

Pyrolysis of post-consumer plastic: from waste to valorized industrial resource

Abstract

In the last century, plastic has increasingly spread in use. However, its general resistance to natural degradation becomes problematic when facing its disposal. In 2022, 26.9 wt.% of the collected plastic waste was sent to recycling, almost exclusively encompassing mechanically recyclable plastics. Non-mechanically recyclable plastics were instead sent to landfill (23.5 wt.% of overall plastic waste) or incineration (49.6 wt.%). To tackle the issues of the landfill soil occupation, and to increase the recycled plastics amount, new sustainable disposal options are imperative. However, not all plastic can be mechanically recycled. Therefore, chemical recycling treatments, including pyrolysis, have been investigated in recent decades, for production of chemicals, new plastics, or fuels.

Plastic waste can be significantly heterogeneous. Municipal plastic waste (MPW) is usually mainly composed of polyethylene (PE, 43 wt.%) and polypropylene (PP, 25 wt.%), whereas waste electrical and electronic equipment (WEEE) plastic is usually mainly composed of acrylonitrile butadiene styrene (ABS, 27 wt.%), and PP (22.4 wt.%). While MPW and WEEE are on average composed of >90 wt.% plastics, automotive shredder residue (ASR) waste is composed of only 28 wt.% plastic, in turn composed of PP (25.6 wt.%), and polyurethane (PU, 16 wt.%). Moreover, metals and semimetals contamination can be significant.

Pyrolysis, particularly suitable for treating contaminated waste, is a thermal degradation of the feedstock under inert atmosphere, at temperatures ranging from 400 to 650 °C for plastics, yielding a gaseous phase, an organic liquid phase (called oil), and a residual solid phase (called char). Usually, oil is the desired product of plastic waste pyrolysis, with PE, PP and PS producing the highest amount of oil. A review of the literature on plastic waste pyrolysis highlighted the feedstock composition and the pyrolysis temperature to be crucial to the yields, with 450-500 °C being the optimal temperature for oil yield, being generally between 55 and 80 wt.%, when pyrolyzing a plastic waste with 0% non-plastic materials at 500 °C. Despite multiple configurations being suitable for plastic pyrolysis, such as the fluidized bed, the stirred tank and the screw reactors were the most commonly employed configurations industrially. An analysis of the composition and physical properties of MPW oil, based on literature data,

revealed that usually the oil contained a roughly even unsaturated aliphatics (35-50 wt.%) and saturated hydrocarbons (up to 40 wt.%) content, and a variable concentration of aromatics (from 1 to 29 wt.%). Also, roughly 30-50 wt.% of the hydrocarbons in the oil were in the typical boiling range of diesel petroleum cuts.

Oil characterization was used to assess its valorization: feedstock for steam cracking ethylene production, substitution of conventional diesel fuels, extraction of styrene for PS production, production of additives for bitumen. The investigation revealed oil not to be suitable as a drop-in material, either due to aromatics and unsaturated hydrocarbons content exceeding steam crackers technical standards (e.g., alkene content <2 wt.%), or not matching the standards for automotive diesels (EN 590). Therefore, an upgrading process of the oil was often required; usually, hydrotreatment was performed, to remove contaminants and convert unsaturated hydrocarbons into alkanes and reduce aromatics content.

The char was investigated for use as sorbent material, testing the adsorption of methylene blue in aqueous solution, simulating textile wastewaters remediation. The study revealed an adsorption capacity of the char (5.8 mg of methylene blue/g of char) comparable to non-activated biochars, confirming the plastic char to be a promising sorbent material, albeit activation would be required to compete with active biochars.

To valorize the pyrolysis gas, two samples were collected from two different pilot-scale reactors, and their lower heating value was compared with empirical thermal requirements of pyrolysis taken from literature. The investigation showed that the amounts of carrier inert gases used for the pyrolysis severely affected the generated energy, as expected, with only one sample being able to fully sustain the pyrolysis.

Lastly, a preliminary life cycle assessment (LCA) study was performed, to assess the global warming impacts of the pyrolysis and compare them with those of incineration. The pyrolysis global warming impacts (590 kg CO₂ eq/t MPW) were lower than those of incineration, with the required electricity to be the highest contributor to the climate change impacts.