

*Bemgba Nyakuma<sup>1,2</sup>, Olagoke Oladokun<sup>1,2</sup>, Yakubu Dodo<sup>1</sup>, Syie Wong<sup>2</sup>,  
Habibu Uthman<sup>1</sup> and Muhamad Halim<sup>3</sup>*

## FUEL CHARACTERIZATION AND THERMOGRAVIMETRIC ANALYSIS OF MELON (*Citrullus Colocynthis L.*) SEED HUSK

<sup>1</sup> Centre for Hydrogen Energy, Institute of Future Energy, Universiti Teknologi Malaysia, 81310 UTM Skudai, Johor Bahru, Malaysia

<sup>2</sup> Department of Chemical Engineering, Faculty of Chemical and Energy Engineering, Universiti Teknologi Malaysia, 81310 UTM Skudai, Johor Bahru, Malaysia

<sup>3</sup> Centre of Polymer Composite Research & Technology (PoCResT), Institute of Science, Universiti Teknologi MARA (UiTM), Shah Alam, Selangor, Malaysia  
bnyax1@gmail.com, bnbevan2@live.utm.my

Received: October 21, 2015 / Revised: January 12, 2016 / Accepted: March 12, 2016

© Nyakuma B., Oladokun O., Dodo Y., Wong S., Uthman H., Halim M., 2016

**Abstract.** The thermochemical fuel properties of melon seed husk (MSH) were characterized to examine its solid biofuel (SBF) potential for future bioenergy utilization. MSH is a cheap, abundant and renewable source of lignocellulosic waste generated from the extraction of vegetable oil from melon seeds. Thermochemical characterization was examined by proximate, ultimate, and thermogravimetric (TG-DTG) analyses, as well as Fourier transform infra-red (FT-IR) spectroscopy. The results showed that MSH exhibits significant volatile matter, fixed carbon, carbon and low nitrogen, sulphur and ash content with a heating value (HHV) of 19.02 MJ/kg. FT-IR analysis indicated functional groups for aliphatic, ester, ketone, alcohol, and aromatic compounds. Thermal decomposition of MSH occurred in three stages: drying (303–448 K), devolatilization (448–673 K) and char degradation (673–1073 K).

**Keywords:** melon, seed husk, biofuel, characterization, thermogravimetry, spectroscopy.

### 1. Introduction

Melon (*Citrillus colocynthis L.*), also known as “Egusi” in Nigeria, is an important cash crop widely cultivated for its high protein and oil-rich seeds [1]. The seed comprises an outer thick husk housing a fleshy oil rich kernel which contains 53 % of unsaturated oil widely utilised as a feedstock in the food beverage, cosmetics and paint industry [2]. The annual cultivation of melon seeds in Nigeria exceeds 500,000 tonnes which are mainly processed into vegetable oils (75 %), domestic consumption (10 %) while a fraction is lost to decay (15 %) [3]

due to lack of long-term storage facilities. In addition, melons are reportedly used as weed suppressants and organic fertilisers, medicinal herbs, and items of socioeconomic and cultural value [1, 4].

The extraction of vegetable oil from melon in Nigeria generates large quantities of lignocellulosic waste generally called melon seed husk (MSH) annually. MSH is a cheap, abundant and renewable source of future solid biomass fuel (SBF) for thermochemical energy applications. Currently, MSH is simply burned in open-air [5] or dumped into landfills, refuse dumps, drainages, or waterways. The inefficiency of these waste disposal strategies requires urgent attention to avert the potential long-term environmental degradation due to increased pollutant emissions. With anthropogenic GHGs emissions set to soar over the next decades [6, 7], the urgency of the task of ensuring the smooth transition from fossil to renewables has become more profound than ever before. According to climate scientists, the continued and unabated increase in global temperatures due to GHGs will greatly impact the future of mankind [8]. In particular, developing countries in sub-Saharan Africa will mostly suffer the effects such as famine, water quality, droughts, soil erosion and crop yields [9–12]. To address these impending issues, scientists and policy makers around the world urgently need to double the current efforts in ensuring clean energy production, energy efficiency and environmental sustainability.

The valorization of biomass through conversion technologies such as torrefaction, pyrolysis and gasification are promising technologies for the sustainable production of clean renewable fuels. In addition, the utilization of solid wastes and agricultural residues as feedstock for biomass conversion is a practical strategy

for waste disposal management and energy production [13-15]. However, the waste to energy valorization process is beset by numerous sociotechnical challenges that have to be addressed to ensure the proposed energy transitions attain fruition. Furthermore, the waste-to-energy (WtE) process requires comprehensive insight into thermochemical fuel properties of the proposed feedstock. This is vital for the engineering considerations required for process design, optimization and scale-up of conversion equipment. The fuel characterisation and thermal decomposition of potential biomass feedstock are frequently investigated using thermogravimetric analysis (TGA) [16-18].

To the best of the author's knowledge, there has been no research in scientific literature on the thermochemical fuel properties and thermal decomposition behaviour of melon seed husk (MSH) as a feedstock for thermochemical biomass conversion. Therefore, this study is aimed at characterizing the thermochemical solid biomass fuel properties of melon seed husk (MSH) as a prospective feedstock for biomass conversion. The study will also examine the thermal behaviour of MSH using TGA analysis under pyrolysis (inert) conditions to ascertain the decomposition temperature profile characteristics of the fuel.

## 2. Experimental

Melon seeds were obtained from a local market in Northern Nigeria, dried and dehulled prior to the characterization tests. The melon seed husks (MSH) were subsequently pulverised in an Elba Dry Miller (Model EBM 9182) and sieved using a 250- $\mu\text{m}$  Endecotts<sup>TM</sup> analytical sieve (Series No. BS410-1986). Ultimate analysis of MSH was determined using the CHNS/O Elemental analyser (Model: Elementar<sup>TM</sup> Vario Micro Cube) according to ASTM D5291 standard. The ASTM standards: E871 for moisture, E872-82 for volatile matter and D1102-84 for ash content were utilized for proximate analysis. The fixed carbon content was obtained by difference using the relation:  $\text{FC} = 1 - \text{M} - \text{VM} - \text{ASH}$  where M, VM, and ASH represent moisture, volatile matter, and ash content, respectively [19]. The higher heating value (HHV) of MSH was calculated from the *Channiwala and Parikh* formula [20]. The ultimate and proximate analysis of MSH is presented in Table 1 and compared with the average literature values deduced by Vassilev *et al.* [21]. The probable chemical structure of MSH was examined by Fourier transform infra-red (FT-IR) Spectrophotometer (Model: Shimadzu IR Prestige-21) using the KBr Pellet method. About 1 % of the sample mixed with KBr crystals was pelletized in a die set before analysis in the FTIR spectrophotometer to determine the chemical functional groups in MSH. A total of 20 scans at the resolution of 8.0 was applied to obtain the FTIR

spectra in the range 4000–400  $\text{cm}^{-1}$ . The thermal decomposition behaviour of MSH was investigated using the Netzsch TG analyser (Model 209 F3). About 10 mg of the powdered MSH sample was heated in an alumina crucible from 303–1073 K at the heating rate of 30  $\text{K}\cdot\text{min}^{-1}$ . The weight loss during TG analysis was recorded and analysed using the Netzsch Proteus 6.1 software to examine the temperature profile and decomposition parameters of MSH.

## 3. Results and Discussion

### 3.1. Ultimate-Proximate Analysis

The ultimate and proximate analysis of MSH is presented in Table 1. The values of FC and O were determined by difference and all values are reported on as received (*ar*) basis. The results were compared to the average values for over 80 lignocellulosic agricultural waste residues evaluated by Vassilev *et al.* [21]. From Table 1, we can observe that the fuel properties of MSH fall within average values reported in literature. Furthermore, the results demonstrate that MSH exhibits low fixed carbon (FC), moisture (M) and ash (A) content. However, a high volatile matter (VM) content greater than 70 wt % was reported for MSH. The high volatile matter content in MSH indicates that the fuel will exhibit a low ignition temperature. This is based on the literature findings for biomass fuels reported in Basu (2010) [22], which indicate that biofuels with high volatile matter content generally display lower ignition temperatures.

In addition, the low ignition temperature of biomass fuels compared to coal can be attributed to the higher volatile matter of the former. The ignition temperature is an important property of solid biofuels since the thermochemical conversion reactions of the fuel such as combustion are usually self-sustaining above it [22]. Therefore, this property has significant implications on the process design, reactor materials and engineering economics of biomass conversion.

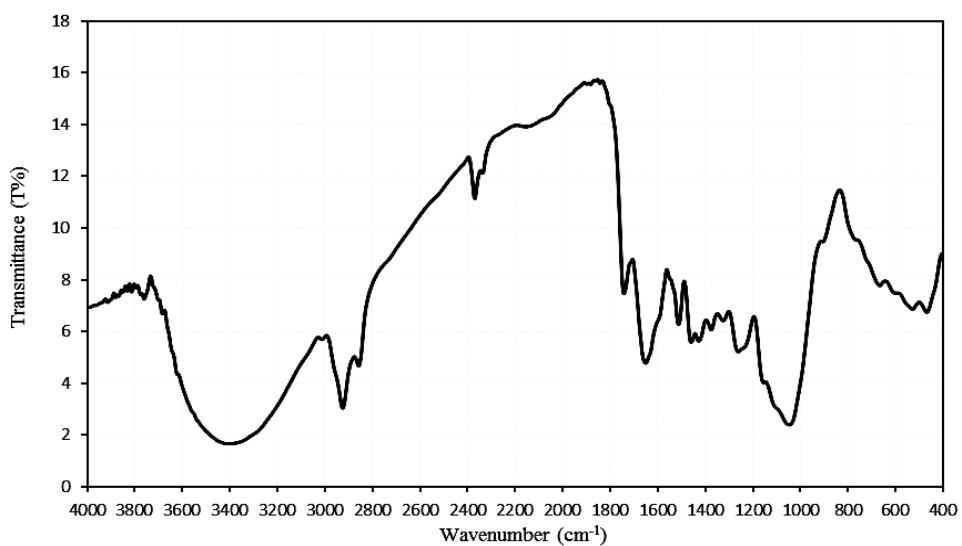
The heating value of MSH (<20 MJ/kg) is significantly lower than that of lignite coal (23.23 MJ/kg) and bituminous coal (26.44 MJ/kg) reported in literature [19, 23, 24]. This is due to the low fixed carbon (FC) and high oxygen (O) content of MSH [25]. Nonetheless, the heating value of MSH indicates the fuel possesses satisfactory calorific energy content for utilization as a solid biomass fuel (SBF). Furthermore, the trace amounts of nitrogen (N) and sulphur (S) in MSH indicate that thermal conversion will yield low  $\text{NH}_x$ ,  $\text{NO}_x$ ,  $\text{SO}_x$ ,  $\text{H}_2\text{S}$  emissions indicating it is potentially an environmentally friendly biofuel for future energy applications. However, this is largely dependent on the choice of biomass conversion technology employed for thermochemical conversion of MSH.

Table 1

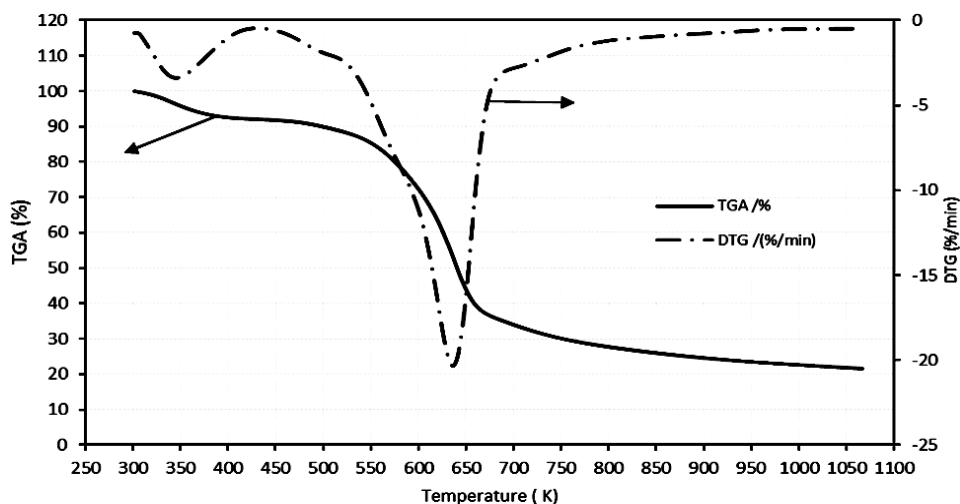
**Proximate and ultimate analysis of melon seed husk (MSH)**

Element	Symbol	MSH, wt %	Literature values**, wt %
Carbon	C	47.54	42–71
Hydrogen	H	6.12	3–11
Nitrogen	N	0.75	0.1–12
Sulphur	S	0.13	0.01–2.3
Oxygen	O*	45.46	4–36
Moisture	M	6.97	3–36
Volatile matter	VM	71.93	48–86
Ash	A	1.88	0.1–46
Fixed carbon	FC*	19.22	1–38
Higher heating value	HHV, MJ/kg	19.07	–

Notes: \* determined by difference; \*\* adapted from Vassilev *et al.*, 2010



**Fig. 1.** FT-IR spectrum of MSH



**Fig. 2.** TG-DTG curves for Melon Seed Husk (MSH)

### 3.2. Fourier Transform Infra-Red Spectroscopy (FT-IR)

The FT-IR spectrum of MSH presented in Fig. 1 shows the characteristic bands fundamentally associated with lignocellulosic biomass components; hemicellulose, cellulose and lignin [25-27].

The strong band in the high-energy zone located from 3000–3600  $\text{cm}^{-1}$  can be ascribed to –OH stretching in the MSH chemical structure. The intensity of the band is a measure of the typical intermolecular bonded –OH groups in lignin, carbohydrates and the symmetric-asymmetric stretch vibrations of water molecules [27, 28]. This is corroborated by the moisture content of MSH reported in Table 1. The medium peak observed at 2924 and 1423  $\text{cm}^{-1}$  can be ascribed to C–H stretching and C–H bending vibrations, respectively, characteristic of alkyl and aliphatic chains. According to McKendry [29], the basic building blocks of lignocellulosic materials consist of aliphatic chains.

The band observed at 2368  $\text{cm}^{-1}$  can be assigned to –C≡C– stretching vibrations distinctive of alkynes. The medium bands observed at 1739, 1512 and 1253  $\text{cm}^{-1}$  are due to C=O stretching vibrations observed in carboxylic, ketone and ester groups. The band at 1647  $\text{cm}^{-1}$  can be attributed to unsaturated –C=C– aliphatic compounds, amides and/or unsaturated aromatic compounds. The strong band observed at 1041  $\text{cm}^{-1}$  can be assigned to C–OH or C–OR typical of alcohols and ester groups [27]. In general, FT-IR analysis indicated that chemical structure of MSH is likely due to functional group contributions from aliphatic, ester, ketone, alcohol, and aromatic compounds present in the lignocellulosic structure of biomass species.

### 3.3. Thermogravimetric Analysis

The TG-DTG curves for MSH at the heating rate of 30  $\text{K}\cdot\text{min}^{-1}$  are presented in Fig. 2. The curves display the typical reverse *s*-shaped curves characteristic of the thermal degradation of lignocellulosic biomass under an inert atmosphere. The TG-DTG curves indicate that the thermal degradation of MSH occurred in three (3) stages, namely drying, devolatilization and char degradation.

The drying stage occurred within 303–448 K with a peak drying temperature of 345 K. Similar observations have been reported in literature for other biomasses [30, 31]. The weight loss during the drying stage was 8.22 %, which is slightly higher than the MSH moisture content 6.97 % (Table 1). The reason for this difference may be that weight loss during TG drying stage is not only due to the loss of surface bounded moisture in MSH but also due to the loss of light volatile compounds.

The second devolatilization stage, characterised by the major peak observed within 448–673 K, was due to major weight loss of 55.40 % of MSH. The weight loss during this devolatilization stage is normally attributed to the major loss of the main organic materials in biomass materials [30]. Consequently, this stage of thermal degradation of biomass is denoted by the region of active pyrolysis. In addition, the “shoulder” on the DTG peak usually attributed to hemicellulose in lignocellulosic biomass materials was observed during MSH thermal analysis [32]. The onset temperature for MSH decomposition during active pyrolysis was observed at 583 K, while the peak decomposition temperature was 636 K with the mass loss rate of 20.37 % and offset temperature of 671 K.

The weight loss during the final stage of MSH degradation was 14.79 %. This is primarily due to char degradation typically denoted by the long tailing observed at 673 K for MSH. The residual mass for MSH degradation was 21.53 %, which denotes the potential biochar yield at the final pyrolysis temperature of 1073 K. By comparing the residual mass to the fixed carbon and ash content in Table 1, we can infer that the char yield of MSH process can be reasonably estimated from thermal analysis.

## 4. Conclusions

The thermochemical fuel properties of melon seed husk (MSH) was investigated using proximate and ultimate, FT-IR, and TG-DTG analyses. The results showed significant volatiles, fixed carbon, carbon content but low nitrogen, sulphur content for MSH. The FTIR analysis indicated that chemical structure of MSH is likely due to functional group contributions from aliphatic, ester, ketone, alcohol, and aromatic compounds. Thermal decomposition of MSH occurred in three stages: drying, devolatilization and char degradation. The most substantial weight loss, 55.40 %, was observed during devolatilization from 448 to 673 K. In addition, 78.5 % degradation of MSH was achieved during the pyrolysis of MSH. The residual char yield of MSH pyrolysis determined from thermal and proximate analysis of the fuel was high. The higher heating value (HHV) of MSH indicates it has sufficient calorific value for utilization as a solid biomass fuel (SBF) for future thermal applications. Therefore, the thermochemical fuel and environmentally friendly properties of MSH indicate it is a potentially promising solid biomass fuel (SBF) for future applications.

## Acknowledgments

The authors wish to acknowledge the contributions of Dr T. A. T. Abdullah of Institute of Future of Energy and the financial support of the Malaysian Ministry of Higher Education (MoHE) Long Research Grant Scheme (LRGS-MOHE) and Universiti Teknologi Malaysia (UTM) GUP Grant (VOT No. 4L817).

## References

- [1] Achigan-Dako E., Fagbemissi R., Avohou H. *et al.*: Biotechnol. Agron. Soc. Environ, 2008, **12**, 393.
- [2] Ezeike G.: Int. J. Food Sci. Technol., 1988, **23**, 511.
- [3] FAO: FAOSTAT Statistics 2008-2013, 2015.
- [4] Ajibola O., Eniyemo S., Fasina O. and Adeeko K.: J. Agr. Eng. Res., 1990, **45**, 45.
- [5] Foo K. and Hameed B.: Desalination Water Treatment, 2012, **47**, 130.
- [6] Van der Werf G., Morton D., DeFries R. *et al.*: Nature Geosci., 2009, **2**, 737.
- [7] Meinshausen M., Smith S., Calvin K. *et al.*: Climatic Change, 2011, **109**, 213.
- [8] Ramanathan V., Crutzen P., Kiehl J. and Rosenfeld D.: Science, 2001, **294**, 2119.
- [9] Godfray H., Beddington J., Crute I. *et al.*: Science, 2010, **327**, 812.
- [10] McMichael A., Powles J., Butler C. and Uauy R.: Lancet, 2007, **370**, 1253.
- [11] Change I.: Genebra, Suíça, 2001.
- [12] Louis M. and Hess J.: Am. J. Prev. Med., 2008, **35**, 527.
- [13] Werle S.: Ecol. Chem. Eng. A, 2013, **20**, 279.
- [14] Ragauskas A., Williams C., Davison B. *et al.*: Science, 2006, **311**, 484.
- [15] Mosier N., Wyman C., Dale B. *et al.*: Bioresource Technol., 2005, **96**, 673.
- [16] Magdziarz A. and Werle S.: Waste Manage., 2014, **34**, 174.
- [17] Słopiecka K., Bartocci P. and Fantozzi F.: Appl. Energy, 2012, **97**, 491.
- [18] Damartzis T., Vamvuka D., Sfakiotakis S. and Zabaniotou A.: Bioresource Technol., 2011, **102**, 6230.
- [19] Basu P.: Biomass Gasification, Pyrolysis and Torrefaction: Practical Design and Theory. Academic Press, New York 2013.
- [20] Channiwala S. and Parikh P.: Fuel, 2002, **81**, 1051.
- [21] Vassilev S., Baxter D., Andersen L. and Vassileva C.: Fuel, 2010, **89**, 913.
- [22] Basu P.: Biomass Gasification and Pyrolysis: Practical Design and Theory. Academic Press, New York 2010.
- [23] Karimipour S., Gerspacher R., Gupta R. and Spiteri R.: Fuel, 2013, **103**, 308.
- [24] Probst R. and Hicks R.: Synthetic Fuels: Courier Corporation, New York 2006.
- [25] Yang H., Yan R., Chin T. *et al.*: Energ. Fuel., 2004, **18**, 1814.
- [26] Zapata B., Balmaseda J., Fregoso-Israel E. and Torres-Garcia E.: J. Therm. Anal. Calorim., 2009, **98**, 309.
- [27] Lopez-Velazquez M., Santes V., Balmaseda J. and Torres-Garcia E.: J. Anal. Appl. Pyrol., 2013, **99**, 170.
- [28] Yang H., Yan R., Chen H. *et al.*: Fuel, 2007, **86**, 1781.
- [29] McKendry P.: Bioresource Technol., 2002, **83**, 37.
- [30] Li L., Wang G., Wang S. and Qin S.: J. Therm. Anal. Calorim., 2013, **114**, 1183.
- [31] Acikalin K.: J. Therm. Anal. Calorim., 2011, **105**, 145.
- [32] Ren S., Lei H., Wang L. *et al.*: Biosystems Eng., 2013, **116**, 420.

## ПАЛИВНІ ХАРАКТЕРИСТИКИ ТА ТЕРМОГРАВІМЕТРИЧНИЙ АНАЛІЗ ЛУШПИННЯ НАСІННЯ КОЛОЦИНТУ (*CITRILLUS COLOCYNTHIS* L.)

**Анотація.** Визначено термохімічні паливні властивості лушпиння насіння колоцинту (ЛНК) з метою його потенційного використання як твердого біопалива. Показано, що ЛНК є дешевим, доступним і відновлювальним джерелом лігноцелюлозних відходів, які одержують при екстракції олії з насіння дині. Проведено дослідження з використанням технічного, елементарного і термогравіметричного (ТГ-ДТГ) аналізу, а також Фур'є-спектроскопії. Встановлено, що ЛНК містить значну кількість летких речовин і зв'язаного вуглецю, а також невелику кількість азоту, сірки і золи з тепловою здатністю понад 19,02 МДж/кг. За допомогою Фур'є-спектроскопії встановлена присутність аліфатичних, естерних, кетонних, спиртових і ароматичних функційних груп. Показано, що термічний розклад ЛНК відбувається в три етапи: висушування (303–448 К), оброблення (448–673 К) і розклад залишку (673–1073 К).

**Ключові слова:** колоцинт, лушпиння насіння, біопаливо, характеристика, термогравіметрія, спектроскопія.