Modeling HDPE thermal pyrolysis

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Highlights

- Kinetic Monte Carlo discloses complex HDPE reaction mechanism
- Phase transition is capable of representing experimental data
- HDPE pyrolysis products can be accurately predicted at different conditions

1. Introduction

Chemical recycling is currently being pursued as one of the most promising technologies to reduce post-consumer plastic's ecological and social impact. Pyrolysis specifically can simultaneously process different post-consumer plastic types in an inert atmosphere, resulting in a liquid stream rich in hydrocarbons, low molecular weight gases, and a char fraction. This technology is the most promising route for the plastics circularity as it does not require pure plastics streams such as mechanical recycling; and has lower energy requirements in comparison with gasification, another chemical recycling technology that leads mainly to a light gas fraction [1].

Currently, the academy and industry aim to understand how pyrolysis oil quality can be predicted in the presence of different feedstocks and contaminants, and also how the process can be optimized, such as best reactor configuration, temperature, and residence time. For polyolefins, the kinetic models are often based on lumped-models, simplifying important details such as pyrolysis oil carbon distribution (i.e. products are represented based on boiling point fractions). In this work, HDPE pyrolysis is modeled via kinetic Monte Carlo (kMC), considering a complex route of chemical reactions [2].

Moreover, understanding the process, such as how process variables (pressure and temperature) can influence the hydrocarbon mixture obtained as a product, is also investigated considering a multicomponent phase equilibrium calculations based on ideal gases and the Peng-Robinson (PR) equation of state (EOS). However, because these models are used for predicting the phase behavior of simple fluids, such as light and moderate hydrocarbons, Perturbed Chain Statistical Associating Fluid Theory (PC-SAFT) EOS is also used as it is known to be a powerful tool to study the phase behavior of complex fluids such as polymers and complex hydrocarbon mixtures [3]. It is shown the thermodynamics is essential to predict the product distribution seen in experimental data.

2. Methods

Kinetic Monte Carlo is used to simulate the kinetics of HDPE pyrolysis, including nine reaction families such as mid-chain scission, hydrogen abstraction, backbiting, and termination by disproportionation, whose kinetic constants were calculated theoretically [4,5]. The kinetic mechanism is coupled with the thermodynamic package, and phase-separation is calculated considering all

hydrocarbons products for the equilibrium calculations based on ideal gas and PR-EOS, but also plastic for PC-SAFT, whose parameters are calculated considering a group contribution method [6]. Volatile products are then removed from the reaction system. Validation experiments are performed on a micropyrolyzer setup, which operates under intrinsic kinetics, at 500 – 650 °C. Products are analyzed using GCxGC with FID and ToF-MS detectors.

3. Results and discussion

Figure 1 compares the experimental and simulated yields of the main pyrolysis products. It shows that the coupled kinetic and thermodynamic model is able to predict the product distribution (which can also be detailed as paraffin, olefins, and diolefins) is obtained. Additionally, kMC is proven to be a powerful tool for understanding the degradation behavior at any instant without considering hypotheses or assumptions that other methods rely on (e.g., a constant distribution). Moreover, it can be easily integrated with a thermodynamic model, which is essential to fully represent the pyrolysis process.
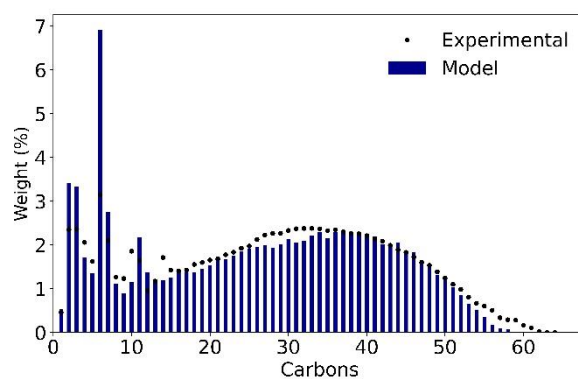

Figure 1. HDPE production distribution at 550 °C (bars are the model results, dots are micropyrolyzer results).

4. Conclusions

For the first time, HDPE pyrolysis is modeled using kMC, and the product distribution accuracy clearly shows that the methodology is robust even when complex reaction networks are considered. Additionally, the integration of a thermodynamic model, phase transition, with the kinetic package is also a novelty – not only employing kMC as a methodology but in plastic pyrolysis modeling. The validation with experimental data can be further extended to different temperatures and pressures, and it is an initial step to validate pilot-scale pyrolysis reactors.

References
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