1 **Pyrolysis of Dedicated Bioenergy Crops Grown on Reclaimed Mine Land in West Virginia**

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ABSTRACT

Dedicated bioenergy crops grown on marginal lands such as reclaimed mine lands and other non-arable lands are auspicious cellulosic sources for sustainable bioenergy production. In this study, characterization of pyrolysis products were documented for two dedicated bioenergy crops grown on reclaimed coal-mine lands in West Virginia. Two clonal varieties (Private and Public varieties) of Miscanthus (*Miscanthus x giganteus*) and two varieties (Bomaster and Kanlow varieties) of Switchgrass (*Panicum virgatum L*) were used in this study. The oven-dried samples were pyrolyzed in a fixed-bed batch reactor under an inert condition and at a temperature of 500 °C to produce biochar and bio-oil (vapor condensate). The pyrolysis product, energy and carbon conversion yields were calculated. Additionally, biochar and bio-oil were characterized for elemental composition, volatile, ash and calorific values. Results showed that there was no significant difference in the biochar yields (about 30.00% yield) obtained from the clonal varieties of Switchgrass and Miscanthus. The bio-oil yields were in the range of 45.00 to 51.00% with the Miscanthus (Private variety) having the highest bio-oil yield of 50.61%. The carbon content of the biomass, biochar and bio-oil were found to be 46.80 – 48.02%, 77.72 – 80.23% and 54.68 – 59.68%, respectively. Average calorific values were found to be 19.49 MJ/kg, 29.01 MJ/kg and 24.98 MJ/kg for the biomass, biochar and bio-oil, respectively. Results for the surface chemistry of the biochars showed carbon and oxygen to be the major chemical constituents of the surfaces of the biochars. Carbon dioxide (CO₂), nitrogen (N₂) and carbon monoxide (CO) were found to be the major components of the non-condensable gas and the CO:CO₂ ratio showed that the non-condensable gas cannot be used as a fluidizing medium.

Keywords: Pyrolysis, Switchgrass, Miscanthus, Bio-oil, Biochar,

1. Introduction

In recent years, there has been a continuous increase in energy demand due to rising population and enhanced energy consumption in various sectors [1]. The dependence of the U.S. on imported crude oil is an obvious issue of national and energy security and has significant environmental implications [2]. According to United States Energy Information Administration [3], the total primary energy consumption per year for all sectors has been projected to increase from 97.1 quadrillion Btu in 2013 to 105.7 quadrillion Btu in 2040, the majority of which is expected to be supplied from fossil resources, a leading source for greenhouse gas emissions. According to an estimate, consumption of gasoline and diesel in the United States resulted in 1522 million metric tons of CO₂ greenhouse gas emissions, which was equivalent to 83% of the total CO₂ emissions by the U.S. transportation sector and 28% of total U.S. energy-related CO₂ emissions [4]. Due to these adverse environmental impacts coupled with the non-renewable and finite nature of fossil fuels, it becomes imperative to develop sustainable and environmental friendly energy sources which will reduce the world's dependency on fossil fuels [5-7] and CO₂ emission. These energy sources are termed renewable energy sources (e.g. biomass, wind, solar and geothermal) because they are continuously replenished, if managed sustainably. About 9% of the energy consumed (total of 97 quadrillion Btu energy) in United States was obtained from renewable resources in 2011 [8].

In the spectrum of renewable energy sources, biomass is the only renewable carbon source, which can be converted into liquid transportation fuel, a possible substitute to crude oils [9,10]. Eaton et al. [11] stated that the United States has the potential to produce over 1 billion dry tons of biomass annually for bioenergy applications, which can be converted into 90 billion gallons of liquid fuels, enough to meet more than 30% of the 2015 U.S. petroleum consumption (297.36 billion gallons).

However, it is noteworthy that the production of these biomass resources will compete with food production in terms of cultivable land use. This has led to investigation on the potential use of marginal lands (including abandoned mine lands and other non-arable lands) for growing dedicated bioenergy crops in order to reduce competition for land between energy and food production. Marginal lands are usually described as unproductive or unsuitable for crop production due to inherent edaphic or climatic limitations or because they are located in areas that are vulnerable to erosion or other environmental risks when cultivated [12,13]. Marginal lands are characterized as having little or no agricultural importance with poor soil qualities, hence making them unsuitable for food production. According to Blanco-Canqui [14], reclaimed mine land is considered marginal because they are often rocky and gravelly, with low soil organic matter concentrations and adverse soil physical and chemical properties. While the United States

has about 4.4 million ha of mine lands, West Virginia is estimated to have about 81,200 ha of mine lands. These lands can be reclaimed and made available for biofuel feedstock production [15,16]. The current state of reclaimed mine lands in West Virginia used for herbaceous biomass production has shown a great potential for high yield. Target yields of 5,000 kg/ha for Switchgrass and 15,000 kg/ha for Miscanthus have been established for reclaimed lands by the WV Department of Environmental Protection [17]. In a study by Skousen et al. [17], 4,900 kg/ha yield was obtained for a variety of Switchgrass and 21,880 kg/ha yield was achieved for a variety of Miscanthus in 2012. While effort is intensified in improving the biomass yield obtained on these marginal lands, there is also a need to investigate the differences in the compositions of the biomass resources grown on cultivable lands and marginal lands. Serapiglia et al. [18] conducted a study on the compositional differences in Switchgrass grown on a prime land and two marginal soils in New Jersey. The authors reported that there was a variation in the mineral contents of the biomass caused by the environment and soil variability across the sites examined. It was found that cell wall composition (cellulose and lignin) of the biomass samples were not significantly affected by location of growth. However, hemicellulose, ash and mineral content of the biomass were significantly affected by the location of growth. Biomass grown on the marginal land had a higher content of micronutrients hence influencing the overall ash content of the biomass. The differences in the composition of the biomass resources obtained from marginal lands and cultivable lands thus provide background information and insight into the distribution and properties of products obtained from the conversion of the biomass resources.

The thermochemical conversion of lignocellulosic biomass has received immense interest as a method for production of liquid fuels and bioproducts as compared to its biochemical counterpart. This is because thermochemical conversion processes can accommodate more diverse feedstock at a time than the biochemical conversion processes. Pyrolysis is defined as the thermochemical conversion process usually conducted at a temperature of 400 to 600 °C in the absence of oxygen to produce a bio-oil (a liquid condensate of pyrolysis vapors) along with some solids (biochar), and some gases (methane, carbon monoxide, carbon dioxide) [19,20]. The pyrolysis product distribution is largely dependent on factors such as operating conditions (temperature, heating rate and vapor holding time) and biomass characteristics (physical characteristics, chemical and mineral composition). The classification of pyrolysis is based on the distribution of pyrolysis products, heating rate and residence time. Fast pyrolysis occurs when the biomass is heated at a rate of 10 – 1000 °C /s within a short residence time. This results in high liquid

yield. Pyrolysis with a low heating rate (0.1 to 1 °C /s) and longer residence time is considered a slow pyrolysis and it results in high biochar yield [13,21].

Research has shown that there is a strong relationship between biomass composition and pyrolysis product distribution and characteristics. Lignocellulosic biomass contains a considerable amount of alkali and alkaline metals, which can affect overall pyrolysis product distribution [22,23]. Presence of low minerals in biomass promotes the production of aromatic hydrocarbons [18] during catalytic pyrolysis. The switchgrass grown on the marginal land produced lower levels of levoglucosan and other oxygenated products due to the greater level of ash and potassium in the biomass [18].

While theoretical estimation of ethanol production from switchgrass grown on reclaimed mine lands has been carried out [24], there is no report on the pyrolysis of biomass resources grown on reclaimed mine lands in West Virginia. Therefore, the objective of this study was to compare pyrolysis product distribution and characteristics of selected dedicated energy crops cultivated on reclaimed mine lands of West Virginia. This article documents the distribution and characteristics of products obtained from the pyrolysis of two clonal varieties of energy crops (Switchgrass and Miscanthus) grown on reclaimed mine land in the State of West Virginia.

2. Materials and Methods

2.1 Sample Collection and Preparation

Samples for this experiment were Public and Private clonal varieties of Miscanthus (*Miscanthus x giganteus*) and Kanlow and Bomaster clonal varieties of Switchgrass (*Panicum virgatum* L.). Details of growth sites and establishment of all the Switchgrass and Miscanthus varieties in the pyrolysis experiments have been documented by Skousen et al. [25]. To be specific, the test samples were harvested from the Alton site, a reclaimed mine land in Upshur County, West Virginia. This site was mined for the Upper, Middle, and Lower Kittanning coal seams. The 30 ha area selected for Switchgrass and Miscanthus plantings was reclaimed in 1985 with less than 15 cm depth of soil being replaced over the mixed overburden and standard reclamation practices were employed. Skousen et al. [25] reported that after the fourth growing season, the dry matter (DM) yield on the Alton sites averaged 5,200 kg/ha for Switchgrass (Kanlow and Bomaster varieties) and 9,000 kg/ha for Miscanthus (Public and Private varieties).

The biomass samples were chopped into small sizes using a kitchen knife and then oven dried at 103 °C for 24 hours prior to the pyrolysis experiment.

2.2 Pyrolysis Experiment

The pyrolysis experiments were performed in a fixed-bed batch reactor having a diameter of 22.86 cm and a height of 25.40 cm. The experimental setup is shown in Figure 1. For a typical experiment, about 400 g of the oven-dried sample was placed inside the airtight reactor. The sample filled reactor was placed in a furnace (Model: BF51728C, Thermo scientific, NC) and nitrogen gas was passed through the reactor to flush out any trapped air for about 10 minutes before heating the furnace. The furnace was heated from room temperature to 500 °C under a nitrogen gas flow of 2 L/min. The temperature was kept constant at 500 °C for 30 minutes. A K-type thermocouple placed inside a thermal well located at a height of 6.35 cm from the bottom of the reactor was used to measure the reactor temperature. The temperature data were logged into the computer via a data acquisition instrument (Model: OM-DAQPRO-5300). The average heating rate recorded for various experiments was approximately 7 °C/min. The nitrogen flow kept the pyrolysis reaction under inert condition and swept the pyrolysis vapors generated in the reactor into a series of ice-bath condensers where the vapors were condensed. This condensate is referred to herein as bio-oil. The bio-oil produced during the pyrolysis was collected from the condensers and a sample of the incondensable gas products given off during the pyrolysis was collected with an airtight syringe (Model: 1000 series, Hamilton, NV) at reactor temperatures of 200, 300, 400 and 500 °C for composition analysis. After the experiment, the reactor was allowed to cool to room temperature under a constant purge of nitrogen gas. Once cooled, the reactor containing char was weighted again. Thereafter the mass of the empty reactor was subtracted from the mass of reactor containing the biochar to obtain the mass of the biochar produced. In addition, the mass of the empty condensers was subtracted from the mass of the condensers containing the bio-oil produced in order to determine the mass of the bio-oil produced.

Figure 1: Experimental setup for biomass pyrolysis [26]

2.3 Analytical Measurements

ASTM D3176-15 standard [27] was followed in carrying out the ultimate analyses (carbon, hydrogen, nitrogen and sulfur mass fractions) of the biomass, bio-oil and biochar samples using a CHNS analyzer (Model: Series II CHNS/O Analyzer 2400, PerkinElmer, Waltham, MA). The calorific values of the biomass, bio-oil and biochar samples were estimated using the unified correlation for computation of higher heating value from the elemental analysis of fuels provided by Channiwala and Parikh [28]. The validity of the correlation has been established for fuels having wide range of elemental composition, i.e. C: 0.00 – 92.25%, H: 0.43 – 25.1%, O: 0.00 – 50.00%, N: 0.00 – 5.60%, S: 0.00 – 94.08% and Ash: 0.00 – 71.4%. However, beyond the specified ranges of C, H, O, N, S and Ash, the predictive accuracy of the correlation does not hold true. Proximate composition (fixed carbon, moisture, volatile matter and ash contents) were carried out on the biomass and biochar samples using a proximate analyzer (Model: LECO 701, LECO Corporation, St. Joseph, MI) following the ASTM D3174 standard [29]. The pH of the bio-oil was measured using an Accumet pH meter (Model: AB 15, Fisher Scientific, Pittsburgh, PA). The viscosity of the bio-oil was measured following ASTM D2983-15 standard [30] using a viscometer (Model: DV2T, Brookfield Middleboro, MA) at a temperature of 50 °C. The composition of the non-condensable gas samples was analyzed using a gas chromatograph (Model: Clarus GC 580, PerkinElmer Waltham, MA).

The mineral composition, Acid Detergent Fiber (ADF), Neutral Detergent Fiber, Acid Detergent Lignin (ADL) and lignin were measured at the University of Georgia Agricultural and Environmental Services Laboratories, Athens, GA. Data on fiber analysis (obtained using the NIR method) and ash content of the varieties were employed to determine the cellulose and hemicellulose contents according to the following equations:

$$\% \text{ Hemicellulose} = \% \text{ NDF} - \% \text{ ADF}$$

$$\% \text{ Cellulose} = \% \text{ ADF} - (\% \text{ Lignin} + \% \text{ Ash})$$

2.4 Biochar and Bio-oil Production Yields

Biochar and bio-oil yields were estimated using the following expression;

$$Y_{\text{Bio-oil/Biochar}} = \frac{\text{Mass of bio-oil/biochar}}{\text{Mass of oven-dried biomass}} \times 100$$

213 The energy yield (η_{Energy}) and carbon yield (C_{yield}) in the biochar were calculated using the following
 214 expressions:

$$215 \quad \eta_{Energy} = Y_{Biochar} \frac{HHV_{Biochar}}{HHV_{Feedstock}}$$

216 where η_{Energy} = energy yield; $Y_{Biochar}$ = yield of bio-char; $HHV_{Biochar}$ = calorific value of bio-char
 217 (MJ/kg); $HHV_{Feedstock}$ = calorific value of the biomass feedstock (MJ/kg).

$$218 \quad C_{Yield} = Y_{Biochar} \frac{C_{Biochar}}{C_{Feedstock}}$$

219 where C_{Yield} = carbon yield; C = carbon content of biochar or biomass feedstock.

220

221 *2.5 Morphological, Textural and Surface Chemistry Characterization of the Biochars*

222 Solid morphology characterization of the biochar samples were performed at the West Virginia University
 223 Shared Research Facilities using a scanning electron microscope (Model: Hitachi-S4700, Hitachi High
 224 Technologies America, Schaumburg, IL). The SEM images were collected using the software available
 225 with the instrument. The characterization of the surface chemical state of the samples was carried out
 226 using X-ray photoelectron spectroscopy (Model: PHI 5000 VersaProbe XPS/UPS, ULVAC-PHI Inc.,
 227 Kanagawa, Japan) with a spectral range of 0 to 1400 eV binding energy and energy resolution of 0.50 eV.
 228 For the analysis, each sample was mounted on a steel specimen disk using an Ultra High Vacuum
 229 approved spectral grade double-sided carbon tape and loaded into the introduction chamber. Afterwards,
 230 the sample was transferred to the analysis chamber where the photoelectron spectra were acquired.

231 The textural characteristics were carried out for two biochar samples produced from Kanlow clonal
 232 variety of Switchgrass and Public clonal variety of Miscanthus. The textural characteristics were
 233 determined by nitrogen adsorption at 77 K using Accelerated Surface Area and Porosimetry System
 234 (Model: ASAP 2020, Norcross, GA, USA). Prior to the analysis, the samples were degassed at a
 235 temperature of 150 °C for 24 hours, cooled to 30 °C and ramped up again to 100 °C for 4 hours before
 236 finally cooling the sample to 30 °C for an hour. The N₂ adsorption isotherms were obtained over a relative
 237 pressure, P/P₀, ranging from 0.01 to 0.99. The BET surface area of the samples were assessed over a
 238 relative pressure range of 0.01 to 0.21.

239

240 *2.6 Experimental design and statistical analysis*

241 A completely randomized design was employed for the experiment. The pyrolysis was carried out in
 242 triplicate for each of the varieties. The *t*-test procedure in SAS statistical software (University Edition)

was used in performing a *t* test (at 95% confidence interval) to determine the effect of biomass types and their varieties on the yield and properties of the pyrolysis products.

3. Results and Discussion

3.1 Feedstock Characterization

3.1.1 Proximate and Ultimate Analyses

The proximate and elemental composition for the Miscanthus and Switchgrass clonal varieties are presented in Table 1. Both energy crops had similar ash and fixed carbon contents of 1 – 2 % and 17 – 18 % respectively. The ash contents were not significantly different irrespective of the varieties. The ash contents of the Miscanthus varieties in this study were lower than that reported in the literature for Miscanthus [31-34]. The ash contents of the Switchgrass varieties (1.2 – 2.02 %) were also relatively lower in comparison to the values reported by Fasina [35] for Switchgrass (2.96 % d.b) and Hu et al.[36] for Alamo whole Switchgrass plant (3.8 %) and Kanlow whole Switchgrass plant (4.0 %). Hu et al.[36] further reported the ash contents of the leaf portion of both Alamo and Kanlow Switchgrass to be 4.6 % while the internodes and nodes portion of the two switchgrass varieties were between 2.1 to 2.5 %. The methods of harvesting the switchgrass were not mentioned but the type of soil used (coarse sandy loam - fine, kaolinitic, thermic typic kanhapludults) was stated. The high ash content of the leaf portion may be due to accumulation of minerals absorbed from the soil by the plants ultimately resulting in the high ash content of the whole plant.

The low ash content reported for the samples in the present research could be due to the harvesting technique employed. The samples were hand clipped and transferred directly into a bag removing any possibility of including dirt or soil with the samples. The low ash content values obtained for the samples are an indication of a low deposit of bulk inorganic material after combustion. The alkali metals contained in ash have been shown to be catalysts for the depolymerization mechanisms during pyrolysis leading to changes in the composition of pyrolysis products, hence the need to quantify the ash content of the biomass[37].

The fixed carbon, which represents the solid combustible residue that remains after the volatile matter has been expelled during heating, was found to be in the range of 16 – 17 %. This result was similar to previous published work [34,38-40]. Kanlow switchgrass had significantly higher volatile matter content

(80.59 %) than the Bomaster Switchgrass (79.56 %) and there was no significant difference ($p < 0.05$) in the volatile content of the Miscanthus varieties. While the volatile matter content of the Miscanthus clonal varieties were not statistically different, less than 1 % difference in volatile matter may cause a significant difference in pyrolysis product yields. Volatile matter content is known to greatly influence bio-oil and biochar yields [41]. The volatile matter content represents the components of a material, except for moisture, which are liberated at a high temperature in the absence of air.

The statistical analysis showed that there was significant difference ($p < 0.05$) in the sulfur content of the biomass varieties with Bomaster Switchgrass having the highest sulfur content of 0.56 % while the hydrogen, nitrogen and oxygen contents were not significantly different for all the varieties. The carbon content of both Switchgrass and Miscanthus clonal varieties ranged between 46 – 48 % while hydrogen was approximately 6 %. The nitrogen and sulfur contents were less than 1 %. A high concentration of nitrogen and sulfur can result in emissions of NO_x and SO_2 , hence a low percentage is desirable in a biomass feedstock[31]. The remaining percentage represents the oxygen content. The elemental compositions for the Switchgrass and Miscanthus clonal varieties were found to be higher than those reported by Imam and Capareda [42] and Bok et al.[34]. Calorific values obtained were between 19 and 20 MJ/kg. The results compare favorably with other published works on calorific values of biomass feedstock [23,43,44]. The calorific value is the total energy content released when the fuel is burned in air, including the latent heat contained in the water vapor and therefore represents the maximum amount of energy potentially recoverable from the combustion of a given biomass source[23]. The calorific value is tightly connected with the biomass elemental composition and it is also influenced by the variation in the cell wall composition and ash content. The proportion of lignin can be used as an indicator of the calorific value due to its relatively low oxygen concentration as compared to holocellulose [31]

Table 1: Characterization of clonal varieties of Miscanthus and Switchgrass feedstock

Property	Miscanthus		Switchgrass	
	Public	Private	Bomaster	Kanlow
Ash (%)	1.37 ± 0.99^a	1.83 ± 0.40^a	2.02 ± 0.26^a	1.21 ± 0.78^a
Fixed carbon (%)	18.06 ± 0.05^a	18.10 ± 0.04^a	18.22 ± 0.20^a	17.03 ± 0.25^a
Volatiles (%)	$80.57 \pm 0.94^{a,b}$	$80.06 \pm 0.37^{a,b}$	79.76 ± 0.08^b	80.59 ± 0.60^a
Carbon (%)	47.00 ± 0.06^a	46.80 ± 0.11^a	48.02 ± 2.31^a	47.03 ± 0.17^a
Hydrogen (%)	6.44 ± 0.04^a	6.45 ± 0.00^a	6.71 ± 0.34^a	6.45 ± 0.03^a
Nitrogen (%)	0.44 ± 0.07^a	0.47 ± 0.05^a	0.52 ± 0.12^a	0.53 ± 0.04^a

Sulfur (%)	0.50 ± 0.01^b	$0.54 \pm 0.01^{a,b}$	$0.56 \pm 0.01^{a,b}$	0.54 ± 0.03^b
Oxygen (%)	45.63 ± 0.09^a	45.74 ± 0.12^a	44.19 ± 2.77^a	45.46 ± 0.16^a
HHV (MJ/kg)	19.29 ± 0.04^a	19.22 ± 0.05^a	20.11 ± 1.50^a	19.34 ± 0.11^a

3.1.2 Mineral Composition

The mineral compositions of Miscanthus and Switchgrass clonal varieties are presented in Table 2. The phosphorus, potassium and calcium contents of the four varieties are similar. However, the magnesium content of the Switchgrass clonal varieties was higher than that of the Miscanthus clonal varieties because the soils where the Switchgrass clonal varieties were grown had higher magnesium content than the soils where Miscanthus clonal varieties were grown [25]. It is expected that the mineral composition of bioenergy crops is directly related to the mineral content of soils in which they are grown. Meanwhile, Private Miscanthus had the highest manganese and sodium concentrations and Public Miscanthus had the highest iron concentration. Jin et al. [39] reported the mineral compositions of the bark, sapwood and heartwood for two woody biomass (red oak and yellow poplar). The zinc and sodium concentrations reported for these two woody biomasses were lower in comparison to the Switchgrass and Miscanthus clonal varieties in this study. However, the manganese and aluminum concentrations reported for the barks of both red oak and yellow poplar were higher than those for the varieties in this study. This variation in the mineral compositions of woody biomass and dedicated energy crops is an important factor, which influences the pyrolysis product distribution.

The percentage of potassium content in the biomass varieties is slightly below average (0.36 – 0.43 %) and it is higher in comparison to phosphorus, calcium and magnesium. Potassium is a strong catalyst for biochar gasification and since CO₂ and H₂O are primary pyrolysis products, they react with biochar in the presence of potassium to form CO and H₂, thereby decreasing biochar yield [45]. Patwardhan et al.[46] and Nowakowski and Jones [47] showed that potassium majorly have a direct effect on the thermochemical breakdown of cellulose and this impact can lower the yields of levoglucosan and increase lower molecular weight deoxygenated compounds during the pyrolysis of cellulose. A higher production of acetic and propanoic acid alongside cyclopentene derivatives and non-methoxylated phenols such as phenol, cresols, and dimethylphenol occurs during cellulose depolymerization catalyzed by potassium. It can reduce ash melting point leading to slag and agglomeration during thermal process thereby lowering

combustion efficiency [48,49]. Bradbury et al. [50] also stated that the yield of organic matter to gas and char is dependent on the inorganic constituents. The inorganic constituents promote secondary reactions which cause break down of higher molecular compounds to smaller ones. Furthermore, Fahmi et al. [37] reported an inverse relationship between biomass mineral contents and lignin content. The study showed that char yield from pyrolysis increased with increase in inorganic constituents; hence, a reduction in lignin content will result in low char yield.

Table 2: Mineral composition in percent (%) and parts per million (ppm) of Miscanthus and Switchgrass clonal varieties (as received)

Minerals	Miscanthus		Switchgrass	
	Public	Private	Bomaster	Kanlow
Phosphorus (%)	0.03	0.03	0.03	0.02
Potassium (%)	0.41	0.43	0.41	0.36
Calcium (%)	0.25	0.30	0.30	0.26
Magnesium (%)	0.03	0.04	0.09	0.09
Manganese (ppm)	74.26	130.19	103.05	62.44
Iron (ppm)	130.79	33.77	37.42	26.38
Aluminum (ppm)	22.84	17.45	15.49	<12.46
Copper (ppm)	<5.00	<5.00	5.73	<5.00
Zinc (ppm)	24.27	21.00	33.31	25.53
Sodium (ppm)	351.20	396.50	352.12	351.95

3.1.3 Chemical Composition

Chemical composition (cellulose, hemicellulose, lignin, and extractive contents) of biomass governs the pyrolysis product yield [51] and kinetics of the pyrolysis process[52]. Raveendran et al. [41] indicated that the actual amount of the individual components present in a particular biomass play a more significant role in determining the characteristics of the pyrolysis products in comparison to the chemical structure of the individual components. This implies that the chemical makeup of the bio-oil and biochar are dictated by the amount of cellulose, hemicellulose and lignin content in the biomass. Bio-oils are composed of differently sized molecules derived primarily from the depolymerization and fragmentation reactions of cellulose, hemicellulose and lignin [53]. Figure 2 shows the chemical composition (cellulose, hemicellulose, lignin and extractive contents) of the Miscanthus and Switchgrass clonal varieties tested. The cellulose content was between 34.44 - 36.94 %, hemicellulose content was between 28.84–31.56 % and lignin content was between 8.84 – 10.31 % for the samples tested. The results obtained for the

chemical composition of the biomass samples were comparable to those reported in the literature [18,23,42,54].

The thermal decomposition of these biomass constituents occurs differently with cellulose decomposing at a temperature of 240- 350 °C to produce levoglucosan and anhydrocellulose, hemicellulose decomposing at a temperature of 200- 260 °C to produce more volatiles, less tars and less biochars, while lignin decomposing at 280 – 550 °C yields phenol via cleavage of ether and carbon-carbon linkages [53]. Mohan et al. [53] further stated that lignin pyrolysis produces more biochar than cellulose or hemicellulose.

Raveendran et al. [41] reported that upon independent pyrolysis of biomass components, cellulose has a biochar yield of 14 %, hemicellulose yields 32 % biochar, and lignin yields 41-47 % biochar. Moreover, simultaneous pyrolysis of all three polymers together does not have any interaction. [45,55]. The percentage referred to as ‘Others’ in Figure 2 are lumped quantities of fat, protein, extractives, pectin etc. which were not individually measured[39].

Figure 2: Cellulose, hemicellulose and lignin compositions of Miscanthus and Switchgrass clonal varieties

3.2 Pyrolysis Product Yields

Figure 3 shows the percent yields of pyrolysis products (biochar, bio-oil and gas) for the two clonal varieties of Miscanthus and Switchgrass. The biochar yield was about 30 % on average for all the varieties. Statistically, there was no significant difference in the biochar yields, which implies that the biomass varieties did not influence the biochar yield. The result also confirmed the implication made for the chemical compositions of the varieties that similar chemical composition would result in similar biochar yield.

The biochar yields (29 -31 %) observed in the present study were relatively higher than the biochar yield (15 %) reported by Boateng et al. [56] for Switchgrass pyrolyzed at a temperature of 480 °C using fluidized-bed (silica sand bed) fast pyrolysis. The difference in biochar yields observed in the current study and in Boateng et al. may be due to the following factors: (1) **Particle size**. Large chopped biomass samples were used in this study while Boateng and his coworkers used switchgrass sample of particle size < 2 mm; (2) **Sample type**. Cave-in-rock switchgrass was used by Boateng et al. whereas the present study used Bomaster and Kanlow Switchgrass; (3) **Pyrolyzer type**. Fast fluidized bed pyrolysis was used by Boateng et al. whereas this study employed moderate fixed-bed pyrolysis [57]. In addition, low pyrolysis temperatures and high vapor-residence times have shown to results in high biochar yield [42,58-60]. This is because the cellulose decomposes at a temperature of 240 to 350 °C, hemicellulose decomposes at a temperature of 200-260 °C whereas lignin decomposes at 280 – 550 °C. Therefore, at low temperatures (below 400 °C) significant amounts of lignin remain uncarbonized, thereby, showing high biochar yields. High biochar yields from complete pyrolysis may be attributed to the high fixed carbon content of biomass. The Switchgrass clonal varieties in the present study had fixed carbon content of 17.63 % whereas it was 13.98 % for the Cave-in-Rock variety used by Boateng et al.[56].

Figure 3: Percent yield (on dry biomass basis) of pyrolysis products of Miscanthus and Switchgrass clonal varieties

The bio-oil yields were in the range of 45 to 51 % for the two clonal varieties of Miscanthus and Switchgrass crops. It is important to note that these bio-oil yields refer to actual condensate (without separation of aqueous phase) collected from the pyrolysis of the oven-dried biomass

The bio-oil yields (45-46 %) obtained for Switchgrass clonal varieties in the present study were higher than the Switchgrass bio-oil yield reported by Imam and Capareda [42]. A bio-oil yield of 23 – 37 % with moisture content of 13% for a Switchgrass ground through a 2mm screen and pyrolyzed at a temperature range of 400 - 600 °C was reported. The distribution of the total bio-oil yield into aqueous and non-aqueous phases showed that the non-aqueous phase constituted about 4 - 12 % of the bio-oil yield while the aqueous phase made up 19 – 25 % of the bio-oil yield [42]. Boateng et al. [56] reported a higher bio-oil yield of about 60.7% with moisture content of 23.02 % wt. from Cave-in-Rock switchgrass, which had higher volatile matter of 83.41 % compared to the two Switchgrass clonal varieties in the present study (80.18 %). Mullen et al. [61] also reported a higher bio-oil yield of 69.50 % for Switchgrass having a particle size of 2 mm and subjected to fast pyrolysis at a temperature of 480 °C.

The bio-oil yields obtained for Miscanthus in this study are similar to that reported by Bok et al. [34] for Miscanthus pyrolyzed in rectangular and cylindrical reactors at a temperature range of 400 to 550 °C. Bio-oil yields of 48.9 % and 50.01 % with moisture content ranging between 13 to 21 % were obtained for the rectangular and cylindrical reactors respectively.

As stated earlier, the yield of the pyrolysis products is influenced by the biomass components and high bio-oil yield correlates with the high content of cellulose and hemicellulose in the biomass. Cellulose pyrolysis will result in low char yield and lignin pyrolysis will give the highest biochar yield along with low liquid and gas yield. This implies that cellulose and lignin hold as the upper and lower limits respectively for the product yields that can be obtained with any biomass sample [41].

The pyrolysis process in this experiment can be classified as Intermediate Pyrolysis. According to Bridgwater [62], in an intermediate pyrolysis, biomass is heated to ~500 °C leading to bio-oil yield (in 2 phases) of about 50 %, biochar yield of 25 % and non-condensable gas yield of ~25 %. Previous work by the co-author [57] and Jones et al. [63] also corroborate that the pyrolysis method in this present study is classified as Intermediate.

3.3 Biochar characterization

Table 3 shows the selected properties of the biochars obtained from the pyrolysis of Miscanthus and Switchgrass clonal varieties. On average, the biochar produced from Miscanthus varieties contained 7.87 % ash whereas biochars made from switchgrass varieties had 6.60 % ash content. The fixed carbon content was between 72 – 75 % for biochars produced from Miscanthus varieties and it was between 74 – 76 % for biochars produced from switchgrass. On average, all the biochars contained 15 – 16 % volatile matter. In comparison with the parent materials, there was a significant increase in the ash and fixed carbon contents in the biochars while the volatile content was drastically reduced. The calorific values for the biochars were also found to be between 28 – 30 MJ/kg. This is comparable to the calorific value for coal [64-66].

The carbon content for Miscanthus biochars ranged from 77 - 79% while Switchgrass biochars had a carbon content of approximately 80%. Comparing this result with the elemental composition of the parent materials, the carbon content significantly increased while there was a reduction in the other elements (i.e hydrogen, nitrogen, sulfur and oxygen). Losses in hydrogen and oxygen are explained by breaking of weaker bonds within biochar's structure and the biochar becoming highly carbonaceous [42]. The biochars produced from the Switchgrass varieties in this study appear to have considerably low ash content, high fixed carbon and carbon content compare to the that reported by Boateng et al.[67] for Switchgrass of particle size <2mm pyrolyzed in a fluidized bed reactor. Boateng et al. reported ash content of 28.67%, fixed carbon content of 43.65%, total carbon content of 63.09%, and volatile matter content of 29.48 %.

Table 3: Characterization of biochar obtained from Miscanthus and Switchgrass pyrolysis

Property	Miscanthus		Switchgrass	
	Public	Private	Bomaster	Kanlow
Ash (%)	8.72 ± 1.21	7.02 ± 0.46	7.00 ± 0.55	6.19 ± 0.54
Fixed carbon (%)	74.59 ± 2.77	77.11 ± 0.33	77.50 ± 0.77	76.78 ± 0.10
Volatile (%)	16.69 ± 1.62	15.62 ± 0.42	15.36 ± 1.00	16.82 ± 0.64
Calorific value (MJ/kg)	28.59 ± 0.31	28.63 ± 0.36	29.34 ± 0.72	29.46 ± 0.55
Carbon	77.72 ± 1.50	78.46 ± 0.62	80.09 ± 1.31	80.23 ± 1.13
Hydrogen	2.94 ± 0.26	2.73 ± 0.07	2.71 ± 0.11	2.77 ± 0.07
Nitrogen	1.08 ± 0.17	0.86 ± 0.15	0.84 ± 0.02	0.64 ± 0.02
Sulfur	0.38 ± 0.10	0.20 ± 0.06	0.17 ± 0.04	0.11 ± 0.03
Oxygen	17.89 ± 0.98	17.75 ± 0.65	16.2 ± 1.44	16.24 ± 1.17
Atomic H/C	0.45	0.41	0.40	0.41
Atomic O/C	0.17	0.17	0.15	0.15
BET surface area (m ² /g)	0.246	-	-	0.981

From Table 3, the biochars have a relatively low H/C and O/C ratio of ~ 0.40 and 0.15 respectively, which depicts a high concentration of carbon. Materials with low H/C and O/C values exhibit high stability and low resistance to degradation due to loss of degradable carbon compounds[68]. It is also an indicator of a very stable structural arrangement of the aromatic rings [69].

An important factor to note is the influence of temperature on the atomic ratio of C-H-O. Increase in the pyrolysis temperature leads to expulsion of the volatile matter, hence reducing the hydrogen and oxygen content of the biochar. This is confirmed with the result obtained by Sadaka et al.[70]. The report showed a decrease in the H/C and O/C ratio for carbonized switchgrass as temperature increased from 350 °C to 400 °C and the char was comparable to the composition of lignite coal. Meanwhile, the biochars obtained for the Miscanthus and Switchgrass clonal varieties pyrolyzed at 500 °C in the present study showed a much lower atomic ratio of hydrogen and oxygen to carbon.

Some peer-reviewed articles have used combination of volatile matter content and atomic ratios of H/C and O/C to determine stability of carbon present in biochar in environment [71]. Low volatile matter content <40% might take more than 100 years to decay in environment [72]. Also, if biochar has O/C>0.6, which means its stability in environment is close to biomass itself. On the other hand, if biochar has O/C close to zero, which means its stability in environment is close to graphite [73]. Therefore, Crombie et al.

[73] stated that the mean residence time of biochar in environment may be as low as 100 years for biochar having $O/C > 0.6$ and as high as 1000 years for biochar having $O/C < 0.2$. Enders et al. [71] proposed following carbon stability classification: 1. No stability if biochar has volatile matter content greater than 80%; 2. Moderate stability if biochar has $< 80\%$ volatile matter content and $O/C > 0.2$ or $H/C > 0.4$; and 3. High Stability if biochar has $< 80\%$ volatile matter and $O/C < 0.2$ or $H/C < 0.4$. Based on this classification, the carbon present in biochars produced in this study may be classified as moderately stable, which might take as long as 1000 years before it can start to decompose.

The scanning electron micrographs of the biochars are presented for Kanlow Switchgrass and Public Miscanthus (Figure 4). The biochars showed a visible presence of pore structure, which is attributable to the removal of volatile content during pyrolysis. Kanlow Switchgrass biochar demonstrated a well pronounced pore structure as compared to the Public Miscanthus biochar. A well-developed pore structure of biochar plays a major role in its use for enhancing soil microbial activities and water retention.

The BET surface area for Public Miscanthus biochar was found to be $0.246 \text{ m}^2/\text{g}$ and Kanlow Switchgrass biochar has a surface area of $0.981 \text{ m}^2/\text{g}$. The low surface area is attributed to particle conglomeration and blocking of pores by decomposition and deposition of tars during pyrolysis [74]. Imam and Capareda [42] reported a surface area of $0.9 \text{ m}^2/\text{g}$ for biochar produced at 500°C . The pore structure of these biochars can be further enhanced when subjected to either physical or chemical activation.

491

492

493 Fig. 4a: Micrograph of Public Miscanthus Biochar

Fig. 4b: Micrograph of Kanlow Switchgrass

494 Biochar

495

496 The X-ray photoelectron spectroscopy was used in identifying and quantifying the surface chemical
 497 composition of the biochars. Figure 5 show the wide scan spectra in the binding energy range of 0 – 100
 498 eV and 0 - 1200 eV for the Kanlow Switchgrass and Public Miscanthus biochar respectively. The XPS
 499 spectra for both biochars showed distinct carbon and oxygen peaks, representing the major constituents of
 500 the biochars. Relatively weak peaks of other minor elements such as calcium and silicon were detected
 501 from the wide scan spectra of the surface of Public Miscanthus biochar. Table 4 summarizes the results of
 502 the C1s and O1s peaks. The minor elements detected on the surface of the Public Miscanthus biochar was
 503 found to be in small quantity (Table 4), which may have been transferred from the parent material during
 504 pyrolysis. These metals are essential nutrients for plant growth when biochar is used for soil amendment.

505 The high resolution carbon C1s and oxygen O1s spectra were deconvolved into four peaks and assigned to
 506 the following known chemical shifts; peak 1 (284.8 eV), graphitized carbon; peak 2 (286.0–286.3 eV),
 507 carbon in phenolic, alcohol, ether or C=N groups; peak 3 (287.3–287.6 eV), carbon in carbonyl or quinine
 508 groups; peak 4 (288.8–289.1 eV), carbon in carboxyl or ester groups. The relative amount of the graphitic
 509 carbon (peak 1) for Public Miscanthus biochar surface was quite higher than the one for Kanlow
 510 Switchgrass biochar.

511 Similarly, the deconvolution of the O1s spectra yielded the following five peaks [42,31]: peak I (531.0–
 512 531.9 eV), carbonyl oxygen of quinines; peak II (532.3–532.8 eV), carbonyl oxygen atoms in esters,
 513 anhydrides and oxygen atoms in hydroxyl groups; peak III (533.1–533.8 eV), non-carbonyl (ether-type)
 514 oxygen atoms in esters and anhydrides; peak IV (534.3–535.4 eV), oxygen atoms in carboxyl groups; and
 515 peak V (536.0–536.5 eV), adsorbed water and/or oxygen [75].

516 Quantitative peak analysis was carried out to quantify the surface element concentrations for the biochars’
 517 surfaces (Table 4). It was found that the surface carbon concentrations were 86.78 % and 85.25 % for
 518 Kanlow Switchgrass and Public Miscanthus biochar respectively. The surface oxygen concentrations of
 519 the Kanlow Switchgrass biochar and Public Miscanthus biochar were approximately 13 %. A comparison
 520 of this result with the bulk elemental compositions of the biochars in Table 3 showed that the surfaces of
 521 both biochars had a higher carbon content and low oxygen content. The low oxygen content is an
 522 indication of low surface oxidation [76].

Table 4: Relative contents of functional groups in C1s and O1s from XPS spectra and their atomic concentration

Biochar	C1s (wt.%)			O1s (wt.%)		Atomic conc. (%)			
	Peak 1	Peak 2	Peak 3	Peak I	Peak II	C1s	O1s	Si2p	Ca2p
Kanlow Switchgrass	78.60	18.33	3.07	46.38	53.62	86.78	13.22		
Public Miscanthus	90.83	9.17		49.84	50.16	85.25	13.18	0.88	0.69

Figure 5a: XPS wide scan spectra of Kanlow Switchgrass biochar

Figure 5b: XPS wide scan spectra of Public Miscanthus biochar

3.5 Bio-oil Characterization

The properties (pH, viscosity, calorific value, density, and elemental composition) of the bio-oil obtained from the pyrolysis of the Miscanthus and Switchgrass clonal varieties are presented in Table 5. From the elemental analysis, the carbon content of the bio-oil across the four clonal varieties varied between 54 and 60%, hydrogen was approximately 7%, nitrogen was ~2 and sulfur was less than 1%. The bio-oils across the clonal varieties are highly oxygenated with oxygen content of 30 – 36 %. This is consistent with values reported in the literature [42,77]. The oxygen in bio-oil is present in most of the more than 300 compounds that have been identified in bio-oil. The high oxygen content of bio-oil leads to low energy density which is less than 50% of that for conventional fuel oils and immiscibility with hydrocarbon fuels. In addition, the high oxygen content of bio-oil results in high acidity of the bio-oil, which in turns makes it extremely unstable [77,78].

Bio-oil is multi-component mixture comprised of different sized molecules derived from depolymerization and fragmentation of cellulose, hemicellulose and lignin [78]. The constituents of bio-oil can be broadly classified into three categories, namely; water, water soluble compounds and water-insoluble compounds. Typically, bio-oils from lignocellulosic biomass and agricultural wastes contain about 10 to 30% wt. water [40,54,57]. The moisture content of the bio-oil depends on the initial moisture

content of the feedstock and water formation during pyrolysis. The water-insoluble constituents basically consist of pyrolytic lignin compounds, which represent high molecular weight oligomeric compounds possibly from low temperature (<500 °C) decomposition of the biomass, which typically yields phenols via the cleavage of ethers and the C-C linkages of the lignin polymer. The water soluble compounds, mainly derived from the decomposition of cellulose and hemicellulose include acids, alcohols, aldehydes, ketones and sugar [56]. Mullen and Boateng [40] reported the water insoluble compounds made up 25 % of the total bio-oils produced from switchgrass pyrolysis, 61.1 % was for water soluble compounds while 13.9 % was water.

The pH of the bio-oils was in the range of 2.55 and 2.76. A similar result for the pH was reported for bio-oil produced from pyrolysis of poplar (2.8), birch (2.5) and pine (2.4) [79], *Miscanthus sinensis* (2.1 – 2.9) [34] biomasses and forest residues (2.2 – 2.6) [38]. The low pH value of bio-oil is a result of the presence of substantial amounts of organic acids, especially acetic and formic acid. The low pH value of the bio-oils in this study, which indicates the acidic nature of the bio-oil, correlates with the high oxygen content reported earlier. This implies that the bio-oils produced in this study will require upgrading before they can be used as liquid transportation fuel.

The calorific values of the bio-oils for both clonal varieties of *Miscanthus* and Switchgrass were not significantly different. The values were in the range of 23 to 27 MJ/kg. The calorific values for the bio-oil were relatively higher than the calorific value obtained for the parent materials (19.0 - 20.0 MJ/kg). He et al. [60] reported a lower value (16.6 – 19.6 MJ/kg) for Switchgrass bio-oil and Bok et al. [34] reported a lower value (16.0 - 18.2 MJ/kg) for *Miscanthus* bio-oil. The difference in the calorific values of the bio-oil may be due to measurement method employed. In this study, the calorific values of the bio-oil were calculated using the equation presented by Channiwala et al. [28], while Bok et al. and He et al. used a bomb calorimeter in determining their calorific value. Another important factor that influences calorific value is the moisture content. Boateng et al. [56] reported two different calorific values for bio-oil produced from Switchgrass pyrolysis collected differently. The bio-oil collected from the condensers have a calorific value of 16 MJ/kg with moisture content of 23.0 % wt. and the bio-oil collected from the electrostatic precipitator had a calorific value of 21.7 MJ/kg with moisture content of 6.21 % wt. The results reported by Bok et al. [34] and He et al. [60] also affirmed that as the bio-oil moisture content increase, the calorific value decreases.

579

580 Table 5: Characterization of bio-oil obtained from pyrolysis of Miscanthus and Switchgrass clonal
581 varieties

Property	Miscanthus		Switchgrass	
	Public	Private	Bomaster	Kanlow
pH	2.76 ± 0.08	2.55 ± 0.09	2.57 ± 0.07	2.59 ± 0.14
Viscosity (cP)	45.17 ± 3.01	16.17 ± 1.61	23.67 ± 1.17	16.33 ± 1.26
Density (kg/m ³)	1033.89 ± 28.12	988.76 ± 16.87	1027.06 ± 28.56	1023.47 ± 18.21
Calorific value (MJ/kg)	25.38 ± 1.76	23.42 ± 4.39	26.62 ± 1.32	24.50 ± 2.28
Carbon (%)	58.21 ± 0.37	54.68 ± 4.64	59.68 ± 1.41	58.15 ± 2.84
Hydrogen (%)	7.10 ± 1.30	6.82 ± 1.79	7.53 ± 0.58	6.42 ± 1.29
Nitrogen (%)	1.96 ± 0.55	1.86 ± 0.44	2.13 ± 0.29	2.12 ± 0.55
Sulfur (%)	0.55 ± 0.09	0.53 ± 0.13	0.61 ± 0.04	0.54 ± 0.10
Oxygen (%)	32.19 ± 1.97	36.11 ± 6.44	30.06 ± 1.78	32.77 ± 2.89
Atomic H/C	1.45	1.47	1.50	1.32
Atomic O/C	0.42	0.50	0.38	0.43

582

583 The densities of the bio-oils were in the range of 988 to 1034 kg/m³. Public Miscanthus bio-oil had the
584 highest density while its counterpart (Private Miscanthus) had the lowest density. The density values
585 obtained in this study were slightly lower than what is reported in the literature for both Miscanthus and
586 Switchgrass bio-oil [34,56,60]

587 Viscosity of bio-oil is one of the major properties considered in the application of bio-oil as a liquid fuel.
588 Viscosity affects the atomization of fuel [80]. The dynamic viscosity of the bio-oil were significantly
589 different ($p < 0.05$) with bio-oil from Public Miscanthus having the highest viscosity (45.17 cP). Private
590 Miscanthus and Kanlow Switchgrass bio-oils have a similar viscosity of ~16 cP. The low viscosity of the
591 bio-oil signifies the ease of flow of the bio-oil, which is a result of the water content of the bio-oil. The
592 dynamic viscosity of the bio-oil is also dependent on the temperature; it decreases with increase in
593 temperature. Furthermore, during the storage of bio-oil, the viscosity of bio-oil has been reported to
594 increase due to chemical reactions between various compounds present in the bio-oil leading to formation
595 of larger molecules [78].

596

597

3.5 Non condensable gas characterization

The percent yields of the non-condensable gas for the four-herbaceous biomasses were between 19 and 29 % (Figure 3) with Private Miscanthus having the lowest gas yield. The gaseous products were sampled during Kanlow and Bomaster Switchgrass pyrolysis when the biomass temperature reached 200 °C, 300 °C, 400 °C and 500 °C and analyzed for gas composition (Figure 6 and Figure 7). Carbon dioxide (CO₂), nitrogen (N₂) and carbon monoxide (CO) are the predominant components of the non-condensable gas samples. Nitrogen has the highest percentage due to the fact that it was the carrier gas.

In terms of the temperature, the carbon dioxide and carbon monoxide volumetric fractions were the highest at a temperature of 400 °C while nitrogen had the lowest volumetric fraction at that same temperature. While there are no tangible variations in the volumetric fractions of other non-condensable gases, the increase in CO and CO₂ volumetric fractions with increase in the temperature is as a result of the oxidation of the carbonized biochars at high temperatures [81,82]. Imam and Capareda [42] reported a similar increase for CO and CO₂ with increase in pyrolysis temperature.

Figure 6a: Volumetric composition (%) of non-condensable gas given off during pyrolysis of Kanlow Switchgrass

Figure 7: Volumetric composition (%) of non-condensable gas given off during pyrolysis of Bomaster Switchgrass

3.6 Carbon yield and energy yield

The mass fraction (%) of biomass carbon and the energy fraction (%) of biomass energy captured in the biochars are presented in Figure 8. These calculations do not account for external heat supplied for pyrolysis. On average, the biochars captured about 50% of the biomass carbon and about 40- 50% of the biomass energy. The remaining energy and carbon were distributed between the bio-oil and non-condensable gas products. Jin et al. [39] reported that pyrolysis of mixed hardwood chips retained 78 % of the feedstock energy and 89 % of the feedstock carbon in its biochars and bio-oils.

Figure 8: Carbon and Energy Yields of Miscanthus and Switchgrass Biochars

4. Conclusion

The clonal varieties of Switchgrass and Miscanthus harvested on reclaimed mine land in West Virginia were pyrolyzed in a batch reactor at 500 °C and the pyrolysis products were characterized in this study. The product yield for the bio-oil, biochar and non-condensable gas were 45- 51%, 29 -31% and 19 – 29% respectively. The carbon and energy yield were ~ 50% and 40-50% respectively. The properties of the pyrolysis products for the clonal varieties for the two herbaceous biomass were similar and comparable to other results reported in literatures.

The surface chemistry analysis of the biochars showed that they have carbon and oxygen as major constituents of the biochars' surfaces. The low pH of the bio-oils indicates the need for upgrading of the fuel before it can be used as liquid fuel. A low viscosity was reported for the bio-oils produced in this study and this was attributed to the water content of the bio-oil. Carbon dioxide (CO₂), nitrogen (N₂) and carbon monoxide (CO) were reported to be the major components of the non-condensable gas and the CO:CO₂ ratio showed that the non-condensable gas cannot be used as a fluidizing medium.

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