

Reduced-order condensed-phase kinetic models for polyethylene thermal degradation

A. Locaspi, T. Faravelli

tiziano.faravelli@polimi.it

CRECK Modeling Lab, DCMIC, Politecnico di Milano, Italy

Abstract

In a circular economy perspective, plastic wastes (PW) can be a source of chemicals, energy vectors and fuels. Pyrolysis, gasification, and partial oxidation technologies can be employed to produce chemicals, fuels, or energy. Modelling the thermochemical valorization requires first the definition of suitable condensed phase pyrolysis mechanisms for each constituent. This work proposes a reduced and a multi-step condensed-phase kinetic model for polyethylene (PE) thermal degradation for CFD applications. The former model employs 50 species and 480 reactions, while the latter involves 10 species and 10 reactions. The degradation rate and the selectivity to the different products is obtained from a validated semi-detailed model. The kinetic mechanisms are complemented by the thermochemistry of gas, liquid, and solid-phase species, accounting for phase-transition through pseudo-chemical reactions. Model validations are performed by comparison with experimental data in terms of mass loss, heat fluxes and product distribution profiles. Extending the proposed approach to other polymers and considering secondary gas-phase reactions offers a powerful tool to model PW chemical recycling processes.

Introduction

Industrial scale implementation of thermochemical recycling is a key step towards circular and sustainable chemical and energy industries [1]. Product distribution optimization, process/reactor design, and pollutant control largely benefit from fluid dynamics and chemical kinetic modelling tools, thus motivating the present work. Studies on PW mixtures have only been emerging recently, while single polyolefins condensed-phase degradation has been extensively studied in the past decades [2]. Several models have been presented for polyethylene (PE) pyrolysis, most being one-step or highly detailed mechanisms [1]. The former describe only polymer mass-loss, while the latter achieve high detail in volatile predictions but are computationally expensive. Industrial applications require accurate but flexible models able to predict the key physico-chemical steps of the degradation, i.e., residence times, heat requirements and product distribution. Reduced-order models capture the phenomena involved at a lower computational cost.

This work proposes a methodology to derive reduced-order CHEMKIN-like condensed-phase kinetic models. A reduced and a multi-step model are obtained for PE pyrolysis, by lumping of a validated semi-detailed mechanism [3]. The resulting

kinetic models offer two levels of compromise between accuracy and cost and prove able to describe a wide range of operating conditions. The models are complemented by thermochemistry of all species. Further work will address secondary gas-phase reactions, while coupling these models to other polymer models enables describing PW valorization. The proposed models are freely available on GitHub [4].

Reduced semi-detailed mechanism (PE-50-480)

The semi-detailed model for PE [3] follows the Functional Groups (FG) methodology, distinguishing polymeric chains in High (HMW) and Low Molecular Weight (LMW) species. The former are represented with pseudo-species representative of the polymer chemical moieties, the latter with species of interest. The reduced mechanism follows the same approach and describes the HMW chains with the same mid- (MC) and end-chain (EC) units. A species representative of the crystalline polymer is also introduced, together with its melting reaction. The LMW distribution is described with real species for $C < C_5$ and by vertical lumping of the $C > C_5$ range introducing paraffin, olefin, and diolefin for C_7 , C_{16} , C_{30} , and C_{60} . A single radical isomer is introduced for each stable species. For instance, as shown in Figure 1, HMW chains decompose forming terminal EC radicals ($P-\dot{C}_{40}H_{80_T}$) that propagate by unzipping, backbiting or stabilize to " $P-C_{40}H_{81}$ ". H-abstraction on this EC forms a secondary radical ($P-\dot{C}_{40}H_{80}$) that decomposes by β -scission. The reduced model lumps them both into " $P-\dot{C}_{40}H_{80}$ ", which undergoes all reactions of the isomers. The selectivity between the pathways is obtained by weighting on the temperature-dependent ratio between the two isomers [5]. The reduced kinetic model employs 50 gas + liquid species and 480 liquid reactions, i.e., a decrease of $\sim 60\%$ and $\sim 85\%$ in species and reactions compared to the semi-detailed mechanism [3].

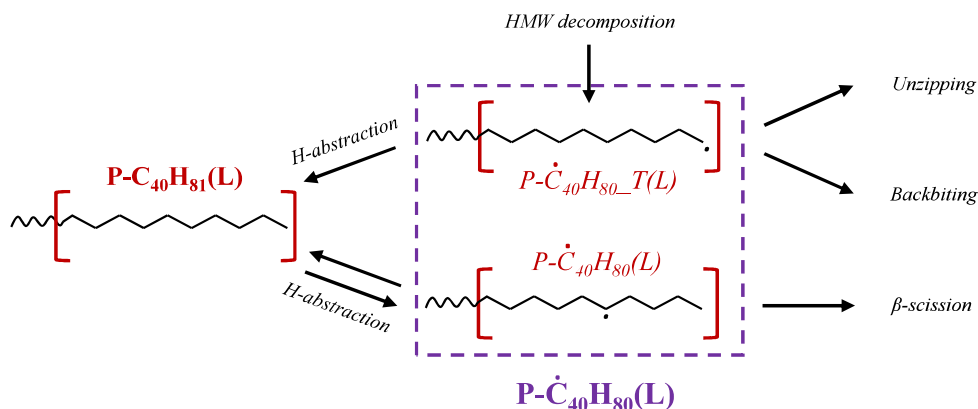


Figure 1. Representation of the radical isomer lumping for EC paraffin radicals.

Multi-step fully lumped mechanism (PE-10-10)

The multi-step model describes only the key aspects of the degradation process to reduce the computational cost. HMW chains are represented only by the crystalline and molten mid-chains, using the same carbon numbers as the reduced model. The LMW distribution is described by real species for the permanent gases (C_2H_4 , C_3H_8 ,

C_3H_6 , C_4H_6) and by lumped species representative of the petroleum cuts (C_5 - C_{60}). Only the olefins are included, introducing NC_7H_{14} for oil cuts (C_5 - C_{10}), $C_{16}H_{32}$ for diesel cuts (C_{11} - C_{20}) and $C_{30}H_{60}$ for waxes (C_{21+}). All species form in gas-phase, except for $C_{30}H_{60}(L)$ that can undergo liquid-phase degradation before evaporating. The multi-step mechanism is sketched in Figure 2. The crystalline phase melts as in the reduced model, and the molten polymer decomposes through 4 major pathways: backbone degradation, allyl formation, backbiting and unzipping. Each step is represented by a lumped reaction that accounts for the products of the semi-detailed mechanism. The rate of backbone degradation is estimated from the steady-state assumption on the total radical pool and assuming β -scissions are rate determining [6]. The selectivity to the other pathways is the same as the reduced model. Overall, this mechanism employs 10 gas + liquid species and 10 reactions, i.e., respectively a decrease of 92% and 99.7% compared to the semi-detailed mechanism [3].

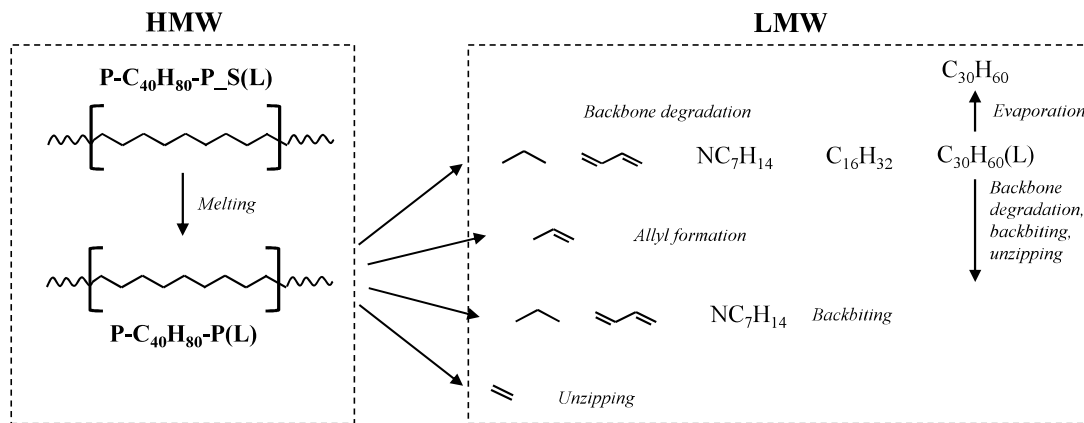


Figure 2. Schematic representation of the multi-step reaction mechanism.

Thermochemistry

The proposed mechanisms involve only irreversible reactions, and the estimation of thermodynamic properties allows to perform energy balances. Species properties are computed starting from gas-phase approaches [7]. Liquid-phase thermochemistry is differentiated according to the species critical temperature (T_c). For $T > T_c$ the gas-phase NASA values are employed, while at $T < T_c$ evaporation properties [8,9] are employed to evaluate the liquid-phase polynomials. To avoid the discontinuity at $T = T_c$, the transition temperature between the liquid and gas polynomials is defined such that the species enthalpy is continuous. On the other hand, the specific heat is intrinsically discontinuous.

The enthalpy and heat capacities of molten MC and EC are evaluated with the same approach, assuming a $T_c \rightarrow \infty$. Conversely, their entropies are estimated as the difference between two real chains of 100 and 110 MC units. The thermochemistry of the crystalline phase is estimated from literature data on heat capacities and melting enthalpies [10]. Above the melting temperature, the Einstein functional form is employed to constrain the high T limit for the heat capacity.

Model Validation

The proposed models are validated with the semi-detailed model [3] and a wide range of experimental data from the scientific literature in terms of mass-loss profiles, heat fluxes, and product distribution as shown in Figure 3 and 4.

Figure 3.a shows the comparison in terms of mass-loss profiles. Both reduced-order models reproduce the polymer degradation with similar accuracy compared to the semi-detailed model. While differences are observed, these are within the author-to-author experimental variability. At low T, the reduced model predicts slightly longer degradation times, possibly because of underestimation of allylic reactivity. The multi-step model predicts a smoother degradation profile, as the simplified reaction kinetics do not account for the time-varying reactivity.

Figure 3.b shows the comparison in predicted heat fluxes at 10°C/min. The models employ the same thermochemistry, and differences are related to the variations in mass-loss predictions. The melting peak is correctly described by the simplified kinetic approach. Conversely, the models underestimate the heat fluxes in the 200–400°C, although a wide scattering is also observed in terms of experimental data. Further experimental work is required to validate the proposed approach.

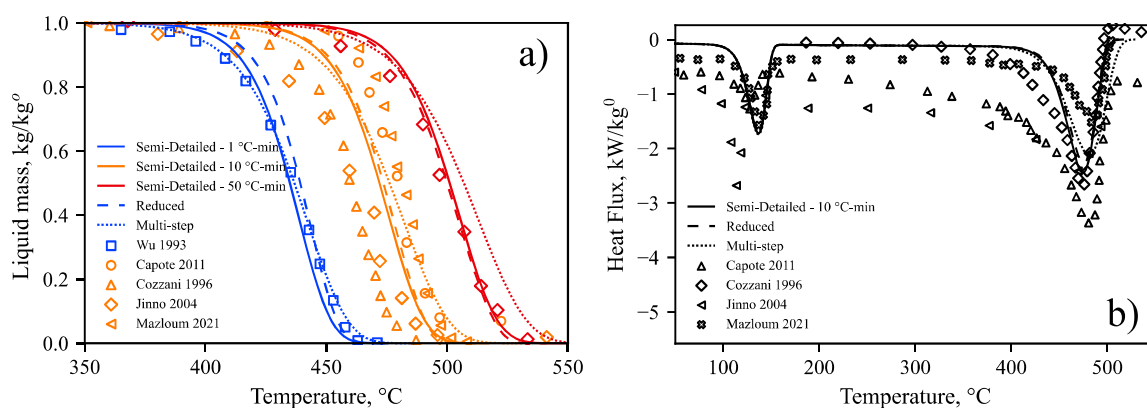


Figure 3. Model validation with data [11–15] on: a) mass-loss, b) heat fluxes.

Figure 4 shows the comparison in terms of mass distribution data. The semi-detailed and reduced models predict the detailed carbon distribution and the differences in unsaturation. Conversely, because of the strong lumping employed, the multi-step model describes only the petroleum cuts formed. Overall, all models capture the trend in the variation of product yields across the considered temperature range. Differences are observed, as the multi-step model neglects CH₄ formation, and the reduced one overestimates C₂H₄. Considering C₃ yields, the semi-detailed and reduced model show similar predictions, while the multi-step mechanism overestimates them. The multi-step model underestimates oil-cuts and underestimates diesel-cuts at high T, possibly due to the strong lumping. The higher oil yields of the reduced model are consequence of the strong simplification in selectivity between terminal and internal radicals.

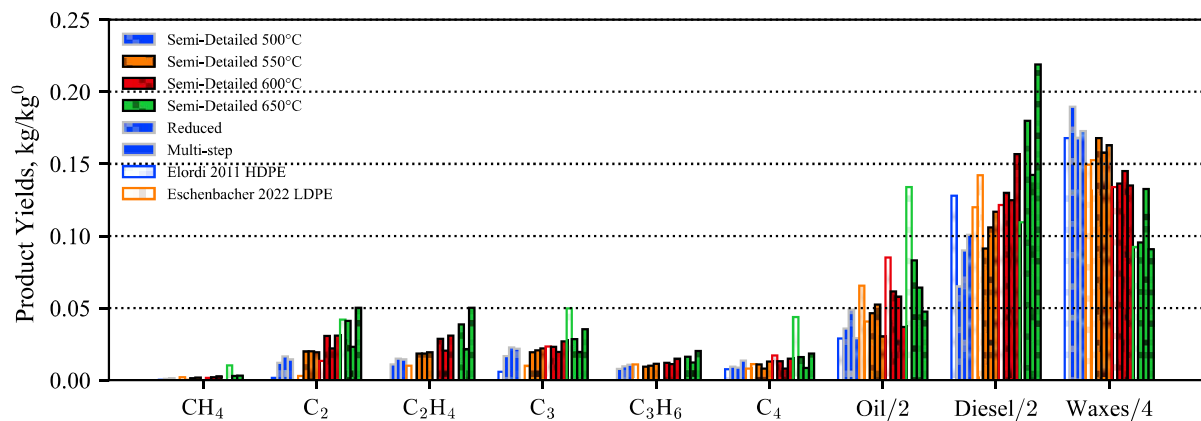


Figure 4. Model validation with mass product distribution data [16,17].

Conclusions

This work proposes a methodology to derive reduced-order condensed-phase kinetic models, employing PE as case-study for validation. A reduced and a multi-step model are proposed, coupled with the estimation of thermochemical properties. The reduced model lumps radical isomers and involves 50 species and 500 reactions, while the multi-step mechanism simplifies the radical chemistry in few global steps and involves 10 species and 10 reactions. The framework is validated with literature mass-loss profiles, heat fluxes, and product yields. Future activity will address evaluation of gas-phase reactions and development of similar reduced models also for other polymers of interest to describe PW valorization.

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