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Experimental Investigation of Fast Pyrolysis of *Isoberlina doka*-Derived Sawdust for Bio-Oil Production

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Abstract

Fast pyrolysis is considered an emerging technology for biomass conversion into liquid oil. In this paper, the conversion of waste from *Isoberlina doka* tree processing into bio-oil using a bench-scale fixed bed reactor with a fluidized behavior within the bed zone has been investigated at temperatures of 400–500 °C and particle size ranges of < 0.5 and 0.5–1 mm. Reactor with the total height of 140 mm consisting of three zones with gas inlet diameter of 10 mm, reaction zone diameter of 70 mm, outlet diameter of 15 mm and a coupled detachable inlet with a diameter 15 mm for biomass loading was used for experimentation. Nitrogen was used as the carrier gas, and the products were biochar, bio-oil and non-condensable gas. Thermogravimetric and derivative thermal analysis (TG/DTA) was carried out in order to understand the thermal behavior of wood particles. Bio-oil produced was analyzed using the gas chromatography mass spectrometry and the Fourier transform infra-red spectrophotometry methodologies. TG/DTA analysis revealed an initial 30.639% mass loss which correlates to hardwood thermal characteristics. Bio-oil yield from bench-scale pyrolysis increased with increasing temperature. A maximum bio-oil yield of 49.84 wt % was observed at the particle size range of 0.5–1 mm, bed temperature of 500 °C and time of 30 min. Volatile generation was at the peak of 54.54% (0.002655 kg/min). However, changes in the chemical composition and functional groups of bio-oil with temperature of production suited it for different usage purposes.

Keywords Bio-oil · *Isoberlina doka* · Pyrolysis · Temperature · Particle size · Time

1 Introduction

The modern world and our societies are highly dependent on energy production. However, growing concerns are raised with the continuous usage of fossil fuel, its unfavorable impact on the environment and the expenses incurred to mitigate the associated negative effects. This has encouraged the use of biomass (a larger, sustainable and carbon–neutral energy resource) as a compliment and an alternative to fossil fuels. Biomass is the term used to refer to all organic matter which can be traced back to photosynthesis as their source [1]. Just as biomass can substitute fossil fuels for energy production, it (and its by-products) can also provide a renewable alternative for industrial products. These bio-based products include foams, plastics, fertilizers, lubricants and speciality

chemicals. Ensyn Corporation has pursued bio-oil as a profitable approach to residue processing and is now marketing a renewable fuel oil [2]. As at 2014, biomass contributed to over 10% of the world's primary energy consumption, making it the 4th largest contributor behind coal, oil and natural gas [3]. In the beginning of 2015, Canada had 70 bioenergy power plants built around the use of woody biomass with a total capacity of 2043 megawatts [4]. Although several systems including a pilot plastic-to-oil conversion plant are operational in south Africa [5], there is, however, a gradual shift occurring in favor of advanced biofuels on the African continent, regarding both biological and thermal conversion processes, underlined by the recognition of the potential of lignocellulosic resources for the sustainable production of biofuels and biochemicals in the near future [6]. In addition, petrochemical-derived waste recycling in Africa is gaining attention; however, sustainability of this new industry is highly dependent on co-pyrolysis with biomass that is readily available and with a well-defined bio-oil characteristic.

Biomass energy use in relation to fixed bed reactors is an important process for power generation and cooking systems

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[7]; therefore, it should be available and accessible without hurting the value chain. *Doka* wood (*Isoberlina doka*) is a hardwood tree native to African tropical savannas and Guinean forest and widely used for construction purposes due to its durability and resilient properties leading to waste dust generation. Hardwood tree can be used directly as a fuel processed into pellet fuel or other forms of fuel. Hence, *Isoberlina doka* sawdust is a good waste energy feedstock. To produce bio-oil, pyrolysis process which is the thermal degradation of the organic components of materials at increased temperatures excluding oxygen to yield combustible gases, biochar and liquid hydrocarbons is favored. The yield distribution of the three classes of product can vary significantly and is highly dependent on the processing conditions. Slow pyrolysis has been found to favor the yield of biochar over other products and is characterized by low heating rate [8]. Short vapor residence times and moderate temperatures maximize the liquid yield from the biomass and is termed "fast pyrolysis." Fluidized bed reactor is usually employed for this type of pyrolysis. However, fixed bed reactor which is not only readily available but being the base design from which other reactors are derived, is used in the present investigation on laboratory scale. Pairing bench-scale investigation with TGA, GC–MS and FT-IR methods facilitates sample and product analysis.

The results of thermogravimetric analysis (TGA) experiments can aid in the prediction of empirical constants of the Arrhenius equation which mostly governs the rate of biomass pyrolysis. Although most of the TGA experiments have been performed under (e.g., less than 50 K/min) due to complex TGA measurement at higher heating rate [9], it can be used to determine the thermal behavior of biomass components. Condensable fraction of volatile generated can also be subjected to Fourier transform infrared (FT-IR) and/or gas chromatography (GC) mass spectroscopy analysis to determine the quality of product.

In this study therefore, hardwood-derived sawdust residue from *Isoberlina doka*, a least concerns category tree on conservation red list [10], was used to investigate a fixed bed which behaves like a fluidized bed reactor within the bed zone. Volatile generation with the intent to focus on the condensable fraction (bio-oil) and the changes in oil composition with temperature in an attempt to explain the yield, quality and the relationship between both is pursued by this study.

2 Methodology

2.1 Sample Collection and Preparation

A milling residue, namely hardwood-derived sawdust from *Isoberlina doka*, which is classified as woody biomass suitable for thermochemical conversion process was generated by the sawmill in Samaru, Zaria, Kaduna State, Nigeria, and obtained for pyrolysis in this experiment. This sample was pretreated to remove sand particles and foreign materials and further milled. Afterward, it was sieved to obtain a size distribution of <0.5 and $0.5–1.0$ mm ranges using the mesh-sized separator. Sieved sawdust particles were labeled according to particle sizes and stored in desiccators.

2.2 Thermogravimetric and Derivative Thermal Analysis of Feedstock

To carry out the TGA analysis, 10 mg of sawdust sample was measured into a crucible and placed in a TGA analyzer (PerkinElmer TGA 4000) with a nitrogen purge of 40 cc/min. Cooling water/algaecide mixture temperature was set to 15 °C; the heating rate was set to 10 °C/min to mimic slow pyrolysis conditions. Data obtained were then subjected to derivative thermogravimetry (DTG) to evaluate the rate of weight loss as a function of temperature.

2.3 Pyrolysis Procedure

The pyrolysis of biomass was carried out in a fixed bed reactor according to the setup described by Kumar and Singh [11]. The reactor which was 13 cm high and 7 cm in diameter was fitted into a heating source (furnace) and a condenser/chiller/circulator attached to the reactor to cool down volatiles exiting at the reactor at the top. The reactor was fitted with nitrogen gas service to create an inert atmosphere, even heat distribution and to aid volatile removal from the reactor. Condensable fraction of volatiles was obtained as bio-oil, while the non-condensable fraction was giving off at the condenser outlet. Temperature monitor and control were achieved with the aid of a digital thermometer, thermocouple attached as well as the temperature control panel of the reactor. In each case, 30 g of the prepared biomass samples was measured into the reactor and the reaction proceeded until the desired conditions were established. The pyrolysis was carried out at temperatures of 400 and 500 °C, reaction times of 10, 20 and 30 min and a constant heating rate of 160 °C/min as shown in Table 1.

2.3.1 Product Yield

In total, 30 g of sample was weighed into the pyrolyzer and pyrolysis carried out. After the completion of each experimental run, char residue was weighed and volume of oil generated recorded. Then after, the yield of liquid, solid and gaseous products was calculated in terms of percentage in line with Chen et al. [12] using Eqs. 1–3.

Table 1 Pyrolysis conditions in a fixed bed reactor

Temperature (°C)	Particle size (mm)	Reaction time (Min)	Heating rate (°C/min)
400	<0.5	10	160
	<0.5	20	160
	<0.5	30	160
	0.5–1.0	10	160
	0.5–1.0	20	160
	0.5–10	30	160
450	<0.5	10	160
	<0.5	20	160
	<0.5	30	160
	0.5–1.0	10	160
	0.5–1.0	20	160
	0.5–1.0	30	160
500	<0.5	10	160
	<0.5	20	160
	<0.5	30	160
	0.5–1.0	10	160
	0.5–1.0	20	160
	0.5–1.0	30	160

%yield of bio - oil

$$= \frac{\text{Volume of liquid product (ml)} \times \text{density (g/ml)} \times 100}{\text{Initial weight of sample (g)}}$$

(1)

$$\text{\%yield of bio - char} = \frac{\text{Weight of solid product(g)} \times 100}{\text{Initial weight of sample(g)}}$$

(2)

$$\text{\%yield of bio - gas} = 100\% - (\%\text{Liquid} + \%\text{Solid})$$ (3)

2.4 Chemical Composition Determination

The GC–MS analysis was carried out using Agilent J & W 19091 J-413 analyzer, and the bio-oil samples were initially dissolved in methanol at a 10 times dilution ratio by weight. The samples were then injected immediately following dilution to minimize interactions between the sample and solvent. Libraries which included NIST11.L and DEMO.L from National Institute of Standards and Technology were used to interpret signal intensity from gas chromatography.

2.5 Functional Group Determination

FT-IR analysis was carried out using Shimadzu 8400 s Spectrophotometer coupled with miRacle A Attenuated total reflectance (ATR) accessory. The liquid was dispensed onto the 2-mm-diameter prism of the ATR. Resolution of the

FTIR device was set to 4 cm^{-1}, spectrum scan frequency was 8 times per minute, and the spectral region was in 600–4000 cm^{-1}. The ATR correction program in the IRsolution software converts the measured ATR spectrum into a normal transmittance measurement by correction of depth penetration differences.

3 Results and Discussion

Figure 1 depicts the thermal behavior of hardwood-derived sawdust particles when subjected to heat under inert conditions. The weight percent, X, and the time derivative of the weight percent, $-dX/dt$, represented by the TG and DTG curves are discussed as a function of temperature. The initial degradation temperature is affected by the number of extractives, which are the less stable components of wood [13]. Components of wood include hemicellulose, cellulose and lignin degrades at different temperature ranges with the former initializing at the temperature of 200 °C. This is the onset temperature of de-volatilization preceded by 2% weight loss due to drying. Hemicellulose decomposition is characterized by an acute weight loss of 30.639%, which explains the fall of the derivative thermal curve to a minimum of − 5.61 at the temperature of 267.75 °C where its total degradation is achieved. The rise of the DTG curve signals the onset of the degradation of cellulose, while lignin component which decomposes at very high temperature is represented by the marginal changes in the plateau above 470 °C on the DTG curve. The TG curve indicates the significant increase in weight loss with increase in temperature to a point where it becomes marginal.

Figure 2a–f shows the weight percent yield of oil, char and gas at selected temperatures and particle sizes. As shown in Fig. 2a–c, the weight percent of gas increases with an increase in temperature at <0.5 mm particle size of the biomass. For example, at 10 min the weight percent of the gaseous product was observed to be 55 and then after increased to 62 as temperature increases from 400 to 500 °C, respectively. However, the weight percent of oil and char individually decreases with an increase in temperature. At 0.5–1.0 mm particle size range as shown in Fig. 2d–f, there is a decrease in the weight percent of gas as temperature increases, whereas the weight percent of oil increases with increase in temperature. The weight percent of char decreases with an increase in temperature from 400 to 450 °C and then after increase as temperature increased to 500 °C.

At 400 °C, Fig. 2a, d reveals a decrease in the weight percent of the gaseous product as the particle size of the biomass increases from <0.5 mm to 0.5–1.0 mm. However, the weight percent of oil and char individually increases with an increase in particle size of the biomass. The same trend of decrease in the gaseous and increase in the oil and char weight

Fig. 1 Thermogravimetric and derivative thermal curve of Hardwood-derived sawdust
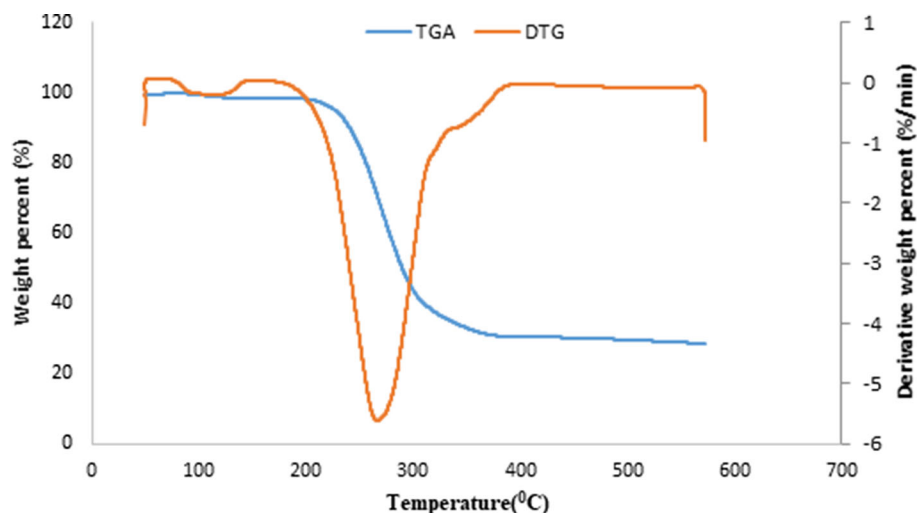
percent with an increase in the biomass particles size are observed in Fig. 2b, c, e, f at temperature of 450 and 500 °C, respectively. This implies that although too large particle size reduces particle resistance to heat distribution [14], very low particle size can affect bed performance by trapping yielded volatiles exposing them to continuous heating.

Figure 3 shows the effect of pyrolysis temperature on the yield of bio-oil from hardwood-derived sawdust. From the results, it can be deduced that bio-oil yield increased with increase in temperature at all particle sizes as well as at all running times investigated. However, percentage oil yield was more temperature dependent at <0.5 mm compared to 0.5–1 mm particle size ranges for all running times with a significant increase ranging from 6 to 10% at the 500 °C when compared with the oil yield at 450 °C. This can be attributed to late response to heating which was not the case with 0.5–1 mm particle size range where oil yield was almost even with temperature increase. Noticeably, a sharp increase of 10.40% in bio-oil yield was observed at the temperature of 450 °C at the particle size range of 0.5–1 mm and 10 min running time after which it increased by only a marginal 0.35%. Overlapping curves on the graph indicates similar response of pyrolysis conditions to temperature treatment over the overlapping areas. It is noteworthy that although oil yield was at its peak at 500 °C for all curves, highest yield was at the particle size range of 0.5–1 mm and running time of 30 min.

This agrees with the reviews of Isahak et al. [15] on bio-oil production using pyrolysis method and Akhtar and Amin [16] on operating parameters for optimum liquid yield.

The effect of reaction time on the percentage yield of bio-oil from hardwood-derived sawdust subjected to pyrolysis is shown in Fig. 4. The result shows that bio-oil yield increased with increase in time but has a weak influence above 10 min. However, significant yield increase beyond 10 min was noticed at fewer conditions which include a

7% increase at 20 min considering the 0.5–1 mm range, 400 °C curve, a 4.55% increase at 20 min considering the 0.5–1 mm range, 500 °C curve and a 4.12% increase considering the <0.5 mm, 500 °C curve. Otherwise, yield increase was marginal ranging from 1.2 to 2% at 20 min and insignificantly less than 1% at the reaction time of 30 min. Bio-oil yield was highest at 30 min for all conditions investigated; however, a peak of 49.84% was recorded at 0.5–1 mm range, 500 °C at 30-min reaction time. These are in accordance with the findings of Stefanidis et al. [17] who with the aid of a bench-scale fixed bed reactor investigated low-quality biomass for bio-oil yield and the report of Mourant et al. [18] who carried out fast pyrolysis on mallee wood studying the effect of alkaline (and alkaline earth) metals on bio-oil yield and composition.

Figure 5 indicates the effect of particle size on the percentage yield of bio-oil from Hardwood-derived sawdust. The result shows a strong influence of particle size in that bio-oil yield increased significantly with increase in particle size. Large particles behavior in a single-particle reactor resulted into lower volatile yield due to various resistance which include porosity and temperature gradient among others [9]. Reduced bed porosity and permeability to carrier and generated gas led to uneven heat distribution [19], which characterized lower yields at <0.5 mm particle size range. At the particle size range of 0.5–1 mm, bio-oil yield of more than 14% increase was recorded at all conditions, while at 10 min, 400 °C as well as 10, 20 and 30 min, 450 °C resulted in yields above 20%. Although oil yield was at its peak of 49.84% at 30 min, 500 °C and closely trailed by a 48.65% yield at 20 min, 500 °C, they only represent a 17.255 and 16.145% increase compared to yields with <0.5 mm range, respectively.

Figure 6 illustrates the rate at which hardwood-derived sawdust is de-volatized with time. The most significant increase in volatile generation was observed at the running
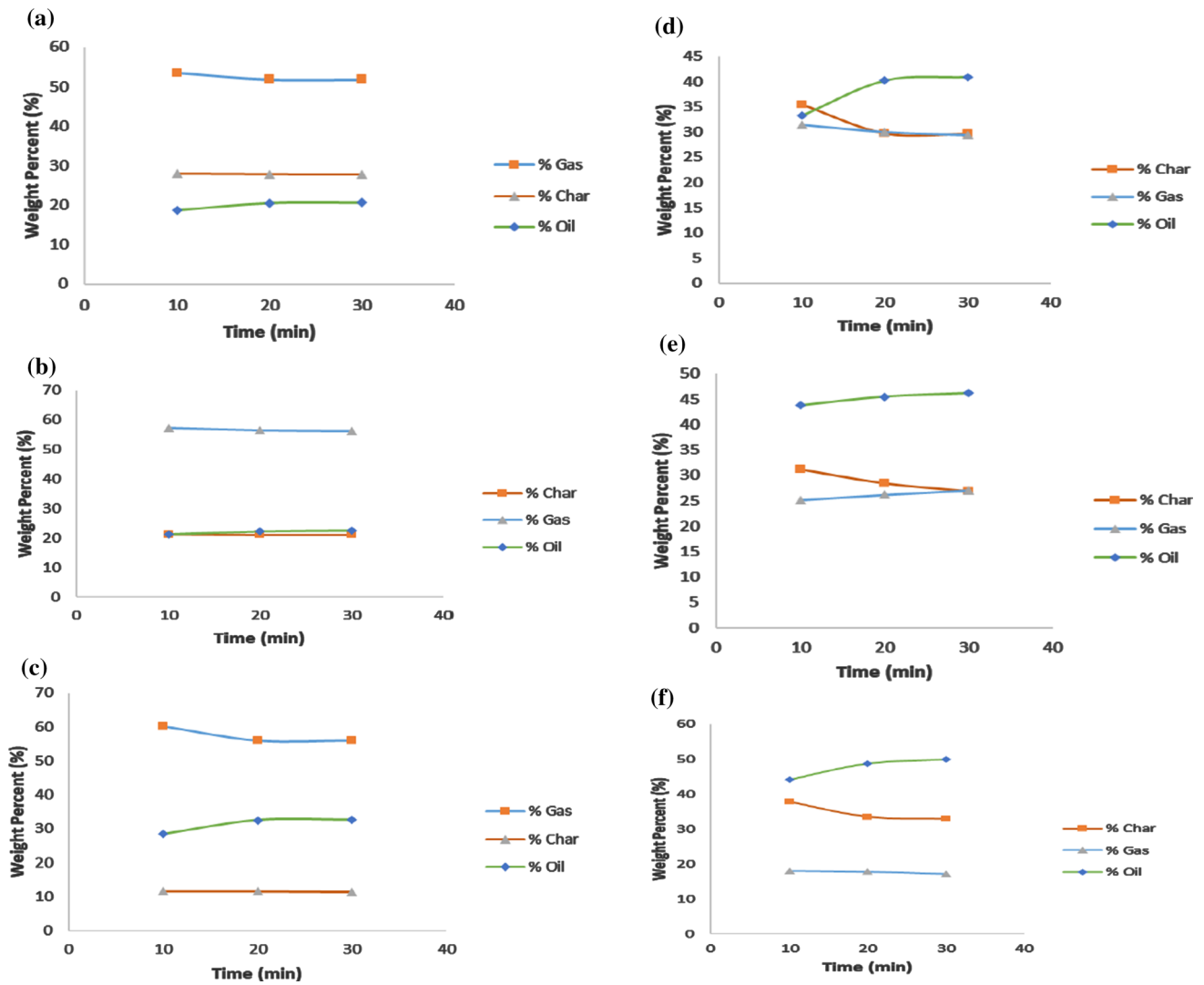
Fig. 2 **a** Product distribution at 400 °C and at < 0.5 mm particle size range. **b** Product distribution at 450 °C and at < 0.5 mm particle size range. **c** Product distribution at 500 °C and at < 0.5 mm particle size range. **d** Product distribution at 400 °C and at 0.5–1.0 mm particle size range. **e** Product 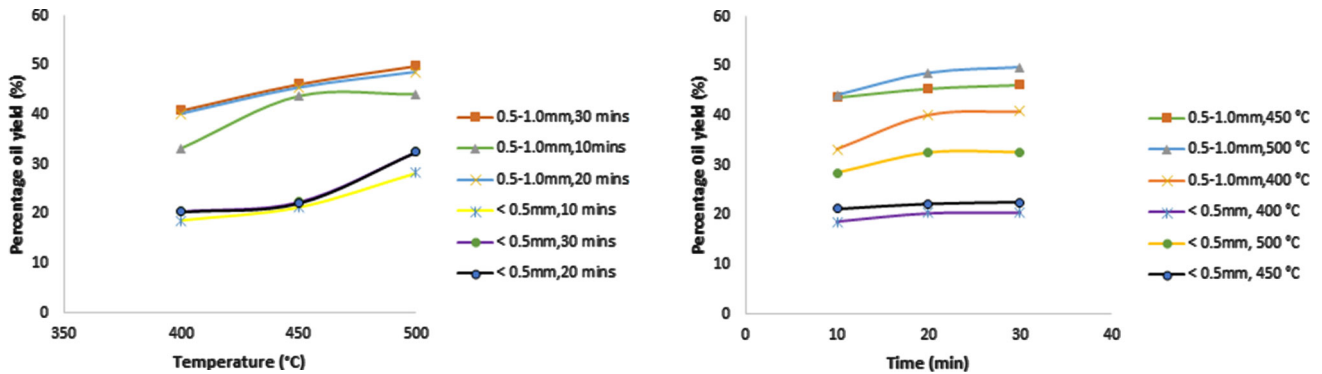distribution at 450 °C and at 0.5–1.0 mm particle size range. **f** Product distribution at 500 °C and at 0.5–1.0 mm particle size range

Fig. 3 Effect of pyrolysis temperature on bio-oil yield
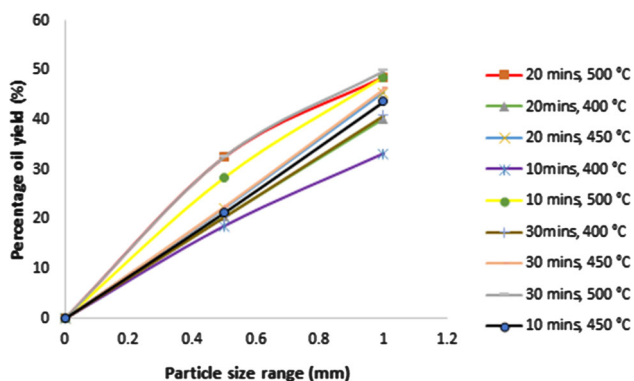

Fig. 4 Effect of reaction time on bioyield
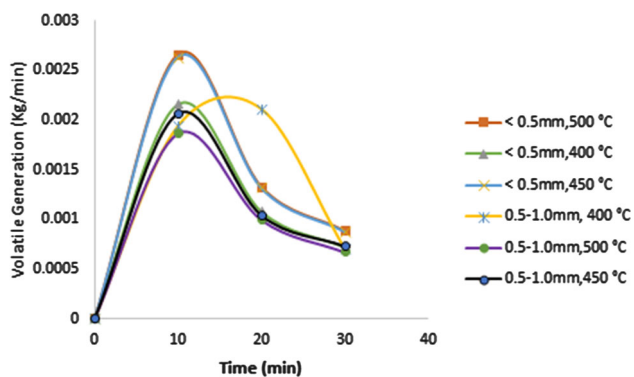
Fig. 5 Effect of particle size on bio-oil yield

Fig. 6 Volatile generation profile of hardwood-derived sawdust

time of 10 min for all curves with the exception of the 0.5–1 mm, 400 °C, which peaked at 15 min. This can be attributed to the fairly higher heating rate which maximizes yield of liquid at shorter generation time [20]. The fall and the tailing of the curves as they approach 20 and 30 min,

respectively, represents a marginal and an insignificant rate of de-volatilization with respect to the energy required to keep the pyrolysis process running up to these times. Component quality and availability in the product stream is dependent on the temperature at which they are produced. While some components are present at all temperature investigated but at increased or reduced quality, others are totally absent at some temperatures. This can be attributed to the fact that they are yet to form or are already broken down to form newer components.

Figures 7, 8 and 9 show the effect of temperature on the chemical composition of hardwood-derived sawdust. From the time of injection to when elution occurs, 20 peaks were observed at the temperature of 400 °C which increased to 22 peaks at 450 °C and then decreased to 15 peaks at the temperature of 500 °C. Signal intensity, however, got weaker with increase in temperature which indicates that new compounds are formed in addition as well as to replace existing ones. This can be attributed to thermal degradation of bio-oil as a result of continuous exposure to heat. In total, 38 components were detected at 400 °C which increased by a significant 23.68% to 47 components at 450 °C. This increase, however, resulted to the total disappearance of compounds like caffeine (1.55%), while some benzene-based compounds were replaced with new ones. At the higher temperature of 500 °C, components decreased significantly by 34.04% to 31 which is accompanied with the production of entirely new components like 1-piperidineethanol. This indicates that bio-oil composition varies with temperature; hence, compound of interest should be targeted at the convenient temperature for production if it is purposed as a raw material for speciality chemicals. It is noteworthy that the
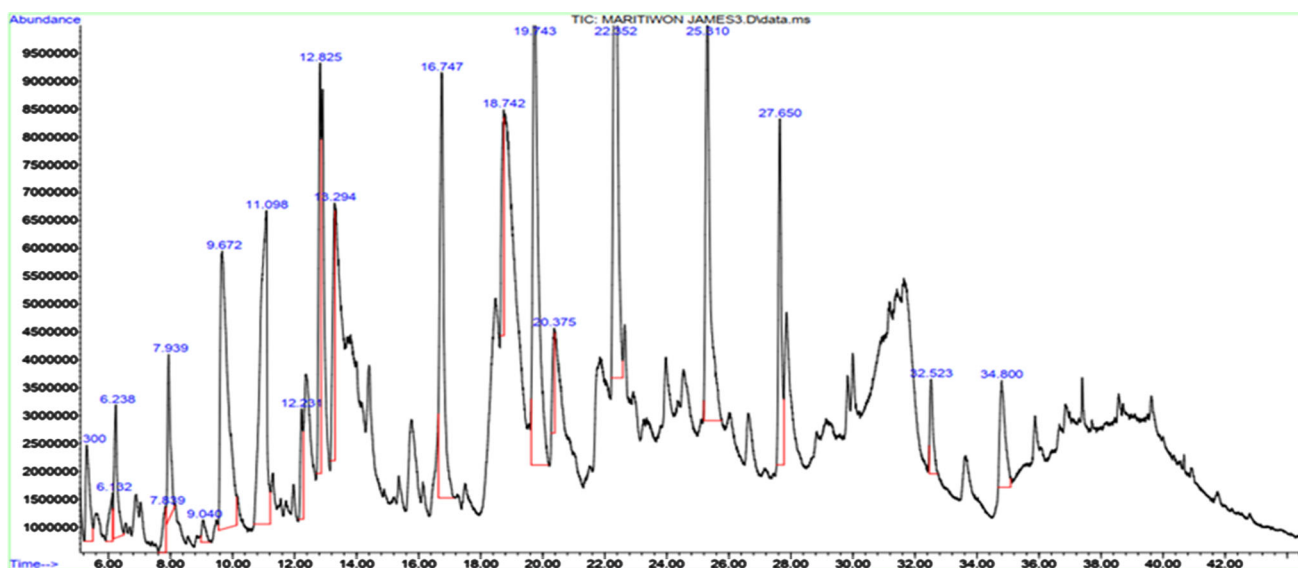

Fig. 7 GC–MS result at 0.5–1.0 mm range, 400 °C and 20 min showing component abundance
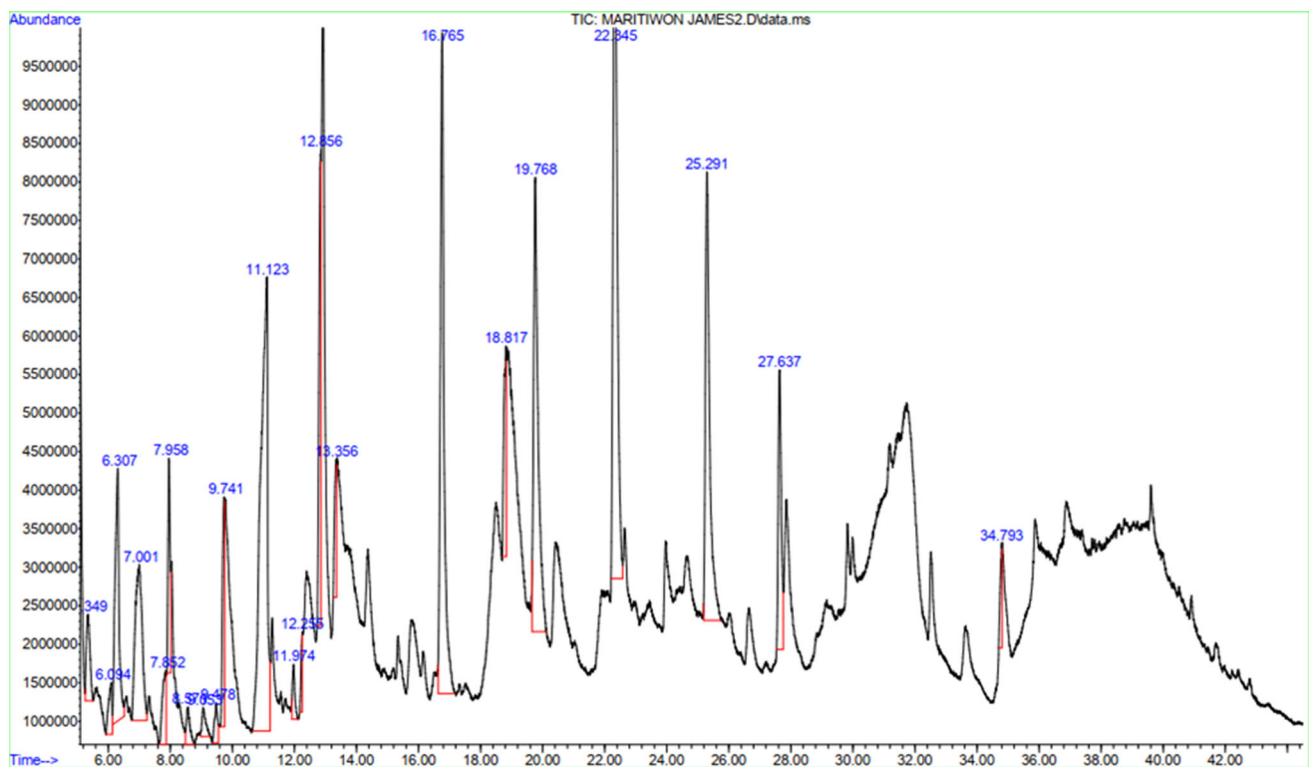
Fig. 8 GC–MS result at 0.5–1.0 mm range, 450 °C and 20 min showing component abundance
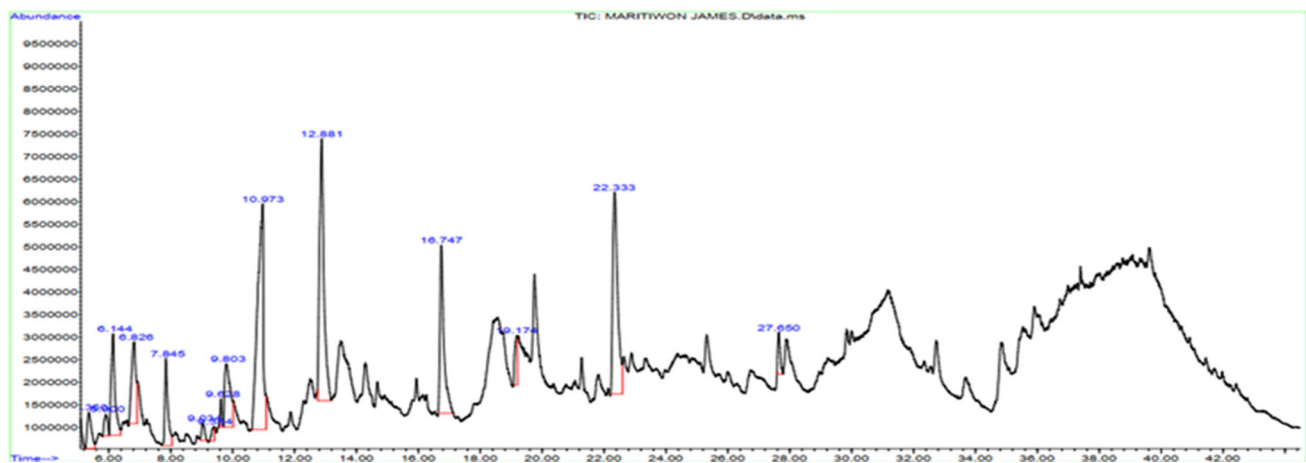

Fig. 9 GC–MS result at 0.5–1.0 mm range, 500 °C and 20 min showing component abundance

number of components increased from 400 °C to peak at 450 °C, while highest bio-oil yield was recorded at the temperature of 500 °C at which the lowest number was observed. Hence, there is no correlation between bio-oil yield and number of components present; therefore, a compromise can be arrived at depending on the purpose for which the bio-oil to be produced is intended. Some of the components detected in bio-oil include mequinol (5.02%, 400 °C; 18.99%, 500 °C), caffeine (1.55%, 400 °C), 5-tert-butylpyrogallol (5.29%, 400 °C; 1.06%, 450 °C; 1.72%, 500 °C), 1-fluoro-2-methoxy-benzene (1.06%, 500 °C), p-cresol (3.11%, 400 °C; 2.06%, 450 °C), butyrolactone (0.85%, 400 °C; 1.21%, 450 °C, 500 °C), 2,4-dimethylfuran (1.43%, 400 °C; 4.33%, 500 °C), phenol (11.08%, 400 °C; 2.45%, 450 °C; 5.92%, 500 °C), creosol (8.81%, 400 °C; 12.34%, 450 °C; 10.74%, 500 °C). The findings of this report were also corroborated by other researchers such as Anca-couce [20] who critically reviewed the composition of bio-oil and Gao et al. [21] who investigated bio-oil from pine-derived hardwood.
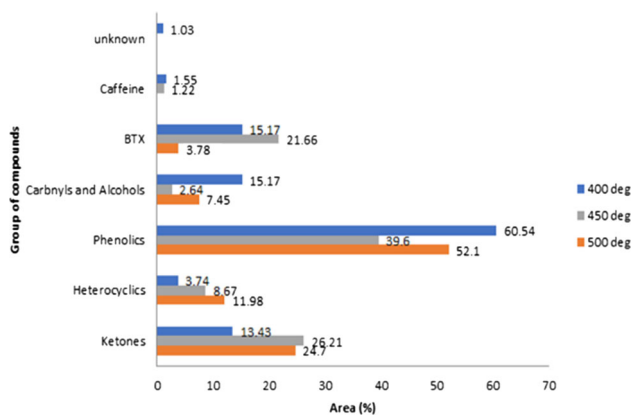
Fig. 10 GC–MS result showing major compounds present in bio-oil produced at 400–500 °C

Djokic et al. [22] and Negahdar et al. [23] identified fast pyrolysis bio-oil as aromatic and non-aromatic oxygenates contained in an extremely complex mixture. These oxygenates include ketones, alcohols, aldehydes, esters, furans, pyrans, carboxylic acids, carbohydrates as well as nitrogen containing compounds and large molecular oligomers. Figure 10 indicates various compounds present in bio-oil at the temperature of 400–500 °C. It can be seen that bio-oil from *Isoberlina doka* contains mostly oxygenated compounds classified as phenolics with an estimated area initially 60.64% at 400 °C which decreased by 20.94% at the temperature of 450 °C. More phenolic compounds were formed at 500 °C as the area increased significantly to 52.1%; nevertheless, this is lower than the area recorded at the initial

temperature. Phenolics were dominated by 2, 6-dimethoxy phenol at lower temperature, but as the temperature increases, creosol and catechol were produced in larger quantities. This can be attributed to the onset of the decomposition of lignin component of biomass at higher temperatures [13, 24]. Heterocyclic compounds containing additional members like sulfur and nitrogen increased with increase in temperature, while ketones content peak at 450 °C and afterward decreased. Component distribution at 500 °C reveals major compounds of interest suitable for raw bio-oil upgrade into combustion fuels, while at 450 °C, industrial and petrochemical raw materials sourcing is favored. At 400 °C however, flavonoids and medically inclined materials like caffeine and mequinol can be sourced. Lignocellulosic components of biomass decomposed by heating contribute to the product in the volatile mixture, compound of several functional groups [25].

Figures 11, 12 and 13 illustrate functional groups present in bio-oil produced at the temperature of 400, 450 and 500 °C, respectively. Functional groups represented by 15 peaks, present in bio-oil produced at 400 °C, were concentrated at wavelengths ranging between 1000 and 1710 cm^{-1} (lower range) and wavelengths ranging from 2962 to 3865 cm^{-1} (upper range). This implies that at 400 °C, the existence of C=O bonds, –C≡C– bonds, N–H bonds, C–N bonds, C=C bonds, C–O bonds, C–H bonds and O–H bonds is indicated in the bio-oil produced. These functional groups validate that organic compounds which include alcohols, phenols, amine, nitriles, alkanes, alkenes, aromatics and acids were present in bio-oil produced [26], which agrees with results
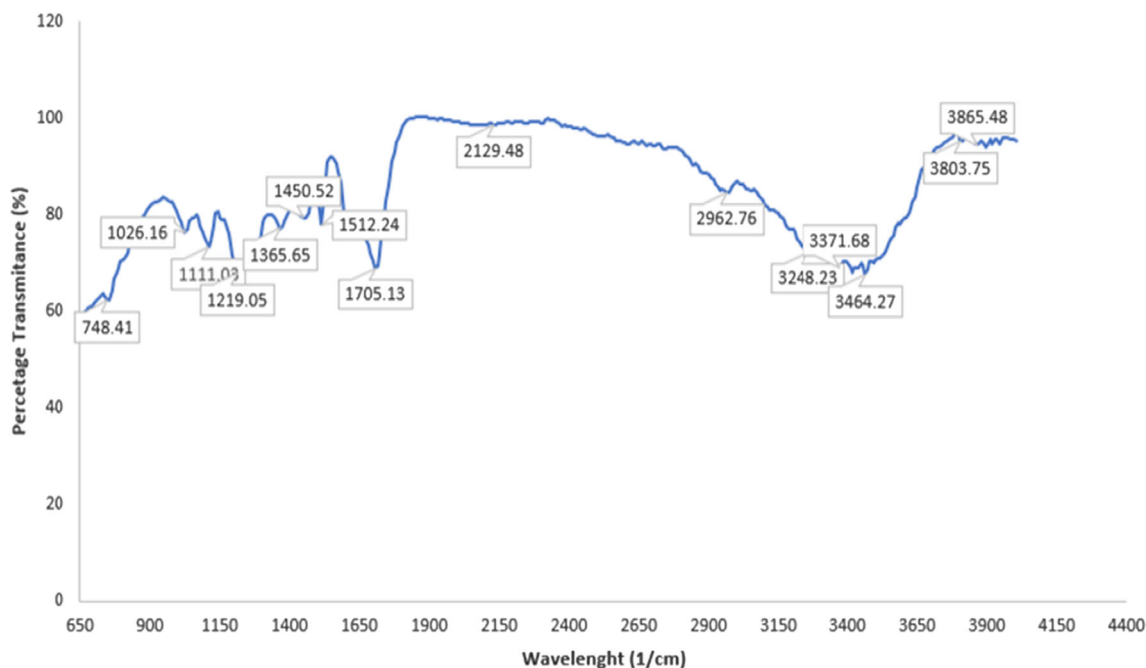

Fig. 11 FT-IR spectra of *Isoberlina doka*-derived bio-oil produced at 400 °C
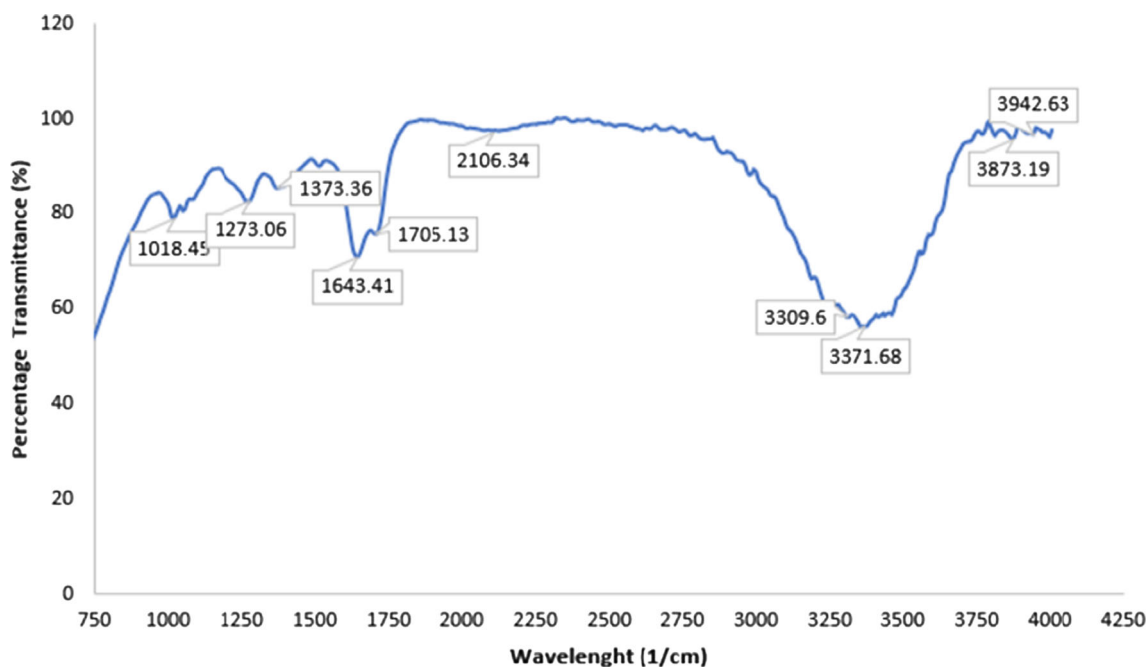
Fig. 12 FT-IR spectra of *Isoberlina doka*-derived bio-oil produced at 450 °C
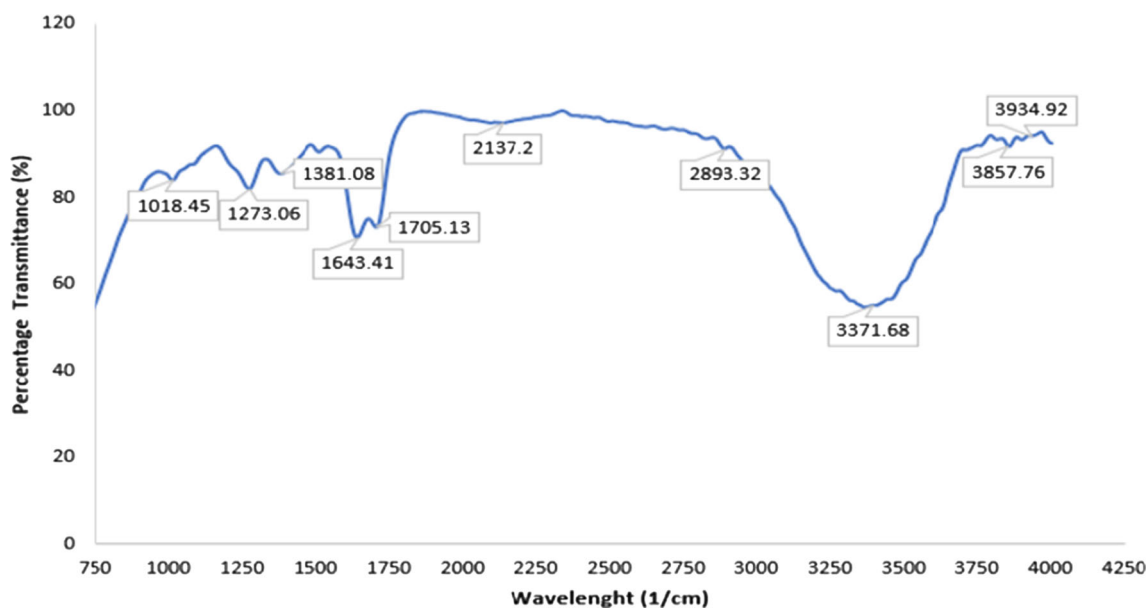

Fig. 13 FT-IR spectra of *Isoberlina doka*-derived bio-oil produced at 500 °C

obtained from GC–MS analysis [27]. However, functional groups present in bio-oil produced at 450 and 500 °C reduced to 10 peaks, respectively, retaining both wavelength ranges present at 400 °C. It is noteworthy that both the upper and the lower ranges of wavelength shrink with increase in temperature. This downsizing represents the disappearance of wave numbers between 1400 and 1550 cm^{-1} from the lower range

and 2962–3250 cm^{-1} from the upper range with the formation of fewer new ones. This phenomenon corroborates the disappearance of some compounds which include caffeine as explained by the GC–MS result.

4 Conclusion

From the experiment carried out, it can be concluded that the thermal behavior of *Isoberlina doka*-derived sawdust is similar to that of other hardwood-derived sawdust except for the early onset of the decomposition of cellulose content at 350 °C. In addition, much of the oil from fast pyrolysis of *Isoberlina doka*-derived sawdust is generated at the early stage of the pyrolysis process after which generation rate shrinks. It can also be concluded that time has a little effect at a higher heating rate; hence, only a scale-up of process could make oil yield tangible beyond 20 min considering a moderately high heating rate of 160 °C/min. It can also be said that although temperature has a significant effect on yield and composition of bio-oil, vapor residence time rather have a minimal effect on bio-oil yield, but do significantly affect bio-oil composition. Again, it can be deduced that bio-oil composition changes with temperature; hence, at 400, 450 and 500 °C, it is more suited for specific purposes of pharmaceutical raw material sourcing, petrochemical sourcing and alternative fuel applications, respectively.

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