Renewable and Sustainable Energy Reviews xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Renewable and Sustainable Energy Reviews

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

# Processing thermogravimetric analysis data for isoconversional kinetic analysis of lignocellulosic biomass pyrolysis: Case study of corn stalk

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ARTICLE INFO

*Keywords:*
Thermogravimetric analysis (TGA)
Kinetic analysis
Biomass pyrolysis
Isoconversional kinetic method
Effective activation energy

ABSTRACT

Modeling of lignocellulosic biomass pyrolysis processes can be used to determine their key operating and design parameters. This requires significant amount of information about pyrolysis kinetic parameters, in particular the activation energy. Thermogravimetric analysis (TGA) is the most commonly used tool to obtain experimental kinetic data, and isoconversional kinetic analysis is the most effective way for processing TGA data to calculate effective activation energies for lignocellulosic biomass pyrolysis. This paper reviews the overall procedure of processing TGA data for isoconversional kinetic analysis of lignocellulosic biomass pyrolysis by using the Friedman isoconversional method. This includes the removal of "error" data points and dehydration stage from original TGA data, transformation of TGA data to conversion data, differentiation of conversion data and smoothing of derivative conversion data, interpolation of conversion and derivative conversion data, isoconversional calculations, and reconstruction of kinetic process. The detailed isoconversional kinetic analysis of TGA data obtained from the pyrolysis of corn stalk at five heating rates were presented. The results have shown that the effective activation energies of corn stalk pyrolysis vary from 148 to 473 kJ $mol^{-1}$ when the conversion ranges from 0.05 to 0.85.

## 1. Introduction

Lignocellulosic biomass can be used to produce renewable electricity, thermal energy, or biofuels, and chemicals via various conversion technologies, such as combustion, gasification, pyrolysis, bio-digestion, fermentation, etc. [1,2]. The advantages that make biomass energy a perfect alternative to fossil fuels include: (1) it is a renewable form of energy; (2) it is carbon neutral; and (3) it is widely available. Lignocellulosic biomass pyrolysis, a thermochemical conversion process of heating lignocellulosic biomass in the absence of oxygen usually at 300–600 °C, has the potential to offer high efficiencies for the production of liquid fuels which can be readily stored or transported [3,4]. The yields of those products are dependent upon the feedstock, thermal environment, heating rate and final pyrolysis reaction temperature [5–8]. Specifically, at a moderate pyrolysis reaction temperature (about 500 °C) and under high heating rates, the main product is bio-oil [9,10]. Biomass pyrolysis can be performed through different types of pyrolysis reactors [11], such as fluidized bed [12], auger [13], rotary kiln [14], down-tube [15], and free fall reactors [16].

A comprehensive understanding of pyrolysis kinetics of a biomass feedstock is important to the process design, feasibility assessment and scaling in industrial applications [17–19]. Fig. 1 shows a schematic flowchart for the overall process design of biomass pyrolysis. In general, the design of biomass pyrolysis processes requires hydrodynamics and transport simulation which involves information about mass and heat transfer as well as kinetics [20]. The optimal parameters for a pyrolysis process should meet the requirements of mass and heat transfer efficiency and pyrolysis kinetics [21,22].

Thermogravimetric analysis (TGA) is usually used for the kinetic analysis of lignocellulosic biomass pyrolysis. According to the search results based on two keywords "thermogravimetric analysis" and "biomass pyrolysis" from the Web of Science Database (http://isiknowledge.com), there are over 1350 papers about biomass pyrolysis kinetic analysis by using TGA published in scientific journals indexed by SCI from 2000. Fig. 2 shows the annual number of publications from 2000 to August 2017, which indicates that TGA has been used to investigate the kinetic mechanism of lignocellulosic biomass pyrolysis by more and more researchers. Recently, Bach and Chen [23]

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http://dx.doi.org/10.1016/j.rser.2017.09.113
Received 14 April 2017; Received in revised form 4 September 2017; Accepted 26 September 2017
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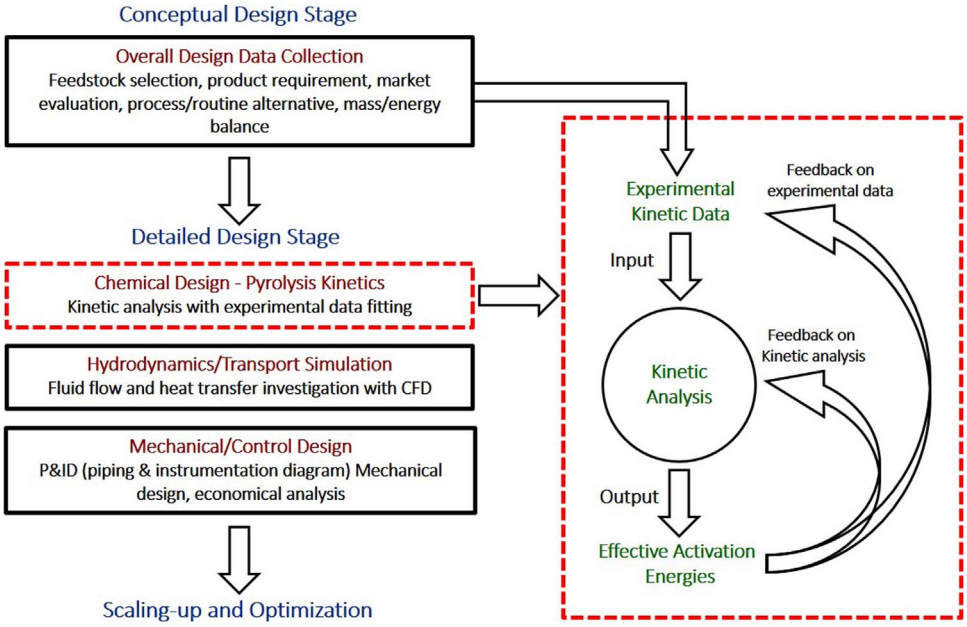


**Fig. 1.** Flow chart of design of biomass pyrolysis processes.

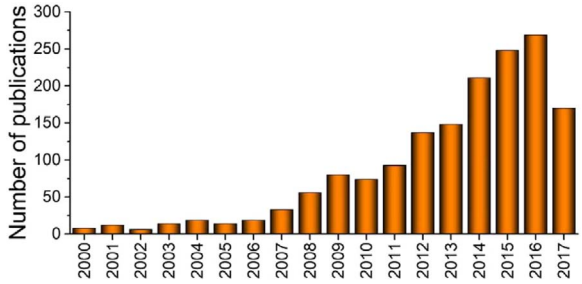


**Fig. 2.** Number of annual publications from 2000 to present on "thermogravimetric analysis" and "biomass pyrolysis" (based on search results from Web of Knowledge Database).

provided a review on recent activities in pyrolysis characteristics and kinetics of various microalgae via TGA and pointed out that the kinetics via TGA was conductive to pyrolysis reactor design, operation optimization, and biofuel production. White et al. [24] concluded that many factors could affect the kinetic parameters based on the processing of TGA data, including process conditions, heat and mass transfer limitations, physical and chemical heterogeneity of the sample, and systematic errors. Saddawi et al. [25] focused on the data analysis method for extracting reliable kinetic data from TGA experiments.

There are two kinds of kinetic methods used for the analysis of biomass pyrolysis kinetics: model-fitting and isoconversional methods [26–28]. According to Sánchez-Jiménez et al. [29], the use of model-fitting methods may reach analogous conclusions: almost any conversion function can satisfactorily fit experimental data at the cost of estimating drastically different kinetic parameter values. The uncertainty in estimating kinetic parameters caused by the use of model-fitting methods can be avoided in the use of isoconversional methods.

There are many isoconversional kinetic methods including the Friedman differential isoconversional method [30], the Ozawa-Flynn-Wall linear integral isoconversional method [31,32], the Kissinger-Akahira-Sunose linear integral isoconversional method [33], the Vyazovkin nonlinear integral isoconversional method [34], the advanced Vyazovkin nonlinear integral isoconversional method [35], and the Cai-Chen iterative linear integral isoconversional method [36]. The corresponding equations for obtaining the effective activation energies, advantages and disadvantages of various isoconversional methods are shown in Table 1. Of those isoconversional kinetic methods, the Friedman isoconversional method is the most widely used isoconversional method because its simplicity and high accuracy. Although the Friedman method is sensitive to data noise, the effect of noise on the isoconversional calculation can be reduced by considering not only data for a specific degree of conversion but also information in its neighborhood [37] or by applying some advanced smoothing methods [38].

When studying the kinetics of lignocellulosic biomass pyrolysis, the variation of activation energy with conversion obtained from isoconversional methods was frequently observed [39–44]. This variable activation energy was also called as the effective activation energy [45]. Processing TGA data is very important to obtain the effective activation energies for lignocellulosic biomass pyrolysis. Researchers have demonstrated some mathematical approaches about it. Caballero and Conesa [46] presented an overview of some relevant mathematical aspects involved in the thermal decomposition processes. Carrier et al. [47] summarized the data preparation and kinetic modeling of biomass pyrolysis by using the Friedman isoconversional method. Although they have discussed some aspects of processing TGA data for isoconversional kinetic analysis, a comprehensive study about the isoconversional kinetic analysis from TGA data of lignocellulosic biomass pyrolysis is still missing in the literature. Thus, the aim of this paper is to present the entire process of processing TGA data for isoconversional kinetic analysis of lignocellulosic biomass pyrolysis taking corn stalk pyrolysis as an example.

## 2. TGA

### 2.1. Brief introduction of TGA

TGA is a thermal analytical technique in which the changes in the mass of a sample is measured as a function of time or temperature as it is subjected to a controlled temperature program in a controlled atmosphere [48]. TGA can provide information about some chemical reactions or about some physical transitions [49]. According to our previous review [50], TGA can be used as an effective tool to perform the proximate analysis of solid fuels. A thermogravimetric analyzer usually consists of a sample pan that is supported by a precision balance [51]. The sample pan is placed in a furnace where the heating temperature and environment are controlled. The mass of the sample is continuously measured and recorded during the experiment.

By coupling a TGA instrument with evolved gas analysis (EGA)

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