A new method to calculate kinetic parameters independent of the kinetic model: Insights on CO_2 and steam gasification

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ABSTRACT

A new method to obtain the rate constant and activation energy independent of a kinetic model is proposed and evaluated for thermochemical conversion, specifically in the steam and CO_2 gasification of coal and biomass. Recent works on gas–solid reactions are based on single-step chemical reaction models that have been increasing in complexity through the use of more regression parameters to fit experimental data. These models fit better; however, sometimes their kinetic parameters are inconsistent, resulting in an incorrect interpretation of the reaction mechanism.

The proposed method, which does not require any assumed kinetic model, is useful in calculating the parameters of the Arrhenius equation using cumulative variables obtained from the experimental data, i.e. conversion and residence time. For this reason, the uncertainty is reduced compared to conventional methods. The new method could be used as a consistency test between different kinetic models by comparing their kinetic parameters with those obtained with the proposed free-model method.

The procedure has been applied to our previous experimental work and other authors' information on CO_2 and steam gasification, verifying that the random pore model is not the best kinetic model to represent gasification and partial oxidation of coal and biomass. The new procedure can be used as a tool for chemical reaction engineering analysis in a broad range of thermochemical reactions under isothermal consideration.

1. Introduction

Gasification is one of the most promising thermochemical conversion technologies to use alternative fuels as feedstock, especially low-rank coals and biomass. Reviews have presented the most significant gasification variables (Di Blasi, 2009; Irfan et al., 2011; Hobbs et al., 1993); however, the kinetics and analysis of its reaction mechanism are complex, since the reaction occurs at high temperatures and the solid characterization usually is performed at very low temperatures.

Kinetic information of partial oxidation and combustion has been reported, since the most common industrial gasifiers inject air to partially combust the fuel, providing the energy that the overall endothermic process requires. Moreover, experiments and modeling for partial oxidation (Loewenberg and Levendis, 1991; Su and Perlmutter, 1985) have been extended for gasification modeling. Studies on gasification have been performed in carbon dioxide (CO_2) (Duman et al., 2014; Jeong et al., 2014; Li et al., 2013; Mandapati et al., 2012; Silbermann et al., 2013; Wang et al., 2013), steam atmospheres (Fermoso

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Nomenclature

E_A	activation energy (kJ/mol)
$f(X)$	function of the conversion in a general rate law (dimensionless)
$G(X)$	integrated form of $dX/f(X)$ (dimensionless)
k	rate constant (min^{-1})
k_o	frequency factor (min^{-1})
m_a	mass of ash (g)
m_o	initial mass of char (g)
m_t	mass of char at the particular time 't' (g)
n	reaction order for the integrate core model
r	reaction rate (min^{-1})
R	ideal gas law constant (kJ mol^{-1} K^{-1})
t	time (min)
T	temperature (K)
X	conversion (dimensionless)

Greek letters

α	intercept of the logarithm of time (min) versus reciprocal of temperature (K^{-1})
ψ	parameter of the random pore model describing char surface (dimensionless)

et al., 2011; Kim et al., 2013; Lin and Strand, 2014), or mixtures of both gasifying agents (Ahmed and Gupta, 2011; Guizani et al., 2013; Ren et al., 2013; Umemoto et al., 2013; Zhang et al., 2014), since the Boudouard reaction, steam reforming and water–gas shifting are the main reactions. Analysis of the reported data in this field is complex, since there is not a criterion consensus (Di Blasi, 2009); and, the modeling of a maximum reaction rate has been the focus of the research on gasification kinetics in recent years (Bhatia and Perlmutter, 1980; Bhatia and Vartak, 1996; Duman et al., 2014; Jeong et al., 2014; Kopyscinski et al., 2013; Li et al., 2013; Lin and Strand, 2014; Mandapati et al., 2012; Singer and Ghoniem, 2011).

Bhatia and Perlmutter (1980) proposed the random pore model (RPM) with a further modification (Bhatia and Vartak, 1996) for gas–solid reactions. This model has been widely accepted due to its nonlinear dependence on char surface, which can predict a maximum reaction rate as observed experimentally. Different modifications to the original model and their applications to fit experimental data have been reported; for example, some of the most recent works present extended and adaptive RPM (Kopyscinski et al., 2013; Singer and Ghoniem, 2011). Modeling improvement is commonly attached to an increase in the number of the fitting parameters, which does not necessarily mean a direct relationship with the reaction mechanism.

Recently, Gomez et al. (2014) demonstrated that the suggested maximum rate is a consequence of a change in the reaction medium, which is generated by an imposition of the experimental procedure, and proposed an alternative experimental method to avoid this effect. In independent studies (Ahmed and Gupta, 2011; Li et al., 2013; Nipattummakul et al., 2010; Popa et al., 2013; Prabowo et al., 2014; Woodruff and Weimer, 2013), the time to observe a maximum rate was constant and independent of the char sample or gasifying agent, as proven by Gomez et al., despite many authors modeled this maximum (Ahmed and Gupta, 2011; Li et al., 2013; Popa et al., 2013). For this reason, simpler expressions can be used to model gasification or other thermochemical reactions where the reaction is chemically controlled and thus one single overall step can be assumed. Therefore, it is important to validate the assumed kinetic model and its respective kinetic parameters (i.e. rate constant and activation energy).

A new procedure is presented to obtain the rate constant and activation energy, based on a deduction from the Arrhenius equation and a general rate law, without transformation of variables or assumption of a particular kinetic model. The aim of this work is the determination of kinetic parameters without restricting the analysis to a particular

kinetic model. From reported data for CO_2 (Kopyscinski et al., 2013; Li et al., 2013; Mandapati et al., 2012; Silbermann et al., 2013) and steam gasification (Fermoso et al., 2011), the activation energy was calculated with the new approach and compared with the reported values, confirming previous findings (Gomez et al., 2014) related to the convenience of using simpler models rather than the RPM for gasification. This new procedure can be used to determine the parameters of the Arrhenius equation for a set of isothermal experiments and can also be used as a tool for scaling industrial processes or testing the consistency of a particular kinetic model.

2. Experimental methods

2.1. CO_2 gasification

Original experimental information from Silbermann et al. related to CO_2 coal gasification was used to determine the activation energy and compare the obtained values with those reported for five different kinetic models (Silbermann et al., 2013). The same procedure was applied to three other works using a nonlinear model (Li et al., 2013) and to the RPM (Kopyscinski et al., 2013; Mandapati et al., 2012). They reported their results as the best fit among the compared kinetic models. It is important to mention that the main experimental difference between Silbermann et al. (2013) and the other references is that its experimental procedure did not induce a maximum rate as a consequence of a gas change, as proven by Gomez et al. (2014).

2.2. Steam gasification

Results for CO_2 and steam gasification follow the same trend, with a higher reactivity of the steam at lower temperatures. Kinetic modeling for steam gasification, using a single-step chemical reaction model, is similar to that of CO_2 gasification (Ahmed and Gupta, 2011). When CO_2 and steam are mixed in different proportions, Langmuir–Hinshelwood (LH) models describe the competition for active sites considering the gas diffusion (Umemoto et al., 2013), but the chemical reaction contribution are assumed with a single-step kinetic model. Information presented by Fermoso et al. (2011) was analyzed in the application of the proposed method to determine the activation energy and compare it with the reported values obtained using the RPM.

3. Kinetics analysis

3.1. Data analysis

Conversion and its associated reaction time were obtained from five independent studies; i.e. Fermoso et al. (2011), Kopyscinski et al. (2013), Li et al. (2013), Mandapati et al. (2012) and Silbermann et al. (2013). Conversion is calculated from the weight at a particular time, which is the original information obtained by thermogravimetic analysis (TGA) or back calculating the information of the gas composition analysis. By definition, conversion is:

$$X = \frac{m_o - m_t}{m_o - m_a} \qquad (1)$$

where m_o is the initial mass of the sample, m_t is the mass at a particular time, and m_a is the mass of the ash.

The conversion rate was not determined in this work, since the proposed method does not require it. This approach