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Thermal and Kinetic Analyses of Maize Cob Combustion under Non-Isothermal and Multiple Heating Rate Thermogravimetric Conditions

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Abstract

The cultivation and processing of maize (*Zea mays* L.) in Nigeria generates large quantities of maize cobs (MC). Current strategies for MC disposal and management are outdated, inefficient, and costly. However, the lignocellulosic nature of MC is suitable for energy recovery through biomass combustion. Studies on the critical examination of the solid-state fuel properties, thermal behaviour, degradation pathways, and temperature profile characteristics (TPCs) of MC are currently lacking in the literature. Therefore, this study seeks to comprehensively investigate the physicochemical, thermal and kinetic properties of MC as solid biofuel for combustion. The results revealed that MC contains high carbon, volatile matter, and fixed carbon along with low ash, nitrogen, and sulphur. Thermal analysis revealed that MC degradation is significantly influenced by temperature and heating rate. Furthermore, higher heating rates from 10 to 30°C/min shifted the TPCs of the TG-DTG plots to higher values. The average TPCs are onset (T_{ons}), midpoint (T_{mid}), and endpoint (T_{end}) temperatures are; 288.21°C, 305.39°C, and 325.71°C, respectively for the TGA combustion of MC. The TGA combustion of MC resulted in ML of 94.22 -95.83% and residual mass (RM) of 4.17-5.78%. The degradation pathway for the TGA combustion of MC occurs in three major stages as evident in DTG peaks from RT – 110°C, 200°C – 500°C. The kinetic analysis revealed that E and A are 125.51 kJ mol⁻¹ and 2.65×10¹⁶ min⁻¹. Overall, the results demonstrate that MC is a highly reactive and practical feedstock for clean energy recovery.

Keywords: Thermal Analyses; Kinetic Modelling, Maize Cob; Combustion, Thermogravimetry.

1. Introduction

Global concerns about greenhouse gas emissions, global warming, and climate change have spurred scientists and policymakers to explore more sustainable sources of energy [1]. Experts posit that anthropogenic activities such as agriculture, land use, and overdependence on fossil fuel energy have exacerbated global warming by 0.8 to 1.2°C above the pre-industrial period [2-3]. For example, the burning of coal emits about 40% of all carbon dioxide (CO₂), whereas energy utilization accounts for approximately 70% or 50 billion tonnes of CO₂ eq. on the planet [4]. Given the current scenario, it is projected that global warming could rise by 1.5°C in 2052 resulting in disastrous socio-economic and environmental challenges [5-7]. Several studies have highlighted the region-specific impacts of global warming and climate change on heavy

rainfall, floods, landslides, epidemics, drought, famine, and loss of biodiversity among other challenges, particularly if mitigating measures are not established soon [8-9].

To mitigate the effects of global warming and climate change, global leaders convened in Paris (France) in 2015 to draft and ratify measures to curb 50 billion tonnes of anthropogenic greenhouse gas emissions by 2065. The so-called Paris Agreement (Climate Accord) was also aimed at charting the course for the transition from fossil fuels to cleaner, sustainable and renewable alternatives such as solar, wind, and biomass. Biomass is regarded as an environmentally friendly, economically viable, and socially acceptable source of clean energy for the future. Due to its carbon-neutral characteristics, various experts project that energy from biomass has the potential to meet the world's growing demand for clean energy, diversify energy mixes, as well as mitigate global warming and climate change. Furthermore, the transition from fossil fuels to renewable biomass energy could potentially create longstanding employment opportunities, increase standards of living, and address the perennial energy crises, particularly in developing countries.

The agricultural sector in Nigeria generates large quantities of solid wastes such as palm wastes, rice husks, cassava peels, sorghum straw, cocoa wastes, maize stover among others. Currently, these wastes are burned in the open air, abandoned in fields or landfilled, which creates human health, safety and environmental challenges. However, the lignocellulosic nature of agricultural wastes could be harnessed for energy recovery through biomass energy technologies such as combustion. Such technologies could effectively provide an avenue to valorise the large stockpiles of agricultural waste streams into energy. Furthermore, combustion could address the waste management, health, safety and environmental challenges posed by the wanton disposal of agricultural wastes.

Various studies have investigated the potential of valorising Maize cobs (MC) wastes as animal feedstuffs, organic fertiliser, mulching material or domestic cooking fuel in the literature. However, these strategies cannot effectively valorise the large stockpiles, estimated at over 5 million tonnes, of MC generated annually by approximately 49.7% of households in the country [10-11]. To this effect, various researchers have investigated the use of MC for various applications such as bioremediation adsorbents [12-13], soil enhancement [14-15], carbon electrode materials [16-17], cementitious materials [18-19], and cellulose extraction [20-21]. Other studies have examined the use of MC as fuel feedstock for briquettes [22], pellets [23], pyrolysis [24], biomethane and biogas production [25].

The combustion properties of MC and related solid fuels such as briquettes have been examined by various research groups [26-29]. However, none of the reviewed literature has embarked on the critical examination of the solid-state fuel properties, thermal behaviour, degradation pathways, and temperature profile characteristics of MC under oxidative thermogravimetric conditions. Therefore, this study seeks to comprehensively investigate the physicochemical, thermal and kinetic properties of maize cob (MC) as solid biofuel for combustion. The physicochemical properties of MC are examined based on ultimate, proximate, and calorific analyses to examine its elemental, proximal and higher heating value contents. The thermal fuel properties of MC are examined by oxidative, non-isothermal, and multiple heating rate conditions to simulate micro-scale combustion, whereas the kinetic properties are computed using the Kissinger model.

2. Methodology

2.1. Chemical analysis

The ultimate, proximate, and calorific analyses of Maize Cobs (MC) was carried out to deduce its chemical fuel properties. The ultimate analysis was carried out to determine the carbon (C), hydrogen (H), nitrogen (N), and sulphur (S) content using the vario Macro Cube CHNS elemental analyser (Germany), while the oxygen (O) was determined by difference. The proximate analysis was employed to determine the moisture content (MC), volatile matter (VM), ash (AC) and fixed carbon (FC) using thermogravimetric analysis based on the procedure described in the literature [30]. The higher heating value (HHV) of MC was determined by

calorific analysis, which was determined using the IKA C200 bomb calorimeter (USA) under isoperibolic conditions.

2.2. Thermal analysis

The thermal properties of MC were examined through non-Isothermal, oxidative, and multiple heating rate thermogravimetric analysis (TGA). The process was carried out to examine the thermal behaviour, degradation pathways, and temperature profile characteristics of MC under oxidative thermal conditions for combustion. For each test, approximately 11 ± 0.87 mg of pulverised MC was weighed and placed in an alumina crucible before heating the furnace from 30°C to 700°C based on the multiple heating rates of $10^\circ\text{C}/\text{min}$, $20^\circ\text{C}/\text{min}$, and $30^\circ\text{C}/\text{min}$. During the TGA, the furnace was purged with air at a flow rate of $100 \text{ mL}/\text{min}$ to create an oxidative atmosphere for the combustion of the MC particles and purge the flue gases generated during the process. At the end of the process, the thermal data were retrieved and analysed to obtain the mass loss (TG, %) and derivative mass loss (DTG, %/min) at various heating rates before plotting the data against temperature ($^\circ\text{C}$). Next, the Shimadzu TG software was used to determine the temperature profile characteristics (TPCs) for the multi-heating TGA combustion of MC based on the procedure described in the literature [31-32]. In this study, the TPCs deduced from the TG plots are; onset (T_{ons}), midpoint (T_{mid}), endpoint (T_{end}) temperatures as well as the total mass loss (ML) and residual mass (RM). In contrast, the TPCs deduced from the DTG plots are; peak temperatures for drying (T_{dry}) and devolatilization for peak I ($T_{\text{dev, I}}$) and peak II ($T_{\text{dev, II}}$).

2.3. Kinetic analysis

In this study, the Kissinger model (KM) was employed to compute the kinetic parameters; activation energy (E , kJ mol^{-1}) and frequency factor (A , min^{-1}) for the TGA combustion of MC under non-isothermal, oxidative, and multi-heating rate TGA. The KM is used to compute the kinetic parameters of thermally degrading materials using the maximum decomposition values of DTG peaks and Arrhenius relation, which is described as follows;

$$k = A \exp\left(-\frac{E}{RT}\right) \quad (1)$$

From Eq. 1, the terms k , A (min^{-1}), E (kJ mol^{-1}), and R ($\text{J mol}^{-1} \text{K}^{-1}$) represent the rate constant, frequency factor, activation energy, and molar gas constant, respectively. For the thermal degradation of MC, the term β is introduced to account for the effect of the heating rates ($10^\circ\text{C}/\text{min}$, $20^\circ\text{C}/\text{min}$, and $30^\circ\text{C}/\text{min}$) on the reaction function described by $f(x)$. After the separation and integration of the variables, governing equations for the KM are deduced as shown in Eq. 2;

$$\ln\left(\frac{\beta}{T_x^2}\right) = \ln\left(\frac{AR}{E}\right) - \ln\left(\frac{E}{RT_x}\right) \quad (2)$$

Therefore, the peak decomposition terms namely; peak temperatures for drying (T_{Dry}), and devolatilization I ($T_{\text{Dev, I}}$) derived from the DTG plots were substituted for T_x in Eq. 2. The kinetic parameters; activation energy (E) and frequency factor (k_o) for T_{Dry} and $T_{\text{Dev, I}}$ were subsequently deduced from the slope and intercept of the plots of $\ln\left(\frac{\beta}{T_x^2}\right)$ against $\frac{1000}{T_x}$ at the various heating rates from $10^\circ\text{C}/\text{min}$ to $30^\circ\text{C}/\text{min}$. The KM kinetic plots are presented in Figures 3 and 4.

3. Results

3.1. Chemical properties

Table 1 presents the chemical fuel properties of MC based on the ultimate, proximate, and calorific analyses as presented on a dry basis (*db*) to provide a comprehensive understanding of its solid biofuel value, waste potentials, and environmental burden [33-35].

Table 1 reveals that the carbon, hydrogen, oxygen, volatile matter, and fixed carbon are contained in high proportions in MC, whereas but the ash, moisture, nitrogen, and sulphur are present in low concentrations.

Table 1. Chemical fuel properties of MC

Fuel Analysis	Fuel property	Symbol (Unit)	Maize Cobs
Ultimate	Carbon	C (wt.%)	46.30
	Hydrogen	H (wt.%)	6.98
	Nitrogen	N (wt.%)	0.91
	Sulphur	S (wt.%)	0.13
	Oxygen	O (wt.%)	45.68
Proximate	Moisture	M (wt.%)	9.88*
	Volatile matter	VM (wt.%)	75.47
	Fixed carbon	FC (wt.%)	17.42
	Ash	A (wt.%)	7.11
Calorific	Higher Heating Value	HHV (MJ/kg)	17.59

The high volatile matter indicates MC could be easily ignited and devolatilised into flue or fuel gases and char during thermal conversion processes such as combustion and gasification, respectively [36]. However, the high content of O may lead to over-oxidation of the MC fuel particles as well as of nitrogen and sulphur into NO_x and SO_x during oxidative thermal processes such as combustion. The higher heating value (HHV) of MC was deduced as 17.59 MJ/kg, which is within range of 14 – 22 MJ/kg typically reported by biomass feedstock in the literature [37]. In general, the ultimate, proximate, and calorific analyses of MC reveal it is a potentially practical biofuel with low waste and environmental burden profiles.

3.2. Thermal properties

Figures 1 and 2 present the TG and DTG plots for the TGA combustion of MC under multiple heating rates from room temperature to 700°C. The process was aimed at examining the thermal behaviour, degradation pathways, and temperature profile characteristics of MC under low-temperature combustion conditions.

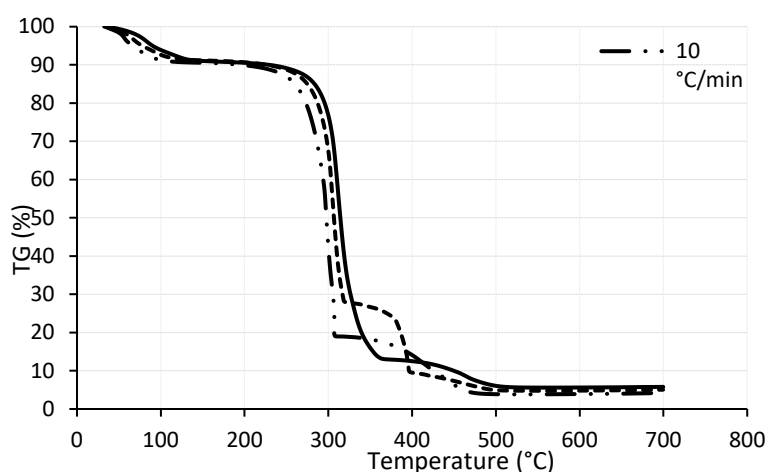


Figure 1. TG plots for MC combustion

The thermal behaviour of MC is characterised by significant mass loss (ML) as evident in the downward sloping TG plots from the left to the right-hand side, as shown in Figure 1. The

TG plots first experienced a steep loss of mass from room temperature to 110°C, before plateauing until 200°C. Subsequently, the sample experienced a more significant ML which terminated at 500°C. After this point, the loss of mass ceased resulting in another levelling as characterised by the tailing observed between 500°C and 700°C indicating the complete degradation of MC or ML of the sample. The ML of biomass samples is typically ascribed to the thermal degradation of hemicellulose, cellulose, and lignin along with the loss of volatile matter (or termed devolatilization) during TGA [38-39].

In addition to the effects of temperature on the process, the TG plots revealed that the change in heating rates also influenced the thermal degradation and ML of the sample during TGA. As observed, the plots shifted to the right-hand side with increasing heating rates from 10°C/min to 30°C/min during TGA. The observed shifts are caused by higher temperature gradient experienced by the thermally degrading particle due to poor heat transfer from the furnace occasioned by the increase in heating rates during TGA. The shifts also changed the characteristics of the TG plots, which are summarised in Table 2. The temperature profile characteristics (TPCs) examined in this study include; onset (T_{ons}), midpoint (T_{mid}), endpoint (T_{end}) temperatures as well as the total mass loss (ML) and residual mass (RM).

Table 2. TG Plot - TPCs of MC combustion

Heating Rate (°C/min)	Onset Temperature (T_{ons} , °C)	Midpoint Temperature (T_{mid} , °C)	Endpoint Temperature (T_{end} , °C)	Mass Loss (ML, %)	Residual Mass (RM, %)
10	283.59	297.11	315.20	95.83	4.17
20	287.66	305.85	325.98	95.50	4.50
30	293.39	313.22	335.95	94.22	5.78

Due to the shifts in the TG plots arising from the increase in heating rates from 10°C/min to 30°C/min, the TPCs also experienced shifts to higher temperatures. As observed, the onset (T_{ons}) increased from 283.59°C to 293.39°C, whereas the midpoint (T_{mid}) was from 297.11°C to 313.22 °C, and lastly the endpoint (T_{end}) was from 315.20 °C to 335.95 °C. The average values of the onset (T_{ons}), midpoint (T_{mid}), and endpoint (T_{end}) temperatures are; 288.21 °C, 305.39°C, and 325.71°C, respectively for the TGA combustion of MC. Therefore, the findings of this study demonstrate that the TGA combustion of MC undergoes ML within the temperature range of 297.11°C and 335.95°C based on the conditions examined in this study. The range of total mass loss (ML) observed during the TGA combustion of MC was between 94.22% and 95.83%, whereas the residual mass (RM) was between 4.17% and 5.78%.

The findings indicate that the MC sample experienced significant thermal degradation or ML of 95.18% and RM of 4.82% on average. In contrast, the TGA pyrolysis of MC by Otolaiye *et al.*, [40] revealed the average onset (T_{ons}), midpoint (T_{mid}), and endpoint (T_{end}) temperatures of 276.09°C, 329.28°C, and 384.59°C, respectively. However, the total mass loss (ML) and residual mass (RM) for the process was 57.52% and 42.48%. The TPC values indicate that the combustion of MC requires relatively lower temperature when compared to the pyrolysis process. Hence, it can be reasonably surmised that the TGA combustion of MC is a more thermally efficient process which resulted in higher conversions and lower operating conditions when compared to the pyrolysis process.

The degradation pathway for the TGA combustion of MC was examined through the DTG plots presented in Figure 2. As observed, the degradation of MC is characterised by numerous peaks observed within the range of RT – 110°C, 200°C – 500°C, which indicates the process occurred in three major stages. The first stage is typically attributed to the loss of moisture due to the low ML (< 10%), whereas the second stage is attributed to the loss of volatiles and degradation of lignocellulosic matter during the TGA. Consequently, the second stage results in significant ML (> 80%), as observed in this study.

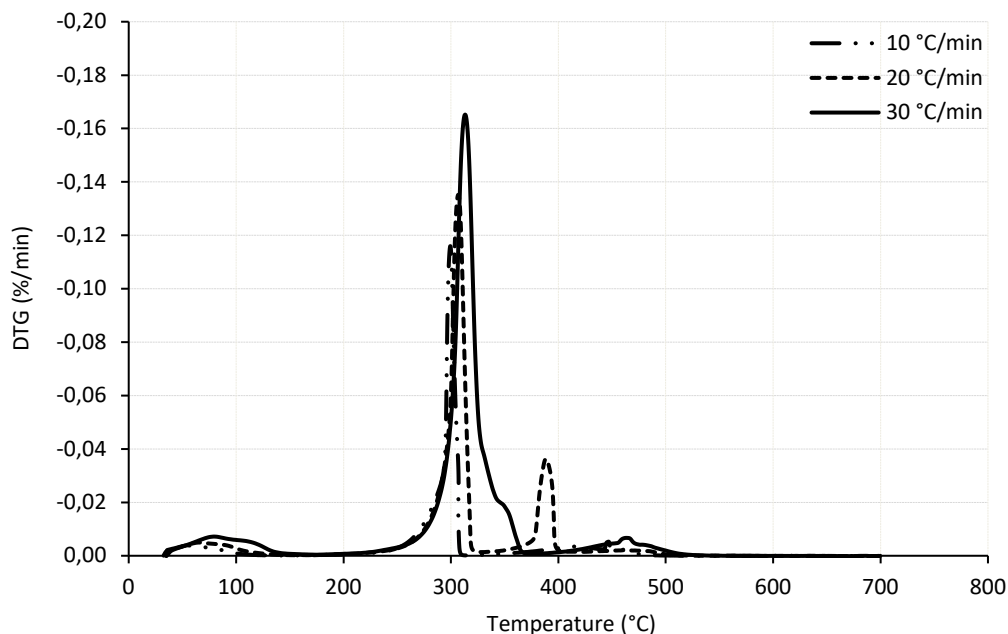


Figure 2. DTG plots for MC Combustion

Table 3 presents the temperature profile characteristics (TPCs) of the DTG plots. The selected TPCs deduced from the DTG peaks in this study are the peak temperatures for drying (T_{dry}) and devolatilization for peak I ($T_{\text{dev, I}}$) and peak II ($T_{\text{dev, II}}$). It is important to state that the thermal degradation of MC at various heating rates produced two peaks each during the second stage of the TGA combustion process, which explains the peak temperatures values for peak I ($T_{\text{dev, I}}$) and peak II ($T_{\text{dev, II}}$) in Table 3.

Table 3. DTG Plot - TPCs of MC combustion

Heating Rate (°C/min)	T_{dry} (°C)	$T_{\text{dev, I}}$ (°C)	$T_{\text{dev, II}}$ (°C)
10	54.22	299.39	313.63
20	66.06	306.83	388.46
30	79.36	312.98	463.29

The peak temperatures for drying (T_{dry}) and devolatilization for peak I ($T_{\text{dev, I}}$) and peak II ($T_{\text{dev, II}}$) enlarged with increasing heating rates. As observed, the T_{dry} values increased from 54.22°C to 79.36°C with an average value of 66.55°C, whereas the $T_{\text{dev, I}}$ was from 299.39°C to 312.98°C or an average of 306.40°C, and lastly the $T_{\text{dev, II}}$ was between 388.46°C and 463.29°C or an average of 425.88°C. In contrast, the TGA pyrolysis of MC by Otitolaiye *et al.*, [40] revealed the average values of T_{dry} , $T_{\text{dev, I}}$, and $T_{\text{dev, II}}$ of 64.93°C, 323.60°C, and 352.27°C, respectively, when compared to the 66.55°C, 306.40°C, and 388.46°C of the combustion process. The relatively higher values of the TGA combustion reported in this study could be explained by the exothermic nature of the process.

3.3. Kinetic properties

The Kissinger model (KM) was employed to compute the kinetic parameters for the TGA combustion of MC under non-isothermal, oxidative, and multi-heating rate TGA. Consequently, the activation energy (E , kJ mol⁻¹) and frequency factor (A , min⁻¹) was deduced from the slope and intercept of the plots of $\ln\left(\frac{\beta}{T_x^2}\right)$ against $\frac{1000}{T_x}$ at the various heating rates from 10°C/min to 30°C/min. Figures 3 and 4 present the KM kinetic plots for the TGA combustion of MC.

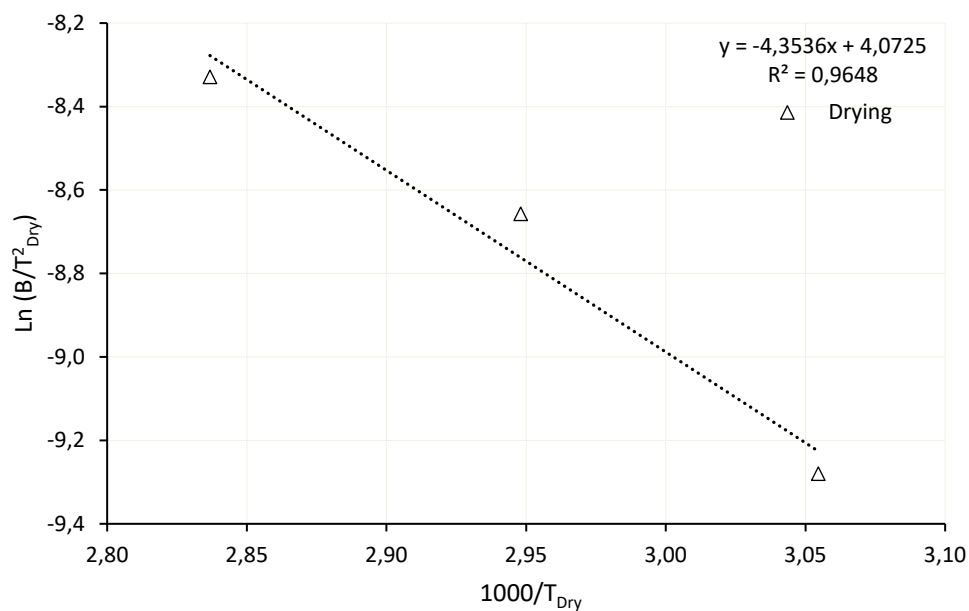


Figure 3. Kissinger kinetic plots for drying stage of MC combustion

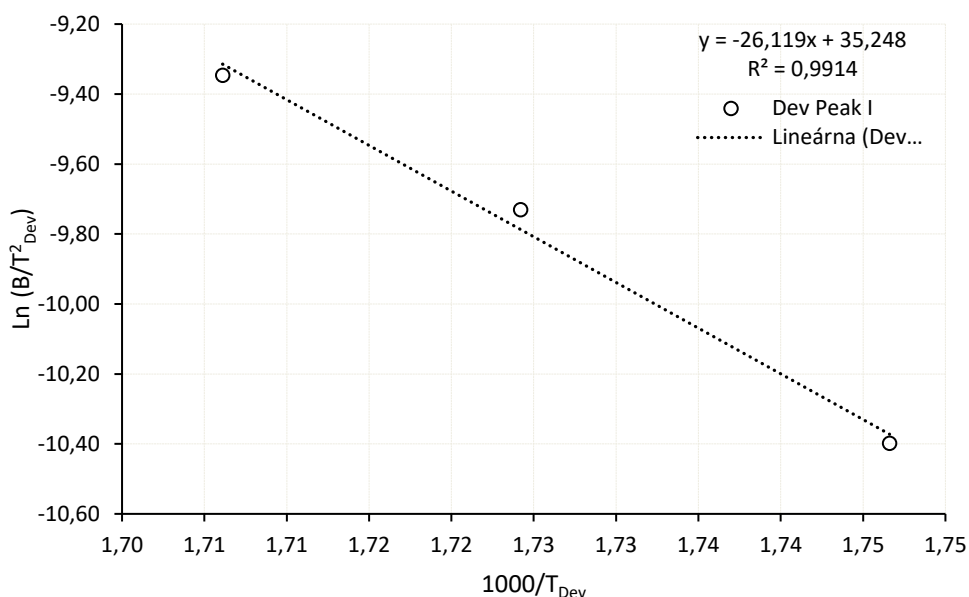


Figure 4. Kissinger kinetic plots for devolatilization stage of MC combustion

Therefore, the activation energy (E , kJ mol^{-1}) and frequency factor (A , min^{-1}) for the drying stage of the MC TGA combustion process are $E = 33.86 \text{ kJ mol}^{-1}$ and $A = 2.39 \times 10^{02} \text{ min}^{-1}$ compared to $37.61 \text{ kJ mol}^{-1}$ and $4.71 \times 10^{02} \text{ min}^{-1}$ for the pyrolysis process reported in the literature [40]. In contrast, the activation energy (E , kJ mol^{-1}) and frequency factor (A , min^{-1}) for the devolatilization stage of the MC TGA combustion process at the peak decomposition temperature I ($T_{Dev, I}$) are $E = 217.15 \text{ kJ mol}^{-1}$ and $A = 5.31 \times 10^{16} \text{ min}^{-1}$ compared to $130.89 \text{ kJ mol}^{-1}$ and $2.32 \times 10^{08} \text{ min}^{-1}$ for the pyrolysis process reported in the literature [40]. On average, the E and A for the TGA combustion of MC are $125.51 \text{ kJ mol}^{-1}$ and $2.65 \times 10^{16} \text{ min}^{-1}$.

4. Conclusions

The study examined the thermal and kinetic properties of maize cobs (MC) under non-isothermal and multiple heating rate thermogravimetric conditions. The objective was to examine the potential of MC as a potential feedstock for the combustion process. In addition, the chemical fuel properties of MC were examined through ultimate, proximate, and calorific analyses. The findings demonstrated that high proportions of carbon, volatile matter and fixed carbon are contained in MC, along with low concentrations of ash, nitrogen, and sulphur. Due to the high volatile matter, MC is considered a potential feedstock for combustion and gasification into flue or fuel gases for clean energy generation. The thermal analysis revealed the thermal behaviour, degradation pathways, and temperature profile characteristics of MC. The TG/DTG plots showed that temperature played a significant role in the thermal degradation or mass loss (ML) during the TGA combustion of MC. The increase in heating rates from 10°C/min to 30°C/min caused a shift in the TG-DTG plots along with the temperature profile characteristics. For all cases, the onset (T_{ons}), midpoint (T_{mid}), endpoint (T_{end}) temperatures and residual mass (RM) increased, whereas the mass loss (ML) decreased with increasing heating rates. Comparison of the TPCs and the kinetic parameters indicated that the MC TGA combustion process is more reactive which results in higher conversion and lower residual mass compared to the pyrolysis process. In general, the findings of the study indicate that MC is a practical feedstock for energy recovery.

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