Systems & Control Transactions

Original Research Article
Peer Reviewed Conference Proceeding
ESCAPE 36 - European Symposium on Computer Aided Process Engineering
Sheffield, UK. 21-24 June 2026

PSE PRESS

Chemical Additives in Plastics: Understanding the Reactions, Fate, and Releases during Pyrolysis

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ABSTRACT

Plastic pyrolysis is widely promoted as a techno-economic industrial scale recycling strategy. Nevertheless, the fate and reactivity of plastic chemical additives during pyrolysis are mostly overlooked in product quality and environmental release assessments. Here, we present an integrated modeling framework to elucidate the role of additives in plastic pyrolysis and evaluate the implications of their transformation products and environmental releases. Using high-density polyethylene (HDPE) as a case study, chemical additives of concern are selected based on occurrence, concentration data, and potential risk to human health and the environment. Bond dissociation energies are predicted using a machine learning model to identify dominant radical species formed under pyrolytic conditions. These additive-derived radicals are incorporated into an automatic chemical reaction mechanism generator that constructs kinetic models composed of elementary chemical reaction steps. These kinetic models are simulated using kinetic Monte Carlo (kMC) methods to predict product distributions and yields. The results show that common additives readily form stabilized alkyl and aryl radicals at energies accessible during pyrolysis, enabling their active participation in polymer degradation pathways. These interactions influence product formation and may contribute to the generation of environmentally relevant by-products. Overall, this study provides a mechanistic and risk-informed perspective on plastic pyrolysis, emphasizing the importance of explicitly accounting for additive chemistry in the development of safer and more sustainable chemical recycling technologies.**Disclaimer**: The views expressed in this work are those of the authors and do not necessarily represent the views or policies of the EPA.

Keywords: Plastic Recycling, Machine Learning, Reaction Engineering, Stochastic Simulations, Environment

INTRODUCTION

Plastic pollution remains a critical global challenge due to rapidly increasing waste generation and the limited effectiveness of existing recycling technologies. Approximately 2.01 billion metric tons of municipal solid waste (MSW) are generated annually worldwide, a figure projected to rise to 3.4 billion metric tons by 2050 [1]. Plastics constitute a substantial fraction of this end-of-life (EoL) material stream, accounting for roughly 7–12% by weight in the United States [2]. Despite ongoing recovery efforts, only 9–10% of plastic MSW is recycled globally, while 12–19% is incinerated, and the majority is landfilled or released into the environment, leading to persistent accumulation and adverse environmental and human health impacts [3].

In this context, pyrolysis has emerged as a promising thermochemical upcycling strategy for converting plastic waste into fuels, monomers, and chemical feedstocks under oxygen-free conditions. However, plastics are chemically complex materials that contain not only polymer matrices but also a wide range of intentionally

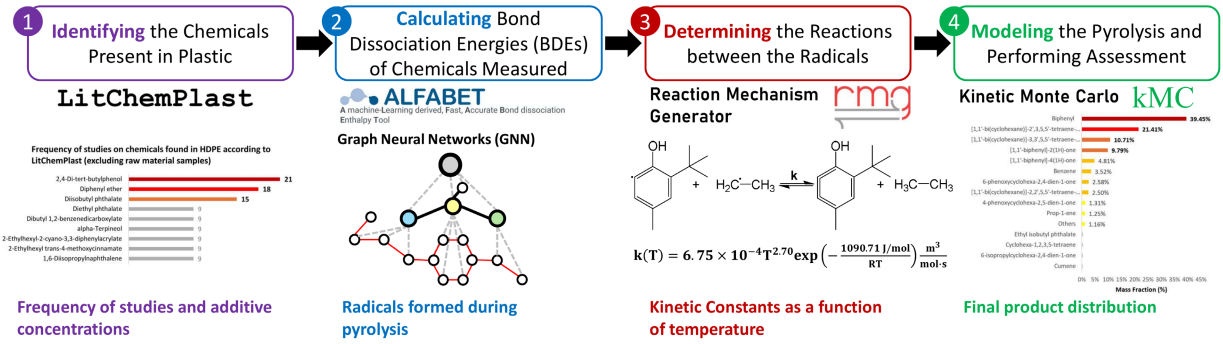


Figure 1. Proposed framework comprising the LitChemPlast database, the machine learning model ALFABET, the Reaction Mechanism Generator (RMG), and kinetic Monte Carlo (kMC) simulations to estimate the reactions, fate, and releases of chemical additives in plastic pyrolysis.

and non-intentionally added substances, including residual monomers, additives, and processing aids. Data from the LitChemPlast database show that over 3, 500 chemicals have been detected in plastics across 372 studies, with more than 16, 000 substances linked to plastic products, including over 4, 200 classified as hazardous [4]. Despite this complexity, most pyrolysis studies focus on polymer degradation, largely overlooking the fate and reactivity of additive-derived chemicals.

Mechanistic modeling approaches, including kinetic Monte Carlo (kMC) simulations, have been widely applied to describe polymer degradation and predict product distributions based on molecular-scale reaction kinetics [5]. However, polymer–additive interactions remain poorly characterized due to limited experimental data and incomplete reaction mechanisms, reducing the predictive capability of conventional models [6]. Machine learning (ML) offers a powerful means to address these limitations by enabling systematic identification of chemically plausible reaction pathways and reactive intermediates [7].

In this work, we integrate ML-based tools with kMC simulations to explicitly account for additive chemistry during plastic pyrolysis. Representative additives are selected based on occurrence and concentration data from the LitChemPlast database. Bond dissociation energies are predicted using ALFABET to identify dominant radical species formed under pyrolytic conditions [8], and their subsequent interactions are explored using the reaction mechanism generator (RMG) [9]. The resulting reaction networks are simulated using kMC to predict product distributions and yields and used to assess the environmental fate and impacts of pyrolysis-derived products. The framework is demonstrated through a case study of high-density polyethylene (HDPE) pyrolysis that incorporates three frequently reported additives (2, 4-di-tert-butylphenol, diphenyl ether, and diisobutyl phthalate).

Methodology

This work introduces an integrated framework to predict product yields and the formation of chemicals of concern during plastic pyrolysis. Machine learning (ML) tools, coupled with kinetic Monte Carlo (kMC) simulations, capture additive-derived reaction pathways often neglected in conventional analyses. The framework identifies representative plastic-associated chemicals, predicts dominant radicals using bond dissociation energy (BDE) analysis, and constructs reaction networks that are used to determine the pyrolysis degradation products. Figure 1 outlines the workflow from chemical identification and radical generation to kMC-based product prediction.

Identifying the Chemicals Present in Plastic

The LitChemPlast database is used to identify and quantify chemicals present in plastics. It compiles and harmonizes chemo-analytical measurements across multiple stages of the plastic life cycle, addressing the limited availability of publicly accessible data on plastic chemical composition. The database includes studies published between 1978 and 2021, identified through systematic searches via Web of Science and SciFinder followed by a two-stage screening process. Extracted data include bibliographic information, sample characteristics (product categories and polymer types), analytical methods, and measured chemicals, with concentrations standardized and reported in parts per million (ppm) [4].

In this study, the comprehensive state-of-the-art open database of chemical additives in plastics, LitChemPlast, is used to identify chemicals of concern with the highest reported occurrence and concentrations across different plastic types and applications. This information enables the selection of representative compounds that are most likely to participate in chemical reactions during the pyrolysis process and therefore influence reaction pathways and product formation.

Calculating Bond Dissociation Energies (BDEs) of Chemicals Measured in Plastics

To predict radical formation during pyrolysis, bonds most susceptible to thermal cleavage must be identified. Bond dissociation energies (BDEs) quantify bond strength and are used to determine bond-breaking under pyrolytic conditions. A BDE is the energy required for homolytic cleavage of a bond (A–B) into radicals ($A\bullet$ and $B\bullet$) [10]. As thermodynamic parameters, BDEs inform reactivity, kinetics, and accessible pathways in radical-driven systems. Bond dissociation is shown in Equation (1), and BDEs are calculated from the enthalpies of formation ($\Delta_f H$) of the parent molecule and the resulting radicals (Equation (2)).

$$A - B \rightarrow A\bullet + B\bullet \quad (1)$$

$$BDE = \Delta_f H(A\bullet) + \Delta_f H(B\bullet) - \Delta_f H(A - B) \quad (2)$$

Experimental determination of BDEs is challenging and restricted to a few techniques, including radical kinetics, photoionization mass spectrometry, and the acidity–electron affinity thermochemical cycle. These methods require high-precision measurements, advanced instrumentation, and strict control, limiting their applicability, particularly for complex or transient species [11]. Quantum chemical approaches, such as density functional theory (DFT), provide accurate BDE estimates but are computationally intensive and sensitive to the level of theory options chosen.

To address these limitations, we employ ALFABET, a machine learning (ML)-based model that predicts homolytic BDEs of organic molecules with near-DFT accuracy at sub-second computational cost. ALFABET is trained on over 290, 000 DFT-calculated BDEs using a graph neural network that operates directly on molecular structures derived from simplified molecular input line entry system (SMILES) strings, eliminating manual feature engineering. The model achieves mean absolute errors of 2.4 kcal mol^{-1} for in-distribution molecules and 3.4 kcal mol^{-1} for out-of-distribution molecules, compared with DFT values of 2.1 kcal mol^{-1} and 2.5 kcal mol^{-1}, respectively. This accuracy loss is compensated by a significant decrease in the CPU time per molecule, where DFT methods require 31.4 h while ALFABET 1 ms [8].

In this work, ALFABET is used to estimate the BDEs of compounds selected from the LitChemPlast database. For each compound, the lowest BDE is used to identify the most probable radical species formed during pyrolysis, which are subsequently incorporated into the reaction network to predict the content of additive-derived chemicals in pyrolysis products and environmental releases.

Determining the Reactions between the Radicals Formed During Plastic Pyrolysis

The reaction network describing interactions between additive-derived radicals is constructed using the kinetic search module of the RMG. Starting from the radical species identified by the BDE analysis, RMG systematically enumerates chemically plausible elementary reactions and assigns temperature-dependent rate coefficients to each reaction. Pressure-independent kinetics are described using a modified Arrhenius expression as shown in equation (3).

$$k(T) = A\left(\frac{T}{T_0}\right)^n \exp\left(-\frac{E_0 + \alpha\Delta H_{\mathrm{rxn}}}{RT}\right) \quad (3)$$

Where A is the pre-exponential factor, n is the temperature exponent, T_0 is a reference temperature, E_0 is the activation energy for a thermoneutral reaction, ΔH_{rxn} is the reaction enthalpy, α is the Evans-Polanyi coefficient, R is the universal gas constant, and T is the system temperature. The Evans-Polanyi corrections are not applied in this work; therefore, α and ΔH_{rxn} are set to zero, and the reported activation energy corresponds directly to E_0.

When assigning kinetic parameters, RMG uses a hierarchical strategy prioritizing data reliability. Parameters are taken from user-provided seed mechanisms, followed by curated reaction libraries, matched training reactions, exact rule-based matches, and, when necessary, estimated average rates. When multiple sources exist within a category, parameters are ranked by level of theory or experimental evidence, with experimental data and high-level quantum calculations prioritized over lower-level estimates [9].

Using this structured approach, RMG generates a consistent and chemically informed reaction network describing radical–radical interactions during pyrolysis. The resulting elementary reactions and associated kinetic parameters are subsequently used as inputs to the kinetic Monte Carlo (kMC) simulations to predict product formation, concentrations, and yields.

Modeling Pyrolysis using Stochastic Simulations

The kMC method is a stochastic simulation framework based on the stochastic simulation algorithm (SSA) originally developed by Gillespie. It enables the time-resolved simulation of chemically reacting systems by explicitly considering the probabilistic nature of individual reaction events [5]. As shown in Figure 2, implementing kMC requires kinetic and system-specific inputs, including reaction-specific pre-exponential factors and activation energies, as well as operating conditions such as temperature, system volume, and the initial populations of all chemical species. The kinetic inputs are obtained from the RMG results, and the process conditions are established based on previous plastic pyrolysis studies.

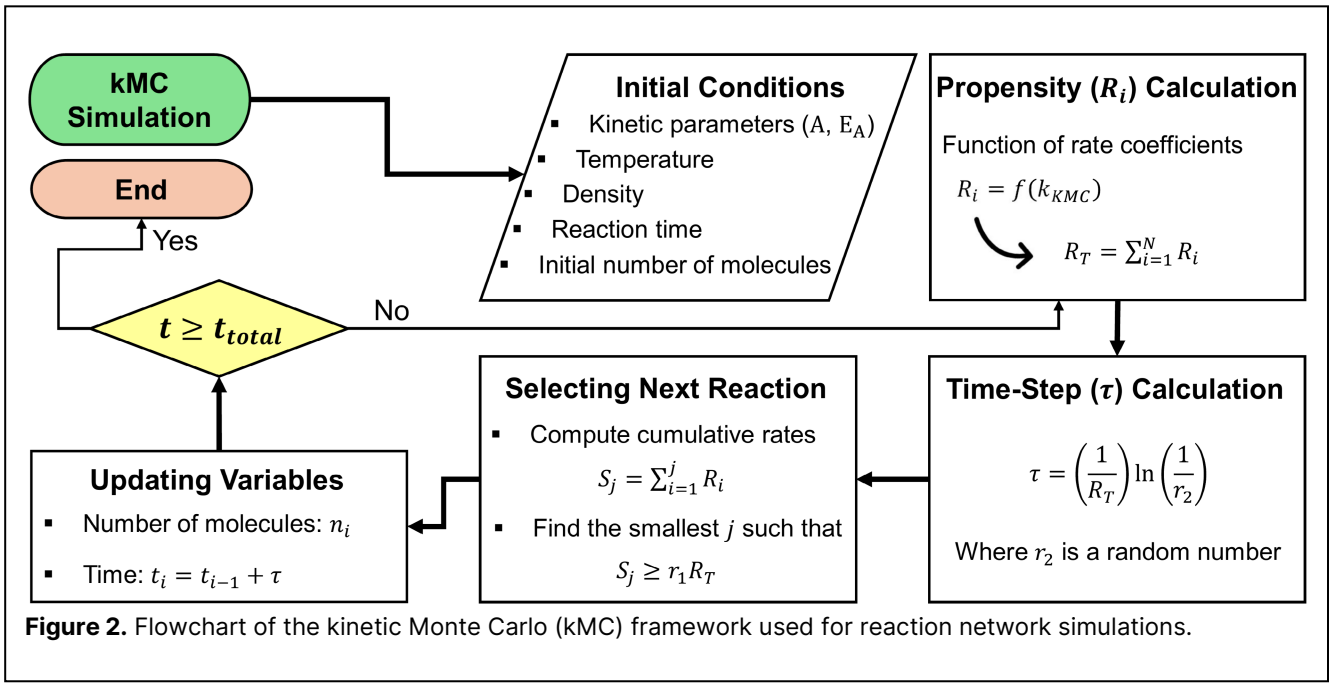


Figure 2. Flowchart of the kinetic Monte Carlo (kMC) framework used for reaction network simulations.

From these inputs, stochastic rate constants are derived from the corresponding macroscopic rate coefficients, accounting for reaction order and molecularity. Specifically, distinct expressions are used for first-order unimolecular reactions, second-order bimolecular reactions between identical species, and second-order bimolecular reactions between different species, as shown from equations (4) to (6), respectively, where $k_a^{\exp}, k_{aa}^{\exp}$, and $k_{ab}^{\exp}$ denote the macroscopic rate coefficients, N_A is Avogadro's number, and V is the control volume [12]. These stochastic rate constants are used to calculate the reaction propensities for each elementary reaction channel. Equation (7) shows the total propensity of the system (R_T), which is obtained by summing up the propensities of all reactions (R_i).

$$k^{MC} = k_a^{\exp} \tag{4}$$

$$k^{MC} = \frac{2k_{aa}^{\exp}}{V \cdot N_A} \tag{5}$$

$$k^{MC} = \frac{k_{ab}^{\exp}}{V \cdot N_A} \tag{6}$$

$$R_T = \sum_{i=1}^{N} R_i \tag{7}$$

The time to the next reaction event is sampled by generating a uniform random number $r_2 \in (0,1)$, which determines the stochastic time increment. A second random number $r_1 \in (0,1)$is then used to select the reaction event by identifying the first reaction whose cumulative propensity exceeds $r_1 \cdot R_T$. Following reaction selection, the populations of reactant and product species are updated according to the reaction stoichiometry. This procedure is repeated, allowing the reaction network to evolve stochastically over time while rigorously preserving the correct statistical distribution of reaction events.

Following the kMC simulations, time-resolved product distributions and final yields are obtained, and high-concentration products are prioritized for downstream analysis due to their relevance for environmental exposure and risk evaluation [13]. This study introduces a fully integrated, mechanistic framework that explicitly links additive-specific reaction chemistry to pyrolysis product formation and environmental releases, which is an aspect that has not been systematically addressed in prior pyrolysis modeling efforts. Whereas most existing models are constrained to polymer-only degradation due to the severe lack of kinetic data for additive-derived reactions, the present approach overcomes this limitation by combining ML-based reactivity prediction, automated reaction mechanism generation, and stochastic kinetic modeling. By doing so, this work enables, for the first time, predictive exploration of additive-driven degradation pathways, improves the reliability of pyrolysis outcome predictions, and supports early identification of environmentally relevant and potentially hazardous degradation products.

RESULTS AND DISCUSSION

This section presents the validation of the proposed methodology through a case study on plastic pyrolysis. The most frequently reported chemicals associated with the selected plastic are identified, and their BDEs are used to determine the dominant radical species formed during thermal degradation. The interactions between additive-derived radicals are then analyzed to determine key reaction pathways and their influence on product

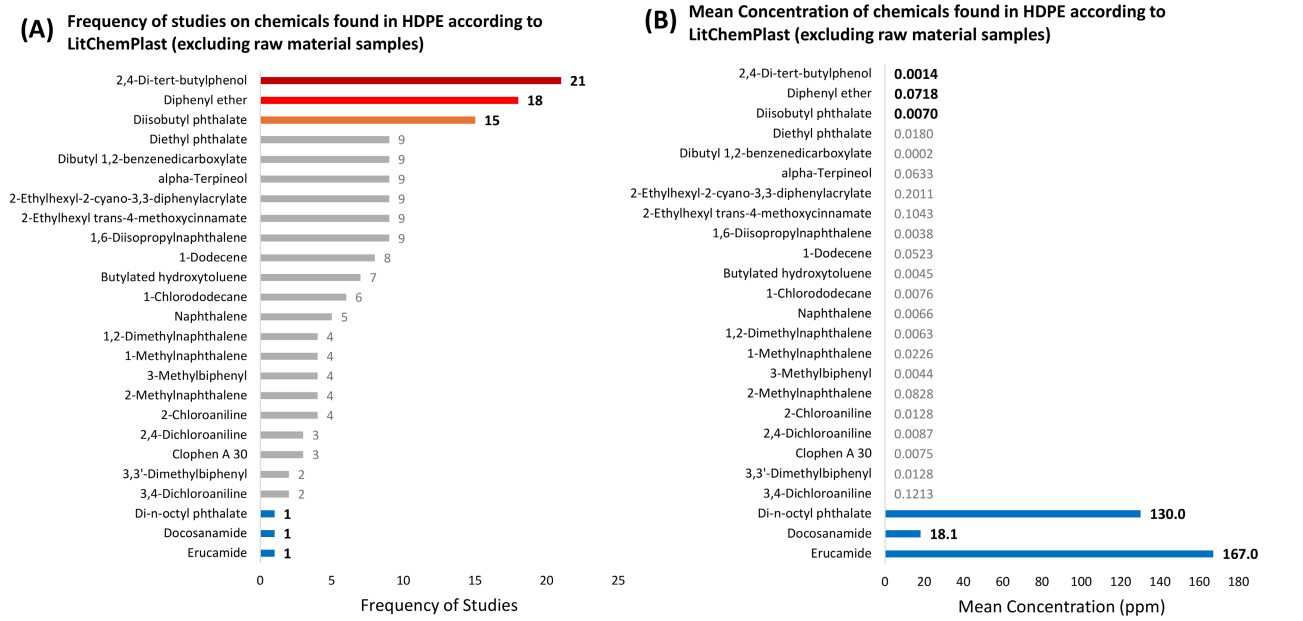


Figure 3. A) Frequency of studies and **B)** Mean concentration in parts per million (ppm) of additives found in HPDE according to the LitChemPlast database, excluding raw material samples.

formation. Based on these reactions, the resulting product distribution is predicted, and the environmental implications and fate of the released chemicals are subsequently assessed.

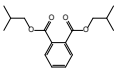
Case Study: Pyrolysis HDPE with Chemical Additives

The case study used to validate the proposed methodology is based on the pyrolysis of HDPE, considering the chemical additives identified in different HDPE samples as reported in the LitChemPlast database. Figure 3 shows the frequency of studies reporting chemicals detected in HDPE and their corresponding mean concentrations, as compiled from the LitChemPlast database [4].

As shown in Figure 3A, the chemicals most frequently reported in HDPE samples are 2, 4-di-tert-butylphenol, diphenyl ether, and diisobutyl phthalate, identified in 21, 18, and 15 samples, respectively. Additive selection was primarily based on occurrence frequency across the LitChemPlast dataset to ensure that the case study compounds are broadly representative of HDPE samples.

In contrast, di-*n*-octyl phthalate, docosanamide, and erucamide were each detected in only a single sample but exhibited the highest concentrations (Figure 3B). While such high-concentration additives represent interesting case studies, their limited occurrence restricts statistical representativeness. Nevertheless, when present in specific EoL streams, their high concentration may significantly influence the emission risk profile: erucamide undergoes autocatalytic degradation below 90°C generating nitrile species and alkyl radicals [14], while di-n-octyl phthalate decomposes via ester bond cleavage to yield oxygenated aromatics [15]. These chemicals were excluded from this case study; however, the proposed framework is generalizable and can readily be applied to such scenarios.

Table 1: Chemical structure, description, SMILES string, and primary hazards of the most measured chemical compounds in HDPE samples.

Information	**2, 4-di-tert-butylphenol**	**Diphenyl ether**	**Diisobutyl Phthalate**
Chemical Structure			
Description	Antioxidant [16]	Degradation product [17]	Plasticizer[18]
SMILES String	CC(C)(C)c1ccc(O)c(C(C)(C)C)c1	c1ccc(Oc2ccccc2)cc1	CC(C)COC(=O)c1ccccc1C(=O)OCC(C)C
Primary Hazards	Corrosive, Irritant, Health Hazard, Environmental [16]	Irritant, Environmental hazard [17]	Health Hazard [18]

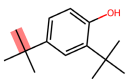
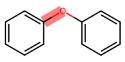
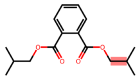
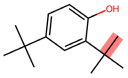
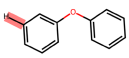
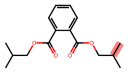
Consequently, this work focuses on the three most frequently reported chemicals in HDPE (excluding raw material samples), as identified in the LitChemPlast database: 2, 4-di-tert-butylphenol, diphenyl ether, and

diisobutyl phthalate. Notably, all three compounds are associated with hazard classifications, including potential carcinogenicity and aquatic toxicity [16] [17] [18]. Table 1 summarizes their key characteristics, including their functional roles in HDPE and SMILES representations, which are subsequently used to compute the corresponding BDEs.

Computing BDEs of Chemicals Measured

The calculated BDEs for the three compounds selected in the case study are summarized in Table 2. For each compound, the two lowest BDE values are reported to provide an overview of the energetically most accessible bond-cleavage pathways.

Table 2: The two lowest BDE values obtained with ALFABET for 2, 4-di-tert-butylphenol, diphenyl ether, and diisobutyl phthalate.

Bond	2, 4-di-tert-butylphenol	Diphenyl ether	Diisobutyl Phthalate
#1	 Bond Type: C-C *BDE(ML):* 76.1kcal/mol	 Bond Type: C-O *BDE(ML):* 84.2kcal/mol	 Bond Type: C-C *BDE(ML):* 87.1kcal/mol
#2	 Bond Type: C-C *BDE(ML):* 76.7kcal/mol	 Bond Type: C-H *BDE(ML):* 110.9kcal/mol	 Bond Type: C-C *BDE(ML):* 89.0kcal/mol

Across all compounds, the lowest BDEs range from approximately 76.1 to 87.1 kcal mol^{-1}, indicating that radical formation from these additives is thermodynamically accessible under typical pyrolysis temperatures (≥ 400-600 °C), where thermal energies are sufficient to activate bond cleavage within this range.

For 2, 4-di-tert-butylphenol, the lowest BDEs (76.1 and 76.7 kcal mol^{-1}) correspond to C-C bond cleavage within the tert-butyl substituents. These values are approximately 10 kcal mol^{-1} lower than the phenolic O-H bond dissociation energy (85.9 kcal mol^{-1}) and nearly 20 kcal mol^{-1} lower than aromatic C-C bond cleavage (96.5 kcal mol^{-1}). This significant energetic preference indicates that pyrolysis is initiated predominantly through the formation of tert-butyl-derived alkyl radicals rather than phenoxy or aryl radicals.

In the case of diphenyl ether, the weakest bond is the aryl-O bond, with a BDE of 84.2 kcal mol^{-1}. This value is significantly lower than the aromatic C-H BDEs (110.9-112.0 kcal mol^{-1}), indicating that homolytic cleavage of the ether bond is the primary pathway for radical formation. The resulting phenyl and phenoxy radicals are stabilized by resonance and are known to participate in secondary reactions that lead to aromatic growth. Therefore, for the formation of alkyl radicals observed in 2, 4-di-tert-butylphenol, diphenyl ether predominantly contributes to aromatic radical species, which may affect the formation of polycyclic aromatic hydrocarbons and char during pyrolysis.

For diisobutyl phthalate, the lowest BDEs (87.1 and 89.0 kcal mol^{-1}) are associated with C-C bond cleavage in the isobutyl side chains. These values are 8-10 kcal mol^{-1} lower than C-H bond dissociation energies in the ester backbone (95.9-96.7 kcal mol^{-1}), indicating that radical formation is dominated by the release of isobutyl radicals rather than direct fragmentation of the aromatic or ester part.

Overall, the BDE analysis demonstrates that additive-derived radicals are thermodynamically favored to form under pyrolytic conditions, and their nature strongly depends on the additive structure. These results provide a quantitative basis for including additive-derived radicals in the reaction network and support their potential role in modifying polymer degradation pathways, product distributions, and the formation of environmentally relevant by-products.

Determining the Reactions between the Radicals Formed During the Plastic Pyrolysis

Based on the BDE analysis obtained using ALFABET, the radical species considered in the pyrolysis simulations are summarized in Table 3. For each additive, the lowest BDE value is selected as the most probable bond-cleavage pathway, resulting in two corresponding radical species that are incorporated into the reaction network. These additive-derived radicals constitute the initial reactive pool used for reaction network generation with the RMG.

To determine the interactions among radical species, binary interactions between all species are assumed. This assumption is widely used in kinetic modeling of pyrolysis and combustion systems, where bimolecular reactions dominate radical propagation, abstraction, and termination pathways. In contrast, higher-order reactions are statistically less probable under typical thermal decomposition conditions due to the low likelihood of simultaneous multi-body collisions. Consistent with this framework, the RMG constructs reaction networks primarily from unimolecular and bimolecular reaction steps based on established kinetic theory [19]. Considering this, Figure 4 summarizes the reaction space generated

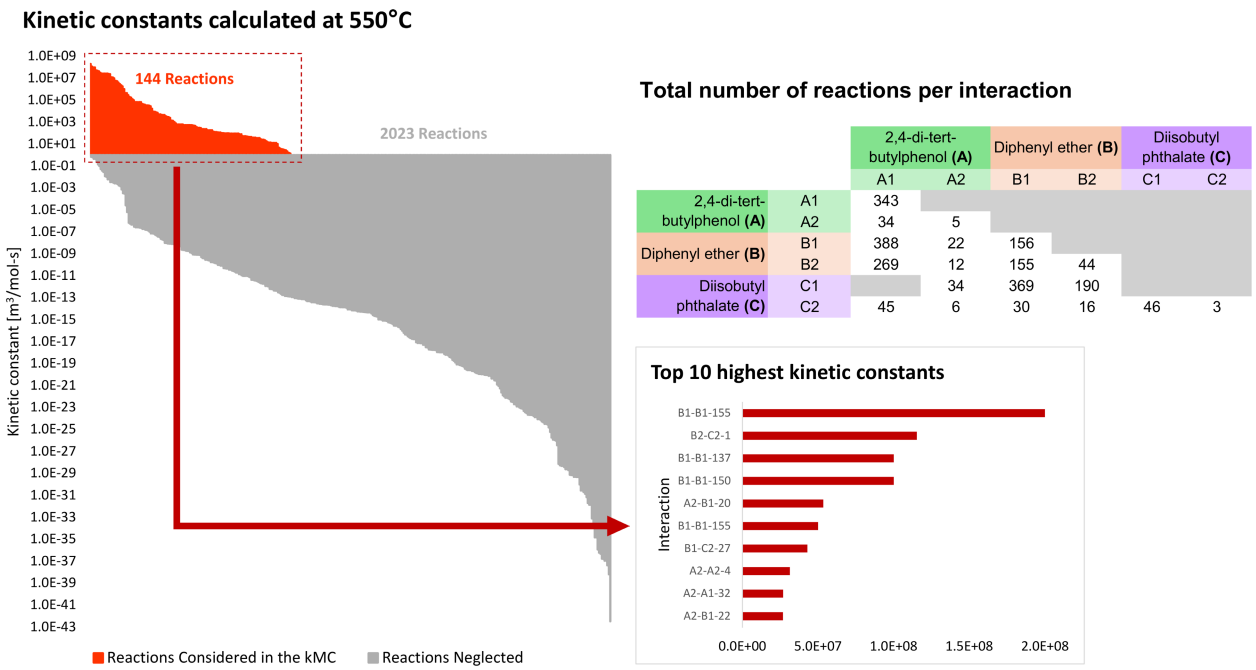


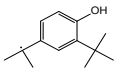
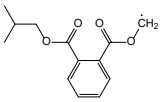
Figure 4. Total number of reactions generated for each radical-radical interaction, along with the corresponding kinetic parameters obtained from the Reaction Mechanism Generator (RMG). Of the 2,167 reactions identified, 144 are selected for inclusion in the kinetic Monte Carlo (kMC) simulations.

by RMG for interactions between additive-derived radicals and the subset retained for kMC simulations. 2, 167 elementary reactions are identified across all radical–radical interactions; however, only 144 reactions are selected based on their kinetic relevance at the pyrolysis temperature (550 °C). These retained reactions exhibit rate constant values several orders of magnitude higher than the remainder of the network, indicating that a relatively small subset of reactions dominates system kinetics.

The distribution of kinetic constants spans more than 40 orders of magnitude, with the fastest reactions primarily involving diphenyl ether-derived radicals (B-type), which account for the highest number of reaction pathways and the largest rate constants. The highest-rate reactions are predominantly radical–radical recombination or hydrogen abstraction events, consistent with expected high-temperature pyrolysis chemistry.

The reduction of the reaction network relies on the assumption that reactions with negligible rate constants do not significantly contribute to product formation within the simulated time scale. This filtering strategy preserves the chemically and kinetically dominant pathways while maintaining computational tractability, enabling efficient and physically meaningful kMC simulations of product formation.

Table 3: Radical species considered for generating the reaction network using the RMG.

Original Compound	Radical ID	Chemical Structure	SMILES
2, 4-di-tert-butylphenol	A1		[C](C)(C)C1=CC(=C(C=C1)O)C(C)(C)C
2, 4-di-tert-butylphenol	A2		[CH3]
Diphenyl ether	B1		C1=CC=C(C=C1)[O]
Diphenyl ether	B2		[c]1ccccc1
Diisobutyl phthalate	C1		CC(C)COC(=O)C1=CC=CC=C1C(=O)O[CH2]C[CH]C
Diisobutyl phthalate	C2		

Modeling the Reaction Network using Stochastic Simulations

Figure 5 presents the product distribution predicted by the kMC simulations, showing the final mass fractions

of the compounds.

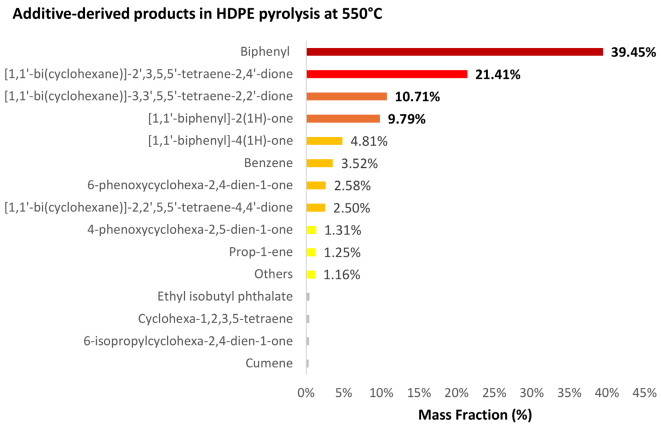


Figure 5. Product distribution predicted by the kMC simulation, considering just the chemicals derived from additives.

The kMC results show that product formation is dominated by a small number of aromatic and partially hydrogenated cyclic compounds, indicating that kinetically favored pathways govern system behavior. Biphenyl accounts for nearly 40 wt% of the additive-derived products, followed by phenolated ketones and cyclohexadienedione derivatives. These findings are consistent with the high stability and reactivity of aromatic radicals identified in the BDE and RMG analyses, especially those originating from diphenyl ether, which exhibits both high reaction connectivity and elevated rate constants.

The prominence of aromatic products suggests that additives can redirect polymer degradation toward aromatic-rich pathways, rather than acting as inert spectators during pyrolysis. This behavior contrasts with conventional polymer-only pyrolysis models, which typically predict product distributions dominated by aliphatic hydrocarbons. The formation of stabilized aromatic species early in the reaction network also explains their persistence at high concentrations in the final product mixture.

From an environmental perspective, several of the dominant products raise concerns. Biphenyl is persistent, hydrophobic, and toxic to aquatic organisms, with documented bioaccumulation potential [20]. Benzene, although produced at lower yields, is a well-established human carcinogen and a regulated air pollutant [21]. Phenolated ketones and cyclohexadienedione derivatives may serve as precursors to polycyclic aromatic hydrocarbons under secondary thermal or environmental conditions, contributing to mutagenic and carcinogenic risks. These results highlight that additive chemistry can significantly influence not only product yields but also the environmental risk profile of pyrolysis outputs.

Overall, these results show that plastic additives actively influence pyrolysis chemistry by serving as radical precursors that redirect degradation pathways and product formation. By integrating additive occurrence data with ML-based bond dissociation analysis, automated reaction mechanism generation, and kinetic Monte Carlo simulations, this study establishes a mechanistic link between additive chemistry, product distributions, and potential environmental impacts. Neglecting additive-derived reactions leads to systematic underprediction of aromatic and environmentally relevant by-products, limiting the reliability of polymer-only pyrolysis models. The proposed framework enables predictive assessment of pyrolysis outcomes and early identification of potentially hazardous degradation products, addressing key challenges associated with scarce kinetic data for additive reactions and supporting safer, more sustainable plastic recycling technologies.

CONCLUSIONS

The framework established in this study offers a risk-informed perspective on plastic pyrolysis by shifting the analytical focus from isolated polymer matrices to consider the complex chemical interactions of additives within EoL streams. By leveraging the ALFABET model to predict bond dissociation energies with near-DFT accuracy at sub-second speeds, we have enabled a systematic, scalable assessment of additives present in commercial plastics. As thermal recycling strategies like pyrolysis are promoted globally, future kinetic and environmental assessments must move beyond polymer-only models to incorporate the additive-derived reaction pathways identified here. Ultimately, the generalization of this framework into a computational tool will be crucial for characterizing other polymers and complex mixtures, ensuring the production of safe, high-value chemical feedstock from plastic EoL material.

ACKNOWLEDGEMENTS

The authors acknowledge the Department of Chemical Engineering at Rowan University and the U.S. Environmental Protection Agency.

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