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A Study of Parallel and Competitive Reaction Schemes in Kinetic Modeling of Plastic Pyrolysis

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ABSTRACT: Pyrolysis is a technology capable of harnessing energy from challenging-to-recycle plastics, thus mitigating the necessity for incineration or landfill disposal. To optimize the plastic pyrolysis process, reliable models for product yield prediction are imperative. This study endeavors to determine the suitability of lumped models, a widely used approach for modeling biomass and coal pyrolysis, in accurately estimating product yields in the context of plastic pyrolysis. To address this question, three lumped models with parallel and competitive reaction mechanisms were compared and fitted to experimental data collected across a broad temperature range. The aim is to identify which models can elucidate the most appropriate reaction pathway for the plastic pyrolysis process. The first model in this study assesses whether the commonly employed wood pyrolysis kinetic models can effectively fit the experimental data from plastic pyrolysis. Subsequently, the final two models introduce additional reactions into the pyrolysis process, prompting the authors to investigate the necessity of these supplementary reaction pathways for accurately predicting plastic pyrolysis outcomes. This investigation seeks to pinpoint the essential terms and discern which ones may be safely omitted from the models. The results of the study reveal that the model incorporating secondary tar reactions with gas, tar, and char is the most precise in predicting the products of plastic pyrolysis, surpassing all other combinations evaluated in this research.

	Kinetic modeling of PMMA pyrolysis
Modeling approach	Models fitting (with a reaction scheme)
Feedstock model	One-component e.g., plastics
Product model	Lumped kinetic model products are lumping to tar (l), char (s), and gas (g)
Reaction scheme	Parallel and competitive reaction scheme

1. INTRODUCTION

Plastics with their widespread and often fleeting use, low cost, and often low recyclability and recycle rates and very slow biodegradability are an environmental issue of wide concern.[1−3] Thermochemical technologies are the leading method to eliminate from the environment the many polymers that are hard or impossible to recycle or even downcycle mechanically or chemically. Combustion, as a thermochemical method, does still, in many cases where pollution control is not strict enough, result in the release of pollutants into the environment, which impacts human health and results in air pollution.[4−6] Pyrolysis can recover more than just heat energy by extracting from plastic waste valuable products in the form of solid (e.g., char), liquid (e.g., pyrolysis oil), or gaseous fuels (e.g., hydrogen and/ or syngas) that may be used in case of pyrolysis oil or syngas as a feedstock to produce alternative fuels or even in chemical synthesis to produce new plastics or chemicals and materials.[7−9] In short, pyrolysis of plastic is a versatile process with a flexible product range that can be easily varied with process parameters like reaction temperature profile and residence time.[10]

Pyrolysis involves numerous reactions that involve a large number of intermediates and end products. As a result, devising a kinetic model for pyrolysis that includes all molecular species and their reactions is not only difficult but

also inevitably involves extensive approximations and parameter fitting.[11] Therefore, model-free and model-fitting methods that lump molecular species into groups, typically solids (with subgroup feed and char or chars), liquid (tar or tars), and gaseous product yields, as opposed to detailed molecular composition, are typically employed to determine the reaction rates and to practically model the yields of solid pyrolysis (Figure 1). The key difference between these two modeling approaches is that model-free methods[12] do not make any assumptions about the reaction scheme between groups for calculating the kinetic parameters, whereas model-fitting methods assume a specific reaction model (parametrized rate expressions) and then determine the kinetic parameters typically by fitting experimental data.[13] Model-fitting methods can be further categorized into one-component or multi-component based on how the initial feed is characterized (e.g., by a specific type of feed or by its components), and lumped or
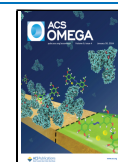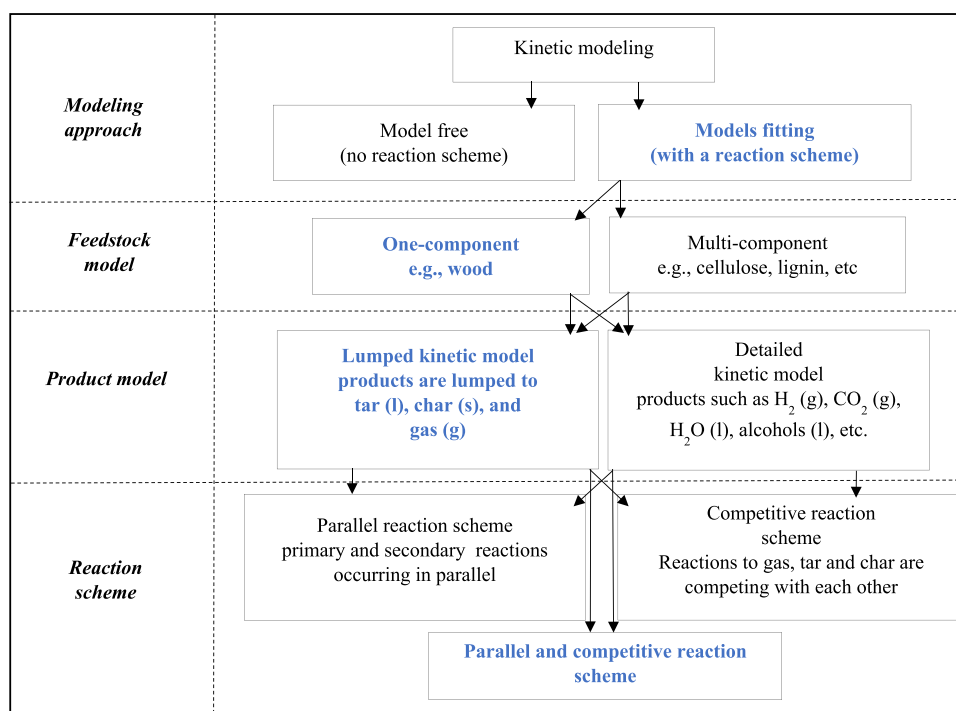
Figure 1. Kinetic modeling approaches. This study used a one-component model-fitting approach, with a parallel competitive reaction scheme lumping the products to tar, gas, and char. Those selected in this study are in blue.

detailed kinetic models based on how the products are defined (e.g., by lumped products such as gas, char, and tar, or by representative or model species in each lumped product).[14] A parallel reaction scheme involves primary and secondary reactions occurring simultaneously. On the other hand, in a competitive reaction scheme, solid mass reactions leading to the formation of gas, tar, and char are in competition with one another. This study employed both parallel and competitive reaction schemes.

Some studies investigate the degradation behavior of plastics pyrolysis with lumped kinetic approaches.[3,6,9,15−19] The majority of kinetic work utilizes lumped models because the kinetics are based on the yields of lumped products (i.e., char, tar, and gas).[6,9,15−18] The conventional parallel competitive reaction model with three primary pyrolysis reactions developed by Agrawal[20] was studied by many authors to predict plastic pyrolysis products.[1,21,22] This model is only suitable where the primary degradation of solid mass occurred (300 and 400 °C), but not at higher temperatures.[21−23] The authors[23] previously used this reaction scheme and investigated its accuracy in predicting pyrolysis products. They concluded that the competitive reaction model with three reactions needs to be expanded to include the secondary decomposition of pyrolysis products to accurately predict yields. Costa et al.[24] used a lumped model with nine reactions to model batch pyrolysis of polyethylene at different temperatures. The pyrolysis products were lumped into lower molecular weight polymer, gas, and light and heavy oil. Ding et al.[25] conducted pyrolysis of polymers at temperatures of 360, 380, 400, and 420 °C. They also developed a four-lump kinetic model to describe the production distribution of the light fractions, middle distillates, and heavy fractions. Their results showed that the model reasonably fitted the experimental data for each of the investigated operating condition. Jiang et al.[26] defined products of polyolefin pyrolysis

lumping into wax, oil, and gas. Kinetic parameters obtained by their model were validated by using isothermal and non-isothermal experimental data. They concluded that the calculated data are only in agreement with the isothermal experimental data. Koo compared five different lumped models with first-order irreversible reactions to evaluate plastic pyrolysis. In all of the models, the pyrolytic products were lumped into char, tar, and gas. According to Koo,[22] models with secondary pyrolysis resulted in more accurate predictions.

Despite the research on plastic pyrolysis reaction schemes and kinetic modeling, there is currently no widely accepted model capable of accurately predicting the pyrolysis rate and resultant products of various materials under a broad range of experimental conditions.[27−29] In addition, there are no studies that considered secondary char reactions in the plastic pyrolysis reaction pathway. In prior work, it was demonstrated that, by expanding the reaction scheme of the conventional lumped kinetic model with only a few specific terms, a new expanded model can predict biomass pyrolysis yields not just for a limited temperature range and a given type of biomass, but the new model can predict biomass pyrolysis yields across various different biomass feedstock and broader temperature ranges.[30] This work investigates whether the previously proposed reaction schemes for pyrolysis of biomass[30] can also accurately predict the product yields of plastic pyrolysis. The same methodology will be followed as in the prior work on biomass.[30] Namely, three lumped models with different primary and secondary reactions will be fitted to experimental data including variations in pyrolysis temperatures (300, 400, and 450 °C).[31] The experimental study by Monteiro Nunes et al.[31] is the only study that has delved into investigating the pyrolysis of the same feedstock under nonisothermal conditions while maintaining consistent experimental parameters across all trials and providing comprehensive data on pyrolytic yields and temperature profiles. Based on exper-

imental data, the authors will estimate the Arrhenius parameters (frequency factor, activation energy) for the reactions by numerical modeling. The ability of the parallel competitive reaction model predominantly used in the literature[32−35] along with two lumped kinetic models previously proposed by authors[30] will be compared to see which, if any, of the selectively added reactions, is necessary or nonnegligible when modeling plastic pyrolysis.

2. MATERIALS AND METHODS

Slow pyrolysis of plastic was conducted in a hot-rod (fixed-bed) reactor operating at different temperatures of up to 450 °C. The heating rate was set to 1 °C s^{-1}, and the corresponding holding time was 900. Throughout the experiments, the pyrolysis was conducted under a helium atmosphere. The detailed experimental methods and data on plastic pyrolysis experiments were conducted by Monteiro Nunes et al. and is published elsewhere.[31] The type of plastic was not reported byMonteiro Nunes et al.,[31] but the ultimate analysis provided is consistent with poly(methyl methacrylate) (PMMA). The oxygen level is 34.7 wt %, and the C/H mass ratio is 7.4.

Data from this experimental study were compared with the predictions of the three reaction kinetic models tested in this study. This study used competing and parallel reaction models (Figure 1). The first model to be tested (denoted here as Model I) is an existing model developed and modified by many authors.[32−34] This first model can be considered a state-of-the-art baseline and has been used as such by the current authors in a previous study in search of a more universal model for biomass pyrolysis.[30] Model I (in black in Figure 2) considers
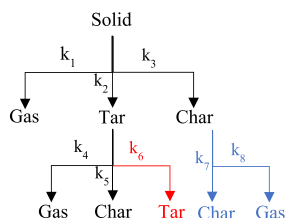
Figure 2. Thermal decomposition of solid with three different reaction schemes was used in this study to predict pyrolytic products. Model I in black color; model II in black and red colors; and model III in black, red, and blue colors.

that solid converts into gases, tar, and char; subsequently, the tar can further decompose into char and gases. Model II is a simple expansion of Model I with the addition of the possibility that primary tar can also convert to an inert secondary tar (the added reaction is illustrated in red). Model III is a further expansion of Model II that includes the addition of the possible formation of an inert secondary char and additional gas from primary char (the added reactions are illustrated in blue). The primary kinetic parameters and other constants used in models I−III are listed in Table 1. The subscripts 1, 2, 3, 4, 5, 6, 7, and 8 are the kinetic parameters of the reactions: solid to gas, solid to tar, solid to char, tar to gas, tar to char, tar to tar, chart to char, and char to gas, respectively. The typical or reported values for these kinetic parameters (A_i E_i) for Model I listed in Table 1 were obtained from the kinetic modeling of plastic pyrolysis conducted by Till et al.[18] To obtain typical values for the kinetic parameters for the secondary char reactions in Model III, it was assumed

Table 1. Primary Kinetic Data as well as the Minimum and Maximum Values of the Arrhenius Parameters of Plastic Pyrolysis Studies in the Literature That Are Used in This Modeling Study

parameters	values	min	max
A_1 (s^{-1})	9.94×10^2	3.60×10^1	2.23×10^9
A_2 (s^{-1})	1.23×10^{16}	1.99×10^4	7.62×10^{19}
A_3 (s^{-1})	1.07×10^{13}	1.18×10^1	1.07×10^{13}
A_4 (s^{-1})	1.18	1.18	1.18×10^1
A_5 (s^{-1})	1.37×10^{-3}	1.37×10^{-3}	6.95
A_6 (s^{-1})	1.24×10^{-1}	1.24×10^{-1}	7.20
A_7 (s^{-1})	1.37×10^{-3}		
A_8 (s^{-1})	1.18		
E_1 (kJ mol^{-1})	86	45	187
E_2 (kJ mol^{-1})	268	71	319
E_3 (kJ mol^{-1})	233	16	233
E_4 (kJ mol^{-1})	386	9	386
E_5 (kJ mol^{-1})	216	48	394
E_6 (kJ mol^{-1})	230	32	230
E_7 (kJ mol^{-1})	216		
E_8 (kJ mol^{-1})	386		

that the reactions have the same kinetic parameters as secondary tar reactions to char and gas.[18,36]

The rate of reaction of the solid phase under nonisothermal conditions is presented using eq 1:[37]

$$\frac{d\alpha}{dT} = \frac{A_i}{\beta} \exp\left(\frac{-E_i}{RT}\right) f(\alpha) \tag{1}$$

where $d\alpha/dt$ is the nonisothermal reaction rate, $\beta = dT/dt$ is the linear heating rate (°C s^{-1}), A is the pre-exponential factor (s^{-1}), E is the activation energy (kJ mol^{-1}), R is the universal gas constant (kJ.K^{-1} mol^{-1}), and T is the absolute temperature (K), and $f(\alpha)$ is the conversion function. In the kinetic models, the rate expression based on the first-order decomposition of the reactive solid is defined in terms of fractional conversion.

The objective is to minimize the difference between experimental data (final yields of gas, tar, and char at the final temperature) and model calculated yields (at the final temperature), by nonlinear least-squares method to estimate Arrhenius parameters (A_i, E_i).[38] A well-proven strategy to avoid mathematical artifacts, and ensure physically relevance of fitted kinetic parameters, is to identify a physically plausible range (expected lower and upper bounds) based on experiments or a survey of experimental work.[30] The authors reviewed the studies that conducted lumped kinetic modeling on plastic pyrolysis and gathered the kinetic parameters in Table 1.[18,21,26,39] The table presents the minimum and maximum activation energies (kJ mol^{-1}) and pre-exponential factors (s^{-1}) for all of the reactions in plastic pyrolysis. The variance in the reported values can be attributed to the diverse utilization of models, feedstock, operational conditions, and heating profiles by different researchers. The kinetic parameters optimized using the nonlinear generalized reduced gradient method, subject to the constraints obtained from the range between the minimum and maximum, are presented in Table 1. The motivation for using these constraints was to ensure that all of the parameters remained within the physically realistic range based on the existing literature.

3. RESULTS AND DISCUSSION

3.1. Arrhenius Kinetic Parameters. In this context, the predictive capabilities of Model I (the existing baseline model[32−34]) will be compared with two potential extensions of Model I, as previously investigated by the authors in their pursuit of a more universally predictive model for biomass pyrolysis.[30]

Unfortunately, plastic pyrolysis data that include trials with widely varying temperature profiles are much rarer than what is available with biomass.[30] Ideally, data should also be available for different polymers, analogous to the wide range of biomass types for which pyrolysis data are available. Upon a review of the literature available on plastic pyrolysis, it became evident that the experimental conditions employed in these studies varied significantly, rendering the utilization of the reported data a challenging endeavor. Specifically, some studies conducted isothermal pyrolysis experiments, while others implemented nonisothermal conditions, albeit with varying heating rates. Additionally, disparities were observed in the reactor lengths and associated temperature profiles. Furthermore, some studies solely reported mass loss without reporting the other pyrolytic yields. Discrepancies in the categorization of pyrolytic yields, as compared to those in our study, further complicated data synthesis. Moreover, some studies exhibited insufficient information regarding the temperature profiles during the pyrolysis process, hindering a comprehensive understanding of their methodologies. Lastly, certain publications presented results exclusively in graphical formats, making data replication virtually impossible due to the absence of numerical values. Based on this review of plastic pyrolysis data, the experiments of Monteiro Nunes et al.[31] was selected as the best available data on plastic pyrolysis to be used to compare the predictive power of the models to be tested here across broad temperature ranges.

The objectives of all models are merely to accurately predict product yields of the feedstock into the three product categories (char, tar, and gas) as a function of the pyrolysis temperature profile. The widely used Arrhenius kinetic equation is used to represent the pyrolysis reaction rates of the models illustrated in Figure 2. The proposed kinetic models optimized a total of 38 kinetic parameters for the three models.

Values for the Arrhenius parameters were obtained by fitting the measured conversion data by using a nonlinear least-squares regression. The kinetic parameters from the literature were employed as the initial guess values.[18,21,26,39] The initial values for the fitting were the kinetic parameters determined for the case of a first-order reaction. The best values of the estimated kinetic parameters for Models I, II, and III based on the experimental data are shown in Table 2. The estimated kinetic parameters are within the predetermined physically realistic range based on the existing literature (Table 1).

The authors previously evaluated the performance of these three models on eucalyptus wood pyrolysis conducted by Monteiro Nunes et al.[31] For the eucalyptus wood pyrolysis, activation energies ranged 88−158, 88−140, and 88−232 kJ mol⁻¹ for Models I, II, and III, respectively. Alternatively, the activation energies inferred herein for PMMA-like plastic while considering the same pyrolysis setup and operational conditions ranged 56−386, 43−386, and 55−386 kJ mol⁻¹ for Models I, II, and III, respectively. This suggests that polymers could have a wider range of temperature sensitivity

Table 2. Kinetic Data Were Obtained by Models I, II, and III for the Plastic Pyrolysis Experiments

| parameters	Model I	Model II	Model III
A_1 (s⁻¹)	5.86×10^4	4.23×10^5	1.54×10^5
A_2 (s⁻¹)	1.99×10^4	1.99×10^4	1.99×10^4
A_3 (s⁻¹)	6.51×10^2	2.28×10^1	2.53×10^2
A_4 (s⁻¹)	1.18	1.18	1.18
A_5 (s⁻¹)	1.37×10^{-3}	1.37×10^{-3}	1.37×10^{-3}
A_6 (s⁻¹)		1.24×10^{-1}	1.24×10^{-1}
A_7 (s⁻¹)			1.37×10^{-3}
A_8 (s⁻¹)			1.18
E_1 (kJ mol⁻¹)	82	96	92
E_2 (kJ mol⁻¹)	78	82	82
E_3 (kJ mol⁻¹)	56	43	55
E_4 (kJ mol⁻¹)	386	386	386
E_5 (kJ mol⁻¹)	216	216	216
E_6 (kJ mol⁻¹)		230	230
E_7 (kJ mol⁻¹)			386
E_8 (kJ mol⁻¹)			244

compared to biomass that can be both higher or lower. The frequency factors obtained for plastic pyrolysis were also lower compared with eucalyptus wood pyrolysis. This indicates that plastic (specifically PMMA in this study) pyrolysis reactions are slower compared to eucalyptus wood pyrolysis at a given temperature.

Arrhenius parameters were determined through nonlinear least-squares regression, utilizing measured conversion data. Initially, literature-derived kinetic parameters[18,21,26,39] served as the starting values, where those established for a first-order reaction guided the initial fitting. The resulting optimal kinetic parameters for Models I, II, and III, based on experimental data, are presented in Table 2, aligning with physically realistic ranges as per the existing literature (Table 1).

In a previous study by Monteiro Nunes et al.,[31] the performance of Models I, II, and III in eucalyptus wood pyrolysis was assessed. For this biomass, activation energy ranges were 88−158, 88−140, and 88−232 kJ mol⁻¹ for models I, II, and III, respectively. In contrast, when applying the same pyrolysis setup and operational conditions to PMMA, activation energies ranged 56−386, 43−386, and 55−386 kJ mol⁻¹ for models I, II, and III, respectively, which is consistent with the trends generally reported in the literature.[40] This discrepancy implies a broader temperature sensitivity range for polymers compared with biomass, encompassing both higher and lower values.

The divergence in activation energies during the primary pyrolysis phase for PMMA, exhibiting lower values than those of eucalyptus wood, suggests a faster initiation of the pyrolysis process. However, the subsequent higher activation energies during the secondary phase indicate an increased energy demand in this zone. This observation underscores the dynamic nature of the pyrolysis process for PMMA, which is characterized by variable energy requirements across distinct phases.

The contrast in energy requirements for breaking bonds between PMMA and cellulosic materials, such as eucalyptus wood, can be ascribed to their differing chemical bonds and molecular structures.[41] PMMA, characterized by robust covalent bonds within repeating methyl methacrylate units, demands substantial energy for the bond cleavage. Conversely, cellulose, a complex polymer with glucose units linked by beta-
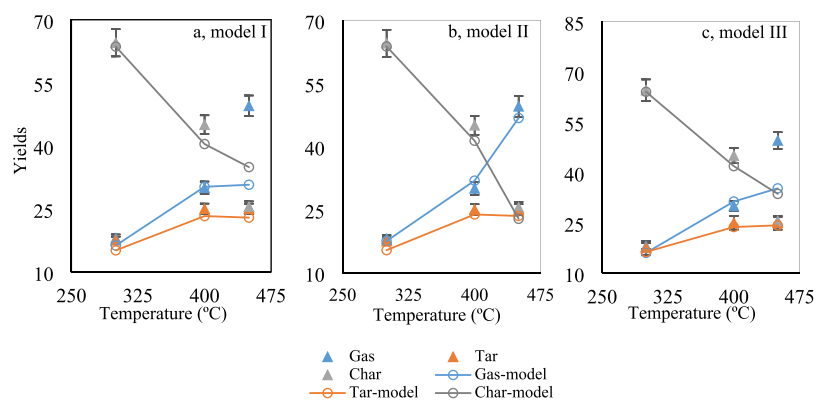
Figure 3. Distribution of the products generated during plastic pyrolysis experiments at different maximum process temperatures and model-predicted yields from models. Panels a−c present data for models I−III, respectively. The legend applies to all of the three figures.

1,4-glycosidic bonds, relies on the strength of numerous hydrogen bonds between adjacent chains, requiring comparatively less energy for bond rupture. This insight reinforces the concept that stronger covalent bonds, as present in PMMA, necessitate more energy for breaking, compared to the weaker hydrogen bonds in cellulose.

Additionally, the frequency factors derived for plastic pyrolysis were found to be lower than those for eucalyptus wood pyrolysis. This discrepancy further underscores the slower nature of plastic (specifically PMMA in this study) pyrolysis reactions compared with their counterparts in eucalyptus wood pyrolysis at a given temperature.

3.2. Pyrolytic Product Yields. The applicability of three kinetic models for plastic pyrolysis was evaluated by using plastic pyrolysis experimental data from the study conducted by Monteiro Nunes et al.[31] The simulated concentration distributions of products, namely, gas, tar, and char, during plastic pyrolysis under nonisothermal conditions are shown in Figure 3. In an ideal scenario, the reaction rates would be measured instantaneously during pyrolysis experiments and could be directly compared with the model's rates. However, the experimental design employed in the models only permitted the collection of final yield measurements at the conclusion of each batch. Consequently, the reported measurements represent the yields achieved at the final temperature when the process concludes. Particularly when integrating tar or immediate solids and their subsequent reactions, the pertinent kinetic properties of tar were sourced from the literature, as they are challenging to measure at the current experimental level. Consequently, the validation of these intricate models necessarily relies on the limited available experimental data.[11] Hence, an approach for calibrating the models with the final experimental yields at three final temperatures 300, 400, and 450 °C was adopted. The models computed the yields for each of the reactions and subsequently reported the combined results for gases, tars, and chars.

The experimental data show that the solid yield drops monotonically with the maximum process temperature, while the tar and gas yields increase with the maximum process temperature for any experiments in the temperature range of 300−500 °C.[23,42] The modeling results from all three models confirmed that, with an increase of the maximum pyrolysis temperature, the final product volume of tar will increase at first and then reach an approximate plateau level for processes that peat at around 400−500 °C.

Figure 3a shows the results of the model-predicted yields compared to the experimentally measured yields for Model I. The model prediction shown is that with the best-fit parameters in Table 2. The fit of the model to the experimental data was only accurate for trials with a maximum pyrolysis temperature of 300 °C. For pyrolysis runs with the maximum temperatures above 300 °C, best fits of Model I achieved less agreement between Model I and experimental data, which could indicate that additional reactions not captured by Model I are not capable of accurately predicting the measured yields for higher temperature. It thus seems that additional conversion pathways are activated above 300 °C while not being captured by Model I.

In Model II of this study, an additional reaction is introduced to enhance Model I. The predicted yields by Model II are depicted in Figure 3b. The model's predictions utilize the best-fit parameters from Table 2 and showcase the results of the proposed model, accounting for secondary (inert) tar formation reactions. This supplementary reaction competes with the primary tar's decomposition into secondary char and secondary gas, favoring the creation of a more stable secondary tar. Consequently, this secondary tar is no longer available for the formation of secondary gases and char. The extra reaction involves converting primary tars into a more stable mixture of tars including various compounds. This conversion process, facilitated by high temperatures and catalysts, progressively generates a refined secondary tar while separating it from secondary gas and char formation.[43,44] Model II explicitly incorporates this aspect. By comparing the predicted results with experimental data, it becomes apparent that the inclusion of a secondary tar reaction in the pyrolysis reaction scheme enhances the accuracy of reaction models when compared to Models I and III. Other researchers have suggested that, at temperatures exceeding 400 °C, secondary pyrolysis occurs concurrently with primary pyrolysis, resulting in the production of secondary gas, tar, and char.[45,46] The modeling work and results presented in Figure 3 support this hypothesis. The fit of Model II is consistent across all of the maximum process temperatures tested in this study. The strong agreement with experimental results implies that Model II could provide a solid foundation for a quantitative understanding of plastic pyrolysis. Naturally, this outcome must be validated for various polymer types and reactor configurations to be considered universally applicable.

Model III builds upon this by introducing the concept that primary char can undergo volatilization, leading to gas

generation through secondary reactions. This results in a more devolatilized solid carbon residue.[47] Computed gas, tar, and char yields from Model III are displayed in Figure 3c. The model employs the best-fit parameters from Table 2 and exhibits the outcomes of the proposed model considering the secondary reactions of tar and char. As evident by Figure 3c, the model aligns well with the experimental data for temperatures up to 400 °C. The results demonstrate that including secondary char reactions does not enhance the precision of predicting plastic pyrolysis products (at least for the PMMA-like polymer examined here) to the same extent as it did for biomass. The kinetic scheme of Model III most accurately predicts the decomposition of biomass pyrolysis.[23,30] Compared to the biomass pyrolysis modeling previously investigated by the authors,[23,30] the behavior of plastic pyrolysis is different. The results here suggest that, in plastic pyrolysis, there is the presence of secondary tar reactions, whereas primary char once formed subsequently acts as an inert substance. Therefore, the addition of secondary char reactions to char and gas (Model III) did not enhance the reaction scheme or improve the accuracy of the yield predictions.

3.3. Validation and Sensitivity Analysis. The standard deviation between model predictions and experimental data was calculated using eq 2.[48] The modeling results showed a small deviation of 0.1 from the plastic experimental data for Model II.

$$\text{standard deviation} = \sqrt{\frac{\sum_{i=1}^{n}\left(\frac{\text{data}_{\text{experiment}} - \text{data}_{\text{model}}}{\text{data}_{\text{experiment}}}\right)^2}{n - 1}} \quad (2)$$

A sensitivity analysis was undertaken to evaluate the significance of incorporating additional reactions into Model II. It is worth considering whether the constraint window, designed to maintain all parameters within physically plausible values and prevent purely mathematical artifacts, may have been either too restrictive or too lenient during the fitting process. To explore the possibility of a narrow window, a sensitivity analysis was performed by expanding the constraint windows for $A_{4,5}$ and $E_{4,5}$ by 20% and subsequently recalibrating the kinetic parameters to the experimental data within these more relaxed constraints. The model was then executed to assess the impact of this relaxation on the optimal-fit kinetic parameters presented in Table 2 for Model II. The consequences of this relaxation on the best-fit kinetic parameters in Table 2 for Model II are shown in Table 3 below. As anticipated, there was an effect, but the absolute deviation was found to be 0%. This deviation is not substantial enough to overturn or invalidate any of the conclusions

reached in this study. This study provided valuable insights into a plausible reaction scheme for plastic pyrolysis, primarily relying on available experimental data. However, to establish its universal applicability, a broader validation is essential.

4. CONCLUSIONS

Pyrolysis is a technology that offers a means of harnessing energy from plastics that are traditionally challenging to recycle. The development of dependable models for predicting product yields is imperative as it underpins the optimization of plastic pyrolysis process parameters, the assessment of its economic viability, and the quantification of its potential environmental advantages. Basing the exploration on the understanding that the pyrolysis process encompasses primary and secondary stages, the goal was to expand the pyrolysis reaction pathway. In prior studies, established models from the existing literature, along with various experimental data for wood pyrolysis, were rigorously examined. The results strongly indicated the necessity for an expanded reaction scheme, offering a logical foundation for the previously proposed models (Models II and III). To validate these models, we utilized earlier experimental data on wood pyrolysis were utilized. Moreover, experimental data from two other studies were incorporated to demonstrate the capability of the proposed model to predict pyrolysis yields across a broader spectrum of experimental conditions and feedstock types.

The aim of the modeling research in this study was to establish a viable reaction pathway for the plastic pyrolysis process within a kinetic model. This model was intended to provide accurate predictions of pyrolysis yields under conditions of nonisothermal heating while fitting the experimental data. The authors employed plastic pyrolysis experimental data obtained from Monteiro Nunes et al.'s study, which utilized identical experimental conditions and equipment for both plastic and biomass pyrolysis. Previously, the authors utilized biomass pyrolysis experimental data to develop a model in their earlier study.

Model I exhibited a satisfactory degree of agreement with experimental results, but only for pyrolysis runs conducted at a maximum temperature of 300 °C. Model III, on the other hand, offered a good fit for most pyrolysis temperatures, with the exception of the highest temperature of 450 °C. Nevertheless, it was Model II that excelled in terms of accuracy and precision when predicting the product outcomes of plastic pyrolysis. Hence, based on the data set, it is proposed that the secondary tar reaction plays a significant role in plastic pyrolysis, particularly at temperatures exceeding 300 °C, while primary char, once formed, behaves as an inert substance up to 450 °C. Furthermore, the incorporation of secondary char reactions into both char and gas, as observed in Model III, did not yield an improvement in yield predictions within this reaction scheme.

Given the limited availability of experimental data, particularly concerning plastic pyrolysis investigations, it is noteworthy that the authors identified only a single paper that presented comprehensive experimental results on plastic pyrolysis. This work furnished an in-depth explanation of the experimental conditions, temperature profiles, and pyrolysis outcomes across various temperature ranges. This highlights the potential for future research endeavors within the field of plastic pyrolysis to conduct comprehensive experimental studies covering a wide spectrum of plastic types, operating temperatures, and process conditions.

Table 3. Results of the Sensitivity Analysis (the Effect of Constraint Window Size on Experimentally Fitted Kinetic Parameters)

parameter	value with original constraint window	value with constraint window ±20%	percent change*
		Model II	
A_4	1.18	1.18	0%
A_5	1.37×10^{-3}	1.37×10^{-3}	0%
E_4	386	386	0%
E_5	216	216	-3.9×10^{-6}%

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Author Contributions

A.S.: conceptualization, formal analysis, validation, investigation, methodology, writing—original draft. C.R.: supervision, writing—review and editing. R.U.: funding acquisition, supervision, writing—review and editing. All authors have read and agreed to the published version of the manuscript.

Notes

The authors declare no competing financial interest.

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