

# Abstract

The global transition towards a less fossil-dependent, circular economy demands innovative technologies for the alternative production of fuels and industrially-relevant chemicals. This should be done in complementarity with the management of persistent waste streams, primarily end-of-life plastics and lignocellulosic biomass. *Ex-situ* catalytic fast pyrolysis (CFP) presents a flexible platform for the valorization of biogenic and non-biogenic carbon sources. This study investigates the potential for upgrading pyrolysis vapours derived from waste polyolefins and olive stone biomass using a dual spouted-bed/fixed-bed pyrolysis unit. It provides insights in the understanding of how these chemically distinct feedstocks behave under comparable process conditions. The influence of key process parameters on product distribution, catalyst performance and deactivation was examined, highlighting the specific challenges and opportunities associated with each material.

This work begins with a detailed state-of-the-art furnishing a comprehensive overview of the potential roles of biomass and plastic waste in the transition towards a sustainable and circular economy and of catalytic cracking of pyrolysis volatiles as a strategy for upgrading raw pyrolysis products. The mechanisms of catalytic fast pyrolysis (CFP) are explored, including the role of different catalyst types (zeolites, metal oxides, and basic materials) in reducing oxygen content, and improving fuel quality. Particular attention is given to the challenges posed by the chemical diversity of biomass- and plastic-derived vapours, and how catalyst design and process conditions can be tailored to address these issues. Subsequently, the materials and methods used in the experimental investigation are described in detail. This includes the characterization of feedstocks (a polyolefin mixture and olive stone biomass), the selection and preparation of catalysts, the design and realization of a dual spouted-bed/fixed-bed pyrolysis reactor and the experimental procedures used to quantify product yields, assess catalyst performance, and evaluate deactivation phenomena.

The results obtained can be synthesized as reported: the investigation into polyolefin upgrading over a HZSM-5 zeolite revealed a trade-off between the production of light olefins and BTX aromatic hydrocarbons. The catalyst is able to completely crack heavy waxes, and a clear optimum was identified for light olefins (C<sub>2</sub>-C<sub>4</sub>) production, achieving a maximum yield of 77.1 wt.% at a space-time of 10 g<sub>cat</sub> min/g<sub>plastic</sub>. Increasing the space-time beyond this point led to secondary reactions, consuming olefins to produce a higher yield of BTX aromatics. Deactivation studies suggested that while higher cracking temperatures (500°C) ensured catalyst stability, lower temperatures (450°C) yielded slightly more BTX despite causing more severe and rapid deactivation due to coking from uncracked wax precursors, resulting in 18.1% loss in BET surface area. Moreover, space-time had a limited effect on deactivation when the temperature was kept at 500°C. Coke content on the catalyst was always lower than 3 wt.% even after 4 h of continuous

operation and was higher for the portion of the catalyst bed immediately in contact with pyrolysis vapour.

For the upgrading of olive stone, the effect of space-time, primary pyrolysis temperature and cracking temperature on product yields and quality and on catalyst deactivation was investigated. The primary pyrolysis temperature was identified as the dominant parameter controlling the initial composition of the bio-oil precursors. Space-time and cracking temperature increase led to lower oil yield and higher yield of gases and water. Deactivation was consistently more severe compared to the case of polyolefin pyrolysis, with a coke content of  $\approx 10$  wt.% after 45 minutes of continuous operation due to the presence of highly reactive phenolic and oxygenated compounds in the biomass-derived vapours, which act as potent coke precursors. Deactivation was also confirmed by the evident reduction in surface area and micropore volume of the zeolite.

A screening of seven catalysts—including zeolites (HZSM-5, HY), metal oxides ( $\gamma$ - $\text{Al}_2\text{O}_3$ ), basic catalysts (dolomite), and homemade iron-based and waste-derived materials—established that catalyst functionality must be tailored to the specific upgrading objective. While HZSM-5 remained the benchmark for aromatization and reduction of light oxygenated compounds, calcined dolomite proved exceptionally effective for bio-oil deacidification, reducing organic acid content from 15.1% to just 0.5% via its basic sites. Other  $\gamma$ - $\text{Al}_2\text{O}_3$ -based catalysts and Fe/dolomite did not exhibit remarkable performances, and more work is needed to explore their potential. This highlights that different catalysts are required to solve the distinct problems posed by biomass-derived vapours (acidity and oxygen content) versus plastic-derived vapours (molecular weight distribution). Ultimately, a “feedstock-aware” approach is essential since the chemical nature of the waste stream, rather than the reactor technology alone, dictates the choice of catalyst and process strategy for effective chemical recycling.

