Bioenergy Potential of Melon Seed Husks

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The valorisation of biomass is the most practical route for the creation of a renewable energy economy. In this study, the bioenergy potential of Melon Seed Husks (MSH) was examined as a potential feedstock for pyrolysis. This involved characterization of the physicochemical, thermal kinetic, and thermodynamic fuel properties of MSH. The results revealed that MSH has high calorific value (HHV = 21.78 MJ/kg) and moisture content (6.97 wt. %). The kinetic parameters ranged from activation energy E_a = 79.89 – 300.51 kJ/mole and frequency factor, A = 1.30 × 10^{06} – 9.18 × 10^{20} s^{-1} with average values of 168.83 kJ/mole and 1.31 × 10^{20} s^{-1} at correlation R^2 = 0.92. The enthalpy ranged from ΔH = 77 – 295 kJ/mol; Gibb's free energy ΔG = 127.73 – 207 kJ/mol, and entropy change ΔS = -140.28 – 141.56 J/mol. The variation in thermokinetic and thermodynamic parameters indicates that the pyrolytic decomposition of MSH is governed by complex, slow, surface-based reactions. In conclusion, the results indicate MSH possesses good fuel properties for future bioenergy production.

Keywords: Bioenergy; Melon seed husks, Thermal kinetics, Thermodynamics, Nigeria

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INTRODUCTION

Melon (*Citrullus colocynthis L.)* is a tropical herbaceous, tendril-bearing, vine plant of the *Cucurbitaceae* family commercially cultivated in various regions in Africa (Nwokolo 1996). It is an essential perennial cash crop cultivated for its fruit and oil-bearing seeds (Nyakuma 2015b). The fruit is ovoid shaped and weighs an average of 1.5 kg. The mesocarp comprises numerous brown coloured oval shaped, *dorsoventrally* flattened seeds enclosed in a brittle cortex (Nwokolo 1996). The seeds contain a white, soft textured oil-rich kernel that is typically dehulled for processing into melon seed oil (MSO) (Giwa *et al.* 2014). The oil content of Melon seed ranges from 22.10 to 53.50% along with a crude protein content of 21.8% (Milovanović and Pićurić-Jovanović 2005). The oil is an important feedstock used for various food (Mabaleha *et al.* 2007; Jarret and Levy 2012), medicinal (Chen *et al.* 2012; Xu *et al.* 2016), biodiesel fuel (Fadhil 2013; Giwa *et al.* 2014), pesticides (Nzelu and Okonkwo 2016), and industrial purposes (Lawal *et al.* 2012; Isaac and Ekpa 2014). According to the FAO (Food and Agricultural Organization), the global production of Melon seeds is between 580,000 and 610,000 tons per annum (Kortse *et al.* 2013). However, the extraction of MSO generates large quantities of lignocellulosic waste known as melon seed husks (MSH). This is the oval-shaped, brown coloured outer coat generated from decortication of the melon seeds. With the growing culinary and medicinal importance of melon seeds, it is estimated that the cultivation and extraction of MSO will result in increased wastes over the coming years (WorldWatch Institute 2017). This will present further waste disposal and management challenges for the communities reliant on the crop for livelihood. In addition, current strategies for the disposal and management of agricultural wastes such as MSH are considered inefficient, unsustainable, and environmentally hazardous (Demirbas 2011). Therefore, practical solutions are urgently required to significantly address the potential challenges of greenhouse gas (GHGs) emissions, global warming, and climate change resulting from open air burning, landfilling, and dumping of agroforestry wastes into the environment.

The utilization of MSH as fuel feedstock for biomass and bioenergy applications is a potential solution for the current waste management challenges. The valorisation of MSH can be achieved through biomass conversion technologies (BCT). Pyrolysis is considered one of the most promising BCT for the production of solid, liquid and gaseous fuels from biomass feedstocks (Basu 2010). Therefore, the pyrolysis of MSH presents opportunities for the production of clean, renewable, and sustainable energy, fuels, and chemicals for the future. Likewise, it is a potentially viable strategy for the efficient disposal and management of future agricultural waste streams. However, BCTs require a comprehensive evaluation of the fuel properties of potential biomass feedstock (Nyakuma *et al.* 2012; Joshua *et al.* 2016; Sadiku *et al.* 2016). This will enable efficient resources mobilization, and the design, development, and optimisation of conversion processes.

Therefore, this study examined the bioenergy potential of MSH as feedstock for pyrolysis. Consequently, the fuel characterization of MSH comprised physicochemical, thermal decomposition kinetics, and thermodynamic analyses. To the best of the authors' knowledge, there is limited research on the area, and new insights will foster the creation of a circular energy economy based on MSH valorisation. Consequently, the paper seeks to present comprehensive knowledge on the bioenergy properties of MSH. The results will provide valuable data for the design, development, and diffusion of future pyrolysis of MSH.

EXPERIMENTAL

The melon seed husks (MSH) were obtained from de-husked melon seeds purchased from a market in Kaduna state, Nigeria. The procedures and standards for the physiochemical, thermal, and kinetic characterization of the MSH are detailed in the previous study on the fuel (Nyakuma 2015b). The ultimate, proximate, and calorific analyses results are presented in Table 1. Thermal analysis was investigated through thermogravimetric (TG) analysis by heating approximately 10 mg of pulverized MSH under the non-isothermal heating program from 30 to 800 °C at 5, 10 and 20 °C/min heating rates under nitrogen gas atmosphere. The analysis was carried on the high precision thermobalance Netzsch 209 F3 Thermogravimetric (TG) analyzer according to the procedure described in literature (Nyakuma 2015a). Subsequently, the resulting TG-DTG data were used to calculate the kinetic parameters for the degree of conversion, α = 0.05 to 0.60 according to the Distributed Activation Energy Model (DAEM). The kinetic parameters; – activation energy, E_a and frequency factor, A – were deduced from the slope and intercept of the equation respectively:

$$ln\left(\frac{\beta}{T^2}\right) = ln\left(\frac{AR}{E_a}\right) + 0.6075 - \frac{E_a}{RT} \quad (1)$$

The theory and assumptions for the DAEM model are described in the literature (Shen *et al.* 2011). Consequently, the thermodynamic parameters; enthalpy (ΔH), Gibb's free energy (ΔG), and entropy change (ΔS) for MSH were calculated based on the kinetic parameters from DAEM using Eqs. 2 to 4 (Maia and de Morais 2016);

$$\Delta H = E_a - RT \quad (2)$$

$$\Delta G = E_a + RT_m . In\left(\frac{K_B T_m}{hA}\right) \quad (3)$$

$$\Delta S = \frac{\Delta H - \Delta G}{T_m} \quad (4)$$

The terms ΔH, ΔG, and ΔS represent the enthalpy, Gibb's free energy, and entropy change, respectively. Furthermore, E_a represents activation energy (kJ/mol), R - molar gas constant (8.314 J/mol K), and T - Temperature (K). The term T_m peak decomposition temperature (K) was determined from the average DTG peaks for MSH degradation. The values were deduced from the Proteus Thermoanalysis Software version 6.0. The term K_B corresponds to the Boltzmann constant (1.38×10^{-23} J/K) and h is Planck's constant (6.626×10^{-34} Js).

RESULTS AND DISCUSSION

Physicochemical Fuel Properties

Table 1 presents the physicochemical properties comprising the ultimate, proximate, and calorific analyses in dry ash free basis (*daf*)* and dry basis (*db*)**.

Table 1: Physicochemical Fuel Properties of Melon Seed Husk (MSH)

Analysis	Element/Property	Symbol/Units	Proportion (wt.%)
Ultimate Analysis*	Carbon	C	51.80
	Hydrogen	H	6.67
	Nitrogen	N	0.85
	Sulphur	S	0.40
	Oxygen	O	40.28
	Higher Heating Value	HHV MJ/kg	21.78
	Lower Heating Value	LHV MJ/kg	20.50
Proximate Analysis**	Moisture	M	6.97
	Volatile Matter	VM	79.52
	Ash	A	1.50
	Fixed Carbon	FC	18.99

The physicochemical properties of MSH indicate that the fuel had high proportions of *C*, *H*, and *FC*, which accounts for its high calorific values *HHV* and *LHV*. In addition, the low moisture and ash content are ideal qualities for the pyrolysis of MSH into solid, liquid, and gaseous biofuels. Furthermore, the low content of pollutant gas precursors *N*, and *S* indicate the fuel is potentially an environmentally friendly feedstock for biofuel and bioenergy production.

Thermal Kinetic Properties

The kinetic parameters E_a and *A* deduced from the slope and intercept of Eq.1 are presented in Table 2. The values are presented for degrees of conversion of MSH from α = 0.05 to 0.60 for pyrolysis decomposition of MSH from 30 to 800 °C.

Table 2: Kinetic parameters for MSH pyrolysis using DAEM

α	Slope	intercept	R^2	E_a (kJ/mole)	A (s^{-1})
0.05	-9.61	18.63	0.9774	79.89	1.18×10^{09}
0.10	-10.45	11.73	0.5048	86.86	1.30×10^{06}
0.20	-20.05	25.36	0.9987	166.72	2.06×10^{12}
0.30	-22.32	27.27	0.9988	185.55	1.55×10^{13}
0.40	-23.90	28.55	0.9988	198.66	5.98×10^{13}
0.50	-19.68	21.02	0.9924	163.61	2.64×10^{10}
0.60	-36.15	44.68	0.9756	300.51	9.18×10^{20}
Average	**-20.31**	**25.32**	**0.9209**	**168.83**	**1.31×10^{20}**

As observed, the kinetic parameters ranged from E_a = 79.89 to 300.51 kJ/mol and $A = 1.30 \times 10^{06}$ to 9.18×10^{20} s^{-1} with average values E_a = 168.83 kJ/mol; $A = 1.31 \times 10^{20}$ s^{-1} and coefficient of determination $R^2 = 0.9209$. The wide variation in kinetic parameters demonstrates that the decomposition is due to complex reactions between the lignocellulosic components of MSH. Furthermore, Maia and de Morais (2016) stated that low-frequency factors $< 10^9$ s^{-1} are due to surface based or closed complex degradation reactions. However, for values $\geq 10^9$ s^{-1} this may be due to a simple complex. Table 3 presents the comparative analysis of the average kinetic parameters of MSH and other biomass investigated in literature.

Table 3. Comparison of the Kinetic Parameters of MSH with other Biomass

Biomass	E_a (kJ/mol)	References
Melon Seed Husk (MSH)	168.83	This study
Cardoon Leaves	350.00	(Damartzis *et al.*, 2011)
Helianthus tuberosus	268.30	(Sun *et al.*, 2012)
Hazelnut Husks	131.10	(Ceylan and Topcu, 2014)
Red Pepper Waste	92.93	(Maia and de Morais, 2016)
Cardoon Stems	224.00	(Damartzis *et al.*, 2011)
Oil Palm EFB Pellets	160.20	(Nyakuma *et al.*, 2015)
Imperata cylindrica	164.93	(Oladokun *et al.*, 2016)

As can be observed in Table 3, E_a values of agroforestry biomass can typically range from 92.93 to 350 kJ/mol, whereas the value for MSH was 168.83 kJ/mol. The activation energy (E_a) is defined as the minimum energy required by reactants in a chemical system to initiate a reaction (Ceylan and Topcu 2014). Therefore, lower E_a values will result in faster reactions and *vice versa*. Furthermore, the degradation of MSH under pyrolysis conditions may be slower compared to Hazelnut husks, *Imperata cylinderica*, Oil palm EFB pellets, and Red Pepper waste. In effect, slow pyrolysis favors the production of solid pyrolysis products such as biochar and bio-charcoal (Basu 2010).

Thermodynamic Fuel Properties

The thermodynamic parameters enthalpy (ΔH), Gibb's free energy (ΔG), and entropy change (ΔS) of MSH were determined based on the kinetic parameters from DAEM. The values of ΔG and ΔS were calculated using the average peak decomposition temperature T_m of MSH. Table 4 presents the thermodynamic properties of the fuel.

Table 4. Thermodynamic Fuel Properties of MSH

α	E_a (kJ/mole)	ΔH (kJ/mol)	ΔG (kJ/mol)	ΔS (J/mol)
0.05	79.89	77.05	127.73	-81.88
0.10	86.86	82.94	169.77	-140.28
0.20	166.72	162.05	176.16	-22.79
0.30	185.55	180.63	184.59	-6.40
0.40	198.66	193.58	190.77	4.53
0.50	163.61	158.44	195.48	-59.84
0.60	300.51	295.09	207.47	141.56

The thermodynamic parameter enthalpy (ΔH) ranged from 77 to 295 kJ/mol with an average value of 164.25 kJ/mol. On the other hand, Gibb's free energy (ΔG) ranged 127.73 to 207 kJ/mol with an average value of 178.85 kJ/mol for the fuel. Lastly, the entropy change (ΔS) was -140.28 to 141.56 J/mol, with an average value of -23.59 J/mol. In comparison, the average values of enthalpy (ΔH) and Gibb's free energy (ΔG) are somewhat higher than the red pepper waste, RPW (ΔH = 119 kJ/mol and ΔG = 136 kJ/mol) examined by *Maia* and *de Morais* (2016). This may be ascribed to the lignocellulosic components, which account for the reactivity and selectivity of products during pyrolytic biomass decomposition. This is corroborated by studies that demonstrate the *holocellulose* content and reactivity of vegetative biomass is higher than husks residues (Ndazi *et al.*, 2008).

CONCLUSIONS

The study examined the bioenergy potential of Melon Seed Husks (MSH) as feedstock for pyrolysis. Consequently, MSH was evaluated based on its physicochemical, thermal kinetics and thermodynamic characteristics. The following conclusions can be drawn from the results;

1. The physicochemical properties of MSH revealed high proportions of elemental fuel constituents; *C*, *H*, *FC* but low ash and moisture content. The calorific value of MSH was significantly high compared to other agroforestry residues in literature. Furthermore, the low content of *N* and *S* demonstrates the environmental friendliness of the fuel.
2. The thermal kinetic properties of MSH demonstrated that E_a and *A* were somewhat higher than other biomass. Therefore, the degradation kinetics of MSH is based on slow surface based pyrolysis reactions, which favour solid products such as biochar and bio-charcoal.
3. The thermodynamic properties of MSH indicated that the ΔH, ΔG, and ΔS are higher than previously reported, which may be due to the high content of unreactive biomass components such as lignin. This indicates that the degradation of MSH will favour solid pyrolysis products.

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