Exploring the Valorization Potential of Pine Residues for Energy Applications through Pyrolysis

Gratitude Charis, Gwiranai Danha, Edison Muzenda, and Bilal Patel

Abstract—**Pyrolysis is explored as a potential cleaner valorization alternative for waste pine-dust and shavings from sawmilling activities in Manicaland, Zimbabwe. The investigation covers the physical and thermochemical characterization of the raw material, pyrolysis using a fixed bed reactor at varying temperatures and subsequent characterization of the products. The ultimate analysis reveals that Pine has a CHNO composition of 45.76%, 5.54%, 0.039% and 48.66% respectively. Thermogravimetry results showed that the residues' ash, fixed carbon and volatiles matter composition was 0.83%, 20% and 79.16%. The high heating value was found to be 17.57 MJ/kg. Pyrolysis runs were carried out for temperatures of 450, 500, 550 and 600ºC. Results indicate a maximum yield of bio-oil of 45.7% at a temperature of 500 ºC, which agrees with literature. Generally, the gas yield increased while the char yield decreased with increase in temperature.**

Index Terms—**Bio-oil, energy, pyrolysis, valorization.**

I. Introduction

In recent years, considerable attention has been turned towards the valorization of biomass, especially its residues and waste into bioenergy and other products [1]-[3]. This comes at the backdrop of climate change issues raised by the continued use of fossil fuels, hence the call for greener approaches like the use of renewable biomass wastes/residues [4]. Biomass is a cheaper, abundantly available, carbon dioxide neutral feedstock with low sulphur and nitrogen compositions, which can be used for heat, power and fuel production [5]. The sawmill industry a central part of timber processing, is one such source of biomass residues in the form of bark, shavings, offcuts, chips and sawdust. Global improvements in timber processing efficiency have enabled the recovery of at least 52% of the logs and downstream valorization of such waste fractions by various industries, leaving approximately 1% of waste [6]. However, in developing nations like Zimbabwe, the case is different as most do not have adequate downstream industries like engineered wood products, pulp, paper and energy to utilize the waste. In these developing nations, Waste-to-energy (WtE) applications are usually limited to steam generation for kiln driers in the larger sawmills and domestic uses, which only take up less than 50% of selected fractions of the waste. Domestic and agricultural uptake of this waste, has not been able to significantly deplete the resource [7]-[9]. From a survey made during a field visit it was established that the most unutilized fractions are sawdust and shavings. The bulk of the waste is improperly disposed of, accumulating at a rate of at least 70,000 tonnes per annum (tpa) marring the aesthetic appeal of timber processing areas and posing various ecological threats like fire and water pollution.

Amongst the valorization options for biomass residues, thermochemical methods like combustion pyrolysis and gasification have been gaining a lot of attention due to their ability to utilize a large range of feedstock and whole parts of lignocellulosic residues. Combustion is the simplest and widely practiced, with many commercialized applications, however it is characterized by low efficiencies and requires extra investments to curb its emissions, which developing regions often skimp. Gasification is efficient but the downside is high investment costs and high technical expertise requirements. Pyrolysis is relatively simpler to operate, with lower investment costs, therefore it is an attractive opportunity for developing nations depending on the value returned from products [10]. The bio oil obtained can be used for heat, power and fuel for stationary engines, or after upgrading, for transportation. The char, which typically contains 25% of the energy from the feed, can provide the energy required for the pyrolysis (typically 15%); making the process self-sufficient [11]. Any extra energy from the process can be exported. A number of studies on pine residues pyrolysis have been done before [12]-[15]. However the variability of climatic conditions for the pine and storage conditions for the residues could potentially result in varying product yields and characteristics compared to those undertaken by other geographical locations, hence, the motivation for this study.

Background, Scope and Methodology

Zimbabwe is a Southern African developing nation, landlocked between four countries. It is therefore typically

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vulnerable to both fuel insecurity and the volatility of oil prices. Moreover, the nation has an energy deficit of about 40%, which it imports from the neighbouring countries [16]. Considering use of bio-oil from pyrolysis for power applications (stationary engines and boilers) and for future transportation fuel applications could be a worthwhile investment in the long term in view of global trends in biomass pyrolysis research. This investigation is one such attempt in this direction, to establish the thermal and chemical characteristics of the feedstock and its potential yields of oil from test runs conducted on a fixed bed pyrolysis reactor.

II. Characterization

Characterization of feedstock is important to be asses the yield potential of any feedstock before conversion. It also informs on the potential environmental impact, especially if there are significant amounts of sulphur or nitrogen output [17]. Prior to the characterization of the samples, the pine residues were ground using a JF 2-D hammer mill and chopper with a sieve size of 0.8mm. Sieving was further done using a 250 µm sieve to eliminate any oversize particles. No prior drying was done since the sawdust had already been dried for an extensive period during dumping.

A. Ultimate Analysis for Elemental Composition

Ultimate analysis was carried out using the Flash 2000 CHNS-O elemental analyzer (Thermo-Fisher Scientific, USA). The biomass samples were weighed, then combusted in an oxygen rich environment. The off gases were carried by helium gas past a copper packed layer, through a GC column where they were separated and detected according to thermal conductivity [18].

B. Thermogravimetric Analysis (TGA)

The moisture content (MC), Fixed Carbon (FC) and Volatile Matter (VM) of the pine samples were determined using LECO TGA 701 Thermogravimetric analyzer (TGA). The analyzer was set to comply with the ASTM E871 for moisture, D1102 & E830 for Ash, E872 and E897 for volatile matter [19].

Moisture content **-** The TGA was set at 107°C and ramped from ambient temperature at 6°C/min according to ASTM E871, to remove all moisture. The drying process was carried out in an inert environment of nitrogen gas until a near constant ‘moisture mass’ was achieved.

*Volatiles content***-** The TGA was set at 550°C for volatization and ramped at 37 °C/min from the 107°C. Volatization occurred in an inert environment of nitrogen gas until a near constant mass was achieved.

*Ashing***-** After burning off the volatiles, the lids on the samples were removed, then the biomass samples were reheated to 550°C at a rate of 3°C/min, this time in an oxygen rich environment. The mass lost during *ashing* is the fixed carbon, which reacts with oxygen.

C. Calorimetry

The High Heating Value (HHV) was determined using a bomb calorimeter, Bomb CAL2K-2, using DIN 51900 T3 standards. The calorimeter was calibrated using benzoic acid.

III. Pyrolysis

For all pyrolysis runs, the residues were ground using a sieve size of 5mm on the mill, then a size range between 1.70 and 5.00mm was separated using appropriate sieves.

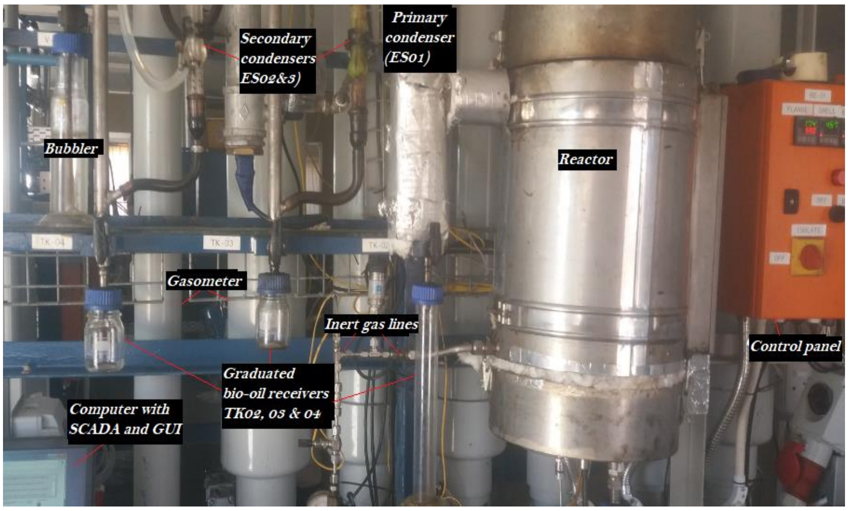

Fig. 1. Pilot plant used for pyrolysis.

A. Pyrolysis Using the Fixed Bed Pilot Plant

The fixed bed pilot plant used for the pyrolysis runs is shown in Fig. 1. A mass of about 200g of pine residues of the selected size range was placed inside the metal holder inside the reactor. The primary condenser was set at 125°C while the other 2 secondary condensers were both set at 25°C. The system was then purged for at least 1 minute using Nitrogen gas which was vented out. The outlet gas vent valve was then immediately closed while simultaneously opening the valve leading to the storage compartment for the gas. The heater was then switched on, at a ramp rate of 66°C/min until it reached 450°C. It was then maintained at that temperature for the rest of the experiment. The experiments was then run until there were no more bubbles to establish the full bio-oil yield. The experiment was then repeated at 500 °C, 550 °C and 600 °C.

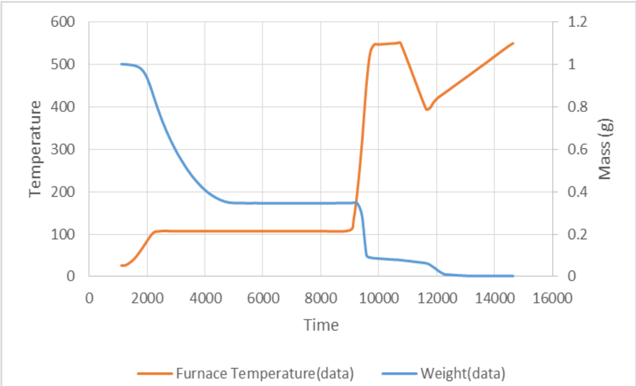

Fig. 2. TGA for one of the pine dust samples, for proximate compositions.

IV. Characterization, Experimental Results and Analysis

A. TGA, Proximate and Calorimetry

Fig. 2 shows the TGA results for the pine samples. The proximate properties are determined from the stagnant regions and shown in Table I.

The C content of 45.8% recorded for the Zimbabwean pine residues is lower compared to results for Canadian (49.0%) and Spanish (48.3-55.4%) pines. However, the H value of 5.54% is comparable with 6.4% and 5.2-7.7% for the Canadian and Spanish pines respectively. The Zimbabwean pine has the lowest nitrogen and sulphur contents compared to N(0.14%) and S(0.01%) for the Canadian and N(0.16-1.6%) and S(0.14-0.45%) for the Spanish pines [13], [20]; implying its ash emissions would has a lower environmental impact. The differences might also be due to the fact that the pine species studied in these regions are different and could also stem from the differences in soils and climatic conditions. The high VM means that pine can have good yields of oil from the condensed vapours.

B. Pilot Pant Pyrolysis

The results of the pyrolysis runs at 450°C, 500°C, 550°C and 600°C are shown in Fig. 3. The standard deviation was 0.443 and standard error 0.22, established by conducting 4 runs at 450°C.

From Fig. 3, the largest yield of bio-oil (45.7%) was obtained at 500°C. This is the same temperature where the maximum yield was obtained from the pyrolysis of Indian pine and Canadian mixed sawdust in a fixed bed reactor. These maximum yields were 39.37% and 45% respectively [14], [21].

TABLE I: Results of Ultimate and Proximate Analyses (Dry Basis) for Pine Residues. FC- Fixed Carbon; VM-Volatile Matter; MC-Moisture Content

	Ultimate analysis- average of 2					Proximate (Dry basis)- averages				**HHV** (MJ/kg)
%	C	H	N	S	O[a]	Ash	FC	VM	MC	
PINEDUST	45.76	5.54	0.039	ND	48.66	0.83	20.00	79.16	6.50	17.568

[a] *Calculated by difference* *ND- Not detected*

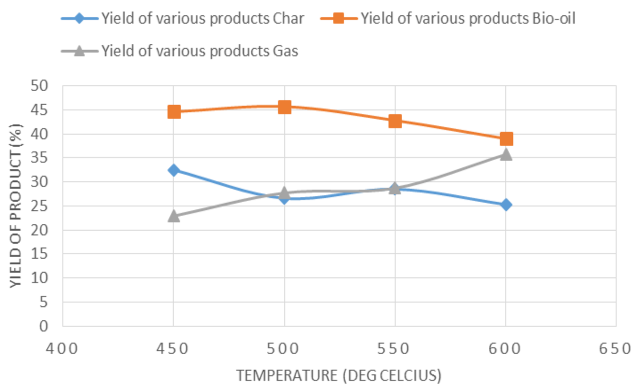

Fig. 3. Yields of char, bio-oil and gas with temperature.

From the graph, the solid yield generally decreases with increase in temperature while the gas yield increases with the increase in temperature. The increase in gas yield can be attributed to secondary reactions of the tar and volatiles, such as thermal cracking and it has to be compensated by a reduction in the char and bio-oil yields. This is consistent with observations by other authors [11], [13], [20]. During the experiments, the increase in gas yield was also observed through the increasing vigour of bubble generation in the bubbler (TK05) for an extensive period at higher temperatures.

V. Discussion and Conclusion

The characterization experiments showed that pine has a good composition of VM, and low Ash which favor a good yield of bio-oil. The decomposition characteristics shown by the TGA results show that the feedstocks can be successfully processed using a thermochemical conversion method like pyrolysis. The characterization results are confirmed by the relatively high yield of bio-oil compared to other material pyrolyzed with a low VM [11]. The optimum temperature for the highest bio-oil was found at 500°C which agrees with two authors who used the same reactor type, though the actual yields were slightly different. The characterization of the oil obtained was still ongoing by the time the paper was due for submission, therefore the authors could not include them and will be reported in the next communication. These results would help to give a fuller picture on any variations of the product with temperature and how its properties compare with bio-oils obtained by other researchers. Overall, the experiments were successful with an acceptable margin of error.

Conflict of Interest

The authors declare no conflict of interest.

AUTHOR CONTRIBUTIONS

Gratitude Charis carried out the research and literature review, while Gwiranai Danha and Edison Muzenda helped with reviewing, proofreading and suggesting things to be added to the paper.

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