Fuel 169 (2016) 93–98

Contents lists available at ScienceDirect

Fuel

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

# Pyrolysis kinetics of soybean straw using thermogravimetric analysis

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## HIGHLIGHTS

- The decomposition zone of soybean straw could be divided into three stages.
- The kinetic of soybean straw pyrolysis was studied by three models.
- Simulation of pyrolysis showed a good agreement with experimental data.
- An insight for future applications of soybean straw was provided.

## ARTICLE INFO

*Article history:*
Received 25 September 2015
Received in revised form 30 November 2015
Accepted 10 December 2015
Available online 17 December 2015

*Keywords:*
Kinetics
Pyrolysis
Thermogravimetric analysis
Soybean straw
Biomass

## ABSTRACT

Thermochemical conversion of crops straw is receiving renewed attention, due to the energy and material recovery that can be achieved. However, it still lacks the kinetic background which is of great importance for a successful design of thermochemical process. In this work, pyrolysis test for soybean straw was performed in a non-isothermal thermogravimetric analysis (TGA) in order to determine the thermal degradation behavior. Pyrolysis experiments were carried out under inert conditions and operated at different heating rates (5, 10, 20, and 30 K/min). Three different kinetic models, iso-conversional Kissinger–Akahira–Sunose (KAS), Ozawa–Flynn–Wall (OFW) models, and Coats–Redfern method were applied on TGA data of soybean straw to calculate the kinetic parameters including activation energy, pre-exponential factor, and reaction order. The activation energy values were 154.15 and 156.22 kJ/mol based on KAS and OFW models, respectively. Simulation of the soybean straw thermal decomposition using the obtained kinetic parameters and comparison with experimental data are in good agreement.



## 1. Introduction

The utilization of biomass wastes including agricultural straw, municipal solid waste, and livestock manure has attracted more and more attention owing to their potential energy property. Agricultural application, landfill, and incineration are the most common disposal processes for the wastes, whereas the traditional disposal routes are becoming increasingly unacceptable due to land limitations and stringent regulations [1,2]. Alternatively, using biomass wastes as energy feedstock for bio-fuel production through thermochemical conversion is regarded as an environmentally friendly disposal route with potential economic benefits. Several thermochemical conversion technologies, including pyrolysis, gasification, and liquefaction conversion, are currently under development [3,4]. Among the techniques, pyrolysis is most widely used in thermal decomposition process and effective for converting biomass waste into useful products of gas, oil, and solid char in an oxygen-free atmosphere [3,5]. The combustible gas and the oil products can be used as fuel due to their high calorific values [6]. Moreover, the bio-oil consists of various organic compounds which can be used as feedstock for value-added chemicals [7,8].

Non-isothermal thermogravimetric analysis (TGA) is one of the most common methods to investigate the kinetics of pyrolysis. Accurate pyrolysis kinetic models are essential to the full utilization of particular biomass wastes. It also contributes to design reasonable, efficient, and competent process and scale to establish in real industrial applications for energy generation. The degradation of biomass wastes is a tremendously complex process, mainly due to the large number and diverse nature of thermochemical reactions. Previous studies [9] showed that the pyrolysis of agricultural biomass consists four individual conversion stages, i.e., moisture evolution, decomposition of hemicellulose, cellulose, and then lignin. Hemicellulose, which is a branched polymer with a low degree of polymerization, is normally decomposed at 493–588 K, where cellulose maintains highly ordered and stable crystalline structures. As a result this, the cellulose undergoes decomposition at 588–673 K [10,11]. Lignin is a three-dimensional polymer

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http://dx.doi.org/10.1016/j.fuel.2015.12.011
0016-2361/

consisting of hydroxyl phenylpropane monomers, and bound adjacent to the cellulose fibers to form a lignocellulose. The lignin is more refractory than the other two components, while having functional groups with widely distributed thermal stability, and this results in a board temperature range of decomposition from 433 to 1173 K [11,12].

In the present work, we investigate the kinetics of pyrolysis process for soybean straw using TGA technique at different heating rates (5, 10, 20, and 30 K/min) under argon atmosphere and determine the kinetic parameters through iso-conversional Kissinger–Akahira–Sunose (KAS) and Ozawa–Flynn–Wall (OFW) models and Coats–Redfern method. The physicochemical properties are firstly determined by elemental analyzer and FTIR spectrometer.

## 2. Materials and methods

### 2.1. Material

The soybean straw sample was obtained from fields of Xuzhou, China. It was pulverized to pass through a 40-mesh sieve followed by drying at 380 K for 24 h and then stored in an airtight container before use. Ultimate analysis was conducted with an Elementar vario MACRO cube CHNS elemental determinator. Table 1 summarizes main characteristics of the soybean straw sample.

### 2.2. TGA

Pyrolysis tests were carried out in a simultaneous differential thermogravimetric analyzer, which combines a heat flux type DSC with a TGA (Mettler Toledo TGA/DSC Stare ESI-0910, Switzerland; with a precision of temperature measurement ±0.15 K, DSC sensitivity ±0.1 mW and microbalance sensitivity ±0.1 μg). Temperature programmed pyrolysis for soybean straw was conducted under a dry argon atmosphere with a flow rate of 50 mL/min. Sample with mass of 15–20 mg was inserted directly into a ceramic crucible and temperature was ramped from room temperature to 380 K and holding for 10 min, then heated to 1173 K with different heating rates of 5, 10, 20, and 30 K/min, respectively. The data of thermogravimetry (TG) and derivative thermogravimetry (DTG) were obtained using the software of the analyzer. The experiments were replicated at least twice.

### 2.3. FTIR analysis

FTIR spectrum of soybean straw was recorded using a Nicolet Magna 560 spectrometer, by collecting 128 scans at a resolution of 4 $cm^{-1}$ in reflectance mode with measuring regions of 4000–400 $cm^{-1}$.

### 2.4. Kinetic study

Biomass pyrolysis is a complex process because more than one reaction is involved. A full kinetic analysis of the complex system is generally not feasible, but some kinds of effective or average kinetic description are still needed. In this work, pyrolysis reaction kinetics was investigated by three different kinetic models, the iso-conversional KAS and OFW models and Coats–Redfern method were applied on TGA data of soybean straw.

**Table 1**
Characteristics of soybean straw.

| Proximate analysis (wt.%)[a] | | | | Ultimate analysis (daf, wt.%) | | | | | H/C |
|---|---|---|---|---|---|---|---|---|---|
| $M_{ar}$ | $A_d$ | $VM_d$ | $FC_d$[b] | C | H | N | S | O[b] | |
| 1.8 | 4.7 | 75.5 | 19.8 | 47.8 | 6.9 | 1.0 | 0.1 | 44.3 | 1.73 |

[a] A: ash; M: moisture; VM: volatile matter; FC: fixed carbon.
[b] Calculated by difference.

#### 2.4.1. The KAS model

The KAS model [13,14] is one of the most widely used iso-conversional methods to calculate pyrolysis kinetics, which is based on the following expression:

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{AE}{Rg(\alpha)}\right) - \frac{E}{RT}$$

where $\beta$ is the heating rate (K/min), $A$ is the pre-exponential factor ($min^{-1}$), $\alpha$ is conversion rate which can be calculated with the lost weight dividing by the total weight of soybean straw, and $g(\alpha)$ is a function depending on the decomposition mechanism. In the plot of $\ln(\beta/T^2)$ versus $1/T$, slope gives $-E/R$ where $R$ numerical valued 8.314 J/(mol·K) is the gas constant. Doing so for the whole range of conversion (0–1) will produce the activation energy for the progressing values of conversion.

#### 2.4.2. The OFW model

Another most common and widely accepted methods in scientific community to compute thermo-kinetic parameter from experimental data is the OFW model [15,16]. The OFW model used a correlation of the heating rate of the samples, activation energy and inverse temperature, which was originally used the Doyle's [17] approximation for the temperature integral. The final form of the OFW equation is expressed as:

$$\log\beta = \log\left(\frac{AE}{Rg(\alpha)}\right) - 2.315 - 0.457\frac{E}{RT}$$

It is evident that a linear plot of $\log\beta$ versus the inverse temperature is sufficient in order to obtain the activation energy corresponding to each conversion step.

#### 2.4.3. The Coats–Redfern method

The Coats–Redfern integral method [18] which is derived from Arrhenius equation was used to analyze the characters of pyrolysis kinetics. Considering the KAS and OFW models are accurate enough for the calculation of activation energy, the Coats–Redfern method can be used to determine the pre-exponential factor as well as the reaction order. The equations for numerical determination of the kinetic parameters using the Coats–Redfern's method are given below.

$$\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right] = \ln\left[\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)\right] - \frac{E}{RT},\ n = 1$$

$$\ln\left[\frac{(1-\alpha)^{1-n}-1}{(n-1)T^2}\right] = \ln\left[\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)\right] - \frac{E}{RT},\ n\neq 1$$

where $n$ is the reaction order which describes the pyrolysis model. As for first-order reaction ($n$ = 1), the slope of curve $\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right]$ versus $1/T$ produce $-E/R$, then the activation energy is derived. For multistep reaction ($n \neq 1$), activation energy can be calculated through KAS or OFW models. Assuming $2RT \ll E$, the intercept can be arranged as $\ln(AR/\beta E)$ where $A$ can be calculated.

## 3. Results and discussion

### 3.1. FTIR analysis

The assignment of structural feature of the soybean straw is based on published interpretation for FTIR spectral data and the standard spectra in FTIR libraries, e.g., Aldrich Condensed Phase FTIR Library [19–22]. As shown in Fig. 1, the spectrum of the soybean straw shows a very strong and board absorption band at