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Exploring the potential of coconut shell biomass for charcoal production

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ABSTRACT

Coconut shells are produced in a vast amount around tropical countries that needs to be utilized properly. Thermochemical methods are the main route for converting biomass to charcoal. Percentage of some relative factors in the biomass such as low-density, low caloric value, high ash, SO_X, NO_X, moisture content, microstructure, and complex elements are its major drawbacks. Nevertheless, no scientific studies were conducted on the carbonization of converting coconut shells to charcoal from local to global scales. Therefore, comprehensive and precise data on its production is limited. To overcome these problems; biomass materials need to be evaluated to assure the suitability of the biomass for the thermochemical process to curtail the yearning of energy demand. For the overall efficiency of the biomass conversion processes into the preference biomass-derived fuel, it is important to understand the physicochemical characteristics of the biomass. The paper aims at understanding the specialties of coconut shell biomass, which is directly used for thermochemical conversion mainly for charcoal production via; chemical structure, energy potential, and morphological analysis. The biomass exhibits a high: density of 412 kg/m^3, a calorific value of 19.4 MJ/kg, fixed carbon of 21.8%, a volatile matter of 70.8%, carbon of 40.1%, and low amount moisture of 5.6%, and ash of 1.8%. EDX and XRF analysis revealed a low amount of complex heavy metals, trace amounts of sulfur, and nitrogen, thus pre-treatment is not required before its utilization, ideal for thermochemical conversion. The coconut shell possesses amorphous and crystalline carbonaceous materials based on the XRD spectrum. The morphology on FESEM images and surface area analysis shows that the coconut shell contains heterogeneous shapes and scales of macro-pores with high surface area and porosity in nature. These essential qualities are suitable for charcoal production, activated carbon, insect repellent, filler, incense sticks, and other applications. Coconut shell possesses remarkable properties such as carbon-rich and environmentally friendly solid fuel to other biomass and coal materials; hence, it is possible to produce alternative energy from coconut shell biomass due to its several characteristics.

1. Introduction

1.1. Conventional energy emission and demand: The state of the art

Conversion of high-quality and most eminent renewable biomass for energy generation is among the barriers that need to be overcome for technological advancement and commercialization to progress. A new method is needed by individuals or energy sectors to generate power. The present research was motivated due to the increasing emissions of CO_2 and the high price of fossil fuel around the globe. The strong linkage between energy demand, fossil fuel utilization, and economic development causes various pessimistic impacts worldwide during the last decades [1]. The UN has

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cautioned and recommended that all countries make remarkable attempts to minimize greenhouse gas levels over the next decade, as emissions rise exponentially, to prevent climate disaster [2]. Based on the UN Environment Programme (UNEP) annual emissions gap report, in the past decade, the CO_2 emissions from deforestation rose to more than 55 gigatonnes equivalent to 1.5% per year on average [2]. To avoid disastrous consequences, scientists say it is necessary from now until 2030 that global emissions should be reduced by 7.6% per year. This makes the world's environmental and energy security issues to explore for a cleaner energy source [2,3]. The rise in oil prices and the growth of the population would raise the energy demand. The energy consumption relies mainly on the current energy resources of crude oil, gas, etc. These energy sources pollute the atmosphere and are not adequate to meet the rising energy future needs. Over time, their use will decline because they are non-renewable sources [4]. The use of renewable energy sources and technology, however, is available, abundant, and economical. Hence, significantly mitigate, if not reduce, carbon emissions without compromising economic growth. Besides, it has driven the use of biomass fuels by the industries. Thus, energy demand, dependence on conventional energy sources, and greenhouse gas emissions may be reduced [5,6].

1.2. The utilization of biomass as a source of energy

Fuel production from biomass waste possesses an alternative option for power generation, which could be due to energy policies and a substantial understanding of the importance of green energy [7]. Biomass appears as a prospective energy source, which has increased sharply in the last few decades [8]. The use of bioenergy as a rich, carbon–neutral renewable source for the development of bioenergy and biomaterials will address the enhancement of a wide range of societal needs. It stands as the third energy resource in the energy market, apart from oil and coal, which could replace non-renewable fuels. Agricultural residues are the most potential biomass, considering their abundant availability worldwide, but they are not fully utilized in harnessing energy [3]. The use of agricultural biomass is necessary to achieve greater remediation efficiency and waste recovery [9]. The use of biomass for energy applications is high in developing countries, as their economies depend predominantly on forestry and agriculture. This could probably tackle the issue of biomass waste disposal if it serves as an energy source. Using raw solid biomass as a fuel poses problems of high moisture content and low energy which results in problems in the conversion technology and additional cost in transporting, handling, and grinding. Biomass should therefore be analyzed for physicochemical properties before processing using physical, biological, and thermochemical conversion methods.

1.3. Interest on coconut shell biomass and its availability

Interest and evaluation of new raw materials are required to guarantee the reduction in emissions, the production of chemicals, and the energy crisis shortly [10]. This indicates an in-depth study of coconut shell biomass as source of energy for power generation. The coconut shell biomass was not completely exploited. While it is used by local people for making utensils, as reinforcement material in concrete mixing [11], automotive applications [12], organic fertilizer [13], and as a combustion fuel by the local blacksmith. However, there has been no thorough analysis of its properties before its usage as feedstock for charcoal and other applications.

Coconut (*Cocos nucifera L*) is an agricultural product grown throughout the year in contrast with other fruits [14]. The major world coconut-producing countries are the Philippines, Indonesia, India, Malaysia, Hawaii, Africa, South America, the Pacific islands, and other locations with tropical climates [15]. The world production of coconut accounts for almost ten million hectares in 92 countries, with 75% of the mass production from Asian countries [14]. Annually, a high amount of coconut fruits are processed for different purposes. Coconut is an excellent source of potassium and is used in many products [15]. The economic importance and potentials of coconut fruit increase its demand. Hence, it contributes to the growth of coconut water, oil and milk processing industries, which discard coconut shells globally as biomass waste in all tropical countries [8].

Malaysia has an interesting biomass-production potential as a positive energy trade balance region. It has the means of capitalizing the country on renewable energy resources to supplement limited petroleum and coal reserves. It has a healthy forest and agro-industries which generates a huge amount of biomass wastes due to the growing generation of agricultural products, particularly the palm family [16,17] for commercial applications in the industry. Malaysia was ranked the 12th major producing coconut country in the world [18] with about 517.6 k tons volume, and the crop stands as the fourth enormous industrial crop. Smallholders encounter hardship as a result of the decline in palm oil prices. This rise the market for coconuts, which makes its prices go up [19]. The coconut industry is emerging in Malaysia and the demand is expanding exponentially. Coconut fruit was utilized for the production of oil only in the past two decades. Currently, apart from the usage of coconut fruit for oil, it is also used for health, beauty, energy, and foods (beverages, cooking oil, powdered milk, fresh milk, and coconut water. As a result, abundant biomass wastes are being generated from coconut industries. The factual abundance of the biomass gives rise to the proportion of the effective residue usage as source of energy. Hence, the coconut shell biomass is readily available for energy generation.

1.4. Understanding coconut shell charcoal production

Charcoal, an energy-dense fuel has an advantage over the use of raw biomass. Thus, reduces the emission of greenhouse gases into the atmosphere. The progress in climate change and economic growth can be achieved by a low-carbon economy. It was known that the coconut shells contain high lignin content [20], this makes it a promising viable alternative biomaterial for the production of charcoal and different raw materials in chemical industries. A more detailed understanding of the complex elements, functional groups, chemical structure, crystalline structure, and morphological composition of the biomass is important for charcoal production. This is important because it demonstrates how the biomass composition influences several factors. Preferably, coconut shells can be transformed to charcoal for additional value-added items using existing technologies for various applications. Coconut shells provide more or less significant benefits that constitute a viable feedstock for charcoal production. It is usable all year round, does not produce any net contribution to the atmosphere when carbonized properly. Furthermore, its usage reduces the dependence on non-renewable fuel, minimizes if not do away with the issue of waste disposal and increase energy supply. Generating effective techniques to utilize and convert biomass will reduce waste disposal and create revenues [21]. For these reasons, the pyrolysis of coconut shells into charcoal provides a good base for solid products that can be used directly and serve as fuel.

Charcoal is a vital player in the world carbon market that offers significant advantages over raw biomass fuels. It has a clean and simple production technology because the process of thermochemical processes (carbonization or slow pyrolysis) reduces particulate emissions. Thus, reduces the risk of developing health and environmental hazards [14]. Carbonization is a thermochemical method that converts biomass fuel into more valuable products (solid (mainly charcoal and biochar), liquid (oil), and gas) in an oxygen-free environment [20]. It is the first stage in any thermal conversion process of carbonaceous materials. The process employs all three by-products. Charcoal is used in pharmaceuticals, cosmetics, animal feed, power sources, a raw material for activated carbon used for water purification and filtration. The liquid bio-oil is used heat, electricity, and chemicals, while the biogas is used as industrial fuel for furnaces, combustors, and reactors. The technology can utilize coconut shells in producing charcoal. Its heat energy encourages the oxidation of complex carbon molecules to break up into carbon or charcoal [20]. However, the biomass nature and the process conditions (temperature, residence time particle size, and heating rate) affect the pyrolysis process and the charcoal composition. Hence, for a systematic way to convert any biomass, it is essential to understand the biomass physicochemical behavior for better charcoal and for designing and optimizing the conversion equipment.

1.5. Advantages of characterizing the biomass

Usually, charcoal from other biomass is used for heat and power generation, but coconut shell charcoal is potentially used as a fuel or as a feedstock for chemicals, as an active carbon (charcoal treated with oxygen) which is considered tremendously effective in purification and other industries, in the production of medicines and cosmetics. As such, to harness the biomass potential to be suitable for the carbonization process to produce such charcoal for this application, detailed physical and chemical analysis of the biomass is first required, to predict the methods of obtaining high-grade charcoal. However, before thermochemical conversion of biomass, it is important to have a clear understanding of its physicochemical properties and carbonization process conditions [22].

A fundamental study on the influence of the physicochemical properties of the biomass is important since all biomass originates from different species and crops; consequently, they possess different chemical compositions. The detailed characterization of fuel biomass has numerous significant characteristics for sustainable development such as climatic management, biodiversity, and carbon storage, etc. It is of interest to know the levels of organic and inorganic elements present in given biomass that can be released during the biomass thermochemical processes. This will help in the modelling, analysis, and designing of energy conversion systems. X-ray diffraction and fluorescence, particle size, and FESEM (field scanning electron microscopy) is the analysis that provides the surface area and morphological structure of the biomass. The thermogravimetric analysis is used to understand the thermochemical behavior of given biomass. XRF analysis quantifies metallic species. The FESEM microscopy determines the morphological properties. XRD presents the crystallinity of the feedstock biomass. Through the FTIR analysis, the existence of particular functional groups and molecules are determined [23].

The effective conversion of biomass into biomass-derived fuel (charcoal) is restricted by the characteristics of the biomass to be used. The explicative treatments of the raw feedstocks account for the predominant price related to their conversion. To optimize the treatments, the biomass composition must be known. Besides, to know whether biomass is suitable for a carbonization process that will reduce the emission of GHGs, chemical analysis is required [24]. The controlled carbonization of the coconut shell is a clean process that has a carbon-negative footprint. Carbon dioxide is among the substantial contributors to global warming as quoted by scientists. Today, for every BTU that is produced in all the conventional energy and power production, coal contains the most CO_2. The combustion of fossil fuels precisely coal produces air pollutants (NO_X and SO_X). The great emission of GHGs, hydrocarbons, chemicals, and organic compounds into the air is largely from industries and factories. These, in turn, affect agricultural products. More so, pesticides and fertilizers that are used in agricultural activities release dangerous chemicals that affect agricultural products [25]. Most of these products are produced from charcoal. Charcoal is also applied directly as fertilizer. As such, a thorough characterization of the coconut shell biomass is required before its use for charcoal production, to determine whether the coconut shell biomass contains harmful chemicals that may contribute to environmental pollution during the carbonization process, and may affect the charcoal composition. With these, the potentiality of the biomass fuel to reduce CO_2 emissions during carbonization could be exploited.

There is some evidence that people are traditionally converting coconut shells into charcoal using the kiln and pit methods in some industries. Nevertheless, there have been no scientific systematic studies conducted on the slow pyrolysis of converting coconut shells to charcoal from local to global scales, thus, comprehensive, precise, and available data on charcoal production from coconut shells is limited. Hence, industries or investors could not tell the best way technically or economically, and environmentally for charcoal production. The handling of its production in the industries is not energy efficient, due to partial combustion. This implies that knowledge of conversion efficiency characteristics is not known, nor are the characteristics of the raw and carbonized final product known. Therefore, as a result, we need to know the biomass first because the exploitation of the coconut shell fuels in the slow pyrolysis processes requires a detailed investigation of its behavior before using it as a feedstock for the thermochemical process. Accurate knowledge of the carbonization related properties such as the essential factors in harnessing its potential for charcoal is needed.

Several studies have been carried out among the thermochemical processes for the employment of biomass at small-scale to medium proportions for power generation as reported in the literature review [23]. Investigations on the effect of the properties of some lignocellulosic biomass on its conversion performance were carried out. Quite a few studies on the physicochemical properties of different feedstock biomass using analytical methods have been carried out. This was to determine the feedstock's energy potential and recovery, and its conversion efficiency [26,27]. For the Canadian next-generation biofuel potentials, specific types of abundant biomass waste found in the country were characterized [28]. Related studies were carried out on different biomass and agro-industrial waste in Colombia for thermochemical processes [23]. Recently, among Malaysian major abundant biomass, six were investigated [26]. Besides, different characterizations of green synthesis nanostructures were carried out [29–31]. Although widely used, almost nothing is known about the structural composition of coconut shell biomass for charcoal production, based on the number of complex elements that hinder thermochemical processes, functional groups, and surface elements, morphological and crystalline qualities. [25], the present study focused on the detailed physical, chemical, structural, and elemental analysis, pyrolytic behavior, reaction chemistry, and bioenergy potential to thoroughly understand the phenomena that control the energy production processes. Furthermore, despite substantial information on various types of biomass in kinds of literature, information on coconut shells is limited in the database of some organizations such as National Renewable Energy Laboratory (NREL) and Deutsches Biomasse Forschungs Zentrum are among the example [23].

The development of an appropriate thermochemical conversion process of coconut shells biomass wastes to produce charcoal entails the knowledge of the characteristics of the biomass, its kinetic properties, and the pyrolytic mechanism. The essential material property of biomass to serve as an energy source is determined through analytical techniques. For a biomass material to be used as an energy source, it should meet the specific thermal requirements.

Considering the ample availability of coconut shells biomass in the Malaysia region, it is thought desirable to study the applicability of such biomass waste for charcoal production. The properties of coconut shells biomass as a value-added feedstock for solid charcoal biofuel for different applications were determined. These properties include but are not limited to; the ultimate and proximate analysis, energy value, density, and a fuel value index. The calorific value, ash, and moisture content should be the most considered for evaluating the biomass quality and the final product [20]. Furthermore, XRD, XRF, FTIR, FESEM analyses were presented as tools to study the elemental, functional groups, particle size, and pore size identification. They serve as a tool for studying the chemical structure and composition of the biomass before the thermochemical conversion process.

2. Materials and methods

2.1. Coconut fruit cultivation and variety

Coconuts are fruits from coconut palm trees that grow on a range of soil types mainly found in coastal coast regions [15,32]. The coconut plant needs a daily temperature of 12 °C and above, the humidity of 70–89%, and a yearly rainfall of 75–100 cm [15]. The maximum height of the tree trunk is up to 60 m [32]. The coconut fruit weighs about 2.5 kg. The Seychelles double coconut is the largest in the world, and that has weighed up to 20 kg [15]. A fully matured coconut consists of 35% fibrous husks, 12% hard shell, 28% white meat flesh, and 25% coconut water [32]. The coconut shell is the outer hard part of the coconut fruit. It is located in between the coconut flesh and the coconut husk that protects the inner part of the fruit. In Malaysia, nearly 12 varieties of coconut plants are grown from small scale to large scale. The Malaysian Tall (MT) is known to be the traditional variety. Other varieties include MAWA, MAMA, MATAG, MARREN, Rennel, Aromatic/Pandan, Malaysian Red Dwarf (MRD), Malaysian Green Dwarf (MGD), Malaysian Yellow Dwarf (MYD), West African Tall, and Tagnanan. The MATAG Hybrid variety has an early maturity period and potential yield. The tree produces up to 140 nuts in a year [32], which makes it the most suitable variety. Other coconut palms are classified as autogamous (self-fertilization), and allogamous (crossed fertilization) varieties. The crossed fertilized varieties are designated as the large coconut palm or Typica which are further divided into two groups. The plants that produce a substantial quantity of medium-sized are the first group and they include the coconut palm found in West Africa, Seychelles Islands, Hebrides, and Lakshadweep Islands in India. The plants that produce an average quantity of large fruits with a large coconut yield are the second category. They are found in Thailand, India, Ramona, and Panama [33]. The autogamous or self-fertilized varieties are known as the dwarf or small coconut palms which are normally very precocious, measures between 10 and 12 m high, and produce large numbers of small coconuts fruit. The classification is based on their colour and inflorescence as a green dwarf (Plumilla), yellow dwarf (Eburnea), and red dwarf (Regia). Furthermore, many types of coconut palms are classified based on botanical regard [33].

2.2. Sample preparation for analysis

The feedstock used for this study was coconut shells biomass and was obtained from a shop in Seri Iskandar, Perak, Malaysia. The coconut shells have certain advantages via; abundance, low initial moisture content, and less preparation time, which makes them suitable as a feedstock for thermochemical conversion process. The feedstock was cleaned manually with a machete to remove the fibrous husk and meat before measuring the initial mass of the coconut shells using a digital scale. This will serve to evaluate the sample's weight loss after moisture removal. The moisture content (Equation (1)) of the feedstock, which is the key factor for thermal conversion, was determined according to [34] ASTM E871-82 procedure. The sample was crushed using a granulator to 5 mm for the pyrolysis process, and some were ground by a grinder and sieved to 250 μm size, to obtain a uniform particle size for the characterization. Detailed analytical characterization of the feedstock was carried out using some techniques described below. Fig. 1 (a) and (b) show the coconut shells and their powdered biomass.

$$MC\% = ((InitialWeight - Finalweight)/Initialweight) \times 100 \quad (1)$$

2.3. Analysis of the physical and chemical properties of the coconut shell biomass

The proximate analysis shows the strong relationship of some characteristics potential of biomass for energy generation [1]. This applies to the ultimate analysis. The proximate test usually describes the certain defining characteristics of the sample with regards to the mass proportion of the moisture content MC, volatile matter VM, fixed carbon FC, and the ash content. The thermogravimetric analyzer (STA 6000) was used to obtain the values of the aforementioned parameters following the ASTM E1131-08 [35] methods. The ultimate analysis is an elemental analysis that discovers the samples' basic constitution of carbon C, hydrogen H, nitrogen N, oxygen O, sulphur S, and volatiles. It was carried out by ASTM D3176-09 [36] standard procedure using the CHNS-932 Leco. The oxygen content was obtained by deducting the values of CHNS content from 100.

The mass of a sample per its volume is referred to as its density. The particle and the bulk density are the two densities usually used to characterized biomass.

The particle density of given biomass refers to the total mass per volume which the particles occupy eliminating the volume of the pore space [37]. The coconut shell sample mass was measured using an electronic digital scale to obtain its density with regards to volume. It was determined using a cylinder of known volume. It was filled with the feedstock biomass and weighed. Water was filled to fill the pore spaces. The mass of the water was recorded to obtain the volume occupied by the water. The relation between the sample weight and the volume of the cylinder yields the bulk density as shown in Equation (2):

$$\rho = M/V \quad (2)$$

where ρ ($kg{\cdot}m^{-3}$) represents the particle density, M (kg) is the sample mass, and V (m^3) is the sample volume.

The bulk density is used in designing handling and transportation logistics systems. The biomass moisture content, particle size and shape, surface characteristics, and particle density are the factors that affect this property. The bulk density was determined according to ASTM standard E873-82 [38].

The increased bulk mass attained after mechanically tapping a container containing the biomass sample is the tapped mass or density. It was determined in accordance with the method described in the literature [39].

Replications were made for a desirable determination of the density property.

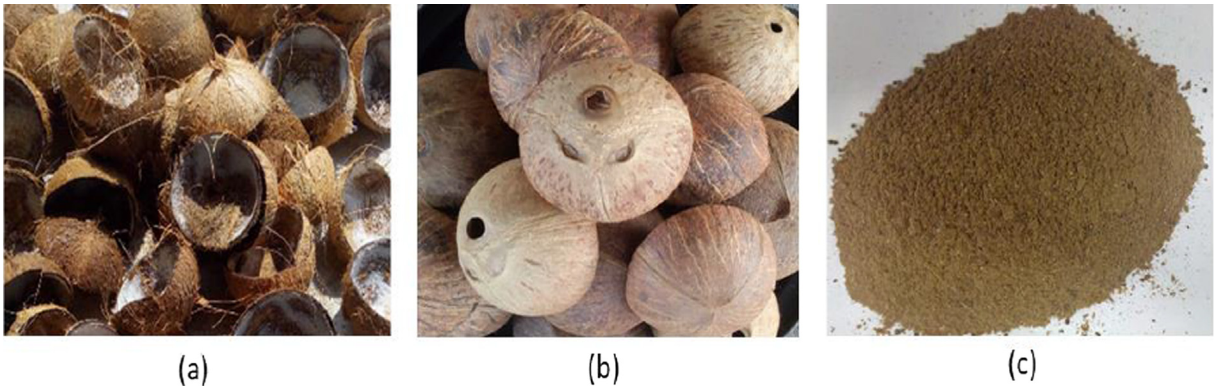


Fig. 1. (a) As received coconut fibrous unclean, (b) cleaned, and (c) powdered coconut shell.

2.4. Measurement of the porosity and compressibility index

The porosity of the given sample biomass is described as the pore space in bulk samples. It is defined as:

$$\varepsilon = 1 - (\rho_b/\rho_p) \tag{3}$$

where ε represents the porosity, ρ_b bulk density, and ρ_p particle density [39].

The compressibility index is a measure of the sample's capacity to be compressed and settle by assessing the relative importance of the inter-particulate interactions [39]. It was obtained by:

$$CompresibilityIndex = (100(V_o - V_F)/V_o \tag{4}$$

where *Vo* represents the unsettled apparent volume (bulk density) and V_F is the final tapped volume (tapped density).

2.5. Measurement of the calorific value and fuel value index

The calorific value determines the samples' energy content. It is an important parameter for thermochemical conversion processes. The calorific value of the raw sample was evaluated with IKA C6000 isoperibol calorimeter according to ASTM D4809-18 standard [40]. The heat released from combustion is measured when the biomass is burnt.

The fuel value index (FVI) of the sample was obtained according to Bhatt and Todaria [41] equation by using the values of ash, moisture, density, and energy content of the coconut shells:

$$FVI = (CV \times D)/Ash) \tag{5}$$

where FVI is the fuel value index, CV and D are the calorific value and density of the coconut shell respectively.

2.6. Measurement of the particle size and surface structure

The sample particle size distribution was determined with Mastersizer 2000. The measurement was taken by an optical bench and the data was analyzed using the Fraunhofer model theory automatically by the Malvern software. The particles were captured at a size range of 0.020 to 2000 μm, a particle RI of 1.740, dispersant RI of 1.330, and a weighted residual of 1.502%.

The porous structural analysis is for the visualization of the material's porous structure. The sample analysis was performed using imaging, mapping, and EDX with Zeiss SUPRA 55 VP model, FESEM, and EDX machine.

2.7. Measurement of the inorganic elements and organic functional groups

The mineral composition or components of the samples were measured by the XRF Bruker S8 Tiger machine in mg/100 g. The structure and the organic functional categories present in the coconut shells biomass were obtained by the FTIR spectrophotometer with a vacuum and flow module (Perkin Elmer). It is an analytical technique that identifies organic materials and also provides information on the molecular structure and the chemical bonds existing in the coconut shells biomass. The FTIR spectra analyses of the samples were recorded between 400 and 4000 cm^{-1}.

2.8. Analysis by X-ray diffraction

The coconut shell sample was analyzed by the XRD analyzer The X-Ray diffraction spectrums of the coconut shell biomass were recorded with a Bruker D8 Advanced diffractometer instrument equipped with a CuKα radiation source. It operates at 40 kV and 30 mA. The analysis was carried out in the central analytical laboratory, Universiti Teknologi Petronas, to determine the structure of the coconut shell biomass.

3. Results and discussion

3.1. Chemical structure

3.1.1. Thermogravimetric analysis

The analysis was carried out to classify the proximate evaluation of the biomass. The feedstock biomass mass loss was measured and plotted versus the temperature. It is also used in categorizing the devolatilization characteristics [42]. The moisture loss is the first phase, followed by a sudden change in mass that indicates the removal of volatile matter. The third phase reveals a sharp slope that captures the fixed carbon content. The last phase that shows a horizontal line represents the amount of the ash content. The initial sample feedstock moisture content (moisture content received) used for all the experiments was calculated according to ASTM E871-82 standard procedure [34] and was found to be 9.21% wt. on a wet basis. This was achieved by using the initial mass of the coconut shell before drying (101.98 g) and the mass after drying (92.6 g).

The results of the studied parameters after the thermogravimetric experiment for the proximate test are obtained from Fig. 2. The results were found to be 5.56% moisture content, 70.82% volatile matter, 21.8% fixed carbon and ash content of 1.8% respectively. This result trend is nearly similar to those obtained on palm kernel shell [43]. In a thermochemical conversion method, a high value of

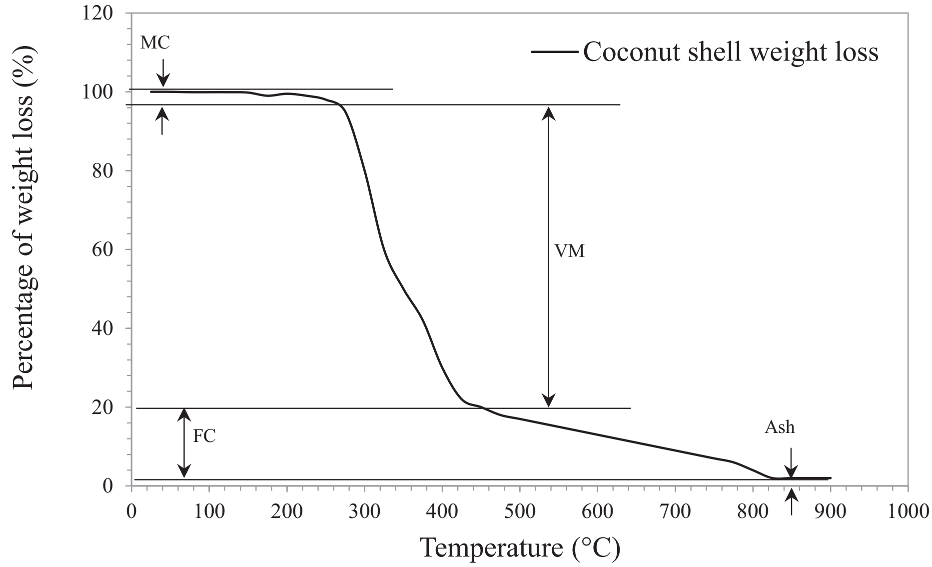


Fig. 2. Thermogravimetric coconut shell weight loss against temperature.

moisture content in a feedstock is one of the serious problems that affect the process. Moisture is a measure of water content present in biomass; it is normally expressed in a percent weight (wet basis). A high amount of moisture affects the thermochemical conversion processes and the heating value of the final product. This indicates the suitability of the biomass after the carbonization process to be used for purification, filtration, and soil amendment by increasing soil carbon. In the combustion of biomass, the volatile matter describes how fuel can be burnt easily. Its presence in a very high amount produces some inorganic compounds [42,44], it normally predicts the fuel reactivity. The volatile matter and the fixed carbon directly have a great influence on the combustion process. The proximate analysis helps in comprehending the performance of the biomass during combustion [1]. Hence, coconut shells will release more energy during the combustion process. In pyrolysis, the volatile matter usually contributes to the increase in the solid by-product (10–20 wt%). It undergoes a condensation reaction due to the prolonged holding time of the gases and volatiles to form solid products. The high amount of volatiles shows feedstock's advantage of undergoing a devolatilization process [42,44]. A high composition of fixed carbon in biomass makes it suitable for energy generation because energy is stored in fixed carbons and volatiles. The shells have a relatively fixed carbon of 21.8%. A key parameter that should be evaluated is the ash content of the given biomass. It predicts the presence of carbon and inorganic constituents in the form of salts and oxides. Normally, the ash content in biomass is less than 10 wt% except for some biomass. Low ash content prevents multiple complications in boilers and furnaces concerning the development of fused solids and high emissions of particulate matter [1]. Most of the biomass presented in Table 1 has an ash content of less than 10 wt% including this study, except rice husk [45]. The characteristic difference among biomass may be due to the variety and sample preparation of the feedstock, weather, and nature of the soil, method of harvesting, season of harvesting, and the humidity of the environment. To evaluate the properties of the biomass, it was compared with the results on other biomass as shown in Table 1. The studied coconut shell biomass is comparable with those that have a considerable value of fixed carbon, volatile matter, and fewer amounts of moisture, and ash content. Besides, from the characteristics behavior, the biomasses can substitute lignite and bituminous coal.

3.1.2. Ultimate analysis

The chemical evaluation of biomass is essential for power generation and also for converting into different compounds [44]. The elements found from the ultimate tests were: carbon 40.08% C, hydrogen 5.22% H, nitrogen 0.22% N, and sulphur 0.17% S as shown in Table 1. The oxygen (54.31%) content which contains other inorganic elements was determined by difference. Carbon was the main element found as it showed the highest percentage. Carbon is the major constituent usually present in given biomass. A high amount of carbon content in biomass is advantageous because its combustion increases the calorific value [46]. Based on the theory; materials with a high amount of fixed carbon present a high value of elemental carbon. The value or amount of oxygen and volatile matter has a relevant connection. Nevertheless, if the results of coal and biomass are compared, the relationship between oxygen and carbon on the solid structure with volatiles content can be established. For instance, the amount of oxygen in coal yielded a low volatile matter of 12%; whereas, in the case of biomass, vola-

Table 1
Physical and chemical characteristics of some raw biomass materials.

Biomass	Proximate Analysis %				Ultimate analysis %					Ref.
	MC	VM	FC	Ash	C	H	N	S	O	
Lignite	2.28	9.09	72.06	16.57	74.5	2.66	1.39	0.48	2.12	[47]
Coal	9.34	25.68	31.59	33.39	72.15	7.19	1.55	0.89	18.21	[48]
Coconut shell	5.56	70.82	21.80	1.80	40.08	5.22	0.22	0.17	54.31	Current Study
Rice husk	8.40	65.33	10.04	24.63	31.60	5.20	0.70	0.09	37.79	[45]
Palm kernel shell	4.00	58.00	43.00	4.00	51.00	7.00	3.00	0.48	39.00	[43]
Sugarcane Bagasse	5.25	82.55	8.30	3.90	46.60	5.92	0.14	43.35	0.09	[23]
Hardwood	7.80	72.30	25.00	2.70	48.60	6.20	0.40	–	41.10	[49]

tiles are around 75% due to the high composition of oxygen [1]. The coconut shells possess a high value of hydrogen (5.22%) which is connected with a powerful influence in a water gas reaction [42]. As a result, the content of nitrogen and sulfur composition is very low. Thus, the coconut shell biomass may produce a low amount of SO_x and NO_x emission during thermochemical conversion, hence, increases the potential of the coconut shell biomass as an eco-friendly renewable energy source [42]. Low sulfur and nitrogen content in biomass indicate fewer SO_x and NO_x that will be produced in boilers and furnaces [1]. The values of the elements obtained are comparable with other biomass (see Table 1).

3.1.3. Analysis by X-ray fluorescence

This spectrometric analysis determined the elemental fractions or compositions of a sample. The main elements present in biomass include chlorine, potassium, silicon, and sulfur. The results of the coconut shell biomass in Fig. 3 illustrates a relative percentages of the elements such as metals; potassium (42.5% K), nonmetals; chlorine (11.1% Cl), phosphorus (4.52% P), and sulfur (1.66% S), metalloid; silicone (1.45% Si), transition metals; iron (18.2% Fe), nickel (0.49% Ni), copper (0.55% Cu), and ruthenium (0.44% Ru), post-transition metal; zinc (0.39% Zn), alkali metal; (0.19% Rb), and alkaline earth metals; magnesium (1.20% Mg), and calcium (17.4% Ca). Potassium was found to have the highest elemental composition (42.2%) in the sample. Potassium burns with a pale pinkish-violet colored flame. It also reacts with water to generate sufficient heat for igniting the hydrogen emitted in a chemical reaction [50]. The concentration of other inorganic elements (Zn, Ru, Cu, Ni, and Rb) was found in less than 1%. The mineral and elemental ions absorb by the plants decrease the biomass energy, change the distribution of the conversion products as well as affecting the operation of the equipment used for thermochemical conversion. During the combustion process, most of the elements present in plant biomass volatilize to become a liquid slag or a solid deposit after cooling. The complex elements in a thermochemical conversion process of biomass are Si, Na, Mg, Ca, Cl, and S [20], and they are considered as thermos-chemical processing systems. This shows that the coconut shell biomass will be good fuel for the thermochemical conversion process because it possesses complex elements in a small amount. Thus, pre-treatment is not required before its utilization, hence good for bio-oil and bio-gas production. The results of this study were similar to those of date palm biomass [51], coconut shells, OPF, and wood chips [42]. However, a higher amount of some of the elements in given feedstock biomass can cause critical problems in handling the ash and the downstream equipment [51]. Therefore, coconut shell biomass will not cause serious problems to the reactor for its processing.

3.1.4. Functional group analysis

The FTIR spectroscopy was used to determine the functional groups existing on the coconut shell biomass. This analysis further predicts a particular functional group and molecules, chemical structure, and composition which can be transformed into products. The degree of transformation of the biomass material to charcoal can be seen by the appearance or non-appearance of the wave [23]. The transmittances by the FTIR spectrum were observed at different intensities which interpret the existence of functional groups (Fig. 4). The spectra help to clearly understand the chemical structure of the biomass. The majority of agricultural biomass possesses almost the same functional groups, such as alcohols, carboxyl groups, phenol, aldehydes, ketones, and ether [52]. The observed wide range apex was in the wavenumber from 400 to 4000 cm^{-1}. The band shifting around the broad apex shows the possible bond of hydroxyl groups, CH, CH_2, CH_3, C = C, C-C carboxyl group, and N-H, Si-O, and O-H functional groups. The band changes were closed to the large peak of 3408 cm^{-1} points out the possible bond of a hydroxyl group due to extensive hydrogen bonding of cellulose [53]. At 2931 cm^{-1}, it displayed the existence of the CH extension which produced vibration of CH, CH_2, CH_3 groups. In 1742 cm^{-1}, it indicated C = C in an aromatic ring. The band 1608 cm^{-1} to 1255 cm^{-1} interpreted the major changes in C-O carboxyl as a result of the activity of the atoms of carboxyl-oxygen, which causes changes in the areas [54]. Furthermore, the change at a peak of 3408 cm^{-1} and 2931 cm^{-1} revealed some vibrations of N-H and O-H. Apex at 1161–1050 cm^{-1} revealed the existence of silica which is imputed to Si-O stretching and bending. This finding agrees with the findings of Lazim et al. [54] on agricultural biomass (durian peel, coir pith, and coconut shell), and Orooji et al. [55], on nanocomposites materials. The spectrum correlates well

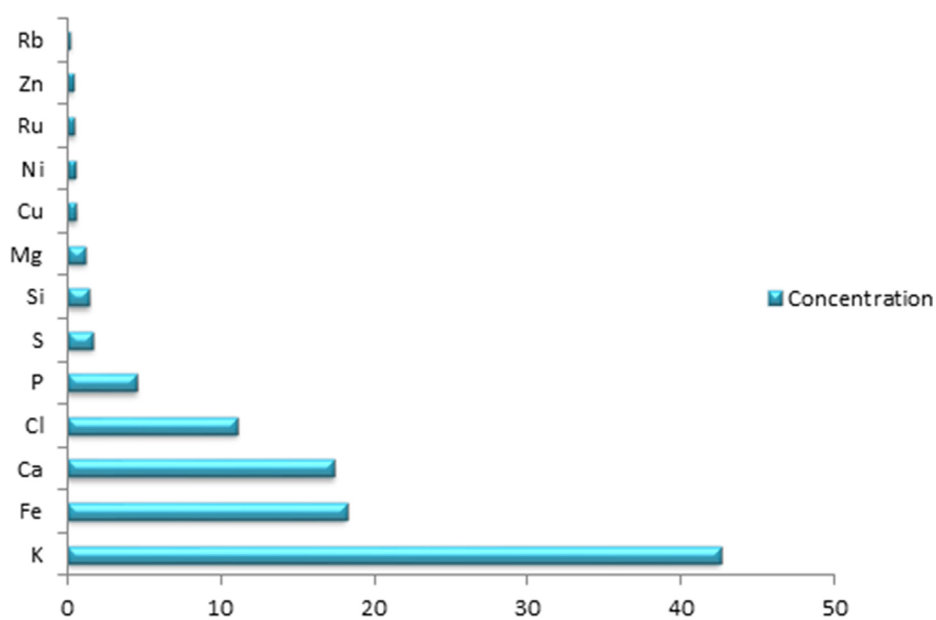


Fig. 3. Elemental composition of coconut shell using X-ray fluorescence.

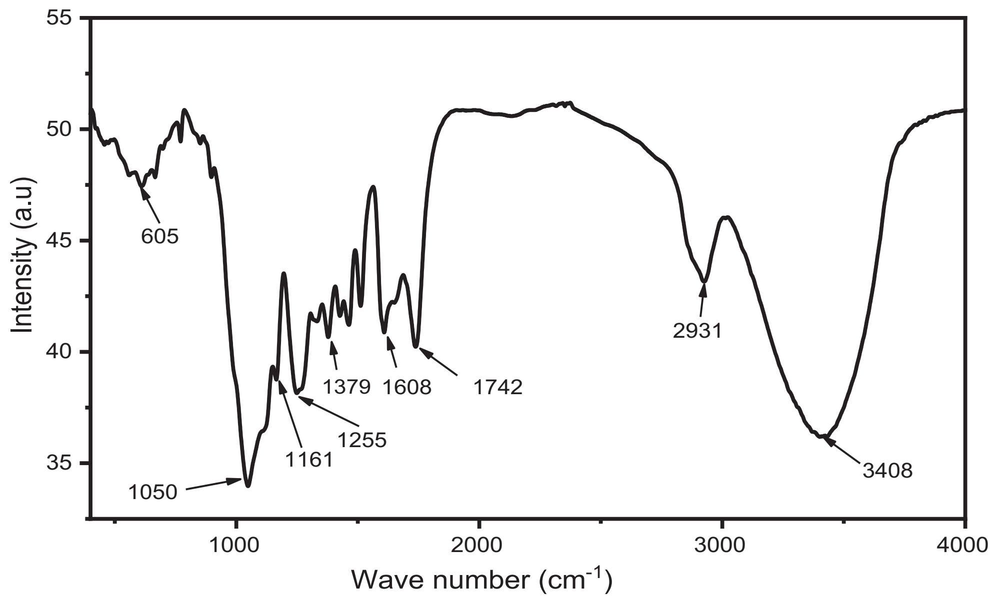


Fig. 4. The Fourier spectrum of the coconut shell biomass.

with the elemental analysis, which also revealed a relatively high amount of retained oxygen content.

3.2. Potential as energy source

3.2.1. Particle, bulk, and tapped density, porosity and compressibility index

The particle mass of the feedstock sample was calculated as 412 kg m^{-3}. This result was in the range of the required basic density. It was quite smaller with those of wood species 500 kg m^{-3} [56]. A high density shows an advantage towards high energy content and permanence while a low density causes an insufficient flow of the material under gravity in operation [14] and poses a challenge for its handling, storage and transportation, and thermochemical conversion processes. The particle mass of a biomass sample is normally employed in thermochemical conversion reactors for the biomass computational fluid dynamics and simulation [37].

The bulk mass and the tapped mass were calculated as 311 kg m^{-3} and 410 kg m^{-3} respectively. It was observed from literature, different biomass materials manifest very great differences in their bulk mass ranging from low values (15–200 kg m^{-3}) to high values of 280–480 kg m^{-3} respectively. Nevertheless, in contrast with the bulk density of coal (about 900 kg m^{-3}), the values of these biomass materials were predominantly low [57]. It can be inferred that compared to other feedstocks, the operations involving handling, transportation, and storage of coconut shells biomass would be less challenging. The parameter is a fundamental characteristic because it affects transportation costs, necessary space for storage, and energy density. It is known that a mass of a biomass material possesses an optimistic linkage with the fuel value index; as such high-density influences the biomass fuel value index for the generation of power [46]. The denser materials contain more specific heat which enables it to burn for longer periods [58]. This indicates the coconut shell can be a good source of energy because it possesses a high value of density which gave rise to the high calorific value. The porosity was found to be 24.39% and the compressibility index was 40.24%. This result agrees with those described by Bello et al. [59]. The density of biomass influences the heat and mass transfer in biomass pyrolysis. It is proportional to the porosity of sample biomass [60].

3.2.2. The energy content and fuel value index

The energy that is released by a unit mass of solid biomass is termed the calorific value. It predicts the potential of biomass as a biofuel [42] for renewable energy applications. The calorific value was found to be 19.4 MJ/kg Table 2. It was reported that 14–20 MJ/kg was the typical biomass range of calorific value [20]. The studied sample showed a high energy value content. The proximate analysis greatly affects the biomass heat energy value. The presence of moisture, ash, and volatiles in a high amount lowers the calorific energy and vice versa. On the other hand, a great value of fixed carbon in biomass increased the calorific energy. A high amount of moisture in given biomass causes a reduction in the net calorific energy, as a result of excessive loss of energy required to eliminate the moisture from the biomass [41]. During the combustion of biomass, the elemental analysis plays a vital role in determining the quantity of energy that will be liberated. The presence of high elemental carbon and low oxygen in coal yielded a higher heating value of 32.3 MJ/kg. For most of the biomass waste, the higher heating value is nearly 20 MJ/kg with 32% having a lesser value [1]. The biomass quantitative and qualitative properties ascertain the quality of fuel. The biomass moisture and ash content, calorific value, and density are the quantitative properties [41].

The fuel value index of the coconut shell fuel material was found to be 4441 (Table 2); therefore, the result of the fuel value index shows that the coconut shell biomass has a high energy

Table 2
Calorific value and fuel value index of biomass.

Biomass	Calorific Value (MJ/kg)	Fuel Value Index	Reference
Lignite	28		[47]
Coal	16.2		[48]
Coconut shell	19.4	4441	Current Study
Rice husk	13.8		[45]
Palm kernel shell	20.4		[43]
Sugarcane Bagasse	16.9		[23]
Hardwood	18.8		[49]
Wood	15.9	4125	[56]

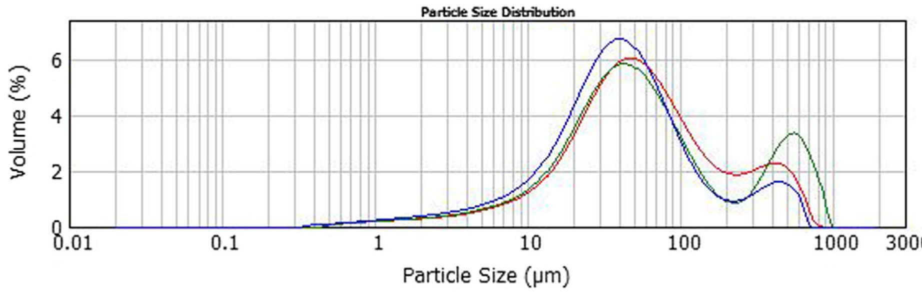


Fig. 5. Particle size distribution.

value when compared to other biomass. The higher value obtained could be probably the consequence of the lesser ash value, higher heating value, and high density of the feedstock material. However, it is comparably with wood species (4125) by Saravanan et al. [56]. Bhatt and Todaria [41] describe biomass materials with a high fuel value index and low ash content as a good fuel with high energy potential. Thus, the potentiality of coconut shells biomass for various energy purposes is high.

3.3. Morphological characterization

3.3.1. The particle size

A broad distribution of sizes ranging from less than 1 to 1000 μm with a specific surface area of 0.39 m^2/g, surface weighted mean (15.3 m), and volumetric weighted mean (81.3 m) was observed (Fig. 5). The particle distribution at d (0.1) explained that 10% of coconut shell biomass was smaller than 9.4 μm, at d (0.5)

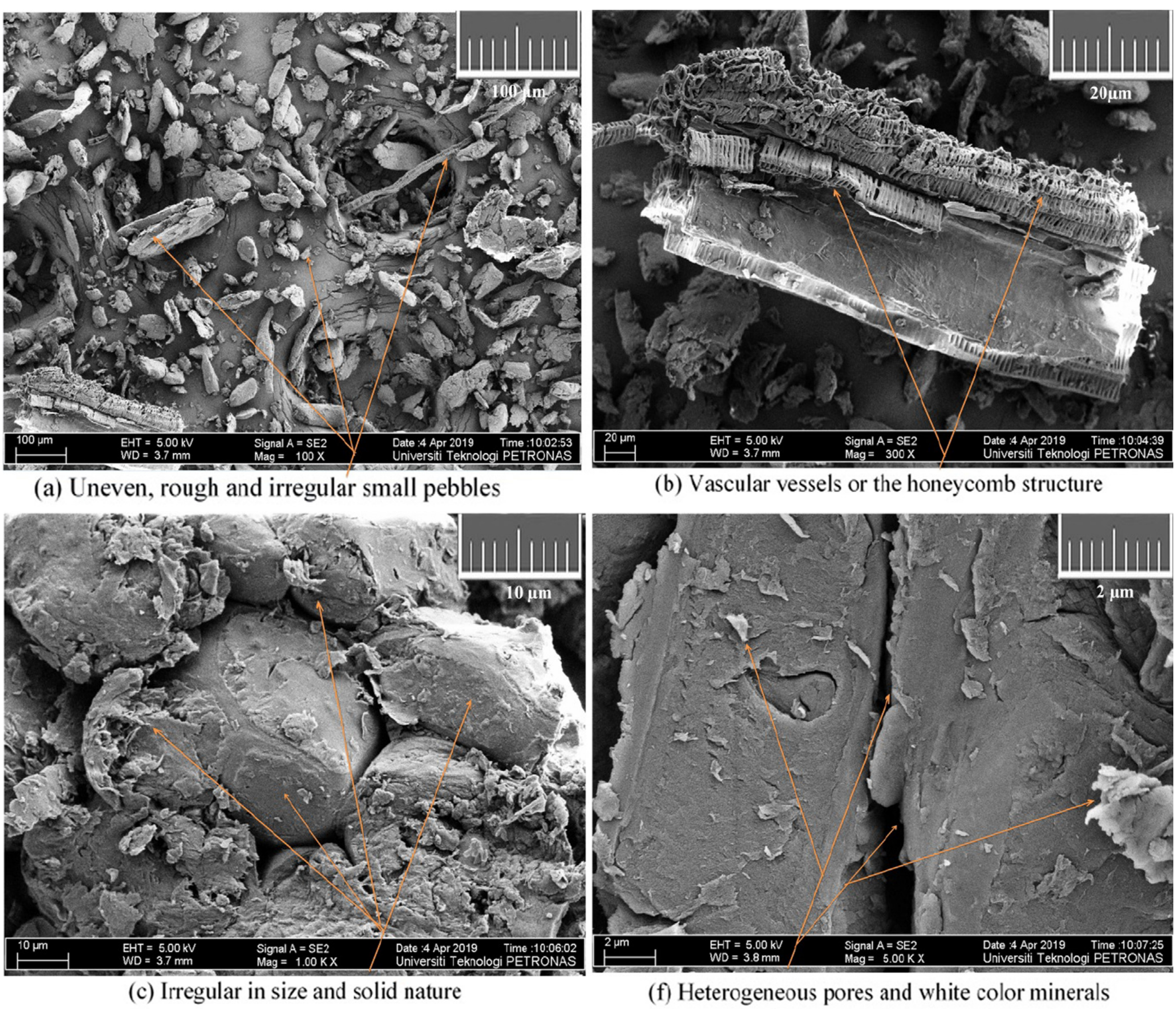


Fig. 6. Coconut shell micrographs detected by field-emission scanning electron microscopy (FESEM) at various magnifications.

means 50% were smaller than 40.5 μm and at d (0.9) described that 90% of the coconut shell biomass were smaller than 200 μm respectively. The smallest particle size was found to be 0.6 μm and the biggest particle size was approximately 1905 μm. This showed that most of the particles were less than 2000 μm. This agreed with the results of FESEM from the present study. The surface area shows the potentiality of the biomass for nutrients adsorption when applied to the soil. For a material-sparing scale, the particle size distribution plays a vital role. It has an impact on the processing and performance of pharmaceutical products [61]. Coconut shell charcoal is known to be applied in pharmaceutical industries.

3.3.2. Porous structural analysis

Fig. 6 is a scanning electron microscopy graph microanalysis (FESEM) which shows the micro-structure/physical surface morphology of the coconut shell. The image of the sample was taken at different magnifications. The porous structure of the sample shows heterogeneous shapes and scales of macro-pores. The micrograph of the coconut shell (Fig. 6a) shows a range of uneven rough, irregular shapes and sizes of small pebble particles to larger particles up to 100 μm. This indicates a high surface area and porosity in nature. In contrast to most biomass, the coconut shells are firmly compacted structures. As such, due to its morphological features, it will not absorb much moisture from the surrounding [42]. The sample looks like a bundle of cylindrically shaped spiral structures interconnected by some large tubes like the lignified vascular xylem vessels or the honeycomb as shown in (Fig. 6b). These structures may be a result of the coconut shell fibers [53]. The sample biomass has a solid nature and is irregular in size Fig. 6c). The sample also exhibits dense surfaces with a complex network of heterogeneous pores (Fig. 6e) [62].

The mapping of the coconut shell biomass sample is presented in Fig. 7. The elements of chlorine, carbon, copper, oxygen, and potassium were detected. The atoms of oxygen, carbon, and potassium in Fig. 7a, 7b, and 7c are closely packed together while those of chlorine and copper are slightly dispersed from Fig. 7d and 7e. The weight percentage of the major elements was analyzed on the spectrum surface by the EDX. The electron image from Fig. 7f shows that the coconut shell contains many crystalline grains, this is as a result of the formation of white color minerals by the pores present in the material's structure [63]. The elements detected by EDX on the sample surface were 59.4% carbon, 49.2% oxygen, 0.1% chlorine and 0.3% potassium. All the elements detected by the EDX and Mapping were also detected from the results of XRF analysis. The elements of carbon and oxygen detected by EDX are higher than those obtained by the ultimate test. This could be due to the non-detecting of nitrogen, sulphur, and hydrogen composition by EDX analysis. These results are comparable with those of different types of date seeds [51], OPF, and wood chips [42]. Moreover, the porous structure shown by the coconut shell indi-

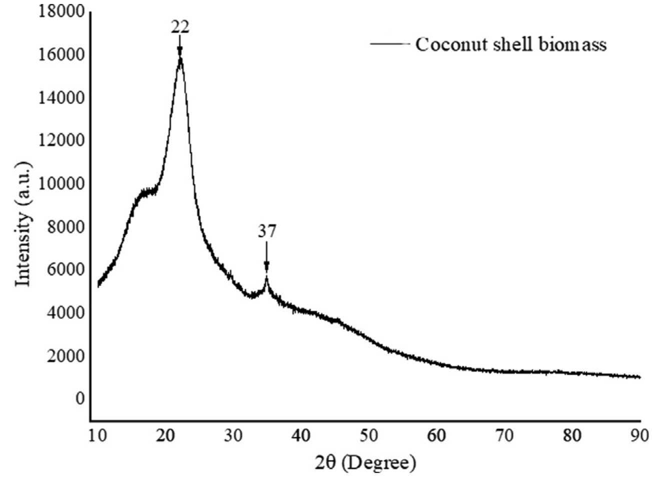
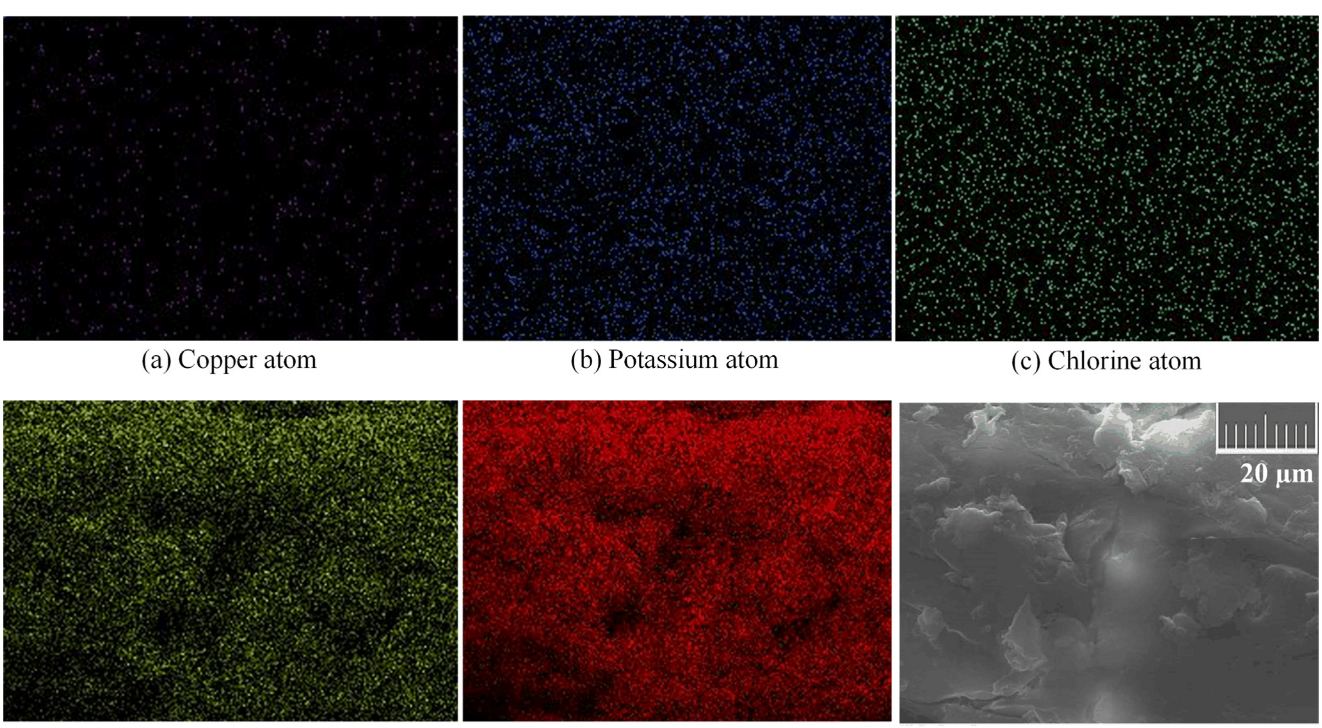


Fig. 8. The X-ray diffraction pattern of coconut shell biomass.



(a) Copper atom (b) Potassium atom (c) Chlorine atom
(d) Oxygen atom (e) Carbon atom (f) Electron image

Fig. 7. Mapping and electron image of the coconut shell biomass.

cates the possibility of its use in purification and adsorption processes from the particle size and surface morphology tests. It was reported, activated carbon produced from coconut shells is better than those obtained from other biomass because of its macropore structure which makes it more effective for purification.

3.3.3. The X-ray diffraction of the coconut shell biomass

The crystalline or amorphous structure of biomass is detected by the X-ray diffractor. The major sharp peaks were at 22° and 37° showing carbonaceous material in the coconut shells (Fig. 8). These peaks show amorphous or nanoparticle-based on the broad peak at 22° [64]. The results are in line with those of on date palm [44] wastes. The observed peaks that split are due to the transformation of carbon from a high to a lower phase. The desirable layer relative positions are one of the characteristics of a crystalline structure of biomass. It forms the sharp peak as shown in Fig. 8 at an angle of 22°. The peak around 37° is characteristic of calcite. There was no appearance of long-range ordered structure (onion-like) in the biomass that will show a few graphite structures [64]. It was known that the crystallinity of given biomass usually depends on the complex bonding of the lignocellulose composition, and the content of wax and cellulose present in the biomass. A sample is said to have predominantly amorphous structures if sharp peaks are absent [65]. Characterization of the biomass reveals a microstructure similar to wood charcoal. Therefore, the coconut shell biomass is said to have an amorphous structure.

4. Conclusion

An in-depth exploration of the factual data and availability of the coconut shell biomass regarding the physiochemical, potential for energy generation, and morphological characteristics concerning the thermochemical conversion-related properties were carried out. This was to investigate thoroughly the economic feasibility and the encouraging perspectives of evaluating the feedstock as a potential alternative for charcoal production. This research can be a starting point for the production of coconut shell charcoal and the selection of biomass species for other energy applications. The coconut shells present a low amount of complex heavy metals, functional groups and are said to have amorphous structures and well required morphological qualities. The feedstock can serve as a promising source of energy because of the good properties of solid-fuel and carbon source. The high content of fixed carbon (21.8%), carbon content (40%), and high energy content (19.4%) will yield a potential carbonaceous material (charcoal). The coconut shell biomass presents superior performance than other biomass in terms of energy and carbon content. Elemental analysis findings such as nitrogen (0.22%) and sulfur (0.17%) show that the biomass is sustainable with zero carbon emissions. Hence, the use of coconut shell biomass for charcoal production could be cost-effective and eco-friendly, because the biomass is abundant at a very low price, and the comprehensive quantitative-characterization of the biomass shows its potential for waste to energy applications through thermochemical technology. Thus, engaging in the processing of coconut shells to charcoal is of great economic significance.

5. Contribution of authors

All the authors have contributed to the achievement of this study.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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