UNCERTAINTY QUANTIFICATION AND PROPAGATION OF PYROLYSIS KINETICS PARAMETERS USED IN FIRE MODELS

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INTRODUCTION

Computational fire modeling has the potential to streamline the development of less flammable materials. Fire models such as the Fire Dynamics Simulator (FDS)[1] are highly effective at predicting smoke and heat transport in building fire scenarios. However, standard fire models such as FDS are less well-validated for predictions of flame spread and fire growth on solid burning items. Model users are typically required to explicitly specify fire growth through an assumed heat release rate (HRR) curve. These relationships giving HRR as a function of time are either roughly estimated through standard design fires or specified by expensive experimental data from oxygen consumption calorimetry performed in heating and ventilation conditions likely to be very different from the specific scenario of interest.

An alternative to HRR curve specification is to improve the ability of existing computational fire models to predict the production of gaseous fuels by burning solids in any specified scenario. A burning solid produces combustible gas as part of a positive feedback loop between the heat being generated by gas-phase combustion and condensed-phase pyrolysis. Predictions of gas phase combustion and fluid dynamics at large scales are well-validated in state-of-the-art fire models, but predictions of the pyrolysis chemistry and heat and mass transport within the condensed phase, along with the coupling between condensed phase mass loss and heat flux from gas phase flames, are relatively less robust. These condensed phase models are physically complex and involve a large number of material properties that must be estimated from various small-scale measurements.

The path to realizing predictive computational fire growth is challenging due to the complexity of condensed phase models, the large amount of measurement data required, and the uncertainties associated with both the models and the data. There are many ways that models may be improved, and better data may be obtained and utilized, but these improvements are not all guaranteed to lead to better predictions of fire growth. Successful progress in measurement and computation for predictive computational fire growth requires the exploration of an extremely large, heterogeneous space of models, sub-models, experiments, and fitting algorithms. Guidance is needed. And that guidance must be driven by clear characterizations of the sources of uncertainty arising from the modeling process and the consequences of that uncertainty on predictions of real fire behavior, such as burning rate, flame spread, and fire growth.

In this paper, a framework is presented for providing guidance on how to systematically reduce uncertainty in the measurements and computational models required for accurate and reliable predictions of fire growth. As an example, and initial step towards achieving this goal, a probabilistic analysis of the kinetic parameters obtained from thermogravimetric analysis (TGA) is presented and applied to several thermoplastic materials.

UNCERTAINTY IN COMPUTATIONAL FIRE GROWTH

Validation and Calibration: Fundamental Relationships of Measurement to Computation

Before characterizing the many layers of uncertainty inherent in fire growth modeling, it is necessary to understand the practical relationships between measurement and computation. At least three processes are of interest: verification (is the model implemented correctly?), validation (is the model correct?), and calibration (what are the best model parameters?). In this paper, the latter two processes are examined in the context of a specific experiment and model as introduced in the next section.

In a forward sense, a computational model should be capable of predicting some measurement data (e.g., fire plume height or temperatures, mass loss, or heat release rate). A favorable comparison of a model prediction to experimental data helps to validate the model. Validation helps build confidence in a computational model's ability to make predictions. The validation relationship between measurement and computation can be expressed very simply as two alternative paths relating a fire scenario to a particular outcome as sketched in Fig. 1a. Experiments result in the measurement of data obtained from a scenario. Models, on the other hand, allow for the prediction of that data given a set of inputs that describe the scenario, along with a set of parameters characterizing the behavior of the materials involved. Many examples of this procedure can be found in the FDS Validation Guide[2], which provides an extensive catalog of validation scenarios used to test the reliability of FDS. Unfortunately, existing fire models are not well-validated in flame spread and fire growth scenarios.

(a) (b)

Figure 1. Relationships between models, parameters, and experiments. (a) Validation as a basic relationship between models and experiments. (b) Model calibration to determine model input parameters.

A necessary prerequisite to validating fire models is the determination of model parameters (i.e., calibration). While in validation, the model is used to solve a forward problem, calibration is a backward or inverse problem. This process of model calibration is sketched in Fig. 1b. Calibration is dependent on a specific scenario (or set of scenarios) and a corresponding experiment (or set of experiments). If the model is well-defined and the calibration is properly performed, the determined model parameters should be applicable to a broad range of scenarios going beyond the specific calibration experiment(s). Inverse problems like calibration are mathematically ill-posed, and so their solutions are instable—i.e., the values of the inferred parameters are highly sensitive to small variations in the scenario and experimental data. Consequently, there is significant uncertainty in determining a single best values of a calibrated parameter since very different values can provide similar predictions. Statistical calibration procedures are therefore extremely helpful in that they allow for the characterization of the uncertainty over a range of parameter values arising from the instability of inverse problems[3].

For the purpose of predictive fire growth, the model parameters to be calibrated are properties governing the condensed phase chemistry, thermodynamics, mechanics, and heat and mass transport of a thermally decomposing, multicomponent material. These physical models require a large number of material properties to be calibrated in order to make accurate predictions. Many of these properties are challenging to measure because of the highly transient behavior of thermally degrading materials. In fact, it is incredibly difficult to isolate the measurement of different material properties in a single

experiment for a rapidly changing sample. In current practice, there are two major approaches to obtaining material properties for fire models: "hierarchical" and "global". A *hierarchical* approach[4] determines properties systematically through a series of experiments working up from milligram scale measurements up to tests at the gram scale. A *global* approach[5] uses a single, relatively complicated test such as the Fire Propagation Apparatus (FPA) or the cone calorimeter to determine all material properties concurrently. Of course, these two approaches represent approximate extremes of a spectrum of methods, and it is worth exploring intermediate techniques that are not as detailed as the standard hierarchical approach but still use more data than purely global approaches. There has been no systematic comparison of the effectiveness of hierarchical versus global methods in their ability to provide robust model parameters capable of predicting fire phenomena in a range of different scenarios. An analysis of the calibrated material property uncertainties arising from these two approaches would help to determine a balanced method for choosing the correct collection of measurements needed for efficient reliable fire model calibration.

Both validation and calibration require experimental data. The difference between validation and calibration relates to how that data is used. Any data set can be used for either calibration or validation, but not for both. It is clear that progress in predictive computational fire growth depends on the advancement of fire measurement science and an increasing, well-cataloged set of experimental data.

Progress in Measurement and Computation for Fire Modeling

To extend the range of application of fire models to fire growth, there needs to be a systematic collaboration between materials scientists, experimentalists, and modelers. A prominent example of an effort to foster such collaboration is the International Association of Fire Safety Science (IAFSS) sponsored working group on Measurement and Computation of Fire Phenomenon (MaCFP)[6,7]. In particular, the stated purpose of the MaCFP Condensed Phase Phenomena subgroup "is to facilitate data sharing and model development to improve computational predictions of thermal decomposition and pyrolysis in fire scenarios." MaCFP has hosted three main workshops prior to the IAFSS symposia in 2017 (MaCFP-1), in 2021 (MaCFP-2), and in 2023 (MaCFP-3). At these workshops, researchers from around the world contribute experimental data and model predictions to validate their models and model parameter sets. By examination and discussion of the validation results, the participants in MaCFP are hoping to pave the path forward for progress in making reliable computational predictions of flame spread and fire growth.

In addition to MaCFP, there are several other current efforts to generate the data necessary to support predictive computational flammability. The NIST Material Flammability Database[8] is currently in development and contains measurement data specifically designed for either model calibration or validation from experiments conducted across multiple scales for nearly 20 unique materials. Similarly, the UL Fire Safety Research Institute is developing the Material and Products (MaP) Database[9] with a focus on material property data for common industrial products. A related symposium on Obtaining Data for Fire Growth Models was hosted by ASTM International in December 2021, during which 17 experts from around the world presented results on the current state of the art in the relationship between fire modeling and measurement[10].

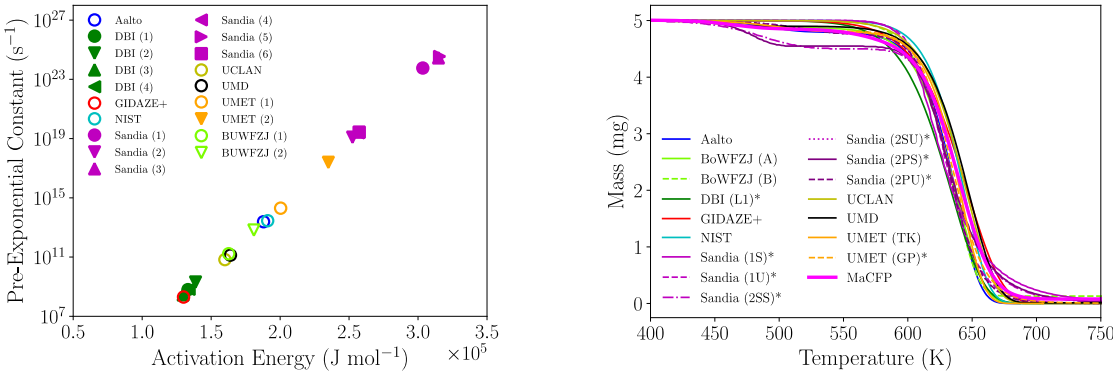
Although these recent efforts provide the fire science community with much of the necessary data to support the integrated improvement of flammability data and fire models, they are not sufficient in themselves to guide experimentalists and model developers in making the most effective targeted improvements to their techniques. There remains substantial uncertainty, driven by the complexity of fire phenomena, in choosing the best experiments for validation and calibration, comparing model predictions, and then making conclusions from these comparisons.

Uncertainty as a Barrier to Progress in Computational Fire Growth Modeling

One of the important initial conclusions of the MaCFP workshops is that there is significant uncertainty involved in modeling the fire behavior of even relatively simple materials. For MaCFP-2, contributors

were asked to calibrate material properties for a black, cast poly(methyl methacrylate) (PMMA). Then, using these calibrated properties, they were asked to make predictions of how the material would respond in response to different heating conditions in a simple one-dimensional slab gasification experiment. It was found that there was considerable variability in both the calibrated properties and the predictions[7].

As an example of calibrated property variability, consider the scatter in Arrhenius kinetic parameters for the pyrolysis of PMMA shown in Fig. 2 (a). The 19 separate contributions demonstrate a great deal of uncertainty in the best estimates of these two model properties, even as they show a strong positive correlation.



(a) (b)

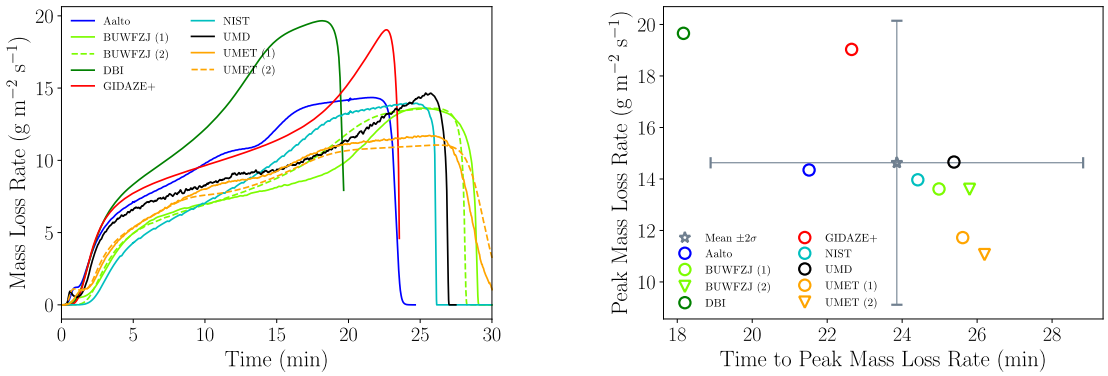
Figure 2. Calibration of poly(methyl methacrylate), PMMA, from various contributors to MaCFP-2[7]. (a) Scatter plot of the Arrhenius pre-exponentials and activation energies shows large uncertainty but a strong correlation. (b) Corresponding predictions of mass versus temperature in TGA results in a relatively small variability at a heating rate of 10 K/min.

Predictions made of mass versus temperature in thermogravimetric analysis (TGA) at a heating rate of 10 K/min show surprisingly less variability in Fig. 2 (b). This observation is the well-known kinetic compensation effect in which changes in the values of the pre-exponential factor and the activation energy can offset each other in a way that produces similar predictions of mass loss. However, it has also been observed that the scatter in kinetically compensated sets of calibrated kinetic parameters can result in large variability in predictions at higher heating rates. Ultimately, calibrated model parameter uncertainty is not important as long as the uncertainty in the predictions of flame spread and fire growth is small enough to make appropriate fire safety decisions. That is, the primary goal is still validation of fire models for predictions of realistic fire scenarios, and model parameter uncertainty is only important insofar as it inhibits reliable predictions in such cases.

Predictions of slab gasification scenarios from MaCFP-2 indicate that the impact of material property uncertainty will be sizeable. Plots of contributor predictions of the gasification of 12 mm thick slabs of the black, cast PMMA exposed to an external heat flux of 25 kW/m^2 are shown in Fig. 3. The predictions of peak mass loss rate, plotted in Fig. 3 (b), vary by around 75 % of the mean value, and the predictions in time to peak mass loss vary by around 40 % of the mean value. This is likely to be an unacceptable degree of uncertainty in a fire safety decision making scenario and is much greater than the experimental uncertainty in typical gram-scale burning experiments such as the controlled atmosphere pyrolysis apparatus (CAPA), the fire propagation apparatus (FPA), and the cone calorimeter. In any case, there is certainly room for improvement even for a relatively simple material (like black, cast PMMA) in a relatively simple scenario (like slab gasification).

The preceding discussion is a clear demonstration that the existing system of fire models and flammability data results in large uncertainties in material property model parameters and model predictions. Reducing these uncertainties requires tools for modeling and working with the

corresponding probabilities and their statistics.



(a) (b)

Figure 3. Predictions of gasification of a 12 mm thick slab of black, cast PMMA exposed to an external heat flux of 25 kW/m^2 using calibrated material property values from various contributors[7]. (a) Mass loss rate versus time. (b) Scatter plot of peak mass loss rates and times to peak mass loss rate.

Characterizing Uncertainty in Computational Fire Growth Models

A high-level overview of uncertainty in predictive computational modeling is sketched in Fig. 6 where uncertainty is represented as probability distributions. Uncertainty in scenario parameters and model parameters (obtained through calibration) result in uncertainty in predictions made by the fire model. In the validation process, the uncertainty in the model predictions must be compared against the uncertainty in the validation experiment. The uncertainty in large-scale experimental data can be reduced by better sensors and tighter controls, but this is often prohibitively expensive or difficult to realize in practice, and so an appropriate validation would be one in which the uncertainty in scenario and model parameters, when propagated through the model, reproduces the uncertainty of the validation experiment—in such a case the probability distributions of the experimental data and the model predictions would approximate each other.

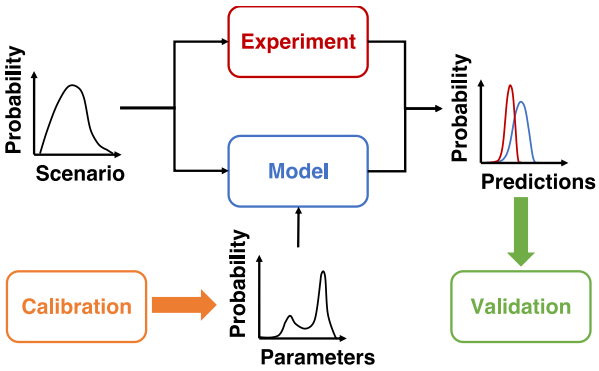


Figure 4. Measurement and prediction under uncertainty.

If the probability distributions in the model output and the experimental data for validation do not agree, then that specific combination of parameters and model should not be used to make predictions in fire safety decision making. In this situation it will be necessary to either (1) make improvements to the model or (2) reduce the uncertainty in the model parameters through more careful calibration (or some combination of (1) and (2)). Option (1) is challenging because fire models are extremely complicated, complex interactions may exist between different submodels, their numerical implementation, or the controlling mechanisms of fire behavior that they simulate, and there are many ways in which they can be modified and possibly improved. Option (2) requires either improving the calibration experiments,

performing more or different calibration experiments, or improving the calibration methods used to estimate the parameters from the data. For a complex system of models and experiments like what is necessary for condensed phase fire modeling, the process of reducing uncertainty in predictions through any of these options is daunting. Fire scientists and engineers need guidance to identify and reduce sources of uncertainty and improve their models and measurements in an efficient manner in order to close the gap between predictions and data for fire growth.

METHODOLOGY

The approach for uncertainty characterization described above involves measurement, calibration, and validation at many scales covering different aspects of fire modelling. In the present paper we demonstrate how to characterize model parameter uncertainty in the calibration of a pyrolysis kinetics model using thermogravimetric analysis data (TGA).

Model of Pyrolysis Kinetics

Any model of solid fuel burning must account for the rate at which combustible gases are produced by the heated solid. Although most polymeric materials undergo fairly complex reaction mechanisms, the most detailed computational condensed phase models used in fire typically assume just several, mostly first order, reactions in series or parallel. Such simple models are usually able to reproduce TGA data for most materials with accuracy within experimental uncertainty. In the following, N parallel reactions are considered of the form

$$\mathrm{R}_i \xrightarrow{k_i} \nu_i \mathrm{C}_i + (1-\nu_i)\mathrm{G}_i, \quad i = 1, \ldots, N \qquad [1]$$

where R_i is the reactant component for reaction i, C_i is an inert "char" component for reaction i, G_i is the volatile gas component produced by reaction i, k_i is the reaction rate constant, and ν_i is a mass-basis stoichiometric coefficient for the char.

The mass of the condensed phase, m, is the sum of the masses of all non-volatile components so that $m = m_\mathrm{C} + \sum_i m_i$ where m_C is the combined mass of all char components, and m_i is the mass of the i^{th} reactant component. The pyrolysis reaction mechanism described by Eq. [1], implies that the system mass changes according to a system of ordinary differential equations

$$\frac{\mathrm{d}m_i}{\mathrm{d}t} = -k_i m_i, \quad i = 1, \ldots, N \qquad [2]$$

$$\frac{\mathrm{d}m_\mathrm{C}}{\mathrm{d}t} = \sum_{i=1}^{N} k_i \nu_i m_i. \qquad [3]$$

Given a set of initial conditions for the component masses, $m_{0,i} \equiv m_i(t=0)$, Eqs. [2-3] can be solved to obtain the component masses at all times $m_i(t)$. The reaction rate constants have the Arrhenius form for temperature dependence $k_i = A_i \exp(-E_i/RT)$ where A_i is the pre-exponential factor, E_i is the reaction activation energy, and R is the gas constant. Note that each reaction in this model requires specification of four parameters: A_i, E_i, ν_i, and $m_{0,i}$. So, for a system of N reactions, the fire model will require $4N$ pyrolysis kinetic parameters.

One advantage of this model is that it has an analytical solution[11] when temperature is increasing linearly at $T(t) = \beta t + T_0$ (as in the case of TGA experiments). That solution, for sufficiently small initial temperatures, is

$$m_i(t) = m_{0,i}\left\{\nu_i + (1-\nu_i)\exp\left[\frac{-A_i T}{\beta}\exp\left(\frac{-E_i}{RT}\right) - \frac{A_i E_i}{\beta R}\,\mathrm{Ei}\left(\frac{-E_i}{RT}\right)\right]\right\}, \quad i = 1, \ldots, N \qquad [4]$$

where $\mathrm{Ei}(x)$ is the exponential integral function evaluated at the argument x. This solution gives $m_i(t \to \infty) = \nu_i$ which does not strictly correspond to Eqs. [2-3] because the analytical solution assigns the residual mass to the reactant component rather than to a separate char species. However, upon summing all N masses in Eq. [4], one obtains the same total mass. In this solution it is apparent that there is a strong correlation between the initial mass, $m_{0,i}$, and the residual mass of reaction, ν_i. In order to simplify the analysis, it was assumed that this coupled effect could be captured in a dimensionless reaction mass loss variable, $\Delta\mu_i \equiv m_{0,i}(1-\nu_i)/m_0$ thus reducing the number of parameters to $3N$. For simplicity, the unknown kinetic parameters will be denoted $\theta = \{(A_i, E_i, \Delta\mu_i)\}$ for $i = 1, \ldots, N$.

Calibration Experiment: Thermogravimetric Analyss

The parameters of the above model need to be estimated for a given material in order to make predictions of fire growth. A standard approach for calibrating pyrolysis kinetic models is through comparison with constant heating rate anaerobic TGA data. In these experiments, a small ($m_0 \approx 5$ mg) sample is heated at a prescribed heating rate, β, in a furnace purged by nitrogen gas. At each experimental time, the sample temperature and mass are recorded yielding a set of time series data of the form $D = \{(t_j, T_j, m_j)\}$ for $j = 1, \ldots, M$ where t_j, T_j, and m_j are the experimental times, temperatures, and masses at the j^{th} point in the series of M points. Generally, after a short initial transient period, the prescribed heating rate is obtained so that $T_{j+1} \approx T_j + \beta(t_{j+1} - t_j)$, and the time sampling rate is approximately constant.

All TGA data were obtained at NIST at a heating rate of $\beta = 10$ K/min for a typical initial sample mass of around 5 mg to 6 mg. In order to further reduce the uncertainty due to initial mass, current NIST data is performed on 5 mg +/- 0.1 mg.

Probabilistic Parameter Estimation

As discussed above, there are several methods for estimating the parameters of a pyrolysis kinetic model from TGA data. Most methods used currently rely on some form of optimization to minimize the error between the TGA data and the model predictions. For example, the pyrolysis model parameters, θ, could be chosen to minimize the root mean square error between the TGA mass data and the model predictions. This not typically a well-behaved optimization problem, but global algorithms have proven to be sufficiently effective to at least find a local minimum for which the model very closely approximates the TGA data[12]. The result is a single calibrated "best fit" set of model parameters.

A single point estimate of all kinetic model parameters is sufficient for making predictions of pyrolysis chemistry, but it does not allow for characterization of the uncertainty of those predictions. There are many sources of uncertainty in this particular calibration problem. These sources can be categorized broadly as measurement uncertainty, material uncertainty, and model uncertainty. Measurement uncertainty in TGA is due to uncertainty in the mass and temperature measurements. Aside from the inherent sensor uncertainty of these measurements, there are also possible systematic sources of error. For example, the temperature in TGA sample is assumed to be spatially uniform, but this assumption is not strictly true and becomes less reasonable for (a) larger samples, (b) higher heating rates, and (c) lower thermal conductivities. Material uncertainty is due to the fact that most materials of interest in fire are complex and so there is irreducible variability from sample-to-sample for a given nominal material obtained from different sources and even within a sample obtained from the same source. Finally, the models being used to predict pyrolysis are reasonable mathematical forms that do not describe detailed chemistry or physics. So even with the best possible point estimate for the set of parameters, it is not known ahead of time if predictions can be made within the measurement and material uncertainties.

A detailed analysis of the sources of uncertainty outlined in the preceding paragraph is very much needed, but such a project is beyond the scope of this paper. However, it should be clear that point estimates of pyrolysis parameters do not give a complete picture of what the experimental data actually

show. A probabilistic analysis can significantly enhance and guide future development of models and measurements for fire growth predictions. The ultimate goal is to produce a probability density function for the uncertain model parameters given TGA data, D. This is expressed as a conditional probability density function (PDF), $p(\theta|D,I)$, where I is shorthand for all of the other background information that is known about the problem such as uncertainties and underlying physics. Bayes' theorem relates this desired probability density to other probability densities that are easier to assign as

$$p(\theta|D,I) = \frac{p(D|\theta,I)}{p(D|I)} p(\theta|I) \quad [5]$$

where $p(D|\theta,I)$ is referred to as the likelihood function, $p(\theta|I)$ is called the prior probability, and $p(D|I)$ is in some contexts called the data evidence. The probability of interest, $p(\theta|D,I)$, is called the posterior probability because it gives the updated probability after the data, D, has been observed. The likelihood function is a model for the probability that the data would be observed if the model parameters were in fact θ. The denominator in Eq. [5] ends up being a normalization factor that can be ignored in parameter estimation problems.

Often, the most challenging part of applying Bayes' theorem in parameter estimation problems is assigning the prior probability, $p(\theta|I)$[13]. In fact, the difficulties surrounding the prior probability are the most common argument against using Bayes' theorem for parameter estimation. However, there are two reasons these challenges are not fatal. First, in most scientific settings, the amount of data overwhelms the prior probability, and the desired posterior probability ends up being approximately proportional to the likelihood function alone, or $p(\theta|D,I) \propto p(D|\theta,I)$ and variations in the prior are negligible. Second, there is a large body of literature in which precise methods for assigning the prior probabilities on parameters have proven to be very successful[13].

In any case, Eq. [5] gives the necessary probabilistic characterization of the pyrolysis kinetic parameters if the likelihood function and prior probability can be specified. As discussed above, there are many sources of uncertainty in TGA calibration problems, and a detailed characterization of the likelihood function would consider all of this information. However, in the absence of this information, there are many reasons for modelling the likelihood with a Gaussian distribution. Aside from the ubiquity of Gaussian distributions in observed data, the Gaussian distribution represents the maximum information entropy if only the mean and variance of the probability distribution are known[13]. Assuming that the deviation in the data is distributed normally about the true model prediction with some standard deviation, σ, then the probability of observing a single point in the TGA time series, D_j, given model parameters θ is:

$$p(D_j|\theta,I) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[\frac{\left(m_j - m_{\mathrm{m}}(t_j,\theta)\right)^2}{2\sigma^2}\right]. \quad [6]$$

The dependence on the scenario parameters, specifically β, has been subsumed into the background information, I, and the details of the model, $m_{\mathrm{m}}(\cdots)$. Assuming that the uncertainty in each data point is independent of all other data points, then the probability of the entire data set is obtained from the product rule of probabilities as $p(D|\theta,I) = \prod_{j=1}^{M} p(D_j|\theta,\sigma,I)$.

A prior probability distribution is necessary to describe the initial uncertainty about the kinetic parameters. In the absence of information, there are many reasons to assume a uniform probability distribution for many uncertain parameters, and so uniform priors, $p(\theta,I)$, will be used for all parameters in the following analysis. Uniform probability density functions must be bounded so that they can integrate to one. Lower and upper bounds for $\ln(A_i)$ and E_i were chosen based on trial and error whereas the mass related parameters were bounded by the logical constraints of mass conservation.

In the next section, Bayes' theorem in was applied to TGA data of three different materials with varied decomposition behavior. Markov Chain Monte Carlo (MCMC) simulations are used to obtain samples from the joint posterior PDF for activation energies, pre-exponentials, and reaction specific mass loss. The posterior PDF was reconstructed from these samples using kernel density estimation. This resultant PDF gives complete information about the relative probabilities of all possible kinetic parameter sets that are consistent with the experimental data. The MCMC simulations are performed using a Python library, PyMC[14], that implements several methods and supporting tools for doing probabilistic analysis. In all cases, the unknown standard deviation, σ, was treated as an unknown nuisance parameter.

RESULTS

High Impact Polystyrene (HIPS)

The first material considered is high-impact polystyrene (HIPS). Inspection of the HIPS data revealed a single distinct reaction peak. Therefore, a kinetic model was chosen for a single reacting component. Four parallel Markov Chains were produced, each containing two thousand samples. Each sample from corresponds to a parameter set, $\theta = \{(A, E, \Delta mu)\}$. So the result of these simulations are 8 thousand possible values of θ that are representative of the state of uncertainty in light of the TGA data. The reconstructed joint posterior PDF for HIPS is given in Fig. 5. The contours of the posterior show, as expected, a strong positive correlation between E and $\log A$ over a range of values. A distinct mode to the joint PDF is observed, but the spread about that mode is only about ± 5 % in either parameter.

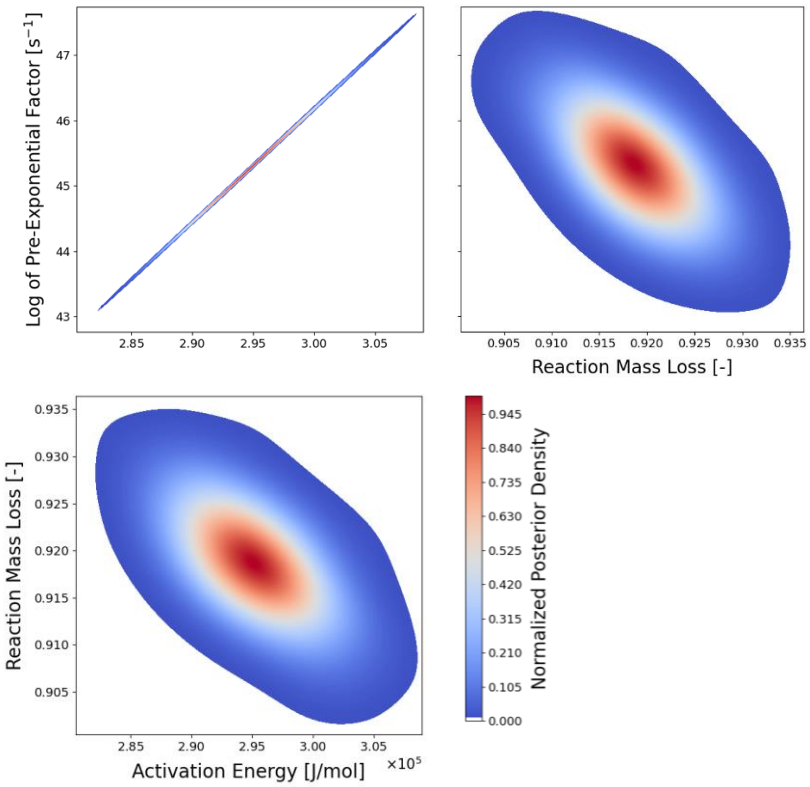


Figure 5. Posterior PDFs for kinetic parameters for HIPS as conditioned by TGA data.

Acrylonitrile Butadiene Styrene (ABS)

It was observed that acrylonitrile butadiene styrene (ABS), like HIPS, degrades with a single distinct reaction peak, and so a single reaction was assumed. Posterior probabilities for these parameters were characterized by using MCMC to simulate four independent two-thousand-sample chains. The

reconstructed joint posterior PDF is plotted as a matrix of bivariate contour plots in Fig. 6. The relationship between E and $\log A$ is seen in the top-left plot where a strong correlation is observed between these kinetically compensating parameters. The other two contour plots in Fig. 6 show the joint probability between the Arrhenius parameters and the total change in dimensionless mass $\Delta\mu$. These plots show a distinct negative correlation, but not nearly as strong as the positive correlation observed between E and $\log A$.This is likely due to the fact that as the Arrhenius parameters increase along a line of constant temperature (the kinetic compensation effect) the reaction peak becomes narrower. A narrower peak can better fit the later reaction masses if the final mass is increased (i.e., smaller $\Delta\mu$).

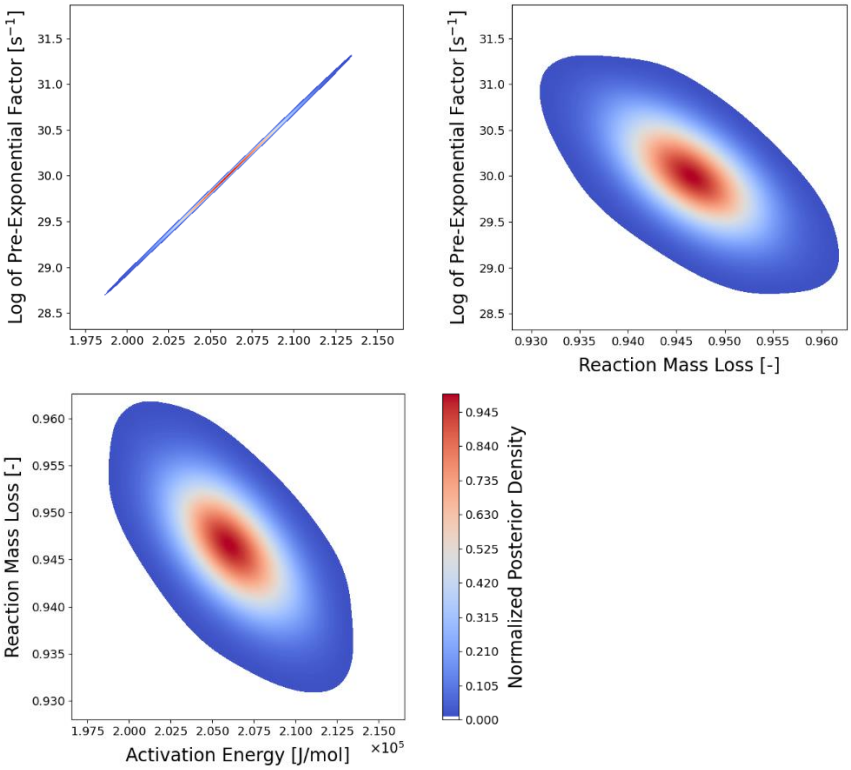


Figure 6. Poster probability distribution for ABS.

Kydex

Finally, Kydex was chosen as a third material because TGA measurements indicate that it degrades in a multistep process, with two distinct reaction peaks, and so a two-reaction model was considered. Four, one-million-sample chains were needed to achieve convergence similar to what was seen for HIPS and ABS. The resultant reconstructed joint posterior PDF is shown in Fig. 7. As before, a strong positive correlation is observed between Arrhenius parameters, but the relationships between these and the mass loss parameters is more varied. Figure 7 gives a complete picture of the uncertainty implied by the TGA data in the parameters that are needed for pyrolysis predictions in fire models. Note that the peak of these contours corresponds to the least-squares fit of the model to the data. The advantage of the MCMC algorithm is that it provides an estimate of the probability of other possible parameter values.

CONCLUSIONS

The results of this paper demonstrate how the tools of probability theory can be used to characterize the uncertainty in estimating pyrolysis kinetic parameters from TGA data. The samples from the MCMC simulations can be used as inputs into large-scale scenarios, ultimately providing an estimate of our uncertainty in predicting flame spread and fire growth. If the process applied in this paper is extended to other calibration experiments, then a more complete picture of prediction uncertainty may be obtained. If this uncertainty compares favorably with the experimental uncertainty in validation cases,

then modelers can have increased confidence in their models, and experimentalists can have increased satisfaction that they are providing sufficient data for model calibration.

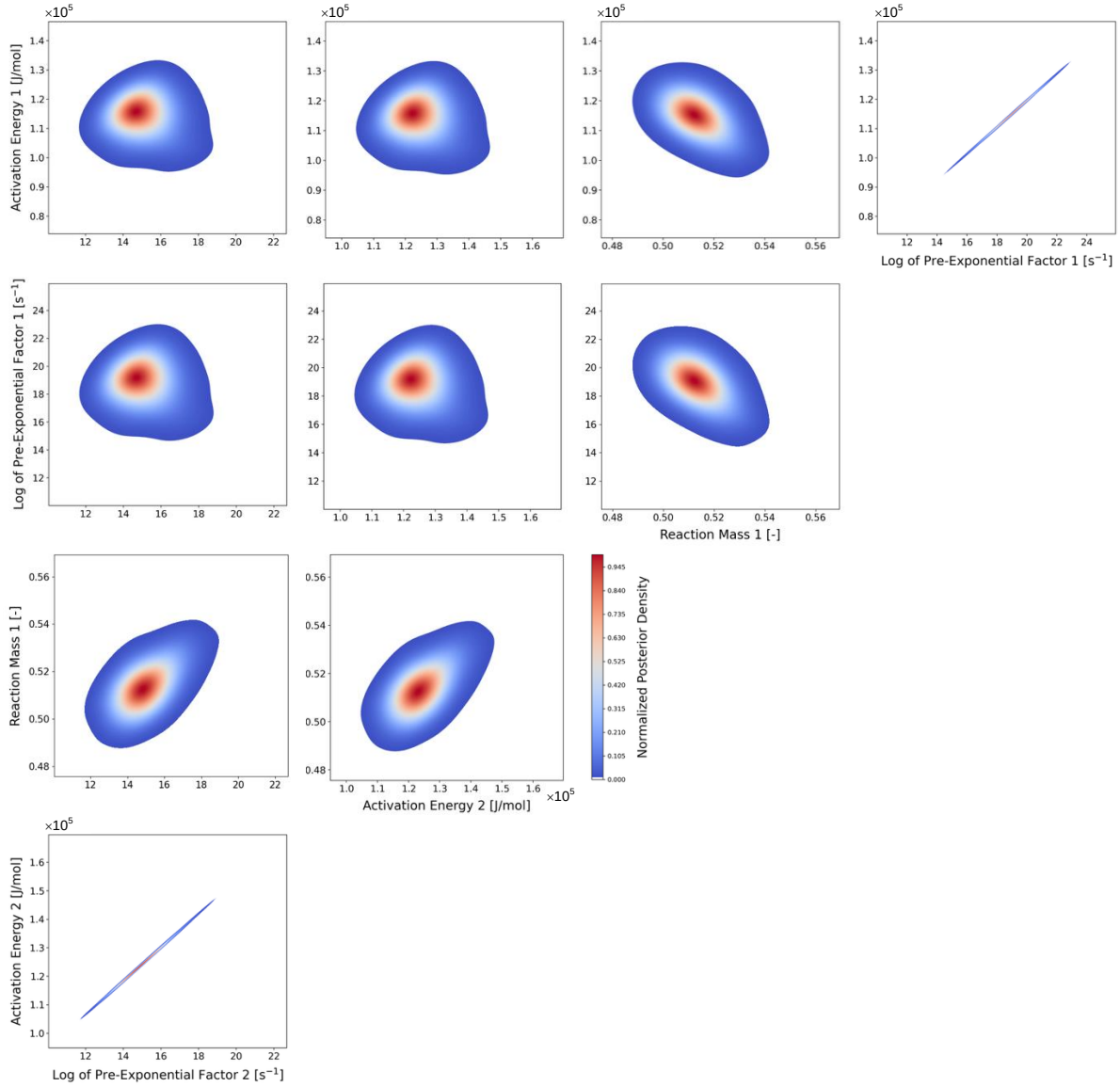


Figure 7. Posterior probability distribution for Kydex.

The results presented are only as good as the underlying model of uncertainty. This uncertainty is encoded in the prior probability distribution and the likelihood function both of which can be challenging to formulate. Fortunately, probability theory tends towards conservative estimates of uncertainty as long as additional assumptions are not introduced. In the present work, the assumptions of uniform priors and Gaussian likelihoods are consistent with this conservative approach—the predicted posteriors can only get narrower with additional assumptions.

In applying this methodology to other data and other problems, two obstacles might present themselves. First, the experimental data could be inaccurate and lead to misleading characterizations of the calibration parameters. Overcoming this obstacle requires carefully conducted experiments with precise statements of uncertainty. Fortunately, bad data can be identified in the model validation process. A second obstacle is that the MCMC simulations might not converge or they might converge too slowly. Not all calibration experiments have corresponding analytical solutions, and it would be prohibitively expensive to run one million simulations that each take one minute. This problem can be addressed from two directions. First, faster surrogate models can be used as long as their uncertainty can be

characterized. It is also not practically unreasonable to run several calibration cases in parallel for several weeks if the outcome is a set of converged posterior samples for a specific material. Second, better sampling algorithms and parameters are available for consideration. In any case, most of the experimental models that are relevant for fire model calibration are relatively fast to simulate.

In future work, the probabilistic tools used here will be applied to characterizing other condensed phase fire model properties using data from other experiments, including differential scanning calorimetry (DSC), microcombustion calorimetry (MCC), and slab gasification data. An initial target validation case will be cone calorimetry, in which not only can a particular model and parameter set be validated under uncertainty, but different approaches for calibration can be easily compared. In particular, a hierarchical approach in which several different calibration experiments are utilized can be compared against a global approach in which a single calibration experiment is considered. Each approach will produce a distinct quantification of parameter uncertainty, and the consequences of this uncertainty can be compared in the validation experiment. Such a comparison will help fire modelers improve their approach to model calibration and guide them in their efforts to improve their models and experiments.

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