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INNOVATIVE TECHNOLOGIES FOR METALS RECOVERY AND PLASTIC VALORIZATION FROM ELECTRIC AND ELECTRONIC WASTE: AN INTEGRATED APPROACH

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Abstract

The increasing diffusion of Hi-tech complex products has raised the attention of scientific community towards their End of Life (EoL) treatment, both in terms of assuring an appropriate disposal, to avoid the dispersion of harmful substances, and at the aim of their exploitation as valuable sources of raw materials. Within this study an integrated approach for waste electrical and electronic equipment (WEEE) end of life treatment is proposed based on the integration of hydrometallurgy for metal recovery and pyrolysis for plastic fraction valorization, with a particular focus on EoL personal computers. An innovative hydrometallurgical process with limited environmental impact for the recycling of added value metals (Au, Ag, Cu, Sn, Pb) from printed circuit boards was developed and thermal technologies were investigated for the valorization of mixed plastic components. The results show metal recovery rates up to 99% and purity grade up to 99%. With reference to plastic valorization, the maximized production up to 95% w/w of both a liquid and gaseous hydrocarbon-based stream to be exploited as a fuel or as source of chemicals was achieved from WEEE plastic fractions.

Key words: hydrometallurgy, mixed plastic, personal computers, printed circuit boards, raw materials, recycling, recovery, thermal technologies, WEEE

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1. Introduction

Technological advancements of these last decades have led to high demand for strategic raw materials, essential for the manufacturing of electrical and electronic devices and to an increase of e-waste generation. Modern electronic equipment can contain more than 60 elements (Circular Economy & Resource Efficiency Experts, 2012) some of which contain harmful substances that require adequate treatment before disposal. On the other hand e-waste could represent a highly valuable source of raw material, while this opportunity is nowadays being lost, since just 15-20% of the world e-waste results to be recycled annually (US Environmental Protection Agency, 2012). This is particularly due to the metal centric approach which is mainly focusing on the recycling precious and high content added value metals, discarding all the rest. As stated also in the UNEP report (UNEP, 2013) a shift from metal centric towards a product centric approach is mandatory in order to achieve higher recycling rates of raw materials and lower production of discarded waste.

In the last years the issue of raw materials supply has emerged worldwide, and especially in

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Europe. Indeed raw materials availability for European industry system is becoming more problematic as shown by a recent report published by the European Commission (European Commission, 2014), identifying a periodically updated list of critical raw materials (20 CRM identified in 2014), most of which are contained in waste electrical and electronic equipment (WEEE).

To solve the issue, EC strategy is based on three main pillars: sustainable mining, recycling and substitution with alternative (not critical) materials. Furthermore, there is a need to address compliance with the EU WEEE Directive (European Commission, 2012), fixing a collection target of 4 kg/capita/year until December 31st 2015, with progressive increments since 2016, and with the EU Landfill Directive (Official Journal, 2003), forbidding the landfilling of waste with a Lower Heating Value (LHV) exceeding 13 MJ kg^{-1}, including in particular plastics which, as a petroleum derived product, show a LHV ranging between 35 and 45 MJ/kg (Green and Perry, 2007).

Within this frame, an integrated approach for the recycling of added value metals and plastic from WEEE is presented, as a part of a wide project named 'Ecoinnovation for Sicily', funded by Italian Government (2011-2015). In particular, the work is focused on the exploitation of WEEE as special source of raw materials. The main objective of this study was to develop and test eco-innovative integrated technology solutions for raw materials recycling and plastic valorization from WEEE, with a special focus on personal computers (PC) external cases and printed circuit boards (PCBs).

Many authors studied recovery of valuable materials from WEEE (Waste Electrical and Electronic Equipment) (Kumar et al., 2014). The novelty of this study consists in the definition of integrated solutions allowing the maximization of materials recovery from end of life complex products and the minimization of discarded waste.

The complexity of WEEE matrices requires the application of an all-round strategy involving the integration of different technologies (De Marco et al., 2008; Ficeriová et al., 2005; Heerman et al., 2001, Hidalgo et al., 2014). With regard to added value metals recycling, an eco-innovative technology was developed and tested, based on hydrometallurgy. Hydrometallurgical techniques were chosen as an alternative to the pyrometallurgy (heat treatment) since they present a series of advantages. Hydrometallurgy, being operative at room temperature, compared to pyrometallurgy has lower requirements in terms of energy consumption and atmospheric emissions; in addition, being based on a sequel of chemical and physical-chemical steps it allows the recovery of low content metals, combined to high selectivity, modularity and flexibility of the operating plants.

With reference to WEEE mixed plastic components valorization, mechanical recycling is generally problematic both for the great heterogeneous composition and for the presence of hazardous substances. Currently mechanical treatments cannot be used on mixed plastics waste with a consistent content in inert and metal fraction, as it frequently happens in WEEE recycled mixed plastics unfortunately has poor mechanical properties and short lifetime, and, therefore it is only exploitable in lower grade applications (Riess et al., 2000). Although plastic reprocessing is technically feasible, ecological-impact studies in the Netherlands and Germany (Brandrup, 1996) have demonstrated that there is a limit of 15%–18% to the amount of thermoplastic waste that can be mechanically recycled with environmental convenience; thus the majority of remaining waste must be recycled by other techniques. For this reason in this study it was decided to focus on the recovery of valuable aliphatic and aromatic fragments (liquid fraction) and valuable gas from PCs mixed plastic components by application of pyrolytic processes.

Following a product-centric approach, an integrated process to recover added value metals and valorize plastic components has been developed: added value metals (i.e. Au, Ag, Cu) were recovered by hydrometallurgical techniques and plastic components were treated by pyrolysis to produce liquid and gaseous hydrocarbon-based streams to be exploited as a fuel or as possible source of chemicals, after an adequate further refining treatment.

2. Experimental

2.1. WEEE materials

The PCs and PCBs were obtained from an authorized Italian WEEE collector after manual dismantling/disassembly of end of life (EoL) household computers.

PCBs wastes are characterized by significant heterogeneity and high complexity with a relatively low metal content: metals are present as a coating of various thickness, and as component of solders, capacitors, resistors etc. The PCBs were checked to manually remove connecting devices when present before undergoing leaching processes. The plastic fraction from PCBs was mixed with that from external housing of PCs.

2.2. Recovery of added value metals from PCBs

All solutions for leaching experiments and metals content evaluation were prepared with analytical grade reagents and de-ionized water. The acids, standards and salts were purchased from Sigma Aldrich, metal ions were determined by Microwave Plasma Atomic Emission Spectrometery (4100 MP-AES, Agilent Technologies); powder composition was determined by X-ray fluorescence spectrometer (Spectro X-LAB 2000 spectrometer). Calibration was carried out for each analysed metal by analyzing at least 5 concentration level standard solutions. Internal quality control checks were carried

out, including procedural blank evaluation. All experiments were performed at 25°C.

Leaching experiments and total content evaluation were performed on 10 whole PCBs samples (ranging from 1 to 3 kg).

The total metal content was evaluated as sum of two successive leachates content (1st leaching on whole PCBs, 2nd leaching on triturated remaining PCBs) and solid residue content, after dissolution in aqua regia.

Comparative leaching experiments were carried out using different acidic media: HNO_3, H_2SO_4, HCl, $HNO_3 + H_2O_2$ with at least 20% w/w acid concentration. Kinetic studies were performed from 0.5 h up to 24 h.

The leached PCBs deriving from leaching treatment were grinded and subject to further leaching experiments with HNO_3, in order to recover the Cu contained inside the plastic/resin slices. A comparison among different operation conditions was carried out, in terms of acid concentration.

The recovery of Cu, Ag, Pb and Fe from leachates was performed using a fractioned precipitation process, varying pH and solubility conditions. The products (salt and/or hydroxides) were purified through a further dissolution and precipitation processes. Ag and Cu were recovered by chemical and/or electrochemical reduction (Donati et al., 2009). The precipitates were washed, dried and weighted, then dissolved again by acidic media to be analyzed.

2.3. Thermo-valorization of plastics from PCBs and small appliances

A pyrolysis process aimed at fuel and/or feedstock production from WEEE mixed plastic fractions was developed. The fixed bed pyrolysis system consisted of a quartz tube reactor, electrically heated, 450 mm in length and 14 mm of inner diameter. Batch runs employed 10-50 g of sample, under N_2 flow at the rate of 2 mL/min to ensure an inert atmosphere. Identification of the type of polymers was carried out using Fourier Transform Infrared Spectroscopy (FT-IR). The oil recovery was assured by a water-cool condenser located downstream the pyrolysis reactor. The gaseous product was sampled by proper gas bags whose content was qualitatively analysed by a Thermofisher Ultra Gas Chromatograph, utilizing a 30 m long and 0.5 mm of inner diameter column, based on synthetic spherical carbon molecular sieves. The char fraction was mechanically collected after each run; moreover, any tar residue stuck to the inner walls of the quartz tube was thermally removed. Both oil and char weight composition were analysed, in terms of %C, %H, %N, %S by an Elemental Vario Macro Cube Instrument. The gas yield was estimated as a difference between the input material and the sum of the oil, char and ash collected from each run. Chemical species in the oil fraction were identified by a FT-IR Thermofisher Nicolet spectroscope on-

line connected. The establishment of the pyrolysis operating conditions has required a preliminary kinetic study which allowed predicting the decomposition reaction time with temperature and conversion.

Thermal analysis experiments were performed on about 10 mg of sample (in a powder form) with a SETARAM 92-16.18 Thermogravimetric Analyser coupled with a Thermofisher Omnic FTIR spectrometer (TGA-FTIR) between 298 and 973 K using four heating rates (2, 5, 10 and 15 K min^{-1}), under an argon carrier gas of 30 mL min^{-1} flow rate. The instrument was calibrated by melting some standard metals in the temperature range of 430 K (Indium) and 1235 K (Silver) and heating rates between 2 and 15 K min^{-1}; the temperature uncertainty was 0.5 K. Because of the buoyancy effect, a preliminary "blank experiment" was carried out before each run.

3. Results and discussion

3.1 Hydrometallurgical process for the recovery of added value elements from PCBs

In Table 1 the average material content distribution in PCBs is shown: data has been evaluated out of three different samples (ranging from 0.5 to 3 Kg) and reported as percentage in weight with a standard deviation below 5%.

Table 1. Average PCBs materials composition

Materials	% w/w
Plastic	18.30
Au	0.02
Cu	12.90
Pb	1.54
Sn	4.30
Ag	0.03
Fe	0.96
Ni	0.53
Zn	0.09
Al	1.45
Mn	0.02
Cr	0.02
Solid residue (resin, glass fiber, etc.)	59.84

It was found that HNO_3 (at least 20%) is the best leaching agent, gold not being dissolved: two consecutive leaching steps were carried out using the selected leaching agent and the solid residue was leached with aqua regia in order to verify mass balances.

In Table 2, as an example, the results using liquid/solid (L/S) ratio equal to 3:1, HNO_3 20% in 24 h are reported. During the treatment tin precipitates as oxide/acid metastannic. This precipitate was separated, then gravimetric and XRF analyses were performed, thus confirming this hypothesis. Applying this leaching conditions, both Au and $SnO_2/Sn(H_2O)_n$ can be recovered from the residue by a physical-mechanical process with a yield of 99%.

Finally the remaining depopulated PCBs, were shredded and leached by nitric acid to recover the remaining 48% of Cu present in the inner layers, to reach an overall yield of 98%, thus demonstrating the process effectiveness.

Table 2. PCBs leaching efficiency of two sequential steps (HNO_3 20%, L/S = 3:1, 24 h). Standard deviation associated to all data is below 5%

Metal	1st leaching on whole PCBs (%)	2nd leaching on triturated remaining PCBs (%)	Leaching solid residue (%)
Cu	45	7	48
Pb	91	3	6
Sn	31	5	64
Ag	99	1	0
Fe	18	37	45
Ni	82	6	12

In Fig. 1 the results of a leaching test performed using HNO_3 20%, L/S ratio 3:1, are reported as function of the time. As confirmed by kinetic curves, Au is not solubilized under this leaching conditions and Sn content decreas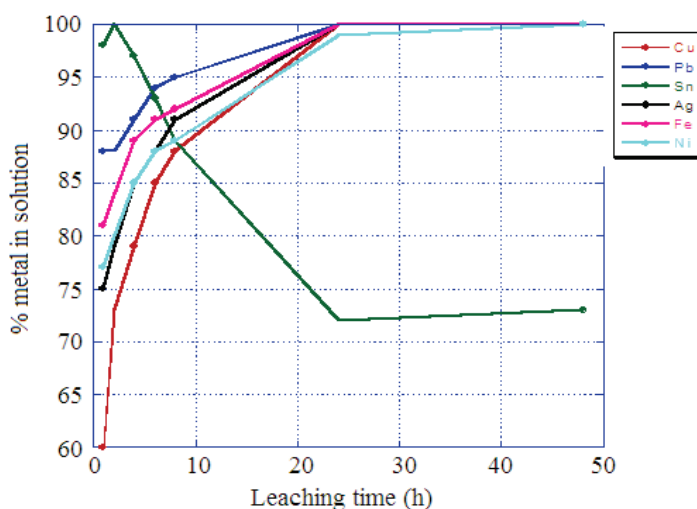es over time, due to precipitate formation $SnO_2/Sn(H_2O)_n$. As shown in Fig. 1, 90% of leached metals can be already recovered after 6 hours leaching.

The leachate coming from the first leaching step contains Ag, Pb, Fe and Cu which can be separated through a fractioned precipitation process. After their recovery, Ag and Cu are treated to obtain the elements as metals via electrowinning and/or chemical reductive processes.

Finally the leached boards resulting completely cleaned from metals on the surface, but still containing significant amounts of Cu inside, were triturated and subjected to new leaching treatment to recover remaining Cu.

As a results of this hydrometallurgical process, a metal recovery up to 99% as yield and purity grade was achieved. Furthermore this process allows treating the whole PCBs, avoiding any preliminary trituration step. The developed hydrometallurgical process is reported in Fig. 2.

3.2. The recovery of mixed plastics from small appliances

3.2.1. Plastic components FT-IR analysis

As it has been previously stated, WEEE plastic fractions enclose a large number of different polymers.

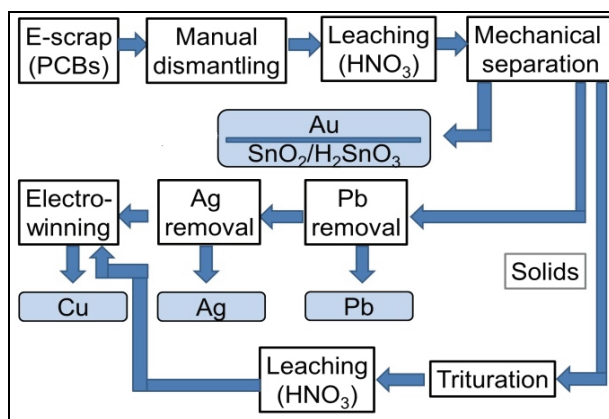**Fig. 1.** Leaching kinetic test (HNO_3 20%, L/S = 3:1)

Fig. 2. Hydrometallurgical process for the recycling of gold, silver, tin, copper and lead from waste printed circuit boards (Fontana et al., 2013)

Polymer identification in mixed plastic components from personal computers (external cases and PCBs) by FTIR analysis revealed the presence of high-impact-polystyrene (HIPS) and acrylonitrile-butadiene-styrene (ABS) as main components for external cases (Fig. 3 sample A); conversely, as far as the PCB is concerned, polybutadientherephtalate (PBT), polyamide 66 (Nylon 66) and polyphenylene sulfide (PPS) were mainly found (Fig. 3 sample B).

Taking into account the results of a field investigation carried out through WEEE sampling and IR analysis and interviews to managers and technicians of some waste treatment plants located in center Italy, a simplified ternary mixture of the three main polymeric constituents (ABS, HIPS and PBT) was defined to be used as representative of personal computers plastic composition.

A simulated PC sample was prepared for process development purposes by mixing defined triturated fractions of the three above mentioned polymeric components.

This sample was defined as "simulated PC" having the following composition: ABS, 64%, HIPS, 33%, PBT, 3%, being considered as representative of plastic composition in personal computers. The work proceeded by investigating a pyrolysis process applied to the sole thermoplastic fraction inside the PCBs, defined as "black slot", which makes up the inner electronic connectors. Finally, pyrolysis was applied to "simulated PC" samples.

3.2.2 Thermal and spectroscopic (TG–FTIR) characterization under pyrolytic conditions

TGA-FTIR results related to the thermal decomposition of black slot samples are showed in Fig. 4. The plot of the Gram-Schmidt curve along with the TG diagram allows describing the reaction trend.
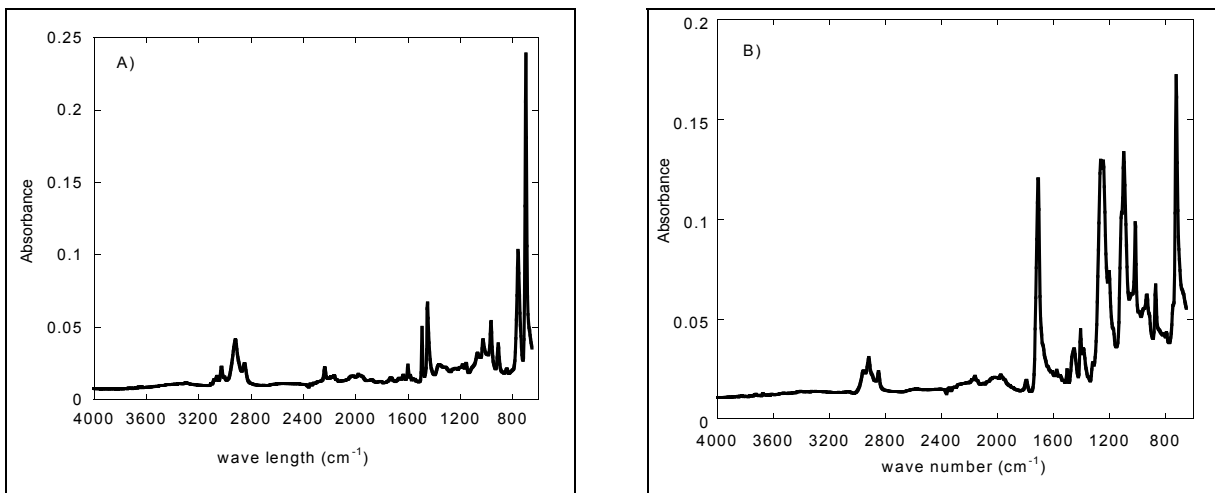

Fig. 3. FT-IR analysis of mixed plastic from PC external case (sample A) and PCBs (sample B)
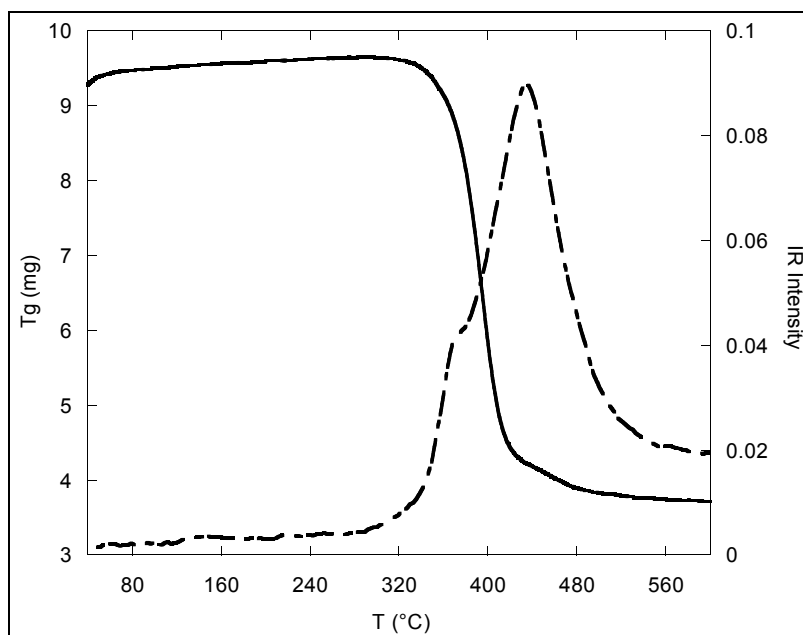

Fig. 4. TG/Gram-Schmidt plot for thermal decomposition of black slot

By examining the TG curve, a sharp mass decrease can be observed at 390°C, corresponding to the thermal degradation, as it is confirmed by the appearance of the Gram Schmidt plot which sums the IR signal intensities of the gaseous products; the TG/FT-IR diagram puts in evidence that thermal degradation occurs in a single step. Besides, the TG curve shows a remarkable residue amount around 22% w/w, which can be attributed to the production of conjugated aromatic rings and the high concentration of flame retardants used in the slots of PCBs (Cafiero et al., 2014). Fig. 5 shows the results of simulated PC sample which is mainly made up with styrene-based polymers. Thermal degradation occurs at 422°C leaving a low residue amount (less than 2% w/w).

IR spectrum of evolved gases from black slot sample pyrolysis is reported in Fig. 6. The bands around 2870 and 2981 cm^{-1} are characteristic of the presence of aromatic ring or substituted phenyl ring.

Absorption bands at about 900 cm^{-1} are related to pulsation vibrations and those at about 1080 cm^{-1} to asymmetric skeletal vibrations of the Tetrahydrofuran (THF) ring (stretch C-O ether). Asymmetrical stretching vibrations of the CH_2 groups at 2981 cm^{-1}, and CH stretching at 2870 cm^{-1} are observed and attributed to butadiene fragment-units. Peaks of carbon anhydride are also visible. These findings are confirmed by literature (Samperi et al., 2004), where PBT degradation is described as occurring in the following steps: the primary formation of cyclic oligomers, their further decomposition to generate unsaturated oligomers (butadiene) plus terephtalic anhydride containing oligomers; besides, THF results to be a secondary product of the polycondensation of PBT from 1,4 polybutanediol and terephthalic acid (Buyle et al., 1981). THF is a cyclic ether used as a solvent in the manufacture of paint, adhesives, impression ink, pharmaceutical products, etc.
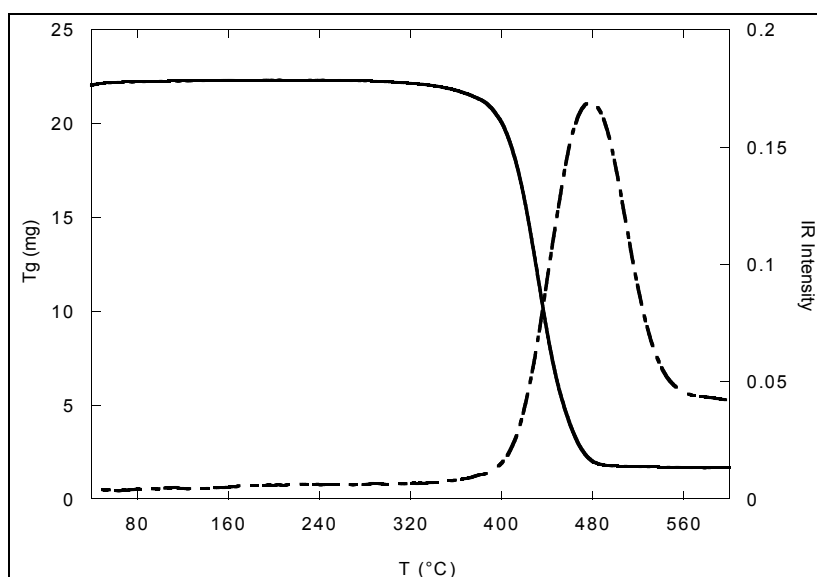

Fig. 5. TG/Gram-Schmidt plot for thermal decomposition of simulated PC
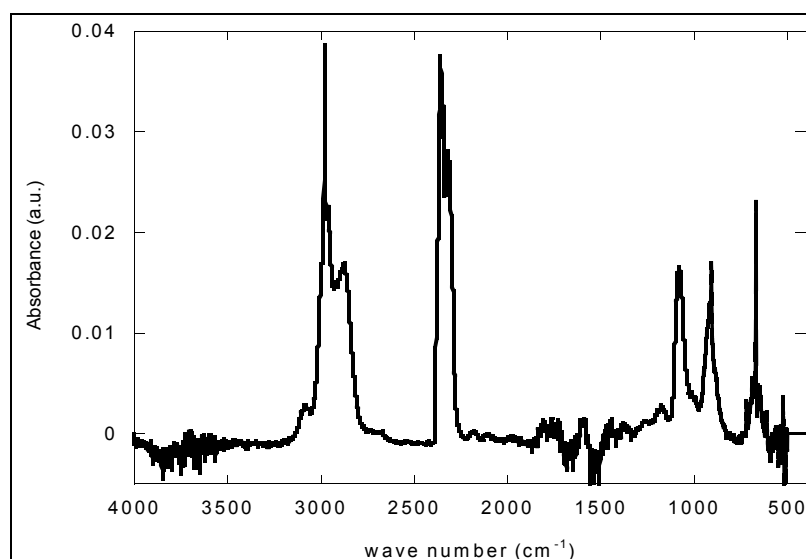

Fig. 6. FTIR spectrum of black slot sample pyrolysis evolved gases

THF most important industrial application is the production of politetramethylene-glycol (PTMEG), necessary in the elaboration of Spandex Fibres, polyurethane and polyester ether (Nexant, 2004). The other obtained product is the butadiene, the largest use of which is the production of synthetic elastomers including styrene-butadiene rubber (SBR) and polybutadiene rubber, employed in the manufacture of tires. Butadiene is also copolymerized into plastics, such as ABS. The FT-IR spectrum of the gas generated by the pyrolysis of simulated PC sample is represented in Fig. 7.

The substance which matches the highest numbers of peaks corresponds to styrene. In addition to the characteristic peaks of styrene, the alchilic peak at 2850 – 2920 cm_{-1} (v –CH_2) probably related to a butadiene fragment and the peak 2200 – 2300 cm^{-1} characteristic of CO_2, coming from the break of the esteric group of PBT can be observed. The fact that styrene appears to be the largest pyrolysis product is also confirmed by the trend of the Gram Schmidt curve reported beside the TG diagram in Fig. 5. This curve is the expression of the sum of intensities associated to the IR signals; its symmetric bell-shape is the sign that a prevalent compound is generated by the personal computer plastic decomposition, without any apparent interference from the evolution of other decomposition compounds. Styrene is a typical petroleum derived chemical with a LHV of 44 MJ/kg (Prosen at al., 1945) and a very important commodity, used mostly in polymer production for PS, ABS and styrene-acrylonitrile (SAN) resins, styrene-butadiene elastomers and latexes, and unsaturated polyester resins.

3.2.3. Kinetic studies

The next step to set up the pyrolysis process is the kinetic study. The determination of the reaction time needed to achieve a given pyrolysis conversion is described by Eq. (1) according to Vyazovkin et al. (2011).

$$t_\alpha = \frac{g(\alpha)}{A\,exp\left(\dfrac{-E}{RT}\right)} \tag{1}$$

where α is the mass conversion, E the activation energy (kJ/mol), A the pre-exponential factor (sec^{-1}), $g(\alpha)$ the reaction model, R the gas constant (8.3441 $Jmol^{-1}\,K^{-1}$) and T the temperature (K).

The adopted procedure has been carried out following the International Confederation for Thermal Analysis and Calorimetry (ICTAC) Kinetics Committee Recommendations (Vyazovkin et al., 2011). The E, A and $g(\alpha)$ of the most representative polymers in WEEE and of a real plastic sample have been estimated from non-isothermal kinetic results by TGA.

As far as the interpretation of kinetic results is concerned, Simon suggested that kinetic parameters represent apparent quantities without a mechanistic interpretation (Simon, 2004): the parameters cannot be used for any theoretical considerations, but they enable modeling the processes for other temperature regimes than those applied in the measurements. Conventional reaction times are taken in correspondence of the 1st derivative TG peak at the thermal degradation step, which occurs with a conversion of 0.6.

Times for black slot and simulated PC samples were 19 min and 3 min respectively. The difference is probably due to the presence of flame retardants in black slot which increases the thermal resistance of the polymer.

In the past, many authors examined the pyrolysis of WEEE plastic as a whole (De Marco et al., 2008; Donati et al., 2009; Guo et al., 2010), but they did not consider the process occurring in each component.
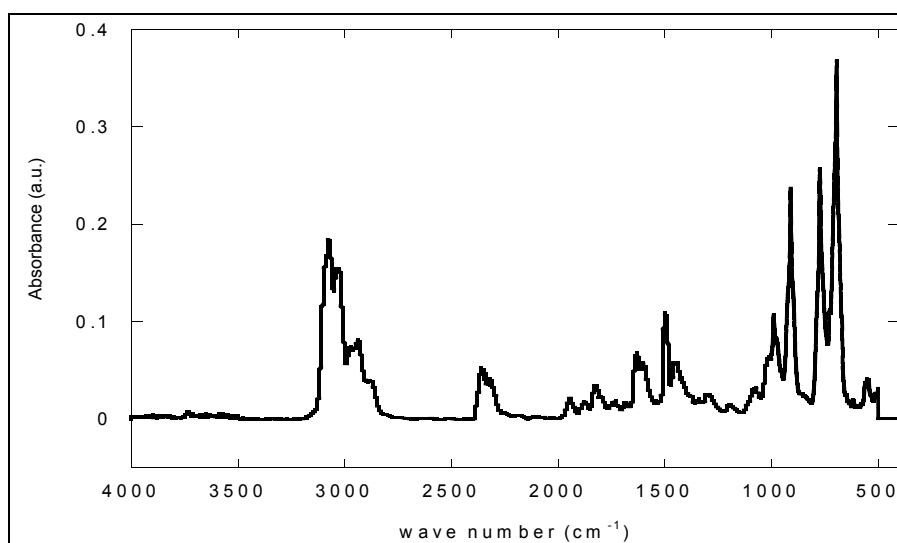

Fig. 7. FTIR spectrum of real WEEE sample pyrolysis evolved gases

On the other hand, a great deal of data on pyrolysis kinetics comes from studies applied to single polymers (Blom et al., 2006; Montaudo et al., 1993; Pramoda et al., 2003), but less to plastic components extracted from WEEE.

3.2.4. Pyrolysis with the bed reactor

Table 3 represents mass balance results for two pyrolysis runs performed on "simulated PC" samples at 400 and 600 °C; these temperatures were chosen on the basis of the results obtained in the previous thermal and spectroscopic (TG–FTIR) characterization experiments carried out under pyrolytic conditions. Besides, high heating value of the oil output, elemental composition of both the oil and the char are also reported.

It can be observed from Table 3 that pyrolysis brings about a strong plastics conversion (over 85% w/w production) into oil at the two temperatures, achieving a yield of 94.1 % w/w at 600 °C; elemental composition as well as the High Heating Value appear unchanged and resemble the one of a typical petrol derived product (Green and Perry, 2007). Gas yield appears not dependent from temperature and contains low chain hydrocarbons such as methane, ethane, ethylene. At higher temperature, char output diminishes from 10.8 % to 2.4 %, mostly at the expenses of oil; at 600 °C its ash content strongly increases, going close to 40 % w/w; at the same time the % C decreases from 70 % to 53 %.

These first tests allow concluding that pyrolysis appears to succeed to treat a heterogeneous plastics charge made up of tecnopolymers, converting it into an energy enriched hydrocarbons mixture from which specific fractions may be subsequently extracted for further valuable uses.

The process tested on the simulated PC sample, which includes both external cases and PCBs plastics, is reported in the sketch shown in Fig. 8, indicating best results obtained carrying out the pyrolysis at 600 °C. The process developed for personal computers plastic components can be extended to other small household appliances as well since they have similar plastic composition.

3.2.5. Economic and environmental considerations

This work has demonstrated the possibility to deliver an integrated approach allowing the recovery of more than 40% weight of PCBs. In Fig. 9 a pie chart evidences the materials that can be recovered by using the developed integrated technology solution presented, as well as future perspectives based on ongoing studies. Furthermore, the overall process includes gas emission treatment, thus matching atmosphere emission reduction and possibility to have product with potential market, and liquid re-use into the overall process is under evaluation. On the basis of these results we can conclude that this approach focuses environmental sustainability.

In order to assess the economic sustainability of the proposed process, we evaluated the average amount of materials recoverable from a ton of PCBs and taking into account the market value of the individual elements (values in September 2014), it is possible to assess a potential value of approximately 9700 euros per ton (Table 4).

Table 3. Mass balance for pyrolysis runs and products elemental composition (C, H, N)

T (°C)	Oil				Char				Gas
400	Mass balance (%)								
	85.3				10.8				3.9
	Elemental analysis (%)			HHV, MJkg	Elemental analysis (%)			Ash (%)	Detected substances: Methane, Ethane, Ethylene
	C	H	N		C	H	N		
	85.0	7.3	4.2	40.01	70.2	2.2	2.6	13.5	
600	Mass balance (%)								
	94.1				2.4				3.5
	Elemental analysis (%)			HHV, MJkg	Elemental analysis (%)			Ash (%)	Detected substances: Methane, Ethane, Ethylene
	C	H	N		C	H	N		
	87.8	7.5	3.4	40.40	52.6	1.4	1.7	38.0	

Table 4. Economic potential of developed integrated technology solution applied to PCBs

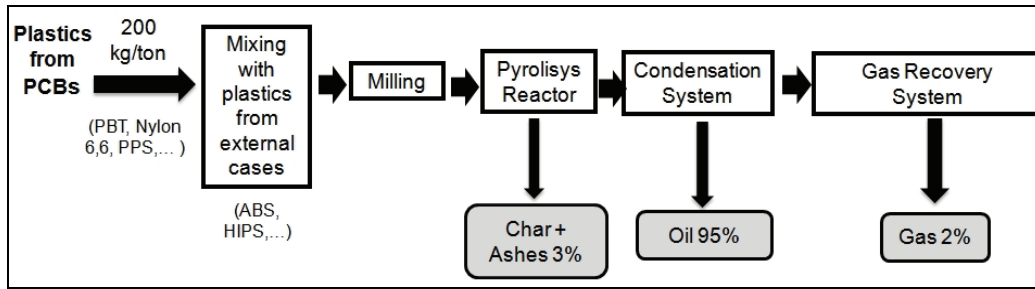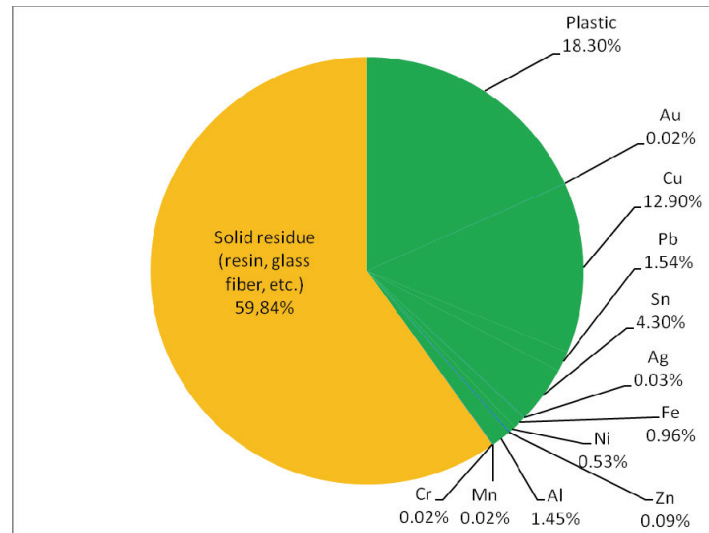| Material	Process recovery kg/ton	Material value (KITCO Market Data - London Metal Exchange – September 2014) €/kg	Estimated value €/ton
Ag	0.350	464	162
Au	0.240	33551	8052
Cu	129	5.30	684
Pb	15	1.62	24
Sn	43	16.53	711
plastic	200	0.37 €/kg oil for electrics	74 €/ton 100% oil for electrics
		0.58 €/kg fuel oil	116 €/ton 100% fuel oil
		Total: 9707	

Fig. 8. Plastic valorization process

Fig. 9. Recovered material distribution following proposed integrated recovery/valorization approach (green) and considering future perspectives (orange)

Considering the End-of-Life pc sold in Italy in 2014, we can assess a potential market of End of Life domestic PCBs at about 19 milion of euros. This evaluation takes into account only domestic PCs, containing PCBs that have on average higher content of added value metals if compared to other small household appliances and lower content if compared professional computers. Overall, it can be concluded that integrated approach, based on the holistic view of all elements contained in an End of Life complex product, supports economic feasibility of process recovery.

Unfortunately not all the hi-tech products on the market become recoverable waste, since about 75% of end-of-life Hi tech products are not currently collected in legal and traceable way (Ecodom, 2013). However, this work could support business plan building in this field and policy makers awareness about economic opportunity in waste management field.

4. Conclusions

The increasing diffusion of Hi-tech complex products has raised the attention of scientific community towards their End of Life treatment, both in terms of assuring an appropriate disposal, to avoid the dispersion of harmful substances, and with the aim of their exploitation as valuable sources of raw materials. PCBs were subjected to an innovative integrated process based on product centric approach to recover all valuable materials, and mixed plastic associated is also treated to maximize the production of valuable liquids and gas, reaching percentages at the highest equal to 95%.

The results obtained with the hydrometallurgical process show recovery rates for gold, tin, silver, lead and copper and purity grade up to 99%. The experiments carried out on personal computers plastic fraction (including PCBs and external cases) allow to conclude that pyrolysis appears to succeed to treat a heterogeneous plastics charge made up of engineered polymers, converting it into an enriched hydrocarbons mixture with yields around 95 % w/w, to be exploited as a fuel, or as possible source of chemicals after an adequate further refining treatment. The process developed for personal computers plastic components can be extended to other small household appliances that have similar plastic composition.

The integration of the developed technological solutions allows the recovery of over 40% weight of materials. The results of this work indicate that the proposed integrated approach, based on the holistic view of all elements contained in an End-of-Life complex product, focuses environmental sustainability and supports economic feasibility of process recovery.

References

Blom K., Yeh R., Wojnarowski R., Ling M., (2006), Detection of degradation of ABS materials via DSC, *Thermochimica Acta*, **442**, 64–66.

Brandrup J., (1996), *Recycling and Recovery of Plastics*, Hanser Publishers, Munich, Germany.

Buyle A., Padias H., Hall K., (1981), Oligomeric bishydroxybutyl terephthalates from terephthalic acid, *Journal of Polymer Science*, **19**, 1021–1032.

Cafiero L.M., Castoldi E., Tuffi R., Vecchio Ciprioti S., (2014), Identification and characterization of some plastics from small appliances and kinetic analysis of their thermally activated pyrolysis, *Polymer Degradation and Stability*, **109**, 307-318.

Circular Economy & Resource Efficiency Experts, (2012), Statistics on the Management of Used and End-of-Life Electronics, Electrical product material composition, US Environmental Protection Agency, On line at: http://www.epa.gov/osw/conserve/materials/ecycling/manage.htm.

De Marco I., Caballero B.M., Chomon M.J., Laresgoiti M.F., Torres A., Fernandez G., Arnaiz S., (2008), Pyrolysis of electrical and electronic wastes, *Journal Analytical Applied Pyrolysis*, **82**, 179–183.

Donati I., Travan A., Pelillo C., Scarpa T., Coslovi A., Bonifacio A., Sergo V., Paoletti S., (2009), Non-cytotoxic silver nanoparticle-polysaccharide nanocomposites with antimicrobial activity *Biomacromolecules*, **10**, 210–213.

Ecodom, (2013), Sustainability Report, Italian Consortium Recovery and Recycling Appliances, On line at: http://www.ecodom.it/Portals/0/Documenti/rapporto_sostenibilita/Ecodom_Rapporto_Sostenibilita_2013vint.pdf.

European Commission, (2012), Directive 2012/19/EU of the European Parliament and of the Council of 4 July 2012 on waste electrical and electronic equipment (WEEE), *Official Journal of the European Union*, **L 197**, 38-71.

European Commission, (2014), Report on critical raw materials for the EU, Report of the Ad hoc Working Group on defining critical raw materials, On line at: http://ec.europa.eu/enterprise/policies/raw-materials/files/docs/crm-report-on-critical-raw-materials_en.pdf.

Ficeriová J., Baláž and P., Gock E., (2005), A processing method of the goldsmiths and electronic Au-Ag containing Wastes, *Acta Montanistica Slovaca*, **1**, 307-310.

Fontana D., Pietrantonio M., Pucciarmati S., Guzzinati R., Torelli, C.G.N., Brunori C., De Carolis R., (2013), Hydrometallurgical process to recover materials from printed circuit boards), Patent Application, No. *RM2013A000549.*

Green D.W., Perry R.H., (2007), *Perry's Chemical Engineers' Handbook*, 8th Edition, McGraw-Hill, New York.

Guo Q., Yue X., Wuang M., Liu Y., (2010), Pyrolysis of scrap printed circuit board plastic particles in a fluidized bed, *Powder Technology*, **198**, 422–428.

Heerman C., Schwager F.J., Whiting K.J., (2001), Pyrolysis & Gasification of Waste, A Worldwide Technology and Business Review, Juniper Consultancy Services, Ltd., Uley, Gloucestershire, England.

Hidalgo D., Corona F., Martín-Marroquín J.M., Gómez M., Aguado A., Antolín G., (2014), Integrated and sustainable system for multi-waste valorization, *Environmental Engineering and Management Journal*, **13**, 2467-2475.

Kumar M., Lee J., Kim M., Jeong J., Yoo K., (2014), Leaching of metals from waste printed circuit boards (WPCBs) using sulfuric and nitric acids, *Environmental Engineering and Management Journal*, **13**, 2601-2607.

Montaudo G., Puglisi C., Samperi F., (1993), Primary thermal degradation mechanisms of PBT and PET, *Polymer Degradation Stability*, **42**, 13-28.

Nexant, (2004), Butanodiol/THF Production, Report Publisher in NEXANT, Researched on January 31, 2007

Official Journal, (2003), Implementation of Directive 1999/31/EC on the landfill of waste, (in Italian), Legislative Decree of 13 January 2003, No. 36, *Official Journal*, No. 59 of 12-3-2003, Suppl. No. 40, On line at: http://www.ambientediritto.it/Legislazione/Rifiuti/2003/dlgs%202003%20n.36.htm.

Pramoda K.P., Liua T., Liua Z., He C., Sue H., (2003), Thermal degradation behavior of polyamide 6/clay nanocomposites, *Polymer Degradation and Stability*, **81**, 47–56.

Prosen E., Rossini F., (1945), Heats of formation and combustion of 1,3 butadiene and styrene, Research RP1628 US National Bureau of Standards, 59-62, On line at: http://nvlpubs.nist.gov/nistpubs/jres/34/jresv34n1p59_A1b.pdf.

Riess M., Ernst T., Popp R., Mueller B., Thoma H., Vierle O., Wolf M., van Eldik R., (2000), Analysis of flame retarded polymers and recycling materials, *Chemosphere*, **40**, 937-947.

Samperi F., Puglisi C., Alicata R., Montaudo G., (2004), Thermal degradation of poly(butyleneterephthalate) at the processing temperature, *Polymer Degradation and Stability*, **83**, 11–17.

Simon P., (2004), Isoconversional Methods: fundamentals, meaning and application, *Journal of Thermal Analysis and Calorimetry*, **76**, 123–132.

UNEP, (2013), Metal Recycling - Opportunities, Limits, Infrastructures, On line at: http://www.unep.org/resourcepanel/Portals/24102/PDFs/Metal_Recycling_Full_Report.pdf.

Vyazovkin S., Burnham A.K., Criado J.M., Pérez-Maqueda L.A., Popescu C., Sbirrazzuoli N., (2011), ICTAC Kinetics Committee recommendations for performing kinetic computations on thermal analysis data, *Thermochim Acta*, **520**, 1-19.