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How to determine consistent biomass pyrolysis kinetics in a parallel reaction scheme

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HIGHLIGHTS

- High scattering in the literature for kinetics of biomass pyrolysis.
- Comparison of isoconversional methods and least squares fitting in a parallel scheme.
- Isoconversional methods can check the reliability of the experiments.
- Isoconversional methods can confirm the employed reaction model in a fitting routine.
- List of four precautions to be taken when determining kinetics of biomass pyrolysis.

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ABSTRACT

This paper discusses a method for determining the kinetics of biomass pyrolysis based on comparing isoconversional methods, such as the Kissinger and KAS methods, and least squares fitting in a parallel reaction scheme with three pseudo-components roughly representing cellulose, hemicellulose and lignin. The activation energies of the different pseudo-components reported in the literature vary widely. This variation could be reduced if care were taken to determine the kinetics of biomass pyrolysis: First, the reference experiments with pure cellulose are reproduced to validate the thermogravimetric analysis. Then, experiments are performed and analyzed with different heating rates and isoconversional methods are employed to verify the reliability of the experiments and to avoid selecting inappropriate reaction models in a fitting routine.

1. Introduction

Biomass, a renewable primary energy source, is expected to play a more important role in the future. Pyrolysis itself is a promising conversion process that produces liquid biofuel and biochar and a main sub-process in gasification, combustion, smoldering or hydrothermal carbonization. However, pyrolysis of biomass entails a very complex set of competitive and concurrent reactions and the exact mechanism remains unknown. The kinetics of biomass is usually determined by thermogravimetric analysis (TGA). Lignocellulosic biomass pyrolysis is assumed to be approximately the sum of the inputs of the respective main components: cellulose, hemicellulose and lignin. Pyrolysis can be described with a parallel reaction scheme in which usually three pseudo-components represent the main biomass components. In diagrams representing the reaction rate as a function of temperature at a constant heating rate, the main peak corresponds to cellulose and the shoulder at lower temperatures to hemicellulose and lignin decomposition covers a wider temperature range, including the tail at high temperatures. In this approach, however, the proportions of each pseudo-component do not correspond to the composition of the real components because of the influence of mineral mater and interactions among the components [1]. The activation energies of the pseudo-components in the parallel reaction scheme usually resemble the activation energies of the original components. As recently published reviews indicated, activation energies vary widely in the literature [2,1]. The widely varying kinetic data reported in the literature in recent years has sparked concern among the biomass pyrolysis community about the reliability of the reported experiments and the analyzed data [2,1,3].

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Gronli et al. [4] suggested pyrolyzing cellulose AVICEL PH 105 and comparing the findings with the findings of their European round robin study in order to verify the reliability of the thermobalance employed. AVICEL PH 105 microcrystalline cellulose yields good reproducibility in thermogravimetric experiments. The basic experimental problem is eliminating limits on heat and mass transport, e.g. thermal lag, the difference in temperature between the sample and the controlling (external) thermocouple caused by the samples thermal inertia and/or reaction energetics. The most evident effects of such a drawback are a shift of the measured mass loss peaks to higher temperatures. The effect is quite significant for cellulose because of the strong endothermicity of the decomposition process [5]. Low initial mass samples and heating rates can be employed to avoid it.

Related to data analysis, there are two main mathematical approaches to obtain the kinetics data: model-based (model-fitting) and isoconversional (model-free) methods. Current studies share a general consensus about the nature of the kinetic models. Conversion (α) is defined in Eq. (1) as a function of the initial mass (m_0), the current mass (m) and the final mass (m_f). The global reaction rate is related to the reaction rate of each pseudo-component in the parallel reaction scheme by Eq. (2). The parameter c_i corresponds to the proportion of the i_{th} pseudo-component. As indicated in Eq. (3), the reaction rate of each pseudo-component ($d\alpha_i/dt$) depends on a pre-exponential factor (A), an Arrhenius-like term related to temperature (T) and activation energy (E) and a final term representing the reaction model. The nth order reaction model, which depends on conversion (α) and the order of reaction (n), is a typical example. The reaction is first order when $n = 1$.

$$\alpha \equiv 1 - \frac{m - m_f}{m_0 - m_f} \tag{1}$$

$$\frac{d\alpha}{dt} = \sum_{i=1}^{n} c_i \frac{d\alpha_i}{dt} \tag{2}$$

$$\frac{d\alpha_i}{dt} = A \exp\left(-\frac{E}{RT}\right)(1-\alpha)^n \tag{3}$$

Model-based (model-fitting) methods were some of the first and most popular methods used to evaluate solid-state kinetics, especially in non-isothermal experiments. In these methods, a reaction model must be postulated first. The most appropriate reaction model can just be selected solely on the basis of the quality of the regression fit. Nonlinear least squares fitting is the method most commonly employed in the biomass community to fit experimental data and evaluate Arrhenius parameters. Differential (DTG) versus integral measurements (TG) are recommended for this method because they show the details of devolatilization better [6]. Least squares fitting of the N analyzed experiments should minimize the sum of Eq. (4) and the fit of the curve obtained to the experimental curve is calculated with Eq. (5).

$$Sum = \sum_{i=1}^{N} \left(\left(\frac{d\alpha_i}{dt}\right)_{exp} - \left(\frac{d\alpha_i}{dt}\right)_{sim} \right)^2 \tag{4}$$

$$fit(\%) = \frac{\sqrt{\frac{Sum}{N}}}{\left(\frac{d\alpha_i}{dt}\right)_{exp,peak}} \tag{5}$$

Isoconversional (model-free) methods compute kinetic parameters without model-based assumptions, such as an a priori first order reaction [7,8]. The Kissinger method calculates activation energy by plotting Eq. (6), obtained from the derivation of Eq. (3), on a logarithmic scale with the temperature data of the peak of the reaction rate (T_m) at each heating rate ($\Delta T/\Delta t$). The activation energy can be calculated from the slope of the line [9]. The Kissinger method is exact when the reaction order is one and remains a good approximation when it is other than one [10]. An extension of this method, the Kissinger–Akahira–Sunose (KAS) method calculates activation energy with certain fixed conversions α. In this study, the temperatures at a certain conversion at different heating rates are used to calculate the activation energy at that conversion [2].

$$\ln\left(\frac{\Delta T/\Delta t}{T_m^2}\right) = \ln\left(\frac{AR}{E}\right) - \frac{E}{R}\frac{1}{T_m} \tag{6}$$

As pointed out by Khawam and Flanagan [7], although the popularity of isoconversional methods has been increasing in the recent, the results obtained from different methods of mathematical analysis are considered to be conflicting rather than complementary. They recommend the complementary use of isoconversional and model-based methods to determine solid state reaction kinetic parameters from experimental data. First, activation energies can be predicted from an isoconversional analysis. Then, based on model-based methods, the most accurate reaction model can be chosen in order to arrive at an activation energy close to the one obtained from the isoconversional analysis. Thus, the selection of the most appropriate reaction model is potentially more consistent than when based on the quality of the regression fit alone [7].

This paper discusses the determination of the kinetics of biomass pyrolysis with isoconversional and model-based (using least squares fitting in a parallel reaction scheme) methods. To the authors knowledge, a combination of both methods for biomass pyrolysis has not been discussed in detail in the literature. The usefulness of isoconversional methods to verify the reliability of experiments and to select appropriate reaction models is demonstrated. This paper is organized as follows: A review of prior literature in Section 2 is followed by a presentation of the experimental materials and methods in Section 3 and the results in Section 4, together with a discussion and a comparison with data from the literature. In closing, the conclusions are expounded.

2. Previous works

As mentioned, there is little consensus in the literature of pyrolysis of lignocellulosic biomass on the kinetic model and activation energies for the parallel reaction scheme. Widely varying kinetic data have been reported in recent years. Although the inputs of the different and difficult-to-separate components in biomass overlap, the activation energies of the pseudo-components in the parallel reaction scheme usually resemble the activation energies of the original components [11]. A general consensus exists on the kinetic model for pure cellulose based on a first order reaction with high activation energy: 228 (191–253) kJ/mol [12]. As recently reviewed by Di Blasi [1], the main component for biomass in the parallel reaction scheme representing the cellulose peak usually has activation energies in the range of 190–250 kJ/mol, close to the commonly accepted values for pure cellulose. Furthermore, the literature usually reports a lower activation energy value for the hemicellulose pseudo-component than for cellulose but it is still high (150–200 kJ/mol). The value for the lignin pseudo-component is usually quite low (<100 kJ/mol), albeit higher values are also reported [1].

Some studies obtain the kinetics of lignocellulosic biomass solely with experiments at one heating rate [11,13]. Branca and colleagues have criticized this, though [14]. Force fitting models to non-isothermal data obtained from a single heating rate can generate very inconsistent Arrhenius parameters that display a strong dependence on the kinetic model selected [2]. Compensation effects can be avoided by employing several heating rates, i.e. different combinations of pre-exponential factors and activation energies