Generalized direct method for pyrolysis kinetic parameter estimation and comparison to existing methods

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Generalized direct method for pyrolysis kinetic parameter estimation and comparison to existing methods

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Abstract
Solid-phase pyrolysis is often modelled using the Arrhenius degradation equation with three unknown parameters: reaction order, activation energy and pre-exponential factor. Since the parameters are model dependent and not directly measurable, several estimation methods have been developed over the years for extracting them from the experimental small-scale data. Lately, the most commonly used methods have been based on optimization and curve fitting. These methods are very efficient for complex problems with multiple reactions but may require significant computational time. Direct (analytic) methods are simpler and faster but often have more restrictions and limited accuracy. This article presents a new, generalized direct method and its performance evaluated along with other commonly used estimation methods. The real usability of the methods is tested also in the presence of small noise.

Keywords
Pyrolysis, modelling, parameter estimation

Introduction
Solid-phase pyrolysis is often modelled using the Arrhenius reaction rate equation with three unknown, model-specific parameters. These parameters are called kinetic parameters as they define the reaction kinetics. Direct measurement of these parameters using any common experimental apparatus is not possible. Knowing the reaction chemistry helps to define the reaction path but for an engineering solution, this may be far too complicated and

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ambitious. In real pyrolysis, several reactions occur simultaneously and may overlap in time and temperature. From the fire modeller’s point of view, it is not necessary or even worthwhile to describe all those reactions but rather approximate the process using as few and as simple reactions as possible. It is a well-known fact that the model parameters are able to compensate the other shortcomings and simplifications in the model.1,2 As the kinetic parameters are associated with a specific reaction scheme having no fundamental physical significance, their values can indeed be chosen freely in order to get the best possible description of reality using the model in hand.

For obtaining the kinetic parameters, one needs to extract them from small-scale experimental data. The most commonly used small-scale experiment is non-isothermal thermogravimetric analysis (TGA), which measures the loss of a very small (few milligrams) sample during constant rate heating. There are basically two approaches to property estimation: curve fitting (mainly evolutionary algorithms)3–8 and analytical methods.8–11 Both have their advantages: curve fitting has very few limitations related to the reaction path or estimated parameters and can operate very effectively for complicated, overlapping reactions and noisy data. Their shortcoming is that they often require significant computational time for the iteration process to converge and some specific software for performing the estimation. It may also be discomforting that – due the compensation effect and other factors – several equally fitting solutions may be found (meaning the solution is not unique). Furthermore, the process is stochastic, which means that the results and the estimation routine cannot be repeated with exactly same results. Analytical methods, on the other hand, use reference points (such as the peak reaction rate) in experimental data to define kinetic parameters. They do operate well for simple, non-noisy and non-overlapping data and give unique solutions without requiring lengthy iterations. They also require just a pencil and paper for obtaining the solutions, so they are fast and efficient solution for an engineer. However, they are often limited to some specific reaction path and well-separated reactions. Noise in the data can lead to difficulties.

In this work, a generalized direct (analytical) method (GDM) for estimating reaction kinetics from TGA data is presented and its performance is compared to alternative common estimation methods. The methods are assessed in terms of accuracy of the results, time consumed and level of user participation and knowledge needed. All the simulations in this work have been made using the pyrolysis model of fire dynamic simulator (FDS) version 6.0.0.12

Estimation methods

Direct method

The direct method (DM) considers a multiple step ($k$ being the reaction index), $N$th order reaction path, where the reaction steps are well separated. By reactions being well separated, we mean that the reaction $k-1$ is completed before reaction $k$ starts. This method is based on the same idea as Friedman used for the one-step reaction.11 The char-yielding reaction of converting material $A$ into material $B$ and fuel gas is described as

$$A \rightarrow (1 - v_k)B + v_k \text{gas}$$

for each reaction $k$. The conversion after the reaction $k$ is defined as
where $m_k$ is the mass after reaction $k$ is complete and $m_0$ is the initial mass of the sample. A reaction progress variable $a_k^*$ corresponding to the mass released from one-step reaction can be defined as

$$a_k^* = \frac{\alpha - \alpha_{k-1}}{\alpha_k - \alpha_{k-1}} \tag{2}$$

An Arrhenius form of the decomposition reaction rate can be written for multiple reactions as

$$\frac{da_k^*}{dt} = A_k \left(1 - a_k^*\right)^{N_i} \exp\left(-\frac{E_k}{RT}\right) \tag{3}$$

Replacing the reaction progress variable with the relation from equation (2) and dividing both sides by the heating rate $\beta = dT/dt$, the Arrhenius equation becomes

$$\frac{d\alpha}{dT} = \frac{A_k}{\beta} \frac{(\alpha_k - \alpha)^{N_i}}{(\alpha_k - \alpha_{k-1})^{N_{k-1}}} \exp\left(-\frac{E_k}{RT}\right) \tag{4}$$

To connect these analytical expressions to the thermogravimetric data, a reference point needs to be specified. In DM, the reference point for each of the reactions is chosen from the peak of the differential thermogravimetric (DTG) curve, as shown in Figure 1. The first derivative (with respect to temperature) of the conversion at the reference point of $k$th reaction is called reference value and is denoted as $r_{pk}$.

$$r_{pk} = \max \left(\frac{d\alpha}{dT}\right) \tag{5}$$
The corresponding temperature and conversion values are denoted as $T_{pk}$ and $\alpha_{pk}$, respectively. The second derivative of the conversion $\alpha$ is zero at reference point. Using these definitions, we can solve the above equation for activation energy

$$E_k = N_k R \frac{r_{pk}}{\alpha_k - \alpha_{pk}} T_{pk}^2$$  \hspace{1cm} (6)$$

Alternatively, the calculation can be made using the reference value based on the first time derivative of the conversion

$$E_k = \frac{N_k R \max (d\alpha/dt)}{\beta} \frac{\alpha_k - \alpha_{pk}}{T_{pk}^2}$$  \hspace{1cm} (7)$$

By substituting the activation energy into equation (4), we obtain an equation for pre-exponential factor

$$A_k = r_{pk} \beta \frac{(\alpha_k - \alpha_{k-1})^{N_k-1}}{(\alpha_k - \alpha_{pk})} \exp \left( \frac{E_k}{RT_{pk}} \right)$$  \hspace{1cm} (8)$$

Now, the only unknown parameter is the reaction order $N_k$. In certain applications, it can be assumed to be one, but for more general approach, some methods from the literature are presented. Gao et al.\textsuperscript{13} listed theoretical limits for the conversion as a function of the reaction order. A very simple curve fit can be made for approximating the reaction order

$$N_k \approx 13.25 \left( 1 - \alpha_{p,k}^* \right)^3 - 4.16 \left( 1 - \alpha_{p,k}^* \right)^2 + 2.3 \left( 1 - \alpha_{p,k}^* \right) - 0.077$$  \hspace{1cm} (9)$$

where $\alpha_p^*$ is the reaction progress variable from equation (2) at the peak. More elaborate methods have been presented by Friedman.\textsuperscript{11} For three different points (1, 2, 3) of a single experimental TGA curve, the reaction order can be calculated as

$$N_k = \ln \left( \frac{r_{2k}}{r_{1k}} \right) - \frac{T_{2k}(T_{3k}-T_{1k})}{T_{3k}(T_{2k}-T_{1k})} \ln \left( \frac{r_{2k}}{r_{1k}} \right)$$

$$+ \ln \left( \frac{1-\alpha_{2k}^*}{1-\alpha_{3k}^*} \right) - \ln \left( \frac{1-\alpha_{2k}^*}{1-\alpha_{3k}^*} \right)$$  \hspace{1cm} (10)$$

If one point is the peak value, $N$ can be estimated using only two reference points (1, $p$)

$$N_k = \frac{\ln \left( \frac{r_{pk}}{r_{1k}} \right)}{T_{pk}(T_{pk}-T_{1k})r_{pk} - \ln \left( \frac{1-\alpha_{pk}^*}{1-\alpha_{1k}^*} \right)}$$  \hspace{1cm} (11)$$

**Generalized Direct Method (GDM)**

The DM is very sensitive to the correct definition of the conversion and the peak value. If the reactions are overlapping at later stage, it may be more convenient to choose the reference point where the reactions do not yet overlap. That is, either before or after the peak value. If the reference point is chosen from where the third derivative is zero (see Figure 1), the activation energy can be calculated as (neglecting the reaction index $k$ for brevity)
$$E = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

(12)

where

$$a = \frac{(\alpha_k - \alpha_{pp})^2}{RT_{pp}}$$

$$b = \frac{-2r_{pp}N_k(\alpha_k - \alpha_{pp})}{RT_{pp}} - \frac{2(\alpha_k - \alpha_{pp})^2}{RT_{pp}}$$

$$c = r_{pp}^2(N_k - 1)N_k - r_{pp}N_k(\alpha_k - \alpha_{pp})$$

Here $T_{pp}$ is the reference point and $r_{pp}$ and $r_{Tpp}$ are the first and second derivatives of the conversion at the reference point, respectively. The second gradient $r_T$ has two peaks and the sign ($\pm$) in equation (12) depends on which peak is chosen. If the first (positive) peak is chosen, the sign is positive. After this, $A_k$ can be calculated at the point $T_{pp}$ as in equation (8) and $N_k$ as previously described for DM. This will be called GDM.

### Data reduction

It is customary to perform the TGAs at different heating rates, typically between 1 and 20 K/min. In fires, the heating rates can, at least for short periods of time, be as high as 1000 K/min. In this work, some approaches to the reduction of the estimation results obtained from different heating rates are studied. First of all, the results from all the heating rates must be somehow averaged for a general result. The averaging can be performed either to the calculated parameter values ($A$, $E$, $N$) or to the reference values ($\alpha$, $T$, $r$).

In addition, the effect of the heating rate range can be considered by giving more or less importance to the extreme heating rates. Different weighting methods examined are listed in Table 1.

<table>
<thead>
<tr>
<th>$w_t$</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$w_1 = \frac{1}{\mu}$</td>
<td>(direct mean)</td>
</tr>
<tr>
<td>$w_2 = \frac{1}{</td>
<td>\beta_i - \mu</td>
</tr>
<tr>
<td>$w_3 = \frac{</td>
<td>\beta_i - \mu</td>
</tr>
</tbody>
</table>

$\mu$ is the mean of the heating rates.

The error (fitness value) between target and estimated curves is calculated as sum of errors in conversions scaled by average relative deviation

$$fV = \frac{\sum_j |\alpha_{mod,j} - \alpha_{exp,j}|}{\sum_j \alpha_{exp,j}}$$

(13)

with the summation going over the values obtained at different temperatures. Small fitness value means good fit in this work.
Other commonly used estimation methods

Several authors have proposed other analytical methods for obtaining the kinetic parameters. Some of the methods are listed in Table 2. These methods are generally easy and quick to use, and they provide relatively unique solutions. Friedman developed his method for a single-step model, but here, it is scaled for multiple steps for generality. McGrattan et al. and Lyon et al.9,10 presented essentially the same equations with slightly different derivations and nomenclature. They both assumed first-order reaction kinetics. Lyon et al. additionally limited the reaction path to just one reaction but offered an alternative method for extracting the reaction parameters using the heat release rate from microscale combustion calorimeter (MCC).10,14 Those equations may have great value for some applications but are not evaluated here since they require different experimental apparatus than the other methods.

Besides the analytical methods, several curve-fitting algorithms have been applied for the kinetic parameter estimation. Evolutionary algorithms are most commonly used, including genetic algorithms (GA),3–7 hybrid genetic algorithms (HGA)7 and shuffled complex evolution (SCE).7,8 Their main idea is based on the survival of the fittest. The algorithm starts from a random set of trial solutions and tests their fitness against the experimental curve. The probability of the stochastic processes depends on this fitness value; the better the fitness value, the greater the probability of the trial solution surviving to the next iteration round. Other processes are crossover (creating new trial solution by uniting two older solutions), mutation (one or more parameters are replaced by a random number) and migration (trial solutions change place between two groups of the solutions). These algorithms are very efficient for complex problems with many parameters, overlapping reactions and even noisy data. They are a bit more complicated to use than the analytical methods and require significant amount of computer resources.

**Results and discussions**

**Simple synthetic material**

Four analytical methods, presented by equations (6) to (12) and Table 2, and two optimization methods (GA and SCE) were tested using a synthetic material sample with two

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**Table 2. Analytical methods used in this work**

<table>
<thead>
<tr>
<th>Method</th>
<th>$E$</th>
<th>$A$</th>
<th>Values to specify/reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct method</td>
<td>$E_k = NkR \frac{r_{pk}}{a_k-a_{pk}} T^2_{pk}$</td>
<td>$A_k = \frac{r_{pk} \beta (a_{k-1}-a_k)^{Nk-1}}{(a_k-a_{pk})^{Nk}} \exp \left( \frac{E_k}{RT_{pk}} \right)$</td>
<td>5: $r_p, T_p, \alpha_p, \alpha_k, \alpha_{k-1}$</td>
</tr>
<tr>
<td>Generalized direct method</td>
<td>$E = \frac{-R}{2a} \ln \left( \frac{2a}{a_k} \right) + N_k \ln \left( \frac{a_k-a_{pk}}{a_k-a_{pk}} \right)$</td>
<td>$A_k = \beta \frac{r_{pk} \alpha_k}{a_k-a_{pk}} \exp \left( \frac{E_k}{RT_{pk}} \right)$</td>
<td>6: $r_{pp}, r_{Tpp}, T_{pp}$, $\alpha_{pp}, \alpha_k, \alpha_{k-1}$</td>
</tr>
<tr>
<td>Friedman11</td>
<td>$E_k = -\frac{R}{2a} \ln \left( \frac{2a}{a_k} \right) + N_k \ln \left( \frac{a_k-a_{pk}}{a_k-a_{pk}} \right)$</td>
<td>$A_k = \frac{r_{pk} \beta (a_{k-1}-a_k)^{Nk-1}}{(a_k-a_{pk})^{Nk}} \exp \left( \frac{E_k}{RT_{pk}} \right)$</td>
<td>8: $r_{1f}, r_{2f}, T_1, T_2, \alpha_{1k}, \alpha_{2k}, \alpha_k, \alpha_{k-1}$</td>
</tr>
<tr>
<td>McGrattan et al.8 and Lyon et al.10</td>
<td>$E_k = \frac{RT^2_{pk} \epsilon_{pk}}{a_k-a_{k-1}} N = 1$</td>
<td>$A_k = \beta \frac{r_{pk} \alpha_k}{a_k-a_{pk}} \exp \left( \frac{E_k}{RT_{pk}} \right)$</td>
<td>4: $r_p, T_p, \alpha_{1k}, \alpha_{k-1}$</td>
</tr>
</tbody>
</table>
well-separated reactions. The synthetic material was chosen because of known target values, simple shape and non-noisy data. The reaction path is shown in Figure 2. Two pseudocomponents are assumed with mass losses of 0.35 and 0.4, respectively, of the original mass, and they were assumed to be known. The first reaction produces water vapour (as some flame retardants) and the second reaction produces fuel gas. The reaction order was calculated using equations (9) and (10) and assuming a first-order reaction for comparison for those models that it was applicable.

The synthetic target data were generated for four different heating rates (5, 10, 30 and 50 K/min), and the results were generalized using the weighting functions (Table 1) for either directly for the estimated parameter values or for the reference points and values. The real performance of the parameters was then tested using target data at 20 K/min and 100 K/min. A summary of the test scheme is shown in Figure 3.

The parameter estimation produced in total 62 sets of kinetic parameters, and they were tested for two different heating rates (20 and 100 K/min). The predicted DTG curves with best fitting parameter sets of each method are presented in Figure 4. In addition to the overall result covering the whole temperature range (Figure 4(a)), the detailed results of

Figure 2. Reaction path for the simple synthetic material.

Figure 3. Test scheme for the estimation methods.
DM: direct method; GDM: generalized direct method; GA: genetic algorithms; SCE: shuffled complex evolution.
the reaction rate peaks are shown in Figure 4(b) and (c). The reaction order in best fitting model for GDM was calculated using the Friedman’s equation (equation (10)), and the curve fit (equation (9)) was used for DM and Friedman’s method. Based on a visual judgement, all the methods reproduced the TGA experiment very well, suggesting that they are adequate for engineering purposes. The fit and the calculated fitness values were significantly better using optimization methods (GA, SCE) than the analytical methods. SCE reproduced the synthetic TGA data most accurately at both validation heating rates. The best fitting parameter sets of each method are listed in Table 3. Between analytical methods, the GDM showed the best performance both at 20 K/min and at 100 K/min heating.

**Figure 4.** Comparison of estimation methods and experimental curve at 20 K/min. (a) Overall results, (b) first peak and (c) second peak.

DM: direct method; GDM: generalized direct method; GA: genetic algorithms; SCE: shuffled complex evolution.
<table>
<thead>
<tr>
<th>Target values</th>
<th>DM, equations (6) and (8)</th>
<th>GDM, equations (8) and (12)</th>
<th>Friedman (Table 2)</th>
<th>McGrattan –Lyon (Table 2)</th>
<th>GA</th>
<th>SCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$ (s$^{-1}$)</td>
<td>$1.50 \times 10^{15}$</td>
<td>$3.10 \times 10^{14}$</td>
<td>$4.11 \times 10^{15}$</td>
<td>$5.83 \times 10^{14}$</td>
<td>$2.67 \times 10^{12}$</td>
<td>$3.41 \times 10^{15}$</td>
</tr>
<tr>
<td>$E_1$ (kJ/kmol)</td>
<td>$1.60 \times 10^{5}$</td>
<td>$1.53 \times 10^{5}$</td>
<td>$1.63 \times 10^{5}$</td>
<td>$1.56 \times 10^{5}$</td>
<td>$1.36 \times 10^{5}$</td>
<td>$1.62 \times 10^{5}$</td>
</tr>
<tr>
<td>$N_1$</td>
<td>1.50</td>
<td>1.43</td>
<td>1.50</td>
<td>1.43</td>
<td>1.00</td>
<td>1.59</td>
</tr>
<tr>
<td>$A_2$ (s$^{-1}$)</td>
<td>$1.00 \times 10^{12}$</td>
<td>$2.48 \times 10^{11}$</td>
<td>$1.17 \times 10^{12}$</td>
<td>$3.15 \times 10^{11}$</td>
<td>$6.05 \times 10^{7}$</td>
<td>$4.52 \times 10^{11}$</td>
</tr>
<tr>
<td>$E_2$ (kJ/kmol)</td>
<td>$2.10 \times 10^{5}$</td>
<td>$2.03 \times 10^{5}$</td>
<td>$2.12 \times 10^{5}$</td>
<td>$2.05 \times 10^{5}$</td>
<td>$1.51 \times 10^{5}$</td>
<td>$2.05 \times 10^{5}$</td>
</tr>
<tr>
<td>$N_2$</td>
<td>2.00</td>
<td>1.92</td>
<td>2.00</td>
<td>1.92</td>
<td>1.00</td>
<td>1.97</td>
</tr>
<tr>
<td>$f/V$ (20 K/min)</td>
<td>–</td>
<td>0.0086</td>
<td>0.0070</td>
<td>0.0085</td>
<td>0.0299</td>
<td>0.0024</td>
</tr>
<tr>
<td>$f/V$ (100 K/min)</td>
<td>–</td>
<td>0.0111</td>
<td>0.0082</td>
<td>0.0109</td>
<td>0.0131</td>
<td>0.0041</td>
</tr>
<tr>
<td>$f/V$ (HRR)</td>
<td>–</td>
<td>0.0832</td>
<td>0.0591</td>
<td>0.0819</td>
<td>0.2463</td>
<td>–</td>
</tr>
<tr>
<td>$f/V$ (MLR)</td>
<td>–</td>
<td>0.0045</td>
<td>0.0022</td>
<td>0.0047</td>
<td>0.0151</td>
<td>–</td>
</tr>
<tr>
<td>Number of reference points (excluding $N$)</td>
<td>10</td>
<td>12</td>
<td>16</td>
<td>8</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Comments</td>
<td>$N_{cf}$ equation (9), Ref. ave, wt3</td>
<td>$N_f$ equation (10), Ref. ave, wt2</td>
<td>$N_{cf}$ equation (9), Ref. ave, wt3</td>
<td>$N = 1$, Par. ave, wt3</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>


‘Ref. ave’ means that reference values were averaged. ‘Par. ave’ means that parameters were averaged. Small fitness value means good fit.

The used reaction order $N$ and information about the parameter averaging are listed in the comments (Table 1).
rates. McGrattan–Lyon method provided the fit with the largest error, but this is to be expected since it is limited to first-order reactions. Of the other analytical methods, only Friedman’s method performed reasonably well when $N = 1$ was assumed.

The effects of the weight functions and two different means of averaging were examined by calculating the fitness values for the validation results of each of the analytical methods. The fitness values with different weight functions are listed in Table 4. For all the other methods except McGrattan–Lyon, the results were much more accurate when the reference values were first averaged prior to calculating the parameters. For the McGrattan–Lyon method, straight averaging of the parameters resulted in better fits. The different weight functions also had some significant effect on the resulting fitness values. Surprisingly, for DM and Friedman’s method, it seems that the $wt^2$ (emphasizing the heating rates closer to mean value) has the better extrapolating ability than $wt^3$ (emphasizing the heating rates far from mean value). For GDM, the opposite was true.

While the analytical methods were very quick to use, the optimization methods required significant computational time even when parallel processing was used to speed up the computations. The set-up time for all the methods was more or less the same. For the analytical methods, the added complexity means increasing number of reference points to be chosen (listed in Table 2). The method of McGrattan and Lyon is the simplest with only four values to specify per reaction, while Friedman’s method is the most complicated one with eight values per reaction. The curve fit reaction order (equation (9)) requires only three reference points, while the Friedman’s equation (equation (10)) needs eight. Of course, the use of the analytical methods could be automated reducing the workload.

The significance of the differences in estimated kinetic parameters was studied by applying the results of the analytical methods to a simulated cone calorimeter test. The

### Table 4. Fitness values of the analytical methods with different weight functions

<table>
<thead>
<tr>
<th>Averaging</th>
<th>DM</th>
<th>GDM</th>
<th>Friedman</th>
<th>McGrattan–Lyon</th>
</tr>
</thead>
<tbody>
<tr>
<td>$fV$ (20 K/min)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Parameters</td>
<td>$wt^1$ 0.0236</td>
<td>0.0570</td>
<td>0.0174</td>
<td>0.0314</td>
</tr>
<tr>
<td></td>
<td>$wt^2$ 0.0210</td>
<td>0.0536</td>
<td>0.0229</td>
<td>0.0316</td>
</tr>
<tr>
<td></td>
<td>$wt^3$ 0.0182</td>
<td>0.0486</td>
<td>0.0207</td>
<td>0.0299</td>
</tr>
<tr>
<td>Reference values</td>
<td>$wt^1$ 0.0100</td>
<td>0.0108</td>
<td>0.0099</td>
<td>0.0453</td>
</tr>
<tr>
<td></td>
<td>$wt^2$ 0.0129</td>
<td>0.0070</td>
<td>0.0130</td>
<td>0.0409</td>
</tr>
<tr>
<td></td>
<td>$wt^3$ 0.0086</td>
<td>0.0084</td>
<td>0.0085</td>
<td>0.0491</td>
</tr>
<tr>
<td>$fV$ (100 K/min)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Parameters</td>
<td>$wt^1$ 0.0311</td>
<td>0.0689</td>
<td>0.0227</td>
<td>0.0132</td>
</tr>
<tr>
<td></td>
<td>$wt^2$ 0.0282</td>
<td>0.0638</td>
<td>0.0292</td>
<td>0.0131</td>
</tr>
<tr>
<td></td>
<td>$wt^3$ 0.0250</td>
<td>0.0603</td>
<td>0.0267</td>
<td>0.0131</td>
</tr>
<tr>
<td>Reference values</td>
<td>$wt^1$ 0.0128</td>
<td>0.0122</td>
<td>0.0123</td>
<td>0.0297</td>
</tr>
<tr>
<td></td>
<td>$wt^2$ 0.0181</td>
<td>0.0082</td>
<td>0.0174</td>
<td>0.0242</td>
</tr>
<tr>
<td></td>
<td>$wt^3$ 0.0111</td>
<td>0.0094</td>
<td>0.0109</td>
<td>0.0342</td>
</tr>
</tbody>
</table>

DM: direct method; GDM: generalized direct method.
The $N$ is calculated as in Table 3.
cone heater was not simulated. Instead, a 50 kW/m² external heat flux was applied to the sample surface in the condensed phase solver. The gas space of the cone calorimeter was simulated with a 1-cm grid resolution to capture the flame heat flux. The thermal parameters of the simulated material are listed in Table 5. The comparison of the simulated cone calorimeter results are shown in Figure 5, and fitness values are shown in Table 3. GDM provides the most accurate prediction of the heat and mass loss rates. The first-order method of McGrattan and Lyon gives the least accurate prediction, as expected according to the TGA results. However, the differences between the methods are relatively small and could be compensated by the thermal parameter values if they were separately estimated using the cone calorimeter data. The differences in the sample’s front and back temperatures were insignificant.

**Noisy synthetic material**

The performance of the analytical estimation methods was also tested in a more realistic case with two, slightly overlapping reactions using synthetic TGA signal that includes noise. According to the previous tests, the optimization methods are known to result in better fitness in most cases and are therefore excluded from this study. The sample is assumed to consist of two pseudocomponents, and the reaction path is seen in Figure 6. The mass losses during the two reactions were 0.25 times the original mass and that was assumed to be known. As in the simple test case, the first reaction yields water vapour and the second fuel gas. The sample data were created at 5 and 50 K/min heating rates and tested at 20 and 100 K/min. The reference points were given equal weights.

Typically TGA experiments have very little noise. According to our own experience on TGA data, the noise is usually associated with the high mass loss rate during the degradation and is by no means constant during the experiment. Two noise types were tested:

\[
\text{Noise } 1 = 1 \cdot 10^{-4} \sin(T) \\
\text{Noise } 2 = 0.0003 \sin(2 \cdot 0.01 \cdot \pi T) + \sin(2 \cdot 0.022 \cdot \pi T) \cdot \left\{ \begin{array}{ll} 
0, & \text{when } T \not\in T_{\text{deg}} \\
0.01 + 1 \cdot 10^{-4} x, & \text{when } T \in T_{\text{deg}} 
\end{array} \right.
\]

\[x \sim N(0, 1)\]

The noise was added to the conversion \( \alpha \). It was generated similarly for both heating rates, but the random numbers were different. Noise 1 is small sinusoidal noise with relatively high frequency. Noise 2 has two parts: small, low frequency sinusoidal noise where nothing is degrading and higher frequency noise with some randomness in the area where

<table>
<thead>
<tr>
<th>Component</th>
<th>( \rho ) (kg/m³)</th>
<th>( \varepsilon )</th>
<th>( k ) (W/m/K)</th>
<th>( c_p ) (kJ/kg/K)</th>
<th>( H_r ) (kJ/kg)</th>
<th>( H_c ) (MJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Component 1</td>
<td>1000</td>
<td>1.0</td>
<td>0.5</td>
<td>3.0</td>
<td>1500</td>
<td>25</td>
</tr>
<tr>
<td>Component 2</td>
<td>1000</td>
<td>1.0</td>
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<td>2.0</td>
<td>200</td>
<td>30</td>
</tr>
<tr>
<td>Residue 1</td>
<td>300</td>
<td>0.8</td>
<td>0.3</td>
<td>1.2</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Residue 2</td>
<td>200</td>
<td>0.9</td>
<td>0.7</td>
<td>1.5</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>
the sample is degrading. The noise levels can be seen in Figure 7. Noise 2 is significantly greater than Noise 1, and it is based on an analysis of real, noisy TGA data. Fitness values were calculated compared to the original, non-noisy data. The noisy data were tested using all the methods listed in Table 2. Due to the strong overlapping of the reactions, the reaction order \((N)\) could not be accurately calculated using the Friedman’s method, and therefore, the curve fit method in equation (9) was used for all methods.

The parameter estimation results are listed in Table 6 and visually presented for Noise 2 in Figure 8. When no noise was added, all the methods where \(N \neq 1\) predicted the DTG curve very accurately. Small sinusoidal noise (Noise 1) did not cause significant error for DM or Friedman’s method, but for GDM, the error increased especially in the second peak. This is probably due to the fact that the magnitude of the error caused by the high-frequency noise increases with each successive derivative, and therefore, small error in the mass data causes greater error in the second derivative. It is also more difficult to define the location of the peak from very noisy data.

Noise 2 was more challenging for all other methods except GDM. The results are shown in Figure 8. The effect of the noise depends on the location of the greatest error, whether it is...
located exactly at the reference point or not. In some cases, the noise can even improve the accuracy of the method, as can be seen for the DM and Friedman’s method for Noise 1 at 100 K/min, compared to the results without any noise. All the methods produced acceptable accuracy for simulation purposes at both noise types.

The sets of kinetic parameters estimated with Noise 2 were tested in cone calorimeter at 50 kW/m² heat flux level. The simulations were made using 1 cm grid size. The thermal parameters were the same as for the simple test case (Table 5), and the heat release rate and mass loss rate at 50 kW/m² are shown in Figure 9. The fitness values of the cone calorimeter results with Noise 2 are listed in Table 6. Only the kinetic parameters estimated using McGrattan–Lyon method caused slightly higher rate and earlier flame out compared to the target results. As expected according to the TGA results, GDM provided the best fit also in the cone calorimeter results. The significance of this difference is very small, as the thermal parameters are known to compensate the inaccuracies in the kinetic model. The kinetic parameters did not have any significant effect on the front and back temperatures of the sample.

**Summary and conclusions**

A DM for estimation of kinetic parameters was generalized for multiple reactions and compared with other commonly used estimation methods. Both analytical methods and optimization algorithms were compared. For analytical methods, different methods for calculating the reaction order were also presented and assessed and different weight functions for the heating rates tested. Synthetic experimental data based on known kinetic parameters were used. The first test was a simple two-step reaction with well-separated reactions and no noise.
<table>
<thead>
<tr>
<th>No noise/Noise</th>
<th>Target</th>
<th>A_1 (s^-1)</th>
<th>E_1 (kJ/kmol)</th>
<th>N_1</th>
<th>A_2 (s^-1)</th>
<th>E_2 (kJ/kmol)</th>
<th>N_2</th>
<th>fV (20 K/min)</th>
<th>fV (100 K/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No noise</td>
<td>Target</td>
<td>1.50 \times 10^{15}</td>
<td>200 \times 10^3</td>
<td>1.50</td>
<td>1.00 \times 10^{10}</td>
<td>1.60 \times 10^5</td>
<td>2.00</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>DM</td>
<td>3.50 \times 10^{14}</td>
<td>1.92 \times 10^5</td>
<td>1.35</td>
<td>6.65 \times 10^1</td>
<td>1.59 \times 10^5</td>
<td>1.96</td>
<td>0.0104</td>
<td>0.0117</td>
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</tr>
<tr>
<td>GDM</td>
<td>8.29 \times 10^{14}</td>
<td>1.96 \times 10^5</td>
<td>1.35</td>
<td>7.25 \times 10^1</td>
<td>1.85 \times 10^5</td>
<td>1.96</td>
<td>0.0105</td>
<td>0.0151</td>
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<tr>
<td>Friedman</td>
<td>6.19 \times 10^{14}</td>
<td>1.95 \times 10^5</td>
<td>1.35</td>
<td>2.78 \times 10^9</td>
<td>1.54 \times 10^5</td>
<td>1.96</td>
<td>0.0103</td>
<td>0.0137</td>
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<tr>
<td>McGrattan–Lyon</td>
<td>1.34 \times 10^{13}</td>
<td>1.75 \times 10^5</td>
<td>1.00</td>
<td>4.55 \times 10^6</td>
<td>1.17 \times 10^5</td>
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<td>0.0576</td>
<td>0.0465</td>
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<tr>
<td>Noise 1</td>
<td>DM</td>
<td>5.59 \times 10^{14}</td>
<td>1.94 \times 10^5</td>
<td>1.35</td>
<td>2.36 \times 10^{10}</td>
<td>1.66 \times 10^5</td>
<td>2.01</td>
<td>0.0104</td>
<td>0.0100</td>
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<tr>
<td></td>
<td>GDM</td>
<td>5.29 \times 10^{14}</td>
<td>1.94 \times 10^5</td>
<td>1.35</td>
<td>1.22 \times 10^{17}</td>
<td>2.55 \times 10^5</td>
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<td></td>
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<td>6.10 \times 10^{14}</td>
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<td>1.35</td>
<td>8.92 \times 10^9</td>
<td>1.60 \times 10^5</td>
<td>2.01</td>
<td>0.0106</td>
<td>0.0119</td>
</tr>
<tr>
<td></td>
<td>McGrattan–Lyon</td>
<td>2.19 \times 10^{13}</td>
<td>1.78 \times 10^5</td>
<td>1.00</td>
<td>8.46 \times 10^6</td>
<td>1.20 \times 10^5</td>
<td>1.00</td>
<td>0.0578</td>
<td>0.0492</td>
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<tr>
<td>Noise 2</td>
<td>DM</td>
<td>2.31 \times 10^{15}</td>
<td>2.01 \times 10^5</td>
<td>1.45</td>
<td>5.07 \times 10^{11}</td>
<td>1.83 \times 10^5</td>
<td>2.40</td>
<td>0.0169</td>
<td>0.0143</td>
</tr>
<tr>
<td></td>
<td>GDM</td>
<td>7.76 \times 10^{14}</td>
<td>1.96 \times 10^5</td>
<td>1.45</td>
<td>1.67 \times 10^{16}</td>
<td>2.43 \times 10^5</td>
<td>2.40</td>
<td>0.0120</td>
<td>0.0181</td>
</tr>
<tr>
<td></td>
<td>Friedman</td>
<td>1.25 \times 10^{16}</td>
<td>2.10 \times 10^5</td>
<td>1.45</td>
<td>7.48 \times 10^{13}</td>
<td>1.98 \times 10^5</td>
<td>2.40</td>
<td>0.0149</td>
<td>0.0093</td>
</tr>
<tr>
<td></td>
<td>McGrattan–Lyon</td>
<td>1.79 \times 10^{13}</td>
<td>1.76 \times 10^5</td>
<td>1.00</td>
<td>7.90 \times 10^6</td>
<td>1.19 \times 10^5</td>
<td>1.00</td>
<td>0.0634</td>
<td>0.0553</td>
</tr>
</tbody>
</table>

DM: direct method; GDM: generalized direct method.
Table 7. Fitness values of cone calorimeter results with Noise 2

<table>
<thead>
<tr>
<th></th>
<th>$f_V$ (HRR)</th>
<th>$f_V$ (MLR)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DM</td>
<td>0.0790</td>
<td>0.0032</td>
</tr>
<tr>
<td>GDM</td>
<td>0.0386</td>
<td>0.0007</td>
</tr>
<tr>
<td>Friedman</td>
<td>0.0629</td>
<td>0.0028</td>
</tr>
<tr>
<td>McGrattan–Lyon</td>
<td>0.3166</td>
<td>0.0146</td>
</tr>
</tbody>
</table>

HRR: heat release rate; MLR: mass loss rate; DM: direct method; GDM: generalized direct method.

Figure 8. Estimation results with different analytical methods for data with Noise 2 at 20 K/min. (a) Overall results, (b) first peak and (c) second peak.
DM: direct method; GDM: generalized direct method.
The second test had two slightly overlapping reactions. Two types of noise were added to the data for testing the performance in a more realistic case with experimental noise.

For the simple sample case, the parameters were estimated at four different heating rates and then averaged using different weight functions. The results were then used at two other heating rates to test the extrapolating ability of the results. Optimization methods turned out to produce better fitting results, but all the methods, including the analytical methods, were able to find parameters that produce a sufficiently accurate fit for most engineering applications. The McGrattan–Lyon method was the simplest and fastest to use without any software. All the analytical methods take just few minutes to obtain results, while the optimization methods take hours or days for running the algorithm.

The noisy sample was tested only using the analytical methods. The parameters were estimated at two heating rates, and the fitness of the solution was tested at two other heating rates. Without noise, all the analytical methods, excluding the first-order McGrattan–Lyon method, reproduced the TGA results very accurately. In case of small high-frequency noise (Noise 1), most method still performed very well but the performance of the GDM was greatly hampered. In case of Noise 2, consisting of lower frequency components, the predictions were significantly less accurate for all the methods except for the GDM. The phase of the noise signal with respect to the selected reference points has somewhat random effect on the performance of the estimation methods. In both test cases, the mass losses of the reactions were assumed to be known exactly. The uncertainties of the methods may be higher if the mass losses are also estimated from the experimental data.

The differences in the TGA predictions did not cause significant errors in the cone calorimeter scale. Furthermore, the thermal parameters are known to be able to compensate small differences in the kinetic models, and therefore, the errors can be reduced if some of the thermal parameters are estimated using the cone calorimeter data itself.

This work demonstrates that the analytical methods can be used efficiently as substitutes to the computationally expensive optimization methods when estimating the parameters of pyrolysis kinetics. There are several methods to choose from, and the choice depends on the

![Figure 9](image-url). The performance of the estimation results in cone calorimeter model at 50 kW/m². (a) HRR and (b) MLR.

HRR: heat release rate; MLR: mass loss rate; DM: direct method; GDM: generalized direct method.
required accuracy, complexity and the experimental data. Methods with fewer reference values work better in case of noisy data and overlapping reactions, while more complicated methods yield more accurate results for clean, simple data. Removing the high-frequency noise from the mass data by filtering is recommended in order to improve the performance of methods relying on higher-order derivatives of the mass data, such as the GDM.

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**Conflict of interest**

Any opinions, findings and conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of the National Science Foundation (NSF).

**References**


**Nomenclature**

\( A \) is pre-exponential factor (s\(^{-1}\))
\( c_p \) is specific heat capacity (kJ/K/kg)
\( E \) is activation energy (kJ/k mol)
\( fV \) is fitness values
\( H_r \) is heat of reaction (kJ/kg)
\( H_c \) is heat of combustion (MJ/kg)
\( k \) is thermal conductivity (W/K/m)
\( m \) is mass (kg)
\( n \) is number of reactions
\( N \) is reaction order
\( r \) is reaction rate (1/s)
R is Gas constant (8.3145 J/(mol·K))
t is time (s)

T is temperature (K, °C)
w is weighting parameter

**Greek**

α is conversion (g/g)
β is heating rate (K/s)
ε is emissivity
μ is mean value of heating rates (K/s)
v is Fuel yield

**Subscripts**

0 is initial, virgin
cf is curve fit
deg is degradation range (temperature)
exp is experimental
f is Friedman’s method
i is heating rate index
j is index of a conversion curve
k is reaction index
model is model value
p is peak value
pp is peak of the second derivative
t is time derivative
T is temperature derivative

**Author biographies**

**Anna Matala** is a Research Scientist at VTT Technical Research Centre of Finland and PhD candidate at Aalto University School of Science. She received her MSc degree in Systems and Operations Research from Helsinki University of Technology in 2008. Her research concentrates on pyrolysis modelling and parameter estimation in fire simulations.

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**Simo Hostikka** is a Principal Research Scientist at VTT Technical Research Centre of Finland. He received an MSc degree in 1997 and a PhD in 2008 from the Department of Engineering Physics and Mathematics of the Helsinki University of Technology. He is one of the main developers of the Fire Dynamics Simulator (FDS) and his expertise covers all the fields of fire modelling.