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Standardization of solid recovered fuels through gravity separation and chemical based imaging techniques

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Abstract

The European politics is addressed, in their last years, more and more towards the abolition of landfills and oriented to verify the possibility to improve their recovery through actions of recycling, composting and energy production. Currently the European Directive 2008/98/EC, through the principle of End of Waste (EoW), is driving the utilization of new methods of waste processing in order to transform them it into a new "renewable" product. The post-consumer plastics resulting from packaging account for about 60% of total plastics waste (i.e. 23 million tons) produced in Europe. The high quality Solid Recovered Fuel (SRF) is a partial solution to the problem of waste and landfill management, becoming integral and essential in the closure of the waste cycle, representing one of virtuous processes for the treatment and recovery of waste. The application of recycling strategies, finalised to polymers recovery, can thus represent an important opportunity to reduce: i) not renewable raw materials utilization (i.e. oil), ii) carbon dioxide emissions and iii) the amount of plastic waste disposed-off. Aim of this work is to study the possibility offered by the integrated utilization of Chemical Imaging (CI) based techniques in order to obtain a good quality SRF characterized by a low content of PVC derived packaging to be used for the production of thermal energy. Packaging "final waste", in fact, is usually characterized by the presence of PolyVinyl Chloride (PVC). Therefore the association of a specific gravity separation architecture with the CI based sensing units, could strongly improve the quality of "final waste" fraction as resulting from classical recycling processes based on milling, classification and density separation. The presence of PVC, in fact, has a negative influence on the combustion and heat recovery of these products due to the production of dioxins and furans. The utilization of the proposed combined approach (i.e. gravity and CI based) could contribute to obtain a SRF characterized by a very low PVC content, thus allowing to certify SRF according to UNI EN 15359:2011 and to correctly utilise it for thermal energy production.

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Keywords - solid recovered fuels; post consumer plastics; plastics waste; PVC; sorting; hyperpsctral imaging.

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1. Introduction

Plastic is a versatile material. In the last 60 years, its production dramatically increased, therefore about 4% of oil and gas world production is used as raw material for plastics, and a further 3 to 4% is exhausted to provide energy for their manufacturing. Several plastic polymers are characterized by a high calorific value and their combustion could replace the use of fossil fuels. Energy recovery of Post-Consumer Plastics Packaging Waste (PC-WPP) by incineration represents an environmental risk, Chlorinated polymers, i.e. PVC particles, produce hydro chloric acid hazardous gas containing chlorine and dioxins. The PolyVinyl Chloride (PVC), considered one of the main sources of toxic effluents, figures among the thermoplastic materials most commonly used worldwide. Its global annual production is 35 million tons and the consumption in Western Europe amount to 5.3 million tonnes [1]. A typical problems for post-consumer wastes separation is the presence of polymers characterized by very close density values, i.e. PolyEthylene Terephthalate (PET) and PVC, with densities of 1.38 to 1.40 g/cm3, respectively [2]. With the introduction of the End of Waste (EoW), the European Community through Directive 2008/98/EC wants to promote the recovery and recycling of waste, in order to transform them into a new "renewable" product. The recycling practices are the only actions allowing to decrease toxic emissions and to reduce the environmental impacts for the natural habitats. Furthermore recovery activities finalised to plastics recycling process can be divided in two main categories: *i.* physical and chemical processing, for implementing a new product with the same properties or lower ones and *ii.* recovery, for energy production [3][4]. In Italy the annual production of municipal solid waste amounts to about 30 million tons and 130 million tons per year of hazardous and non-hazardous [5], the use of Solid Recovered Fuel (SRF) represents a partial solution to the problem of waste management and landfilling, becoming an integral and essential part in the closure of the waste cycle, representing one of the virtuous processes for the treatment and recovery of waste. The main material constituting the SRF is represented by: *i.* post-consumer plastic packaging (with higher fractions of containers in polyethylene terephthalate - PET, with a calorific value of about 46 kJ/g), *ii.* containers in Polyethylene - PE, polyolefins rigid packaging and *iii*. plastic boxes and packaging film. The post-consumer plastics resulting from packaging account for about 60% of total waste plastics (i.e. 23 million tons) produced in Europe. In Italy the technical criteria for the determination of EoW is indicated in the Legislative Decree, n°. 152/06 - Part IV (art. 184-ter of) abolishing definitely the name of *CDR* and *CDR - Q*. The regulation establishes a system of classification and properties for SRF, through specific parameters such as: Net Calorific Value (NCV), chlorine content and mercury content. According to the combination of these parameters up to 125 different types of SRF can be defined. Further parameters (i.e. heavy metal content) can be specifically requested by the purchaser. In this latter case “specifications” are introduced. The main focus of this work is the PVC polymers separation, selecting the polymer particles from post-consumer wastes using an experimental separation technique named Reflux Classifier (RC), which is normally used for mineral processing, in order to set up efficient and reliable recovery strategies. The association of a specific architecture of a gravity separation with the combined use of an innovative Chemical Imaging (CI) based sensing architecture, could allow the further processing of plastics packaging “final waste” fraction as resulting from classical recycling processes based on milling, classification and density separation. PVC presence, in fact, plays a negative role on combustion and heat recovery due to dioxins and furans production. The combined detection operative logic, based on gravity and proposed CI approach, therefore aimed to obtaining a SRF with a low content of PVC, allowing to certify materials (in according to UNI EN 15359:2011) to be correctly used for thermal energy production. The final aim of this work is thus to obtain a SRF characterized by a low PVC content thanks to the possibility to perform a full characterization by CI. A comparison of this innovative approach and the results commonly obtained by classical analyses referred to specific plastic waste stream characteristics, with reference to chlorine amount, was carried out and the results critically evaluated in order to set up control strategies finalised to a low environmental SRF impact production.

2. Materials and methods

1.1 The analysed samples

Samples under investigation are composed of the residual fraction resulting from a plastic waste sorting plant and representing the sink fraction of the sedimentation tanks. The feed is mainly composed of heterogeneous post-consumer polymeric packaging: PoliEtilene Tereftalato (PET), PolyPropylene (PP), PolyEthylene (PE), PVC, Acrylonitrile-Butadiene-Styrene (ABS), PolyStyrene (PS) and PolyCarbonate (PC). The heavy fraction resulting from the sorting plant processing is of about 120.000 ton/year of product. Feed is composed by high percentage of PVC (24.90 % in weight, later indicated as % w/w) and in order to reduce the presence of chlorine, a separation of PVC product was carried out. This approach allows to generate a better SRF, characterized by lower dioxins and hydrogen chloride gas emissions. A typical composition of this product as well as the pictorial appearance of it, are reported in Table 1.

Table 1. Example composition of PC-PPW sample.

PC-PPW	PET	PVC	Rubber	PS/ ABS	PA/PBT and other polymers	PE/PP (added)	PE/ PP	PAPER /FIBER	METAL/ INERTS
% w/w	26.8	24.9	3.1	9.6	5.4	11.9	5.5	4.2	8.6

1.2 Overview of the performed analyses

The results obtained by Bonifazi, et al., 2014 [6] have allowed to extend the topic of this study. To facilitate and speed up the experimental process, the sink fraction has been reduced in size by a cutting mill, the resulting product was then separated by the RC device. After the separation process a FT-IR analysis was carried out to perform a full identification of the different polymers. The identified polymers and the particles/aggregates, not preliminary analysed by Fourier Transform Infrared Spectroscopy (FT-IR) analysis, and characterized by a strong fibres/polymers intergrowth, have been thus manually selected and tested by means of calorimetric analysis to determine the emission of chlorine. Each polymer particle was then analysed by HSI in order to identify its spectral signature in the VIS-NIR (1000-1700 nm) wavelength range and to build an "ad hoc" reference spectra library to use for the recognition. A reference sample of about 708 g was utilised for the experimental separation. The results of the studies developed by the different analytical approaches (i.e. density characterization, FT-IR) to asses and quantify the presence of chlorine contained are reported in Fig. 1. The class density plot clearly shows as most of the chlorinated particles are characterized by a density ranging between 1150 kg/m^3 and 1300 kg/m^3 about 80% of the total chlorinated particles are in this range (Fig. 1).

3. Experimental Separation

The RC is an innovative fluidized bed, this device can provide an innovative solution to classify the particles according to size and density [7]. It is typically used in mining and suitable for the separation of coal and minerals [8][9]. The sink fraction was previously milled to make the material more homogeneous and to allow the particles liberation (i.e. plastic, paper, fibres, and metals). A sample of 120g was split and put in water to simulate the initial conditions from the sedimentation tanks.

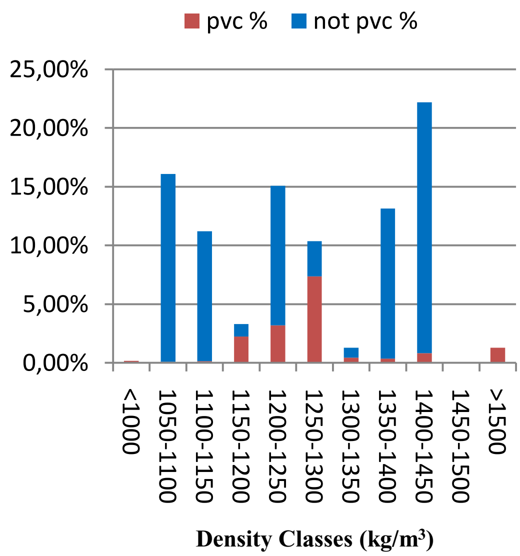


Fig. 1. Density distribution of the coarse product selected from the sink fraction resulting from laboratory sink-float separation of the heavy fraction as resulted from the industrial processing. The distribution of the PVC particles is displayed in red, are displayed in blue the particles which do not contain PVC.

The RC device was modified and adapted to perform a better processing according to complex physical-chemical samples attributes. A zone of turbulence was created in the lower part of the device utilising two pipes, 12 mm each, feeding a constant water flow. The resulting turbulent eddies effect, on the fluid upward motion, facilitates the particles release and their disaggregation. Interaction between particles of different composition can, in fact, contribute to increase the sedimentation rate, decreasing the separation effect. The turbulence generated in a confined space increases the speed of heavy particles (i.e. Aluminium and plastic polymers) enhancing their separation according to their density values. A screen was put at a height of about 14.5 cm to block the falling material, in this way the material was concentrated in the area of maximum turbulence. The RC setup allowed separating the sample in three products: *i*. float material, *ii*. SRF sample and *iii*. heavy fraction.

4. Fourier Transform Infrared Spectroscopy (FT-IR)

The sink fraction was dried and 292 coarse particles were selected to perform FT-IR analysis. The selected particles were acquired and analysed one by one utilising a Perkin Elmer FT-IR Spectrum™ 100.

5. Near Infrared Hyperspectral Imaging (NIR HSI)

The core of the sensing unit is constituted by a NIR HSI, capable to simultaneously measuring the optical spectrum components and the spatial location of an object surface.

The unit was specifically designed and set up for both industrial and research use. An ImSpectorTM N17 (Specim, Finland) sensing device, working in the NIR range (1000-1700 nm) with a spectral resolution of 5 nm for a total of 131 wavelengths, was utilised . This approach is particularly suitable to be utilised to develop and implement on-line analytical strategies and certificate the SRF sample. The Spectral data analysis was carried out in both cases utilizing the PLS_Toolbox (Version 6.5.1, Eigenvector Research, Inc.) running inside Matlab® (Version 7.11.1, The Mathworks, Inc.), adopting standard chemometric techniques [10][11]. The Partial Least Square-Discriminant Analysis (PLS-DA) was used to find a model able to perform an optimal discrimination among classes of samples and for prediction in new images. PLS-DA is a supervised classification technique, requiring a prior knowledge of the data [12]. The result of PLS-DA applied to hyperspectral images is a "prediction map", where the class of each pixel can be identified using color mapping. A PLS-DA model, based on Baseline, 2nd Derivate and Mean Centering (MC) spectra pre-processing, was thus developed to discriminate between plastic waste material heavy fraction.

6. Calorimetric Test

Analysis has been performed according to DIN EN ISO/IEC 17025, in order to determine the true content of chlorine in the samples. The UNI EN 15359 standards (in substitution of the UNI CEN/ TS 15359: 2006) was followed to classify the SRF sample, the SRF classes are reported in Table 2.

Table 2 SRF classified according to Directive UNI EN 15359

Classification characteristic	Statistical measure	Unit	Classes 1	2	3	4	5
Chlorine (Cl)	Mean	%	≤ 0,2	≤ 0,6	≤ 1,0	≤ 1,5	≤ 3

7. Results and discussion

1.3 Experimental Separation by RC device

The separation process was developed to standardize the output products and to certify the product, furthermore the experimental process has produced two main streams, that is: *i*. SRF samples, *ii*. heavy fraction, being previously mentioned "float product" constituted by fine particles in a very limited quantity. The SRF sample is composed of paper fibers and with some small residual of plastics and on the other hand the heavy fraction samples is composed of clean thick flakes of plastics and metals. Afterwards the chlorine content of heavy fraction was verified analyzing 292 particles (10.5 g) with FT-IR analysis and HSI imaging technique.

1.4 FT-IR Analysis of heavy fraction

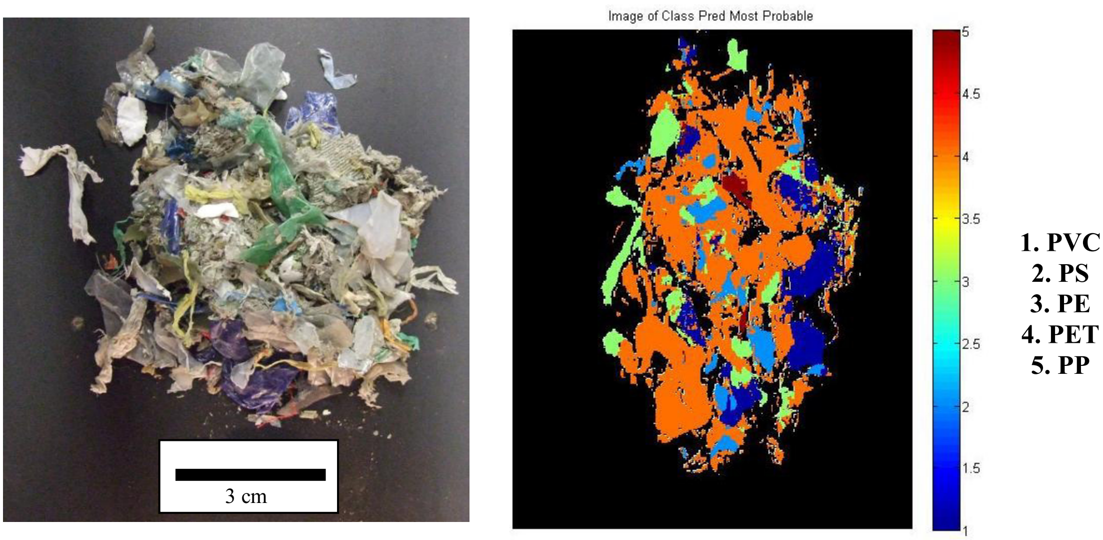
The results of FT-IR analysis are reported in Table 3. FT-IR analysis showed as PVC particles constituted about the 12.54% w/w of the investigated sample.

Table 3 Results of FT-IR analysis carried out on a representative set of particles coming from the sink fraction as resulting from laboratory test.

	PET	PE	PP	PS	PVC	Other
% w/w	50.50	1.42	2.30	2.97	12.54	30.28

1.5 Hyperspectral Imaging

The application of PLS-DA model to a representative SRF sample is shown in Fig. 2. The PLS-DA analysis has allowed to realize a good classification of samples. Therefore the classification and recognition of the material that constitutes the SRF is analysed to find correspondence with the results previously carried out with the FT-IR analysis, showing a high presence of PET.



a. b.

Fig. 2. SRF representative sample (a) and predicted image (b) as resulting from PLS-DA modelling.

1.6 Calorimetry Test

The results of the calorimetry test, reported in Table 4, showed the content of chlorine in the investigated samples. The heavy fraction samples is characterized by a high chlorine content, of about 5%, it is thus not suitable for incineration. On the contrary, the product named SRF sample shows a chlorine content of about 3%, according to UNI EN 15359 standards (classification system for SRF) the sample is not classified as waste but as a SRF class 5.

Table 4 Results of the content of chlorine in the samples.

	Big-Bag (feed)	Heavy fraction	SRF samples
% w/w	3.8	5.0	3.0

8. Conclusions

The different analytical approaches adopted to perform a Post-Consumer Plastics Packaging Waste (PC-PPW) characterization, finalised to their sorting, showed a different response in terms of PVC physical-chemical identification/characterization in respect to the adopted separation. All the tests have been carried out with reference to the heavy fractions resulting from a density based separation.

The Reflux Classifier (RC) was utilised to separate the PVC particles from the original samples, the separation process has achieved an acceptable result considering the homogeneity of the output.

Therefore the results of the calorimetric test, ensure a decrease in chlorine content, the separation process can be improved to reach the levels indicated by standard and classify the material as SRF quality. Finally, HSI permitted to fully identify all the different polymers constituting the PC-PPW.

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Biography

Giuseppe Bonifazi is full professor of raw materials beneficiation at the Department of Chemical Materials Environment Engineering (DICMA), Faculty of Civil and Industrial Engineering at La Sapienza - University of Rome. He has more than 30 years experience on the characterization of particles and particulate solids materials by image processing.