



Fast Pyrolysis of Nigeria Danta Hardwood (*Nesogordonia papaverifera.*) and Obeche Softwood (*Triplochiton scleroxylon*) Sawdust.

By

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Abstract

Biomass resources have received comparatively little research and development focus despite their abundance in Africa. This work presents the use of a fixed bed fast pyrolysis system for the conversion of indigenous wood species, hardwood and softwood, from sawmill residues to bio-oil. The hardwood produced slightly more liquid product than the softwood although both wood species yielded similar amounts of bio-char of 31 wt%. The bio-oil yield for hardwood was 48.1 wt% compared to 45.8 wt% for the softwood. FTIR spectrometric scan of the liquid products detected nineteen different functional groups in both hardwood and softwood bio-oils. This is indicative of similar chemical species in bio-oils produced from wood sources. The softwood however contains slightly more phenolic and alcoholic compounds than the hardwood. This could explain the slightly higher values of viscosity and density of softwood bio-oil than hardwood bio-oil. The density and viscosity of softwood are 1082 kg/m³ and 2 cst respectively compared to 1074 kg/m³ and 1.3 cst for hardwood. Also, 28 of the chemical species found in the bio-oil were also present in fossil diesel suggesting a possibility of blending bio-oil with conventional diesel.

Keywords: Bio-oil, Hardwood, Softwood, Sawdust, Fast pyrolysis, Africa.

Introduction

Biomass derived fuels have been recognized as a major renewable energy source to supplement fossil fuel sources of energy and it is expected to play a pivotal role in the world's future energy supply¹. As a result, transformation of biomass into useful and sustainable forms of energy is a common concern of researchers globally. Most biomass sources widely investigated are those that are native to or grown in the developed and emerging countries where almost all research and development have been undertaken^{2,3,4}. Comparatively, biomass in Africa has not received significant research attention and thus remains largely unexplored⁵. There is, however, a

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¹ IRENA (2015), A background paper to "Renewable Energy in Manufacturing", March 2015. IRENA, Abu Dhabi. www.irena.org/remap/IRENA_RE_Potential_for_Industry_BP_2015.pdf

² Butler, E., Devlin, G., and McDonnell, K. (2011): A review of recent laboratory research and commercial developments in fast pyrolysis and upgrading. *Renewable and Sustainable Energy Reviews*, 15 (8): 4171-4186

³ Isahak, W.N.R.M., Mohamed, W.M. H., Mohd, A.Y., and Taufiq-yap Y.H. (2012): Review on bio oil production from biomass by using fast pyrolysis method. *Renewable and Sustainable Energy Reviews*. 16: 5910-5923.

⁴ Meier, D., Beld, B.V., Bridgwater, A.V., Elliott, D., Oasmaa, A., and Preto, F. (2013): State-of-the-art of fast pyrolysis in IEA bioenergy member countries. *Renewable and Sustainable Energy Reviews*. 20: 619-641

⁵ Bensah, E.C., Kadar, Z., and Mensah, M.Y. (2015). Ethanol production from hydrothermally-treated biomass from West Africa. *BioResources* 10(4): 6522-6537.

gradual shift occurring in favour of advanced biofuels on the African continent, both in biological and thermal conversion processes, underlined by recognition of the potential of lignocellulosic resources for the sustainable production of biofuels and biochemicals in the near future. According to Kuye and Edeh⁶, about 13 million tonnes of agro-forestry waste is generated annually in Nigeria. Popoola *et al.*⁷ investigated the theoretical potential of converting wood residue to bio-oil in Nigeria and an assessment of biofuel potential from various biomass residues in Ghana has been undertaken⁸.

In sub-saharan Africa, the conversion of biomass waste to energy also provides an opportunity for waste management. In Ghana for instance, about 90% of solid waste generated are organic with the combustible composition ranging from 45-55%⁹. These biomass wastes can be converted to biofuels using different technologies including pyrolysis. Pyrolysis is a process which involves thermal decomposition of the organic polymers (hemicelluloses, cellulose, and lignin) found in biomass in the absence of oxygen which results in the formation of bio-oil, bio-char, and gaseous fractions in varying proportions depending on reaction conditions. Pyrolysis can generally be classified as slow or fast. Slow pyrolysis is often related to the production of charcoal while fast pyrolysis is related with production of bio-oil. Slow pyrolysis of biomass will produce high content of charcoal¹⁰. At present, researchers are focusing on fast pyrolysis since it is the promising routes in producing bio-oil as it can yield up to 75 wt% of bio-oil on wet basis¹¹.

Researchers in Africa are making efforts to study the pyrolysis process for bio-oil production from different feedstocks. A review of some of the methodologies used reveal that most the processes can best be described as slow pyrolysis. Ogunjobi and Lajide¹², Adegoke *et al.*¹³, and Ogunsina *et al.*¹⁴ have converted corn cob, wood residue and palm fruit bunches to bio-oil

⁶ Kuye, A.O., Edeh. I. (2013). Production of bio-oil from biomass using fast pyrolysis – A critical review. *Journal of Minerals Research*. 1(1): 1-20.

⁷ Popoola, L.T., Gutti, B., and Adeniran, J.A.(2013): The potentials of waste-to-energy system in Nigeria: A study of pyrolysis conversion of wood residue to bio-oil in major cities of south-western Nigeria. *Advances in Applied Science Research*. 4: 243-251.

⁸ Kemausuor, F., Kamp, A., Thomsen, S.T., Bensah, E.C., and Ostergard, H. (2014): Assessment of biomass residue availability and bioenergy yield in Ghana. *Resources, Conservation and Recycling*. 86: 28-37.

⁹ Ahiekpor, J.C. Kuye, A.O., Osei-Wusu. A. (2015). Liquid fuels production by pyrolysis from waste – opportunities and challenges in Africa. 2nd International Conference on Applied Sciences and Technology. Kumasi, Ghana. 28-30th October, 2015.

¹⁰ Bridgewater A.V. (2003). Renewable fuels and chemicals by thermal processing of biomass, *Chemical Engineering Journal*. 91: 87–102.

¹¹ Ahiekpor, J.C., and Kuye, O.A. (2015). Production of bio-oil in Nigeria: Challenges and Prospects. *Petroleum Technology Development Fund Journal*. (In press).

¹² Ogunjobi, J.K., and Lajide, L. (2013). Characterisation of bio-oil and bio-char from slow pyrolysed Nigerian yellow and white corn cobs. *Journal of Sustainable Energy and Environment*. 4:77-84.

¹³ Adegoke, O.A.; Fuwape, J. A.; Fabiyi, J. S. (2014). Combustion properties of some tropical wood species and their pyrolytic products characterization. *Energy and Power*. 4(3):54-57.

¹⁴ Ogunsina, B.S., Ojolo, S.J., Ohunakin, O.S., Oyedeji, O.A., Matanmni, K.A., and Bamgboye, I.A. (2014). Potentials for generating alternative fuels from empty palm bunches by pyrolysis. *JOMAR*.8:50-60.

respectively. Osayi *et al.*¹⁵ reportedly used fast pyrolysis in a fixed bed to pyrolyze natural rubber in South Africa at a heating rate of 15 °C/min which is lower than rates recommended for fast pyrolysis¹⁶.

The conditions sufficient for fast pyrolysis process to produce high yield and good quality bio-oil include: high heating rates of above 30 °C/min¹⁷; carefully controlled pyrolysis reaction temperature; short hot vapor residence time; and rapid cooling of pyrolysis vapors¹⁷. Fast pyrolysis may be performed in different reactor configurations with the fixed bed reactor being the simplest but also the least efficient. As fast pyrolysis is not well advanced in many countries in Africa, developing and improving the yield and quality of bio-oil using the fixed bed pyrolysis reactor may be a step towards understanding the fast pyrolysis mechanism. This will enhance the development of more efficient and advanced reactor configurations such as fluidized bed and rotating cone reactors.

In fixed bed pyrolysis, the feed material is fed into the reactor and heat is applied externally. Usually nitrogen is used as inert gas and for evacuating the volatile gases from the reactor. This work reports on the progress being made to understand the production of bio-oil from selected wood species in Nigeria. A laboratory scale fixed bed reactor made from stainless steel was used with a modified furnace as the heating source. The yield and characteristics of bio-oil produced from hardwood and softwood sawdust using the pyrolysis system are presented. The liquid products were analyzed using an FTIR spectroscopy.

Methodology

Pyrolysis process

The sawdust of Danta hardwood (*Nesogordonia papaverifera*) and Obeche softwood (*Triplochiton scleroxylon*) were sampled from Dagodo and Aluu sawmills respectively in Port Harcourt, River State. The samples were used as collected from the two sawmills. The experimental setup is shown schematically in Figure 1.

¹⁵ Osayi, I.J., Iyuke, S., Diakanua, N.B., and Ogbeide, S.E. (2015). Liquid fuels production from natural rubber. 1st *International Oil Flow Conference*, Uniport, Port Harcourt, Nigeria.

¹⁶ Ronse, F., Hecke, Van S., Dickinson, D., and Prins, W. (2013): Production and characterization of slow pyrolysis biochar: influence of feedstock type and pyrolysis conditions. *Bioenergy*. 5: 104-115

¹⁷ Meier, D., Beld, B.V., Bridgwater, A.V., Elliott, D., Oasmaa, A., and Preto, F. (2013): State-of-the-art of fast pyrolysis in IEA bioenergy member countries. *Renewable and Sustainable Energy Reviews*. 20: 619-641

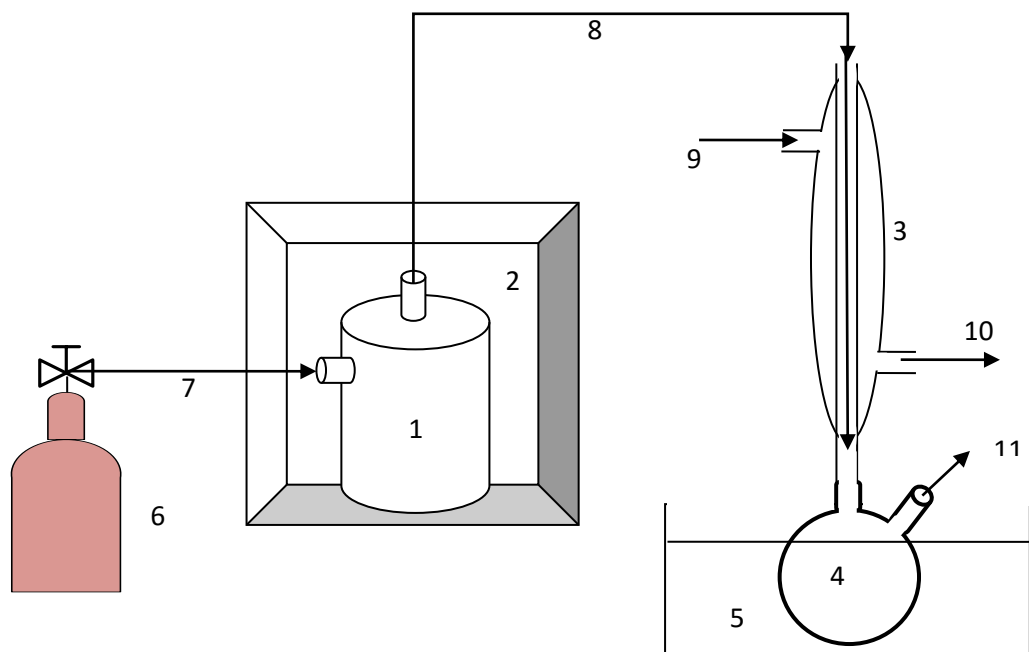


Figure 1: Schematic of experimental set-up: 1. Reactor, 2. Furnace, 3. Reflux condenser, 4. Bio-oil collector 5. Ice trap, 6. Nitrogen bottle, 7. Inert/sweep gas inlet, 8. Product outlet, 9. Cooling water inlet 10. Hot water outlet 11. Non-condensable gas outlet

The reactor (see Figure 1) is placed in a muffle furnace (J.P. Selecta, S.A, 582543 S/N, 230 VAC, 00-C/2000367, 50/60 Hz, 3500W, Spain) with a temperature controller and capable of heating up to 1100 °C. Nitrogen gas was used as the inert gas and also used to evacuate the volatile products. Bio-oil was collected using a reflux condenser and a round-bottom flask immersed in an ice bath.

During any experiments, 200 g of sawdust is charged into the reactor which is covered air-tight and placed in the furnace. The reactor has two openings (see Figure 1). One opening located on the side of the reactor and above the level of sawdust in the reactor is connected to the nitrogen gas cylinder using a stainless steel pipe to serve as the inlet for the nitrogen gas which is both an inert and carrier gas for the process. The other opening is located on top of the reactor and serves as the outlet for both nitrogen gas and volatile fractions to the condensation unit.

Once the sawdust was fed into the reactor, the system was purged with nitrogen gas for about 5 minutes before the experiment was commenced. A free board was created in the reactor by not filling it up totally in order to allow for easy passage of gaseous products. The temperature of the furnace was then set to a reaction temperature of 500 °C using electronic temperature controller at a heating rate of 30 °C/min. The volatile products were quickly removed by opening the nitrogen valve. The reaction was stopped forty (40) minutes of reaching reaction temperature (500 °C) since there was no more liquid product condensing from the ice trap. The liquid products were collected and stored in an air-tight container for analysis.

The condensation unit was made of a single pass reflux condenser and a round bottom flask with two openings, immersed in an ice bath. The condensable fractions of volatile fractions were first condensed in the reflux condenser using water at ambient temperature and further condensed in the round bottom flask immersed in the ice bath. This double cooling was aimed

at maximizing the yield of liquid products. Non condensable gases were allowed to escape through the outlet of the bio-oil collector via a flexible tube.

When no more condensation was noticed, the flow of nitrogen gas was stopped and furnace turned off. The system was allowed to cool, the round bottom flask was then disconnected from the reflux condenser and the reactor removed from the furnace. The pyrolysis products (bio-oil and char) were collected and weighed. The weight of the non-condensable gases was determined by the difference between the sum of the weight of bio-oil and char from the total weight of sawdust used for the experiment.

Analysis of pyrolysis liquid products

The bio-oil as produced was analysed for some physical and fuel properties and was compared with similar properties of fossil diesel acquired from AP filling station at the University of Port Harcourt main entrance, Choba. The properties determined included density (ASTM, D4052), viscosity (ASTM D445), pour point (ASTM D97), flash point (ASTM D92), and pH (ASTM D6423). The viscosity, pour and flash points were determined in an external laboratory at RofNel Energy Services Ltd in Port Harcourt, Nigeria. An FT-IR analysis was also performed using a Shimadzu FT-IR instrument at Fugro Nigeria Ltd to generate the IR spectra and identify the functional groups present in the bio-oil and fossil diesel.

3. Results and discussion

Bio-oil, bio-char and non-condensable gases were the three products obtained from the fast pyrolysis of softwood and hardwood Nigerian sawdust. Table 1 shows the mean yield of the various products together with their standard deviation. Hardwood sawdust gave slightly higher yield of bio-oil than softwood but both gave similar bio-char yield. This could probably be due to the softwood having more volatile fractions that are non-condensable.

Table 1 *Distribution of bi-oil, bio-char and non-condensable gas from pyrolysis of softwood (SW) and hardwood (HW) sawdust compared with other results of fixed bed pyrolysis*

Author	Feedstock	Bio-oil (%)	Bio-char (%)	Gas (%)
This work (2015)	SW	45.8± (0.92)	31.1±0.71	23.1±0.21
	HW	48.1±0.40	31.1±0.83	20.8±1.15
Salehi <i>et al.</i> ¹⁸	Sawdust	45	33	22
Ogunjobi and Lajide ¹⁹	Corn cob	42.6	33.3	24.1
Ogunsina <i>et al.</i> ²⁰	Palm fruit bunches	33.6	25.1	41.3

¹⁸ Salehi, E., Abedi, J., and Harding, T. (2009). Bio-oil from sawdust: pyrolysis of sawdust in a fixed-bed system. *Energy and Fuels*, 23 (7): 3767–3772.

¹⁹ *ibid*

²⁰ *ibid*

The yields of this work are comparable to the results of Salehi *et al.*²¹ who used a fixed bed reactor to study the pyrolysis of wood sawdust but differs greatly from the results of other authors who used different feed stocks. This confirms the reports that pyrolysis product yields and their distributions are greatly influenced by the type of feedstock and their compositions amongst other factors.

Samples of the bio-oil produced are shown in Figure 2. After centrifuging, the bio-oil separated into two layers; a light brown coloured liquid and a dark brown liquid as shown in Figure 3. This phenomenon could be as a result of the different chemical composition of bio-oil. According to Oasmaa and Peacocke²², the amount and type of extractives in a wood feedstock could cause the separation of bio-oil into phases. Also, high water content could cause phase separation of bio-oil. Two phase product with a larger aqueous phase and a viscous oily phase may be produced if feedstock with high water content (> 10 wt%) is used²³. Bio-oils can be considered as micro emulsions of water and water-soluble organic compounds with water-insoluble, mostly oligomeric, lignin-derived material. The ratio of these fractions depends on the feedstock, process conditions, and production and storage conditions²⁴.



Figure 2: Bio-oil samples

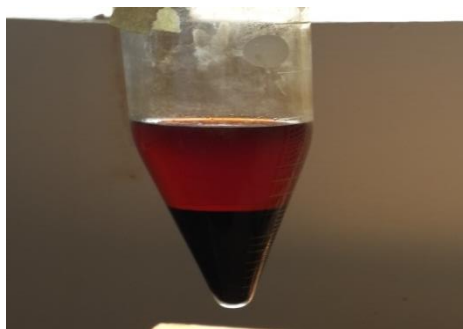


Figure 3: Bio-oil after centrifuging

Composition of bio-oil and diesel from FTIR analysis

In determining the functional groups present in the bio-oil from softwood and hardwood sawdust, an FT-IR analysis was performed on the bio-oil samples. The FTIR spectrum for

²¹ *ibid*

²² Oasmaa, A. And Peacocke, C. (2010). A guide to physical property characterisation of biomass-derived fast pyrolysis liquids. A guide. Espoo: VTT. VTT Publications 731. <http://www.vtt.fi/inf/pdf/publications/2010/P731.pdf>.

²³ Lehto, J., Oasmaa, A., Solantausta, Y., Kyto, M., and Chiamonti, D. (2013). Fuel oil quality and combustion of fast pyrolysis bio-oils. VTT Technology.

hardwood bio-oil, softwood bio-oil and fossil diesel are shown in Figures 4, 5, and 6 respectively. Nineteen different functional groups were detected in both bio-oil samples. Qualitative analysis of the peaks suggests that the organic composition of the bio-oil from both hardwood and softwood is very similar. However, the softwood contains more phenols and alcohol compounds than the hardwood. This could possibly make bio-oil from hardwood sawdust more thermally stable than bio-oil from softwood sawdust since oxygen-containing reactive functional groups have been reported to be responsible for thermal instability and ageing of bio-oils²⁴.

Aldehydes, carbonyls, nitro compounds and phenols were not detected in the diesel sample. Also, fewer quantities of alcohols were present in the diesel sample compared to both bio-oil samples although fifteen different functional groups were common to both diesel and bio-oil samples. This suggests the possibilities of blending bio-oil and diesel for use directly as fuel without upgrading. As expected, the diesel contains more alkanes than bio-oil and the functional groups dominant in both diesel and bio-oil samples are alcohols, alkanes, alkenes, aromatics, carboxylic acids, esters and ethers.

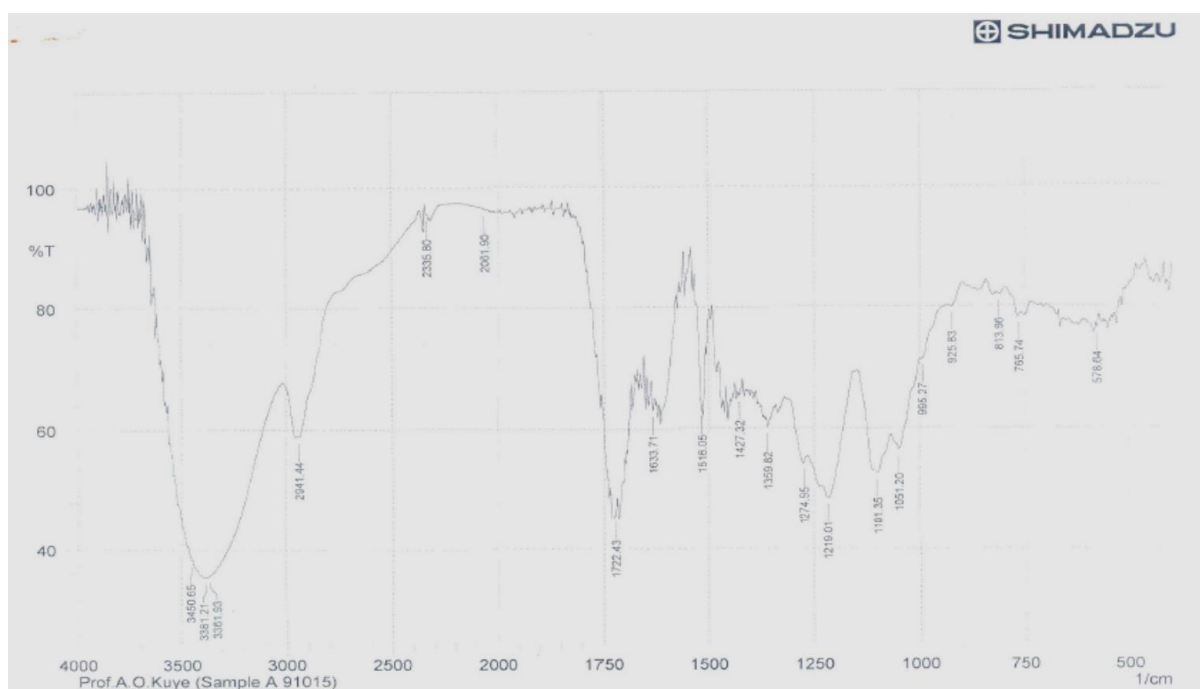


Figure 4: FTIR spectrum of hardwood sawdust bio-oil

²⁴ Salehi, E., Abedi, J., Harding, G.T., Seyedeyn-Azad, F. (2013): Bio oil from sawdust: Design, operation, and performance of a bench-scale fluidized bed pyrolysis plant. *Energy and Fuels* 27: 3332-3340.

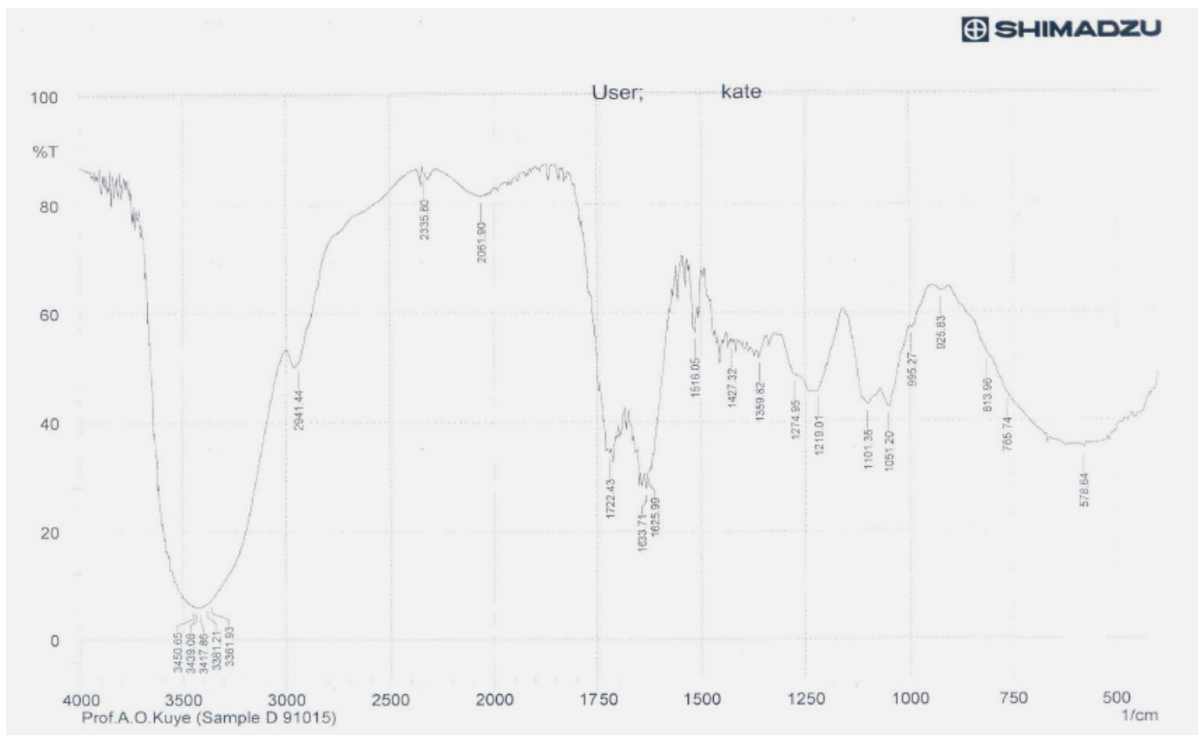


Figure 5: FTIR spectrum of softwood sawdust

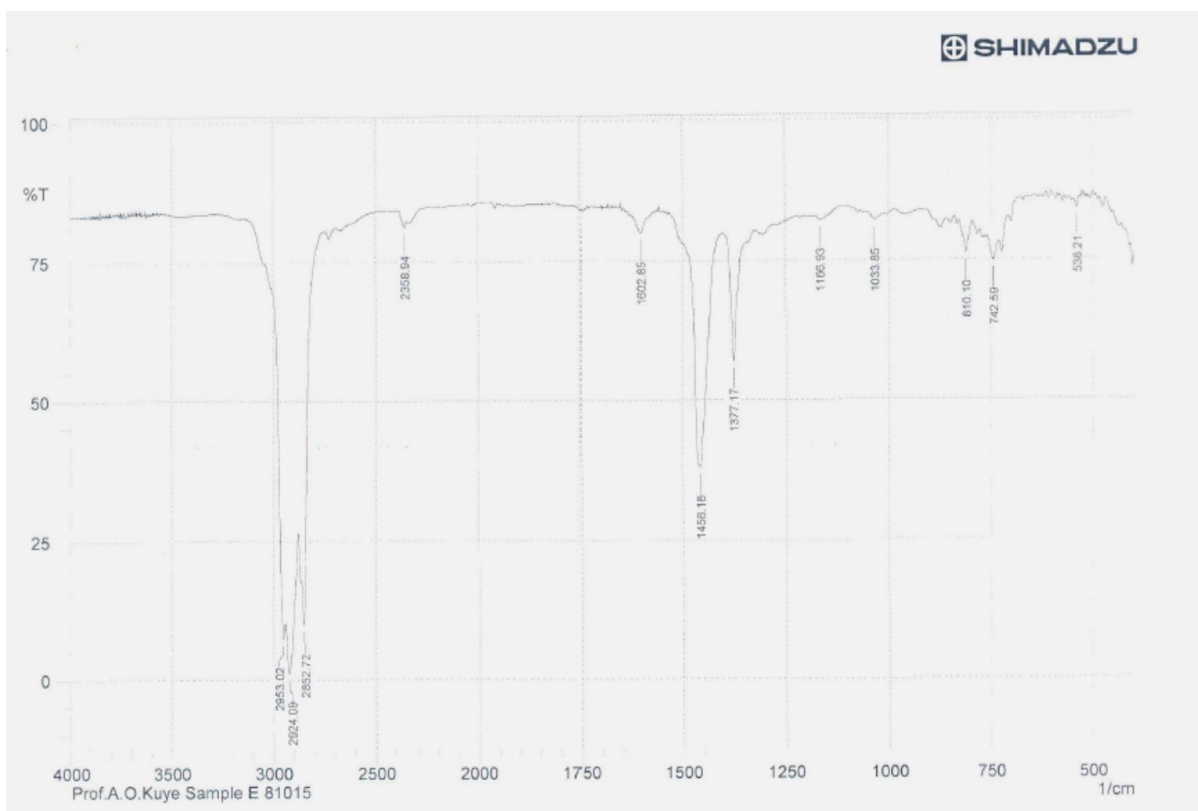


Figure 6: FTIR spectrum of fossil diesel

Fuel properties of bio-oil and diesel

The characterization was performed on a homogenous mixture of the bio-oil and the results of the test are shown in Table 2.

Table 2 Bio-oil properties

Property	Method	Hardwood Bio-oil	Softwood Bio-oil	Diesel
Viscosity, cSt @40 °C	ASTM D445	1.3	2	3.8 (2-0-4.5)
Viscosity, cSt@100 °C		0.6	0.7	1.5
Density, kg/m ³ @15.5 °C	ASTM D4052	1074	1082	895 (810-890)
pH	ASTM D6423	2.25	2.33	2.54
Flash point °C	ASTM D93	107	110	165
Pour point, °C	ASTM D97	-11.8	-12.3	(-40 to -30)

Values in brackets are standard values for No.2 diesel.

Viscosity, which is a measure of a fluid frictional property, is an important factor in considering the performance of a liquid fuel with respect to resistance to shear of flow in engines, must not be too high. The viscosity of the bio-oil produced was 1.3 cst and 2 cst for hardwood and softwood respectively. Both values are lower than that of diesel which has a viscosity of 3.8 cst at 40 °C. The recommended viscosity for commercial No.2 diesel is between 2 and 4.5 cst. Our bio-oil is at the lower limit of this range which makes it easier to pump and atomize. According to Lehto *et al.*²⁵ the viscosity of bio-oil could also be an indication of its water content. The lower viscosity of the bio-oil compared to fossil diesel could be as a result of the bio-oil containing more water than the diesel and hence could not necessary represent a better atomisation and ignition properties. Likewise, the bio-oil from the hardwood sawdust might contain more water than the softwood bio-oil on the basis of their viscosities.

The density of bio-oil determined at 15 °C is usually in the range of 1100 -1400 kg/m³²⁶ and depends on the type of feedstock and pyrolysis conditions. The density of bio-oil is also a measure of its water content, as lower bio-oil density is an indication of higher water content (Lehto *et al.*, 2013). Generally, the density of bio-oil is higher than that of fossil diesel because of higher water content in bio-oil and presence of macromolecules such as oligomeric phenolic compounds. Softwood bio-oil has a slightly higher density than hardwood bio-oil probably due to the former having more compounds than the later as indicated by the FT-IR spectroscopy.

²⁵ Lehto, J., Oasmaa, A., Solantausta, Y., Kyto, M., and Chiaramonti, D. (2013). Fuel oil quality and combustion of fast pyrolysis bio-oils. VTT Technology.

²⁶ Qi, Z., Jie, C., Tiejun, W., and Ying, X. (2007): Review of biomass pyrolysis oil properties and upgrading research. *Energy Conversion and Management* 48: 87–92

The bio-oil produced is very acid with pH of 2.25 and 2.33 for hard and softwood respectively. Hence, handling and storage of the bio-oil must be done with caution. The pH of the diesel sample is also acidic with a value of 2.54.

The pour point is the lowest temperature at which liquid fuel will no longer flow. The pour point for the bio-oil is -12.3 °C and -11.8 °C for softwood and hardwood respectively. Temperatures in sub-saharan Africa never get to these levels, hence this will not be a problem in these regions. However, the standard pour point for commercial diesel is between -40 °C and -30 °C.

Finally, an attempt was made to measure the flash point of bio-oil. The flash point is an indication of the maximum temperature at which it can be stored and handled without serious fire hazard. The flash point of bio-oil was determined according to ASTM D 93-10 using a Pensky-Martens closed-cup tester. During this measurement, the temperature remained at 100 °C for about 10 minutes while the bio-oil was boiling perhaps due to its water content. After appreciable amount of water was evaporated, the temperature started rising very fast and the flash point for soft and hardwood bio-oil was determined at 110 °C and 107 °C respectively.

Conclusions

A fixed bed fast pyrolysis unit was used to convert biomass to bio-oil. Initial test running of the reactor on hardwood and softwood indigenous wood species yielded 48.1 wt% and 45.8 wt% liquid products respectively at 500°C. The reactor could be used to perform further optimization and kinetic experiments of fast pyrolysis. Analysis of the liquid products using FTIR spectroscopy indicates the presence of nineteen function groups for both wood species. A total of 56 chemical species were identified in the softwood sawdust compared to the 52 compounds in the hardwood bio-oil. The physical properties for the bio-oil and chemical composition were similar to results of other authors. All twenty-eight chemical species detected in conventional diesel fuel were also detected in the bio-oil samples. This makes it possible to upgrade or refine the bio-oil to diesel or even consider blending the bio-oil with diesel with minor pre-treatment procedures.

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