ASSESSMENTS OF PYROLYSIS KINETICS AND MECHANISMS OF CELLULOSE USING THERMOGRAVIMETRY

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ABSTRACT

Pyrolysis is one of the most promising thermolysis processes for biomass conversion. In this study, pyrolytic mechanism and the thermal degradation behavior of cellulose were investigated at 20 K min^{-1} using NETZSCH 409 PC thermogravimetric analyzer (TGA). The thermal degradation behavior has been utilized to determine kinetic parameters. Coats-Redfern as a model fitting method for kinetic calculations was applied to estimate the activation energy and pre-exponential factor. The reaction regions, peak temperatures, mass loss, maximum mass loss rate of the celluse sample were also determined by using Proteus software. The calculated values for pyrolytic mechanism and kinetic parameters are in good agreement with literature.

Keywords: *Cellulose, Pyrolysis, Thermogravimetry, Kinetics, Coats-Redfern*

INTRODUCTION

In recent years, the demand for alternative energy resources to replace fossil fuel was greatly enhanced due to an acceleration in global warming, inevitably depletion of other energy resources such as fossil fuels, and various environmental pollution problems [1]. To satisfy this demand, it is extremely important to pass from the fossil fuels to the renewable energy sources [2].

As one of the various sources of energy, biomass is one of the newest energy resources that can substitute fossil fuels, due to its abundance and carbon neutral nature, stable provision and low sulfur content [1-3]. Biomass consists of the mixture of lignin, cellulose, hemicellulose and a small bulk of other organic materials that each of them pyrolyse or decay at various rates and by different pathways and mechanisms [4]. The main processes to obtain energy from biomass are pyrolysis, combustion, gasification, alcoholic fermentation, anaerobic digestion, hydro gasification, trans-esterification and liquefaction [5].

Pyrolysis of the biomass that is a well-known thermochemical process and quite sufficient to supply intensive energy demands, can decompose biomass into combustible gas, solid bio-char and liquid bio-oil in an oxygen-free atmosphere at 300–900°C [6] [7]. The behavior of each biomass in the pyrolytic environment is different and the choice of biomass according to the desired result is critically important. Cellulose is a sort of a biomass that is worth examining with regard to its thermal degradation process, because the kinetic results are computed according to its degradation curve [1].

The subject of kinetic analysis of pyrolysis has attracted numerously investigators for years [8]. In the kinetics study, one of the essential aspects for pyrolysis process is knowing the thermal deterioration mechanism, the reaction parameters for estimating the distribution of the product, and the ratio of reaction. The kinetic data is required to select the reactor, and optimize the operation conditions at the step of design and application, and operating efficiency of the reactor [9, 10].

A number of kinetic methods have been offered to investigate and explain pyrolysis process [11]. Model-fitting methods are quite ideal techniques for computing kinetic parameters. Model-fitting methods contain to fit various models to temperature curves and synchronously defining both the and Arrhenius constant (A) and activation energy (E) [12]. This kinetic method that used a single-heating-rate, and singlestep decay model demonstrate just a series of kinetics triplet which is predicted after reducing the deflection among experimental and simulated data to minimum [10].

One of the most popular approach in the model-fitting methods is Coats–Redfern method [13]. Coats–Redfern is formed of to fit the experimental data to the theoretical kinetic model based upon specific physic–geometrical conjectures which are hard to carry out in real systems [11].

Model-fitting approach associated with thermogravimetric analysis (TGA) for pyrolysis is prevalently utilized to assess all of kinetics parameters of this thermal degradation process such as reaction model, and pre-exponential factor, and activation energy (kinetics triplet) [10].

There are extremely less studies in the literature about the pyrolysis mechanisms and kinetic modelling of cellulose. The study of Zhang et. al. compared the pyrolysis properties of cellulose of different biomass samples that are pure cellulose, poplar wood, pine wood, and wheat straw, attained from Sigma Aldrich and Avicel using Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscope (SEM), and X-ray di□ractometer (XRD), and they carried on the pyrolysis operations handling a thermogravimetric analyzer (TGA) within nitrogen atmosphere from room temperature to 823K at $10 Kmin^{-1}$ heating rate [14]. Yang et. al. examined the pyrolysis properties of cellulose utilizing TG–FTIR and TGA, proposed an altered reaction model to work pyrolysis of cellulose, and utilized the random scission model to explain the kinetics of cellulose pyrolysis process. In this study, the identical kinetic parameters were utilized for various linear heating rates (10–100°C/min) and isothermal segment conditions [15]. Jun Yi Yeo et. al. research the thermal decay conduct and pyrolytic mechanism of lignin, hemicellulose and cellulose, using thermogravimetric analysis (TGA) equipment at various heating rates range from $10\ Kmin^{-1}$ and $100\ Kmin^{-1}$ with a step-size of $10\ Kmin^{-1}$ [16].

The aim of this work is to research the pyrolysis properties of cellulose that is one of the most promising biomasses for obtaining energy in a thermogravimetric analyzer (TGA), and to analyze its thermal kinetic properties using Coats-Redfern method.

MATERIALS & METHODS

2.1. Sample

To this study, the cellulose samples (cotton linter pulp) were taken from by Macherey, Nagel & Co (Düren, Germany). The α-cellulose concentration was almost 92% and its average degree of polymerization (DP) was used about 350–400.

2.2. Thermogravimetry

In this study, a thermogravimetric analyzer (TGA), model Netzsch STA 409, was employed as a cellulose pyrolyzer. In each experiment, the mass of cellulose sample was taken 10.0 mg. Argon was utilized as a carrier gas for pyrolysis operation at 45 mL/min flow rate. The samples were heated from 25 °C to 900 °C at 20 K /min heating rate.

2.3. Kinetics

Utilization of model-fitting methods is very practical and efficient to perform the kinetic modeling of the pyrolysis because of their simplicity. (makale 15). Coast Redfern method that is the most reliable and low error rate model fitting method, where Arrhenius factor and activation energy remain constant over the entire temperature range [17], uses the expansion of asymptotic series to approximate the exponential integral given in Equation (1);

$$In\left(\frac{g(\propto)}{T^2}\right) = In\left[\left(\frac{k_0\, R}{E_a\, \beta}\right)\left(1-\frac{2RT}{E_a}\right)\right] + \frac{-E_a}{RT}$$

(1)

the plot of $In(g(\propto))-2In(1/T)$ versus $1/T$ helps to find k_0 and E_a from the intercept and slope, respectively [8].

RESULTS AND DISCUSSION

3.1. Thermogravimetry

The weight loss and the derivative of weight loss curves of cellulose are shown in Fig. 1. The pyrolysis process of cellulose was investigated into one step occurring at 270°C - 600°C, with the weight loss of 86.18%, which is corresponded to degradation of cellulose. The pyrolysis peak was at 342 °C and the peak height value as the DTG curve is nearly flat over a long period of time. After 334.6°C, the pyrolysis rate apparently decreased rapidly, and as a result, some small loss in sample mass was maintain as long as the temperature enhanced up to 1000 ° C.

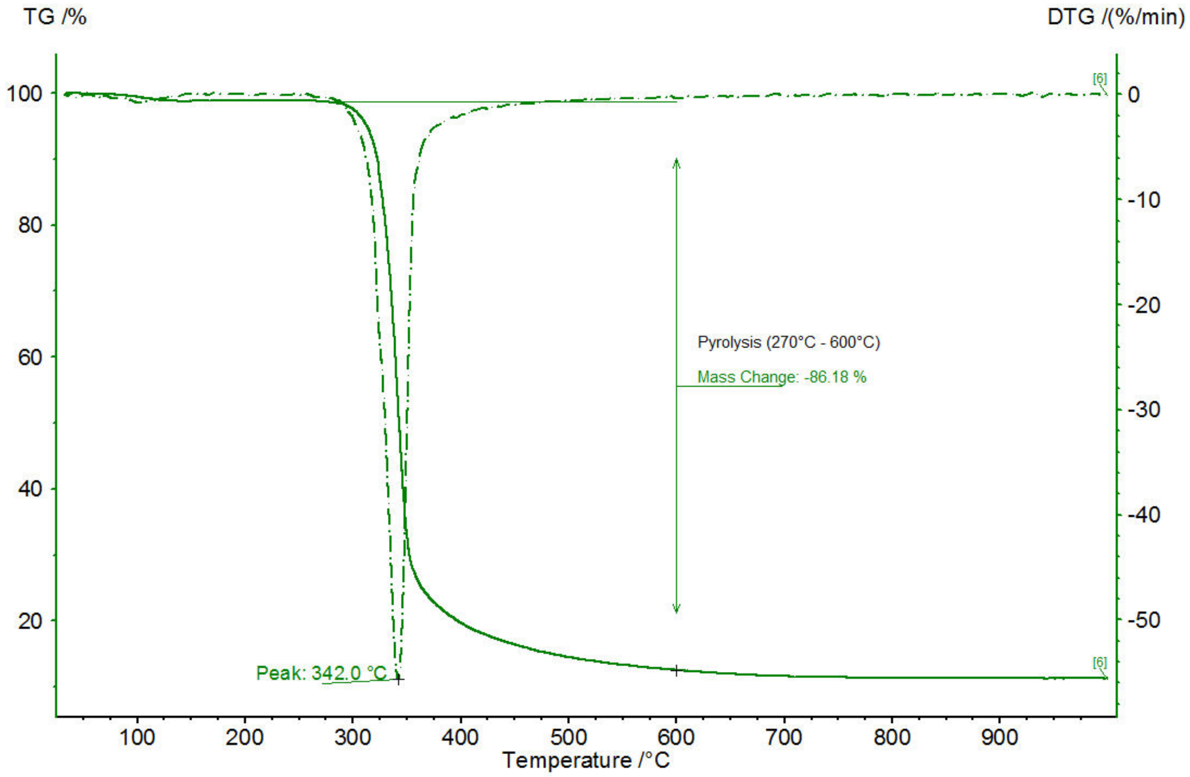

Figure 1. The TG and DTG curves of cellulose. The curve with the solid line belongs to TGA, and the curve with the dash line belongs to DTG.

3.2. Kinetics

The pyrolysis temperature was selected as 270 °C – 600 °C depends on the DTG results. The graph of In(g(∝))-2In(1/T) versus 1/T according to Coats-Redfern methods gives kinetic results for pyrolysis of cellulose. The results for Arrhenius factor and activation energy were calculated as 450.519 kJ/mol and Arrhenius factor of 4.47×10^{35} s^{-1}, respectively.

CONCLUSION

A reasonable thermogravimetric study and kinetic remark was conducted. In this study, the kinetic model for pyrolysis of cellulose based on the reaction models was offered which is first order reported in previous studies. The results for activation energy and Arrhenius factor are high and it is in good agreement with literature.

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