



Kinetic Modeling and Gas Composition Analysis During Sawdust Pyrolysis

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Abstract. This research paper deals about kinetic modeling and gas composition analysis of sawdust pyrolysis. The thermal degradation of sawdust at lower (10 °C/min), medium (20 °C/min) and higher (50 °C/min) heating rates were conducted using Beijing Henven Thermo Gravimetric (TG) analyzer. The sawdust pyrolysis gave 98% gas and 2% char, 80% gas and 20% char, and 70% gas and 30% char for lower, medium and higher heating rates. The Flynn-Wall Ozwa (FWO) model free method and the Arrhenius equation was used to estimate kinetic parameters and rate of this pyrolysis process. The rate equation was 93% fit with the medium heating pyrolysis data, which was better fit than the other heating rates. The Thermo Gravimetric analyzer and Jesco 6600 Fourier Transform Infrared (FTIR) analyzer were connected and the released gases at medium heating were investigated. Using TG-FTIR analysis carbon monoxide, carbon dioxide, water, hydrogen and char were released during pyrolysis of sawdust at medium heating rate.

Keywords: Sawdust · Pyrolysis · Kinetic modeling · Gas composition analysis

1 Introduction

Biomass is any organic matter, typically plant-based matter that is available on a renewable or recurring basis. Biomass resources include forest and mill residues, agricultural crops and wastes, wood and wood wastes, animal wastes, livestock operation residues, aquatic plants, fast-growing trees and plants, and municipal and industrial wastes. Biomass can be used in its solid form or gasified for heating applications or electricity generation, or it can be converted into liquid or gaseous fuels [1].

The process usually begins with drying process, and then followed by pyrolysis. The pyrolysis process leads to breaking down of the biomass, into solid matter (charcoal) gaseous mixture (mainly CO₂, CO, CH₄ and H₂) and liquid matter (tar) [2].

Biomass contains cellulose, hemicelluloses and lignin, during the heating biomasses decomposes and releases the volatiles. Volatile generates due to the presence of cellulose and hemicelluloses and remaining char generates due to the lignin. Biomass decompositions started at temperature range 250–300 °C and volatile release at 300–350 °C temperature and complete decomposition carried out above 500 °C. In present work, kinetics study and the gas composition analysis of sawdust pyrolysis were carried out.

2 Materials and Methods

The pine sawdust obtained from furniture manufacturing companies in Bahir Dar city, Ethiopia. This sawdust was ground in the laboratory ball mill and then sieved into an average size less than one mm.

2.1 Thermo Gravimetric Analysis

The non-isothermal experiments were performed in atmospheric pressure under nitrogen environment with a flow rate of 36 mL/min from room temperature to 960 °C. Pyrolysis was carried out at 10 °C/min, 20 °C/min and 50 °C/min, the particle size of less than 1 mm and initial weight of 16.6 mg sample was used. Weight losses occurring in correspondence to temperature rises were continuously recorded with a computer fitted in Beijing Henven TGA instrument. In this study, all the experiments were replicated twice with an uncertainty of less than 3% [2–4].

2.2 FTIR Analysis

Chemical compounds and functional groups identified from wood saw dust sample by using FTIR analyzer. A TGA device was coupled with JASCO FT/IR 6600 infrared spectrometer through 10 cm gas cell. The gas flow rate through the transfer line and gas cell was kept constant. Infrared spectra over the range of 4000 to 650 cm^{-1} were collected every 15 s at a resolution of 4 cm^{-1} . The absorption bands of each spectrum collected are simultaneously integrated over the entire spectral range. Gram-Schmidt curves are obtained by plotting this integration from each spectrum as a function of temperature. These curves were used to have an overview of volatile production throughout the test [5–7, 8, 9].

2.3 Kinetic Modeling of Sawdust Pyrolysis

The results obtained from thermo gravimetric analysis were elaborated according to model-free methods to calculate the kinetic parameters. The activation energy (E_a) and pre-exponential factor (A) were obtained using Flynn-Wall-Ozwa (FWO) methods. The FWO method is based on the following equation: [11]

$$\ln(B) = \ln\left(\frac{AE}{Rg(x)}\right) - 5.331 - 1.052 \frac{E}{RT} \quad (1)$$

Where: B is heating rate, A is exponential factor, R is gas law constant and $g(x)$ is the integral conversion.

Therefore the plot of natural logarithm of heating rates versus $1000/T$ gives a straight line plot. The slope and y-intercept were used to find the activation energy and the exponential factor parameters. The regression equations and the square of the correlation coefficient (R^2) is also presented. The activation energies (E_a) and pre-exponential factor (A) were derived from the slope and intercept of plotting regression line, respectively.

The rate equation for sawdust decomposition was assumed n^{th} order and percent weight loss with respect to temperature was expressed as follows:

$$R1 = \frac{dx}{dT} = A/B \exp((-E/RT))(1 - X)^n \quad (2)$$

3 Results and Discussion

3.1 Pyrolysis of Sawdust

The weight loss curve in Fig. 1 shows the loss of mass with temperature at different heating rates for Sawdust. As can be seen from the plot, the de volatilization process begins at about 380 K and proceeds rapidly with increasing temperature until about 600 K and then the weight loss decreases slowly to the final temperature. The first weight loss, around 110 °C, corresponds to the moisture loss of the sample. At temperatures below 110 °C, moisture content is reduced by up to 5% of the sample weight. The second weight reduction corresponding to increasing the temperature to 900 °C is attributed to de volatilization and pyrolysis of mainly organic materials. All the volatiles were evolved at below 600 °C for the three heating cases. In this step, the yield of the volatile material is up to 70% for 50 °C/min, 80% for 20 °C/min and 98% for 10 °C/min heating rates respectively.

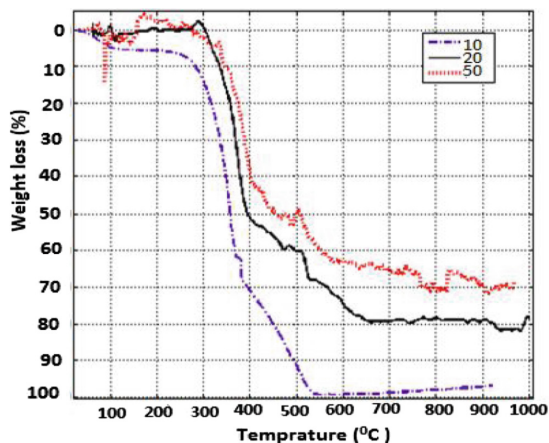


Fig. 1. Sawdust weight loss at different heating rates

It can be seen that the TG curve shifted up as the heating rate increased. As the heating rate increased the char yield increased and the gas release is decreased. At the lower heating rate, fewer char and high gasses are produced. In contrast, at higher heating rate, the de volatilization process occurred sooner due to the increased rate of heat transfer. Faster heating rates give the high amount of char and low gas release.

3.2 Kinetic Modeling of Sawdust Pyrolysis

The parameters obtained from FWO model free method are 5.057 kJ/mol and $8.93 \times 10^4 \text{ min}^{-1}$ for activation energy (E) and pre-exponential factor (A), respectively. The correlation coefficient (R^2) is 88% (Fig. 2).

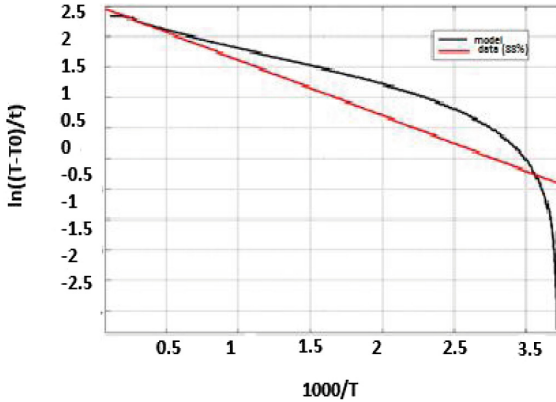


Fig. 2. Logarithm of heating rate with inverse temperature

The reaction assumed is first order and get the following relation for percent weight loss and temperature (Fig. 3).

$$R1 = \frac{dx}{dT} = \frac{8.93 \times 10^4}{20} \exp\left(\frac{-5.057}{8.314 \times T}\right) (1 - X) \tag{3}$$

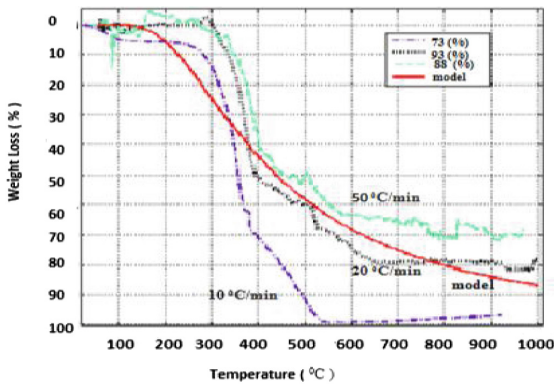


Fig. 3. Model fit with the at different heating rate data

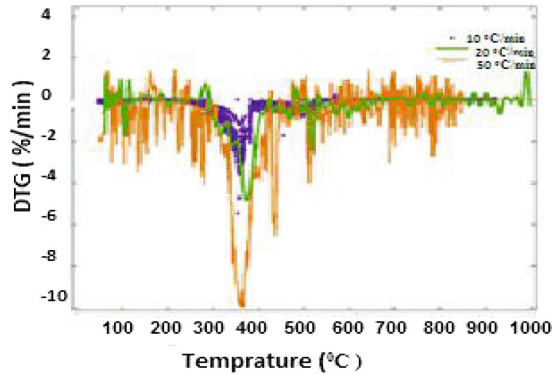


Fig. 4. DTG analysis of Sawdust at different heating rates

When we integrate the above equation, the percent weight loss becomes

$$X = 1 - \exp\left(\frac{-2715.84}{T}\right) \exp\left(\frac{-0.61}{T}\right) \quad (4)$$

The Flynn model fits 73% with higher heating rate (50 °C/min), 93% with medium heating rate (20 °C) and 88% with lower heating rate (10 °C). Therefore the first order assumption is reasonable for pyrolysis of sawdust at medium heating rate.

3.3 DTG Analysis of Sawdust Pyrolysis

The derivative thermo gravimetric (DTG) curve could assist in explaining the TG curve.

The spread of the decomposition over temperatures of 25–900 °C appears as a relatively broad peak. The area under the peak represents the weight loss during the reaction. Thus, relative mass losses may be compared. When initial slow decompositions are followed by fast decompositions above 200 °C then a second slow decomposition initiates at 380 °C, there is a gradient change in the DTG curve. This information is used in this study to distinguish the different stages of each process and their gas evolution.

Higher heating rate has given maximum weight change per time compared to the medium and lower heating rates. The DTG curve indicates that different gases released during pyrolysis of sawdust at different temperature. These peaks are important to estimate amount and type of gases released.

3.4 FTIR Analysis of Sawdust Pyrolysis

In the wave number range $3600\text{--}3150\text{ cm}^{-1}$ indicating the release of H_2O , $3000\text{--}2730\text{ cm}^{-1}$ indicating H_2 is released, $2400\text{--}2160\text{ cm}^{-1}$ indicating the existence of CO_2 , $2260\text{--}1990\text{ cm}^{-1}$ indicating the existence of CO , $1900\text{--}1650\text{ cm}^{-1}$ indicating aldehydes released, $1500\text{--}950\text{ cm}^{-1}$ phenols/ethers released and $900\text{--}650\text{ cm}^{-1}$ hydrocarbons released [12].

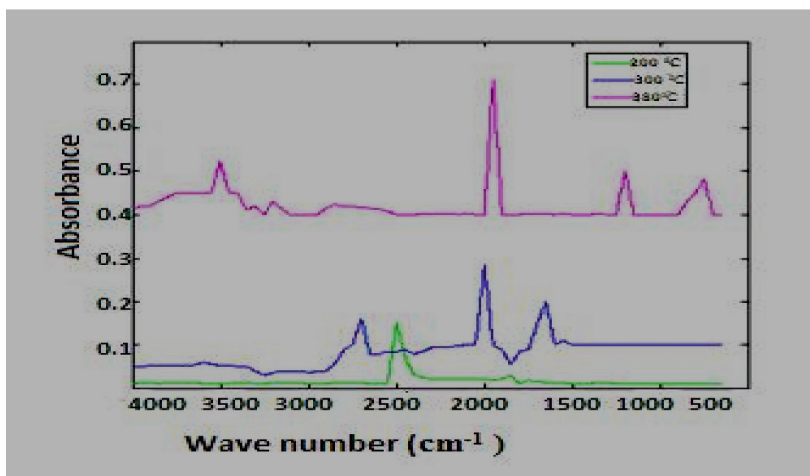


Fig. 5. FTIR analysis of saw dust

At the first stage of the temperatures between 100 and $420\text{ }^{\circ}\text{C}$, the curves of evolved gases (Figs. 5 and 4) revealed the presence of CO_2 , H_2 and CO , as well as small amounts of some organic volatile compounds such as aldehydes and acids. The first peak at approximately $100\text{ }^{\circ}\text{C}$ represents the water vapor release. The second complex peak confirms the release of volatiles in two steps during active pyrolysis. Individual compounds identified are carbon dioxide, carbon monoxide, hydrogen and char. From DTG & FTIR curve there are many peaks that correspond to functional groups, but major peaks are considered in this work. The progress of released volatile peaks and the temperature interval of their evolution are similar to that observed in this work. The results of sawdust pyrolysis were published by Gu et al. [12]. The pyrolysis process was divided into the following three steps: below $250\text{ }^{\circ}\text{C}$ production of the water vapor. Carbon dioxide, carbon monoxide and hydrogen are produced in the range of $250\text{--}500\text{ }^{\circ}\text{C}$. Above $500\text{ }^{\circ}\text{C}$ char formation process is resulted. Speculative path ways for the mechanism of cellulose, hemicellulose and lignin pyrolysis also presented. The first carbon dioxide signal was detected at approximately $250\text{ }^{\circ}\text{C}$, reach maximum peak of at $320\text{ }^{\circ}\text{C}$ and decreased up to $450\text{ }^{\circ}\text{C}$ is agreement with the results obtained in this study. However based on the results presented in this study carbon dioxide and hydrogen are released at slightly higher temperatures.

4 Conclusion

The mass loss of sawdust sample during pyrolysis was model using Flynn-Wall-Ozwa model free method. The model was compared with the TG data and 93% of fit was achieved for medium heating rate. The differential analysis shows that higher heating rate has given maximum weight change per time compared to the medium and lower heating rates. The higher heating rate also gives maximum char conversion and low gas release. The DTG & FTIR curve peaks were revealed that for gas release of CO₂, H₂ and CO, as well as small amounts of some organic volatile compounds such as aldehydes and acids.

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