Modelling PS pyrolysis combining the Method of Moments and full chemistry simulations

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Highlights
- Construction of an innovative detailed, hybrid kinetic model for polystyrene pyrolysis
- Successful combination of small chain free-radical chemistry with Method of Moments
- Validation of the kinetic model for a wide range of operating conditions and PS feeds
- Detailed model insights will lead to efficient design of industrial pyrolysis processes

1. Introduction

Solid plastic waste (SPW) has become one of the world's most pressing environmental problems. The accumulation of large SPW volumes in the environment makes a clear case for developing efficient recycling processes. Polystyrene (PS) is an important SPW stream and contaminant of typical polyolefin-rich wastes [1]. Recycling PS is thus essential for creating a circular chemical industry. Mechanical recycling leads to inherent downcycling, whereas chemical recycling shows great potential for upcycling PS back into high-value chemicals, for instance, styrene.

Chemical recycling through thermal pyrolysis, which decomposes PS at high temperatures (over 500 °C), is the most promising chemical recycling route and is being rapidly implemented in the chemical industry [2]. Due to the complex interplay of kinetics and transport phenomena [2], designing industrial processes requires fundamental process insights to be obtained via detailed modelling. Constructing detailed (kinetic) models that can be solved in a reasonable time remains a significant challenge. This work develops a novel, detailed, deterministic model for PS pyrolysis is developed as a proof of concept. The hybrid model combines the accuracy of detailed radical chemistry simulations with the computational efficiency of the Method of Moments (MoM). The main product yields, as predicted by our model, are validated against experimental data from a micropyrolyzer unit These experimental data are obtained from PS feedstocks covering a large range of chain length distributions (CLD), proving the model's robustness to variations in the PS starting material.

2. Methods and materials

Our model employs the simultaneous integration of two sets of differential equations, as shown in Figure 1. The first set of equations explicitly captures all reactions of small chains, while the second set of moment equations focuses on the averaged reactions of heavy species and interactions between light and heavy species. Both sets of equations share the same rate coefficients, adopted from [3], and reaction network. In the second set of equations, we apply the MoM to aggregate population balances, that describe reactions for individual chain lengths, into a smaller number of moment equations. The latter describes the evolution of statistical properties of the CLDs of
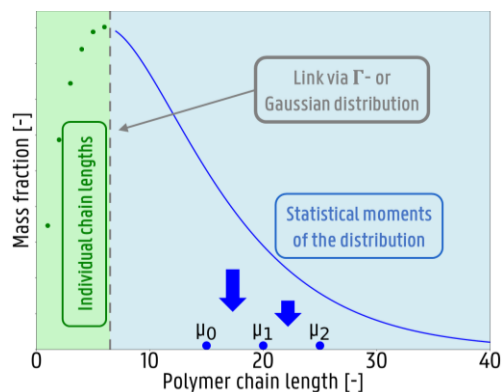

Figure 1. The adopted hybrid modelling methodology relies on a connection between the full chemistry (left, green) and the Method of Moments (right, blue).

all species in the PS pyrolysis process. Both numerical solvers, depicted in blue and green in Figure 1, strongly interact. For example, chain-shortening like β-scission reactions produce small species from large compounds with specific chain lengths. To determine the concentrations of those specific chain lengths, relevant CLDs are reconstructed at each timestep using a gamma or Gaussian distribution.

Validation experiments are performed on a micropyrolyzer setup, which operates under intrinsic kinetics, free from secondary gas-phase reactions. Thermal pyrolysis experiments are performed at 500, 550, and 600 °C, using anionically polymerized PS standards with molar masses of 2000, 4000, and 100 000 g/mol. Products are analysed using GC × GC with FID and ToF-MS detectors.

3. Results and discussion

Figure 2 compares the experimental and simulated yields of the main pyrolysis products, for the 4000 g/mol PS sample. The simulations are performed using gamma distributions, while Gaussian distributions yield almost identical results. Figure 2 clearly shows that the model accurately predicts the experimental monomer, dimer, and trimer yields. Similar benchmarks are acquired for the 2000 and 100000 g/mol PS. Furthermore, our model successfully manages to simulate the chemistry of light and heavy compounds at the same time. This example demonstrates a clear proof of concept for our novel kinetic model. In addition, whereas other kinetic models often focus on a small set of operating conditions and feedstocks, the strength of our model is that it can capture a wide range of temperatures and starting CLDs, as confirmed by additional validation
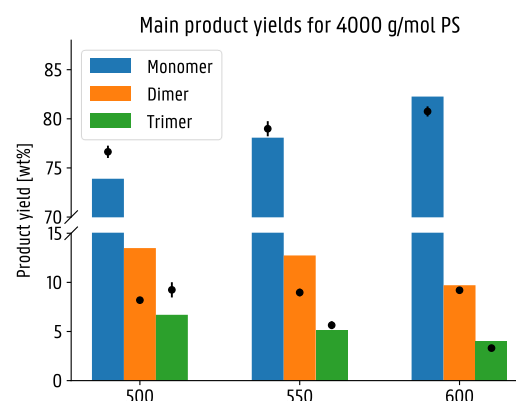

Figure 2. Yields of the main pyrolysis products of 4000 g/mol PS. Bars indicate simulation results, dots experimental values.

Furthermore, our model is used to perform a thorough sensitivity analysis, quantifying the impact of selected kinetic parameters and the initial CLD on the yields of the main pyrolysis products. Even more, a detailed reaction path analysis is performed, showing how different elementary reactions and reaction families influence the degradation of PS. They are thus also excellently suited to describe the impact of additional non-kinetic phenomena, such as diffusion limitations.

4. Conclusions

A hybrid kinetic model for the pyrolysis of polystyrene, that combines the Method of Moments for long polymer chains and detailed chemistry simulations for short chains, is presented. The model is validated over a wide range of operating conditions and PS grades based on micropyrolysis experiments. The subsequent insights boost our knowledge of the fundaments of PS pyrolysis, paving the way to a more accurate and efficient design of industrial pyrolysis processes. The model can be easily extended to other polymers, significantly advancing their chemical recycling potential.

References

[1] Roosen M, Mys N, Kleinhans K, Lase IS, Huysveld S, Brouwer M, et al. Expanding the collection portfolio of plastic packaging: Impact on quantity and quality of sorted plastic waste fractions. Resources, Conservation and Recycling 2022;178:106025.
[2] Dogu O, Pelucchi M, Van de Vijver R, Van Steenberge PHM, D'Hooge DR, Cuoci A, et al. The chemistry of chemical recycling of solid plastic waste via pyrolysis and gasification: State-of-the-art, challenges, and future directions. Progress in Energy and Combustion Science 2021;84:100901.
[3] Levine SE, Broadbelt LJ. Reaction pathways to dimer in polystyrene pyrolysis: A mechanistic modeling study. Polymer Degradation and Stability 2008;93(5):941-51.