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Robust Extension of the Coats-Redfern Technique: Rapid and Realiable Reactivity Analysis of Complex Fuels Decomposing in Inert and Oxidising TGA Atmospheres

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Abstract

Thermogravimetric analysis (TGA) is well-established for rapid reactivity assessment for reactions described by temperature and mass data alone. Many methods have been presented to quantify reactivity rates from TGA data and some have been over-extended in the literature creating a range of contrasting data for similar decompositions. A novel formalisation of the Coats-Redfern method extended to encompass overlapping multi-stage reactions, such as in biomass combustion, is presented. The method is tested with a range of theoretical decompositions containing numerous stages with varying stage-overlap and illustrates current reporting of TGA data is often insufficient. To increase robustness and confidence of predictions an increase in the amount of data reported is suggested along with a novel method of comparing reactivities between experiments. The method is shown to compare decompositions using

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only the small amounts of data available when reactions overlap with tolerable accuracy for screening and indicative applications. By way of example the method is then applied to two biomass samples (willow and shea meal) decomposing in air and oxygen-enriched combustion environments. The method is able to accurately represent the willow decomposition but the convoluted nature of the shea meal decomposition reduces the method's ability to model this reaction. However, comparison of the reactivities produced by the model with changes in the temperature at maximum rate of decomposition indicate that for both biomasses the trends of oxygen enrichment of combustion atmospheres enhances combustion reactivity.

Introduction

Since Coats and Redfern introduced their idea of extracting kinetic data from the results of thermogravimetric analysis (TGA) nearly half a century ago,[1] a plethora of papers have subsequently been published. These papers use, refine or criticise the techniques available for investigating the properties of reactions that can be approximated by temperature and mass measurements alone, see for example.[2–5]

Although originally, and often still, used to characterise single reactions, at some point the method of estimating kinetic parameters from TGA was applied to fuels. Despite clear scientific evidence to the contrary, much research still purports to estimate with a relatively high degree of accuracy kinetic rates of decomposition for complex fuels decomposing due to a range of parallel and series reactions. There are several reasons why the technique has endured, notable among them being that few other options exist for characterisation; that despite limited scientific precedent, the characterisation superficially appears to be applicable; and equally a continuing refusal by academic oversight communities to extend guidelines for extracting TGA-derived data for single reactions to more complex overlapping, multi-stage reactions. This reticence is understandable considering the litany of misappropriation of kinetic theory to areas beyond its limitations. Indeed, despite the availability of clear methods for, and the limitations of, extracting rate constants from TGA data non-adherence is rife in the research community. It is unfortunate that many examples exist in which ‘kinetic rates’ are extracted from TGA data which bear little semblance to the reactions they are attempting to characterise as evidenced by, for example, the range of activation energies and orders of reaction reported for the combustion of various biomasses. It is believed researchers working with complex multi-stage reactions (such as pyrolysis or combustion of multi-component fuels) will continue to use TGA data since it offers rapid, indicative results. Thus, a formalisation of the procedure which is difficult to find in the literature is reported herein. The availability of several comprehensive works which detail the procedure for single-stage reactions[4–6] and recent work identifying mechanisms in multi-stage reactions[7] is acknowledged. In this work, the methods explained and collected therein have been extended to demonstrate applicability to overlapping multi-stage reactions in complex fuels.

This work was borne out of a need to rapidly and economically assess the probable effects on rate of combusting a variety of fuels in a variety of atmospheres. The research matrix for this series included over 50 unique experiments thus an expensive set of characterisations was not feasible. Instead a robust method was needed to estimate with relative confidence the effect of altering the reaction atmosphere on the decomposition of each of these fuels. The particular benefit of this idea was to provide estimates for rate data using only a minimal number of heating rates. Iso-convsersional methods such as those developed by Kissinger-Akira-Sunose[8,9] and Flynn-Wall-Ozawa[10,11] may provide more accurate rate parameter estimates but at the cost of at least three temperature ramp rates.[4,12] Equally, the development of distributed activation energy models (DAEM) and extensive curve-fitting techniques have elsewhere been employed in attempt to further increase the accuracy of predicting pyrolysis and oxidative reactions of fuels with varying degrees of success, for example see.[13–17] In short it is acknowledged that a considerable amount of work exists that aims to extract rate parameters for reactivity analysis from TGA data. However, while other methods are reported to display marginal increases in accuracy, this is invariably at the cost of at least three heating rates or the application of relatively complex solver techniques. Dissimilar to work which can actively employ the TGA results in modelling studies, it is noted that while rate data extracted from TGA experiments show correlation with larger scale combustion,[18] the orders of magnitude difference in heating rate predicate any extrapolations can only be qualitative.[19] Furthermore, it is widely accepted that the 'rate' data extracted from TGA devices is dependent on the experiment and so it is felt that TGA results should realistically only be used for comparison within the confines of an experiment and not compared with external data as to extrapolate further would be beyond the limitations of the procedure. Thus, for comparative work between fuels and atmospheres emphasis is placed on rapid, indicative techniques which are more likely to be useful to industry and screening of fuels by assessing trends. Since the use of TGA-derived data in accurately predicting full-scale combustion is qualitative in nature, it is felt methods which involve substantial extra effort (either materially by repeated experiments or through complex curve fitting) are difficult to justify. In summary, this work does not intend to duplicate available literature which details the potential for pitfalls during TGA studies. Instead, it aims to provide a method which can sit within the guidance provided by standards, which is powerful, rapid, traceable and therefore useful. It is also noted that for a non-specialist TGA literature can be misleading and contradictory and so this work attempts to provide a method for which those who adopt it clearly understand the inherent limitations.

Rather than a completely new method, the outline below is mainly concerned with an increase in the amount of data reported and used for comparisons. At present, data reporting is often lacking in literature where in some cases it has become common practice to omit reporting of the pre-exponential constant in the Arrhenius equation. Indeed, even where reported, this important parameter is rarely used in discussions regarding comparisons of reactivity which are normally reduced solely to the activation energy. This work highlights that for graphical methods, such as those proposed by Coats and Redfern, a temperature range which the linear fit is made across is essential in providing robustness of the data. It will also be demonstrated that while the square of the Pearson product moment correlation coefficient (R^2) is necessary for the data fitting section, to provide an overview of the whole reaction it is equally useful to provide the correlation between collected data and that reconstructed from predicted reactivities.

In this work, the initial case examines the effect of smoothing and how subjective curve fitting can affect the estimated parameters. The work is then extended to include a decomposition consisting of two reactions with minor overlap and finally a decomposition that includes three reactions with substantial overlap. Finally, the developed methodology is applied to a worked example comparing the reactivity of willow and shea meal in two oxidising atmospheres.

Materials and Methods

In this work both idealised and experimental data is used to develop and test the method which follows. For experimental situations a brief overview of data collection is initially presented and followed by the procedure used to generate idealised data used in the majority of the results in this work. The process of identification of reaction zones follows while the effects of curve fitting, data smoothing and overlapping data are discussed in the following section.

Experimental Data

The experimental data was generated according to ASTM standards E1641 and E2550. In order to mitigate the effect of particle size of the sample on its combustion behaviour,[20] the sample particle size was reduced to $<212\,\mu\text{m}$ using a SPEX 6770 Freezer Mill which prevented the formation of waxes and volatiles from escaping during size reduction.[21,22] For each experiment $5 \pm 0.5\,\text{mg}$ of each biomass sample was accurately measured into an open alumina crucible and the sample was introduced to a Mettler-Toledo TGA/DSC1 device. Once air was purged by the test atmosphere the sample was then heated to 383 K and held for 30 min to drive off moisture. The sample was then heated at the test heating rate to a temperature of 1023 K while the test atmosphere was pumped into the chamber at a rate of $50\,\text{ml}\,\text{min}^{-1}$. The sample was held at the final temperature for a further 30 min to ensure combustion was complete. The procedure was repeated at heating rates of $10\,\text{K}\,\text{min}^{-1}$ and $40\,\text{K}\,\text{min}^{-1}$ for short rotation coppiced (SRC) willow and shea meal (SM) samples decomposing in air and a synthetic atmosphere of 30 % O_2 and 70 % N_2.

Idealised Data

Throughout this section recommendations are made regarding how TGA data should be treated. As a basis for these recommendations an idealised set of TGA results has been created which aims to illustrate the potential errors associated with data processing. For simplicity, the initial case assumes an irreversible, single-stage first order reaction described by the Arrhenius relationship that consumes all of the solid reactant. This concept is then extended to include two and then three non-competing reaction stages in the decomposition with a differing extent of overlap between reactions. A heating rate (β) of $1\,\mathrm{K\,s^{-1}}$ is assumed and mass remaining at each time-step (M_i) is calculated according to the following equations. The pre-exponential activity coefficient is considered to remain constant across the relatively narrow temperature range of each reaction. The parameters used in the idealised reactions are presented in table 1.

Arrhenius Model

The Arrhenius equation (eq. (1)) forms the basis for most parameter estimation from TGA data and is widely documented in the literature. Equation (2) demonstrates how the remaining reactant mass is calculated at each time-step for the idealised and reconstructed datasets.

$$k_{a,i} = A_a e^{\frac{-E_{A,a}}{RT_i}} \tag{1}$$

$$M_i = \sum_{a=1}^{a=N} m_{a,i-1} - k_{a,i} m_{a,i-1} \tag{2}$$

where

- k is the rate constant
- a is the reaction stage number
- i is the time-step

- A is the pre-exponential constant
- E_A is the activation energy
- R is the universal gas constant
- T is the temperature
- N is the number of reaction stages occurring in the decomposition (1 - 3 in the following examples)
- m is the mass of each reactant, the sum of which (M) is the total mass decomposing.

Identifying Reactions and Leading Edges

One of the biggest problems with using the Coats-Redfern technique to analyse TGA data from fuel decompositions is that single reactions cannot be isolated from the overall decomposition. Indeed from the derivative thermogram (DTG) graphs of multi-stage reactions presented throughout this work, it can be seen that the rising edge of initial reactions often overlap with the falling leg of the subsequent reaction. Thus in order to estimate the kinetic parameters it is necessary to investigate how well the kinetic parameters may be estimated using only a small part of the data.

In this work identifying reactions is completed by adopting the following method where it is assumed that all decompositions comprise of a series of non-competing, first-order, single-stage reactions obeying Arrhenius laws. The following procedure is demonstrated with the 3-stage decomposition illustrated in fig. 1.

A tangent is drawn to the reaction leading and trailing edges on the DTG curve. At the intersect of this tangent with the zero line (or the preceding or subsequent reaction line in the case of overlapping reactions) a bisection of the point is extended until it reaches the DTG trace. When the bisect reaches the DTG trace this is labelled as the start of the reaction zone (and the end of the previous reaction zone). For overlapping shoulder zones, the crossover point is found by taking the midpoint between where the two leading edges meet the tangent at the crossover.

The leading edge of each reaction is defined as the section of the DTG that aligns with the tangent where rate is typically increasing at its fastest rate with increasing temperature (the steepest slope), just before the maximum rate is found.

Assigning Reactions Compositional Mass

When reconstructing overlapping multi-stage reactions, as will be performed later, it is necessary to estimate the fraction of the total mass consumed by each reaction stage. Additionally, if experiments are conducted under different heating rates the temperature ranges which the reactions occur across may change. However, at the heating rates which can be studied in TGA devices and within the tolerance of experimental errors, the mass loss due to each reaction should be consistent at different heating rates for most cases of interest. Thus, as well as providing data for reconstruction, this additional procedure builds confidence that data is being compared between experiments fairly.

Applying the Coats-Redfern Procedure

The Coats-Redfern procedure is widely reported in the literature, for example see[4] and references therein, and will not be duplicated here. Following the established procedure for each reaction stage separately, the extent of reaction (α) is calculated by comparing the mass at time i (M_i) with the initial (M_0) and final (M_f) masses as per eq. (3).

$$\alpha = \frac{M_0 - M_i}{M_0 - M_f} \tag{3}$$

Then, according to the procedure for first order reactions plotting $\ln\left(-\ln\left(1-\alpha\right)/T^2\right)$ against $1/T$ yields a straight line, the slope of which is $E_{A,a}/R$ and the intercept equal to $\ln\left(AR/\beta E\right)$.

The Importance of Reconstruction

In the literature the robustness and accuracy of the Coats-Redfern method at predicting kinetic parameters is often described by linearity of the Coats-Redfern plot or a section of it. In order to test the accuracy of the technique presented here it is more useful to recreate the entire mass and DTG curves (since these are the focus of the model). To do this, the estimated values for activation energy, pre-exponential constant and mass fraction for each reaction stage are substituted into eqs. (1) and (2) to generate mass and DTG curves which can be directly compared to the original data which is similar to work in biomass pyrolysis.[14,23,24] Although useful for the researcher, it would be unpractical to provide a graph of every plot in a publication, so the square of the Pearson product moment correlation coefficient (R^2) between the initial and the reconstructed data for the mass loss and DTG profiles is instead calculated. This procedure protects against false-confidence in the data which could occur if the Coats-Redfern plot, or a section of it, was highly linear but not necessarily appropriate for the reaction. Also, if sufficient data is provided (reaction stage temperature range, mass loss during reaction stage, activation energy, pre-exponential constant and order of reaction) the mass and DTG profiles may be reconstructed using eqs. (1) and (2) to a degree of accuracy provided by the correlation coefficient. This is not possible with the majority of data available in the literature which either provides an overall energy of activation encompassing several decomposition stages, or alternatively individual reactivity parameters without the constituent masses consumed by each reaction within the decomposition. It is believed the approach in this work is considerably different to much combustion literature which only reports the linear fit to the Coats-Redfern plot.

It is important to note that the comparison of the data should only be carried out in region of the reaction and the original data should be normalised to this range. Otherwise any extra data points either side of the reaction will artificially boost the value of the correlation coefficient. Equally, if other reactions are occurring outside of the reaction zone, such as the continued mass loss seen in biomass ashes, this will not have a large effect on the coefficient (in this instance to artificially reduce its value).

Overcoming the Compensation Effect

The compensation effect has been widely discussed by a number of works available in the literature, for example[4,5,25] and for this reason it is felt that the output of this model should be only compared qualitatively with TGA data already in the literature. The issue is that by using a graphical technique to estimate a function, especially when a degree of freedom such as the order of reaction being modelled is fixed, a numerical output of the model cannot be viewed singularly. In short, although widely practised, it is judged that comparison of activation energies alone is insufficient to describe relative reactivities and can even be misleading. For example, a more reactive decomposition may be represented by a higher activation energy than a less reactive decomposition so long as the pre-exponential constant is sufficiently lower than that of the less reactive case. Since in this method the order of reaction is fixed to unity, the model output only requires evaluation of two terms. This allows reactivity comparisons to be simply completed by normalising the reactivity to a reference case value for activation energy ($E_{A,0}$) and pre-exponential function (A_0). Once the reference case is established, the following simple equation can be used to discern the reactivity of a fuel relative to the reference case (R_i).

$$R_i = \frac{\ln A_i}{\ln A_0} - \frac{E_{A,i}}{E_{A,0}} \tag{4}$$

where if

- $R_i < 0$ then the decomposition is less reactive than the reference case
- $R_i = 0$ then the decomposition and the reference case are equally reactive
- $R_i > 0$ then the decomposition is more reactive than the reference case

To provide a basis for comparison for the trends presented by any variation found in R_i, the temperature at which maximum rate of reaction ($T_{max,i}$) for each stage was also calcuated. This was then normalised to the reference case ($T_{max,0}$) to indicate a change in reactivity as $T_{max,N} = \left(T_{max,0} - T_{max,i}\right)/T_{max,0}$.

Results and Discussion

Effect of Fitting Range (One-Stage Decomposition)

Simulated plots of the mass and DTG shown in fig. 2 generated by substituting the data in table 1 into eqs. (1) and (2) for a single-stage decomposition were analysed according to the procedure. The Coats-Redfern plot for this example is shown in fig. 3. In order to investigate the usefulness of fitting data to the leading edge of the reaction, the figure also shows the fitting ranges that are used to produce the parameter estimates displayed in fig. 4. Here, although the α value is calculated for the entire reaction, the range of data the Coats-Redfern line is fitted to is varied as the lines of best fit are fitted to all the data, the central 90, 80 and 60 % of the data and the leading edge respectively. From this it can be concluded that the 'tail' of the Coats-Redfern plot created at the start of reaction (which appears at the right in fig. 3 as the plot is against $1/T$) has the largest effect on the slope of the line and therefore most distorts the parameter predictions arising from it. In this instance the Coats-Redfern method tends to overestimate both the activation energy and the pre-exponential factor emphasising the need for caution when comparing with reactivity data obtained by other methods. However, it can be confidently stated that relative to fitting to the entire dataset, a single-stage reaction may be well-estimated by simply fitting the Coats-Redfern line to the reaction's leading edge temperature interval.

Effect of Smoothing (One-Stage Decomposition)

During TGA volatility present in the results due to experimental inaccuracies and feedback loops that control the TGA device manifest as noise. Despite being regularly employed, the amount to which data is smoothed to reduce this volatility is rarely reported and is not mentioned in standard methods for extracting kinetics from TGA data. To analyse the effect of smoothing on the estimation of rate parameters a 10% random error as shown in eq. (5) is applied. Prior to undergoing the Coats-Redfern technique, various levels of smoothing are employed using a moving point average (eq. (6)). The idealised data with random noise along with a 10, 20 and 50 point either side smooth (respectively corresponding to 10 % 19 % and 46 % of the data for this reaction at this heating rate) are shown in fig. 5. Following the same data-fitting procedure employed without smoothing allowed parameter estimation and subsequent reconstruction of the mass and DTG curves (not shown). Comparing these reconstructed curves with the original data produced the results shown in fig. 6 where it is apparent that an increased degree of smoothing of the mass reading can have a substantial effect on not only the DTG profile but also the parameters that are predicted. Thus, it is suggested that a small amount of smoothing may be employed to graphically identify reaction zones more easily, but that any smoothing causes the Coats-Redfern method's accuracy to diminish and as such if used should be reported with the data and should be kept to a minimum function of the dataset, or if possible avoided completely.

$$M_i = \sum_{a=1}^{a=N} \left[m_{a,i-1} - (0.9 + 0.2 \times Z)\, k_{a,i} m_{a,i-1}\right] \tag{5}$$

where Z is a random number between 0 and 1 and the average mass $\bar{M}_t$ is given by

$$\bar{M}_t = \frac{\sum_{i=t-x}^{t+x} M_i}{2x+1} \tag{6}$$

Two-Stage Decomposition with Slight Overlap

Having proved that fitting the Coats-Redfern method only to the leading edge is able to estimate the rate parameters for one-stage decomposition, it is now useful to simulate overlapping reactions as is the case in most TGA data for fuels. This was completed by considering mass loss due to two independent, parallel reactions that overlap slightly as presented by the data in table 1 and shown in fig. 2.

Separating the decomposition into two stages and then following the same procedure as for the single-stage decomposition for each of the reaction stages, the estimates of parameters shown in table 2 were derived where trends similar to those seen for the single-stage decomposition were found. These figures indicate that modelling the leading-edge using the Coats-Redfern technique is able to provide a relatively good approximation of the reactivity even when the full extent of the reaction is convoluted in the TGA data by the presence of subsequent reactions. In fact, in this case, the overlap acts to reduce the overestimation of parameters by the Coats-Redfern method compared to the single-stage predictions. Using the results from the estimation procedure for the leading edge, the mass loss and DTG for the sample were recreated and compared with the original data displaying good agreement with R^2 values of 0.999 and 0.984 for correlation between the original and model-derived mass and DTG curves respectively.

Three-Stage Decomposition with Overlap

Further extending the previous work, a scenario that involves two initial reactions with considerable overlap followed by a third reaction set mostly apart from the first two was simulated using the values in table 1 which created the mass loss and DTG curves shown in fig. 2.

Due to the considerable overlap that occurs between the first two reactions it was not possible to investigate the effect of data fitting as in the previous examples (as is the case with realistic data it was impossible to separate the reactions graphically). In this scenario, the three reaction stages were identified and following the same procedure as detailed previously the results shown in table 3 were generated again displaying a similar trend to the single-stage decomposition results (fig. 4). The plot in fig. 7 was generated for the values estimated from the leading-edge temperature range.

The significant overlap between reactions in this example convolutes the data and reduces the ability of the method to accurately estimate single rate parameters. However, as shown in fig. 7 the method still manages to capture the overall reactivity of the decomposition well with R^2 values of 0.999 and 0.960 for the mass and DTG respectively, hence providing relative confidence for application of this method to real fuels.

Experimental Results

From the collected data, the mass and its first derivative were plotted in order to identify the reaction zones, leading edges and mass fraction per reaction which are presented in table 4. Using this data, the Coats-Redfern procedure as detailed above was then applied. An example plot for each of the three reaction stages along with the fitting range for the leading edge are shown in fig. 8 for willow decomposing in air at a heating rate of $10\,\mathrm{K\,min^{-1}}$. For conciseness estimations for activation energy and the pre-exponential factor are presented in table 4 rather than graphically. These parameters and the mass attributed to each reaction were then substituted into eqs. (1) and (2) to recreate the mass and DTG profiles which are shown in fig. 9 for willow and in fig. 10 for shea meal decomposing at $10\,\mathrm{K\,min^{-1}}$ in air in both cases. The recreated willow data was generally found to correlate well with the experimental data across the reaction temperature range with correlation R^2 values typically greater than 0.997 and 0.842 for the mass and DTG curves respectively. However, the inability to identify distinct reaction zones for the shea meal sample rendered the model less able to predict this decomposition with R^2 values of greater than 0.976 for the mass curve and in the region on 0.55 for the DTG curve. The relative reactivity (R_i) was then calculated using the air case at each heating rate as the reference case. The results shown in fig. 11 also include the normalised difference between the temperature at which maximum rate was found for each sample and the air case $T_{max,N}$. Comparing these two sets of results with the actual DTG profiles (see supporting material) it can be concluded that although the shea meal is relatively poorly characterised by the kinetic parameters (illustrated by the poor reconstruction correlation), the change in reactivity assessed by the procedure correlates well with changes in DTG. However, for the variation in the value of $T_{max,N}$ on unsmoothed data this is not the case as measurement noise can cause the maximum rate loss to be artificially predicted due to an outlier. Slight smoothing of the data tends to reduce this but has been shown also to affect the estimation of rate parameters. In this case, if smoothing is not employed it appears the model output (R_i) is a better indication of change in reactivity than $T_{max,N}$. However, if $T_{max,N}$ is found from slightly smoothed data the changes in this value and R_i correlate well. Moreover, although comparison of the rate parameters with external data would be questionable, comparison with trends in reactivity assessed by R_i is possible even with decompositions that have relatively complex overlapping reactions. For the willow sample the trends for both R_i and unsmoothed $T_{max,N}$ correlate well.

The findings for both biomasses broadly indicate an overall increase in reactivity with an increase in oxygen concentration which is in agreement with published literature.[26] This is even the case for reactions where the activation energy falls, emphasising the need for comparison of activation energy and pre-exponential values together. Figure 11 also shows that relatively small differences in reactivity are seen for the first two (devolatilisation) stages, which may even be considered negligible, while the reactivity during the final char combustion stage substantially benefits from the increase in oxygen concentration.

Comparison with Literature

As the R^2 values suggest, the actual parameters generated by the Coats-Redfern technique may not necessarily well-reflect changes in reactivity when compared separately and may not well reflect the decomposition they are modelling when considered individually. For this reason it is felt only the trends found and not the actual values should be compared with wider literature.

Conclusions

The simple, rapid Coats-Redfern procedure which is widely used by academe and industry has been formalised and further developed. This method's ability to estimate rate parameters for multi-stage overlapping reactions has been demonstrated by testing it on a variety of idealised decompositions where greater rigour in evaluating predictions against real data, and greater reporting of results than currently practiced is employed. The method's ability to identify changes in reactivity are demonstrated by comparing the decomposition of two biomass samples in two combustion atmospheres. The model was found to characterise the decomposition of willow well while an inability to distinguish separate reaction stages in the decomposition of shea meal rendered the method less able to characterise this decomposition. Nevertheless, changes in reactivity of the samples between the two combustion atmospheres were identified where the char reaction in particular was found to be more reactive in a combustion atmosphere with a higher oxygen concentration.

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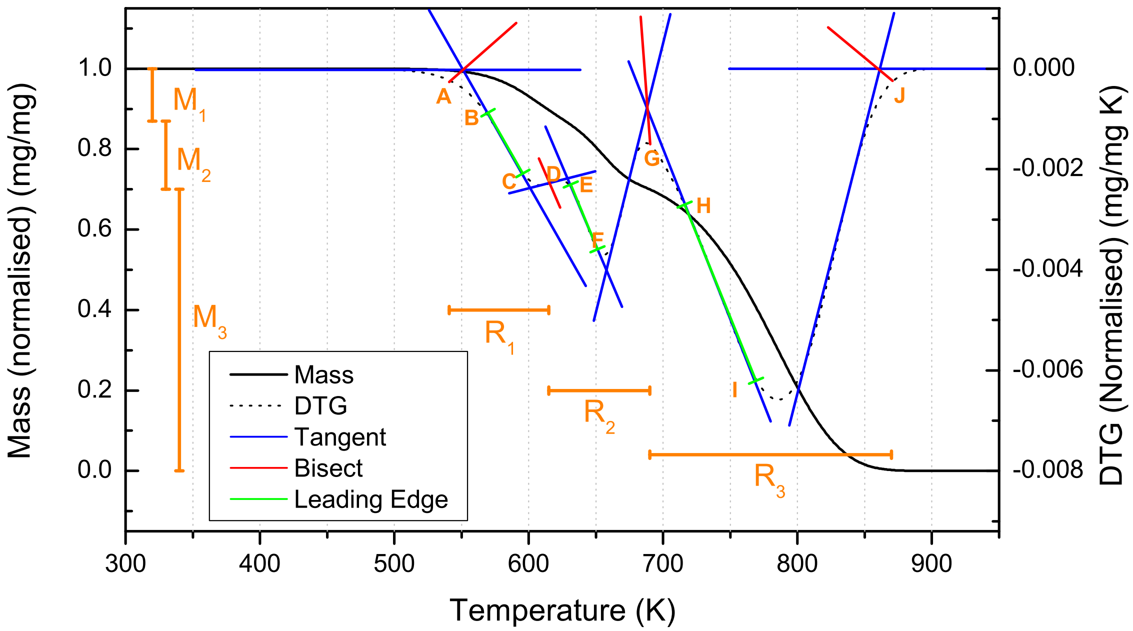

A	Stage 1 - Start	F	Leading Edge 2 - End
B	Leading Edge 1 - Start	G	Stage 2/3 Crossover
C	Leading Edge 1 - End	H	Leading Edge 3 - Start
D	Stage 1/2 Crossover	I	Leading Edge 3 - End
E	Leading Edge 2 - Start	J	Stage 3 - End

Figure 1: Graphical procedure for identifying reactions from DTG Data using three-stage decomposition as an example

Table 1: Rate parameters for generating idealised TGA data

Number of stages:	1	2		3		
Reaction:	i	i	ii	i	ii	iii
m_i	1	0.25	0.75	0.1	0.15	0.75
$E_{A,i}$ (kJ mol^{-1})	100	100	120	135	190	110
ln(A$_i$)	15.2	15.2	13.8	23.9	32.0	13.0

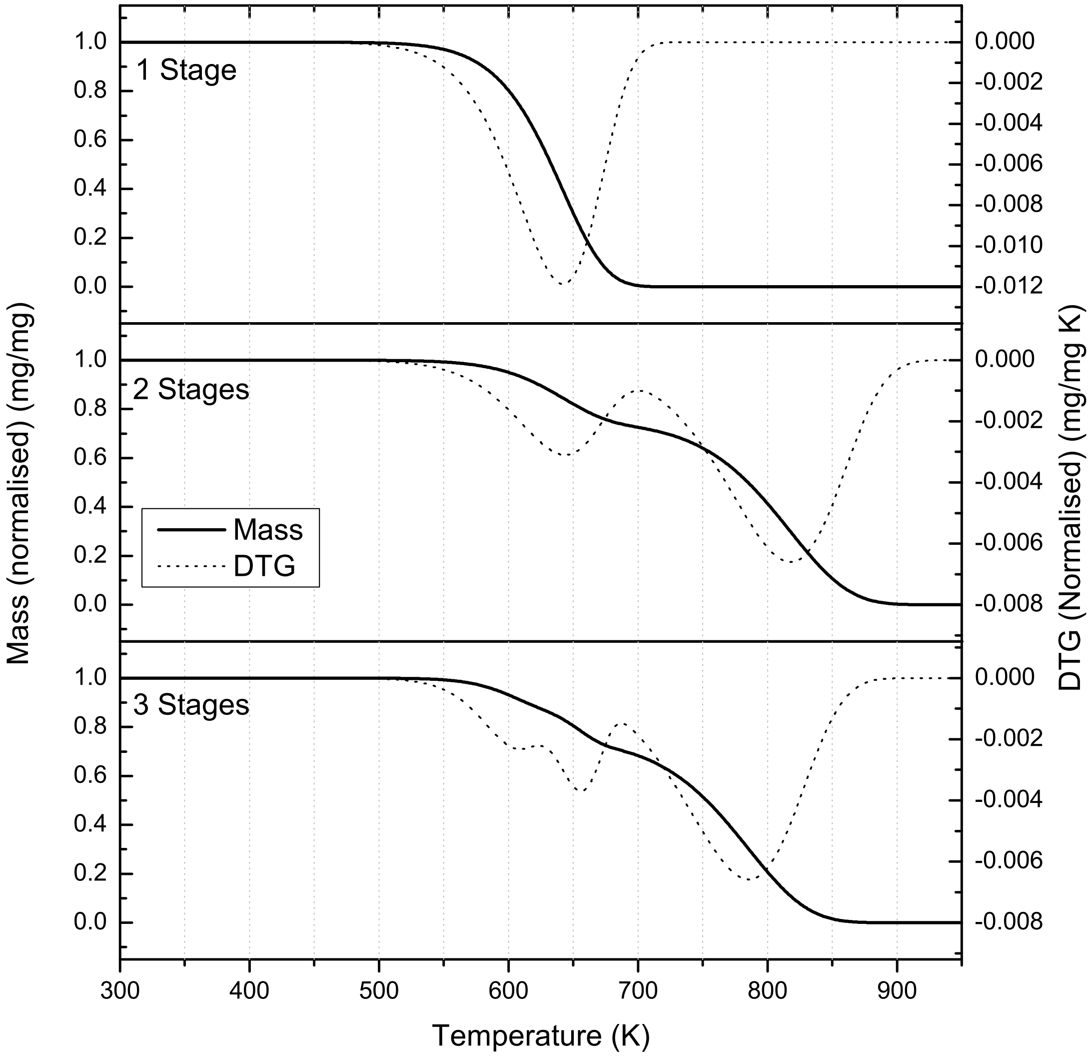

Figure 2: Idealised mass and DTG data for 1-, 2- and 3-stage decompositions

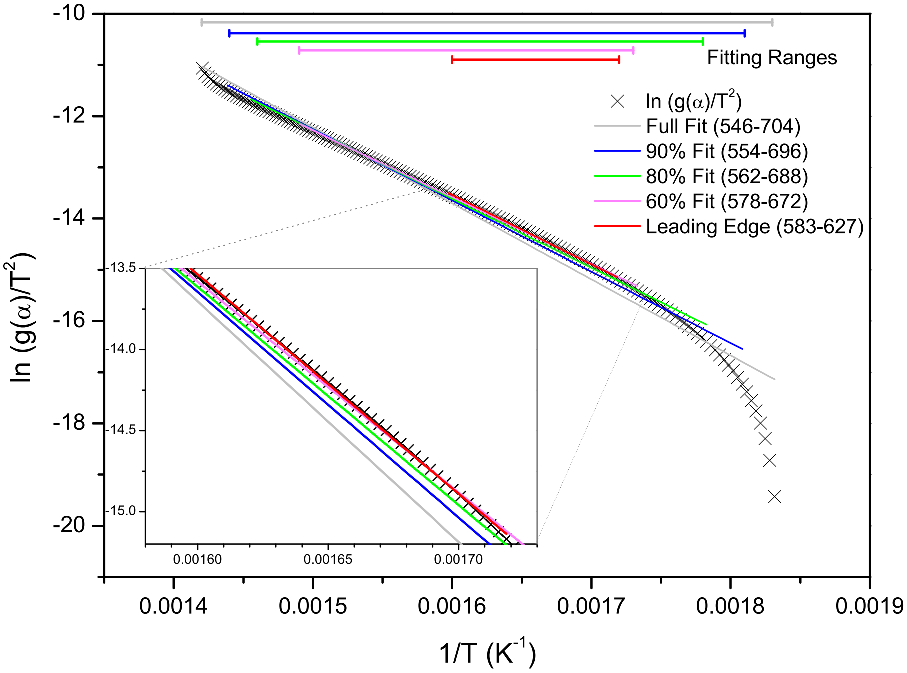

Figure 3: Coats-Redfern plot for dataset fitted to various proportions of the data

Table 2: Estimated rate parameters for 2-stage decomposition for varying widths of fit to the Coats-Redfern plot

	Full	90%	80%	60%	Leading Edge	Model
Stage 1: (545 K to 704 K), Leading Edge (590 K to 630 K)						
$E_{A,i}$ (kJ mol^{-1})	119.0	111.8	107.0	104.2	108.3	100
ln(A$_i$)	18.60	17.20	16.28	15.78	16.64	15.20
R^2	0.9584	0.9842	0.9933	0.9978	0.9996	n/a
Stage 2: (704 K to 903 K), Leading Edge (746 K to 793 K)						
$E_{A,i}$ (kJ mol^{-1})	152.9	142.9	136.7	132.0	143.8	120
ln(A$_i$)	18.68	17.17	16.24	15.53	17.46	13.81
R^2	0.9607	0.9881	0.9956	0.9988	0.9989	n/a

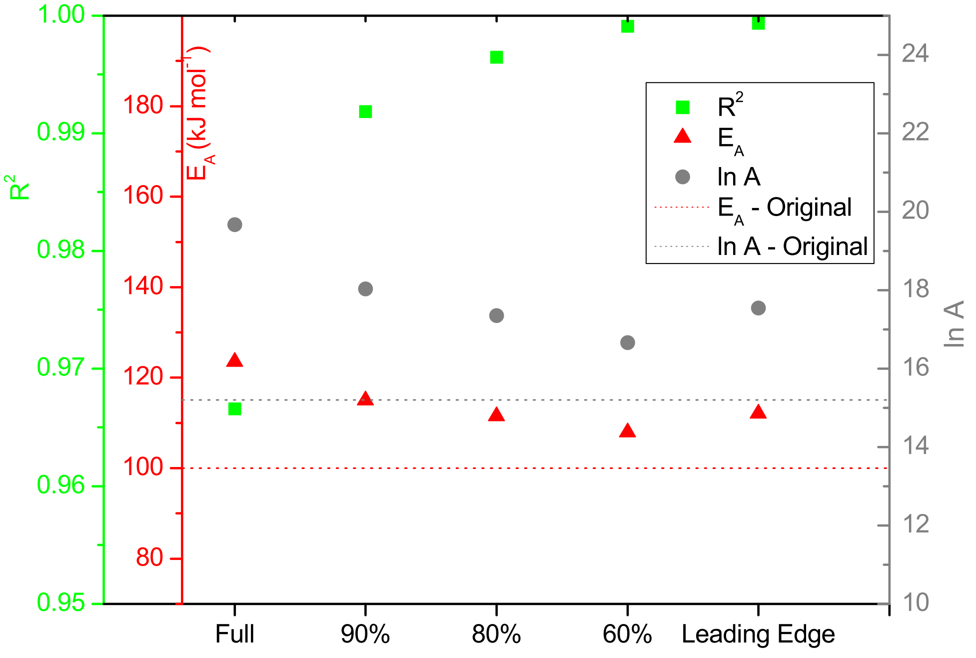

Figure 4: Variation in Coats-Redfern estimation for single-stage reaction depending on amount of data fitted to

Table 3: Estimated rate parameters for 3-stage decomposition for varying widths of fit to the Coats-Redfern plot

	Full	90%	80%	60%	Leading Edge	Model
Stage 1: (537 K to 617 K), Leading Edge (595 K to 627 K)						
$E_{A,i}$ (kJ mol^{-1}) ln(A_i) R^2	192.0 35.89 0.9628	182.5 33.89 0.9814	169.5 31.16 0.9948	161.5 29.47 0.9985	154.0 27.89 0.9999	135 23.94 n/a
Stage 2: (617 K to 688 K), Leading Edge (635 K to 650 K)						
$E_{A,i}$ (kJ mol^{-1}) ln(A_i) R^2	217.2 36.75 0.9486	204.7 34.42 0.9762	191.0 31.88 0.9930	185.3 30.83 0.9978	199.9 33.65 0.9995	190 32 n/a
Stage 3: (688 K to 873 K), Leading Edge (720 K to 760 K)						
$E_{A,i}$ (kJ mol^{-1}) ln(A_i) R^2	146.5 18.58 0.9529	136.6 17.03 0.9838	129.5 15.92 0.9941	124.5 15.16 0.9982	147.6 19.05 0.9977	110 13 n/a

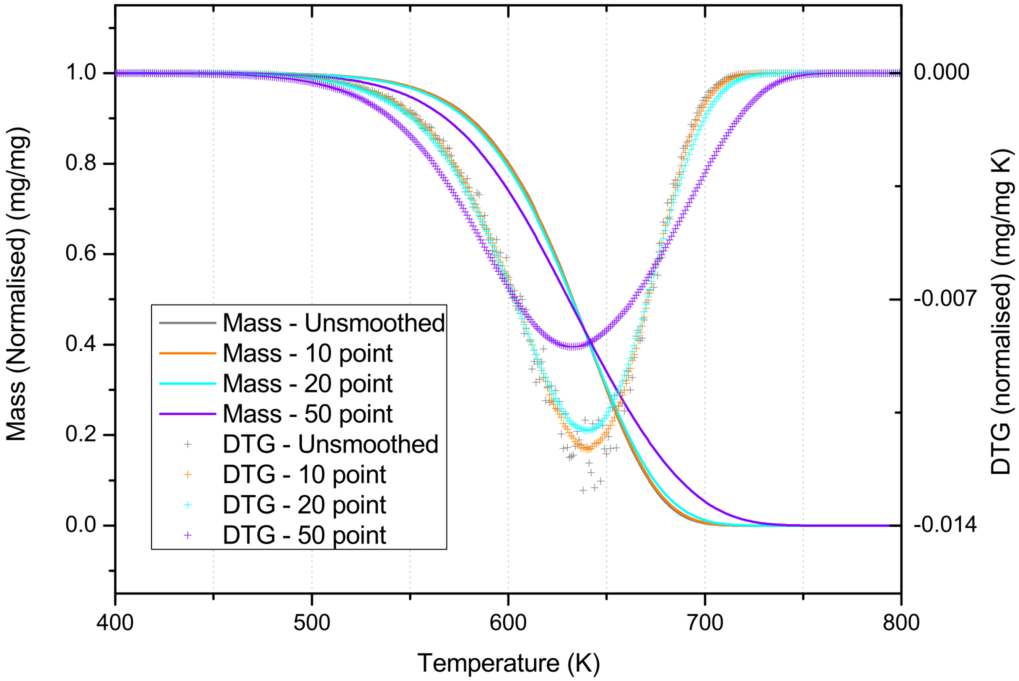

Figure 5: Effect of smoothing on mass and DTG data

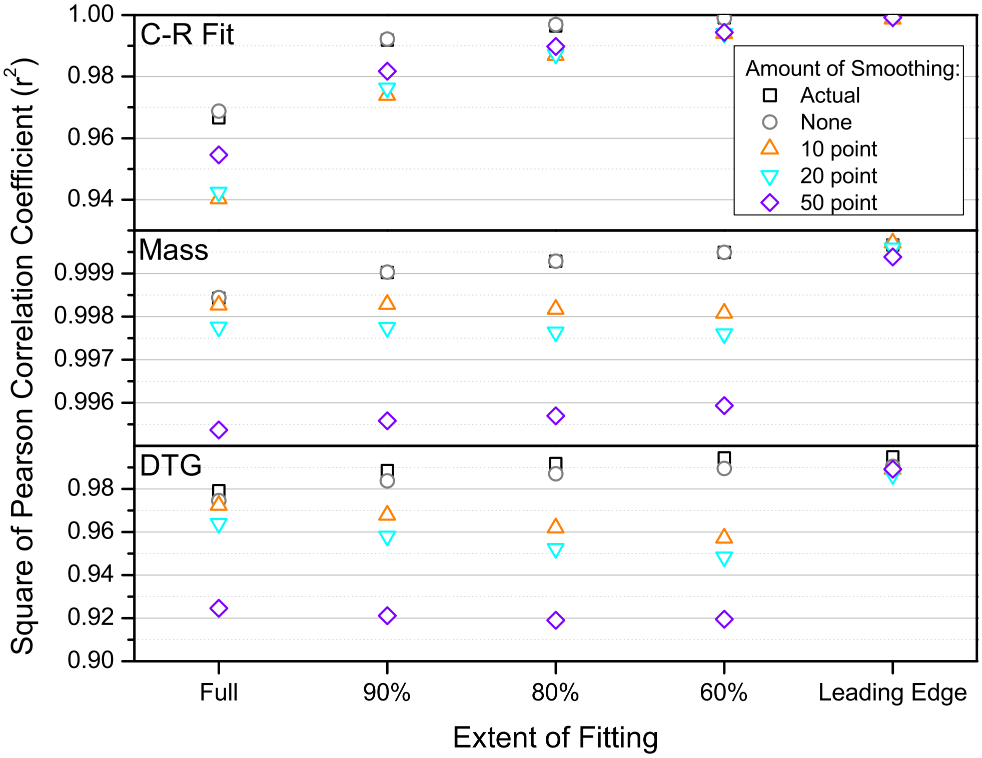

Figure 6: Variation in correlation between original data and that recreated by parameter estimation depending on level of smoothing performed prior to undergoing the Coats-Redfern procedure

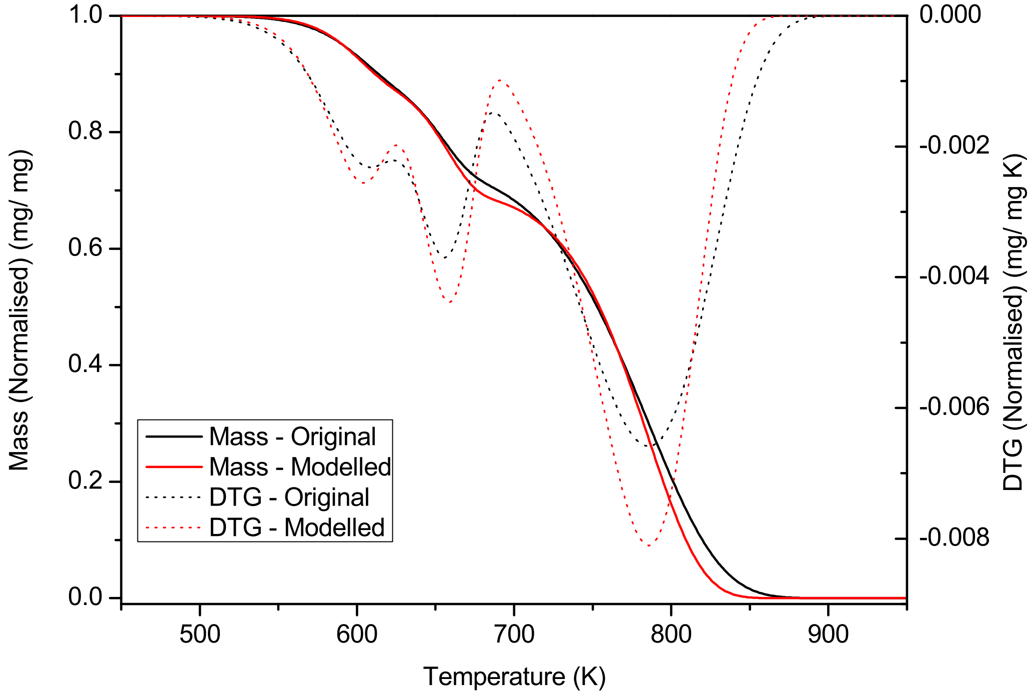

Figure 7: Original and recreated mass and DTG curves for 3-stage decomposition

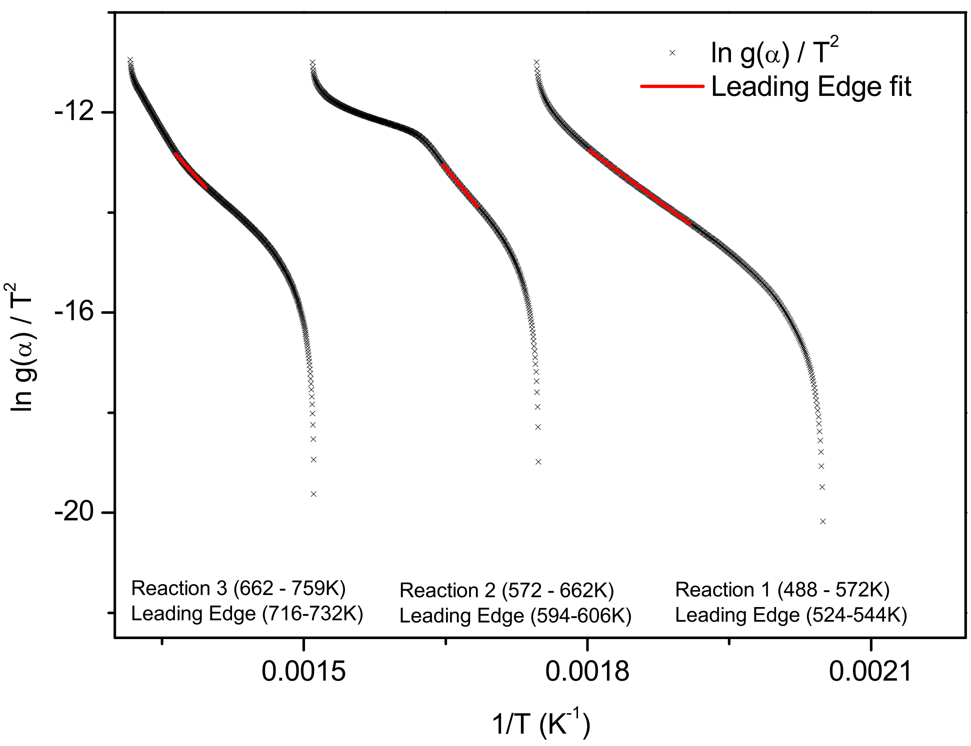

Figure 8: Coats-Redfern plots for willow reacting in air at $10\,\mathrm{K\,min^{-1}}$

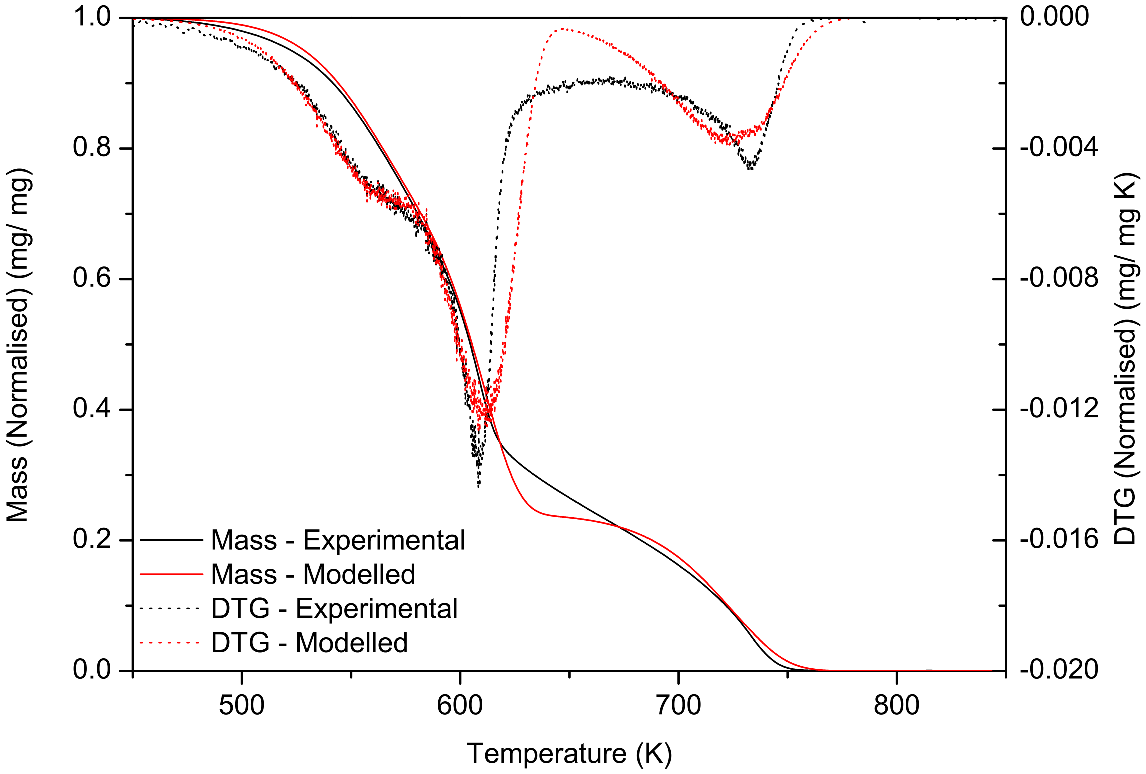

Figure 9: Comparison of experimentally derived and modelled mass and DTG data for willow decomposing in air

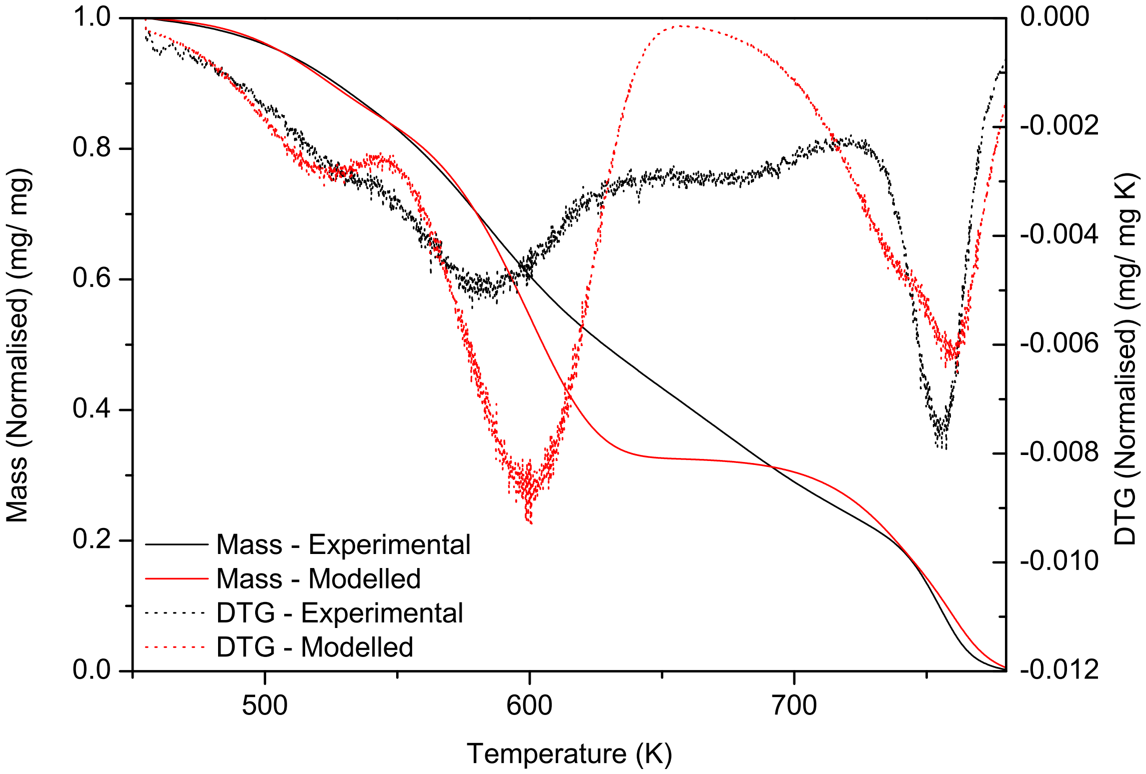

Figure 10: Comparison of experimentally derived and modelled mass and DTG data for shea meal decomposing in air

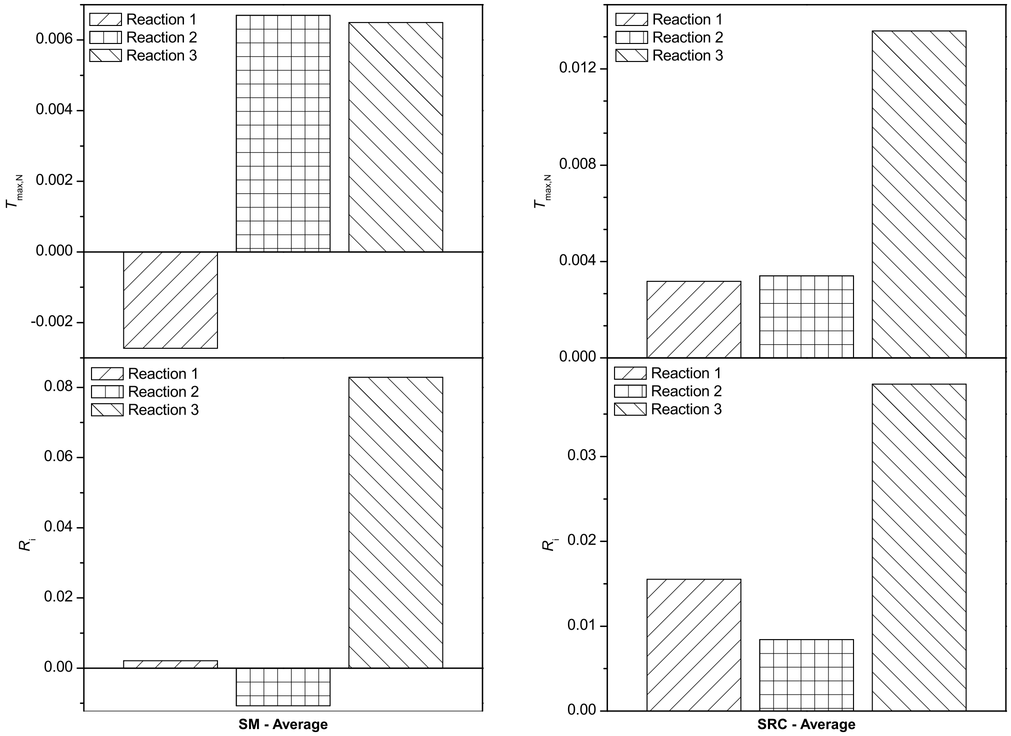

Figure 11: Averaged reactivity (R_i) and change in maximum rate temperature ($T_{max,N}$) of willow (SRC) and shea meal (SM) decomposing in oxygen-enriched air relative to air

Table 4: Parameters derived for willow and shea meal decomposition

O$_2$ %	β K min^{-1}	Stage	Reaction Range K	Leading Edge K	m_i	CR Fit R^2	E_{Ai} kJ mol^{-1}	ln A$_i$	Mass Rebuild R^2	DTG Rebuild R^2	$T_{max,i}$ K
Willow (SRC)											
21	10	1	488−572	522−544	0.25	0.9992	114.7	19.85	0.9977	0.8332	572.9
21	10	2	572−662	594−606	0.51	0.9994	188.4	32.51			608.3
21	10	3	662−759	716−732	0.24	0.9946	173.7	23.83			734.0
21	40	1	510−594	546−576	0.23	0.9994	118.4	21.06	0.9983	0.8809	593.8
21	40	2	594−688	616−632	0.50	0.9999	175.8	29.90			633.6
21	40	3	688−808	756−774	0.26	0.9976	143.8	18.70			777.2
30	10	1	496−570	530−552	0.24	0.9996	124.7	22.15	0.9970	0.8242	569.6
30	10	2	570−660	592−604	0.53	0.9993	196.6	34.38			605.6
30	10	3	660−750	714−724	0.24	0.9962	196.8	28.05			724.0
30	40	1	514−594	548−576	0.24	0.9996	122.0	21.83	0.9976	0.8895	593.3
30	40	2	594−690	614−628	0.50	0.9998	178.6	30.49			632.1
30	40	3	690−794	746−766	0.25	0.9964	163.1	22.11			766.7
Shea meal (SM)											
21	10	1	454−534	494−524	0.12	0.9975	100.3	18.38	0.9766	0.4936	530.2
21	10	2	534−686	548−578	0.55	0.9911	116.2	18.25			578.3
21	10	3	686−784	738−752	0.33	0.9914	208.8	28.47			757.4
21	40	1	462−554	503-540	0.14	0.9989	98.6	18.51	0.9874	0.5912	549.3
21	40	2	554−698	570−596	0.43	0.9932	119.4	19.56			606.6
21	40	3	698−868	760−788	0.44	0.9984	97.5	10.18			796.0
30	10	1	445−532	460−554	0.12	0.9985	101.8	18.85	0.9797	0.5298	532.3
30	10	2	532−685	548−578	0.57	0.9936	111.4	17.25			575.7
30	10	3	685−776	734−748	0.31	0.9925	218.1	30.31			750.3
30	40	1	460−554	500−540	0.14	0.9989	96.2	17.95	0.9839	0.5829	550.2
30	40	2	554−708	570-596	0.47	0.9936	117.9	19.19			601.3
30	40	3	708−842	758−776	0.39	0.9988	138.1	16.90			793.1

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Supporting Material

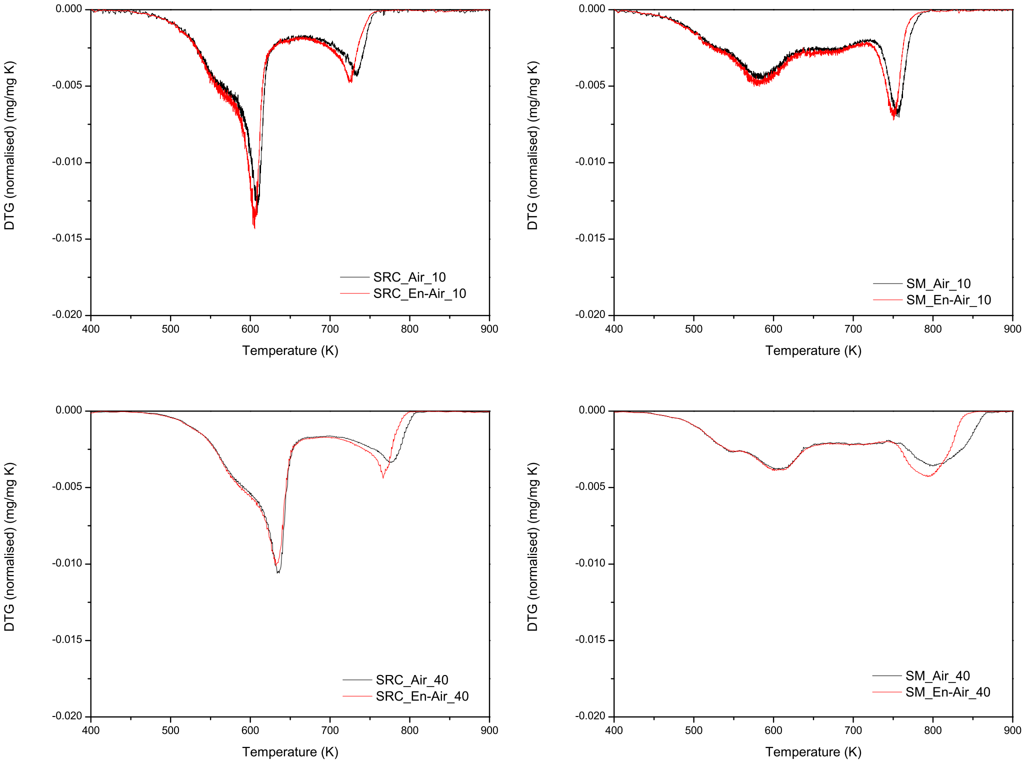

Figure 12: DTG curves of willow (SRC) and shea meal (SM) decomposing in air and oxygen enriched air at 10.40 K min^{-1}