A Preliminary Modeling Study of a Fluidized Bed Pyrolyser for Plastic Wastes

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1. Introduction

The amount of plastic wastes is continuously growing and the fraction of plastic material in municipal solid wastes and refuse derived fuels is progressively increasing. Pyrolysis and gasification processes are promising routes for the upgrading of solid wastes to more usable material such as synthesis gas [1]. The characterization of pyrolysis behaviour of plastic wastes is then of interest in the optimization of pyrolysis processes for the recovery of valuable products. Moreover, a pyrolysis and devolatilization step is always present in the initial stages of gasification and combustion of solid fuels.

Compared to the other technologies for gas-solid reactions, fluidized bed reactors are particularly suitable for the pyrolysis of plastic wastes, such as polypropylene (PP) and polyethylene (PE). Bubbling fluidized bed hydrodynamics deeply affects physical and chemical properties such as the heat and the mass transfer, the gas-solid mixing, their contact and their residence time. The degree at which these properties are influenced, depends on many important variables such as the kind of polymer feeding (in-bed or over-bed), the operating temperature, the height of the freeboard, the size and density of bed particles, the height to diameter ratio of the bed [2]. Particularly, it has been experimentally proved that in a bubbling fluidized bed, operated at 600°C, in which plastic such as PE and PP are fed over-bed, the pellets completely melt during their passage through the freeboard [3]. Thus, they reach the bed in a liquid phase and soon envelope the sand particles, forming a whole aggregate. At the operating temperature the PE and PP viscosities are particularly low, so that the liquid-liquid surface tension is weaker than the liquid-solid one. As a result the aggregate soon separate in many singular sand particles each enveloped by the melted polymer.

2. Fluidized bed pyrolyser

2.1. Experimental apparatus

A sketch of the experimental apparatus is reported in Fig. 1. The bubbling fluidized bed reactor, in which the runs were carried out, has an internal diameter of 110mm and a height of 1.05m. The whole reactor is warmed by means of an electric heater and the temperature is monitored in the bed and in the freeboard. The former is controlled, so that it is preserved at a value of 600°C during the process. The latter is just measured and experimentally has been observed that it reaches values up to 900°C in the upper part of the reactor (∼0.90m). This temperature is the result of the combination of the sensible heat of the gas coming from the fluidized bed (∼0.15m) and the heat directly supplied by the electric heater.

The experiments were carried out by feeding polyethylene (PE) over-bed, by means of a screw-feeder located at the top of the freeboard. The plastic material melts during its passage

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along the freeboard, so that it reaches the bubbling bed in a liquid phase, enveloping sand particles.

Figure 1 Experimental apparatus for the gasification and pyrolysis of plastic materials.

2.2. Schematization of the system

Rising along the bubbling fluidized bed, the bubbles coalesce and grow, carrying clusters of solids (fuel and sands) up to the surface. During this rising, part of the carried solids slide down, thus guaranteeing a very effective gas-solid mixing in the bed. As a consequence of this phenomenon and of the high thermal capacity of the sand, isothermal conditions set up in the bed region. On these basis, this part of the reactor can be modeled as an isothermal perfectly stirred reactor (PSR) at 600°C. A typical gas contact time in the fluidized bed is about 0.5-1 s.

When bubbles reach the interface between the bed and the freeboard, they burst tossing the part of solids they were carrying on their upper surface. Because of this phenomenon, the so called splash, the mixing reached in this zone is high enough to model even this part of the system with a similar isothermal PSR. Then, a plug flow of the gas is hypothesized in the freeboard, so that a plug flow reactor with given temperature profile can be reasonably used. Temperature profile moves from the bed temperature (600°C) up to the temperature measured at the freeboard top (900°C). This schematization of the pyrolyser with a very simple sequence of ideal reactors gives useful preliminary information and is reported in Fig. 2. The degradation of polyethylene and the successive reactions in the gas phase will be discussed in the next paragraphs.
2.3. Polyethylene decomposition

The detailed kinetic model of PE and PP thermal decomposition is already described elsewhere [4]. This model is able to predict the degradation of the polymers in a wide range of operating conditions, both in isothermal conditions and in dynamic runs with different heating rates. As a matter of simplicity, here we only consider PE degradation.

Figure 3 reports a couple of comparisons between model predictions and experimental measurements of PE decomposition at different heating rates (5°C/min and 8°C/min), the model agrees well with the experimental measurements in both cases. This detailed model is also able to predict the product distribution under different conditions. Figure 4 shows an example of comparison between predicted and experimental alkene distribution for isothermal pyrolysis of PE at 600°C. As already discussed, this product distribution is released in the fluidized bed and is subject to successive degradation rising along the freeboard.
2.4. Kinetic modeling of products formation from PE pyrolysis

As already shown in Fig 2, the successive evolution of these products in the gas phase is studied in an ideal plug flow reactor. To these purposes, a detailed kinetic scheme is used for the homogeneous pyrolysis of hydrocarbons [8, 9]. Preliminary simulation results clearly indicate that the product distribution at the end of the freeboard is only weakly sensitive to the initial product distribution. The residence times (0.5-2.5s) and temperatures (600-1000°C) investigated in the freeboard allow the system to rapidly transform the initial heavy products mainly into hydrogen, methane and ethylene, regardless of the starting distribution as long as the H/C ratio remains about 2. These observations make the preliminary calculations simpler and n-cetane (nC_{16}H_{34}) can be directly used as a surrogate of the primary PE degradation products. Indeed, the product distributions at the exit of the freeboard calculated with the detailed PE distribution or with n-cetane are very similar in both cases.

![Graph comparing calculated and experimental alkene product distribution](image1.png)

*Figure 4* Alkene product distribution from isothermal pyrolysis at 600°C. Comparison between experimental data and model results [7].

![Graph showing mass fraction profiles of alkenes vs. residence time](image2.png)

*Figure 5* – Mass fraction profiles of alkenes vs. residence time in an isothermal plug flow reactor at 1100 K (left) and 1200K (right).
These points are better clarified in Figure 5, where the evolution of alkenes are plotted along the contact time at 1100 K and 1200 K. The initial degradation of the polymer surrogate to form small alkenes is very fast, in fact species with more than 4 carbon atoms, once formed, are rapidly consumed in the earliest stages of the reactor, in less than 0.1-0.3 s. Propene and ethylene are relatively more stable. At 1200 K only ethylene survives at residence times similar to those of the freeboard. These model predictions well agree with the preliminary experimental measurements obtained in the pilot units at different fluidization velocity (0.1-0.3 m/s). Alkenes with 3 or more carbon atoms are not observed at the end of the freeboard.

Figure 6 shows the mass fraction profiles of the major species, always at reference temperatures of 1100 K and 1200 K. In these long residence time and high temperature conditions, the most important pyrolysis products are H2, CH4, C3H4, C2H2 and also aromatic species, such as benzene and naphthalene. These condensation products account for more than 20% of the total mass. The formation of aromatic species will be better discussed in the next paragraph. Acetylene, allene, propadiene and butadiene are important precursors of aromatics. Mainly acetylene fraction is a good indicator of the peak temperature in the system.

\[\text{Figure 6} – \text{Mass fraction profiles of major species vs. residence time in an isothermal plug flow reactor at 1100 K (left) and 1200K (right).}\]

### 2.5. Pollutant formation (PAH)

High temperature pyrolysis of PE and PP, but also the gasification of plastic materials under sub-stoichiometric conditions, favors the formation of benzene and Polycyclic Aromatic Hydrocarbons (PAH), even if the plastic material fed to the reactor does not contain aromatic structures. Important pathways responsible for this formation of PAH are the HACA mechanism (H-abstraction and C2H3 addition) [10] and the recombination of resonantly stabilized radicals such as cy-C3H5 [11] and C3H3 [12]. Both these mechanisms are included in the kinetic model, together with the formation of cyclopentadiene, important precursor of benzene in these conditions.

Mass fractions of important PAH as predicted by the model at the end of the freeboard are reported in table 1. The sum of PAH increases with increasing temperature, while benzene and naphthalene slightly decrease because of successive reactions forming larger species.
Table 1 – Mass fractions of aromatic species at the end of the freeboard

<table>
<thead>
<tr>
<th></th>
<th>900°C</th>
<th>950°C</th>
<th>1000°C</th>
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<tbody>
<tr>
<td>Benzene</td>
<td>0.12</td>
<td>0.12</td>
<td>0.11</td>
</tr>
<tr>
<td>Styrene</td>
<td>0.015</td>
<td>0.022</td>
<td>0.025</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>0.11</td>
<td>0.115</td>
<td>0.10</td>
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<tr>
<td>Phenanthrene</td>
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<td>0.023</td>
<td>0.031</td>
</tr>
<tr>
<td>Pyrene</td>
<td>0.008</td>
<td>0.016</td>
<td>0.023</td>
</tr>
</tbody>
</table>

3. Conclusion

A preliminary kinetic study of PE pyrolysis in a fluidized bed reactor was carried out by means of a detailed kinetic scheme in very simplified conditions. The mechanistic model of plastic degradation correctly predicts the conversion profiles and the primary product distribution. Model predictions showed that the product distribution mainly depends on the conditions in the freeboard rather than in the bed, due to the long residence times and the high temperatures. Aromatic species account for more than 20% of the products, on mass basis.

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5. References