



Physico-Chemical Properties of Bio-Oil from the Pyrolysis of *Pinus caribea* (Morelet) Needles

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Abstract

Biomass is a renewable natural resource per excellence for the present and the future as well and it appears to have formidable positive eco-friendly properties. The high regenerative ability and decay resistance of pine needles has influenced its continual relegation as an unimportant forest product. There is need to transform these species residues (needles) into forms that will make their combustion easier and more efficient. In this study, the physical and chemical properties of Bio-oil from *Pinus caribea* Needles were investigated. Pine needles were collected from felled tree in the Department of Zoology (University of Ibadan) and grounded to 6 mm particle size to yield sufficiently small particles. Approximately 4.92kg of pine needles was oven dried at $100\pm 3^{\circ}\text{C}$ until constant weight to determine the moisture content. 820g of shredded pine needles was loaded into the vacuum pyrolysis chamber reactor at 600°C and 700°C in triplicates. Physico-chemical and compositional analyses of the bio-oil were achieved through carbon-hydrogen-nitrogen-sulphur (CHNS) studies, Calorific Value, Fourier transform-infrared (FT-IR) spectroscopy and Gas chromatography-mass spectrometry (GC-MS) through standard procedures (American Standard for Testing and Materials). Data were analysed using t-test at $\alpha 0.05$. The pyrolytic product at 700°C had higher bio-oil yield, Density, Moisture content and pH of 10%, 1.0975kg/dm^3 , 4.76% and 6.635 respectively. Ultimate analysis for the following elements C, H, O ranged from (83.97 - 85.43%), (13.29-14.23%) and (0.40-0.53%) for 600°C and 700° respectively, while Sulphur and Nitrogen were available in trace amounts at both temperature regime. The proximate analysis was favourable at 700°C with lower Ash content and higher heating value of 0.67% and $48.96\pm 0.1825\text{Mj/Kg}$ respectively. The functional groups with FT-IR analysis include alcohols, esters, alkynes with most of the compounds characterized by saturated bonds. GC-MS of the bio-oil showed mostly hydrocarbons including aromatic compounds (phenols and alkenes) and some aliphatic compounds. The result of this study is an indication that bio-oil of *Pinus caribea* needles revealed its potential for fossil fuel substitution and bio-chemical production.

Keywords: *Pinus caribea*, Needles, Pyrolysis, Physical Properties, Ultimate Analysis, FT-IR, GC-MS.

Introduction

Ever since the inception of shortage of petroleum resources accompanied with the global energy crisis in the 1970s, attention has been on development of alternative energy (fuels) due to the concerns of global warming and climate change from anthropogenic emissions of greenhouse gases (Brown *et al.*, 2011). The price of fossil fuels is on the increase and this would lead to a switch in interest of people or a change of focus to renewable energy (Sukumaran *et al.*, 2010). Therefore, it has been discovered through scientific studies that biomass is one of the important renewable natural resources and in contrast to other renewable resources; its yields contain solid (Bio-char), bio-fuel and gas (Bridgewater and Peacocke, 2000).

Renewable biomass sources can therefore be converted to oils and can be a logical choice to replace fossil fuels (Islam *et al.*, 2013. Biomass

energy is said to be desirable because unlike fossil fuels, it takes away Carbon from the atmosphere while growing, and returns it when it is burned. This happens in order to maintain a closed Carbon cycle within and increase in atmospheric CO_2 levels (He *et al.*, 2009). *Pinus caribaea* is an evergreen and resinous trees growing to 3 – 80 m tall with needle-like gray-green leaves that grow in pairs. Essential oils from *Pinus* species have been reported to have various therapeutic properties (Sonibare and Olakunle, 2008, Kirima *et al.*, 2020). Pine needles are abundantly found as under-exploited biomass in coniferous forests and are responsible for forest fires and air pollution (Merila *et al.*, 2008). As forest residue during logging, it would be wasteful to leave the energy content of pine needles unexploited especially during times of increasing energy dependence. In addition, a higher level of utilization of pine needles could curtail ecological damages in hill

conditions, and consequently, slow down the depletion of fossil fuel reserves (Fuentes, 2017). One of the promising utilization techniques is through pyrolysis process. For the production of bio-oils, lignocellulosis biomass are thermally degraded via pyrolysis at higher temperature with varying heat rates in the absence of Oxygen (Czernik and Brigdewater, 2004).

In certain residential areas, pine trees which are planted for aesthetic purposes have been considered as an unsuitable urban tree due to its shedding of leaves. This is because these land owners are clueless about the benefits and potentials of the pine needles. The high regenerative ability and decay resistance of pine needles has also influenced its continual relegation as an unimportant forest product. Besides the low bulk density and dusty characteristics of the biomass, there are also problems that are associated with their transportation, handling and storage (Husan *et al.*,

2002). Therefore, there is the need to transform these species residues into forms that will make their combustion easier and more efficient. Pine needles were chosen for this study because of its slow rate of decomposition and no record of adequate information of its pyrolysis in Nigeria.

Materials and Methods

Study Area

The samples of *Pinus caribea* needles were collected from the Department of Zoology, University of Ibadan, Akinyele Local Government, Oyo state. It is situated within Latitude 7.443°N and Longitude 3.8995°E while the University is located in Northern part of Ibadan city which is between latitude 7°26'N and 7°28'S and longitude 3°52'W and 3°55'E at an altitude of 227m above the sea level. Ibadan is situated at the latitude 7°23'16"N and Longitude 3°53'47"E of the equator and 750m above the sea level. (Figure 1).

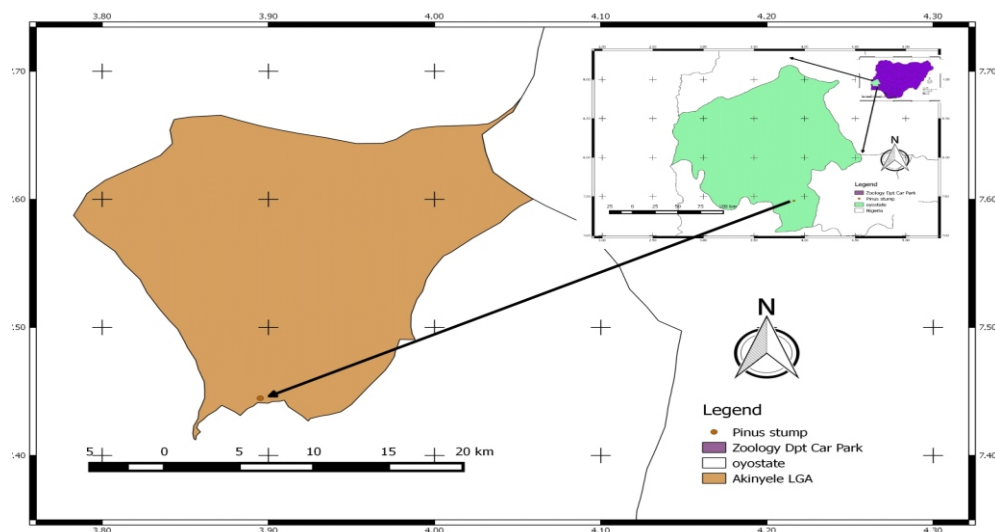


Figure 1. Map of Akinyele LGA showing Pinus stump (material source) in Department of Zoology, University of Ibadan

Sample Collection and Feedstock Preparation

The samples (Pine needles) were collected and the needles were bagged at the site of collection to aid haulage, after which they were air-dried to moisture content of 19°C before shredding to ensure easy pyrolysis (Plate 1). The biomass was grounded and a sieve of 6mm was used to obtain a yield of sufficiently small particles, in order to

ensure rapid reaction in the reactor (Plate 2). Approximately 4.92kg of pine needles was oven dried at 100±3°C until constant weight was obtained to determine the moisture content. The air-drying is essential to avoid adverse effects of water on stability, viscosity, pH, corrosiveness and other liquid properties in the pyrolysis product.



Plate 1a: *Pinus caribea* showing the needles and branches



Plate 1b: shredded *Pinus caribea* needles in Ziploc Bag.

Bio-oil Extraction

Shredded pine needles (820g) was loaded into the pyrolytic reactor at 600°C and 700°C heating rate. The temperature was varied to determine the differences between the two temperature ranges in terms of yield, physical and chemical properties. Each production was replicated three times. The

gas was distilled in the condenser to form bio-oil which was collected into a conical flask. The moisture in the bio-oil was precipitated according to AOAC, 1990 method of drying to a constant weight in an oven. However, was determined using the equation below:

$$\text{Moisture content} = \frac{\text{Weight of } (W_o) - \text{Weight oven dried Sample } (W_i)}{\text{Weight of oven dried Sample } (W_i)} \dots\dots\dots(1)$$

Determination of Bio-oil Yield and Char

Bio-oil yield

It is calculated as the percentage of the oven dry pine needles that was condensed as bio-oil, using Equation

$$\text{Bio - oil yield} = \frac{\text{Weight of bio - oil}}{\text{Weight of pine needles}} \times 100 \dots\dots\dots 2$$

Char Yield

It is calculated as the percentage of the oven-dry pine needles which is converted to a solid carbonized (char), using Equation.

$$\text{Bio - char} = \frac{\text{Weight of char}}{\text{Weight of pine needles}} \times 100 \dots\dots\dots 3$$

The mass of the char and bio-oil are given within the experimental error of $\pm 3 \text{ wt.}\%$.

Gas Yield

It is calculated as the yield of non-condensable gases was calculated using a mass balance equation:

$$\text{Bio - oil}(\text{wt.}\%) + \text{Bio - char}(\text{wt.}\%) + \text{NCG}(\text{wt.}\%) = 100(\text{wt.}\%) \dots\dots\dots(4)$$

Physical Properties of Bio-Oil

Table 1. Physical properties and Methods used in their determination

Physical Properties	Method Used
Determination of Moisture content	ASTM D-1744 (1988)
Determination of pH	ASTM E-70 (2007)
Determination of Density	ASTM D-4052 96 (1998)
Determination of Kinematic Viscosity	ASTM D-445 (1988)
Determination of Flash point	ASTM D-93(1999)
Determination of Fire point	ASTM D-10 (1999)
Determination of Cloud point	ASTM D-5200 (1988)
Determination of Pour point	ASTM D-97 (1993)

Characteristic of Bio-oil

Ultimate Analysis

Two (2g) gram of bio-oil sample was weighed in a platinum crucible and placed in a leibig-pregle condenser chamber containing magnesium perchlorate and sodium hydroxide. The sample was burnt off to produce carbon dioxide and water. The CO₂ was absorbed by sodium hydroxide while water was absorbed by magnesium perchlorate. Generally the high oxygen content of biomass samples results in a low heating value (Czernik and Bridgwater, 2004). Total sulfur of bio-oil samples was determined according to ASTM D 3177 (2002).

Ultimate analysis of the bio-oil products was carried out using ASTM D3174-76 (2009). The result of Carbon, Hydrogen, Nitrogen and Sulphur were obtained while oxygen was calculated using formula)

$$\%O = 100 - (\%C + \%H + \%N) \dots\dots(5)$$

Proximate Analysis

Percentage Volatile Matter Determination

A known mass of pyrolysed oil sample was weighed into a closed crucible and heated in a Gallenkamp muffle furnace set at 600°C for six minutes, followed by heating for another 6 minutes at a temperature of 900°C. The amount of volatile present is equal to loss in weight which was calculated using the equation

$$\%V @ 900^\circ C = \frac{W_i - W_f}{W_i} \times 100 \dots\dots(6)$$

Where = W_i = Initial mass of the sample,
 W_f = Final constant mass of the sample

Percentage Ash Content Determination

The ash content is one of the most influential parameters in the pyrolysis process. Agricultural residues generally have higher ash contents than woody-biomass. High ash contents in biomass are not desirable because ash catalyzes reactions that compete with biomass pyrolysis, leading to increased formation of water and gas at the expense of liquid organics. It also reduces the temperature at which maximum organic liquids are yielded. A sample was injected into a known mass crucible and placed in a muffle furnace set at 900°C for 6 hours till a whitish greyish matter is obtained, The amount of residual white grey matter is determined by difference in accordance to ASTM D 482-07 (2007).

$$\%Ash\ content = \frac{M_a - M_o}{M_s} \dots\dots\dots(7)$$

Where M_a = Mass of Crucible plus ash, M_o = Mass of empty crucible, M_s = Mass of sample

Percentage fixed Carbon Determination

The amount of fixed carbon is calculated using equation)

$$100 - (\% Ash\ content + \% Volatile\ content) \dots\dots(8)$$

Heating value (Hv)

The heating value of bio-oil was determined by burning a weighed sample in an oxygen-bomb calorimeter, Leco AC-350 under controlled conditions in accordance to ASTM D-240 (1998). The test procedure consists of adding the weighed of bio oil samples to the cup (approximately 0.5–1.0mL), installing a fuse, and charging the bomb with oxygen to approximately 200psi. The

energy value was calculated from temperature observations before, during, and after combustion, with proper allowance for thermochemical and heat transfer corrections. It is the most important fuel property of any liquid fuel.

Fourier Transform Infrared (FT-IR) Spectroscopy

FT-IR analysis was carried out on the oil samples to determine the possible functional groups present in the bio-oil samples. The response of the possible functional groups were characterized by observing the transmission of infrared radiations and comparing with known standards in order to identify the type and nature of the functional groups present in the bio-oil sample. The data interpretations were surveyed using extensive elucidation based on Pavia *et al.*, 2001.

Gas Chromatography-Mass Spectrometry

The *Pinus caribea* oil was analysed using Gas Chromatography-Mass Spectrometry. The mass spectrometer detected the ionized fragments using their mass-charge ratio. After fragmentation, by an electron multiplier diode, it turned the ionized mass fragment into an electrical signal which was then detected. The quantitative analysis for pyro-oil will be conducted by comparing the average peak area of the internal standards to total areas. The spectrum of the component was compared to that of the known spectrum, the components saved in NIST library ver 2.0 (National Institute of

Standards and Technology) (Lafferly, 1980 and Stein's 1990). The name, molecular weight, and formula of components of the test material was ascertained.

Results nad Discussion

Bio-oil Yield

The mean content of bio-oil and bio-char were determined at two temperature regime; 600°C and 700°C. The yield of bio-oil decreased with increase in temperature from 4.47 to 10% for 600°C and 700°C respectively (Figure 2). This depicts that change in temperature significantly influence bio-oil yield. This correlates the findings of Koufapanos *et al.*, (1989); Sadakata *et al.*, (1987) which explains that an increase in pyrolysis temperature increases the yield of bio-oil yield and decreases bio-char production. Though the values of bio-oil yield (4.47 and 10%) was slightly lower than 16.63 wt% yield of bio-oil obtained from sugarcane straw (Durange *et al.*, 2013). The value is also lower than yield of bio-oil obtained from wood of same specie and other biomass in the range of (60-95 wt%) (Mohan *et al.*, 2006). The results from this study is in consonance with the work of He *et al.*, (2012) which leaves give lower yield organics in bio-oil than the wood of mallee trees. However, oil from pine needles can be used to supplement another conventional hydrocarbon fuel (Jones *et al.*, 2009), while the bio-char can be converted into an energy source through briquette production.

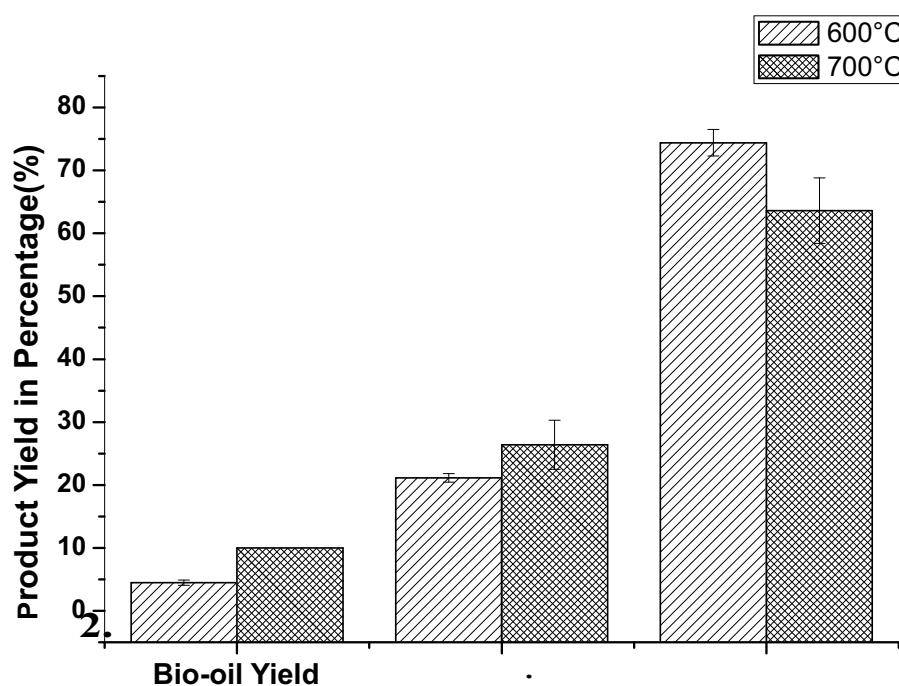


Figure 2. Mean product yield of pyrolysis at varying temperature.

Physical Properties of Bio-oil

The needles of *Pinus caribea* though light-brown in colour was observed to produce bio-oil that is dark brown in colour (Plate 2), a free-flowing organic liquid and has a distinctive smoky odour which is in line with Garcia-perez, (2006).

In this study, the physical properties (pH, density and moisture content) of bio-oil were shown in Figure 3, where it was observed that increase in temperature increased the pH to 4.89,

Density to 1.10kg/dm³ but reduces the Moisture content to 5.77%. On the other hand, Figure 4 presented the result of pour point, cloud point, fire point, flash point and kinematic viscosity. The Flash point and fire point shows slight increase with increase in temperature which averaged 181.125°C and 190.75°C respectively, while viscosity averaged 465.5cSt, cloud point (13.65°C) and pour point (12.03°C) decreased with increase in temperature.



Plate 2: Bio-oil of Pinus Needles

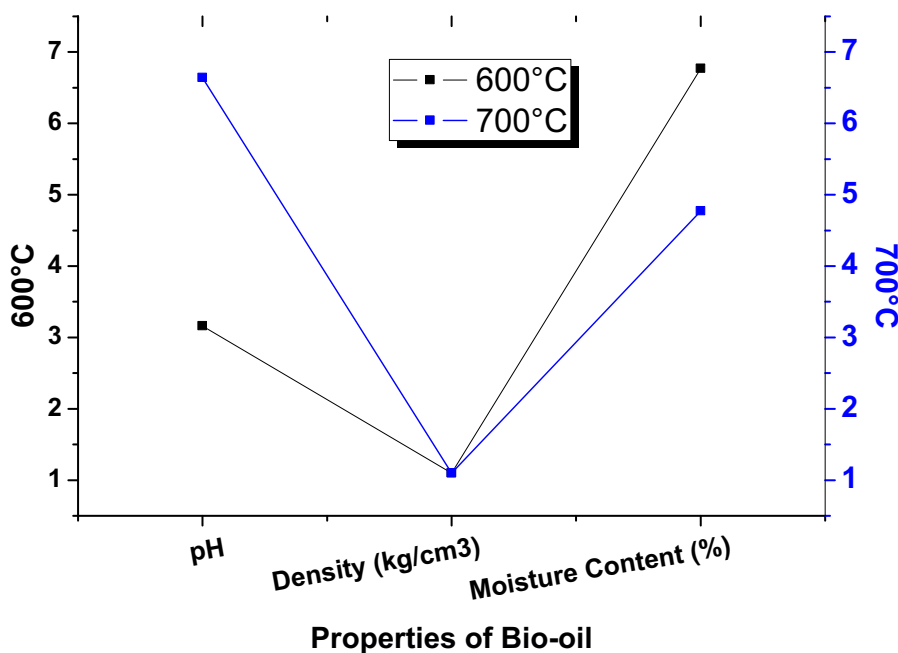


Figure 3. Physical Properties (pH, Density and Moisture content) of Bio-oil

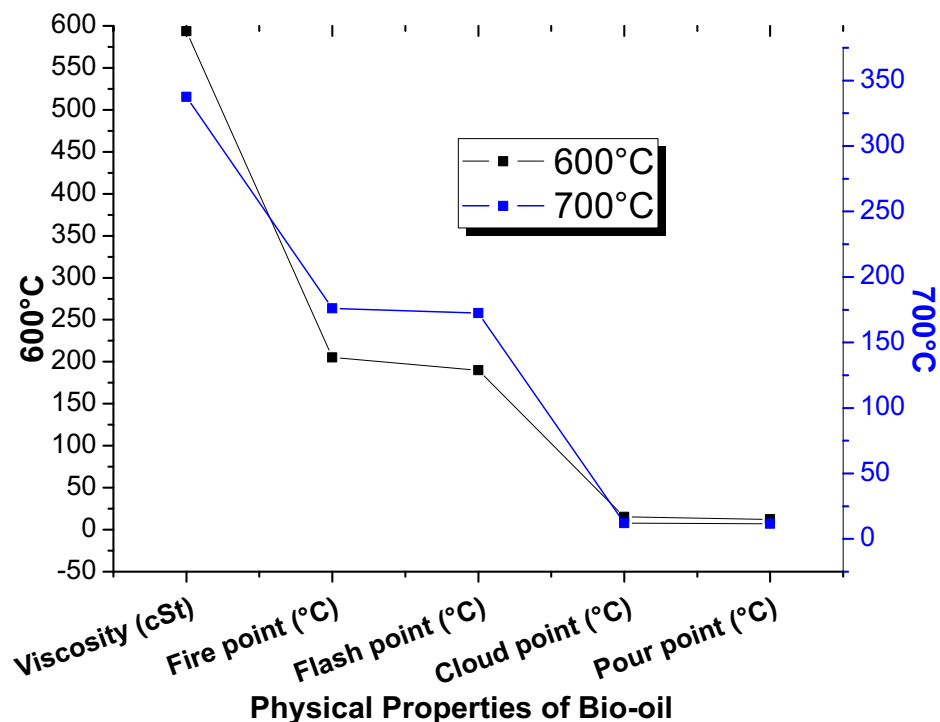


Figure 4. Physical Properties (Viscosity, Fire, Flash, Cloud and Pour point) of Bio-oil

Density is an important property that is used in the characterization of bio-oil products. Bardalai and Mahanta, 2015, opined that density of bio-oil affects its heating value: increase in density results in increased heating value. This study obviously showed that density decreases with increase in temperature as recorded by Perez *et al.*, (2002); Asadullah *et al.*, (2007); Yin *et al.*, (2011). Further comparison showed that Czernik and Bridgewater, (2004) agreed that density increases when temperature increases.

The higher amount of moisture content in bio-oil leads to phase separation that could make bio-oil become difficult for application, Qiang *et al.*, 2009. It is therefore very important to reduce the moisture content in the feed stock below 10wt.%. The results of moisture content showed that 6.77-4.77% was lower than the 15-30wt.% reported by Aarsen, (1985); Mohamad *et al.*, (2009). Also, according to Aarsen, (1985), the results show an advantage to the use of bio-oil because it increases the heating rate and shelf life of the bio-oil due to the negative effect of high water content on the heating value and the phase separation.

Bio-oil contains mostly organic acids such as formic acid, Carboxylic acid and acetic acid: as the pH becomes less, the oil becomes more acidic (Bardalai and Mahanta 2015). Also, according to

Tsai *et al.*, (2006), temperature could possibly cause increase in the pH of bio-oil. The pH of bio-oil in this study is in agreement with Oasmaa and Czernik (1999); Czernik and Bridgewater, (2004), at 700°C it showed that there is continual reaction and breakdown of organic acids which gives rise to non-acidic compounds.

The range for the pour point depicts results parallel to the findings of Oasmaa and Peacock (2001). The results conformed to the ranges of wood bio-oil at (12-33°C) (Mohan *et al.*, 2006). According to Czernik and Bridgewater, (2004), high pour point leads to high viscosity value which affects the pumpable conditions and increases engine deposits. While moisture content lowers flash point and increases delay in ignition (Qiang *et al.*, 2009).

The suitability of oil for specific work can be identified from its physical and chemical properties (Bardalai and Mahanta, 2015). These oils cannot be used directly as transport fuel but need to be treated (Bertero *et al.*, 2012). According to Dragos *et al.*, (2013), fuels with high viscosity tend to form larger droplets on injection which can cause poor fuel atomization during the spray, increases the engine deposits, needs more energy to pump the fuel and wears fuel pump elements and injector.

Ultimate Analysis of Bio-oil

The result in Figure 5 shows that temperature slightly influence the percentages of the elements present in the bio-oil of Pine needle C-(83.97 and 85.43%), H-(13.29 and 14.23%), N-(1.33 and 0.63%), O- (0.40 and 0.53%) and S-(1.13 and 0.8667%) for 600°C and 700°C respectively.

The amount of Oxygen content in oil is due to the moisture content present (Bardalai and Mahanta 2015). it is necessary to remove O₂ from oil to make it economical and attractive. The amount of O₂ shows low heating value of the oil sample (Czernik and Bridgewater, 2004; Kiky *et al.*, 2015). The high O₂ is due to the presence of

many highly polar groups in the bio-oil, which causes it's low calorific value (Lu *et al.*, 2008; Lu, 2008). The Carbon content in the bio-oil is higher than the 48.0-63.5% obtained in bio-oil of pine sawdust (Braz and Cmkovic, 2014). Hydrogen was observed to be lower compared to the result obtained in bio-oil of pinewood H-5.31 (Fei *et al.*, 2007). The content of nitrogen connotes that the bio-oil is environmental friendly Czernik and Bridgewater, (2004). The low proportion of sulphur connotes that the bio-oil is of good quality and environmental pollution arising from the high sulphur content will not be applicable to the bio-oil produced from the same oil (Pattiya *et al.*, 2007).

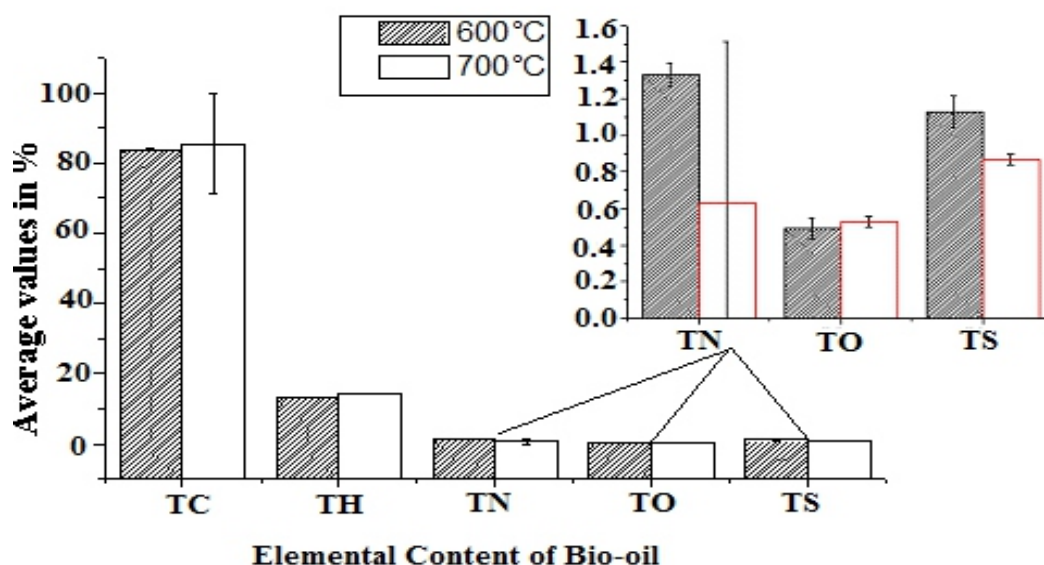


Figure 5. Variation in elemental content in Bio-oil of *Pinus caribea* needles

Proximate Analysis of Bio-oil

The result in Table 2 showed the proximate analysis of bio-oil. Percentage volatile matter (77.33 and 79.17%), Percentage Ash content (0.86 and 0.667%), Percentage Fixed carbon (21.81 and 20.16%) while Heating value (Hv) was discovered to be 46.97 and 48.93MJ.kg⁻¹ for 600 and 700 pyrolysis respectively.

The heating value or calorific value of oil indicates the energy content of it. They are believed to be the largest factors and important properties in fuel economy which defines the energy density of fuels (Oghenejoboh and Umukoro, 2014). The heating value depends on

some factors; water and oxygen content which according to Xiuyuan *et al.*, (2011) are said to have negative impact on the Hv. The Hv was observed to be higher when compared to typical values of bio-oil (15-24.3 MJ/Kg) but correlates slightly with values of heavy fuels (40 MJ/Kg), (Czernik and Bridgewater, 2004). Oluwadare *et al.*, (2016) inferred that the lower the ash content of a fuel material, the higher the heating value. The calorific value obtained in this study indicates a high energy dense fuel adding to its combustion quality. The presence of O₂ and Moisture content lowers Hv, (Qiang *et al.*, 2009; Zhang *et al.*, 2007).

Table 2. Means of Proximate Analysis of Bio-oil of *Pinus caribea* needles

Variables	Ash (%)	Content (%)	Volatile matter (%)	Fixed Content (%)	Heating Value (Mj/Kg ⁻¹)
Temperature					
600°C	0.86 ± 0.03 ^a	77.33 ± 0.088 ^a	21.81 ± 0.2 ^a	21.81 ± 0.2 ^a	46.97 ± 0.25 ^a
700°C	0.67 ± 0.089 ^b	79.17 ± 0.12 ^b	20.16 ± 0.12 ^b	20.16 ± 0.12 ^b	48.93 ± 0.18 ^b
Pooled Mean	0.77 ± 0.049	78.25 ± 0.049	20.98 ± 0.25	20.98 ± 0.25	47.97 ± 0.46
P-values	0.013	0.01	0.00	0.00	0.007

Values with the same alphabet in each column are not significantly different at $\alpha=0.0$ using the two sample T-test *p-values > 0.05 are significant (Laboratory work, 2018)

Chemical Properties of Bio-oil

FT-IR of Bio-oil at 600°C

The compounds observed from the FT-IR analysis of Bio-oil at 600°C in Table 3 were Phenols (O-H), alkenes(C=C), aromatics (C-C), ethers (C-O) and aliphatic amines (C-N). The types of bonds present in the compounds were single bonds with the exception of alkenes. It was also observed that the aliphatic amines and aromatic compounds were of medium intensities while phenols and ethers had strong bonds. However, fig. 6 shows the absorption peaks. There are unidentified groups with equivalent frequencies (4346.00, 3910.00,

and 416.30 cm⁻¹) which may indicate the presence of undesirable contaminant in this sample. The presence of more saturated chemical groups may influence the cloud point positively, invariably, it can affect the performance of bio-fuel during cold weather operations (Younis *et al.*, 2009). The presence of alkenes (unsaturated) in bio-oil may require catalytic cracking and reforming by oil refineries to create alkanes from them. However, this property may be improved upon by injecting cold flow into bio-fuel. Generally the prevalence of saturated bonds indicates that the oil sample is stable and cannot vaporize easily.

Table 3. Frequency, Functional Group and relevant compounds present in Bio-oil at 600°C

Frequency(cm ⁻¹)	Functional Groups	Type of vibration	Compounds	Intensity
3426.00	O-H	Stretch	Phenols	Strong broad bond
1643.29	C=C	Stretch	Alkenes	Medium Intensity
1428.00	C-C	Stretch(in-ring)	Aromatics	Medium Intensity
1264.00	C-O	Stretch	Ether	Strong bond
1102.00	C-N	Stretch	Aliphatic amines	Medium Intensity

C=Carbon, H= Hydrogen, N=Nitrogen, O= Oxygen. Unidentified peaks are not represented above (Laboratory work, 2018).

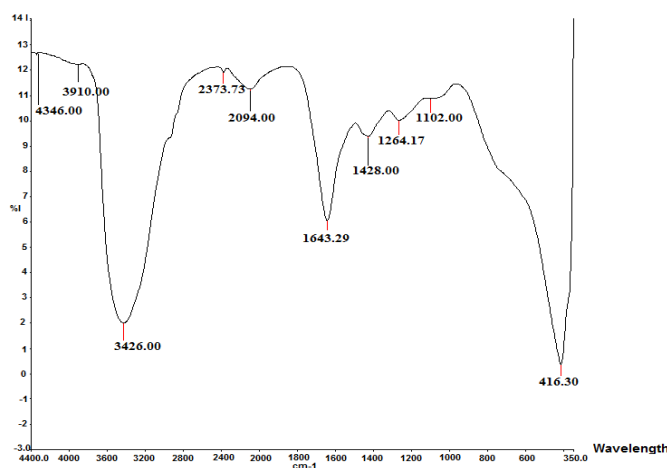


Figure 6: FT-IR spectral analysis for Bio-oil at 600°C, FT-IR of Bio-oil at 700°C

Table 4 is the FT-IR analysis obtained in the sample and it suggested the following functional groups: Phenols (O-H), Aromatics(C-C), Alkynes (C≡C), Alkyl Halides(C-H(-CH₂X)), Primary Amines(N-H) and Aliphatic amines (C-N). The absorption peaks which are the wave numbers are clearly seen in Fig. 7. Appearance of unidentified compounds could indicate the presence of impurities that would have contaminated the samples during handling and extraction process. These unidentified samples have frequency of 4329, 4258, 3907 and 423.84cm⁻¹. At 700°C, there

are more saturated compounds obtained when compared to oil at 600°C. The presence of more saturated bonds will affect the performance of bio-oil positively during cold weather engine operation (Younis *et al.*, 2009). The high quantity of phenol (strong bonds) in the bio-oil is of interest because phenol isolated from bio-oil could be alternative to phenol produced from petroleum and it would ease the production of phenolic resins due to its high reactivity (Tessarolo *et al.*, 2013).

Table 4. Frequency, Functional group and relevant compounds present in Bio-oil at 700°C

Frequency (cm ⁻¹)	Functional Groups	Type of vibration	Compounds	Intensity
3415.00	O-H	Stretch	Phenols	Strong broad bonds
2103.00	C=c	Stretch	Alkynes	Weak Intensity
1643.41	N-H	Bend	Primary Amines	Medium Intensity
1562.00	C-C	Stretch (in-ring)	Aromatics	Medium Intensity
1424.00	C-C	Stretch (in-ring)	Phenols	Medium Intensity
1274.00	C-H(-CH ₂ X)	Stretch	Alkyl halides	Medium Intensity
1065.00	C-N	Stretch	Aliphatic amines	Medium Intensity

C=Carbon, H= Hydrogen, N=Nitrogen, O= Oxygen. Unidentified peaks are not represented above (Laboratory work, 2018).

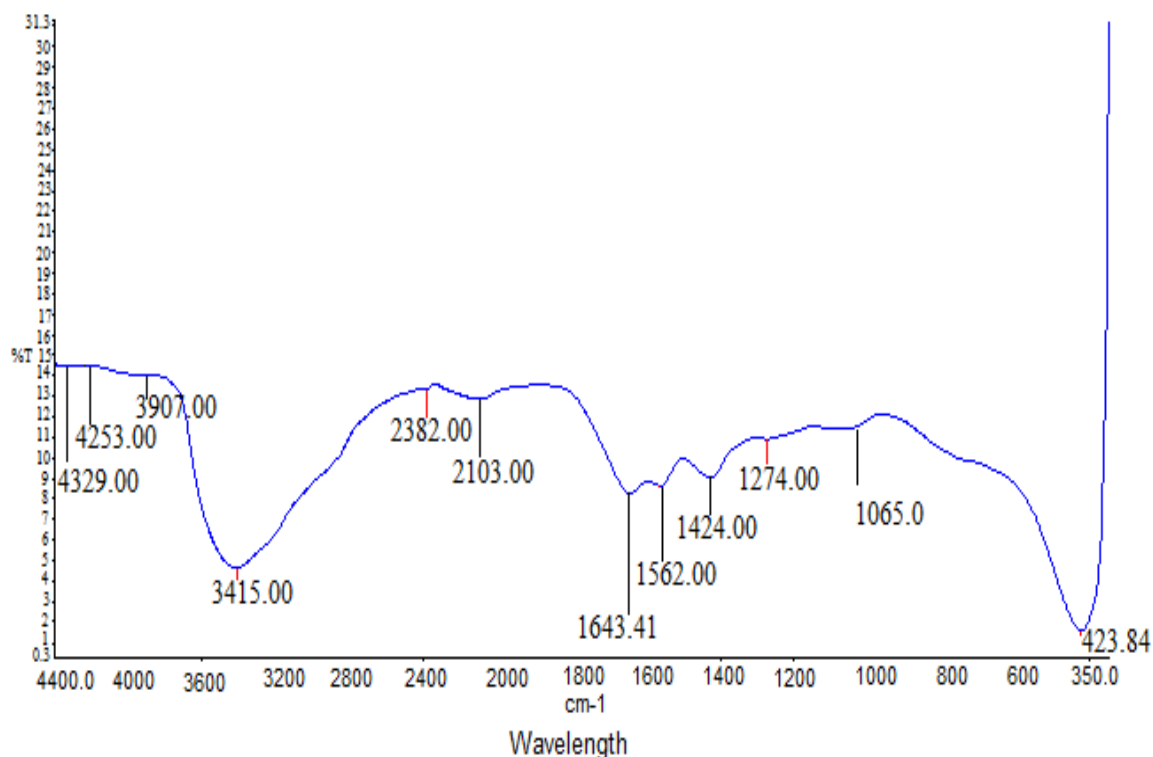


Figure 7. FT-IR spectral analysis for Bio-oil at 700°C, GC-MS of Bio-oil

Table 5 and 6 shows the results of chromatogram for bio-oil produced from the pyrolysis of *Pinus caribea* needles. The results were matched with NIST library to identify the compounds present: the identification of the compounds based on the peak area, molecular weight and molecular formula. GC-MS chromatogram in Fig. 8 detected 11 peaks for 600°C and the prominent peaks were observed to range between 4.50-30.52 min. The peak at 9.335 retention time has the highest percentage 47.13% peak area; this was identified as 3-ethylphenol with the molecular formula C₁₀H₈ and Molecular weight of 128.17. The lowest peak is shown to have its values at 23.508 retention time with percentage peak area of 1.72% identified as Fluorene with molecular formula C₁₃H₁₀ and molecular weight of 166.22, it can be used to make dyes, plastics and pesticides. While Fig. 9 presented prominent peaks that ranged between 0.00-6.70 min. The peak at 4.49 retention time has the highest percentage 60.43% peak area; this was identified as a phenol with the molecular formula

C₆H₅OH and Molecular weight of 94.11. The lowest peak is shown to have its values at 3.688 retention time with percentage peak area of 2.29% identified as Butyrolactone with molecular formula C₄H₆O₂ and molecular weight of 86.08.

Zhang *et al.*, (2006) explained that the chemical composition of the bio-oil depends on a great extent to the composition of the biomass or the residue from which it was produced from and the parameters that were used during pyrolysis.

Through observation, the GC-MS analysis explains that the compounds present in the bio-oil sample at 600°C is composed of hydrocarbon; Phenols and Alkenes. Also, bio-oil sample at 700°C is composed of hydrocarbon; approximately 83.33% aromatic compounds and 16.7% of aliphatic compound. These compounds are mostly Phenols and Alkenes. Alkenes are used as starting materials in the synthesis of alcohols, plastics, lacquers, detergents and fuels. The presence of aromatic compounds can be attributed to its biopolymer structure such as cellulose and hemicellulose (Tsai *et al.*, 2008).

Table 5. Bio-active Compounds detected and their groups in pyrolysed oil at 600°C

Peak Area	RT	PA %	MW	MF	Bioactive Compounds	Group
1	4.497	4.61	94.11	C ₆ H ₅ OH	Phenol	Aromatic
2	6.636	6.19	108.1378	C ₇ H ₈ O	Phenol, 4- methyl	Aromatic
3	8.275	1.54	122.167	C ₈ H ₁₀ O	Phenol, 2,6 -dimethyl	Aromatic
4	8.831	2.15	122.167	C ₈ H ₁₀ O	Phenol, 3 - ethyl	Aromatic
5	9.355	47.13	128.174	C ₁₀ H ₈	<u>Naphthalene</u>	Aromatic
6	12.939	7.17	142.201	C ₁₁ H ₁₀	2- methyl - <u>Naphthalene</u>	Aromatic
7	13.527	2.14	142.2	CH ₃ C ₁₀ H ₇	1- methyl - <u>Naphthalene</u>	Aromatic
8	18.566	10.53	152.19	C ₁₂ H ₈	<u>Biphenylene</u>	Aromatic
9	19.873	3.12	156.228	C ₁₂ H ₁₀	<u>Naphthalene, 2 - ethenyl -</u>	Aromatic
10	23.508	1.72	166.223	C ₁₃ H ₁₀	<u>Fluorene</u>	Aromatic
11	30.52	13.7	178.234	C ₁₄ H ₁₀	<u>Phenantrene</u>	Aromatic

RT=Retention Time, PA%=Peak Area Percentage, MW=Molecular weight, MF= Molecular Formula.

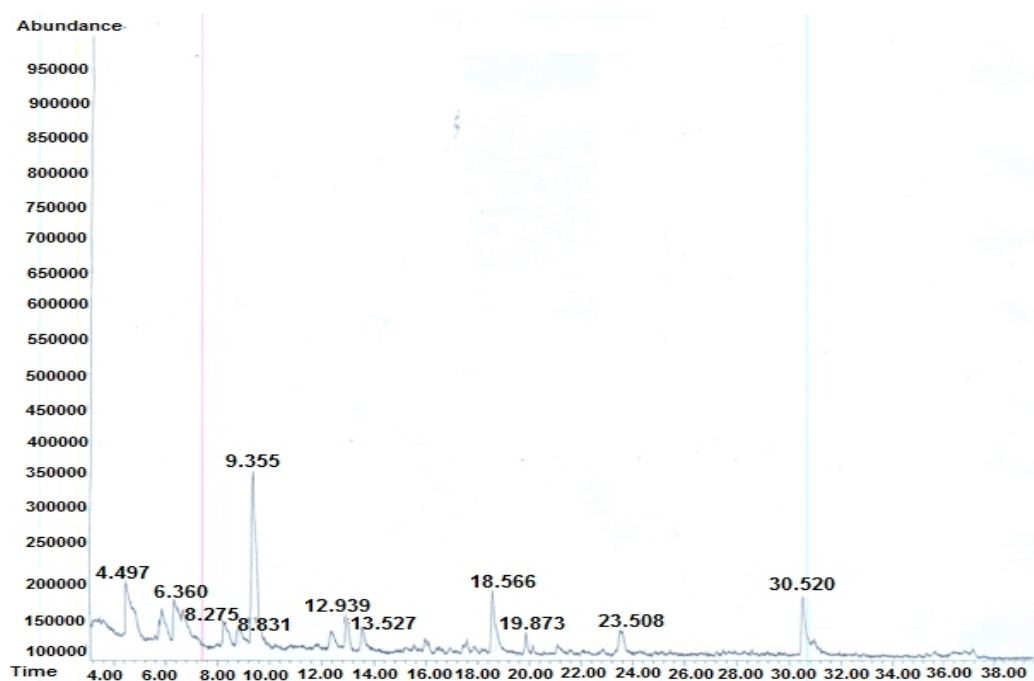


Figure 8. GC-MS of Bio-oil at 600°C

Table 6. Bio-active Compounds Detected and Their Groups in Pyrolysed Oil at 700°C

Peak Area	RT	PA %	MW	MF	Bioactive Compounds	Group
1	3.688	2.29	86.08	C ₄ H ₆ O ₂	Butyrolactone	Aromatic
2	4.49	60.43	94.11	C ₆ H ₅ OH	Phenol	Aromatic
3	5.377	2.96	112.13	C ₆ H ₈ O ₂	2 -Cyclopenten -1- one, 2- hydroxy - 3- methyl-	Aliphatic
4	5.875	1.85	108.1378	C ₇ H ₈ O	Phenol, 2- methyl	Aromatic
5	6.334	19.47	108.14	CH ₃ C ₆ H ₄ OH	Phenol, 4- methyl	Aromatic
6	6.709	12.99	124.14	C ₇ H ₈ O ₂	Phenol, 4- methyl	Aromatic

RT=Retention Time, PA%=Peak Area Percentage, MW=Molecular weight, MF= Molecular Formula (Laboratory work, 2018).

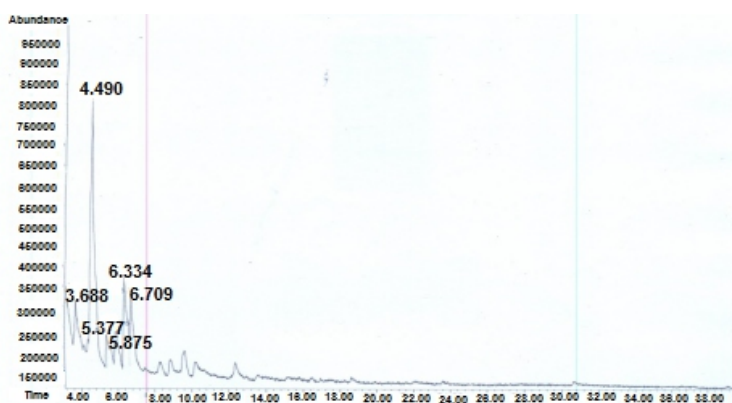


Figure 9. GC-MS of Bio-oil at 700°C

Conclusion

In conclusion, Sulphur, nitrogen and oxygen content had lower values which connotes its suitability. It serves as a potential source for clean renewable bio-fuel. The heating value of bio-oil with the low ash content confirms it as a good source of fuel. It could be deduced from FT-IR that increase in the temperature of bio-oil result to larger amount of compounds. The results showed that there was increased amount of saturated compounds than unsaturated. GC-MS Spectrum was comprised mostly of aromatic hydrocarbons (phenolic in nature) and some aliphatic compounds. Also, the composition of the hydrocarbons varied with the increase in temperature. The knowledge of chemical compositions will aid its use as fuel and as raw material in chemical industries.

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