

# Extraction and Physicochemical Characterization of Lignin from Cameroon's Three Raffia Palm Species (*Raffia Farinifera*, *Raffia Hookeri* and *Raffia Vinifera*) and Africa Oil Palm (OPEFB)

Beckley Victorine Namondo\*, Ekane Peter Etape, Josepha Foba-Tendo, Fomogne Cyrille Yollandev, Mih Vanacius Nsom, Nzegge William

Department of Chemistry, Faculty of Science, University of Buea, Buea, Cameroon

## Email address

[namondo31@gmail.com](mailto:namondo31@gmail.com) (B. V. Namondo)

\*Corresponding author

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**Abstract:** The goal of this study was to extract lignin from palm cellulosic biomass (*Raffia Farinifera*, *Raffia Hookeri* and *Raffia Vinifera*) and one species of Africa Oil palm (OPEFB) by Klaxon and organosolv processes for potential use as a partial replacement for the phenol precursor in resole phenolic systems. The isolated lignin samples were purified and characterized by Fourier transform Infrared Spectroscopy (FTIR), Thermogravimetric analysis (TGA/DTG) to compare the thermal properties, proximate analysis to compare the chemical composition, Scanning Electron Microscopy coupled to Electron Diffraction spectroscopy (SEM/EDS) to compare the morphology and the chemical composition of the samples. Analyses based on FT-IR finger print spectral region revealed no significant qualitative differences in the functional groups of the different lignin. However, chemical compositional, morphological and thermal analyses indicated that the lignins isolated by klaxon method were thermally more stable and had a greater char yield which ranged from 46-54% while the source of the lignin sample by plant species and part of the plant was observed to affect the thermal properties. Generally, the variability observed was within the range of plants of the same species. SEM / EDS analysis showed that all the sample fibers were covered with silica bodies embedded in defined craters and the silica bodies were elementally composed of silicon and oxygen.

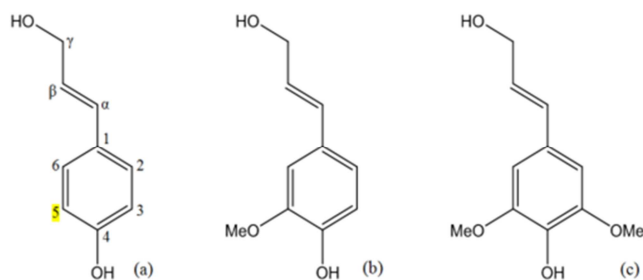
**Keywords:** Raffia Palm Fibers, Lignin, Chemical Composition, Thermal Stability, Morphology

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## 1. Introduction

Lignin is a plant component with important implications for various agricultural disciplines. It confers rigidity to cell walls, and is therefore associated with tolerance to abiotic and biotic stresses and the mechanical stability of plants [1]. It makes up about 20-40% of wood and annual plants (depending on the species). Together with cellulose and hemicellulose, they form lignocellulose, which is the main constituent of plant cell walls, with lignin acting as a linker

between sets of cellulose and hemicellulose. As a natural polymer, Lignin is traditionally formed from three monomers, the so-called monolignols (p-coumaryl, coniferyl, and sinapyl alcohols) shown in Figure 1 [2]. These alcohol sub units lead respectively to the Characteristic constituent units of lignin; guaiacyl (g), syringyl (S) and p-hydroxyphenol propane (p-H). The structure of the monolignols differ only by the number of substituted methoxy groups at the phenyl ring.

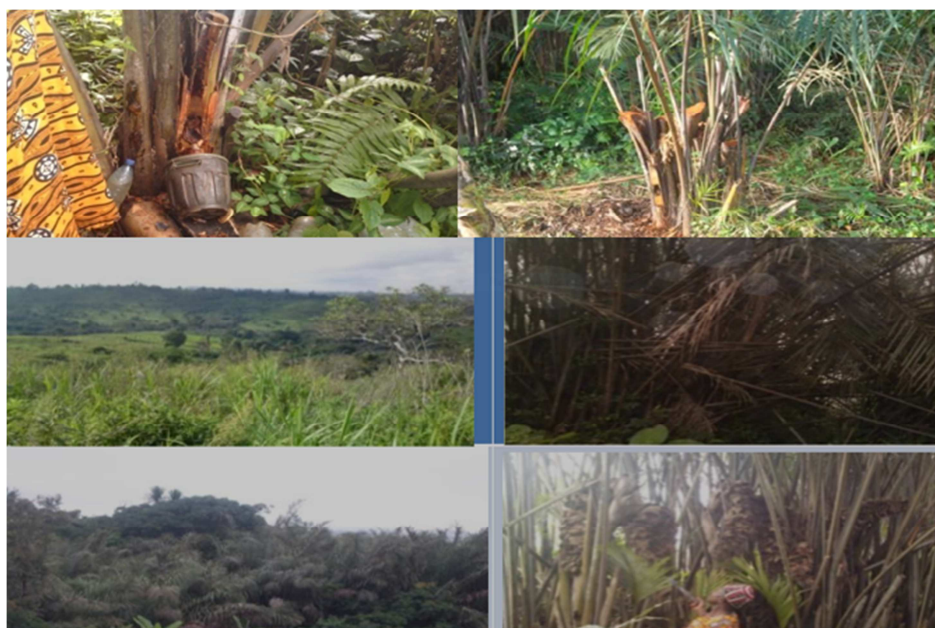


**Figure 1.** Lignin monomers: (a) *p*-coumaryl, (b) coniferyl and (c) sinapyl alcohols.

One of the ways to obtain lignin is by direct isolation from the plants and the Lignin are classified according to the precursors of the polymer. Guaiacyl lignin (G) is typical of softwood species and it is formed mostly of trans-coniferyl alcohol precursors, with the remainder consisting mainly of trans-*p*-coumaryl alcohol which contains *p*-hydroxyphenyl (H) units. In contrast, generally guaiacyl-syringyl (GS) lignins found in hardwood species are mainly composed of trans-coniferyl alcohol and trans-sinapyl alcohol type units in varying ratios. Grass lignins are also classified as guaiacyl-syringyl lignins, although they contain some structural units derived from trans-*p*-coumaryl alcohol and some aromatic acid residues [3]. Lignins show great diversity in composition, molecular structure, and reactivity, as a function of source and extraction method. The physico-chemical characteristics of lignins strongly influence the response of biomass to pretreatment processes and the conversion of biomass to bioethanol. The resistance of biomass to acid or enzyme digestion to sugar residues is to a greater extent due to lignin and has been referred to as biomass recalcitrance. Commercial lignins have been traditionally obtained as by-products of paper pulping mills and this has been the main source of commercial lignins. The continuous expansion of bio-based industries has however opened up more sources of lignin. Some lignin-based products include: Activated

carbon, Carbon fiber and Phenols. As a renewable aromatic resource for the chemical industry, lignin from new sources need to be characterized for the basic properties which are structure dependent. Generally to enhance the industrial use of lignin, there is need for a continuous supply of new lignin biomass products with constant quality which are related to purity, chemical composition, and functional properties [3].

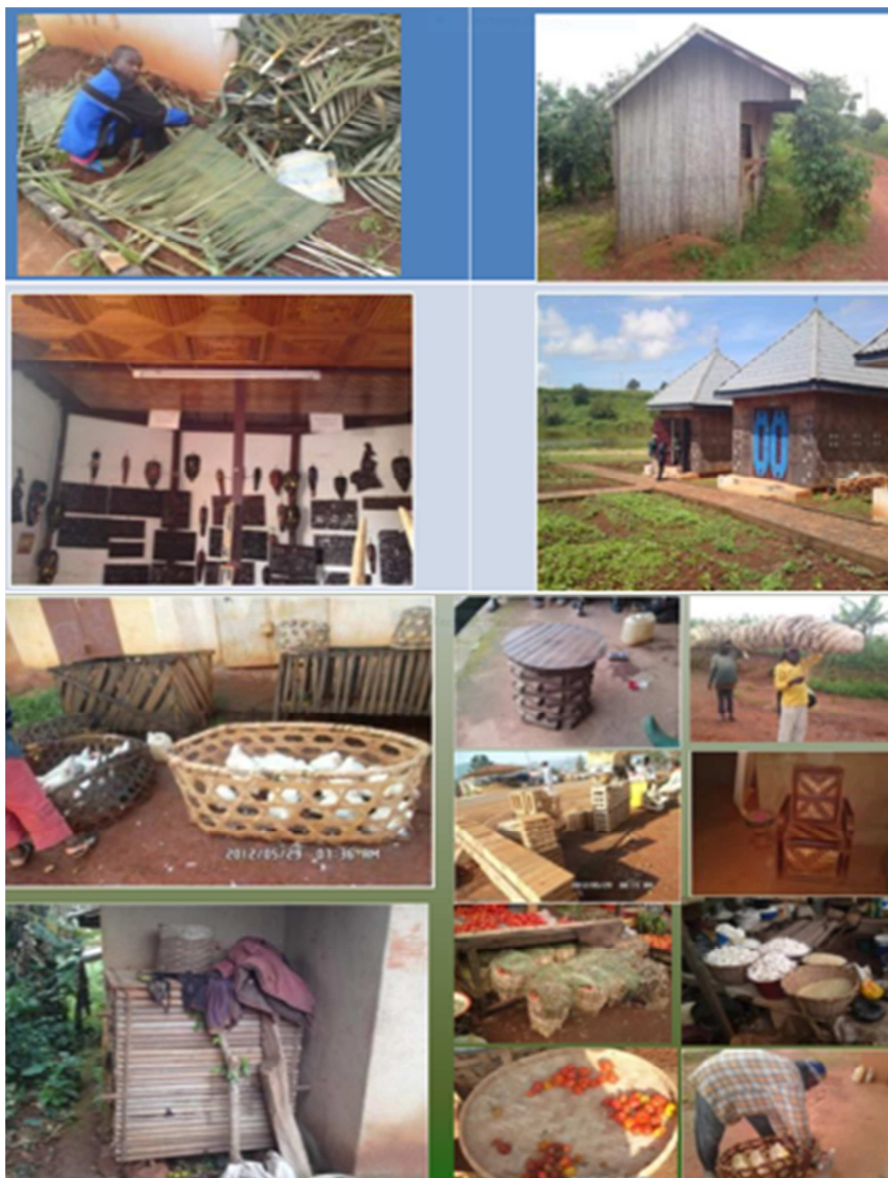
Agro-forestry Lignocellulosic biomass sources range from trees to agricultural residues and Palms constitute a family of the agro-forestry biomass with a fibrous network structure in most of its parts (fruit bunches, fronds or bamboo, leaves and even the stem). Some palms species such as the oil palm, coconut and dates, have been exploited industrially and constitute an important source of biomass for the industries. They have been exploited for food, feed, materials and energy while others such as the Raffia Palms, Areca catechu are less known and have been exploited mostly for traditional uses. Raffia Palms are native to tropical Africa where they constitute an important ecosystem. The palm cultivation has been traditionally practiced in family estates and farms, and small hold scheme plantations over different eco-climatic zones of West and Central Africa. These palm plantations are relatively fast growing and harvesting of the stems does not require heavy equipment. The Raffia Palms are mostly found growing in wetlands, especially around flood plains and river valleys. Their presence in several regions in Cameroon has led to the growth and development of particular plant and animal species which are linked up into a complex web of feeding relationships. Raffia and other palm species have been locally exploited in the palm wine industry. These areas of local exploitation has produced waste such as palm fronds or bamboo. Figure 2 represents the local exploitation of raffia palm and the generation of abundant biomass waste which is abandoned. The abundant biomass waste is a rich natural source of fiber and can be used as a potential reinforcing material in polymer composites.



**Figure 2.** Illustrations of abandon biomass waste from reduced exploitation [4].

To address this problem, the palm wine wastes have been recycled in some applications. Some of the socio-economic and cultural applications in communities in Cameroon include extraction of fiber used in the agricultural, art and craft sectors, symbol during traditional ceremonies and treatment of hemorrhoids, bamboo used to make tooth pick,

building construction materials and furniture, leaves used for treatment of liver ailments and fruits used for the treatment of liver (leaves) and interior decoration as shown in Figure 3. Even with these recycling applications much biomass waste from raffia palms has increasingly been discarded in large quantities.



**Figure 3.** Some illustrations of Construction of houses, huts, Household goods and containers [4].

These bamboo are composed of biomass which is highly lignocellulosic and it is possible for these palms to be cultivated and harvested in a sustainable manner for renewable biomass required for manufacturing lignin-based products. The Raffia plantations are very accessible and the stem require relatively little pre-treatment before extraction of lignin and cellulose. The promotion of raffia palm cultivation as a source of biomass for African bio-refineries, if economically exploited could be beneficial to the preservation of ecosystems (that are under threat), contribute to food security, reduce the amount of agro forestry waste and sustain indigenous small

businesses in the art and craft sector. In this paper we report on the viability of raffia palm as a potential source of lignin and the influence of extraction method on physico-chemical characteristics of extracted lignin.

## 2. Experimental

### 2.1. Materials and Method

Three raffia palm species; *Raffia Hookeri* (RHoF), *Raffia Farinifera* (RFaF), *Raffia Vinifera* (RViF), and oil palm fruit



bunch (EFB) were sampled from four different locations and de-fibered manually. The fibers were sampled from different parts of the plants; core, midrib (mid), periphery (peri), spikelet (sp) and stalk (st). These fibers were air dried and cut into small sizes to pass a mesh sieve size of about 0.2-0.4cm. The fibers were dewaxed with ethanol for 8 h in a Soxhlet extractor to remove all the oil and wax in the fibers (extractives).

### 2.1.1. Extraction of Lignin

Two methods were used to extract the lignin of the fibers; Klaxon lignin or acid insoluble lignin (AIL) and Organosolv processes. According to Klaxon method, the dewaxed fibers were dried at 105°C and treated with 72% sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) in the ratio of 1g fiber per 15ml of solution with frequent stirring at 4°C temperature in a refrigerator for 5mins or until the samples were completely soaked in the acid. The samples were hydrolyzed for 2hrs at room temperature and stirred every minute to ensure complete mixing. Hydroxylates were transferred into a 1000ml flask and diluted to a 3% acid concentration with 560ml of distilled water. The later were placed on a heating mantle attached to a reflux condenser and heated for 4hrs. The hydrolysis solution was later removed and filtered through a sintered glass and washed thoroughly with hot distilled water. The residue was collected, dried and the weight recorded. These fibers were named the lignified fibers (RHoF, RViF, RFa<sub>16</sub>F, EFB<sub>st</sub>, and EFB<sub>sp</sub>).

### 2.1.2. Organosolv Process

The organosolv lignin was produced from organosolv pulping though with some slight modifications. OPEFB and *Raffia* fiber fractionations were carried out by an organosolv (ethanol-water) process, using a 7 L MK digester (M/K Systems, Inc., Maryland) with liquor circulation, under different conditions. The ratios of liquor/ fiber and ethanol/water remained constant at 14/1 (v/w) and 50% (% v/v), respectively. The time to reach the maximum temperatures of 180°C was 30 minutes while the reaction run time was 90 minutes. Acetic acid (2 g/L) and sulfuric acid (0.5, 1.0 and 2.0 g/L) were used as catalysts [5]. Acidified water was added to the known volume of liquid fraction in order to precipitate lignin. The lignin was separated by centrifugation (400rpm) for 20 minutes and dried at 50°C for 30minutes.

### 2.1.3. Ash Content of Lignin

The ash content was determined gravimetrically by heating the lignin in a muffle furnace at 800°C until it reached a constant weight.

## 2.2. Characterization

The structural and functional group of fiber samples and lignin were studied by Fourier Transform Infrared (FTIR) spectroscopy (Perkin Elmer, Model: spectrum one FT-IR spectrometer). FTIR analysis was carried out by using a FTIR Varian 600-IR, equipped with a Mercury Cadmium Telluride (MCT) detector and attached with ATR unit (PIKE

Miracle). 2mg of air dried lignin sample was impregnated in 200mg of dried potassium bromide (KBr) to make a KBr plate and similar pressure was applied for all measurement by using the pressure applicator attached with a torque knob. The wavenumber range was chosen in the 4000-600 cm<sup>-1</sup> range with a 150 scan and resolution of 4 cm<sup>-1</sup>. The spectra were detected in absorption mode. Background scanning and correction were performed before running new sample. The relative peak absorbance was normalized (the intensity of highest absorbance peak normalized to unity) for all the IR bands of each lignin sample. Thermal analysis was conducted using a Thermal Analyzer (PerkinElmer STA 6000), which can serve as TGA to generate TGA graphics. Approximately 30mg of lignin sample was heated from 30°C up to 600°C (10°C/minute) in a nitrogen atmosphere. The samples were carbon coated (fine carbon tape) to study the morphology. The phase constitution after equilibration was characterized by scanning electron microscopy both in the back scattered and secondary electron imaging mode (HITACHI, Model No. S-3400N). The relative proportions of carbon, hydrogen and nitrogen in the air dried samples was determined with a Perkin Elmer Model 2400II CHN analyzer. Calibration was done with acetanilide before each test. The air-dried sample weight was corrected for moisture. The total sulfur content of the oven-dried lignin samples were evaluated by the microwave acid digestion, and inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis. The percentage of oxygen was obtained by subtracting the sum of C, H, N and S contents from 100 percent (including the ash) [6]. However, the nitrogen and sulfur could be included in ash content as well. We assumed that nitrogen and sulfur are totally bonded to lignin.

## 3. Results and Discussion

### 3.1. The Yield Percentage of the Isolated Lignin

The percentage yield of lignin from different Palm sources after Klaxon and organosolv treatments was determined gravimetrically and the results presented in Table 1.

**Table 1.** The percentage yield of the isolated lignin from RViF, RHoF, RFaF, EFB<sub>st</sub> and EFB<sub>sp</sub>, for various processes.

| Methods    | RViF | RhoF | RFaF | EFB <sub>st</sub> | EFB <sub>sp</sub> |
|------------|------|------|------|-------------------|-------------------|
| klaxon     | 22.6 | 36.9 | 28.9 | 28.5              | 25.2              |
| ORganosolv | 22.6 | 26.9 | 23.8 | 26.5              | 25.2              |

The results indicated that for Klaxon process, RHoF fibers yielded the highest lignin content of 36.9% followed by RFaF, EFB<sub>st</sub>, EFB<sub>sp</sub> and RViF fiber with lignin content of 28.9%, 28.5%, 25.2% and 22.6% respectively while for the organosolv process, RHoF yielded the highest lignin content of 26.9% followed by EFB<sub>st</sub>, EFB<sub>sp</sub>, RFaF and RViF fibers with lignin content of 26.5%, 25.2%, 23.8% and 22.6% respectively. The klaxon treatment showed a greater yield for almost all the palm species though the percentage yield varied with both the process and the palm species. This

observation was attributed to the fact that lignin from different plants could be different.

### 3.2. FT-IR Analysis

FT-IR Spectroscopy has been widely used for identification in lignin preparation and in this study the FT-IR results for the lignin samples from various methods of preparation (Klaxon and organosolv) produced similar results both in the number of bands and frequency though the band intensities varied. The FT-IR profiles for the Klaxon and organosolv isolated lignins are shown in Figures 4 and 5 respectively. The strong broad band in the range  $3500\text{cm}^{-1}$ - $3100\text{cm}^{-1}$  present in all the lignin samples is related to OH

stretching vibrations which indicated the presence of alcohol and phenolic hydroxyl groups involved in hydrogen bonding. The intensity of the band increased during demethylation on the one hand and decreased during methylation on the other hand. This can be explained by the fact that, during demethylation the  $-\text{OCH}_3$  bonds in methoxyl groups bonded to the 3<sup>rd</sup> or 5<sup>th</sup> carbon atom of the aromatic ring are split and the  $-\text{CH}_3$  is replaced by a hydrogen atom producing a new OH group while during methylation, the O-H bonds are broken and H replaced by  $-\text{CH}_3$  leading to the decrease in intensity of the band. The band within the ranges  $2940$ - $2900\text{cm}^{-1}$  is related to asymmetric vibration ( $\text{V}_{\text{as}}\text{CH}_2$ ) of guaiacyl-syringyl.

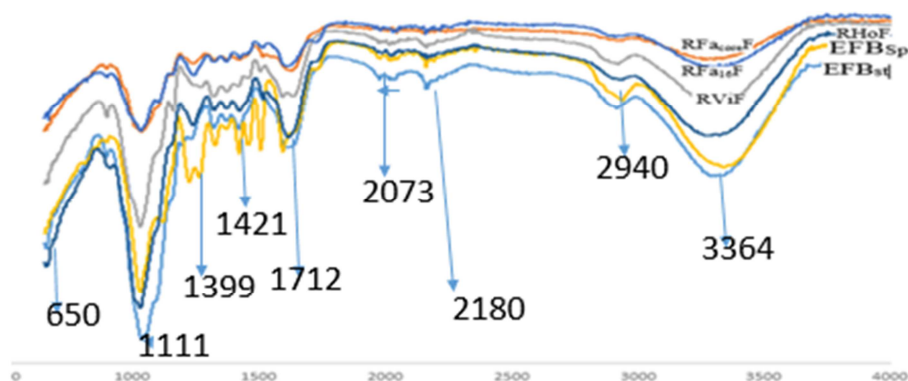


Figure 4. FT-IR profile for the Klaxon Isolated Lignin samples.

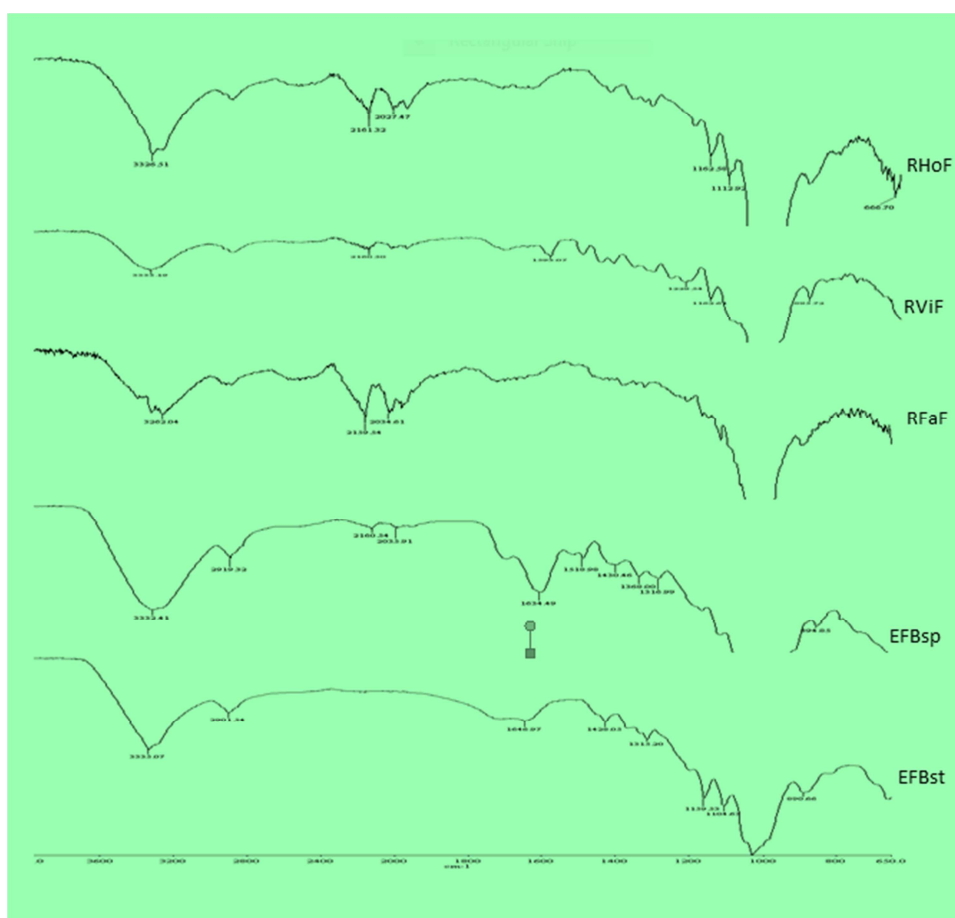


Figure 5. FTIR profile for the organosolv isolated lignin.

The band at  $2165\text{--}2100\text{cm}^{-1}$  is related to  $\text{C}=\text{C}=\text{O}$  (ketones) and indicated the presence of ketenes. The other two bands within the ranges  $2033\text{--}2000\text{cm}^{-1}$  and  $1978\text{--}1970\text{cm}^{-1}$  are  $\text{C}=\text{C}$  asymmetric stretch while those at  $1737\text{--}1700\text{cm}^{-1}$  and  $1665\text{--}1615\text{cm}^{-1}$  are attributed to the stretching vibration of carbonyls (unconjugated carbonyls). The band in the range  $1100\text{--}1117\text{cm}^{-1}$  is due to the ether stretching while that at  $830\text{--}840\text{cm}^{-1}$  indicated the C-H deformation and ring vibration. The strong and sharp band at  $620\text{cm}^{-1}$  is attributed to the precipitation from sulfuric acid and due to C-S stretching vibrations. Bands occurring from  $1600$  and  $1500\text{cm}^{-1}$  are characteristics of aromatic compounds (phenolic hydroxyl groups) and are attributed to aromatic skeleton vibrations. The bands at  $1300\text{cm}^{-1}$  (syringyl) and  $1200\text{cm}^{-1}$  (guaiacyl) indicated the presence of both syringyl and guaiacyl in lignin's chemical structure. The band at  $1350\text{cm}^{-1}$  which is characteristic of an  $\text{N}=\text{O}$  stretching indicated the presence of nitrogen in the lignin structure which conforms to the observation from proximate analysis.

In addition, the bands at  $1327\text{--}1307\text{cm}^{-1}$  and  $1274\text{--}1213\text{cm}^{-1}$  are attributed to the vibration of syringyl and the stretching vibrations of C-O bonds and guaiacyl rings, and stretching vibrations of C-O bonds. Those at  $1043\text{cm}^{-1}$ ,  $1089\text{cm}^{-1}$ ,  $1091\text{cm}^{-1}$ ,  $1110\text{cm}^{-1}$  and  $1107\text{cm}^{-1}$  could be attributed to  $\text{C}=\text{O}$ , C-H, C-O-C and C-O deformations or stretching vibrations of different groups in lignin and carbohydrates. The ones at  $1110\text{--}1100\text{cm}^{-1}$ ,  $1089\text{--}1072\text{cm}^{-1}$  and  $1043\text{--}1024\text{cm}^{-1}$  could be attributed to vibrations of C-O bonds in primary and secondary alcoholic groups and sometimes dialkyl ether bonds while those at  $915\text{--}910\text{cm}^{-1}$  and  $854\text{--}770\text{cm}^{-1}$  are related to  $=\text{CH}$  aromatic ring (guaiacyl-syringyl) and deformation vibrations of C-H bonds on the benzene ring. The various properties of natural fiber in general and lignin in particular are a function of hydrogen bonding. Therefore the closer the lignin chain, the greater the

interaction between the adjacent fragments resulting in more and stronger hydrogen bonds which leads to greater packing of lignin chains resulting to higher mechanical and thermal properties.

Inter molecular hydrogen bonds in lignin are observed at around  $3568\text{--}3577\text{cm}^{-1}$  [7]. Intra molecular hydrogen bonding vibrations in cellulose and lignin appear at lower frequencies around  $3432\text{cm}^{-1}$  while others normally appear in the range  $3300\text{--}3342\text{cm}^{-1}$  which indicate that both intra molecular and inter molecular bonds are involved in the formation of the giant lignin molecule [8].

### 3.3. Chemical Composition of the Fibers and the Isolated Lignin

The chemical composition of the fiber samples was carried out to determine the percentage by weights of Ash and the elements; Carbon, Hydrogen, Nitrogen and Sulfur. The results are summarized in Tables: 2, 3 and 4, and the results show that Nitrogen was detected in the lignin isolates. It is suggested in literature [15] that nitrogen was part of the protein-lignin complex that formed during the delignification process. The percentage of nitrogen in the lignin isolates was significant which supported the suggestion that, nitrogen was bound tightly to lignin molecules as a protein while the sulfur content might have resulted from the method of isolation. The oxygen content was calculated by subtracting 100 from the total of C, H, N and S content. The elemental composition of OPEFB in this study falls in the range reported in literature [9]. The ash content of lignin from Raffia (3.39-4.37%), is far lower relative to those observed for OPEFB (7-10.58%). This difference in the elemental compositions may be a variable associated to the palms species.

Table 2. Chemical Composition for cations.

| Res#                | % Total N | % Ca | % Mg | % K  | % Na   | % Ash Content |
|---------------------|-----------|------|------|------|--------|---------------|
| RHoF                | 0.08      | 0.26 | 0.02 | 0.09 | 0.0049 | 3.39          |
| RViF                | 0.14      | 0.48 | 0.02 | 0.34 | 0.0014 | 4.37          |
| RFa <sub>16</sub> F | 0.15      | 0.18 | 0.06 | 1.05 | 0.0031 | 3.58          |
| EFBSt               | 0.65      | 0.31 | 0.13 | 4.03 | 0.046  | 10.58         |
| EFBSP               | 0.63      | 0.22 | 0.14 | 1.75 | 0.027  | 7.07          |

The elemental compositions of the organosolv and klaxon isolated lignin samples have been presented in Tables 3 and 4 respectively. The results showed that the klaxon lignin have a low carbon and higher oxygen content indicating that the Klaxon lignin from our samples contain higher number of

methoxyl group relative to the organosolv lignin which contain lower number of methoxyl group. This observation could be related to the number of syringyl groups and consequently to the methoxyl content in lignin molecules.

Table 3. Chemical composition of organosolv from RFa16F, RViF, RHoF, EFBst and EFBsp.

| Code                | C     | H    | N    | S    | O     | empirical formula                                                              | HHV (MJ/Kg) | H/C  |
|---------------------|-------|------|------|------|-------|--------------------------------------------------------------------------------|-------------|------|
| RFa <sub>16</sub> F | 44.01 | 7.39 | 1.75 | 0.00 | 46.85 | $\text{C}_{3.66}\text{H}_{7.39}\text{O}_{2.93}\text{N}_{0.125}$                | 18.37       | 2.02 |
| RViF                | 43.07 | 6.92 | 1.00 | 0.16 | 48.85 | $\text{C}_{3.59}\text{H}_{6.92}\text{O}_{3.05}\text{N}_{0.07}\text{S}_{0.006}$ | 16.67       | 1.93 |
| RHoF                | 42.94 | 7.62 | 1.58 | 0.00 | 47.86 | $\text{C}_{3.58}\text{H}_{7.62}\text{O}_{2.99}\text{N}_{0.11}$                 | 17.71       | 2.23 |
| EFB <sub>st</sub>   | 43.88 | 7.43 | 0.98 | 0.00 | 47.71 | $\text{C}_{3.66}\text{H}_{7.43}\text{O}_{2.98}\text{N}_{0.07}$                 | 17.85       | 2.03 |
| EFB <sub>sp</sub>   | 44.72 | 7.27 | 0.95 | 0.20 | 46.86 | $\text{C}_{3.73}\text{H}_{7.27}\text{O}_{2.93}\text{N}_{0.67}\text{S}_{0.005}$ | 18.04       | 1.95 |

**Table 4.** Chemical composition of Klaxon Lignin from RViF, RFa<sub>16</sub>F, RHoF, EFBst and EFBsp.

| Code                | C     | H    | N    | S    | O     | Empirical formula                                                                             | HHV (MJ/Kg) | H/C  |
|---------------------|-------|------|------|------|-------|-----------------------------------------------------------------------------------------------|-------------|------|
| RViF                | 51.11 | 4.32 | 1.11 | 0.64 | 42.82 | C <sub>4.259</sub> H <sub>4.32</sub> O <sub>2.676</sub> N <sub>0.079</sub> S <sub>0.02</sub>  | 16.55       | 1.01 |
| RFa <sub>16</sub> F | 43.66 | 6.34 | 0.40 | 0.09 | 49.51 | C <sub>3.64</sub> H <sub>6.34</sub> O <sub>3.094</sub> N <sub>0.029</sub> S <sub>0.003</sub>  | 16.02       | 1.74 |
| RHoF                | 51.75 | 4.94 | 0.31 | 0.84 | 42.16 | C <sub>4.313</sub> H <sub>4.94</sub> O <sub>2.635</sub> N <sub>0.022</sub> S <sub>0.026</sub> | 17.87       | 1.15 |
| EFB <sub>st</sub>   | 49.59 | 6.44 | 1.82 | 1.19 | 40.94 | C <sub>4.133</sub> H <sub>6.44</sub> O <sub>2.559</sub> N <sub>0.13</sub> S <sub>0.037</sub>  | 19.27       | 1.56 |
| EFB <sub>sp</sub>   | 46.73 | 6.44 | 0.78 | 1.12 | 44.93 | C <sub>3.894</sub> H <sub>6.44</sub> O <sub>2.808</sub> N <sub>0.056</sub> O <sub>0.035</sub> | 17.80       | 1.65 |

Lignin with higher number of methoxyl groups contain lower percentage by weight of carbon and higher percentage by weight of oxygen. This results suggested that lignin extracted by organosolv route contain less number of methoxyl groups relative to lignin extracted by klaxon. The elemental composition of lignin has been used to predict the empirical formula of each lignin as shown on Tables 3 and 4. A considerable amount of sulfur was exhibited by both the organosolv and klaxon lignins ranging from 0.09-1.19%. However, the Raffia species showed a much lower sulfur content generally less than 0.5% (for organosolv) and 1.5% (for Klaxon). The organosolv lignin in this study could be considered commercial sulfur-free since they exhibited a low percentage of sulfur (0.1- 0.47%) and the Lignin from raffia

generated by organosolv method could be utilized as a sulfur-free lignin for different industrial applications where sulfur may interfere in the process. The percentage of nitrogen in each lignin varied due to the differences in source of the plant. The lowest amount of nitrogen content was present in the klaxon lignin (0.31-1.82%), while the organosolv lignin contained a higher nitrogen content (0.95 -2.96%) in comparison with other lignins.

The energy value of the lignin is an important characteristic since lignin is commonly used in combustion and gasification applications. The energy value of the samples was predicted from their elemental composition using Dulong's equation (Equation 1).

$$\text{HHV (MJ/Kg)} = 0.335 (\%C) + 1.4323 (\%H) - 0.154 (\%O) - 0.145 (\%N) \quad (1)$$

A higher proportion of carbon in the lignin molecule is preferable as it will lead to higher energy generation in a combustion process [10]. Comparison of the higher heating value among the lignin samples showed that klaxon lignin have the highest energy value and this was attributed to the highest carbon and lowest oxygen content, while the lowest carbon and highest oxygen content was found in the organosolv lignin with the lowest energy value. Also the EFB showed a greater energy value relative to the raffia species. Higher H/C ratio indicate more reactivity in the fuel and as a result it would be a better source for gasification. For instance, organosolv and klaxon lignin have H/C ranges of 1.95-2.23 and 1.01-1.74, respectively. In this regard, the molar ratio of H/C for all lignin samples was found to be in the range of 1.01 to 2.23, which indicated that there was no much difference between the H/C ratios of lignin. However, klaxon lignins are a better source of energy while the organosolv lignins are a better source of gasification.

The empirical formulae of the lignin from the same species but generated by different methods were different which was an indication that the lignins were modified by the various methods of extraction.

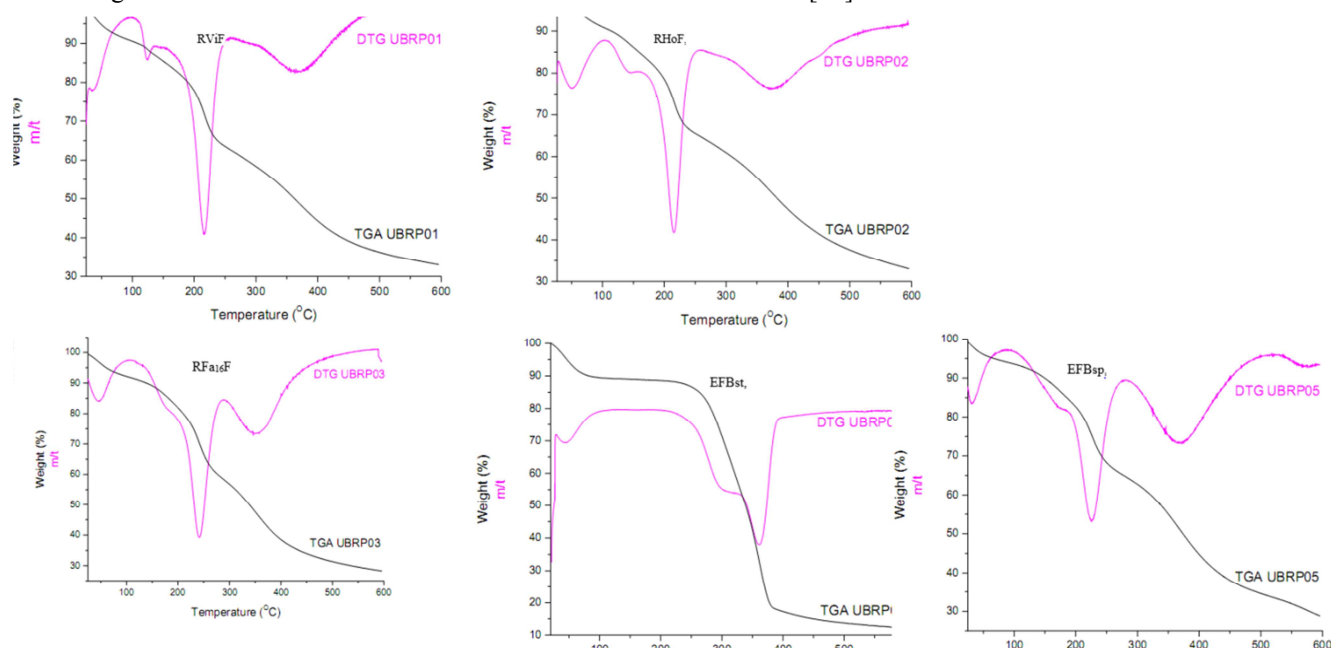
### 3.4. Thermal Decomposition

Thermal stability and decomposition of organic polymers have been commonly determined using TGA under nitrogen environment. The thermal stability of natural fibers used as a filler or reinforcement in polymer composites is of great importance [11]. This is because manufacturing of composites requires the mixing of lignocellulosic materials and the polymer matrix at temperatures of around 200°C for the most common thermoplastic polymers. Also, the degradation of lignin due to high temperatures at the time of

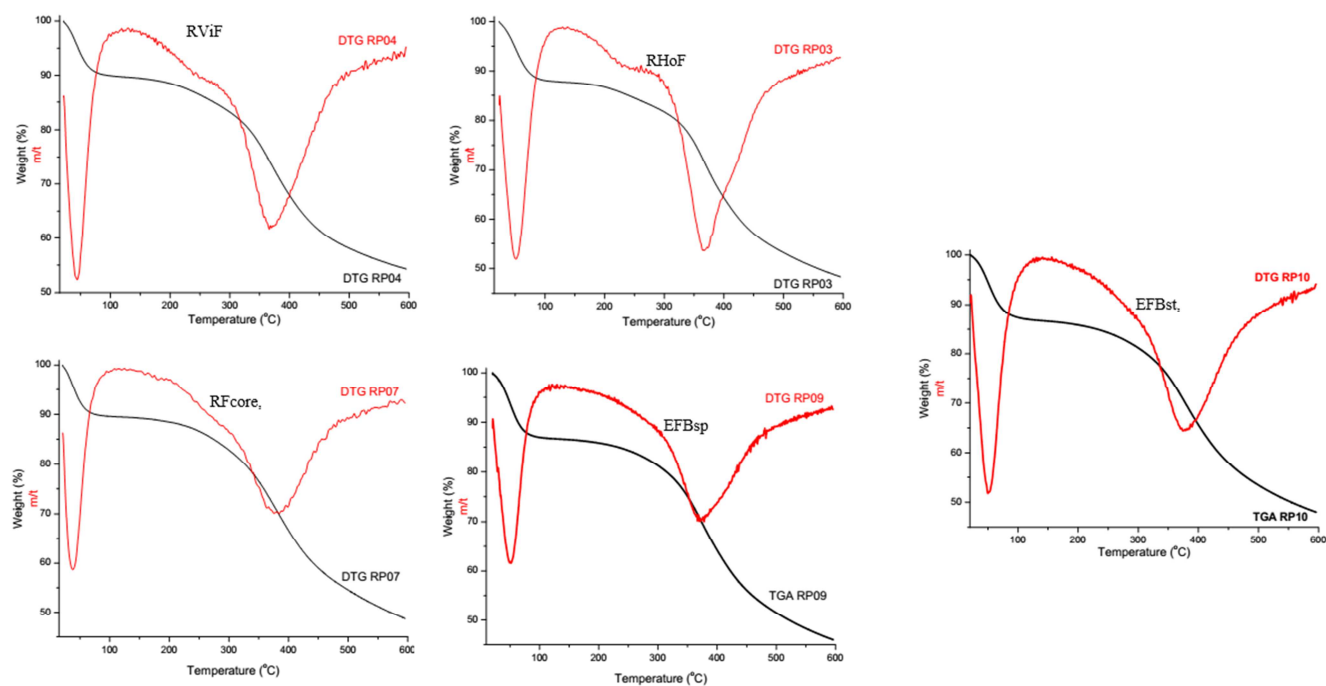
processing may lead to undesirable composite properties, such as odors and browning, added to a reduction in mechanical properties. Therefore, it is important that the degradation profile of the lignin from the fibers be determined. TGA/DTG profiles represented in Figures 5 and 6 for organosolv and Klaxon respectively, revealed the weight loss percentage of materials with respect to the temperature of thermal degradation. In order to determine the best extracted lignin, thermal stability study was conducted on extracted lignin from various sources mentioned in the previous section. Thermal degradation data indicated weight loss and the first derivative (DTG) indicated the corresponding rate of weight loss. The peaks of this curve (DTG<sub>max</sub>) represented a measure of thermal decomposition and have been used as a means to compare thermal stability characteristics of different materials and methods. In this study all the raffia lignin isolated by the same process showed similar peaks in number, position, intensity and even broadness. However, RFaF showed only one peak and a shoulder while RViF showed an anomaly in the lignin peak intensity. Lignin molecular structure is composed of mostly aromatic rings having various branching. These chemical bonds lead to a wide range of degradation temperature from 100 to 600°C with 30 to 40 wt.% of all organosolv and 40-54% klaxon lignin samples still remaining un-volatilized at 600°C. This is attributed to the formation of highly condensed aromatic structures which have the ability to form char. Degradation of the lignin samples were divided into three stages. In stage one, the initial weight loss step occurred at 30-100°C for organosolv and 30-120°C for klaxon lignin which was attributed to the evaporation of water absorbed. Stage two for organosolv lignin was sub divided into two thermal events as shown in Table 5. This stage occurred

around 100–250°C while in the klaxon lignin this was reflected in just one thermal event, as represented in Table 6 and was attributed to the degradation of components of carbohydrates in the lignin samples which were converted to volatile gases such as CO, CO<sub>2</sub>, and CH<sub>4</sub>. The final stage of degradation occurred over a range of temperatures beyond 300°C. Within this stage, degraded volatile products derived from lignin including phenolics, alcohols, aldehydes, acids along with the formation of gaseous products which were evolved. It was also observed from the TGA curve that thermal degradation was not initiated until the materials had

absorbed a certain amount of heat energy. Therefore, heat initiated the degradation processes and the breaking down of the structure causing molecular chains to be dissolved. It can be suggested that the lignin's thermal properties are a function of the source while the weight loss portion that occurred between 250 and 600°C, was attributed to the slow degradation of lignin. This also reveals the significant thermal stability properties of both lignins at high temperature which could be allotted to the high degree of branching and the extremely condensed aromatic structures formation [12]



**Figure 6.** TGA / DTG of Organosolv isolated lignin From RViF, RFaF, RHoF, EFBst, and EFBsp.



**Figure 7.** TGA/ DTG of Klaxon Isolated lignin from RViF, RF<sub>core</sub>, RHoF, EFBsp and EFBst.



Table 5. Organosolv lignin.

| Source of lignin  | Temp. to 5% wt. loss (°C) | 1 <sup>st</sup> Thermal event |              |                       | 2 <sup>nd</sup> Thermal event    |                         |              |                       |                                  |
|-------------------|---------------------------|-------------------------------|--------------|-----------------------|----------------------------------|-------------------------|--------------|-----------------------|----------------------------------|
|                   |                           | T <sub>onset</sub> (°C)       | Wt. loss (%) | T <sub>max</sub> (°C) | Wt. loss at T <sub>max</sub> (%) | T <sub>onset</sub> (°C) | Wt. loss (%) | T <sub>max</sub> (°C) | Wt. loss at T <sub>max</sub> (%) |
| RViF              | 81                        | 101                           | 8            | 142                   | 13                               | 152                     | 15           | 230                   | 28                               |
| RHoF              | 81                        | 103                           | 10           | 150                   | 14                               | 170                     | 16           | 220                   | 27                               |
| RFa <sub>16</sub> | 75                        | 107                           | 8            | 180                   | 14                               | 190                     | 17           | 240                   | 34                               |
| EFBst             | 74                        | 102                           | 8            | 164                   | 8                                | 179                     | 16           | 239                   | 31                               |
| EFBsp             | 72                        | 102                           | 7            | 170                   | 12                               | 187                     | 14           | 232                   | 28                               |

Table 5. Continued.

| Source of lignin  | Temp. to 5% wt. loss (°C) | 3 <sup>rd</sup> Thermal event |              |                       |                                  | Resid. Wt. at 600°C |
|-------------------|---------------------------|-------------------------------|--------------|-----------------------|----------------------------------|---------------------|
|                   |                           | T <sub>onset</sub> (°C)       | Wt. loss (%) | T <sub>max</sub> (°C) | Wt. loss at T <sub>max</sub> (%) |                     |
| RViF              | 81                        | 250                           | 37           | 400                   | 56                               | 36                  |
| RHoF              | 81                        | 270                           | 37           | 400                   | 54                               | 37                  |
| RFa <sub>16</sub> | 75                        | 300                           | 42           | 380                   | 57                               | 33                  |
| EFBst             | 74                        | 285                           | 39           | 380                   | 56                               | 18                  |
| EFBsp             | 72                        | 290                           | 36           | 370                   | 53                               | 35                  |

Table 6. Klaxon Lignin.

| Source of lignin  | Temp. to 5% wt. loss (°C) | 1 <sup>st</sup> Thermal event |              |                       | 2 <sup>nd</sup> Thermal event    |                         |              |                       |                                  | Resid. Wt. at 600°C |
|-------------------|---------------------------|-------------------------------|--------------|-----------------------|----------------------------------|-------------------------|--------------|-----------------------|----------------------------------|---------------------|
|                   |                           | T <sub>onset</sub> (°C)       | Wt. loss (%) | T <sub>max</sub> (°C) | Wt. loss at T <sub>max</sub> (%) | T <sub>onset</sub> (°C) | Wt. loss (%) | T <sub>max</sub> (°C) | Wt. loss at T <sub>max</sub> (%) |                     |
| RViF              | 50                        | 150                           | 11           | 250                   | 13                               | 270                     | 15           | 370                   | 26                               | 36                  |
| RHoF              | 50                        | 150                           | 12           | 250                   | 14                               | 270                     | 17           | 370                   | 29                               | 37                  |
| RFa <sub>16</sub> | 48                        | 148                           | 11           | 250                   | 13                               | 2800                    | 14           | 390                   | 30                               | 33                  |
| EFBst             | 52                        | 142                           | 13           | 250                   | 16                               | 300                     | 17           | 390                   | 30                               | 18                  |
| EFBsp             | 52                        | 145                           | 13           | 250                   | 14                               | 300                     | 19           | 390                   | 29                               | 35                  |

DTG<sub>max</sub> appeared between 250 and 400°C for all lignin samples (Figures 6 and 7, and Tables 5 and 6). In this region, pyrolytic degradation is expected to occur. This degradation process involves fragmentation of inter-unit linkages, releasing of monomers and derivatives of phenol into the vapor phase. The results indicated that the thermal degradation of organosolv lignin began at about 100°C (T<sub>onset</sub>) against the klaxon lignin which began at 135°C T<sub>onset</sub>. This means that the organosolv lignin are thermally stable

only until about 100°C while klaxon lignin are thermally stable until about 135°C. Therefore Lignin from klaxon extraction had the highest thermal stability and highest char yield 46-56% attributed to the formation of aromatic hydrocarbons, hydroxyphenolic and guaacyl-syringyl type compounds. Isolated lignin sample produced char when heated at 600°C which should match with the sum of fixed carbon and ash content measured from proximate analysis.

### 3.5. Morphological Study (SEM/EDS)

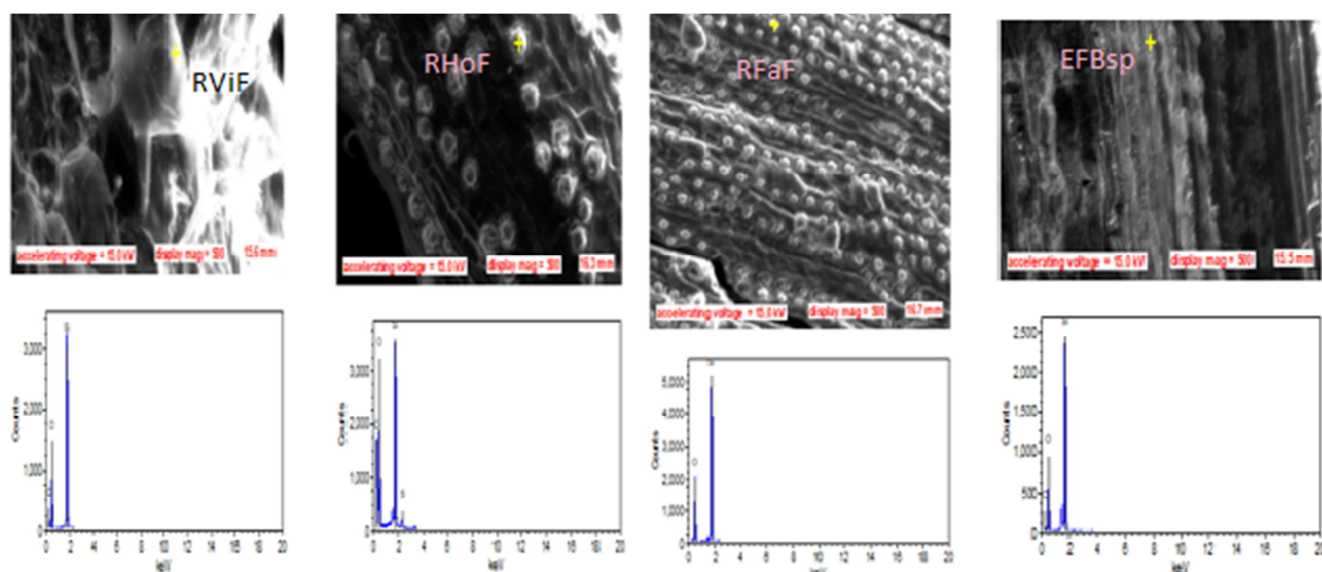


Figure 8. SEM for the organosolv lignin.

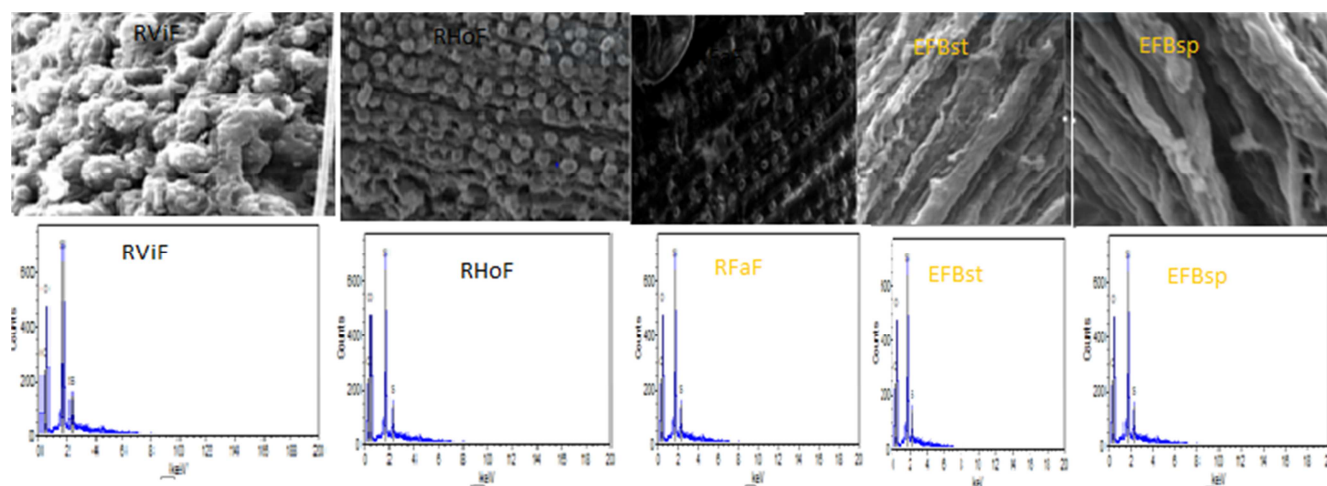


Figure 9. Morphology of klaxon isolated lignin.

The morphology of the fibers was studied using the SEM/EDS and the profiles are shown in Figures 8 and 9. The SEM results revealed that the structure of the fibers looked complex and made up of distinct cell wall layers with different textures. The layers seemed to be made up of linearly and fairly rigid fibrillar which are impregnated with silica bodies embedded within an amorphous material between the fibrils. In most cases the amorphous material were removed leaving the silica bodies exposed while in other parts both the silica bodies and amorphous portions were removed leaving voids and/ or interfibrillar, and an underlying skin core structure. In the cases where the silica bodies were removed, they left behind empty holes leading to a porous surface morphology. The silica bodies contribute to the strength and rigidity of the fiber, and removal of the silica bodies opens up the siliceous pathway as a result exposing the more amorphous region of the fiber [13]. The various methods of treatment had different effects as shown on the various micrographs.

## 4. Conclusion

This study investigated the extraction of lignin from different palm species biomass resources; RHoF, RFaF, RViF, EFBsp and EFBst, using organosolv and Klaxon processes which were then characterized through FTIR, TGA/DTG, Proximate and SEM/EDS testing methods. FTIR spectra of the Lignin samples indicated that there were no significant qualitative differences among the lignin samples irrespective of the isolation method (klaxon or organosolv), palm species or part of the plant from which the fiber sample was collected. It was found that lignin isolated by Klaxon method provided the greatest yield of 36.9% and RHoF fibers provided the greatest yield of the various palm species. There was no much difference between the H/C ratios of lignin samples from various methods however, klaxon lignin samples indicated to be a better source of energy while the organosolv lignins are a better source of gasification. The source of the lignin was seen to affect the thermal properties of the isolated lignin. Generally, lignin extracted by Klaxon method had the greatest thermal stability and highest char yield of 46-54%. The increase in

thermal degradation allows char to be formed on the surface which keeps the underling layer from getting burnt. Therefore, providing a greater char yield indicated that the Klaxon isolated lignin samples have greater fire resistant properties which was attributed to their chemical structure and can provide enhanced thermal properties when they are used as partial replacement in phenolic resin systems. Finally SEM/EDS test method indicated that all fiber samples were made up of filamentous fibrillar embedded with silica bodied chemically constituted of silicon and oxygen.

## Conflict of Interest

There is no conflict of interest.

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