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FLUIDIZED BED GASIFICATION OF MIXED PLASTIC WASTES: A MATERIAL AND A SUBSTANCE FLOW ANALYSIS

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ABSTRACT

Gasification as a reliable and convenient waste-to-energy process for the economic analysis of mixed-plastic waste (MPW) was investigated. To this end a pilot scale bubbling fluidized bed air gasifier was fired with two commercially available MPWs to obtain syngas composition and characterization of the bed material, cyclone collected fines and purge material from the scrubber. These results were then processed by means of Material and Substance Flow Analyses to evaluate the main process performance parameters for the two MPWs tested.

INTRODUCTION

Pervasive use of plastics as packaging materials makes this the most important fraction of municipal solid waste to be considered to reach a gradually larger intensity of separate collection (6). The sorting process of this fraction after a household separate collection generally produces a high percentage of residues, together with some completely recyclable streams and a not negligible fraction of a non homogeneous plastic scrap, called mixed plastic waste (MPW). This latter stream contains several types of plastic polymers that often are together with a not negligible amount of ferrous and non-ferrous metals. Due to its heterogeneity MPW can be utilized to substitute virgin materials only for a limited number of goods. On the other hand, its high calorific value makes thermal treatment an environmental sustainable and economic attractive alternative (9,1).

The study investigates the possibility to utilize the gasification as a reliable and convenient waste-to-energy process for the economic valorisation of mixed-plastic waste. To this end a pilot scale bubbling fluidized bed air gasifier, having a thermal capacity of 500kJ/s, was fired with two commercially available MPWs. The results have been combined with an environmental assessment tool, the Material Flow Analysis, which is named Substance Flow Analysis when it is referred to a specific chemical. MFA/SFA is a systematic assessment of the flows and stocks of materials and elements within a system defined in space and time. It connects the sources, the pathways, and the intermediate and final sinks of each species in a specific process (7). In this study MFA/SFA was applied to a system boundary that includes the BFB gasifier and the cleaning system for ash separation (cyclone and wet scrubber). The BFB gasifier was further divided into two sections: the first corresponds to the dense bed and splashing zone; the second to the freeboard.

THE PILOT SCALE FLUIDIZED BED GASIFIER

The utilized pilot scale BFB gasifier has the characteristics schematically listed in Table 1. An olivine - a magnesium-iron silicate, $(Mg,Fe_2)SiO_4$ - was selected as material for the fluidized bed on the basis of results of previous investigations carried out on the same pilot-scale BFBG [Arena et al., 2010a] that indicated olivine as an interesting candidate to act as a bed catalyst for the tar cracking

reactions in waste-derived fuel gasification, even taking into account its low cost and excellent resistance to attrition in the fluidized bed reactor. The main characteristics of the utilized olivine are reported in Table 2.

Table 1. Main design and operating features of the pilot scale bubbling fluidized bed gasifier.

<i>Geometrical parameters</i>	ID: 0.381m; total height: 5.90m; reactive zone height: 4.64m
<i>Feedstock capacity</i>	100 kg/h
<i>Typical bed amount</i>	145 kg
<i>Feeding system</i>	over-bed air-cooled screw feeder
<i>Bed temperatures</i>	700-950°C
<i>Fluidizing velocities</i>	0.3 –1m/s
<i>Flue gas treatments</i>	cyclone, scrubber, flare

Table 2. Characteristics of the olivine particles utilized as bed material in the pilot scale bubbling fluidized bed gasifier.

<i>Mineral</i>	Mg-Fe silicate
<i>Chemical composition, %</i>	
<i>SiO₂</i>	39-42
<i>MgO</i>	48-50
<i>Fe₂O₃</i>	8-10.5
<i>CaO</i>	<0.4
<i>K₂O</i>	-
<i>TiO₂</i>	-
<i>Al₂O₃</i>	0.8
<i>Cr₂O₃</i>	
<i>Mg₃O₄</i>	
<i>LOI (loss of ignition)</i>	0.20
<i>Size range, μm</i>	200 ÷ 400
<i>Sauter mean diameter, μm</i>	298
<i>Particle density, kg/m³</i>	2900

In the reported experiments, air was used as reducing agent and always injected at the bed bottom while the fuel was fed by means of an over-bed feeding system. The fluidizing air stream was heated up to 450°C by a two electric heaters before entering the reactor. The fuel and blast flow rates were mutually adjusted so that, at the fixed fluidizing velocity, the desired equivalence ratio ER was obtained (where ER is defined as the ratio between the oxygen content of air supply and that required for the stoichiometric complete combustion of the fuel effectively fed to the reactor). The cylindrical BFB reactor was heated up to the reaction temperature by the sensible heat of pre-heated blast gases and by a set of three external electrical furnaces. The gas generated in the reactor was sent to a high efficiency cyclone and then to a wet scrubber (for the removal of tars, residual fly ash and acid gases) and finally incinerated by a safety flare. An accurate description of the plant and of experimental procedures is provided elsewhere (3). Here it is sufficient to highlight that gas composition was on-line measured upstream and downstream of the syngas conditioning section as well as at the reactor height corresponding to the end of splash zone. The diagnostic apparatus utilizes IR analyzers for the main syngas components (carbon monoxide and dioxide, hydrogen, methane) and two micro-gas-chromatographs equipped with different columns for the detection of light and heavy hydrocarbons as well as of carbon monoxide and dioxide, hydrogen, nitrogen and water.

EXPERIMENTAL RESULTS

The plant was fed with one of the two mixed plastic wastes taken in consideration, both obtained as by-products of the sorting process of end-of-use plastic packaging from separate collection (Table 3). The first, named GS3, is a mixture of recycled polyolefins obtained from plastic packaging for food and beverages by means of sorting and washing treatments. The second, named SRA, is a mixture of several plastic wastes obtained from separate collection of packagings made of plastic as well as ferrous and non-ferrous metals, as resulting after an intensive treatment aimed to produce a fuel that can meet even high quality standards, as those of metallurgical industry.

Table 3. Chemical characterization of the two MPWs utilized in the study.

Mixed Plastic Wastes	GS3	SRA
<i>Ultimate analysis, % wb</i>		
C (min-max)	84.4 (84.3-84.8)	79.5 (75.9-83.1)
H (min-max)	14.0 (13.5-14.2)	13.1 (12.8-13.4)
N (min-max)	0	0.2 (0.15-0.25)
S (min-max)	0	0.1 (0.08-0.12)
Moisture (min-max)	0.3	0.7 (0.6 – 0.8)
Ash (min-max)	1.3	1.9 (1.4 – 2.4)
O (by difference)	0	4.5
<i>HHV^a, MJ/kg_{fuel,db}</i>	46.0	43.4 (41.8-45.0)
<i>LHV^b, MJ/kg_{fuel,ar}</i>	42.9	40.2 (38.6-41.8)
<i>Size (diameter and height), mm</i>	7, 1	irregular
<i>Bulk density, kg/m³</i>	460	310

a) evaluated by means of relationship proposed by Channiwala and Parikh (2002).b) evaluated by the HHV on dry basis by taking into account the latent heats of vaporization of fuel moisture and water obtained as product of hydrogen combustion;wb= weight basis; db=dry basis; ar=as received.

The pilot scale BFBG was operated with the mixed plastic wastes in a bed of olivine particles fluidized at a velocity of 0.7m/s, at a bed temperature of about 850°C, preheated air of about 450°C and an equivalence ratio of 0.27. The performances of the BFBG were measured and recorded only when the chemical composition of the produced syngas and the temperature profile along the reactor reached steady-state conditions. The experimental activity provided the complete chemical composition of gas stream at two levels of BFB gasifier (2m above the air distributor and at the reactor exit) together with those of streams leaving the cyclone and the wet scrubber system. These latter data, (Table 4), have been elaborated and used for the substance flow analysis of carbon, hydrogen, iron, magnesium and other elements and for the feedstock energy flow analysis (5).

THE MFA/SFA ANALYSIS

Figures 1-3 report the quantified flow diagrams resulting by the MFA/SFA applied to the above cited sections of the bubbling bed gasifier (dense bed + splashing zone and freeboard zone) and of the cleaning system (cyclone for ash separation +wet scrubber for gas cleaning) of the pilot scale gasification system, when operated with the two MPWs.

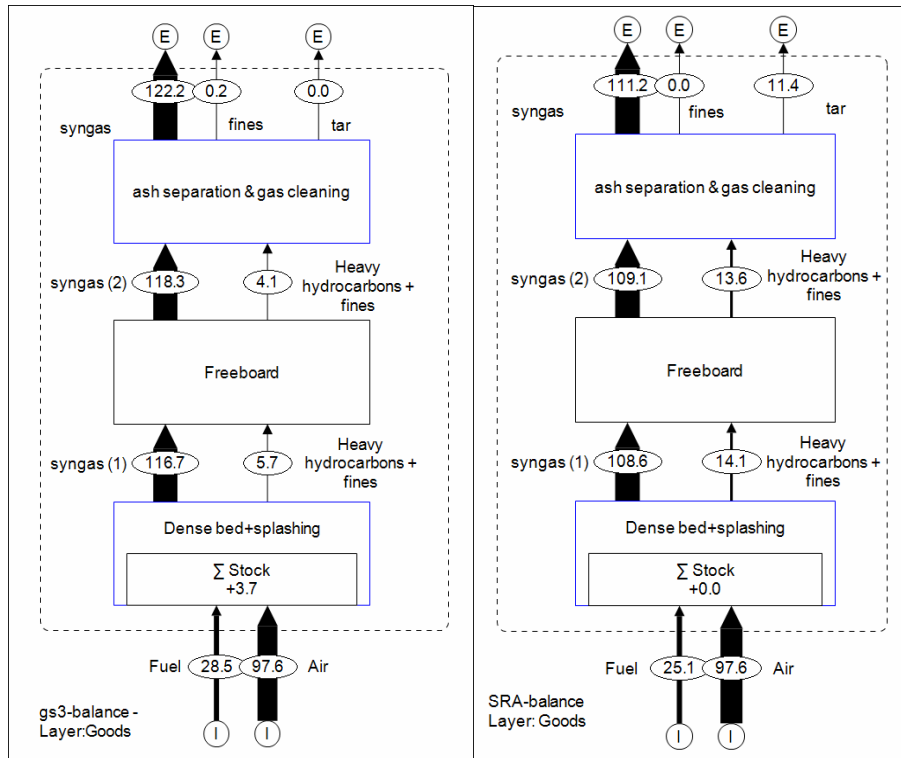


Figure 1. Layers of total mass balances (kg/h) throughout the pilot scale gasifier, for test with GS3 (left) and SRA (right) mixed plastic waste fuels.

The layer of total mass flow rate is reported in Figure 1. The input flows to the BFBG unit are the stream of plastic fuel and that of air used as oxidizing agent and fluidizing gas. The output flow stream from the dense bed and splashing zone is that of the obtained syngas, which still contains heavy hydrocarbons and entrained fines. This stream is visualized in Figs. 1-3 as two different arrows, one indicating the syngas, i.e. the mixture of N_2 , CO , H_2 and C_nH_m with $n < 6$, the other indicating the contaminants, mainly heavy hydrocarbons and entrained fine particles. The output from this first section moves throughout the freeboard and then to the cyclone for dust abatement and to the wet scrubber for removal of tars and inorganic compounds. Along these paths both chemical and physical reactions occurred so that the mass flow and composition of each stream were modified (Figs. 1-3).

By looking at Figure 1 it is evident the different process performances obtained with the mixture of polyolefin plastic waste (GS3) and with the other mixed-plastic waste (SRA). The analysis of the results of the test with GS3 in a bed of olivine indicates a great performance, with the almost complete absence of tar (Fig. 1), a consequently high value of the specific syngas conversion efficiency $(122.2/(28.5+97.6)=0.97)$ and a high concentrations of molecular hydrogen and carbon monoxide in the syngas (Table 4). Specific studies about the role of olivine as a tar removal catalyst during the gasification of polyolefin plastic wastes [Arena et al., 2009; 2010a] indicated that magnesium and iron, both largely present in the olivine particles, activate the endothermic decomposition reactions of hydrocarbon fragments that are the first precursors of tar formation. The very low tar concentrations are always coupled with low concentrations of methane (less than 3%), ethane, ethylene, acetylene, propylene or, in other words, with high extension of the cracking and dehydrogenation reactions (10).

Table 4. Operating conditions and performance parameters of the pilot scale BFBG operated with the SRA fuel under two values of equivalence ratio.

Mixed Plastic Wastes	GS3	SRA
<i>Operating Conditions</i>		
ER (equivalence ratio), -	0.27	0.27
AF (air/fuel ratio), kg _{air} /kg _{fuel}	3.95	3.59
<i>Output Process Data</i>		
Temperature of fluidized bed, °C	830	890
Q _{syngas} , m ³ _N /kg _{fuel}	5.82	3.75
LHV _{syngas} , kJ/m ³ _N	6850	6430
Specific energy, kWh/kg _{fuel}	11.1	6.7
CGE (cold gas efficiency), -	0.83	0.77
<i>Syngas composition (downstream of cyclone and scrubber)</i>		
N ₂ , %	46.25	65.11
CO ₂ , %	1.50	9.80
CO, %	21.07	5.34
H ₂ , %	28.18	8.58
CH ₄ , %	2.31	7.30
C ₂ H ₄ + C ₂ H ₆ + C ₂ H ₂ + C ₃ H ₆ , %	0.55	3.76

The analysis of the results for the SRA fuel indicates that syngas has very low concentrations of H₂ and CO and larger concentrations of CH₄ and C₃H_m together with a higher content of tar ($11.4/(25.1+97.6)=0.093$) and a correspondingly lower specific syngas yield ($111.2/(25.1+97.6)=0.91$): this suggests that the catalytic action of olivine is not present. Moreover, the role of the freeboard section appears negligible since the decreasing of heavy hydrocarbons and elutriated fines fraction between the exit of dense bed and splashing zone and the reactor exit is very low (3.5%).

Figure 2 reports the results of the mass balances applied to the carbon element, i.e. the carbon layer of SFA, for both MPWs. It provides the carbon conversion efficiency CCE, defined as the ratio between the mass flow rate of the carbon present in the syngas as CO, CO₂, CH₄ and light hydrocarbons (until C₅H_m) and the mass flow rate of the carbon that enters the reactor with the fuel.

In the case of the GS3, the CCE increases from the value of 0.77 at the exit of the splashing zone to 0.81 and 0.83 related to the freeboard and cleaning system exit, respectively. These values confirm that the largest part of fuel conversion into syngas occurs in the dense bed and splashing zone, which is characterized by an intense turbulence of gas phase and by the effect of heterogeneous and/or catalytic reactions (dehydrogenation and carbonization).

Analogous calculations can be made for the SRA test (right side of Fig. 2). In this case, the CCE does not vary between the three measurement points and remains almost equal to 0.76. This different behaviour is confirmed by the value of carbon accumulated in the bed (that is almost zero) as well as by that of carbon fines elutriation rate (that is negligible). The absence of carbon fines along the freeboard can affect the type of reactions occurring in this region: oxygen is absent and heterogeneous reactions cannot occur, so that the only expected reactions are those of recombination of reactive molecules that can lead to an increasing of heavy hydrocarbons (tar).

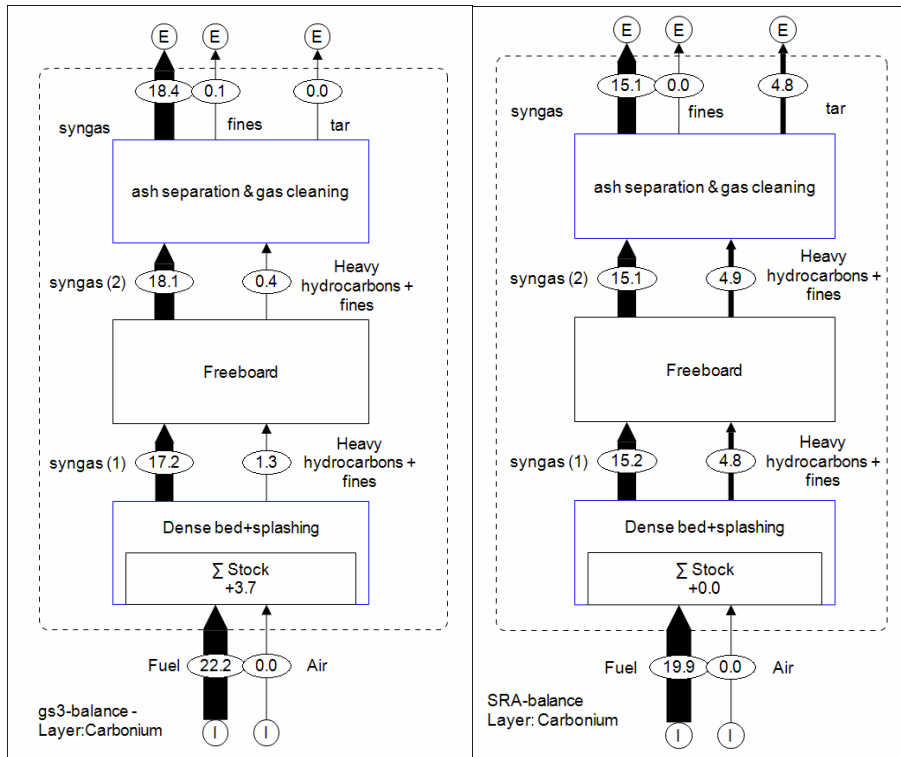


Figure 2. Layers of total carbon balances (kg/h) throughout the pilot scale gasifier, for test with GS3 (left) and SRA (right) mixed plastic waste fuels.

The graph on the left side highlights the completely different behaviour of the GS3 waste. The carbonization was so present, and strong, that an accumulation of carbon on the bed particles surface was present: the stock of 145kg of bed particles was progressively incremented (3.7kg/h) as a result of opposite effects of elutriation losses and carbon accumulation. The fines collected at the cyclone in the run with GS3 were mainly produced by the attrition between the bed particles and the carbon layer deposited on their surface. They contained quantity of iron larger than that entering the reactor with the fuel (4): this means that part of the elemental iron of olivine, linked with the carbon by coordination complexes, was then detached from the particle by mechanical attrition and entrained out of the reactor in the syngas.

This behaviour allowed that, in the test with GS3, less than 6% of the fuel carbon was used to produce tar precursors while, in that with SRA where this mechanism was inactive, the 24% of the fuel carbon was transformed into heavy compounds in the dense bed+splashing zone. These considerations can be repeated and further supported by analyzing the hydrogen layer (Fig. 3).

In the test with GS3 the hydrogen conversion into syngas moved from 0.82 to 0.89 and to 1, i.e. the dehydrogenation of the fuel was completed. All the fuel hydrogen was transferred into syngas as H₂ and light hydrocarbons. No hydrogen was present as tar compounds and as carbon fines. This result was due to the completion of carbonization/dehydrogenation reactions that largely occurred in the dense bed and partly occurred in the freeboard and in the cyclone, thank to the contact between the carbon fines (that contained metal active particles absorbed over and inside its surface) and heavy hydrocarbons not yet converted into small molecules in the dense bed+splashing zone. The dehydrogenation was

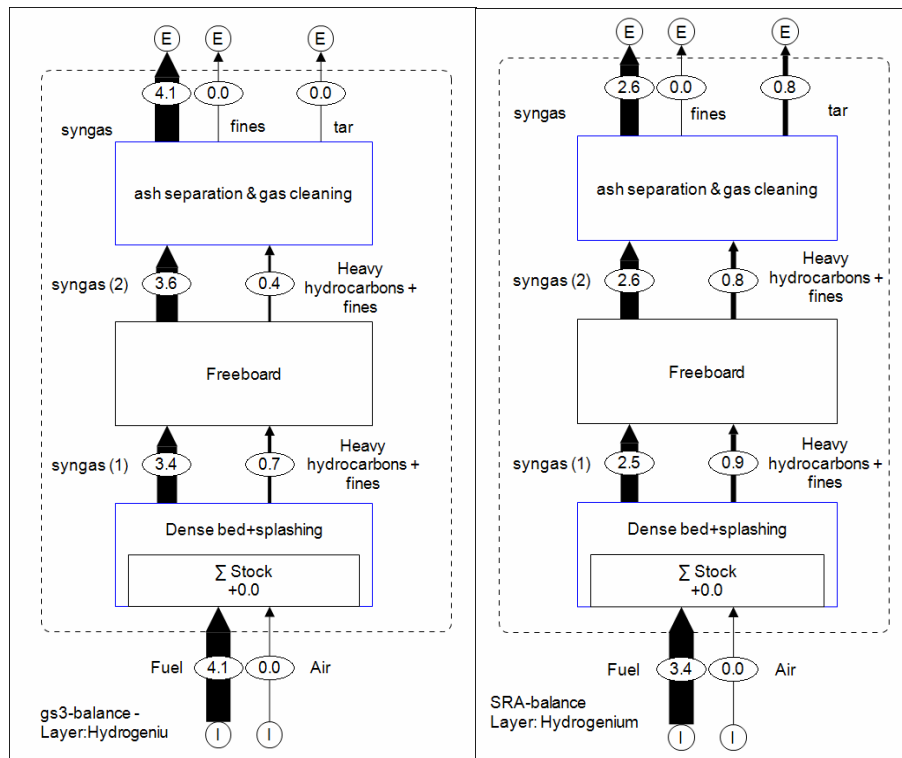


Figure 3. Layers of total hydrogen balances (kg/h) throughout the pilot scale gasifier, for test with GS3 (left) and SRA (right) mixed plastic waste fuels.

due to the increasing of aromatization until to the complete hydrogen abstraction from heavy hydrocarbons and PAHs.

The hydrogen flow analysis of SRA test shows, again, a different behaviour (Fig. 3). In this case, the increasing of hydrogen conversion into syngas components moved from 0.74 to 0.75 and to 0.77. The values are, as with CCE, very close to each other, and the final value was very far from the total conversion obtained with GS3. This result was due to the absence of any heterogeneous reactions in the dense bed as well as in the other zones of gasifier: the carbon accumulation rate was almost zero and, as a consequence, the carbon elutriation rate too.

CONCLUSIONS

The industrial application of plastics-to-energy gasifiers was investigated. The process performances of two mixed-plastic wastes, gasified in a pilot scale bubbling fluidized reactor having a bed of olivine have been evaluated. Experimental measurements taken at different points inside and downstream of the gasifier, combined with mass balances and material and substance flow analyses, indicated the MPW that offers the higher performance and reliability. In particular, SRA, a MPW obtained from a separate multi-material collection (plastics+ferrous+non-ferrous packaging) processed by an intense treatment, presently designed to be utilized in the metallurgic industry, appeared convenient for a gasification-based, plastics-to-energy plant only if a downstream recovery and valorization of tar stream is provided. On the contrary, GS3, a more homogeneous MPW, mainly made of polyolefin plastics with a substantial absence of ferrous or non-ferrous packaging, and just processed by means of a shredding and washing treatment gave the best performance.

During the gasification of SRA, the catalytic effect of olivine particles appeared absent or limited: carbonization was practically absent and the produced tar was captured by the wet scrubber so determining a not negligible environmental burden and a remarkable energetic loss and, then, a relevant economic cost. It is likely that the catalytic support to the cracking and isomerization was always active (the heavier fragments are broken and a number of unsaturated hydrocarbons with two or three carbon atoms are formed) but the catalytic enhancement of the dehydrogenation and carbonization determined by active sites of iron was absent (the hydrogen content remains low and the tar formation was not inhibited).

During the gasification of GS3, the catalytic effect of olivine particles was so strong that no tars were detected downstream of the cleaning section and the endothermic reactions of carbonization clearly reduces the bed temperature. The negative aspect of this mechanism is that an amount of carbon continuously accumulates in the bed, indicating the necessity of an overflow of exhausted olivine particles and a corresponding make-up of fresh particles. Exhausted olivine could be regenerated by burning the carbon layer covering the external surface (2).

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REFERENCES

1. Arena U. and M.L. Mastellone (2006) Fluidized Bed Pyrolysis of Plastic Wastes. Chapt. 16 in Feedstock Recycling and Pyrolysis of Waste Plastics, J. Scheirs and W. Kaminsky (Eds). J. Wiley&Sons Ltd, ISBN: 0-470-02152-7, pp. 435-474
2. Arena U, L. Zaccariello, M.L. Mastellone (2008) Gasification of a plastic waste in a fluidized bed of olivine. Proc. of CFB9 - 9th Int. Conf. on Circulating Fluidized Beds. J. Werther, W. Nowak, K.-E. Wirth and E.-U. Hartge /eds.), ISBN 978-3-930400-57-7, p. 691-696
3. Arena U., L. Zaccariello, M.L. Mastellone (2009) Tar Removal During the Fluidized Bed Gasification of Plastic Waste. Waste Management, 29:783-791
4. Arena U., L. Zaccariello, M.L. Mastellone (2010a). Fluidized Bed Gasification of Waste-Derived Fuels. Waste Management, 30:1212-1219
5. Arena U., F. Di Gregorio, L. Zaccariello and M.L. Mastellone (2010b) Fluidized bed gasification of biomass: a substance flow analysis, in Fluidization XIII, S.Done Kim, Y. Kang, J.Keun Lee and Y. ChilSeo (Eds), Engineering Conferences International, ISBN 978-0-918902-57-3, pp. 805-812
6. Brandrup J., M. Bittner, W. Michaeli and G. Menges (Eds.) (1996). Recycling and recovery of plastics, New York, NY: Hanser Publ
7. Brunner P.H. and V. Rechberger (2004) Practical Handbook of Material Flow Analysis. CRC Press LLC, Boca Raton (FL)
8. Channiwala S.A and P.P. Parikh (2002). A unified correlation for estimating HHV of solid, liquid and gaseous fuels, Fuel, 81:1051-1063
9. Hermann C., F.J. Schwager, K.J. Whiting (2001).Pyrolysis & Gasification of Waste.A Worldwide Technology & Business Review. 2nd Edition. Juniper Consultancy Services Ltd
10. Mastellone M.L. and U. Arena (2008). Olivine as a Tar Removal Catalyst During Fluidized Bed Gasification of Plastic Waste. AIChE Journal, 54/6: 1656-1667