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Parameterization and Validation of Pyrolysis Models for Polymeric Materials

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Abstract

A methodology for parameterization of pyrolysis models for polymeric solids is proposed. This methodology is based on a series of experiments including thermogravimetric analysis, differential scanning calorimetry, infrared radiation absorption measurement and controlled atmosphere, radiation-driven gasification experiments involving simultaneous sample mass and temperature monitoring. These experiments are interpreted using a transient pyrolysis model run in an infinitely fast (0D) and one-dimensional (1D) transport modes to derive a complete property set. This property set is subsequently validated by comparing the mass loss rate histories obtained from the gasification experiments to the model predictions. For a range of previously studied materials, these predictions were found to be, on average, within 10-20% of the experimental values. This manuscript provides an overview of this methodology, accompanied by examples of its application, identifies its imitations and suggests paths for future development.

Key Words: fire modeling; material flammability; polymer properties; ThermoKin

1. Introduction

Pyrolysis is arguably the least understood process among phenomena comprising fire growth. Detailed chemical kinetics of the thermal decomposition of even the simplest pyrolyzable solids such as polyethylene are still being debated in the literature [1]. And a lack of experimental methods capable of direct, time-resolved measurement of the concentration of intermediate species formed in the condensed phase virtually ensures that many of the debated questions remain unresolved in the foreseeable future. What makes the pyrolysis process even

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more difficult to analyze is an extremely strong coupling between the chemical processes and heat and mass transfer in the condensed phase. Not only do chemical transformations affect all transport properties, they also produce profound macroscopic changes in the condensed-phase morphology (formation of bubbles, fissures, etc.). While a numerical model of pyrolysis incorporating all these elements is clearly within reach of the modern computational capabilities, this model will require a very large number of parameters most of which are unknown and very difficult to determine.

A more feasible approach to development of a pyrolysis model is to assemble it from relatively simple, semi-empirical submodels. Each of these submodels can be formulated to reflect overall physics of a component process or a group of related processes and parameterized based on experiments. Rather than trying to capture all potentially significant aspects of each process, the submodels' complexity is dictated solely by the requirement to represent available experimental data with the accuracy comparable with the experimental uncertainty.

Over the past several years, our group has been working on developing a set of experiments and related analytical procedures that represents this pyrolysis model development philosophy. An attempt was made to achieve a rational compromise between detailed quantification of each process comprising pyrolysis and minimization of time and effort required to collect relevant data. This attempt has culminated in a methodology that relies on simultaneous thermal analysis experiments including thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) to determine kinetics and thermodynamics of the thermal decomposition of a pyrolyzable solid. These experiments yield semi-global decomposition reaction kinetics, heat capacities, heat of melting and heats of decomposition reactions.

The other key experimental element of our methodology is radiation-driven gasification experiments involving simultaneous monitoring of mass and temperature of a coupon-sized sample. The gasification temperature data are combined with the results of the thermal analysis experiments and simple radiation absorption measurements to characterize the condensed-phase heat transfer as a function of temperature and local composition. Both thermal analysis and gasification experiments are analyzed and interpreted using numerical modeling. The last, but nevertheless, critical step in the model development is validation. In our methodology, this step

is accomplished by comparing the mass loss rate histories obtained from the gasification experiments to those predicted by the fully parameterized model.

This methodology has been successfully applied to a number of non-charring [2-3] as well as charring [4-5] synthetic polymers and a lignocellulosic composite [6-7]. The purpose of this manuscript is to summarize significant findings of these studies and identify remaining challenges. Unlike the previous manuscripts, the focus is not on technical details of particular procedures but rather on the overall workflow and reasoning behind selection of the key technical elements. It is also demonstrated that, despite some differences in the submodel formulations among modern pyrolysis codes [8-10], parameters obtained using one code can be utilized in another with a reasonable expectation for similar predictions.

Before proceeding with a description of our methodology, it is important to recognize that its development rests on a number of important contributions. Henderson et al. [11] and Vovelle et al. [12] were among the first researchers who formulated and implemented numerical pyrolysis models, and applied them to the analysis of experiments on simple polymers and composites. Subsequent studies by Di Blasi [13] and Staggs [14] extended applicability of these models to lignocellulosic materials and charring thermoplastics. Stoliarov and coauthors [8] and Lautenberger and Fernandez-Pello [9] were among the first to develop generalized pyrolysis modeling codes capable of simulation of a wide range of degradation, smoldering and flaming combustion scenarios with a customizable level of complexity.

Stoliarov and coauthors were also among the first researchers who demonstrated that models for both non-charring [15] and charring [16] materials can be parameterized using experiments that isolate individual processes comprising pyrolysis. These works laid a foundation for the studies summarized in the current manuscript. In parallel, Lautenberger, Rein and Fernandez-Pello [17] developed a methodology for pyrolysis model parameterization based on fitting bench-scale fire test data using an evolutionary optimization algorithm. This approach was subsequently advanced by Chaos and co-authors [18]. Finally, a hybrid methodology, involving a combination of fitting and direct measurements, has been proposed in a recent publication by Kim and Dembsey [19].

2. Model Development Process

2.1 Kinetics of Thermal Decomposition

Kinetic analysis of TGA data, which can be presented as mass or mass loss rate dependence on sample temperature, consists of selection of a mathematical model and determination of parameters of this model. A large number of mathematical models have been proposed in the literature; and a good portion of them was reviewed by Vyazovkin and Wight [20]. None of these models have a well established physical relationship to the solid decomposition processes. The main motivation behind their development is frequently to enable representation of complex TGA curves using the minimum number of adjustable parameters.

In our attempt to analyze kinetics of polymer decomposition, we have made a decision to deviate from the traditional approaches employed in the field of thermal analysis and model TGA data using a set of the first and second order reactions governed by the Arrhenius rate constants. This decision was based on an observation that these are the only reaction rate laws that have a firm theoretical foundation: they can be derived for the principals of statistical thermodynamics [21]. TGA curve complexity was captured by increasing the number of reactions. These reactions were chosen to be consecutive (i.e., $A \rightarrow B + C$, $B \rightarrow D + E$, etc.) unless there was a clear indicator of parallel chemical processes (such as changes in the final yield of solid residue with heating rate).

The selected reaction mechanism was solved using an in-house numerical pyrolysis code, ThermaKin [8], which was run in an infinitely fast transport mode (i.e., the solid was programmed to follow the heating rate set in the TGA experiment and all volatiles were instantaneously removed from the solid). The Arrhenius pre-exponential factor, activation energy, and product yields of each reaction were adjusted until a desirable agreement, measured by the coefficient of determination (R^2) and visual data comparison, with the experimental data was reached. The parameters were changed in small increments, which direction (+ or -) and relative magnitude were determined according to the rules summarized elsewhere [4]. Provided that the minimum number of reactions was used to achieve the prescribed level of agreement, this procedure generated a unique parameter set.

Both experimental sample mass and mass loss rate curves were used simultaneously as optimization targets. While these curves represent the same information, they emphasize different aspects of the mass loss dynamics. Examples of TGA modeling results obtained with this approach are shown in Figure 1. A single, first order reaction was used to capture the

decomposition of poly(acrylonitrile butadiene styrene) (ABS), while two consecutive reactions were employed to represent the decomposition of poly(ethylene terephthalate) (PET), which produced a notable amount of residue or char.

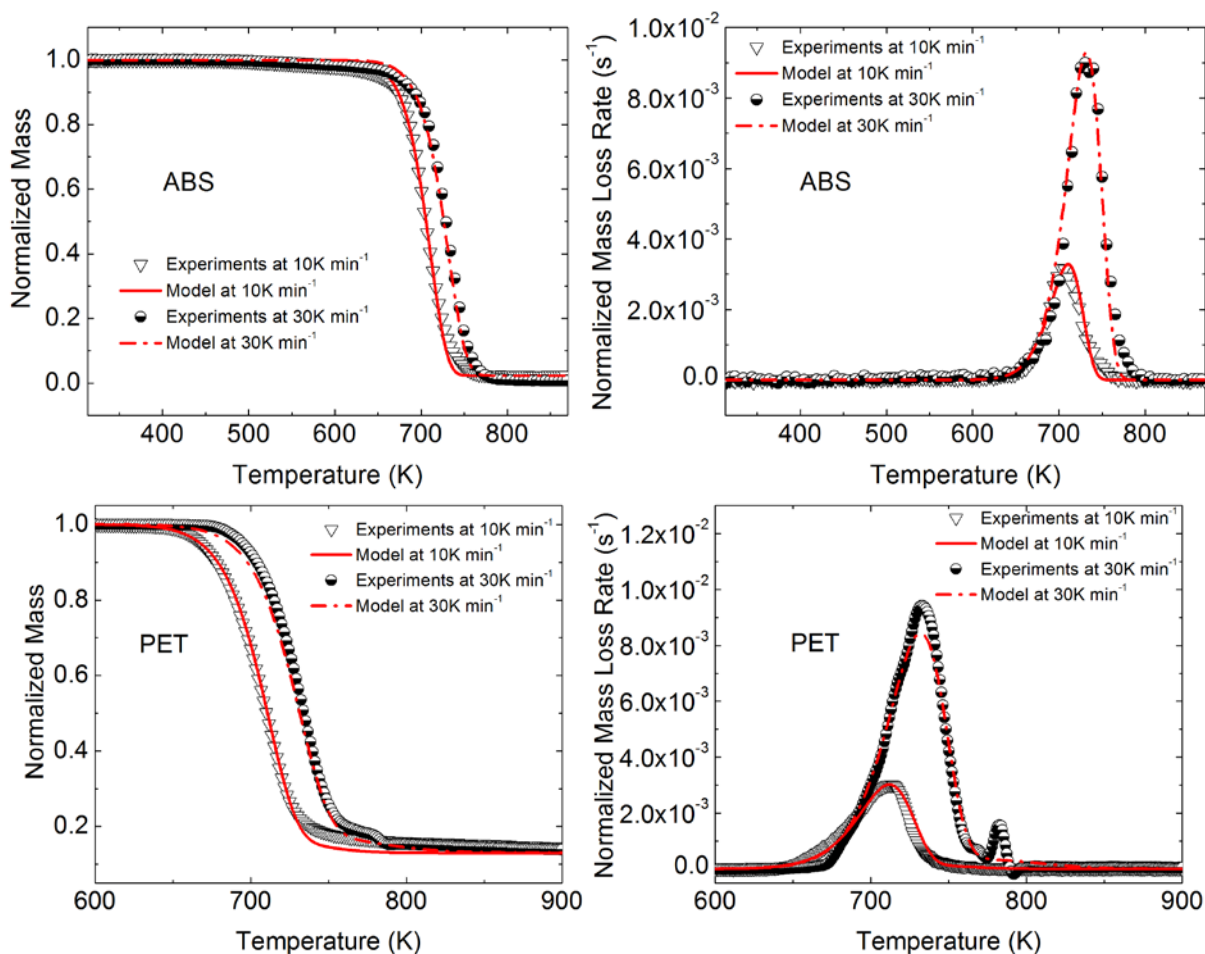


Figure 1. Experimental and simulated TGA data obtained at 10 and 30 K min⁻¹ heating rate, in nitrogen atmosphere [2,4].

Only experimental data obtained at 10 K min⁻¹ were utilized in the model parameterization. This decision was based on a theoretical analysis [22] that indicates that this is the maximum heating rate (for <10 mg samples) that achieves fully spatially uniform sample temperature, even when the heat of decomposition is large. In principle, simultaneous use of higher heating rate data for parameterization is advantageous because it extends the range of temperature over which the decomposition is analyzed toward fire-like conditions. However,

this extension tends to be small, 30-70 K per a factor of 10 increase in the heating rate. And the trade off is significant. In the absence of temperature uniformity, the main advantage of a TGA (or DSC) experiment, its ability to provide quantitative information on thermally induced processes free from contributions by heat transfer, is lost.

As the data in Figure 1 suggest, a moderate increase in the heating rate, to 30 K min⁻¹, does not compromise a good agreement between the model (derived from 10 K min⁻¹ data) and experiment, while providing partial validation for the model parameters. However, our experience indicates that this is not always the case. For example, 30 K min⁻¹ experimental data on poly(oxymethylene) (POM), which has a relatively high heat of decomposition, deviate from the corresponding predictions notably [2]. This deviation is thought to be a consequence of inability of POM samples to keep up with the analyzer's temperature sensor at this rate of heating.

2.2 Thermodynamics of Thermal Decomposition

Unlike TGA measurements, which results are hardly affected by a choice of the instrument or sample container (as long as the heating rate is kept within 3-30 K min⁻¹), the outcome of DSC analysis of the thermal decomposition can be significantly impacted by the choice of hardware. Our experience indicates that traditional DSC instruments, where sample and reference containers are located in a non-heated enclosure, are not well suited for the heat of decomposition measurements due to a highly non-linear and unstable baseline associated with the deposition of volatile decomposition products on internal instrument surfaces. An early attempt to correct for these non-linearities and instabilities [23] was only partially successful.

On the other hand, simultaneous thermal analyzers (STAs), where sample and reference containers are typically fully immersed into a furnace, possess a much better baseline stability. And the sensitivity of their heat flow sensors has improved considerably over the past decade. These instruments also provide an additional benefit of generating TGA and DSC data from a single experiment.

Most of our recent thermal analysis experiments were conducted in a Netzsch F3 Jupiter STA. Platinum-rhodium sample containers with lids equipped with a small orifice for ventilation were used in all experiments to maximize the thermal contact between a degrading sample and the heat flow sensor. Presence of the lids also helped with the baseline stability. The heat flow

sensor was calibrated periodically using a set of 8 organic and inorganic compounds with known melting points and heats of melting. This calibration procedure, described in detail elsewhere [2], was time consuming (it took over a week to complete) and heating rate specific (only 10 K min⁻¹ experiments were calibrated), but necessary to ensure the quality of the measurements.

Each STA experiment on a given material was repeated 7-10 times. Empty container baseline was run prior to each of these experiments; the baseline heat flow was subtracted from the corresponding sample data. Subsequently, the average heat flow curve was computed and used in further analysis. Averaging of multiple experiments significantly reduced the impact of random baseline shifts, which were not completely accounted for by the empty container baseline subtraction. The average heat flow was found to be sufficiently accurate to be used for determination of material heat capacity [2].

Regions of the average heat flow curve not associated with melting or decomposition were normalized by instantaneous heating rate and fitted with linear temperature functions representing heat capacities of the corresponding components in the TGA-derived decomposition mechanism. If melting process was detected, an additional first order reaction representing this process was added to the mechanism. Component mass fractions (with respect to the initial sample mass), which temporal evolution was computed by ThermaKin, were multiplied by the corresponding heat capacities to obtain sensible heat flow baseline. Subtraction of this baseline from the total heat flow and subsequent integration of the difference produced the values of the heat of melting and heats of decomposition. These heats (renormalized by the initial reactant masses) were assigned to the corresponding reactions.

At the last stage of analysis, the fully parameterized reaction model was verified by comparing ThermaKin-calculated heat flow with that observed in the experiments. Examples of this comparison are shown in Figure 2. The experimental and simulated heat flow agreement is not perfect because the instantaneous experimental heating rate fluctuates considerably around its set point. The integral heat flow (right graphs in Figure 2) is captured very well. This agreement demonstrates that the presented measurement and analysis procedure, which detailed description can be found in earlier publications [2,4], yields a semi-global reaction model that simultaneously reproduces both TGA and DSC experiments.

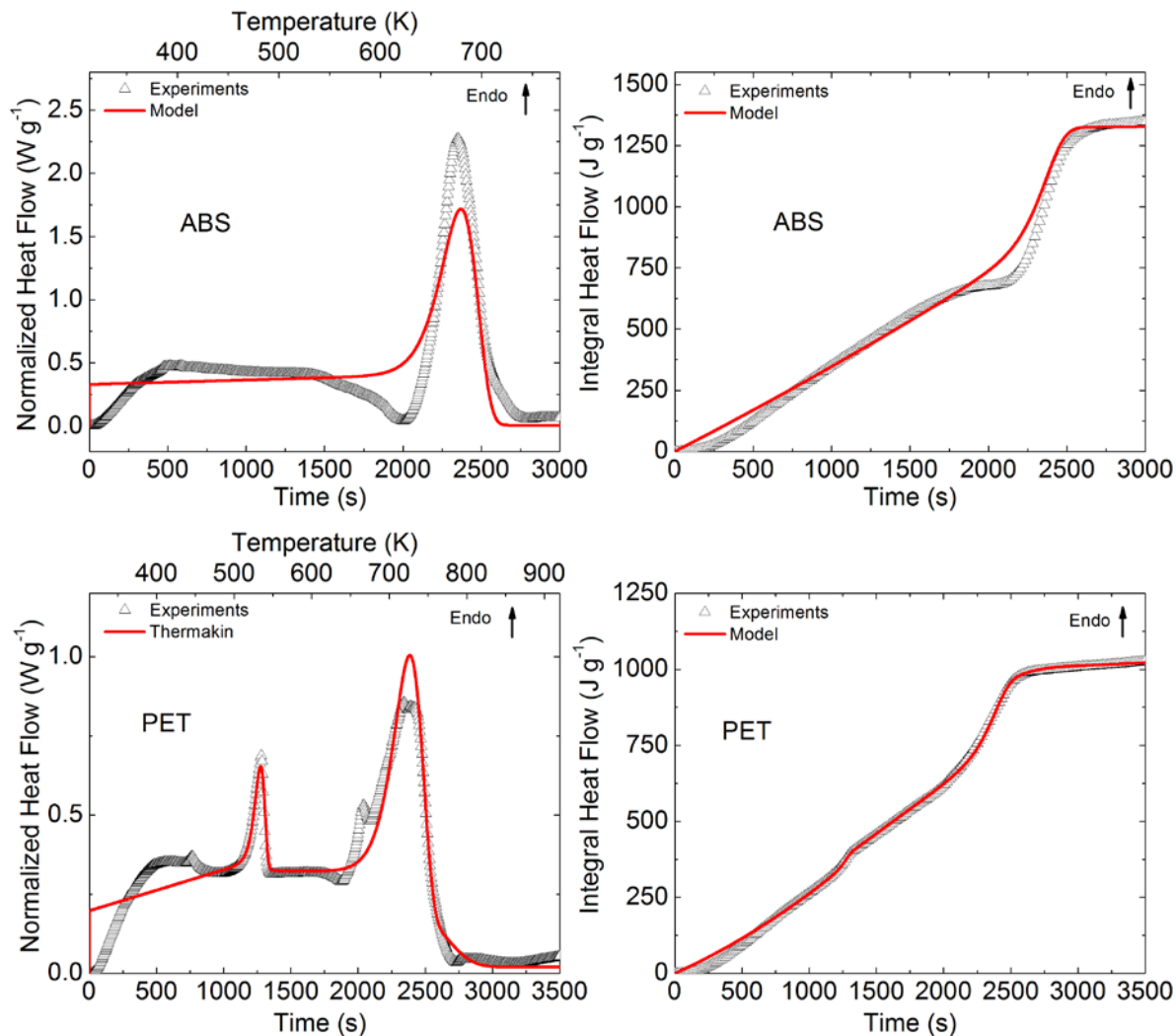


Figure 2. Experimental and simulated DSC data obtained at 10 K min^{-1} heating rate, in nitrogen atmosphere [2,4].

2.3 Optical Properties

A rigorous calculation of the rate of heat transfer from an external radiator through a pyrolyzing solid requires a solution of three-dimensional radiation transport equations taking into account wavelength dependences of the source intensity, solid emissivity, refraction index and absorption coefficient [24]. An introduction of such complexity into the framework of a pyrolysis model is hardly justifiable because of significant evidence [25] indicating a limited role of this energy transfer mode in the overall process. This is the reason why, in the state-of-the-art pyrolysis codes [8-10], this transfer is taken into account by invoking a number of simplifying assumptions including one-dimensional geometry and wavelength-independent (average)

absorption coefficient and emissivity (which, in the framework of the current discussion, is assumed to be equal to absorptivity).

Försth and Roos [26] and Linteris et al. [27] performed calculation of average emissivities for a wide range of synthetic polymers using wavelength-resolved data from an integrating sphere equipped with infrared spectrometer and by assuming 1025-1081 K grey body source (emulating an external fire). Most of the emissivity values were found to be above 0.9. Based on this observation and due to a lack of specialized equipment required for these measurements, 0.95 emissivity was assumed for virgin and semi-degraded polymers in all our pyrolysis models [3,5]. The validity of this assumption can be examined further by conducting gasification experiments on surface-modified samples as explained in the next subsection. Due to apparent high carbon content of the final condensed-phase products of polymer decomposition, their emissivity was assigned a value obtained for graphite, 0.86 [28].

Average infrared absorption coefficients of virgin materials can be estimated by placing a thin film of the material of interest between a radiant heater and a water-cooled Schmidt-Boelter heat flux gauge and determining the fraction of radiation transmitted through this film. This approach was previously utilized by Jiang et al. [29] and Linteris et al. [27]. In our most recent adaptation of this approach [5], 1.5 mm thick film samples were exposed to 35 kW m^{-2} produced by a cone calorimeter heater. The data on transmitted radiation were collected for the first 5 s after the beginning of exposure to minimize contributions associated with the conduction through the sample.

A Beer-Lambert-law-based expression taking into account radiation reflection at the polymer-air interfaces [15] was used to compute the absorption coefficients from the data on transmitted radiation. It should be noted that the average absorption coefficients obtained from this type of measurement depend on the thickness of material sample [27]. However, as long as the measured values indicate that most of the radiation is absorbed within a relatively small (<0.5 mm) depth, the impact of ignoring this dependence on the overall heat transfer is expected to be negligible.

2.4 Heat Transfer

Bottom surface temperature histories of $80 \times 80 \times (5-8)$ mm horizontally mounted samples whose top surface was exposed to a steady and nearly uniform radiant heat flux were used to

compute the thermal conductivities of virgin materials and their condensed-phase decomposition products. The samples were gasified in a nitrogen atmosphere using the Controlled Atmosphere Pyrolysis Apparatus (CAPA), which was installed under the heater of a cone calorimeter. A temperature-calibrated infrared camera was employed to obtain non-contact, spatially-resolved measurement of the bottom surface temperature, which was performed simultaneously with the mass loss measurement. A detailed description of this experimental setup and procedure, which evolved through a series of modifications [6-7] from the standard cone calorimetry [30], can be found elsewhere [3,5].

Fully quantified radiative and convective heat fluxes at the top and bottom surfaces of the CAPA samples enabled simulation of these gasification experiments. These simulations were carried out using the one-dimensional version of ThermaKin [8]. The model was parameterized with the properties derived from the thermal analysis experiments and radiation absorption measurements. The thermal conductivities of the condensed-phase material components (the only undefined properties remaining in the model) were adjusted until a good agreement with the experimental bottom surface temperature was achieved. Examples of this agreement are shown in Figure 3 (the modeling results obtained with the Fire Dynamics Simulator or FDS [10], also shown on this figure, are discussed in the next subsection). The thermal conductivities of all components with the exception of those representing the final residues were expressed as a linear function of temperature. The thermal conductivities of the final condensed-phase products were assumed to have an additional third power term, which was used to account for a potential contribution of radiative transport across pores [16].

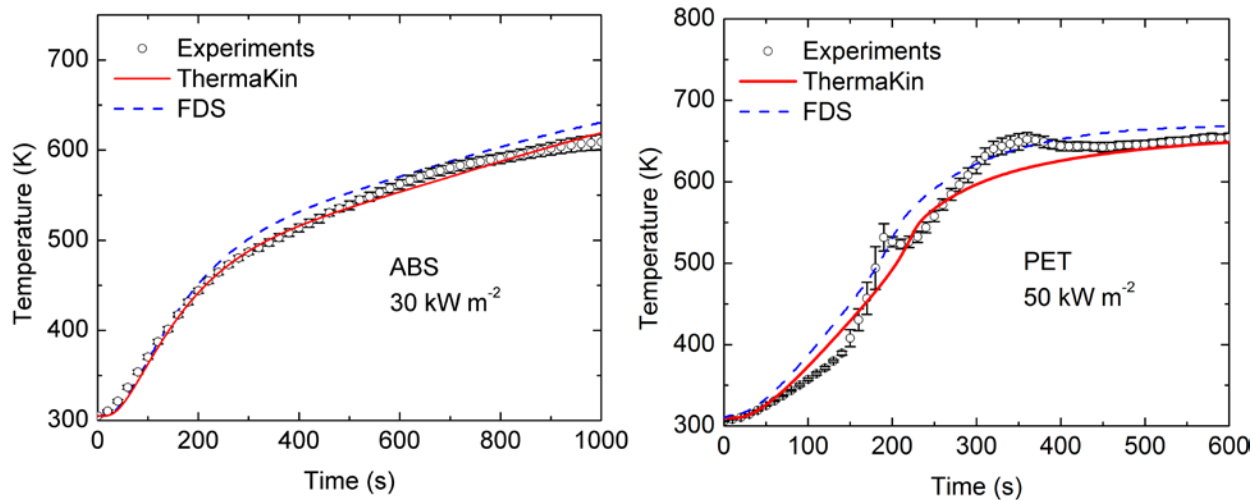


Figure 3. Experimental and simulated bottom surface temperature histories of samples pyrolyzed in CAPA, under nitrogen, at 30-50 kW m⁻² of external heat flux. Details of these experiments and ThermaKin simulations are provided elsewhere [5].

The gasification experiments were conducted at several radiant heat fluxes between 20 and 90 kW m⁻². However, only the lower heat flux (20-50 kW m⁻²) experiments were used in the heat transfer parameterization because these experiments were believed to be associated with the most certain boundary conditions. The rest of the experiments were utilized for validation (discussed in the next subsection).

Repeating these experiments using samples whose top surface was painted with a high (0.95) emissivity, thermally resistant paint provided additional information on the radiation transport. An increase in the bottom surface temperature due to this surface modification indicated that the sample surface emissivity was in fact significantly lower than the assumed value of 0.95. A decrease in the bottom surface temperature indicated that the external radiation penetration into the sample was notable and had to be taken into account in the heat transfer calculation. Beyond the qualitative assessment, this information could be utilized to arrive to more accurate heat transfer properties by modeling the temperature data from both surface-modified and non-modified experiments as illustrated in an earlier publication [6].

2.5 Validation

A comparison of the rate of production of gaseous decomposition products measured in the gasification experiments to that predicted by the model was used to validate the model's parameters. This rate, also referred to as mass loss or burning rate, multiplied by the effective heat of combustion of these products, yields the heat release rate, which is the single most important quantity characterizing material flammability [31]. A good agreement between the experimental and modeled rates, especially when observed for a wide range of external heat fluxes, is indicative of the validity of the material decomposition kinetics, thermodynamics and heat transfer parameters because all of these properties contribute to the definition of the mass loss rate dynamics [25] and none of them were derived from the mass loss rate data. A poor agreement indicates that either the model failed to take into account an important process or at least one measured property value or gasification boundary condition parameter is incorrect and needs to be reevaluated.

Representative comparisons between the experimental and simulated mass loss rates are shown in Figure 4. All ThermaKin mass loss rates demonstrate a reasonable agreement with the corresponding experiments. The most significant discrepancies are observed for the middle sections of the PET curves. These discrepancies are believed to be a consequence of this material's tendency to drip and spatter during pyrolysis, which is not taken into account in the model. This tendency is also responsible for large uncertainties in the height of the first peak of the PET experimental curve obtained at 50 kW m⁻².

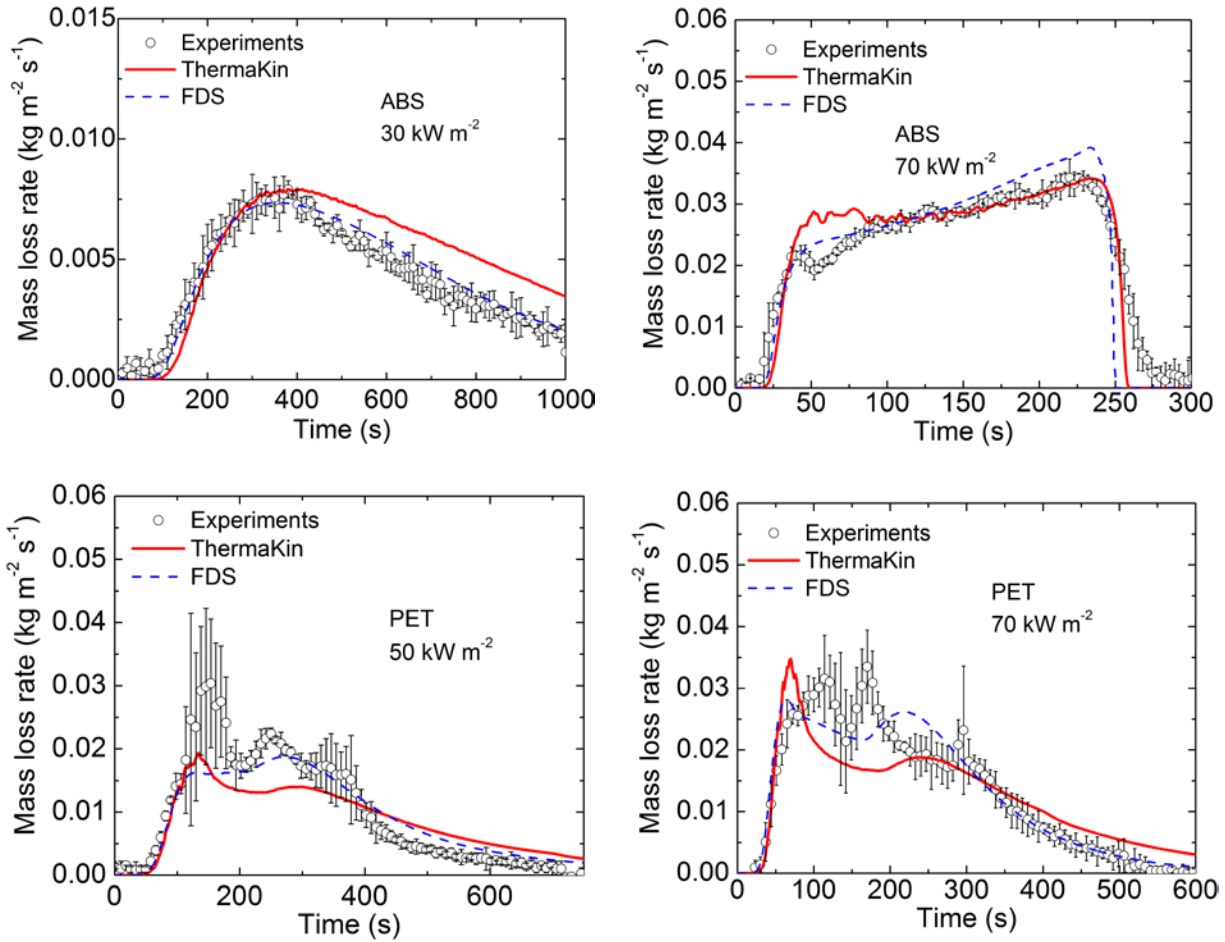


Figure 4. Experimental and simulated mass loss rate histories of samples pyrolyzed in CAPA, under nitrogen, at 30-70 kW m⁻² of external heat flux. Details of these experiments and ThermaKin simulations are provided elsewhere [5].

Figure 4 also shows the results of the simulations obtained using a pyrolysis model implemented in the FDS [10]. This pyrolysis model was parameterized using the same property values as those employed in the ThermaKin simulations. However, due to some differences in

the model formulations, the results are not completely identical. More specifically, an inability of the FDS to simulate convective heat flow associated with the movement of gaseous decomposition products (inside the condensed phase) and minor differences in the radiation submodel and boundary condition descriptions, resulted in slightly higher net heat transfer rates into the samples in the FDS simulations (see Figure 3). These model differences also produced a reduction in the mass loss rates at the early stages of pyrolysis and an increase at later stages, which appeared to slightly improve the overall agreement between the simulations and experiments. More ThermaKin and FDS comparisons can be found in a related work [32].

3. Conclusions

The presented pyrolysis model development methodology is hierarchical; i.e., the properties obtained from a set of experiments are used to interpret the results of the next set of experiments and extract more properties. This approach considerably improves efficiency (less experimental work is required to obtain necessary parameters) and also enables determination of properties, such as thermal conductivity of a decomposition intermediate, for which it is practically impossible to carry out a direct measurement. The main drawback of this approach is that a significant error in a single measured property value may propagate and compromise other properties. The validation step in the development process ensures that an existence of such error is detected. However, an identification of the true source of an observed discrepancy may still represent a significant challenge.

The presented methodology has been tested on a wide range of polymeric materials [2-7] and an on-going work in our group is directed toward extending it to fiber-reinforced and layered composites. Overall, the results of these tests have been positive. However, some issues were identified for charring polymers that exhibit a highly intumescent behavior [5]. Substantial swelling of these materials produced large uncertainties in the boundary conditions of the gasification experiments, which made the data collected at late stages of these experiments unreliable. Improving gasification experiments to extend the time during which well-defined conditions are maintained for highly intumescent materials will be a subject of future work. In addition, the current way of parameterization of condensed-phase component densities, which is based on the measurement of the mass and volume of initial and completely pyrolyzed material samples at room temperature, does not fully capture the material's swelling dynamics. A more

sophisticated physical submodel and parameter estimation approach are likely to be required to correctly simulate this aspect of the pyrolysis process.

The last but not the least is the effect of oxygen. All experiments used in the presented parameterization process were conducted in an essentially anaerobic environment. This environment imitates the behavior of a material covered by a continuous laminar flame sheet. However, before ignition, after cessation of the flame or in the case where this flame is turbulent, the solid is exposed to environmental oxygen. A chemical reaction between the solid and oxygen may significantly alter the dynamics of the pyrolysis process and affect key flammability characteristics such as the maximum burning rate [33] or the time to ignition [34]. Development of a robust procedure for quantification of this behavior is an important step toward comprehensive modeling of material flammability.

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