

## Co-pyrolysis of polyethylene with products from thermal decomposition of brominated flame retardants

### ABSTRACT

Co-pyrolysis of brominated flame retardants (BFRs) with polymeric materials prevails in scenarios pertinent to thermal recycling of bromine-laden objects; most notably the non-metallic fraction in e-waste. Hydro-dehalogenation of aromatic compounds in a hydrogen-donating medium constitutes a key step in refining pyrolysis oil of BFRs. Chemical reactions underpinning this process are poorly understood. Herein, we utilize accurate density functional theory (DFT) calculations to report thermo-kinetic parameters for the reaction of solid polyethylene, PE, (as a surrogate model for aliphatic polymers) with prime products sourced from thermal decomposition of BFRs, namely, HBr, bromophenols; benzene, and phenyl radical. Facile abstraction of an ethylenic H by Br atoms is expected to contribute to the formation of abundant HBr concentrations in practical systems. Likewise, a relatively low energy barrier for aromatic Br atom abstraction from a 2-bromophenol molecule by an alkyl radical site, concurs with the reported noticeable hydro-debromination capacity of PE. Pathways entailing a PE-induced bromination of a phenoxy radical should be hindered in view of high energy barrier for a Br transfer into the para position of the phenoxy radical. Adsorption of a phenoxy radical onto a Cu(Br) site substituted at the PE chain affords the commonly discussed PBDD/Fs precursor of a surface-bounded bromophenolate adduct. Such scenario arises due to the heterogeneous integration of metals into the bromine-rich carbon matrix in primitive recycling of e-waste and their open burning.

**Keyword:** Polymeric materials; Brominated flame retardants; Reaction mechanism; Co-pyrolysis