

# Microwave-assisted valorisation of unsortable thermoplastic waste

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## Introduction

Increasing plastic demand, its imprudent accumulation and landfill disposal are well widely known as critical burdens for the current environmental crisis. For this, chemical recycling is accepted as the most promising pathway to readily access plastic depolymerisation, accessing to new feedstock for the production chain; however, most plastic chemical recycling strategies have evidenced to still lack of a clear viability on substituting linear fossil economy. Generally, the complexity of plastic waste streams and the chemical process fragility, both often lead to deficient process efficiency and stability, plus insufficient carbon recuperation from waste polymers to new plastic monomers. Among chemical recycling pathways, thermo-chemical reactions represent the most robust strategy, which do not need of severe feedstock pre-treatment and offer higher process flexibility to heterogeneous plastic waste compositions.<sup>1</sup> In this framework, microwave-assisted pyrolysis emerges as a potential technology to improve plastic waste and biomass conversion to fuel or chemical feedstock for new plastic production. The selective MW-heating and the immediate effect of microwave power source switching on sample heating and cooling permit the unrivalled control of operational parameters and gas-phase reaction quenching, thus, establishing a promising enhanced control over the process chemistry and product's distribution.<sup>2</sup>

The aim of this work is to validate the benefits of plastic waste valorisation through novel microwave-assisted pyrolysis (MAP) technology and enroll further efforts to overcome its main barriers hindering technological maturity and upscaling. Despite its potential and rapidly growing interest, the use of MAP for plastic waste valorization is still an incipient field, and, as such, examples of operating pilot or demonstration plants are still scarce.<sup>3</sup> So far, the most hindering bottlenecks for the technology validation are:

- 1) Processing volume/mass microwave absorption correlation with feedstock's dielectric properties
- 2) Reactor cavity design
- 3) Precise operational parameters control for bio-oils fraction properties and optimization

With these limitations, our work aims to tackle synergically the previous challenges to overcome the former technology bottlenecks and validate a production methodology for bio-oil with suitable properties to new plastic production starting from unsortable thermoplastic waste mixtures based on polyethylene, polypropylene and polystyrene (PE, PP and PS).

## Experimental procedure

For this purpose, residual low-density polyethylene (LDPE)-rich samples containing variable amounts of PP and PS were selected as target plastic stream to be valorized using the proposed MAP technology. First, a deep assessment of LDPE dielectric properties was carried towards with silicon carbide (SiC) as chosen microwave susceptor to ensure the fast and moderately homogeneous pyrolysis temperature achievement of LDPE:SiC mixtures. Figure 1 shows preliminary studies of dielectric properties (dielectric constant, dielectric loss, and loss tangent) of SiC particles (particle diameter,  $d_p = 1 - 2$  mm) for microwave heating.

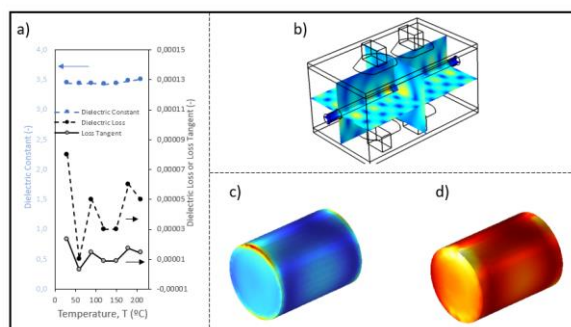


Figure 1. a) Temperature-dependent dielectric properties characterization for plastic waste/MW-susceptor blends; b) Simulation of the electromagnetic field distribution (EMFD) within a 800 mL tubular reactor and rectangular MW cavity featured with four mode stirrers, irradiated at 2.45 GHz by a 3.2 kW power magnetron; c) simulated EMFD at fixed bed sample volume; d) simulated temperature distribution at the plastic/susceptor blend.

The previous results served as key inputs for the cavity modelling by COMSOL Multiphysics software, which integrates numerical methodologies to simulate the electric field distribution and resonant modes enabled inside the cavity

by the samples, ultimately simulating the theoretical efficiency of the microwave-assisted heating. reports current studies of authors' microwave oven cavity and its electromagnetic (EM) field distribution upon LDPE/SiC blended samples heating (configured as 10 cm long fixed bed placed inside a cylindrical quartz tube reactor), whilst c and 1d report resulting preliminary EM field and temperature distribution along the sample volume, respectively.

In parallel, an experimental MAP set-up was arranged for empirical trials in order to test and optimise the MW-assisted thermochemical contactor configuration and the waste LDPE suitability for bio-oil production. Figure 2a and 2d show current experimental set-up and sample arrangement, highlighting the potential of the MAP system for reaching very high local temperatures at the sample volume ( $> 800^{\circ}\text{C}$ ), if required. Figure 2b shows a thermal image of the heated sample, in which a temperature gradient beyond  $300^{\circ}\text{C}$  is measured between the sample bed and the surrounding void region, demonstrating the great heating efficiency that MAP can attain over conventional convective heating. Furthermore, Figure 2c shows a sample of bio-oil recovered from waste LDPE valorisation via MAP.

## Results

The obtained bio-oils from plastic waste streams must suit characterized specific properties, composition, and criteria required for steam cracking refinery-like facilities, such as low aromatic contents. Hence, operational parameters as reaction and residence times, temperatures and/or hydrocarbon chain lengths selectivities must be experimentally assessed. The key advantage of the proposed system and main finding of this work was the mitigation of downstream secondary gas-phase reactions due to the sharp temperature decay beyond the sample bed, thus, obtaining primary cracking products as pyrolysis oil. The obtained hydrocarbons are mainly linear in the range C10 – C20 with up to 1 or 2 chain insaturations, avoiding the production of aromatics and, thus, increasing the H/C atomic ratio in the resulting oil. As a result, this hydrocarbon pool is preferred in case the oil is further employed as naphtha additive for sustainable steam cracking purposes.

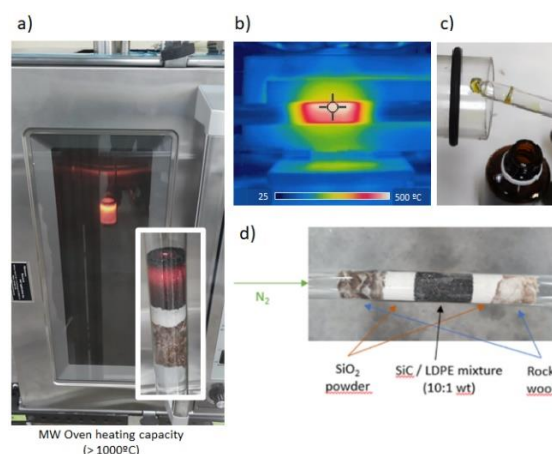


Figure 2. a) Experimental MAP plastic waste operation b) Thermal gradient IR measured image; c) bio-oil recovery d) experimental set-up of plastic waste- SiC bed in MW-transparent quartz tube.

## Conclusions

This research work targeted the integration of processed bio-oils into new plastic production environments for circular economy demonstration via energy-efficient MW-assisted pyrolysis. This technology succeeded in the generation of highly hydrogenated linear oils, thanks to the selective heating provided by MW irradiation and the significant temperature gradient attained between the heated sample and the comparatively colder surrounding atmosphere. An additional advantage of MAP systems lays in the fact that the process can be fully driven using energy from renewable sources and, thus, contributes to thermo-chemical processes decarbonisation.

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