An efficient and general analytical approach to modelling pyrolysis kinetics of oil shale

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HIGHLIGHTS

- Novel approach to analytical modelling pyrolysis kinetics of oil shale is presented.
- The methodology is generic which can model many types of reaction kinetics.
- The model is efficient, accurate, easily implemented and application-independent.
- Comparison with measurements and numerical simulations shows excellent agreement.
- Favorable generalizations and extensions of the modelling approach are presented.

ARTICLE INFO

ABSTRACT

This paper presents a new approach to analytical modelling pyrolysis kinetics of oil shale based on Arrhenius equation which is inherently nonlinear allowing no exact analytical solution. The proposed method introduces an approximation which leads to a significant simplification of the closed-form solution and the calculation and allows for rapid estimates of kinetic parameters. The analytical model is successfully validated by both experimental data and the numerical model ($R^2 > 0.99$). In addition, the developed methodology and model are sufficiently general which can be applied to other types of fuel resources and chemical reactions. To demonstrate, some generalizations and extensions of representative kinetic models in wide-area applications are presented. The proposed modelling approach improves over the state-of-the-art methods for pyrolysis kinetics models in its efficiency, simplicity, generality and application-independence. The model is easy to implement and computationally attractive.

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1. Introduction

As an energy source, oil shale pyrolysis has been produced over hundreds years through heating the oil shale to a temperature that the kerogen, the organic portion of the oil shale, decomposes into gas, oil and coke [1,2]. Broadly, two basic oil shale retorting processes, in situ (underground) and ex situ (aboveground), are used. Both techniques require energy to heat the oil shale to pyrolysis temperature. Modelling the pyrolysis kinetics of oil shale for an understanding of the decomposition mechanisms and kinetic parameters are significant for designing and operating an energy efficient pyrolysis process because pyrolysis is a very complicated thermochemical conversion process involving extremely complex reactions and the end products depend on numerous factors [3]. Hence, despite extensive knowledge of the process, an exact mechanism and kinetic modelling for oil shale pyrolysis is difficult or practically impossible. Therefore, many comprehensive pyrolysis models are based on Arrhenius-type kinetic equation for interpreting fundamental mechanism of the entire pathway or specific mechanisms within the pathway. Arrhenius model has a long history of use as pyrolysis kinetics and revisiting the mechanisms for pyrolysis and the relevant models so far developed demonstrate its generality which has proven to be a valuable analysis tool with wide applications [3–8].

Arrhenius kinetics for decomposition is modelled based on the two most important and frequently used parameters: activation energy and pre-exponential factor (e.g. [4]). Since an accurate Arrhenius model equation is inherently nonlinear in nature allowing no exact analytical solution, numerical techniques become necessary to find the solutions and the parameters (e.g. [9]).

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The underlying mechanisms remain elusive with numerical approaches.

The analytical model, on the other hand, has an advantage that it can provide a clear description of the primary kinetics and parameters for the underlying mechanisms. It is suited to understand the outcomes and to interpret the experiments. Extensive analyses, therefore, have been performed to explore thermal decomposition kinetics and to determine kinetic parameters for pyrolysis kinetics of oil shale as well as for other types of biomass using analytical models (see, for example, [10,11], for general reviews). Two basic principles regarding the methodology can be identified among the analytical models: integral and differential methods based on Coats–Redfern [12] and Friedman [13] approaches and their modifications [6,14–16]. Typically, Thermogravimetry (TG) and Differential Thermal Analysis (DTA) experiments are conducted under either isothermal or non-isothermal condition. The TG/DTG data are analyzed and the kinetic parameters are adjusted based on the kinetic model equation using goodness of fit assessment [17]. Graphical methods are often used to evaluate goodness of fit.

Although simple, an obvious disadvantage with these methods is that it describes observations of the data only without showing the underlying mechanism by which the data are produced. Another relevant disadvantage which is directly tied to this is that graphical methods generally suffer from poor statistical properties (see, for example, [10]). Attempts have been made to improve these methods and majority of the improvements are made to better approximate the Arrhenius temperature integral (see [4,6,18,19] for a general review). The temperature integral is always encountered which permits no analytical solution. The approximation of the temperature integral is usually done through predefined formula, which is undoubtedly related to the unknown kinetic mechanisms. Accuracy is often sensitive to the form of the assumed kinetic mechanisms [6,20,21], which presents a major challenge in kinetics analysis. This requires prior knowledge of the kinetic mechanisms which is often inaccessible in practice.

This paper presents a radically new analytical methodology to address such an issue to improve upon past analytical models. We approach the temperature integral problem differently than existing models in that the proposed model does not make any assumptions on the temperature integrals or kinetic mechanisms. The developed model provides a closed-form expression of the decomposition kinetics based on kinetic parameters. Experimental and numerical validations show an exceedingly high accuracy of the model ($R^2 > 0.99$).

One significant aspect of the developed modelling method is the straightforward formalism for the final model solution which represents a significant simplification of the closed-form solution and calculation and allows for rapid estimates of kinetic parameters. The proposed approach is highly efficient, simple, accurate, yet universal which can be easily modified and extended to accommodate other reaction kinetic features. To demonstrate, we present its generality and practicality through representative wide-area applications and show that many popular existing models can be expressed as instances of our model. Therefore, although the paper concentrates on oil shale pyrolysis, the proposed methodology will be of great interest to researchers and engineers for modelling other types of chemical reactions for fuels [22]. Finally, the implementation is extremely simple which can be achieved with a few lines of code or with spreadsheets or even with a pencil and paper.

2. Methods

2.1. Kinetic model

The kinetics of kerogen decomposition to shale oil is described in two steps [23,24]:

$$kerogen \rightarrow bitumen + gas \rightarrow oil + gas + residue$$

and modelled as an n-order reaction equation as [25] for retorting process

$$\frac{dX}{dt} = k(1-X)^n \tag{1}$$

where X is the weight loss or mass fraction or conversion (%) defined as

$$X = \frac{w_0 - w_t}{w_0 - w_f} \tag{2}$$

w_0: initial weight;
w_t: weight at time t;
w_f: final weight;
k: rate coefficient given by Arrhenius equation:

$$k = A \exp\left(-\frac{E}{RT}\right) \tag{3}$$

A: pre-exponential factor;
E: activation energy;
R: gas constant;
T: temperature.

Assuming a constant heating rate $\beta = \frac{dT}{dt}$, an integration of Eq. (3) results in a plot of $\ln\left(-\frac{\ln(1-X)}{T^2}\right)\left(\ln\left(\frac{1-(1-X)^{1-n}}{(1-n)T^2}\right) \text{ if } n > 1\right)$ against $1/T$ being a straight line. The kinetic parameters are determined using its slope and intercept. This graphical method is based on Coats–Redfern method which is the most commonly used parameter estimation approach. Despite of ease of use, graphical method has some limitations as described in Section 1. In the following we propose a new model to overcome these limitations.

2.2. The proposed approximate analytical model

Assume $n = 1$. As we'll see later that this assumption is for a simple illustration only and the reaction order is not limited to linear one. Since a constant heating rate $\beta = \frac{dT}{dt}$ is the most common case in applications, Eq. (1) leads to

$$\frac{dX}{1-X} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right)dT \tag{4}$$

Integration of Eq. (4) gives

$$\int_{X_0}^{X} \frac{dX}{1-X} = \int_{T_0}^{T} \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right)dT - \ln(1-X)\Big|_{X_0}^{X}$$

$$= \frac{A}{\beta} \int_{T_0}^{T} \exp\left(-\frac{E}{RT}\right)dT \tag{5}$$

The right-hand integral cannot be calculated analytically. We propose its approximation as follows:

$$\int_{T_0}^{T} \exp\left(-\frac{E}{RT}\right)dT = \frac{RT^2}{E} \exp\left(-\frac{E}{RT}\right)\Big|_{T_0}^{T}$$

$$- \int_{T_0}^{T} \frac{2RT}{E} \exp\left(-\frac{E}{RT}\right)dT \tag{6}$$

Rearrange of the terms containing integrals together leads to

$$\int_{T_0}^{T} \left(1 + \frac{2RT}{E}\right) \exp\left(-\frac{E}{RT}\right)dT = \frac{RT^2}{E} \exp\left(-\frac{E}{RT}\right)\Big|_{T_0}^{T} \tag{7}$$

For a small temperature change ΔT, $1 + \frac{2RT}{E}$ is approximately constant. Therefore, Eq. (7) can be approximated as