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Combustion Characteristics and Decomposition Kinetics of Melon Seed Husks Based on the Distributed Activated Energy Model

Bemgba B. Nyakuma[1]*, Olagoke Oladokun[1], Tertsegha J-P. Ivase[2], Moses I. Ayoosu[3], Jamila Baba Ali[4], Samuel Moveh[5], Yakudu A. Dodo[6]

[1] *School of Chemical and Energy Engineering, Faculty of Engineering, Universiti Teknologi Malaysia, 81310 Skudai, Johor, Malaysia*
[2] *Bio-Resource Development Centre, National Biotechnology Development Agency, Makurdi, Benue State, Nigeria*
[3] *Faculty of Built Environment and Surveying, Universiti Teknologi Malaysia, 81310 Skudai, Johor, Malaysia*
[4] *Department of Polymer and Textile Engineering, Faculty of Engineering, Ahmadu Bello University, Samaru Zaria, Kaduna State, Nigeria*
[5] *School of Mechanical Engineering, Faculty of Engineering, Universiti Teknologi Malaysia, 81310 Skudai, Johor Bahru, Malaysia*
[6] *Faculty of Engineering and Built Environment, Universiti Sains Islam Malaysia (USIM), 71800 Nilai, Negeri Sembilan, Malaysia*

Abstract

This paper examined the thermal decomposition kinetics of melon seed husks (MSH) under multi-heating rates and non-isothermal oxidative conditions by thermogravimetric analysis (TGA), temperature profile characteristics (TPCs), and the distributed activated energy model (DAEM). The thermal analysis resulted in 95.06 – 95.77% mass loss (M_L) and 4.01 – 4.94% residual mass (R_M). The TPCs indicated that the midpoint (T_{mid}), endpoint (T_{end}), peak drying and peak devolatilization temperatures (I and II) increased with incremental heating rates except for the ignition (T_{ons}). In addition, the changes in temperature and heating rates significantly influenced the thermal behaviour, degradation mechanisms, and TPCs as evident in TG/DTG plots. Kinetic analyses indicated the activation energy (E_a) and frequency factor (A) also fluctuated significantly during TGA. The values of E_a were from 46.53 kJ/mol to 533.82 kJ/mol, whereas A was from 3.62 min^{-1} to 1.68 × 10^{51} min^{-1} with average values of 215.56 kJ mol^{-1} and 8.85 × 10^{49} min^{-1}, respectively. Overall, the MSH displayed high thermal reactivity during thermal and kinetic analyses. Hence, combustion is a potentially practical route for the valorisation of MSH into clean energy for a sustainable environment.

Keywords: Combustion; Kinetic analysis; Melon seed husks; Activated energy; DAEM.

1. Introduction

Melon seed (*Citrullus colocynthis, L*.) otherwise called *Egusi* is an important perennial cash crop extensively cultivated in Nigeria. It is a yearly, monoecious and herbaceous non-creeping plant of the *Cucurbitaceae* family that survives in the tropics, subtropics, temperate or parched regions worldwide [1]. With an oil content of 45-60%, the melon seed is commonly consumed as food, condiment or processed into a vegetable oil termed melon seed oil (MSO) in many parts of Nigeria and West Africa [2-3]. Over the years, MSO has become a vital vegetable oil and feedstock for biodiesel production, cosmetics, fine chemicals, and traditional medicines [4-8]. As a result, the demand for melon seeds and its rich oil has increased significantly, resulting in the cultivation of over 500,000 tonnes of the crop annually [9].

Typically, the extraction of oil from melon seed generates MSO, seed cake, and the outer seed coat called the husks or shells [1]. The seed cake is currently utilised as an essential

source of protein, carbs, and minerals for animal feeds and food supplements for humans [10]. However, the melon seed husk (MSH) is discarded as wastes in dumpsites, open pits or land-fills. Other known disposal strategies include utilisation as cooking fuel, organic manure, mulching material, biochar feedstock and bio-herbicides [11-15]. Over the years, the low efficiencies of the outlined waste disposal and management strategies have resulted in MSH accumulation in the environment. Hence, the open-air burning of MSH has soared over the years, thereby resulting in airborne pollution with aggravated risks to human health and safety in the affected areas. Therefore, more sustainable approaches are required to effectively address the current and impending problems arising from the poor disposal and management of MSH.

Given its lignocellulosic nature, the valorisation of MSH through biomass conversion technologies is proposed as an efficient approach to effectively dispose and manage the growing stockpiles of MSH. Previous studies have examined the thermal conversion of MSH under pyrolysis conditions [9, 16-17]. The study by Nyakuma [17] examined the solid biofuel potentials of MSH as feedstock for clean energy and power generation. The thermal and kinetic properties were also examined under non-oxidative (pyrolysis) conditions using thermogravimetric analysis (TGA).

In a separate study, Nyakuma [9] examined the bioenergy potential along with the physicochemical and thermodynamic fuel properties of MSH as feedstock for pyrolysis. The findings indicate that MSH has a high energy content, heating value, and combustible elements for thermochemical conversion into clean energy. However, the limitations of the non-oxidative nature, product selectivity, and distribution of pyrolysis products require further investigation of the potential of MSH as solid biofuel feedstock. Since current energy conversion processes and infrastructure in biomass power plants are based on pulverised combustion, it is expedient to explore the oxidative thermal conversion of MSH for future applications.

Therefore, this study seeks to examine the oxidative thermal properties of MSH as a potential feedstock for combustion in future biomass power plants. In addition, the thermal degradation and kinetic behaviour of MSH will be examined through the Distributed Activated Energy Model (DAEM). To the best of the authors' knowledge, there is currently no publication on the oxidative thermal analysis and combustion kinetics of MSH in the literature. Hence, this study presents novel insights into the bioenergy potential of MSH during combustion for future clean energy generation.

2. Experimental

In this study, the melon seed husks (MSH) examined were purchased from a popular market in Kaduna State, Nigeria. Next, the MSH was characterised to determine its physiochemical (ultimate and proximate) and calorific fuel properties, as reported in our previous studies in the literature [9, 16-17]. Based on the results, MSH can be effectively utilized as feedstock for thermochemical energy conversion through pyrolysis, gasification or combustion.

In this study, the thermal and kinetic characterisation of the MSH was examined under oxidative thermal conditions for combustion applications. Therefore, the thermal properties of MSH were examined through thermogravimetric analysis (TGA). The tests were performed under non-isothermal conditions by heating 8 mg of the pulverised MSH sample in an alumina crucible from 30°C to 800°C at different heating rates 10°C/min, 20°C/min, and 30°C/min using the Shimadzu TG-50 (Japan) thermal analyser. During TGA, the furnace was purged with air at a flow rate of 20 ml/min to flush out the evolved gases. In the end, the mass loss (%) was computed as a function of temperature to determine the thermogravimetric (TG, %) and derivative (DTG, %/min) plots, presented in Figures 1 and 2.

Next, the thermal degradation behaviour of MSH was examined to determine the temperature profile characteristics (TPCs) using the Shimadzu TA Workstation thermal analysis software. Hence, the onset (ignition) (T_{ons}), midpoint (T_{mid}), endpoint (T_{end}), and devolatilization peak (T_{max}) temperatures were computed along with mass loss (M_L) and residual masses (R_M) under oxidative (combustion) conditions during TGA. Based on the TG plots, the degrees of conversion (a) of MSH were determined at the various corresponding temperatures to compute the kinetic parameters; activation energy (E_a) and frequency factor (A) using the distributed activation energy model (DAEM). The model was proposed by Vladimir Vand in 1943 [18]

and has since been successfully adapted to characterise the kinetic changes occurring in thermally degrading components during TGA. Based on DAEM, the devolatilization of thermally reacting species can be described by the equation:

$$1 - \frac{V}{V_\infty} = \int_0^\infty \Phi(E_a, T) f(E_a) dE_a \tag{1}$$

Where the terms V, V_∞, $\Phi(E_a, T)$, $f(E_a)$, and A represent the total volatiles changed at the time, t; efficient fuel volatile content; temperature-dependent activation energy E_a; normalised activation energy distribution curve for the irreversible first-order reactions and frequency factor, respectively. By applying the Arrhenius relation, which accounts for the effects of heating rate (β) on the change in volatiles, the mathematical relation for DAEM can be deduced as expressed by the relation;

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{AR}{E_a}\right) + 0.6075 - \frac{E_a}{RT} \tag{2}$$

Hence, the activation energy, E_a, and frequency factor, A, can be deduced from the slope and intercept of the fitted linear curve, respectively.
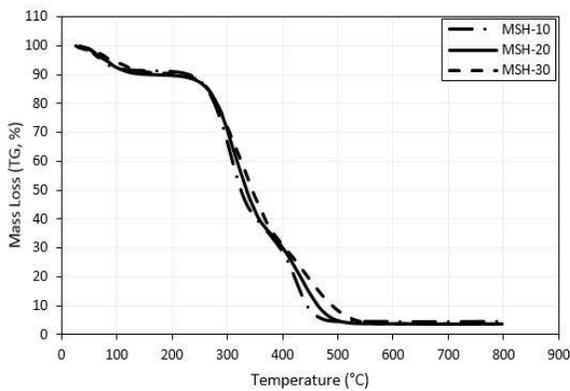
3. Results and discussion

Figure 1. Plots for oxidative TG analysis of MSH

Figure 1 presents the thermogravimetric (TG) plots for the oxidative thermal analysis of MSH. As stated earlier, the TG analysis aims to examine the thermal degradation behaviour of MSH under non-isothermal oxidative conditions, which simulates the combustion of the fuel under multiple heating rates. As observed, the TG plots exhibited a downward sloping trend from the left to the right of Figure 1 with increasing temperature at the various heating rates adopted in this study. The trend indicates that the higher temperatures thermally degraded MSH during TGA under the oxidative conditions examined in this study. The observed trend could be ascribed to the thermal degradation of the lignocellulosic components (lignin, cellulose and hemicellulose) in MSH into evolved flue gases, char, and ash.

Similarly, the change in heating rates affected the rate of thermal degradation of MSH. As observed, there was a shift in the TG plots to the right-hand side of Figure 1 as the heating rates increased from 10°C/min to 30°C/min. Although the shapes and forms of the TG plots for all the heating rates remain unchanged, the rate of thermal degradation and corresponding temperature profile characteristics (TPCs) were significantly modified. This observation could be ascribed to the thermal lag that occurs during multiple heating rate degradation of biomass materials [19-20]. As a result, the plots shifted to the right-hand side or higher temperatures as observed from the TPCs presented in Table 1.

Table 1 TG TPCs for Oxidative Thermal Analysis of MSH

°C/min	T_{ons}, °C	T_{mid}, °C	T_{end}, °C	M_L, %	R_M, %
10	259.39	321.32	388.86	95.06	4.94
20	256.86	332.34	412.59	95.99	4.01
30	249.99	342.77	444.39	95.77	4.23

The TPCs computed for MSH in this study include; onset (T_{ons}), midpoint (T_{mid}), and endpoint (T_{end}), temperatures along with mass loss (M_L) and residual masses (R_M). As observed

in Table 1, the onset (T_{ons}) temperature decreased from 25939 °C to 249.99°C. However, the midpoint (T_{mid}) increased from 321.32°C to 342.77°C, whereas the endpoint (T_{end}) temperature increased from 388.86°C to 444.39°C. Lastly, the mass loss (M_L) and residual mass (R_M) were in the ranges; 95.06% to 95.99% and 4.01% to 4.94%. The results indicate that the change in heating rates significantly affected the TPCs for MSH during TGA.

Next, the thermal degradation mechanism was examined through the DTG plots presented in Figure 2. As observed, the thermal degradation of MSH resulted in three sets of DTG peaks in the range from RT to 200 °C and 200°C to 600°C during TG analysis.
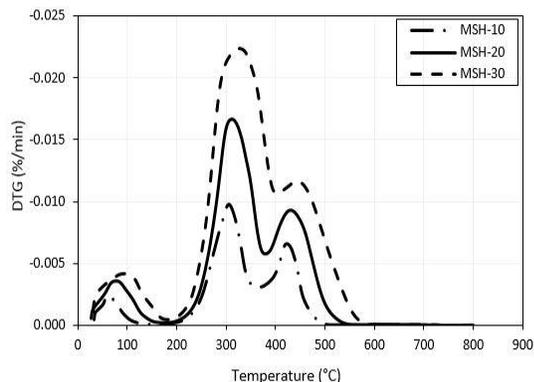

Figure 2 Plots for oxidative DTG analysis of MSH

The first set of peaks below 200°C could be ascribed to drying and loss of low molecular weight volatile compounds. The second set of DTG peaks observed between 200°C and 600°C could be attributed to the devolatilization of major organic compounds during TGA. However, this primary devolatilization stage was characterised by two sets of peaks denoted as devolatilization peak temperatures I and II, which occurred in two different range of temperatures (I = 200°C to 400°C and II = 400 C to 600°C) during TGA. Table 2 presents the temperature profile characteristics of the MSH based on the DTG in Figure 2.

Table 2. DTG TPCs for Oxidative Thermal Analysis of MSH

Heating Rate °C/min	Peak Drying Temp. (°C)	Peak Devolat. Temp. I (°C)	Peak Devolat. Temp. II (°C)
10	60.46	305.34	423.77
20	76.88	310.75	500.34
30	94.02	327.51	446.33

As observed, the peak drying temperatures increased from 60.46°C to 94.02°C, whereas the peak devolatilization temperatures I increased from 305.34°C to 327.51°C and peak devolatilization temperatures II were in the range 423.77°C to 500.34°C. The findings show that the thermal degradation of the MSH occurred in three stages under oxidative (combustion) conditions. These include; drying, devolatilization, and lastly, char combustion characterised by the long tailing observed after 600°C for all heating rates during TGA. The findings indicate that MSH is thermally reactive and can be efficiently degraded under the conditions examined in this study. To further examine the thermal reactivity of MSH during combustion, its kinetic properties were computed through the governing equations of the DAEM Model detailed in section 2 [18].

3.1. Kinetics

The DAEM model proposed by Vladimir Vand in 1943 [18] was adopted to examine the kinetic parameters; activation Energy (E_a) and frequency factor (A) for MSH during the oxidative thermal degradation or combustion process. The kinetic parameters were determined for different degrees conversion from a =0.05 to 0.95 (increments Δ = 0.05). Consequently, the E_a and A were computed from the slopes and intercepts of the DAEM Equation. As observed, the activation energy (E_a) was in the range from 46.53 kJ/mol to 533.82 kJ/mol, whereas the frequency factor ranged from 3.62 min^{-1} to 1.68×10^{51} min^{-1} based on the R^2 of 0.86 to 1.00. The findings indicate that the kinetic parameters for the oxidative or combustion of MSH fluctuated significantly during TGA.

Table 3. Computed kinetic parameters for Oxidative Thermal Analysis of MSH

(*a*)	R^2	(E_a)	(A)
0.05	0.9140	46.53	9.25×10^{01}
0.10	0.9855	533.82	1.68×10^{51}
0.15	0.9564	298.15	2.30×10^{24}
0.20	0.9959	260.41	9.05×10^{19}
0.25	0.9949	263.92	6.92×10^{19}
0.30	0.9837	235.32	6.02×10^{16}
0.35	0.9835	218.25	7.95×10^{14}
0.40	0.9998	176.34	6.40×10^{10}
0.45	0.9847	152.33	2.76×10^{08}
0.50	0.9937	148.88	8.49×10^{07}
0.55	0.9386	125.80	4.39×10^{05}
0.60	0.9133	190.78	8.68×10^{10}
0.65	0.8908	367.35	6.51×10^{24}
0.70	0.9753	346.49	1.81×10^{22}
0.75	0.9974	290.20	1.67×10^{17}
0.80	0.9365	142.58	3.32×10^{05}
0.85	0.9518	114.62	1.46×10^{03}
0.90	0.9637	96.71	4.28×10^{01}
0.95	0.8582	87.12	3.62×10^{00}

Based on the findings, the average values of E_a and A for MSH were; 215.56 kJ/mol and 8.85×10^{49} min^{-1}. Furthermore, the lowest (46.53 kJ/mol) and highest (533.82 kJ/mol) E_a values were observed at a = 0.05 and a = 0.10, respectively. This indicates that MSH is highly reactive at a = 0.05, which resulted in a rapid fluctuation of the kinetic parameters, as observed during the analysis. Hence, it can be reasonably surmised that MSH is a potentially practical feedstock for thermal conversion through combustion due to its high thermal reactivity. However, this submission requires macro-scale reactor tests to effectively observe its thermal degradation and reactivity for large scale combustion applications.

4. Conclusion

The study presented findings on the thermal decomposition kinetics of MSH under non-isothermal, oxidative, and multiple heating rate conditions. The thermal degradation and kinetic behaviour of MSH were examined through thermogravimetric analysis (TGA), the temperature profile characteristics (TPCs), and the distributed activated energy model (DAEM). The findings showed that the variation in temperature and heating rates significantly influenced the thermal behaviour, degradation mechanisms, and TPCs as observed in the shape, size and orientation of the TG and DTG plots. Lastly, the kinetic analysis indicated that MSH is highly thermally reactive as evident in its rapidly fluctuating kinetic parameters; activation energy (E_a) and frequency factor (A) during the thermal and kinetic analyses. Overall, the results showed that combustion is a potentially practical route for the valorisation of MSH.

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To whom correspondence should be addressed: Dr. Bemgba B. Nyakuma, School of Chemical and Energy Engineering, Faculty of Engineering, Universiti Teknologi Malaysia, 81310 Skudai, Johor, Malaysia,
E-mail: bbnyax1@gmail.com