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Waste thermoplastic pyrolysis in a reactive distillation system

Godinho T.[1,*], Lemos M.A.N.D.A.[1], Lemos F.[1]

[1]CERENA, Chemical Engineering Department, Instituto Superior Técnico, Lisboa, Portugal;

* tiago.dos.santos.carrasco.godinho@tecnico.ulisboa.pt;

Motivation

The world plastic production has been increasing continuously, mostly due to the increase in world population and the development of the Chinese market. Although it had positive effects, the increase in plastic production also caused increases in the consumption of fossil carbon and in the accumulation of plastic waste with consequences in global warming and environmental pollution (Plastics Europe, 2019). Efficient management of plastic waste is therefore necessary to minimize those problems, having this to be based on the maximization of recycling and energy recovery processes, which will help to promote the reduction of landfill usage and a more circular economy (Figure 1).

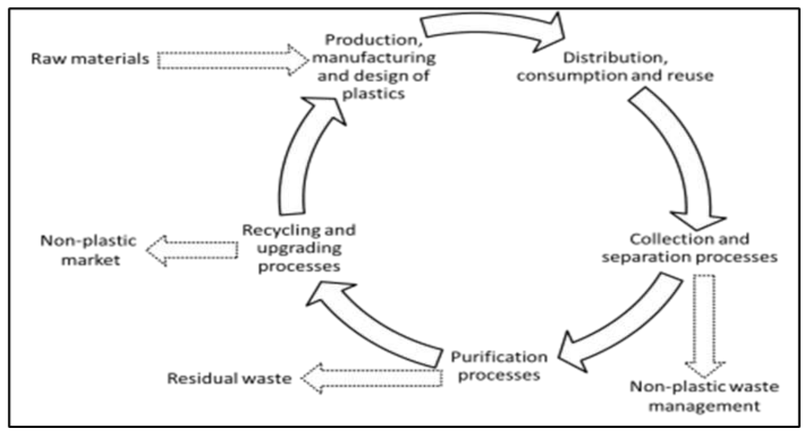

Figure 1- Circular economy of plastics.

One way to increase plastic waste recycling is with the use of tertiary recycling processes, as they are capable of processing contaminated or mixed plastics, that would otherwise be incinerated or landfilled, converting them into high-value products.

Plastic pyrolysis has been studied in many contexts, being this mostly studied in laboratory scale equipment. Extensive work is often done on the thermal degradation of pure plastics, although there are some studies on contaminated plastics, which can show many operational problems, as these don't usually degrade entirely to lighter molecules, producing also heavy compounds that can be deposited on process lines (S. Dayana et al., Energy Convers. Manag., vol. 115, pp. 308–326, 2016). However, since waste plastics are cheap and widely available, it's highly important to develop methodologies to allow their recycling, as the resulting processes are essential to improve on the current plastic pyrolysis technology.

Thus, this work focuses on the study of an innovative pyrolysis process of major fractions of plastic waste, Polypropylene (PP), High-Density Polyethylene (HDPE), Low-Density Polyethylene (LDPE) and Polystyrene (PS) to evaluate the feasibility of performing efficient pyrolysis on waste plastic, reducing the operational problems caused by high boiling-point species.

Methods and Results

Experiments using waste single type plastics (PP from food packages, HDPE from detergent bottle, LDPE from film and PS from coffee cups) were carried-out in a simultaneous thermal analyzer (DSC-TG) and in a semi-batch bench-scale reactor. Before use, all waste plastic samples were cleaned and crushed/shredded into small size particles with a granulometry between 2-4 mm using a cutting mill Retsch 2000.

DSC-TG

All experiments were performed in a Perkin-Elmer simultaneous thermal analyser 6000 in dynamic conditions with a sample size of around 20 mg in alumina pans under a nitrogen flow of 20 ml/min.

The temperature was initially stabilized at 40 ºC for 10 minutes and then heated at 10ºC/min, up to 700ºC; this temperature was maintained for 10 minutes, before cooling. Blank experiments with empty pans were used to establish adequate DSC baselines.

The results are depicted graphically in Figure 2.

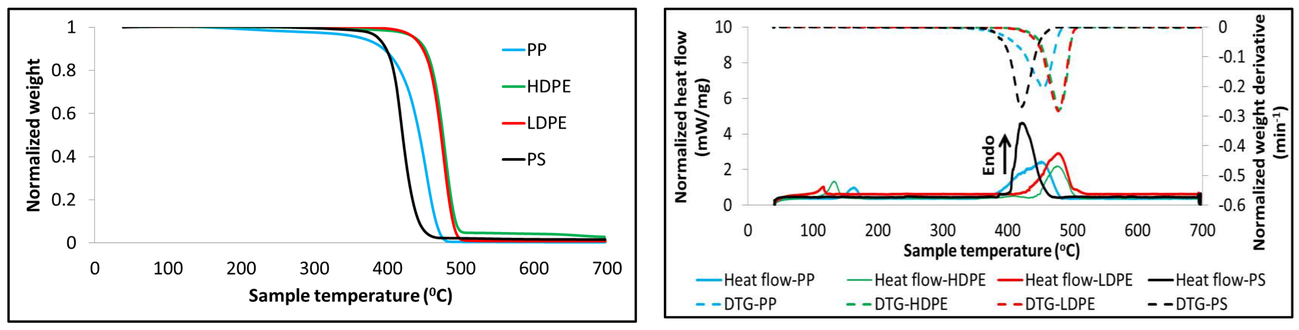

Figure 2- Thermal analysis of waste thermoplastics.
Left) Normalized weight loss. Right) Normalized weight derivative and heat flow.

Semi-batch reactor

A lab-scale semi-batch reactive distillation system previously described was used (E. Santos et al., Catalysis Today, vol. 379, pp. 212–221, 2021). The temperature inside the reactor was measured continuously and the products (heavy mixture, liquid and gas) were separated. Liquid products were analyzed in a Perkin-Elmer Clarus 680 gas chromatograph.

In a typical run, around 5 g of the reactant was introduced into a Schlenk-type glass reactor of 0.1 dm³. The reactor was placed in an oven and connected to a liquid collection system, topped by a condenser cooled by water at 20 ºC. The outlet of the condenser was connected to a gas burette. The system was filled with nitrogen and the reactor was heated, at a rate of 10 ºC/min, up to 500ºC, which was kept for 90 minutes.

Product yields were calculated by weighing the corresponding fractions, except for gas yield which was computed by difference. The results are represented in Figure 3.

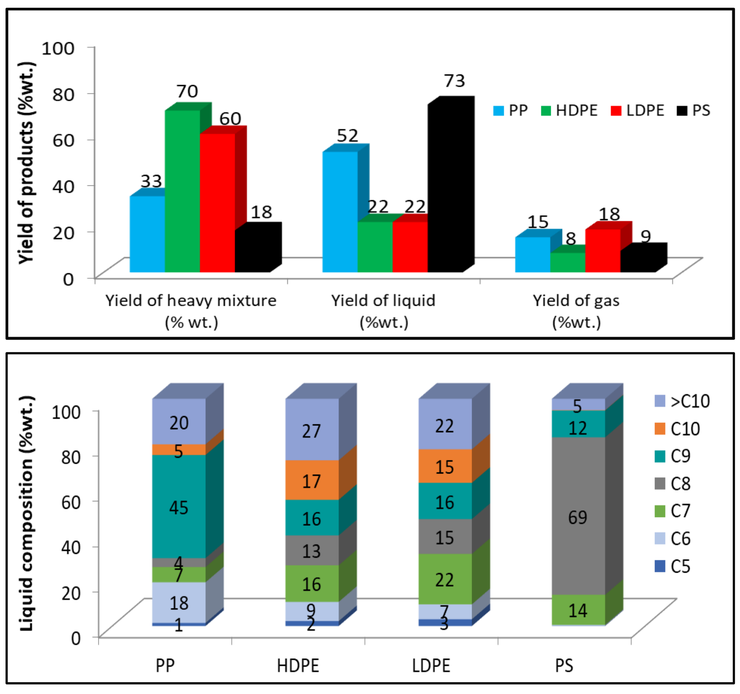

Figure 3- Yield and composition of the liquid products obtained in the semi-batch reactive distillation system.

Main conclusions:

- Waste plastic degrades at operating temperatures below 500ºC, into useful hydrocarbons, which have a very high olefinic content and can be introduced in petrochemical production lines;
- PE plastics have low melting temperatures, conversions, and productions of olefinic light distillates, while having high degradation temperatures;
- PP plastics have high melting temperatures and moderate degradation temperatures and conversions;
- PS plastics degrade at low temperatures, have high conversions and produce high amounts of aromatics;
- It's feasible to perform a viable pyrolysis with high-quality light products from low quality waste polymers, particularly of PS and PP types, which can promote a more circular economy, while also minimizing the harmful impacts of the conventional cycle of consumption and production of plastics and improving the current state of the plastic pyrolysis technology.

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