

Characterisation of KwaZulu Natal Pine and Eucalyptus Biomass Waste to Evaluate the Potential of Using Their Mixtures as Feedstock for Wood Vinegar Production.

Thembelihle Portia Lubisi^{1,3}, Phuti Cedric Tsipa^{1,2}, Jonas Johakimu³, Ntandoyenkosi Malusi Mkhize¹

Abstract—Refinery of biomass via pyrolysis is critical in producing bio fuels, chemicals, and char. Using biomass feedstock mixtures increases the feedstock available for processing and may eliminate sorting costs. The present study evaluates the potential of using biomass mixtures in place of single biomass waste as feedstock for the pyrolysis process in bio-oil production. The South African samples characterised were pine sawdust (PSD), eucalyptus sawdust (ESD), sawdust mixtures containing pine and eucalyptus (EPSD), pine bark (PB), eucalyptus bark (EB), and a mixture containing both sawdusts and barks (EPSDB). Characterisation included proximate, elemental, structural, HHV, and thermogravimetric analysis.

The results showed that PSD contains the highest volatiles (79.7 to 80.6 wt%), which means its likelihood to yield higher bio-oil at investigated heating rates of 5, 10, 20, and 40 °C/min. The volatile content of EPSD was similar to that of PSD. Including 5% bark in the mixture reduced the volatile content (78 to 78.9 wt%). The ash content of bark samples was high, while the ash content in PSD, ESD, EPSD, and EPSDB was less than 1 wt%, though including bark in the mixture slightly elevated the ash content. The TGA/DTG curves showed the temperature where significant thermal degradation occurs, and this temperature increased with increasing heating rates for all samples. The Py-GCMS results showed ESD contains highest ketones and phenols, with <1 % acids, which means better quality of wood vinegar will be produced. Though PSD contains highest volatiles, the biomass mixtures EPSD and EPSDB proves to be better feedstock for wood vinegar production than PSD due to their higher ketones and phenol content. The bark samples were found to be poor quality feedstock for woodvinegar production. It concluded that biomass mixtures are suitable for pyrolysis feedstock in wood vinegar.

Keywords—Bio-mass, Blends, Eucalyptus, Pine, Pyrolysis.

Thembelihle Portia Lubisi^{1,3} is with the University of KwaZulu Natal and Council for Science and Industrial Research, Mazisi Kunene Rd, Glenwood, Durban South Africa. (corresponding author's e-mail: theportia@yahoo.com).

Phuti Cedric Tsipa^{1,2} is with the University of KwaZulu Natal, Mazisi Kunene Rd, Glenwood, Durban South Africa and Nelson Mandela University, Centre for Rubber Science & Technology; Department of Chemistry, P O Box 77000, Port Elizabeth, 6301.

Jonas Johakimu³ is with the Council for Science and Industrial Research, Mazisi Kunene Rd, Glenwood, Durban South Africa. (corresponding author's e-mail: Jjohakimu@csir.co.za)

Ntandoyenkosi Malusi Mkhize², is with the University of KwaZulu Natal, Mazisi Kunene Rd, Glenwood, Durban South Africa. (corresponding author's e-mail: MkhizeN7@ukzn.ac.za).

I. INTRODUCTION

Lignocellulosic biomass waste simultaneously presents a disposal challenge and economic opportunity as a cost-effective feedstock for value addition [1], [2]. KwaZulu-Natal (KZN) is a South African forestry region. Consequently lignocellulosic biomass waste is abundant in KwaZulu-Natal (KZN). The primary products of KZN forestry are pine and eucalyptus, which constitute approximately 90% of the trees in KZN forestry plantations. For utilisation of lignocellulosic biomass waste, value addition would make economic sense to utilise pine and eucalyptus biomass waste as this guarantees reliable supply chains. An extensively utilised biomass waste value addition technique is pyrolysis which is a thermochemical technique [3], [4]. Pine and eucalyptus biomass waste can be utilised individually as pyrolysis feedstock or blended in co-pyrolysis. Within the South African context, bio-oil production as a value-added product from co-pyrolysis pine and eucalyptus is of interest from an economic and environmental perspective.

The present study characterises lignocellulosic biomass waste of pine and eucalyptus biomass bark, trunk sawdust and blends as a preparatory investigation for the co-pyrolysis of pine and eucalyptus biomass for wood vinegar production. Wood vinegar is the aqueous fraction of the pyrolysis oil (bio-oil) constituting of a complex combination consisting of water (22.5±2.5%) and miscible polar organic molecules (77.5±2.5% of polysaccharides, hydroxyaldehydes, phenolic derivatives, hydroxyketones, acetic and formic acid levels) [5], [6]. Application of bio-oil range from insecticidal properties [7], biofertiliser fermentation catalyst [8], herbicide [9] and seed germination enhances [10].

Characterisation of pyrolytic feedstock is critical as it informs feedstock preparation, pyrolysis parameters and product treatment techniques to ensure quality products and enhance process economics [11]. The study utilises proximate and ultimate analysis, Fourier Transform Infrared Spectroscopy (FTIR), Thermogravimetric Analysis (TGA) and Pyrolysis gas chromatography mass spectrometry (Py-GCMS) characterisation techniques.

While there has been significant research in pyrolysis and co-pyrolysis, biomass co-pyrolysis is limited as literature has primarily focused on employing biomass as blends such as sludge, coal, tyre or plastic polymers [11], [12]. Consequently, there is comparatively limited co-pyrolysis characterisation literature [13], [14]. Additionally, there are conflicting data on the impact of biomass co-pyrolysis, and processing biomass blends presents a substantial difficulty because of the wide variability in the physicochemical characteristics of the separate biomass [15]. It has been shown that although the individual biomass undergoes physical, chemical, or biological changes throughout the process, there may be several interactions between them during co-pyrolysis [16], [17]. Determining these positive or negative synergistic impacts is also essential for the appropriate design and process optimisation of biomass blend-based operations. Our analysis has brought important insights into the pre and post-pyrolytic upgrade operations to enhance bio-oil production.

II. METHODS

A. Collection and Processing of Biomass

Biomass of eucalyptus (*Eucalyptus Grandis* (EG)) and pine (*Pine Patula* (PP)) in the form of barks and sawdusts were collected from Evergreen Saw Mill in KZN, SA. All the biomass was thoroughly washed with distilled water to eliminate all contaminants. Biomass was dried at 60 ± 2 °C for 12 hours. Drying at 60 °C facilitates gradual evaporation, preventing rapid moisture loss that could warp or damage the wood. The dry biomass was crushed and sieved through a 2 mm woven sieve on a vibratory shaker (conforming to ISO3310-1). The 2 mm sieve underflow biomass was packed in airtight polyethylene bags and stored in dry conditions at standard room temperature and pressure prior to experiments.

B. Preparation of Biomass Blends

Blends were prepared on a weight basis (weight percentage (wt%)) utilising an analytical precision balance (Mettler-Toledo, Model ME802E, least count: 0.1 mg). The weighed samples were mechanically mixed for uniformity. Six samples were prepared: bark, trunk sawdust (sawdust), and blends of varying compositions. The proportions of blends considered the anatomy of the tree and also the availability of tree type. Table I lists the samples and details the sample description, the blend ratios and the sample identity utilised in the paper.

TABLE I
SAMPLE NAMING

Sample number	Sample description	Sample identity
1	100% PP bark	PCB
2	100% EG bark	EB
3	100% PP sawdust	PSD
4	100% EG sawdust	ESD
5	50/50 PSD and ESD	EPSD
6	47.5% PSD, 47.5% ESD, 2.5% EB and 2.5% PB	EPSDB

C. Characterisation of Blended Feedstocks

ASTM standards protocols were utilised for proximate analysis (moisture content: ASTM E871–82, ash content: Tappi T 211 om-85, volatile matter content: ASTM E872–82). Fixed carbon content was calculated based on mass difference. C, H, N, S, and O % content was determined by an elemental analyser (Perkin Elmer, Model 2400, Series II CHNS analyser). HHV can be measured in a bomb calorimeter. HHV was determined using an oxygen bomb calorimeter (PARR, Model 1341 EB) utilising an ASTM standard D-2015 (withdrawn by ASTM 2000 and not replaced). Thermal degradation of the blends was studied using a thermal gravimetric analyser (TGA) (Perkins Elmer Simultaneous Thermal Analyzer 6000). The functional group identification was accomplished through Fourier transform infrared spectroscopy (FTIR) analysis (Shimadzu, Model: IRAffinity–1). Py-GC/MS was used to identify pyrolysis products by comparing their mass spectra with the mass spectra in a library database. A multi-shot pyrolyzer, EGA/PY-3030 D, (Frontier Lab, Japan) attached to an ultra-alloy capillary column (30 m x 0.25 mm, 0.25 μ m) was used with 1.2 mL/min Hydrogen column flow rate. 0.2mg of the biomass samples were used in Py-GCMS analysis.

III. RESULTS AND DISCUSSION

The samples under investigation were analysed as per methods given in Section II, and the characterisation results are tabulated in Table II.

TABLE II
CHARACTERISATION RESULTS

	PB	EB	PSD	ESD	EPSD	EPSDB
Proximate analysis						
Moisture content, (wt%)	9.72 \pm 0.05	9.77 \pm 0.07	8.98 \pm 0.04	9.75 \pm 0.06	9.34 \pm 0.05	9.63 \pm 0.02
Ash content, wt %	3.23 \pm 0.11	3.18 \pm 0.06	0.21 \pm 0.09	0.27 \pm 0.07	0.23 \pm 0.04	0.35 \pm 0.12
Volatiles, wt %	60.0 \pm 0.62	74.6 \pm 0.54	79.8 \pm 0.51	78.0 \pm 0.15	79.6 \pm 0.68	78.2 \pm 0.49
Fixed carbon*, wt %	27.1 \pm 0.17	12.45 \pm 0.21	11.01 \pm 0.2	11.98 \pm 0.26	10.83 \pm 0.24	11.82 \pm 0.08
Elemental analysis						
Carbon, C, %	45.64	41.39	40.99	42.53	42.03	42.50
Hydrogen, H, %	5.30	5.24	5.73	5.61	5.60	5.50
Nitrogen, N, %	0.28	0.19	0.10	0.30	0.23	0.10
Sulphur, S, %	0.10	0.07	0.12	0.08	0.09	0.11
O*, %	45.45	49.93	52.85	51.21	51.82	51.44

H/C*	1.39	1.52	1.68	1.58	1.60	1.55
molecular ratio						
O/C*	0.75	0.91	0.97	0.91	0.93	0.87
molecular ratio						
Structural analysis						
Holocellulose, %	63.56	67.89	67.34	67.84	66.24	65.62
Klason Lignin, %	34.05	33.87	32.27	31.37	32.10	32.84
Solvent Extractives, %	3.40	2.40	1.40	1.99	1.53	1.80
HHV (calculated)	18.29	16.91	17.27	17.63	17.27	17.57

A. Proximate Analysis Results

The proximate analysis results are with reference to Table II. According to a number of studies, in order to enhance heat transfer, the ideal feedstock for pyrolysis should have a moisture content of less than 10% [18]. The blends' moisture content ranged from 8.98 wt% for PSD to 9.68 wt% for EPSDB, indicating that they were appropriate for co-pyrolysis. Low biomass moisture content would result in less moisture-containing bio-oil. Additionally, due to the high heat capacity of water, a high moisture content above 10% will significantly increase the energy demand for pyrolysis. The results show that treatment at 60 °C is effective and uses less energy than drying at 100 °C as proposed in other studies on blends [11]. The volatile matter content of PB was the lowest at 60%, while the volatiles of all other samples were at or above 75%. The volatiles component of the samples reflects the content of the bio-oil fraction (condensable) and syngas fraction (incondensable gases). Higher volatile matter implies a likelihood of increased bio-oil production [19], [13]. This result illustrates that PB is unsuitable for bio-oil products, and the other samples are suitable for obtaining bio-oil as there is no significant difference between sawdust and blends.

Fixed carbon is inversely correlated to the total volatiles in the feedstock. From Table II, it can be seen that the feedstock with a higher amount of volatiles wt% had low fixed carbon. The fixed carbon in PB was significantly higher than the fixed carbon in all other samples. The fixed carbon in samples 2 to 5 was comparable, ranging from 11.01 for PSD to 12.45 for EB. Also, fixed carbon influences the heating value of the feedstock. The feedstock with higher fixed carbon content had a higher calorific value. A feedstock's ash concentration is indicative that metal oxides or inorganic components are present. Reactors with high fuel ash content experience slagging, fouling, and corrosion in addition to decreased calorific value [20]. The ash content in PB and EB were magnitudes of order higher than in the other four samples. This result is in line with the literature as it is reported that typically, a higher ash content is likely in the leaves and bark

of the tree and a lower ash content in the wood stem [19]. The ash content in blends with bark is more significant than in blends without bark, signifying that ash content is primarily contributed by bark irrespective of the tree.

B. Elemental Analysis Results

The elemental analysis results are with reference to Table II. All samples investigated contained lower sulfur and nitrogen, which were <0.15% and <0.4%, respectively. This implies that pyrolysis products from the samples under investigation will generate a minor quantity of SO_x and NO_x emissions when utilised as feedstock. On the other hand, the ratios of oxygen to carbon (O/C) and atomic hydrogen to carbon (H/C) in a particular solid fuel are the factors associated with the amount of energy contained inside the solid fuel.

To provide a preliminary estimate of the amount of hydrogen required to convert the hydrocarbon into a gas and/or liquid, the H/C ratio is a helpful calculation. When the H/C ratio is greater, the fuel has better energy efficiency, and the CO₂ emissions that result from its burning are lower. The typical molecular H/C ratio of fuel materials composed of lignin and cellulose, such as biomass, is approximately 1.5 [21], [22]. Biomass with a higher H/C ratio would likely produce a higher pyrolysis oil yield and a lower solid yield. PSD displayed the highest H/C ratio, while PB displayed the lowest H/C ratio [19]. EPSD and EPSDB displayed H/C ratios of 1.6 and 1.55, respectively. PSD displayed the highest O/C ratio of 0.97, while PB showed the least O/C value of 0.75. Fuels with a high O/C ratio have a smaller heating value than those with a low O/C ratio [23]. EPSD and EPSDB displayed an O/C ratio of 0.92 and 0.91, respectively. PB displayed the lowest H/C value, the lowest O/C value, and the highest energy content, as reflected by the calculated HHV.

C. Structural Analysis Results

The structural analysis results are with reference to Table II. The structure of the feedstock affects the co-pyrolysis product that is produced as well as the yields of those products. When biomass has a low lignin concentration, the quantity of oxygen in the oil created during pyrolysis is reduced. Table II shows that bark samples generally contain higher lignin than sawdust and blend samples. However, since lignin is transformed into organic oxygenates, phenolic compounds, acids, char, and non-condensable gases, the difference in lignin is not statistically significant. A larger bio-char production might result from a higher lignin concentration because stable structures are present. [24]. Table II shows that the bark sample contained the highest solvent-soluble extractives, with PB showing the highest 3.4 % followed by EB at 2.4 %. High volatile content in biomass is associated with uncontrollable burning when the product is heat degraded, and as an increase in the extractive content occurs, the heating value of biomass increases [25]. Bark samples generally have higher extractives than wood stems [26]. The results in Table II, also show a

generally higher extractive content in ESD (1.99 wt%) than in PSD (1.40 wt%). However, characterisation results reflected generally higher extractives in hardwood than in softwoods [27], [28]. Mixing all samples together, EPSD resulted in extractive content of 1.43 wt% while adding bark to a mixture (EPSDB) elevated the extractives content to 1.8 wt%.

D. Functional Group Spectra

Fig. 1 depicts the FTIR spectra of all six samples. It is clear that the peaks vary significantly from each other terms of wave number and transmittance. height and breadth. In essence, these peaks indicate various functional groups present in the feedstock. In the FTIR spectra of two sets of mixes, the 3400 to 3900 cm^{-1} , 2300 to 2400 cm^{-1} and the 1400 to 1900 cm^{-1} band has the most noticeable peak. 3400 to 3900 cm^{-1} . The 3400 to 3900 cm^{-1} is a result of stretching of the O-H bond as shows the points to the presence of alcohols and phenols. The 2300 to 2400 cm^{-1} shows a stretch of the nitriles and alkynes double bond. The 1400 to 1900 cm^{-1} shows single bonded compounds up to 1700 then the carbon oxygen stretch bonds. The chemical structure of the samples seem to be comparable in terms of presence of bond structures.

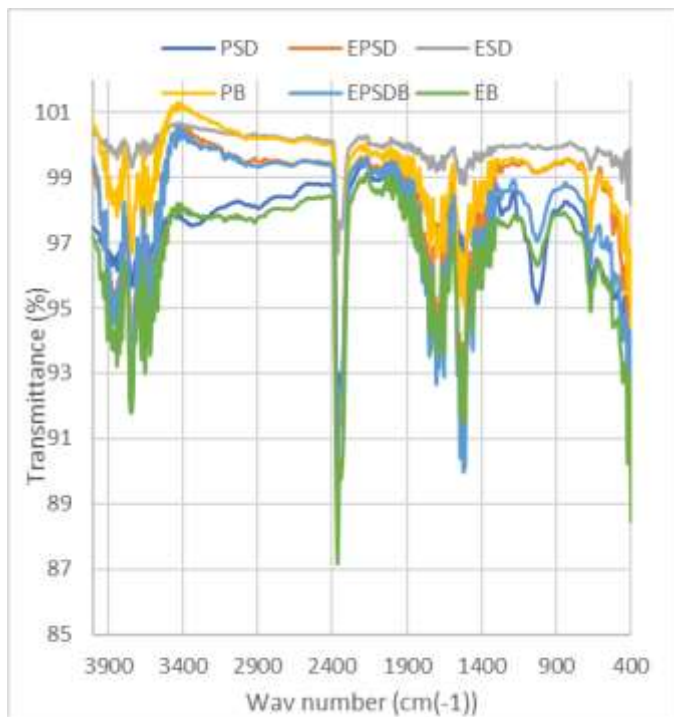


Fig. 1 FTIR spectra of feedstock

E. Thermal Degradation

Thermal degradation is important as it informs the maximum temperature of operation and thus prevents excessive heating with no potential product quantity and quality gain.

The experiments were conducted at a constant heating rate (non-isothermal), as the temperature was raised from 30 °C to 700 °C. The heating rates used in this study were 5, 10, 20, and 40 °C/min; however, the discussion will use the values for

EPSDB at 40 °C/minutes. Fig. 2 and Fig. 3 show the TGA and DTG analysis curves of the samples under investigation, where they reflect the material decomposition behaviour of the biomass samples. These curves allow for identifying the temperature range within which primary bio-oil production or yield is prevalent and are critical in selecting the temperature range to use when conducting the pyrolysis process.

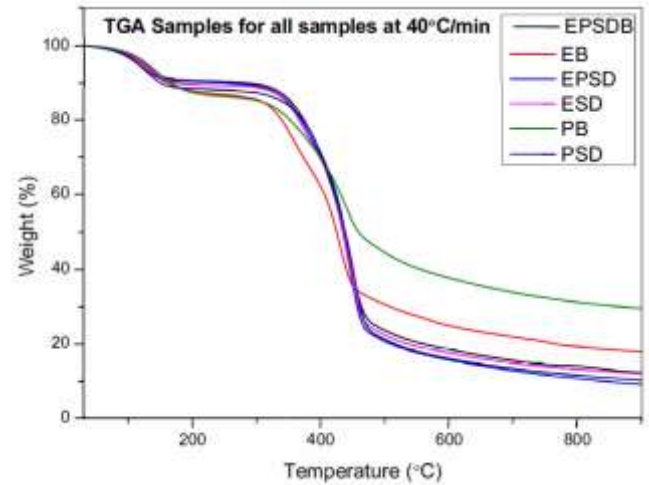


Fig. 2 Feedstock TGA curves at heating rates 40 °C/min

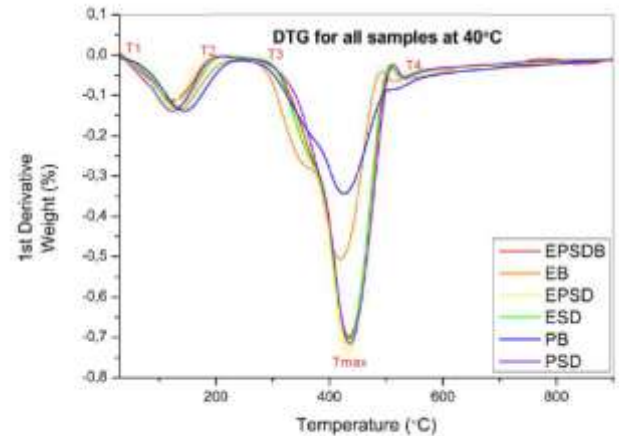


Fig. 3 Feedstock DTGA curves at heating rates 40 °C/min

Fig. 2 and Fig. 3 show the TGA and DTGA results. Fig. 2 and Fig. 3 show distinct but comparable profiles. There are four stages of mass loss in the profile. The first stage (T_1 - T_2) which indicates moisture in the fiber's structures and evaporative water loss. The breakdown of low molecular weight components may potentially also be included in the first stage. The first stage was from 30 °C to 160 °C for EPSDB. The second phase (T_2 - T_3) shows stable physiochemical conditions in the samples since there is no significant mass change from 160 °C to approximately 325 °C.

The third stage (T_3 - T_4) shows the decomposition, degradation, and the release of volatile materials causing a large mass loss at this stage, which is basically what devolatilisation entails. For EPSDB at 40 °C/min this was 325

°C – 510 °C. For some samples the DTGA curves showed two peaks (e.g. PB, ESD and EB) that represented stage 3 breakdown (devolatilisation), before T_{max} . T_{max} depicts the point at which the maximum reaction rate occurs and this was 445 °C for EPSDB at 40 °C/min. The breakdown of hemicellulose is responsible for the first peak. Short-chain hetero-polysaccharides, which make up hemicellulose, readily break down at comparatively low temperatures [29]. The second peak is in line with the breakdown of cellulose. Ether bonds join the D-glucose units in cellulose to form a collinear polysaccharide. Compared to hemicellulose, which has a major amorphous aspect, cellulose is more resistant to degradation because of its crystalline structure [30]. The most resistant component of the biomass, namely lignin and other composite chemicals that are more thermally stable, broke down after T_{max} , which is the final stage of breakdown. The aromatic structures that makeup lignin, a composite organic polymer, crosslink hollecellulose.

In addition, Stage 4 establishes the offset degradation temperature T_4 , which effectively translates into a minimal mass loss with temperature rise or DTGA curve flattening. Thus stage is referred to as charring stage.

TABLE III
TGA AND DTGA TABLE OF RESULTS

	Region	PB	EB	PSD	ESD	EPSD	EPSDB
5°C/min	$T_3 - T_4$ (°C)	250-	245-	270-430	260-	270-	240-
		415	400		450	430	375
	T_{max} , °C	380	370	400	380	400	325
10°C/min	Volatile %	62.0	77.2	80.6	77.9	79.3	78.5
	$T_3 - T_4$ (°C)	280-	250-	300-450	300-	300-	250-
		450	420		450	450	400
20°C/min	T_{max} , °C	400	400	410	410	410	360
	Volatile %	60.3	74.4	80.5	78.5	78.7	78.9
	$T_3 - T_4$ (°C)	290-	275-	305-455	305-	305-	260-
40°C/min		450	430		455	455	410
	T_{max} , °C	410	420	425	420	425	375
	Volatile %	60.5	77.7	80.5	78.5	79.7	78
40°C/min	$T_3 - T_4$ (°C)	310-	310-	325-510	325-	325-	325-
		480	475		510	510	510
	T_{max} , °C	435	430	445	445	445	445
	Volatile %	57.4	69	79.7	78.7	80.8	78.0

Table III shows thermogravimetric analysis results for all samples at 5, 10, 20 and 40 °C/min. All samples, at the heating rates investigated, displayed similar degradation trend with existence of moisture removal zone, devolatilization zone and charring zone. However, the temperature range for these zones varied. The differences may result from variations in the structural components of those materials (cellulose, hemicellulose, and lignin, respectively) [17]. Increasing the heating rate resulted in shifting towards increasing value of a region of high depolymerisation and increase in the peak temperature, T_{max} , was also found to be increasing as the

heating rate increased. This trend was observed for all samples investigated. EPSD was observed to behave similar to PSD in terms of devolatilisation temperature and T_{max} at all heating rates. Devolatilization for EPSDB started at the lowest temperature than the rest of the samples, which means its pyrolysis can be done using lower temperatures.

For all heating rates, it was observed that the bark samples (EB and PB) were observed to have lesser degradation, which is further shown by low volatile content with PB showing the lowest volatiles. The higher ash concentration and higher lignin in the bark, is said to cause less deterioration. It is anticipated that the pyrolysis of bark samples shall lead into lower bio-oil yield and higher char yield.

PSD was consistently found to contain highest volatiles and the values were quite comparable with EPSD for all heating rates investigated. Soft woods higher bio-oil yields than hard wood [31]. Adding bark to the saw dust mixture resulted in slight decrease in volatile content, as shown by EPSDB. This shows that pyrolysis of binary mixture is likely to produce high bio oil yields that are comparable with soft wood, which is known to produce higher quantities of bio-oil. There was no major difference in volatiles content of each sample as heating rate changed. However, it must be noted that the volatiles reported herein are a sum of condensable and non condensable gases, which is an indirect bio-yield indicator but does not reflect on the exact bio-oil yield. The values obtained will be used to decide on the pyrolysis temperature range during bio-oil production experiment.

The practical implication of the results in Table III is that the type of biomass and blending will not significantly affect pyrolysis operating temperature.

The TGA results in Fig. 2 reflected that no weight loss was recorded after 600 °C, which denotes the charring stage.

F. Py-GCMS

Bio-oil is a complex liquid containing oxygenated polar compounds, which are majorly resulting from degradation of hemicellulose, cellulose and lignin. Some of these compounds found in the aqueous phase of the bio-oil are acids, aldehydes, esters, ketones and phenols + alcohols. In the present study these compounds percentages were looked at using pyro-gcms and the results are shown in Table IV.

Table IV
DISTRIBUTION OF OXYGENATED COMPOUNDS OBTAINED FROM PYRO-GCMS

	PB	EB	PSD	ESD	EPSD	EPSDB
Acids	4.85	1.51	0.5	0	3.54	0.66
Alcohols	2.23	1.48	0.3	0.89	6.25	6.93
Aldehyde	4.43	7.16	9.34	9.75	11	7.48
Esters	9.32	7.3	19.7	3.94	0.48	4.55
Ketones	13.2	17.71	15	21.7	16.8	24.66
Phenols	0.09	3.57	14.6	30.6	26.5	16.27

The results showed that PSD pyrolysis gas had lower phenol and ketone content but higher esters present than in ESD. The acid and alcohol content was <1 % in both PSD and ESD but the aldehyde content was similar. Higher phenol and ketone content in pyrolysis gas is an indicator that the wood vinegar to be produced from that feedstock will have better antibacterial, antifungal, aromatics and solvent properties [32], [33]. PB contained higher acid than the rest of the samples. Higher acid content means the boil oil produced will likely be of lower pH. Additionally, high acid has a negative impact on the stability of the bio-oil making storage and transportation. Mixing the saw dust samples (EPSD) was observed to lead into higher phenols, ketone and aldehyde content than PSD. Adding bark into saw dust mixture (EPSDB) somewhat reduced the phenol and ketones content but increased esters. However, the ketone and phenol content for EPSDB was higher than that of PSD. The alcohol content was observed to be higher for EPSD and EPSDB. Alcoholic compounds are known to exhibit antimicrobial properties thus adding to the overall effectiveness of wood vinegar as a natural pesticide or antifungal agent in agricultural applications. A significant decrease in esters was seen in EPSD, while in EPSDB a reduction in acids was observed.

IV. CONCLUSION

The thermal degradation of single, binary and ternary saw dust samples were observed to display similar trend in terms of volatilization temperature at 20, 30 and 40 °C/min. PSD generally showed highest volatile content and is likely to produce higher yield of bio-oil. The volatiles content of binary and ternary mixtures were quite comparable with that of single saw dust sample. The degradation peak shifted to a higher site without impacting degradation performance, according to thermal stability study of biomass at dynamic heating rates.

ESD will produce better wood vinegar as it contains highest ketone and phenols and acids <1%. Though PSD displayed higher volatiles content, it is likely to produce lesser quality wood vinegar than binary and ternary mixtures due to its lower ketones and phenols content. This shows that the biomass mixtures are eligible feedstock for wood vinegar production. The wood vinegar from binary mixture EPSD is expected to have lower pH than that of EPSDB.

Considering that bark constitutes estimated 5% of the tree and adding the findings that it contains lesser volatiles, it is therefore not a preferable feedstock for pyrolysis where bio-oil is the desired product.

The saw dust biomass from EG and PP, either as separate raw materials or in blends, showed significant promise as a raw material for woodvinegar production. Although the findings of this research are encouraging, more precise and reliable models are still required to forecast biomass co-pyrolysis.

ACKNOWLEDGMENT

This research was supported by the Council for Science and Industrial Research (CSIR) and University of KwaZulu Natal.

REFERENCES

- [1] H. P. Vu, L. N. Nguyen, M. T. Vu, M. A. H. Johir, R. McLaughlan, and L. D. Nghiem, "A comprehensive review on the framework to valorise lignocellulosic biomass as biorefinery feedstocks," *Science of the Total Environment*, vol. 743, p. 140630, 2020.
- [2] M. Broda, D. J. Yelle, and K. Serwańska, "Bioethanol production from lignocellulosic biomass—challenges and solutions," *Molecules*, vol. 27, no. 24, p. 8717, 2022.
- [3] J. A. Okolie *et al.*, "Waste biomass valorization for the production of biofuels and value-added products: A comprehensive review of thermochemical, biological and integrated processes," *Process Safety and Environmental Protection*, vol. 159, pp. 323-344, 2022.
- [4] S. Jha, S. Nanda, B. Acharya, and A. K. Dalai, "A review of thermochemical conversion of waste biomass to biofuels," *Energies*, vol. 15, no. 17, p. 6352, 2022.
- [5] K. Asdal and H. Reinertsen, *Doing document analysis: A practice-oriented method*. Sage, 2021.
- [6] A. V. Bridgwater, "Review of fast pyrolysis of biomass and product upgrading," *Biomass and bioenergy*, vol. 38, pp. 68-94, 2012.
- [7] C. Mattos, M. C. C. Veloso, G. A. Romeiro, and E. Folly, "Biocidal applications trends of bio-oils from pyrolysis: Characterization of several conditions and biomass, a review," *Journal of Analytical and Applied Pyrolysis*, vol. 139, pp. 1-12, 2019/05/01/ 2019, doi: <https://doi.org/10.1016/j.jaap.2018.12.029>.
- [8] U. Pangnakorn, S. Watanasorn, C. Kuntha, and S. Chuenchooklin, "Application of wood vinegar to fermented liquid bio-fertilizer for organic agriculture on soybean," *Asian Journal of Food and Agro-Industry*, vol. 2, pp. 189-196, 2009.
- [9] X. Liu *et al.*, "The use of wood vinegar as a non-synthetic herbicide for control of broadleaf weeds," *Industrial Crops and Products*, vol. 173, p. 114105, 2021.
- [10] X. Luo *et al.*, "Effect of co-application of wood vinegar and biochar on seed germination and seedling growth," *Journal of Soils and Sediments*, vol. 19, pp. 3934-3944, 2019.
- [11] H. H. Muigai, B. J. Choudhury, P. Kalita, and V. S. Moholkar, "Co-pyrolysis of biomass blends: Characterization, kinetic and thermodynamic analysis," *Biomass and Bioenergy*, vol. 143, p. 105839, 2020.
- [12] X. Chen, L. Liu, L. Zhang, Y. Zhao, and P. Qiu, "Pyrolysis characteristics and kinetics of coal-biomass blends during co-pyrolysis," *Energy & fuels*, vol. 33, no. 2, pp. 1267-1278, 2019.
- [13] X. Wang *et al.*, "Thermogravimetric kinetic study of agricultural residue biomass pyrolysis based on combined kinetics," *Bioresour. technology*, vol. 219, pp. 510-520, 2016.
- [14] D. Mallick, M. K. Poddar, P. Mahanta, and V. S. Moholkar, "Discernment of synergism in pyrolysis of biomass blends using thermogravimetric analysis," *Bioresour. technology*, vol. 261, pp. 294-305, 2018.
- [15] X. Jin, N. Chen-yang, Z. Deng-yin, G. Yan-hui, H. Qi-min, and X. Yu-hong, "Co-pyrolysis of rice straw and water hyacinth: characterization of products, yields and biomass interaction effect," *Biomass and Bioenergy*, vol. 127, p. 105281, 2019.
- [16] P. Tanger, J. L. Field, C. E. Jahn, M. W. DeFoort, and J. E. Leach, "Biomass for thermochemical conversion: targets and challenges," *Frontiers in plant science*, vol. 4, p. 218, 2013.
- [17] S. Wang, G. Dai, H. Yang, and Z. Luo, "Lignocellulosic biomass pyrolysis mechanism: A state-of-the-art review," *Progress in energy and combustion science*, vol. 62, pp. 33-86, 2017.
- [18] N. Bordoloi, R. Narzari, R. S. Chutia, T. Bhaskar, and R. Katakai, "Pyrolysis of *Mesua ferrea* and *Pongamia glabra* seed cover: characterization of bio-oil and its sub-fractions," *Bioresour. Technology*, vol. 178, pp. 83-89, 2015.

- [19] Q. Zhou, F. Han, R. Arnold, Y. Xie, and S. Chen, "Energy and material characteristics of different component tissues of eucalyptus urophylla× grandis," in *2011 International Conference on Materials for Renewable Energy & Environment*, 2011, vol. 1: IEEE, pp. 469-474.
- [20] I. Y. Mohammed, Y. A. Abakr, S. Yusup, and F. K. Kazi, "Valorization of Napier grass via intermediate pyrolysis: Optimization using response surface methodology and pyrolysis products characterization," *Journal of Cleaner Production*, vol. 142, pp. 1848-1866, 2017.
- [21] Z. Xiong *et al.*, "Assessing the chemical composition of heavy components in bio-oils from the pyrolysis of cellulose, hemicellulose and lignin at slow and fast heating rates," *Fuel Processing Technology*, vol. 199, p. 106299, 2020.
- [22] D. Chen *et al.*, "Insight into biomass pyrolysis mechanism based on cellulose, hemicellulose, and lignin: Evolution of volatiles and kinetics, elucidation of reaction pathways, and characterization of gas, biochar and bio-oil," *Combustion and Flame*, vol. 242, p. 112142, 2022.
- [23] R. M. Rowell, *Handbook of wood chemistry and wood composites*. CRC press, 2005.
- [24] C. Li *et al.*, "Impact of heating rates on the evolution of function groups of the biochar from lignin pyrolysis," *Journal of Analytical and Applied Pyrolysis*, vol. 155, p. 105031, 2021.
- [25] A. P Singh Chouhan and A. K Sarma, "Critical analysis of process parameters for bio-oil production via pyrolysis of biomass: a review," *Recent Patents on Engineering*, vol. 7, no. 2, pp. 98-114, 2013.
- [26] M. Roser and H. Ritchie, "Yields and land use in agriculture," *Our world in data*, 2013.
- [27] G. Giannotas, V. Kamperidou, M. Stefanidou, P. Kampragkou, A. Liapis, and I. Barboutis, "Utilization of tree-bark in cement pastes," *Journal of Building Engineering*, vol. 57, p. 104913, 2022.
- [28] W. Guidi, E. Piccioni, M. Ginanni, and E. Bonari, "Bark content estimation in poplar (*Populus deltoides* L.) short-rotation coppice in Central Italy," *Biomass and bioenergy*, vol. 32, no. 6, pp. 518-524, 2008.
- [29] S. Wang *et al.*, "Pyrolysis mechanisms of typical seaweed polysaccharides," *Journal of Analytical and Applied Pyrolysis*, vol. 124, pp. 373-383, 2017.
- [30] H. Huang, J. Liu, H. Liu, F. Evrendilek, and M. Buyukada, "Pyrolysis of water hyacinth biomass parts: Bioenergy, gas emissions, and by-products using TG-FTIR and Py-GC/MS analyses," *Energy Conversion and Management*, vol. 207, p. 112552, 2020.
- [31] I. D. V. Torri *et al.*, "Bio-oil production of softwood and hardwood forest industry residues through fast and intermediate pyrolysis and its chromatographic characterization," *Bioresource technology*, vol. 200, pp. 680-690, 2016.
- [32] J. Cheng, Z.-C. Geng, J.-L. Zheng, L. Qiu, and F. Jiao, "Characterization of the pyrolygneous acids generated from the pyrolysis of four types mulberry branches," *Industrial Crops and Products*, vol. 183, p. 114949, 2022.
- [33] A. K. Gautam, P. K. Singh, and M. Aravind, "Defensive role of plant phenolics against pathogenic microbes for sustainable agriculture," *Plant Phenolics in Sustainable Agriculture: Volume 1*, pp. 579-594, 2020.