A study on the fast pyrolysis of millet and sorghum straws sourced from arid and semi-arid regions of Nigeria in a twin-screw mixing reactor

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ABSTRACT

In this study, fast pyrolysis of sundried sorghum straw (*Sorghum bicolor*, SS) and millet straws (*Pennisetum glaucum* (L). R. Brown, MS), was conducted in a 10 kg.h^{-1} pyrolysis pilot plant. The aim was to compare their pyrolytic products with products derived from other widely used straw biomasses. Gas chromatography with flame ionization detection (GC–MS/FID), as well as proximate and ultimate analyses, were conducted to characterize the feedstocks and fast pyrolysis products. Compared to other ash-rich feedstocks (such as wheat straw), SS and MS yields recorded lower yields of organic-rich condensate (ORC) and aqueous condensates (AC); but higher yields of pyrochar and pyrolysis gas. The mass balance results showed that the ORC yields from pyrolysis of SS and MS were within a close range of 24–25 wt%, db. The ORC derived from SS and MS retained up to 34 wt% and 32 wt% of renewable carbon from their respective raw biomass. Furthermore, O:C atomic ratio slightly decreased in ORCs from 0.8 to 0.7 for SS, and from 0.9 to 0.7 for MS. However, the H:C atomic ratio increased significantly resulting in an elevated heating value from approx. 18 MJ.kg^{-1} in feedstocks to approx. 24 MJ.kg^{-1} in both ORCs. GC–MS/FID analysis showed that these condensates contain substantial quantities of acids, non-aromatic ketones, lignin-derived phenols, and levoglucosan. The ORCs obtained from these straw biomasses (SS and MS) exhibited similar characteristics to ORCs from the commonly valorized straws of wheat and miscanthus except that the concentrations of vital organic compounds are considerably low. This in effect also makes them promising for fuel applications and as precursors for the production of chemical platforms.

1. Introduction

There is currently a pressing need to restore biomass to its former prominence, which it lost during the industrial revolution. This is because of the carbon imbalance resulting from the excessive use of fossil fuels. Kwon et al. [1] reported that the use of fossil fuels contributed up to 84% of global energy consumption in 2020, resulting in a significant release of 34.8 billion tons of anthropogenic CO_2 emissions. Therefore, carbon-containing materials, including biomass, solid wastes, and livestock manure, were proposed as alternatives to fossil fuels to mitigate the disastrous effects of CO_2 emissions, such as global warming [1,2].

Renewables, biomass, and waste accounted for only 3 % of Nigeria's total primary energy consumption in 2017 [3]. The nation's

renewable energy master plan projects (2021), however, intend to increase renewable energy usage to about 26.7 % and, reduce CO_2 and greenhouse gas emissions by 40 % by 2030 [4]. A circular, sustainable, and transformative bioeconomy strategy would effectively achieve the later aim. The European Commission states that a sustainable bioeconomy is essential for achieving a carbon–neutral future. It has the potential to transform biomass wastes into valuable resources and encourage stakeholders' innovations and incentives [5]. The bioeconomy starts with biomass production [6]. Interestingly, Nigeria occupies the second position in the world's millet and sorghum production after India and the United States of America, respectively [7]. Over 12 million tonnes of residues were estimated to be generated annually from sorghum and millet crops, capable of generating about 203.9 PJ of energy [8]. This excludes annual residues from other cereal plant crops grown in Nigeria. Studies showed that a significant portion of the residues end up in landfills or are burnt [9,10].

This study proposes the conversion of these agricultural residues: sorghum straws (SS) and millet straws (MS), from waste to

valuable products via fast pyrolysis. Fast pyrolysis is a thermo-chemical conversion technology. It degrades a variety of feedstocks such as domestic, agricultural, and industrial wastes. The end product is primarily a liquid product called pyrolysis oil or bio-oil, along with solid (pyrochar) and gaseous products [11,12]. The technique's success in high liquid yield is due to several factors. These include a moderately high temperature of approximately 500 ℃, a high heating rate, and a short vapor residence time (<2 s) at the reaction temperature. This is followed by rapid quenching of the reaction and cooling of the product gas into bio-oil [13,14]. Moreover, the type and design of the pyrolysis reactor and the physical and chemical composition of the feedstock have a critical influence on the pyrolysis product yield distribution [12].

Research groups from the Karlsruhe Institute of Technology (KIT) have worked for over a decade using wheat straw in a bioliq® process aimed at producing syngas from bioslurry [15–17]. Bioslurry is a mixture of bio-oil, and pyrochar [18]. The blend contains approximately 90 % of the energy content in the original biomass feedstock [18,19]. The bioliq® process consists of a decentralized fast pyrolysis plant for the pretreatment of different biomasses into unified and densified bioslurry [19]. Afterward, a high-pressure, entrained flow gasifier is employed to gasify the mixture to produce tar-free syngas [16,19]. The syngas is used to produce organic platform chemicals or transportation fuels [20]. On the other hand, the syngas can be burnt in a gas turbine to generate electricity [21]. We thought this bioliq® concept could be adapted to drive Nigeria's renewable energy master plan using its vastly spread straw wastes in the arid and semi-arid zones.

Twin-screw mixing fast pyrolysis reactor specialized for the pyrolysis of high-ash feedstocks (that is, straws) is used in the bioliq® process. A detailed description of the reactor is provided in the literature [18]. The reactor effectively mixes the biomass feed with pre-heated heat carriers, such as steel balls or sand, resulting in a high heat transfer rate [18]. Furthermore, the setup uses the fractional condensation principle to split the produced bio-oil into two streams: organic-rich condensate (ORC) and aqueous condensate (AC). A variety of different biogenic residues have been tested in this setup including beech wood, as reference materials. The bio-oil yield, reported on a dry biomass basis, significantly decreases from around 50% for ash-free material to 25% for residues with an ash content of about 10% [17]. Studies to improve the bio-oil yield of high-ash residues have been considered by varying process parameters, including moisture contents in feedstocks. Fonseca et al., 2019 investigated the impact of moisture content and sweeping gas flow rate on the wheat straw fast pyrolysis product yield. In their study, wheat straws were conditioned to three different moisture contents (1.2%, 9.3%, and 24%, dry basis), categorized as dry, medium, and moist. The moist feedstock produces the highest amount of bio-oil, however, medium feedstock gave the largest ORC. Increasing sweeping gas was also found to increase bio-oil quantity and quality [22].

Numerous studies have extensively investigated the pyrolysis of biomasses utilizing various reactor types, while also attempting to optimize process conditions [14,23–25]. However, the specific biomass type considered in this study has received limited attention in the literature. Dhyani et al., 2017 reported the effect of the reaction environment (N$_2$ and CO$_2$ environments) on the quality of bio-oil produced from slow pyrolysis of sorghum straws [26]. They noted a higher yield of furans, an essential industrial compound, in bio-oil produced in a CO$_2$ environment and fewer acids and aromatic compounds. In comparison, pyrolysis of the same straws in an N$_2$ environment favors a higher yield of ketones, phenols, and their derivatives. Piskorz et al., 1998 studied the fast pyrolysis of Italian sweet sorghum and sweet sorghum bagasse in a bench scale continuous fluidized bed unit. They reported a

maximum liquid yield of approx. 69 wt% (on dry basis) at a pyrolysis temperature of 510 °C and vapor residence time of 0.5 s. They observed that sorghum bagasse (crushed sweet sorghum stalks) gave a higher bio-oil yield and had better quality, which could serve as an alternative fuel, compared to liquid products from sweet sorghum when pyrolyzed [27]. However, Naik et al., 2017 reported a maximum bio-oil yield of about 16 % by mass of the sorghum bagasse feedstocks pyrolyzed in a laboratory-scale fixed bed reactor at a pyrolysis temperature of 450 °C [28]. Millet straw and polythene bags were subjected to flash pyrolysis in a kiln device coupled with two gas analyzers [29]. The study focused on identifying and measuring the amount of carbonaceous and nitrogenous species compounds in the gaseous products. Millet straw yields an average of 45 wt% carbonaceous compounds (comprising CO, CO$_2$, and C$_2$–C$_6$ light hydrocarbons) and 15 wt% nitrogenous compounds (NO$_2$, NO, N$_2$O, HCN, and NH$_3$). Although plastic pyrolysis is not related to the current study, it is interesting to know that higher carbonaceous gas, up to 68 wt%, and the same 15 wt% of nitrogenous gas released from pyrolysis of plastic bags compared to biomass.

After conducting a thorough literature review [26–29], it appears that there is a lack of studies investigating the fast pyrolysis of sundried sorghum and millet straws, including the characterization of their pyrolysis products. Furthermore, the above-mentioned studies were conducted on only a lab scale. To address this knowledge gap, the present study aims to investigate the fast pyrolysis of sundried sorghum and millet straw on a pilot-scale twin-screw reactor using the reactor's current optimal operating conditions. Additionally, this study will characterize the organic-rich condensate, aqueous condensate, pyrochar, and evolved gaseous products resulting from the pyrolysis process.

2. Materials and methods

2.1. Materials

Straw wastes of sorghum (*Sorghum bicolor L.*), locally known as guinea corn in Nigeria and pearl millet (*Pennisetum glaucum L. R. Br.*), plants were sourced from farmlands in the arid and semi-arid regions of Nigeria, in West Africa. About 80 kg of each of the two biomass straws were gathered on farmlands between February and April 2020. For ease of packaging and transportation from Nigeria to Germany, the straw biomasses were first milled in a hammer mill fitted with a 7 mm sieve. Due to the reactor's particle size requirement for optimum operation, the biomasses were further grounded in a power cutting mill (25.203/105; construction year: 1998) supplied by Fritsch GmbH, Germany, using a sieve size of 4 mm. The resulting biomass was characterized and used as feedstocks for the fast pyrolysis experiment. The feedstock properties are presented in Table 1.

2.2. Fast pyrolysis experiments

The fast pyrolysis of sorghum and millet straw residues was conducted in a 10 kg h^{-1} twin-screw mixing fast pyrolysis reactor at the process development unit (PDU) at Karlsruhe Institute of Technology. A detailed description of the pyrolysis unit is available elsewhere [18]. A schematic representation of the setup is depicted in Fig. 1.

Grounded biomass was fed in batches to prevent clogging through a buffer silo that feeds the screw that controls the rate at which feedstocks enter the pyrolysis reactor continuously. The pyrolysis occurs in a thermally isolated twin-screw reactor in which biomass feedstock mixes with steel beads of about 1.5 mm in diameter. The rotation of the twin-screw reactor is

Table 1
Physical and chemical properties of sundried sorghum and millet straws.

Straw biomass	Moisture (%, ar)	Proximate analysis (wt.%, db)			Elemental analysis (wt.%, db)					Fiber component[a] (wt.%, db)			Calorific value (MJ.kg^{-1})
		VM	FC	Ash	C	H	N	S	O*	Hemicellulose	Cellulose	Lignin	
Sorghum	6.7 ± 0.7	69.9 ± 0.7	24.5 ± 0.7	5.6 ± 0.9	46.2 ± 0.0	5.6 ± 0.0	0.6 ± 0.0	0.0 ± 0.0	42.1 ± 0.9	19.1	46.3	8.1	18.2 ± 0.1
Millet	4.9 ± 0.0	69.8 ± 1.5	22.4 ± 2.2	7.9 ± 0.6	46.5 ± 0.0	4,9 ± 0.0	0.4 ± 0.1	0.0 ± 0.0	41.0 ± 1.8	15.3	50.5	10.7	17.6 ± 0.2

* calculated value, db: dry basis
[a][8].
C: Carbon.
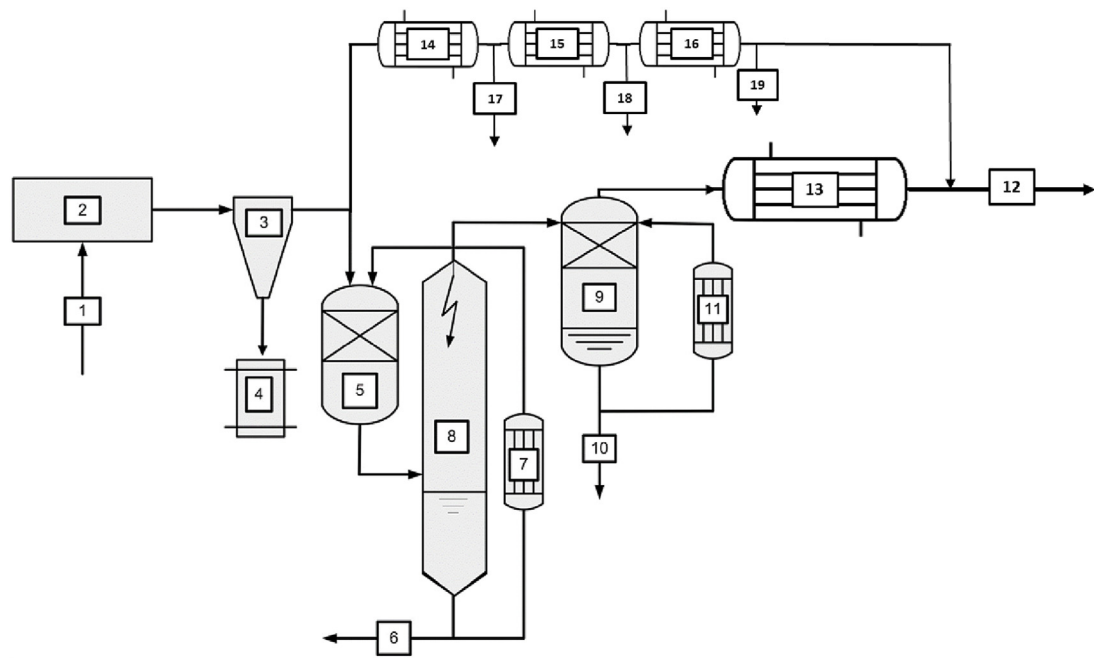H: Hydrogen.
N: Nitrogen.
S: Sulfur.
O: Oxygen.

Fig. 1. Scheme of the fast pyrolysis process development unit (PDU): 1: Biomass Feed, 2: Pyrolysis screw reactor, 3: Cyclone, 4: Solid products, 5: Quenching Condenser 1, 6: Organic-rich condensate (ORC), 7: Heat exchanger 1, 8: Electrostatic precipitator, 9: Quenching Condenser 2, 10: Aqueous condensate (AC), 11: Heat exchanger 2, 12: Gaseous product, 13: Third condensation unit, 14: Bypass condenser 1, 15: Bypass condenser 2, 16: Bypass condenser 3, 17: ORC bypass, 18: AC bypass, 19: AC bypass. (Adapted from Ille et al. [30]).

140 rpm and the steel beads act as heat carriers. They are electrically heated before entering the reactor and recirculated using bucket elevators during the pyrolysis process. Biomass feeding into the reactor begins once the reactor outlet temperature reaches 500 °C. Each pyrolysis experimental run takes about 3 h. It is assumed that the pyrolysis process is a steady-state process, as the reactor temperature is maintained throughout the runtime at 500 °C in the absence of oxygen.

After the biomass undergoes pyrolysis conversion in the reactor, the resulting organic vapors and pyrochars are directed through a double cyclone. This process is used to recover the pyrochar, which is collected in char collection vessels. The organic vapors are then directed to the first condensation loop, where the vapors are quenched using cooled condensate at a temperature of approximately 90 °C. This quenching process results in the formation of the organic-rich condensate that is collected in the first condensation unit (C1). Some char particles were entrained into the first condensation unit in the process and would be referred to as 'solids in bio-oil'. After the first stage, the uncondensed vapor passes through an electrostatic precipitator to capture aerosols and

combine them with the condensate. The organic condensate collected in the first condensation unit is recirculated, cooled, and then re-injected as a quenching medium. For initial cooling, the first condensation system employs ethylene glycol, which is stable and readily miscible with the organic condensates. Consequently, the organic-rich condensate produced contains a significant amount of ethylene glycol and was subtracted in the analytic method used to determine the actual product formed. The second condensation loop to recover aqueous condensate is designed similarly to the first but operates at lower temperatures, about 15 °C. Water is used as the cooling medium for this condensation loop. The noncondensable gasses were analyzed online using a process gas chromatograph before being expelled. At the end of each experimental trial, both quenching systems were emptied, and the condensates and char were collected, weighed, and sampled. Yields of condensates are calculated by subtracting the initial ethylene glycol and water filling, respectively. To recover undiluted pyrolysis liquid products, a bypass condensation loop (units 14, 15, and 16 in Fig. 1) is installed and connected just before the quench. This is necessary because the ORC and AC obtained from

the main condensation loops are heavily diluted with ethylene glycol and water, respectively. The bypass condensation loops are shell and tube condensers with similar operating temperature conditions to the main quenching condensation loop. All experiments were conducted in duplicates for reproducibility.

2.3. Analytic methods

Moisture content in all samples was measured following DIN EN 18134–3. Volumetric Karl-Fischer titration using methanol with Hydranal Composite-V was used to determine the water content in all condensates. Reaction water is calculated by the difference of total water content in the products minus biomass moisture [30]. The ash content of raw biomass and pyrochar, volatile matter analysis of feedstocks, and the elemental analysis of feedstocks and pyrochar were analyzed following DIN EN ISO 18122, DIN EN ISO 18123, and DIN EN ISO 16948, respectively. The calorific values of the raw biomass, pyrochar, and organic-rich condensate were calculated as the high heating value (HHV, on a dry basis) using equation **(1)** [31]. GC–MS/FID analysis of the pyrolysis liquids (ORC and AC) was carried out using the method discussed by Funke et al. [18]. The product gas composition was measured during the experiment using process gas chromatography (Daniel 700, Emerson, United States). A constant flow of neon gas was injected into the reactor during the experiment as a reference. The mass of H_2, CO, CO_2, N_2, O_2, CH_4, alkane, and alkenes C_2–C_5 gases released was calculated based on the reference volumetric flow, the average gas composition ratio, the duration of the experiment, and the density of the gas specie.

$HHV = 349.1C + 1178.3H + 100.5 S – 103.4O – 15.1 N – 21.1 Ash$

1.

Where HHV is the higher heating value in (KJ kg^{-1}, dry basis), C, H, S, O, and N are percentages of carbon, hydrogen, sulfur, oxygen, nitrogen, and ash as determined by elemental analysis.

3. Results and discussion

3.1. Product yield distribution

Fast pyrolysis products from the KIT pyrolysis unit include the liquid products: organic-rich condensate and aqueous condensate; solid product (pyrochar) and the pyrolysis gas (which are the non-condensable gaseous products) [30].

The product yields and mass deficits from fast pyrolysis of SS and MS are presented in Fig. 2. The figure shows the average yields on an 'as received' basis. The organic-rich condensate yield (including 'solids in bio-oil') is 42.4 ± 0.2 wt% and 39.9 ± 0.8 wt% for SS and MS, respectively. The pyrochar yield is found to be 20.1 ± 0.4 wt% from fast pyrolysis of SS and 25.9 ± 0.0 wt% for MS. 25.2 ± 0.4 wt% of noncondensable gases were released during fast pyrolysis of SS and 23.9 ± 0.8 from MS. Comparatively, SS was observed to give slightly higher condensates (ORC and AC) and gas yields, while MS yielded higher pyrochar. The higher pyrochar yield from MS can be attributed to the higher lignin and ash contents found in MS (Table 1). Studies on the thermal degradation of lignin have shown that lignin decomposes over a broader range of temperatures of 150–900 °C [32–35]. Up to 30–50 % of lignin has been reported to end up in pyrochar after thermal degradation [33]. Cellulose, however, decomposes to produce liquid products (bio-oil) during thermal degradation [36]. Although the ash content in MS is higher than in SS, the gaseous product released during the pyrolysis of SS was higher. High pyrolysis gas is usually associated with the catalytic effect of metal ions in ash [37]. It shows that the impact of the fiber composition in the two feedstocks supersedes that of the catalytic of alkaline elements in ash, perhaps at the
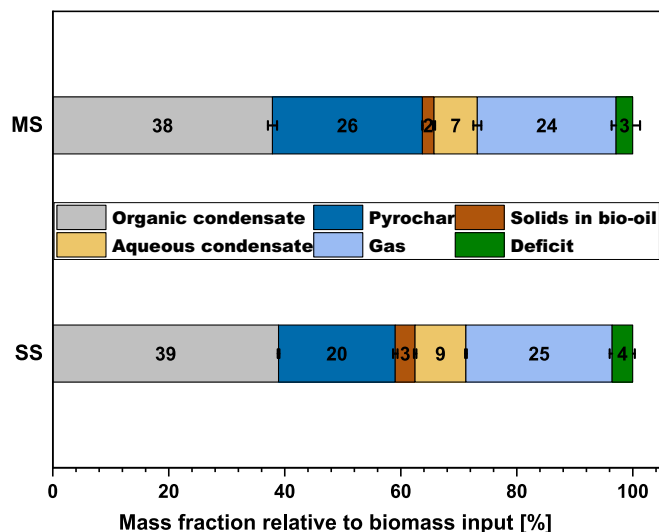

Fig. 2. Experimental mass balance on an 'as received' basis. The mass fraction in percentages of product yield from fast pyrolysis of sorghum stalk (SS) and millet stalk (MS): Error bars represent standard deviation.

pyrolysis temperature used. Table 1 shows that SS contains higher hemicellulose than MS. Hemicellulose is highly reactive [38], degrades in a comparatively shorter and low-temperature range (220–315 °C) [39], and favors the production of gaseous products [40]. The results demonstrate that fast pyrolysis of SS and MS can produce approximately 71 wt% and 73 wt% of bioslurry on an "as received" basis, respectively. These values are lower than the bioslurry yields of scrap wood (81 wt%), miscanthus (77 wt %), and wheat straw (78 wt%) [18].

The estimated experimental mass deficits for SS and MS were 3.6 ± 0.4 wt% and 2.9 ± 2.6 wt% respectively. However, on a 'dry basis,' the estimates were 15.0 ± 0.8 wt% for SS and 14.9 ± 2.1 wt % for MS. The mass balance deficit is an issue yet to be studied but often reported [18,19,41]. Henrich et al., 2016 suspected that the deficit is a result of the escape of undetected oxygenate vapors, such as methylene oxide (=formaldehyde, T_{boil} = 253.8 K), methoxy methane (=dimethyl ether, T_{boil} = 248.2 K), methanol (T_{boil} = 337.8 ± 0.3 K), etc., together with the pyrolysis gas during the second condensation step [19]. Alternatively, the possible formation of ammonia gas can occur as a result of the conversion of organic nitrogen in biomass protein compounds into molecular nitrogen gas. The nitrogenous gases are often not analyzed but were reported to have caused an increase in the pH value of bio-oil [19].

Table 2 shows a comparative yield on a dry basis from different biomass feedstocks that were pyrolyzed using the twin-screw mixing reactor. Reporting the fast pyrolysis products on an 'as received' and 'dry' basis is necessary because an 'as received' basis gives the actual product distributions that could otherwise be concealed and are beneficial for equipment and storage capacities design. Mass balances on a 'dry basis', however, exclude the effect of the differences in the moisture content of the raw biomass feedstocks on the organic-rich and aqueous condensate yields. Thereby making it a more suitable method for comparing fast pyrolysis product yields [12,15,18].

Table 2 shows that, under the same process conditions and setup, the organic-rich condensate produced from sundried SS and MS is relatively low compared to wheat straw, miscanthus, and scrap wood. While this trend is consistent with previously reported effects of ash content on organic oil yield, SS and MS exhibit a comparably low organic oil yield for the ash they contain [17]. The suspected ash effect could be traced to the concentration of alkaline metal ions, especially potassium, which is more abundant

Table 2
Summary of products yields on a 'dry basis' of some biomasses pyrolyzed using the twin-screw reactor at a similar process setup.

Biomass (Feed)	Feed moisture content (wt.%, ar)	Ash in feed at 550 °C (%, db)	Organic-rich condensate* (wt. %, db)	Reaction water (wt. %, db)	Pyrochar (wt. %, db)	Pyrolysis gas (wt. %, db)	Ref
Sorghum straw	6.7 ± 0.7	5.6 ± 0.9	25.3 ± 0.0	4.1 ± 1.0	21.6 ± 0.6	26.1 ± 0.3	This study
Millet straw	4.9 ± 0.0	7.9 ± 0.6	24.4 ± 0.8	3.4 ± 0.5	27.2 ± 0.0	24.4 ± 0.9	This study
Wheat straw	9.6	9.2	35	14	–	–	[18]
Wheat straw	≤ 10	5–6	31–37	–	21–24	17–25	[17]
Miscanthus	10.1	2.7	46	14	–	–	[18]
Scrap wood	5.2	1.5	50	12	–	–	[18]

ar – 'as received' basis.
db – dry basis.
* excluding solids in bio-oil

in MS (K = 19. 3 mg.g^{-1}) and SS (K = 15.2 mg.g^{-1}), compared to 4.1 mg.g^{-1} and 2.1 mg.g^{-1} reported in miscanthus and wheat straws, respectively [8,42,43]. High K values in SS and MS can be attributed to the soil's nutrient requirement in their source location. The use of the NPK (nitrogen, phosphorus, and potassium composition) fertilizers is reported to have caused significant improvement in the growth and yield of these cereal crops [44]. Due to their high reactivity, potassium and sodium ions promote secondary reactions and favor gas yield at the expense of bio-oil production during pyrolysis [25,45]. Gaseous yield comparison (in Table 2) shows higher pyrolysis gas yield compared to wheat straw and miscanthus. Perhaps, using different experimental parameters could improve the pyrolysis liquid yield of SS and MS. Lowering fast pyrolysis temperature was observed to cause a reduction in the catalytic effect of potassium in rape stalk (K = 5.4 mg.g^{-1}), resulting in a higher organic condensate yield [46]. The bio-oil produced from rape stalk increased by 44 percent when pyrolyzed at decreasing temperature of 550–450 °C [46]. Likewise, Naik et al., 2017 reported a maximum bio-oil yield from sorghum bagasse at a lower pyrolysis temperature of 450 °C [28]. Process parameters, such as reduced vapor residence time in the reactor, feedstock particle size, and varying condenser temperature, have been employed to optimize pyrolysis liquid yield from high ash biomass feedstocks [27,47]. The estimated water of reaction in this study is surprisingly low, 3–4 wt%, considering the ash content of the investigated feedstocks. Hodgson et al. [48] reported high ash produces high water of reaction due to catalytic cracking of organic vapors. However, SS with lower ash content was observed to yield more reaction water than MS, which is difficult to explain. Factors, such as the difference in cellulose and lignin in both feedstocks, might have contributed more significantly than the effect of ash concentration in the feedstock. The same goes for the pyrolysis gas released by both feedstocks, especially MS, which yielded a comparative pyrolysis gas with wheat straw. However, due to its high ash content, MS pyrochar yield is higher than that of SS and compared biomasses in Table 2.

3.2. Products characterization and heating values

3.2.1. Organic rich condensate

Table 3 shows the results from the physical and chemical characterization of the organic-rich condensate produced from the fast pyrolysis of SS and MS. The organic condensates are free-flowing liquids, dark brown, and have a distinctive smoky odor, typical of the description of bio-oils [49]. The water content of 9.9 ± 0.1 wt % and 14.0 ± 0.2 wt% on 'as received' was measured for SS and MS organic-rich condensates, respectively. Water in organic condensate results from the initial moisture in biomass. The water produced during the thermal degradation reaction is called the water of reaction [14]. The presence of high water content in the organic-rich condensate can contribute to phase separation, corro-

Table 3
Some properties of bio-oils from fast pyrolysis of sorghum and millet straws.

Properties	Sorghum straw (SS)	Millet straw (MS)
Water content (wt. %, ar)	9.9 ± 0.1	14.0 ± 0.2
Homogeneity	homogenous	Homogenous (but undergoes phase separation in storage)
Elemental composition (wt. %, *db.* excluding solids in bio-oil)		
Carbon	46.4 ± 0.3	45.5 ± 0.1
Hydrogen	10.6 ± 0.0	10.6 ± 0.0
Oxygen	42.8 ± 0.3	43.7 ± 0.3
Nitrogen	0.2 ± 0.0	0.2 ± 0.2
Sulfur	n.d	n.d
Heating values (MJ kg^{-1}, *db.*)		
HHV	24.3 ± 0.1	23.9 ± 0.0

n.d – not detected, db – dry basis.

sivity, and instability of the organic condensate [50]. Therefore, it is desirable to have a low water content in the organic-rich condensate. Comparatively, the water content in MS organic condensate (14 wt%, 'as received') is slightly higher than that in SS condensate (ca. 10 wt%, 'as received). This is suspected to have caused the phase separation of the MS organic-rich condensate later in storage, while SS organic-rich condensate remained homogenous. Phase separation of MS condensate was unexpected considering its lower reaction water but a possibility because of its high ash concentration. It shows that the MS condensate experienced a slow-phase split, contrary to when the water content in the organic condensate is higher, ≥ 25 wt%, which could cause immediate phase separation [19,51]. Phase separation or aging is an indication of fuel instability. During this process, chemical reactions like polymerization, acetalization, oxidization, or dimerization take place between unsaturated and reactive components in bio-oil. These reactions can lead to the loss of valuable organic compounds such as phenols, esters, ketones, sugars, furans, and aldehydes present in bio-oil [51]. It is essential to note that water's presence in organic-rich condensate has pros and cons. Water is reported to lower the organic condensate's heating value and flame temperature because it delays ignition and combustion rates compared to fossil fuels. However, water in organic condensate improves its flowability by decreasing the viscosity of the organic condensate, and it is beneficial for pumping and atomization [13]. Depending on biomass type and process conditions, the water content in organic condensate varies widely in the range of 12–35 wt% [13]. The feedstock composition and chosen condensation temperature affect water content in the condensates, so it is difficult to compare results from many studies. Oasmaa et al., 2010 reported a water content range of 21–27 wt% in homogenous organic condensate produced from wood and reed canary grass fast pyrolysis; and 39–51 wt% of water in heterogenous organic condensate from timothy hay, barley, and rape seed straws [25].

It could be observed that SS and MS organic-rich condensates have similarities in their elemental compositions (Table 3). The carbon content of 46.4 ± 0.3 wt% on a 'dry basis' was measured in SS organic condensate and 45.5 ± 0.1 wt% carbon content in that of MS. The carbon content of ORC reported in the literatures varies widely, which might be due to the differences in analytics and reaction methods. Nevertheless, on a dry basis, the carbon content of organic-rich condensate of SS and MS compares well with that reported for pine saw dust (41 wt%), fresh (green) and stored (brown) forest residues (41 wt%), and eucalyptus *crandis* (42 wt %) [25]. However, Greenhalf et al., 2013 reported carbon contents between 54 wt% and 63 wt% for organic condensate produced from wheat straw, switchgrass, miscanthus, willow SRC and beech wood [14]. In contrast, hydrogen content in SS and MS organic condensate (approx. 11 wt%) was observed to be higher than that reported (<10 wt%, db.) for the previously compared biomass organic condensates [14,25]. The contents of nitrogen remain low in SS and MS organic condensates ($\leq$0.2 wt%), while sulfur was not detected. It implies that SS and MS bio-oils are likely to produce very low NO_x and SO_x volatiles when combusted for energy.

The organic-rich condensate of SS and MS had oxygen contents of 42.8 ± 0.3 wt% and 43.7 ± 0.3 wt%, respectively. This high oxygen content is typically due to oxygenated organic compounds, particularly organic acids like acetic and formic acid, which are the major components of the organic condensate. [52,53]. The presence of organic oxygen is the rationale behind the difference between bio-oil and hydrocarbon-based fuels [54]. Up to 50 wt% of oxygen content in organic condensate has been reported in different works. The variation depends on the biomass type and the fast pyrolysis process condition [55]. High organic oxygen content is undesirable in organic-rich condensate because it is the primary cause of instability of the organic condensate, thereby resulting in aging [51]. It also leads to low heating value (LHV) and immiscibility of condensates with hydrocarbon fuels [13,55]. Mishra and Mohanty [56] suggested catalytic pyrolysis to produce organic condensate with low oxygen content and minimize the undesirable effects. They reported a lower oxygen content in bio-oil produced via CaO, CuO, and Al_2O_3 catalyzed pyrolysis reaction compared to that of thermal pyrolysis (without catalyst). Thereby resulting in organic condensate with lower viscosity, higher heating value, and lower acidity. Similarly, Black et al. (2016) mentioned that blending a catalyst with biomass before being pyrolyzed caused partial deoxygenation of the condensate. However, both studies revealed that catalytic pyrolysis produces higher moisture content in the ORC. Thus, the choice between thermal pyrolysis and catalytic pyrolysis would depend on the specific application and the desired fuel properties. Alternatively, the oxygen content in the organic condensate can be lowered through upgrading termed deoxygenation. These can be achieved through hydrotreating and catalytic vapor cracking [13,57].

The heating values of the ORC (Table 3) were calculated on a 'dry basis,' using the carbon, hydrogen, nitrogen, and oxygen contents. Ash was neglected because the quantity of the organic condensate presented above is without ash-containing solids (solids in bio-oil). According to Banks and Bridgwater, biomass ash is almost entirely contained in pyrochar after pyrolysis [52]. However, a small amount of fine pyrochar particles can be entrained into the organic-rich condensate. The estimated HHV of SS and MS bio-oil were approx. 24 MJ.kg^{-1} compared to approx. 18 MJ.kg^{-1} in the original feedstocks.

Table 4 shows the different functional groups of compounds identified by the GC–MS/FID analysis of the organic-rich condensate produced from SS and MS. Pyrolysis liquids (ORC and AC) are complex mixtures of organic compounds containing over 300 chemical components [51,58]. The GC–MS/FID analysis of SS and MS organic condensate, however, identified about 66 and 71 organic compounds, respectively. A detailed compound list is available in supporting information, Table A. Both MS and SS condensate fractions are mainly composed of organic acids, non-aromatic ketones, lignin-derived phenols, guaiacols, syringols, sugars, some furans, and their respective derivatives. The difference in the distribution of these compounds in SS and MS organic-rich condensate is non-significant. Approximately 41 wt% (total anhydrous mass) of these compounds were identified in SS organic condensate and about 42 wt% in that of MS. The organic acids have the highest concentration of ca. 11 wt% for SS and ca. 13 wt% for MS, made up of acetic and propionic acids, which are major products formed from hemicellulose [58]. It implies that hemicellulose in both feedstocks experienced extensive degradation at the pyrolysis temperature of 500 °C and products condensed into organic-rich condensate. These groups of hemicellulose derivatives might have resulted in the high oxygen content of the ORC (Table 3). Phenolic fractions are the second most abundant compound in SS organic condensate, consisting of 4-ethenyl phenol (3.3 wt%), 4-ethylphenol (3 wt%), phenol (1.2 wt%), and small fractions of cresols and xylenols. These are organic chemicals of great industrial importance, and the ketones [59]. The ketones are second and occupy third in abundance in MS and SS organic-rich condensate, respectively. SS and MS organic condensate predominantly consist of straight-chain ketones, acetol (hydroxy propanone), about 3.4 wt% and 4.2 wt% in the organic condensate of SS and MS, respectively. Some traces of cyclic ketones were detected. Cyclic

Table 4
Main compounds identified in ORC after fast pyrolysis of tropical sorghum and millet straws.

Compounds	Sorghum straw (wt.%)		Millet straw (wt.%)	
	Wet	Dry	Wet	Dry
Non-aromatic Compounds				
Acids	10.0 ± 0.1	11.1 ± 0.1	10.8 ± 0.1	12.6 ± 0.1
Non-aromatic Ketones	7.8 ± 0.0	8.7 ± 0.0	9.1 ± 0.1	10.6 ± 0.1
Heterocyclic Compounds				
Furans	0.8 ± 0.0	0.8 ± 0.0	1.1 ± 0.0	1.3 ± 0.0
Aromatic Compounds				
Benzenes	0.1 ± 0.0	0.1 ± 0.0	0.1 ± 0.0	0.1 ± 0.0
Lignin-derived Phenols	8.6 ± 0.1	9.5 ± 0.2	6.0 ± 0.1	7.0 ± 0.1
Guaiacols (Methoxy phenols)	3.3 ± 0.1	3.6 ± 0.1	4.2 ± 0.0	4.9 ± 0.0
Syringols (Dimethoxy phenols)	2.1 ± 0.0	2.3 ± 0.0	2.5 ± 0.0	2.9 ± 0.0
Carbohydrates				
Sugars	4.2 ± 0.3	4.7 ± 0.4	2.4 ± 0.0	2.8 ± 0.0

ketones are leading components of an organic condensate fraction because they possess desirable combustion characteristics and high resistance to autoignition. These properties make them suitable for application in combustion engines, among other benefits [60]. Straight-chain ketones are reported to be derived from hemicellulose decomposition, while cyclic or ring ketones are formed from cellulose decompositions [61,62].

The main groups of the lignin derivatives identified in both SS and MS organic condensate fractions were phenols and guaiacols, while catechols were not detected. A small percent of furans with furfural (only about 0.2 wt% in both SS and MS organic condensate fraction), and carbohydrates, especially levoglucosan (2.9 wt% in ORC from SS and 2.0 wt% in ORC from MS), were detected. Due to the low levoglucosan content, the fast pyrolysis of the investigated feedstocks may require shorter vapor residence times. According to Ronsse et al. (2012), levoglucosan production is favored under higher pyrolysis temperatures and a faster heating rate. And because levoglucosan easily undergoes secondary reaction, prolonged residence of the organic vapor in the pyrolysis reactor can cause the breakdown of its vapor into the water and secondary char [63].

The weight yield of chemical compounds in analyzed fractions of SS and MS organic condensate is relatively low compared to that reported for other biomass types such as sorghum bagasse, wheat straw, switchgrass, miscanthus, etc [14,58]. The chemical composition of organic condensate is known to be influenced by various fast-pyrolysis conditions such as temperature, heating rate, vapor residence time, pressure, gaseous environment, vapor filtration type, condensation medium, and biomass type [49,64].

3.2.2. Aqueous condensate

The chemical properties of the AC produced from fast pyrolysis of SS, and MS are presented in Table 5. As expected, the AC contains a high amount of water. Up to 83 wt% and about 85 wt% of water was found in a fraction of AC produced from SS and MS, respectively, after subtracting the initially charged water in condenser 2. This agrees with Charis et al., 2020 that inherent bound moisture in biomass contributes a more significant fraction of AC's water [65]. Total organic carbon (TOC) of approx. 148 $g \cdot L^{-1}$ and 244 $g \cdot L^{-1}$ in AC from SS and MS, respectively, and chemical oxygen demand (COD) of approx. 698 $g \cdot L^{-1}$ and 899 $g \cdot L^{-1}$ in AC from SS and MS, respectively. These measured values a considerably high and significantly exceed the acceptable limits of 5 $mg \cdot L^{-1}$ and 40 $mg \cdot L^{-1}$ for TOC and COD standards by EPA (Environmental Protection Agency, Ireland) and NIS (Nigerian Industrial Standard) reported by Adewoye et al. [66]. Similarly, it exceeds the limit of TOC of 125 $mg \cdot L^{-1}$ O_2 and COD of 25 $mg \cdot L^{-1}$ O_2 concentration set by the Council of the European Communities [67]. It implies that AC produced from fast pyrolysis of SS and MS would require treatment for safe disposal. Dahmen et al. (2012) utilized AC for bioslurry production when mixed with organic condensate and a sufficient

amount of fine pyrochar, which is a suitable feedstock for gasification [15]. Recent studies demonstrate the use of aqueous condensate as a substrate for downstream microbial cultivation, resulting in a cost-efficient detoxification of AC [68,69]. However, it is important to note that aqueous condensate is not recovered in commercial fast pyrolysis installations. Instead, it is burnt (as vapor without condensation step) together with pyrolysis gases and pyrochar to provide the heat for the heat carrier loop and, in ideal cases, even provide heat and electricity to local customers via an integrated steam cycle [70].

The GC–MS/FID analysis identified about 77 chemical components in AC produced from SS and 67 in AC from MS. A detailed list of these compounds is also provided in Table A of the supporting information. Analysis showed that, on a dry basis, the AC contains a higher mass fraction of organic acids (SS − 34.4 wt%; MS – 29.8 wt%), non-aromatic ketones (SS − 38.9 wt%; MS – 35.4 wt%), and furans (SS − 4.2 wt%; MS – 3.7 wt%) than that in the organic condensate. In addition, unlike in the organic condensate, non-aromatic esters, alcohols, and aldehydes were detected in AC, presented in Table 6. The difference in chemical composition between ORC and AC is due to variations in compound properties such as molecular weight and boiling temperature [71]. Fractional condensation of fast pyrolysis vapor is an ideal method to address this discrepancy. Both condensers (C1 and C2) operate at different temperatures. Lower molecular weight compounds with lower boiling points are likely to condense on condenser 2, which operates at a temperature near room temperature. An example of a typical compound is the propanoic acid found in AC, which will not condense at the first stage (operating at 90–95 °C), but only at the much lower temperature of condenser 2 (about 15 °C), due to its boiling point of 79.9 °C.

3.2.3. Pyrochar

The effects of pyrolysis process conditions are pronounced on the pyrochars produced from fast pyrolysis of SS and MS. Table 7 shows a severe reduction of the oxygen content in SS and MS pyrochars compared to that in the original feedstocks and bio-oils. The pyrochars contain <10 wt% oxygen, similar to the reported oxygen content in pyrolyzed corn stover, rape stalks, sunflower stalks, and wheat straws [72].

It could be observed that the carbon content in MS pyrochar is low due to its high ash content. Subsequently, resulting in a lower heating value in MS pyrochar than expected and compared to SS pyrochar. However, the HHV of SS and MS compares very well with the heating values of pyrochar produces from different biomass feedstocks at the same pyrolysis temperature [12,23,24]. Ash content in fuels is an important parameter that inversely influences the fuel's calorific value [23]. Ash is known to be composed of alkaline and alkaline-earth metal salts such as sodium, potassium, manganese, and zinc [73]. These metals (as ions) are primarily retained in solid products after the thermal degradation of biomasses. In contrast, non-metal elements, such as sulfur and chlorine in biomass, mostly form volatiles and are released into the gaseous phase [74]. Similar to the SS and MS pyrolysis liquid products, low nitrogen content and negligible sulfur content were observed in SS and MS pyrochars.

3.2.4. Pyrolysis gases

The composition of noncondensable gases released during the fast pyrolysis of SS and MS is presented in Fig. 3. The gas composition is given in percent volume of the total dry gas volume minus nitrogen supplied to create the inert environment necessary for the pyrolysis reaction. -

The main constituents of the released gases are CO_2 and CO. The CO_2 and CO yields are 54.4 ± 0.6 vol% and 30.1 ± 0.8 vol%, respectively, of the total gas released during the pyrolysis of SS. In com-

Table 5
Some physicochemical properties of aqueous condensates (AC).

Properties	Aqueous condensates	
	Sorghum straw (SS)	Millet straw (MS)
Physicochemical properties (excluding initial water, ar)		
Water content (%)	82.8 ± 0.2	84.6 ± 0.2
TOC (gL^{-1})	147.6 ± 0.8	244.0 ± 1.2
COD (gL^{-1})	697.7 ± 1.8	899.4 ± 0.8
Ultimate analysis (dry basis)		
Carbon (wt. %)	31.9 ± 3.1	40.9 ± 4.5
Hydrogen (wt. %)	18.5 ± 0.2	15.7 ± 0.2
Oxygen (wt. %)	49.6 ± 3.3	43.4 ± 4.3

Table 6
Main compounds identified in aqueous condensates.

Compounds	Sorghum straw (wt.%)		Millet straw (wt.%)	
	wet	dry	wet	dry
Non-aromatic Compounds				
Acids	6.0 ± 0.2	34.4 ± 1.1	4.6 ± 0.0	29.8 ± 0.1
Esthers	0.0 ± 0.0	0.1 ± 0.0	0.0 ± 0.0	0,0.1 ± 0.0
Alcohols	0.1 ± 0.0	0.4 ± 0.0	0.1 ± 0.0	0.5 ± 0.0
Aldehydes	0.3 ± 0.0	1.8 ± 0.1	0.2 ± 0.0	1.4 ± 0.0
Ketones	6.7 ± 0.3	38.9 ± 1.5	5.4 ± 0.0	35.4 ± 0.1
Heterocyclic Compounds				
Furans	0.7 ± 0.0	4.2 ± 0.2	0.6 ± 0.0	3.7 ± 0.0
Aromatic Compounds				
Aldehydes	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.1 ± 0.0
Lignin-derived Phenols	0.2 ± 0.0	9.5 ± 0.2	0.3 ± 0.0	1.2 ± 0.0
Guaiacols (Methoxy phenols)	0.1 ± 0.0	3.6 ± 0.1	0.1 ± 0.0	0.8 ± 0.0
N-compound	0.0 ± 0.0	0.1 ± 0.0	0.0 ± 0.0	0.1 ± 0.0

Note: water content > 80 wt%.

Table 7
Elemental analysis and ash content of SS and MS pyrochars.

Pyrochars	Elemental analysis (wt.%, db)				Ash (%, d)	HHV (MJ kg^{-1})
	C	H	O	N		
SS	66.2 ± 2.1	2.9 ± 0.0	7.4 ± 0.8	1.0 ± 0.0	22.1 ± 1.3	25.3 ± 0.9
MS	51.3 ± 0.1	2.4 ± 0.2	7.7 ± 1.0	0.6 ± 0.0	37.9 ± 0.4	19.2 ± 0.5

db: dry basis.

parison, the CO_2 and CO released by MS are 49.5 ± 0.7 vol% and 35.1 ± 0.1 vol%. The results compare well with that reported for hardwood, softwood, wheat straw, and wheat bran [19]. As previously explained, the high volume of both gases can be traced to the catalytic effect of potassium salts in MS and SS. The minor constituents are other gases that include H_2, CH_4, and gaseous hydrocarbons (C_2–C_5 alkanes and alkenes), and their percent volume is similar for both feedstocks investigated. The pyrolysis gas contains syngas' main components (CO_2, CO, and H_2) and can be utilized as an energy source [52].

Fig. 3. Percent volume composition of pyrolysis gas released during fast pyrolysis sorghum straw (SS) and millet straw (SS). Error bars represent the standard deviation.

3.3. Van Krevelen diagram

The atomic ratios, O:C and H:C, were estimated from the elemental analysis of the feedstocks, organic-rich condensate, and pyrochars and are represented in the Van Krevelen diagram shown in Fig. 4. The plot shows that fast pyrolysis conditions significantly reduced the O:C and H:C atomic ratios of the pyrochar, indicating a highly carbonaceous solid with increased carbon–carbon bonds compared with the original biomass. These conditions, however, have a slight effect on reducing the O:C atomic ratio of organic condensate but increased its H:C atomic ratio. As discussed in previous sections, this resulted in the organic condensate calorific value being higher than that of the feedstocks. Generally, pyrolyzing SS and MS enhanced the fuels' energy content, making them more viable energy sources [75].

3.4. Carbon balance

Carbon in biomass is the only renewable (biogenic) carbon source [18]. The accurate knowledge of how carbon in biomass is distributed in fast pyrolysis products is key to effectively utilizing the byproducts generated from the process (pyrochar and gas). Fig. 5 shows the percent weight distribution of carbon in the pyrolysis products based on the solid elemental and gas compositional analyses. The result indicates that the amount of carbon retained in the SS and MS organic-rich condensate (without solids) is higher than the carbon fraction in the pyrochars. Up to 20 wt% carbon was estimated to be in noncondensable gases released by both feedstocks, which implies an effective use of the gases should also be considered.

A similar trend was reported for the elemental carbon distribution in the fast pyrolysis products of wheat straw, miscanthus, and scrap wood [18].
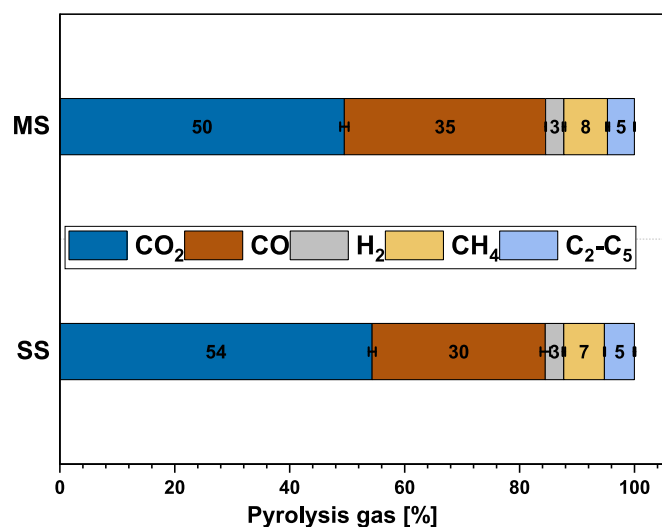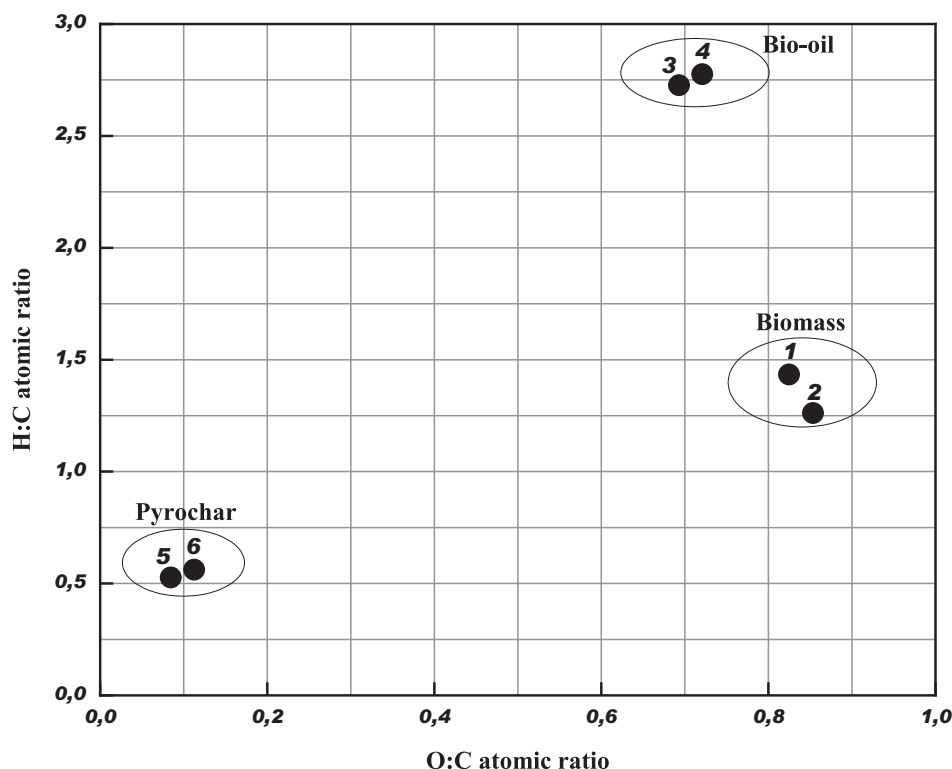
Fig. 4. Van Krevelen of raw feedstocks, bio-oils, and pyrochars (raw SS-1, raw MS-2, SS bio-oil-3, MS bio-oil-4, SS pyrochar-5, MS pyrochar-6).
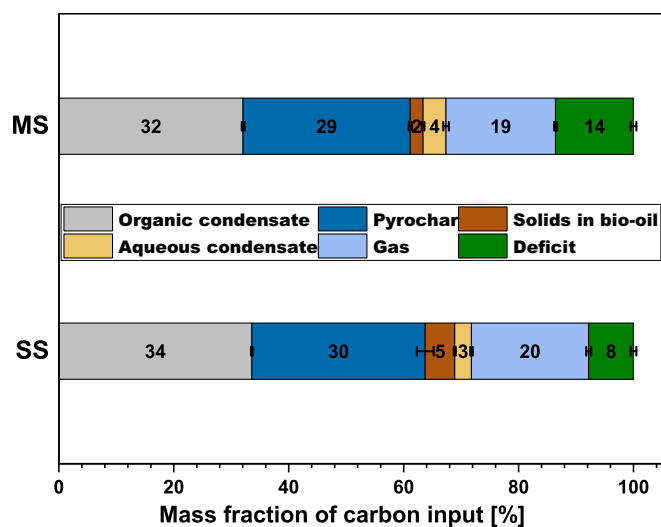

Fig. 5. Carbon distribution in the fast pyrolysis products of sorghum straw (SS) and millet straw (SS). Error bars represent standard deviations of measurements.

4. Conclusion

Fast pyrolysis of sundried sorghum straw (SS) and millet straw (MS) sourced from arid and semi-arid regions of Nigeria was conducted using a 10 kg.h^{-1} twin-screw mixing reactor. Organic-rich condensate (ORC) produced from both feedstocks exhibited similar properties. It is noteworthy to mention that hemicellulose content is suspected to have a greater impact on the pyrolysis gas yields of SS and MS than the effect of the ash they contained. Moreover, the ash content in the feedstock seems to reduce the ORC yield. MS, despite its higher cellulose content, yielded lower ORC than SS, due to its higher ash content. Furthermore, compared to other ash-rich feedstocks such as wheat straw and miscanthus, SS and MS recorded lower yields of ORC and higher yields of pyrochar

and pyrolysis gas. The low ORC produced from both feedstocks was characterized by low water content (<10 and 15 wt%, for SS and MS respectively) which might be attributed to the effect of sun drying.

More organic compounds were detected in the ORC recovered from MS compared to SS. ORC from MS is more acidic with an acids content of approx. 12.6 wt%, dry. Although less phenolic in concentration, and contained lignin-derived phenols of about 14.8 wt%. It had more lignin-derived phenol's derivative compounds than that from SS with acids and lignin-derived phenols contents of 11.1 wt %, and 15.4 wt%, dry, respectively. Some other important organic compounds identified in ORCs from SS and MS, useful for industrial applications, include levoglucosan, furans, and ketone derivative compounds. These compounds, however, were found in low concentrations. Therefore, SS and MS pyrolysis products are considered suitable for bioslurry production, which can be gasified into syngas or combusted to produce heat and electricity. Nonetheless, more studies are required to improve the yield and quality of ORCs from SS and MS. Further research would include the effect of feedstock pretreatment (such as washing and particle size), and the effects of the pyrolysis temperature, condensation temperatures, and organic vapor residence time in the reactor. These efforts can lead to the more efficient and sustainable conversion of sundried SS and MS into valuable products.

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CRediT authorship contribution statement

Joshua Oluyinka Ajikashile: Conceptualization, Writing – original draft, Data curation, Methodology. **Muhammad-Jamal Alhnidi:** Visualization, Investigation, Data curation, Formal analysis.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.mset.2023.03.007.

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