



Advances in modeling plastic waste pyrolysis processes

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Abstract

The tertiary recycling of plastics via pyrolysis is recently gaining momentum due to promising economic returns from the generated products that can be used as a chemical feedstock or fuel. The need for prediction models to simulate such processes is essential in understanding in depth the mechanisms that take place during the thermal or catalytic degradation of the waste polymer. This paper presents key different models used successfully in literature so far. Three modeling schemes are identified: Power-Law, Lumped-Empirical, and Population-Balance based equations. The categorization is based mainly on the level of detail and prediction capability from each modeling scheme. The data shows that the reliability of these modeling approaches vary with the degree of details the experimental work and product analysis are trying to achieve.

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1. Introduction

Plastic materials have been around for a long time. They can be traced back to 1847. Their commercialization was onset after the shortage in supply of natural rubbers during the Second World War. Plastics are light in weight, easily molded, highly durable, and come at a low cost [1]. Besides, they have a wide range of applications as in plastic bags, bottles, accessories, chairs, tables and electronic devices. Consequently, more plastic wastes are thrown into the environment raising serious concerns as landfill areas are shrinking continuously. The fact that plastic wastes are non-biodegradable makes them reside in landfills for longer periods. In addition to taking up valuable land space, these wastes are a direct culprit in causing irreversible damage to the soil, under-ground water and nearby communities (e.g. fires and toxic fumes).

Alongside landfilling, incineration (known as quaternary recycling) is an economically viable route to get rid of plastic wastes and recover valuable energy from their high calorific value. This method however is highly questionable due to the emissions of toxic compounds such as dioxins and furans [2]. On the other hand, bringing the plastic waste back into the production/consumption cycle via recycling is proven a successful alternative. One of the most promising types is tertiary recycling which involves thermally degrading plastics at high temperatures to crack the polymer chains to a variety of hydrocarbon molecules. These can act as a feedstock in a chemical production process or can be upgraded to be used as a fuel similar to that derived from crude oil.

The development of a mathematical model that can simulate the pyrolysis of plastic waste is of great value. It can be used in computer-aided simulations to analyze product distribution and yield. Also,

modeling the thermal degradation kinetics would help optimize and improve the degradation process in terms of energy, product quality and reaction time. There have been mainly three successful approaches to model the thermal degradation process. These can be grouped under: Power-Law, Lumped-Empirical, and Population-Balance.

2. Power-law modeling

In this type of modeling, the degree of conversion of the polymer uses a rate of reaction expressed as,

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (1)$$

where $k(T)$ is the rate constant and $f(\alpha)$ is a function of conversion that describes the type of reaction. $k(T)$ follows the well-known Arrhenius equation.

Equation (1) can be expanded to give,

$$\frac{d\alpha}{dt} = \frac{d\alpha}{dT} \frac{dT}{dt} = \frac{d\alpha}{dT} \beta \quad (2)$$

where T and β are the absolute temperature and the heating rate respectively.

After substitution and rearrangement the following is obtained,

$$\frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \exp(-E/RT)dT \quad (3)$$

Setting $G(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)}$ and integrating gives,

$$\ln G(\alpha) = \ln \frac{AE}{R} - \ln \beta + \ln p(x) \quad (4)$$

Such that $p(x) = \frac{e^{-x}}{x} - \int_x^\infty \frac{e^{-x}}{x}$ where $x=E/RT$. Various solutions for the function $p(x)$ are proposed in the literature as listed below,

- Doyle's approximation [3],

$$\ln p(x) = -5.3305 + 1.052x. \quad (5)$$

This gives,

$$\ln \beta = \ln \frac{AE}{R} - \ln G(\alpha) + -5.3305 + 1.052x \quad (6)$$

- Friedman's method [4],

$$\ln \frac{d\alpha}{dt} = \ln \beta \frac{d\alpha}{dT} = \ln[Af(\alpha)] - \frac{E}{RT} \quad (7)$$

- Coats-Redfern's method [5],

$$\ln \frac{G(\alpha)}{T^2} = \ln \left[\frac{AR}{\beta E} \left(1 - \frac{2RT}{E} \right) \right] - \frac{E}{RT} \quad (8)$$

- Flynn-Wall-Ozawa's method [6, 7],

$$\ln p(x) = -2.315 - 0.4567x. \quad (9)$$

This after substitution becomes,

$$\ln \beta = \ln \frac{AE}{RG(\alpha)} - 2.315 - 0.4567 \frac{E}{RT} \quad (10)$$

- Kissinger-Akahira-Sunrose's method [8, 9] is based on Coats-Redfern approximation $p(x) = \frac{e^{-x}}{x^2}$ such that,

$$\ln \frac{\beta}{T^2} = \ln \frac{AR}{Eg(\alpha)} - \frac{E}{RT} \quad (11)$$

When the left hand side in the above equation is plotted against $1/T$, the activation energy can be found from the slope of the line for a fixed conversion α . As for $f(\alpha)$, it represents a function of the kinetic model. It may be written in a general form of $f(\alpha) = (1-\alpha)^n \alpha^m [-\ln(1-\alpha)]^p$ where m and p are exponents and n is the order of reaction. An assessment of the various models proposed was done in a previous review [10]. The findings state that low heating rates tend to overestimate the activation energy and that equations of first and second order tend to be in agreement with the activation energies found in literature. The common models [11] used for $f(\alpha)$ are described in Table 1,

Table 1. Models of kinetic function $f[\alpha]$

Model	$f[\alpha]$
Phase boundary – controlled reaction [contracting area]	$[1 - \alpha]^{1/2}$
Phase boundary – controlled reaction [contracting volume]	$[1 - \alpha]^{2/3}$
Random nucleation–Unimolecular decay law	$[1 - \alpha]$
Reaction nth order	$[1 - \alpha]^n$
Johnson–Mehl–Avrami	$n[1 - \alpha][-\ln[1 - \alpha]]^{1-1/n}$
Two-dimensional growth of nuclei [Avrami equation]	$2[-\ln[1 - \alpha]^{1/2}][1 - \alpha]$
Three-dimensional growth of nuclei [Avrami equation]	$3[-\ln[1 - \alpha]^{2/3}][1 - \alpha]$
One-dimensional diffusion	$1/[2\alpha]$
Two-dimensional diffusion	$1/[-\ln[1 - \alpha]]$
Three-dimensional diffusion [Jander equation]	$3[1 - \alpha]^{2/3}/2[1 - [1 - \alpha]^{1/3}]$
Three-dimensional diffusion [Ginstling–Brounshtein]	$3/2[[1 - \alpha]^{1/3} - 1]$
n-dimensional nucleation [Avrami–Erofeev equation]	$n[-\ln[1 - \alpha]]^n [1 - \alpha]$
Reaction of first order with autocatalysis	$[1 - \alpha][1 + K_{cat}\alpha]$
Reaction of n th order with autocatalysis	$[1 - \alpha]^n [1 + K_{cat}\alpha]$
Prout– Tompkins equation	$[1 - \alpha]^n \alpha^a$

After adopting a function that describes the degradation mechanism, the activation energy, pre-exponential constant and order of reaction can be calculated. The fractional weight can be expressed as a function of the fraction of a structural quantity, such as a group, a constituent, a broken bond, or any other.

It should be noted that no matter what the rate is function of (e.g. conversion α , concentration, chain bonds, etc.), the procedure for getting the pre-exponential constant and activation energy remains the same. Plotting the left hand side of the various equations vs. $1/T$ ought to generate a straight line. From the slope of this line, one can determine the activation energy and consequently the pre-exponential constant.

The power law modeling approach is direct and simple to implement. It is adopted by many researchers as summarized in Table 2. It is both computationally and time efficient. However, the mutual correlation of activation energy and pre-exponential constant makes these types of models apparent and not intrinsic because the activation energy from a model is often validated from a Thermo Gravimetric Analysis

(TGA) run. Also, this kind of modeling does not fully describe the mechanisms of the degradation process unless coupled to product identification equipment such as gas chromatography and/or mass spectrometry or other analytical equipment. It should be also noted that unless the sample is small enough for the TGA experiment, there will be mass and heat transfer restrictions thus, affecting the fitting process of a model using thermogravimetry.

3. Lumped-empirical modeling

In this approach, the model groups together the degradation products in a set of differential equations of mass concentrations that depict the formation of a predefined set of lumps. The solution of the differential equations determines the rate constants of the various formed lumps. Many researchers have used this type of modeling as shown in Table 3.

Table 2. Summary of Power-Law models

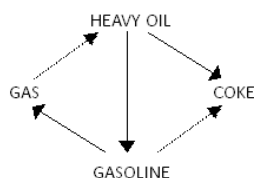
Reference	Parameters investigated	Estimated kinetic parameters	Findings
[10]	Rate of weight loss	Pre-exponential constant, Activation energy	Low values of the heating ramp overestimate the activation energy. First and second reaction orders provide good fit.
[11]	Rate of weight loss	Pre-exponential constant, Activation energy, Coefficient of partial process contribution	Employs a coefficient that expresses the contribution of partial processes to overall mass loss.
[12-15]	Concentrations of intermediates, volatiles	Pre-exponential constant, Activation energy, reaction order	Takes account of catalyst in model. Equations were integrated using the Euler method. Model is capable of simultaneously correlating experiments with catalysts studied.
[16]	Rate of weight loss	Pre-exponential constant, Activation energy	Reaction of first order. As the heating rate increases, gas yield increases and vice versa for liquid yield.
[17]	Fraction of broken bonds	Pre-exponential constant, Activation energy	Not every bond-broken in the main chain leads to volatile products.
[18]	Rate of weight loss	Pre-exponential constant, Activation energy	First order or nth-order $f[\alpha]$ are different from that of random scission mechanisms.
[19]	Rate of change of the number of each bond type	Pre-exponential constant, Activation energy	Measures intrinsic rather than apparent kinetic parameters taking into account that not every broken bond leads to volatilization. Model proved to be valid for the entire conversion range. Cannot be used above 400°C.
[20]	Rate of weight loss	Pre-exponential constant, Activation energy	A comparison of all available functions $f[\alpha]$ in literature was done.
[21]	Around 60 real and lumped species and radicals	Rate constant, Activation energy	Most reactions were of zero or first order.

Table 3. Summary of various Lumped-Empirical models

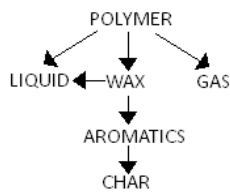
Reference	Product Lumps	Estimated kinetic parameters	Findings
[22]	Concentrations of Gasoline, Gas, Coke	Rate constant and activation energy	The kinetic parameters were evaluated by nonlinear least-squares regression.
[23]	Concentrations of Gas,	Pre-exponential	High residence time affects fit.
[24]	Liquid, Wax, Aromatics, Char	constant, Activation energy	
[25]	Concentrations of Intermediates, Paraffin, Vinyl Olefin, Tertiary Olefin, Internal Olefin, Residue	Reaction constant	Reactions of first order. Good fit of model. Olefinic double bonds are shifted from the terminal to internal position of the carbon chain under catalysis.
[26-29]	Concentrations of Complex of hydrocarbon and catalyst, n/isomeric olefins and carbenium, Intermediates, paraffins, olefins, HCl, Coke/BTX	Rate constants	Differential equations were solved with Runge-Kutta algorithm in Matlab. Model incorporated activity decay function for the catalyst.
[30]	Concentrations of Plastic mixture, solid lower molecular weight polymer, gas, light liquid fraction, heavy liquid fraction	Rate constants	All reactions are first order and irreversible. Logarithmic form of the Arrhenius equation did not display linearity thus deduced not to be the best approach for the calculation of activation energy and pre-exponential factor.
[31-33]	Fractions of Alkane, Alkene, and Dialkene	Rate constant and activation energy	Rate constants of different elementary reactions were found such as β -scission, H-abstraction [intermolecular & intramolecular], Recombination and Disproportionation reactions. Primary secondary and tertiary radicals were taken into account as well as liquid and gaseous phase reactions. Schultz distribution was assumed. Numerical integration was done through an implicit multi-step Adams-Moulton method or explicit Adams algorithm. Was able to replicate the TGA runs with good fit.

This approach is used to get the rate constants of the various lumps and determine their final concentrations. This type of modeling is somehow limited since it does not describe the reaction mechanisms and is limited to the proposed lumps in the model; below are some schemes identified by different researchers,

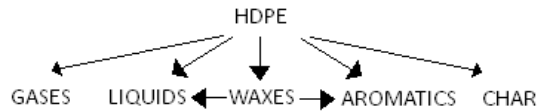
- Songip et al. [22],



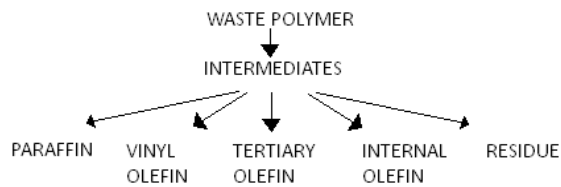
- Elordi et al. [23],



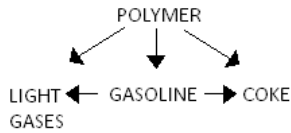
- Al-Salem et al. [24],



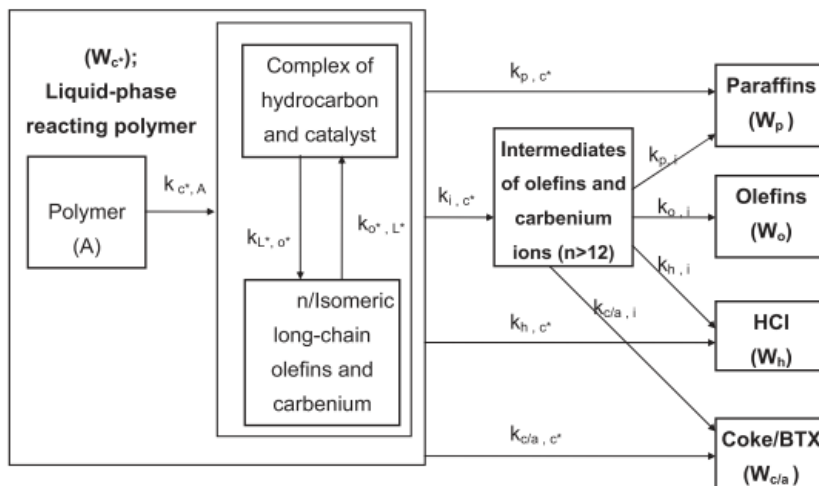
- Miskolczi et al. [25],



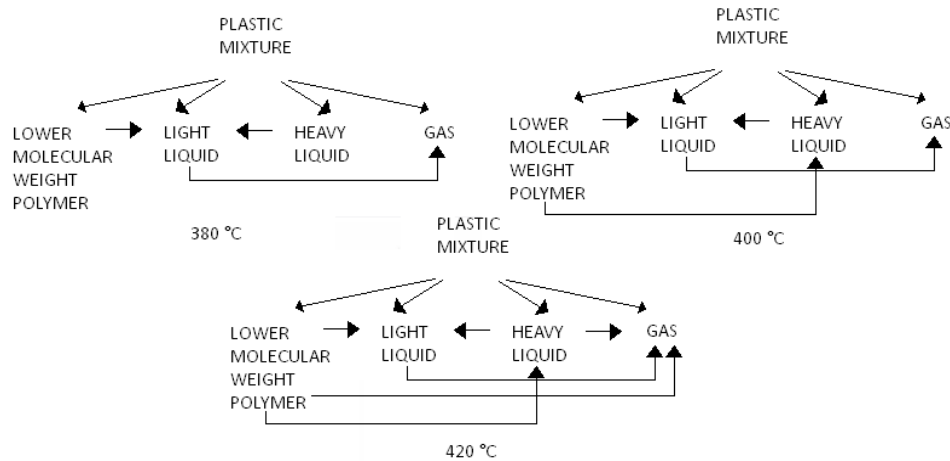
- Lin [26],



- Lin et al. [27-29],



- Costa et al. [30],



4. Population-balance based modeling

The population balance equations can be used to describe the evolution of the frequency distributions of polymeric chains with different molecular weights/sized fragments. Unit fragments can either yield random or parabolic distributions of binary daughter-products or specific distribution of products [34]. Molecular-weight distributions [MWD] can be determined experimentally by gas permeation chromatography. A general mechanism was proposed for the thermal degradation of addition polymers [35]. It entails the following set of reactions,

- Initiation reactions:
 - End-chain scission

$$\sim\text{CH}_2 - \dot{\text{C}}\text{HX} - \text{CH}_2 - \text{CH}_2\text{X} \rightarrow \sim\text{CH}_2 - \dot{\text{C}}\text{HX} + \dot{\text{C}}\text{H}_2 - \text{CH}_2\text{X}$$
 - Random scission

$$\sim\text{CH}_2 - \text{CHX} - \text{CH}_2 - \text{CHX} \sim \rightarrow \sim\text{CH}_2 - \dot{\text{C}}\text{HX} + \dot{\text{C}}\text{H}_2 - \text{CHX} \sim$$
- Depropagation

$$\sim\text{CH}_2 - \text{CHX} - \text{CH}_2 - \dot{\text{C}}\text{HX} \rightarrow \sim\text{CH}_2 - \dot{\text{C}}\text{HX} + \text{CH}_2 = \text{CHX}$$
- Hydrogen chain transfer reactions:
 - Intermolecular transfer reaction

$$\begin{aligned} \sim\text{CH}_2 - \dot{\text{C}}\text{HX} + \sim\text{CH}_2 - \text{CHX} - \text{CH}_2 - \text{CHX} - \text{CH}_2 \sim &\rightarrow \sim\text{CH}_2 - \text{CH}_2\text{X} + \sim\text{CH}_2 - \text{CHX} - \dot{\text{C}}\text{H} = \text{CHX} + \dot{\text{C}}\text{H}_2 \sim \\ \sim\text{CH}_2 - \dot{\text{C}}\text{HX} + \sim\text{CH}_2 - \text{CHX} - \text{CH}_2 \sim &\rightarrow \sim\text{CH}_2 - \text{CH}_2\text{X} + \sim\text{CH}_2 - \dot{\text{C}}\text{X} - \text{CH}_2 \sim \end{aligned}$$
 - Intramolecular transfer reaction

$$\sim\text{CH}_2 - \text{CHX} - \text{CH}_2 - \text{CHX} - \dot{\text{C}}\text{H}_2 \rightarrow \sim\dot{\text{C}}\text{H}_2 + \text{CHX} = \text{CH} - \text{CHX} - \text{CH}_3$$
- β -Cleavage of secondary radicals:

$$\sim\text{CHX} - \text{CH}_2 - \dot{\text{C}}\text{X} - \text{CH}_2 \sim \rightarrow \sim\dot{\text{C}}\text{HX} + \text{CH}_2 = \text{CX} - \text{CH}_2 \sim$$
- Branching

$$\begin{aligned} \sim\text{CH}_2 - \dot{\text{C}}\text{HX} + \sim\text{CH}_2 - \dot{\text{C}}\text{X} - \text{CH}_2 \sim &\rightarrow \text{CH}_2 - \text{CX} - \text{CH}_2 \sim \\ &| \\ &\text{CHX} - \text{CH}_2 \sim \\ \sim\text{CH}_2 - \dot{\text{C}}\text{X} - \text{CH}_2 \sim + \sim\text{CH}_2 - \dot{\text{C}}\text{X} - \text{CH}_2 \sim &\rightarrow \sim\text{CH}_2 - \text{CX} - \text{CH}_2 \sim \\ &| \\ &\sim\text{CH}_2 - \text{CX} - \text{CH}_2 \sim \end{aligned}$$
- Termination
 - Bimolecular coupling

$$\sim\text{CHX} - \dot{\text{C}}\text{H}_2 + \dot{\text{C}}\text{HX} - \text{CH}_2 \sim \rightarrow \sim\text{CHX} - \text{CH}_2 - \text{CHX} - \text{CH}_2 \sim$$
 - Disproportionation

$$\sim\text{CH}_2 - \text{CHX} - \dot{\text{C}}\text{H}_2 + \dot{\text{C}}\text{HX} - \text{CH}_2 - \text{CH}_2 \sim \rightarrow \sim\text{CH}_2 - \text{CHX} - \text{CH}_3 + \text{CHX} = \text{CH} - \text{CH}_2 \sim$$

It should be noted that other reactions, such as cyclization, aromatization, isomerizations and recombination, might take place throughout. This usually increases the degree of branching while the length of the polymer chain is reduced.

The population balance equations can be written for the above reactions using both discrete and continuous MWDs. If the MWD allows integrals to represent averages of the distribution, only then the

continuous kinetics are valid. Let us consider a random degradation of a polymer P with molecular weight x' . Then it will degrade into two fragments of lower molecular weights x and $x'-x$ according to the following equation:



The governing equation is then [36],

$$\frac{\partial p(x, t)}{\partial t} = -k(x)p(x, t) + 2 \int_x^{\infty} k(x')p(x', t)\Omega(x, x') dx' \quad (13)$$

where $\Omega(x, x')$ is the stoichiometric kernel that determines the distribution of scission products and $k[x]$ is the rate coefficient prone to have the form,

$$k(x) = k_p(x - x_0)^p \quad (14)$$

where x_0 is the smallest molecular weight chain that can crack. The general form of the stoichiometric kernel is,

$$\Omega(x, x') = x^m(x' - x)^m \Gamma(2m + 2) / [\Gamma(m + 1)^2 (x')^{2m+1}] \quad (15)$$

This can be reduced to $\Omega(x, x') = 1/x'$ in the case of totally random fragmentation; where $m=0$ and $m=\infty$ correspond to random and midpoint chain scission, respectively. In the case of proportioned, specific product release, or depolymerization, the stoichiometric kernel can be written in the form of a Dirac Delta function: $\Omega(x, x') = \delta(x - bx')$ where b is a fraction number.

The gamma function is defined by applying Stirling's formula as,

$$\Gamma(x) \approx (2\pi/x)^{1/2} x^x \exp(-x) \quad (16)$$

There are many ways to solve the integro-differential population balance equations. The moments' method, similarity method, numerical methods or any other method can be used to solve the aforementioned balance equations. Various solutions of the integro-differential population balance equations were discussed [37]. The most popular is to either differentiate the population balance equations to obtain a set of partial differential equations or to convert the equations into moments where the n^{th} moment is defined by:

$$p^{(n)}(t) = \int_0^{\infty} p(x, t) x^n dx \quad (17)$$

From here one can distinguish the following,

- The zeroth moment [$n=0$] is the time-dependent total molar concentration
- The first moment [$n=1$] is the mass concentration
- The normalized first moment produces the average MW, $p^{avg} = p^{[1]}/p^{[0]}$
- The mass average is given by, $M_w = p^{[2]}/p^{[1]}$
- The molar average is $M_n = p^{avg}$
- The Polydispersity index $D = M_w/M_n = p^{[2]} p^{[0]}/[p^{[1]}]^2$

$p^{[0]}$, p^{avg} , and p^{var} describe the shape characteristics of the distribution. The gamma distribution is also constructed from these three moments. It should be noted that the Gaussian, Poisson, and exponential distributions are special cases of the gamma distribution. The zeroth moment alone is usually required to determine the rate coefficient from experimental data. Applying the moment operation to the governing equation yields,

$$dp^{(j)}/dt = kc^{(j)}(1 - j)/(1 + j) - Kc^{(r+j)} \quad (18)$$

The moments represent the distribution via,

$$p(x) = [p^{(0)}/\beta\Gamma(\alpha)]y^{\alpha-1}\exp(-y) \quad (19)$$

where $y = [x - x_0]/\beta$, x_0 is the minimum size of a molecule, α and β are related to the first and second moments in expressions that define the average and variance of the gamma distribution function,

$$\begin{aligned} p^{(1)}/p^{(0)} &= x_0 + \alpha\beta \\ p^{(2)}/p^{(0)} - [p^{(1)}/p^{(0)}]^2 &= \alpha\beta^2 \end{aligned} \quad (20)$$

An advanced model was developed to track the evolution of the molecular weight distribution, for the pyrolysis of high density polyethylene, using elementary steps to govern the moment equations [38]. From here we can depict the elementary reactions and their corresponding moment equations. These are listed here for completeness.

- Random fission

$$\begin{aligned} D_n &\xrightleftharpoons{k_f, k_c} Re_i + Re_{n-i} \\ \frac{dD^m}{dt} &= -k_f(2D^{m+1} - e_f D^m) + \frac{1}{2}k_c \sum_{j=0}^m \binom{m}{j} Re^j Re^{m-j} \\ \binom{m}{j} &= \frac{m!}{j!(m-j)!} \end{aligned} \quad (21)$$

$$D^3 = \frac{2D^2 D^2}{D^1} - \frac{D^2 D^1}{D^0}$$

$$\begin{aligned} \frac{dRe^m}{dt} &= 2k_f C_m (2D^{m+1} - e_f D^m) - k_c Re^m Re^0 \\ C_m &= \frac{1}{m+1} \end{aligned}$$

- Specific Chain Fission/Radical Recombination

$$\begin{aligned} D_n &\xrightleftharpoons{k_{fs}, k_{cr}} Re_{n-s} + r_s \\ \frac{dD^m}{dt} &= -k_{fs} D^m + k_c \sum_{j=0}^m \binom{m}{j} Re^{m-j} (s)^j [r_s] \\ \frac{dRe^m}{dt} &= k_{fs} \sum_{j=0}^m \binom{m}{j} (-s)^j D^{m-j} - k_c Re [r_s] \\ \frac{d[r_s]}{dt} &= k_{fs} D^0 - k_c Re^0 [r_s] \end{aligned} \quad (22)$$

- Hydrogen Abstraction

$$\begin{aligned} Re_n + D_i &\xrightleftharpoons{k_{tr,e}, k_{tr,m}} D_n + Rm_i \\ \frac{dD^m}{dt} &= -N_H^m k_{tr,e} Re^0 (D^{m+1} - e_t D^m) + N_H^m k_{tr,e} Re^m (D^1 - e_t D^0) + N_H^e k_{tr,m} Rm^m D^0 - N_H^e k_{tr,m} Rm^0 D^m \\ \frac{dRe^m}{dt} &= N_H^m k_{tr,e} Re^m (D^1 - e_t D^0) + N_H^e k_{tr,m} Rm^0 D^m \\ \frac{dRm^m}{dt} &= N_H^m k_{tr,e} Re^0 (D^{m+1} - e_t D^m) + N_H^e k_{tr,m} Rm^m D^0 \end{aligned} \quad (23)$$

- β -Scission/Radical Addition

$$\begin{aligned} Rm_n &\xrightleftharpoons{k_{bs}, k_{ra}} Re_i + D_{n-i} \\ \frac{dRm^m}{dt} &= -2k_{bs} Rm^m + k_{ra} \sum_{j=0}^m \binom{m}{j} Re^j D^{m-j} \\ \frac{dRe^m}{dt} &= 2k_{bs} C_m Rm^m + k_{ra} Re^m D^0 \\ \frac{dD^m}{dt} &= 2k_{bs} C_m Rm^m - k_{ra} Re^0 D^m \end{aligned} \quad (24)$$

- Depropagation/Propagation

$$Re_n \xrightleftharpoons[k_p]{k_{dp}} Re + M$$

$$\frac{dRe^m}{dt} = -k_{dp} Re^m + k_p \sum_{j=0}^m \binom{m}{j} Re^{m-j} [M] + k_{dp} \sum_{j=0}^m \binom{m}{j} (-1)^j Re^{m-j} - k_p Re^m [M]$$

$$\frac{d[M]}{dt} = k_{dp} Re^0 - k_p Re^0 [M]$$
(25)

- Backbiting

$$Re_n \xrightleftharpoons[k_{bbf}]{k_{bbr}} Rm_n$$

$$\frac{dRe^m}{dt} = -k_{bbf} Re^m + k_{bbr} Rm^m$$

$$\frac{dRm^m}{dt} = k_{bbf} Re^m - k_{bbr} Rm^m$$
(26)

- Specific β -Scission

$$Rm_n \xrightleftharpoons[k_{ra}]{k_{bs}} Re_{n-s} + d_s$$

$$\frac{dRm^m}{dt} = -k_{bs} Rm^m + k_{ra} \sum_{j=0}^m \binom{m}{j} Re^{m-j} (s)^j [d_s]$$

$$\frac{dRe^m}{dt} = k_{bs} \sum_{j=0}^m \binom{m}{j} (-s)^j Rm^{m-j} - k_{ra} Re^m [d_s]$$

$$\frac{d[d_s]}{dt} = k_{bs} Rm^0 - k_{ra} Re^0 [d_s]$$
(27)

- Disproportionation

$$Re_n + Re_i \xrightarrow{k_d} D_n + D_i$$

$$\frac{dD^m}{dt} = k_d Re^m Re^0 + k_d Re^0 Re^m$$

$$\frac{dRe^m}{dt} = -k_d Re^m Re^0 - k_d Re^0 Re^m$$
(28)

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 chain lengths in terms of the number of monomer units and the superscripts denote the moments.

The advantage of this type of modeling is its directness in deriving expressions for monomers of the frequency distributions. Many authors and researchers have used the moment's method as a solution for the population balance equations and have discussed them in great details. It was pointed out that the gamma distribution cannot satisfactorily represent the initial conditions [39]. Hence, the solution obtained from both the partial differential equations and the moment's method is similar but differs with long reaction times. In all cases, the moment's method proves to be the most valid when using analytical results obtained from gas permeation chromatography [39-44].

5. Conclusion

The need to define product distributions and specify products is of utmost importance when the aspects of the plastic waste thermal degradation process are being assessed. Different kinetic models can be used to achieve certain degrees of detail. These include,

- The Power Law modeling approach which is mainly used for thermogravimetric experiments. This method is usually not applicable to reactor based experimentation where heat and mass transfer take

place. It shows good fit but lacks the detail in product distribution required in advanced experiments. It only tackles the kinetics of the reaction such as activation energy and rate constant.

- The Lumped-Empirical model is used to specify products as gas, liquid, wax, char, or any other lump. It retains good fit with experimental results. However, given that it follows a pre-specified lumping scheme and that it does not give detailed carbon chain length product distribution makes it disadvantageous in that sense.
- The Population-Balance based modeling surpasses the weak point of the Lumped-Empirical model and depicts a wide range of products according to the carbon chain length. This can be done by tracing reaction paths of the polymer chain, which is made up of thousands of monomer units, that undergo thousands of reactions. Its disadvantage lies in its dependence on numerical methods such as the moments' method to solve the population balance equations. In most cases it proves to be computationally very demanding. Adopting only the first three moments to keep the size of equations computationally manageable can produce noticeable discrepancies in certain product distributions [45]. The need for a novel numerical approach for solving the population balance equations in a computationally efficient manner can prove to be very crucial in assessing the overall process performance.

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