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Pyrolysis of Pearl Millet and Napier Grass Hybrid (PMN10TX15): Feasibility, Byproducts, and Comprehensive Characterization

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Abstract- A novel hybrid of pearl millet and napier grass (*Pennisetum glaucum* [L.] R. Br. x *Pennisetum purpureum* Schumach), PMN10TX15, was characterized and investigated as an alternative energy source. Pyrolysis reactions of the PMN10TX15 were carried out in a batch reactor operated at 400-600 °C and atmospheric pressure, aiming to investigate its feasibility for energy conversion and products generation. Initially, the biomass was expected to generate great quantities of bio-oil owing to its high volatile matter (86.94%) and energy content (16.44 MJ/kg). However, not only bio-oil was obtained, but also interesting yields and composition of syngas and biochar. Bio-oil, biochar, and syngas products obtained at 600 °C achieved the highest heating values of 19.9, 28.7, and 4.1 MJ/kg, respectively. Phenols detected in the liquid byproducts could establish an alternative route for its petroleum primarily source, offering potential application to the plastic industry. Furthermore, the pyrolysis at 500 °C yielded the highest mass balance of 94.4% and energy recovery of 82.8%.

Keywords renewable energy, biomass, perennial hybrid, *Pennisetum glaucum* [L.] R. Br., *Pennisetum purpureum* Schumach.

1. Introduction

Nowadays, the world is facing an energy crisis caused by many factors altogether, which includes global warming linked to the use of fossil fuels and coal, the increasing price and diminishing supply of such fuels, and the depleting resources related to development and rapid population growth. Hence, sustainable renewable energy will become the most promising and attractive alternative for displacement of the traditional fossil and coal fuels [1]. Every renewable energy such as solar, wind, geothermal, hydropower, and biofuels, must be profitable with potential for industrial production, sustainable for the environment, and accessible to population [2].

Biomass has been widely applied as an energy source. This type of feedstock can be continuously regenerated in contrast to fossil fuels, which take long to generate and explore, and consists of cellulose, hemicellulose, lignin, and minor amounts of other organics, such as sugars [3]. Environmental concern increases urgent demand for energy sources such as biomass that can provide lower (or zero) balance of greenhouse gases emissions through its production and use chain. Advantages of this raw material need to be combined with governmental subsidy aiming to guarantee economic and technical viability [4]. In addition, district energy systems from agricultural biomass have emerged as a great approach, providing a local and affordable energy supply. It represents opportunity for cities to move towards climate-resilient, resource-efficient, and low-carbon pathways [5].

Despite the complexity associated with biomass as a feed for bio-oil production [6], the use of biomass is an outstanding field towards the desire of clean energy from alternative sources that are sustainable, affordable and environmentally benign [7]. Furthermore, vegetal biomass is an important source that plays fundamental role in energy generation in agricultural based developing Countries. In 2017, the Brazilian Ministry of Mines and Energy document reported that 25.5% of the internal energy supply of Brazil was obtained exclusively from sugarcane, wood, and vegetal coal [8].

Among several vegetal biomass possibilities as feedstocks, the pearl millet-napier grass (PMN) hybrids (*P. glaucum* [L.] Br. X *P. purpureum* Schumach) outstand with tolerance to drought and diseases, seed size, and quality of millet combined with the hardness, aggressiveness, and high quality dry matter of napier grass [9]. PMN hybrids provide high yields of tropical perennial grasses, such as sugarcane (*Saccharum spp.*), in addition to integrated cultivation systems of large-seeded annual grasses, such as sorghum (*S. bicolor [L.]* Moench) [10]. Therefore, one of the greatest advantages that PMN hybrids offer over other grasses is the mechanical cultivation possible with seeds.

Additionally, the establishment of perennial grasses in marginal lands are estimated to produce as many as 377 million tons of biomass in the U.S. alone [11]. The use of abandoned agricultural lands to grow bioenergy crops, such as PMN hybrids, aims to avoid deforestation along with consequent carbon stored emissions in the atmosphere [12]. Moreover, this C4 N-fixing warm-season grass can be high yielding in marginal areas, benefiting these areas with nutrient leaching and minimizing soil erosion occurrence [13]. Altogether, both use of marginal and abandoned agricultural areas besides particular advantages, imply less competition with arable lands, resulting in less food security threats.

Giving a great vegetal biomass, one promising way of conveying such feedstock into bioenergy and useful products is through thermochemical conversion. Pyrolysis is the thermochemical decomposition of biomass conducted in the absence of oxygen that can generate mainly solid (biochar), liquid (aqueous and bio-oil), and gaseous (syngas) products [14]. Although these byproducts are expected, the yields depend on the pyrolysis type and respective operational parameters chosen [15]. Slow pyrolysis has received attention regarding the yield of its byproducts [16].

Some interesting studies have addressed thermal conversion of the elephant or napier grass (*Pennisetum purpureum* Schum.). Strezov et al. (2008) studied conversion of elephant grass to syngas, biooil, and biochar generation at two different heating rates, and concluded theoretical potential production of 1.2 Gt of biochar and average of 2 Gt of biooil per year under Brazilian non-arable soils [17]. Braga and collaborators (2014) have investigated kinetics of elephant grass under water and acid solution pre-treatments. The study concluded that the treated biomass is suitable for fast pyrolysis application providing good yields of biooil [18]. However, there is lack of studies performed to elucidate the potential and applicability of PMN hybrids and pearl millet as feedstocks for energy generation. Considering this scenario and the potential of the grass, the aim of the present work was to characterize and evaluate PMN10TX15 hybrid as feedstock for thermochemical conversion, under different operational temperatures.

2. Material and Methods

This study was planned, organized, and performed at Bio-Energy Testing and Analysis Laboratory (BETA Lab), at Texas A&M University, College Station, TX. The biomass used to develop this study was a hybrid between pearl millet and napier grass named PMN10TX15. The feedstock was obtained from the Perennial Grass Breeding Program, Soil and Crop Sciences Department at Texas A&M University, College Station, TX.

2.1 PMN10TX15 Preparation and Characterization

The PMN10TX15 particle size was reduced using a Wiley mill (Model 4, Thomas Scientific), and was then sieved to less than 2.0 mm size (ASTM E11) to obtain a uniform biomass feedstock [19]. The moisture content (MC) of the biomass was determined based on ASTM E 1756 [20]. Since there was less than 10% MC (Table 1), the biomass was used for slow pyrolysis without any additional drying.

2.2 Slow Pyrolysis

Pyrolysis reactions were performed in a commercial batch reactor (Series 4570 HP/HT, Parr® Instrument Company) operated at 400, 500, and 600 °C temperatures. The PMN10TX15 feedstock weighing 200 g was placed inside the reactor, which was then carefully sealed. Before heating, the reactor was purged with nitrogen gas (Airgas© Inc.) for at least 15 minutes to remove the oxygen. The biomass was stirred and heated at a rate of 3.0±0.5 °C/min until the desired temperature was reached. A reaction time of 30 min after reaching the desired temperature was set. After reaction, the system was cooled to room temperature. All runs were performed in triplicates. The liquid product was obtained from the condensable gases cooled by a glycol-water mixture at -4 ºC in the condenser, resulting in a mixture of aqueous (inorganic phase) and bio-oil (organic phase) products. The phases were separated by density difference, and then properly stored in a chiller. Non-condensable gases were collected in Tedlar sampling bags for volume and composition determination. The biochar was obtained from the reactor and placed in air-tight bags.

2.3 *Analytical Methods*

2.3.1 *Raw PMN10TX15 Biomass and Biochar Samples*

The PMN10TX15 biomass and biochar samples were characterized using proximate analysis, which includes volatile combustible matter (VCM), ash, and fixed carbon (FC), performed following ASTM D3175-11 [21]. The higher heating value (HHV) was obtained according to ASTM D2015-00, using a bomb calorimeter (Model 6200 Calorimeter, Parr Instruments) [22]. The Fourier Transformed Infrared Spectrophotometer (FTIR), Shimadzu IRAffinity-1S (Shimadzu©, Inc.), was used in order to infer about existence of chemical functional groups. Ultimate analysis involves the measurement of carbon (C), hydrogen (H), nitrogen (N) and sulfur (S) content of the samples. Approximately 2.0 mg of the sample was prepared and analyzed using an elemental analyzer (Vario Micro Elementar Analysensysteme© GmbH).

2.3.2 *Gas Product*

The gas chromatography (GC) analysis was performed to obtain the composition of syngas released during slow pyrolysis. The samples were assumed to be at standard temperature and pressure conditions (STP). The syngas samples were injected into the gas chromatograph (SRI Multiple Gas Analyzer #1, SRI© Instruments) equipped with two columns: a 6' Molecular Sieve 13X and a 6' Silica Gel column. Helium was used as the carrier gas. The gas chromatograph was calibrated with a standard gas mixture (Airgas© Inc.) that consisted of C_2H_2, CO_2, CO, C_2H_6, C_2H_4, H_2, CH_4, N_2, O_2, C_3H_8, and C_3H_6. The temperature of the column was initially set as 62 °C before raising to 280 °C at a rate of 4.6±0.3 °C/min.

2.3.3 *Liquid Product*

The chemical composition of the liquid products was determined using a gas chromatograph-mass spectrometer (GC-MS, Model QP2010, Shimadzu, Inc.) equipped with a ZB-5MS column (30 m x 0.25 mm x 0.25 μm film thickness). The samples were filtered (0.45 μm PTFE syringe filter, Whatman®) to remove any solid residues and diluted in methylene chloride (>99.5% pure, Fischer Scientific©) in 10% v/v concentration before each analysis. The prepared samples were placed in the auto-sampler (AOC-20s) and directed to the auto injector (AOC-20i). The injection temperature was 295 °C, with ultra-high purity helium (Airgas© Inc.) used as the carrier gas at a flow rate of 1.5 mL/min. The column temperature was held at 45 °C for 4 min, then heated up to 250 °C at a rate of 5 °C/min and then maintained for 10 min.

2.3.4 *PMN10TX15 Compositional Analysis*

The compositional analysis was performed in accordance to LAPs of NREL in the following sequence of procedures: prepared according to NREL-42620 [23]; determination of extractives in the samples (NREL-42619) [24]; structural carbohydrates and lignin content were then obtained based on NREL-42618 [25]; and acid-soluble lignin concentration was achieved using UV-Vis spectroscopy (NREL-42617) [26]. Total sugar was calculated by difference.

2.4 *Statistical Analysis*

Analysis of variance (ANOVA) at 95% confidence level was performed in the SISVAR 5.6 software to determine the statistical significance of the experimental parameters and results. The standard deviations were represented in the results as indication of experimental errors.

2.5 *Mass and Energy Balances*

The total mass, m_g (g), and higher heating value, HHV_g (MJ/kg), of the syngas product were calculated using Eq. (1) and (2), respectively. The $m_{g,i}$ is the mass of each gas component (g), x_i is the volumetric fraction of the component obtained from the GC, V_T is the total gas volume (m^3), M_i is the molecular weight of the component (g/mol), P is the atmospheric pressure (Pa), R is the universal gas constant (8.314 J/mol-K), T is the absolute temperature (K), and $HHV_{g,i}$ is the heating value of the gas component (MJ/kg). The product yield (wt%) and energy distribution were obtained using E. (3) [1] and (4) [27], respectively.

$$m_g = \sum m_{g,i} = \sum \frac{x_i V_t M_i P}{RT} \tag{1}$$

$$HHV_g = \frac{\sum HHV_{g,i} m_{g,i}}{m_g} \tag{2}$$

$$Product\ Yield\ (wt\%) = \frac{Product\ Weight}{Initial\ biomass\ weight} \text{x}100\% \tag{3}$$

$$\%\ Energy\ Recovery = Product\ Yield\ (wt\%)\ X\ \left(\frac{HHV\ Product}{HHV\ biomass}\right) \quad (4)$$

3 Results and Discussion

3.1 *Characteristics and Properties of PMN10TX15*

The composition and properties of PMN10TX15 presented in Table 1 showed some similarities with the characteristics of napier grass [28]. The proximate analysis shows that the biomass had 86.9% VCM, more than the 85.17±0.21 VCM content of napier grass. Similar with napier grass, PMN10TX15 also obtained low ash content (6.53%). The relatively low ash content of the PMN10TX15 is attractive in pyrolysis process due to the reduction of slagging, fouling and corrosion problems during thermochemical conversion [29].

Table 1. Compositional analysis of PMN10TX15 in comparison with napier grass (– indicates data not available)

Characteristics	PMN10TX15	napier grass[a]
Moisture content (wt%), db[b]	6.8[c]	74.22±0.17[c]
Higher heating value (MJ/kg), db	16.44	16.58±0.10
Proximate Analysis (wt%), db		
Volatile comb. matter (VCM)	86.94	85.17 ± 0.21
Fixed carbon (FC)	6.53	8.49 ± 0.04
Ash	6.53	6.4 ± 0.01
Ultimate Analysis (wt%), db		
Carbon (C)	40.39	45.10 ± 0.70
Hydrogen (H)	5.49	5.93 ± 0.15
Nitrogen (N)	0.40	1.45 ± 0.04
Sulfur (S)	0.04	0.35 ± 0.01
Oxygen (O)[d]	47.15	47.17 ± 0.71
Compositional Analysis (wt%)		
Extractives	13.35	4.7 ± 1.4
Water	9.97	-
Ethanol	3.38	-
Lignin	25.31	-
Acid Insoluble	5.61 ±0.16	-
Acid Soluble	19.7 ± 0.18	-
Protein	2.48	-
Total sugar	52.33 ± 0.98	-

[a] Values adapted from [28].
[b] dry basis
[c] MC as received basis
[d] Oxygen obtained by difference including ash

It is also important to note the very low sulfur content of the PMN10TX15 compared to napier grass, which is a desirable characteristic of a feedstock for energy conversion and biofuel generation. It leads to decrease in formation of SO_x compounds when processed [30]. The authors were not able to find a comprehensive characterization and compositional data of *Pennisetum glaucum* [L.] Br. species in literature. Furthermore, some properties were found regarding its morphological structure [31], protein, dry matter, ash, starch, and minerals [32]. The elemental composition and HHV of PMN10TX15 hybrid falls within other perennial crops used as potential raw material for thermal conversion and energy production [28,30-32].

3.2 *Effect of Operational Temperature on Product Yield*

The slow pyrolysis of PMN10TX15 generated the expected biochar, syngas, and the liquid byproducts, this last consisting of the bio-oil and aqueous phase. Yields of byproducts obtained and presented in this study were higher than the average values for slow pyrolysis reactions reported by Sharma et al. (2015) for liquid products (30%) and biochar (35%), although syngas produced was inferior (<35%) [33]. The effect of varying the pyrolysis temperature on the yield of each product is presented in Fig. 1.

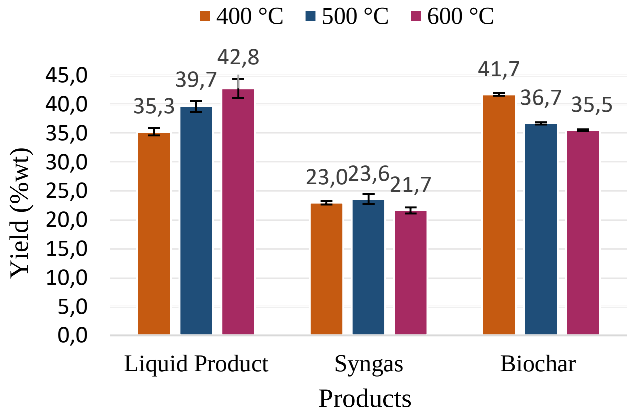


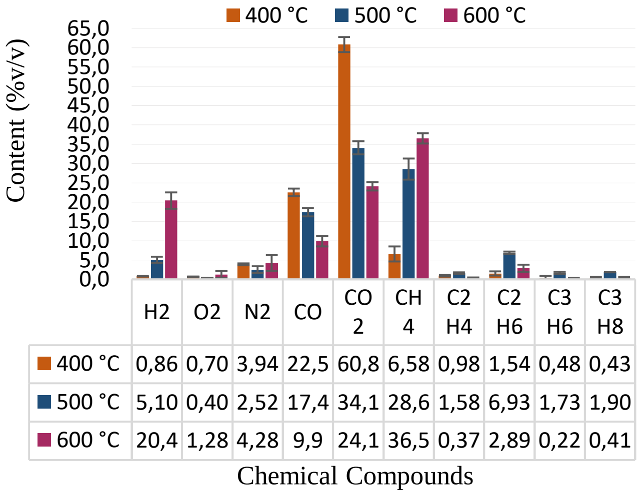
Fig. 1. Product yields at different operational temperatures.

The liquid product yield increased from 35.3 to 42.8% when the temperature was elevated from 400 to 600 °C. On the other hand, the highest biochar yield of 41.7% was obtained at 400 °C and decreased by 6.2% when the operational temperature raised to 600 °C. Therefore, whereas the thermal conversion is performed at lower temperatures and heating rates, dehydration and fragmentation dominate, leading to the production of biochar [34]. Additionally, the maximum gas yield (23.6%) was achieved at 500 °C, and its minimum yield of 21.7 wt% at 600 °C. Results of the ANOVA performed at 95% confidence level verified that the operational temperature significantly affected the syngas and biochar yields, with their p-value < 0.05, but did not affect the liquid products (p-value = 0.077). Trend described and observed in previous studies [14, 27]. The trend of this study is comparable to achievements reported by Jahirul and collaborators (2012), whereas the temperature increases in a range set, less biochar is produced with yield of the liquid and gaseous byproducts increased [15].

3.3 Effect of Operational Temperature on Characteristics and Properties of Byproducts

3.3.1 Syngas

The increase of temperature had significant effect (p-value < 0.05) on the increase of volume of syngas produced, according to ANOVA at 95% confidence level. Although the lowest syngas yield was observed at 600 °C, the maximum gas volume of 41.4 L was reached at this temperature. The composition of the gas product is reported for each operational temperature in Fig. 2, wherein ten compounds were detected in the samples. At 400 °C, low concentrations of H_2, CH_4, and other hydrocarbon gases were detected compared to higher temperatures, while CO and CO_2 were at their highest concentration. Gas components, such as C_2H_4, C_2H_6, C_3H_6, C_3H_8, were highest at 500 °C, while H_2 and CH_4 were found at their maximum concentrations when the operational temperature was set to 600 °C. Considering the molecular weights of the components, it is reasonable that the syngas yield was lowest at 600 °C despite the large volume obtained due to the significant decrease (p-value < 0.05) in the concentration of the heavier gases, such as CO and CO_2, when temperature was increased. This reduction is favorable considering the threats brought about by greenhouse gases, such as their role in global warming, and consequently, climate change.



	H2	O2	N2	CO	CO 2	CH 4	C2 H4	C2 H6	C3 H6	C3 H8
400 °C	0,86	0,70	3,94	22,5	60,8	6,58	0,98	1,54	0,48	0,43
500 °C	5,10	0,40	2,52	17,4	34,1	28,6	1,58	6,93	1,73	1,90
600 °C	20,4	1,28	4,28	9,9	24,1	36,5	0,37	2,89	0,22	0,41

Fig. 2. Relative composition (v/v%) of syngas produced at different operating temperatures.

Figure 3 shows the HHV of the feedstock and pyrolysis products obtained at different temperatures. The higher heating value can be defined as the amount of heat given out by a substance when submitted to combustion [35]. The HHV of the gas at 500 and 600 °C is observed to have significantly higher values compared to 400 °C (p-value < 0.05), mainly due to the increase in the concentration of H_2, CH_4 and other hydrocarbons. The H_2 has a HHV of 120.21 MJ/kg [36], which is higher than any other component of the syngas. The syngas produced could be interesting for commercial purposes, especially for direct combustion, engines and turbines as prime mover, to obtain synthetic natural gas (SNG) [37], and to produce bio-methanol through sustainable processes design [38].

The HHV values of PMN biochar are comparable with biochar from other feedstocks such as orange bagasse and corn starch, around 29 MJ/kg. These biochars can be suitable for briquette production, which are forms of solid fuels with higher HHV value, useful for agricultural areas, and that can consequently contribute to avoid deforestation [39].

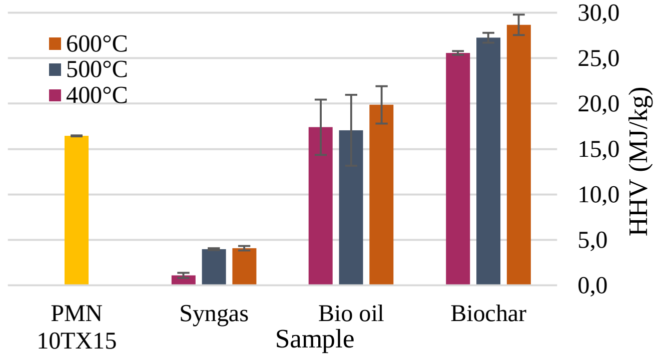


Fig. 3. HHV of the biomass and pyrolysis products at different temperatures.

3.3.2 Liquid products

The aqueous phase obtained from the pyrolysis process was yellowish, while the bio-oil phase was viscous and dark-colored. The HHV of the aqueous samples was reported undetectable by the bomb calorimeter analysis, owing to its very low calorific value, similarly as in previous studies with Jatropha cake as raw material for pyrolysis reactions [27]. The HHV of the bio-oil at 400 °C was 17.4 MJ/kg, and decreased to 17.1 MJ/kg at 500 °C (Fig. 4). The maximum bio-oil HHV in the study was obtained at 600 °C (19.9 MJ/kg).

According to previous studies, the yield and quality of the bio-oil could be further improved using different catalysts [40]. Upgrading methods to enhance the oil quality, such as hydrodeoxygenation, can be applied to produce gas and/or diesel range hydrocarbons and other high value chemicals [6]. Therefore, depending also on the upgrade path chosen, bio-oil could be directed to the engine fuels marketplace [41], be blended with some other bio-based fuels to increase their quality [42], directed to the plastic industry [43], among other uses.

The elemental composition of the aqueous phase and bio-oil are given in Table 2. It can be observed that the concentration of C, H and N increased, while the O decreased, following the rise of operational temperature of the range set. In addition, the amount of C of the bio-oil for all temperatures was observed to be approximately 5-8 times higher compared to the aqueous phase, while the amount of O and H when compared with aqueous phase were 2-3 times lower. Likewise, in the aqueous phase, the N content was considerably low among the other components.

Table 2. Elemental composition of the aqueous phase, bio-oil and biochar products

Sample	Compound content (wt%)				
	C	H	O [a]	N	S
Aq. phase 400 °C	6.81	7.75	85.4	0.00	0.00
Aq. phase 500 °C	9.43	9.41	80.4	0.81	0.00
Aq. phase 600 °C	11.1	9.45	78.4	1.08	0.00
Bio-oil 400 °C	47.9	5.60	45.3	1.18	0.01
Bio-oil 500 °C	62.2	7.26	29.2	1.32	0.02
Bio-oil 600 °C	50.2	6.69	42.1	1.04	0.03
Biochar 400 °C	62.9	3.90	19.1	0.92	0.07
Biochar 500 °C	66.2	3.13	13.0	0.87	0.10
Biochar 600 °C	69.1	2.48	9.94	0.95	0.10

[a] Obtained by difference of the elements and ash

The chemical groups present in the aqueous phase and bio-oil were determined by GC-MS analysis and are listed in Table 3. The detailed chemical composition of the bio-oil obtained at 500 °C is presented in Table 4. Phenols were found to be in majority of the compounds detected in the bio-oil for all temperatures. High concentration of phenols in bio-oils were already reported in literature, where such concentration of this compound could offer a feasible and market valuable alternative route for the plastic industry [43] and in the aqueous phase produced at 500 and 600 °C. The ketones in the bio-oil samples were only detected at 500 °C, and the acids concentration was observed to decrease as the operational temperature increased.

Table 3. Relative content (%) of the chemical groups present in the liquids obtained at different temperatures

Chemical group	Bio-oil (°C)			Aqueous Phase (°C)		
	400	500	600	400	500	600
Acids	2.62	1.91	1.79	-	1.00	1.31
Alcohols	2.84	14.21	8.94	16.30	15.37	16.24
Alkanes	5.37	3.16	10.70	-	-	1.32
Aromatics	5.31	2.28	5.70	-	-	-
Ketones	-	10.82	-	36.61	28.54	26.45
Phenols	72.52	48.83	66.99	27.53	36.20	36.42
Phenyls	1.69	1.69	-	-	-	-
Others	9.65	18.08	5.87	19.55	18.90	18.25

Table 4. Relative content of chemical compounds at 500 °C bio oil detected by GC-MS analysis (**Bold** – chemical functional groups)

Compound	Relative Content (%)	Compound	Relative Content (%)
Acids	1.91	**Phenols**	48.83
n-Hexadecanoic acid	1.91	Phenol	7.14
		Phenol, 2-methyl-	4.29
Alkene	3.16	Phenol, 4-methyl-	5.97
Toluene	2.27	Phenol, 2-methoxy-	9.73
Naphthalene, 1-methyl-	0.89	Phenol, 2-ethyl-	1.27
		Phenol, 4-ethyl-	7.06
Alcohols	14.21	Phenol, 2-methoxy-4-methyl-	3.23
2-Furanmethanol	4.62	Phenol, 2-ethyl-5-methyl-	1.07
2-Furanmethanol, tetrahydro-	4.85	Phenol, 4-ethyl-2-methoxy-	5.3
2-Methoxy-4-vinylphenol	4.74	Phenol, 2,6-dimethoxy-	2.28
		Phenol, 2-methoxy-4-(1-propenyl)-, (Z)-	1.49
Aromatics	2.28		
Ethylbenzene	1.43	**Phenyls**	1.69
Benzene, 1-ethyl-4-methoxy-	0.85	2-Propen-1-one, 1-phenyl-	1.69
Ketone	10.82	**Others**	18.8
2,3-Pentanedione	1.55	Furfural	13.61

Compound	Relative Content (%)	Compound	Relative Content (%)
Ketone		**Others**	
1-Hydroxy-2-butanone	2.81	Benzofuran, 2,3-dihydro-	5.19
2-Propanone, 1-(acetyloxy)-	3.85		
2-Cyclopenten-1-one, 2-methyl-	1.92		
2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-	0.69		

3.3.3 Biochar

The biochar obtained was black, had a fluffy texture, and no relevant smell. The highest HHV achieved at 600 °C (Fig. 3) is related to the high presence of carbon. The biochar HHV increased with pyrolysis temperature; however, ANOVA at 95% confidence level confirmed that the operational temperature had no significant effect on the biochar HHV. The proximate analyses of the biochar samples at different pyrolysis temperatures in comparison with the raw PMN10TX15 are shown in Fig. 4.

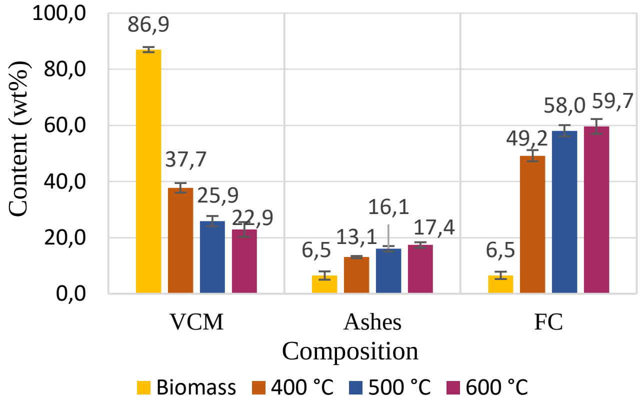


Fig. 4. Proximate analysis report of the biochar, and the PMN10TX15 biomass in comparison.

After a series of devolatilization reactions through slow pyrolysis, the ash remained in the solid product which caused its increase as more VCM content disappeared with temperature [44]. Based on ANOVA at 95% significance level (*p*-value > 0.05), the pyrolysis temperature was found to have no statistical significance on the variations in VCM, FC and ash contents. The biochar produced through pyrolysis reactions has recently received attention for its interesting application possibilities. This carbon-rich by-product when activated can be compared to activated carbon in relation to adsorption. Oleszczuck et al. (2012) concluded that the biochar from the pyrolysis of corn straw and paper waste as an effective agent in the removal of polycyclic aromatic hydrocarbons (HAPs) from the family of persistent organic pollutants (POPs) in sewage sludge when compared to activated carbon [45]. In addition, the PMN biochar itself or after activation could be incorporated in Brazilian fields, aiming to contribute with increase of water retention and nutrient use efficiency [46].

According to the profile identified through FTIR analysis (Fig. 5.), chemical groups were inferred for biomass and biochar samples. The spectrum of PMN10TX15 showed wide peaks from 3600-3100 referring to O–H stretching vibrations that suggested presence of alcohols, amines, amides, and/or water. Such peaks disappeared after reactions, most probably due to dehydration/removal of water and other volatile compounds, such as alcohols, phenols. The peaks at 3000-2800 cm^{-1} refer to C–H, suggesting the presence of alkanes, which disappearance can be inferred due devolatilization. C–O stretching vibrations found in the range of 1750 and 1600 cm^{-1} can be due presence of aldehydes, alkenes, carbonyls, carboxylic acids, esters, and ketones. Previous study reported transmittance peaks at 1727-1260 cm^{-1} range, suggesting the presence of hemicellulose in Napier grass. In addition, peaks at 3430 $cm^{−1}$ and 2923 $cm^{−1}$ range suggested the presence of α-cellulose, and reminiscent bands belonged to lignin [47]. The biochar spectrum shows peaks from 3100-2900 cm^{-1} and 1350-1500 cm-1, inferring C–H stretching vibrations and bending, and the presence of alkanes. The absorbance peak at 2400-2600 cm^{-1} range have suggested the presence of acids. The 1750-1500 cm^{-1} absorbance peak suggests N–H bending and the presence of amides and ketone. The absorbance peak that occurred at 1300-1000 cm^{-1} and infers C–O/C=O stretching vibrations, suggesting the presence of ethers, and/or esters. The 1000-700 cm^{-1} peak refers to –C=H, suggesting the presence of alkanes. Finally, Peaks at the inorganic region (below 1000 cm^{-1}) intensified, most probably due to increased concentration of ash in the biochar.

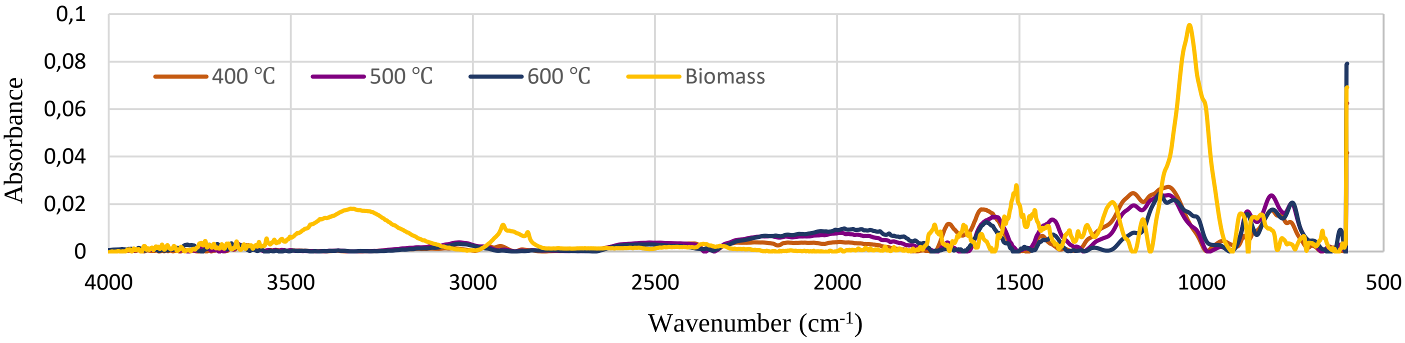


Fig. 5. Fourier transform infrared spectroscopy of biochar samples (FTIR) analyses of biochar at different operation temperatures, in comparison with PMN10TX15 biomass.

3.3.4 Mass and energy distributions

The mass and energy distribution of the PMN10TX15 pyrolysis byproducts were determined based on product yields and HHV and are reported in Figures 6 and 7., respectively. As the temperature increased, more mass was converted into liquids and less remained as biochar.

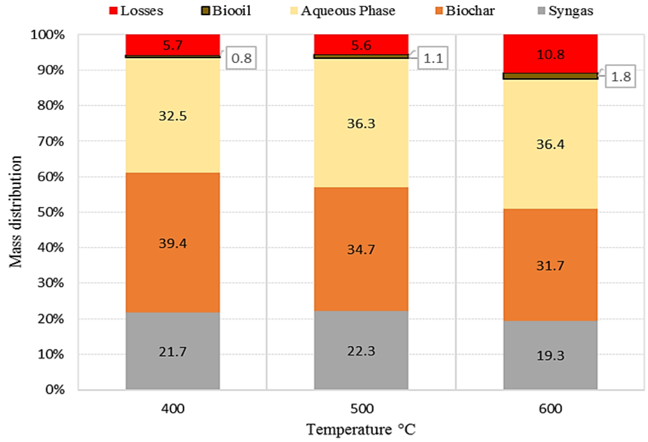


Fig. 6. Mass distribution of pyrolysis byproducts for the three different operational temperatures.

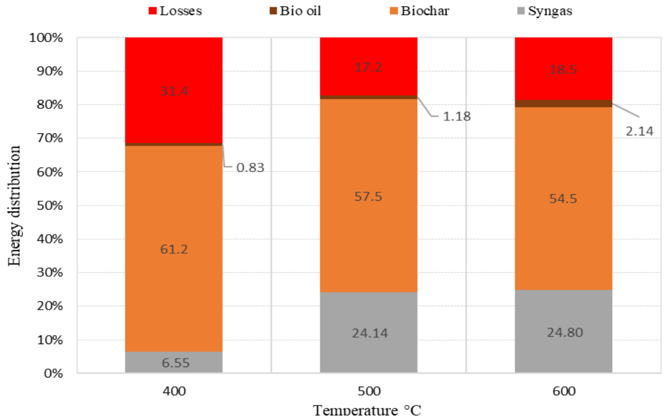


Fig. 7. Energy recovery of pyrolysis byproducts for the three different operational temperatures.

Mass and energy balances are crucial analysis for efficiency, feasibility and recovery of the system. It can be observed in Fig. 7 that biochars had the highest energy contribution among byproducts in all pyrolysis temperatures, with lower yield (Fig. 6.) and higher C concentration detected at 600 °C. The syngas energy yield was observed to increase with operational temperature, which can be explained by the increase in *H_2*, *CH_4* and other hydrocarbons with high HHV [36]. Bio-oil had considerable HHV, however, its low energy yield evident in the mass distribution resulted in the very low mass yield compared to the other pyrolysis byproducts. The lowest energy and mass losses were acknowledged at 500 °C, indicating this operational temperature to be the most efficient in this study.

4. Conclusion

The results obtained through the slow pyrolysis of PMN10TX15 indicated that the change in operational temperature had effect in the yields and characteristics of the solid, liquid and gaseous products generated. The analyses revealed the hybrid as a potential perennial grass for feedstock regarding its HV, low ash, and high sugar contents. Considerable amounts of phenols contained in the liquid products were also observed in this study, with the highest content yield achieved at 600 °C. The temperature increase led to biochar with high HHV and the decrease of CO and CO_2 with increase of H presence in syngas that contributed to a cleaner gas with higher HHV. According to the mass and energy balance distributions, the optimal pyrolysis process was at 500 °C, where 94.4% of mass was recovered and 82.8% of energy recovery was reached.

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