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Gasification of polyethylene in a bubbling fluidized bed operated with the air staging

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HIGHLIGHTS

- ▸ Experimental tests were carried out by feeding polyethylene in a BFB gasifier.
- ▸ The fluidized bed gasifier is an intrinsic two-stage reactor.
- ▸ The gasifying agent was injected with and without its splitting.
- ▸ The staging of the air stream can be a valid method to reduce tar formation.

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ABSTRACT

Gasification is a thermochemical process that converts different solid fuels into a synthetic gas (syngas) that can be utilized for different purposes. The possibility to gasify different kind of waste, as alternative to the traditional combustion processes, is attractive for several reasons, by way of an example the small scale of plants and the related social acceptability can be cited. Main constraint to a wide utilization of gasification is the parallel and undesired production of by-products that are mainly constituted by heavy hydrocarbons condensable at ambient temperature (tar) and carbonaceous particle fines. This work is conceptually divided into two parts: a description of the main reaction pathways occurring in a bubbling fluidized bed reactor operated as gasifier (BFBG) with the aim to highlight what is the pathway (and the reactor zone) that favors the heavy hydrocarbons formation; a discussion about experimental results obtained by operating a pre-pilot BFB gasifier under different operating conditions with the aim to reduce the formation of heavy hydrocarbons. The experimental tests have been carried out by feeding polyethylene in a BFB gasifier and by injecting the air stream, utilized as gasifying agent, in different positions: (a) at bed bottom (indicated also as primary zone) without any splitting of the flow rate; (b) at bed bottom and in the splashing zone, that is the volume just above primary zone, by splitting into two streams the necessary air flow rate; (c) at bed bottom, in the splashing zone and in the freeboard region, by splitting into three streams the air flow rate. Results indicate that staging of air stream can be a valid method to impede or reduce the formation of condensable compounds provided that air is well distributed in order to avoid segregation, the injection is made in the zone were heavy stable hydrocarbons are not yet formed and the splitting rates between primary and secondary streams is accurately calculated.

1. Introduction and scope

Gasification is a process that converts a fuel, e.g. coal, biomass, solid waste or a mixture of them (co-gasification), into a syngas mainly constituted by carbon monoxide and hydrogen, that can be addressed to an end-use apparatus to produce electric energy and heat with high efficiency or to a series of refining processes to obtain chemical feedstock [1]. Recently, the scientific literature focused on the possibility to gasify several type of waste (plastics, biomasses, wood, etc.) fed alone or together with traditional fuels like coals [2–5]. The main restriction to a wider utilization of gasification as a reliable process to obtain chemical feedstock is the parallel and undesired production of by-products that are mainly constituted by heavy hydrocarbons condensable at ambient temperature (tar) and carbonaceous particle fines [6]. These by-products lower the heating value of the syngas and limit the

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Abbreviations: ER, mass of oxygen provided for reactions/mass of oxygen necessary for stoichiometric combustion; Good, total mass used as reference in a balance; PAHs, poly-aromatic hydrocarbons; Tar, a mixture of heavy hydrocarbons with a molecular weight larger/equal of benzene.

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possibility to address the syngas to further high-performing process units. Definition of the best operating conditions and reactor design should be the main way to minimize the production of these undesired by-products rather than focusing most of the efforts to clean the "dirthy" syngas. In other words, the preferable methods to obtain minimization of these compounds should be the "primary" methods that allow avoiding expensive cleaning operations of the producer syngas downstream the gasifier. The primary methods include the utilization of catalysts [7,8], the optimization of operating conditions and the reactor design variation [9,10]. With particular reference to fluidized bed gasifier these primary methods can be all conceptually applied but their individual or synergistic benefits on the overall performance must be evaluated. A possible operating condition that could promote positive effects on the performance is the air splitting between different locations along the reactor. This method is well known with reference to combustion processes and it is utilized in order to favor the finalization of volatile oxidation. In the case of gasification, the range of operational modes by means of those the staging can be realized is wide: splitting of air; addition of pure oxygen (or carbon dioxide, steam, etc.) to one or more streams are examples of possible operation. The application of specific staging operations of the gasifying agent during a gasification process can be useful or not depending on the fuel characteristics and reactor hydrodynamics.

This work describes the experimental results obtained by operating a bubbling fluidized bed gasifier by feeding polyethylene and by injecting air as gasifying agent in three different modes: (a) at the bed bottom (indicated also as primary zone) without any splitting of the flow rate and (b) at the bed bottom and in the splashing zone, just after the primary zone, by splitting into two streams the air flow rate; (c) at the bed bottom, in the splashing zone and in the freeboard region, by splitting into three streams the air flow rate. The syngas has been sampled and analyzed at the exit of the reactor and the data have been elaborated to obtain the total and the elementary mass balances. All data have been further utilized in order to obtain some important performance parameters: carbon conversion efficiency, fraction of energy transferred from the fuel to syngas, syngas specific chemical energy and tar concentration in the syngas.

2. Descriptive model – the fluidized bed gasification as an intrinsic two-stage process

The bubbling fluidized beds are reactors characterized by a complex hydrodynamics due to the presence of different phases and different mixing degrees. The hydrodynamic structure of the bubbling fluidized bed is intrinsically not homogeneous since, at least, three macro-zones having different hydrodynamic behavior can be individuated: dense bed, splashing zone and freeboard. These zones are the places where complex meso-structures are formed and mixing/segregation patterns of gaseous and solids affect the effective rate of reactions. Specifically, the gaseous reactants as well the volatiles produced by the degradation of the fuel, just after its injection in the hot bed, are characterized to have a not uniform axial distribution and induce segregation phenomena [11,12]. Most of the research activity on mixing/segregation of volatile matter with respect to the fluidizing gas was based on coal and addressed to the combustion process but Nienow and Rowe [12] studied the devolatilization of plastic spheres in a hot bubbling fluidized bed and documented the formation of bubbles of volatile matter around gas-emitting particles. Experimental evidence led these authors to conclude that a "pseudo-buoyancy" force associated with volatile bubble formation acted on fuel particles and was ultimately responsible for particle segregation at the bed surface. Fiorentino et al. [11,12] have reported a comprehensive experimental and theoretical study of the bubble formation process around volatile-emitting particles, including high-volatile non-fossil solid fuels. They highlighted the conditions under which interaction between the gas-emitting particle and the emulsion phase results into the formation of an endogenous volatile bubble that eventually rises to the bed surface. The gas-emitting fuel particle may be dragged to the bed surface by the uprising endogenous bubble according to either single bubble segregation (SBS) or multiple bubble segregation (MBS) patterns. The former occurs when the first generated volatile bubble is able alone to "lift" the fuel particle to the top of the bed. This behavior has been confirmed by experimental studies on plastic gasification by Mastellone and Arena [13] that demonstrated that the actual reaction volume where devolatilization and oxidation reactions were concluded was a limited space between the upper side of dense bed and splashing zone. Therefore, the differences in terms of mixing efficiencies between the dense bed, the splashing zone and the freeboard have been enough well deepened in the literature even though the effect that this inhomogeneity has on the kinetic rate and the final composition of the gas produced in the BFB reactor is less clear [14], particularly with reference to gasification of non fossil fuels.

The main effect of the gas segregation, in the three macro-zones of the reactor and inside the dense bed, is that the oxygen necessary for gasification reactions could not be available where oxidation should occur by promoting undesired reactions of volatiles produced by the fuel cracking. In the specific case of gasification process, for which the oxygen-to-fuel ratio is lower respect to combustion process, the large part of the primary air, injected by means of the distributor located at the reactor bottom, is confined in the bubbles formed at distributor level and becomes progressively available for reactions during the bubbles raising along the dense bed until their eruption in the splashing zone. This implies that the equivalence ratio in the bed is much less than the value fixed as operating parameter. In other words, the gasification of volatiles produced by the thermal/catalytic cracking occurring in the dense bed does not occur homogeneously in the bed at the desired oxygen-to-fuel ratio but at a lower value that, on the other hand, depends on the spatial position since the establishment of an axial distribution of the oxygen concentration along the bed height.

The establishment of reducing conditions in the bed zone due to very low values of oxygen-to-fuel ratio leads to production of large amount of hydrocarbons, acids and ammonia that cannot be oxidized inside the bed and should be converted when and where there is the oxygen availability. The knowledge of reaction patterns, the kinetic rates of the main products as well as the identification of the reactor zones where these reactions occur is crucial to design and operate in a correct way a bubbling fluidized bed gasifier.

A schematic representation of the type of reactions mainly occurring in the above cited macro-zones of a BFB with the indication of the main intermediate and final products is given in Fig. 1. With reference to this scheme and by taking in mind what it has been before underlined related to the effective oxygen availability, is possible to draw the following considerations.

The oxidative reactants amount in the dense bed is not large enough to guarantee the oxidation of all the fragments produced by the cracking. These intermediates undergo two parallel reaction pathways: the small fragments in contact with the oxidizing reactants are converted to small stable molecules (CO, CO_2, CH_4, H_2O, H_2); another part of the produced volatiles undergoes uni- or bimolecular reactions to produce heavy stable molecules (benzene, naphthalene, phenantrene, etc.) [15]. The production of these heavy molecules is undesired since they constitute the precursors and the constituents of the so-called "tar" stream. Find a suitable meth-