

# Approximations to the Distributed Activation Energy Model for Pyrolysis

C.P. Please,<sup>1</sup> M.J. McGuinness,<sup>2</sup> D.L.S. McElwain.<sup>3</sup>

A full-length article submitted to *Combustion and Flame* in April 2002, then resubmitted after minor revisions in September 2002.

## Abstract

*The Distributed Activation Energy Model (DAEM), used for the pyrolysis of a range of materials (including coal, biomass, residual oils and kerogen), assumes that the thermal decomposition of numerous components is described by a distribution of activation energies. Existing theories are reviewed with particular focus on methods used to evaluate solutions quickly and efficiently. This paper demonstrates that previous approaches taken to simplify the solution methods can usually be identified as belonging to one of two distinct and physically relevant regimes. A careful analysis in these two regimes is given based upon asymptotic expansions, leading to systematic methods for rapidly finding accurate approximations. The new theory results in simple expressions for the devolatilisation rate of a given distribution of reactants. The method thereby provides a rapid and highly effective method for estimating kinetic parameters and the distribution of activation energies. Comparison of the simplified results with existing theories and with calculations of the full model are given. The methods provide a useful basis for calculations of coupled models of volatilisation and combustion, and for models with spatially varying temperatures.*

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<sup>1</sup>Department of Mathematics, University of Southampton, England SO17 1BJ

<sup>2</sup>Victoria University of Wellington, PO Box 600, Wellington, New Zealand

<sup>3</sup>School of Mathematical Sciences, QUT, GPO Box 2434, Brisbane Q 4001, Australia

## Nomenclature

DExp	the double exponential term	$E$	activation energy (J/mol)
$e$	energy rescaled to order one	$f$	distribution of volatiles
$H$	Heaviside or step function	$h$	exponent
$k$	rate coefficient ( $s^{-1}$ )	$k_0$	frequency factor ( $s^{-1}$ )
$m$	rate of temperature change ( $K/s$ )	$R$	ideal gas constant
$T$	temperature ( $K$ )	$t$	time ( $s$ )
$V$	mass fraction volatilised	$V^*$	initial value of $V$
$v$	mass fraction not yet volatilised	$Y$	LambertW function
$y$	nondimensionalised energy		

### Subscripts:

$i$	volatile constituent label	$s$	a central value
$w$	a value representing width		

### Superscripts:

$e$	extremum
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### Greek Symbols:

$\alpha$	a parameter	$\tau$	nondimensionalised time
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## 1 Introduction

The distributed activation energy model (DAEM) has proven very successful in describing the pyrolysis of various coals under differing temperature histories. While our focus here is primarily on parameter values relevant to coal, the DAEM also applies to the pyrolysis of other materials, including biomass, residual oils, resin chars [1], and kerogen [2]. Calculations of solutions to this model may require many evaluations of double integrals, involving rapidly varying functions and this creates significant numerical difficulties. The aim of this paper is to use asymptotic methods to make accurate approximations to the integrals and thereby allow rapid calculation of DAEM solutions. Existing approximations in the literature are reviewed, and are noted to have had varying degrees of success. Next one of the main sources of numerical difficulty, namely the

double exponential term arising in the DAEM, is investigated for various temperature histories. This double exponential term acts over a narrow range of activation energies, which changes as time progresses. The key to our approach is to recognise the importance of the relative width of the double exponential term compared with the width of the initial distribution of volatiles.

## 2 Mathematical Model

A single block of coal and the time evolution of its constituent parts is considered, averaged over the whole block. Such an approach ignores any spatial variation of temperature, and is appropriate for pulverised coal, or as a component of a more complicated travelling wave model. The development here follows Howard [3] and Solomon and Hamblen [4]. The coal's constituents are numbered  $i = 1 \dots n$ , and the released (volatilised) mass fraction for the  $i$ th constituent is  $V_i(t)$ . The initial mass of constituent  $i$  in the coal is  $V_i^*$ . Each reaction is assumed to be first order, so that the rate of pyrolysis is

$$\frac{dV_i}{dt} = k_i (V_i^* - V_i) . \quad (1)$$

The rate coefficient  $k_i$  is taken to be Arrhenius in form,

$$k_i(t) = k_{0i} e^{-E_i/RT(t)} ,$$

where  $k_{0i}$  is the pre-exponential or frequency factor ( $s^{-1}$ ),  $E_i$  is the apparent activation energy for constituent  $i$  (J/mol),  $R$  is the ideal gas constant, and  $T(t)$  is the time-dependent temperature of the coal (K). Equation (1) has the solution

$$\frac{V_i^* - V_i}{V_i^*} = \exp \left( - \int_0^t k_i(u) du \right) .$$

If  $i = 1$ , the model is referred to as the single first-order reaction model (SFOR). In contrast the distributed activation energy model (DAEM) allows for a more complicated set of reactions by considering a continuous distribution of reactants. In the DAEM the dependence on volatile number

$i$  is replaced by a continuous dependence on activation energy  $E$ , so that the total amount of volatile available for release from the coal is taken to be a distribution satisfying

$$dV^* = V^* f(E) dE .$$

The solution then becomes

$$\frac{V^* - V}{V^*} = \int_0^\infty \exp \left( - \int_0^t k_0(E) e^{-E/(RT(u))} du \right) f(E) dE . \quad (2)$$

This model is gaining acceptance for capturing the required diversity of reaction time scales for coal volatilisation, and is an essential element of any devolatilisation model [3, 5].

This model is used for two main purposes. The first is to assume the initial distribution of volatiles  $f(E)$  and the pre-exponential factors  $k_0(E)$  and then find the resulting time-dependence of the volatiles. The second is the inverse problem, where the rate of volatilisation  $dV/dt$  is measured and the distribution of volatiles must be determined. This second problem is one of estimating parameters, and there are significant difficulties in determining accurately both  $f(E)$  and  $k_0(E)$  as they are highly correlated. A common assumption is then to take all the pre-exponential, or frequency factors,  $k_{0i}$  to have the same value  $k_0$ . This simplifies much of the later analysis and is reasonable given much of the uncertainty over the reactant distributions. Formally the inverse problem then becomes one of solving a Volterra integral equation of the first type for the function  $f(E)$ . Such problems are invariably ill-posed and it is necessary to regularise the problem, with conditions such as  $f(E)$  being as smooth as possible or being of a particular form, in order for solutions to be properly defined.

In this paper approximations for the time-dependence of the volatiles are determined first, when the DAEM for volatilisation is given by Eq. (2), with  $k_0(E)$  replaced by the constant  $k_0$ .

Within the integral the integrand consists of the product of the double exponential term

$$\text{DExp} \equiv \exp \left( - \int_0^t k_0 e^{-E/(RT(u))} du \right) ,$$

and a term representing the initial distribution  $f(E)$ . DExp is determined only by the temperature conditions used in the experiment and the initial distribution is determined only by the coal being considered. Another way to write the double integral is in the form

$$v = \int_0^\infty \exp(h(E)) dE ,$$

where  $v = 1 - (V/V^*)$  and is the fraction of the volatile matter not yet released, and

$$h(E) \equiv - \int_0^t k_0 e^{-E/(RT(u))} du + \ln(f(E)) .$$

### 3 Previous Simplifications

One of the main difficulties with the solution as written in Eq. (2) is that evaluating the integral can require significant computing resources, particularly when it needs evaluating many times. Previous approximations to the solution, especially those seeking to convert the DAEM back to an equivalent SFOR model, suffer from difficulties in extrapolating to other heating regimes, and difficulties in extracting the volatile distribution  $f(E)$  from experimental measurements. These approaches to simplifying this problem are discussed further in this section.

Niksa and Lau [5] have explored the relationship between the DAEM and the SFOR model with an approach based on holding the activation energy fixed, and defining an effective or nominal rate constant  $\langle k \rangle$ , which varies with time, as

$$\frac{dV}{dt} = \langle k \rangle (V^* - V) .$$

Calculation of  $\langle k \rangle$  requires fully evaluating the DAEM. They note [5] that there is a large variation in  $\langle k \rangle$  with time or temperature, and also a more modest variation with coal rank.

Niksa and Lau [5] also derive approximate analytical approximations to the DAEM for temperatures undergoing linear or exponential ramping. Their approach is based on exploiting the rapid changes occurring in DExp. They

first note that in the physically relevant regime where  $E/(RT) \gg 1$ , it is possible to make the approximation, e.g. in the case where the temperature ramps as  $T = mt$ , that

$$\int_0^t k_0 e^{-E/(RT(u))} du \sim \frac{k_0 RT^2}{mE} \exp(-E/(RT)) .$$

The resulting rapidly-varying double exponential function is then approximated by a piece-wise linear function that has three regions: one where DExp is zero, one where it is unity and one in between where it rises linearly from zero to one. The width and location of the linear region varies with time. In the case where the initial distribution is Gaussian, use of this simple piece-wise linear approximation results in integrals that can be easily evaluated.

Niksa and Lau indicate that this procedure provides accurate approximations to the full DAEM for all parameters of interest. Their work represents a refinement of the ideas in Suuberg [6], who uses a simple step-function approximation to DExp (see also [3, 7, 8]) which jumps from zero to one at an energy that varies with time. Such a step-function approximation leads to simple integrals and for the case of a Gaussian initial distribution gives an error function approximation to the DAEM. Niksa and Lau note that there remain some problems in using their approximation at lower temperatures, especially with the numerical solution of the equations for the position of the piece-wise linear approximation.

Miura and Maki [9] (and see also [10, 11]) consider the inverse problem and present a method for estimating the distribution  $f(E)$  and the frequency factor  $k_0$  from volatilisation data associated with three sets of experiments with different heating profiles. For a linearly ramping temperature, they replace DExp with a step-function, and find that  $f$  is proportional to the rate of change of released volatile with time. They then use this relation to find  $f$  from the data.

In the following section, a more accurate approximation to DExp is first developed, which is then used in the two cases of narrow and wide distributions.

## 4 Systematic simplifications

The integrand in (2) consists of two parts. The first part (DExp) depends on time through the temperature history experienced by the sample. The second part is independent of time, and depends on the distribution of volatiles in the sample. The behaviour of the temperature dependent part DExp is considered first, and approximations are derived that are useful for physically relevant problems. Both constant and ramping temperature histories are investigated, together with simple distributions of volatiles.

### 4.1 The double exponential integrand

Approximations to the double exponential

$$\text{DExp} = \exp\left(-\int_0^t k_0 e^{-E/(RT(u))} du\right)$$

are considered, where  $T(u)$  is specified and  $E$  can take any positive value. The approach taken is similar to that of Niksa and Lau [5] but uses more systematic methods and a more accurate approximation.

In order to motivate the systematic simplifications of this integrand it is useful to consider the typical values of the parameters and functions on which it depends.

The frequency factors are typically in the range  $k_0 \sim 10^{10}\text{--}10^{13} \text{ s}^{-1}$ , while the activation energies of interest are in the region 100–300 kJ/mole. The temperatures considered depend on the particular experiments but 1000–2000°C are typically used. Note however, that the DAEM model is also of interest for combustion problems where the temperature range can be significantly larger, and it is therefore useful to be able to extrapolate the simplifications made in the temperature range of 1000–2000°C to these higher regimes.

To motivate and demonstrate the simplification method exploited later, the case of constant temperature (when the integral is particularly simple

anyway) is considered first. Taking  $T(u) = T_0$ , DExp becomes

$$\exp\left(-tk_0e^{-\frac{E}{RT_0}}\right).$$

Taking typical values,  $E/(RT_0) \sim 10$  while  $tk_0 \sim 10^{10}$ . The large size of both of these parameters makes the function very rapidly varying with  $E$ . This is further illustrated if the function (4.1) is re-written in the form

$$\exp\left(-\exp\left(\frac{E_s - E}{E_w}\right)\right).$$

where

$$E_s \equiv RT_0 \ln(tk_0) \quad \text{and} \quad E_w \equiv RT_0.$$

For  $E$  much less than  $E_s$  the function is nearly zero while for  $E$  much greater than  $E_s$  the function is nearly one. The function changes from zero to one in a range of  $E$  values within a distance of approximately  $E_w$  of  $E_s$ . Using the data above, this implies that the function changes within about  $E_w \approx 10$  kJ/mole of  $E_s \approx 100$  kJ/mole, and hence that the change is reasonably rapid.

For more complicated time histories the same ideas hold but the integral needs more careful attention. For example if the temperature is taken to ramp linearly with  $T = mt$ , DExp becomes

$$\exp\left(-\int_0^t k_0 e^{-\frac{E}{Rmu}} du\right).$$

The integral in the exponent can be approximated using the conventional Laplace approach where the parameter  $E/(Rmt)$  is assumed to be large and hence the dominant contribution from the integral is when  $u$  is near  $t$  (and the temperature is near its maximum). This gives the following well-known asymptotic approximation to the function:

$$\exp\left(-\int_0^t k_0 e^{-\frac{E}{Rmu}} du\right) \sim \exp\left(-\frac{k_0 Rmt^2}{E} e^{-\frac{E}{Rmt}}\right) \quad \text{as } \frac{E}{Rmt} \rightarrow \infty. \quad (3)$$

This approximate function is now written in the form

$$\exp\left(-\exp\left(\frac{E_s - E}{E_w}\right)\right),$$



where again the function switches rapidly from zero to one as  $E$  increases, over a range of size  $E_w$  around  $E_s$ , and this can be approximated as follows. Defining

$$g(E) = (E_s - E)/E_w$$

then (3) can be written as

$$\exp(-\exp(g(E)))$$

where

$$g(E) \equiv -\frac{E}{Rmt} + \ln\left(\frac{k_0 Rmt^2}{E}\right).$$

Because only the behaviour near  $E_s$  is of interest, this function is expanded in a Taylor series,

$$g(E) \sim g(E_s) + (E - E_s)g'(E_s) + \dots$$

Hence using this equation and the definition of  $g(E)$ ,  $E_s$  and  $E_w$  are chosen so that

$$g(E_s) = 0 \quad \text{and} \quad g'(E_s) = -1/E_w.$$

Solving these gives

$$E_s = Rmt Y(k_0 t) \quad \text{and} \quad E_w = \frac{Rmt E_s}{Rmt + E_s}$$

where  $Y(x)$  is the LambertW function defined to be the one real root of the equation

$$Y e^Y = x.$$

It is useful to note that approximations to  $Y(x)$  for small and large  $x$  (corresponding to short and long times) are [12]

$$Y \sim x - x^2, \quad x \ll 1,$$

and

$$Y \sim \ln\left(\frac{x}{\ln\left(\frac{x}{\ln x}\right)}\right), \quad x \gg 1.$$

DExp has been observed to be like a smoothed step-function, rising rapidly (for large values of  $tk_0$ ) from zero to one in a range of activation energies of

width  $E_w$  around the value  $E = E_s$ , where both  $E_s$  and  $E_w$  vary with time. In the total integrand of (2) DExp is multiplied by the initial distribution  $f(E)$ . The initial distribution is typically centered around a value  $E_0$  and has a width designated by  $\sigma$ , both of which are constant. Typically a Gaussian may be used but much of what is considered later applies to more general distributions. There are two different limits of interest, that of a relatively wide initial distribution compared with the width of DExp, and that of a relatively narrow distribution. The general way that the shape of the total integrand changes with time depends on which limit applies. When the initial distribution is relatively wide compared to  $E_w$ , the total integrand is initially the distribution  $f(E)$ , but then it is progressively chopped off from the left by the step-like DExp as time proceeds. The location of the maximum of the total integrand can move significantly, and the shape becomes quite skewed. When the initial distribution is relatively narrow, the total integrand remains similar in shape to the initial distribution, with an amplitude that is progressively reduced by DExp as time proceeds. The total integrand remains more symmetrical than in the wide distribution limit, although the location of its maximum does move.

To demonstrate the approach, consider the special case where the initial distribution  $f(E)$  is Gaussian, centered at  $E_0$  with standard deviation  $\sigma$ . Approximations are sought to the integral

$$v = \frac{1}{\sigma\sqrt{2\pi}} \int_0^\infty \exp(h(E)) dE ,$$

where

$$h(E) = -\exp\left(\frac{E_s - E}{E_w}\right) - \frac{(E - E_0)^2}{2\sigma^2}$$

and  $E_s$  and  $E_w$  are functions of  $t$  as defined earlier.

Energy is now rescaled as  $y = E/E_0$ . so that the problem becomes

$$v = \sqrt{\frac{\alpha}{\pi}} \int_0^\infty \exp\left[-\exp\left(\frac{y_s - y}{y_w}\right) - \alpha(y - 1)^2\right] dy \quad (4)$$

$$h(y) = -\exp\left(\frac{y_s - y}{y_w}\right) - \alpha(y - 1)^2 \quad (5)$$

where the constant parameter  $\alpha = \frac{E_0^2}{2\sigma^2}$ . Note that in practice  $\alpha \gg 1$ .

Note also the time dependence in the following two special temperature history cases that are commonly encountered.

For constant temperature  $T = T_0$ ,

$$y_s = \frac{RT_0}{E_0} \ln \tau, \quad y_w = \frac{RT_0}{E_0}.$$

For linear ramping temperature  $T = mt$ ,

$$y_s = \frac{Rm\tau}{k_0 E_0} Y(\tau), \quad y_w = \frac{y_s}{1 + Y(\tau)},$$

where  $Y$  is the LambertW function defined in (4.1) and time has been rescaled as  $\tau = k_0 t$ .

These results show that in the ramping temperature case the location  $E_s (= E_0 y_s)$  moves with time in a similar manner to the constant temperature case, with the log replaced by a LambertW function. However, the width of DExp,  $E_w (= E_0 y_w)$ , is narrower at early times. It is this second feature that accounts for the major difference in the appearances of the curves of released volatile versus time, between the ramping and constant temperature cases. In the constant temperature case, the amount of released volatile begins to change perceptibly even at very early times, whereas in the ramping temperature case the amount of released volatile does not change perceptibly until the critical time is reached when the two parts of the integrand overlap significantly.

Note that the ramping temperature case is easily generalised to the case of a nonzero initial temperature  $T_0$ , by simply replacing  $t$  with  $t + T_0/m$  everywhere. The analysis is otherwise unchanged.

Approximations to Eq. (4) are now studied, noting that the initial distribution is centered around  $y = 1$  with width  $1/\sqrt{\alpha}$  while DExp jumps from zero to one around  $y = y_s$  with a width  $y_w$ .

## 5 The Wide Distribution Case

First the case where the initial distribution is much wider than DExp is considered. To do this, the limit  $y_w \sqrt{\alpha} \ll 1$  is taken. In this limit, as previously discussed, DExp jumps from zero to one near  $y = y_s$ , in a manner that has previously [3, 6, 7, 8] been approximated by the step-function

$$H(y - y_s) = \begin{cases} 0, & y < y_s \\ 1 & y \geq y_s \end{cases}$$

The following approach improves upon this, and upon the linear ramp approximation used in [5].

Motivated by previous work, Eq. (4) is rewritten in the form

$$\begin{aligned} v &= \sqrt{\frac{\alpha}{\pi}} \int_0^\infty \left[ \exp\left(-\exp\left(\frac{y_s - y}{y_w}\right)\right) - H(y - y_s) \right] \exp(-\alpha(y - 1)^2) dy \\ &\quad + \sqrt{\frac{\alpha}{\pi}} \int_{y_s}^\infty \exp(-\alpha(y - 1)^2) dy . \end{aligned}$$

The second integral in this equation is a conventional error function, or normal distribution, and hence straightforward to compute. In fact many previous simplifications (the step-function approximations) use just this term and neglect the first integral. Note that in the first integral, the integrand is the initial distribution multiplied by a function that is very small everywhere except in a neighbourhood of size  $y_w$  around the point  $y = y_s$ . This integrand can therefore be approximated by expanding the initial distribution term as a Taylor series about  $y = y_s$  giving

$$\begin{aligned} &\sqrt{\frac{\alpha}{\pi}} \int_0^\infty \left[ \exp\left(-\exp\left(\frac{y_s - y}{y_w}\right)\right) - H(y - y_s) \right] \exp(-\alpha(y - 1)^2) dy \\ &= \sqrt{\frac{\alpha}{\pi}} \int_0^\infty \left[ \exp\left(-\exp\left(\frac{y_s - y}{y_w}\right)\right) - H(y - y_s) \right] \\ &\quad (1 + (y - y_s)2\alpha(y_s - 1) + \dots) \exp(-\alpha(y_s - 1)^2) dy . \end{aligned}$$

Each of the integrals arising from a term in the Taylor series can now be integrated separately to yield

$$v \sim \frac{1}{2} \operatorname{erfc}(\sqrt{\alpha}(y_s - 1)) + \sqrt{\frac{\alpha}{\pi}} y_w e^{-\alpha(y_s - 1)^2} [A_0 - 2\alpha y_w (y_s - 1) A_1]$$

$$+\alpha y_w^2 \{2\alpha(y_s - 1)^2 - 1\} A_2 + \frac{2}{3} y_w^3 \alpha^2 \{2(y_s - 1) + 2\alpha(y_s - 1)^3 + 1\} A_3 \Big], \quad (6)$$

where the integrals remaining to be evaluated are represented by

$$A_i \equiv \int_{-\infty}^{\infty} x^i \left( e^{-e^{-x}} - H(x) \right) dx \quad i = 0, 1, 2, \dots .$$

These  $A_i$  need only be evaluated once, as they are independent of any parameters, and the first few values are

$$A_0 \approx -0.5772, \quad A_1 \approx -0.98906, \quad A_2 \approx -1.81496, \quad A_3 \approx -5.89037.$$

Formally this expansion is only valid when  $\alpha y_w (y_s - 1) \ll 1$  and in the limit  $y_w \sqrt{\alpha} \rightarrow 0$ , but in practice the expansion is quite robust, as the formal errors occur only at the extremes of the distribution. Further terms in this expansion are easily found if it is desired to improve the accuracy of the approximation or the approximation can be made simpler by taking fewer terms. For example the approximation used by [3, 6, 7, 8] is just the first term in this series.

For a general initial distribution  $f(E)$ , which is wide compared to  $y_w$ , this asymptotic approach gives the general result

$$v \sim \int_{y_s}^{\infty} f(y) dy + y_w A_0 f(y_s) + y_w^2 A_1 f'(y_s) + y_w^3 A_2 f''(y_s)/2 + y_w^4 A_3 f'''(y_s)/6 \quad (7)$$

where, as usual, the symbol ' is used to indicate the derivative.

## 5.1 Inverse Problems

For the general result (7), the rate of volatilisation can be written in the form

$$\begin{aligned} \frac{dv}{d\tau} \sim & \left[ -f(y_s) + y_w A_0 f'(y_s) + y_w^2 A_1 f''(y_s) + y_w^3 A_2 f'''(y_s) \right] \frac{dy_s}{d\tau} + \\ & \left[ A_0 f(y_s) + 2A_1 y_w f'(y_s) + 3y_w^2 A_2 f''(y_s) \right] \frac{dy_w}{d\tau}. \end{aligned} \quad (8)$$

This last equation gives a method for considering the inverse problem with greater accuracy than previously considered (these neglected all terms with  $A_0, A_1, A_2$  etc.).

Since in this case  $E_0$  is not known beforehand, it is best to rewrite Eq. (8) in the dimensional form

$$\frac{dv}{dt} \sim \left( -\frac{dE_s}{dt} + A_0 \frac{dE_w}{dt} \right) f(E_s) + A_0 E_w \frac{dE_s}{dt} f'(E_s) + \dots \quad (9)$$

Note that the original Volterra integral equation of first type for  $f$  has been approximated by a differential equation. The left hand side is known,  $E_s$  and  $E_w$  are known functions of  $t$  (provided that  $k_0$  is known), and we need to determine  $f(E_s)$ . As explained by Niksa and Lau [5], dependence on  $t$  may be replaced by dependence on  $E_s$ , by inverting  $E_s(t)$ .

A perturbation approach to solving Eq. (9) takes advantage of the narrow double exponential (compared with the width of the distribution) by considering  $E_w \equiv \epsilon e_w$ ,  $\epsilon \ll 1$ . Then to order  $\epsilon$  for example,

$$\epsilon A_0 e_w \frac{dE_s}{dt} f'(E_s) + \left( \epsilon A_0 \frac{de_w}{dt} - \frac{dE_s}{dt} \right) f(E_s) = \frac{dv}{dt}.$$

Usually when higher derivatives are multiplied by small parameters, the problem requires singular perturbation techniques, and consideration of boundary layers. However, here the boundary conditions ( $f \rightarrow 0$  when  $E_s \rightarrow 0$  or  $\infty$ ) are automatically satisfied by the zeroth-order (or outer) solution, and regular series expansion techniques provide a simple way to approximate  $f$ . Hence  $f$  is expanded as a power series in  $\epsilon$ ,  $f \sim f_0 + \epsilon f_1 + \epsilon^2 f_2 + \dots$ , and coefficients of powers of  $\epsilon$  are equated to obtain

$$f_0 = -\frac{\frac{dv}{dt}}{\frac{dE_s}{dt}}, \quad (10)$$

$$\epsilon f_1 = A_0 \left( E_w \frac{df_0}{dE_s} + \frac{\frac{dE_w}{dt} f_0}{\frac{dE_s}{dt}} \right). \quad (11)$$

The zeroth-order approximation  $f_0$  is the same as that obtained by Miura and Maki [9]. Adding  $\epsilon f_1$  gives an improved formula, and higher-order terms are similarly easily calculated. However, each improvement requires

higher-order derivatives (differences) of  $v$  to be calculated, and without some form of prior smoothing this will eventually lead to numerical errors large enough to swamp the results.

## 6 The Narrow Distribution Case

The analysis and expansions presented by McGuinness et al. [13] prove to be accurate only for relatively narrow distributions  $f(E)$ , in particular for ramping temperature histories which satisfy  $\sigma \ll \sqrt{2} RT_1$  where  $T_1$  is the temperature of the point of inflection in a plot of released volatiles versus temperature. The development in this section is aimed at the same case of narrow distribution, but differs from the approach of [13] by considering simultaneously the behaviour of the initial distribution  $f(E)$  and of the term DExp, in a manner analogous to the method of the moving maximum for Laplace problems [14]. In contrast the method presented in [13] is equivalent to taking the maximum of the total integrand to remain fixed at the maximum of the initial distribution and then proceeding in a manner analogous to that of a standard Laplace problem. The present approach yields results that are more robust and more accurate over a wider range of operating parameters, because it allows for the fact that the maximum of the integrand moves in a time-dependent manner.

The assumption of a narrow distribution for the Gaussian distribution corresponds to taking  $\sigma \ll RT$  in both temperature history cases, with  $T = T_0$  for constant temperature, and  $T = mt$  in the ramping temperature case. Formally this corresponds to taking  $y_w \sqrt{\alpha} \gg 1$  in (4).

Although the integral in (4) is not in Laplace form, the method of Laplace motivates the approach taken here. The value  $y^e$  of  $y$  is sought, where the function  $h(y)$  given in (5) is at an extremum, by finding the point where  $h'$  is zero. Hence since

$$h'(y) = \frac{e^{\frac{y_s - y}{y_w}}}{y_w} - 2\alpha(y - 1) .$$

it is necessary to find  $y^e$  that satisfies the equation

$$e^{\frac{y_s - y^e}{y_w}} = 2\alpha y_w (y^e - 1) .$$

The solution is given by

$$y^e = 1 + y_w Y \left( \frac{1}{2\alpha y_w^2} \exp \left( \frac{y_s - 1}{y_w} \right) \right),$$

where  $Y$  the LambertW function.

A Taylor series expansion of  $h$  about  $y^e$ , truncated after the quadratic term, gives

$$h(y) \sim h(y^e) + h''(y^e)(y - y^e)^2/2. \quad (12)$$

Noting that the second derivative of  $h$  is

$$h''(y) = -\frac{e^{\frac{y_s - y}{y_w}}}{y_w^2} - 2\alpha$$

the leading behaviour of  $v$  in (5) is

$$\frac{\exp(h(y^e))}{\sigma \sqrt{|h''(y^e)|}}.$$

and this may be written in the form

$$\frac{\exp[-\alpha(y^e - 1)(y^e + 2y_w - 1)]}{\sqrt{1 + \frac{y^e - 1}{y_w}}},$$

where  $y^e$  is defined above.

This approach to approximating the volatiles when the initial distribution is narrow compared to  $y_w$  can be used for other distributions but it will always require finding the maximum of the total integrand and this is not easy to generalise.

## 7 Numerical Comparisons

In this section the asymptotic approximations are compared with full numerical calculations of the double integral (2) and with the approximations of Niksa and Lau [5]. The case of a Gaussian distribution is



used, with a linearly ramping temperature. For a wide range of parameter values, the asymptotic approximations derived here are found to be more accurate than previous work, and our approximations are generally found to be accurate enough to give  $v$  vs  $t$  plots that are indistinguishable from plots generated from the full calculations. Furthermore, in the narrow distribution case, the asymptotic method provides accurate approximations of the integrand of the energy integral, as it evolves in time. In these comparisons,  $T_0 = 273$  K and  $E_0 = 2.05E05$  J/mol.

All calculations were performed using Maple, which has built-in support for LambertW functions. The full numerical calculations were done by first rewriting the double integral in terms of exponential integrals, and are accurate to four significant figures.

## 7.1 Wide Gaussian

In the case that the Gaussian distribution is relatively wide, both the asymptotic results and those of Niksa and Lau are indistinguishable from plots of the full calculations of  $v$ , as illustrated in Fig. (1).

Note from the plot of the differences between full and asymptotic results, that our results are more accurate than those of Niksa and Lau. The parameter values used are indicated in Table (1).

Table 1: Parameter values used for comparisons.

case	$k_0$ ( $s^{-1}$ )	$E_0$ (kJ/mol)	$\sigma$ (kJ/mol)	$m$ (K/s)
Fig. (1)	1.07E10	205	40	650
Fig. (2)	1.0E13	205	50	650
Fig. (3)	1.07E10	205	1	650
Fig. (4)	1.07E10	205	2	650

The inverse problem of determining the distribution from measurements of  $v$  versus time is illustrated in Fig. (2). The circles indicate the underlying Gaussian distribution used to generate values of  $v$  versus time by using full calculations of the DAEM as in Eq. (2). The parameter values used are

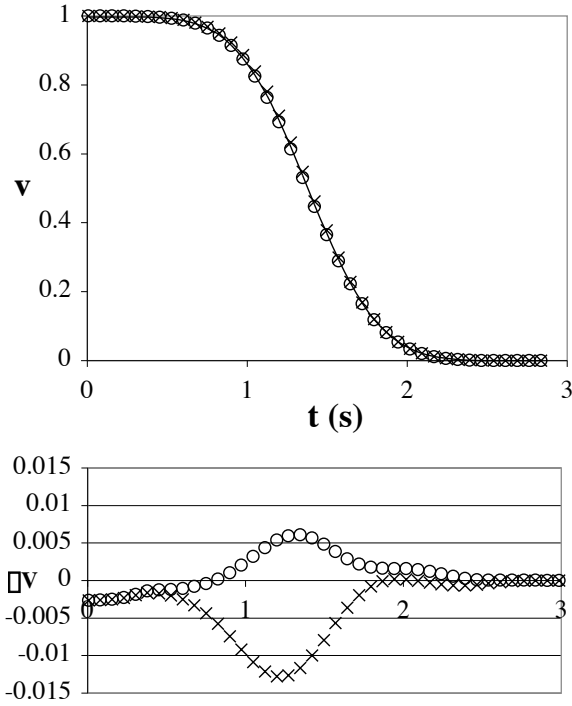


Figure 1: Comparisons of  $v$  values obtained from accurate integrations and asymptotic results . See Table (1) for parameter values used. The first plot shows  $v$  values, from full calculations (solid curves), from our asymptotic results (circles), and from the work of Niksa and Lau (crosses). The second plot shows differences between full calculations and asymptotic values obtained for  $v$ , with circles indicating our results, and crosses the results of Niksa and Lau.

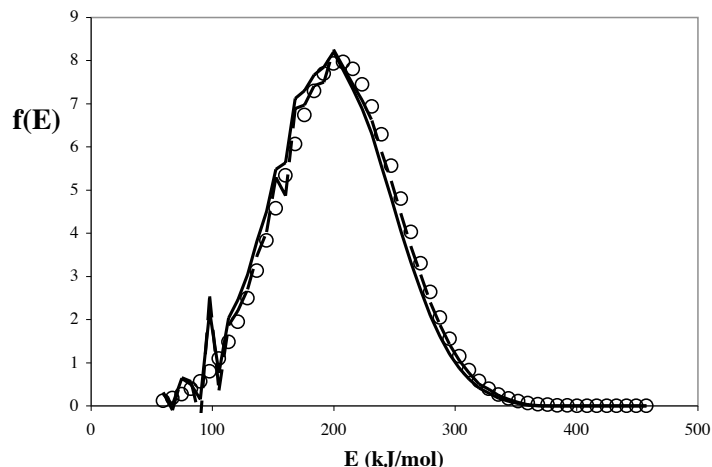


Figure 2: Comparisons of the underlying Gaussian distribution with distributions estimated inversely from  $v$  values versus time. See Table (1) for parameter values used. The actual distribution is indicated by circles, the leading-order result by a solid line, and the higher-order result by a dashed line.

indicated in Table (1). The solid line shows the result of calculating just the leading-order term  $f_0$  using Eq. (10), and the dashed line is the result obtained by adding our higher-order correction term from Eq. (11). It can be seen that adding  $\epsilon f_1$  does provide a more accurate estimate of the underlying distribution in the DAEM, but also that errors due to differencing are becoming more significant, as the  $v$  values were only generated accurate to 4 significant figures. This is particularly apparent in Fig. (2) at energies less than 125 kJ/mol, and could be improved in practice by first fitting an appropriate smooth function (perhaps a power times an exponential) to the data, or by using a running polynomial fitted over just a few nearby points.

## 7.2 Narrow Gaussian

Typical results for the case of a relatively narrow Gaussian are displayed in Fig. (3).

The parameter values used are listed in Table (1). In the first plot, circles

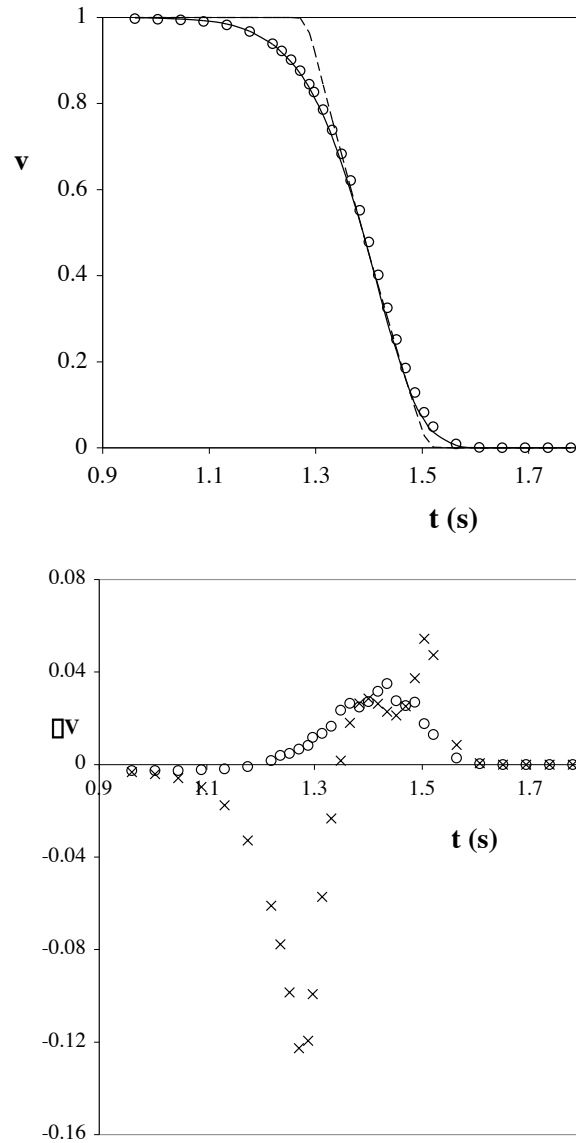


Figure 3: Comparisons between full calculations, our asymptotics, and those of Niksa and Lau, for the narrow Gaussian case. The first plot shows the amount of volatile  $v$  remaining to be released versus time, with the solid line being full calculations, the circles our results, and the crosses those of Niksa and Lau. The second plot shows differences between  $v$  values obtained from asymptotic results and from full calculations, using our results (circles) and those of Niksa and Lau (crosses).

indicate full calculation values, the solid line is our asymptotic result, and the dashed line is the result of Niksa and Lau. The second plot shows differences between our asymptotic results and full calculations (circles), and between the results of Niksa and Lau and full calculations (crosses). The asymptotic results can be seen to be better, especially at early times.

It is also useful to compare full calculations of the time-dependent integrand with our approximation based on Eq. (12). Figure (4) shows a comparison at different times for Savage Mine lignite [3](see Table (1) for parameter values used). The symbols are full calculations for the DAEM integrands, and the solid curves are our asymptotic approximations.

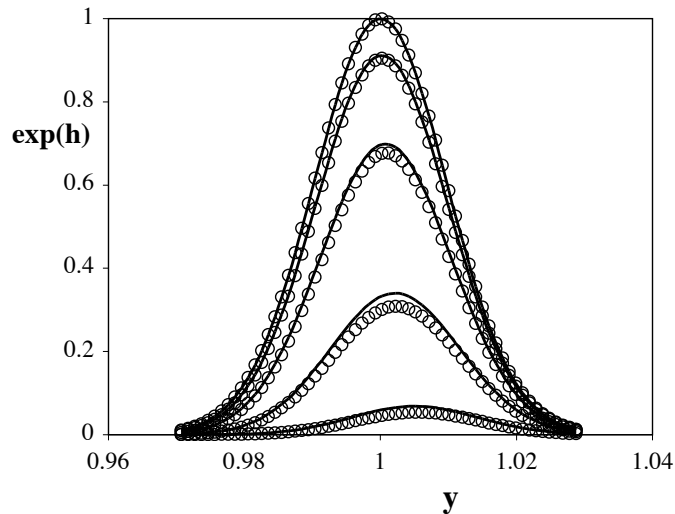


Figure 4: Comparisons between integrands for full calculations (curves) and our asymptotic results (circles), as they evolve in time in the case of a narrow Gaussian. The abscissa is the rescaled energy variable,  $y$ . The times used, from the highest curve down, are 0, 1.25, 1.35, 1.43, and 1.51 seconds respectively.

These figures are illustrative of results obtained over a wide range of parameter values. Tables (2) and (3) summarise these results in more detail, by showing the maximum errors (differences in  $v$  values) obtained

when comparing our results (and those of Niksa and Lau) with full calculations, for a selection of the parameter values we considered.

Table 2: Table showing the maximum error, that is, the maximum difference between approximate and full calculations of  $v$ , for a range of parameter values. The calculations have been done for asymptotic results ("AsW") using the wide distribution case, and for those of Niksa and Lau ("NL").

$m$ (K/s)	$\sigma$ (kJ/mol)	$k_0$ s <sup>-1</sup>	AsW	NL
1.0E+00	20	1.0E+10	.011	.023
1.0E+00	20	1.0E+12	.007	.021
1.0E+00	20	1.0E+14	.005	.019
1.0E+00	50	1.0E+08	.013	.016
1.0E+00	50	1.0E+12	.010	.012
1.0E+00	50	1.0E+16	.009	.012
1.0E+02	50	1.0E+08	.020	.014
1.0E+02	50	1.0E+12	.010	.010
1.0E+02	50	1.0E+16	.013	.013
1.0E+04	50	1.0E+08	.031	.031
1.0E+04	50	1.0E+12	.013	.016
1.0E+04	50	1.0E+16	.010	.012

In particular, our results have been numerically checked against accurate evaluations and against the approximations of Niksa and Lau, for  $E_0 = 205$  kJ/mol; and for  $\sigma$  taking the values 1, 5, 10, 20, and 50 kJ/mol; and for  $k_0$  taking the values 1E08, 1E10, 1E12, 1E14, and 1E16 s<sup>-1</sup>; and for  $m$  taking the values 0.1, 1, 10, 100, 1000, and 10000 K/s. In nearly all cases our approximation fitted the accurate results more closely than that of Niksa and Lau.

The wide distribution results were used for the cases in Table (2), and the narrow distribution results were used for the cases in Table (3). Note that while all of the cases in Table (2) have wide distributions, and some of the cases in Table (3) have narrow distributions, a number of the cases in Table (3) have distributions of similar width to DExp. It is clear that the approach taken here when assuming narrow distributions yields results that are robust enough to be applicable even when the distribution is not

Table 3: Table showing the maximum error, that is, the maximum difference between approximate and full calculations of  $v$ , for a range of parameter values. The calculations have been done for asymptotic results ("AsN") using the narrow distribution case, and for those of Niksa and Lau ("NL").

$m$ (K/s)	$\sigma$ (kJ/mol)	$k_0$ s <sup>-1</sup>	AsN	NL
1.0E-01	1	1.0e+10	.02	.13
1.0E-01	1	1.0e+14	.02	.12
1.0E-01	1	1.0e+16	.02	.12
1.0E+00	1	1.0e+10	.03	.13
1.0E+00	1	1.0e+16	.02	.12
1.0E+01	1	1.0e+10	.03	.13
1.0E+01	1	1.0e+16	.02	.12
1.0E+02	1	1.0e+08	.04	.13
1.0E+02	1	1.0e+16	.02	.12
1.0E+03	1	1.0e+08	.04	.13
1.0E+03	1	1.0e+16	.02	.12
1.0E+04	1	1.0e+08	.05	.13
1.0E+04	1	1.0e+16	.03	.12
1.0E-01	10	1.0E+08	.015	.048
1.0E-01	10	1.0E+16	.039	.033
1.0E+00	10	1.0E+08	.017	.051
1.0E+00	10	1.0E+16	.035	.035
1.0E+01	10	1.0E+08	.024	.054
1.0E+01	10	1.0E+16	.033	.036
1.0E+02	10	1.0E+08	.023	.057
1.0E+02	10	1.0E+16	.029	.038
1.0E+03	10	1.0E+08	.030	.061
1.0E+03	10	1.0E+16	.025	.040
1.0E+03	10	1.0E+08	.034	.065
1.0E+04	10	1.0E+16	.022	.042
1.0E+00	20	1.0E+08	.049	.026

narrow. We have also found it to be better than the previous results of McGuinness et al [13].

Some comments are included here to help with decisions about whether the distribution is wide or narrow. In our calculations,  $\sigma$  is compared with a critical value  $\sigma_c$ , which is found by setting the width  $y_w$  of DExp equal to the distribution width  $3\sigma_c/E_0$ . This requires calculating the time  $t_c$  when DExp is passing through the center of the distribution ( $y = 1$ ). Reasonable results are obtained by using

$$\sigma_c \equiv \frac{E_0 R m t_c}{3(R m t_c + E_0)},$$

where

$$t_c = (t_{\min} + t_{\max})/2$$

and  $t_{\min}$  is the time when DExp just begins to encounter the distribution, found by solving

$$y_s + 2y_w = 1 - 3\sigma/E_0,$$

that is,

$$\frac{TY(k_0 t)(3 + Y(k_0 t))}{1 + Y(k_0 t)} = \frac{E_0 - 3\sigma}{Rm},$$

while  $t_{\max}$  is the time when DExp has just moved past the distribution, found by solving

$$y_s - y_w = 1 + 3\sigma/E_0,$$

that is,

$$\frac{tY^2(k_0 t)}{1 + Y(k_0 t)} = \frac{E_0 + 3\sigma}{Rm}.$$

## 8 Discussion

A detailed investigation has been presented of the behaviour of the double exponential time-dependent part of the double integral that arises in the DAEM, here called DExp. Two limits were considered, one in which the distribution of volatiles is wide compared with DExp, and one in which the distribution is comparatively narrow. In each case, asymptotic approximations for the amount of volatile released in the full DAEM were



derived, and have been found (for Gaussian distributions) by numerical testing to be more accurate than previous approximations, particularly in the case of a narrow distribution.

The narrow distribution results have also been found to be useful in cases where the distribution is of similar width to DExp.

Furthermore, for the case of a wide distribution, an improved way to calculate the actual volatile energy distribution directly from the experimental rate of release of volatile is presented. A numerical investigation of this inverse problem for a model Gaussian distribution indicates that our higher-order correction term provides an improved estimate of the underlying distribution. The results and approach here are general enough to apply to any form of energy distribution (provided it is wide compared with DExp), and to be used for multiple distributions (as when several volatiles with different mean and standard deviation are combined).

## Acknowledgements

CPP and MJM wish to acknowledge the generous support given by CiSSaIM at Queensland University of Technology during the course of this research. MJM also thanks the EPSRC for the Visiting Fellowship (GR/R56570/01) that supported much of his work on this project, and Victoria University of Wellington for the Research and Study Leave that made it all possible.

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