Plastic Solid Waste Valorisation via Two-Stage Pyrolysis

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Plastic solid waste (PSW) management is a global challenge due to its growing production and non-biodegradability. Despite improvements in recycling, incineration and landfilling are still largely used, highlighting the need for alternative strategies. Among thermochemical processes, pyrolysis has emerged for decomposing PSW into value-added gas, liquid, and solid products under oxygen-free conditions. This research project explores the valorisation of real PSW through a three-phase approach. Initially, a two-stage lab-scale pyrolysis process was developed and optimized to enhance volatile recovery, providing a dataset for process modelling. The second phase involved the process modelling, targeting the generation of 500 kWe feeding the pyrolysis gas as fuel in an internal combustion engine (ICE). The model was followed by a CO_2 emission assessment under Renewable Energy Directive (REDIII) criteria and a techno-economic analysis, confirming the feasibility of producing renewable recycled carbon fuels (rRCF). A pivotal outcome from these phases was the significant impact of the solid pyrolysis residue (pyro-char) on the overall process sustainability. When treated as a waste, pyro-char can negatively affect both environmental and economic performances. Thus, in the current third work phase the research shifted the focus toward understanding and valorising this fraction. The ongoing work investigates how pre-impregnation of PSW with iron(II) acetate affects pyro-char formation and properties, while also impacting the overall pyrolysis dynamics. Indeed, iron-derived species formed during thermal treatment may act as in-situ catalysts, allowing to self-catalytic reactions that enhance the conversion efficiency and alter the product distribution. Experimental results show that iron loading significantly alters char yield and structure, particularly at 900 °C, where a notable catalytic effect reduces char mass while potentially increasing gas and liquid fractions. The pyro-char was characterized using X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDS). These analyses revealed the presence of iron carbides and oxides, suggesting the formation of catalytic phases during pyrolysis. These findings open new pathways for tuning char properties, reducing process residue, and enhancing energy recovery. By focusing on the often-neglected solid fraction, this work contributes to a more comprehensive understanding of PSW pyrolysis. It proposes an auto-catalytic strategies to shift process dynamics, supporting the transition toward efficient, sustainable, and decarbonized energy systems.

Keywords: *plastic waste recycling, CO_2 emissions, process feasibility, pyro-char valorisation*