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On the development of a polyolefin gasification modelling approach

Susana Martínez-Lera, Javier Pallarés Ranz *

University of Zaragoza/CIRCE, Mariano Esquillor Gómez 15, 50018 Zaragoza, Spain

HIGHLIGHTS

- A polyolefin air/steam gasification model for fluid bed reactors was developed.
- Contribution on the definition of pyrolysis, homogenous reactions and tar evolution.
- Model validation was performed against experimental tests and data from literature.
- The model is able to reproduce key gasification variables with acceptable error.
- The model provides a satisfactory prediction of tar generation.

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ABSTRACT

Gasification is a promising alternative for polymeric waste valorization when mechanical recycling is unfeasible on account of its heterogeneity or partial contamination, or simply when it yields a product of lower quality than what the market requires. Apart from its application for electricity generation, the waste-derived syngas shows a great potential for chemical waste recycling for the synthesis of hydrogen, methane, natural gas or methanol. In spite of the effort devoted so far to the experimental demonstration of these processes to enable this technology to access commercial stage, it is still necessary to develop detailed models of the process that allow a precise prediction of the resulting syngas composition, as well as tar formation and global efficiency of the process. This research work presents the development of a polyolefin gasification model for fluidized bed reactors. The model details the behaviour of primary pyrolysis and homogeneous reactions of oxidation, steam reforming, aromatization and thermal cracking. To accomplish this, it adopts new modelling strategies for the definition of primary tar species in order to reflect their twofold nature (aliphatic and aromatic), as well as to describe kinetics and stoichiometry involved in thermal cracking processes of tar species. The model is able to successfully predict the generation, volume composition and heating value of the syngas, final tar generation and global efficiency of the process.

1. Introduction

Plastic waste has a high potential for thermal valorization, since it is characterized by a high heating value and a wide availability. According to Plastics Europe [1], during the last decades polymeric material demand has continuously increased, reaching 48 million tonnes in Europe in 2014. The most demanded polymers in Europe are polyethylene (both high- and low-density), which accounts for 29% of the plastic market, and polypropylene, which represents 19%. Among these, packaging plastics (mainly composed of these two polyolefins) account for 39% of the global demand, a large part of which ends up in landfills after a brief useful life. As a consequence, a huge amount of residues is generated from these materials, which involves an enormous waste of resources and a constant source of pollution.

Despite the ongoing initiatives to reduce their volume by means of mechanical recycling, these residues are usually too mixed or partially polluted with organic matter. When this is the case, recycling means too great an effort to separate and pre-treat collected waste prior to its processing, and it often yields a secondary product with a considerably lower quality than what the potential market requires; this makes energy recovery much more attractive than recycling both in economic and environmental terms [2].

In this sense, different researchers [2–4] and international environmental institutions have so far recognized the energy potential of waste derived from these materials, and have analyzed the existing alternatives for their energy use. Among these, gasification

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* Corresponding author.
E-mail address: jpallare@unizar.es (J. Pallarés Ranz).

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processes seem to be easier to apply than direct combustion for particularly difficult waste (wet, low heating value, residual…) and, aside from electricity production, gasification-derived syngas shows a great potential for chemical recycling for the synthesis of hydrogen, methane, natural gas or methanol [5,6]. On the other hand, gasification requires a lower investment in gas cleaning for thermal processes, given its much lower volume gas production, and it also leads to lower emissions of nitrogen oxides, particles, dioxins, furans and unburned species [3,7].

Although plastic waste gasification is still at research stage, its technical feasibility is supported by a variety of studies of different research groups. In scientific literature, numerous publications can be found in relation to gasification experiments of plastic materials such as polystyrene [8,9], polyethylene [1,2], polypropylene [3,4,9], PVC [10], PET [11], used tyres [12], plastic residues and waste-derived fuels [13,14], as well as co-gasification of plastic and other fuels [15,16].

Nevertheless, one of the greatest challenges that waste gasification faces is the lack of a precise control of syngas properties as a function of the fuel (in particular, regarding its characteristic heterogeneity) and of operation parameters in terms of composition, tar production and efficiency [17–19]. Plastics are decomposed by means of thermal cracking based on radical depolymerisation, which takes place by random scissions of aliphatic chains [20]. This process leads to greater hydrocarbon content in the resulting syngas in comparison with other fuels, which in addition involves a larger residual tar production that must be eliminated prior to the gas valorization in internal combustion engines [21–23]. For this reason, in order to enable the transition of this technology to commercial scale, it is essential to develop models of the process that allow the facility design and control according to the requirements of the desired final product.

There are two main strategies to represent polyolefin pyrolysis in the model. The first one, represented by models such as those by Ranzi [20], Mastral [24], Levine [25] or Gascoin [26], carries out a comprehensive definition of radical generation and recombination processes, in which hundreds of chemical species and reactions take place. Even though this kind of models can provide detailed information on the final compound distribution, they require an extensive amount of input parameters and phenomena that must be modelled, such as [27]: the kinetics related to each of the existing chemical bonds; both physical and chemical properties of the huge number of involved molecules, including fusion and evaporation points, thermal phenomena, etc.; the definition of the ramification and saturation degree of each of the substances, as well as their tendency to evolve towards species of different nature; statistical definitions for each of the various reaction paths that a molecule can randomly take, etc.

The second alternative proposes a simplified representation of the process. Researchers such as Westerhout [27], Conesa [28], Aboulkas [29] or Al-Salem [30] have experimentally proved that it is possible to simplify the modelling of the processes, since at high conversion degrees the process fits well in simple pseudo-mechanisms ruled by first-order kinetics. This evidence is also supported by Wallis [31], who states that the process is best described by incorporating the experimentally measured initial distribution and approximating the population balance equations by lumping into representative compounds; when applied to a global model these compounds would later interact with each other through reactions expressed by means of simple kinetics. Typically, these are grouped as a function of their physical state (gas, liquid, solid waxes), their molecular weight (heavy, intermediate, light) or their chemical nature (aromatic, char, wax).

Basing on the described premises, this research work presents the development of a polyolefin gasification model for fluidized bed reactors. The model details the behaviour of homogeneous reactions of oxidation, reforming, aromatization and thermal cracking, and it adopts new modelling strategies for the definition of primary tar species in order to reflect their twofold nature, aliphatic and aromatic, and the kinetics and stoichiometry involved in tar thermal cracking. As reference fuel, low-density polyethylene (LDPE) was chosen for its greater availability in comparison to other polymeric residues and taking into account that, unlike other common plastics such as PVC, nylon or polystyrene, its direct recycling through reextrusion or depolymerisation is notably difficult [32], whereas its high heating value renders it particularly appropriate for high-efficiency thermal valorization.

Finally, the model was subjected to double validation by means of experimental tests performed in our pilot plant and also against other empirical data extracted from scientific literature, both of which have proven the model capable of reproducing the system behaviour under different operation conditions with acceptable error.

2. Polyolefin gasification model

The base structure of the simulation model is depicted in Fig. 1. Its main input parameters are, besides the reactor geometry, the properties of the involved solids (fuel and bed material) and operation conditions in terms of temperature (T), pressure (P), equivalence ratio (ER, defined as the molar relation between actual incoming O_2 and the amount that would be required for stoichiometric combustion), steam ratio (SC, defined as actual relation between incoming mass flows of steam and fuel at input conditions) and fuel mass flow (m_{fuel}).

Fuel is defined in the model by means of its immediate and elemental analyses, as well as its heating value. As for gasification agent flows, they are defined through the combination of several input parameters, namely fuel mass flow, equivalence and steam ratios. Given these parameters and the operation temperature, the first step of the simulation is the initialization of the variables that determine fuel and gasification agent conditions at their access to the reactor, including primary fuel devolatilization.

Simulation proceeds upwards in a sequential way by means of axial discretization of the reactor tank, so that it is assumed that there are no radial variations of concentration or temperature. The mesh divides the fluid bed into 1500 cells, whereas the solid-free narrow zone and the freeboard are each divided into 500 cells. Perfect mixing is assumed within a certain control volume, and for each one of these reaction velocities are evaluated as a function of gas concentrations that exit the previous lower cell. Initial concentrations at the base of the reactor are calculated basing on input conditions of the gasification agent, whereas instant primary pyrolysis is considered for incoming fuel at the height where the feeding system is located, according to the geometry of the reactor.

When thermal degradation of pure polyolefins is analyzed by means of thermogravimetric experiments (TGA) under inert N_2 atmosphere and heating rate of 10 °C/min (see Fig. 2), only a negligible amount of residue remains after the plastic decomposition, which corresponds to the limited amount of ash previously present in the materials, which shows that they contain no fixed carbon. This allows concluding that polymeric materials such as the ones considered here are fundamentally composed by volatiles so, unlike with other solid fuels, heterogeneous reactions will not take place in the gasification process.

In general terms, three sub-models can be considered in the global model:

1. Fluid dynamic model of the fluidized bed
2. Primary pyrolysis model