

Research Article

Pyrolytic Kinetic Study of Sugarcane Bagasse using Thermogravimetric Analysis

K. Nithiya^{*1}, P. Subramanian¹, D. Ramesh¹, D. Uma² and A. Surendrakumar³

¹Department of Renewable Energy Engineering, AEC&RI, TNAU, Coimbatore

²Department of Biochemistry, AC&RI, TNAU, Coimbatore

³Department of Farm Machinery and Power Engineering, AEC&RI, TNAU, Coimbatore

Abstract

The pyrolysis of sugarcane bagasse is studied using thermogravimetric analyser under nitrogen environment. The present study investigates the thermal degradation behaviour and determination of kinetic parameters such as activation energy (E_a) using Kissinger-Akahira-Sunose method. The experiments are conducted at different heating rates of 10, 20, 30, 40 and 50°C min⁻¹ at non-isothermal conditions with nitrogen gas flow rate of 60 ml min⁻¹. The results revealed that the maximum degradation of rice husk increases from 4.56 to 23.98 per cent as the heating rate increases from 10 to 50°C min⁻¹. Activation energy values were in the range of 110-116 kJ mol⁻¹ for different heating rates under non-isothermal conditions. The activation energy varied with the degree of conversion, indicating that pyrolysis is a multi-step process involving several reactions. The current investigation proves the suitability of sugarcane bagasse as a potential feedstock for pyrolysis.

Keywords: Pyrolysis, Sugarcane bagasse, Activation energy

*Correspondence

Author: K. Nithiya

Email id: k.b.nithiya@gmail.com

Introduction

Renewable energy is becoming a priority in this modern era due to decline in petroleum resources along with necessity for emission reduction resulting from the use of fossil fuel resources. Biomass is considered as a promising renewable energy resource to substitute conventional fossil fuels. The availability of biomass energy potential in India is estimated as 26 GW [1]. Biomass can be converted to various fuels, chemicals and also for energy generation through thermochemical pathways viz., combustion, gasification and pyrolysis. Among the thermochemical conversion techniques, pyrolysis is considered as most efficient process due to its higher feed to fuel ratio compared to combustion and gasification process [2]. Thermogravimetric analysis is one of the important techniques to study the primary reactions of decomposition of solids. It is also used to study the devolatilization of biomass under inert and oxygen atmospheres as it provides accurate data on the occurrence of intrinsic reaction [3]. Kinetic study of biomass is of utmost importance because it is needed for the design of pyrolysis reactors and gasifiers [4,5].

Pyrolysis is the thermal decomposition of biomass in the absence of oxygen to obtain solid, liquid and gaseous products. It is classified in terms of temperature and heating rate as, slow pyrolysis for the production of biochar and fast pyrolysis (higher heating rate) for the production of bio-oil. Thermal decomposition kinetics of biomass is a key component in the efficient design of thermochemical processes for the conversion of biomass into energy and products [6]. Cellulose, hemicellulose and lignin are the basic units of biomass and the thermal degradation of these components ranges between 470 and 770 K starting with hemicellulose at 470-530 K, followed by cellulose at 570 to 620 K and then by lignin at 550 to 770 K [7, 8]. Nocera et al. [9] conducted pyrolysis experiments at different heating rates to study the decomposition temperature of different polymers. They found that the mass loss and its rates were strongly affected by the heating rates and the depolymerisation temperature was mainly between 200 and 400°C. The effect of particle size on slow pyrolysis kinetics was studied by Suriapparao and Vinu [10]. The study revealed high yield of aromatics with medium sized particles (0.3 - 0.5mm); and reduced yield of phenolics and linear hydrocarbons and increased production of gases (CO and CO₂) with particle size.

In the present study, pyrolysis of sugarcane bagasse at five different heating rates were conducted using thermogravimetric analyzer (TGA) to study thermal degradation of the biomass. Non-isothermal kinetic study of the sugarcane bagasse was carried out by the application of KAS kinetic model and the activation energy of the process was also calculated [11].

Materials and Methods

Sample Preparation

The sugarcane bagasse samples were obtained from nearby areas in and around TNAU, Coimbatore. The raw sample as received contained 45 (%)w moisture. The moisture content was lowered to 8-10 (%)w by drying in hot air oven at $103 \pm 5^\circ\text{C}$. The air-dried samples were ground and sieved to obtain uniform particle of size in the range of 0.1 - 0.2 mm. The samples were also subjected to proximate and biochemical analysis and the results are given in Table 1.

Table 1. Characteristics of sugarcane bagasse

Parameters	Values
Proximate analysis (%)	
Volatile matter	79.00
Ash content	16.19
Fixed carbon	13.17
Biochemical analysis (%)	
Cellulose	36.19
Hemicellulose	31.57
Lignin	18.67
Extractives	11.71

From table 1, volatile and ash content of the sample was found to be 79 and 16.19 (%)_w. Fixed carbon in the sugarcane bagasse was 13.17 per cent. Cellulose, hemicellulose and extractives in the sample was 36.19, 31.57 and 18.67 while extractives were 11.71 per cent, respectively.

Experimental technique

The pyrolysis experiments were done using thermogravimetric analyser (Model: TGA Q50, TA instruments) coupled with data processor. Thermogravimetric analysis is used to determine a material's thermal stability by monitoring the weight change that occurs during heating in controlled atmosphere. The instrument has a wider range of operating conditions from room temperature to 1100°C . Nitrogen was used as purge gas at flow rate of 60 ml min^{-1} . The experiments were carried under non-isothermal conditions from room temperature to 950°C by placing the sugarcane bagasse sample in the TGA platinum pan and varying the heating rate from $10^\circ\text{C min}^{-1}$ to $50^\circ\text{C min}^{-1}$. In this study, approximately 10 mg of sample is used for each analysis. The samples undergo different stages such as drying and depolymerisation during pyrolysis process. Weight losses with respect to temperature rise were continuously recorded with computer working simultaneously with furnace.

Kinetic study

Thermogravimetric curves were used to obtain the kinetic parameters such as activation energy (E_a) and frequency factor (A) by Kissinger-Akahira-Sunose (KAS) method. General kinetic equation of non-isothermal degradation process is given by,

$$\frac{dx}{f(x)} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) dT \quad \dots (1)$$

where,

x - degree of conversion; A - frequency factor; R - gas constant; β - heating rate; T - temperature
 E - activation energy

Integrating from the initial condition of $x=0$ at $T=T_0$, we obtain

$$\int_0^x \frac{dx}{f(x)} = g(x) = \frac{A}{\beta} \int_{T_0}^T e^{-E/RT} dT \quad \dots (2)$$

For KAS method, Coats-Redfern approximation is used for temperature integration [12] and the above equation is transformed into,

$$g(x) = \frac{A}{\beta} \cdot \frac{RT^2}{E} \cdot \exp\left(-\frac{E}{RT}\right) \quad \dots (3)$$

Taking logarithm and rearranging the above equation,

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{RA}{Eg(x)}\right) - \frac{E}{RT} \quad \dots (4)$$

by plotting $\ln \beta/T^2$ versus $1/T$, a regression line could be derived at different temperature heating rates. The activation energy and frequency factor can be calculated from the slope.

Results and Discussion

TGA

Pyrolysis experiments were performed with sugarcane bagasse biomass at five different heating rates and thermogravimetric curves are given in Fig. 1.

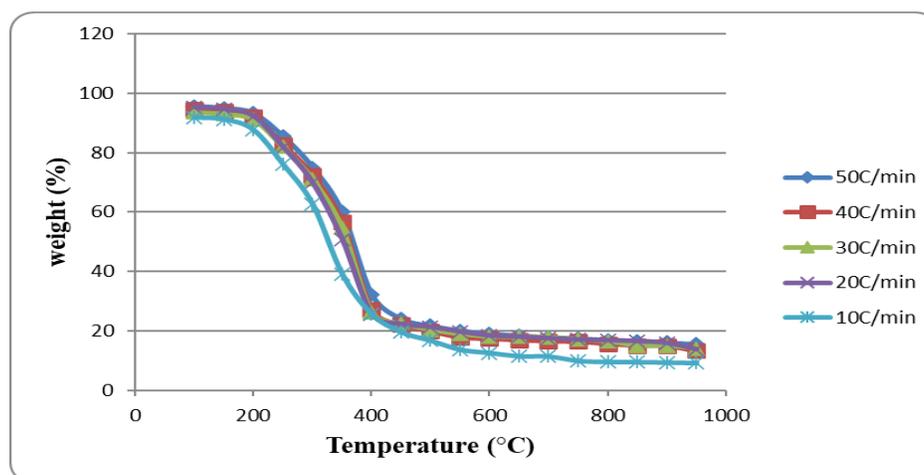


Fig.1. Thermogravimetric curves at different heating rates.

From the thermogravimetric curves, almost similar trend of degradation was observed regardless of heating rates. Generally, the pyrolysis process is divided into three stages viz., (i) dehydration stage at temperature below 150°C in which the water molecules and lower molecular weight compounds were removed, (ii) devolatilization stage from 150 to 500°C consists of two exothermic processes where the main components, hemicellulose, cellulose and lignin were decomposed and a higher amount of volatile vapours formation occur [13]. This stage is referred as active pyrolysis stage. During this stage, higher molecular weight compounds (i.e., oligomeric components from the depolymerization of hemicellulose, cellulose and lignin) are depolymerized to lower molecular weight compounds such as phenols, acids, aldehydes, ketones etc. with the exposure to continuous heat. During decomposition of cellulose, the bonds associated with cellulose are split into monomers at lower temperature and with the increase of temperature, integration of bonds resulted to the formation of liquid [14]. (iii) At final stage, lignin was endothermically decomposed at temperatures above 500°C at a slower rate. Char is the major product during this stage (passive pyrolysis).

Fig. 1. depicts the major weight losses that occurred at different heating rates. Heating rate is considered as one of the important factors in pyrolysis process. It can be observed that 70 per cent of weight loss occurred between 300 and 400°C which was mainly due to the degradation of cellulose and hemicellulose. The residue (char) at the end of the reaction ranges between 9.11 (10°C min⁻¹) and 15.42 (50°C min⁻¹) per cent, respectively. TGA curves indicate that, increase in heating rate from 10 to 50°C min⁻¹ resulted into increased char obtained during thermal decomposition. It may be due to the fact that the lower heating rates resulted to better effective heat transfer to the inner core and among the surface of the particle causing more weight loss in the form of volatile content. Thus, at the higher heating rates, the char residue at the end of pyrolysis experiments also increased. Similar results were observed by Regina *et al.*, [15].

The weight loss curves shifted to a higher temperature region as the heating rate was increased from 10 to 50°C min⁻¹. The peak temperature at the four different heating rates was found to be 316.14, 330.12, 334.23, 345.78 and 355.7°C, respectively. The shift of temperature profile to the right might be due to the thermal lag in the heat transfer between the inner and outer surface of the biomass [14]. Due to the prolonged residence time at lower heating rate (10°C min⁻¹), the temperature profile along the cross-section of the biomass is linear with the outer surface area, and the inner core of biomass is maintained at the same temperature for a specific period. At higher heating rates (40°C min⁻¹), the temperature profile was different between outer and inner core of biomass along the cross section [16]. From the TG-DTG thermographs, it was observed that the different trends are mainly attributed to the chemical composition viz., cellulose, hemicellulose and lignin components.

Thermal degradation kinetics

TGA analysis of the biomass was conducted at five different heating rates and KAS method was used to determine the kinetic parameters. The regression lines based on the above method was plotted and the values of R², activation energy and frequency factor are listed in Table 2.

Table 2. Kinetic parameters by KAS method

Heating rate (°C min ⁻¹)	R ²	Activation energy (Ea, kJ mol ⁻¹)	Frequency factor (A, s ⁻¹)
10	0.94	115.25	7.89
20	0.96	112.16	7.85
30	0.96	112.40	7.85
40	0.96	113.03	7.87
50	0.96	110.76	7.85

It can be seen that the values of determination coefficients are higher than 0.90 in all the heating rates. The activation energies are in the range between 110 and 116 kJ mol⁻¹ which was lower than the values reported in the literatures [13, 17]. This may be due to the various kinetic models viz., Flynn-Wall-Ozawa method and Vyazovkin method used for the calculation of kinetic parameters. The value of frequency factor lies in the range from 7.85 to 7.89. The variation in A values signified the complex reactions during the thermal degradation of biomass [18]. Activation energy in the process must be lower during a chemical reaction. Higher value of activation energy represents difficulty in the occurrence of reaction. It also determines the reactivity and rate of the reaction. Thus, different activation energies at different heating rates illustrated the various characteristics of thermal decomposition process of sugarcane bagasse samples. It also indicates the complexity of physical and chemical transformations at different reaction stages. The activation energy obtained were found to be similar as reported in the literature for different biomass. The values were found to be lower than value obtained for elephant grass (183.8 kJ mol⁻¹), eucalyptus (208 kJ mol⁻¹) [19] and rice husk (221 kJ mol⁻¹) [20].

Conclusion

Pyrolysis of sugarcane bagasse was experimented in thermogravimetric analyser to study the thermal degradation and determination of kinetic parameters using Kissinger-Akahira-Sunose method. The pyrolysis reaction occurred in the temperature range of 290 – 410 °C. Activation energy values were in the range of 110 - 116 kJ mol⁻¹ for different heating rates under non-isothermal condition. Frequency factor values were in the range between 7.85 and 7.89. The results confirmed that the sugarcane bagasse can be used as potential feedstock for the production of good quality fuels and value-added chemicals.

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