Pyrolytic kinetics of coconut shell waste using Ramped PyrOx

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Abstract: Biomass pyrolysis is an efficient and economical conversion process. The kinetics of biomass conversion is still not fully understood mainly because this complex material is composed of numerous compounds with very different reactivities. In this work an inverse model is used to determine the nonparametric probability density function p(E_a) of activation energy (E_a) for coconut shell waste (CSW) pyrolysis via the Ramped PyrOx (RPO) method from the time-series and temperature-series mass conversion data. In this method, the degradation rates are described by inverting distributed activation energy model (DAEM). This method does not require p(E_a) to follow any particular parametric form furthermore the modelling results are independent of experimental conditions such as heating rates. The pyrolytic kinetics is modelled considering first-order degradation mechanism. The activation energies of pseudo-components were estimated as $246.5\ kJ \cdot mol^{-1}$, $264.2\ kJ \cdot mol^{-1}$, $290.4\ kJ \cdot mol^{-1}$ *and* $319.7\ kJ \cdot mol^{-1}$ *.*

Keywords: Coconut shell waste; Pyrolysis; Inverse modelling; Ramped PyrOx; Pseudo-components

1. INTRODUCTION

The thermal conversion of the biomass is typically carried out in a thermogravimetric analyser where the mass loss is recorded as a function of time and temperature. The obtained decomposition data describes the dynamics of the conversion process. The complexity of the conversion process is because of the different constituting components with varying reactivities and mechanisms. In order to better understand the process, it is necessary to properly interpret the dynamics from the decomposition rate data. In this study, a regularized inverse method is used. The data is first inverted to obtain a discrete distribution of degradation rates which give rise to an ill-conditioned system of algebraic equations. The inverted discretized system of equations is then regularized to get a meaningful approximate solution. The kinetic parameters are obtained from the best-fit rate distribution. The extent of regularization (ω) is set by the L-curve criterion at an optimum balance between the residual error and the roughness. This distributed model treats first order parallel degradation reactions described by probability density function $p(E_a)$ of the activation energy (E_a). As compared with the previous studies (LAKSHMANAN & WHITE, 1994: pages 1158–1167; CAI & LIU, 2007: pages 971–975; DE CAPRARIIS, DE FILIPPIS, HERCE, & VERDONE, 2012: pages 6153–6159), the inverse method does not require $p(E_a)$ to follow a particular parametric form, but rather estimates a nonparametric E_a distribution for the material left at any time which is independent of heating rates. Inverse methods are highly sensitive to noise, so the solution needs smoothening using smother regularization techniques such as Tikhonov regularization (TIKHONOV, 1977; HANSEN & O'LEARY, 1993: pages 1487–1503).

2. MATERIAL AND METHODS

2.1. Material

Whole coconut fruit was obtained from local market. The dried outer husk, shell and the inner fruit were separated carefully. The fragments of the coconut shell waste (CSW) were cleaned with water and air dried prior to its grinding to a fine powder in a hammer mill. The obtained powder was sieved and the fraction of the particle size less than 0.149 mm as per Tyler standard mesh screen was kept in air dried container for further characterisation.

2.2. Characterization

Elemental analysis of the CSW was carried out in CHN/S analyser and the proximate analysis was carried out using standard test methods. Thermogravimetric analysis was carried out in Perkin Elmer's the TGA 4000. The pyrolytic study was conducted in an inert atmosphere with a continuous supply of pure nitrogen gas. 10, 15 and 15 C/min heating rates were used separately to analyse the thermal behaviour of CSW in terms of mass loss. The details of the characterizing techniques and results can be found elsewhere (ALI, BAHAITHAM, & NAIBULHARAM, 2017: pages 1–11).

2.3. Kinetics analysis

Thermoanalytical instruments such as thermogravimetric analyzer (TGA) is frequently used to study the thermal reactivity of biomass samples (WHITE, CATALLO, & LEGENDRE, 2011: pages 1–33). Kinetic parameters of biomass pyrolysis are estimated from the mass-dependent differences in the degradation rates during heating. The rate constant at any temperature can be described by Arrhenius equation

$$k = A_0 \cdot \exp\left(-\frac{E_a}{RT}\right) \quad (1)$$

where A_0 is the Arrhenius pre-exponential factor and R is the ideal gas constant

Biomass is composed of pseudo-components during decomposition each one of these have unique kinetic parameter. During pyrolysis, the degradation rate of a particular pseudo-components i is often described with respect to the conversion of component i at any time t

$$\frac{d\alpha_i}{dt} = k_i \cdot f(\alpha_i) \quad (2)$$

where k_i is the dynamic first-order rate coefficient associated with component i at time t. Rate constant of component i can be determined as a function of E_{ai} following the Arrhenius equation

$$k_i = A_{0i} \cdot \exp\left(-\frac{E_{ai}}{RT}\right) \quad (3)$$

where A_{0i} is the Arrhenius pre-exponential and E_{ai} is the activation energy of the component i

For non-isothermal systems, time-dependent decay coefficients can therefore be described by the average E_{ai} at any heating rate as the DAEM is valid for any measured time-temperature history.

$$\frac{d\alpha_i}{dt} = A_{0i} \cdot \exp\left(-\frac{E_{ai}}{RT}\right) \cdot f(\alpha_i) \tag{4}$$

$$\frac{d\alpha_i}{f(\alpha_i)} = A_{0i} \cdot \exp\left(-\frac{E_{ai}}{RT}\right) dt \tag{5}$$

For a first order degradation of a pseudo-component referred to a single first-order reaction model

$$\alpha_i = 1 - \exp\left[-\int_0^t A_{0i} \cdot \exp\left(-\frac{E_{ai}}{RT}\right) dt\right] \tag{6}$$

Distributed activation energy model (DAEM) is a promising method to describe the non-isothermal decay of complex material such as biomass (BRADBURY, SAKAI, & SHAFIZADEH, 1979: pages 3271–3280; WHITE ET AL., 2011: pages 1–33) during thermogravimetric analysis. At lower heating rates, it correlates really well to the experimental data. For discrete DAEM, the overall conversion can be represented as the sum of the individual pseudo-component conversions involved in a number of parallel reactions.

$$\alpha = \sum_{i=1}^{N} \gamma_i \cdot \alpha_i \tag{7}$$

where γ_i is the fractional conversion of pseudo-component i

$$\alpha = \sum_{i=1}^{N} \gamma_i \cdot \left\{1 - \exp\left[-\int_0^t A_{0i} \cdot \exp\left(-\frac{E_{ai}}{RT}\right) dt\right]\right\} \tag{8}$$

In contrast a continuous DAEM considers a continuous distribution of reactants for more complicated set of reactions. In this case, an integral over all possible non-negative values of E_a is used

$$\alpha = 1 - \int_0^\infty \exp\left[-\int_0^t A_0 \cdot \exp\left(-\frac{E_a}{RT}\right) dt\right] p_0(E_a) \cdot dE_a \tag{9}$$

where $p_0(E_a)$ is the initial probability density function of activation energy and $p_0(E_a) \cdot dE_a$ is the fraction of probability density associated with the infinitesimal range of activation energy. The equation contains double-layer of integrals, including E_a to vary from 0 to infinite which makes it harder to compute. Normalizing $p(E_a) \cdot dE_a$ yields

$$\int_0^\infty p_0(E_a) \cdot dE_a = 1 \tag{10}$$

At any time, $p(E_a) \cdot dE_a$ can be calculated from the product of $p_0(E_a) \cdot dE_a$ and double exponential decay

$$p(E_a) \cdot dE_a = \exp\left[-\int_0^t A_0 \cdot \exp\left(-\frac{E_a}{RT}\right) dt\right] p_0(E_a) \cdot dE_a \tag{11}$$

$$\alpha = 1 - \int_0^\infty p(E_a) \cdot dE_a$$

DAEM usually consider *nth*-order non-isothermal kinetic models (BRAUN & BURNHAM, 1987: pages 153–161; WHITE ET AL., 2011: pages 1–33) , superposition of parallel first-order reactions. Differentiating with respect to time, the total rate of degradation at any time t is given by the equation:

$$\frac{d\alpha}{dt} = \int_0^\infty A_0 \exp\left(-\frac{E_a}{RT}\right) \cdot \exp\left[-\int_0^t A_0 \cdot \exp\left(-\frac{E_a}{RT}\right) dt\right] p_0(E_a) \cdot dE_a \tag{12}$$

$$\frac{d\alpha}{dt} = \int_0^{\infty} A_0 \cdot \exp\left(-\frac{E_a}{RT}\right) \cdot p(E_a) \cdot dE_a \tag{13}$$

2.4. Inverse Modelling

The matrix form of the DAEM can be written as

$$\mathbf{g} = \mathbf{A} \cdot \mathbf{p} \tag{14}$$

The vector E over a discretized interval can be represented as

$$\Delta E_{a_l} = \frac{1}{2}\left(E_{a_l} - E_{a_{l-1}}\right) + \frac{1}{2}\left(E_{a_{l+1}} - E_{a_l}\right) \tag{15}$$

The vector p representing the discretized E can be described as

$$p_l = \frac{1}{\Delta E_{a_l}} \int_{\frac{1}{2}\left(E_{a_l}+E_{a_{l-1}}\right)}^{\frac{1}{2}\left(E_{a_l}+E_{a_{l+1}}\right)} p_0(E_a) dE_a \tag{16}$$

The matrix A is the obtained discretised Laplace transform operator

$$A_{jl} = exp\left\{-\sum_{u=0}^{j} A_0 exp\left[-\frac{E_{a_l}}{RT(t_u)}\right]\Delta t_u\right\}\Delta E_{a_l} \tag{17}$$

In inverse modeling, the degradation rates are described by inverting distributed activation energy model (DAEM).

$$\mathbf{p} = \mathbf{A^{-1}}.\mathbf{g} \tag{18}$$

The minimization criterion is fulfilled by solving the constrained least squares problem according to the following vectorial form

$$\min_P \|\mathbf{A} \cdot \mathbf{p} - \mathbf{g}\|^2 \tag{19}$$

This first derivative of the solution vector as a measure of roughness can be written as

$$\left\|\frac{dp_0(E_a)}{dE_a}\right\| = \sqrt{\sum_{l=1}^{n_l}\left[\frac{p_{l+1}(E_a) - p_l(E_a)}{E_{a_{l+1}} - E_{a_l}}\right]^2} = \|\mathbf{R} \cdot \mathbf{p}\| \tag{20}$$

where R is the bi-diagonal operator, the solution is obtained by minimizing the sum of the residual error and the roughness of the data.

$$\min_P \|\mathbf{g} - \mathbf{A} \cdot \mathbf{p}\|^2 + \omega\|\mathbf{R} \cdot \mathbf{p}\|^2 \tag{21}$$

where ω is the regularization parameter which control the data fitting with residual error.

The nonparametric probability density function $p(E_a)$ of the activation energy (E_a) was obtained from the inverse model using the open-source "rampedpyrox" version 0.2 (HEMINGWAY, 2016).

3. RESULSTS AND DISCUSSIONS

Figure 1, shows the thermogram and fractional mass of volatile matter remaining with respect to time and temperatures. The DTG curves indicates multicomponent degradations in the active pyrolysis zone with overlapping peaks.

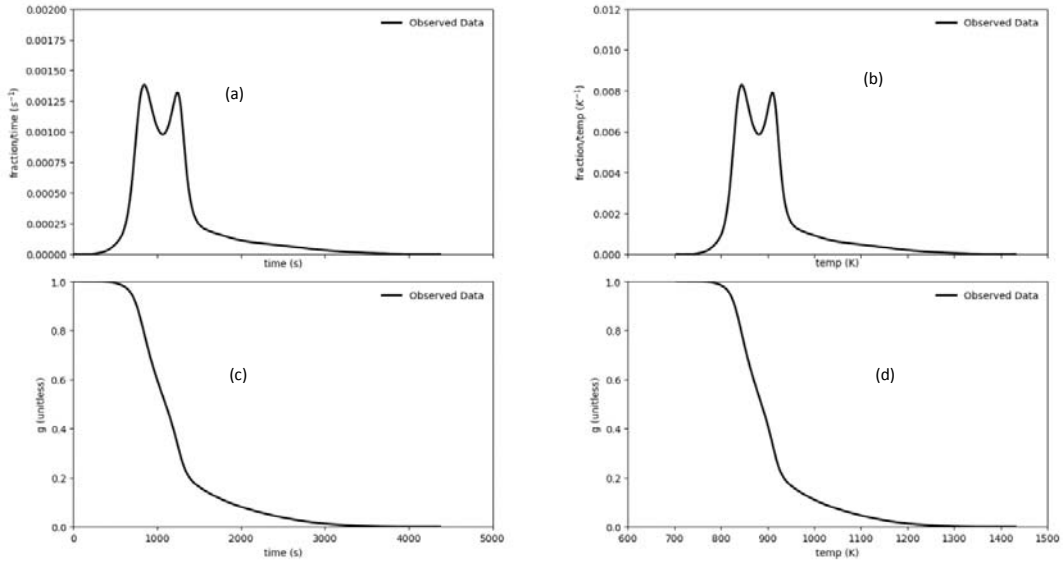

Figure 1 a) DTG curve with respect to time, b) DTG curve with respect to temperature, c) fraction volatiles remaining with respect to time and d) fraction volatiles remaining with respect to temperature

To determine the optimum value of regularization parameter (ω), an L-curve method was adopted (HANSEN & O'LEARY, 1993: pages 1487–1503). The best-fit gives smooth solution of $p_0(E_a)$ while residual error is the measure of uncertainty.

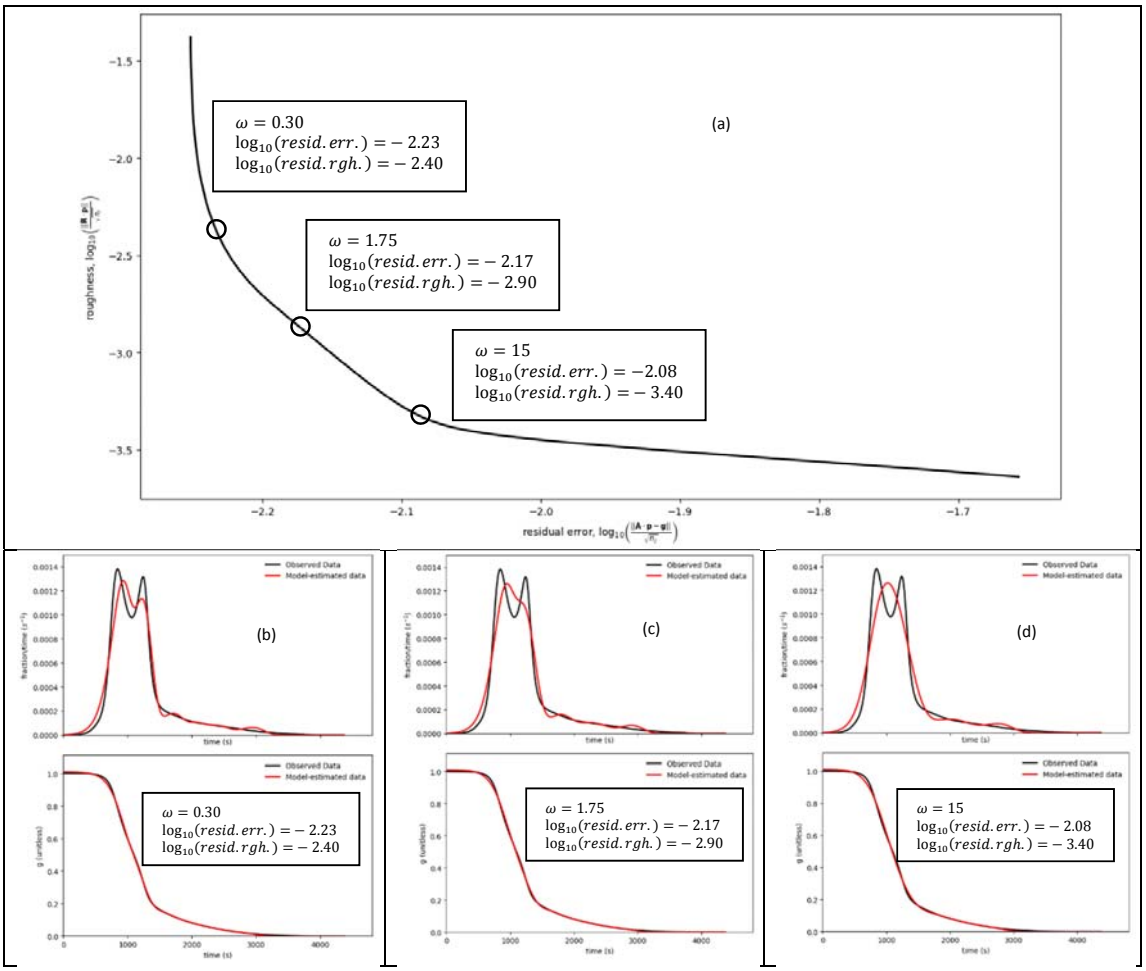

Figure 2 a) L-curve, b) DTG and fraction volatile remaining curves corresponding to $\boldsymbol{\omega = 0.3}$, c) DTG and fraction volatile remaining curves corresponding to $\boldsymbol{\omega = 1.75}$ and, d) DTG and fraction of volatile remaining curves corresponding to $\boldsymbol{\omega = 15}$

The $\boldsymbol{\omega = 0.3}$ corresponds to best fit with higher residual error, whereas $\boldsymbol{\omega = 15}$ lowers residual error at the expense of loose fitting of the data. An average between the best-fit and residual error with $\boldsymbol{\omega = 1.75}$ however can be considered acceptable as it represents a tradeoff between the residual error and best fit.

The non-parametric $p_0(E_a)$ is shown in Figure 3. It is indicated that there are four distinct peaks with activation energies of $246.5\ \mathrm{kJ \cdot mol^{-1}}$, $264.2\ \mathrm{kJ \cdot mol^{-1}}$, $290.4\ \mathrm{kJ \cdot mol^{-1}}$ and $319.7\ \mathrm{kJ \cdot mol^{-1}}$. Each peak corresponds to a pseudo-component while the identification of the pseudo-components as the constituents of the CSW is not evident.

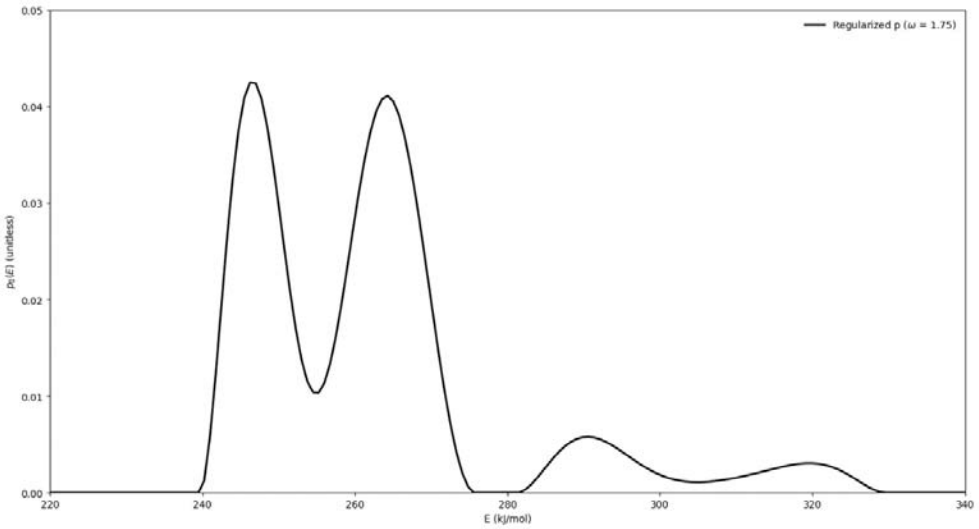

Figure 3 Probability density function of activation energies

The values obtained from the inverse model are higher than previously reported using model-free and model-fitting methods (ALI ET AL., 2017: pages 1–11). This method has an advantage over other methods as the $p_0(E_a)$ does not require parametric form. The disadvantage of inverse problem is that it is an ill-posed problems where there is no guarantee of a unique solution. The kinetic parameters obtained from this method can be used to predict the non-isothermal experimental data at other heating rates.

4. CONCLUSIONS

This study describes the use of inverse model for the kinetic study of the coconut shell waste (CSW) pyrolysis. The experimental thermogravimetric data was modelled as first-order degradation. The optimised solution of inverse problem was chosen to be a trade-off between the best fit and the residual error. The activation energies of pseudo-components were found to be $246.5\ kJ \cdot mol^{-1}$, $264.2\ kJ \cdot mol^{-1}$, $290.4\ kJ \cdot mol^{-1}$ and $319.7\ kJ \cdot mol^{-1}$. Although this method does not require pyrolytic data at different heating rates and parametric form of distribution for DAEM but it lacks the ability to distinguish the pseudo-components. Moreover, the pre-exponential factor also require to be inputted from other method. Despite of these uncertainties, the kinetic parameters derived from non-isothermal experiments can be used to predict or forward model non-isothermal experimental data.

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