swept away by the flowing stream of argon. Therefore, to maintain P_v constant, more of the vapour is produced. This leads to a decrease in T_s , when the flow rate of argon is increased.

However, when the flow rate of argon is increased further, this disturbs the heat transfer. With increasing flow rate of argon, the actual temperature of the sample decreases and is lower than the measured temperature. Therefore, this leads to an apparent increase in T_s , on increasing the flow rate of argon.

At the lowest flow rate of argon, the 'pyrolysis-start' temperature is less than the recorded heating in air (259^oC and 270^oC, respectively), at the same heating rate. The difference between the two temperature increases at the optimum flow rate of argon (256^oC). Whereas, a total mass loss of 42% was recorded at the optimum flow rate of argon, this was only 30%, at the same heating rate in air.

From the discussion above, it can be concluded that pyrolysis in a flowing stream of argon would reduce energy consumption due to a decrease in the pyrolysis temperature and also enhance the recovery of valuable matter. There is an optimum flow rate of argon at which these benefits are maximum.

The "pyrolysis start" temperature T_s is not significantly influenced by the heating rate at the lowest flow rate of argon used in the TGA runs. The same is true for the total mass loss of the sample.

The influence of the holding temperature on the degree of pyrolysis is examined. A hypothetical case was considered where the maximum holding temperature was changed from 300^oC to 400^oC. The change in the mass of the sample in this temperature interval is examined as a function of heating rate. In both cases, i.e. heating in argon and in air, the fraction of mass loss in the considered temperature interval decreased with increasing heating rate. This must be factored in the design of the pyrolysis process for commercial

exploitation. Only 6% of the total mass loss occurs in this temperature interval, at the optimum flow rate of argon.

3.3. Electron Probe Micro Analysis of WPCBs

Two types of particles could be identified under Scanning Electron Microscope (SEM) combined with Electron Probe Micro Analysis (EPMA). One of them was rich in carbon. This exhibited a well-woven structure of carbon-rich fibres. The same type of particles were identified under SEM, irrespective of the environment during pyrolysis and the temperature of pyrolysis Figure 1. gives the micro-structure of the carbon-rich particle and its chemical analysis (EPMA).

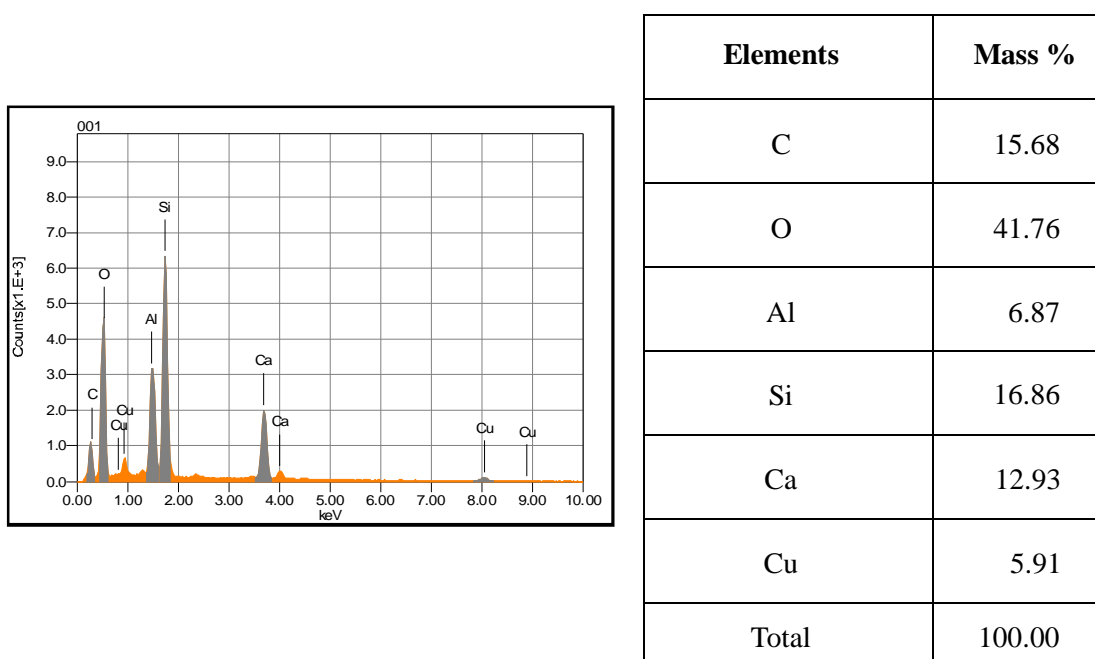


Figure 1. Chemical Analysis of carbon-rich particle

3.4. Characterization of Oil

Characterisation studies were carried out using FT-IR to confirm the application of oil collected during pyrolysis and it is produced in Figure 2. It shows the presence of O-H, C-C, C-H and C-O bonds. And almost same is also reported by Zhou et. al., [2] states that alcohols/ phenols between $3500 - 3300 \text{ cm}^{-1}$ associated with O-H stretches, methyl/methylene between $3000 - 2800 \text{ cm}^{-1}$, C=C stretches between $1650 - 1400 \text{ cm}^{-1}$, between the range of $900 - 650 \text{ cm}^{-1}$ deformation vibration in benzene ring with the association of C-H and during the analysis of phenols, bands are always found in the range of $1390 - 1220 \text{ cm}^{-1}$. The result confirms that the oils and gases obtained during pyrolysis can fulfill fuel requirements of pyrolysis or in other purposes as per requirements due to high calorific value present.

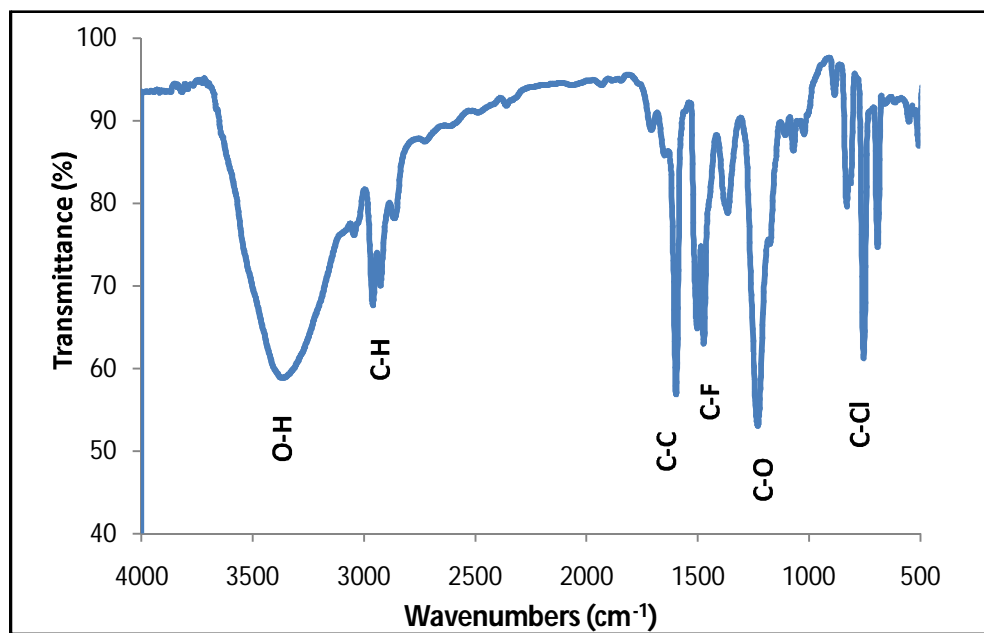


Figure 2. FTIR of collected oil of Pyrolysis investigation

4. CONCLUSIONS

Based on the above studies, the following conclusions were drawn:

- ❖ After the thermo-gravimetric study for the pyrolysis of WPCBs under argon and air atmosphere, it was found that the process consisted of three zones: (a) at low temperatures, up to about 250 °C, there was a gradual decrease in the mass of the sample, (b) at a characteristic temperature, around 250 °C, there was a drastic change in the mass, (c) at higher temperatures the mass change was not rapid but faster than that observed at temperatures less than 250 °C.
- ❖ The temperature at which the rapid mass loss occurred is termed as the “pyrolysis-start temperature”, T_s . T_s decreased significantly with decreasing heating rate in air. Heating rate did not significantly alter this temperature in the case of pyrolysis under argon.
- ❖ The total mass loss was higher in argon compared to heating in air. The flow rate of argon influenced T_s , significantly. There was an optimum flow rate, at which T_s was the lowest.
- ❖ The total mass loss was the highest at this optimum flow rate.
- ❖ The activation energy for volatilisation of the WPCBs decreased with decreasing heating rate.
- ❖ After the laboratory experiment under argon atmosphere, about 10% of the mass of the WPCBs could be recovered as oil. The oil was characterized using FT-IR and found to contain radicals of O-H, C-C, C-H and C-O.
- ❖ Pyrolysis did not occur at 250 °C but it was practically complete at 300 °C. The degree of pyrolysis was not significantly enhanced on increasing the pyrolysis temperature from 300 °C to 400 °C.
- ❖ Recovery of oil and degree of pyrolysis were higher in argon stream compared to pyrolysis under vacuum.

- ❖ Computation of the energy requirement of the process showed that there is a huge potential for converting this process into a viable technology for the recovery of metals and oil rich in phenol and its derivatives, on industrial scale.

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REFERENCES

- [1] Li J, Lu H, Xu Z, Zhou Y, 2008, Critical rotation speed model of the rotation roll electrode in corona electrostatic separation for recycling waste printed circuit board, *Journal of Hazardous Materials*, 154, pp. 331-336.
- [2] Zhou Y, Wu W, Qiu K, 2010, Recovery of materials from waste printed circuit boards by vacuum pyrolysis and vacuum centrifugal separation, *Waste Management*, 30, pp. 2299-2304.
- [3] Hester RE and Harrison RM (Eds.), 2009, *Electronic Waste Management: Design, Analysis and application*, Royal Society of Chemistry Cambridge, UK, pp. 49-95.
- [4] Li J, Duan H, Yu K, Wang S, 2010, Interfacial and mechanical property analysis of waste printed circuit boards subject to thermal shock, *Journal of the Air and Waste Management Association*, 60, pp.229-236.
- [5] Moyo T, Chiirume BH, Petersen J, 2020, Assessing alternative pre-treatment methods to promote metal recovery in the leaching of printed circuit boards, *Resources, Conservation and Recycling*, 152, 104545.
- [6] Bernardes A, Bphliger I, Rodriguez D, Milbrandt H, Wuth W, 1997, Recycling of printed circuit boards by melting with oxidizing /reduction top blowing process, *Extraction processing Division (Proceeding of the 1997 TMS Annual Meeting)*, pp.363-376.
- [7] Zhao Y, Wen X, Shi H, Jiao H, TAO Y, 2006, Study on metals recovery from -0.074 mm printed circuit boards by enhanced gravity separation, *Chinese Journal of process Engineering*, pp. 201-204.
- [8] Zhou G, Luo Z, Zhai X, 2007, Experimental study on metal recycling from waste PCB, *Proceeding of the International Conference on Sustainable Solid Management*, 5-7 September 2007, Chennai, India. pp.155-162.
- [9] Yoo J-M, Jeong J, Yoo K, Lee J-c, Kim W, 2009, Enrichment of the metallic components from waste printed circuit boards by a mechanical separation process using a stamp mill, *Waste Management*, 29, pp. 1132-1137.
- [10] Kers J, Kulu P, Goljandin D, Kaasik M, Ventsel T, Vilsaar K, Mikli V, 2008, Recycling of electronic wastes by disintegrated mills and study of separation technique of different materials, *Materials Science (Medziagotyra)*, 14 (4), pp.296-300.
- [11] Eswaraiah C, Kavitha T, Vidyasagar S, Narayanan SS, 2008, Classification of metals and plastic from printed circuit boards (PCBs) using Air Classifier, *Chemical Engineering Processing*, 47, pp. 565-576.

- [12] Barontini F, Marsanich K, Petarca L, Cozzani V, 2005, Thermal degradation and decomposition products of electronic boards containing BFRs, *Industrial and Engineering Chemistry Research*, pp. 4186–4199.
- [13] Blazso M, Czegeny Z, Csoma C, 2002, Pyrolysis and debromination of flame retarded polymers of electronic scrap studied by analytical pyrolysis, *Journal of Analytical and Applied Pyrolysis*, 64, pp. 249–261.
- [14] Chiang H-L, Lin K-H, Lai M-H, Chen T-C, Ma S-Y, 2007, Pyrolysis characteristics of integrated circuit boards at various particle sizes and temperatures, *Journal of Hazardous Materials*, 149, pp. 151–159.
- [15] Chien Y-C, Wang H-P, Lin K-S, Huang Y-J, Yang YW, 2000, Fate of bromine in pyrolysis of printed circuit board wastes, *Chemosphere*, 40, pp. 383–387.
- [16] Kumar V, Lee J-c, Jeong J, Jha MK, Kim B-s, 2015, Recycling of printed circuit boards (PCBs) to generate enriched rare metal concentrate. *Journal of Industrial and Engineering Chemistry*, pp.805-813.
- [17] Yoo J-M, Jeong J, Yoo K, Lee J, Kim W, 2009, Enrichment of the metallic components from waste printed circuit boards by a mechanical separation process using a stamp mill, *Waste Management*, 29, pp. 1132-1137.
- [18] Cui J and Forssberg E, 2003, Mechanical recycling of waste electric and electronic equipment: a review, *Journal of Hazardous Materials*, B99, pp. 243-263.
- [19] Sohaili J, Muniyandi SK, Mohamad SS, 2012, A review on printed circuit boards waste recycling technologies and reuse of recovered nonmetallic materials, *International Journal of Scientific & Engineering Research*, 3(2), pp. 2229-5518.
- [20] Menad N, Bjorkman B, Allain EG, 1998, Combustion of plastics contained in electric and electronic scrap, *Resource Conservation and Recycling*, 24, pp. 65-85.