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# Characterisation of selected Nigerian Biomass for Combustion and Pyrolysis Applications

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## Abstract

Biomass is the most utilised form of renewable energy, especially in developing nations, and is a possible replacement for fossil fuel in power generation. The most commonly used method for recovering energy from biomass is combustion. Many countries are exploring the utilisation of energy crops and indigenous residues to deliver sustainable sources of biomass. For these bio-resources, detailed characterisation of the fuel properties is essential in order to optimise the combustion processes. In this study, some potential energy crops and woods from Nigeria, namely *Terminalia superba, Gmelina arborea, Lophira alata, Nauclea diderrichii*, and also one abundant agricultural residue, palm kernel expellers (PKE) were characterised for their combustion properties. Standard characterisation methods such as proximate and ultimate analyses, metals analysis, and ash fusion test were used for this purpose and the results were compared to some UK biomass. In addition, their thermal conversion was assessed by thermogravimetric analysis and pyrolysis-gas chromatography–mass spectrometry. Finally, combustion studies were conducted by suspending single biomass particles in a methane flame to obtain information on reactivities and combustion characteristics. Results indicate that the ash fractions in the Nigerian woods were low in K, Si, and Ca, resulting in low calculated alkali indices, hence these fuels are not predicted to cause severe fouling problems. Furthermore, the analysis of the evolved product during devolatilisation from Py-GC-MS suggests that the content of oil is high in *Gmelina*. Finally, the results from the single particle combustion experiments revealed longer char burn out rate for *Lophira* and *Nauclea* when compared with those of *Terminalia* and *Gmelina*.

Keywords: biomass, torrefaction, energy, combustion, pyrolysis.

## 1.0 Introduction

Nigeria has large reserves of gas and solid minerals, and the largest oil reserves in Africa. Consequently the country has a very high dependence on crude oil, which contributes approximately 27% of the gross domestic product [1]. The current electricity generation capacity, based largely on fossil fuel sources, is at present about 6GW, in a country with an approximate population of 170 million people [1]. Thus, only about 40% of Nigerians are connected to the national grid [2, 3]. Nigeria also has vast renewable energy resources, comprising mainly hydro, solar, wind and biomass [4] and these remain largely untapped.

At present, bioenergy sources are used by a significant number of people in rural areas to meet their basic energy needs (cooking, lighting and heating), but this is achieved in an inefficient way, with a negative impact on people's health as well as on the environment. It is therefore important to take adequate measures to modernize its supply, conversion and use in a sustainable way. Biomass resources in Nigeria include woods, agricultural wastes, crop residues, sawdust, wood shavings, bird and animal litter and dung as well as industrial and municipal solid wastes [5]. These were estimated in Mt as 39.1 fuel wood, 11.2 agricultural wastes, 1.8 sawdust, and 4.1 municipal solid wastes [5]. The highest quantity of woody biomass is found in the rain forest in southern Nigeria, and the highest quantities of crop residues is from the guinea savannah in the north central region of Nigeria. Agricultural residues include cornstalks, rice husk, cassava peels, palm kernel shells, coconut shells and sugarcane bagasse.

Nigeria is a member of the "non-Annex 1" countries who are signatories to the Kyoto protocol agreement. As such, Nigeria has no limit or emission restriction, but needs to initiate Clean Development Mechanism projects (CDM) in order to reduce emissions of greenhouse gases in the atmosphere. The success of CDM projects can earn Nigeria carbon credits which can also be traded to Annex 1 countries who are trying to achieve their emission limits. The World Bank identified over 750 CDM projects in Nigeria, which, if implemented, could generate 100 million tonnes of carbon emission reductions annually [3]. As a consequence, the Federal government of Nigeria has initiated four CDM's, three of which concern gas flare reduction, recovery and processing, while the fourth is "Save 80 Fuel Wood Stoves" aimed at introducing the energy-saving and low polluting "Save 80" wood stove to the Nigerian Market. According to World Energy Council (WEC) [6], the Federal government of Nigeria has also signed a Memorandum of Understanding (MoU) to develop forest carbon projects in the country, as well as to establish a carbon centre for the West African region. Several afforestation projects covering several thousand hectares in many States in Nigeria are completed. These have involved establishing seedling nurseries, and plantation management [7]. Woods in the plantations include *Gmelina, Terminalia*, teak, eucalyptus, and pine. Tropical rain forest is the major source of timber supply and energy crops in Nigeria with high plant diversity of over 4,600 plant species. The forest covers 10% of the country's land area with over 560 tree species at a range of about 30 to 70 species per hectare for trees ≥ 5 cm diameter at breast height (dbh) [8].

*Terminalia superba* is a tree found in the tropical lowland forest in Nigeria. The tree is planted around April at the beginning of the rainy season, and thrives on rich, well-drained alluvial soils, although it can also be cultivated on other soil types namely lateritic sands, gravel and clays, lava, black basaltic clays and crystalline soils. The wood air dries rapidly, degrades slightly and is lightweight to medium-weight, with a density ranging from 370–730 kg/m$^3$ at a moisture content of about 12% [9]. Once the wood is dried, it becomes stable. The chemical composition has been measured as 14–17.5% of hemicellulose, 40 to 45% of cellulose, 28 to 35% lignin [9].

*Nauclea diderrichil* is a tree species found in the humid tropical rainforest of Nigeria and is one of the known trees in the early stage of forestry practice in Nigeria. This tree is one of the few local trees that records success under plantation management, although the Forest Commission of Nigeria considers *Nauclea* to be vulnerable and endangered due to the exploitation since the 19th century [10], and this has led to its rarity in natural forests. In order to ensure regeneration of this species, recent attention has been directed towards plantations, and success is recorded in the Oluwa and Omo forest reserves, with the establishment of about 1,354 ha of *Nauclea* plantations [10]. The trees range from 9- 23.6 m in height and the total above ground biomass varied from 32.5 t $ha^{-1}$ to 287.5 t $ha^{-1}$ between 5 and 30 years [11].

*Lophira alata* is a tree species in the Ochnaceae family. The tree grows to a maximum height and a diameter at breast height (dbh) of 50m and 180cm respectively, and can also be found in freshwater forest, around the Niger delta's large coastal rivers, mainly Osun, Ogun and Osse [12].

*Gmelina arborea* is a short rotation coppice, deciduous tree species, belonging to the verbenaceae family. *Gmelina* is from India and Burma, but has a natural distribution extending from the Himalayas in Pakistan to Nepal, Cambodia, Vietnam and southern provinces of China [13]. *Gmelina* has a life span of 30–50 years and grows fast during the first 5–6 years [14]. In Nigeria, *Gmelina* is mostly found in the tropical rain forest, and covers an estimated 112,000ha [15]. The tree has high biomass yield, ranging from 83.2 t $ha^{-1}$ (5 years) to 394.9 t $ha^{-1}$ (21 years) [8]. *Gmelina* has been shown to tolerate a wide range of conditions with mean annual rainfall from 1778 to 2286mm and mean annual temperature of 18 to 28°C [16]. Thus, *Gmelina* has been considered to be highly favoured in plantations due to its adaptability to a wide range of soil and climatic conditions. The extensive range of site and environmental conditions that *Gmelina* tolerates, together with its fast growth rate, ease of propagation from seeds and cuttings, good coppicing and short rotation, has contributed to its success in plantations [14, 15]. A study conducted by Fuwape and Akindele [14] showed that *Gmelina* has high heating value and can be used as fuel in the energy supply chain.

Palm Kernel Expeller is an oil palm residue and Nigeria is one of the largest producers of palm oil. Harnessing this enormous agricultural waste for energy utilization to serve as feedstock for power plants and also for the production of bio-oils is considered important. The fact that they are abundantly available are amongst the economic reasons of employing them as the major source for renewable energy [17].

While the forest industry for timber is well established in Nigeria, the sawmill residues are under utilised. It has been estimated that the volume of waste wood generated nationwide (in approximately 2000 sawmills) is 104,000 $m^3$ per day [18]. Clearly, this is an untapped resource. There is very little information in the open literature concerning the fuel properties of woods and energy crops in Nigeria and this paper aims to characterise some of the plantation and timber species (*Terminalia superba*, *Nauclea diderrichil*, *Gmelina arborea*, *Lophira alata*) and one agricultural residue (palm kernel expeller (PKE), for their fuel, pyrolysis and combustion characteristics. Results are compared with some typical UK energy crops (willow SRC, miscanthus giganteus, eucalyptus) and one UK residue (wheatstraw).

## 2.0 Experimental Methods

### 2.1 Materials

Biomass samples were obtained from sawmills in Nigeria and supplied by Quintas Renewable Energy Solutions Limited, in the form of chip with average dimensions of 2.5cm x 2.2cm x

1.1cm. Prior to analysis, the fuels were reduced to smaller particle sizes using a Retsch cutting mill SM 100, and milled further using the Retsch PM100 planetary ball mill. The milled fraction was sieved and the particle size less than 600$\mu$m was collected and dried overnight in the oven at a temperature of 60$^0$C, before being stored in a desiccator for further analysis.

## 2.2 Proximate and ultimate analyses

The moisture, volatile and ash contents were determined using the British standards BS EN 14774-1:2009, BS EN 15148:2009 and BS EN 14775:2009, respectively. The reproducibility for the proximate analyses was ≤ 0.2%. The fixed carbon content was estimated by difference. A CE instruments Flash EA 1112 Series elemental analyser was used for measuring the C, H and N contents of the fuel samples milled to <600$\mu$m. The measurements were performed in duplicate and a mean value is reported. The oxygen content was obtained by difference. The relative error for the analysis of C was in the range of 0.1–1.8%, but for H and N the relative error was ≤ 0.2%. The sulfur content of the samples was below the detection limits.

## 2.3 High heating values

The high heating values (HHV) of the five Nigerian biomass samples were measured experimentally in a bomb calorimeter and were compared with values calculated using the correlation developed by Friedl et al. [19]. The HHV (dry basis) were calculated using the elemental analysis on a dry basis as follows:

$$HHV = 3.55C^2 - 232C - 2230H + 51.2C \times H + 131N + 20{,}600 \qquad (1)$$

The standard error was calculated as ±405 kJ/kg.

### 2.4 Determination of lignocellulosic fractions

The determination of the lignocellulosic fractions were carried out by the IBERS Analytical Chemistry Laboratory at the University of Aberystwyth. The gravimetric measurements of Neutral Detergent Fibre (NDF), Acid Detergent Fibre (ADF) and Acid detergent Lignin (ADL) were made using the Gerhardt fibrecap system, which is the improved version of Van Soest's methods [20, 21]. The NDF, which is regarded as the total cell wall is the residue, corrected for ash, left after refluxing for 1 h in a neutral buffered detergent solution [21]. ADF, the ash corrected residue remaining after refluxing the samples in a solution of Cetyl Ammonium Bromide (CTAB) in 2 M sulphuric acid is a measure of cellulose and lignin only [21]. ADL was measured by treating ADF with 72% sulphuric acid to solubilise the cellulose to determine crude lignin. Ash was determined in the samples after heating at 600°C in a muffle furnace for at least 4 h. The concentration of hemicelluloses and cellulose were calculated according to Equations (2) and (3) respectively.

$$\text{Hemicellulose } \% = \text{NDF}\% - \text{ADF}\% \tag{2}$$

$$\text{Cellulose } \%= \text{ADF}\% - \text{ADL}\% \tag{3}$$

### 2.5 Metal analysis

The ash analysis was performed by TES Bretby Ltd, UK. The ash was obtained according to the British standard method BS EN 14775:2009, and was analysed by inductively coupled plasma spectrometry (ICP) following acid digestion. The metal contents determined were converted to theoretical weight percent oxides and are presented in Table 3.

## 2.6 Ash fusion test

Ash Fusion Tests (AFT) were performed on all fuels under oxidising conditions. Cylinders of ash samples were heated, under an air flow rate of 50 ml/min, in a Carbolite Digital Ash Fusion Furnace with a black and white camera to capture the deformations of the ash cylinder. The samples were heated to 1600°C under a controlled heating rate of 7°C/min, and images were recorded at temperature intervals of 5°C for the temperature range of 550–1600°C. The ash was prepared as described in section 2.5. Further details of the method can be found in Baxter et al. [22]. The images captured at different temperatures were analysed to determine the shrinkage temperature, deformation temperature, hemisphere temperature and flow temperature using the European standard DD CEN/TS 15370-1:2006.

## 2.7 Fuel pyrolysis and char combustion behavior by thermogravimetric analysis (TGA)

The devolatisation and char combustion behavior of the fuels were investigated using a TA Q5000 Thermogravimetric analyser. For pyrolysis, a typical mass of ~10 mg of sample was heated at rate of 25°C $\text{min}^{-1}$ to 700°C in a purge of nitrogen at a flow rate of 50 ml/min. This was followed by cooling to ~40°C before heating up again at a rate of 25°C $\text{min}^{-1}$ to a final temperature of 900°C under a constant flow of air (50 ml/min) to obtain the char burning profile.

## 2.8 Single particle combustion

In order to obtain an insight into the combustion behavior of the Nigerian woody biomass at flame temperatures, single biomass particles were combusted in a methane-air flame. The experiment involved suspending cubed shaped fuel particles (~2x2x2mm) on a steel needle in a natural gas flame from a Meker type-burner, at a temperature of ~1200°C and oxygen concentration of 10.8±0.3 mol%. The needle was kept in place in a ceramic housing and was covered by a protective water-cooled sheath when first placed in the flame. For the experiment, the protective sheath was retracted to expose the fuel particle to the methane-air flame. A Fuji HS10 video camera was used to record the images of the combustion at a speed of 33 frames per second (fps). The images recorded were transferred to the computer and analysed.

### 2.9 Pyrolysis-Gas Chromatography-Mass Spectrometry (Py-GC-MS)

Py-GC-MS analyses were performed on the samples using a CDS 1000 pyroprobe attached to a HP 5890 series II Gas Chromatograph fitted with a Rtx 1701 60m capillary column (0.25 id and 0.25μm film thickness). The oven was held at a temperature of 70ºC for 2 min and then the temperature was increased at a rate of 20ºC $\mathrm{min}^{-1}$ to a final temperature of 250ºC, and held for 15 min. Approximately 2 mg of sample were placed in a 20 mm silica tube between two plugs of quartz wool. The sample was then pyrolysed at a maximum temperature of 600ºC with a nominal ramp rate of 20°C $\mathrm{ms}^{-1}$ and a final dwell time of 20s. Pyrolysis products were identified from the chromatograms with the assistance of a mass spectral detection library (NIST 05A MS library) and also by comparisons with values found in Nowakowski et al. [23].

## 3.0 Results and Discussion

### 3.1 Proximate and ultimate analyses

The results from the proximate analysis of the Nigerian fuels are listed in Table 1 and compared to some energy crops and an agricultural residue (wheat straw). The moisture content of *Nauclea* was over 40% and therefore required further air-drying at 60ºC for 72hr in order to prevent biological deterioration. Both moisture contents, before and after drying, are reported in Table 1. The results show that all the Nigerian woods have lower ash contents than the UK energy crops included in this study. *Gmelina* and *Nauclea* have particularly low ash at ≤ 1.0%. The fixed carbon contents of the Nigerian woods show a similar range to UK woods- *Lophira* and short rotation willow coppice are comparable (20.3 and 19.8 wt.% respectively), while *Terminalia,* eucalyptus, and wheat straw have lower fixed carbon contents- between 17.4-17.6 wt.%.

Table 1. Proximate analysis of the fuels studied

| **Fuels** | **Moisture (wt.% ar)** | **Moisture (wt.% ad)** | **Volatiles (wt.% db)** | **Fixed carbon (wt.% db)[a]** | **Ash (wt.% db)** |
|---|---|---|---|---|---|
| PKE | 9.6 | 8.9 | 76.1 | 21.0 | 2.9 |
| *Lophira* | 13.9 | 12.0 | 78.1 | 20.3 | 1.6 |
| Willow (SRC) | 9.8 | n/a | 77.6 | 19.8 | 2.6 |
| *Nauclea* | 42.0 | 4.2 | 80.6 | 18.8 | 0.7 |
| *Gmelina* | 39.9 | 4.9 | 80.9 | 18.1 | 1.0 |
| Eucalyptus | 23.7 | 6.1 | 79.9 | 17.6 | 2.6 |
| Wheat straw | 6.1 | n/a | 74.1 | 17.6 | 8.3 |
| *Terminalia* | 17.4 | 5.2 | 80.2 | 17.4 | 2.4 |
| Miscanthus | 7.2 | n/a | 82.9 | 14.7 | 2.5 |

ar, as received
ad, after air drying at 60°C
db, dry basis (after air drying at 60°C)
n/a: not applicable
[a]Calculated by difference

Table 2 shows the ultimate analysis of the fuels. The C content of the Nigerian fuels is comparable to that of willow and it is >50 wt.%, except for *Terminalia*. PKE and *Nauclea* record the highest C contents (>53 wt.%). The higher than average C contents of the Nigerian fuels were confirmed by their corresponding relatively higher experimental HHVs obtained, which were in the range 19.4-21.1 MJ $kg^{-1}$. The experimental HHVs are also listed in Table 2, and were in good agreement with the calculated values (<4% error). The H content in miscanthus and wheat straw is low (< 5 wt.%), while the nitrogen content of the fuels is <1%, and range from 0.2 to 0.7%. The fuels with the highest nitrogen contents are *Nauclea* and willow (0.6-0.7%). The contents of sulphur and chlorine in all the fuels were below the detection limits, except for miscanthus and wheat straw, which resulted in a chlorine content of 0.31 and 0.42 wt.%, respectively.

Table 2. Ultimate analysis and HHV of the fuels on a dry basis (db).

| **Fuel** | **C (wt.%)** | **H (wt.%)** | **N (wt.%)** | **Cl (wt.%)** | **O (wt.%)**[a] | **HHV (MJ/kg)**[b] | **HHV (MJ/kg)**[c] |
|---|---|---|---|---|---|---|---|
| Nauclea | 53.1 | 5.7 | 0.6 | N.D. | 40.6 | 21.2 | 20.9 |
| PKE | 53.6 | 5.1 | 0.5 | N.D. | 40.8 | 21.0 | 21.0 |
| Gmelina | 51.4 | 5.7 | 0.2 | N.D. | 42.7 | 20.4 | 20.8 |
| Lophira | 51.8 | 5.0 | 0.3 | N.D. | 42.9 | 20.3 | 21.1 |
| Willow | 51.1 | 5.3 | 0.7 | N.D. | 42.9 | 20.2 | - |
| Terminalia | 48.9 | 5.2 | 0.3 | N.D. | 45.5 | 19.2 | 19.4 |
| Eucalyptus | 46.3 | 5.1 | 0.5 | N.D. | 48.1 | 18.3 | - |
| Miscanthus | 46.1 | 4.9 | 0.2 | 0.31 | 48.5 | 18.1 | - |
| Wheat straw | 42.8 | 4.9 | 0.5 | 0.42 | 51.38 | 17.6 | - |

[a] Calculated by difference,
[b] Calculated using Eq. (1)
[c] Determined experimentally
N.D. Not detected (<0.01 wt.%)
- Not determined

## 3.2 Slagging and fouling indices

It is known that the occurrence of alkali and alkaline earth metals in the fuel causes slagging and other forms of fireside deposits [24]. The metal salts in biomass will combine with oxygen to form metal oxides in the ash during combustion, together with chlorides, sulphates and phosphates. Depending upon the ash characteristics it might form hard deposits on the heat exchanger surfaces and boiler walls. K and Na, together with $SiO_2$ form low melting point ash mixtures. Thus high alkali content in fuels causes severe slagging on the boiler grate or in the bed and because of its volatility, also results in fouling of convection heat transfer surfaces [24]. Table 3 lists the main components of the fuels ash. *Terminalia* and *Lophira* have high CaO content, while the most abundant component in the *Gmelina* and *Nauclea* ash is $K_2O$. Therefore, these two pairs of woody biomass are expected to have very different ash melting behavior. In the case of PKE, silica is the main ash component.

Table 3. Ash composition of the fuels (wt. %)

| **Elemental oxide** | **Terminalia** | **Gmelina** | **PKE** | **Nauclea** | **Lophira** |
|---|---|---|---|---|---|
| $SiO_2$ | 1.7 | 8.9 | 57.1 | 9.5 | 10.5 |
| $Al_2O_3$ | 0.3 | 1.0 | 11.0 | 0.9 | 0.3 |
| $Fe_2O_3$ | 0.1 | 0.6 | 6.0 | 0.9 | 0.2 |
| $TiO_2$ | <0.1 | <0.1 | 0.6 | 0.4 | <0.1 |
| CaO | 41.7 | 19.6 | 5.8 | 9.3 | 41.0 |
| MgO | 1.0 | 2.8 | 1.8 | 3.0 | 2.7 |
| $Na_2O$ | 0.1 | 0.3 | 0.4 | 0.3 | 0.4 |
| $K_2O$ | 8.4 | 29.9 | 2.5 | 32.0 | 8.2 |
| $Mn_3O_4$ | <0.1 | <0.1 | 0.2 | 0.2 | 0.4 |

| | | | | | |
|---|---|---|---|---|---|
| $P_2O_5$ | 0.7 | 0.5 | 0.7 | 6.4 | 2.2 |
| $SO_3$ | 1.5 | 1.7 | 1.5 | 4.1 | 3.5 |

The alkali index (AI) presents the quantity of alkali oxide in the fuel per unit of fuel energy (kg alkali $GJ^{-1}$). The alkali index is frequently used as a threshold pointer for fouling [24]. The upper limit for the alkali index is 0.34 kg alkali GJ $kg^{-1}$- above this point, fouling is definitely expected to occur [24, 25]. The alkali indices for the fuels studied were calculated using equation (4) and are shown in Table 4.

$$AI = kg\ (K_2O + Na_2O)/GJ. \tag{4}$$

The base to acid ratio index is normally used to predict the slagging tendency of a fuel. The base to acid ratio ($R_{b/a}$) is defined as the ratio of the basic metal oxides to the acidic oxides in the ash, as presented in equation (5) [26].

$$R_{b/a} = \%\ (Fe_2O_3 + CaO + MgO + K_2O + Na_2O)\ /\ \%(\ SiO_2 + TiO_2 + Al_2O_3 + P_2O_5) \tag{5}$$

Thus as the $R_{b/a}$ value increases, due to the higher concentration of basic components in the ash, there is a tendency for lowering of the ash melting point, and therefore increasing its potential for slagging. The base to acid ratios and base percentage calculated for the Nigerian fuels are also shown in Table 4. Generally, the intrinsic mineral matter contained in biomass is lower than in coal, although this can be considerably higher in some species of grasses and agricultural residues [24]. The ash content of the Nigerian fuels are lower or at least comparable to those from the UK energy crops listed in Table 1, and are much lower than wheat straw. From Table 4, it is observed that the alkali index for all the fuels is below the 0.34 GJ $kg^{-1}$ threshold value and hence these fuels are not predicted to cause severe fouling problems. Gmelina is expected to be the most problematic, nevertheless its alkali index is still below the "fouling probable" indicator. Table 4 also shows the base to acid ratios ($R_{b/a}$) calculated for the Nigerian fuels. From the $R_{b/a}$ in Table 4, we can observe that *Terminalia*, *Gmelina*, and *Lophira* can be expected to have a higher tendency to form ash deposits in the combustion chamber than *Nauclea* and PKE. However, the Nigerian PKE presented a lower value for $R_{b/a}$ in comparison to the value reported for the imported PKE in Darvell et al. [26], which was calculated at 2.93.

Table 4. Slagging and fouling indices

| **Parameter** | **PKE** | **Lophira** | **Gmelina** | **Terminalia** | **Nauclea** |
|---|---|---|---|---|---|
| Alkali Index (kg alkali/GJ) | 0.04 | 0.07 | 0.15 | 0.10 | 0.11 |
| $R_{b/a}$ (including $P_2O_5$) | 0.24 | 4.04 | 5.12 | 19.00 | 2.65 |
| Base Percentage (%) | 16.5 | 52.5 | 53.2 | 51.3 | 45.5 |

### 3.5 Ash fusion test

The temperatures for the four ash melting characteristic states: shrinkage, deformation, hemisphere, and melting, were determined for all the samples studied and are listed in Table 5. It is to be noted that these temperatures are determined visually, therefore there is an inherent error in their estimations. In the case of the estimation of the shrinkage temperature, this error may be larger, since the contrast of the images collected at lower temperatures is poor. Descriptions of the melting behaviour of the test pieces are also included in Table 5. It was observed that the ashes from both PKE and miscanthus shrink then swell during the deformation stage, this is followed by bubbling and then melting. *Nauclea* ash was also observed to swell upon deformation (before melting). Further comparison of the deformation temperature can be made with values found in the literature [22, 27]. The deformation temperatures of lignites and several biomass are seen to pass through a minimum (parabolic curve) when plotted against base percentage; the minimum being in the range 35-55% basic oxides in the ash. The base percentage of the Nigerian woods also fall in this range (see Table 4) and thus it can be assumed that, like many other woods and biomass fuels, deposition will require careful monitoring and control if these fuels are utilized in high temperature combustion systems. However, it is also important to note that the values reported in this paper represent an average composition of the wood fuels, including the bark component. Clean white wood fuels have much lower ash contents and different ash compositions than those with bark [28, 29]; furthermore there is variability in ash composition depending on the type of fibre (heartwood, branch wood, top branches, etc.) [28]. Thus, good fuel quality management is used by most power companies to help alleviate potential fuel deposition problems [30-32] and, based on these results, similar fuel quality management is recommended for the Nigerian energy crops and woods.

Table 5. Ash Fusion Test (AFT) characteristic temperatures (°C)

| **Fuel** | **Shrinkage Temp.** | **Deformation Temp.** | **Hemisphere Temp.** | **Flow Temp.** | **Observations** |
|---|---|---|---|---|---|
| Wheatstraw | 950 | 980 | 1095 | 1140 | Shrinks, swells at deformation and then melts |
| Miscanthus | 960 | 1000 | 1300 | 1325 | Shrinks, swells at deformation, bubbles up and then melts |
| Willow | 990 | 1075 | 1520 | 1525 | Shrinks, and then melts |
| PKE | 1080 | 1130 | 1365 | 1380 | Shrinks, swells at deformation, bubbles up and then melts |
| Gmelina | 1030 | 1185 | 1490 | 1505 | Shrinks, and then melts |
| Terminalia | 1065 | 1265 | 1510 | 1520 | Shrinks, and then melts |
| Nauclea | 1070 | 1375 | 1480 | 1505 | Shrinks, swells at deformation and then melts |

| **Fuel** | **Shrinkage Temp.** | **Deformation Temp.** | **Hemisphere Temp.** | **Flow Temp.** | **Observations** |
|---|---|---|---|---|---|
| Eucalyptus | 950 | 1430 | 1445 | 1455 | Shrinks and then melts |
| *Lophira* | 1110 | 1430 | 1455 | 1475 | Shrinks, and then melts |

## 3.6 TGA Analysis

The devolatilisation and char burning profiles of the UK and Nigerian fuels were used to study their combustion behaviour. Typical plots of the derivative of the mass loss curve with time (DTG) obtained during the temperature programmed pyrolysis and char combustion of the fuels in a thermogravimetric analyser are shown in Figures 1(a)-(e). There is a very small peak observed at a temperature <100$^o$C on the devolatilisation profile, which is due to moisture evaporation, whilst the second (main) peak between 200-400$^o$C is due to volatile release. During this stage the lignocellulosic components decompose at different rates. Often two peaks are seen corresponding to hemicellulose followed by cellulose decomposition over a narrow temperature window, as can be observed in the PKE plot (Fig. 1(d)). The DTG curves of *Terminalia* and *Lophira* show a main peak with a shoulder at lower temperatures, which is normally considered to arise from hemicellulose decomposition due to its less stable structure, while the main peak is considered to be mainly due to the degradation of cellulose. In contrast, only one peak can be observed for the devolatilisation of *Gmelina* and *Nauclea* (after drying). These observations are consistent with the comparative amounts of hemicellulose found in the fuels. The lignocellulosic composition of the Nigerian fuels are shown in Figure 2. It can be observed that the fuels with higher hemicellulose content, e.g. PKE and *Terminalia* resulted in a more pronounced shoulder/peak due to hemicellulose decomposition (see Fig. 1(d) and (e)). Lignin decomposition occurs over a wide temperature range because of its cross-linked structure and aromatic nature, resulting in a much broader peak [33]. It can be noted that very small peaks can be observed in the DTG plots for *Lophira* and *Terminalia* at a temperature range 460-620$^o$C. These peaks can be attributed to the decomposition of calcium present in the fuels. This was investigated by TGA pyrolysis studies of the fuels with added $CaC_2O_4$ (results not shown), which confirmed that the occurrence of these peaks in the DTG curves for *Terminalia* and *Lophira* result from the decomposition of CaO, which accounts for ~41% of their ash (see Table 3). The mass remaining after pyrolysis is the char, which was cooled down before being heated up in air to obtain the corresponding char burning profile. The char burning profiles have also been plotted in Figs. 1(a)-(e) for the fuels studied. In these DTG plots, a single peak can be observed at temperatures ~300-500$^o$C due to the char combustion stage. The peak temperatures for the devolatilisation and char combustion stages for all the fuels studied are listed in Table 6. The devolatilisation and char combustion peak temperatures are often used as indicators of fuel reactivity- the lower the peak temperature, the more reactive the fuel is [34]. The respective peak temperatures for the devolatilisation of *Gmelina* and *Nauclea* are lower compared to the rest of the Nigerian fuels suggesting that these fuels would be the most reactive. Their tendency to pyrolyse faster than the other fuels is likely due to their relatively high potassium content, since it is known to catalyse pyrolysis reactions [23, 34]. Previous work has shown that the peak temperature for volatile combustion decreases as the potassium content of the fuel increases [23, 34, 35]; still potassium remains a problem in biomass ash as it causes slagging and fouling issues in the combustion chamber.

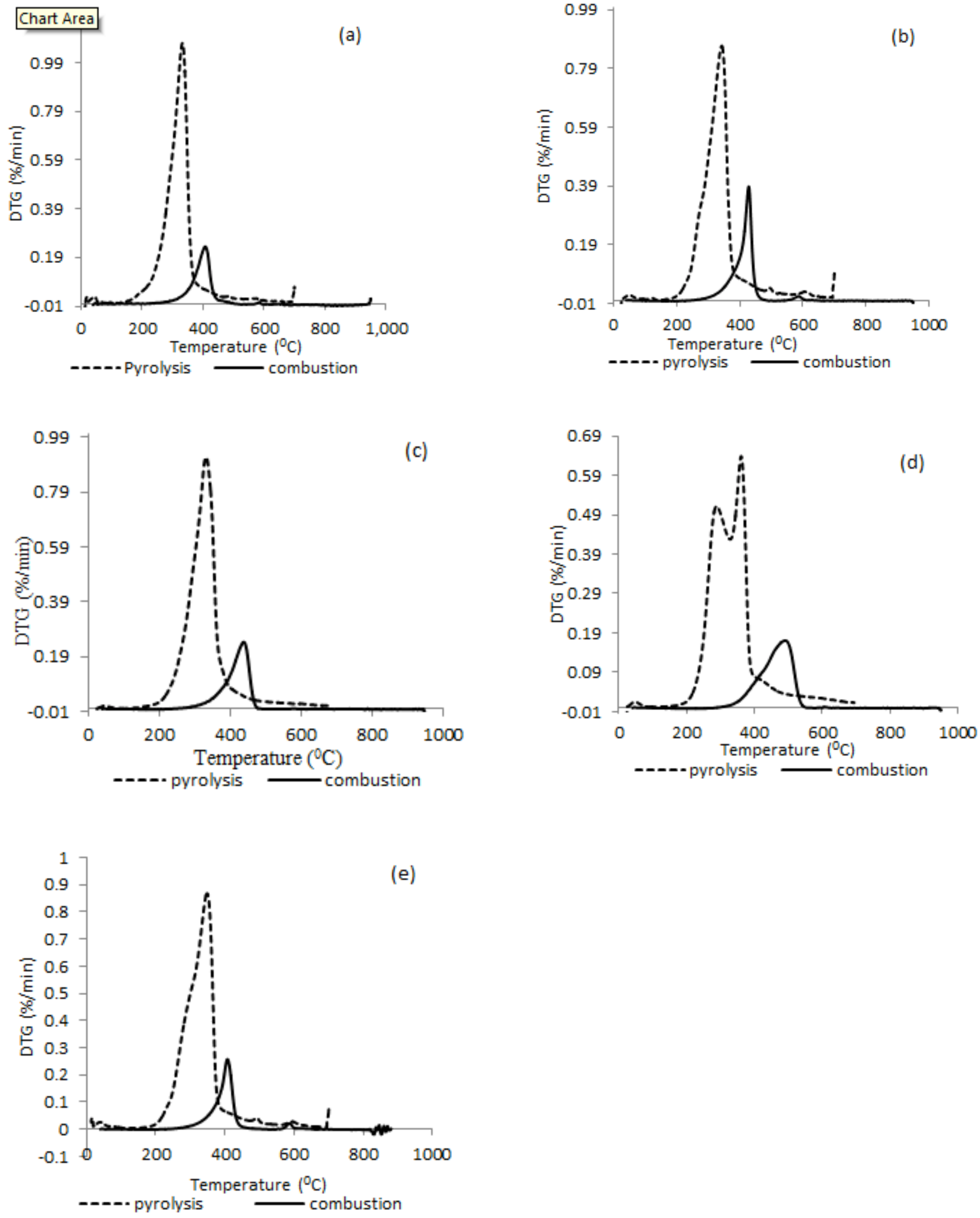


Chart Area
(a)
DTG (%/min)
0.99
0.79
0.59
0.39
0.19
-0.01
0
200
400
600
800
1,000
Temperature (⁰C)
Pyrolysis
combustion
(b)
DTG (%/min)
0.99
0.79
0.59
0.39
0.19
-0.01
0
200
400
600
800
1000
Temperature (⁰C)
pyrolysis
combustion
(c)
DTG (%/min)
0.99
0.79
0.59
0.39
0.19
-0.01
0
200
400
600
800
1000
Temperature (⁰C)
pyrolysis
combustion
(d)
DTG (%/min)
0.69
0.59
0.49
0.39
0.29
0.19
0.09
-0.01
0
200
400
600
800
1000
Temperature (⁰C)
pyrolysis
combustion
(e)
DTG (%/min)
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
-0.1
0
200
400
600
800
1000
Temperature (⁰C)
pyrolysis
combustion

Figure 1. DTG plots for the pyrolysis in nitrogen to 700ºC and subsequent char combustion in air to 900ºC of the fuels, where: (a) *Gmelina*, (b) *Lophira*, (c) *Nauclea*, (d) PKE and (e) *Terminalia*.

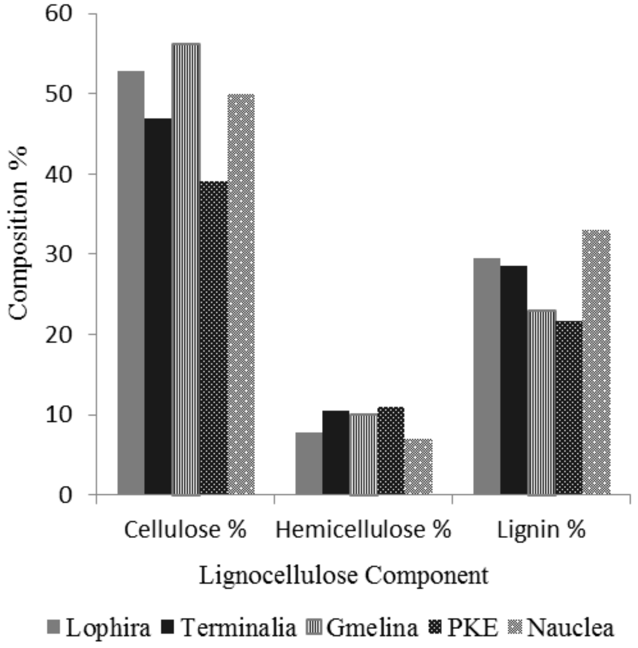


Figure 2. Lignocellulosic composition of the fuels.

The kinetic parameters for the pyrolysis of the fuels were estimated from the TGA mass loss curves obtained and are listed in Table 6. For this, it was assumed a global first-order reaction rate [36-41] and the pre-exponential factors A ($s^{-1}$) and activation energies Ea (kJ/mol) were calculated according to the reaction rate constant method [41-43]. The correlation coefficients ($R^2$) are also reported in Table 6. The ranking of the Ea follows the same order with the rate of reactivity using DTG peak pyrolysis temperature except for PKE, which showed the highest peak temperature but resulted in a slightly lower activation energy than both *Terminalia* and *Lophira*. For comparison purposes, the pyrolysis reactivities of the fuels were estimated at 573K ($k_{573}$), using the kinetic parameters obtained, and these are also listed in Table 6. The higher the value of k at the reference temperature, the more reactive the fuel is [41, 43, 44]. From the data in Table 6, we can expect that at 573K *Nauclea* and *Gmelina* would pyrolyse faster than *Terminalia* and *Lophira,* and that PKE would be the least reactive fuel. As expected, the same order of reactivity is obtained when comparing the peak temperatures for devolatilisation.

Table 6. Kinetic parameters for the devolatilisation of the fuels and DTG peak temperatures.

| **Fuel** | **Devolatilisation Temp ($^0$C)** | **Char combustion Temp ($^0$C)** | **Ln A ($s^{-1}$)** | **Ea (kJ $mol^{-1}$)** | **$k_{573}$ ($s^{-1}$)** | **$R^2$** |
|---|---|---|---|---|---|---|
| *Nauclea* | 325 | 428 | 9.88 | 77.8 | 0.00157 | 0.9953 |
| *Gmelina* | 325 | 398 | 10.03 | 78.8 | 0.00150 | 0.9947 |
| *Terminalia* | 343 | 403 | 15.57 | 110.2 | 0.00052 | 0.9982 |
| *Lophira* | 345 | 425 | 15.92 | 112.0 | 0.00051 | 0.9801 |
| PKE | 352 | 485 | 14.53 | 107.5 | 0.00033 | 0.9985 |

### 3.7 Combustion at flame temperatures

The video images recorded from the single particle combustion in a methane flame experiments were analysed to gain an insight into the combustion behaviour of the fuels at high heating rates/high temperature, and the following stages could be clearly identified from these images: ignition, volatile combustion, and char combustion. Consequently, the visual analysis of the images allowed the estimation of the ignition delay, and of the duration of the volatile and char combustion stages. In this work, the ignition of a fuel particle was assumed once flaming combustion was visible, after exposure to the flame. When the biomass particle enters the flame it undergoes the process of heating-up, moisture evaporation and then ignition [45, 46]. For the particle size studied here, the ratio of heat convected to the surroundings to heat conducted to the surface, i.e. the Biot Number, which is affects the heating-up process and the ignition delay, can be significantly influenced by the moisture content. However, in these experiments the biomass was oven dried (~5- 12% moisture). Ignition usually marks the beginning of volatile combustion and the end of moisture release. In combustion processes, the moisture content in the fuel particle is important because the requirement to dry the particles in the flame before they heat up and ignite causes a delay in the ignition process and can result in lifted or unstable pulverized fuel flames [47]. The lignocellulosic components of the fuels differ - softwoods have a smaller fraction of hemicellulose and a higher fraction of lignin when compared to hardwoods, and hemicellulose reacts faster at the lowest temperature when compared to cellulose and lignin [48]. A plot of the ignition delay against particle original dry mass is presented in Figure 3.

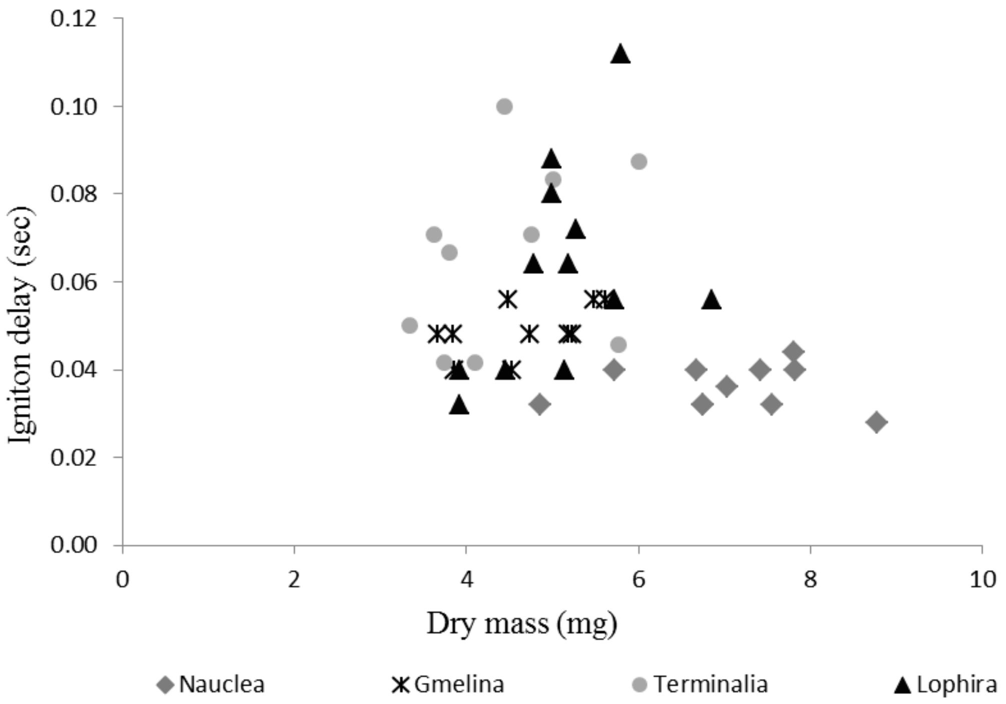


Figure 3. Plot of the ignition delay against particle dry mass.

From Figure 3, it can be observed that there were differences in the ignition delay of the studied Nigerian fuels. The ignition delay for *Nauclea* and *Gmelina* show a smaller dependence on particle mass than *Terminalia* and *Lophira*. However, in this case this is probably due to the chemical composition of *Nauclea* and *Gmelina* and both fuels having significantly low moisture contents when compared with *Lophira*. Density and thermal conductivity differences of the woods will also influence moisture and volatile diffusion rates as well as heating rates. The ignition delay of *Nauclea*, *Terminalia*, *Lophira* and *Gmelina* ranged from 0.03 – 0.05s, 0.04 – 0.10s, 0.03 – 0.11s and 0.04 – 0.06s respectively, with error ≤ ± 0.008s due to video frame speed. The spread in ignition delay arises in part from the difficulty in cutting particles to exactly the same size and also, in part, to the homogeneity of moisture content in individual particles. On average, *Nauclea* and *Gmelina* ignite faster- indicating that these fuels may be more reactive. As discussed in section 3.6, the temperature of maximum volatile production rate is ~ 20°C lower for *Nauclea* and *Gmelina* compared to *Terminalia* and *Lophira* (see Table 6).

Video interrogation of the combustion of single particles revealed overlap of volatile (flaming) combustion and char (glowing) combustion in most cases, where char combustion proceeded at the bottom of the particle while volatile release and combustion occurred from the top of the particle. Even so, the combustion processes were analysed as independent steps, which are discussed in this section. Volatile combustion was observed as the first stage following ignition, where the particles pyrolysed and volatile organic compounds were released. Figure 4 shows the duration of volatile combustion plotted against the particles' initial dry mass. During this stage, the particles were seen to undergo devolatilisation and the volatile materials released were combusted resulting in a flame. The volatile content, and therefore its rate of release, differ for all the fuels due to their composition (see Table 1), and also due to the differences in mass. This accounted for the variation in the duration of devolatilisation/volatile combustion of the fuels. The duration of flame combustion is comparable for all the fuels, except for *Nauclea*, as can be seen in Figure 4. There is quite a clear distinction between *Nauclea* and the other fuels, as similar sized particles are heavier in mass when compared to the other fuels. This resulted in a relatively lengthier volatile combustion stage (3.37-5.26s). The flame duration for *Terminalia*, *Lophira* and *Gmelina* ranged from 2.38-3.53s, 3.22-4.21s and 2.02-3.74s, respectively (error ≤ ± 0.008s). *Lophira* also had slightly longer flame duration than *Terminalia*, and *Gmelina* possibly due to slower release of volatile matter and also to variations in wood density. After flaming combustion, when all volatiles have been released, the volatile flame extinguishes, and oxygen can reach the residual char particle and heterogeneous char combustion commences. This process continues until the char is eventually reduced to a small mass of ash. It was also observed that shortly after devolatilisation, the particle started to shrink and then shrinks more rapidly towards the end of the combustion reaction until the residual ash was left attached to the supporting needle, i.e. the video evidence is consistent with a "shrinking sphere" model for char combustion (Zone II or III) where there is a contribution to the observed combustion rate from diffusion processes. For this work, the duration of char burnout was estimated from the end of volatile combustion until complete char burn out was evident. Figure 5 shows the plot of char burnout duration versus dry mass for the fuels.

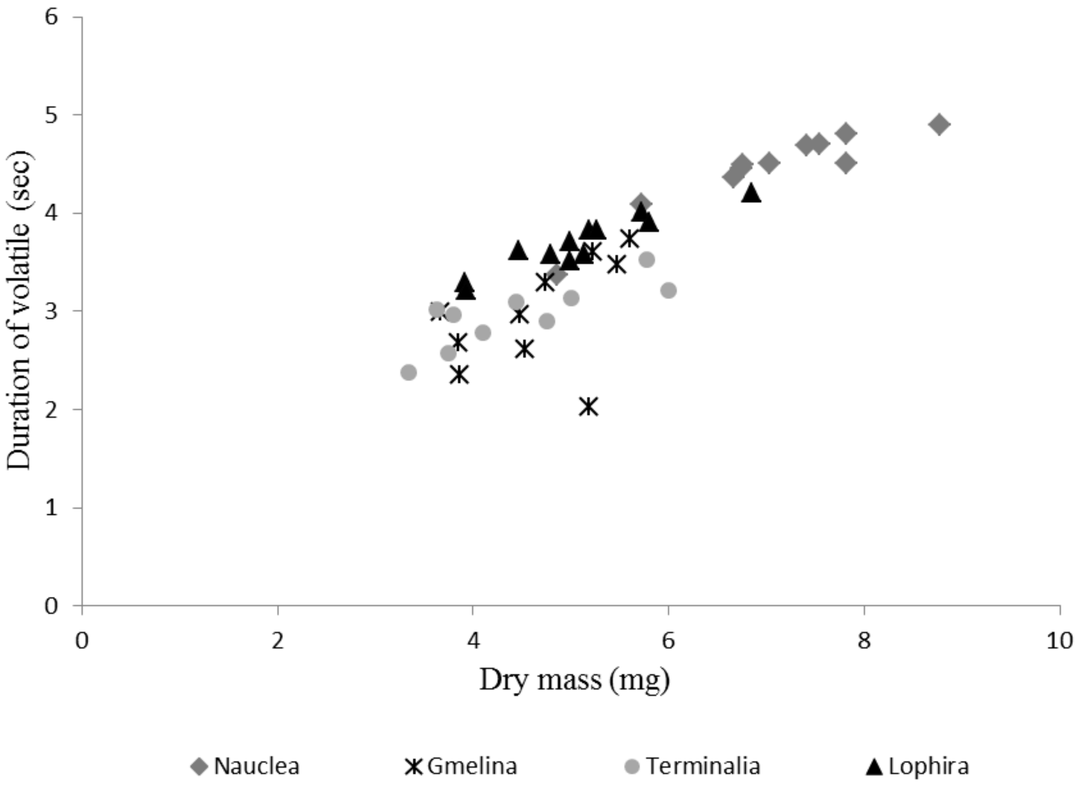


Figure 4. Duration of volatile combustion versus dry particle mass of the fuels.

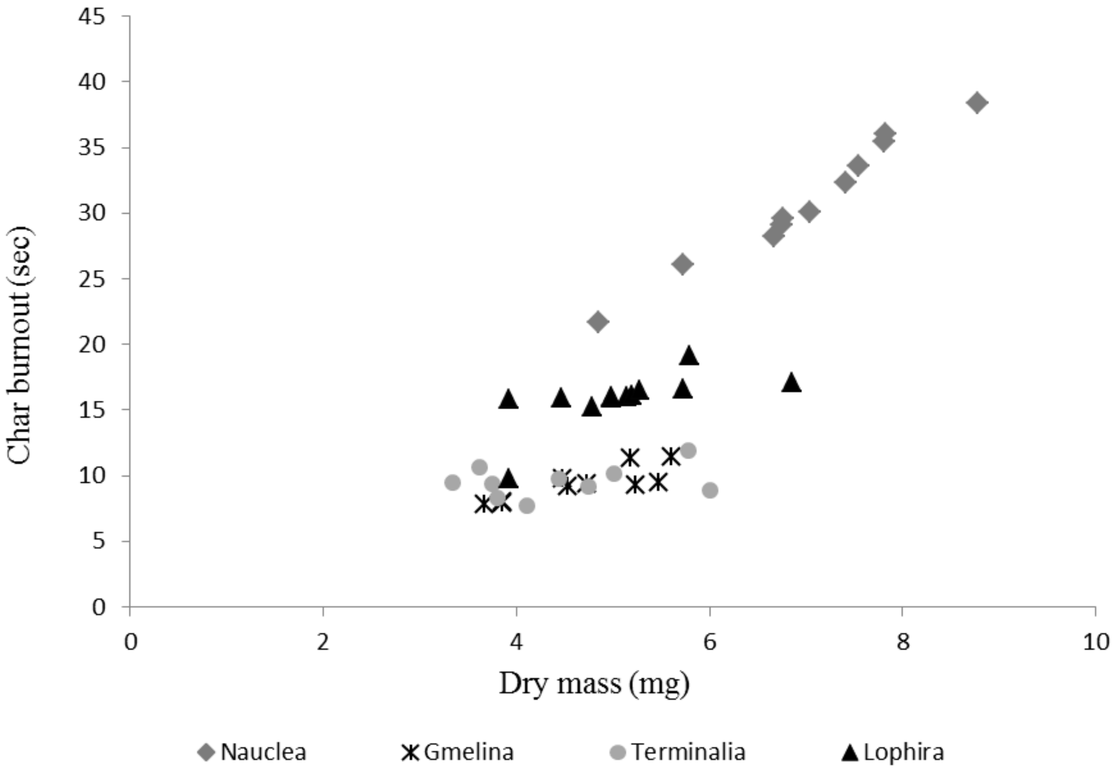


Figure 5. Duration of char burnout versus initial fuel particle dry mass.

From figure 5, it can be seen that the duration for char burnout for *Terminalia*, and *Gmelina* were comparable, and ranged from 7.7-11.9s (error ≤ ± 0.008s), whilst the *Lophira* and *Nauclea* particles showed distinctly longer char burnout stages (9.7-19.1s and 21.6-39.5s respectively). The major factors controlling char burnout are (i) the mass of char remaining after devolatilisation, (ii) the chemical factors determining the amount of high-temperature volatiles produced and on the development of char porosity, (iii) the amount of catalytic metals present in the char (iv) the chemical reaction rate of the char combustion, and (v) the diffusion rates. *Lophira* and *Nauclea* have higher fixed carbon contents and higher heating values than the other fuels, which could have resulted in a larger mass of char and therefore longer char burnout. Variations in the density of the raw material, the elemental carbon content of the resultant char and porosity may also contribute to differences in char combustion rates. *Terminalia,* which has an average wood density of 550 kg m$^{-3}$ and *Gmelina w*ith average wood density of 530 kg m$^{-3}$ are classified as medium density woods, while *Nauclea* (760 kg m$^{-3}$ average wood density) and *Lophira* (with 940 kg m$^{-3}$ average wood density) are classified as high-density woods. The higher mass per unit volume as well as possible depletion of amount of catalytic metals present in the resultant chars of could be responsible for the longer burn out rate of *Lophira* and *Nauclea*'s chars when compared with those of *Terminalia* and *Gmelina*; further work will establish the porosity development during devolatilisation and provide added insight into the observed differences in burnout rates. The slightly higher burnout times observed in *Nauclea* compared to *Lophira* could be due to *Nauclea*'s relatively higher elemental carbon content (see Table 2).

### 3.8 Pyrolysis-Gas Chromatography-Mass Spectrometry

Pyrolysis Gas Chromatography-Mass Spectrometry was used to investigate the different organic groups in the volatiles released. The technique involves rapid heating of the fuels which results in the release of volatile organic compounds and other volatile components from cellulose, hemicellulose and lignin in a similar way to flash pyrolysis [49]. The analysis highlights the differences in biomass composition and structure of the fuels. Table 7 shows the selected marker compounds for oil and lignocellulosic fractions in the Nigerian fuels, including PKE. The chromatograms obtained from the pyrolysis–GC–MS of the Nigerian fuels (with assignments to the main peaks) are presented in figures 6 – 10. The main peaks were assigned from the mass spectral detection NIST05A MS library and also from the literature [23, 35]. A wide variation of decomposition products from lignocellulose and also products from oil components in the fuel, including long chain fatty acids, are observed in the chromatograms. Figure 11 shows a comparison of the decomposition products from the Py-GC-MS analyses for the fuels studied against their dry weight percentage. The peak area percentages were calculated from the chromatograms and normalised per mg of volatile products as detailed in Nowakowski et al. [23]. The decomposition products are also grouped into their various lignocellulosic components as shown in Table 7. The peak area percentages were calculated from the chromatograms and quantified as a percentage of the fuel sample dry weight, which are listed in Table 8. The main products from their pyrolysis are methoxyphenols- originating from the degradation of their lignin fraction in the temperature ranges from 250-500$^{O}$C [50, 51]. The fast pyrolysis of the lignin fraction resulted in monomeric phenolic compounds and oligomers with different degrees of polymerization- these lignin-derived products are primarily responsible for the high-molecular weight and viscosity of bio-oils [49]. The conversion process and resultant products in fast pyrolysis depend on several operating parameters [52]. The most important parameters are the pyrolysis temperatures and heating rates, which determine the final yields of products obtained: bio-oil, noncondensable gases or char [33, 49, 52-54]. The mineral content in biomass also affects the quantity and quality of the products yields [53]. The literature suggests that high contents of monovalent potassium and divalent calcium in fuels are responsible for the lower organic volatile yield and may promote dehydration of holocellulose and demethoxylation of lignin units during pyrolysis [33, 49, 52-56]. This is consistent with our findings, since *Terminalia*, which has the highest CaO content (41.7 wt.%) records the highest peak area % for lignin products especially for methoxy-phenols and phenols (see figure 11). Depolymerization is the main process responsible for the decomposition of holocellulose during fast pyrolysis [56]. Qiang et al. [55] reported that the depolymerization process results in the formation of various anhydrosugars (mainly levoglucosan), furans and other products, although the high content of CaO in the fuel reduces the formation of levoglucosan. The presence of calcium promotes glucose fragmentation instead of cellulose depolymerisation [56]. Levoglucosan, is often the main product formed from the depolymerisation reaction of cellulose [56]. Further cellulose degradation also leads to formation of furan and acids. During the pyrolysis of PKE, most of the furan compounds form from the dehydration of carbohydrates [57]. Table 8 shows the relative percentages of the volatile products that originate from the decomposition of the different lignocellulosic fractions and oil. It can be observed that *Gmelina* and PKE are the only fuels that present oily compounds in their volatile fraction. Finally, the volatile yields from the py-GC-MS experiments (Table 8) are slightly higher than the measured volatile content (Table1). This is expected, since the pyroprobe is a flash pyrolysis technique that involves the rapid heating of samples and faster heating rates are known to favour higher volatile yields than slow pyrolysis.

Table 7. Classification of pyrolysis products into lignocellulosic groups [23, 51, 58].

| **Component** | **Degradation temperature** | **Evolved compounds** |
|---|---|---|
| Hemicellulose | 150-350ºC | 1,3-Pentadiene,<br>3-Methyl-1,2-cyclopentanedione,<br>1-methyl-4-(1-methylethenyl)-cyclohexanol |
| Cellulose | 275-350ºC | Furan,<br>2-methyl furfural,<br>1,2-Cyclopentanedione, |
| Lignin | 250-550ºC | 2-methoxylphenol; 2-methoxy-4-methylphenol; 4-methylphenol; 4-ethyl-2-methoxyphenol;<br>2-Methoxy-4-vinylphenol; Eugenol;<br>2,6-dimethoxyphenol; Phenol,<br>2-methoxy-4-(prop-1-enyl) phenol,<br>1,2,4-Trimethoxybenzene;<br>1-(4-hydroxy-3-methoxyphenyl)-ethanone<br>3',5'-Dimethoxyacetophenone<br>1-(4-hydroxy-3-methoxyphenyl)-2-propanone<br>2,6-dimethoxy-4-(prop-2-en-1-yl) phenol<br>Methylparaben; Vanillin. |
| Extractives | 250-550ºC | Decanoic acid<br>Desaspidinol<br>Hexadecanoic acid<br>6-Octadecenoic acid, |

Table 8. Quantification of volatile yields into lignocellulosic groups (peak area %)

| **Sample** | **Hemicellulose** | **Cellulose** | **Lignin** | **Extractives** | **High-heating rate volatile yields** |
|---|---|---|---|---|---|
| *Lophira* | 2.8 | <1 | 97.2 | <1 | 87.1 |
| *Terminalia* | 11.1 | 1.1 | 87.8 | <1 | 82.5 |
| *Gmelina* | 0.6 | 5.5 | 81.4 | 12.5 | 84.2 |
| *PKE* | <1 | 25 | 72.3 | 2.7 | 79.6 |
| *Nauclea* | 13.6 | <1 | 86.4 | <1 | 83.9 |

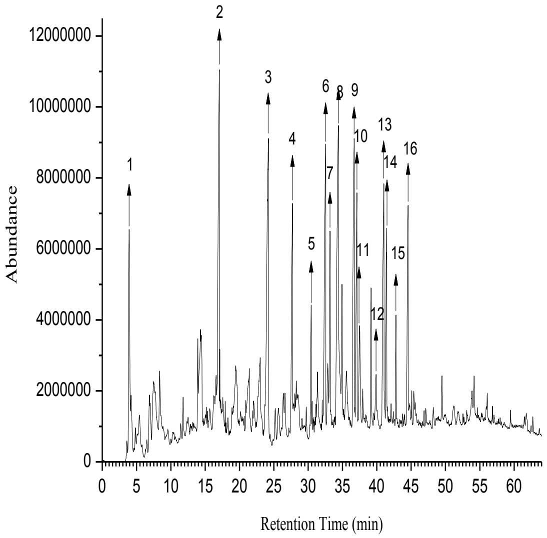


Figure 6. Py GC-MS chromatogram of *Nauclea* showing assigned peaks. The main peaks are assigned as follows: 1: 1,3-pentadiene, 2: cyclohexanol, 1-methyl-4-(1-methylethenyl)-, acetate; 3: 2-methoxyphenol; 4: 2-methoxy-4-methylphenol; 5: 4-ethyl-2-methoxyphenol; 6: 2-methoxy-4-vinylphenol; 7: eugenol; 8: 2,6-dimethoxyphenol; 9: 2-methoxy-4-(1-propenyl) phenol -; 10: 1,2,4-trimethoxybenzene; 11: vanillin; 12: ethanone, 1-(4-hydroxy-3-methoxyphenyl); 13: 3',5'-dimethoxyacetophenone; 14&15: 2,6-dimethoxy-4-(2-propenyl)phenol.

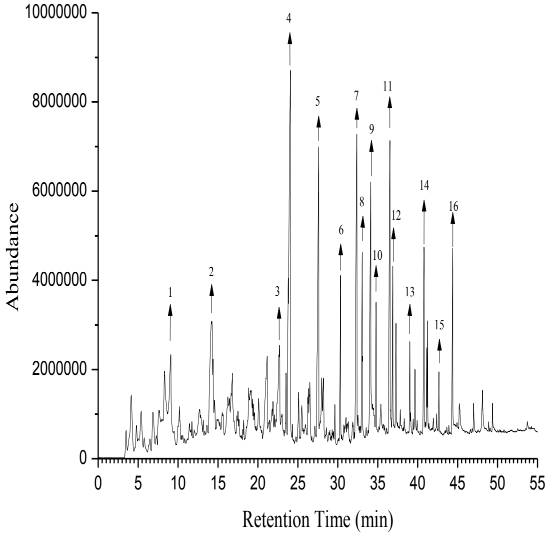


Figure 7. Py GC-MS chromatogram of *Terminalia* showing assigned peaks. The main peaks are assigned as follows: 1:1,3-pentadiene, 2: cyclohexanol, 1-methyl-4-(1-methylethenyl)-, acetate; 3: 1,2-cyclopentanedione, 3-methyl; 4: phenol; 5: 2-methoxyphenol; 6: 2-methoxy-4-methylphenol; 7: 4-ethyl-2-methoxyphenol; 8: 2-methoxy-4-vinylphenol; 9: eugenol; 10: 2,6-

dimethoxyphenol; 11: 2-methoxy-4-(1-propenyl)-phenol; 12: 1,2,4-trimethoxybenzene; 13: vanillin; 14: ethanone, 1-(4-hydroxy-3-methoxyphenyl); 15: 3',5'-dimethoxyacetophenone; 16: 2,6-dimethoxy-4-(2-propenyl)phenol.

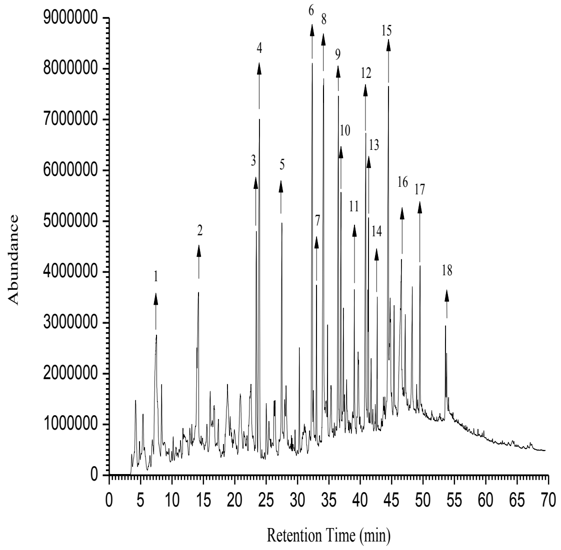


Figure 8. Py GC-MS chromatogram of PKE showing assigned peaks. The main peaks are assigned as follows: 1: furan, 2-methyl-; 2: furfural; 3: phenol; 4: 2-methoxyphenol; 5: 2-methylphenol; 6: 4-methylphenol; 7: 2-methoxy-4-methylphenol; 8: 4-ethyl-2-methoxyphenol; 9: 2-methoxy-4-vinylphenol; 10: 2-methoxy-3-(2-propenyl)phenol; 11: 2,6-dimethoxy-phenol; 12: 2-methoxy-4-(1-propenyl)-phenol; 13: 1,2,4-trimethoxybenzene; 14: vanillin; 15: 3',5'-dimethoxyacetophenone; 16: 2,6-dimethoxy-4-(2-propenyl)-phenol; 17: n-hexadecanoic acid; 18: 6-octadecenoic acid.

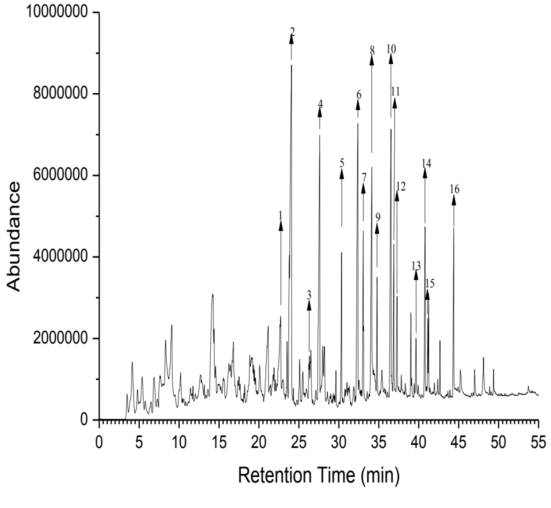


Figure 9. Py GC-MS chromatogram of *Lophira* showing assigned peaks. The main peaks are assigned as follows: 1: 1,2-Cyclopentanedione, 3-methyl; 2: 2-methoxyphenol; 3: 2-methoxy-3-methylphenol; 4: 2-methoxy-4-methylphenol; 5: 4-ethyl-2-methoxyphenol; 6: 2-Methoxy-4-vinylphenol; 7: eugenol; 8: 2,6-dimethoxyphenol; 9: 2-methoxy-4-(1-propenyl)phenol; 10: 1,2,4-trimethoxybenzene; 11: vanillin; 12: ethanone, 1-(4-hydroxy-3-methoxyphenyl)-; 13:

3',5'-dimethoxyacetophenone; 14: 2-propanone, 1-(4-hydroxy-3-methoxyphenyl)-; 15: 2,6-dimethoxy-4-(2-propenyl)phenol; 16: 2,4-hexadienedioic acid, 3,4-diethyl-dimethyl ester.

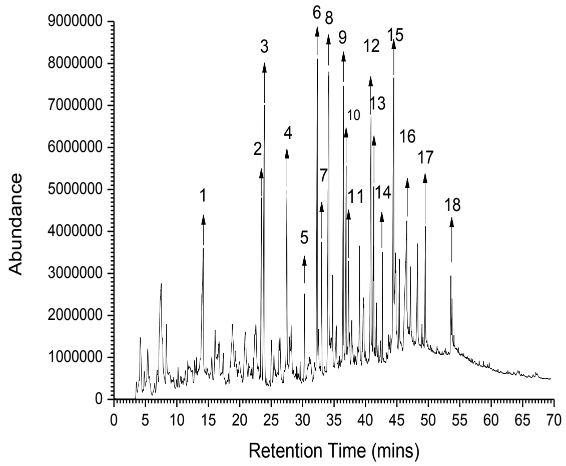
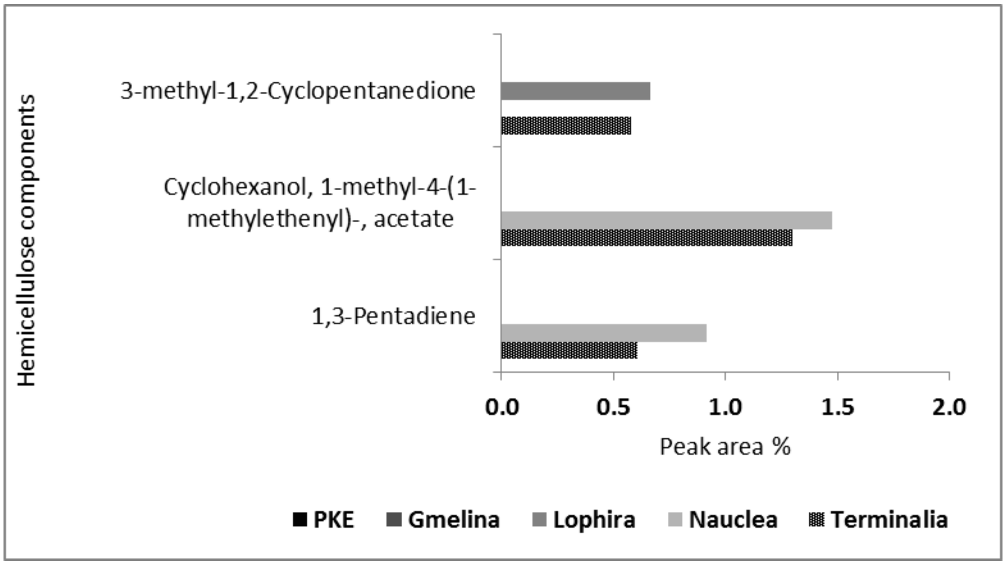
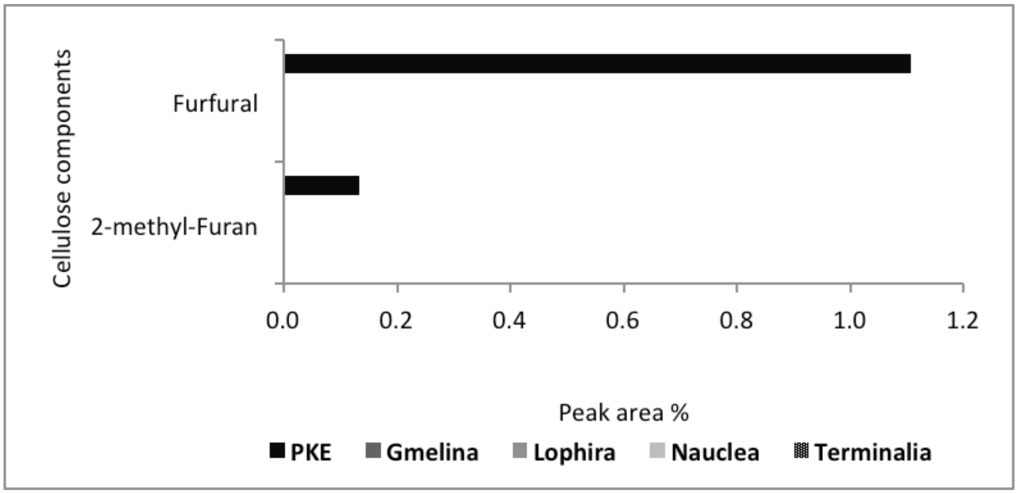
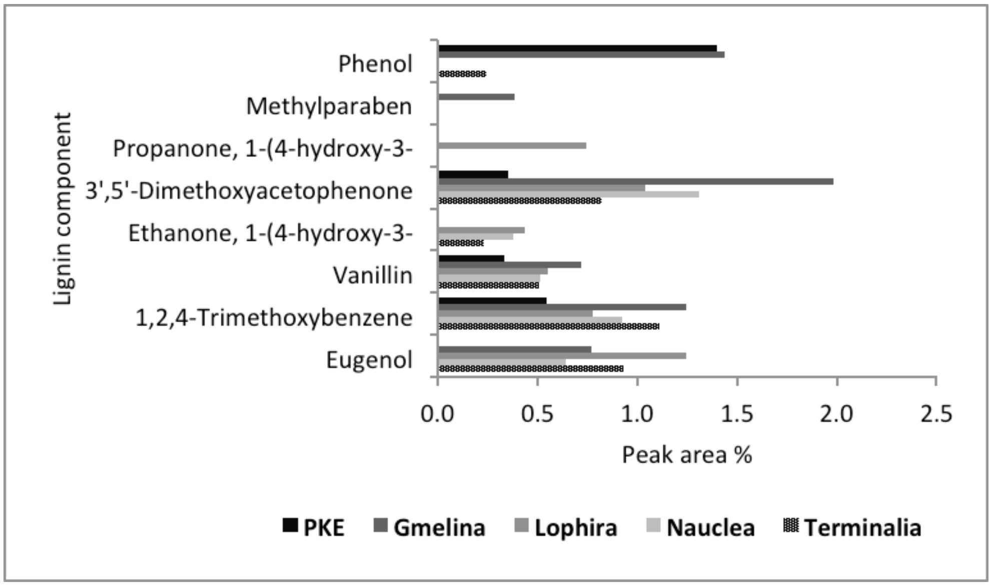
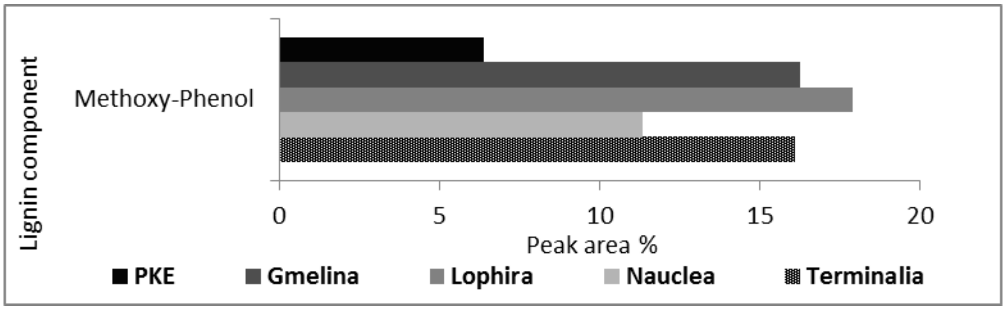


Figure 10. Py GC-MS chromatograms of *Gmelina* showing assigned peaks. The main peaks are assigned as follows: 1: 3,5-dimethylpyrazole-1-methanol; 2: phenol; 3: 2-methoxyphenol; 4: 2-methoxy-4-methylphenol; 5: 4-ethyl-2-methoxyphenol; 6: 2-methoxy-4-vinylphenol; 7: eugenol; 8: 2,6-dimethoxyphenol; 9: 2-methoxy-4-(1-propenyl)phenol; 10: 1,2,4-trimethoxybenzene; 11: vanillin; 12: 3',5'-dimethoxyacetophenone; 13: 2,6-dimethoxy-4-(2-propenyl)-phenol; 14: methylparaben; 15: decanoic acid; 16: desaspidinol; 17: hexadecanoic acid; 18: 6-octadecenoic acid.




Cellulose components
Furfural
2-methyl-Furan
0.0
0.2
0.4
0.6
0.8
1.0
1.2
Peak area %
PKE
Gmelina
Lophira
Nauclea
Terminalia


Lignin component
Phenol
Methylparaben
Propanone, 1-(4-hydroxy-3-
3',5'-Dimethoxyacetophenone
Ethanone, 1-(4-hydroxy-3-
Vanillin
1,2,4-Trimethoxybenzene
Eugenol
0.0
0.5
1.0
1.5
2.0
2.5
Peak area %
PKE
Gmelina
Lophira
Nauclea
Terminalia


Lignin component
Methoxy-Phenol
0
5
10
15
20
Peak area %
PKE
Gmelina
Lophira
Nauclea
Terminalia

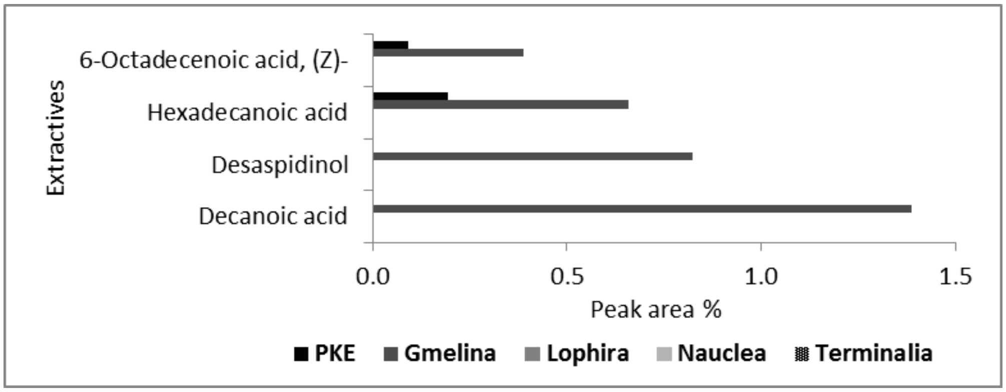


Figure 11. Key markers from the Py-GC-MS analysis of the Nigerian fuels.

## 4.0 Conclusions

Four Nigerian woods: *Gmelina*, *Lophira*, *Terminalia*, and *Nauclea*, and a residue- palm kernel expeller (PKE) have been characterised and studied for their combustion properties. The fuels were characterised by proximate and ultimate analysis and compared with some UK energy crops. Additionally, pyrolysis and char burning profiles of the fuels were obtained by thermogravimetric analysis to assess their combustion properties, and the ash slagging and fouling propensity of these fuels were also estimated. It was found that the Nigerian fuels studied here have higher carbon contents (49-53% dry basis) than the UK energy crops included in this study -for comparison purposes. Their higher carbon content resulted in the relatively high (for woody biomass) calorific values of 19-21 MJ kg$^{-1}$ (dry basis). Ash contents are relatively low and fall in the range of 0.7-2.2 wt.% (dry basis). The ash compositions are dominated by calcium oxide, potassium oxide and silica. Ash compositions are very different between the four Nigerian woods with silica contents ranging from 1.7-10.5%, potassium oxide contents ranging from 8.2-32% and calcium oxide contents ranging from 9.3-41.7%. Although the potassium oxide content in the ash is high, particularly in the case of *Gmelina* and *Nauclea*, their low ash contents mean that the predicted fouling behavior is not foreseen to cause major problems in boilers. The base percentages fall in the range 45-53%, which is the expected range for low melting ashes, although the ash fusion test results under oxidizing conditions show that these ashes begin to deform at temperatures above 1200ºC (except for Gmelina- at 1185ºC). These mixed findings suggest that careful management of fuel quality (such as debarking) and boiler operation would be advisable for high temperature combustion applications. Analysis from TGA showed differences in the combustion properties of these fuels. The high content of potassium in *Gmelina* appears to influence the combustion properties of the fuel, since the peak temperature for volatile combustion is lower than for all other fuels (except wheat straw), indicating that the fuel is more reactive. The results from the single particle combustion experiments revealed that *Lophira* and *Nauclea* showed relatively longer char burnout stages than *Gmelina* and *Terminalia*. This may be due to the differences in wood density. Further work is needed in order to examine porosity development during char formation and how this impacts on char combustion rates.

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