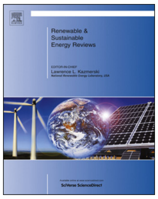
Renewable and Sustainable Energy Reviews 36 (2014) 236–246

Contents lists available at ScienceDirect

Renewable and Sustainable Energy Reviews

journal homepage: www.elsevier.com/locate/rser



An overview of distributed activation energy model and its application in the pyrolysis of lignocellulosic biomass

Junmeng Cai [a,b,*], Weixuan Wu [a], Ronghou Liu [a]

[a] Biomass Energy Engineering Center, Key Laboratory of Urban Agriculture (South) Ministry of Agriculture, School of Agriculture and Biology, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, PR China
[b] State Key Laboratory of Heavy Oil Processing, China University of Petroleum, 18 Fuxue Road, Beijing 102249, PR China

ARTICLE INFO

Article history:
Received 5 August 2013
Received in revised form
27 February 2014
Accepted 27 April 2014
Available online 20 May 2014

Keywords:
Distributed activation energy model (DAEM)
Lignocellulosic biomass
Pyrolysis
Kinetics
Parameter estimation method
Numerical calculation

ABSTRACT

Research interest in the conversion of lignocellulosic biomass into energy and fuels through the pyrolysis process has increased significantly in the last decade as the necessity for a renewable source of carbon has become more evident. For optimal design of pyrolysis reactors, an understanding of the pyrolysis kinetics of lignocellulosic biomass is of fundamental importance. The distributed activation energy model (DAEM) has been usually used to describe the pyrolysis kinetics of lignocellulosic biomass. In this review, we start with the derivation of the DAEM. After an overview of the activation energy distribution and frequency factor in the DAEM, we focus on the numerical calculation and parameter estimation methods of the DAEM. Finally, this review summarizes recent results published in the literature for the application of the DAEM to the pyrolysis kinetics of lignocellulosic biomass.

Contents

1. Introduction

The pyrolysis of lignocellulosic biomass has attracted considerable attention because it is the thermochemical process that converts lignocellulosic biomass into liquid fuel (bio-oil), which is easy to store and transport when compared to raw biomass [1,2]. Knowledge of the kinetics is important in the computational fluid dynamics modeling of biomass pyrolysis process [3]. And in the pyrolysis process of lignocellulosic biomass, the relative rates of decomposition, cracking, and repolymerization/condensation reactions influence the quantity and quality of bio-oil produced as well as the long-term storage stability of the bio-oil [4].

The distributed activation energy model (DAEM) is a multiple reaction model, which is widely used in the pyrolysis of

---

[*] Corresponding author at: Biomass Energy Engineering Center, Key Laboratory of Urban Agriculture (South) Ministry of Agriculture, School of Agriculture and Biology, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, PR China. Tel./fax: +86 21 34206624.
E-mail address: jmcai@sjtu.edu.cn (J. Cai).

http://dx.doi.org/10.1016/j.rser.2014.04.052
1364-0321/

lignocellulosic biomass [5]. The model assumes the decomposition mechanism take a large number of independent, parallel, first-order or *n*th-order reactions with different activation energies reflecting variations in the bond strengths of species. The difference in activation energies can be represented by a continuous distribution function [6]. The DAEM is not only used to describe the pyrolysis kinetics of lignocellulosic biomass and its main components, but also to describe the pyrolysis kinetics of coal [7–9] and other thermally degradable materials [10–13].

In order to better understand the DAEM and its application in the pyrolysis of lignocellulosic biomass, an overview of the research and development in the DAEM for the pyrolysis of lignocellulosic biomass is conducted. The derivation of the DAEM was first presented. Then, the activation energy distribution and frequency factor in the DAEM are overviewed and the numerical calculation of the DAEM is discussed. In Section 5, the methods for the estimation of the DAEM kinetic parameters are critically studied. Finally, the up-to-date research efforts in the DAEM for the pyrolysis of lignocellulosic biomass are summarized.

2. Derivation of DAEM

The concept of an activation energy distribution was originally proposed by Vand [14] and later used by Pitt [15] and Anthony [16]. The DAEM for lignocellulosic biomass pyrolysis may be applied to either the total amount of volatiles released, or to the amount of an individual volatile constituent. The description in this work follows the total amount volatiles released. It is assumed that lignocellulosic biomass has many chemical groups which are numbered $i=1,\ldots,s$, and the released mass fraction for the *i*th group is $V_i(t)$. The contribution of the decomposition of the *i*th group is assumed to be described by the pseudo-*n*th-order rate equation

$$\frac{\mathrm{d}(V_i/V_i^*)}{\mathrm{d}t}=k_i\left(\frac{V_i^*-V_i}{V_i^*}\right)^n=A_i\exp\left(-\frac{E_i}{RT}\right)\left(\frac{V_i^*-V_i}{V_i^*}\right)^n \tag{1}$$

where V_i^* is the total released mass fraction for the *i*th group, n is the reaction order and k_i is the reaction rate constant, A_i is the frequency factor, E_i is the activation energy, R is the universal gas constant, T is the temperature, and t is the time.

Eq. (1) can be written in its integral form

$$\frac{V_i}{V_i^*}=\begin{cases}1-\left[1-(1-n)\int_0^t A_i\ \exp\left(-\frac{E_i}{RT}\right)\mathrm{d}t\right]^{1/(1-n)} & n\neq 1\\ 1-\exp\left[-\int_0^t A_i\ \exp\left(-\frac{E_i}{RT}\right)\mathrm{d}t\right] & n=1\end{cases} \tag{2}$$

The complexity of lignocellulosic biomass pyrolysis is such that a continuous distribution $f(E)$ of activation energies is assumed where $\int_E^{E+\Delta E} f(E)\mathrm{d}E$ describes the probability that chemical groups with a sample have an activation energy in this range E to $E+\Delta E$. The mass fraction of potential volatile material with activation energies between E and $E+\mathrm{d}E$, $\mathrm{d}V^*$, at a given time t is $V^*f(E)\mathrm{d}E$.

$$\mathrm{d}V^*=V^*f(E)\mathrm{d}E \tag{3}$$

Then, V_i^* and V_i are replaced by $\mathrm{d}V^*$ and $\mathrm{d}V$, respectively. Then Eq. (2) becomes

$$\mathrm{d}V=\begin{cases}V^*\left\{1-\left[1-(1-n)\int_0^t A\ \exp\left(-\frac{E}{RT}\right)\mathrm{d}t\right]^{1/(1-n)}\right\}f(E)\mathrm{d}E & n\neq 1\\ V^*\left\{1-\exp\left[-\int_0^t A\ \exp\left(-\frac{E}{RT}\right)\mathrm{d}t\right]\right\}f(E)\mathrm{d}E & n=1\end{cases} \tag{4}$$

The integration of Eq. (4) leads to

$$\alpha=\frac{V}{V^*}=\begin{cases}1-\int_0^\infty\left[1-(1-n)\int_0^t A\ \exp\left(-\frac{E}{RT}\right)\mathrm{d}t\right]^{1/(1-n)}f(E)\mathrm{d}E & n\neq 1\\ 1-\int_0^\infty\exp\left[-\int_0^t A\ \exp\left(-\frac{E}{RT}\right)\mathrm{d}t\right]f(E)\mathrm{d}E & n=1\end{cases} \tag{5}$$

where α is the degree of conversion.

Differentiating Eq. (5) with respect to t, the expression of $\mathrm{d}\alpha/\mathrm{d}t$ is

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=\begin{cases}\int_0^\infty A\ \exp\left(-\frac{E}{RT}\right)\left[1-(1-n)\int_0^t A\ \exp\left(-\frac{E}{RT}\right)\mathrm{d}t\right]^{n/(1-n)}f(E)\mathrm{d}E & n\neq 1\\ \int_0^\infty A\exp\left[-\frac{E}{RT}-\int_0^t A\ \exp\left(-\frac{E}{RT}\right)\mathrm{d}t\right]f(E)\mathrm{d}E & n=1\end{cases} \tag{6}$$

Most laboratory experiments involving the pyrolysis of lignocellulosic biomass are performed at temperatures linearly varying with time from a starting temperature, T_0 [17]. Under the linear heating program, Eqs. (5) and (6) can be rewritten as Eqs. (7) and (8)

$$\alpha=\begin{cases}1-\int_0^\infty\left[1-(1-n)\int_{T_0}^T\frac{A}{\beta}\ \exp\left(-\frac{E}{RT}\right)\mathrm{d}T\right]^{1/(1-n)}f(E)\mathrm{d}E & n\neq 1\\ 1-\int_0^\infty\exp\left[-\int_{T_0}^T\frac{A}{\beta}\ \exp\left(-\frac{E}{RT}\right)\mathrm{d}T\right]f(E)\mathrm{d}E & n=1\end{cases} \tag{7}$$

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T}=\begin{cases}\int_0^\infty\frac{A}{\beta}\exp\left(-\frac{E}{RT}\right)\left[1-(1-n)\int_{T_0}^T\frac{A}{\beta}\exp\left(-\frac{E}{RT}\right)\mathrm{d}T\right]^{n/(1-n)}f(E)\mathrm{d}E & n\neq 1\\ \int_0^\infty\frac{A}{\beta}\exp\left[-\frac{E}{RT}-\int_{T_0}^T\frac{A}{\beta}\exp\left(-\frac{E}{RT}\right)\mathrm{d}T\right]f(E)\mathrm{d}E & n=1\end{cases} \tag{8}$$

where β is the heating rate.

3. *f*(*E*) and *A* in DAEM

A popular choice for the activation energy distribution is the Gaussian distribution centered at E_0 with standard deviation σ

$$f(E)=\frac{1}{\sigma\sqrt{2\pi}}\exp\left[-\frac{(E-E_0)^2}{2\sigma^2}\right] \tag{9}$$

The disadvantage of the Gaussian distribution is that it is symmetric whereas the actual reactivity distributions tend to be asymmetric [18]. The asymmetry can be accounted for by replacing the Gaussian distribution with other distributions, e.g. the Weibull [19–21] or Logistic [22,23] distributions.

The Weibull distribution was first proposed to describe chemical reactivity distributions for the pyrolysis of petroleum source rocks [19]. For the Weibull distribution, $f(E)$ is given by

$$f(E)=\frac{\lambda}{\eta}\left(\frac{E-\gamma}{\eta}\right)^{\lambda-1}\exp\left[-\left(\frac{E-\gamma}{\eta}\right)^{\lambda}\right] \tag{10}$$

where λ is the shape parameter, η is the width parameter, and γ is the activation energy threshold ($E\geq\gamma$). The mean activation energy E_0 and the standard deviation σ of the Weibull distribution are defined by

$$E_0=\gamma+\eta\Gamma\left(1+\frac{1}{\lambda}\right) \tag{11}$$

$$\sigma=\sqrt{\eta^2\Gamma^2\left(\frac{2}{\lambda}+1\right)-\eta^2\Gamma^2\left(\frac{1}{\lambda}+1\right)} \tag{12}$$

where Γ is the Gamma function. Because of the activation energy threshold, Eqs. (7) and (8) should be written in the following forms if the Weibull distribution is considered