Investigation of Kinetic, Thermodynamic and Performance Parameters during Devolatilization of Agricultural biomass Waste via TGA

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ABSTRACT

Agricultural biomass waste is a renewable energy source with numerous environmental benefits of particular importance in the bioenergy sector. This study examines the thermal decomposition behavior of khat stem (KS) as a renewable energy source using thermogravimetric analysis (TGA) during the pyrolysis process. The kinetic, thermodynamic, and performance parameters such as flammability, combustibility, ignition, and burnout were analyzed using TGA data collected at various heating rates (10, 20, 30, 40, 50, and 100 °C/min) in the temperature range of 30-800 °C in an inert atmosphere. The results show that KS has three distinct decomposition zones for water removal, hemicellulose, cellulose, and lignin degradation. The mass loss occurred mainly between 200 and 500 °C. The findings also revealed that increasing the heating rate caused the TGA/DTG curves to move to higher temperatures, possibly due to improved transport pathways, increased thermal energy, and thermal inertia. KS's activation energy and pre-exponential factor were 110.55 kJ/mol and 8.01E+11 min-1 using the Flynn-Wall-Ozawa (FWO) model and 106.06 kJ/mol and 1.29E+14 min-1 using the Kissinger-Akahira-Sunose (KAS) model. The difference between the average activation energy values and enthalpy change was approximately five kJ/mol using FWO and KAS models at different heating rates. The study found that KS has low flammability, combustibility, ignition, and burnout temperatures at lower heating rates, making it a suitable renewable fuel resource that can replace fossil fuels.

Keywords: FWO/KAS model, Pyrolysis, TGA/DTG, Thermal performance, Thermodynamic parameters

INTRODUCTION

Agricultural biomass waste is a renewable energy source with numerous environmental benefits (Miljkovic et al., 2019) and of particularly significant to the bioenergy sector due to its carbon neutrality (Balogun et al., 2021). Agricultural residues, which are easy to collect and inexpensive, are expected to be used for biofuel production soon (Van de Velden et al., 2010). By and large, renewable energy from biomass only accounts for 10% of energy consumption. In particular, Ethiopia has a surplus of biomass available at about 141.8 million tons per annum, comprising woody biomass, crop residues, agricultural wastes, and animal manure resources (Benti et al., 2021). Currently, the potential for utilization is about 71.9 million tons annually (Benti et al., 2021). Therefore, elucidating the concept of de-carbonization, dematerialization, and zero waste in promoting these materials' reduction, reuse, and recycling can provide the best possible solution to multidimensional problems and economize the overall process (Afessa et al., 2022).

Much research has been conducted to convert biomass into usable value-added products and produce biofuel (bio-oil, biochar, and syngas) (Verma et al., 2012), where the resulting product is highly dependent on operating conditions such as reaction temperature, residence time, particle size, and heating rate (Van de Velden et al., 2010). Thermochemical processes such as pyrolysis, gasification, combustion, hydrothermal liquefaction, and carbonization are the various technologies that have been extensively studied. Pyrolysis is an endothermic process that decomposes carbonaceous materials in a low-oxygen atmosphere to produce Pyrolytic bio-oil are light gases and char as solid residues (Van de Velden et al., 2010). The process consists of several steps. Initially, heat is transferred from a heat source, increasing the biomass particle's temperature. Subsequently, this temperature increase triggers the pyrolysis reactions. These reactions produce charcoal and lightweight volatiles, which results in heat transfer between these hot gases and the unreacted biomass. The subsequent stages of biomass pyrolysis correspond to the thermal decomposition of the organic components (cellulose, hemicellulose, and lignin). Figure 1 shows a representation of the biomass conversion pathway described above.

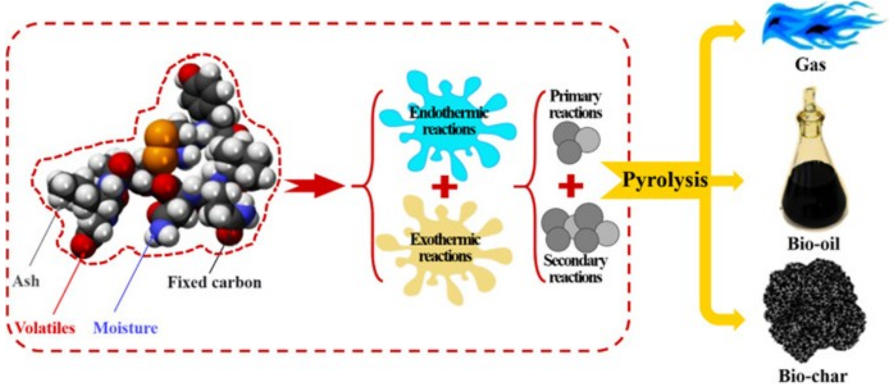

Figure 1. Thermal decomposition pathway for biomass particle.

Pyrolysis technology has yet to be very successful commercially due to the complex feedstock chemistry, bio-oil instability, poor fuel properties, and variations in product composition associated with feedstock chemistry and reaction conditions (Van de Velden et al., 2010). Recently, however, extensive experimental studies have been conducted to investigate the decomposition properties and reaction kinetics of solid biomass. Although the devolatilization process looks simple, the reaction sequence is complex. It involves both endothermic and exothermic processes (strongly influenced by temperature variations), and its thermodynamics and Kinetics are poorly understood (Sobamowo et al., 2017). The complex interactions between the kinetics and the physical and morphological changes and transport processes within the particle extensively influence this process. Decomposing biomass material with a small sample size to neglect the diffusion effect and kinetically controlled thermal decomposition is preferable to efficient and controlled processes (Onsree et al., 2018). Contrarily, if the heat input is insufficient, large thermal gradients occur, leading to slow pyrolysis and incomplete reactions in the particle's core and favoring char formation. Smaller particles have a larger specific surface area. They are more mobile within the reactor volume, resulting in improved heat transfer and lower temperature gradients (Van de Velden et al., 2010), which attributes to improving the thermal conversion properties of biomass. Representative sample weight and particle sizes are desired to avoid inter-particle heat and mass transfer limitations throughout TGA experimental measurements(Vyazovkin et al., 2011). On the other hand, particles more significant than the critical limit can be affected by internal and external temperature gradients, thermal inertia due to the heat capacity effect, and the relatively significant diffusion effect, which can strongly influence temperature variations due to endothermic or exothermic reactions (Miller & Bellan, 1997).

Thermogravimetric analysis (TGA) is a powerful technique that measures the devolatilization rate of biomass samples as a function of time\temperature (Cardona et al., 2015). It is used to investigate biomass material's mass-loss profile, thermal stability, reactivity, decomposition kinetics, and compositional analysis (Emiola-Sadiq et al., 2021). However, TGA cannot detect phase transitions, polymorphic transformations, or reactions in which the mass is invariant. In TGA, chemical kinetics mainly controls the process, and the influence of mass and heat transport can be minimized. However, for industrial-scale applications, the sample size in actual pyrolysis furnaces is up to several centimeters, much larger than in lab-scale setups like TGA. Large particle sizes and high sample loading introduce heat and mass transfer phenomena quite different from the thermal decomposition behavior studied in typical TGA. In the previous publication, the kinetic parameters of the same sample were reported at lower heating rates (Afessa et al., 2022). To the best of the authors' knowledge, no research has been conducted on the analytical investigation of the thermal decomposition of the sample to investigate the thermodynamic and thermal performance characteristics. Similarly, no effort was made to quantify the thermodynamic and thermal performance parameters at different heating rates (10, 20, 30, 40, 50, 100°C/min) between 30 - 800 °C.

In general, studying the kinetic, thermodynamic, and performance variables during the devolatilization of agricultural biomass waste using TGA can offer insightful information in guiding the development of more environmentally friendly and effective energy conversion techniques to exploit the potential of this waste as a renewable energy source, which can reduce global dependence on fossil fuels and mitigate the effects of climate change.

MATERIALS AND METHODS

Biomass samples characterization

Khat (Cathaedulis), also spelled "qat" or "chat," stem, were obtained from a local farm in Ethiopia (Jimma town). The biomass sample was selected because of the need for adequate investigation in previous literature and their higher potential availability in Ethiopia. Comprehensive physiochemical characterization of the sample was performed in earlier work (Afessa et al., 2022) and reported in Table 1.

Nonisothermal Thermo-gravimetric (TG) analysis

The biomass sample was subjected to dynamic heating measurements in a Perkin Elmer TGA-7 instrument. The heating temperature was ramped up from ambient conditions (30 °C - 800 °C) at different heating rates (10, 20, 30, 40, 50, and 100 °C/min). The carrier gas was N2 with a 40 mL/min flow rate. The data obtained were analyzed using Pyris v11 software. Small homogeneous samples of 20 mg and particle sizes smaller than 500 µm were used to ensure uniform heating and avoid problems with transport phenomena through the sample bed in the crucible. The simulation was recorded twice for all experimental conditions considered to minimize experimental uncertainties (Afessa et al., 2022).

Formulation of Mathematical Model

Kinetic Modelling Using TGA Data

Several kinetic modeling techniques are available to assess the experimental TGA data. Model fitting and model-free (Isoconversional) kinetic models are the most often utilized. These models were created to extract kinetic parameters for solid-state processes from experimental data that was thermally triggered (TGA, DSC, DTA, etc.). Many model-free (isoconversional) approaches, such as Flynn-Wall-Ozawa (FWO) and Kissinger-Akahira-Sunose (KAS), are described in the literature. Model-free approaches are commonly used to calculate the activation energy of a reaction process without determining reaction types or understanding the kinetic mechanism of the process. The Kinetics of reactions in isothermal and homogeneous systems is determined by Equation (1-6), from which nonisothermal and heterogeneous systems' kinetic reactions are derived. The two kinetic models used to determine kinetic parameters are the KAS and FWO; their linear equations are presented in Equations (7–9).

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (1)$$

$$k_{(T)} = A\exp\left(\frac{-E}{RT}\right) \quad (2)$$

$$\alpha = 1 - \frac{m_{(t)} - m_r}{m_o - m_r} \quad (3)$$

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

$$f(\alpha) = (1-\alpha)^n \quad (5)$$

$$\frac{d\alpha}{dT} = \frac{A}{\beta}.e^{\left(\frac{-E}{RT}\right)}.(1-\alpha)^n \quad (6)$$

KAS $$ln\frac{\beta}{T_i{}^2} = ln\frac{AR}{Eg(\alpha)} - \frac{E}{RT_i} \quad (7)$$

FWO $$ln\beta = ln\frac{AE}{Rg(\alpha)} - 5.331 - 1.052\frac{E}{RT_i} \quad (8)$$

Thermal performance parameters

The thermal performance parameters, namely, ignition temperature (T_i), the temperature at the maximum DTG (T_{max}), burnout temperature (T_b), corresponding time (t_i, t_{max}, t_b), the maximum and average DTG ($-Rp$ and $-R_v$) were obtained from the TGA and DTG measured data. All these parameters were used sequentially to estimate the thermal performance parameters for the various pyrolysis conditions. These include comprehensive flammability (S), combustibility (C), ignition (Di), and burnout (Db) according to Equations (9) - (12)(Balogun et al., 2021).

$$S = \frac{-R_p \times -R_v}{T_i^2 \times T_b} \quad (9)$$

$$C = \frac{-R_p}{T_i^2} \quad (10)$$

$$D_i = \frac{-R_p}{t_i \times t_b} \quad (11)$$

$$D_b = \frac{-R_p}{\Delta t_{1/2} \times t_p \times t_b} \quad (12)$$

Analysis of Thermodynamic Parameters

Theoretically, the peak temperature is the temperature at which a chemical reaction should proceed spontaneously from the point of view of equilibrium thermodynamics (peak temperatures are kinetically controlled and coincide with the maximum decomposition reaction rate (Archer et al., 2013). The thermodynamic parameters, such as the change in Enthalpy (ΔH), Entropy (ΔS), and Gibbs free energy (ΔG) of the biomass material during devolatilization, were characterized by thermogravimetric analysis. All these parameters were derived and quantified from kinetic parameters obtained from conventional methods (FWO and KAS) reported in previous work based on a first-order chemical reaction model (Balogun et al., 2021). Equations (13) – (15) were used to evaluate the parameters (Balogun et al., 2021; Xu & Chen, 2013).

$$\Delta H = E_{\alpha} - RT \tag{13}$$

$$G = E_a + RT_{max} \ln(\frac{k_B T_{max}}{hA_a}) \tag{14}$$

$$\Delta S = \frac{\Delta H - \Delta G}{T_{max}} \tag{15}$$

Wherek_B and h are the Boltzmann constant (1.381 x 10^{-23} J/K) and Planck constant (6.626 x 10^{-34}Js), respectively.

RESULTS AND DISCUSSION

Ultimate and proximate analyses

The proximate and ultimate analysis results are shown in **Error! Reference source not found.** The sample has high volatile matter content (> 70 wt.%), which contributes favorably to fuel ignition at lower temperatures implying a high reactivity and hence, improving the thermal conversion process (Saffe et al., 2019). The sample has low amounts of ash (< 3.5 wt.%), which can facilitate high combustion rates, minimize processing costs and residue disposal issues, and avoid energy conversion problems (Mishra & Mohanty, 2018) (e.g., incrustation, reactor corrosion, and slag formation). The emission of fuel-NO_x and SO_x from this sample should be minimal as the amount of nitrogen and sulfur in the biomass sample is very low. The ultimate analysis shows a carbon content of 50.5 wt. % for khat stem, confirming that the sample is suitable for renewable fuel sources. Comparable results of proximate and ultimate are reported in the literature (Gebregziabher et al., 2021). The ignition performance of the sample was also related to the sum of fixed carbon (FC) and volatiles (VM). The higher sum of FC and VM indicated that the sample had a superior ignition performance (Xu et al., 2020). The sum of VM and FC of the biomass sample (KS) is nearly 90.36 %, which can be evidence for better ignition performance of the KS. These values from analyses are comparable with various lignocellulosic materials reported in the literature(Afessa et al., 2022). Therefore, the khat stem used in this study could be a potential source for bioenergy production and will offer the potential to replace fossil fuel requirements in certain specific applications.

Table 1: Ultimate and proximate analyses of Khat stem

Sample	Ultimate analysis [%]
C	50.50 ± 2.1
H	5.52 ± 1.1
N	0.65 ± 0.1
O*	43.32 ± 1.8
S	n.d.**
Proximate analysis [%]	
MC	6.57 ± 0.77
VM	70.90 ± 0.72
FC	19.36 ± 0.69
Ash	3.17±0.75

*Calculated by the difference;**Not detectable

TGA and DTG characteristics of Khat stem (KS)

The reactions during a devolatilization process are divided into three main phases (Afessa et al., 2022). First, at temperatures below 200ºC, the moisture trapped in the biomass structure evaporates and dries the biomass sample. It is also noted that the free water in the biomass sample is essentially removed after this evaporation stage. This biomass particle devolatilization stage is a nonisothermal drying process with a linear heating rate (Chen et al., 2012). The weight loss increases as the devolatilization temperature of the sample increases. Figure 2 shows the thermogravimetric (TGA) and differential thermogravimetric (DTG) curves of the sample as a function of pyrolysis temperature and time at a heating rate of 20°C/min. In a temperature range between 200 ºC and 500 ºC, the formation of primary products occurs through a mechanism that mainly involves a slow process of depolymerization and restructuring with low mass loss (in which the bonds between the monomers in the polymer chain are broken). Then, the materials undergo a complex thermo-chemical reaction called fragmentation (in which covalent bonds in different parts of the polymer chain are thermally broken) and the formation of primary carbon (Altantzis et al., 2021). In this process, many volatiles are released, and the TGA curve drops sharply (Chen et al., 2012). Volatile molecules formed by polymerization reactions have a relatively high molecular weight and therefore condense easily, thus forming the liquid (tar) primary products (Altantzis et al., 2021). The final devolatilization process involves the slow decomposition of residues (mainly lignin), where the TGA curve is relatively apartment. In general, the devolatilization gas released in the subsequent stages of devolatilization always contains a large amount of water vapor. This is because the crystallized water of the biomass sample is released under high temperatures, and a lot of water is produced from a series of thermal, chemical reactions of the organic components (Chen et al., 2012).

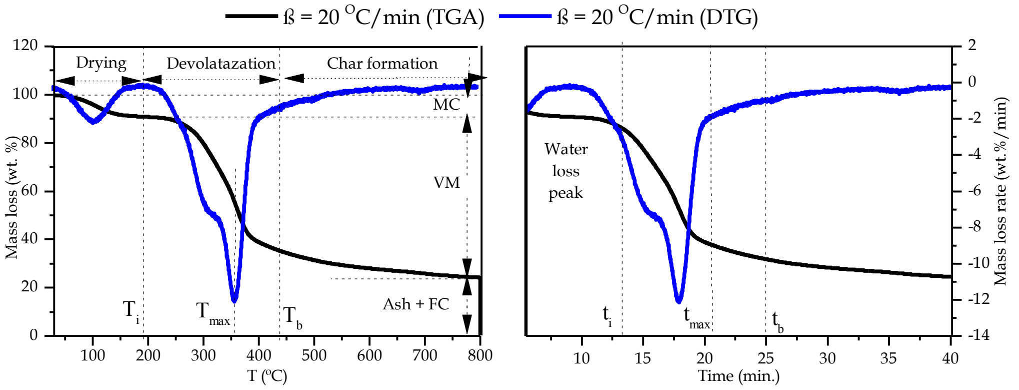

Figure 2. TGA and DTG curves (Ti - ignition temperature, Tp - peak temperature, Tb - burnout temperature with respective time ti Ignition time, tp peak time and tb burnout time)

The heating rate is an important parameter in commercial applications because it can be used to determine the type of reactor used for large-scale applications. In Figure 3, results of the thermogravimetric experiments are presented for the khat stem at four different heating rates of 10, 30, 50, and 100 °C/min to show the effect of the heating rate during the devolatilization process. The heating rate was considered for the reason that it had some influence on conversion and product distribution.

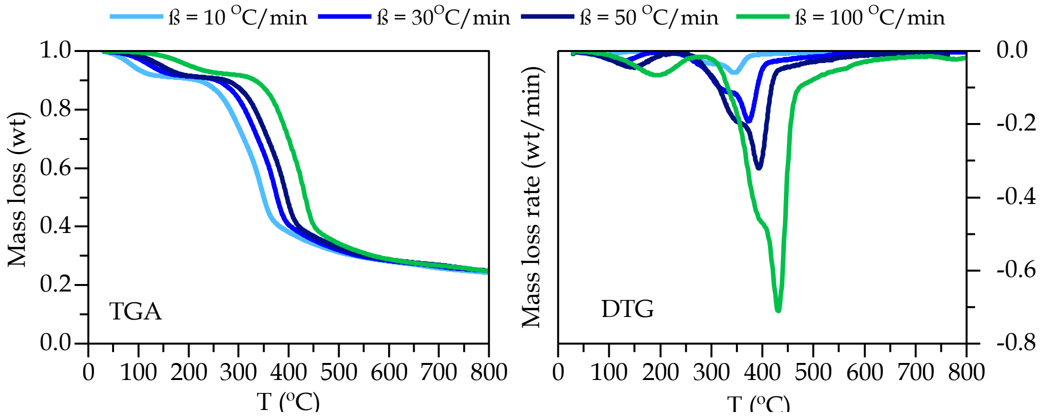

Figure 3. TGA and DTG devolatilization curves of Khat stem at different heating rates

From Figure 3, it can be seen that the DTG curves of the biomass sample at different heating rates comprise one small peak, one pronounced peak, and one long tailing. This experiment showed that increasing the heating rate shifted the TGA/DTG curves to higher temperatures during the devolatilization of the biomass particle. For instance, when the heating rate was changed from 10 °C/min to 30 °C/min, the shifting of the TGA/DTG curve was nearly 10 °C, whereas it was higher than 80 °C on the DTG peaks when the heating rate changes from 10 °C/min to 100 °C/min. At the low heating rate, the shape of the DTG curve was narrow and short but became broader and higher at higher heating rates. For the characteristic temperatures, increasing the heating rate shifted the ignition, peak, and burnout temperatures to higher values. Those trends are probably attributed to improved transport processes and increased thermal energy (Afessa et al., 2022). It can also be inferred that at higher heating rates, the peak temperatures can only shift to higher values during the experiment without noticeable changes in thermal profiles of decomposition characteristics. This can also result from the increasing effect of the thermal inertia during the devolatilization process with decreasing characteristic time (Rasool et al., 2019). These thermal inertia effects were more pronounced in the higher heating rate experiments. At a given temperature, a higher heating rate implies that the material reaches the temperature in a shorter time (Chen et al., 2014). Moreover, thermal energy was available to facilitate better heat transfer between the surroundings and the inside of the samples at the higher heating rate (Onsree et al., 2018).

Thermal performance parameters of Khat stem (KS)

The thermal performance parameters for the khat stem (KS) during the devolatilization process are summarized and presented in Table 2. All the parameters were obtained based on thermogravimetric experimental data using equations (9) – (12). The thermal performance parameters, S, C, Di, and Db, had demonstrated enhancement with heating rates. It is substantial that the improvement was pretty much of the same order of magnitude for all heating rates. Previous research revealed that high values of Di indicated better ignition capability of the biomass sample. Again, a rise in heating rates led to a corresponding increase in the ignition, peak, and burnout temperatures with a corresponding decrease in time. This trend agrees with data in published literature (Balogun et al., 2021). The results confirm that devolatilization of the Khat stem had the lowest comprehensive flammability (S) of 3.28E-08 (%2/(min2K3), flammability (C) of 2.41E-05 (%/(minK2), ignition (Di) of 7.17E-03 (%/(min3) and burnout (Db) of 1.11E-04 (%/(min4) at all the lower heating rate of 10 ^{o}C/min.

Table 2. Thermal performance parameters during devolatilization of KS at different heating rates

Khat Stem – KS													
β	T_i	T_{max}	T_b	t_i	t_p	t_b	$\Delta t_{1/2}$	$-R_p$	$-R_v$	S	C	D_i	D_b
10	504.34	616.35	667.18	21.77	33.81	39.29	41.70	6.13	0.91	3.28E-08	2.41E-05	7.17E-03	1.11E-04
20	513.34	632.84	686.14	11.45	17.84	20.72	20.84	11.70	1.82	1.18E-07	4.44E-05	4.93E-02	1.52E-03
30	527.66	640.84	699.47	8.19	12.20	14.31	13.88	19.02	2.69	2.64E-07	6.83E-05	1.62E-01	7.84E-03
40	545.60	653.79	712.21	6.69	9.55	11.13	6.94	24.99	3.62	4.27E-07	8.39E-05	3.35E-01	3.39E-02
50	548.05	666.66	732.21	5.42	7.92	9.31	7.89	32.30	4.71	6.92E-07	1.08E-04	6.40E-01	5.56E-02
100	597.04	704.44	762.29	3.32	4.44	5.04	4.30	70.22	9.02	2.33E-06	1.97E-04	4.19E+00	7.29E-01

Where all parameters with respective unit: β (Heating rate) in (^{o}C/min), ((Ti-Ignition temperature, Tp - peak temperature, Tb - burnout temperature, in K), (ti Ignition time, tp peak time and tb burnout time in min), (-Rp and –Rv in (%/min)) S in (%2/(min2K3)) , C in (%/(minK2)), Di (%/(min3)) and Db in (%/(min4))

Activation energy and thermodynamic parameters Analyses

All thermodynamic parameters (ΔH, ΔG, and ΔS) were calculated based based on the experimental kinetic parameters (E and A) values derived from the FWO and KAS model and also reported in the previous work (Afessa et al., 2022). All the parameters were calculated at peak temperature since this temperature characterized the highest devolatilization rate in biomass conversion. The disparities in those parameters with a degree of conversion for the biomass sample at multiple heating rates are shown in Figures 4, 5, 6, and 7, respectively.

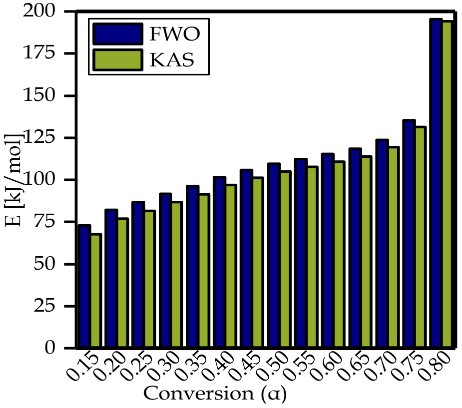

Figure 4. Variation of activation energy with the degree of conversion using FWO and KAS model

The ΔH denotes the amount of internal energy contained in the system of thermodynamics coupled with the amount of energy used to perform activities on a material, where the value can be positive or negative (Muzayyin et al., 2020). The ΔH also measures the heat exchange between complex activated components and reactants; this means that high values of ΔH indicate high reactivity and a fast reaction rate. This study showed no significant difference between the change in Enthalpy and the heating rate. However, both the kinetic and ΔH vary significantly with conversion, highlighting the complexity associated with the thermal conversion of the biomass sample (Balogun et al., 2021). The variation of Enthalpy also follows a similar trend as the activation energy. The values of ΔH during the degassing process of KS for different heating rates (10-100 ^{o}C/min) were in the range of 105.42-104.69 kJ/mol using FWO and 100.93 - 100.20 kJ/mol using the model KAS. Positive values of ΔH indicate an endothermic reaction, while the opposite case is called an exothermic reaction. The difference between the activation energy values and the enthalpies reflects the probability that the pyrolysis reaction will occur. A more negligible difference indicates that product formation is more accessible during the process. A difference of ~5 kJ mol-1 was observed between the E and ΔH values, indicating little potential energy barrier to achieve product formation, implying that product formation would be easier (Ahmad et al., 2019). This is consistent with findings in the literature (Ahmad et al., 2017). Figure 5 illustrates the variation of Enthalpy with conversion efficiency using the FWO and KAS models.

The ΔG is a measure of the total energy increase during a reaction in a thermal process (Ivanovski et al., 2021). It also provides valuable information about the spontaneity and direction of the reactions. A positive value of ΔG indicates non-spontaneity, while a significant value indicates better reaction rates (Muzayyin et al., 2020). The mean values of ΔG for FWO vary in the range of (163.89 kJ/mol - 172.31 kJ/mol) and (141.21 kJ/mol - 147.02 kJ/mol) for the model KAS for the different heating rates (10 -100 ^{o}C/min). Figure 6 illustrates the variation of Gibbs free energy values with the degree of conversion using the FWO and KAS models. The ΔG data obtained for the sample in this study are of the same order of magnitude and show slight variation between the upper and lower limits. The variations of average ΔG values during the degassing process of KS for different heating rates (10-100 ^{o}C/min) using both models were in the range of (6-8 kJ/mol). In general, the Gibbs free energy indicates the total energy gain of the system for the formation of the activated complex and reflects the bioenergy potential of the biomass. The results obtained in this work agree with the findings of (Muzayyin et al., 2020).

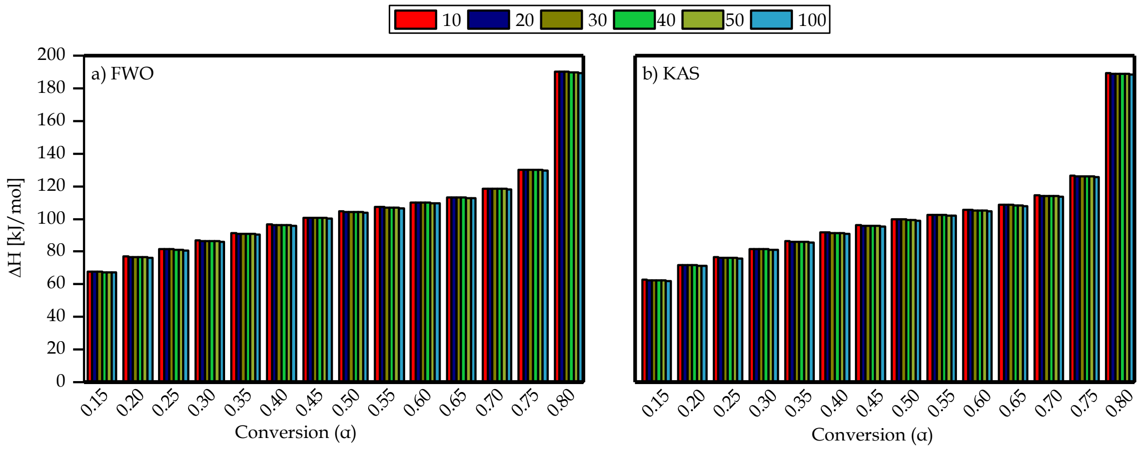

Figure 5. A plot of change in Enthalpy (ΔH) at 10, 20, 30, 40, 50,100 oC/min based on (a) FWO and (b) KAS

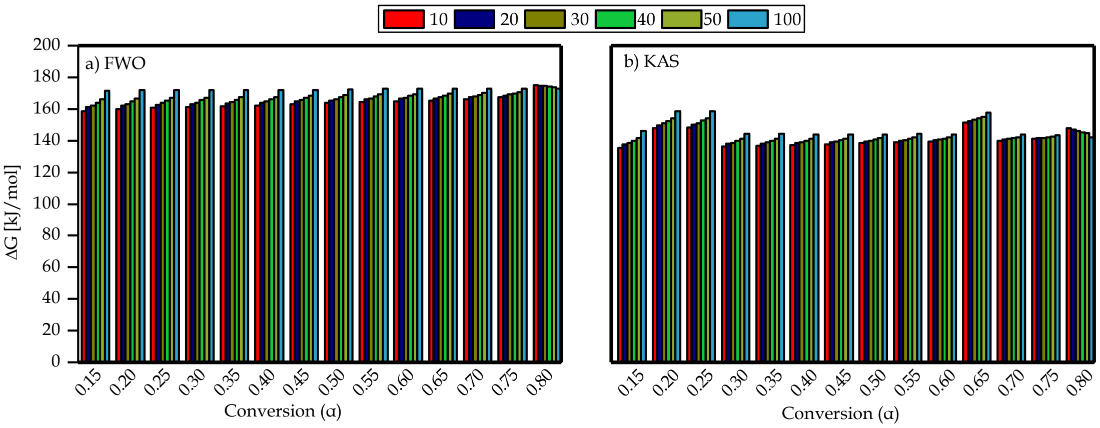

Figure 6. A plot of change in Gibbs free energy (ΔG) at 10, 20, 30, 40, 50,100 oC/min based on (a) FWO and (b) KAS

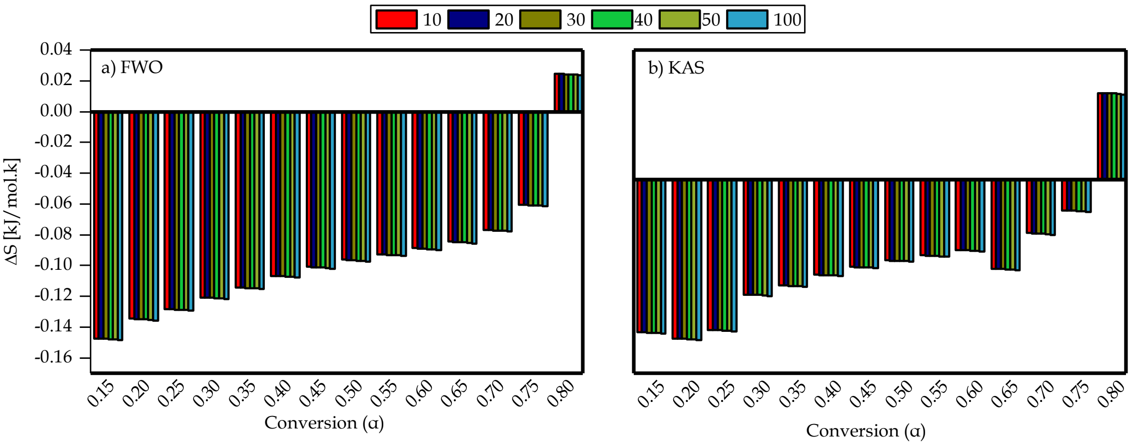

Figure 7. A plot of change of Entropy (ΔS) at 10, 20, 30, 40, 50,100 oC/min based on (a) FWO and (b) KAS

Figure 7 elucidates variation of change in Entropy (ΔS) values with degree of conversion using FWO and KAS model. The change in Entropy decides the degree of disorder for any reaction during the thermal degradation process, ΔS. From the calculation, results in the changes in Entropy (ΔS) were both negative and positive, which reflects the complexity of the thermic degradation of the sample into final products (Xu & Chen, 2013). The typical values are within the range of (-0.094 – 0.096 kJ/mol. K for FWO and (-0.0065 – 0.067 kJ/mol.K for KAS model) for the various heating rates (10 –100 ^{o}C/min), respectively. The negative value in ΔS verifies the product disorder within the sample through bond separation below the initial reactant (Muzayyin et al., 2020). A low ΔS means that the product was near its thermodynamic equilibrium state, and the material showed low reactivity.

In contrast, a high ΔS means high reactivity and less time consumed to form an activated complex. To our knowledge, no literature reported similar calculations for khat stem pyrolysis. Even though similar calculations for khat stem pyrolysis have not been reported, comparable results were reported compared to other feedstocks available in the literature (Ivanovski et al., 2021).

CONCLUSION

The devolatilization of agricultural biomass waste using TGA is a complex process that is impacted by various factors such as biomass type, heating rate, particle size, and atmospheric conditions. Kinetic analysis can provide insights into the devolatilization process's reaction mechanisms and rate-limiting steps, optimizing the process for maximum yield and efficiency. Determining kinetic mechanisms and rate constants for the pyrolysis process has been mainly carried out under regimes controlled by chemical Kinetics, using microscopic samples in powder form so that effects of transport phenomena such as heat and mass transfer can be neglected. In this way, the particle temperatures can be shown to be nearly the same as the surface temperature. Thermodynamic analysis can provide information on the thermodynamic stability and energy content of biomass waste and released gases, which can aid in designing optimal process conditions and selecting appropriate equipment. According to thermodynamic parameters from this investigation, reactions were relatively more straightforward at the early stages of decomposition. Performance characteristics can also considerably impact the devolatilization process and the subsequent products, thus, must be carefully monitored and optimized. It was also demonstrated that the thermal performance parameters increased with the heating rates. The difference between the average activation energy values and enthalpy change was approximately 5 kJ/mol. It could be concluded that khat stem had potential as a renewable energy source; its availability in plenty also supported this.

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