Analysis of Adenanthera *pavonine* L. (Febaceae) Pod and Seed as Potential Pyrolysis Feedstock for Energy production

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Abstract

Though countless possible bioenergy feedstocks are available, the lack of information on their characteristics has made them unusable for industrial purposes. This study revealed the bioenergy potential of seed and pod of *Adenanthera pavonine* by analyzing their physicochemical, ultimate, proximate, kinetic, thermodynamic, thermal, and higher heat value. The seed presented 19.90%, 2.12%, 24.40% and 14.73% cellulose, hemicellulose, lignin and extractive respectively, while the pod has 21.35%, 25.15%, 23.50% and 11.63%. From the proximate analysis the pod has higher volatile matter (92.79%), and fixed carbon (1.40%), while the seed has higher moisture (6.36%), ash (0.84%), and higher heat value (18.63 MJ kg^{-1}). The kinetic and thermodynamics results present the seed with Ea 23.73 kJmol-1, ΔH 14.06 kJmol-1, ΔG 10.74 kJmol-1 and ΔS -78 Jmol-1, while the pod has 21.3 kJmol-1, ΔH 12.20 kJmol-1, ΔG 10.98 kJmol-1 and ΔS -83 Jmol-1. The probable energy blockade between Ea and ΔH for the seed and pod was 9.72. The high value of H: C and low O: C, with the higher heating values recorded for the pod and seed, presented them as better biofuel candidates. The study results have supplied necessary information for the industrial utilization of *Adenanthera pavonine* seed and pod as valuable feedstocks for bioenergy conversion.

1. Introduction

An increase in world population coupled with rapid industrialization and urbanization is causing a reduction in fossil fuel energy resources. Also, the negative environmental greenhouse gas effect of fossil fuel is calling for alternative replacement for fossil fuel energy.

Plant biomass is renewable, abundant, and easily adaptable is being considered as the capable replacement for fossil fuel energy. It can supply a hygienic, renewable, dependable, and low-carbon print fuel. About thirteen percent of the world's energy can be derived from biomass, is converted directly to heat, biofuels, and value-added chemicals through various reaction pathways [1].

Nevertheless, using biomass as a raw material for fuel generation has its drawback, there are numerous character differences between and within various biomass types and species. Therefore, knowledge of the physicochemical properties and the energy value of biomass are very vital for its proper utilization [2]. The chemical constituent of biomass such as moisture, cellulose, lignin, hemicellulose, extractive, and ash play different vital roles in determining the suitability of the mate-

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rial for particular end-use. The moisture content of biomass can affect the higher heating value if too high and also impact negatively the bio-oil properties. The elemental composition of fuel-derived biomass is very important for the control and prevention of ash fouling and slag formation which could affect thermochemical processing delivery pipes. Biomass with high cellulose or hemicellulose content would produce a higher yield of bio-oil, while those with higher lignin content will give rise higher yield of char [3].

To obtain the inherent energy content of biomass, a thermochemical processing system is needed, this cannot be constructed without the knowledge of its thermal behaviour and chemical composition [4]. Thus, information on the pyrolytic behavior of the biomass from its thermogravimetric (TG) characterization is essential before the industrial utilization in a thermochemical plant. Parameters such as rate of biomass decomposition and the activation energy valuable for engineering design of thermochemical conversion unit are obtained from TG using Coats and Redfern model [5]. Thermodynamic parameters; entropy (ΔS), enthalpy (ΔH), and Gibbs free energy (ΔG) are useful to verify the visibility of the pyrolysis occurrence, operation condition, and possible products

Proximate analysis is a valuable means of defining and envisaging the heating values of biomass, it helps to reveal the fuel behavior of the biomass at various stages during combustion [6]. Whereas, the biomass fuel efficiency and cleanness can be predicted using both the proximate and ultimate analysis [7]. Higher heating value (HHV) is used to quantify the energy worth of biomass fuel. Experimentally, HHV of biomass fuel can be determined using a bomb calorimeter, however, because of the cost and time-consuming nature of the procedure, various authors have utilized data obtained from the proximate and ultimate analysis to determine the HHV of different biomass through the use of empirical models [8-12].

Adenanthera pavonina L. is a wild underutilized plant that can be exploited for firewood, shade, ornamental, medicinal, and dyeing purposes [13]. The ability of *Adenanthera pavonine* as low-cost biosorption for Pb (II) and Cd (II) from wastewater has been demonstrated and it was reported that the seed has a good sorption capacity for the two metallic ions [14]. Extracted galactomannan from *Adenanthera pavonina L* has been reported as a good binder in cement-based hydroxyapatite composite [15]. Medicinal importance of the various parts of the plant has been documented by various authors; anti-inflammatory [16], anti-blood pressure [17], and anti-diabetic [18].

Due to the lack of data on the biofuel potential of pod and seed of *Adenanthera pavonine,* this research work is aimed at the exhaustive analysis of the pod and seed of *Adenanthera pavonina* to reveal their bioenergy possibility and provide data for designing a thermochemical conversion system for the industrial utilization.

2. Material and Method

2.1. Material

Samples were obtained from *Adenanthera pavonine* tree at the Federal University of Technology, Akure, Ondo State, Nige-

ria. Contaminants were sorted out, the seeds were removed from the pods and the materials were sundry (72 h). The materials were pulverized and sieved to obtain 450 m particle size and then stored in an airtight container at room temperature.

2.2. Extractive free sample

A biomass (B_1) was Soxhlet extracted (4 h) serially with (1: 2) ethanol (985%): toluene, ethanol (4 h), distilled water (500mL x 3), then dried (105 ^{o}C) to a constant weight (B_2) [19]. Percentage extractive was calculated thus after a triplicate experiment:

$$\text{Extractive content (\%)} = \left[\frac{(B_1 - B_2)}{B_1}\right] \times 100 \qquad (1)$$

2.3. Acid-insoluble lignin

To the extracted biomass (E) was added sulphuric acid (72%, 15 mL) at 20 ℃ (2 h). The experiment was stopped by adding deionized water (560 mL), before heating (95 ℃, 4 h) and then allowed to cool (24 h). The filtered was obtained as acid-soluble lignin and the solid as the acid-insoluble lignin (washed to pH 7) after oven-dried to a known weight (L) [20]. A triplicate experiment was done and acid-insoluble lignin was calculated thus:

$$\text{Klason lignin, (\%)} = \frac{L \times 100}{E} \qquad (2)$$

2.4. Acid-soluble lignin

To acid-soluble lignin filtrate volume (V = 575 mL) was diluted with sulphuric acid (3%) and the ultraviolet absorbance (AB) read at 205 nm, with sulphuric acid (3%) being the reference sample [21]. Lignin content in the filtrate (B in g/1000 mL) was calculated as follows:

$$B = \frac{AD}{100} \qquad (3)$$

Where: D= The dilution factor of the filtrate, 110 = Absortivity or extinction coefficient. The acid acid-soluble lignin was calculated as follows:

$$\text{Lignin (\%)} = \frac{110BV}{1000w} \qquad (4)$$

2.5. Holocellulose

A mixture of extractive free biomass (W_e), distilled water (150 mL), glacial acetic acid (0.2 mL), and sodium chlorite (1 g) was subjected to heat treatment (70 ℃). The procedure was repeated three times but without the addition of distilled water and biomass. The solid sample was washed free of chlorine, oven-dried (105 ^{o}C) to weight (W_h) [22]. A Triplicate experiment was performed and the holocellulose content was determined as:

$$\text{Holocellulose content (\%)} = \left[\frac{w_e}{w_h}\right] \times 100 \qquad (5)$$

2.6. Alpha-cellulose

The obtained holocellulose was treated with sodium hydroxide (17.5%, 50 mL, 20°C), distilled water (50 mL) was added after 29 min. The solid particle obtained was washed to neutral pH with deionized water [22] and then oven-dried (105 ^{o}C) to constant weight (w_{00}). A triplicate experiment was done and cellulose was determined with the following formula:

$$\text{Cellulose } (\%) = \left[\frac{w_9}{w_{oo}}\right] \times 100 \tag{6}$$

2.7. Instrumental analysis

Perkin Elmer STA 6000, was used for the determination of the sample proximate composition (moisture content, volatile matter, ash content, and fixed carbon). Scanning Electron Microscope (SEM) coupled with-Energy Dispersed X-ray (EDX) (FEI FIB/SEM Nova 600 Nanolab) was used for the morphological characteristic and elemental composition of the samples using the ash component. Thermogravimetry analysis (TG/DTG) was conducted (TGA TA STD Q6000) in a nitrogen atmosphere, flow rate 20 mL min^{-1} at a temperature (30 and 900 ^{o}C), and heating rate 10 ^{o}C min^{-1}, about 10.0 mg sample was used for the thermal characterization. Perkin Elmer CHNS was employed for ultimate analysis determination of percentage carbon, hydrogen and sulfur content, while oxygen (%) was calculated by difference {(O =100 − (C+H+N+S+Ash)}[23]. The H/C and O/C ratios were determined using empirical methods [24, 25] as follows:

$$\frac{H}{C} = \frac{\text{number of H atoms}}{\text{number of C atoms}} = \frac{\%H/1}{\%C/12} \tag{7}$$

$$\frac{O}{C} = \frac{\text{number of O atoms}}{\text{number of C atoms}} = \frac{\%O/16}{\%C/12} \tag{8}$$

2.8. Higher heating value

Higher heating value (HHV) or gross calorific value were using the empirical formula [26] as follows;

$$HHV(MJ/kg^{-1}) = 0.0877L + 16.4951 \tag{9}$$

2.9. Kinetic and thermodynamic parameters

Modified Coats and Redfern model (Equation 10) [5] was employed for the determination of the activation energy (Ea), pre-exponential factor (A), and Regression coefficient (R^2) through the graph plot of ln [ln (1- x)] against 1000/T. Thermodynamics parameters such as entropy (ΔS), enthalpy (ΔH), and Gibbs free energy (ΔG) were calculated using equations (11-14) [27,28]. Different factors such as Boltzmann constant K$_B$ (1.381 x10^{-23} J/K), Plank constant h (6.626 x 10^{-3}4 J/s), and TG peak temperature (T$_m$/K) are usually used in the calculation and other necessary values during the calculation are obtained from the TG data.

$$\ln\left[-\ln\left(1-x\right)\right] = \ln\frac{ART^2}{\beta E_a} - \frac{E_a}{RT} \tag{10}$$

$$A = \frac{\left[\beta * Exp\left(\frac{E}{RT_m}\right)\right]}{RT_m^2} \tag{11}$$
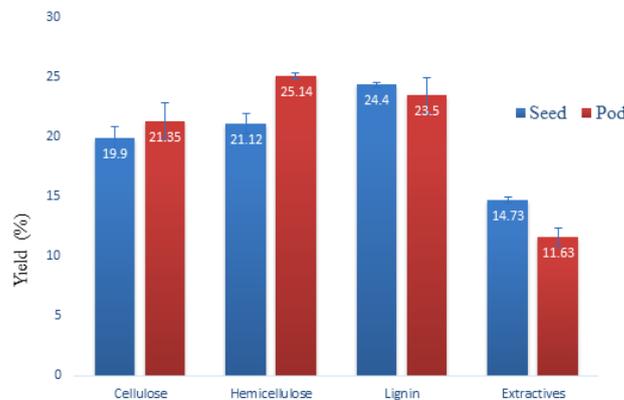
Figure 1: Percentage composition of biomass

$$\Delta H = Ea - RT \tag{12}$$

$$\Delta G = Ea + RT_m \ln\left(K_B T_m / hA\right) \tag{13}$$

$$\Delta S = \Delta H - \Delta G / T_m \tag{14}$$

3. Results and Discussions

3.1. Composition of biomass

The seed and pod of *Adenanthera pavonine* displayed distinct characters. The extractive results revealed 13.73 % for the seed while the pod recorded 11.63 %. This is expected because the chemical composition of biomass can be influenced by the nature of such material. It has been reported that both saturated and unsaturated fatty acids are abundant in *Adenanthera pavonine* seed [29]. The percentage extractive presented in this study is higher than 7.78% and 9.75%, but lower than 13.82% to 32.86% reported for different date palm residue [30]. The high extract content of the seed suggests that it can support biomass burning and ignition ability, an added advantage if used in composite briquette compounding. The pod recorded 21.14% cellulose and 23.50% hemicellulose, both are higher than the 19.90% and 21.12% for cellulose and hemicellulose of the seed. On the other hand, the 24.40% lignin content of the seed was higher than 23.50% of the pod. The cellulose content of the seed and pod are lower than 45-50 % for hardwood -and soft wood-cellulose [31], but compared favourably with 12-29% reported for lignocellulosic residue [32], while the hemicellulose was in agreement with 15-35% for hardwood and 20-31% for softwood [31]. However, the lignin content of both the seed and pod was higher than 11-22 reported for lignocellulosic biomass [32]. It can be inferred from the results of the hemicellulose and cellulose of the pod and seed that biomass will experience faster thermal degradation, thus saving energy cost during pyrolysis, though at the expense of higher heating value that the lignin would have supplied.

3.2. Proximate analysis of biomass

The pod has a lower moisture content of 5.22% against 6.36% of the seed. The higher moisture content of the seed

might be due to its high extractive content (fatty acid, resin, gum) which could have prevented the evaporation of bond water.

The reported moisture contents (pod and seed) were lower than 8.00% [33] and 7.02% [34] for Lantana camara by different authors. The low moisture content of the pod agreed with the low value reported for the pod *Acacia mangium* amongst all its various parts [35]. The moisture contents of the pod and seed are lower than fifteen percent recommended for pyrolysis required biomass [36]. Higher moisture content is expected to engineer microbial degradation, which will invariably affect the fuel quality of the biomass. Thus, the seed and the pod would be good fuel oil-producing feedstock [37]. High volatile matter is desirable in pyrolysis feedstock because it would aid ignition and support the biomass burning ability. After all, they are expected to produce a high quantity of bio-oil [38]. There is no significant difference between the volatile matter of the seed (91.79%) and pod (92.79%), suggesting that those materials would have good ignition ability. The higher volatile matter reported in this study was not an isolated case, higher volatile values have been reported for the pod of *Acacia mangium* [35] and *Bauhinia monandra* [39]. The volatile matter the seed and pod here reported is higher than 69.82 to 74. 85% for various part *Acacia mangium* [35], 74.30% to 87.50% for date palm [30]. The difference in the volatile matter of the different biomass could be linked to the plant types, nature of the biomass, and the state of the biomass before analysis. The oxides of the elements present in the biomass represent the ash content, which can be determined as the solid inorganic component after the thermal degradation of the biomass. The worth and durability of thermochemical products and plant-unit are mostly influenced by the ash feedstock content. Slag development during the thermochemical process would corrode the system [4], the corrosion indirectly affects the quality and quantity of the biofuel, increasing the energy need and cost of system maintenance. Thus, feedstock with minima ash content is desirable for thermochemical conversion. It has been affirmed that biomass feedstock with ash values ranging from 1.41 to 2.69% is a good candidate for bioenergy utilization [35]. Hence, ash values of 0.84% (seed) and pod 0.59% (pod) make these materials better feedstock and it is envisaged that the associated ash problem of biomass would be eliminated or minimized if these materials are utilized as thermochemical feedstock. The pod and the seed ash values are lower than 4.5 to 10.5% switchgrass [40] and 2.68% grapevine pruning, 1.94% olive pruning, and 2.25% riverbank residue [41]. The ash differences of the various biomass can be ascribed to various factors such as soil type, ecological reason, plant types, and part. The thermochemical undecomposed part of the biomass is the fixed carbon [35], which can be employed in biochar preparation. However, low biochar feedstock is preferable for thermochemical biofuel application because of the expected high bio-oil yield. The two materials examined in this study; pod and seed presented 1.01% and 1.40% fixed carbon respectively, probably the reason for the high volatile matter content of those materials. It is therefore assumed that the pod and seed of *Adenanthera pavonine*, would be a good candidate for bioenergy production. The fixed carbon of this study is very low compared with 14.47 to 18.31% from different parts of Acacia mangium [35], but are higher than 0.34% and 0.623% for *Delonix regia* seed and pod.

From the HHV analysis of the biomass using [26] formula for non-wood lignocellulosic fuels. It was revealed that the pod and the seed have higher but different values; the seed has 18.63 HHV values, while the pod recorded 18.56. The higher value of the seed could be the effect of its high lignin and extractive values, both of which have been documented to increase HHV [26]. The HHV reported in this study are lesser than 20-25 MJ kg-1 of sweet sorghum [42], but are higher 15.00 MJ kg-1 for camel grass [43], 15.10 MJ kg^{-1} of para grass [44], and 17.20 MJ kg-1 of *A. donax* [45], all of which are notable fuel biomass. Thus, the seed and pod of Adenanthera *pavonine* can be adjudged to be good energy biomass.

3.3. Ultimate analysis of biomass

The CHNS carbon, hydrogen, sulphur, and oxygen values for the seed are 38.26%, 6.30%, 1.92%, and 52.68% against 43.01%, 5.785. 1.63% and 48.99% of the pod. All the obtained values are in agreement with literature values for various biomass [26]. The pod is richer in carbon and oxygen, while the seed is richer in hydrogen and sulphur. The fuel potential of the biomass can be predicted from carbon, oxygen, and hydrogen, making those elements important in the biomass thermochemical process. The knowledge of sulphur content would help in preventing possible environmental pollution from its gaseous products. The H: C ratio of 1.97 and 1.61 were recorded for the seed and the pod respectively. These values are within the range of 1.46 to 2.18 for different non-edible biomass [46] and 1.54 to 1.67 for various walnut shells [47]. Also, 1.03 and 0.85 recorded for the O: C ratio is within the range of 0.72 to 0.99 for different date palm residues [30]. The higher H: C fraction and lower O: C fraction of the pod and seed, indicate them as better biofuel candidates [48]

3.4. Elemental analysis of biomass

The mineral content of biomaterial for bio-energy research is very essential, considering the negative effect those metals could have on the desired products and the processing unit. The EDX analysis of the ash presents the presence of K, Na, Ca, Mg, P, and O in the seed while Na was not detected in the seed, Si and other elements in the seed are detected. The seed has a higher content of Na (1.330), Mg (7.36), and P (1.81), while the pod has K (44.71), and Si (0.93). The low level of Silica in the pod and its absence in the seed, coupled with the absence of heavy metals in both the seed and the pod signifies the safeness of these materials as a good feedstock for bioenergy production. The ash is rich in essential minerals (K, Na, Mg, and P) for plant growth; therefore, the ash can be utilized as a biofertilizer.

However, alkali earth metals are known to induce in-situ reactions such as cracking which often led to low oil yield and high gas production [49]. Also, those metals can inhibit microorganisms if those biomasses are used biochemical for purposes [50]. Hence, there is a need for pretreatment of the biomass to reduce the metal content during thermochemical conversion
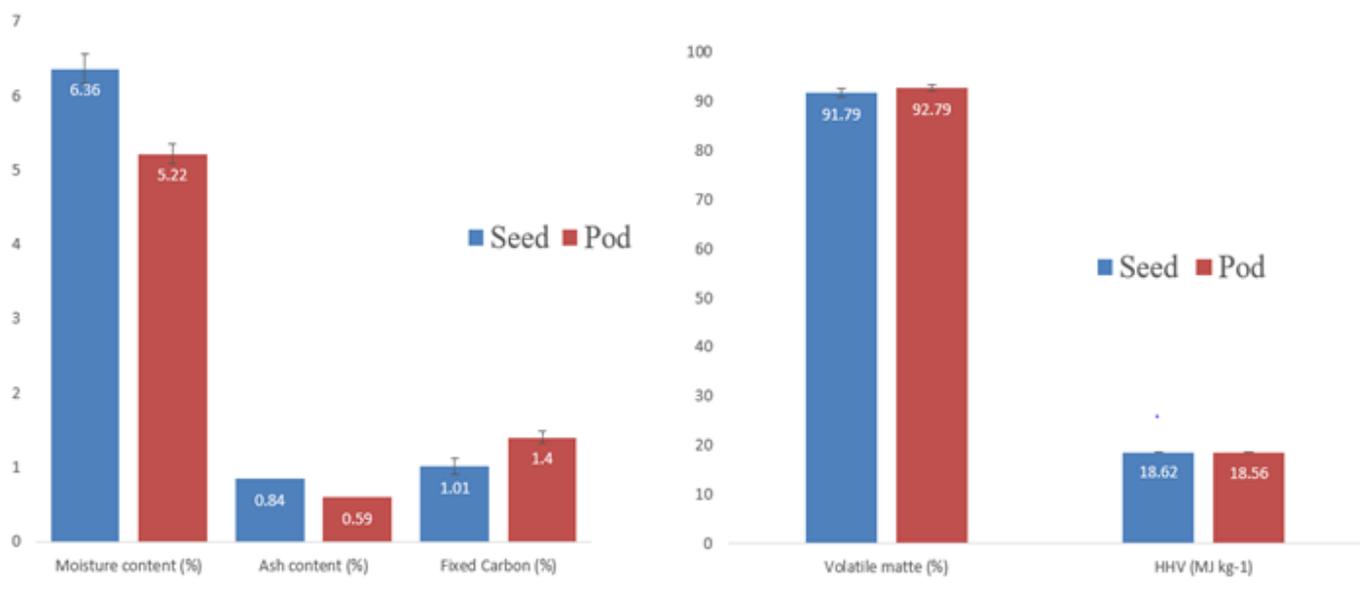
Figure 2: Proximate analysis of biomass (Fixed carbon calculated by difference)
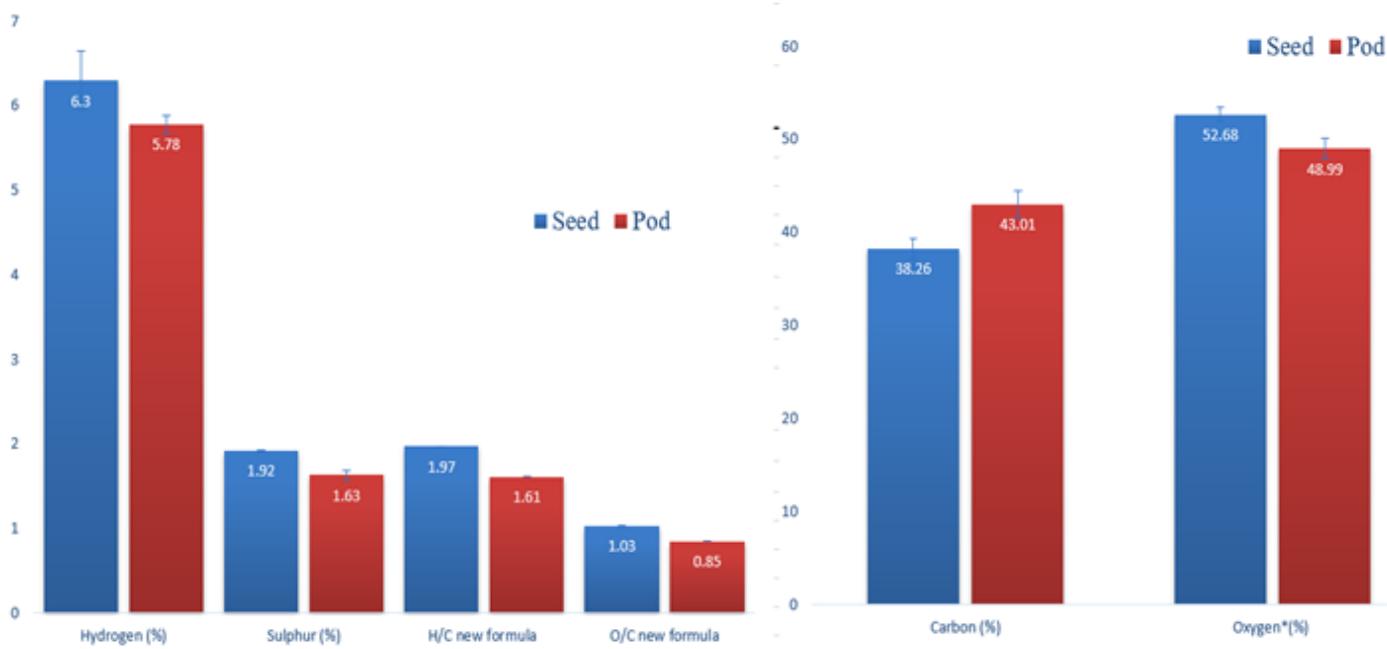
Figure 3: Ultimate analysis of biomass (O* Calculated by difference)

3.5. Thermogravimetry analysis

The major chemical composition of biomass is cellulose, hemicellulose, lignin, extractive, and ash. The chemical compositional similarity and the proximity in the proximate, ultimate and elemental analyses of the two analyzed materials in this study, could be responsible for the sameness of their different TG/DTG curves. The curves presented the initial weight loss from zero to 150 ℃ ascribed to moisture loss. The second weight loss (150 - 400 ℃) is due to the decomposition of hemicellulose and cellulose. While the pod presented a single peak at this temperature, the seed presented about two peaks, which suggests that there is hemicellulose/cellulose decomposition overlap in the pod but this was not so in the seed that presented two distinct peaks as revealed by the DTGA. Lignin being thermally stable than cellulose and hemicellulose were the last to be degraded. This experienced a long duration from 400 - 900℃. The seed experienced higher degradation energy at 357.36 ℃, while that of the pod was at 353.28℃, indicating
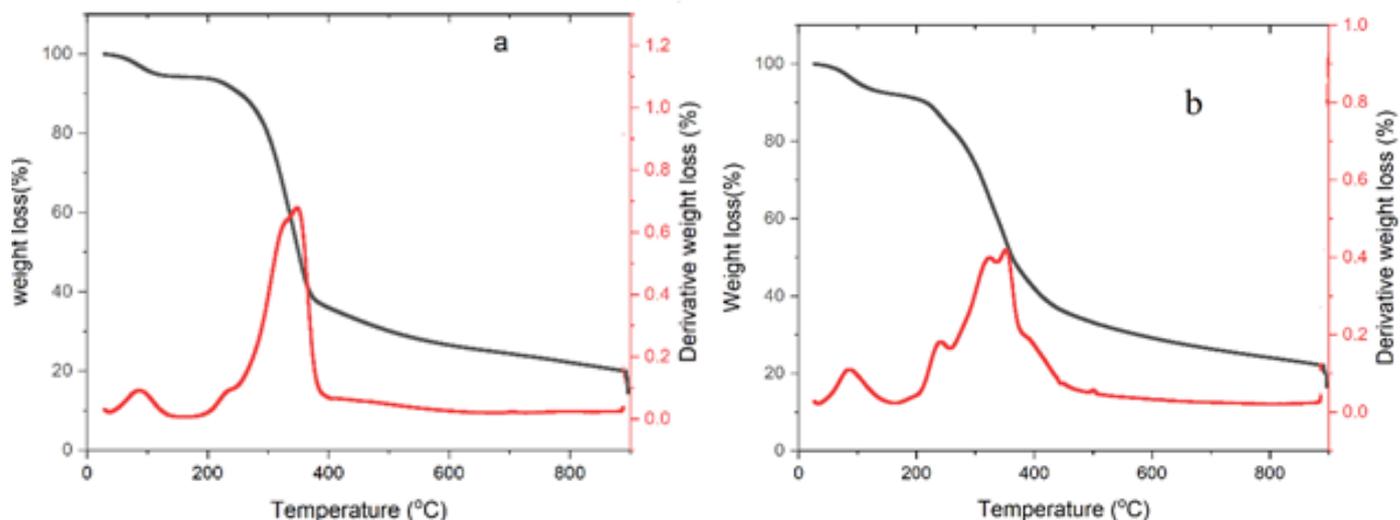
Figure 4: TG/DTG of pod (a) and seed (b)

Table 1: EDX Analysis result

Element (%)	Seed	Pod
Potassium	36.66	44.71
Sodium	1.33	Not detected
Calcium	6.11	4.5
Magnesium	7.36	1.98
Silica	Not detected	0.93
Phosphorous	10.81	1.00
Oxygen	37.73	46.83

that higher energy is required for degradation of the seed.

3.6. Morphology Characterization

The SEM investigation revealed a noticeable variance in the morphology of the seed and the pod of *Adenanthera pavonine*. When the pod appeared as a smooth surface, ball-like, and not too densely packed material, the seed presents a rough surface, flat-like, densely packed, and irregular shape material. Though, the two materials are composed of the same chemical composition the differences in the amount present and their location could have influenced the surface morphology

3.7. Kinetic and thermodynamics

Activation energy signifies the minimum energy that biomass must acquire before its main constituents (such as cellulose, hemicellulose, and lignin) can be converted to various pyrolytic products such as gas, liquid, and solid char. The higher activation energy ($23.78 kJmol^{-1}$) of the seed over that of the pod ($21.92 kJmol^{-1}$) can be linked to its high lignin content. Thermally lignin is stable than cellulose and hemicellulose, and higher energy is required in breaking the lignin bond. The high Ea of the seed agreed with the literature finding that the higher Ea of Kaner seed was as a result of its volatile constituents such as fatty acid [51]. Ea observed in this study are lower than 221-229

$kJ mol^{-1}$ (rice husk) [52] and tobacco residue [53]. The difference between the Ea and ΔH values for the seed and pod was found to be $9.72 kJmol^{-1}$ which is higher than approximately 5 $kJmol^{-1}$ reported to signify fastness in converting the biomass to products [54]. The higher Ea of the seed can be supported from the thermal analysis in which the seed's highest degradation temperature was higher (357.36 ℃) than that of the pod (353.28 ℃), revealing that much energy was consumed by the seed in breaking its components.

The energy released by biomass during pyrolysis is quantified by Gibbs free energy and values of $10.74 kJmol^{-1}$ (seed) and $10.98 kJmol^{-1}$ (pod) suggest a non-spontaneous process. The result implies that the pod will supply more bioenergy than the seed. The values obtained in this study were lower than those reported by [54]. The results of ΔH follow the same pattern as that of Ea, the seed has the higher value. Though, the positive ΔH predicts that heat would be absorbed during the breaking down of the precursor components. The lower ΔH value of the pod indicates that its products can be easily separated during pyrolysis. The higher ΔH recorded by the seed might be associated with its chemical composition because it contains high lignin and extractive contents. Both of which will require extra energy in bond breaking. The ΔH reported in this study was lower than those reported for Kaner seed, flaxseed, and microalgae with a 5 to 20 ℃/min heat rate [51]. The entropy ΔS reflects the disorderliness the biomass precursor underwent under chemical or physical treatment owing to thermal treatment [55]. The higher ΔS of the seed implies that it would be more reactive and require less reaction time to reach the activation complex, while the pod will experience the opposite [28]. Undoubtedly, The reactivity of the seed is not unconnected with its higher Ea and ΔH.

4. Conclusion

The bioenergy ability of the seed and pod of Adenanthera *pavonine* has been evaluated. The chemical composition of both ma-
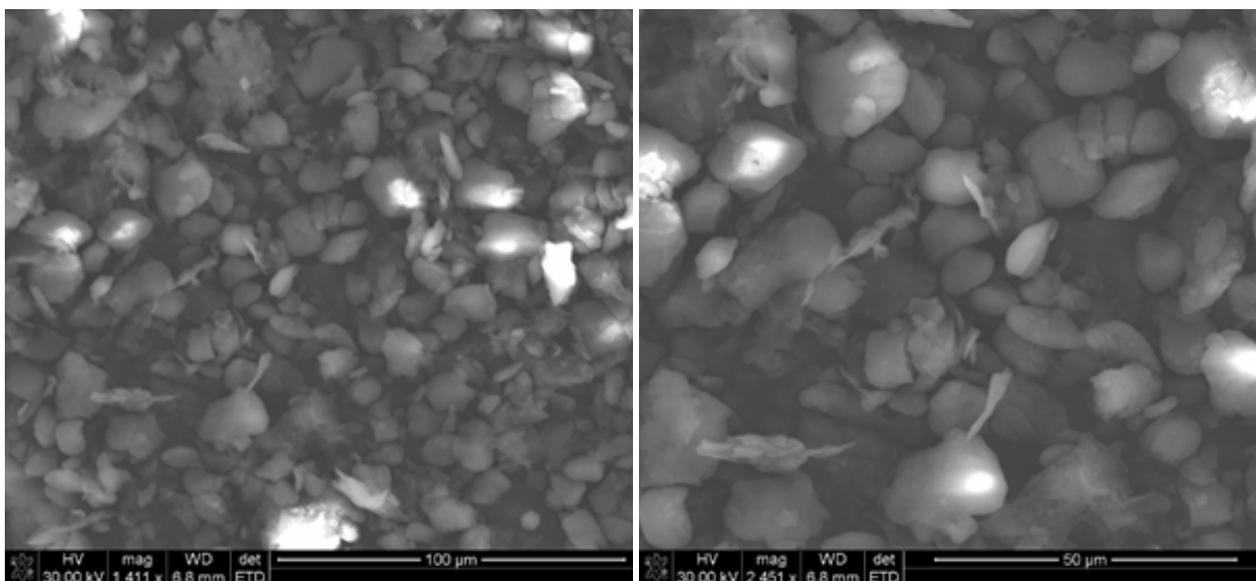
(a)
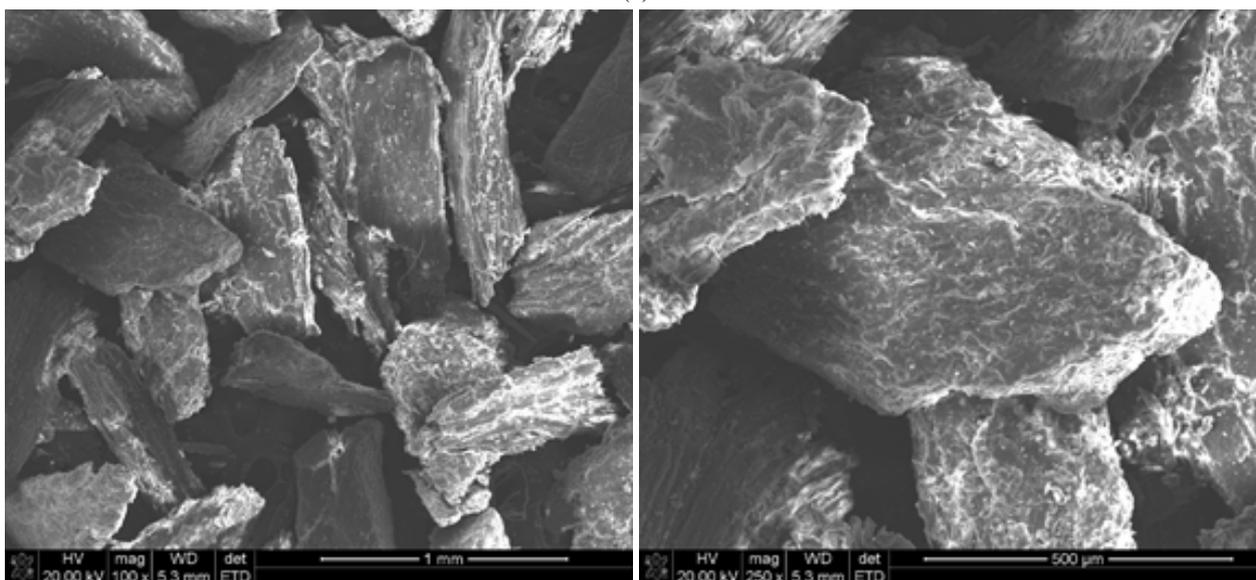
Figure 5: SEM of the pod (a) and seed (b)

Table 2: Kinetics and thermodynamics results

	Seed	pod	Ea-ΔH
Ea	23.78 kJ mol^{-1}	21.92 kJ mol^{-1}	9.72
A	0.01648985sec	0.0106400833sec	
R^2	0.9432	0.9433	
ΔS	-79.82 J mol^{-1}	-83.466 J mol-1	
ΔH	14.06 kJ mol^{-1}	12.20 kJ mol^{-1}	9.72
ΔG	10.74 kJ mol^{-1}	10.98 kJ mol^{-1}	

terials revealed the presence of lignocellulose constituents that can support biomass-bioenergy. The ultimate analysis showed that the materials have a high volatile matter, suggesting their good ignition ability and they could be used as composite for biomass with low ignition prowess. The high heating values recorded for the pod and seed were in tandem with the good bioenergy characteristic as suggested by the ultimate analysis, compositional analysis, and higher H: C fraction and lower O: C fraction of the pod and seed. The results have demonstrated that the seed and pod are good bioenergy candidates and the thermochemical conversion unit can be constructed from the generated data.

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