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Physico-Chemical Characterization of Nine Agricultural Biomasses of the Togolese Flora

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Abstract

Green coal or bio-coal is coal produced with rich biodegradable materials, elaborated from agricultural and household residues with a high percentage of carbon. This green charcoal (fuel briquettes) is an alternative to charcoal. Well known for its contribution to greenhouse gas emissions, charcoal is one of the causes of tree felling. The valorization of waste by the manufacture of biofuels could be an alternative to the use of charcoal. The general objective of the present study is the valorization of nine biomasses from Togo as raw materials. Specifically, physico-chemical characteristics such as dehydration, acidity, and conductivity were determined. Information on the structure and composition of the biomass was found. These data on the nature of the biomass were found through the use of Fourier Transform Infrared (FTIR) and Thermogravimetry (TGA). The promising results inform on the nature of the analyzed samples and allow the selection of the best biomass which would give an important thermal conductivity for the manufacture of the briquettes, but also of the binders to be used according to the physico-chemical characteristics like the pH.

Keywords

Biomass, Valorization, Briquettes, Material, Fuels, Physicochemical Characterization

1. Introduction

In today's industrialized world, raw materials and energy resources, particularly hydrocarbons and gas, have become a major concern on a global scale. Energy is an unavoidable need for all of us and it meets our basic needs. Thus, several human activities and various incomplete combustions of lignocellulosic biomasses, carbonization, and forest fires result in the release of nitrous oxide, carbon monoxide, and other harmful gases into the atmosphere and contribute negatively to the climate alert [1]. An evolution for a green world leans towards the use of chemicals, and more respect for the environment. Wood energy remains the main source of cooking energy in African countries. Its consumption is estimated at more than three quarters of household energy consumption. According to Abassi *et al.* [2], its consumption is largely dominated by 72% of firewood against the use of 28% for charcoal production. The use of wood as an energy source is very unevenly distributed in the world, and this depends mainly on the countries and their lifestyles. This concerns about 0.7% of industrialized countries and 20% of developed countries [3]. However, the interest in substitution of the so-called "traditional" energies for other forms of energy is extremely delicate to solving many problems, namely deforestation and pollution. The valorization of our products in the agricultural and agro-industrial sectors, which generates an enormous amount of waste after the use of agricultural products, allows the preservation of the fauna and flora. The energetic development of biomass makes it possible to overcome the problems facing our planet. Biomass consists mainly of carbon, hydrogen, and oxygen [4]. Moreover, it mitigates the effect of the very high air pollution caused by the use of gas and oil. The continuous increase of oil and gas prices (Russia-Ukraine war) on the world markets and in many European and African countries is alarming. Renewable energies offer nowadays important opportunities for economic development which are real in our localities and their mastery will allow the creation of numerous jobs. This energy constitutes a real economic source that allows an improvement and an intensification of the results in the agricultural and industrial sectors. Nine biomasses selected for the production of briquettes (peanut shells, palm nut shells, coconut shells, corn cobs, corn straws, corn stalks, cassava stalks, papaya stalks, and sawdust) will be characterized. This choice was made on the basis of the relative availability of these substrates in Togo and especially since these biomasses are not valued. Their abandonment pollutes our city and our districts and also clogs our gutters. The physico-chemical characteristics of these agro materials will be determined, because their knowledge allows identifying the quality of the biomass because their influence is determining the performance of briquettes. The thermal conductivity of a material designates its power to let heat through, and according to the Wiedemann-Franz-Lorenz law, there is a relationship between thermal and electrical conductivity. Moreover, in the choice of the binders to be used for the manufacture of biochars, the pH is important to know. Indeed, in order to limit the alkaline attacks as in the use of clay, it is necessary to make, consequently, the choice of the adapted materials based on the pH.

2. Material and Method

The plant material consisted of peanut shells. Other raw materials such as palm nut shells, coconut shells, corn cobs, corn straws, corn stalks, cassava stalks, papaya stalks, and sawdust constitute the biomass used in the manufacture of briquettes.

2.1. Preparation of the Raw Material

The nine collected biomasses were dehydrated. After the collection of the raw materials, a sorting was performed. Those with a size ranging from 10 cm to 15 cm were selected. They were then dried in an oven at 105˚C for 16 h or 24 h depending on the nature of the biomass. Once the drying is completed, a part is crushed for physico-chemical characterization. The rest is carbonized directly for the manufacture of ecological coal. This technique allows reducing the humidity contained in the fuel without chemical decomposition of the biomass.

2.2. Biomass Characterization

The following physico-chemical characterizations were carried out on the biomasses: acidity: the acidity was measured thanks to the pH-meter Hanna instruments PH 211/RS with the use of the standard AFNOR NF ISO 10-390 according to [5] [6]. Conductivity: It was measured with the conductivity meter model cond 3110 serial number 20,311,469 with a precision of the conductivity measurement 0.5% of the measured value ± 1 digit. Fourier Transform Infrared (FTIR) was performed using Bruker VERTEX 70 spectrometer with an absorption band range between 400 and 4000 cm^{-1}. Thermogravimetric Analysis (TGA) of the samples was performed by a TG 209 F1, ASC-Netzch apparatus in a dry environment with a heating rate of 10˚C/min at room temperature at 1000˚C.

3. Results and Discussion

3.1. Study of Dehydration

Before the carbonization stage or the actual manufacture of the consolidated material, the dehydration process is essential. The drying of the biomass was carried out in an oven at 105˚C. The mass variation of the biomass is determined and the process is stopped when the mass becomes stable. The loss of water mass in the sample varies from 5% to 25%; % H_{bs} (10.37, 6.4, 5.6, 7.46, 8.56, 12.49, 20.48, 19.20, 5.6) and % H_{bh} (9.4, 6, 5.28, 6.94, 7.89, 11.1, 17, 16.11, 5.28) for the biomasses (**Table 1**).

3.2. pH Measurement

The performance and quality of the briquettes are determined from physico-chemical parameters such as pH, density, etc. The pH of the uncharred residues is all acidic or close to neutral for some before charring as shown in **Table 2**. These elements all become basic but the most basic are palm kernel shells, coconut shells and corn stalks which have pH of 10.23, 10.27 and 10.06 respectively, as shown in **Table 3**. This increase in pH is due to the addition of the binders and the effect of carbonization performed during the briquette design process. Biomass with higher pH values performs better.

Table 1. Dehydration of biomass before analysis.

	Mass before the oven	Mass after the oven	$\%H_{bs}$	$\%H_{bh}$
Peanut shell	100 g	90.6 g	10.37	9.4
Palm kernel shell	100 g	94.0 g	6.4	6
Coconut shell	100 g	93.98 g	5.6	5.28
Corn raid	100 g	93.06 g	7.46	6.94
Corn straw	100 g	92.11 g	8.56	7.89
Corn stalk	100 g	88.9 g	12.49	11.1
Cassava stem	100 g	83 g	20.48	17
Papaya stem	100 g	83.89 g	19.20	16.11
Sawdust	100 g	94.72 g	5.6	5.28

$\%H_{bs}$ and $\%H_{bh}$ = percentage in moisture content.

Table 2. Physico-chemical characteristics (pH and conductivity) for non-carbonized material.

Material	pH	σ
Peanut shell	5.27	1.426 ms/cm
Palm kernel shell	6.15	1.297 ms/cm
Coconut shell	6.32	2.110 ms/cm
Corn raid	5.97	1.110 ms/cm
Corn straw	6.21	2.03 ms/cm
Corn stalk	7.44	1.768 ms/cm
Cassava stem	7.71	1.115 ms/cm
Papaya stem	7.27	0.993 ms/cm
Sawdust	6.27	1.049 ms/cm

Table 3. Physicochemical characteristics (pH and conductivity) for carbonaceous material.

Material	pH	σ
Peanut shell	9.15	1.446 ms/cm
Palm kernel shell	10.23	2.140 ms/cm
Coconut shell	10.27	10.040 ms/cm
Corn raid	9.68	4.200 ms/cm
Corn Straw	8.64	0.962 ms/cm
Corn stalk	10.06	9.020 ms/cm
Cassava stem	9.52	7.880 ms/cm
Papaya stem	9.27	6.260 ms/cm
Sawdust	7.46	1.257 ms/cm

3.3. Infrared Characterization of Biomasses

This technique can provide information on the nature, reactivity and arrangement of surface functional groups. Reflectance can be used to determine the chemical bonds of a sample. This method requires very little sample preparation and can be used to analyze both liquids and solids. In this technique, the wave penetrates only a few microns into the sample and it also allows to do surface characterization, as in the case of materials. The advantage of this technique in the preparation of the sample is that it allows analyses on raw samples. The Fourier transform infrared spectra of the studied samples (**Figures 1-9**) reveal several peaks that can be identified as follows: in all figures appear, in the interval 3327.21 - 3339 cm^{-1}, peaks that correspond to the stretching vibration of the OH and N-H groups [7]. The stretching vibrations of the aliphatic C-H alkyl groups present in the cellulose and hemicellulose of the studied biomaterials, appear in the interval 2822.31 - 2919.37 cm^{-1}. The peaks recorded in the interval 1632.76 - 1732.76 cm^{-1} correspond to the valence vibrations of the carbonyl group C=O as in carboxylic acids. The bands recorded between 1506.68 cm^{-1} and 1634.56 cm^{-1} can be attributed to C-O carboxylic groups (**Table 4**).

3.4. Thermal Analysis of Biomass

To characterize the thermal behavior of the biomass, a thermal analysis was performed. A mass of 3.7729 mg of sample powder was measured under nitrogen atmosphere with a heating rate of 20˚C/min. The crucible used is made of aluminum oxide (Al_2O_3). Thermogravimetric Analysis (TGA) is a technique that

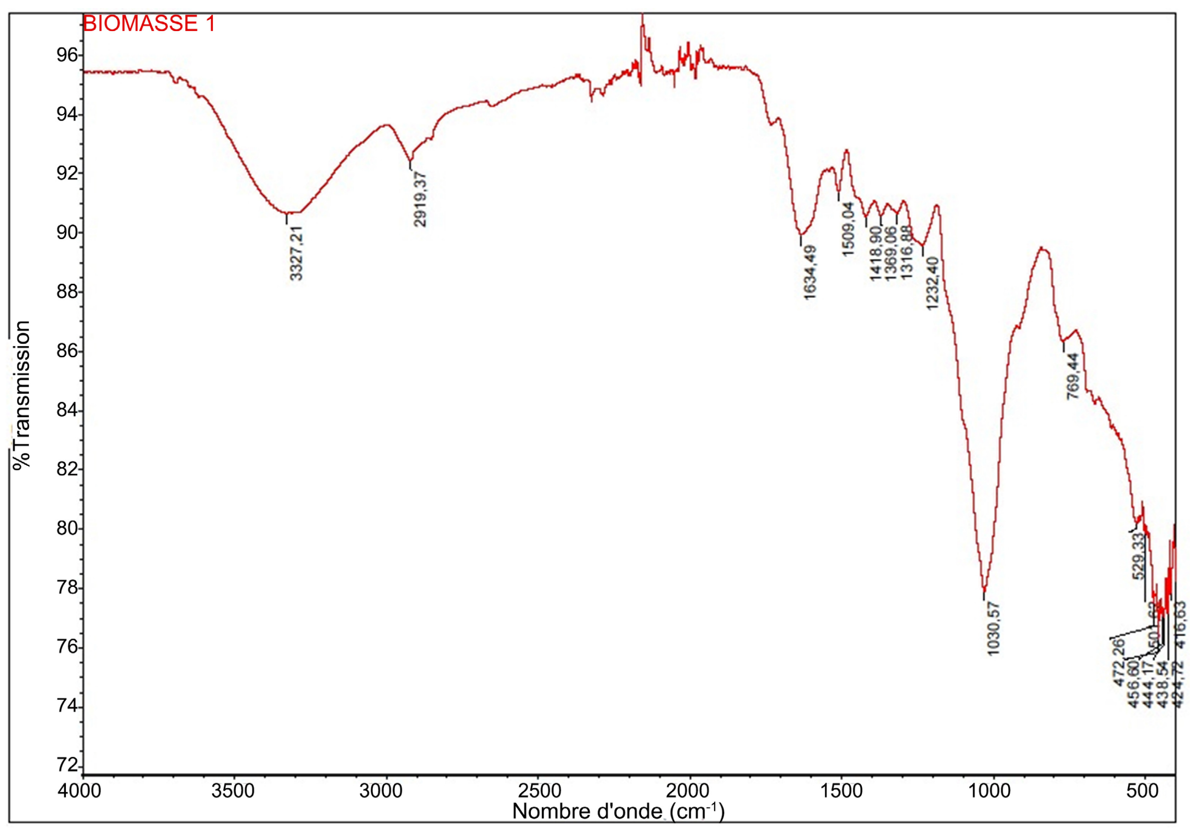

Figure 1. Infrared on the peanut shell.

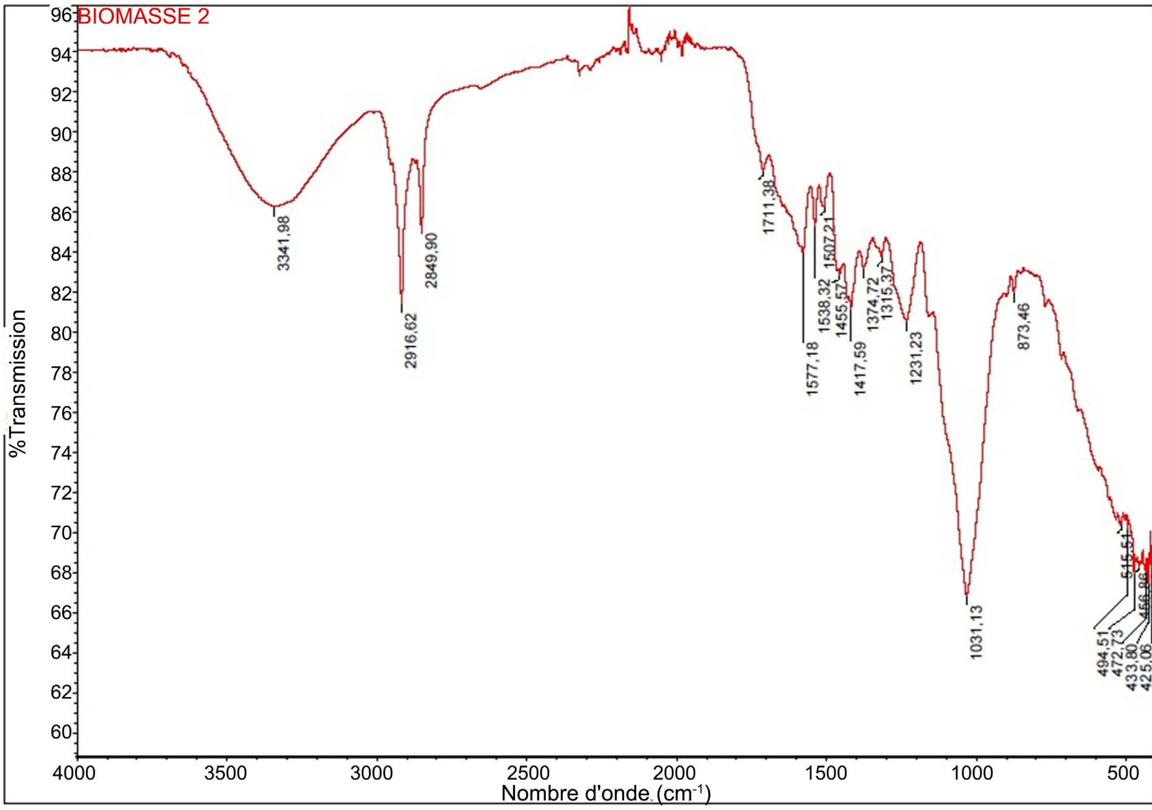

Figure 2. Infrared on the palm hull.

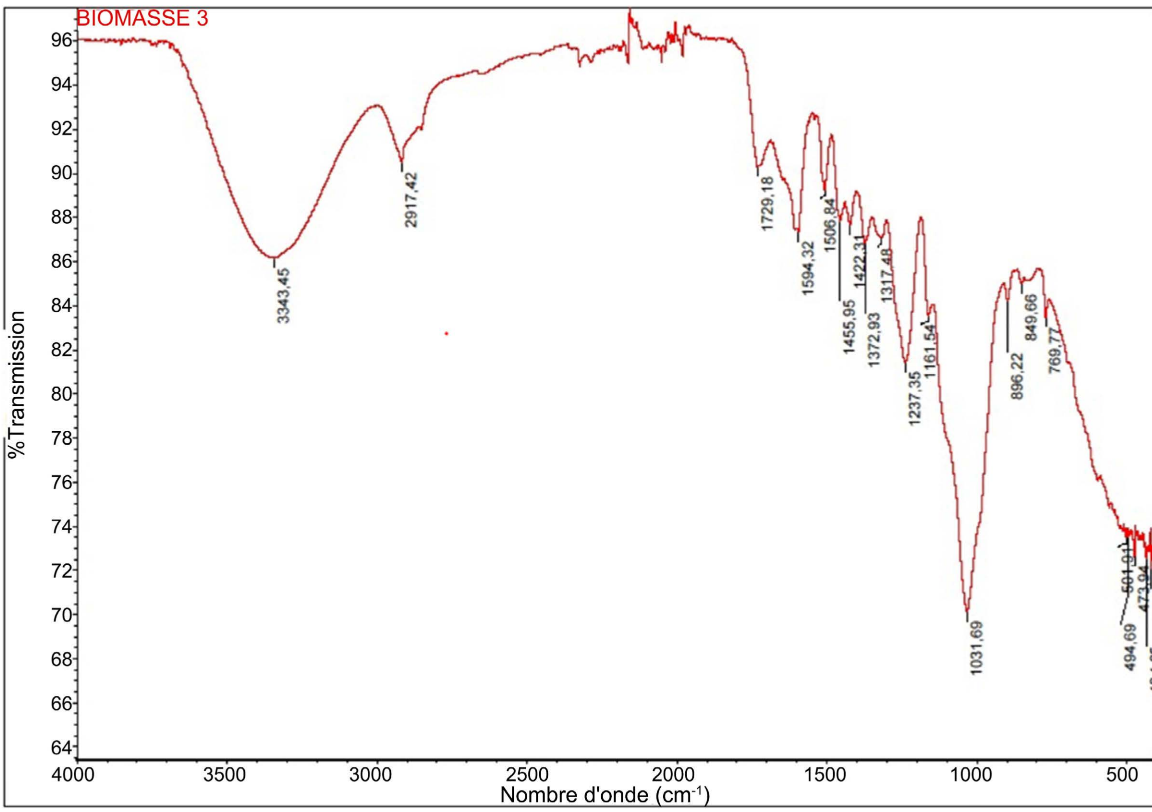

Figure 3. Infrared on the coconut shell.

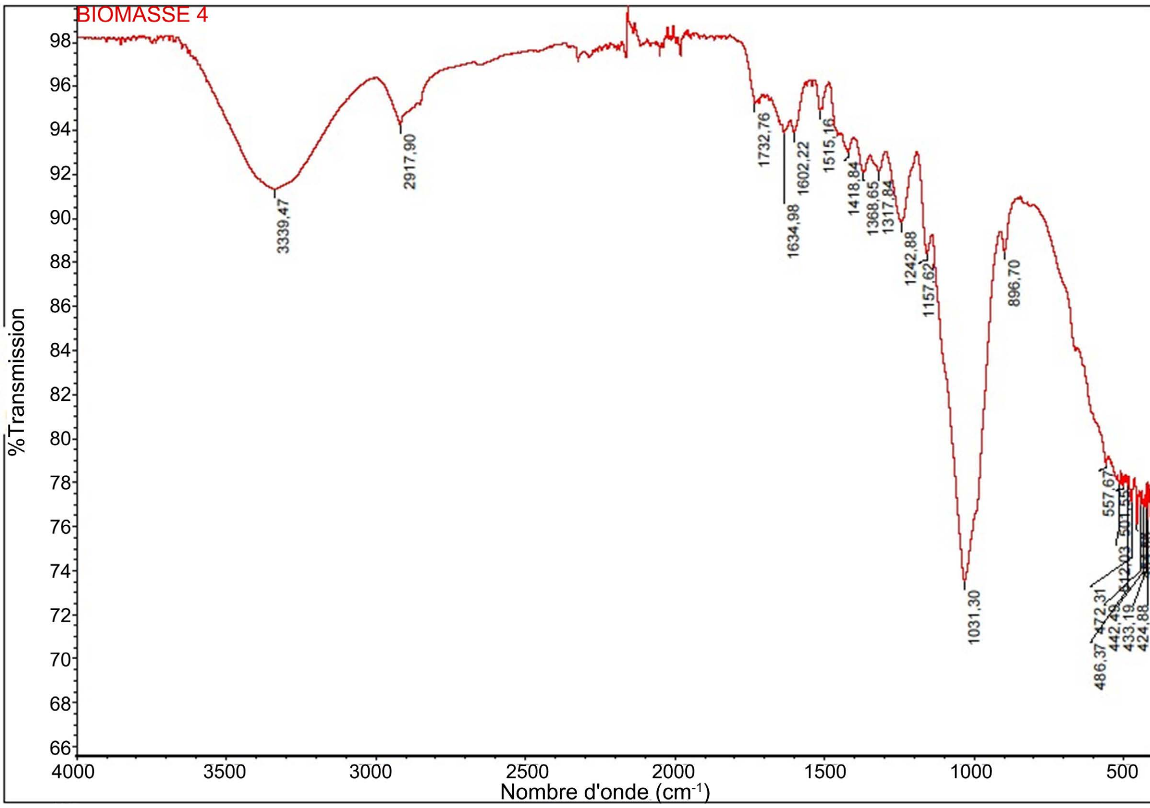

Figure 4. Infrared on corn cobs.

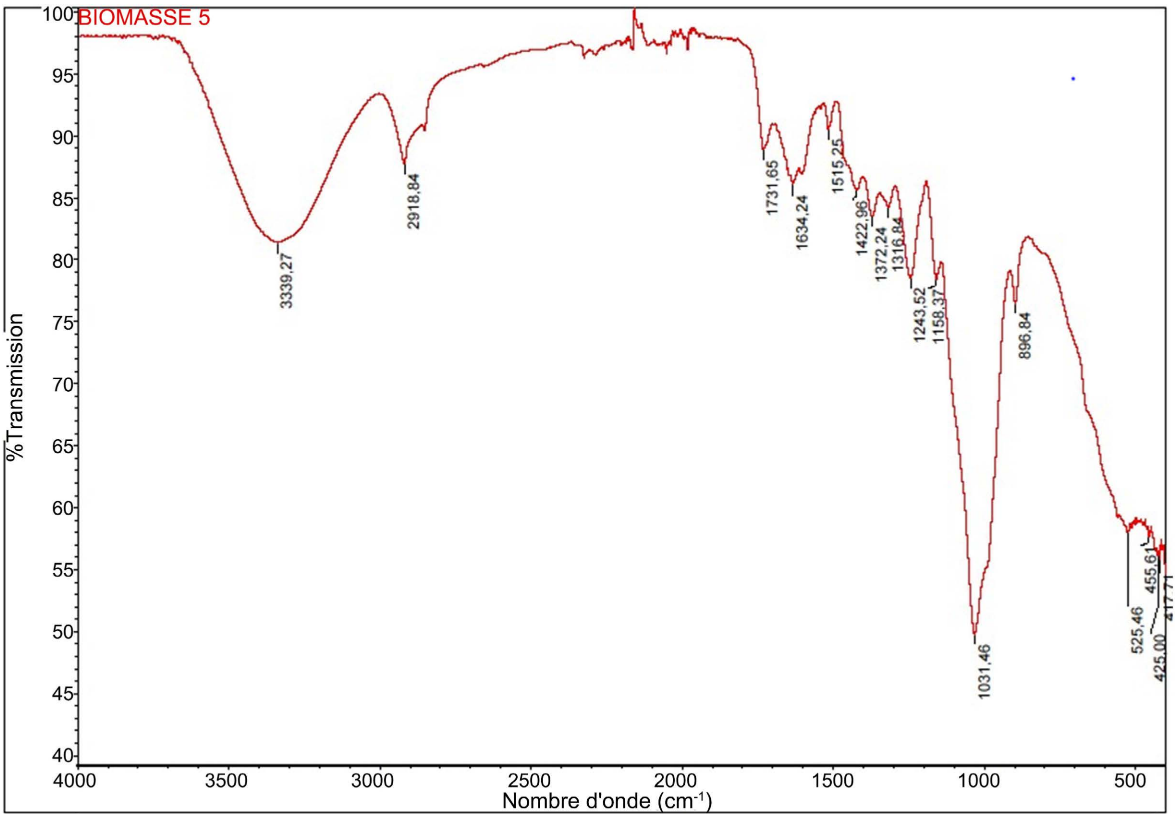

Figure 5. Infrared on corn straw.

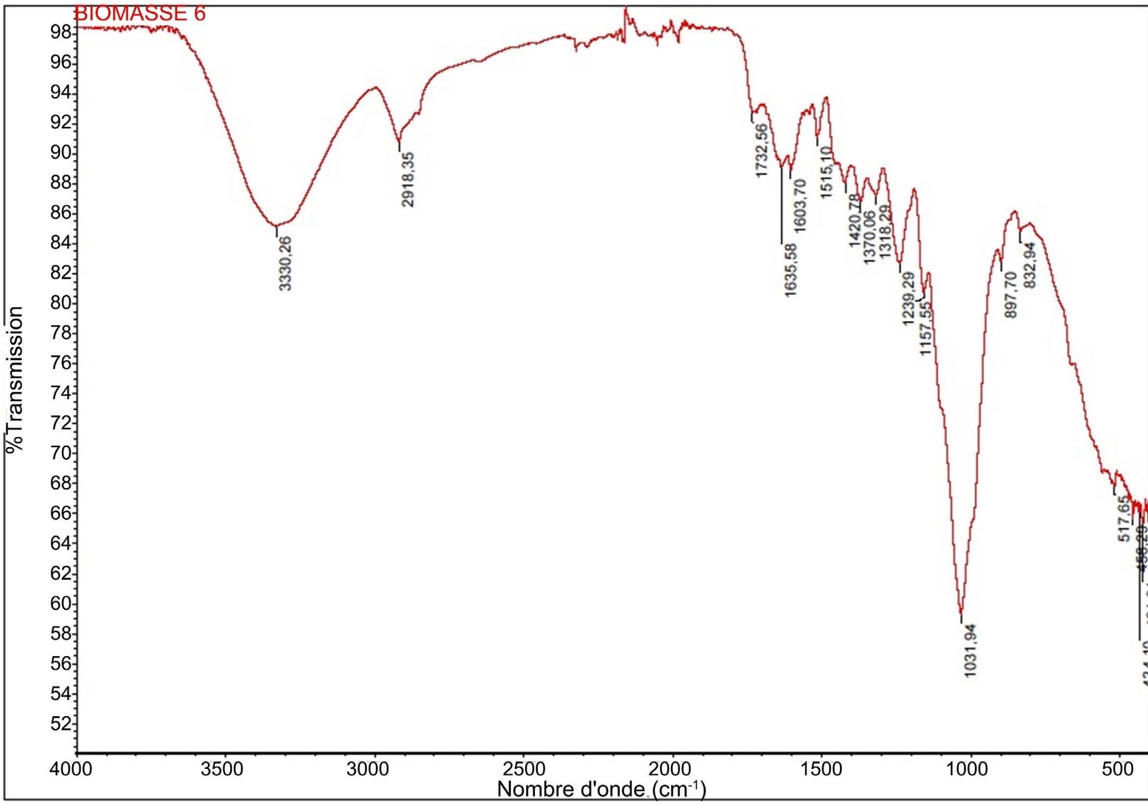

Figure 6. Infrared on the corn stalk.

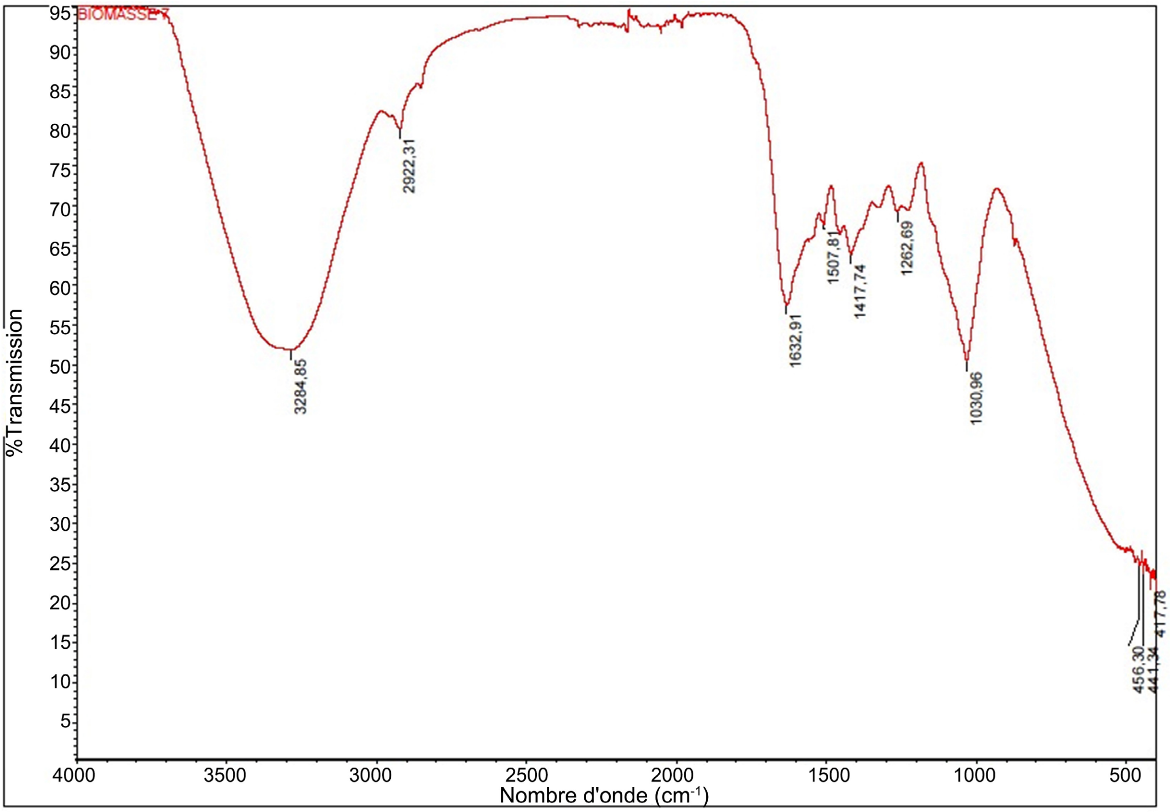

Figure 7. Infrared on the cassava stem.

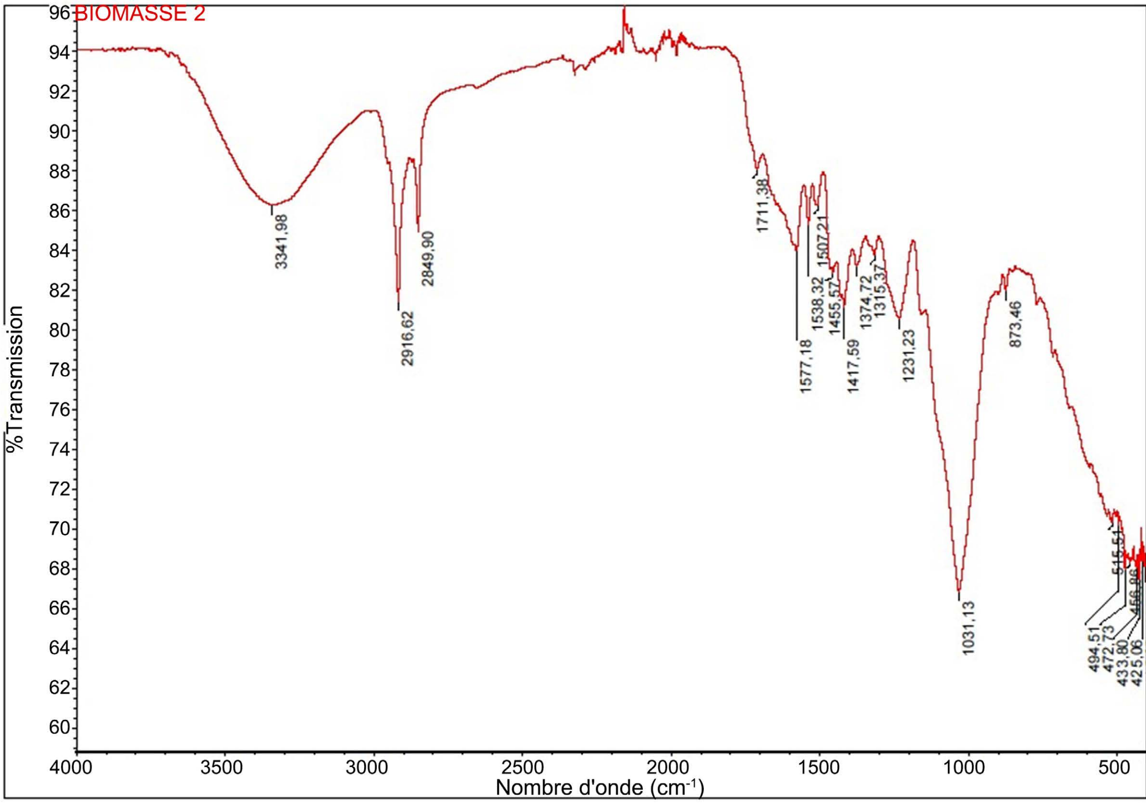

Figure 8. Infrared on the papaya stem.

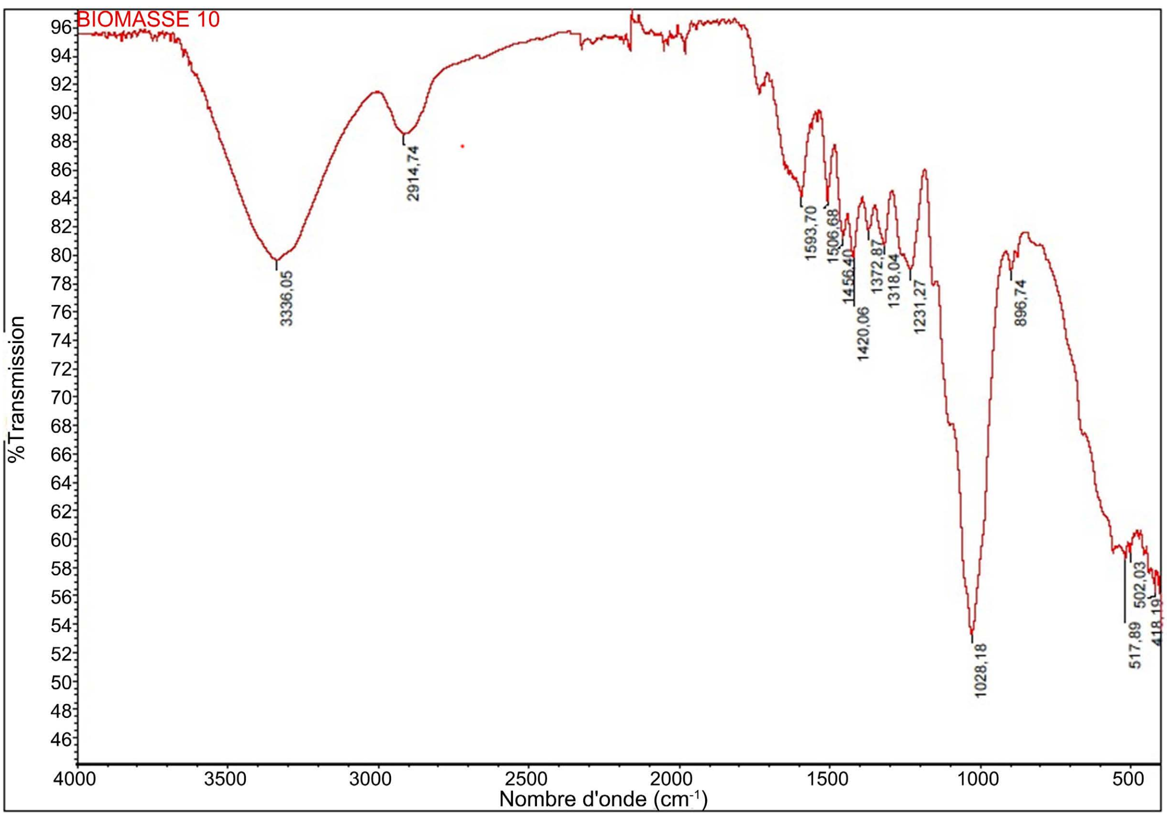

Figure 9. Infrared on sawdust.

has been used extensively to study biomass pyrolysis [8]-[15]. Peanut shells, papaya stems and sawdust show two peaks. The first loss of mass which is found between 25˚C to 125˚C, denotes the first peaks corresponding to a loss of 6.49% of the total mass for peanut shells. Between 125˚C - 175˚C a loss of 7.90% is observed for the papaya stems and 7.37% for sawdust. The second loss of mass for these three samples is in the temperature range of 125˚C to 1000˚C with 79.91% for peanut shells, 80.40% for papaya stems and 82.33% for sawdust. These changes are due to a loss of free water contained in the biomass after drying the material. The second loss can be segmented into several steps and between 170˚C to 600˚C,

Table 4. Summary of Infrared data.

	Liaison OH	Liaison C-H	Liaison C=O	Liaison C-O
Peanut shell	3327.21 cm^{-1}	2919.37 cm^{-1}	1634.49 cm^{-1}	1509.04 cm^{-1}
Palm kernel shell	3341.98 cm^{-1}	2916.62 cm^{-1}	1711.38 cm^{-1}	1577.18 cm^{-1}
Coconut shell	3343.45 cm^{-1}	2917.42 cm^{-1}	1729.18 cm^{-1}	1594.32 cm^{-1}
Corn raid	3339.47 cm^{-1}	2917.90 cm^{-1}	1732.76 cm^{-1}	1634.98 cm^{-1}
Corn straw	3339.27 cm^{-1}	2918.84 cm^{-1}	1731.65 cm^{-1}	1634.24 cm^{-1}
Corn stalk	3330.26 cm^{-1}	2918.35 cm^{-1}	1732.56 cm^{-1}	1635.58 cm^{-1}
Cassava stem	3284.85 cm^{-1}	2922.31 cm^{-1}	1632.91 cm^{-1}	1507.81 cm^{-1}
Papaya stem	3326.27 cm^{-1}	2918.42 cm^{-1}	1635.24 cm^{-1}	1507.29 cm^{-1}
Sawdust	3336.05 cm^{-1}	2914.74 cm^{-1}	1593.70 cm^{-1}	1506.68 cm^{-1}

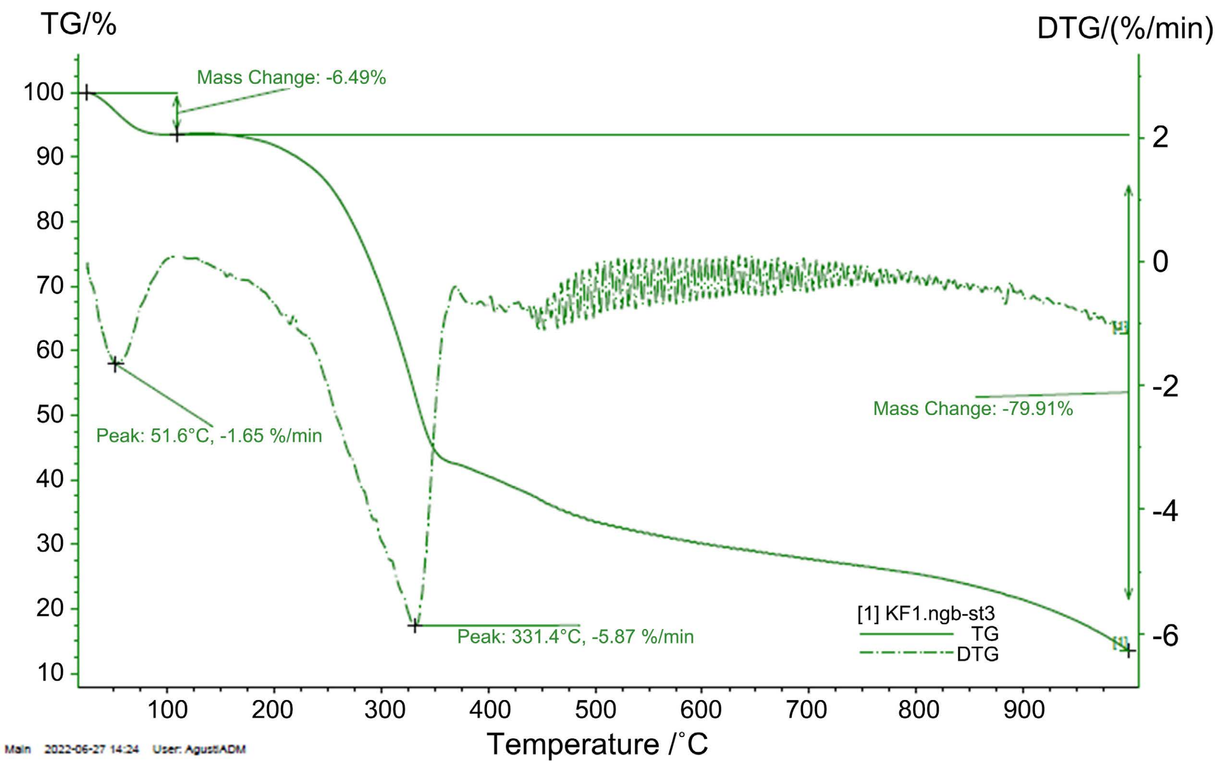

Figure 10. Thermal analysis on peanut shells.

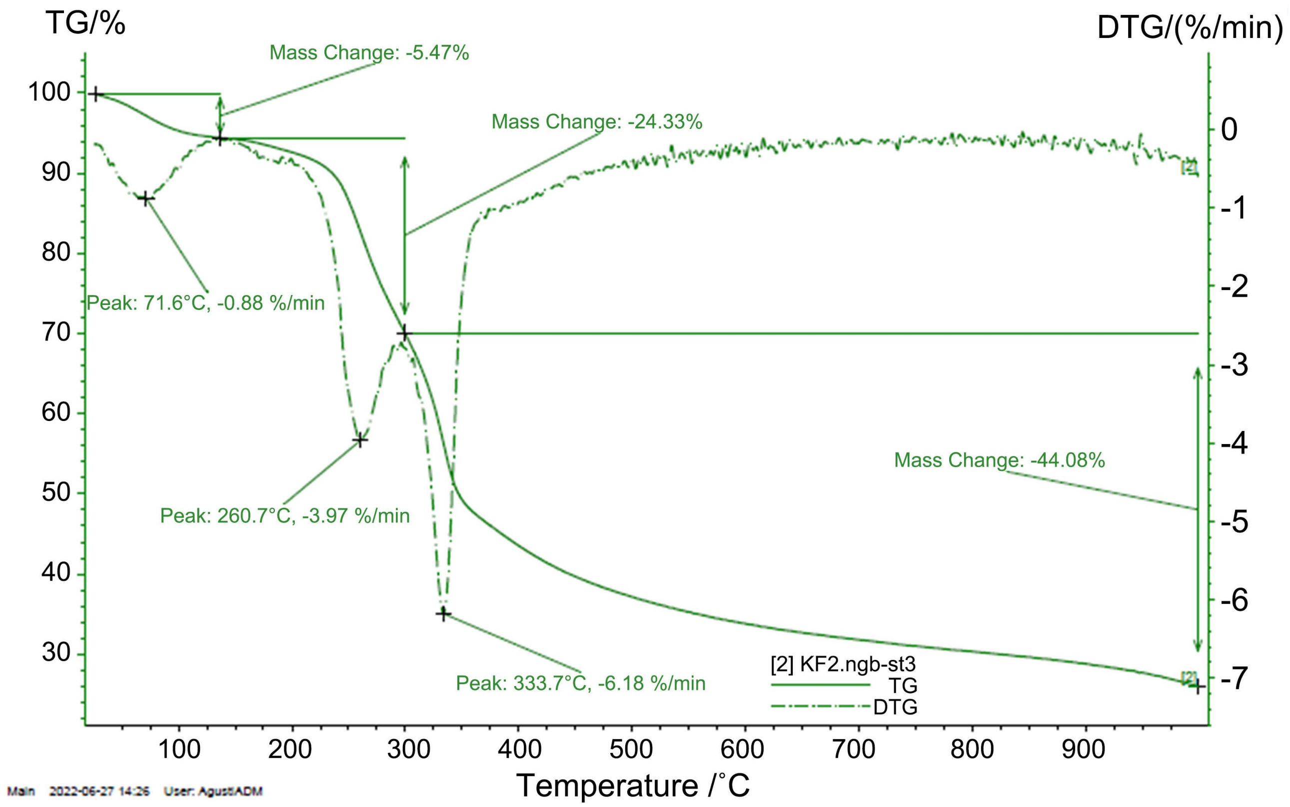

Figure 11. Thermal analysis of palm kernel.

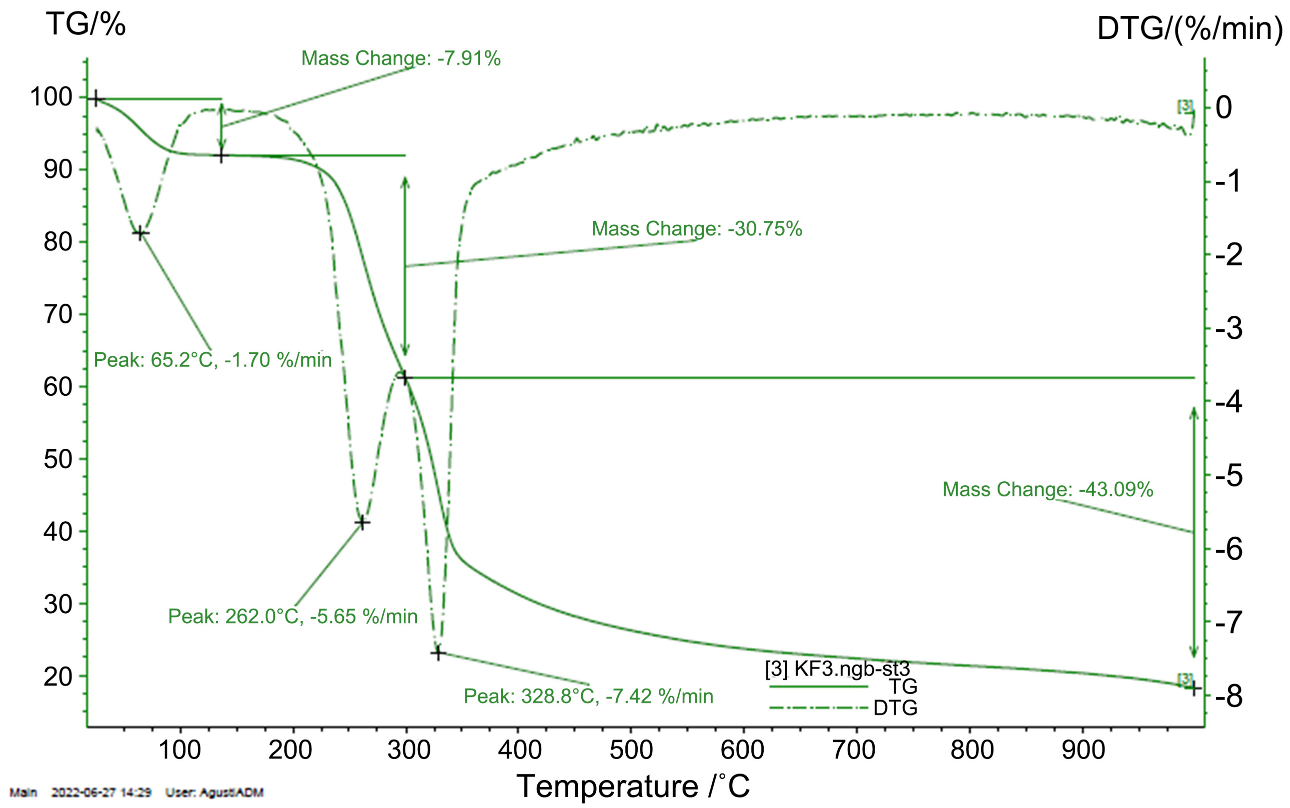

Figure 12. Thermal analysis on coconut shell.

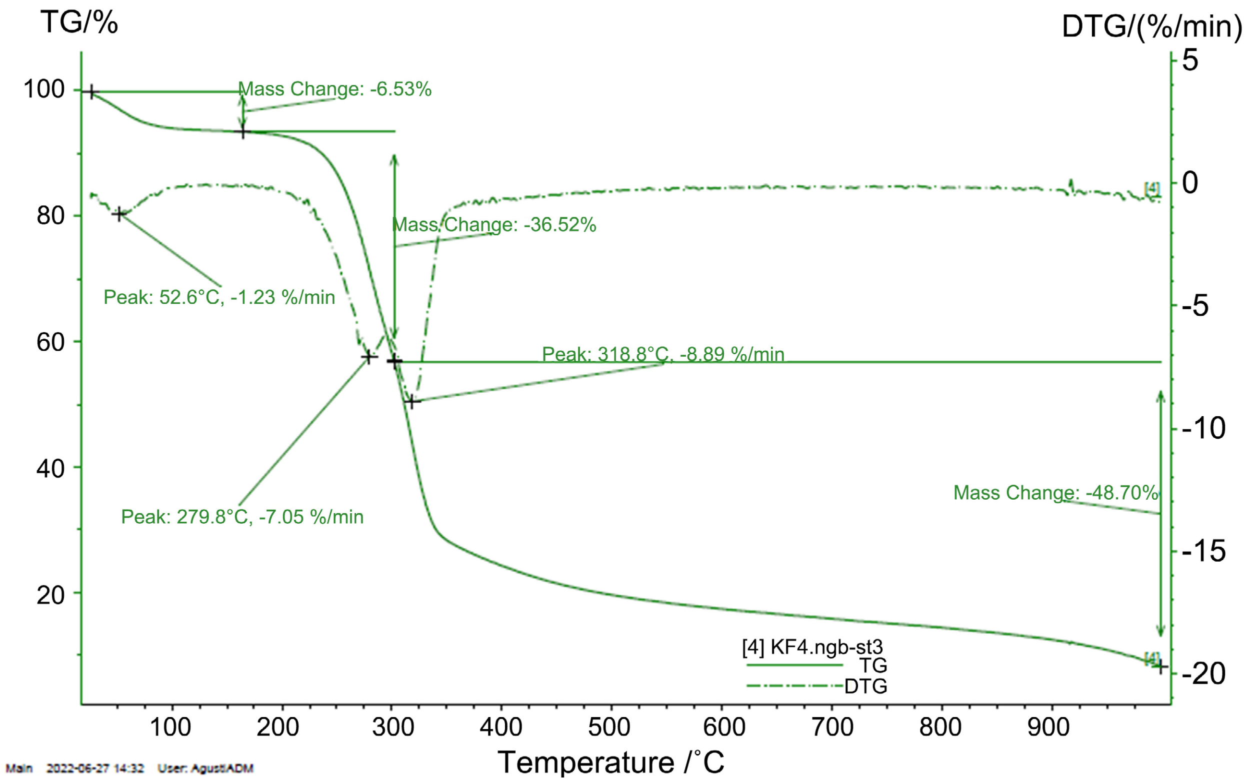

Figure 13. Thermal analysis of corn cobs.

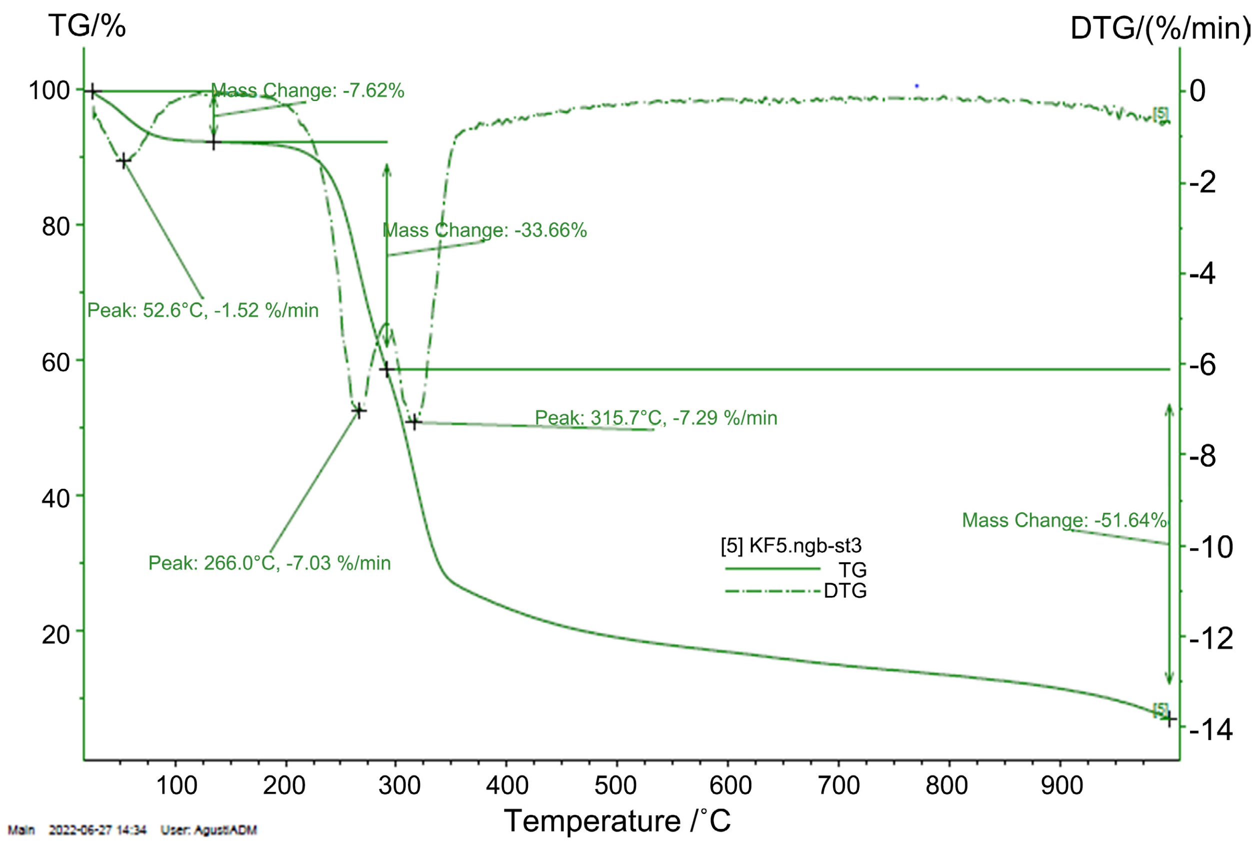

Figure 14. Thermal analysis of corn straw.

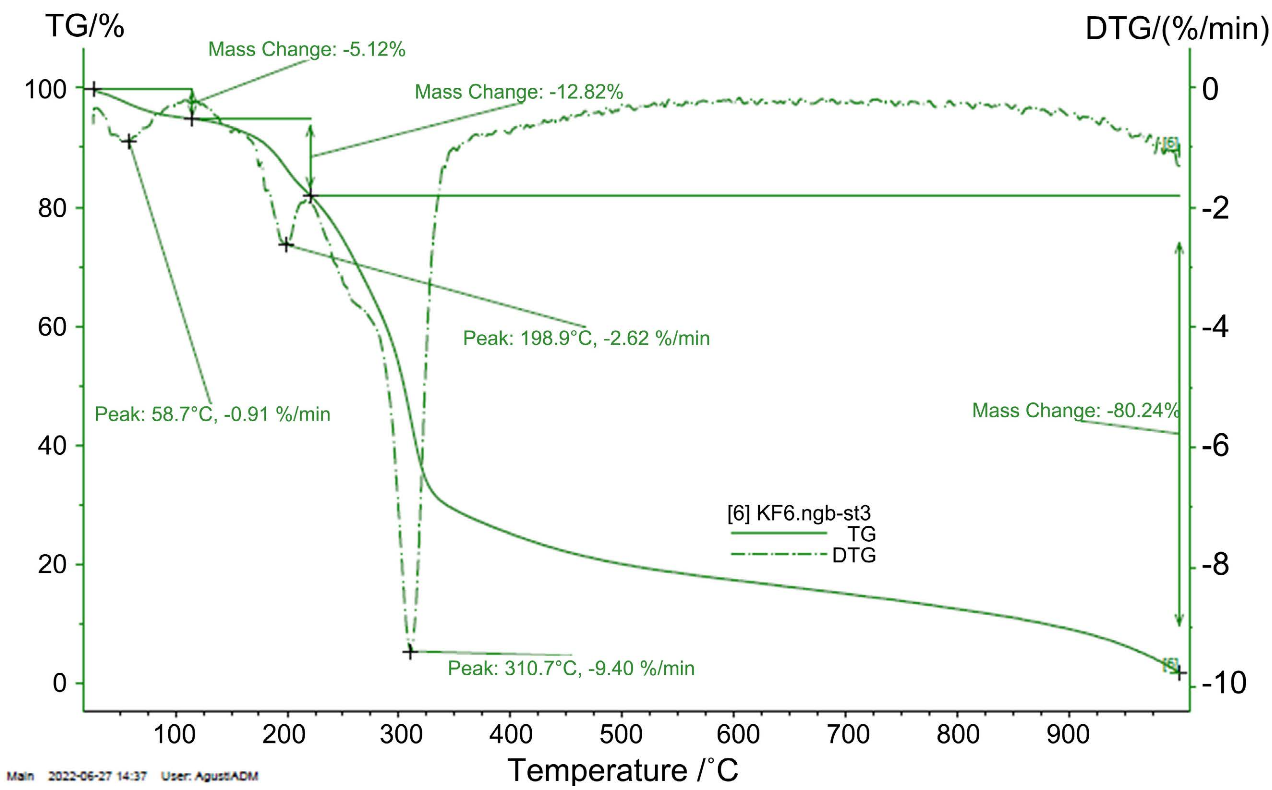

Figure 15. Thermal analysis on the corn stalk.

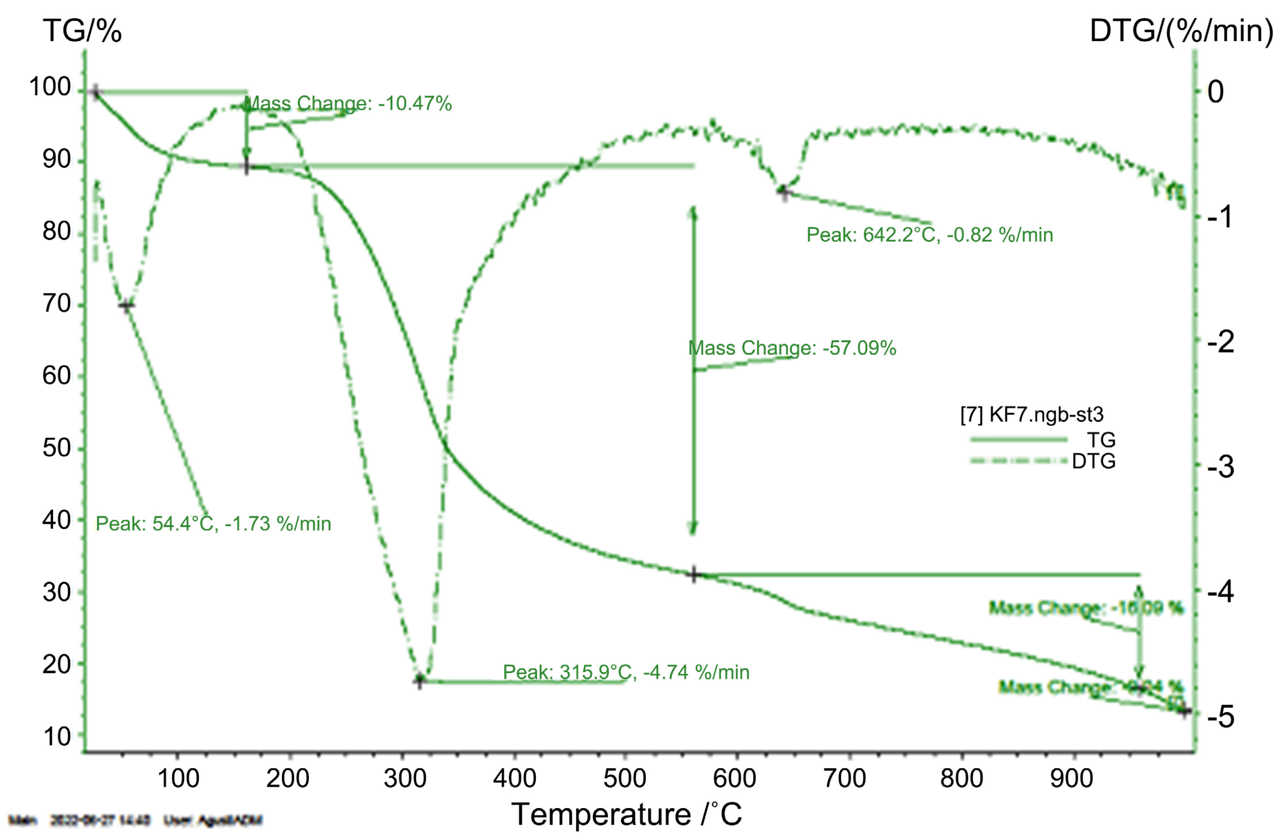

Figure 16. Thermal analysis on cassava stem.

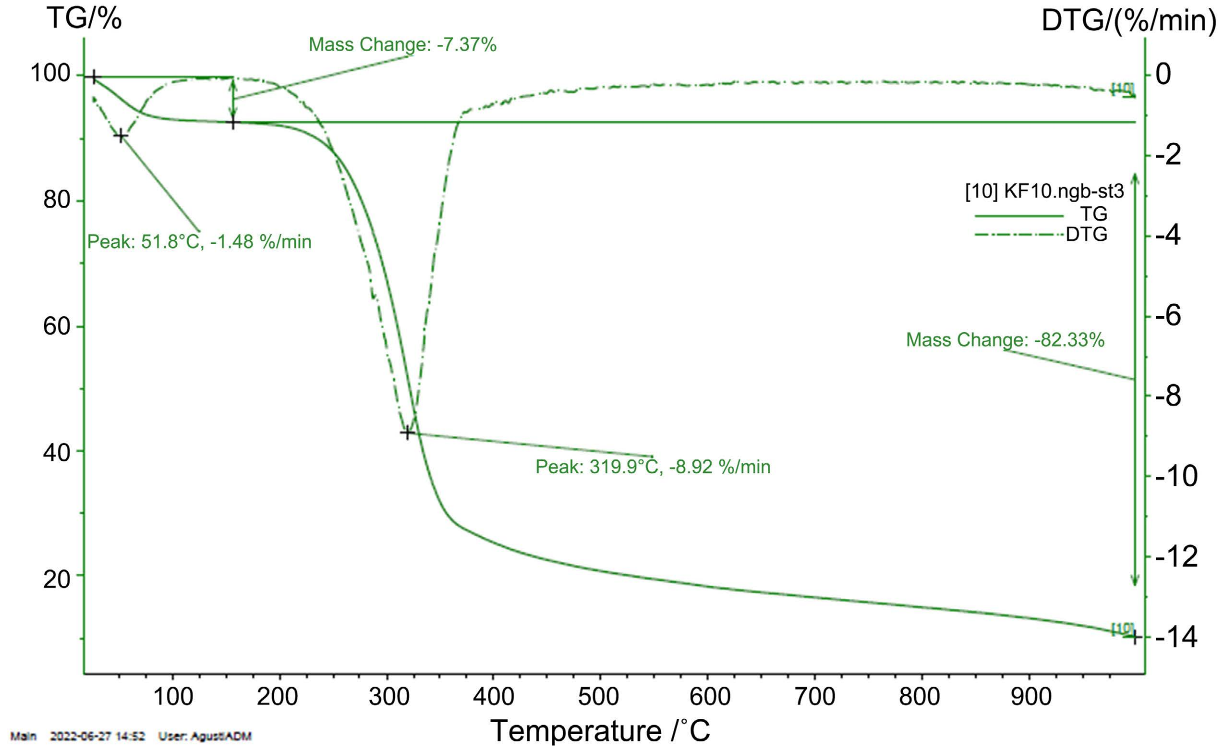

Figure 17. Thermal analysis on the papaya stem.

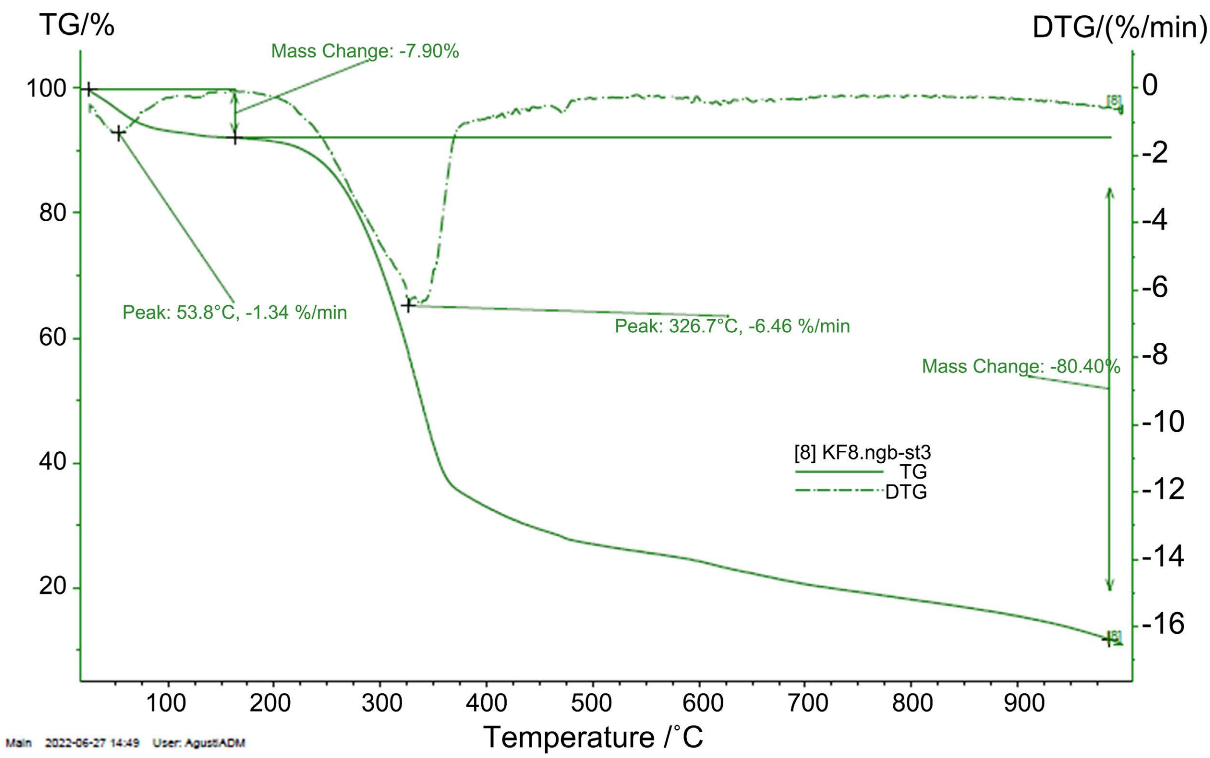

Figure 18. Thermal analysis on sawdust.

according to [8] it refers to the volatile organic matter. According to the theory [9]-[21], that the main constituents of the biomass, cellulose, hemicellulose and lignin, decompose thermochemically in the following temperature range: 150˚C - 350˚C, 275˚C - 350˚C, 250˚C - 500˚C, respectively. Still in the second loss, there is a loss of structural water, linked to OH hydroxyl groups, which starts from 500˚C. Palm hulls, coconut shells, corn cobs, corn straws, corn stalks, and cassava stalks show three peaks. Between 25˚C and 150˚C the first losses are respectively 5.12% to 10.47%. These losses correspond to a loss of free water or surface water contained in the biomass. The second mass loss for the biomass having three peaks is 12.82% to 57.09% spread respectively over the temperature interval from 150˚C to 300˚C with a last step which shows a mass loss is 16.09% to 80.24% between 300˚C to 1000˚C (**Figures 10-18**).

4. Conclusion

On a planetary scale, the demand for energy has not ceased to increase since the 1970s due to the exponential growth of the population, but the crisis linked to the war in Ukraine has shown that the search for other alternatives is necessary, especially in developing countries. After the analysis of the biomasses produced from the Togolese flora, physico-chemical characteristics such as acidity, conductivity, and density were determined. Information on the structure and composition of the material is found through ThermogravimetricAnalysis (TGA) and the use of Fourier Transform Infrared (FTIR). The promising results provide information on the nature of the analyzed samples and allow the selection of the best biomass in the manufacturing of briquettes.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this article.

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