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Research Article
Potentials of Milled-wood Residue and Kraft Lignin of *Ficus exasperata* Vahl.

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Abstract

Background and Objective: Wood and other industrial waste or residues are loaded with great potentials that can serve as raw materials for bio-energy and bio-refinery usage. In this study the active constituent present in milled-wood residue (MWR) and kraft ficus lignin (KFL) was analyzed using Ultimate (CNHOS), FT-IR, GC-MS and proximate analysis. **Materials and Methods:** Lignin was isolated by precipitating from Black liquor and purified by acidification. The Ultimate analysis (CHNOS) was carried out using ASTM 3174-76 (2009), FT-IR spectroscopic analysis and GC-MS analysis was carried out. **Results:** Ultimate analysis irrespective of pulping temperature varied significantly in MWR and KFL. Carbon was most abundant in MWR with highest value of 33.13% and lower value of 32.12% in KFL. FT-IR presented various peaks with strong, medium, broad and weak intensities that indicated the diverse bond types such as O-H, C=O, N-H, C-O-H, C-O and C-H with emergence of phosphine and bicarbonate in MWR and carboxylic acid in KFL. The GC-MS analysis of KFL revealed that 23 peaks were detected; Oxalic acid ($C_{19}H_{36}O_4$) with retention time of 27.74 had the highest peak area 18.45% while methyl tridecanoate ($C_{14}H_{28}O_2$) with retention time 10.66 had lowest peak area 0.35%. Calorific value of the 2 energy materials gave ash (%) content of 4.22 and 24.66% with average heating value of 32.19 and 25.37 MJ kg^{-1} for MWR and KFL respectively. **Conclusion:** MWR and KFL revealed that *F. exasperata* as a raw-material (Oxalic acid, vanillin, synthetic tannins and polymer filters) has the potential for bio-energy and bio-chemical production.

Key words: *Ficus exasperata*, milled-wood residue, kraft lignin, ultimate analysis, bioenergy

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Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

Lignocellulosic biomasses are in abundance and possess great potentials for the production of fuels and chemicals[1]. In developing country like Nigeria, forest, Agricultural and industrial waste management has always been a major challenge due to rapid growth in population, socio-cultural change and widespread poverty which have all contributed to waste disposal challenges and environmental degradation[2]. The conversion of this waste to energy will be an opportunity to confront both the menace of waste and also the domestic fuel challenge. In this present time, the management of waste from industrial and domestic products brings about problem with the consequence of pollution to the environment[3]. However, the aim of wood pulping is to remove lignin from wood fibre in order to use the fibre in paper production. There are several methods used for removing lignin, but the most common is Kraft pulping which produces strong pulps for use. The Kraft process utilizes a solution of sodium hydroxide and sodium sulphide to treat wood chips at an elevated temperature around 170°C. Black liquor is a waste generated during pulp and paper production, it contains high lignin content (kraft lignin) that gives the black liquor the dark brown to black color[4,5]. The black liquor of kraft pulping contains some amount of lignin and residual pulping chemicals which should not be flushed into the downstream but could be enhanced as raw material for bio-energy and bio-chemical production.

The reason for lignin precipitation from black liquor is to produce fuel and other products that can serve as sources of income/revenue generation[6]. Also, the use of renewable resources is important and only sustainable processes that transform such resources into useful products can achieve beneficial economic growth[7].

This study investigated the wood residue and kraft lignin of *F. exasperate* for the purpose of identifying their potentials for better utilization as biomaterial so that the economic importance of the species becomes more pronounced, this might directly help in reducing over exploitation of other known species.

MATERIALS AND METHODS

Sample collection: Milled-wood residue (MWR) was obtained from the Department of Forest Products Development and Utilization, Forestry Research Institute of Nigeria in 2017. The institute is located along latitude 7°23'34''N to 7°23'36''N and longitude 3°51'36''E to 3°51'36''E. The MWR was air dried for 4 weeks in order to reduce the moisture content to about 12% and was subjected to ultimate (FT-IR) and proximate analysis. Black liquor (a waste from pulping) was collected and used for this experiment in order to compare it's potentiality.

Lignin precipitation and purification: Kraft ficus lignin obtained was isolated by precipitating kraft ficus lignin (KFL) from KBL by acidification. The procedure of lignin precipitation and purification followed published method by Ben and Ragauskas[8]. KBL was separated through a filter paper on a funnel. Approximately 100 mL of ethanol was added to 300 mL of KBL. The solutions were stirred for 1 h. The KFL was allowed to settle down for 15 h after which it was decanted. Precipitates were poured into a glass funnel and washed twice with cold water by vigorous stirring. However, semi-solid precipitate obtained were air dried and extracted for 8 h in a soxhlet extractor using pentane to remove excess sulphur and other impurities. The KFL precipitates were suspended in a 9:1 H_2SO_4:H_2O solution and stirred for an hour in order to complete the purification process. The precipitates were washed again with 9:1 H_2SO_4:H_2O and stirred. Purified KFL was dried and the yield determined after H_2SO_4 was removed by evaporation. The recovered lignin was determined and subjected to the following test: FT-IR, GC-MS, ultimate and proximate analysis.

Characterization of MWR and KFL

Ultimate analysis: The following elements were determined using[9] ASTM 3174-76; Carbon (C), Hydrogen (H), Nitrogen (N), Oxygen (O) and Sulphur (S) content.

FT-IR: Spectroscopic analysis was performed using Perkin ELMER 1600 to know the functional groups present in both the MWR and KFL.

GC-MS: The KFL obtained was methylated and analysed using gas chromatography-mass spectroscopy. The GC-MS analysis was done using the instrument Trace GC Ultra Thermo Scientific DSQ II, equipped with a VF-5ms fused silica capacity column of 30 m length, 0.25 mm diameter and 0.25 µm film thickness. For GC-MS detection, an electron ionization system with ionization energy of 70 Ev was used. Helium gas 99.99% of purity was used as a carrier gas as well as an eluent. The flow rate of helium gas was set to 1.5 mL min^{-1}. The sample injector temperature was maintained at 200°C. Initially oven temperature was maintained at 140°C for 1 min and the temperature was gradually increased up to 300°C for 5 min. About 1 µL of sample was auto injected for analysis.

In identifying the various components, the relative percentage amount of each component was calculated by comparing its average peak area to the total areas. The detection employed by using[10,11] the NIST (National Institute of Standards and Technology) library version 2.0. Interpretation of GC-MS was conducted using the database of NIST library having more than 62,000 patterns. The spectrum of the component was compared with that of a known spectrum, the components saved in the NIST library version 2.0. The name, molecular weight and molecular formula of components of the test materials were ascertained.

Proximate analysis

Volatile matter (%): This was determined by separately placing 2 g of the samples (MWR and KFL) in a crucible of known mass and oven-dried to a constant mass, after which it was heated in the furnace at temperature of 600°C for 10 min:

$$\text{Volatile matter (\%)} = \frac{B - C}{B} \times 100 \quad (1)$$

where, B is the weight of oven dried sample (g) and C is the weight of sample after 10 min in the oven (g).

Ash content (%): This follows the same procedure as volatile matter, except that the samples were heated in the furnace for about 2 h:

$$\text{Ash content (\%)} = \frac{D}{B} \times 100 \quad (2)$$

where, B is the weight of oven dried sample (g) and D is the weight of ash (g).

Fixed carbon (%): This was obtained by subtracting the value of the addition of percentage volatile matter and percentage of ash content from 100%. This is expressed using the Eq:

$$\text{Fixed carbon (\%)} = 100 - (V + A) \quad (3)$$

where, FC is the percentage of fixed carbon, V is the percentage volatile matter while A is the percentage ash content.

Heating value (Hv): This was calculated using Gouthal Eq:

$$\text{Heating value} = 2.326\,(147.6C + 144V) \quad (4)$$

where, H_V is the heating value (MJ kg^{-1} or KJ kg^{-1}), C is the percentage fixed carbon and V is the percentage volatile matter.

Statistical analysis: A one-way analysis of variance (ANOVA) was used for kraft lignin Yield. Data were subjected to statistical analysis of 3×3 factorial experiment in a completely randomized design (CRD) and Mean±SEM.

RESULTS

Kraft ficus lignin yield: The mean values of precipitated KFL from KBL are presented in Table 1. The yield increased with increase in pulping temperature from 18.8% at 140°C to 21.3% at 160°C and then decreased with further increase in pulping temperature 19.2% at 180°C. Analysis of variance shows that pulping temperature had significant influence on the kraft lignin yield (p = 0.038) (Table 2).

Ultimate analysis: Observation made on variation in ultimate analysis of MWR and KFL in Fig. 1 shows that carbon content in MWR (33.13%) was higher than that of KFL (32.12%).

Table 1: Influence of pulping temperature on the yield of kraft ficus lignin

Pulping temp. (°C)	Ethanol (mL)	Black liquor (mL)	Kraft lignin (%)
140	100	300	18.8±0.26
160	100	300	21.3±0.22
180	100	300	19.2±0.23

Table 2: Analysis of variance for kraft ficus lignin yield

SV	Df	SS	MS	F-cal	Sig.
Tree	2	1.209	0.605	97.274	<0.001
Temp	2	0.001	0.001	0.119	0.038
T×temp	4	0.017	0.004	0.687	0.610
Error	18	0.112	0.006		
Total	26	1.339			

p-values>0.05 are not significant, SV: Source of variation, Df: Degree of freedom, SS: Sum of square, MS: Mean square, Sig: Significance, F-cal: F-calculated

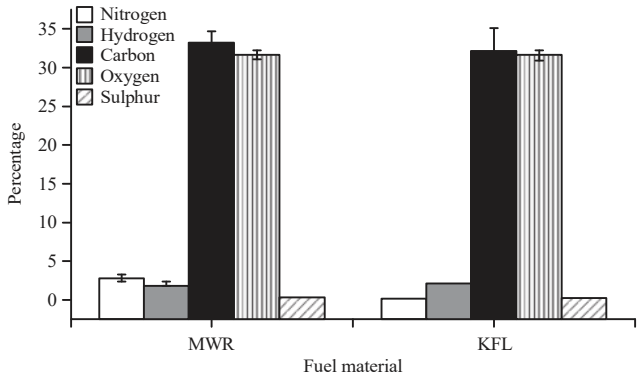

Fig. 1: Mean values of ultimate analysis of MWR and KFL

Table 3: Frequency, functional group and compounds present in milled-wood residue

Frequency (cm^{-1})	Functional group	Type of vibration	Compounds	Intensity
3781.26	O-H	Stretching	Phenols	Broad and intense peak
3415.00	N-H	Stretching	Amines	Strong band
2922.15	C-H	Stretching	Alkanes	Strong band
2354.21	P-H	-	Phosphine	Strong broad
2044.81	$NaHCO_3$	-	Bicarbonate	Very weak
1735.65	C=O	Stretching	Aldehyde	Double bond
1611.37	C=O	Stretching	Ketones	Double bond
1426.57	C-O-H	Bending	Phenols	Broad and weak peak
1370.62	C-O-H	Bending	Phenols	Broad and weak peak
1324.13	C-O-H	Bending	Phenols	Broad and weak peak
1258.31	C-O	Bending	Ethers	Strong band
1049.37	C-O	Bending	Ethers	Strong band
895.10	C-H	Plane bending	Aromatic	Strong band
776.02	C-H	Plane bending	Aromatic	Strong band
662.93	C-H	Bending	Alkenes	Very strong
608.29	C-H	Bending	Alkynes	Very Strong

H: Hydrogen, C: Carbon, O: Oxygen, N: Nitrogen, Na: Sodium, P: Phosphorus

Oxygen content was also higher in MWR (31.12%) than 9.62% obtained in KFL. While trace of sulphur 0.29 and 0.21% was obtained in MWR and KFL, respectively.

FT-IR of MWR: The result of fourier transform infrared spectroscopy of MWR of *F. exasperata* fractions is presented in Table 3. It was observed that various peaks with strong, medium, broad and weak intensities were found indicating different bond types such as O-H, C-O, N-H, C=O C-O-H and C-H was obtained in the wood residue of *F. exasperata*. The O-H and N-H stretching vibrations was because of phenols (broad and intense peak) and amines (strong), whereas the C-O bending vibrations were from aromatic, alkenes and alkynes. Similarly, C-O-H having a bending vibration of broad and weak intensity was due to the presence of Phenols. Moreover, strong bands signify the presence of ethers with C-O stretching vibration. However, C=O with stretching type of vibration indicates the presence of aliphatic aldehyde and ketones. While C-H indicated the presence of alkanes with strong intensity. While the presence of phosphine (PH) and bicarbonate ($NaHCO_3$) in MWR was observed to have a strong band and broad and weak band respectively (Table 3).

Fourier transform infrared spectroscopy of KFL: The result in Table 4 shows all the various peaks with strong, medium, broad and weak intensities present. It also indicated the diverse bond types such as O-H, C=O, N-H, C=C, C-O-H, C-O and C-H in kraft ficus lignin. The O-H and C-H with stretching vibrations were from phenols having broad and intense peak and alkanes with strong intensity. Whereas the functional group of C=O having stretching vibrations were from aldehydes and ketones. Also, N-H with a bending vibration and broad band intensity was because of secondary amines. Similarly, group of C-O-H with a bending vibration shows broad and weak intensity from phenols while C-O stretching with medium intensity indicated the presence of carboxylic acid. The C-O stretching vibration indicated the presence of secondary and primary alcohol with broad and weak intensity. (Table 4).

GC-MS: Observation made on GC-MS of kraft ficus lignin in Table 5 detected 23 peaks. NIST library was used to identify the compounds present. The name of identified compounds in the kraft ficus lignin with their retention time (RT), molecular formula (MF), molecular weight (MW) and peak area percentage were also present. The peak at 27.74 retention time was observed to be the highest with peak area of 18.45% and the bioactive compound presents oxalic acid (OA) with molecular formula $C_{19}H_{36}O_4$ and molecular weight of 328. While the peak at 10.66 retention time had the lowest peak area percentage of 0.35% with the presence of methyl tridecanoate having molecular formula $C_{14}H_{28}O_2$ and molecular weight of 228. The acid present in GC-MS of kraft lignin appear to be oxalic acid.

In general, the GC-MS result showed that kraft ficus lignin is composed mostly of 43.85% oxygenated, hydrocarbons; approximately 24.91% aliphatic (C_{10}-C_{21}) and 16.08% are aromatic (C_7-C_{10}). Other compounds observed were 5.78% ketones, 3.93% nitrogenated, 4.54% alkanes and 0.81% alkenes (Fig. 2).

Proximate analysis: The result in Fig. 3 compared the calorific value of the 3 energy sources in this study, it was recorded that MWR contains higher percentage volatile matter averaged 82.89%, compared to 64.52% in KFL. Lower percentage ash content of 4.22% was recorded in MWR

Table 4: Frequency, functional group and compounds present in kraft ficus lignin

Frequency (cm^{-1})	Functional groups	Type of vibration	Compounds	Intensity
3394.8	O-H	Stretching	Phenol	Very broad and Intense
2924.2	C-H	Stretching	Alkanes	Strong band
2854.7	C-H	Stretching	Alkanes	Strong band
1735.9	C=O	Stretching	Aldehydes	Double bond
1712.8	C=O	Stretching	Ketones	Double bond
1589.4	N-H	Stretching	Amines	Broad band
1504.5	C-O-H	Stretching	Phenols	Broad and weak peak
1458.2	C-O-H	Bending	Phenol	Broad and weak peak
1419.6	C-O-H	Bending	Phenol	Broad and weak peak
1419.6	C-O-H	Bending	Phenol	Broad and weak peak
1373.3	C-O-H	Bending	Phenol	Broad and weak peak
1319.3	C-O	Bending	Carboxylic	Medium intensity
1265.7	C-O	Bending	Carboxylic	Medium intensity
1226.7	C-O	Bending	Carboxylic	Medium intensity
1103.3	C-O	Bending	Alcohols (secondary)	Broad and weak intensity
1026.4	C-O	Bending	Alcohols (primary)	Broad and weak intensity
1026.1	C-O	Bending	Alcohols (primary)	Broad and weak intensity
910.4	C-H	Plane bending	Alkenes	Very strong

H: Hydrogen, C: Carbon, O: Oxygen, N: Nitrogen

Table 5: Bioactive compounds detected and their functional groups in kraft ficus lignin

Peak no.	RT (min)	PA (%)	MW (g mol^{-1})	MF	Bioactive compounds	Groups
1	4.40	3.93	68	$C_3H_4N_2$	Pyrazole	Nitrogenated
2	6.76	1.72	124	C_9H_{16}	Cyclohexane	Ketones
3	6.15	0.41	142	$C_{11}H_{10}$	1,4-Methanonaphthalene	Aromatic
4	9.94	0.45	320	$C_{21}H_{36}O_2$	11,14,17-Eicosatrienoic acid	Oxygenated
5	10.66	0.35	228	$C_{14}H_{28}O_2$	Methyl tridecanoate	Aliphatic
6	12.96	0.45	278	$C_{12}H_{23}BrO_2$	Methyl 11-bromoundecanoate	Aliphatic
7	13.87	1.39	101	$C_5H_{11}NO$	Decanamide	Amide
8	15.19	6.02	330	$C_{19}H_{83}O_4O$	2,3-dihydroxypropyl ester	Oxygenated
9	15.66	0.50	284	$C11H_{22}O_2$	Decanoic acid	Oxygenated
10	17.19	1.14	119	$C_{12}H_{25}NO$	Myristic acid	Amide
11	18.90	4.54	184	$C_{13}H_{28}$	Lauric acid	Alkane
12	20.49	2.40	227	$C_{14}H_{29}NO_4$	Tetradecamide	Amide
13	21.64	5.29	330	$C_{19}H_{38}O_4$	2,3-Dihydroxypropyl ester	Oxygenated
14	22.24	0.81	272	$C_{17}H_{33}Cl$	1, Chloro-7-heptadecene	Alkene
15	22.62	8.28	281	$C_{18}H_{35}NO$	9-Octadecenamide	Amide
16	22.85	2.56	283	$C_{18}H_{37}NO$	Octadecenamide	Amide
17	23.06	1.94	266	$C_{18}H_{34}O$	13 Octadecanal	Aliphatic
18	23.52	10.72	210	$C_{14}H_{26}O$	2,11-Tetradecadien-1-ol	Oxygenated
19	23.73	2.42	286	$C_{12}H_{26}O$	2-butyl-1-octanol	Oxygenated
20	24.33	11.88	298	$C_{20}H_{42}O$	Eicosanol	Aliphatic
21	24.87	4.06	450	$C_{31}H_{62}O$	Dipentadecyl ketone	Ketone
22	27.09	10.29	296	$C_{21}H_{44}$	2,6,10,14 tetramethyl heptadecane	Aliphatic
23	27.74	18.45	328	$C_{19}H_{36}O_4$	Oxalic acid	Oxygenated

RT: Retention time, PA (%): Peak area percentage, MW: Molecular weight, MF: Molecular formula

while the higher content of 24.66% was obtained in KFL. On average, percentage fixed carbon recorded was 12.89% and 9.00% for MWR and KFL respectively. However, it was observed that the heating value was higher 32.19 MJ kg^{-1} in MWR while KFL had a lower heating value of 25.37 MJ kg^{-1}.

DISCUSSION

Lignin is a good source of energy suitable in the production of fuel, steam and syngas[12,13]. The yield of KFL is said to be high though the level of purity is not different from kraft eucalyptus lignin. This is because KFL recorded 0.26% sulphur and ash content of 24.66%. However, this is in line with kraft eucalyptus lignin that presented very low purity levels with a high amount of ash content (>20%)[14]. Vakkilainen and Valimaki[15] were of the opinion that precipitating lignin from black liquor could be used as substitute for fuel in the kilns. It could also be upgraded and use as raw material for production of composites, adhesives and other chemicals. Also, it is said to be a multipurpose

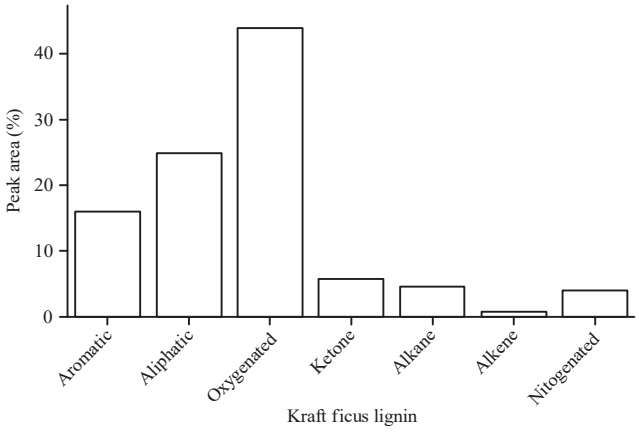

Fig. 2: Compounds identified in kraft ficus lignin based on their peak area percentage

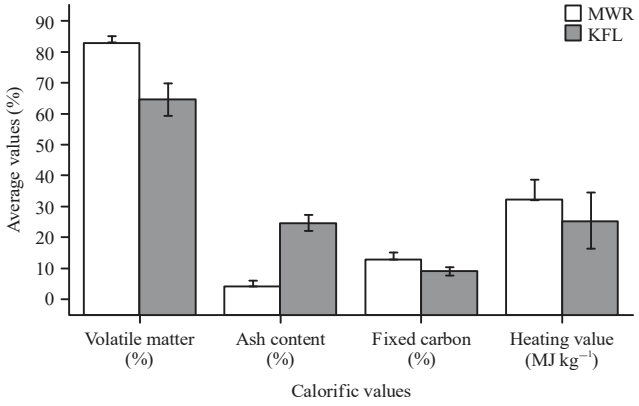

Fig. 3: Proximate analysis of MWR and KF

(versatile) raw-material that can be channelled into the production of so many valuable products, such as vanillin, synthetic tannins and polymer filters[16,17].

From ultimate analysis of the two materials, it was observed that oxygen content of MWR is said to be considerable because high oxygen content results in low heating value[18]. The content of H, C and O in KFL irrespective of the pulping temperature was observed to be lower than the result obtained in kraft eucalyptus lignin and kraft spruce lignin. However, it is likely that some trace amount of acid used during the precipitation and purification of the lignin samples affected the results of the elemental analysis[14]. Whereas, the content of sulphur in KFL is lower when compared to the result of Sahoo *et al.*[19]. The low content of sulphur in kraft ficus lignin is a sign that lignin was properly washed because Vakkilainen and Valimaki[15] was of the opinion that if lignin washing is not properly carried out, the sulphur might be high and can cause problem during burning.

The FT-IR shows that C-O stretching vibrations between 1510 and 1610 cm^{-1} was because of ketones and secondary amines, whereas the O-H stretching vibrations between 3268 and 3450 cm^{-1} were from phenols and alcohols[20]. The 2924 and 2854 cm^{-1} region is assigned as stretching of C-H saturated bonds with a strong band intensity, 1712 and 1735 cm^{-1} as C=O stretching of the carbonyl functionalities with double bond, 1519 cm^{-1} as N-H stretching and 11504 of the C-H stretching vibration with broad and weak intensity, 1458-1373 cm^{-1} as C-O-H bending vibration of the phenolic functionalities and 1103-1026 as C-H bending with broad and weak intensity while t 910 cm^{-1} as C-H plane bending with a very strong intensity. In the region of 1800 and 900 cm^{-1}, many absorption bands were associated with various components and those vibration modes were due to the derivatives of carbohydrates and lignin[21]. However, the presence of Phosphine in *F. exasperata* could be from the soil where the tree was fell.

Sparkman *et al.*[22] defines GC-MS as an analytical method that brings together the features of gas chromatography and mass spectrometer to detect different constituents within a test sample.

Out of the 23 peaks detected in the GC-MS of kraft ficus lignin, oxalic acid with abundant hydrocarbons were identified which are useful Co-products use in meat browning, food flavour, preservatives, adhesives and other useful chemicals[23]. Moreso, the presence of oxalic acid in kraft lignin is an indication that it can be used in bleaching pulp and also used in baking powder[24]. Wiley and Helliker[25] stated that OA serves as a reducing agent and its conjugate base is known as oxalate; it is used as a chelating agent for mostly metal cations.

Lignocellulosic biomasses are useful in the production of fuels and chemicals, they are said to be abundant in nature[1]. The heating value of MWR (32.19 MJ kg^{-1}) in this study is higher than 26.6 MJ kg^{-1} obtained in pine wood, which could be due to variation in the genetic make up of the wood species[26].

However, KFL irrespective of the varied pulping temperature with an average heating value of 25.37 MJ kg^{-1}, exhibited higher heating value than 18.3 and 23.0 MJ kg^{-1} reported by García *et al.*[27] for kraft eucalyptus and spruce lignin respectively. Also, as reported by other researchers[14,28,29] KFL had acceptable properties to be used for energy generation. This also attest to the fact that KFL is an energy bearing compound in wood and could be used to predict the energy value of wood[30]. The low heating value of kraft ficus lignin could be as a result of removal of extractive and other component of the wood during pulping process that should have added to the heating value.

CONCLUSION

From the results of this study, the following conclusions were drawn: GC-MS conducted on KFL shows the presence of oxalic acid, which can be used as a mordant in dyeing processes as well as remove calcium from wastewater, as grinding agent for polishing marble etc..

The two energy materials compared (MWR and KFL) shows that the heating value of KFL (25.37 MJ kg^{-1}) attest to the fact that lignin is an energy bearing compound in wood and could be used to predict the energy value of wood. It is therefore recommended that further studies are needed to better evaluate other activities and potentials of the plant for biochemical production. Also, more studies should be carried out to determine the mechanical properties of *F. exasperata* wood to be able to subject it to full utilization as a small diameter timber.

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SIGNIFICANCE STATEMENT

This research would be helpful as new theory on utilization of the species as biomaterial for production of value-added products: The presence of oxalic acid in kraft ficus lignin would be beneficial because the discovery would help to identify critical areas of oxalic acid utilization as co-product use in meat browning, food flavour, preservatives, adhesives and cleansing agent to many researchers.

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