Effect of Temperature on the Pyroligneous Oil from Selected Tropical Woody Biomass in a Fixed-Bed Reactor

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Abstract

The influence of temperature on the yield and properties of pyroligneous oil produced from biomass from Apa wood (*Afzelia africana*), Iroko wood (*Melicia excelsa*) and palm kernel (*Elais guineensis*) shells were investigated at 400, 500, 600, 700 and 800 °C in an in-house fabricated fixed-bed reactor. The syngas and pyroligneous oil namely: pyrolysis oil and tar were studied. The biomass species and pyrolysis temperature significantly influenced the oil yield ($p < 0.05$). The chemical compositions of the pyrolysis oil were characterized using Fourier transform infrared (FTIR) and the spectra showed the presence of ketonic (acid) and olefinic compounds. The ketonic acid is responsible for the high acidic nature of the oil. Density of the pyrolysis oil obtained from Apa, Iroko and PKS were not temperature and biomass source dependent.

Keywords: biomass, pyrolysis, fixed bed reactor

Introduction

Biomass is an aggregate of all biologically produced matter, which is abundantly available on earth in form of wood and wood wastes, forest and forest products, agricultural crops and their waste or by-products, municipal solid wastes, animal wastes, wastes from food processing, and aquatic plants including sea weeds and algae (Agarwal and Agarwal, 1999). It is a major source of energy fuel in many developing countries where the use of fuel wood for cooking and heating predominates about 56% especially in some rural areas (Ramachandra and Kamakshi, 2005) . Woody biomass is a versatile and renewable energy resource that could be upgraded to high dense energy and chemical by-products through various biochemical and thermochemical conversion routes. The current forest and agricultural activities in Nigeria possess enough potential to produce adequate biomass residue for effective economic conversion to energy. This could serve as a supplement to the nation's fossil derived energy needs.

Pyrolysis, which is one of the ways of converting biomass to energy, is the technique of applying high heat to organic matter (lignocellulosic materials) in the absence of oxygen or in restricted air supply (Buekens and Schoeters,1987; Diebold and Bridgwater,1997;

Bridgwater,1999). The polymeric constituents of the organic matter, such as cellulose, hemicelluloses and lignin structure degrade thermally to produce charcoal, condensable organic liquids (pyrolytic oil), non-condensable gases, acetic acid, acetone, and methanol (Dietrich and Oasmaa, 1999). Biomass rate of structural decomposition and products' yield can be controlled by regulating the pyrolysis conditions. These conditions include: final pyrolysis temperature, heating rate, residence time, particle size, biomass chemical composition and moisture content (Fuwape,1996; Nurgul *et al.*,2008). Pyrolysis oil possesses half of the heating value of the fossil oil (34 MJ/kg) while its elemental composition is similar to that of the original biomass (Athanasion *et al.*,2005). Therefore, it has the potential to be used as a fossil fuel substitute (Nurgul *et al.*,2008; Raph, 2004). Chemicals have been isolated from pyrolysis oil industrially and the recovered commodities include: methanol, acetone, acetic acid and mixture of phenols (Goh et al., 2006). Similarly, valuable pure phenols like phenol, cresols, guaiacol, 4-methylguaiacol, catechol and syringol had been recovered from *Eucalyptus* wood pyrolytic tar

(Goh et al., 2006). Production of pyrolysis oil has many potentials and uses. For examples, biodiesel can be used for generator and automobiles operation while phenol is used for bioadhesive or bioplastic. Cresols can be used in the manufacturing of synthetic resins, herbicides, fumigants in photographic developers and explosives, and as antiseptics, disinfectants, and parasiticides in veterinary medicine. Guaiacol can be used as antiseptic, anesthetic and dye in chemical reactions. Catechol is used in the production of perfumes, cosmetics, anticorrosion and bonding agents. Additionally, the tar from pyrolysis can be used for paint and preservatives production. Despite these numerous pyrolysis products uses and large turnout of woody biomass residues/wastes, there is inadequate information available in published literature on the pyrolysis of some Nigerian woody biomass.

In this study, three biomass selected include Apa wood (*Afzelia africana*), Iroko wood (*Melicia excelsa*) and palm kernel (*Elais guineensis*) shells. Densities of Apa, Iroko and palm kernel shell are 785, 673 and 350 kg/m^3, respectively. Their wastes are readily available and abundant but less consider as economic products in Nigeria. So these wastes cause environmental pollution. Converting through pyrolysis technology would helps solve pollution problems and simultaneously address fuel and chemical production need of the society. This thermal conversion technique offers a pragmatic approach to waste consumption and its consequent upgrade to valuable energy and chemical by-products. Against this backdrop, an electrically-fired, fixed-bed reactor with automatic controls for biomass conversion to energy fuels and chemicals was in-house fabricated.

This study aimed at evaluating the effect of temperature on the yield of pyrolysis products (oil, tar and gas) from three selected tropical biomass (Apa, Iroko and palm kernel shell). It also considered the density and pH of the pyrolysis oils. Chemical analysis of the oils was conducted using Fourier transform infrared.

Materials and Method

An electrically fired in-house fabricated fixed-bed pyrolysis plant of 1.85 kW power rating was used for the pyrolysis of the selected biomass materials (Fig. 1). It consists of a furnace with two 12Ω heat resistance heaters connected in parallel, 2.34×10^{-3} m^3 reactor chamber equipped with vapor delivery tube, cross-flow condenser, a step down transformer and automatic control system, 500×10^{-6} m^3 pyroligneous liquid recovery unit and measuring vessels. The furnace chamber was made of an insulating fire-clay, and designed to completely retain the heat generated within it, with minimal loss. The reactor is a top loading plant. Its designed insulating cover is made of the same material with which the furnace wall is built. The outside wall of the furnace is insulated concentrically with a layer of 0.05 m fiberglass, which equally provides mechanical shock resistance for the plant. The concentric walls of kaolin and fiberglass are finally encased in a steel cylindrical housing, on which a pair of handle is attached, for easy handling and to permit free movement of the furnace chamber. The reactor chamber is made of brass plate with 0.004 m thickness and rolled into a cylindrical shape. It has a sealed bottom and a dismountable cover and provides an oxygen deficient environment for enclosed feedstock particles. It is provided with a riser and delivery pipe connected to the condensing unit of the pyrolysis plant, which provides an outlet for the pyrolysis aerosol. The volumetric space of the thermal reactor chamber is made robust enough to accommodate 0.5 kg of biomass feedstock together with the temperature probe for monitoring the reaction temperature at its centre.

Wood feedstock used was obtained as off-cuts from a sawmill factory in Akure, Ondo state, Nigeria. Apa wood (*Afzelia africana*), Iroko wood (*Melicia excelsa*) (10 kg each) were processed into a surface machined rectangular pin chip particles size of 10 mm × 10 mm × 50 mm. The and palm kernel (*Elais guineensis*) shells (PKS) was obtained from local palm oil processing plant at Okitipupa, Ondo state, Nigeria; the shells were processed by screening, cleaning, and drying prior prolysis.

Experimentation

The three selected lignocellulosic materials: Apa wood (*Afzelia africana*), Iroko wood (*Melicia excelsa*) and palm kernel (*Elais guineensis*) shells were oven dried in accordance with ASTM: E 871 - 82 standard procedure (ASTM, 2006). The average (%) expelled moisture from 20 batches of each of the selected biomass was determined following equation (1).

$$\text{Total expelled moisture } (\% \text{wt/wt}) = \frac{1}{N} \sum_{i=1}^{N} \left(\frac{m_{pw} - m_{pd}}{m_{pw} - m_{envelope}} \right)_i \times \frac{100}{1} \tag{1}$$

where:

N = total number of batches of selected materials,
m_{pw} = mass of each batch before drying + mass of envelope,
m_{pd} = mass of each batch after drying to constant weight + mass of envelope,
$m_{envelope}$ = mass of envelope

Fifteen batches weighing 500 g net weight per batch for each of the oven-dried selected materials were used as feedstock in the reactor. A total of 45 pyrolysis experiments were conducted on the reactor at an average of 15 experiments per biomass species at various pre-set temperatures of 400, 500, 600, 700 and 800 °C. The tests were replicated three times for each pyrolysis temperature. The reaction atmosphere was free of oxygen (air tight). The feedstock residence time, furnace temperature and pyrolysis (reaction) temperature were recorded at five minutes intervals. The pyroligneous liquor, which consists of pyrolysis oil and tar, was recovered in the condensate bottles while the volume of the non-condensable gas was determined by water displacement method. The char residues (charcoal) were recovered from the reactor chamber after attaining room temperature and their weights were determined. The residual fractions were recovered and their yields were measured.

Physical Properties and Chemical Compositions

Physical properties of the pyrolysis oil were determined following standard methods. The pH-values were determined according to ASTM D1067 standard (ASTM , 2011). The density was determined using the relationship between mass of the recovered oil and its volume (equation 2).

$$\rho = \frac{m}{V} \tag{2}$$

Where: ρ = density, m = mass of pyro-oil and v = volume of pyro-oil

Chemical property of the pyrolysis oil was characterized using Fourier transform infra-red (FTIR) spectroscopy. This was considered as a function of temperature in triplicates.

Results and Discussion
Physical characterization of pyrolysis products

The yields of pyro-oil from the three selected lignocellulosic materials as a function of temperature are presented in Table 1 and Fig. 2. Palm kernel shell (PKS) had the highest yield of 186.93 g at 800°C from 500 g parent stock carbonisation. Iroko wood pyrolysis yielded 182.93 g at 800°C while Apa wood yielded 175.27 g at 800°C. It is not very clear why the trend in Apa wood was completely different from that of Iroko wood and PKS, but it was observed that Apa wood had thermally degraded to char and syngas between 600°C-700°C. This type of reaction that occurred at such elevated temperatures is termed secondary reaction which could either be endothermic, exothermic or a combination of both. The yield of pyro-oil is significantly different within species (p<0.05). Although there was no significant difference between 400°C and 500°C as well as 600°C and 800°C pyrolysis temperature settings; the difference that was observed occurred between 500°C and 600°C. The significant differences obtained for the species is similar at the various temperatures.

The yield of tar from the three selected biomass species did not follow a particular trend with the carbonisation temperature (Fig. 3). Pyrolysis temperature significantly affected the tar yield for all the biomass. Thermal cracking of tar was noticed between 500°C to 600°C in all

the samples. This undoubtedly had an adverse affect on its yield. Therefore, short residence time for volatiles and the use of carrier gas may be considered because tar is highly susceptible to thermal cracking at elevated temperatures. Maximum tar yield was observed for Apa, Iroko and PKS at 700, 600 and 500°C, respectively. This is an indication that tar yield depends on the degree of polymerisation and density of the biomass; increase in biomass density causes increase in temperature at which maximum tar yield occur. Note that densities of Apa, Iroko and palm kernel shell are 785, 673 and 350 kg/m^3, respectively. Pyrolysis syngas yield from Apa wood (*Afzelia africana*), Iroko wood (*Melicia excelsa*) and palm kernel (*Elais guineensis*) shells increased with increase in pyrolysis temperature (Fig. 4).

Table 1. Effect of temperature on the density of pyrolysis oil and tar from the different biomass

| Biomass | Products | Temperature (^{o}C) | | | | |
		400	500	600	700	800
Apa	Pyro Oil	1.02±0.001	1.03±0.005	1.03±0.021	1.04±0.005	1.03±0.006
Iroko		1.02±0.002	1.01±0.001	1.03±0.007	1.02±0.007	1.01±0.007
PKS		1.01±0.004	1.02±0.004	1.02±0.000	1.01±0.003	1.01±0.004
Apa	Tar	1.05±0.003	1.07±0.032	1.08±0.035	1.07±0.032	1.05±0.010
Iroko		1.05±0.013	1.05±0.012	1.07±0.020	1.06±0.003	1.05±0.005
PKS		1.06±0.031	1.04±0.005	1.04±0.009	1.04±0.006	1.04±0.010

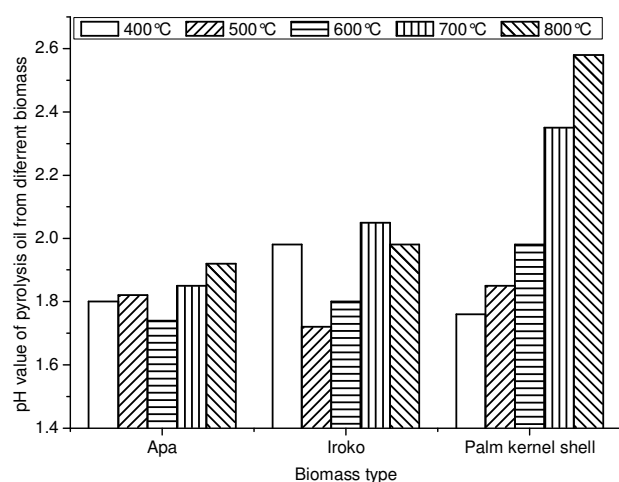Fig. 1. Pyrolysis unit showing oil produced in a flat bottom flask

Fig. 2. Acidity level of the pyrolysis oil obtained from Apa wood (*Afzelia africana*), Iroko wood (*Melicia excelsa*) and palm kernel (*Elais guineensis*) shells at different temperatures.
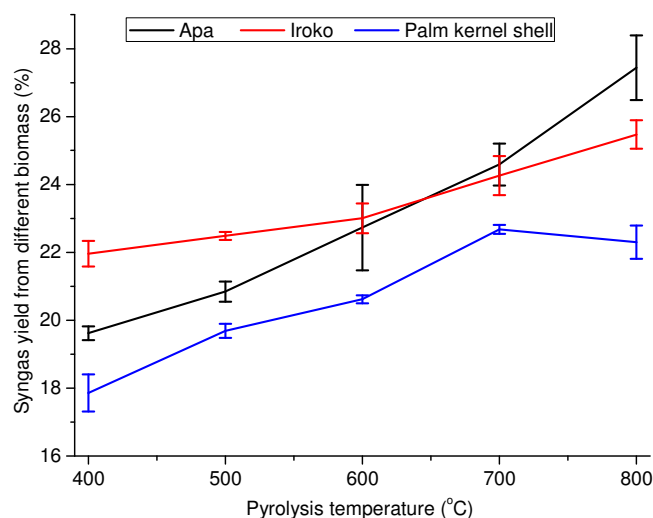

Fig. 4. Pyrolysis syngas yield from Apa wood (*Afzelia africana*), Iroko wood (*Melicia excelsa*) and palm kernel (*Elais guineensis*) shells at different temperatures.
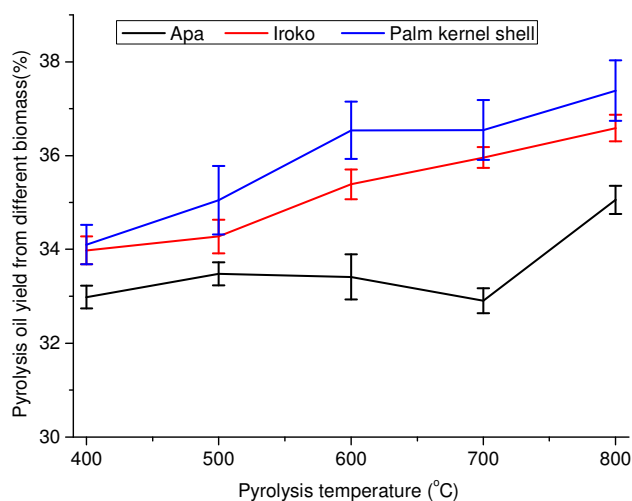

Fig. 3. Pyrolysis oil yield from Apa wood (*Afzelia africana*), Iroko wood (*Melicia excelsa*) and palm kernel (*Elais guineensis*) shells at different temperatures.

The practical implications of the percentage yield results of the pyrolysis products obtained in this study are as follows. The fixed-bed reactor requires 1,000 kg of Iroko wood to produce maximum yield of 339.8 kg of pyrolysis oil, 99.14 kg of tar and 219.6 kg of pyro-gas. The values vary drastically across carbonisation temperatures to 365.86 kg of pyrolysis oil, 100.2 kg of tar and 254.74 kg of pyro-gas at 800 ℃. Similarly, 1,000 kg of Apa wood is required to produce maximum yield of 329.86 kg of pyrolysis oil; 80.26 kg of tar, and 196.2 kg of pyro-gas. This yield varies across temperatures, to 350.54 kg of pyrolysis oil, 104.66 kg of tar and 274.4 kg of pyro-gas at 800℃. Also, at 400 °C, 1,000 kg of PKS is required to produce maximum yield of 341 kg of pyrolysis oil, 91.94 kg of tar and 178.6 kg of pyro-gas. The yield of pyro-oil, tar and syngas is therefore significantly enhanced by temperature.

The densities of the pyrolysis oils from Apa, Iroko and PKS are very similar ranging from 1010 and 1040 kg/L. This range is lower compared to that of fast pyrolysis biomass oils, which was about 1.2 kg/L as reported by Solantausta *et al.*(1993). In the present study, the system was operated as slow pyrolysis,

therefore, this may have been responsible for the lower density oils than for fast pyrolysis. It must be noted that the density of the pyrolysis oil differs from that of fossil fuel. The density of pyrolysis oil is based on the oxygen content while the main contributing chemical is that of polycyclic aromatic. So the density of these pyrolysis oils cannot be compared directly with that of fossil fuel. In addition, the observed densities reveal that the oxygen content of the oils of Apa, Iroko and PKS are very similar. From Table 1, temperature and biomass density did have noticeable effect on the pyrolysis oil density.

The pH values of pyrolysis oils obtained from Apa, Iroko and PKS are shown in Fig. 2. It ranged from 1.74 to 1.92, 1.72 to 2.05 and 1.76 to 2.58 for Apa, Iroko and PKS, respectively. For PKS pyrolysis oil, the pH increased with increase in temperature while there is no distinctive trend observed for oils from Apa and Iroko. This implies that increase in the pyrolysis temperature will cause increase in carboxylic acid content of the oil from PKS and consequently increasing its corrosiveness of engine tank (mild steel, aluminum, and so on).
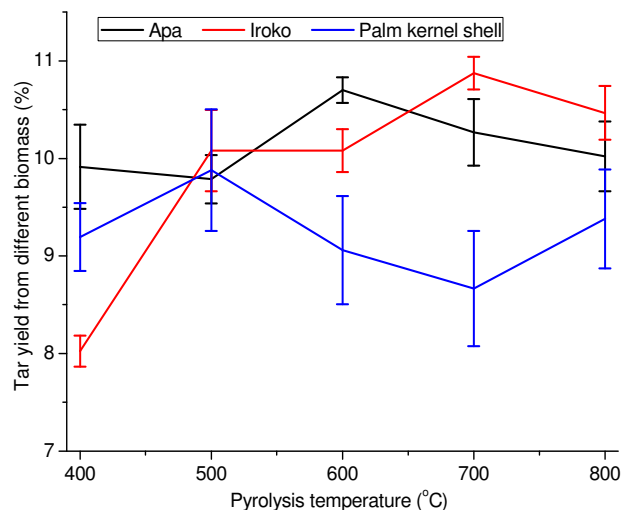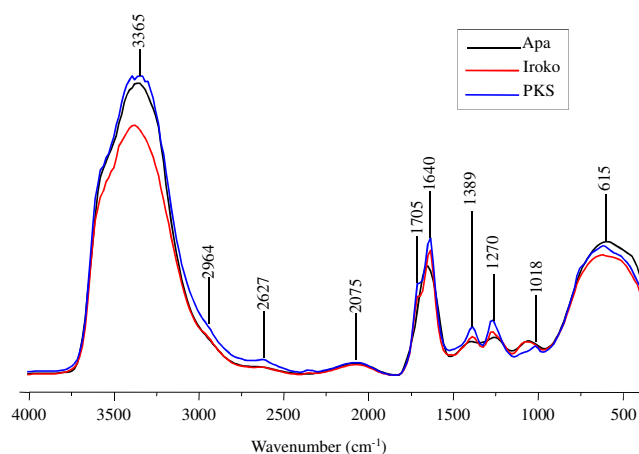

Fig. 6. Fourier transform infrared spectra of Apa wood (*Afzelia africana*), Iroko wood (*Melicia excelsa*) and palm kernel (*Elais guineensis*) shells at 800°C
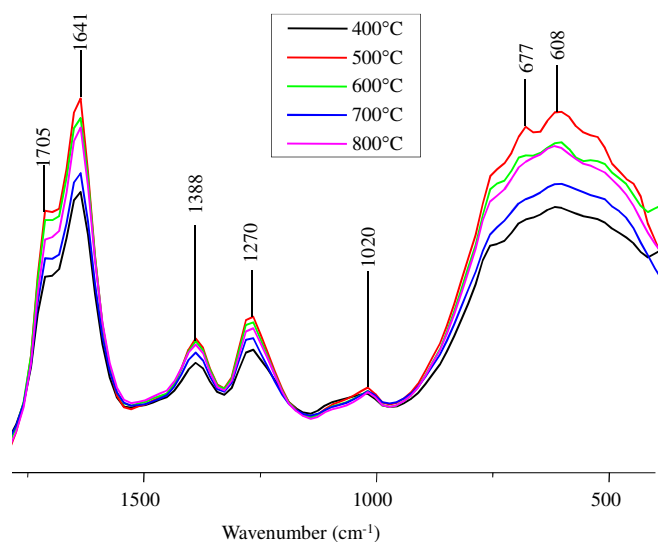

Fig. 7. Fourier transform infrared spectra of palm kernel (*Elais guineensis*) shells at different temperatures

Fig. 5. Pyrolysis tar yield from Apa wood (*Afzelia africana*), Iroko wood (*Melicia excelsa*) and palm kernel (*Elais guineensis*) shells at different temperatures.
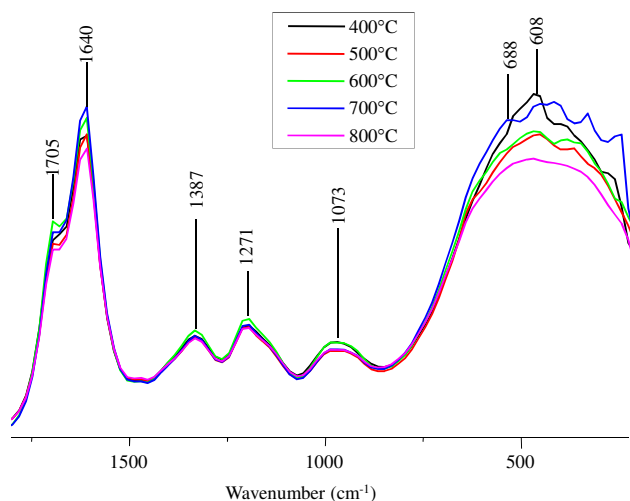
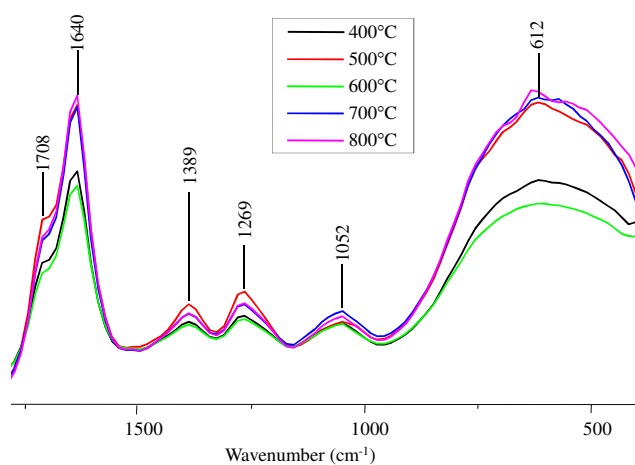Fig. 8. Fourier transform infrared spectra of Iroko wood (*Melicia excelsa*) at different temperatures

Fig. 9. Fourier transform infrared spectra of Apa wood (*Afzelia africana*) at different temperatures

Chemical Composition of Pyrolysis Oil

Infrared spectra of pyrolysis oils obtained from Apa, Iroko and PKS at different temperatures are presented in Figs. 1 and 2. The spectra for the oils contained a large and intense peak around 3365 cm^{-1} which is an indication of the presence of polymeric O-H (especially phenols and alcohols) in the oils. This is evidence in the out-of-plane bending at 677 cm^{-1}. The peaks at 2964 cm^{-1} (CH stretching vibrations) and 1389 cm^{-1} (CH deformation vibrations) indicate the presence of long aliphatic carbon chains, alkanes groups (paraffinic compounds). Structural moieties of fatty acids may be the major composition of these aliphatic carbon chains. Ketonic and olefinic (alkenes) compounds are identified by the C=O stretching vibration at 1705/1708 cm^{-1} and C=C stretching vibration at 1640cm^{-1}, respectively. The band between 1200 and 980 cm^{-1} were due to the presence of primary, secondary and tertiary alcohols, ethers and esters due to the C–O stretching and O–H deformation vibration of these functional groups. The absorbance peak between 900 and 650 cm^{-1} indicated the possible presence of mono, polycyclic and substituted aromatics groups (Özbay *et al.*, 2008). The prominent oxygenated functional groups of O–H, C=O, C–O and aromatic compounds showed that the oil were highly oxygenated and therefore, very acidic. This is corroborated by the obtained high pH values. The fact that these pyrolysis oils are dominated by oxygenated functional groups suggests that there is the need to upgrade the oils through deoxygenation process before use in biodiesel engines. The presence of hydrocarbon groups C–H, C=C and alcohols indicate that the oils produced from the selected biomass have a potential to be used as fuel. It is very clear from the infrared spectra that phenols and substituted phenols are the main constituents of the pyrolysis oils produced from the three selected biomass sources.

Conclusion

The influence of temperature on pyrolysis oil, tar and syn-gas yields as well as chemical composition and pH values of the oils produced from Apa wood (*Afzelia africana*), Iroko wood (*Melicia excelsa*) and palm kernel (*Elais guineensis*) shells (PKS) were investigated. It was observed that the yield of pyrolysis oil increased with increasing pyrolysis temperature for the selected biomass. The variation of pyrolysis oil yield among biomass also confirmed a difference in their degree of polymerisation and structural composition. Hence, the yield of pyrolysis oil is also biomass

dependent. The pH-value showed very high acidic values for oils produced. In addition, infrared analysis showed that oxygenated chemical compounds dominated the pyrolysis oil. . This suggests that these oils need to be upgraded through deoxygenation process to avoid corrosion problem. Density of the pyrolysis oil obtained from Apa, Iroko and PKS were not temperature and biomass dependent.

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