

Molecular Characterization of Heteroatomic Compounds in Pyrolysis Oils from Epoxy and Phenolic Resins Using GC-Combustion-MS for Advanced Recycling Applications

Tiziana Orlando^{abcd}, Marco Piparo^{ab}, Jean-François Focant^c, Brice Bouyssiere^{bd} and Pierre Giusti^{abd}

^a TotalEnergies One Tech TotalEnergies Research & Technology Gonfreville, BP 27, 76700 Harfleur, France

^b International Joint Laboratory – iC2MC: Complex Matrices Molecular Characterization, TRTG, BP 27, 76700 Harfleur, France

^c Organic and Biological Analytical Chemistry Group, MolSys Research Unit, University of Liège, 4000 Liège, Belgium

^d Université de Pau et des Pays de l'Adour, E2S UPPA CNRS, IPREM, Institut des Sciences Analytiques et de Physico-chimie pour l'Environnement et les Matériaux UMR5254, 64053 Pau, France

Introduction

The increasing use of fiber-reinforced composite materials, particularly epoxy and phenolic resins, in high-performance applications raises significant end-of-life (EoL) management challenges due to their resistance to degradation and material complexity. Pyrolysis has emerged as a promising route for recovering valuable products from these types of materials. However, the presence of heteroatomic species especially oxygen-, nitrogen-, and sulfur-bearing compounds, can negatively impact downstream upgrading processes and catalyst stability. Therefore, a detailed molecular-level characterization of the pyrolysis oils is essential to better understand their composition and to optimize the recycling strategies.

Methods

In this study, pyrolysis oil derived from epoxy and phenolic resins were analyzed using a GC-Combustion-MS system (ELEM-SPOT, Shimadzu). This innovative instrument couples gas chromatography (GC) with an online combustion interface, where the separated compounds are quantitatively oxidized into their volatile species (CO₂, NO, H₂O and SO₂), followed by a mass spectrometer (MS)[1]. This approach allows for an absolute quantification of the heteroatoms

without the need for compound-specific calibration standards, providing a comprehensive elemental distribution across chromatographic peaks.

Results

The developed approach enables the identification and absolute quantification of O-, N-, and S- containing molecules in the pyrolysis oil from both resin types. Distinct compositional differences were observed: phenolic-derived oils exhibited a higher abundance of N-, and O-bearing molecules. All the oxygenated and nitrogenous species have been quantified and classified according to their chemical composition (ether, ketones, ...). The study provided clear insights into the distribution of functional groups and highlighted the influence of polymer chemistry on pyrolysis product composition. The potential of the GC-Combustion-MS system has also been demonstrated for the advanced characterization of complex recycling streams and contributes to improving the management and valorization of composite materials.

References

[1] J. García-Bellido *et al.*, « Potential of GC-Combustion-MS as a Powerful and Versatile Nitrogen-Selective Detector in Gas Chromatography », *Anal. Chem.*, vol. 95, n° 31, p. 11761-11768, août 2023, doi: 10.1021/acs.analchem.3c01943.