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Mathematical Modelling and Kinetics of Thermal Decomposition of Corn Stover using Thermogravimetry (TGA-DTG) Technique

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Abstract. Lignocellulosic biomass could be pyrolytically converted into value-added products and one of the steps during the pyrolysis is thermal decomposition which involves multiple reactions. Therefore, mathematical modelling of thermal decomposition could provide molecular insight into thermal degradation reactions by providing accurate prediction of the phases of the multi-component reactions in particular nucleation, growth and boundary-phase reactions occurring under different working conditions. In this study, thermal decomposition behaviour of Corn Stover was explored using thermogravimetry technique (TGA-DTG) at heating rates of 20, 30, 40 and 50 °C/min under nitrogen gas flow (55 mL/min) and oxygen gas flow at 15 mL/min. The Flynn-Wall Ozawa (FWO) and Kissinger Akahira Sunose (KAS) models were used to estimate the kinetic parameters such as apparent activation energy, pre-exponential factor and order of reaction so as to be able to design the pyrolytic reactor that could be used for the biomass conversion. The hemicellulose maximum mass loss rate was at 300 °C, cellulose at 410 °C and lignin decomposition from 190 °C to 620 °C. The apparent activation energies calculated ranged from 44.39 -134.81 kJ/mol using the FWO method while the KAS method gave 87.83 – 282.41 kJ/mol. The variation of the apparent activation energy represents the four different stages occurring during the thermal decomposition process for the corn stover. The Friedman's model was used with reaction-order model to estimate the order of reaction. The predicted model fitted well with the experimental data showing that the complex degradation process followed a first-order reaction.

Keywords: Thermogravimetry; Corn Stover; Kinetics; Lignocellulosic biomass; Kissinger Akahira Sunose; Flynn-Wall Ozawa

INTRODUCTION

Renewable energy is fast becoming popular as it is regarded to being a potential future source of energy to the global energy challenges and because trends reveals that the world will soon face limitations regarding the use of fossil fuels. The usage of biomass has enticed global interest, due to the exhaustion of fossil fuels and increase in energy demand in addition to the ever-growing environmental concerns regarding the emission levels of carbon dioxide (CO₂), sulphur dioxide (SO₂) and nitrogen oxides (NO_x) which are depleting the ozone layer and contributing to global climate change [1].

Most developing countries have economies which are largely driven by agriculture and forestry due to contribution they have on Gross Domestic Product (GDP), therefore, embracing the participation in biomass conversion technologies [2]. The annual local production of corn in South Africa is about 6.7 million tonnes. The global corn

production is about 0.5 million metric tonnes (MMT), and amongst such global yields 1.7 % of this production is generated in South Africa [3]. This vast amount of agricultural residues ploughed annually leaves huge quantities of biomass waste generated during the process. These agricultural waste are dumped into open spaces as waste or incinerated in the open land. This practice of burning agricultural waste has catastrophic effects on the environment, such as air pollution and affects human health [4]. In addition, the soil matter and its nutrients are negatively affected by the disposal of the crop waste [5].

The agricultural residues of corn stover could be used as valuable raw material in the manufacturing process of liquid biofuels, bioenergy and chemicals products [6]. Corn stover is a lignocellulosic material that has attracted interests from researchers as potential replacement for non-renewable fossil fuels. However, lignocellulosic biomass decomposition is a complex process because the biomass is a composite material and therefore contains different chemical components [6].

Numerous research efforts have acknowledged the fact that thermal degradation process for lignocellulosic biomass is solely dependent on the reaction rates and thermos-kinetics of their constituents namely, lignin, cellulose, hemicellulose and other lower substances such as extractives [7]. It is thus imperative to assess the thermal deconvolution behaviour of biomass and the degradation of its main constituents so we could study the rate of the chemical reaction taking place [7]. Furthermore, the thermal deconvolution of lignocellulosic biomass is quite intricate and complex as it tends to take place via multiple reactions that occurs at different decomposition rates and therefore kinetic models are important as they provide molecular insight for pyrolysis reactions [8].

Thus, this study investigates different kinetic modelling techniques, which includes the Flynn Wall ozawa (OFW) and Kissinger Akahira Sunose (KAS), to determine the kinetic parameters during pyrolysis of lignocellulosic biomass (E.g. Corn stover). Friedman's method was used for better understanding of the reaction-based order models.

EXPERIMENTAL METHODS

Materials

The pre-treated corn stover sample used in this study was obtained from a source in Nigeria. The sample was dried and crushed into smaller particles. The biomass sample was further pulverized into fine particles suitable for TGA and other analysis in the laboratory. The samples were kept dry in small bottles and ziplock in plastic bag. The Scanning Electron Microscopy (SEM) was used to analyse the surface morphology and composition of Corn Stover. It also checks the crystalline structure of the cellulose polymers tightly bonded to the cell walls via the lignin and hemicellulose monomers. The corn ctover sample was coated with 60/40 % of Gold and Palladium (Au/Pd) prior to scanning to prevent charge up.

Thermal Decomposition

About 50 mg biomass sample was weighed into the TGA aluminium pan. For each experimental sample run, the sample was held at 25 °C for 15 minutes, thereafter, the temperature was raised to 105 °C whilst temperature being held constant for 30 minutes. The Nitrogen gas, which aids as the protective gas in the TGA for pyrolysis process, was kept at a constant flowrate of 55 mL/min during the experimental runs. The dried sample was heated up to 700 °C at differing heating rates of 20°C/min, 30°C/min, 40°C/min and 50°C/min. At this stage the hemicellulose decomposes within the range of 160°C – 360°C while cellulose decomposing at 240 °C-390 °C [9]. For the combustion of formation of solid char, the temperature was maintained at 700 °C further for 30 minutes with the oxygen flowrate into the system kept at constant flowrate of 15 mL/min and Nitrogen being kept at constant flowrate of 55 mL/min.

Bomb Calorimetry

In this experiment, about 0.5 – 1 g of corn stover sample was burnt using the Drycal Modular Calorimeter to obtain the heating value for combusting the sample. Benzoic acid was used to calibrate the instruments prior to commencement of experiment. The crucible in the bomb calorimeter was initially tare to zero. The crucible was then loaded with biomass sample and fuse wire was hanged onto the sample crucible. The grinded corn stover sample was then placed into the bomb bucket and observation for any possible leaks was done. The oxygen pressure was set

at 20 bars. The electrodes were then connected to the top of the bomb and tightened with the lid closed and the experiment was conducted.

Kinetic Study

Lignocellulosic biomass thermal degradation process is complex as its main constituents contain different chemical composition and degrade at different temperature intervals whilst undergoing pyrolysis. During the thermal decomposition of biomass, it is essential to observe the rate of chemical reaction occurring through studying its kinetic parameters. Therefore, isoconversional methods are used to estimate the kinetic parameter values, and the pre-exponential factor and activation energy are calculated as a function of the conversion and temperature. The most generally utilised equation in defining the rate of decomposition reactions in the non-isothermal devolatilization kinetics is presented as Eq. 1:

$$\frac{d\alpha}{dt} = kf(\alpha) \quad (1)$$

Denotes the degree of conversion, t is time, k , indicating the rate constant whilst $f(\alpha)$ referring to the reaction model.

The reaction rate constant, k , is largely dependent on temperature and is therefore expressed by the Arrhenius equation in Eq. 2:

$$K = A. e^{-\frac{E_a}{RT}} \quad (2)$$

Where E_a refers to the activation energy (KJ/mol), T is the absolute temperature in kelvin (K), R is the gas constant (8.314 J/mol.K) and A is the pre-exponential factor (min^{-1}).

The conversion rate (α) is obtainable as follows:

$$\alpha = \frac{m_i - m_a}{m_i - m_f} \quad (3)$$

And from the above equation, we can deduce that m_i denotes initial mass of the sample, m_a depicting mass at time t , while m_f is referring to the final mass of sample.

The combination of Eq. 1 and Eq. 2 will yield the elemental equation of analytical methods used to estimate the kinetic parameters, which is expressed in Eq. 4:

$$\frac{d\alpha}{dt} = A. f(\alpha). e^{-\frac{E_a}{RT}} \quad (4)$$

The thermogravimetric analysis takes place at different heating rates, and incorporating it into Eq. 4 gives:

$$\beta = \frac{dT}{dt} \quad (5)$$

Dividing equation 4 by β (Eq. 5) gives Eq.6:

$$\frac{d\alpha}{dT} = \left(\frac{A}{\beta}\right) e^{-\frac{E_a}{RT}}. f(\alpha) \quad (6)$$

The model-free and model-fitting techniques are utilized for the assessment of the parameters for the lignocellulosic biomass reaction kinetics. Both isoconversional models and fitting-model techniques were applied in this study to roughly calculate the kinetic parameters. The iso-conversional methods used are Kissinger –Akahira Sunose (KAS) and Flynn-Wall Ozawa (FWO) methods. For the model fitting, the Friedman’s method together with the reaction-based order model were used to determine reaction order. The kinetic models used to evaluate the kinetic parameters are outlined below:

The Flynn Wall Ozawa Method

The Flynn Wall Ozawa method is the most prevalent and widely preferred method within the scientific community when it comes to computing kinetic parameters from experimental data. This is because, it does not assume any reaction model when computing the kinetic parameters in activation energy and pre-exponential factor.

The model is expressed in Eq. 7:

$$\ln\beta = \ln \frac{AE}{f(\alpha)R} - 2.315 - 0.4567E/RT \quad (7)$$

The Activation energy will thus be obtained by constructing a straight line plot of $\ln\beta$ vs $1/T$ with a gradient of $-0.4567E/RT$. From the intercept of the resulting straight line, the pre-exponential factor values can be obtained.

The Kissinger Akahira Sunose (KAS) Model

This is an isoconversional method in which the reaction order is omitted whilst estimating the activation energy. The values of the activation energy at different conversion rates is determined from the numerical approximations of the Arrhenius integral across a wide range of thermal history [10].

The model expression is as shown in Eq.8:

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{AR}{E f(\alpha)}\right) - E/RT \quad (8)$$

The plot of $\ln(\beta/T^2)$ vs. $1/T$ produces a straight line. The activation energy values and pre-exponential factor will be estimated from the intercept and slope without assuming any particular reaction model.

Friedman's Method

The main assumption made from the Friedman's method is that the thermal degradation process does not necessarily depend on reaction temperature, however, the rate of mass loss affects the reaction progress. Hence, the function of conversion is constant at any given conversion. The model expression is given as follows:

$$\ln\beta \frac{d\alpha}{dT} = \ln[k_0 f(\alpha)] - \frac{E_a}{RT} \quad (9)$$

The plot of $\ln\beta \frac{d\alpha}{dT}$ versus the inverse temperature, the activation energy can be estimated from the slope, $\frac{E_a}{RT}$.

Reaction Order Based Model

The reaction order is one of the most widely used for the estimation of the reaction kinetics of solid mass conversion:

$$f(\alpha) = (1-\alpha)^n \quad (10)$$

Sestak and Berggren introduced an empirical model, known as SB model [10].

$$f(\alpha) = (1-\alpha)^n \cdot \alpha^m \cdot [-\ln(1-\alpha)]^p \quad (11)$$

From equation 11, the reaction order is denoted by symbol n, while m and p denotes accelerating behaviour and nuclei growth mechanisms, respectively. Therefore, if we incorporate SB into Eq. 6:

$$\frac{d\alpha}{dt} = \frac{k_0}{\beta} e^{(-E_a/RT)} \cdot (1-\alpha)^n \cdot \alpha^m \cdot [-\ln(1-\alpha)]^p \quad (12)$$

The reaction order parameters were estimated at each heating rate by using the non-linear square method in Eq. 13:

$$OF = \sum \left(\frac{d\alpha}{dt} \downarrow exp - \frac{d\alpha}{dt} \downarrow pred \right)^2 \quad (13)$$

RESULTS AND DISCUSSION

Surface Morphology of Corn Stover

Figure 1 shows the SEM morphology of the corn stover revealing the crystalline form of cellulose structure embedded in the flat and compactly arranged surface, supported by the lignin and hemicellulose components. The clearly defined components of the corn stover sample as shown in Figure 1 revealed no damage or indication of loose bonds prior to the thermal degradation process. The hemicellulose function is to connect the lignin and cellulose fibrils and offer rigidity to the entire network of cellulose-hemicellulose-lignin within the corn stover biomass sample. The xylan polymer bonds are embedded within the hemicellulose structure.

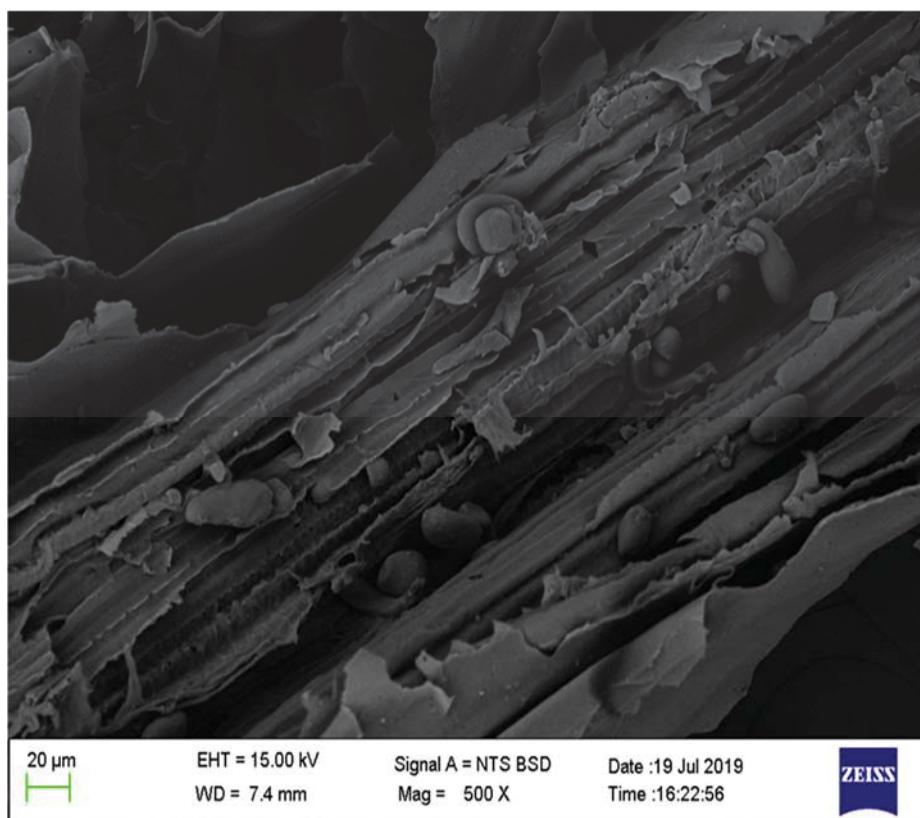


FIGURE 1. Surface morphology of cellulose-rich raw corn stover

Thermal Decomposition

The thermal decomposition (Weight loss) profile of corn stover at different heating rates is depicted in Figure 2. The thermal degradation behaviour of corn stover was investigated as a function of mass loss versus temperature and time using thermogravimetric analysis at 55 mL/min N_2 flow rate and operating at different heating rates of 20, 30, 40 and 50 °C/min. The release rates of the different components of lignocellulosic biomass during the degradation process vary with change in heating rate. However, the thermal behaviour shows general trend which illustrates the thermal deconvolution in 4 stages. According to Sittisun *et al.* [4] such a trend implies that same reactions occurred at all heating rates. The corn stover degradation process had undergone four distinct mass loss stages and it was in agreement with the findings from Jutakridsada *et al.* [11]. The first stage can be deduced to being the dehydration stage of biomass sample occurring at temperature ranges of 25°C to 170°C corresponding to the release of moisture content and the beginning of the polysaccharide hydrolysis process, where the water molecule starts breaking down the covalent bonds of polymerized monosaccharides such as glucose on the lower molecular hemicellulose part of lignocellulosic biomass constituents [9]. Subsequent to the initial degradation stage, there was minimal weight loss due to moisture release before rapid weight loss of sample took place at around 180 °C to 400 °C which signals the start of stage 2. Lignocellulosic biomass consists of hemicelluloses, celluloses and lignin as major constituents. According to Varhegyi *et al.* [12] hemicelluloses typically decomposes in temperature ranges of 160 °C – 360 °C, while celluloses degrades within higher temperature ranges between 240 °C – 390 °C, and lignin decomposition occurs at much slow pace over wide temperature range of 180 – 900 °C for Corn Stover. On the derivative thermogravimetric (DTG) curve outlined in Figure 2 the temperatures at which maximum rate of mass loss took place are outlined by the position of the peaks in the curve. Two major peaks could be detected in the decomposition curve in Figure 2 and it is attributed to phase change process whereby the hemicellulose and cellulose components in lignocellulosic biomass are undergoing decomposition. From the results we could deduce that the hemicellulose constitutes decomposed first, subsequent to that was the cellulose structural decomposition and lastly the lignin bonds. The corn stover devolatilization temperature was within the ranges of 170 °C – 400 °C with peak

temperatures at 270 °C – 320 °C, 280 °C – 330 °C, 290 °C-330 °C and 300 °C – 340 °C at heating rates of 20, 30, 40 and 50 °C/min respectively. The values obtained for the devolatilization temperature in stage 2 and the peak temperatures were in similar magnitude to those obtained by Sittisun et al. [4] for corn stover at heating rates of 10, 30 and 50 °C/min. This stage can be attributed to further mass loss of lignin and fixed carbon, with residues of lignin and some cross-linking cellulose contents undergoing further exothermic polymerization stage of char [13]. During the final stage that took place above 680 °C and 690 °C for corn stover complete combustion of biomass took place with ash contents of both biomass samples.

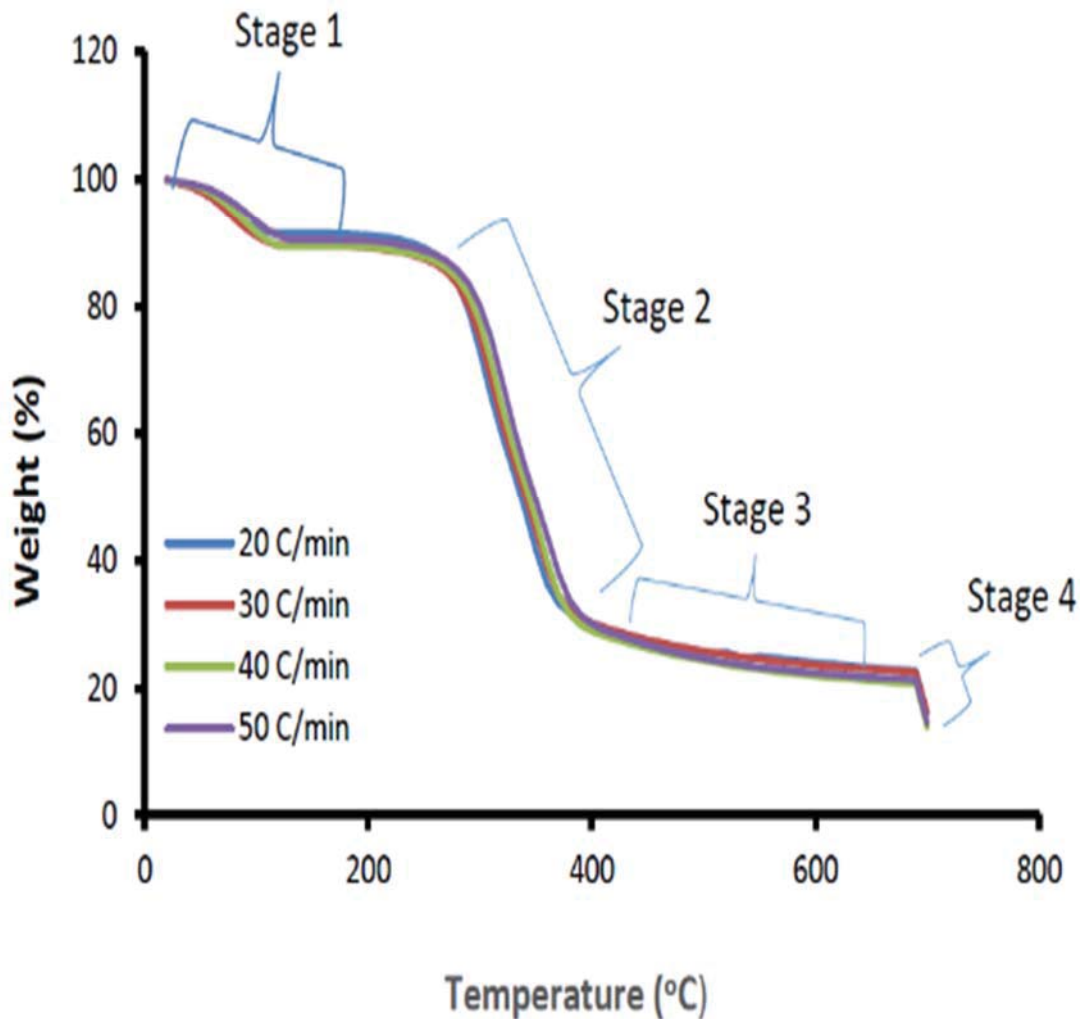


FIGURE 2. TGA profile of Corn Stover at different heating rates

Effect of Heating Rate on Thermal Decomposition of Corn Stover

The influence of the heating rate was considered as one of the research objectives mainly because of its great influence on the conversion of lignocellulosic biomass and product distribution [6]. In this study, the TGA results as shown in Figure 2 revealed that increasing heating rate showed an increase in temperature within stage 2, which is the devolatilisation stage. However, there has been no effect of heating rate within stage 1, 3 and 4 as the trends were more similar for corn stover sample. This could be due to the fact that corn stover is a cellulose rich structure,

and cellulose is interconnected with hemicellulose and lignin. Therefore, the thermal stability of the biomass sample at the second stage was impacted by the higher heating rate as the material reached higher temperature within short period of time once the hemicellulose polymers and cellulose bonds were broken. The observation from the DTG curves was in good agreement with results of Onsree et al. [6] and Aboyade et al. [9]. Figure 3 clearly shows that the relationship between heating rate and lignocellulosic biomass components decomposition. At lower heating rates, the shape of DTG curve is narrow while at higher temperatures the shape is broader and shifts to the right showing phase boundary reactions. From the derivative curve for corn stover sample, it could be seen that increasing heating rate shifted the initial temperature, the peak temperatures and final temperatures to higher temperatures. According to Onsree *et al.* [6], such a behaviour has been caused by the increased thermal lag and more thermal energy was available to make it possible to achieve better transfer of heat between the surroundings and the inside of particles at higher heating rates.

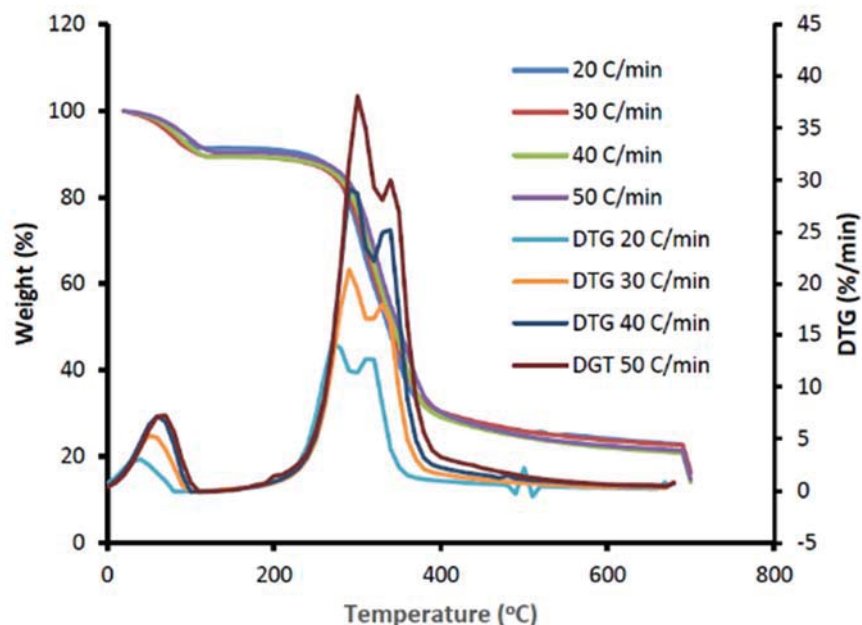


FIGURE 3. TGA-DTG graph of corn stover at different heating rates

Kinetic Analysis

The kinetic parameters such as activation energy and pre-exponential factor defining the overall weight loss of corn stover sample using thermogravimetric analysis data were determined from the Flynn Wall Ozawa (FWO) and Kissinger Akahira Sunose (KAS) method. Figure 4 depicts the kinetic study of corn stover, using FWO method. The conversion range from 0 – 15 % is attributed to the moisture release and the lower lignocellulosic biomass contents decomposition [9]. The devolatilisation stage occurred from 20% conversion rate and temperature of 280 °C with activation energy values ranging from 44.39 KJ/mol–134.81 KJ/mol as stated in Table 1 using the FWO method. At this stage, volatile release is taking place as the hemicellulose polymers are being broken down as well as the cellulose microfibrils which are embedded within the cell wall structure of lignocellulosic biomass [4]. This also means that the activation energy differed largely within the oxidative decomposition process. The lignin constituent of biomass required more energy to break because the reactivity of the lignin adhesive bonds took time to react. The results from this study is similar to the findings of Aboyade et al. [9] and Sittisun et al. [4].

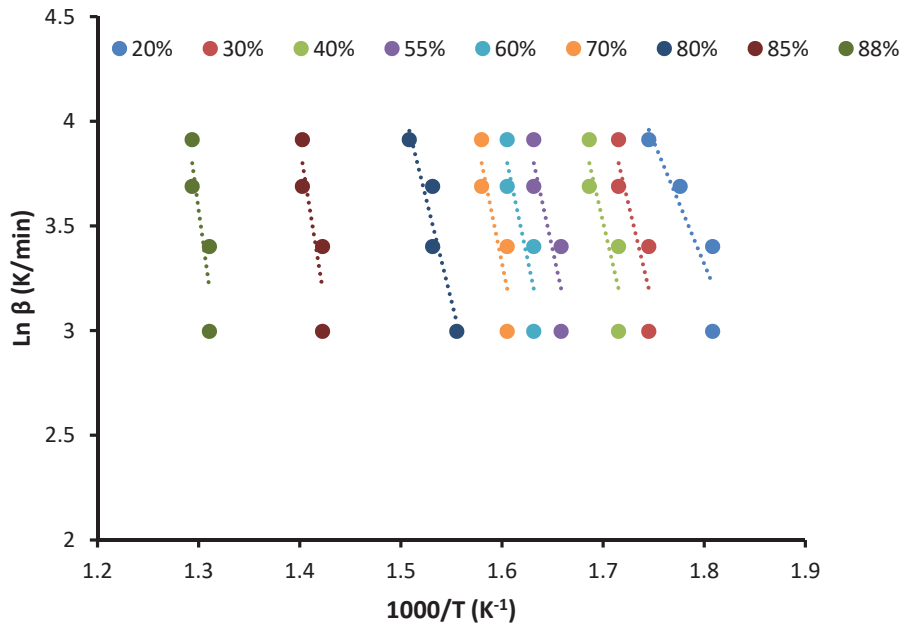


FIGURE 4. Kinetic study of corn stover using Flynn Wall Ozawa (FWO) method

TABLE 1. Activation energy values for corn stover using Flynn Wall Ozawa (FWO) method

Conversion (α)	E_a (kJ/mol)	A (s^{-1})	R^2
0.2	44.39	1.2×10^5	0.80
0.3	76.36	7.8×10^{10}	0.77
0.4	79.02	1.4×10^{11}	0.77
0.55	84.49	4.3×10^{11}	0.77
0.6	87.29	7.5×10^{11}	0.77
0.7	90.14	1.3×10^{12}	0.77
0.8	74.27	6.3×10^8	0.90
0.85	114.57	1.3×10^{14}	0.77
0.88	134.81	4.1×10^{15}	0.77
Average	87.26		

Figure 5 depicts the linear plots obtained for the kinetic study of corn stover, using the KAS method at different conversion rates. The activation energy was found to be higher than those calculated using the FWO method. The activation energy values ranged from 87.83 kJ/mol – 282.41 kJ/mol as shown in Table 2 using the KAS method and cellulose and hemicellulose lignocellulosic biomass constituents were decomposed in this range [9]. The Kissinger Akahira Sunose (KAS) method indicated that the cellulose and lignin decomposition displayed higher activation energy values as stipulated in Table 2 from 40% conversion rate to 90%. This means that the depolymerisation process of cellulose polymer chain via the trans-glycosylation process required more energy to break the glycosidic bonds which held the cellulose structure together within the microfibrils section of corn stover fibres [4]. The thermal degradation process was largely influenced by the crystalline structure of corn stover which was rich in cellulose and tightened together with strong adhesive lignin forces, therefore requiring higher activation energy to decompose [4]. This results are in agreement with results reported in literature [4,9].

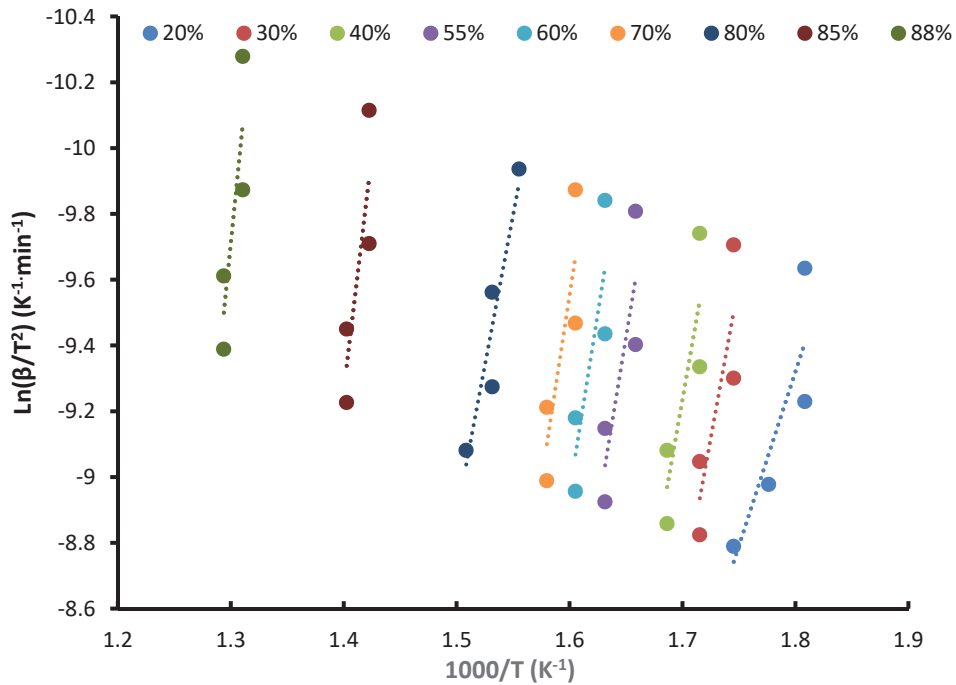


FIGURE 5. Kinetic study of corn stover using Kissinger Akahira Sunose (KAS) method

TABLE 2. Activation energy values for corn stover using Kissinger Akahira Sunose (KAS) method

Conversion (α)	E_a (kJ/mol)	A (s ⁻¹)	R^2
0.20	87.83	2.86×10^3	0.77
0.30	157.54	5.47×10^{12}	0.75
0.40	163.25	1.00×10^{14}	0.75
0.55	174.89	3.34×10^{13}	0.75
0.60	180.86	6.10×10^{13}	0.75
0.70	186.93	1.12×10^{14}	0.75
0.80	151.75	3.27×10^{10}	0.88
0.85	239.09	1.39×10^{16}	0.75
0.88	282.41	5.15×10^{17}	0.76
Average	180.51		

Table 3 shows the activation energy values obtained in literature by Onsree et al. [6] using the Flynn-Wall Ozawa method. Comparing Table 3 with the results obtained in this study in Table 1 and Table 2, it could be observed that activation energy value of 70 kJ/mol at conversion rate of 20% was obtained by Onsree et al. [6], whereas in this present study at same conversion rate, the activation energy was lower at 44.39 kJ/mol. The difference in those values could be attributed to the fact that both experiments occurred under different heating rates and within that stage, it is the hemicellulose component which undergoes decomposition. Therefore, it could be that the biomass sample used in this study was less thermally stable than the ones used for Onsree *et al.* [6], Aboyade et al. [9] and Sittisun et al. [4]. From this present study (Table 1), an activation energy of 79.02 kJ/mol was obtained at 40% conversion rate. However, an activation energy of 63 kJ/mol was obtained by Onsree et al. [6]. Within that range of

conversion, normally the crystalline form of cellulose undergoes degradation into volatiles so the amount of energy required to break the glycosidic bonds should increase as such a trend was observed in present study. However, with the corn stover pellet used by Onsree et al. [6], the activation energy decreased and this could mean most of the reactions would have occurred in the boundary section of the particle and not within the core of the sample particle. It could also mean that, there great heat and mass transfer limitations occurred during experiment and their sample size was bigger and during thermal decomposition, bigger particle sizes experiences slow reactions. According to Ali et al [10], the thermal deconvolution of the biomass constituents which contains similar chemical structure will thus decompose over similar narrow temperature ranges and therefore high-loading and non-uniform distribution of the biomass sample into the furnace will result in the homogenous reactions which affects the activation energy trend. The activation energies calculated from 80% conversion rates in studies conducted by Onsree et al. [8], Aboyade et al. [9] and Sittisun et al. [4] as well as this present study are higher, indicating the fact that most of the simultaneous multi-component reactions occurred at the boundary phase of particle as that is where the lignin and hemicellulose component are located.

TABLE 3. Calculated activation energies from TGA by the FWO method using corn stover as biomass sample [6]

Conversion	E_a (kJ/mol)	R^2
0.1	60	0.935
0.2	70	0.941
0.3	65	0.957
0.4	63	0.969
0.5	63	0.975
0.6	62	0.977
0.7	63	0.975
0.8	68	0.939
Average	64	

Model-Fitting Method

Estimation of the Order of Reaction for Corn Stover Using the Reaction Order-Based Model

The Flynn-Wall Ozawa and Kissinger Akahira Sunose methods were used to obtain the kinetic parameters without necessarily assuming any reaction order. This is to avoid problems regarding the uncertainties that may arise if a reaction order is assumed, because biomass pyrolysis does not assume a single reaction mechanism. Hence, the reaction order calculation is omitted when estimating kinetic parameters using FWO and KAS [7]. Lignocellulosic biomass is composed of many components and hence, it would be beneficial to understand the reaction mechanism, reaction scheme and influence which various biomass components have on the biomass conversion process. In this study, the Friedman's model was used to examine the reaction order value. The calculations were performed using Microsoft excel. Using the activation energy values obtained from the Friedman method, the predicted conversion rate was calculated at each heating rate using the differential model (Eq. 4). The experimental conversion rate at every heating rate was plotted with calculated predicted conversion rates against furnace temperature as illustrated in Figure 6 (a-d). This is aimed at determining if the reaction order based model can best possibly describe the multi-component reaction mechanism of the Lignocellulosic biomass components.

From the simulated DTG curves as illustrated in Figure 6 (a-d), it can be seen from the predicted curves that reaction order of 1 is more closely fitted to the experimental curve as compared to the other two reaction orders at all four heating rates. As the reaction order is increased from 1 to 3, the difference between the experimental and predicted values increases as indicated by the Objective function (OF) and Fit (%) shown in Table 4. This is an evidence that the multi-component decomposition reaction for corn stover follows a lower reaction order [10]. The corn stover reaction mechanism was reportedly found to follow first order reaction rate. This is an indication that, rate at which the thermal degradation process occurs in converting corn ctover biomass into char, volatiles and gases is solely dependent on its concentration [14]. The observation from this study is similar to the findings of Ali et al. [10] and Onsree et al. [6].

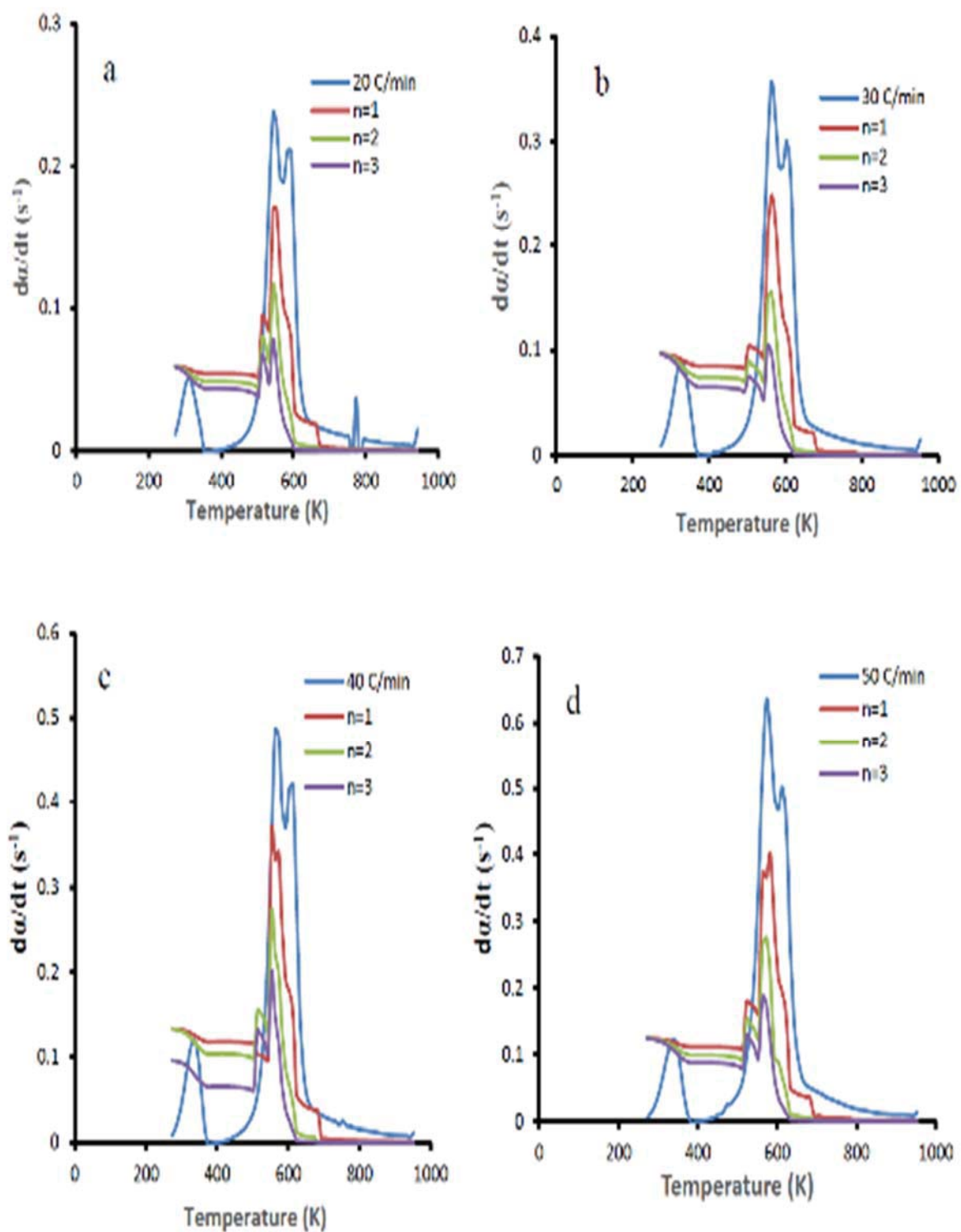


FIGURE 6. DTG best-fit plot of Corn Stover with different reaction orders at (a) 20°C/min (b) 30 °C/min (c) 40 °C/min (d) 50 °C/min

TABLE 4. Reaction order parameters calculated at different heating rates for Corn Stover

Reaction Order	°C/min	A (s ⁻¹)	OF (s ⁻²)	N	Fit (%)
1	20	0.1387	0.007	1	64.17
	30	0.1926	0.0017	1	83.61
	40	0.2734	0.0429	1	43.67
	50	0.3292	0.4874	1	-74.65
Average		0.2334	0.1348	1	
2	20	0.1387	0.58		
	30	0.1926	0.955		
	40	0.2734	0.9731		
	50	0.3292	5.2417		
Average		0.2334	1.9374		
3	20	0.1387	1.226		
	30	0.1926	2.314		
	40	0.2734	6.016		
	50	0.3292	9.508		
Average		0.2334	4.76		

CONCLUSION

This current study successfully examined the thermal decomposition and calculated the kinetic parameters for the pyrolysis reaction of corn stover in a nitrogen atmosphere at four different heating rates. The following conclusions could be drawn from this study;

- SEM image for corn stover revealed crystalline form of cellulose structure embedded in the flat and compactly arranged surface supported by the lignin and hemicellulose components.
- The activation energy for corn stover was from 44.39 – 134.81 kJ/mol using the Flynn-Wall Ozawa method and between 87.83 – 282.41 kJ/mol using the Kissinger-Akahira Sunose method. Results showed that Kissinger-Akahira is considered a reliable method that could help defining the decomposition reaction for biomass compared to Flynn-Wall Ozawa due to its better temperature approximation for the integral kinetic model equation.
- Furthermore, the results show that, Friedman method can complement the reaction-order based model in defining the multi-component lignocellulosic biomass decomposition rate. The order of reaction for corn stover decomposition was found to be 1.

This study has successfully estimated the kinetic parameters for corn stover using FWO, KAS and Friedman's models. However, in order to further explore the reaction kinetics through the development of empirical fit parameters such as the accelerating behaviour and nuclei growth mechanisms, other model-fitting method such as the Sestak and Berggren model could be considered.

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