## Multicriterial methodology for mixed plastic waste pyrolysis management

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The problem of plastic waste represents one of the most critical environmental challenges of our time. While mechanically recyclable plastics find their way into established reuse circuits, a significant fraction of plastics are mixed and difficult to recycle and are destined for landfill or incineration (Liu et al., 2024). Plastic films, multimaterials, additive-laden polymers, and thermoset plastics fall into this category of problematic waste, for which mechanical recycling is challenging for reasons of recycled material quality, separation costs, and degradation of physical-mechanical properties (Lorang et al., 2022).

To address this critical issue, chemical recycling, in particular, enables the transformation of polymers into valuable chemical compounds, and offers the possibility of processing plastics that traditional mechanical recycling is not yet able to process. Among chemical recycling technologies, pyrolysis is emerging as one of the most promising solutions for processing heterogeneous and difficult-to-manage plastic waste (Fadillah et al., 2021)

Pyrolysis is a thermal process in the absence of oxygen that converts plastics into a mixture of gas, oil and solid residue. The main advantage of this technology is the ability to process mixed plastics without the need for careful separation of the polymers, producing pyrolysis oils that can be reused as feedstocks for the synthesis of new polymers or fuels, or as feedstock for refineries, which are able to produce the starting monomers of the plastics themselves for recycling (Peng et al., 2022).

However, not all polymers behave the same during pyrolysis. Polyethylene (PE) and polypropylene (PP), for example, decompose with high yields in oil, making them ideal materials for this process. Polystyrene (PS) decomposes mainly into styrene monomers, which can be easly recovered and reused (Onwudili et al., 2009). In contrast, polymers containing heteroatoms, such as PET and PVC, pose significant issues: PET releases undesired oxygenates, while PVC produces hydrochloric acid, leading to corrosion issues and the need for specific treatments to neutralize gaseous effluents (López et al., 2011).

In addition to the production of different chemical compounds, the various polymers thermally degrade in similar but in some cases different temperature ranges. These differences in behavior during the process raise questions about the optimal configuration of a pyrolysis plant for the treatment of waste plastics. In a context where pyrolysis is being adopted on a large scale, the question arises whether it is preferable to adopt a single reactor capable of processing mixed plastics or a configuration with several reactors in parallel, each optimized for a specific type of polymer. A single reactor simplifies process management and reduces investment costs but could result in lower yields and difficulties in product quality control. In contrast, a configuration with multiple reactors allows the process to be optimized for each polymer, improving the selectivity and quality of the final products, but introduces additional energy costs and greater operational complexity, requiring hard sorting of incoming plastic waste. Understanding which plant configuration is most appropriate for pyrolysis of waste plastics is essential to maximize the benefits of this technology and ensure more sustainable management of waste plastics.

In this study, a methodology was developed to evaluate the best plant configuration for pyrolysis of the most common mixed waste plastics (LDPE, HDPE, PP, PS, PET, and PVC).

To do so, a pyrolysis model was implemented in Matlab that includes both the chemical kinetics of each polymer, but also the thermodynamics of the process so that the energy aspects could also be evaluated. The reactor chosen is a plug flow, which is divided into two sections: the upper one where the volatiles released during the pyrolysis process are located along with the carrier gas used to transport those volatiles, in this case nitrogen; the lower one where there is the incoming feedstock that over time transforms into its products. The simulations carried out thus investigated three general scenarios: pyrolysis of each polymer within a single reactor, pyrolysis of mixes of plastics within a single reactor, and finally intermediate configurations were investigated, such as a reactor dedicated to pyrolysis of polyolefins and other single reactors for each polymer. An example of a result related to the pyrolysis simulation of one of the investigated polymers, in this case HDPE, is shown in Fig. 1

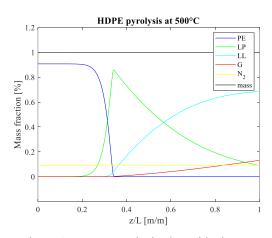


Figure 1. HDPE pyrolysis alongside the reactor

Where: PE is the polyethylene feed, LP is the heavy oil, LL is the light liquid, G is the gas and  $N_2$  is the nitrogen mass flow. All the process has to guarantee a total mass balance equal to 1.

Finally, a configuration performance index (CPI) written as:

$$CPI = w_1 * F_{yield} + w_2 * F_{quality} - w_3 * F_{energy}$$

where:

- $F_{oil}$  = Factor associated to oil and gas yield.
- F<sub>quality</sub>= Factor associated to products quality (taking in to account contamination concentration, paraffins/olefins, aromatics content).
- $F_{energy}$  = Factor associated to the requested energy during the process
- $w_i$  = importance weights of parameters.

The three factors, namely  $F_{\text{oil}}$ ,  $F_{\text{quality}}$ ,  $F_{\text{energy}}$ , are evaluated for obtaining a maximum CPI equal to 100. The higher this index, the better the performance of that configuration. Table 1 shows the indices for the three configurations considered.

Table 1. CPI of the considered plant configuration

|     | Single reactor | Multiple reactor | Intermediate configuration |
|-----|----------------|------------------|----------------------------|
| CPI | 39             | 58               | 63                         |

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