

Thermochemical recycling of LDPE through fast pyrolysis & catalytic upgrading towards naphtha range hydrocarbons

P.N. Soldatos^{1,*}, A.G. Margellou¹, A.A. Lemonidou², K.S. Triantafyllidis^{1,3}

¹Department of Chemistry, Aristotle University of Thessaloniki, Thessaloniki, Central Macedonia, 54124, Greece

²Department of Chemical Engineering, Aristotle University of Thessaloniki, Thessaloniki, Central Macedonia, 54124, Greece

³Centre for Interdisciplinary Research and Innovation (C.I.R.I.), Aristotle University of Thessaloniki, Thessaloniki, Central Macedonia, 57001, Greece

Keywords: Chemical recycling, Solid plastic waste, Heterogeneous catalysis, Fast pyrolysis

*Presenting author email: psold@chem.auth.gr

Introduction

Plastics play a vital role in daily life, but their increasing production-projected to reach 580 Mt/year by 2050 for key thermoplastics (PE, PP, PET, PS, and PVC)-poses significant challenges for waste management (Abbas-Abadi et al., 2023). With only 18% of plastic wastes currently recycled, the majority is either incinerated or landfilled, exacerbating solid waste management issues. Conventional mechanical recycling struggles with the heterogeneous nature of post-consumer municipal plastic waste, often resulting in final products with inferior properties. On the other hand, thermochemical recycling shows promise in converting these wastes into valuable intermediates, including monomers, oligomers or other desired fractions, addressing the complexities of plastic waste management (Dogu et al., 2021; Tan et al., 2022). From this perspective, this study investigates (catalytic) fast pyrolysis as a viable method for recycling plastics, particularly focusing on LDPE, a common component of municipal plastic waste. The primary objective is to convert LDPE into pyrolysis oil that closely resembles valuable petroleum fractions. Through in situ upgrading, various catalysts were employed to optimize “light” pyrolysis oil yields and enhance selectivity towards naphtha range hydrocarbons, essential for monomers production via stream cracking. This approach aims to address plastic waste management challenges while promoting circular and sustainable polymer production.

Materials & Methods

The experimental setup consists of a bench-scale fixed-bed reactor designed to simulate fast pyrolysis conditions, operating under a constant N₂ flow. Thermal and catalytic tests were performed over a temperature range of 450-600 °C. Prior to this, preliminary screening of thermal and catalytic degradation of the polymer was examined via thermogravimetric analysis (TGA) in a temperature range of 25-700 °C, under N₂ flow, with a heating rate of 10 °C/min. The Polymer/Catalyst ratio for TGA experiments was 4-5/1 to ensure the desired contact of the polymer-catalyst mixture, while in the fast pyrolysis experiments, different ratios (ranging from 2/1 to 10/1) were tested. The catalysts studied include a variety of zeolites with different properties (acidity, porosity, morphology) such as ZSM-5, Beta, USY, amorphous silica-alumina, as well as mixed oxides. Pyrolysis oil was collected using CS₂ and analyzed by GC-MS/FID, while non-condensable gases were analyzed using GC-FID/TCD. Fresh and spent catalysts underwent characterization by XRD, N₂ sorption, elemental analysis or other relative techniques.

Results & Discussion

In the TGA tests, the decomposition profile of LDPE was identified in the range of 454-480 °C, with a maximum degradation peak at 468 °C. The use of highly acidic aluminosilicate catalysts notably decreased the

DTG_{max} by up to 80 °C. Variations in catalysts pore structure, size, and acid site abundance resulted in diverse degradation profiles. During thermal pyrolysis in the fixed-bed reactor, the primary pyrolytic products were wax (C₁₆₊), with minimal temperature-dependent changes in product distribution. Wax production was higher at 450 °C (90 wt.%) and decreased to 70 wt.% at 600 °C, while both py-oil and gas yields followed an inverse trend remaining low (3-5 wt.%) at 450 °C, and slightly improving up to 10-12 wt.% at 600 °C. Highly acidic catalysts induced wax cracking towards py-oil even at 450 °C (up to 45 wt.% with a Plastic/Catalyst ratio of 10). Increasing temperature further enhanced py-oil yield, reaching a maximum of 65 wt.% at 550 °C. However, higher temperatures or lower plastic/catalyst ratios induced subsequent cracking of oil-intermediate hydrocarbons to gaseous products (yields up to 35 wt.%), primarily consisting of propylene, ethylene, and isobutylene. Catalyst properties influenced the chemical profile of pyrolysis oil, with highly Brønsted acidic zeolites enhancing cracking and producing olefin-rich py-oil. Depending on catalyst's pore size/structure, aromaticity and condensation towards PAHs were also observed. The carbon number distribution of py-oil compounds closely resembled that of naphtha, with maximum at C₇-C₁₂. Tuning zeolite acidity could induce a shift towards a more paraffinic nature of py-oil. This effect was also observed with mixed oxides, which, due to their lower acidity, decreased olefinic-aromatic content, while increasing the carbon number of compounds (C₁₄-C₂₄).

Acknowledgements

This project has received funding from the European Union's Horizon Europe Research and Innovation Programme under Grant Agreement No. 101058412.

References

- M. Abbas-Abadi, Y. Ureel, A. Eschenbacher, F. Vermeire, R. Varghese, J. Oenema, G. Stefanidis, K. Van Geem, *Prog. Energy Combust. Sci.* **2023**, 96, 101046.
- O. Dogu, M. Pelucchi, R. Van de Vijver, P. Van Steenberge, D. D'hooge, A. Cuoci, M. Mehl, A. Frassoldati, T. Faravelli, K. Van Geem, *Prog. Energy Combust. Sci.* **2021**, 84, 100901.
- T. Tan, W. Wang, K. Zhang, Z. Zhan, W. Deng, Q. Zhang, Y. Wang, *ChemSusChem* **2022**, 15, e202200522.