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Product yield distribution and Essential Oil Composition of Eucalyptus Terminalis Sawdust Pyrolysis

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Abstract. In this study, pyrolysis of sawdust sample (Western blood-wood- Eucalyptus terminalis) was investigated. Experiments were performed at six temperature levels ranging from 300 °C to 800 °C under N_2 atmosphere. The weights of char, tar and gas yields produced in each experiment were measured and recorded in percentage of initial weight of the pyrolyzed sample. Results of the study showed that product yield of Eucalyptus terminalis char, tar and gas of 41.28% at 300 °C, 45.10% at 300 °C and 57.20% at 800 °C, respectively were produced. Proximate analysis shows that volatile matter, fixed carbon, ash content and moisture content of sawdust sample were 75.53%, 15.35%, 1.56% and 7.56%, respectively. Result of the elemental analysis shows that the carbon, hydrogen, nitrogen, oxygen and sulphur contents of the sawdust sample were 54.19%, 7.05%, 0.97%, 37.15%, and 0.64%, respectively. The higher heating value and pH of the sawdust sample are 23.40 kJ/g and 2.30% respectively. This indicate that char and tar yields decrease with increased pyrolysis temperature while gas yield increases as pyrolysis temperature increases for the sawdust sample. The value of the correlation coefficient obtained indicate a fairly high degree of accuracy of the regression models to predict experimental result when used within the temperature range considered in this study. Result of analytical Py-GC/MS shows that the proportion of phenolic compounds identified was more than 50% with *trans*-2-octadecadecen-1-ol, *cis*-10-pentadecen-1-ol, 9-octadecenal and methyl-1-cyclohexenyl ketone dominating. This study establishes the fact that pyro-oil can not only be used as a fuel but can also be purified and serves as raw materials for chemical and processing industries.

Key Words: Sawdust sample, pyrolysis, pyro-oil, proximate analysis, GC-MS analysis

1. Introduction

Research into renewable energy sources are being pursued vigorously at both national and international levels. There are many factors leading to this turn of events. One compelling factor is the depleting tendency of fossil fuels, coal and natural. As a non-renewable and finite resource, fossil fuels as sources of energy are limited in supply because they are time-bound [1]. There are indications that fossil fuel will begin to dwindle out in the 21st century. Since they take millions of years to be produced, replacement of fossil fuels is a

gradual process that cannot be relied on to continue serving future energy needs. There is concern over the security of fossil fuel supplies and their rising cost [2].

Another important issue driving the use of renewable energy is the growing concern about the environment specifically in the area of climate change. This seems to be one of the most important factors [3]. Burning of fossil fuels to produce energy leads to the release of gases, including carbon dioxide, carbon monoxide, sulphur dioxide, nitrogen oxides, methane, and other gases termed as greenhouse gases [1]. Their release into the current atmosphere causes an imbalance in the composition of these gases especially carbon dioxide and carbon monoxide leading to trapping of heat from the earth surface and a consequent increase in the atmospheric temperature of the earth termed as global warming. Renewable energy seems to be the answer to future energy needs. All sources of energy that when properly managed can be an unlimited source in terms of time are referred to as renewable energy [4]. So far, solar energy, wave energy, tidal energy, geothermal energy, hydropower and biomass energy are some of the renewable energy sources currently in use.

Thermochemical conversion of biomass is a promising route for energy and fuel production (Huber, el at, 2006), which is also considered as the easiest process to adapt to current energy infrastructure [5]. More attentions have been focused on fast pyrolysis for bio-oil production as the substituent for transported fuels [6]. The feedstock ranges from barkwood, agricultural wastes/residues, nuts, seeds, algae,grasses, and forestry residues to energy crops such as miscanthus and sorghum. Wood materials are widely used as they can give high liquid yields, up to 80% (by mass) on dry feed basis at 500-520 °C with residence time not more than 1 s.

The problem of solid waste disposal has become an alarming environmental problem facing many cities in Nigeria with lack of efficient waste management systems. However, sustainable energy can be generated from these wastes thereby putting an end to environmental pollution generated from them. In this study, the potential of bio-oil production from wood residues using pyrolysis had been examined. Pyrolysis had been considered because of its superiority to other systems of waste-to-energy conversion as it operates at atmospheric pressure and modest temperatures with yields of bio-oil exceeding 70 wt % [7].

According to [8], the price of this potential bio-oil at ₦50/litre in Nigeria is quite lower than the current price of diesel (₦180/litre) in which both are being used in many static applications such as boilers, furnaces, engines and turbines for electricity generation. Hence, adequate consideration should be given to this alternate means of energy generation thereby, reducing over-dependence on fossil fuels which are very expensive for industrial purposes. Also, Nigerian energy policy should be reviewed so as to encourage both local and foreign investors in bio oil production.

Comparatively, biomass in Africa has not received significant research attention and thus remains largely unexplored [6]. There is, however, a 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 [9] about 13 million tonnes of agro-forestry waste is generated annually in Nigeria.

However, the utilization of these natural resources is limited. Furthermore, with regard to fast growing population of the country and substantial waste production, waste management policy in different sectors especially biomass wastes demand novel solutions. One of the best options to reduce waste and produce green energy is energy recovery from bio-based wastes.

Presently, in Nigeria Eucalyptus terminalis is commonly used for furniture making and as building materials, it forms large percentage of wastes and constituting nuisance to the environment. Researchers in Africa are

making efforts to study the pyrolysis process for bio-oil production from different feedstock. [10] have converted corn cob, wood residue and palm fruit bunches to bio-oil, respectively.

Better management of the wastes from wood industries utilizing Eucalyptus terminalis could be achieved by producing clean energy from the materials. The clean energy is derived from pyrolysis liquid serving as source of chemical energy (fuel) and useful industrial chemicals. This study was focused on characterizing chemical composition of bio-oil yields using analytical Py-GC/MS and investigate the effects of pyrolysis temperature on product yield distribution from pyrolysis of wood residue within the temperature range of 400 ºC and 800 ºC in a fixed bed reactor. Regression equations were also developed from product yield curves of wood residue for the purpose of predicting pyrolytic yields.

2.   Materials and Methods

2.1 Feed Materials

The wood specimen used in this study were obtained in July 2016 from Ota, South-Western Nigeria, (6º 38´ 0´´ N, 3º 6´ 0´´ E). It was air dried and ground to particle size of 500 µm using Philip milling machine.

2.1.1 Experimental Set-up

The pyrolysis unit comprised a fixed-bed reactor, retort, pipes, condenser, and a carrier gas cylinder. Fixed-bed reactor heats up the pre-loaded retort by a 4-kW furnace with automatic temperature control, hence the giving off of the volatile stream. The product pipes channel the volatile stream into the condenser which are immersed in an ice-bag (tar trapper). Staged tar trapping was employed so as to collect tarry components which escaped the first tar trap in order to ensure efficient trapping of the tar. Figure 1 shows the assembly view of the pyrolysis unit for this study.
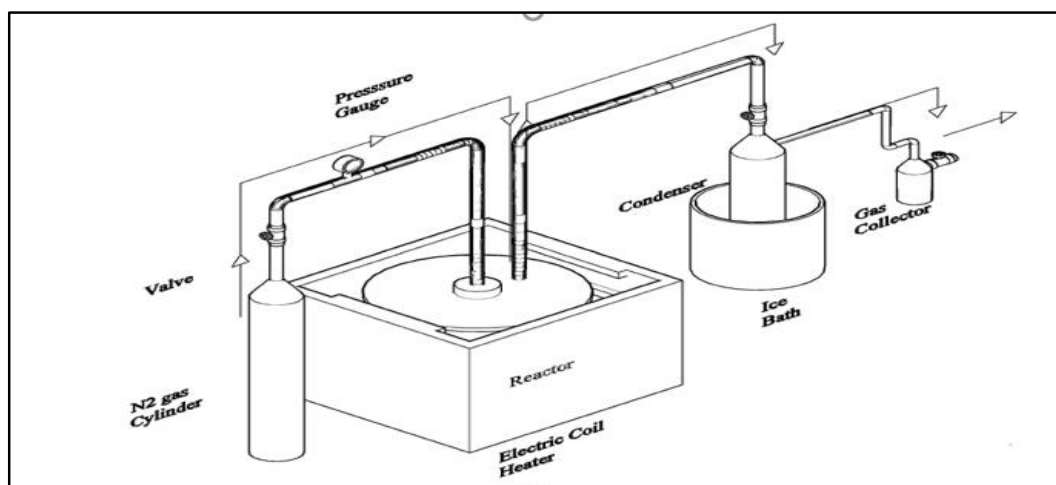

Figure1. Experimental set-up of the pyrolysis unit.

2.1.2 Experimental procedure
For the experimental investigation, six (6) temperature levels were considered i.e. 300ºC to 800ºC at interval of 100ºC were considered in this study. Nitrogen was introduced into the reactor at pressure lower than 10 psi at a fixed holding time of ten (10) minutes and vacuum pressure. The reactor was raised to the desired pyrolysis temperature and the retort, already loaded with the sample of approximately 100 g of wood sawdust sample, was then put in the reactor with its lid firmly secured in place by using the hold down bolts with the gasket in position. The product collected were weighed to ascertain their initial weights and afterwards immersed in ice-bags. The stopwatch was set to a thirty minutes countdown. At the lapse of the thirty minutes residence time, the retort was removed from within the furnace chamber. The collected tar was measured on the weighing balance while the retort was allowed to cool. The bolts holding the retort lid in position were then loosened and a tong was used to collect the char from the retort. The char was then weighed thereafter and its value recorded. From the measured weight of tar and char, the weight of gas let off was obtained as well as the percentage weight of all products. The furnace temperature was raised again to the desired temperature and the entire process was repeated for other runs and temperature levels.

2.2 Product Analysis

 The pyrolysis unit was built in such a way to assist separating the tar and gas in the volatile stream. The char remained in the retort while the fluids were transferred to condenser and gas moved to gas collector based on the simple principle of condensation. The parameters for comparison include weight of char, tar and gas produced in each experiment. A digital weighing scale of accuracy ±0.1 g was employed in measuring the weight of the samples and the products. Product yields were expressed in percentage of the initial weight of the pyrolyzed wood samples.

2.3 Compositional Analysis
Compositional analysis was conducted using both observation and instrumental analytical methods to obtain the extractive and lignin contents according to ASTM D1108-96 and ASTM D1106-96, respectively.

2.4 Heating values
The Higher Heating Value (HHV) of biomass product was calculated from a correlation developed by [11] as shown by the following equation:

 HHV_{dry} (MJ/kg) = -1.3675 + 0.3137C + 0.7009H + 0.0318O*   (1)
Where C, H are percentages on dry basis of carbon, hydrogen, respectively
The lower heating value (LHV) was calculated from HHV and the hydrogen content by the following equation (ECN-Phyllis, 2012):
LHV_{dry} (MJ/kg) = HHV_{dry} – [2.442 x 8.936(H/100)]   (2)

3.   **Results and Discussion**
3.1. Physical characterization

 The results were discussed in terms of the physical and chemical properties of the solid raw sample. The main characteristics of the feed material are listed in Table 1.

Table 1. Main characteristics of the raw wood sawdust sample (%)

Proximate analysis[a] (wt. %)		Ultimate analysis[b] (wt. %)	
Moisture content	7.56	Carbon	54.19
Volatile matter	75.53	Hydrogen	7.05
Fixed carbon	15.35	Nitrogen	0.97
Ash	1.56	Oxygen[c]	37.15
pH	2.30	Sulphur	0.64
HHV(MJ kg^{-1})	23.40		
LHV(MJ kg^{-1})	17.35		

3.2 Product yields

The product yield distribution from the pyrolysis of Western blood-wood (Eucalyptus terminalis) sample at different temperature levels are presented in Table 2, respectively. As shown in the Table, char and tar yields from the wood sawdust pyrolysis decreased from 41.28% and 45.10% at 300 ^{0}C to 24.15% and 18.65% at 800 ^{0}C, respectively. However, gas yield increased from 13.62% at 300 ^{0}C to 57.20%.

Table 2: Product yield distribution from Western blood-wood (Eucalyptus terminalis)

Temperature (^{o}C)	Char yield (wt %)	Tar yield (wt %)	Gas yield (wt %)
300	41.28	45.10	13.62
400	32.52	37.05	30.43
500	28.40	34.25	37.35
600	25.80	30.45	43.75
700	25.45	25.30	49.25
800	24.15	18.65	57.20

3.3 Effect of Temperature on the Product Yields

Figure 2 shows product (tar, pyro-gas and char) yield at different pyrolysis temperature. From Figure 2, it can be seen that tar and char yield decreases with increase in temperature. This is because bio-oil secondary reactions yields more gas and char at temperatures above 500 ^{0}C. This is similar to results of Fagbemi et al. (2001).Char yield decreases from 41.28 wt% to 24.15 wt% with increased pyrolysis temperature. This may be due to increase rate of primary decomposition at high temperature or through secondary decomposition of the solid residue. This result is consistent with that of [12]. and Gheorghe [13]. It is observed that as temperature increases from 300^{0}C to 800^{0}C the bio-gas yield increases from 13.62 wt% to 57.20 wt%.
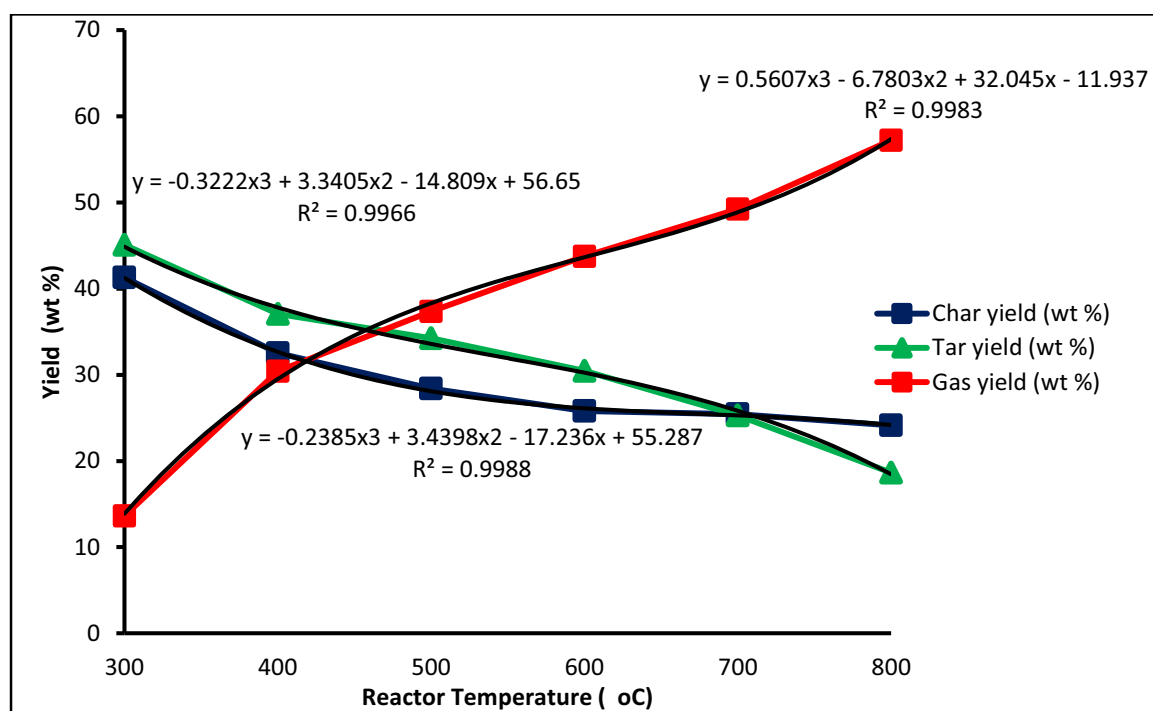
Figure 2. Product yield at different reactor

3.4 Regression Models between Reactor Temperature and Product Yields

The regression models between the reactor temperatures and product yields, and the respective value of the coefficient of correlation (R^2) for Western blood-wood (Eucalyptus terminalis) were obtained and are given as

Char: $Y_c = -0.2385T^3 + 3.4398T^2 - 17.236T + 55.287$ $R^2 = 0.9988$ (3)

Tar: $Y_t = -0.3222T^3 + 3.3405T^2 - 14.809T + 56.65$ $R^2 = 0.9966$ (4)

Gas: $Y_g = 0.5607T^3 - 6.7803T^2 + 32.045T - 11.937$ $R^2 = 0.9983$ (5)

Where Y_c is the char yield, Y_t is the tar yield, Y_g is the gas yield and T is the reactor temperature. The models (equations (3) to (5)) are instrumental for predicting the response of wood feedstock pyrolyzed in a fixed-bed reactor between 300˚C-800˚C. The values of the correlation coefficients obtained indicate a fairly high degree of accuracy of the regression models to predict experimental results when used within the temperature range considered.

3.5 Composition of the Volatile oil of Western Blood-wood (Eucalyptus terminalis).

The bio-oil yields obtained from the pyrolysis of the wood sample were subjected to Gas Chromatography (GC) and Gas Chromatography-Mass Spectrometry (GC-MS) analyses. This   was done for detailed identification of various compositions in the complex mixture. These compositions are presented in Table 5. The retention indices of each identified component were also calculated based on their retention time in order to confirm the identification.

The GC-MS analysis of the bio-oil yield revealed the presence of of 21 compounds (99.4% of the volatile extract). The main components are palmitic acid (13.0%), oleic acid (16.3%), cis-1, 9-hexadecadiene (12.5%), *cis*-10-pentadecen-1-ol (12.4%), 9-octadecenal (10.9%), *trans*-2-octadecadecen-1-ol (10.0%), myristic acid (5.1%), stearic acid (5.0%) and other compounds (14.8%).

Table 3: Chemical composition

No.	Compounds	Retention Index	Percentage Composition	Group
1	Luprosil	676	4.0	$C_3H_6O_2$
2	2,5-dimethylfuran	732	2.3	C_6H_8O
3	1,4-dimethyl-1H-pyrazole	804	0.7	$C_5H_8N_2$
4	2-methylbutyric acid	811	1.2	$C_5H_{10}O_2$
5	*trans*-3-Octene	824	0.3	C_8H_{16}
6	*cis*-3-octene	824	0.3	C_8H_{16}
7	5-methyl-3-methylene-5-hexen-2-one	887	0.6	$C_8H_{12}O$
8	4,5-dimethyl-1H-imidazol	927	0.6	$C_5H_8N_2$
9	Cyclooctane	959	0.3	C_8H_{16}
10	Corylone	972	0.5	$C_6H_8O_2$
11	3-methylcyclopentane-1,2-dione	1003	0.5	$C_6H_8O_2$
12	methyl-1-cyclohexenyl ketone	1027	1.2	$C_8H_{12}O$
13	*o*-guaiacol	1090	0.3	$C_7H_8O_2$
14	2-nitroethylpropionate	1067	0.8	$C_5H_9NO_4$
15	*cis*-1,9-hexadecadiene	1610	12.5	$C_{16}H_{30}$
16	*cis*-10-pentadecen-1-ol	1763	12.4	$C_{15}H_{30}O$
17	myristic acid	1769	5.1	$C_{14}H_{28}O_2$
18	palmitic acid	1968	13.0	$C_{16}H_{32}O_2$
19	9-octadecenal	2007	10.9	$C_{18}H_{34}O$
20	*trans*-2-octadecadecen-1-ol	2061	10.0	$C_{18}H_{36}O$
21	stearic acid	2167	5.0	$C_{18}H_{36}O_2$
22	oleic acid	2175	16.9	$C_{18}H_{36}O_2$
	Percentage Total		**99.4**	

4. Conclusion

In this study, the potentials of waste-to-energy system had been assessed by considering the production of bio-oils from wood residue collected from south-western Nigeria using pyrolysis conversion. The chemical compositions of fast pyrolysis bio-oils from wood have been studied by GC-MS analysis and a fairly high

degree of accuracy of the regression models to predict experimental results was obtained. Results of this show that the bio-oil produced met the qualities of other liquid products from other energy classified woody biomass already screened. The difference in level of phenolic compounds, oleic acid, aromatic hydrocarbons and nitrogen-contained compounds suggest that it could be a good source of natural antioxidants to be used in medicinal and food products to promote human health and prevent diseases,

This study establishes the fact that understanding the compositions of bio-oils from energy crop will add to the use in thermochemical conversion platforms, as this information will be extremely important in evaluating the bio-oils' stabilities, properties, and toxicities. It will also be useful in identifying and solving challenges associated with further refining of bio-oils into liquid fuels and that selected sawdust sample have the potential of being used as alternative source of energy and serve as good source of extraction of chemical compounds.

Acknowledgements

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