The Crucial Role of the Process Modelling During the Design of a Bubbling Fluidised Bed Gasifier of Plastics

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***Abstract* — Gasification is a thermochemical process that aims to convert solid fuels into a synthetic gas that can be addressed to an end-use apparatus to produce electric energy and heat or can be further refined to be transformed in chemical valuable products. Many solid fuels, included waste (wood, biomass, plastics, municipal solid waste, etc.), can be gasified under different operating conditions (pressure, temperature, reactants) in different kind of reactors. This paper aims to correlate the descriptive model for the gasification of a mixture of commodity plastic waste to the basic design of a bubbling fluidized bed gasifier on the basis of experimental data and mathematical calculations.**

***Index Terms* — Bubbling Fluidised Bed, Gasification, Plastics**

I. INTRODUCTION

GASIFICATION can be considered an “old-*but*-innovative” process because of its 50 years of application time in well known petrochemical processes but also of the recent exploit of “new” application of the same processes to different type of fuels: the waste. The change of the fuel characteristics as well as the change of the main aim of the process requires a deepening of the effect that the specific waste has on the process performance. Waste gasification is in fact a not yet wide commercial utilization process because of conversion efficiency losses and syngas cleaning concerns [1], [2]. The reactor technology has also an important effect on the gasification performance as well as the reactants type and the operating conditions (temperature and pressure) [3]. The understanding of the process development, strictly related to the fuel structure and kinetic behavior under gasification conditions, is crucial to correctly operate the gasifier in the case of single fuel feeding as well as under co-gasification conditions [4]. Typical undesired by-products of gasification process are heavy hydrocarbons condensable at ambient temperature (tar) and carbonaceous particle with very small mean size (few microns).

This paper aims to correlate the descriptive model for the gasification of a mixture of commodity plastic waste – to the basic design of a bubbling fluidized bed gasifier on the basis of experimental data and mathematical calculations.

II. MODELLING

A. Brief description of the bubbling fluidised bed hydrodynamics

A bubbling fluidized bed can be described by means of three schemes, useful for different purposes: the graphical scheme (Fig. 1a) shows a visual representation of the typical aspect of a bubbling fluidized bed (BFB) characterized by a zone where a bed made by particles is suspended by the fluidising gas (emulsion phase) coming from the bottom distributor and crossed by bubbles streams (bubble phase) characterized by a size and mean velocity distribution along the bed height due to the coalescence and by a zone where the voidage increases, bubbles disappear, turbulence decreases (freeboard). The changeover from the dense zone to the dilute zone is enough quick and discontinuous by creating a sort of “transition” zone that can be identified with the name of “splashing”.

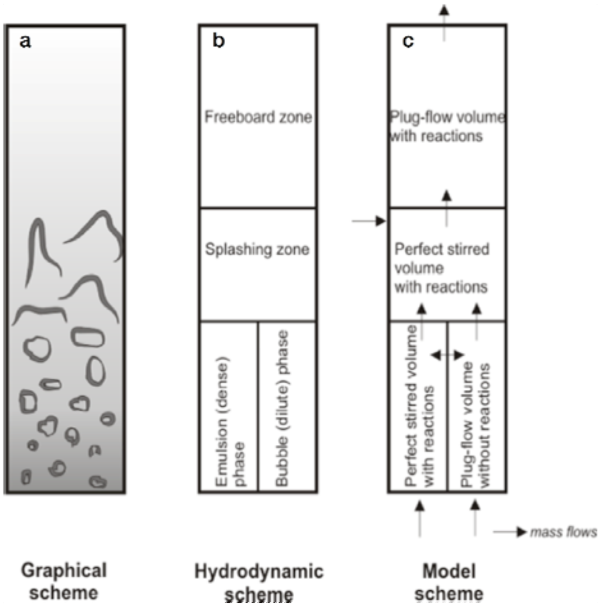

Fig. 1 Schemes of the bubbling fluidised bed gasifier utilised as reference for the model.

In the case of a typical BFB, operated under conditions of a true bubbling regime, the hydrodynamics can be described by means of a model applied to system boundaries as reported in the Fig. 1b and the kinetic modelling can be carried out by referring to a combination of ideal reaction

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volumes as reported in the same Fig. 1c. This representation highlights the peculiarity of a BFB reactor that can be seen as a combination of four zones: emulsion zone in the dense bed, bubble phase in the dense bed, splashing zone above the dense bed and freeboard zone between the splashing and the reactor exit. These zones have hydrodynamic regimes different from each to other and are connected by mass and energy exchange flows. The overall process rate can be then obtained by considering a combination between the attendant aspects: the physical kinetics i.e. mass transfer and interphase exchange rates and the chemical "intrinsic" kinetics (i.e. rate of chemical reactions with no mass transfer limitation) of each process step. The knowledge of the process rate is obviously the basis for the reactor design so that a way to evaluate it on the basis of both experimental and modelling data is given in the following.

B. Process reactions occurring in the dense bed

The peculiar aspects correlated to the thermal treatment of plastic waste are: the very low content of ashes; the very low content of char; the low specific heat value of the solid polymer; the stickiness of the molten polymer; the very high devolatilization rate due to the low energy necessary to break the C-C and C-H bonds. Another crucial aspect must be recalled in the case plastics are fed into a bubbling fluidized bed: the agglomeration phenomenon between the molten polymer and the bed particles and the related effects of this interaction on the heat exchange and mass transfer rates. If the agglomeration occurs, the hydrodynamic variables, like the size and density of the bed particles and the fluidization velocity having a key role in determining the overall performance of the reactor [5], can dramatically change.

Just after the injection into the hot fluidized bed, a very fast heat transfer mechanism leads the polymer pellet external surface up to the softening temperature. The time necessary to reach this state can be evaluated by means of the dynamic energy balance on the single plastic pellet:

$$m_{fuel} \cdot c_p \cdot dT/dt = A \cdot h_{bed} \cdot (T_{bed} - T_{melting}) - r_{melting} \cdot \Delta H_{melting} \quad (1)$$

where: m_{fuel} is the mass of the fuel, c_p is the specific heat capacity of fuel, T is the time-depending temperature of the pellet surface, A is the external pellet surface, h_{bed} is the heat transfer coefficient between the bed and the pellet, T_{bed} is the bed temperature, $T_{melting}$ is the temperature at which the pellet melts, $r_{melting}$ is the rate of melting, $\Delta H_{melting}$ is the latent heat of melting. The term related to the melting process absorption can be neglected compared with the heat transferred by the fluidized bed that can be evaluated by means of the following relationship proposed:

$$h_{bed}=Nu \cdot k_{fuel}/d_{fuel}=272 W/m^2K \; (d_{fuel}=6mm \text{ at } 850°C) \quad (2)$$

Where: Nu is Nusselt number (calculated by [6]), k_{fuel} is the fuel conductivity and d_{fuel} the fuel pellet diameter.

The solution of the energy balance is:

$$T(t) = T_{bed} + (T° - T_{bed}) \cdot \exp(-h_{bed} \cdot A / m \cdot c_p) \quad (3)$$

With reference to data reported in Table I, the estimated time necessary for the softening of external surface is less than 1s (Fig. 2). This means that the agglomeration between the plastic pellets and the bed particles starts just after the injection in the fluidized bed. Starting time for degradation (350-400°C for thermoplastic polymers) is about 5s at 850°C and 30s at 450°C.

TABLE I
INPUT AND OUTPUT DATA FOR THE ENERGY BALANCE

Parameter	Value	Units
Temperature (T)	850	°C
Gas viscosity (μ)	4.91E-05	Ns/m^2
Gas density (ρ)	0.315	kg/m^3
Inert particle diameter (d_{bed})	0.00035	m
Inert particle density (□$_{bed}$)	2600	kg/m^3
Gas conductivity (k)	0.016	cal/s m° C
Fuel diameter (d_{fuel})	0.005	m
Density of fuel (ρ_{fuel})	950	kg/m^3
Specific heat of fuel (c_p)	0.55	kcal/°C kg
□□□□□□□□□□□□□ of fuel □$\Delta H_{melting}$)	23.8	kcal/kg
Softening temperature of fuel	135	°C
Conductivity of fuel (k_{fuel})	0.46	cal/s m °C

Fig. 3 reports the photos of the transversal section and of the external surface of a PE pellet having 6mm diameter kept in a fluidized bed at 450°C for 15s. This experimental evidence confirms the calculation reported in the Fig. 2.

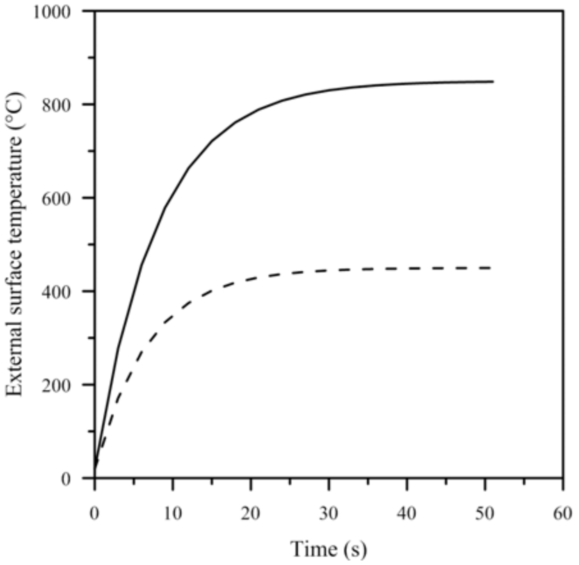

Fig. 2 Temperature increasing of the external surface of a PE pellet in a BFB at 850°C (continuous line) and 450°C (dot line).

C. Fuel-bed interaction (agglomeration)

Once the pellet surface molten (i.e. very rapidly at bed temperatures greater than 450°C), several sand particles stick on the plastic surface, forming an *aggregate* that has

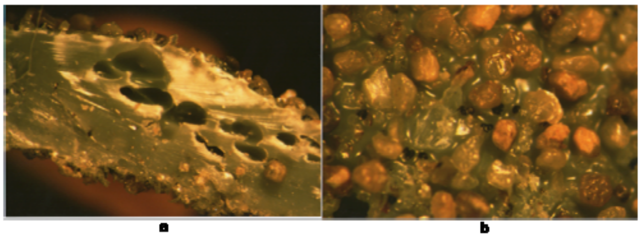

Fig. 3 Photos of a PE pellet kept 15s in BFB at 450°C. Transversal section (a); external surface (b).

the external shell made of sand particles and the internal core made of polymer not yet molten (Fig. 3).

The molten polymer flows throughout the bed particles forming the external shell, so forming a uniform coating over and between them and by promoting an adhesion increasing of other bed particles that are close to the aggregate. Moreover, depending on the nature of polymer, and in particular on the absence or not of a sticky carbon residue, the polymer flowing throughout the bed particles can lead to a fast crumbling of the aggregates or can promote the adhesion of several layers of inert material, until the polymeric mass completely flowed throughout the sand. The time necessary to complete this process is related to several factors and to the diffusion rate of plastic molten throughout the inert "hot" particles. The evaluation of this time is strongly depending by the temperature. In any case, at bed temperature as high as 800°C the formation and crumbling of the aggregates are almost undistinguished [7]. This is due also to the parallel beginning of the cracking of the carbon–carbon bonds of the polymer chain (occurring at a mass temperature of about 400°C), i.e. to the beginning of the devolatilization process that starts when the polymer has already covered the bed particles. Therefore, it is not related to the whole molten pellet, but to a layer of polymer, which coats and adheres on the external surfaces of single sand particles.

D. Intrinsic kinetic stage - primary cracking of polymer

As above reported, the crumbling occurs when the polymer forming adhesive bridges between the particles undergo devolatilization i.e. thermal cracking. This latter duration can be evaluated by considering the internal heat transfer resistance of the polymer layer (not more than few micrometers thick) as negligible. The polymer temperature can be assumed constant everywhere since the heat transfer rate to and within the polymer layer is very fast as compared to the primary cracking rate. As a consequence, the rate of mass loss results independent of the polymer temperature profile and the solution of the related equation can be strongly simplified. In other words, if ρ_x is the density of solid residue; A is the pre-exponential factor; E is the apparent activation energy; T is the polymer temperature, the general equation:

$$-\frac{\partial \rho}{\partial t} = A\exp(-E/RT)(\rho - \rho_x)$$

becomes

$$\frac{\rho - \rho_\infty}{\rho_0 - \rho_\infty} = \exp\left\{ -\int_0^t A\exp\left(-\frac{E}{\Re T}\right) dt \right\} \qquad (4)$$

Therefore, the devolatilization time evaluated by means of the recalled phenomenology can be evaluated to be equal to 4.6×10^{-3}s (at 650°C) and to 1.1×10^{-6}s (at 850°C).

By the above reported calculations it can be argued that the limiting stage of the in-series-process *heating-aggregation-devolatilization* is the heating stage.

Just after the devolatilization stages there is the beginning of a complex set of reactions pathways involving the primary volatiles.

E. Reactions involving primary volatiles

The pathways of reactions involving the volatiles produced by the thermal cracking are tentatively represented in the sketch of Fig. 4 by highlighting that the numerous reactions occurring during a gasification process could be divided into three types: a) bimolecular reactions involving primary volatiles and oxygen (e.g. CO formation); b) heterogeneous reaction of primary volatiles with metals present in the bed or in the fuel ashes (e.g. formation of metal-carbon complexes, catalytic de-hydrogenation); c) monomolecular reactions in a reactor zone where the conditions not allow the volatiles oxidation (e.g. reaction of ethylene to form benzene); d) condensation reactions that lead to heavy molecules formation (e.g. polycondensation of benzene or n-rings molecules to form Polycyclic Aromatic Hydrocarbons [PAHs]).

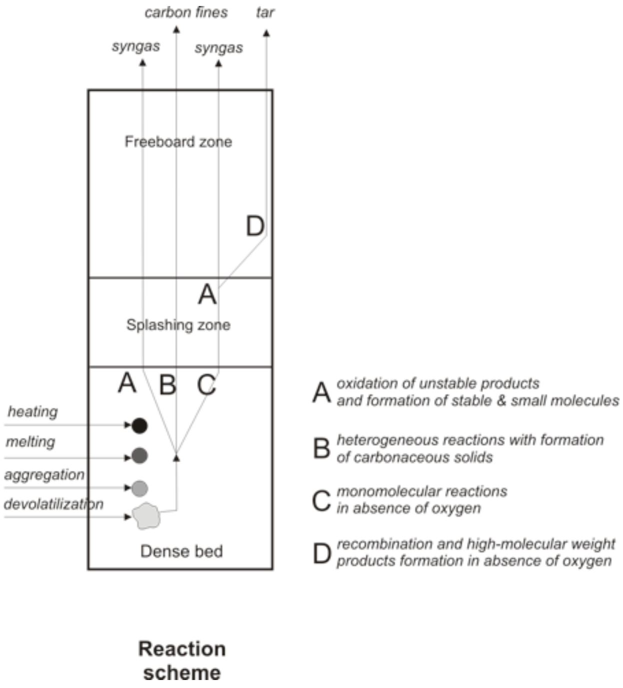

Fig. 4. Scheme of reactions as occurring in a BFB gasifier fed by plastics.

Thank to the aggregation between bed particles and melting plastics and to the very fast heating-devolatilization process it is unquestionable that the thermal cracking is carried out in the emulsion phase of dense bed. In this zone the oxygen content is low, as clearly demonstrated in the following paragraph, so that only a small fraction of primary volatiles undergo the reactions indicated with the path "A" in Fig. 4, that is those of oxidation to small molecules. The other fraction of volatiles reacts in different ways following different reaction mechanisms: a possible pathway includes the heterogeneous reaction between metals (iron, magnesium, nickel, etc.) and unsaturated volatiles (B); another parallel pathway is the reaction of small reactive molecules (like ethylene, propylene or other C_nH_m) to form 1-ring molecules (C); these latter molecules can condensate to form heavy hydrocarbons or PAHs as well as oxygenated aromatic hydrocarbons (D).

This scheme shows that the reducing environment of dense bed enhances the formation of PAHs and, then, of tar because of the limited progressing of path A respect to B-C and D. This feature gives an important information to the designer of a bubbling fluidised bed gasifier i.e. increasing of oxygen inside the dense bed. The oxygen mass transfer rate inside the dense bed is, as a consequence, the key designing variable that must be taken into account in order to favour the mechanism indicated as “A”. Moreover, it must be noted that the addition of oxygen in other zones of reactor (e.g. by means of secondary streams in the freeboard) could not guarantee any positive reduction of tar yield because the PAHs formed in the dense bed are so stable that cannot be transformed in CO, H_2, H_2O, etc. The oxidation of their chemical structure can lead to the formation of oxygenated heavy compounds (e.g. phenols) instead of the desired small molecules.

The mechanism indicated with “B” is related to the presence of metals in the dense bed that, under reducing conditions, promotes the carbonization reactions [8]–[14].

The metals can be extracted by the bed material, reactor parts and by plastic ashes. The size and nature of metals can lead to a strong accumulation of carbon inside the fluidized bed or to the elutriation of carbon fines towards the reactor freeboard. For example, if metals are linked to the bed material the carbon accumulates over the bed material particles by changing the composition of bed itself with a limited elutriation due to the mechanical attrition. If, on the contrary, the metals are extracted as nano-sized clusters the carbon accumulates over these nano-clusters that are entrained out the reactor. The knowledge of these behaviours is crucial information for the designer because of consequence on the correct operation of the reactor and on the performance of process.

III. Oxygen distribution in the dense bed

The extension of oxidizing reactions in the dense bed, or, better, in the emulsion phase of dense bed, depends on the effective availability of oxygen in that zone. A crucial aspect of BFB gasification modelling is related to the real availability of gas reactants with respect to the chemical reactions. The unavailability of oxygen, or any other oxidising agent, determines the occurrence of molecular rearrangement of hydrocarbons fragments and radicals into stable and heavy molecules (pathways B and C in Fig. 4). These latter are precursors of the most undesired by-products of gasification of plastics: carbonaceous particles and, overall, tars (pathway D in Fig. 4).

The equation related to the mass balance on oxygen with reference to the bubble phase is:

$$\frac{dC_{O_{2,b}}}{dz} = -k_m/U_b\cdot\left(C_{O_{2,b}}\Big|_z - C_{O_{2,e}}\Big|_z\right) \qquad (5)$$

In the case of complete consumption of oxygen in the emulsion phase due to the oxidation reactions the $C(O_{2,e})|_z=0$ and the equation can be solved as in the following:

$$C_{O_{2,b}}(z) = C_{O_{2,b}}(0)\cdot\exp(-k_m/U_b\cdot z) \qquad (6)$$

where: k_m is the mass exchange coefficient.

Following equation puts into relation the single bubble rising velocity (U_b) with the superficial gas velocity (U_g), minimum fluidization velocity (U_{mf}), bed diameter (D_{bed}) and bubble diameter (D_b):

$$U_b(z) = 0.35\cdot(32.2\,D_b/0.3048)^{0.5}\left\{\tanh[3.6(C_{b,z}/D_b)^{0.5}]^{1.8}\right\}^{1/1.8} \qquad (7)$$

This latter variable is obtained by:

$$D_b = \frac{0.62}{32.2^{0.2}}\left[\left(\frac{U_g-U_{mf}}{0.3048}\right)^{0.4}\right]\cdot\left\{\left[z+3.37\left(\pi D_{bed}^2/4\right)/N_{nozzles}\right]^{0.5}\right\}^{0.8} \qquad (8)$$

This model allows correlating the concentration of oxygen in the bubble phase at different level of the dilute phase of the bed with the main operating conditions and geometrical parameter of the reactor.

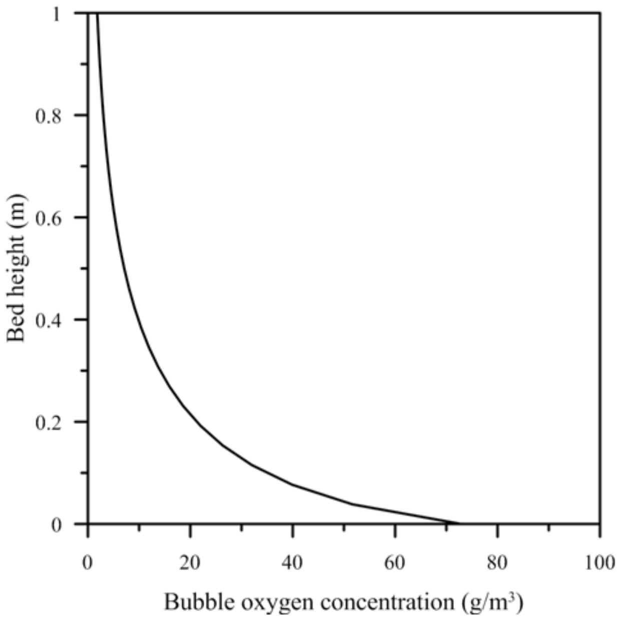

Fig. 5. Oxygen concentration profile (D_{bed}=1m).

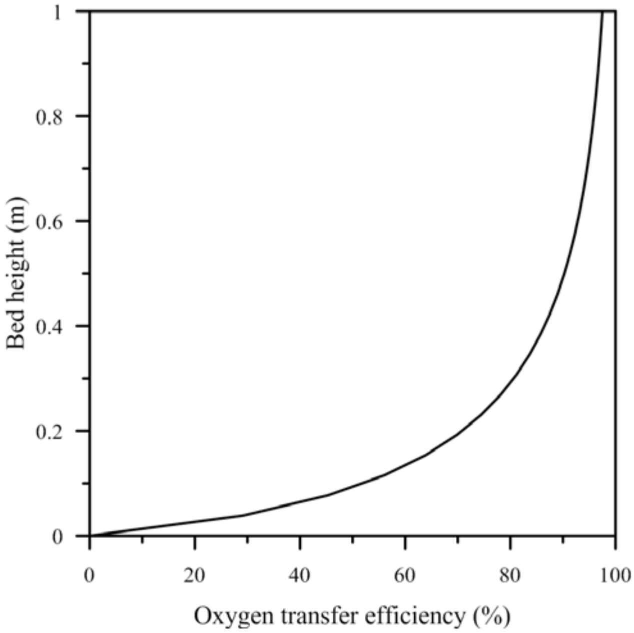

Fig. 6. Transfer oxygen efficiency (D_{bed}=1m).

Fig. 5 and 6 reports the oxygen concentration profile and the transfer efficiency of the oxygen along the dense bed as evaluated by using (6). It is evident that the bed height must be fixed in such a way to obtain the completeness of oxygen transfer in order to have the desired equivalence ratio in the dense bed (bed diameter has been fixed to 1m).

IV. DESIGN OF A BFB GASIFIER FOR PLASTIC WASTE

The design of a bubbling fluidised bed used to gasify plastic waste must taken into account both the typical hydrodynamics of a bubbling bed and the specific characteristics of the thermochemical transformation of the plastic waste. As reported in the previous paragraphs the gasification process performance of plastic waste is strongly linked to the BFB gasifier design and operation: type of bed material, bed height, position of fuel injection, freeboard height are variables that strongly affect the values of performance parameters and process stability. Figure 4 shows the inter-correlations between the main variables that affect the process performance of a gasifier. The role of bed temperature is crucial because of its influence on the heating rate, on the intrinsic kinetic rates of thermal cracking and chemical reactions as well as on aggregates lifetimes, as clearly demonstrated in the previous paragraphs. This means that its value must be fixed in a well-defined range and its optimal value must be guaranteed, for instance, by tuning of pre-heating temperature or by using a thermal wheel (e.g. steam). The temperature profile along the gasifier depends on the distribution and extension of endothermic and esothermic reactions as well as of thermal transport efficiency. In fact, as previously reported, the BFB gasifier is not an homogeneous reactor and the gasification process can be seen as a complex series-parallel sequence of reactions in a series-parallel sequence of reacting volumes having different hydrodynamics behaviour. This complexity leads to have a distribution of endo- and eso-thermic reactions in the reactor that affects the temperature profile.

In particular, the devolatilization process (drying and cracking) begins during the fuel falling down from the feeding location towards the dense bed (Fig. 3), here it is completed by determining heat absorption. Heat necessary to these physical and chemical transformations is provided by partial oxidation of the fuel (under form of radicals, fragments and char) in the dense bed (pathway A in Fig. 3). As before recalled, the extension of oxidizing reactions in the dense bed, or, better, in the emulsion phase of dense bed, depends on the effective availability of oxygen in that zone.

A crucial aspect of BFB gasification modelling is related to the real availability of gas reactants with respect to the chemical reactions. The unavailability of oxygen, or any other oxidising agent, determines the occurrence of molecular rearrangement of hydrocarbons fragments and radicals into stable and heavy molecules (pathways B and C in Fig. 3). These latter are precursors of the most undesired by-products of gasification of plastics: carbonaceous particles and, overall, tars (pathway D in Fig. 3). The formation of these products can be limited by increasing the equivalence ratio (λ), i.e. the overall oxygen content, from values of about 0.20 to values of about 0.35. The increasing of oxygen ratio leads to a decreasing of heating value of syngas, an increase of mean temperature and an increase of the syngas yield due to the shift between large fragments (liquids and solids) to gaseous products. A correct value of λ can be set on the basis of experimental data or industrial experiences but, in any case, its increasing to the maximum acceptable values does not guarantee the absence of undesired products due to hydrodynamic concerns. In fact, at given value of λ it is mandatory designing and operating the gasifier in order to enhance the contact between oxygen and fuel volatiles. The importance of this design step has been demonstrated by evaluating the oxygen distribution between the different zones of the BFB as highlighted in the Figs 5 and 6.

The mean value of oxygen mass exchange between bubbles and emulsion zone as evaluated in the case of Figs 5 and 6 is 26g/m^{2}s and it if referred to the transversal section occupied by the emulsion zone. For a typical lab-scale BFB of 100mm ID the mean value of oxygen mass exchange between bubbles and emulsion zone is about the same but, for a same ratio h_{bed}/D_{bed}, the oxygen transfer efficiency decreases to a fraction of 30%. This explains why the uncorrect value of h_{bed}/D_{bed} led to a strong production of intermediates, tars and PAHs. Another interesting feature to be taken into account during a gasifier design is the effect on the oxygen mass exchange between bubbles and emulsion zone of initial oxygen concentration. In fact, this rate increases up to 44g/m^{2}s for a fluidization stream composed by 35% oxygen instead of that typical of air (21%) because of the increased driving force. The utilization of oxygen-enriched air can then be a practical solution to reduce the reactor size and increase the mass transfer rate of oxygen.

V. CONCLUSIONS

Gasification of plastics in a bubbling fluidized bed is characterized by the peculiar mechanism of fuel-particles interaction that enhances the residence time of the fuel in the dense bed until the devolatilization (thermal cracking) is completed. The time necessary to complete the process from the beginning of heating (just after the injection) to the completion of devolatilization can be estimated by considering the heating stage as limiting the overall process rate. In the specific case reported in this paper, the plastic pellets having 6mm of mean size in a bed at a temperature of 850°C needs about 5s to complete the first step of the gasification process i.e. the transformation of the solid fuel into primary gaseous volatiles. The main indication for a correct design is the proper location of the injection of plastics that must be above the bed and not inside it. A proper location of the injecting point well above the dense bed allows to avoid the excessive and uncontrolled growing of the aggregates size that can occur if the plastics is injected directly into the hot dense bed/splashing.

The successive chemical reactions that primary volatiles undergo are of different types depending on the structure of primary volatiles and on the availability of reactants (oxygen, steam, carbon dioxide, etc.). The hydrodynamics of a bubbling fluidized bed is complex and the segregation of the oxygen in the bubble zone can favour the monomolecular as well as the recombination reactions of volatiles in the emulsion zone. The correct height of the bed, correlated to several geometrical and operating parameters, is crucial in order to guarantee a fast and complete mass interphase exchange of oxygen from bubbles to emulsion zone.

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