# TGA Maximum Heat Release Rate and Mass Loss Rate and Comparison with the Cone Calorimeter 

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#### Abstract

Thermogravimetric analysis (TGA) is a fundamental tool to study the degradation and pyrolysis behaviours of milligram-sized samples in inert or oxidising atmospheres. One of the most important outputs of TGA measurements is the maximum heat release rate (MHRR) or the maximum mass loss rate (MMLR). Analytical solutions of the MHHR/MMLR have been developed for infinitely fast heat transfer between the gas and solid. It has also been proposed that the MHRR in a TGA apparatus is proportional to the heat of combustion divided by the heat of gasification of the material. This conclusion was reached by the observed nearly linear relation of the MHRR in the TGA with the heat release rate per unit area in the cone calorimeter for thermally thick samples. In this work, we investigate the MMLR in the TGA for both finite and infinite rates heat transfer by analytical solutions and numerical calculations. A universal expression between the MMLR and equipment and material parameters is deduced. The derived expression is subsequently validated against experimental data of two polymers (PA6 and PBT). Finally, we discuss how the pyrolysis rate or heat release rate for a thermally thick solid, as measured for example in a cone calorimeter, is related with the MMLR in the TGA apparatus.


KEYWORDS: TGA, heat release rate, mass loss rate, cone calorimeter.

## NOMENCLATURE

| $A$ | pre-exponential factor $(1 / \mathrm{s})$ | $x$ | dimension into solid $(\mathrm{m})$ |
| :--- | :--- | :--- | :--- |
| $C_{l}$ | characteristic parameter, $=h_{c} /(\rho \delta L)$ | $X$ | fractional mass loss |
| $c_{p}$ | specific heat $(\mathrm{J} / \mathrm{kg}-\mathrm{K})$ | Greek |  |
| $E$ | activation energy $(\mathrm{J} / \mathrm{mol})$ | $\beta$ | heating rate $(\mathrm{K} / \mathrm{min})$ |
| $h_{c}$ | heat transfer coefficient $\left(\mathrm{W} / \mathrm{m}^{2} \cdot \mathrm{~K}\right)$ | $\delta$ | characteristic size of the sample $(\mathrm{m})$ |
| $\Delta H_{g}$ | total heat of pyrolysis $(\mathrm{kJ} / \mathrm{kg})$ | $\gamma$ | exponent in the MMLR in Eq. 1 |
| $\Delta H_{c}$ | heat of combustion $(\mathrm{kJ} / \mathrm{kg})$ | $\Theta$ | dimensionless MLR in Eq. 18b |
| $k$ | thermal conductivity $(\mathrm{W} / \mathrm{m} \cdot \mathrm{K})$ | $\lambda$ | reaction order |
| $L$ | latent heat of pyrolysis $(\mathrm{kJ} / \mathrm{kg})$ | $\Pi$ | dimensionless variable in Eq. 18b |
| $M$ | mass $(\mathrm{g})$ | $\rho$ | density $\left(\mathrm{kg} / \mathrm{m}^{3}\right)$ |
| $\dot{q}_{n e t}^{\prime \prime 2}$ | net heat flux $\left(\mathrm{kW} / \mathrm{m}^{2}\right)$ | subscripts |  |
| $S$ | surface area $\left(\mathrm{m}^{2}\right)$ | $g$ | gas |
| $t$ | time $(\mathrm{s})$ | $\max$ | temperature at which MHHR occurs in TGA |
| $T$ | temperature $(\mathrm{K})$ | $o$ | Initial condition |
| $V$ | volume $\left(\mathrm{m}^{3}\right)$ | $s$ | surface |

## INTRODUCTION

Thermogravimetric analysis (TGA) involves heating a milligram-sized sample in inert or oxidising atmospheres and measuring the weight and also, the temperature of the sample if the experiment is combined with differential scanning calorimetry (DSC). The weight and temperature changes over specific temperature ranges provide indications of the chemical degradation of the sample and thermal stability of the material. One of the most important outputs of TGA measurements is the maximum heat release rate (MHRR). The MHRR in a TGA apparatus can be found in three ways: a) indirectly, by multiplying the maximum mass loss rate (MMLR) in the TGA experiments in nitrogen by the heat of combustion of evolved gases obtained by simultaneous mass spectroscopy analysis [1], b) directly, by oxygen depletion
after the evolved gases from TGA are completely burned online in a micro furnace [2] and c) by bomb calorimetry. In Refs. [3,4], an analytical solution of the MHRR was proposed, which was then used to correlate with the steady HRR of a thick sample in the cone colorimeter. The analytical solution of the MHRR for non-charring materials takes the following form (for high heat transfer rates and high activation energy);

$$
\begin{equation*}
\dot{q}_{c, \max }=\frac{\Delta H_{c} \beta E}{e^{\gamma} R T_{\max }^{2}} \tag{1a}
\end{equation*}
$$

or in terms of the MMLR:

$$
\begin{equation*}
\frac{d X}{d t}_{\max }=\frac{\beta E}{e^{\gamma} R T_{\max }^{2}} \tag{1b}
\end{equation*}
$$

where $T_{\max }$ is the temperature at which the MHRR occurs, $R$ the universal constant, and $\gamma$, the exponent of the natural number $e$ in the denominator, having the following form [3]:
$\gamma=\left[1+\frac{2 R T_{\text {max }}}{E}\right]^{-1}$

For large values of activation energy, i.e. $E /\left(R T_{\max }\right) \gg 1, \gamma$ is approximately one.
It has been shown in Ref. [3] that Eqs. 1a-c correlate well with TGA measurements of PMMA, polyethylene (PE) and phenolic triazine (PT) at heating rates from 1 to $200 \mathrm{~K} / \mathrm{min}$. However, an important assumption in deriving Eqs. 1a-c is that the temperature of the solid sample is the same as the gas temperature in the TGA, which would only be the case for infinitely fast heat transfer. This assumption renders that Eq. 1 is invalid for the cases with finite rates heat transfer, which sometimes have to be applied in order to produce a measurable difference between the gas and material temperatures. For example, in a DSC apparatus this temperature difference is used to calculate the heat of melting or the heat of pyrolysis.

The first objective of this study is thus to extend the MMLR in TGA for finite rates heat transfer by taking into account the effects of the equipment and material characteristics (i.e., the heat transfer coefficient and density, thickness and heat of pyrolysis of the material). Analytical and numerical results show that the relation in Eq. 1b is valid only when a characteristic parameter, $C_{l}=h_{c} /(\rho \delta L)$ (where $h_{c}$ is the effective total heat transfer coefficient, $\rho$ sample density, $L$ latent heat of pyrolysis, and $\delta$ the characteristic size of the sample) is sufficiently large. For smaller values of $C_{l}$, i.e., the cases of finite rates heat transfer, the MMLR is found to be a function of $C_{l}$. A universal expression of the MMLR is deduced numerically. Finally, the derived expression is validated against TGA measurements of PA6 and PBT at different heating rates. The last section before the conclusions addresses how the pyrolysis rate or heat release rate for a thermally thick solid, as measured for example in a cone calorimeter, is related with the MMLR in the TGA apparatus.

## METHODOLOGY

## Mass and Energy Balance in the TGA Apparatus in an Inert Atmosphere

The heating of the solid in an inert atmosphere occurs in three regimes as sketched in Fig. 1 plotting the fractional mass loss or the conversion fraction $(X)$ versus the solid temperature. In the first regime I, only heating occurs, followed by pyrolysis in regime II at a nearly constant temperature and by further heating in regime III if there is char remaining. This behaviour is specifically applicable when the activation energy is high ( $E / R T \gg 1$ ).


Fig. 1. Three regimes for the heating of the solid in an inert atmosphere, showing the fractional mass loss or the conversion factor $(X)$ as a function of the solid temperature.

As usual in TGA experiments, we consider samples small enough that they behave as thermally thin. In addition, we consider experiments in an inert atmosphere where the gas temperature increases at a steady rate with time. This condition is satisfied if the diffusion time into the solid ( $\delta^{2} / \alpha$, where $\delta$ is a characteristic size and $\alpha$ the thermal diffusivity) is both less than a time characteristic of the gas temperature rise in the TGA (e.g. $\left[d T_{g} / d t / T_{g}\right]^{-1}$ and a characteristic reaction time for the decomposition of the solid.

The energy balance and mass balance equations including pyrolysis of the material from solid to gas are:
$c_{p} M \frac{d T}{d t}=h_{c}\left(T_{g}-T\right) S+\frac{d M}{d t} L$
where the solid mass $M$ decays following a first order global Arrhenius degradation reaction:
$\frac{d M}{d t}=-M A e^{-\frac{E}{R T}}$

In Eqs. 2 and 3, $h_{c}$ is the total effective heat transfer coefficient including both convection and radiation, and $S$ the surface area of the solid.

For simplicity but without loss of generality, we assume that the volume of the solid remains constant so the density decreases as $\rho=M / V$ and the following transformations are possible:
$M=M_{o}(1-X), \rho=\rho_{o}(1-X)$

Substituting Eq. 4 in Eqs. 2 and 3, we obtain:

$$
\begin{align*}
& c \rho_{o}(1-X) \frac{d T}{d t}=h_{c}\left(T_{g}-T\right) S / V-\rho_{o}(1-X) A e^{-\frac{E}{R T}} L  \tag{5}\\
& \frac{d X}{d t}=(1-X) A e^{-\frac{E}{R T}} \tag{6}
\end{align*}
$$

Note that the ratio of surface to volume is the inverse of the characteristic size of the material, namely:

$$
\begin{equation*}
\frac{S}{V}=\frac{1}{\delta} \tag{7}
\end{equation*}
$$

The gas temperature in Eq. 5 increases at a steady rate with time:

$$
\begin{equation*}
\frac{d T_{g}}{d t}=\beta \tag{8}
\end{equation*}
$$

## Determination of the Temperature at which the MMLR Occurs

By taking the time derivative of the RHS of Eq. 6 and noting that the MMLR occurs when the time derivative of the LHS of Eq. 6 is zero, we obtain:
$A e^{-\frac{E}{R T_{\max }}}=\frac{d T_{\max }}{d t} \frac{E}{R T_{\max }{ }^{2}}$
where $T_{\max }$ denotes the solid temperature at which the MMLR occurs.
We also note that in the second regime in Fig. 1 where decomposition occurs the temperature is nearly constant so that the term on the LHS of Eq. 5, can be ignored, one obtains
$h_{c}\left(T_{g}-T\right) / \delta-\rho_{o}(1-X) A_{r} e^{-\frac{E}{R T}} L=0$


Fig. 2. Three terms in Eq. 5 calculated by the numerical model, verifying that the term on the LHS in Eq. 5 is less than the two terms on the RHS by more than an order of magnitude.
To support this proposition, we plot in Fig. 2 the three terms in Eq. 5 as a function of temperature obtained by numerically integrating Eqs. 5 and 6 for PMMA. Numerical integrations were performed using the subroutine HPCG, where evaluation was done by Hammings modified predictor-corrector method [5], and a fourth order Runge-Kutta method [6] was used for adjustment of the initial increment and for computation of starting values. Figure 2 clearly shows that at the main degradation temperature range the transient term on the LHS of Eq. 5 is less than the two terms on the RHS by more than an order of magnitude. The model parameters used are: $\beta=10 \mathrm{~K} / \mathrm{min}, c_{p}=1500 \mathrm{~J} / \mathrm{kg} \cdot \mathrm{K}, L=0.8 \times 10^{6} \mathrm{~J} / \mathrm{kg}$ [7], $\rho_{o}=1190 \mathrm{~kg} / \mathrm{m}^{3}, \delta=0.2 \mathrm{~mm}, h_{c}=5000 \mathrm{~W} / \mathrm{m}^{2} \cdot \mathrm{~K}, A=3.2 \times 10^{9} \mathrm{~s}^{-1}, E=1.42 \times 10^{5} \mathrm{~J} / \mathrm{mol}$ [8].
Rearranging Eq. 10, we obtain

$$
\begin{equation*}
\frac{h_{c}\left(T_{g}-T\right)}{\rho_{o} \delta L}=C_{1}\left(T_{g}-T\right)=\frac{d X}{d t} \tag{11a}
\end{equation*}
$$

where $C_{1}=\frac{h_{c}}{\rho_{o} \delta L}$

Taking the time derivative of Eq. 11a and noting that the MMLR occurs when the time derivative of the RHS is zero, so
$C_{1} \frac{d\left(T_{g}-T_{\max }\right)}{d t}=0$ or $\frac{d T_{\max }}{d t}=\frac{d T_{g}}{d t}=\beta$

Equation 12 indicates that at the MMLR the derivative of the solid temperature, $d T_{\max } / d t$, is equal to the heating rate, $\beta$. This relation is verified by the numerical result in Fig. 3 showing the derivate of the solid temperature ( $d T / d t$ ) for different heat transfer coefficients. For a very high heat transfer coefficient $h_{c}=5000 \mathrm{~W} / \mathrm{m}^{2} \cdot \mathrm{~K}$, the history of $d T / d t$ is almost the same as $\beta$ since heat transfer is very fast. For lower heat transfer coefficients, $d T / d t$ is initially less than $\beta$ but becomes equal to $\beta$ at around 636.3 K regardless of the heat transfer coefficient.


Fig. 3. Predicted derivative of the solid temperature $(d T / d t)$ as a function of the solid temperature for different heat transfer coefficients.

This temperature, corresponding to the temperature at which the MMLR ( $T_{\max }$ ) occurs, can also be derived analytically by substituting Eq. 12 into Eq. 9:

$$
\begin{equation*}
A e^{-\frac{E}{R T_{m, \max }}}=\beta \frac{E}{R T_{m, \max }^{2}} \tag{13}
\end{equation*}
$$

Equation 13 indicates that $T_{\max }$ is independent of equipment and material parameters, such as $h_{c}, L, \delta, \rho$, but only depends on the heating rate and the kinetic parameters (activation energy and pre-exponential factor).

This result is further supported by the numerical results in Figs. 4 a and 4 b , where the MLR is plotted against time and the solid temperature respectively for different heat transfer coefficients. Although the times to reach the MMLR are different for different heat transfer coefficients as shown in Fig. 4a, the temperatures at which the MMLR occurs are the same as noted in Fig. 4b. The value of the MMLR with a heat transfer coefficient of $5000 \mathrm{~W} / \mathrm{m}^{2} \cdot \mathrm{~K}$ is $0.00276 \mathrm{~s}^{-1}$, which is close to the one given by Eq. 1 b , i.e.,
$0.00277 \mathrm{~s}^{-1}$. However, at lower heat transfer coefficients, the MMLR is significantly lower. The fact that the MMLR decreases as the heat transfer coefficient decreases can be explained by examining Eq. 6. Because $T_{\max }$ is the same for different values of $h_{c}$, the MMLR is proportional to (1- $X_{\max }$ ), where $X_{\max }$ is the fractional mass loss at the MMLR, which would be higher for lower heat transfer coefficients as shown in Fig. 5.


Fig. 4. Predicted MLR as a function of: (a) time; (b) the solid temperature for different heat transfer coefficients.

## Determination of the MMLR as a Function of $C_{1}=h_{c} /\left(\rho_{o} L \delta\right)$

Equation 11a shows that the MMLR is a function of $C_{l}$. In order to determine the dependence of the MMLR on $C_{l}$, we randomly generated one hundreds sets of values for $\rho_{o}, h_{c}$, and $L$, and $\delta$ using Eq. 14 .
$L=L_{\text {min }}+r_{1}\left(L_{\text {max }}-L_{\text {min }}\right)$
$h_{c}=h_{c, \text { min }}+r_{2}\left(h_{c, \text { max }}-h_{c, \text { min }}\right)$
$\rho_{o}=\rho_{o, \text { min }}+r_{3}\left(\rho_{o, \text { max }}-\rho_{o, \text { min }}\right)$
$\delta=\delta_{\text {min }}+r_{4}\left(\delta_{\text {max }}-\delta_{\text {min }}\right)$


Fig. 5. Predicted fractional mass loss as a function of the solid temperature for different heat transfer coefficients.
where $r_{1}, r_{2}, r_{3}$ and $r_{4}$ are random numbers uniformly distributed in the range of $[0,1]$, and the minimum and maximum values of each individual parameter are given in Table 1. The other parameters remain the same as those used to generate the results of PMMA in Figs. 2-5, i.e. $\beta=10 \mathrm{~K} / \mathrm{min}, c_{p}=1500 \mathrm{~J} / \mathrm{kg}-\mathrm{K}$, $A=3.2 \times 10^{9} \mathrm{~s}^{-1}, E=1.42 \times 10^{5} \mathrm{~J} / \mathrm{mol}$.

Table 1. Minimum and maximum values of $\rho_{o}, h_{c}$, and $L$, and $\delta$.

| $L_{\text {min }}$ <br> $(\mathrm{J} / \mathrm{kg})$ | $L_{\max }$ <br> $(\mathrm{J} / \mathrm{kg})$ | $h_{c, \min }$ <br> $\left(\mathrm{~W} / \mathrm{m}^{2} \cdot \mathrm{~K}\right)$ | $h_{c, \max }$ <br> $\left(\mathrm{~W} / \mathrm{m}^{2} \cdot \mathrm{~K}\right)$ | $\rho_{o, \min }$ <br> $\left(\mathrm{~kg} / \mathrm{m}^{3}\right)$ | $\rho_{o, \max }$ <br> $\left.\mathrm{~kg} / \mathrm{m}^{3}\right)$ | $\delta_{\text {min }}$ <br> $(\mathrm{mm})$ | $\delta_{\max }$ <br> $(\mathrm{mm})$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $0.5 \times 10^{6}$ | $3 \times 10^{6}$ | 5 | 5000 | 500 | 3000 | 0.05 | 0.4 |

Figure 6 shows the calculated MMLR against $C_{l}$, as well as the analytical solution calculated using Eq. 1 b . Clearly, Eq. 1b is only valid when $C_{l}$ is sufficiently large (above $0.01 \mathrm{~K}^{-1} \cdot \mathrm{~s}^{-1}$ for the present parameters). As expected, this threshold value would vary with the equipment and material parameters. The next objective is thus to derive a universal expression of the MMLR.


Fig. 6. Predicted MMLR versus $C_{1}$; the constant value for $0.00227 \mathrm{~s}^{-1}$ is calculated by Eq. 1 b . In total, 100 sets of data of $\rho_{o}, h_{c}$, and $L$, and $\delta$ were randomly generated using Eq. 14.

Analytical asymptotic solutions for the MMLR have been derived by taking the time derivative of the terms in the energy balance Eq. 10 and using Eq. 6. Namely, the time derivative of the sample temperature using Eq. 6 is:

$$
\begin{equation*}
\frac{d T}{d t}=\frac{C_{1} \beta+(1-X)\left(A e^{-E / R T}\right)^{2}}{C_{1}+A(1-X) e^{-E / R T}\left(E / R T^{2}\right)} \tag{15}
\end{equation*}
$$

From Eq. 6 and using Eq. 15 we can find the variation of the conversion factor with the sample temperature:

$$
\begin{equation*}
\frac{d X}{d T}=\frac{d X / d t}{d T / d t}=A(1-X) e^{-E / R T} \frac{C_{1}+A(1-X) e^{-E / R T}\left(E / R T^{2}\right)}{\beta C_{1}+(1-X)\left(A e^{-E / R T}\right)^{2}} \tag{16}
\end{equation*}
$$

Next, we can integrate Eq. 16 from the initial sample temperature to the maximum sample temperature, which is given by Eq. 13. Some consistent asymptotic analysis shows that at the MMLR conditions the following functional relation is valid:

$$
\begin{equation*}
1-X_{\max }=\operatorname{fcn}\left(\frac{A e^{-E / R T_{\max }}}{\sqrt{\beta C_{1}}}\right) \tag{17}
\end{equation*}
$$

The temperature at the MMLR is given by Eq. 13. We can not obtain analytically the functional relation in Eq. 17. However, for small values of $\left(A e^{-E / R T_{\max }}\right) / \sqrt{\beta C_{1}}$ (e.g. large values of the heat transfer coefficient) and large values of activation energy (i.e. $E / R T_{\max } \gg 1$ ), we obtain :
$1-X_{\text {max }}=1 / e$ when $\frac{A e^{-E / R T_{\text {max }}}}{\sqrt{\beta C_{1}}} \ll 1$

Note that this result agrees with the previous solutions [3,4] as shown in Eqs. 1a-c. This result is also supported by the numerical results in Fig. 7, where we plot a modified MMLR
$\Theta=\frac{(d X / d t)_{\max }}{\sqrt{\beta C_{1}}}=\left(1-X_{\max }\right) \frac{A e^{-E / R T_{\max }}}{\sqrt{\beta C_{1}}}=\left(1-X_{\max }\right) \Pi$ as a function of $\Pi$
where $\Pi=\left(A e^{-E / R T_{\text {max }}}\right) / \sqrt{\beta C_{1}}$


Fig. 7. Dimensionless maximum mass loss rate, $\Theta=\left(1-X_{\max }\right)\left(A e^{-E / R T_{\max }}\right) / \sqrt{\beta C_{1}}$, as a function of $\Pi=\left(A e^{-E / R T_{\max }}\right) / \sqrt{\beta C_{1}}$ for a heating rate of $10 \mathrm{~K} / \mathrm{min}$. In total, 100 sets of data of $\rho_{o}, h_{c}$, and $L$, and $\delta$ were randomly generated using Eq. 14.

As mentioned earlier, we could not obtain analytically the functional relation in Eq. 17 for larger values of $\Pi$. However; this can be achieved by besting fitting the numerical results. In order to generate all possible values of $\Pi$, we performed calculations with a wider range of heating rates (from 1 to $500 \mathrm{~K} / \mathrm{min}$ ), for each of which 10 sets of data were generated for $\rho_{o}, h_{c}$, and $L$, and $\delta$ using Eq. 14. The numerical results are shown in Fig. 8, where all data collapse into one single curve, indicating the validity of Eq. 17 for all heating rates.


Fig. 8. Calculated $\Theta$ as a function of $\Pi$ at different heating rates. For each heating rate, 10 sets of data of $\rho_{o}, h_{c}$, and $L$, and $\delta$ were randomly generated.
Having in mind that $\Theta$ equals to $\Pi /$ e for small values of $\Pi$, we used a polynomial expression to best fit the data in Fig. 8. After trial-and-error, we obtain the following expression:
$\Theta=\frac{\Pi / \mathrm{e}+0.12 \Pi^{2}}{1+0.36 \Pi^{1.542}}$
which givens an excellent agreement with the calculated data as shown in Fig. 8. Note that Eq. 19 takes into account both the equipment and material parameters, and as a result it is valid for all cases. Consequently, it can be used to determine equipment or material parameters based on the TGA measurements, such as the heat transfer coefficient and the heat of pyrolysis.

## Effects of reaction order

For simplicity, we have assumed that the degradation of material follows a first-order Arrhenius expression, which would not be the case for most practical materials. For generality we assume that the reaction rate of a given material can be approximated as: $\frac{d X}{d t}=(1-X)^{\lambda} A e^{-\frac{E}{R T}}$, where $\lambda$ is the reaction order, which can be considered as a material constant and obtained numerically by fitting the mass loss curves at different heating rates in the TGA apparatus. In order to verify that Eq. 19 is valid for any reaction order, we repeated the calculation as for Fig. 2, however, the reaction order of PMMA was artificially varied between 0.5 and 2. The results in Fig. 9 shows that with an increase in the reaction order, there is an increase in the sold temperature at which the MMLR occurs ( $T_{\max }$ ) and thus the reaction rate. The normalised MMLR, $\Theta$, can, however, be expressed as the same function of $\Pi$ using Eq. 19.


Fig. 9. Effect of reaction order on the dependence of the dimensionless MMLR, $\Theta$, on $\Pi$

## Application to PA6 and PBT

In order to further validate Eq. 19, we performed numerical calculations for two polymers, PA6 and PBT, for which we have conducted measurements in TGA at different heating rates ( $1,2,5,10$, and $20 \mathrm{~K} / \mathrm{min}$ ). The thermal properties were deduced by ignition tests at different heat fluxes in the cone colorimeter whereas the kinetic parameters are obtained using the thermokinetic software by Netzsch, which are summarized in Table 2. $h_{c}=5000 \mathrm{~W} / \mathrm{m}^{2} \cdot \mathrm{~K}$ and $\delta=0.2 \mathrm{~mm}$ were used for all calculations. The results are shown in Fig. 10.

Table 2. Thermal and kinetic parameters of PA6 and PBT.

|  | $\rho$ <br> $\left(\mathrm{kg} / \mathrm{m}^{3}\right)$ | $c_{p}$ <br> $(\mathrm{~J} / \mathrm{kg} \cdot \mathrm{K})$ | $L$ <br> $(\mathrm{~J} / \mathrm{kg})$ | $E$ <br> $(\mathrm{~J} / \mathrm{mol})$ | $A$ <br> $\left(\mathrm{~s}^{-1}\right)$ | $\lambda$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| PA6 | 1130 | 2300 | 1.4 | $2.11 \times 10^{5}$ | $2.51 \times 10^{13}$ | 1.1 |
| PBT | 1310 | 865 | 1.6 | $1.78 \times 10^{5}$ | $2.95 \times 10^{11}$ | 1.59 |



Fig. 10. Calculated $\Theta$ as a function of $\Pi$ for PA6 and PBT at different heating rates.
Because a higher value of $h_{c}$ was used, the data is mostly within the region of small values of $\Pi$, where we have verified that $\Theta$ is proportional to $\Pi$. More importantly, although there are large differences in the thermo and kinetic parameters for PA6 and PBT, the calculated normalized MMLR $\Theta$ still follows the same function given by Eq. 19. This figure, along with results in Figs. 7-9, demonstrates that the validity of Eq. 19 for materials with different thermal properties and/or kinetic parameters.

## EXTENSION TO THERMALLY THICK SOLID EXPOSED TO CONSTANT HEAT FLUX

When a thermally thick solid is exposed to a constant heat flux, the conduction equation governing the heat transfer inside the solid is:

$$
\begin{equation*}
\rho c_{p} \frac{\partial T}{\partial t}=k \frac{\partial^{2} T}{\partial x^{2}}-\dot{m}^{\prime \prime \prime}(t) \cdot L \tag{20}
\end{equation*}
$$

where, $\dot{m}^{\prime \prime \prime}$ is the volumetric mass loss rate, which can be calculated as assuming first-order reaction:

$$
\begin{equation*}
\dot{m}^{\prime \prime \prime}=A \rho e^{-E / R T} \tag{21}
\end{equation*}
$$

The boundary conditions on the front and back surfaces are given by Eqs. 22a and 22b respectively:

$$
\begin{align*}
& \left.k \frac{\partial T}{\partial x}\right|_{x=0}=\alpha \dot{q}_{e x t}^{\prime \prime}-\varepsilon \sigma\left(T_{s}^{4}-T_{\infty}^{4}\right)-h_{c}\left(T_{s}-T_{\infty}\right)  \tag{22a}\\
& \left.k \frac{\partial T}{\partial x}\right|_{x=l}=0 \tag{22b}
\end{align*}
$$

where $x=0$ represents the top surface which recedes during pyrolysis.
The mass loss rate is related to the Arrhenius expression at steady state by:
$\rho A \int_{0}^{\infty} e^{-E / R T} d x=\frac{\dot{q}_{n e t}^{\prime \prime}}{\Delta H_{g}}$
where $\Delta H_{g}$ is the total heat of pyrolysis, consisting of both the latent heat of pyrolysis, L , and the sensible heat, $c_{p}\left(T_{s}-T_{0}\right)$, where $T_{s}$ is the surface temperature.

From Eq. 23, an asymptotic expression can be derived for large values of $E / R T$ if we know the temperature gradient at $x=0$. In the thin reaction region close to the expose surface, the reaction layer conduction is balanced by the reaction term at steady state (note that outside the reaction zone conduction is balanced by convection for a stationary front):
$k \frac{d^{2} T}{d x^{2}}=\rho A L e^{-E / R T}$

By multiplying Eq. 23 by $d T / d x$ and integrating, the gradient $d T / d x$ varies significantly inside the reaction layer except if the latent heat of pyrolysis is zero. Asymptotic analysis shows that the following relation is valid:

$$
\begin{equation*}
A e^{-\frac{E}{R T_{s}}}=\left[\frac{E}{R T_{s}^{2}}\right]\left[\frac{\dot{q}_{n e t}^{\prime \prime 2}}{\rho k \Delta H_{g}}\right] \operatorname{fcn}\left(\frac{L}{\Delta H_{g}}\right) \tag{25}
\end{equation*}
$$

This equation for the surface (pyrolysis) temperature in the cone calorimeter is similar to the relation for the temperature in the TGA (see Eq. 9) but with an effective heating rate, $\dot{q}_{n e t}^{\prime \prime}{ }^{2} / \rho k \Delta H_{g}$, which depends on several material parameters including the conductivity of the material. The function on the RHS of Eq. 9 is one for $L \rightarrow 0$. This is verified numerically in Fig. 10, where the LHS term, $A e^{-\frac{E}{R T_{s}}}$, at steady state is plotted against $\left[\frac{E}{R T_{s}^{2}}\right]\left[\frac{\dot{q}_{n e t}^{\prime \prime}}{\rho k \Delta H_{g}}\right]$ for different heat fluxes for PMMA $(10 \mathrm{~cm})$, where the latent heat of pyrolysis was set to zero. The other properties and parameters used in the calculations are the same as those used in the TGA. For the range of heat fluxes considered, there is an excellent agreement between the two sets of data.

It has also been proposed in Ref. [3] that the HRRs of various materials in the cone calorimeter are proportional to a heat release capacity, $\Delta H_{c} E / e R T_{\max }{ }^{2}$. This conclusion was reached by the observed empirical relation of the MHRR in the TGA with the heat release rate per unit area in the cone calorimeter for thermally thick samples. To verify this finding, we conducted calculations with different values of activation energy (ranging from 142 to $192 \mathrm{~kJ} / \mathrm{mol}$ ) and the calculated steady HRR is plotted in Fig. 12 versus the heat release capacity determined from the TGA at a heating rate of $10 \mathrm{~K} / \mathrm{min}$. In Fig. 12, temperature, $T_{s}$, in the ordinate is the surface temperature of a thermally thick sample in the cone calorimeter, whereas the temperature, $T_{\max }$, in the abscissa is the temperature at which the maximum MLR occurs in TGA.It appears that there exists a linear relation between the HRR in the cone calorimeter and the heat release capacity in the TGA as suggested by Ref. [3]. However it should be emphasized that the relation is not universal but depends on the material properties such as the conductivity and latent heat of pyrolysis as shown in Fig. 12, where the conductivity and latent heat of pyrolysis were set to half/ twice of their original values. The change in the latent heat of pyrolysis has a fundamental effect on the HRR whereas the effect by changing the conductivity is marginal.


Fig. 11. Calculated $A e^{-\frac{E}{R T_{s}}}$ as a function of $\left[\frac{E}{R T_{s}{ }^{2}}\right]\left[\frac{\dot{q}_{n e t}{ }^{2}}{\rho k \Delta H_{g}}\right]$ for different external heat fluxes at steady state of a PMMA ( 10 cm ) in the cone calorimeter by setting the latent heat of pyrolysis equal to zero.


Fig. 12. Predicted steady HRR with different values of activation energy in the cone calorimeter against the heat release capacity in the TGA at a heating rate of $10 \mathrm{~K} / \mathrm{min}$.

We show and propose here that the change in the HRR in the cone calorimeter with the heat release capacity in the TGA is primarily related to the change of surface temperature. As the surface temperate is nearly proportional to $E / R$ (based on Eq. 9 or Eq. 25 ), an increase of activation energy, $E$, will result in an increase of surface temperature but a decrease of the heat release capacity in the TGA ( $\left.\Delta H_{c} E / e R T^{2}\right)$ (assuming the heat of combustion does not change). The increased surface temperature has two effects on the mass loss rate in the cone calorimeter: a) decreased net heat flux owing to an increase of surface reradiation losses and $b$ ) increased sensible heat. Both factors contribute to the decrease of the MLR, where estimates and numerical results show that the former is the primary cause.

## CONCLUSIONS

Numerical calculations and analytical solutions have been performed to derive the maximum mass loss rate (MMLR) in the TGA apparatus (the heating rate increases at a steady rate with time) for finite rates heat transfer. The main conclusions of this work are:

- At the MMLR, the time derivative of the solid temperature is equal to the heating rate. The temperature at which the MMLR occurs is independent of equipment and material parameters but depends only on the heating rate and kinetic parameters.
- Present result verified that the MMLR relation in Ref. [3] is valid only for infinite fast heat transfer, or when a characteristic parameter $C_{1}=h_{c} /(\rho L \delta)$ is large, where $h_{c}$ is the total heat transfer coefficient, $\rho$ the sample density, $L$ the heat of pyrolysis, and $\delta$ the characteristic size of the sample. For small values of $C_{l}$, the MMLR is a function of $C_{l}$ as indicated by Eq. 19 with symbols defined in the nomenclature. Application of the numerical model to the TGA data of two polymers, PA6 and PBT, verified that this function is also independent of the heating rate or the kinetic parameters.
- For thermally thick materials exposed to a constant heat flux in the cone calorimeter, the pyrolysis temperature (Eq. 25) is similar to the one in the TGA (Eq. 9), but additionally it depends on the ratio of the latent heat of pyrolysis and total heat of pyrolysis. When this ratio is small, the steady pyrolysis rate can be calculated using Eq. 25. We have concluded that the proposed empirical relation in Ref. [3] that the HRR in the cone calorimeter is proportional to a so-called heat release capacity ( $\Delta H_{c} E / e R T^{2}$ ) is not fundamentally appropriate. Although our results showed that there is a nearly linear relation between them, this relation is not universal but depends on the material properties such as the conductivity and latent heat of pyrolysis (see Fig. 12). The change in the HRR in the cone calorimeter with the heat release capacity was mainly due to the change of sample surface temperature.
- The present methodology can also be used to check and optimise the operational characteristics of the DSC, e.g. by changing the gas flow rate and hence the heat transfer coefficient.


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