Energy Conversion and Management xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Energy Conversion and Management

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

A combined genetic algorithm and least squares fitting procedure for the estimation of the kinetic parameters of the pyrolysis of agricultural residues

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ARTICLE INFO

Article history:
Received 16 November 2015
Received in revised form 24 April 2016
Accepted 29 April 2016
Available online xxxx

Keywords:
Biomass
Pyrolysis
Thermogravimetry
Genetic algorithm
Evaluation function
Least squares

ABSTRACT

The main objective of this study is to implement a two-step fitting procedure to estimate the kinetic parameters of two distinct pyrolysis models to study the pyrolysis of pine bark, wheat straw and rice husk. Thermogravimetric curves were obtained for the three biomass fuels for heating rates of 5, 10 and 15 K/min in an inert atmosphere of Argon to investigate the impact of the type of biomass in the pyrolysis behavior under different heating conditions. Distinctive thermogravimetric and differential thermogravimetric curves were obtained owing to the different composition of the biomass fuels. For the conditions examined, the impact of the heating rate on the profile curves was marginal. In order to better understand the impact of the biomass composition in the pyrolysis, their main components were estimated. Additionally, a two-step algorithm was used to calibrate the global kinetic parameters of a single reaction model and of a three parallel reaction model, based on the fitting of predicted curves to the experimental ones. The first step was a genetic algorithm procedure. An evaluation function that minimizes the deviation between the experimental and predicted pyrolysis yields, while preserving the characteristics of the mass decomposition during pyrolysis, is presented in this work. The second step was a least squares minimization that was used for further refining the solution obtained in the first step. The method showed excellent repeatability. For each biomass fuel, all heating rates were globally fitted, with errors of the order of ~5% for the single reaction model and of less than 1.6% for the three parallel reaction model. The activation energies obtained by fitting each model to the experimental data are generally within the values reported in the literature. Finally, a sensitivity analysis showed that the variation of the composition of each biomass used in this study does not affect significantly the predictions of the three parallel model.

1. Introduction

Biomass is one of the most abundant and used sources of renewable energy in the world with reduced impact on global warming. Biomass is becoming more relevant as an energy carrier due to its high diversity and availability. It includes plants, leftovers from agricultural materials and forestry processes, as well as organic, industrial, animal and human wastes. Agricultural wastes, in particular, contain high amounts of organic constituents (cellulose, hemicellulose, lignin and minor amounts of other organics) and possess high energy content [1]. Biomass can be upgraded through pyrolysis, which is a form of thermal treatment that decomposes organic materials into liquid, solid and gaseous forms in the absence of oxygen. All three-output fractions have potential as fuels for transports, power generation and combined heat and power [2]. Most biomass upgrading processes are optimized to woody biomass [3]; however, due to economic and environmental reasons, only a part of the available forest biomass can be used. In this context, in addition to forest biomass, it is critical to use also agricultural residues for energy purposes. The extreme variability of the biomass feedstock demands for an extensive investigation on the impact of its composition in their pyrolysis behavior.

Thermogravimetric (TG) and differential thermogravimetric (DTG) curves allow studying the pyrolysis behavior, relate it to the feedstock properties and isolated it from transport processes when heating rates are low, i.e., under these conditions it can be assumed that temperature and species concentration gradients inside the sample are marginal. Di Blasi [4] made an extensive review of a large number of studies focused on modelling the biomass pyrolysis process based on thermogravimetric studies. In her review, Di Blasi describes the single first order reaction model

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http://dx.doi.org/10.1016/j.enconman.2016.04.104
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(SFOM), which considers only one component and one stage of decomposition, and the three parallel model (3PM), which describes the decomposition of the cellulose, hemicellulose and lignin assuming that there are no interactions between these components, and that these reactions occur at the same time. Until very recently, the most common procedures used to estimate the kinetic parameters in the referred models were based in Arrhenius plot methods such as Kissinger–Akahira–Sunose (KAS) [5] and Flynn–Wall–Ozawa (FWO) [6]. These are linear regression methods that are only able to estimate two kinetic parameters (activation energy and pre-exponential factor) of one or multiple conversion stages of one single component [5]. However, when multi-component mechanisms with the occurrence of several parallel reactions are taken into account, the usage of these methods can be quite difficult and its results can become questionable [7]. With the continuous increase of computing power, optimization methods such as genetic algorithm (GA) and least squares procedures have emerged as an alternative for the estimation of multiple kinetic parameters, as these have significant advantages when compared to the Arrhenius plot method. Firstly, optimization methods can be used for optimizing parameters from a broad range of empirical models, e.g., SFOM and multiple-PM, where more than two constants of the Arrhenius equation can be estimated using the latter method. Furthermore, fitting procedures make use of all experimental data available (no information is lost), whereas in the Arrhenius plot method the conversion stages are treated in a discrete way, i.e., information is lost.

Recent studies where least squares fitting procedures have been used in the context of biomass pyrolysis include those of Vamvuka et al. [8], Grønli et al. [9], Di Blasi [4] and Cai and Ji [10]. In these studies, TG and DTG curves were obtained for heating rates between 10 and 30 K/min. Cai and Ji [10] fitted the kinetic parameters using a least squares solver applied to the TGA data of peanut shells at a heating rate of 10 K/min, and obtained a very small deviation between the experimental and predicted mass fraction curves. Vamvuka et al. [8] fitted a 3PM curve to the respective DTG curves using a least squares procedure, with the goal of studying the effects of the composition of the biomass fuel and concluded that different amounts of each component lead to distinctive pyrolysis peaks and width. Grønli et al. [9] obtained the kinetic parameters for the pyrolysis of hardwoods and softwoods by fitting a 5PM rate curve to the respective DTG curves using a least squares procedure. The authors showed that unified activation energies for the three biomass components are able to describe the pyrolysis behavior with good accuracy. Burhenne et al. [3] applied the kinetic parameters derived by Di Blasi [4] and Grønli et al. [9] to model the pyrolysis of woody biomass (spruce and bark) and agricultural biomass (wheat and rape straw). In this work [3], the mass fractions of the three main biomass components were obtained by fitting the pyrolysis DTG curves using a least-squares procedure. These last studies showed that the lignin content of any biomass feedstock is the main controlling factor in pyrolysis. They also showed that, at higher heating rates (20–30 K/min), the distinct peaks associated with the different constituents may not appear because some of them can be thermally decomposed simultaneously, overlapping each other in the DTG profiles.

There are a few studies that used GAs as a fitting procedure for the estimation of biomass pyrolysis parameters. Jiang et al. [7], for instance, studied the pyrolysis of extruded polystyrene and rigid polyurethane at heating rates between 5 and 20 K/min, and obtained a good agreement between calculated and experimental results for all heating rates. In this study, where the SFOM was used to describe the process of pyrolysis, the activation energies obtained using the GA were consistent with those obtained by isoconversional methods. Vascellari et al. [11] and Rabaçal et al. [12] used the GA to fit calculated pyrolysis curves using empirical models to predict pyrolysis curves using predictive models. In both cases, predictive pyrolysis models were used to obtain a decomposition curve for the initial stage of coal conversion. Dhumal and Saha [13] fitted the kinetic parameters using the GA applied to TGA data at heating rates between 20 and 40 K/min. These authors highlighted the simple implementation of the GA and that this tool provides good results for multivariable optimization problems. Finally, it is worth mentioning the study of Authier et al. [14] that used the GA combined with a least squares method as a fitting procedure in the case of coal devolatilization during combustion in a TGA and a drop tube furnace, evidencing that this two-step fitting procedure leads to more accurate and reliable results. There was not much focus given to the evaluation function of the GA in these previous studies, probably because the decomposition was considered only for one-rate models, which produce curves that are relatively trivial to fit. Note that when the three main components of biomass are considered at low heating rates, the pyrolysis yield and rate curves present distinctive features for which fitting may not be trivial.

It is generally agreed that the extreme variability of the biomass residual feedstock composition can have an impact on the pyrolysis behavior. In this context, the main objective of this work is to implement a two-step fitting procedure to estimate the kinetic parameters of two distinct pyrolysis models to study the pyrolysis of agricultural residues. Pine bark, wheat straw and rice husk were selected given a lack of studies addressing these specific types of biomass in the literature, filling a gap still existing in the kinetic modelling of non-woody biomass. Thermogravimetric experiments were performed using different heating conditions (5, 10 and 15 K/min) in order to investigate the influence of the type of biomass. The TG and DTG curves were used as a reference to fit the predicted curves based on a single component and a three component modeling assumption. The empirical models (SFOM and 3PM) were used to describe the biomass pyrolysis, of which the kinetic parameters were estimated using a fitting procedure consisting of a genetic algorithm combined with a least squares (LSQ) fitting. The GA does not need an initial guess and rapidly converges to an optimal solution. This solution is then used has an initial guess for the non-linear LSQ fitting procedure to provide an adequate start, refining further the solution given by the GA. A definition of the evaluation function for the GA that minimizes the deviation between the experimental and the predicted pyrolysis yield curves, while preserving the characteristics of the mass decomposition during pyrolysis, is presented. The pyrolysis rate curve is usually characterized in terms of the beginning and end of the global decomposition and of the devolatilization peaks [9]. Individual evaluation functions are defined for the deviation between the experimental and the predicted pyrolysis yield curves and for the deviation between the experimental and predicted characteristics of the pyrolysis rate curves. In previous works, only the deviation between the experimental and the predicted yield curves was considered. The obtained set of optimized kinetic parameters and associated fitting errors for all biomass types and heating rates are presented and discussed. Subsequently, a sensitivity analysis was performed, considering the variation of the biomass composition for the specific case of the 3PM.

2. Materials and methods

2.1. Biomass composition

The tests of each biomass sample for proximate analysis were carried out using a thermogravimetric analyzer TGA701, while for the elemental analysis was used a TruSpec Micro CHNS.