CHARACTERIZATION OF SWITCHGRASS CHAR PRODUCED IN TORREFACTION AND PYROLYSIS CONDITIONS

Guillaume Pilon and Jean-Michel Lavoie*

In this research, char was prepared from Switchgrass (*Panicum virgatum*) cave-in-rock species and characterized from the perspective of value addition either as a soil amendment or as a feedstock for energy production. Char from torrefaction/pyrolysis was produced in a fixed bed lab-scale reactor, using a N_2 flow at three temperatures (300, 400, and 500°C) and for two residency times (2.5 and 5 minutes). Proximate and ultimate analyses as well as calorific value tests were done on each of the chars obtained. Chars scanning electron microscopy (SEM) pictures were taken. Organic composition of char leachates was characterized using gas chromatography-mass spectrometry (GC-MS) following a Soxhlet extraction with dichloromethane. Char was analyzed using FTIR-ATR. No significant difference was observed in most char characteristics between 2.5 and 5 min residency times, for each temperature studied. Among the compounds identified, two may be of particular interest with respect to the biochar domain. 1-undecanol, a compound commonly used as a growth regulator in agriculture, was observed in 300 and 400°C chars for 5 and 2.5 min residence time, respectively. Naphthalene, commonly used as an ingredient in pesticide products, was the only polycyclic aromatic hydrocarbon (PAH) observed in chars and was found solely in the extracts obtained from the char produced at 500 °C (for both residency times).

Keywords: Char; Pyrolysis; Torrefaction; Biochar; Switchgrass; Soxhlet extraction; PAH

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INTRODUCTION

Biomass char, for a long time considered as a residue, may play a major role in a biomass value addition chain. Char from torrefied biomass (≤ 300 °C) can contribute to the economic feasibility of a biomass supply chain as "solid fuel" by reducing the energy requirements during grinding, as well as transportation via densification, while improving storage stability (Felfli et al. 2005; Phanphanich and Mani 2011; Uslu et al. 2008; Zwart et al. 2006). For energy production, char may be advantageous for the overall process, either for gasification (CO_2 environment) or for combustion (Boateng 2007 and Prins et al 2006a). As reported by Phanphanich and Mani (2011), torrefaction char, in comparison to raw biomass, may also produce less tar during gasification, while its energy content is superior to the original feedstock. Nevertheless, char "solid fuel" feasibility still depends on its final price for the gasification or combustion user. Char obtained at higher severity conditions may also serve as a soil amendment, which can increase crop yield, store carbon (CO_2 reduction), and reduce the leaching of nutrients due to surface adsorption (Lehmann 2007).

Torrefaction techniques have been studied for a long time, and numerous findings have been reported. However, its investigations have mostly emphasized the use of wood as the original feedstock. In the past 5 years, published results using other lignocellulosic biomass as feedstock have been observed. Nevertheless, reported results usually have involved long reaction times, while convection within the reactor was rarely high. Sadaka and Negi (2009) studied how torrefaction of wheat straw, rice straw, and cotton gin waste with from 0 to 60 min treatment at 260 °C improved physical and thermochemical properties of the feedstocks for further utilization. Bridgeman et al. (2008) studied torrefaction of reed canary grass and wheat straw using thermogravimetric analysis (TGA) with the specific reacting conditions provided by TGA apparatus (low convection and few mg of powdery form material). However, torrefaction at 300 °C, at high heating rates, high convection, and short residence time (<10 min) of non-woody lignocellulosic biomass, investigating physicochemical characteristics of char has been, to our knowledge, sparsely reported in the literature.

As for pyrolysis char (>300 °C), especially for soil amendment applications (biochar), multitudes of factors influence its properties (Joseph et al. 2009). Strictly looking at physical properties, the factors considered to have a possible major effect on biochar properties are the original biomass (chemical composition, ash composition, size biomass), the operating conditions (temperature, heating rate, mass transfer rate, residence time, oxidative conditions, pressure, type of input (gas – vapour), catalyst), the pre-treatment (drying, crushing), and the post-treatment (activation, crushing) (Downie et al. 2009). Among these factors, the highest reacting temperature was reported as the major factor influencing on physical properties, while heating rate and pressure came in second. The overall biochar characterization domain with respect to production conditions is in development. According to Krull and co-workers (2009), some characterization methods such as solvent-extractable components of biochar have rarely been attempted and could provide valuable insight on characterization and eventually application of char as a soil amendment. Extraction of chars, followed by compound analysis, conducted on different wood charcoal barbecue briquettes have previously been reported in the literature. Authors found the presence of various PAHs, although no details on the production of the wood briquette were specified (Kushwaha et al. 1985). More recently, extraction of chars obtained from pyrolysis of plastic, wood, and tires wastes mixture (at 0.41 MPa and 420 °C for 15 min) were conducted in order to reduce their organic contaminants composition (Bernardo et al. 2009, 2010).

In this research, char was prepared from switchgrass (*Panicum virgatum*), a species that is being considered as an energy crop in many geographical locations in North America, including in Quebec (Canada). Switchgrass was selected due to its potential as a dedicated crop for energy production as well as for its agronomic attributes (Samson et al. 2005). Chars physicochemical characteristics as a function of temperature (300, 400, 500 °C) and residence time (2.5 and 5 min), at high heating rate and moderately high convection were analyzed. Such residence times were chosen in order to verify conditions that might be beneficial for smaller reactor sizing as well as for the biomass supply and transformation chain rate. Chars were characterized for proximate and ultimate analyses as well as calorific value tests. Scanning electron microscopy (SEM) pictures were taken to follow the changes of biomass physical structure. BET analysis was carried out to study effects related to surface area. FTIR using attenuated total reflectance equipment (ATR) was also utilized to follow char chemical transformation as function of temperature. Organic composition of char leachates were qualified using gas chromatography-mass spectrometry (GC-MS) following a preliminary Soxhlet extraction with dichloromethane.

EXPERIMENTAL

Biomass

Feedstock used for the experiments was Switchgrass (*Panicum virgatum*), cave-in-rock species. The feedstock was grown in the Eastern Township region of Quebec, Canada. Crops were cultivated in a clay soil, the material selected had a 1.5 years root system and was harvested in Fall (November 2009). The biomass was harvested and baled in 500 kg bales with moisture content below 10% and stored for about 6 months under open structures protected from rain before samples were taken in laboratory. Switchgrass samples used for this research were maintained in unsealed plastic bags at room temperature for 1 to 4 months (20 to 25 °C).

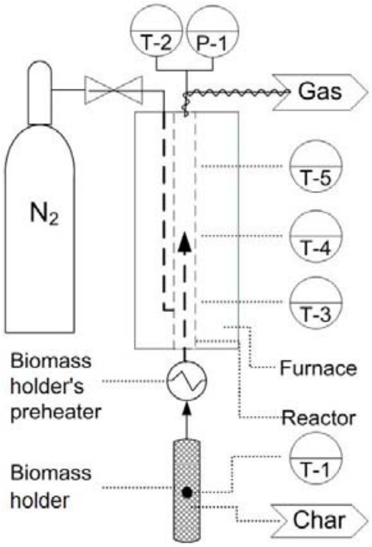
Experimental Setup and Biomass Char Production

Char production was conducted in a lab-scale fixed bed reactor. The reactor consists of a stainless steel tube installed within a furnace and mounted vertically (Fig. 1). Switchgrass was cut into pieces shorter than 10 cm. Biomass moisture levels, which varied all along experiments, typically ranged from 4 to 10% (dry basis). Before each test, a biomass holder (Figs. 2 and 3) was preheated to the reactor's temperature outside the reactor, using a preheater installed underneath the reactor, open to ambient air environment. This step was used to simulate the feeding of biomass into a reactor; such biomass would suddenly enter the reactor, therefore achieving high heating rates. The short contact with ambient air while passing from preheater to reactor simulates air that can enter in minor quantity within a non-purged continuous feeding system. For each batch, biomass was inserted in the preheated biomass holder, at 1g/batch and quickly inserted in the reacting chamber using a thermocouple as a displacing rod. This technique resulted in an almost instantaneous biomass heat-up to the desired reacting temperature (Fig. 4). The thermocouple (displacing rod) allowed monitoring of temperature variations within the biomass holder (Fig. 1 to 3). A quick connection around the thermocouple allows the sealed connection with the reactor when biomass holder and thermocouple are inserted. High convection around particles was obtained for a N_2 flow at 0.115 L/s (STP: 101.3 kPa – and 25 °C) using an inline flowmeter. The N_2 flow resulted in a superficial velocity estimated at 0.33 m/s in the holder (STP). These conditions were estimated to be slightly below minimum fluidization of the biomass particles. The inert gas was preheated at reactor's temperature using an inline preheater and passed within the furnace before entering the reactor (Fig. 1). Chars were produced at 300, 400, and 500 °C (± 5°C) for two distinct residence times in the reactor (2.5 and 5 min.) calculated from the instant biomass was inserted in the reactor (Fig. 4). Once the time of reaction was successfully reached, char was quickly taken out of the reactor, transferred in a pan and maintained into desiccator. Chars produced in several batches from specific conditions were homogenized as a unique sample prior to analysis. Further details about the reactor, the experimental setup, and the operating conditions were presented in a previous report (see Pilon and Lavoie (2011)).

Feedstock and Char Characterization

Proximate analysis, organic elemental analysis, calorific value and specific surface

Analytical methods for proximate analysis, organic elemental analysis, calorific value determination, BET surface area as well as cellulose, hemicellulose, and lignin content in the original biomass were all reported previously (Pilon and Lavoie (2011)).



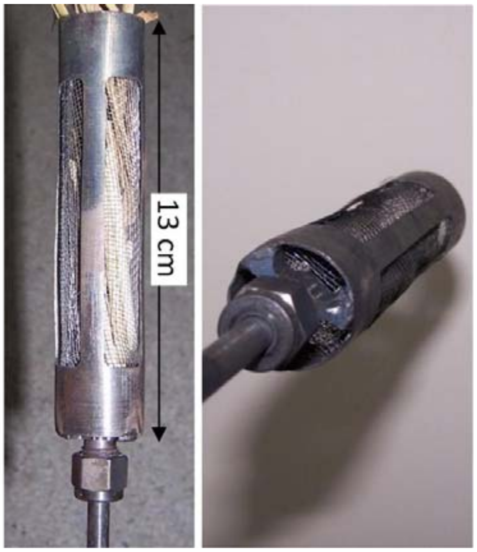


Fig. 1. Schematic representation of the experimental setup
Fig. 2 and 3. Side and bottom view of biomass holder

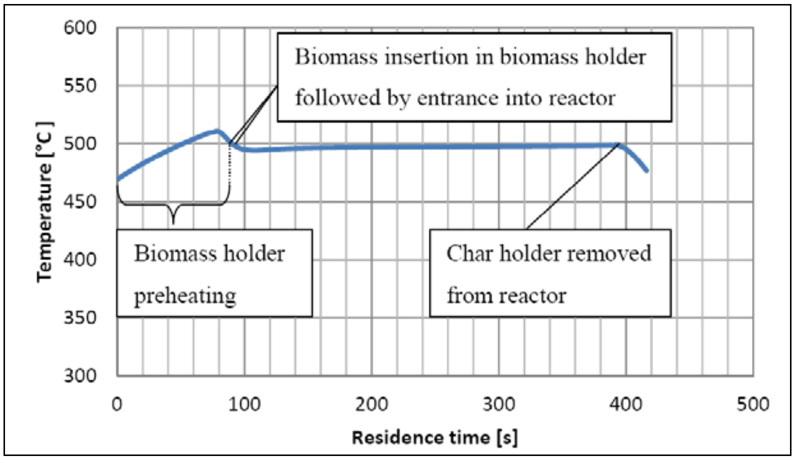


Fig. 4. Example of representative temperature profile within biomass holder during batch test for 500 °C – 5 min test

Scanning electron microscopy pictures

Scanning electron microscopy was performed using a Hitachi model VPSEM S-3000N device. Prior to SEM analyses, char was first applied on an autosticking carbon and its surface metalized, thus allowing conduction. Metallisation was done using an Anatech Hummer VI sputtering system using a 60%Au-40%Pd electrode. Pictures presented were taken at a magnification of 45X and 500X. Representative pictures were selected from pictures taken on a few samples.

Organic components extraction and GC-MS analysis

For each extraction, one gram of ground char (~90% 10-200 mesh particles size) was placed in cellulose cartridges of (25 mm ID X 90 mm) and extracted with 150 mL of dichloromethane. All extractions were done in triplicates. Extractions were conducted 8 hours at about 10 cycles/hr. After extraction, the solvent and extracts were filtered to remove any char particles and transferred into a round flask for concentration using vacuum roto-evaporator. Each concentration was done at 40 °C under a vacuum of 20 kPa relative to ambient pressure. Reduction was done until complete solvent evaporation. The concentrated product was collected using about 1-2 mL of dichloromethane, and the vials were kept at 4°C prior to injection in the GC-MS. The gas chromatograph utilized was a HP 5890 Series II equipped with HP 5971A Mass Selective Detector and HP 7673 Controller. The column was an HP-1ms GC column (Agilent Technologies). Each sample was analyzed in a splitless mode. Gas chromatography and mass spectroscopy were performed using temperatures of 325 °C (inlet) and of 280 °C (detector). The oven's temperature method consisted in an initial temperature of 90 °C for 1 min, followed by a temperature increase at 10 °C/min up to 180 °C. The heating rate was then changed to 5 °C/min up to 270 °C, where it was maintained for a total run time of 58 min. Compounds were identified using the Wiley7 library.

Char FTIR analysis

Solid char was analyzed by infrared spectroscopy using attenuated total reflectance (FTIR-ATR). The FTIR used in this experiment was a model 640 (Varian), while the ATR was purchased from Pike Technologies. Char pieces obtained for every studied condition were analyzed in four replicates. For each sample, 300 scans were run between 600 and 4000 cm^{-1}.

RESULTS AND DISCUSSION

Balance on Char Production

Figure 5 depicts char yield reduction behaviour with increasing temperature. Despite a slight reduction at 300 and 400 °C, ANOVA statistical method showed no significant difference among each residence time for all temperatures investigated ($\alpha = 0.05$). Char yields and analytical results (on a char basis) are presented in Table 1. Based on values obtained in Table 1, biomass losses (on an original biomass basis), in function of temperature, are shown in Table 2 in order to follow the composition of feedstock losses. For the char obtained at 300 °C (2.5 or 5 min.), volatile content seemed to be the main loss (Table 2). Volatiles losses were mostly related to oxygen losses, which were found to be a twofold value in comparison to the carbon losses (Table 2). The 30-32% mass loss for the char produced at 300 °C (Table 2; expressed as CHON or volatile losses) could correspond mostly to hemicelluloses decomposition; hemicelluloses are known to decompose at temperatures ranging from 225 to 300 °C (Prins et al. 2006b). Hemicelluloses in switchgrass cave-in-rock species were evaluated at 36.3% (determined by difference between holocellulose and α-cellulose; Pilon and Lavoie 2011) (Table 3), a value close to what was reported by Lemus and co-workers (2002), who quantified the hemicelluloses to reach up to 32% for cell wall components. On the other hand, char losses cannot be related solely on hemicelluloses degradation. Despite their conversion, hemicelluloses volatiles may also condense to form tar or coke, partly constituting char (Sharma et al. 2002). Cellulose and lignin are known to decompose from 305 to 375 °C and from 250 to 500 °C respectively, therefore these two biomass constituents, especially lignin, must also account, to a certain extent for the losses observed at 300 °C.

Results obtained at 300 °C can be compared with those of Gilbert and co-workers, who torrefied switchgrass at 250 °C for 2h and obtained char yields of 72%$_{\text{d.b.}}$ with elemental and proximate analysis fairly similar to results observed in this study (Table 1) (Gilbert et al. 2009). This suggests that within much shorter residence time (2.5 min), much higher heating rates and superficial velocity (about 100X more), and 50 °C temperature increase, similar torrefied biomass properties could be obtained. As a result, this could represent a potential improvement of torrefaction systems in terms of energy requirements, system production rate, and reactor sizing due to lower residence time. Further research should therefore be conducted on these operating conditions with respect to torrefied feedstock properties.

For char production at temperatures of 400 °C and 500 °C, char yield was drastically reduced (27.3-25.3 and 12.4-12.3% respectively) (Table 1). Hemicelluloses, cellulose and lignin are known to decompose at temperatures of 225 to 300 °C, 305 to 375 °C and 250 to 500 °C respectively (Prins et al. 2006b). Cellulose was reported by Lemus and co-workers to represent 37.8% of the bone-dry mass of switchgrass (Lemus et al. 2002), which is comparable to the 33.7% cellulose contained in the biomass from this study (Table 3); therefore the 73% mass reduction at 400 °C may very well correspond to the total holocellulose of switchgrass (see Table 3) and part of lignin. Lignin must have continued its decomposition further when pyrolysis temperature was increased to 500 °C, resulting in the 87% mass lost from original biomass for the char produced at 500 °C. Boateng and co-workers (2007) worked on the same feedstock, using a bench-scale fluidized bed fast pyrolysis reactor. They ran their tests at 500°C and obtained 12.9% of char yields. Their results are comparable to the values (12.4 and 12.3%) that were obtained in the present research for 2.5 and 5 min retention time respectively (Table 1). Nonetheless, at 500 °C, the contact of air with biomass while entering the reactor resulted in momentary ignition, while on exiting the reactor it presented signs of char glowing red (oxidative pyrolysis). These momentarily conditions necessarily contributed to mass losses. This may also account for the char ash losses observed at 500 °C (see Table 2). No ignition or red glowing char was noted for 400 °C; however short oxidation may have occasioned char yield reductions. Sharma and co-workers (2002) observed char yield reduction during oxidative pyrolysis of tobacco under similar conditions. Brewer and co-workers (2009) also produced switchgrass char at 500°C using a fluidized bed reactor and obtained slightly higher char yields (15-20 %).

Char moisture content increased with process temperature (see Table 1). This behaviour is consistent with hydrophobic character of torrefaction chars and water sorption properties of pyrolysis biochar (Felfli et al. 2005; Rutherford et al. 2010).

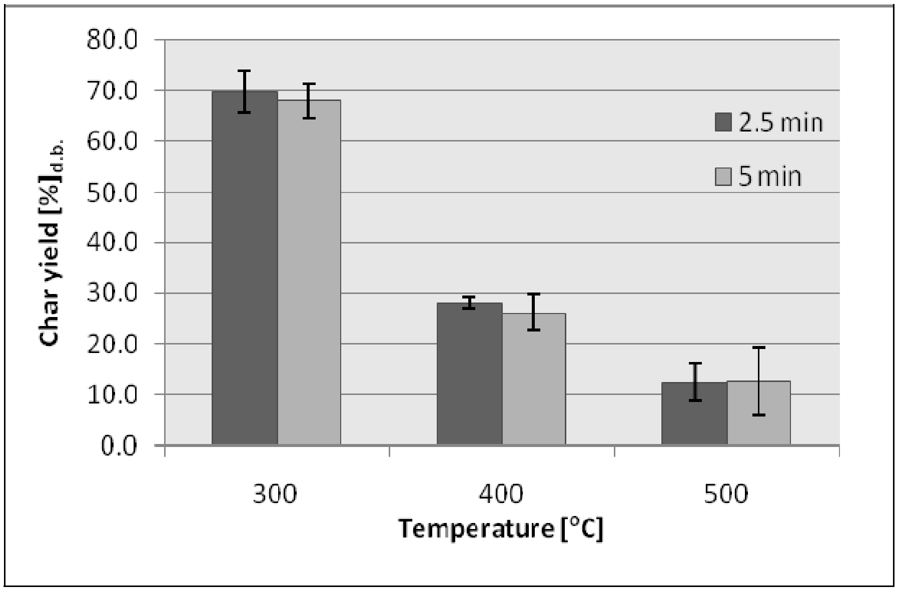


Fig. 5. Char yield obtained from pyrolysis of Switchgrass at 300, 400 and 500°C, for 2.5 and 5 minutes. (d.b.: dry basis WRT original biomass). Error bars correspond to standard deviation.

Heating Value

The maximum higher heating value (HHV) was obtained for the char produced at 400°C (Table 1). Under these conditions, the 2.5 and 5 min processes resulted in increases of 36.6% and 23.1% respectively with reference to the original feedstock. ANOVA statistical analysis showed that there was no significant difference between chars produced for the two residence times of 2.5 and 5 min for each specific production temperature ($\alpha = 0.05$). The decrease in heating value at 500 °C could be resulting from the decreasing volatile content and the increasing ash content (Table 1). HHV obtained for the 500°C char (19.6 and 22.4 MJ/kg for 2.5 and 5 min respectively) are comparable to values obtained by Boateng and co-workers (2007), who obtained 19.4 MJ/kg using a bench-scale fluidized bed reactor (see Table 1).

SEM Figures and BET Results

Scanning electron microscopy pictures (see Fig. 6 and 7) present the degree of decomposition as function of temperature at two enlargement levels, 45X and 500X respectively. The 45X enlargement (Fig. 6) shows the structural breakage as temperature increases, which is consistent with observations from previous research aimed on structural breakage during devolatization (Downie et al. 2009). These results are consistent with the observations made during grinding of material, where original biomass grinding was a tedious process, 300 °C char crumbled easily, and a powdered material was obtained much more easily at 400 and 500 °C.

Table 1. Production Mode, Yield, Composition, Heating Value, and Surface Area of Representative Switchgrass Chars

Mat.	R.Bed	T°	RT	HR	Conv	Yield	C	H	O	N	H/C	O/C	MC	Ash	VC	FC	HHV	S.A.	References
		[°C]	[min]	[°C/min]	*	[%][1]	[%][1]	[%][1]	[%][1]	[%][1]	**	**	[%]	[%]	[%]	[%]	[MJ/kg]	[m^2/g]	
RSG	na	na	na	na	na	na	44.5	5.8	45.7	0.5	1.55	0.77	6.2	3.7	81.0	15.3	19.5	<1	Pilon and Lavoie[2]
SGC	Fixed	300	2.5	Fast	++	70.9	51.3	5.5	38.8	0.5	1.30	0.57	0.4	6.7	72.8	20.5	20.3	<1	Pilon and Lavoie[2]
SGC	Fixed	300	5	Fast	++	65.6	51.7	5.5	37.7	0.5	1.28	0.55	0.2	5.3	69.9	24.7	22.7	<1	Pilon and Lavoie
SGC	Fixed	400	2.5	Fast	++	27.3	65.4	3.8	20.9	0.7	0.70	0.24	1.8	11.8	34.2	53.9	26.6	3.6	Pilon and Lavoie
SGC	Fixed	400	5	Fast	++	25.3	67.2	3.7	19.6	0.6	0.66	0.22	1.6	14.6	33.2	52.2	24.0	4.5	Pilon and Lavoie
SGC	Fixed	500	2.5	Fast	++	12.4	63.9	2.6	15.0	0.6	0.48	0.18	1.3	26.6	20.8	52.6	19.6	66.6	Pilon and Lavoie[2]
SGC	Fixed	500	5	Fast	++	12.3	67.5	2.8	13.8	0.6	0.49	0.15	2.4	23.8	21.7	54.6	22.4	84.6	Pilon and Lavoie
SGC	Fixed	250	120	10	+	72.0	50.9	5.6	37.3	0.8	1.33	0.55	3.7	4.8	70.7	20.8	20.6	n/a	Gilbert et al. 2009
SGC	Fluidized	480	quick	Fast	+++	12.9	60.7	4.0	8.7	0.8	0.79	0.11	3.8	25.9	28.4	42.0	19.4	7.8	Boateng et al. 2007
SGC	Fluidized	500	0.025	Fast	+++	15-20	39.4	1.3	6.1	0.7	0.4	n/a	0.9	52.5	7.1	39.5	15.37	50.2	Brewer et al. 2009

n.b. [1]: Percentages are expressed on a dry basis. [2]: Part of these results are presented in (Pilon and Lavoie 2011) along a complementary study.
Legend: Mat.: material, R.Bed: reactor bed, RSG: raw switchgrass, SGC: switchgrass char, T°: temperature, na: not applicable
RT: residence time, HR: heating rate, Conv: convection, MC: moisture content, VC: volatile content, FC: fixed carbon,
HHV: higher heating value, S.A.: surface area, n/a: not available, *: medium "++" to very high "+++", **: molar basis.

Table 2. Losses Occurring from Original Switchgrass for Char Production

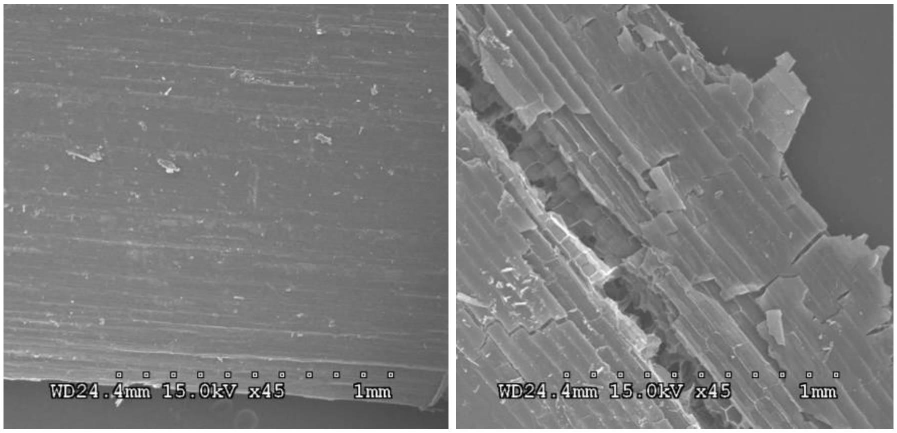
Comparison Conditions	C	H	O	N	CHON losses	Ash	VC	FC	VC + FC losses
	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]
RSG to SGC 300°C	9.1	2.0	19.3	0.2	30.6	0	32.3	0	32.3
RSG to SGC 400°C	26.8	4.7	40.1	0.4	72.0	0.2	72.2	1.4	73.6
RSG to SGC 500°C	36.1	5.4	43.7	0.5	85.6	0.5	78.4	9.0	87.9

n.b.: Percentages are expressed on a dry biomass basis & RT 2.5 and 5 min results were averaged for every temperature condition.

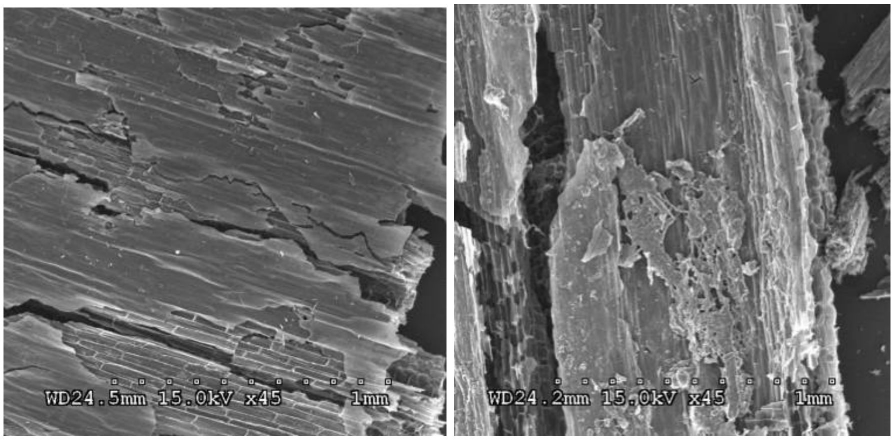
Table 3. Switchgrass Characterization

Identification	Mass Units *(± S.D.)**
Ash	3.7 *(± 0.2)*
α-cellulose	33.7 *(± 0.7)*
Hemicellulose	36.3 *(± 1)*
Lignin	17.3 *(± 0.6)*
Total	**100**

* Expressed in terms of 100 mass units of oven dry switchgrass straw.



Raw Switchgrass 300°C - 5 min

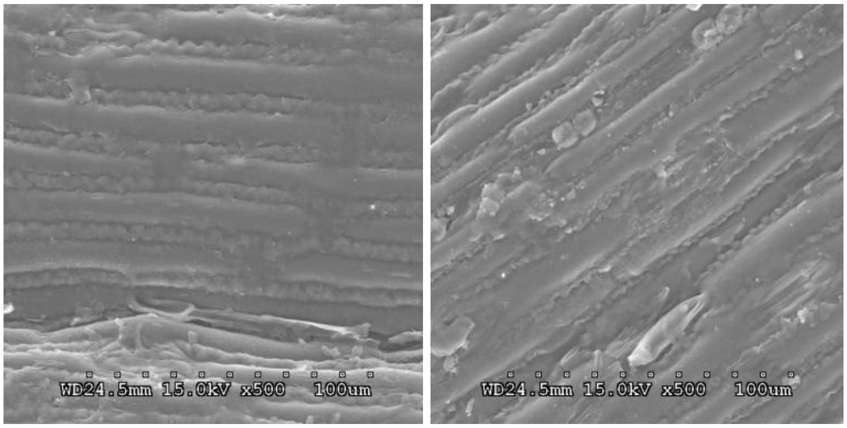


400°C – 5 min 500°C – 5 min

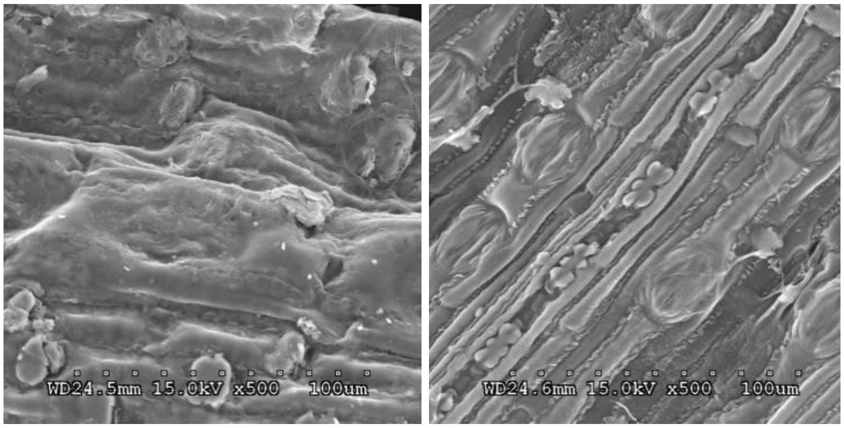
Fig. 6. Scanning electron microscopy pictures of raw switchgrass and switchgrass chars for 45X enlargement.

At 500X enlargement (Fig. 7), it is not possible to observe such structural modifications. Magnification (see Fig. 7) showed that, as temperature increased, some biomass sublayers and structures tend to appear more pronounced, which might contribute to increased surface area of char (Table 1). As reported by Downie and co-workers (2009), temperature increase may result in enhancement of char micropores development to some extent. However, it is not possible to discern such micropore development from the pictures taken (Fig. 6 and 7). It has to be noted that the surface presented is the side of an original plant structure and not the tip of a cut plant structure, where cavities resulting from inner plant structure could appear more pronounced. Such types of cavities (side view) may be observed in Fig. 6, resulting from structural breakage at higher temperatures.

Despite the fact that pore development could not be observed using the SEM (see Fig. 7), BET surface area increased at 500 °C, reaching values ranging from 66.6 to 89.0 m^2/g for 500 °C at 2.5 min and 5 min respectively. Increasing BET surface area at 500 °C may result from this structural breakage, allowing access to inner plant cavities, enhanced by devolatilization. High heating rates such as the one obtained along these experiments, combined with the higher temperature levels are reported to enhance devolatilization, resulting in structure breakage (Biagini et al. 2009). BET surface area results obtained for 500 °C are similar to those reported by Brewer and co-workers (2009) who obtained 50 m^2/g using a fluidized bed reactor. On the other hand, Boateng (2007) got a BET surface area of 7.8 m^2/g for their char produced in fluidized bed reactor. Despite the increasing BET surface area, values obtained in this study for the 2.5 and 5 min chars (500 °C) have shown no significant statistical difference.



Original 300°C - 5 min



400°C - 5 min 500°C – 5 min

Fig. 7. Scanning electron microscopy pictures of raw switchgrass and switchgrass chars for 500X enlargement

Char Extractions and Composition Analyses

The compounds identified in the dichloromethane char extracts are reported in Table 4. In addition, the content of extracted compounds is presented in Table 5. Among the identified compounds, aliphatic compounds were observed only at 300 and 400 °C, while none was identified at 500 °C. This observation is consistent with the work of Sharma and co-workers (2002), who observed from FTIR and NMR char analyses a rapid loss in aliphatic groups and an increase in aromatics for temperatures above 450 °C. Additionally, the same authors reported that chars formed from cellulose below 400 °C had a higher concentration in aliphatics than chars obtained at higher temperature. This assumption could be supported by the FTIR-ATR analysis on char, where bands growing around 800 cm^{-1} as well as around 1600 cm^{-1} with increasing temperatures (Fig. 8) were observed. In both cases, the band appeared suddenly at temperatures starting from 400 °C. Wavenumbers of 700 to 900 cm^{-1} can be associated with aromatics, as well as the peak at 1600 cm^{-1}, which can correspond to a conjugated C=C link, also common in aromatic compounds. The band decreasing between 2800 and 3000 cm^{-1} would also be consistent with this assumption, since this band may correspond to two aliphatic bands (aliphatic CH_3 (2946-2987 cm^{-1}) and aliphatic CH_2 (2888-2946 cm^{-1})). The observation is also supported by the H/C and O/C ratios, decreasing with increasing temperature (Table 1) which may correspond to an increase in aromatic structure concentration (Krull et al. 2009). Other results at wavenumber of 885 cm^{-1}, consistent with observations of Uchimiya and co-workers (2011), indicated the appearance of aromatic C-H at temperature higher than 500 °C.

The appearance of naphthalene, a polycyclic aromatic hydrocarbon (PAH), observed at operating conditions of 500 °C, also supports the previous assumptions (Table 4). PAH formation usually increases with operating temperature, where aromatic rings may loose their functional groups, eventually combining into PAH (McGrath et al., 2001; Nakajima et al., 2007). Additionally, this temperature corresponds to the level at which lignin thermal decomposition is enhanced; therefore aromatisation of dimeric fractions from lignin may have occurred, leading to naphthalene formation. Sharma and co-workers (2004) concluded that char aromatic content and inorganics may act as catalyst in PAH formation. As reported by McGrath and co-workers (2001), appearance of naphthalene might be critical for further thermochemical transformations, since heavier PAH can be created from aliphatic substrate through naphthalene.

Naphthalene has been classified as a group 2B chemical, a category regrouping compounds possibly carcinogenic to humans (Nakajima et al. 2007). The same product is also commonly sold as mothballs, and naphthalene containing products are already used in soil as a fumigant pesticide under risk mitigation measures (EPA 2008). Extraction yields at 500 °C correspond to 1.3-1.1mg of extract per g of char (2.5 and 5 min respectively) (Table 5). Linked with the relative content of naphthalene obtained, these value could provide a rough estimate on how much char produced under these specific conditions could be applied on soil with respect to environmental regulations. However, because several other compounds remain to be identified and quantified as well as their effect and interaction with soil and plant remains to be clarified, these values provide a first estimate for further research in the domain, which should rely on an exhaustive qualification and quantification of the all the compounds extracted from the char.

The 1-undecanol that was identified at 300 °C – 5min and 400 °C – 2.5min is a compound that could be of interest for biochar as soil amendment, since this compound is already sold as a growth regulator (ScFinder 2011). Occurrence of such a compound highlights the necessity to investigate more intensively the chemical composition of char with respect to char test conducted in soil in order to possibly establish some relationship.

It can be observed that vanillin, a single benzene ring, was found only at 300 and 400 °C (CAS # 121-33-5). Since vanillin was shown to decompose only at temperatures above 550 °C (Shin et al. 2001), it is most likely that this compound disappeared simply due to its phase change, its boiling point being estimated at 285 °C (Lide 2008). These results are consistent with softwood lignin volatiles analysis reported by Sharma et al. (2004), mentioning that they contained mostly vanillin and guaiacol. Guaiacol was also observed at a temperature of 300 °C (CAS #90-05-1, Table 4).

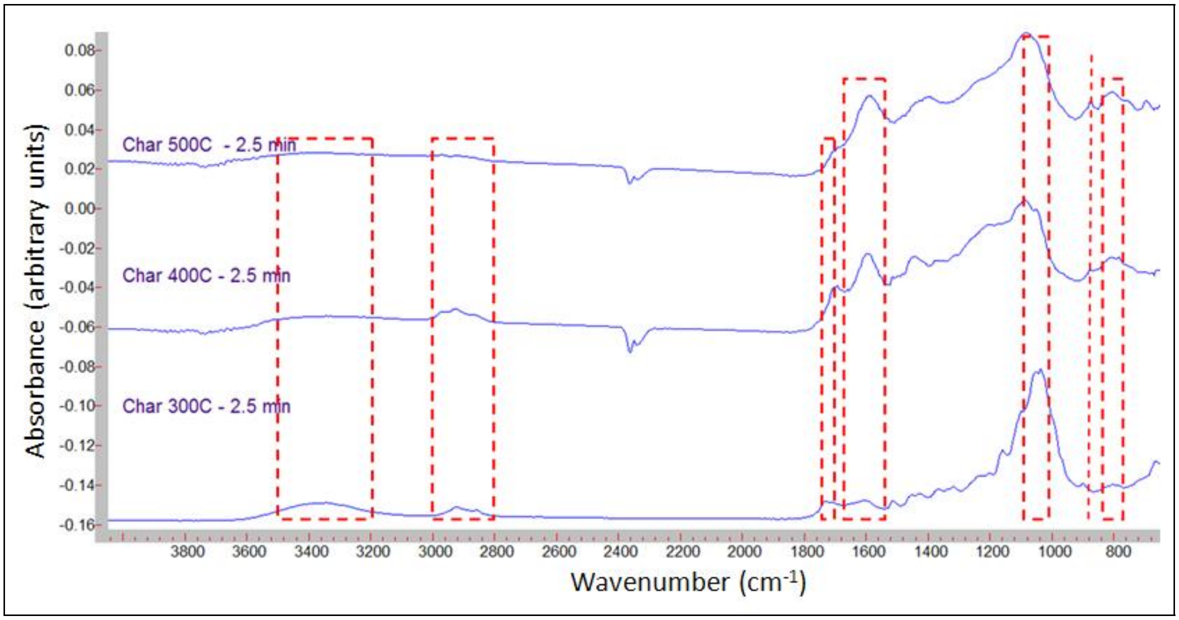


Fig. 8. FTIR spectrums of chars obtained using attenuated total reflectance equipment (ATR) for 300-500 °C and 2.5 min pyrolysis conditions

As reported by Uchimiya and co-workers (2011), the decrease in bond stretching between 3200-3500 cm^{-1} while increasing temperature from 300 to 500 °C represents a decrease in O-H related to hydrogen bonded hydroxyl groups. These findings may correspond to water formation, possibly linked to the aqueous content found in pyrolysis oils. The 1700-1740 cm^{-1} wavenumbers showed an increase from 300 to 400 °C and a decrease from 400 to 500 °C which can be associated with a carboxylic acid group (Fig. 8). However, the only compound identified containing a carboxyl group is hexadecanoic acid observed at 300 °C 2.5 min (Table 4). A decrease in the IR absorbance from 1030-1100 cm^{-1} for 300 to 400 °C chars may be the decreasing amount of C-O bonds, which would be consistent with high reduction in volatiles and oxygen content (Table 2), an observation that can be correlated with IR results presented by Uchimiya and co-workers (2011). The negative peak observed near 2350 wavelength corresponds to a main CO_2 wavelength; the latter may become negative during background subtraction due to laboratory environment gas variations.

As presented in Table 5, the amount of extracts from char behaves as could be expected; it decreases with increasing temperature as well as with increasing reactor residence time. It is known that compounds present on char may result from volatile products condensation (Sharma et al. 2002) and that increasing temperature and residence enhances further conversion of these condensed volatiles. The amount of extracted products (Table 5) with the relative amount of compounds (Table 4) provides an approximation of identified compound presence. Further analyses with compounds quantification would beneficiate the results. In addition, char characterization studies could gain from having higher char reactor productivity; char content for extraction could also be increased in order to increase abundance response. In terms of value addition, especially for biochar as a soil amendment, char could be produced with a specific content of desired or undesired compounds, which will necessarily have to be considered along technology and product development. These results give some initial insights. However, follow-up work is needed for the understanding and sustainable development of this domain. For instance, work is needed to clarify why the char may contribute in soil and plant productivity in some conditions and less in others, and in defining conditions under which chemical characteristics appear, in concert with physical characteristics.

Table 4. Identified Compounds from DCM Extractions of Switchgrass Chars

Identified Compounds*	CAS	RT (min)	300°C 2.5 min	300°C 5 min	400°C 2.5 min	400°C 5 min	500°C 2.5 min	500°C 5 min
Molecular chains								
1-Decene	872-05-9	10.44	3.1					
1-undecanol	112-42-5	10.47		3.2	17.9			
Heptadecane	629-78-7	12.44			7.7	2.3		
1-Tetradecanamine, N,N-dimethyl-	112-75-4	14.08	12.5	6.6				
Hexadecanoic acid	57-10-3	18.02	2.1					
1 Benzene cycle and derivatives								
Phenol, 2-methoxy-	90-05-1	5.12		4.0				
Phenol, 4-ethyl-2-methoxy	2785-89-9	7.70	2.0	5.3				
Phenol, 2,6-dimethoxy-	91-10-1	8.53	2.1	12.1				
Benzaldehyde, 4-hydroxy-3-methoxy-	121-33-5	9.15	13.1	19.4	10.0	2.3		
Benzaldehyde, 3,4-dimethoxy-	120-14-9	10.12			6.3			
Benzaldehyde, 4-hydroxy-3,5-dimethoxy-	134-96-3	12.64	9.5	9.5				
Polycyclic aromatic hydrocarbons								
Naphthalene, decahydro-, trans-	493-02-7	5.04					41.5	25.4
Naphthalene, decahydro-, cis-	493-01-6	5.61					16.8	18.0

RT: retention time *Presence of compound is indicated by its relative content.

Table 5. Amounts of DCM Extractions from Switchgrass Chars

T°	°C	300	300	400	400	500	500
RT	min	2.5	5	2.5	5	2.5	5
Extract	mg/g char	2.8	2.5	1.9	1.5	1.3	1.1

CONCLUSIONS

1. Among the identified compounds from char extractions, two compounds are already used in agriculture under risk mitigation measures: the 1-undecanol-1, a growth regulator, and naphthalene, a product compound used in soil as a fumigant pesticide. Naphthalene was the only polycyclic aromatic hydrocarbon found in the chars.
2. Char production at a temperature of 400°C allowed the maximum HHV increase over the original biomass. Nonetheless, mass reduction with respect to original biomass was much greater at 400 °C (72%) than for 300°C (31%). At 300 °C, it was also shown that char yields and properties were fairly similar to results obtained by other authors operating at 250 °C for 2 hours, but for differing process conditions.
3. Residence time increasing from 2.5 to 5 min did not lead to significant difference between most char characteristics.
4. Scanning electron microscopy pictures showed that charred switchgrass surface does not appear more porous under the studied conditions. The increasing BET surface area at 500 °C would mostly be the result of a structural breakage at these temperature levels, allowing an access to inner plant cavities, enhanced by devolatilization.

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