

Advanced Modeling of High Density Polyethylene Pyrolysis

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Abstract

This work presents a novel approach for predicting product composition during the pyrolysis of high density polyethylene (HDPE) into fuel. A coupled two-model framework is suggested: A lumped-empirical model depicts the products from the first stage in terms of gas, oil and waxes; and a population-balance model tracks the latter evolved products using mechanistic reactions to predict the carbon-chain length distribution in the end products. The lumpedempirical model is developed specifically for this purpose and is based on literature data, whereby, reaction kinetics were estimated using a parameter estimation technique. The mechanistic model tracks 181 species according to their carbon-chain length distribution in a computationally efficient manner showing good fit with literature data.

Keywords: Pyrolysis model, plastic waste to fuel, chain length distribution.

1. Introduction

Pyrolysis is an effective method that converts waste (biomass, municipal waste and plastic waste among others) into fuel [1]. Several researchers, thus, have been developing tools to understand in depth the mechanisms that drive the thermal and catalytic degradation of polymer waste and predict their kinetics as well as product distributions. The need to define product distributions and specify end products is of utmost importance when the fuel quality along with the economic, environmental, and energy aspects of the plastic waste thermal degradation process are being considered. Hence, the development of high-fidelity models that describe the frequency distribution of products is taking special attention nowadays.

This work aims at presenting a new approach to modeling high density polyethylene (HDPE) pyrolysis. Both a pathway model (Lumped-Empirical) and a mechanistic model (Population-Balance) were combined for that purpose. The population balance equations describe the mechanistic reactions that occur at the molecular level during the thermal degradation or pyrolysis of high density polyethylene. The population balance equations found in the work of Kruse et al. [2] constitute a strong foundation for this purpose. However, in this work, unlike most models found in literature, the population balance equations do not use the moments' method, rather, they are solved explicitly. The characteristics of this modeling scheme are: (a) Identify, in the first stage, the intermediate lumped products from polyethylene pyrolysis such as wax, low molecular weight product and gas using a lumped-empirical

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model. (b) Use the intermediate lumped products from the first stage as an input to the population-balance model to produce the carbon chain length spectrum of the final products.

The details of these two models are illustrated in subsequent sections of this report, and the prediction capability of the hybrid approach is assessed against data available in the literature for the thermal pyrolysis of HDPE at 420°C.

2. Modeling the Two-Stage Pyrolysis Process

The overall pyrolysis process is modeled in two stages including the thermal breakage of the polymer into a predefined set of lumped products, and the degradation of the product lumps obtained from the first stage into a range of products which are described according to their carbon chain length.

2.1. Modeling the First Pyrolysis Stage

The first stage of the overall modeling process is composed of a lumped-empirical model that predicts the mass (and molar) yield of various product lumps. The mass yields of low molecular weight products (oil) and gases from Levine et al. [3] at 420°C were used to construct the lumped-empirical model. A parameter estimation technique was applied to determine the reaction rate constants [10].

The proposed model involved five lumps including the polymer (P) that assumed to form Oil, gas (G), heavy wax (Hw), and light wax (Lw). It should be noted that Oil is assumed to have a carbon-chain length ranging from five up to

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twenty three. As for the wax products, they range from a carbon-chain length of twenty four up to forty four. The following illustration shows the considered model pathways,



Fig. 1. Schematic of the proposed pyrolysis pathway model

The governing differential equations that model this process are as follows:

 $dP/dt = -k_1P - k_2P - k_3P - k_4P$ $dHw/dt = k_4P - k_8Hw - k_9Hw$ $dLw/dt = k_1P - k_6Lw - k_5Lw$ $dOil/dt = k_2P + k_5Lw + k_9Hw - k_7Oil$ $dG/dt = k_3P + k_6Lw + k_7Oil + k_8Hw$

where P is the polymer undergoing pyrolysis, Hw is heavy wax, Lw is light wax, Oil is liquid oil, and G is gas. The estimated rate constants for the above model are listed in Table 1.

Table 1: Estimated rate constants at 420°C

Parameter	Value (1/min)
\mathbf{k}_1	0.170488
\mathbf{k}_2	2.43E-08
k ₃	0.0301269
\mathbf{k}_4	0.206132
k5	0.0146288
\mathbf{k}_{6}	0.0103907
k ₇	2.25E-14
\mathbf{k}_8	0.0204982
k 9	3.48E-10

2.2. Modeling the Second Pyrolysis Stage

Kruse et al. [2] developed a highly detailed mechanistic model to predict the product species from HDPE waste pyrolysis. In fact, the carbon chain length in a polymer is quite large (ranging in ten to hundred thousand) as such a large number of equations are required to model the carbon chains from the polymer down to the end short-chain products. The moment method is generally used to solve the associated large set of population balance equations by using only the first three moments for each species. This reduces the computational load and stiffness of the problem. The population balance equations are written for the dead chain polymer, D, the mid-chain radicals, Rm, and the end chain radicals, Re. The subscripts denote the carbon chain length with *i* taking any value between 1 and *n*, where *n* is the maximum number of carbon chains in the polymer. The following mechanistic reactions are used:

1- Random Fission/Radical Recombination

$$D_n \stackrel{k_f,k_c}{\longleftrightarrow} Re_i + Re_{n-i}$$

$$\begin{aligned} \frac{dD_n}{dt} &= -k_f (n-1)D_n + k_c \sum_{i=1}^{n+1/2} R_{\theta_i} R_{\theta_{n-1}} \\ \frac{dR_{\theta_i}}{dt} &= k_f (n-1)D_n - k_c Re_i Re_{n-i} \\ \frac{dR_{\theta_{n-i}}}{dt} &= k_f (n-1)D_n - k_c Re_i Re_{n-i} \end{aligned}$$

2- Specific Chain Fission/Radical Recombination

$$\begin{split} D_n & \stackrel{k_{fs},k_{cr}}{\longleftrightarrow} Re_{n-s} + r_s \\ \frac{dD_n}{dt} &= -k_{fs}(n-1)D_n + k_c Re_{n-s}r_s \\ \frac{dRe_{n-s}}{dt} &= k_{fs}(n-1)D_n - k_c Re_{n-s}r_s \\ \frac{dr_s}{dt} &= k_{fs}(n-1)D_n - k_c Re_{n-s}r_s \end{split}$$

The dead polymer chain here can break at a specific point chosen to be a gaseous product of length 1 representing s. Specific chain fission can occur for any of the products. This requires that n be variable from the smallest chain length, here 2, up to n giving all the products the possibility to undergo specific chain fission. Note that the factor n-1 represents the number of breakable carbon chains and is used to favor the breakage of the species with higher carbon chain lengths.

3- Hydrogen Abstraction

$$\begin{aligned} & \text{Ke}_n + D_i \stackrel{k_{tr,e};k_{tr,m}}{\longrightarrow} D_n + Rm_i \\ & \frac{dD_i}{dt} - -N_H^m k_{tr,e} Re_n (n-1) D_i + N_H^e k_{tr,m} Rm_i D_n \\ & \frac{dD_n}{dt} = N_H^m k_{tr,e} Re_n (n-1) D_i - N_H^e k_{tr,m} Rm_i D_n \\ & \frac{dRe_n}{dt} = -N_H^m k_{tr,e} Re_n (n-1) D_i + N_H^e k_{tr,m} Rm_i D_n \\ & \frac{dRm_i}{dt} = N_H^m k_{tr,e} Re_n (n-1) D_i - N_H^e k_{tr,m} Rm_i D_n \end{aligned}$$

Where N_H^m and N_H^e are the number of abstractable hydrogen atoms from the mid-chain and end-chains respectively. *n* varies between the smallest chain length up to *n*. This gives all the products the possibility to undergo chain fission. Note that it is not possible to have a mid-chain radical with a carbon chain length of less than 3, hence the minimum value that *n* can take here is 3. The factor *n*-1 represents the number of breakable carbon chains and is used to favor the forward hydrogen abstraction process and formation of mid-chain radicals.

4- -Scission/Radical Addition

$$Rm_n \stackrel{k_{br} \cdot k_{ra}}{\longleftrightarrow} Re_i + D_{n-i}$$

$$\frac{dRm_n}{dt} = -2k_{bs}Rm_n + k_{ra}\sum_{i=1}^{n+1/2} Re_i D_{n-i}$$
$$\frac{dRe_i}{dt} = 2k_{bs}Rm_n - k_{ra}Re_i D_{n-i}$$
$$\frac{dD_{n-i}}{dt} = 2k_{bs}Rm_n - k_{ra}Re_i D_{n-i}$$

The free electron on the mid-chain radical can reside anywhere along the chain length except for the ends of the chain. This results in the possibility of having -Scission anywhere along the chain length. For any value of n, -Scission can occur at any point up to the middle of the chain, n+1/2, resulting in the summation to include all the possibilities of scissions. Because the minimum number of carbon atoms for a mid-chain radical is 3, n varies from the latter up to n to fully include all the species that can undergo -Scission.

5- Depropagation/Propagation

$$\begin{aligned} & Re_n \stackrel{k_{dp}:k_p}{\longrightarrow} Re + M \\ & \frac{dRe_n}{dt} = -k_{dp}Re_n + k_pReM \\ & \frac{dRe}{dt} = k_{dp}Re_n - k_pReM \\ & \frac{dM}{dt} = k_{dp}Re_n - k_pReM \end{aligned}$$

Monomer formation in depropagation is straight forward and can occur at any chain length thus the variation of n should be between 3, the smallest chain length to yield a monomer, up to-n.

6- Backbiting

$$\begin{aligned} & Re_n \stackrel{k_{bbf}; k_{bbr}}{\longleftrightarrow} Rm_n \\ & \frac{dRe_n}{dt} = -k_{bbf} Re_n + k_{bbr} Rm_n \\ & \frac{dRm_n}{dt} = k_{bbf} Re_n - k_{bbr} Rm_n \end{aligned}$$

Although this is a reaction not resulting in a change of carbon chain length, it consists of several reactions of hydrogen shifts. End-chain hydrogen shifts include 1-4, 1-5, 1-6, and 1-7 and mid-chain hydrogen shifts include x-x+3, x-x+4, x-x+5 where x is the position of the free electron on the product chain.

7- Specific -Scission/Radical Addition

$$Rm_{n} \stackrel{k_{bs};k_{ra}}{\longleftrightarrow} Re_{n-s} + d_{s}$$
$$\frac{dRm_{n}}{dt} = -k_{bs}Rm_{n} + k_{ra}Re_{n-s}d_{s}$$
$$dP_{n}$$

$$\frac{aRe_{n-s}}{dt} = k_{bs}Rm_n - k_{ra}Re_{n-s}d_s$$

$$\frac{dd_s}{dt} = k_{bs}Rm_n - k_{ra}Re_{n-s}d_s$$

The mid-chain radical undergoes scission at a specific point chosen to be a gaseous product of length 4 representing *s*. Specific -Scission can occur for any of the products. This requires that *n* be varying from the smallest chain length, here 5 due to the size of the selected product, up to *n*, giving all the products the possibility to undergo specific -Scission.

8- Disproportionation

$$Re_{n} + Re_{i} \xrightarrow{\kappa_{d}} D_{n} + D_{i}$$

$$\frac{dD_{n}}{dt} = k_{d}Re_{n}Re_{i}$$

$$\frac{dD_{i}}{dt} = k_{d}Re_{n}Re_{i}$$

$$\frac{dRe_{n}}{dt} = -k_{d}Re_{n}Re_{i}$$

$$\frac{dRe_i}{dt} = k_a Re_n Re_i$$

dt

This termination reaction can cover all the range of products with n starting at 1.

The rate constants for the former reactions follow Arrhenius law and were adopted from literature [3, 5]. For completion, they are listed in Table 2.

Table 2: Mechanistic rate parameters for HDPE pyrolysis

Reaction Type	Symbol	Frequency factor, A (1/s or L/(mol.s))	Activation Energy (kcal/mol)
Chain fission	\mathbf{k}_{f}	1E+16	89.66
Allyl chain fission	\mathbf{k}_{fs}	1E+16	75.2
Radical recombination	k _c	1.1E+11	2.3
Disproportionation	\mathbf{k}_{d}	1.10E+10	2.3
End-chain -scission	\mathbf{k}_{dp}	1.32E+13	28.386
End-chain -scission backwards	\mathbf{k}_{p}	1.32E+13	28.386
Mid-chain -scission	k _{bsm}	5.35E+14	28.9028
-scission to LMWS	k _{bs}	2.33E+13	28.8572
Radical addition	k _{ra}	2.88E+07	5.8728
Hydrogen abstraction forward	k _{tre}	2.75E+08	10.43
Hydrogen abstraction backward	$\mathbf{k}_{\mathrm{trm}}$	2.75E+08	10.43
1,4-hydrogen shift	$\mathbf{k}_{\mathrm{bbf}}$	1.58E+11	20.8
1,5-hydrogen shift	$\mathbf{k}_{\mathrm{bbf}}$	1.82E+10	13.7
1,6-hydrogen shift	$\mathbf{k}_{\mathrm{bbf}}$	1.05E+10	18.3
1,7-hydrogen shift	\mathbf{k}_{bbf}	3.00E+09	18.3
x,x+3-hydrogen shift	\mathbf{k}_{bbr}	1E+11	21.2
x,x+4-hydrogen shift	\mathbf{k}_{bbr}	1.26E+11	14.7
x,x+5-hydrogen shift	\mathbf{k}_{bbr}	7.24E+09	18.1

The mechanistic reactions of the population-balance model are involved in bond-breaking and formation of radicals to various products. Different reactions account for different product formation. They can be summarized in the table below:

Table 3: Product formation from different reaction types

Reaction Type	Product Formed
Random Fission	End-chain Radical
Specific Chain Fission	Mid-chain Radical
Radical Recombination	Single-bond Product
Hydrogen Abstraction	Single-bond Product and Mid-chain Radical
-Scission	Double-bond Product and End-chain Radical
Specific -Scission	Double-bond Product and End-chain Radical
Radical Addition	Mid-chain Radical
Depropagation	Double-bond Product and End-chain Radical
Propagation	End-chain Radical
Backbiting	Mid-chain Radical (forward); End- chain Radical (backward)
Disproportionation	Single-bond Product and Double- bond Product

The product yields from the second stage model differentiate between single-bond and double-bond products. It should be noted that double-bond products are formed with the following mechanistic reactions:

-Scission

 $\sim CH_2 - CH_2 - CH_2 - CH_2 - CH_2 \sim \rightarrow$ $\sim CH_2 - CH_2 - CH_2 - CH_2 + CH_2 = CH_2 \sim$

Specific -Scission

$$\sim$$
CH₂ - CH₂ - CH₂ - CH₂ - CH₂ - CH₃ \rightarrow

$$\sim CH_2 - CH_2 + CH_2 = CH_2 - CH_2 - CH_3$$

Depropagation

$$\sim CH_2 - CH_2 - \dot{C}H_2 - CH_3 \rightarrow$$
$$\sim CH_2 - \dot{C}H_2 + CH_2 = CH_2$$

Disproportionation

$$\label{eq:CH2} \begin{split} \sim & \operatorname{CH}_2 - \operatorname{CH}_2 - \operatorname{CH}_2 + \operatorname{CH}_2 - \operatorname{CH}_2 - \operatorname{CH}_2 \sim \rightarrow \\ \sim & \operatorname{CH}_2 - \operatorname{CH}_2 - \operatorname{CH}_3 + \operatorname{CH}_2 = \operatorname{CH}_2 - \operatorname{CH}_2 \sim \end{split}$$

3. Results and Discussion

The combined model is designed to work in a sequential manner. The pathway model is solved with the purpose of delivering the proper initial conditions for the mechanistic model as such the mass yield of the different product lumps are taken at the time where the mass yield of the polymer is near negligible (0.01 percent) thus having no significant effect on the final products. By doing so, the mechanistic model does not make use of the original polymer high carbon chain length. This dramatically reduces the number of equations to be solved. The moment method is not applied in this case, and the differential equations in section 2.2 are explicitly solved without any further transformations. The mass yields of the low molecular weight lumps obtained from the pathway model (Fig. 2) are used as initial values by the mechanistic model. The yields of the pathway model are distributed evenly for the oil products [3], and with experimental wax distribution [6] for the wax-ranged products.



Fig. 1. Time evolution of the product lumps molar yield

Wax-range products are considered to be the highest carbonchained products in this model. They include products of up to 44 carbons in the backbone chain [7] (under a pyrolysis temperature of 420°C). Therefore, the mechanistic model tracks the decomposition of carbon chains with *n* varying between 1 and 44 including products with single and double bonds. The combined model thus tackles 181 species. Further model assumptions are made to help solve the set of equations,

- Isothermal conditions for the entire reaction time
- Even spatial distribution for the polymer melt
- Relatively small time and reaction scales allowing species to react before they leave the polymer melt

The illustrations in Figures 3-6 show a comparison between the model results and literature experimental results of Levine et al. [3] for a carbon-chain length ranging between 8 and 23.



Fig. 2. Comparison between model and literature results of condensable alkene yields for HDPE pyrolysis at 420 °C after 90 minutes



Fig. 3. Comparison between model and literature results of condensable alkene yields for HDPE pyrolysis at 420 °C after 150 minutes



Fig.4. Comparison between model and literature results of condensable alkane yields for HDPE pyrolysis at 420 °C after 90 minutes

The results of the condensable alkenes and alkanes fit quite well with the literature experimental results. It is evident that the results of the double-bonded products are more closely matched to the literature data than their single-bonded counterparts. This can be attributed to two factors. One is the initial condition provided by the pathway model and the other would be the lack of structural modeling such as branching, cyclization and aromatization. The pathway model fits well with the adopted literature data. However, the evolutions of the lumps of products follow a profile typical of that of a first order system as seen in the literature [8]. Also, the lack of data for the Hw and Lw lumps which were calculated separately, made the pathway model assembly more difficult to mimic the results of oil and gas lumps. The initial conditions that were entered into the mechanistic model slightly differed from the data provided by Levine et al. [3]. Nonetheless, the model adopted the same mechanistic reactions in the literature [3,9] thus, does not have a different approach to the mechanistic aspect of the solution for modeling the product evolution. Rather, it approaches the solution in a different way.

The model tracks mid-chain and end-chain radicals. This was important for explaining the evolution of the products as well as their behavior. Moreover, model simulations showed that the presence of both mid-chain and end-chain radicals is at most times 84 percent of the overall mix of products. This means that as the reaction proceeds and the polymer starts to undergo different mechanistic reactions starting with random fission reactions, the presence of mid-chain and end-chain radicals is dominant. Little is known about the behavior of radicals in a pyrolysis process, except for their very high rate of formation and transformation to dead polymers. This model offers an insight on radical presence in a pyrolysis which is quite important for future process development and enhancements.



Fig. 5. Comparison between model and literature results of condensable alkane yields for HDPE pyrolysis at 420 °C after 150 minutes

3. Conclusion

A new approach was introduced to model polymer pyrolysis by coupling a lumped-empirical (pathway) model with a population-balance (mechanistic) model. The main aim behind this strategy was to reduce the number of equations to be solved (and minimize computational load) while maintaining the high fidelity of the model in terms of predicting accurately the chain length distribution in the final products. The two models were validated in this work based on literature data. The pathway model was designed with five lumps of products including the polymer itself.

The coupled models were successful in tracking 181 species during the pyrolysis of HDPE at 420 °C. The model displayed a good fit for condensable alkanes and even better for alkenes. The discrepancy in some of the results can be attributed to the absence of branching, weak bonds, cyclization and aromatization reactions in the adopted reaction equations.

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