



Non isothermal model free kinetics for pyrolysis of rice straw



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HIGHLIGHTS

- Study of pyrolysis behavior and kinetics of rice straw.
- Indication of complex multistep mechanism for RS pyrolysis using isoconversional plot.
- Determination of reaction mechanism using master plots and compensation effects.
- Isothermal predictions from non-isothermal data for validation of kinetic results.

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ABSTRACT

The kinetics of thermal decomposition of rice straw was studied by thermogravimetry.

Non-isothermal thermogravimetric data of rice straw decomposition in nitrogen atmosphere at six different heating rates of 5–40 °C/min was used for evaluating kinetics using several model free kinetic methods. The results showed that the decomposition process exhibited two zones of constant apparent activation energies. The values ranged from 142 to 170 kJ/mol ($E_{avg} = 155.787$ kJ/mol), and 170 to 270 kJ/mol ($E_{avg} = 236.743$ kJ/mol) in the conversion range of 5–60% and 61–90% respectively. These values were used to determine the reaction mechanism of process using master plots and compensation parameters. The results show that the reaction mechanism of whole process can be kinetically characterized by two successive reactions, a diffusion reaction followed by a third order rate equation. The kinetic results were validated using isothermal predictions. The results derived are useful for development and optimization of biomass thermochemical conversion systems.

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1. Introduction

Environmental protection and fossil fuel depletion are some of the driving forces which push technological research towards the development of alternative fuels. Second generation biofuels from biomass is an interesting route, able to transform an abundant and well distributed feedstock into fuels with properties similar to conventional fossil fuels (Mendes and Figueiredo, 2011). Biomass is a source of short-cycle carbon, which is of utmost importance for future energy needs (Wongsiriamnuay and Tippayawong, 2010). Moreover the lignocellulosic biomass is low in sulfur, resulting in a more ecological fuel (Catoire et al., 2008). Thermochemical conversion is one of the main approaches used to produce bio-oils, derived from the de-polymerization and fragmentation reactions of the three key biomass building blocks: cellulose, hemicellulose and lignin (Guillaume and Thierry, 2013). The variation in thermal response exhibited by biomass is

attributed to the varying proportion of these constituents from biomass to biomass. Biomass can be converted into useful forms of energy using thermo-chemical and bio-chemical processes but thermo-chemical conversion technology finds its dominance because of its high efficiency in conversion to gaseous, liquid and solid products under thermal conditions (Zhang et al., 2006).

Pyrolysis can be used as an independent process for the production of useful energy holders (fuels) and/or chemicals. It also occurs as the first step in a gasification or combustion process. The development of thermochemical processes for biomass conversion and proper equipment design requires the knowledge of several process features which include a good understanding of the governing pyrolysis mechanisms, the determination of the most significant pyrolysis parameters and of their effect on the process and knowledge of the kinetics (Koufopoulos et al., 1989). A precise conception of solid state pyrolysis kinetics is very crucial in designing and operating industrial biomass conversion systems. Thermogravimetric analysis (TGA) is the most commonly applied thermoanalytical technique in solid-phase thermal decomposition studies (Ninan, 1989), and it has gained extensive recognition in thermal studies of biomass pyrolysis.

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The precision and accuracy of the kinetic expression governing the reaction mechanism and the kinetic parameters inferred from kinetic analysis have a profound dependence on the reliability of the evaluation methods used to study the decomposition behavior of biomass under different conditions of temperature and/or atmosphere. Numerous researchers have investigated the decomposition kinetics of biomass using model fitting approaches involving global or semi-global mechanisms. Di Blasi presented a comprehensive review of the different classes of mechanisms proposed for the pyrolysis of wood and other cellulosic materials (Di Blasi, 1993). One step global model involving a single global reaction has been used widely but it is extremely simplified and is unsuitable to predict the complex nature of decomposition of biomass (Varhegyi et al., 1989). Varhegyi used the independent reaction model of three pseudo-components. This model ensures the possibility of simultaneous decomposition of pseudo-components. The biomass decomposition results reported in the literature (Varhegyi et al., 1997; Orfao et al., 1999; Gronli et al., 2002) show that this model provides consistent parameter values with low fitting errors. The macroscopic kinetics of biomass pyrolysis is complex as it includes information about simultaneously occurring multiple steps. Unraveling the macroscopic kinetics presents a certain challenge that can only be met by the computational methods that allow for detecting and treating multi-step processes (Vyazovkin and Sbirrazzuoli, 2006). According to the results of the ICTAC Kinetics Project (Brown et al., 2000), isoconversional methods are among a few methods that are up to this challenge.

This study aims to investigate the characteristics and kinetics that describes the thermal decomposition process of rice straw. Rice straw is one of the main cereal straws and is created as by-product of the rice milling processes in large quantities worldwide every year. Asia contributes to total production of rice straw with an important ratio of 92% (Putun and Apaydin, 2004). The pyrolysis behavior of rice straw is investigated using thermogravimetric analyzer. Isoconversional analysis methods, generalized master plots are used to determine the kinetic triplet. The work compares the different isoconversional methods available for kinetic analysis in detail for rice straw and provides basis for further applications of the thermochemical conversion of rice straw as a potential feedstock.

2. Experimental method

2.1. Sample preparation and characterization

The rice straw sample used in the study was subjected to several treatments before analysis. It was dried at room temperature and was milled and sieved to an average particle size of 50 μm . The Moisture content of the feed has been obtained from the HR-83 Mettler Toledo Halogen Moisture Analyzer. The calorific value measured using a Parr 6300 bomb calorimeter came out to be 13.414 MJ/kg. The proximate analysis of rice straw sample showed that it contains 11.95% moisture, 19.74% ash and fixed carbon of 7.25%. The volatile content of rice straw was 73.015%. The ultimate analysis showed that rice straw contains 34.11% carbon, 6.52% hydrogen, 0.174% nitrogen and sulfur less than 0.1 wt%. The oxygen content was calculated by difference and was found as 59.2%. The trace metal analysis of rice straw sample has been carried out in the DRE, PS-3000 UV, Leeman Labs Inc., Inductively Coupled Plasma- Atomic Emission Spectroscopy. A high content of silica of 1,04,235 ppm is found in rice straw. The elemental analysis showed presence of potassium (17,360 ppm), calcium (8161 ppm), magnesium (1077 ppm), aluminum and manganese with traces of sodium, zinc, copper, and lead in rice straw.

2.2. Experimental techniques

The experiments were carried out in a thermogravimetric analyzer, DTG-60 (Shimadzu, Japan), to measure and record the sample mass change with temperature over the course of the pyrolysis reaction. Rice straw samples of average particle size of 50 μm were taken in alumina crucibles with sample mass in the range of ca. 10 mg. The samples were heated from room temperature to 700 $^{\circ}\text{C}$ at six different heating rates of 5, 10, 20, 30 and 40 $^{\circ}\text{C}/\text{min}$ and the results obtained were used in the kinetic analysis. Nitrogen gas at a flow rate of 100 ml/min was used as an inert purge gas to displace air in the pyrolysis zone, thus avoiding unwanted secondary reactions and oxidation of the sample. The experimental results were tested to ensure reproducibility.

2.3. Kinetic models-theoretical background

The fundamental equation used for study of kinetics of heterogeneous solid-state thermal decomposition can be described as follows,

$$\frac{d\alpha}{dt} = kf(\alpha) = A \exp\left(\frac{-E_x}{RT}\right)f(\alpha) \quad (1)$$

where, the reaction rate ($d\alpha/dt$) can be expressed as a function of a temperature dependent term $k(T)$ and the dependence of extent of conversion(α) on reaction model $f(\alpha)$. The value of α typically reflects the progress of the overall transformation of a reactant to products. The overall transformation can generally involve more than a single reaction or, in other words, multiple steps each of which has its specific extent of conversion (Vyazovkin et al., 2011).

The rate constant $k(T)$ is generally expressed by Arrhenius equation as follows,

$$k(T) = A \exp\left(\frac{-E_x}{RT}\right) \quad (2)$$

where A is the pre exponential factor (in min^{-1}), E_x is the apparent activation energy (in kJ/mol), T is the temperature (in K) and R is the gas constant (8.314 kJ/mol K). The conversion α can be defined as

$$\alpha = \frac{m_0 - m_t}{m_0 - m_\infty} \quad (3)$$

where m_0 is the initial sample weight, m_t is the sample weight at time, t , and m_∞ is the final sample weight. For dynamic analysis of non-isothermal data a term β as the heating rate (in K/min) is introduced into the equation and the final equation obtained is as follows,

$$\frac{d\alpha}{dT} = k(T)f(\alpha) = \frac{A}{\beta} \exp\left(\frac{-E_x}{RT}\right)f(\alpha) \quad (4)$$

The various methods for kinetic analysis can be broadly classified into two groups as “model fitting kinetics” and “model free kinetics”. Model fitting methods involve forcible fitting of kinetic parameters into the equation which results in ambiguous kinetic interpretations where more than one reaction mechanism satisfactorily fits into the data at the cost of drastic variations in the Arrhenius parameters, which compensate for the difference between the assumed form of $f(\alpha)$ and the true but unknown reaction model (Vyazovkin and Wight, 1999). The model-free approach does not require assumption of specific reaction models, and yields unique kinetic parameters as a function of either conversion (isoconversional analysis) or temperature (non parametric kinetics) (Vyazovkin, 2000). Of the two main model free methods the isoconversional approach is more frequently adopted, and is increasingly being used in biomass thermochemical conversion research (Aboiyade et al., 2012).

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