CHEMICAL ENGINEERING TRANSACTIONS

VOL. 106, 2023

A publication of
AIDIC
The Italian Association
of Chemical Engineering
Online at www.cetjournal.it

Guest Editors: Jeng Shiun Lim, Nor Alafiza Yunus, Peck Loo Kiew, Hon Huin Chin

ISBN 979-12-81206-05-2; **ISSN** 2283-9216

DOI: 10.3303/CET23106057

Novel Production Methods of Biochar from Durian (*Durio Zibethinus*) Rind to be Used as Smokeless Fuel

Tuyen Boi Ly[a], Co Dang Pham[a], Kien A. Le[b], Phung K. Le[a,*]

[a]Faculty of Chemical Engineering, Ho Chi Minh City University of Technology (HCMUT), VNU-HCM, Ho Chi Minh City, Vietnam
[b]Institute for Tropicalization and Environment, 57A Truong Quoc Dung Street, Phu Nhuan District, Ho Chi Minh City, Vietnam
phungle@hcmut.edu.vn

Durian (*Durio zibethinus*) fruit processing discards out waste shells, which accounts for more than 60 % by weight of the fruit into landfills, leading to serious issues regarding environmental pollution and public health risks. Despite the extensive research available on converting this biomass source into high carbon content biochar, little has been discussed on its susceptibility towards microbial degradation and fungal growth and the effects these contaminations may have on the obtained products. In this study, two types of durian shells, composted and non-composted types are collected by an evaluation of pretreatment conditions, and carbonised for recovery of biochar material. FTIR, SEM and TGA/DTG were utilised to show significant differences in the structure and thermal properties between the composted durian shell and the non-contaminated one. By making use of these differences, for the first time ever, novel briquetting methods of mechanically pressing at normal and elevated temperature were applied on composted shells to produce biochar fuels with varying shapes and combustion properties to suit different applications. A higher yield of more than 50 % with a higher fixed carbon content of up to 51 % could be attained without any need for a binding material from the composted material by the pressing method with incorporation of heat. The results from this research can encourage developing different approaches towards making use of source materials with recalcitrant structures for specific desirable properties.

1. Introduction

In 2021, the global production of durian (*Durio zibethinus*) - a delicacy found in Southeast Asian countries, is 2 Mt and this number is expected to rise with increasing demands for consumption and exports to countries like China (Durian Harvests, 2021). Within Thailand, one of the major durian-producing countries, this high increase in demand even led to increased cultivating of fields for durian production, allowing for a forecasted 2 times increase in production capacity to 2 Mt in 2022 (VNA, 2021). This shell takes up about 60 % of the fruit and is commonly treated by composting with low efficiency or on-site burning which generates a large volume of gaseous pollutants (Jamnongkan et al., 2022). The peel is a kind of lignocellulose biomass, whose composition can reach up to 60.5 % cellulose, 13.1 % hemicellulose and 15.45 % lignin, as reported by Tan et al. (2017), indicating a high potential for carbon recovery. With low production costs, eco-friendly properties, and applicability for different purposes, including waste treatment, greenhouse gas reduction and energy generation (Bong et al., 2021), biochar and activated carbon from durian peel have been studied to develop various applications (Gómez et al., 2021).

In current real time manufacturing, a large amount of durian shell wastes is left discarded on fields for multiple days before collection and treatment, which allows for growth of microbes, including bacteria and fungi. This biological degradation alongside the highly recalcitrant structure of the shell would affect the properties of the material. In one research, anaerobically digested sugarcane bagasse was pyrolysed to produce biochar with distinct porous structure and an enhanced lead adsorption capacity (Inyang et al., 2011). One similar concept was also developed where combined anaerobic digestion and pyrolysis was used to treat biomass to simultaneously obtain both biogas product and biochar material (Feng & Lin, 2017). This approach has been developed but is yet to be applied and tested on an experimental setup. By considering the different aspect in

Paper Received: 30 May 2023; Revised: 28 June 2023; Accepted: 9 July 2023
Please cite this article as: Ly T.B., Pham C.D., Le K.A., Le P.K., 2023, Novel Production Methods of Biochar from Durian (Durio Zibethinus) Rind to be Used as Smokeless Fuel, Chemical Engineering Transactions, 106, 337-342 DOI:10.3303/CET23106057

technology for treatment for durian shell, this study investigates the properties of the shells after microbial degradation, develops the process to produce biochar fuel and suggests different fuel-based applications to suit each of the attained material.

2. Materials and methods

2.1 Biochar production

Durian shell was obtained from Tien Giang Province, Vietnam. The shells are subjected to different physical (chipping, shredding) and thermal (sun drying, convectional drying) pretreatment methods. Shells that have been left discarded for over 3 days were collected from durian manufacturers in Tien Giang to experience noticeable fruit rot and fungal contamination Briquetting was performed by a briquetting press machine using manual rotation at normal temperature and at an elevated temperature of 80 °C. Pyrolysis was carried out using a SXII-4-10 box-type muffle furnace with a residence time of 2 h.

2.2 Characterization methods

Fourier-transform infrared spectroscopy (FT-IR) analysis were executed on a Bruker Tensor 37 spectrometer in the range of 4,000-500 cm^{-1}. Thermogravimetric analysis (TGA) was performed using Mettler Toledo TGA/DSC Stare System to analyse the structure of the materials and their combustion properties by heating the materials at 10 °C/min from 30 °C to 800 °C under N_2 or air atmosphere. A Prisma E scanning electron microscope (SEM) was utilised for analysis of their surface structure.

Proximate analysis of fixed carbon was determined following ASTM D3172, ASTM D3174 and ASTM D3175 following the determination of moisture, volatile matter and ash content of the biochar sample where moisture content analysis was performed using a YOKE DSH-10A Moisture analyser. Calorific value of the briquette was measured according to ASTM D5865 using a PARR calorimeter.

Drop strength test was performed by dropping the samples from a height of 1.5 m onto a steel plate and the ratios between the weight of a biochar shape before and after the drop test were determined.

3. Results and discussions

3.1 Pre-treatment of durian shell

The effect of pre-treatment of durian shell was investigated, as seen in Figure 1 to discuss the conditions leading to the growth of microbial degradation of the samples. When first recovered, raw durian shells (DS-01) are noticeably wet and the green thorn layer can be clearly seen over a white soft and spongy layer. The common treatment method for large scale manufacturing – drying under sunlight cannot allow these chips to fully dry, letting fungi develops (DS-02). This can be used to explain the degradation of durian shells into a dark-brownish substance as evidenced in the durian shells collected from manufacturers in Tien Giang province (DS-03). These contaminants have been studied by Piasai et al. (2021) to be characteristic of fruit rot diseases caused by fungi such as *Phytophthora* and *Sclerotium*. Therefore, it is concluded that a stronger drying conditions. such as convectional drying technology are required if these contaminants are to be prevent, as seen in samples DS-04 – DS-06.

Figure 1: Durian shell samples under different pre-treatment conditions

After 24 h of convectional drying, even though the chipped durian shell achieved a significantly lower moisture content of 8.02 % in comparison to the initial 76.82 % (Figure 2a), the variation between samples is still high which may be explained by the recalcitrant multilayer structure of the shell letting moisture escape unevenly. For a standardised material to ensure high-efficiency and high-quality conversion to biochar, increasing the drying time or shredding the material prior to drying would be required. This is evidenced in DS-05 and DS-06 shells where the moisture content was determined to be lower, being 3.73 % and 6.17 % respectively, with a low deviation between different samples. For the composted material, because the porous structure to trap moisture is not as significant, the moisture content is lower than the raw material, but is still considerably high (60.86 %).

FTIR results from Figure 2 show that both non-contaminated and contaminated shells contain functional groups that are characteristic of lignocellulose where a broad peak can be observed at around 3,400 – 3,200 cm^{-1} corresponding to the phenol functional group in cellulose, hemicellulose and lignin. The peaks that signify C=C aromatic bond at around 1,700 – 1,600 cm^{-1} can be found for lignin and proteins, and the peak at around 1,000 cm^{-1} is assigned to be the asymmetric stretch of C-N bonds in substitute amines.

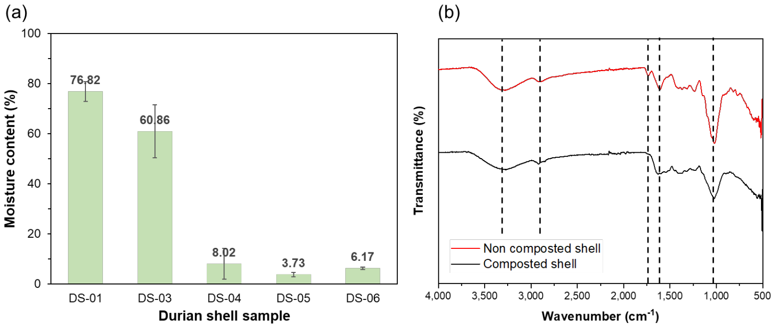

Figure 2: (a) Moisture content and (b) FTIR results of different durian shell samples

Under electron microscope (Figure 3), in can be concluded that this microbial degradation process would affect the natural porous structure of the durian shell, leaving no noticeable pore and a rough surface.

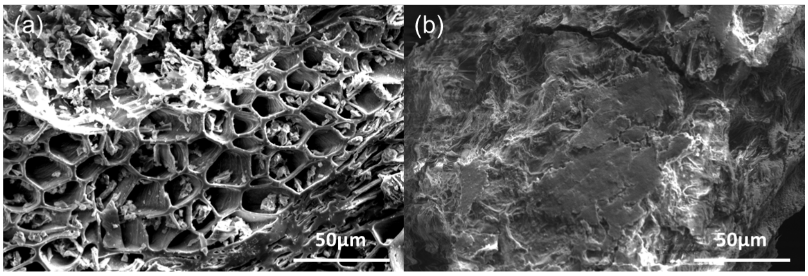

Figure 3: Surface structure of (a) raw durian shell (DS-01) and (b) durian shell after composting (DS-02)

3.2 Effect of pyrolysis temperature

For analysis of pyrolysis condition for biochar production, non-composted DS-05 and composted DS-03 shells were used. Thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) results of both samples (Figure 4) correspond to the 4 stages of thermal degradation of lignocellulosic materials previously recorded by Escalante et al. (2022). From room temperature to about 200 °C, moisture and light volatiles removal takes where more peaks were observed for non-contaminated shells in DTG curve, indicating its complicated layered structure that traps moisture and volatiles. The decomposition that happens around 200 – 400 °C is mainly characteristic of cellulose and hemicellulose breakdown. Finally, the thermal degradation process of lignin can occur over a wide range of temperature, from around 400 °C up to over 600 °C. From this analysis, it can be expected that the shells can be sufficiently carbonised at around 500 °C – 600 °C.

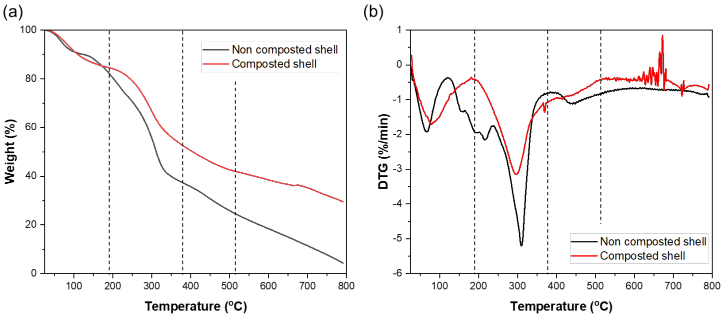

Figure 4: (a) TGA and (b) DTG plot of durian shells under N_2 atmosphere

The TGA results correspond to the biochar mass recovery of biochar shown in Figure 5a where even though the overall trend is on the decrease because of the volatile matter escaping from the biomass, little differences can be observed at pyrolysis temperature between 500 °C and 600 °C because the samples have been fully carbonised. Simultaneously, an increase in fixed carbon content can be seen that elevates the suitability of carbon materials for applications in fuel materials. The mass recovery of biochar for durian shell after composting (DS-02) is continuously higher than the raw durian chip, which might be thanks to the composting process allowing for consumption of volatile matter by microbes prior to pyrolysis. It can be concluded that in large scale manufacturing where durian shells are often left discarded in dumpster prior to collection and treatment, the shells material can be of high potential to be directly used without any standardization for biochar production by pyrolysis under 600 °C.

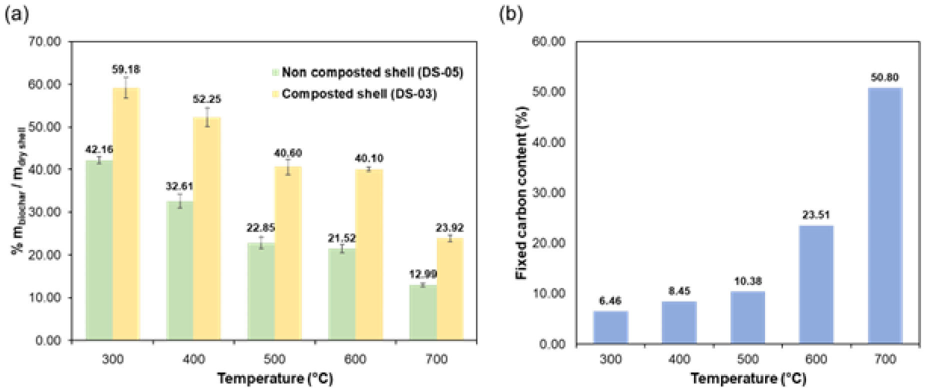

Figure 5: Effect of pyrolysis temperature on (a) mass recovery for DS-03 and DS-05 shells and (b) fixed carbon content for DS-03 shells of biochar products

3.3 Effect of biochar shaping methods

Different types of biochar with different shaping technologies are pyrolysed under the same conditions for comparison, as shown in Figure 6. It is noteworthy that DS-03 shells have a softer structure making it easy to be briquetted by pressing using mechanical forces at normal and elevated temperature.

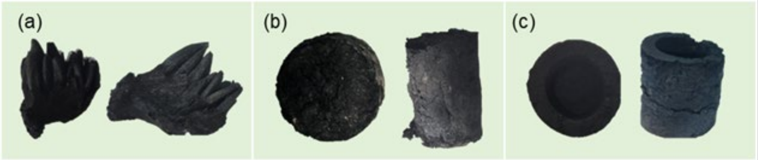

Figure 6: Durian derived biochar from (a) raw shell chips (B-01), and composted shell after mechanical press under (b) normal temperature and (c) at 80 °C

As seen in Figure 7, the biochar samples have different surface structure. The biochar from directly pyrolyzing chips of DS-05 raw dried durian shells (B-01) would retain the original well-defined porous structure of durian shells. On the other hand, as the composted shell loses its original shell structure, mechanically pressing the shell without incorporation of high heat prior to pyrolysis (B-02) results in biochar briquettes with strands of material softly layered, creating a slightly different porous material. Heat pressing creates tightly compacted durian shell fibres to produce a dense material with no evidence of any porous structure even after carbonization (B-03).

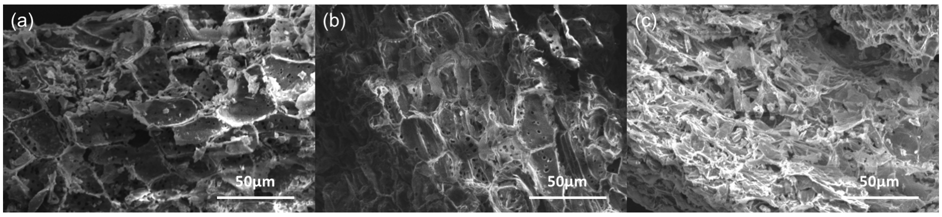

Figure 7: Surface structure of biochar (a) from raw shell chips (B-01), (b) from mechanical press of composted shell (B-02) and (c) from heat press of composted shell (B-03)

The results from surface structure then corresponds to data relating to the physical properties of the attained biochar material. More specifically, according to Table 1, mechanically pressed durian shells after pyrolyzing would be the less dense material, with the lowest bulk density (124.6 kg/m^3) and high pore space to allow for the highest moisture capture. This loosely combined structure also makes this briquette sample exhibits the lowest mechanical strength by testing via the drop test where only 68.03 % of the weight of the briquette remains after dropping. Heating while pressing creates a densely packed, heavy (773.9 kg/m^3) and mechanically strong briquette that can withstand a much higher mechanical impact. This indicates that the method of heat pressing for formulation of biochar briquette can be a notable alternative to the current methods of using gums or starch as binders, which have been reported in research such as one by Haryati et al. (2018) to experience a reduced fuel calorific value. One interesting factor is that since B-01 samples retain the thorny structure that was originally designed to withstand the load of the fruit upon falling (Ha et al., 2020), even though the sample has a significantly lower bulk density than B-03, the drop strength is slightly higher at 98.94 %.

The calorific value correlates to the properties of the shell precursors where the calorific value is similar between B-02 and B-03 biochar because they both originates from DS-03 shells and experiences similar thermal degradation. This calorific value is higher than B-01 biochar, which may be explained by the aid of microbial contaminants in degradation of the char prior to heat treatment, producing a higher fixed carbon content.

Table 1: Physical properties of the different biochar samples

	B-01	B-02	B-03
Moisture (%)	7.63 ± 0.58	14.78 ± 4.73	4.85 ± 0.89
Bulk density (kg/m^3)	403 ± 20.7	124.6 ± 22.1	773.9 ± 28.7
Calorific value (MJ/kg)	14.2 ± 0.3	22.0 ± 0.7	21.6 ± 0.4
Drop strength (%)	98.94 ± 0.80	68.03 ± 4.74	95.28 ± 2.43

After the thermal decomposition process, the obtained biochar experience major differences in structural characteristics in comparison to their shell precursor, but the functional groups are similar among the different samples (Figure 8a). The surface functionalities that are characteristic of cellulose at around 3,400 – 3,200 cm^{-1} somewhat remains after pyrolysis, meaning that increased pyrolysis conditions should be utilised for better fuel properties. The most distinguished peaks for samples are near 1,600 cm^{-1} which can be assigned to the aliphatic C=C bonds in structures of carbonaceous materials.

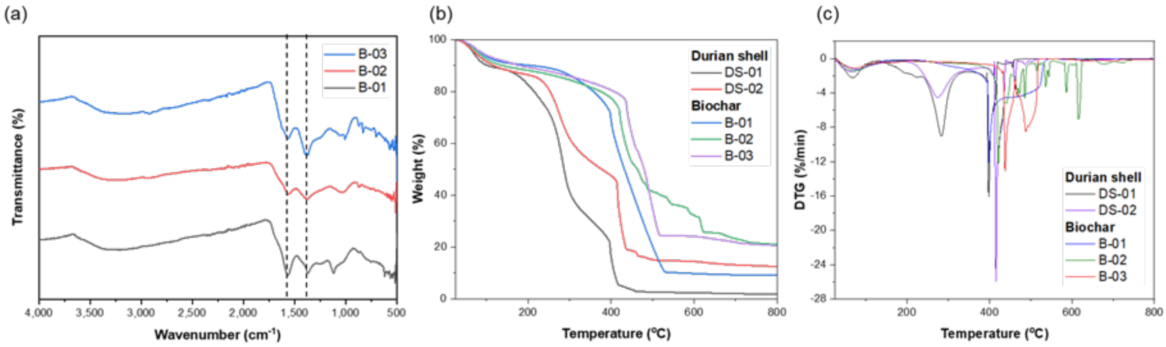

Figure 8: (a) FTIR of biochar (b) TGA and (c) DTG analysis of durian shell and shell biochar under atmosphere condition

The fuel property was evaluated for shells and biochar by TGA under conventional air condition (Figure 8b, c). In comparison to biochar, durian shell experiences loss in mass earlier, starting at around 200 °C, which can be explained by the loss of moisture and volatile content which is not available in high quantity for biochar. Similarly, the peaks at around 200 – 400 °C account for the thermal and oxidizing decomposition of hemicellulose and cellulose which can only be seen in the raw biomass. From 400 – 600 °C, sharp peaks that are distinguished of the combustion process can be observed. It is noteworthy that sample B-03, which has the densest structure has a higher initial combustion point, suggesting that it would take more heat and a longer heating period for the material to be able to sustain burning. B-01 and B-02 experiences similar thermal decomposition trend, indicating a similar burning behavior.

In practical applications, wood chips with lower density, calorific value but with larger surface area and smaller moisture content would be more ideal to be used as a starter-type fuel to begin ignition or for cooking applications. For briquette shaped carbon residential heating is more suitable where longer burning time sustained heating time are required, especially for the much denser B-03 biochar where, for the same volume, a much higher energy release and directional heating is allowed.

4. Conclusions

In this paper, novel strategies for processing durian shells derived biochar by considerations of the drying conditions and shaping methods were developed to produce 03 types of biochar fuels with varying calorific values, densities and mechanical strengths. Conventional chipping and convectional drying of durian shells can produce biochar with a lower calorific value of 14.2 MJ/kg but with a high drop strength of 98.84 % and a porous structure that can be easily combusted to be used as cooking fuels and as chips to promote ignition of heavier briquettes. Shells that have been biologically degraded from microbes can be briquetted at elevated temperature to produce biochar fuels with high calorific values of up to 21.6 MJ/kg and a much denser structure of 773.9 kg/m3, making them suitable for elongated combustion in cases of domestic heating applications. From this foundation, this paper suggests that more in depth evaluation into practical problems in larger scale manufacturing, such as the effect of fungi and bacterial on shell material, should be conducted more in the scientific community and the processing industry.

Acknowledgments

We acknowledge Ho Chi Minh City University of Technology (HCMUT), VNU-HCM for supporting this study.

References

Bong, C. P. C., Lim, L. Y., Lee, C. T., Ong, P. Y., Fan, Y. V., Klemeš, J. J., 2021, Integrating compost and biochar towards sustainable soil management, Chemical Engineering Transactions, 86, 1345–1350.

Durian Harvests, 2021, Global Durian Production, Durian Harvests <durianharvests.com/production> accessed 18.06.2023.

Escalante, J., Chen, W.-H., Tabatabaei, M., Hoang, A. T., Kwon, E. E., Andrew Lin, K.-Y., Saravanakumar, A., 2022, Pyrolysis of lignocellulosic, algal, plastic, and other biomass wastes for biofuel production and circular bioeconomy: A review of thermogravimetric analysis (TGA) approach, Renewable and Sustainable Energy Reviews, 169, 112914.

Feng, Q., Lin, Y., 2017, Integrated processes of anaerobic digestion and pyrolysis for higher bioenergy recovery from lignocellulosic biomass: A brief review, Renewable and Sustainable Energy Reviews, 77, 1272–1287.

Gómez, K. Y., Quevedo, N. R., Molina, L. D. C., 2021, Use of the Biochar Obtained by Slow Pyrolysis from Ulex Europaeus in the Removal of Total Chromium from the Bogotá-Colombia River Water, Chemical Engineering Transactions, 86, 289–294.

Ha, N. S., Lu, G., Shu, D., Yu, T. X., 2020, Mechanical properties and energy absorption characteristics of tropical fruit durian (Durio zibethinus), Journal of the Mechanical Behavior of Biomedical Materials, 104, 103603.

Haryati, S., Rahmatullah, Putri, R. W., 2018, Torrefaction of Durian peel and bagasse for bio-briquette as an alternative solid fuel, IOP Conference Series: Materials Science and Engineering, 334, 012008.

Inyang, M., Gao, B., Ding, W., Pullammanappallil, P., Zimmerman, A. R., Cao, X., 2011, Enhanced Lead Sorption by Biochar Derived from Anaerobically Digested Sugarcane Bagasse, Separation Science and Technology, 46(12), 1950–1956.

Jamnongkan, T., Intaramongkol, N., Kanjanaphong, N., Ponjaroen, K., Sriwiset, W., Mongkholrattanasit, R., Wongwachirakorn, P., Lin, K. Y. A., Huang, C. F., 2022, Study of the Enhancements of Porous Structures of Activated Carbons Produced from Durian Husk Wastes, Sustainability (Switzerland), 14(10), 5896.

Piasai, R., Chalmers, P., Piasai, O., & Khewkhom, N., 2021, Postharvest fungicide dips to control fruit rot of ‘Monthong’ durian (Durio zibethinus), European Journal of Plant Pathology, 160(2), 325–336.

Tan, Y. L., Abdullah, A. Z., Hameed, B. H., 2017, Fast pyrolysis of durian (Durio zibethinus L) shell in a drop-type fixed bed reactor: Pyrolysis behavior and product analyses, Bioresource Technology, 243, 85–92.

VNA, 2021, Thailand to become world’s top durian producer in five years, Vietnam Plus, Hanoi, Vietnam.