Biomass char production at low severity conditions under CO_2 and N_2 environments

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Abstract

In a perspective of biomass value addition, biomass char, a thermochemical product, long time considered as a residue, is now getting attention and may represent a vector in the sustainability of the whole biomass sector. Some char types were shown to have great potential as a solid fuel or precursor for further transformations as well as having attributes for storage and transportation. Other types showed potential as a soil carbon sequestration technique and soil amendment enhancing biomass yields. Depending on several factors, but mostly on biomass and production conditions, biomass char physico-chemical characteristics may vary tremendously. Therefore, in order to be used in accordance for specific utilizations, its characteristics must be carefully understood and controlled. In this study, chars with varying properties were produced in a custom-made lab-scale fixed bed reactor. Along these experiments, various biomass chars were produced under CO_2 and N_2 for temperatures of 300 and 500 °C. Char was produced from switchgrass (*Panicum virgatum L.*) an energy crop grown in Canada. It was then characterized for ultimate and proximate analysis as well as for calorific value. In addition, specific surface was characterized by Brunauer-Emmett-Teller (BET) technique. Char organic content composition was verified by Soxhlet extractions using dichloromethane and extracts were analysed by GC-MS.
Keywords: BET, biochar, biomass, bio-oil, char, CO_2, pyrolysis, torrefaction.

1 Introduction

Biomass char refers to biochar with respect to soil amendment, and to charcoal when referring to the charred organic matter used as a source of energy

(Lehmann and Joseph [1] and McLaughlin *et al.* [2]). The latter has been shown to be a potential soil amendment that would enhance biomass production/hectare. It was also shown to have positive effects on soil health as well as being able to store carbon for reduction of CO_2 emission (Gaunt and Lehmann [3] and Lehmann [4]). Another application, potentially complementary to soil amendment [5], stated that biomass char also had potential to provide the required heat for pyrolysis' endothermic reaction along bio-oil production. Furthermore, it was shown to be advantageous as a feedstock for combustion or for syngas production through gasification (Boateng [6] and Uslu *et al.* [7]).

Biomass char can be obtained through different thermochemical processes operating at low oxygen content using varying degree of severity. In chronological order of severity, torrefaction, slow and fast pyrolysis and gasification are processes under which biomass char can generally be obtained. Torrefaction can be defined as the conversion of lignocellulosic material occurring without oxygen, within a temperature range of 200 to 300 °C at atmospheric pressure (Prins *et al.* [8] and Uslu *et al.* [7]). It consists mostly in hemicellulose degradation resulting in a solid material with low moisture content, hydrophobic properties and high calorific value if compared to original biomass. Most likely, biomass char obtained under torrefaction may not meet biochar stable soil characteristics since original biomass requires sufficient temperature (≥300 °C) in order to produce carbonized material with modified chemical bonds, which are less likely biodegradable (McLaughlin *et al.* [2]). Slow pyrolysis operates usually at temperature between 300 and 500 °C, at heating rates lower than 2 °C/s and long residence time (min to days), conditions that were shown to enhance char production over non-condensable gases and oil. Fast pyrolysis operates at higher heating rate (up to 10 000 °C/s), shorter residence time (<1s to 30s) and enhances biooil over char and non condensable gases yields (Brewer *et al.* [9] and Mohan *et al.* [10]). Gasification conditions operate with low-mid level of oxygen, yielding generally to about 5-10% biomass char. Despite their lower char production yield compared with slow pyrolysis, the potential of fast pyrolysis and gasification char were recently considered as having a soil amendment potential (Brewer *et al.* [9]).

Biochar physico-chemical properties vary to a large extent depending on a multitude of factors, especially the reacting conditions at which it is prepared (Joseph *et al.* [11]). The operating parameters that have been reported to influence its properties are the heating rate, the highest operating temperature, the pressure, the reaction residence time, the reactor design, the biomass pretreatments, the flow rate of inputs and the post treatments (Downie *et al.* [12]). Among these numerous factors, temperature is considered one of the most important factors affecting char properties as it provides the necessary activation energy of the implied reactions, furthermore it influences physical changes as volatilization and structural melts. Studies on wood showed that the three main biomass components have been reported to decompose at temperature ranging from 200 – 325 °C for hemicelluloses, from 240 to 375 °C for cellulose and from 280 to 500 °C for lignin (Prins *et al.* [8] and Downie *et al.* [12]). Demirbas [13] studied carbonization (medium rate pyrolysis at 10 °C/s) for several agricultural

and forest residues, for temperatures ranging from 300 to 900 °C. For every feedstock, solid products were found to decrease, gases increased and liquid fractions decreased, furthermore, higher heating values (HHV) were also found to increase for increasing temperature.

Pyrolysis gaseous environment also plays a major role. Conventionally, pyrolysis operates within an environment free of oxygen, therefore using inert gases such as nitrogen. CO_2 is also an inert gas at room temperature, however, increasing temperature, CO_2 becomes reactive and tends to react with carbon char through the reverse-Boudouard reaction, eqn (1).

$$C + CO_2 \rightarrow 2\,CO \qquad (1)$$

There are numerous thermochemical processes that could take beneficial advantage of using CO_2. In combustion field, especially in coal industry, the Oxyfuel Technology which consists of using flue gases with pure oxygen (CO_2, H_2O and O_2) instead of air (N_2, O_2, CO_2 and H_2O) appears as a promising technology especially from output CO_2 purity and sequestration point of view (Buhre [14]). In addition, use of flue gases as a gas source contains residual heat which is beneficial for energy flows within the overall process (Butterman and Castaldi [15]). In gasification, use of CO_2 to enhance Boudouard reaction and CO formation for syngas production is also a common practice. In physical activation of char for activated carbon, CO_2 is the medium used for surface area and pore enhancement. Physical activation is usually done at temperature around 900 to 1200 °C (Jindarom *et al.* [16]). In the presence of CO_2, char yield is usually reduced towards formation of volatiles (Minkova [17] and Butterman and Castaldi [15]). Jindarom *et al.* [16] observed that for temperatures around 350 to 750 °C, the use of CO_2 in comparison of N_2 resulted in chars with higher char specific surface and basicity levels.

High specific surfaces as well as high porosity are two desired characteristics for soil amendment applications since it may represent a favourable site for beneficial microorganisms proliferation as well as an exchange surface for nutrient retention or water absorption attributes (Lehmann and Joseph [1]). Under pyrolysis conditions, specific surface was observed to reach peak values at temperatures varying from 350 to 700 °C depending among a few factors, such as biomass types (Sharma *et al.* [18] and McLaughlin *et al.* [2]). Decrease in specific surface area at higher temperature was attributed, by some researchers, to melts in char structure. Increasing retention time was also shown to increase porosity since it allowed most volatilization reactions to reach completion. As for the heating rates, lower heating rates would allow volatile release with less morphological changes, therefore maintained natural porosity in comparison with higher rates which would even lead to morphological transformation of cell structure (Downie *et al.* [12]).

In this research, char was prepared from switchgrass (*Panicum virgatum*). Switchgrass was chosen due to its beneficial characteristics as an energy crop such as its hardiness in harsh climate conditions and poorer soils (He *et al.* [19] and Martel and Perron [20]). In a first step, a homemade fixed bed reactor was

tested along specific conditions simulating a high heating rate reactor operating under N_2 atmosphere. In a second step, the same reactor was then operated at lower heating rate, but adding new atmosphere conditions, first under N_2 and secondly under CO_2. Temperature, heating rate and gas atmosphere were the two main parameters studied and their effect on char physico-chemical characteristics was analysed. Char obtained was characterized for proximate and ultimate analyses, for BET as well as for its calorific value. Some of the chars organic content compositions were verified by Soxhlet extractions using dichloromethane and extracts were analysed by GC-MS. Bio-oil yield was also verified and the ones from slow heating rate were analyzed by GC-MS.

2 Materials and method

2.1 Biomass

Switchgrass (*panicum virgatum*) Cave-in-Rock specie utilized for the experiments was grown in the Eastern Township region of Quebec, Canada. The crop was grown in a clay soil and had a 1.5 years root system. The feedstock was harvested in Fall (November 2009) at moisture content below 10% in 500 kg bales and stored in open structures protected from rain. Switchgrass samples used for experiments were maintained in unsealed plastic bags at room temperature (20-25 °C).

2.2 Experimental setup

For experimentations, a lab scale fixed bed pyrolysis reactor was used. It consists in a stainless steel (SS) cylindrical reactor of 26.6 mm ID and 0.44 m length installed in a 2400W electric tube furnace mounted vertically. Biomass is added to reactor using a biomass carrier, fig. 1. The latter is 13 cm long, 25 mm OD in diameter and is made of stainless steel. Carrier's top, bottom and along the length is partially opened in order to allow gas flow through its structure. A wire mesh is installed within the carrier to retain the biomass from falling down. Reactor's entrance is controlled via a gate valve equipped with a motor for a quick control.

During the first experimental tests operating at higher heating rate, a preheater installed underneath the reactor was used in order to preheat the biomass carrier at reactor's temperature. The carrier has a top opening in order to fill it with biomass. The action of filling the reactor and taking it into the reactor is done for every test in less than 10 s. During the second step of experiments, at lower heating rates, preheater for biomass carrier was not used. Biomass carrier is attached to a thermocouple (T/C), which serves as a rod to move it into the reactor. The T/C also provides an indication on temperature progress within biomass carrier.

Nitrogen and carbon dioxide are the two gas vectors utilized while also serve to enhance heat and mass transfer between gases and feedstock. Gas flow input is maintained at 0.115 L/s (STP: 101.3kPa – and 25 °C) for every tests and is

controlled by a flowmeter before entering the reactor. The flowmeter is calibrated with respect to each gas. Nitrogen gas and CO_2 are respectively preheated before entering the reactor using an inline gas heater and while passing in the annulus region between reactor and tube furnace. Gases and volatiles exiting the reactor pass by a heated line maintained around 200 °C +/- 25 °C before being diverted to an exhaust system.

For pyrolysis vapours mass balance, vapours are collected within two consecutive glass condensers; both are kept within isothermal container filled with dry ice. Pyrolysis gases are obtained by difference from char and condensable liquid yields.

Real time temperature monitoring is done on the overall system using National Instrument Data Acquisition System NI cDAQ-9172 equipped with Labview software. Thermocouples are positioned all along the system as shown in figure 1. In figure 1, T corresponds to thermocouples, where T1 refers to biomass carrier, T2 to gas outlet, T3, T4 and T5 to annulus region between tube furnace and reactor, T6-T9 to outlet gas line, inside and at surface temperature and T10 at gas inlet to monitor gas inlet temperature. Pressure (P1, fig. 1) is
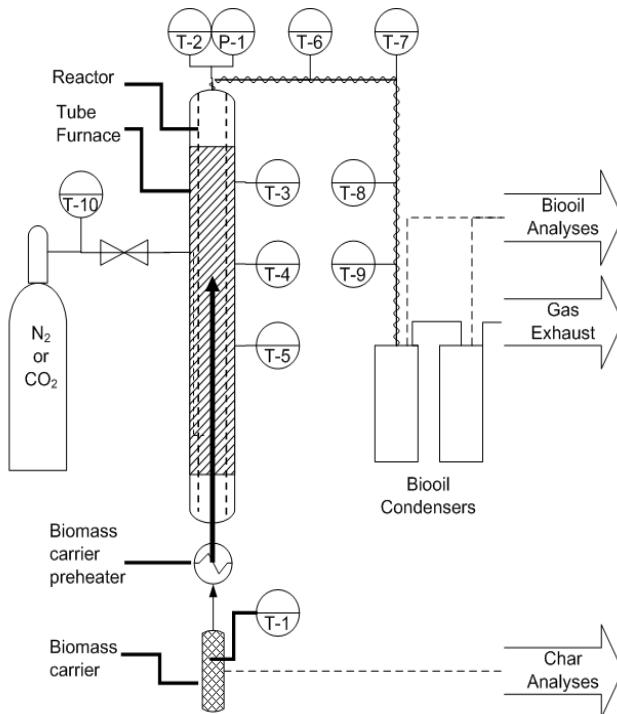

Figure 1:   Schematic representation of the experimental setup.

verified at reactor exit using a mechanical pressure gauge in order to maintain an absolute pressure close to 101.3 kPa in the reactor.

2.3 Biomass char production and products mass balance

Biomass was first cut into pieces shorter than 10 cm and humidity level, which ranged between 4 and 10%, was monitored all along the char production periods. Typically one gram of switchgrass was inserted in the biomass carrier per batch. For each batch operating at higher heating rates, the biomass carrier was first preheated until reaching reactor's temperature, before being rapidly filled with biomass and inserted in the core of the reactor. This resulted in an almost instantaneous heat up of biomass. Gas environment used at higher heating rate is N_2. At lower heating rate, a comparison between N_2 and CO_2 was done. In these latter conditions, the biomass carrier was not preheated, biomass was inserted in the carrier, approached to reactor's opening to flush air and rapidly entered within the reactor. Biomass is kept in reactor for a desired residence time of 2.5 minutes, after what it was removed from the reactor, emptied, its content cooled down within a desiccator and transferred within hermetic containers until further analysis. Along experiments at high heating rate, time was monitored from the moment the biomass was inserted in the preheated carrier. For moderate heating rates, time was counted once the temperature reading indicated the desired temperature. It took about 7.5 and 9.5 min. to reach 500 and 300 °C respectively for slow heating rates conditions. For all batches, tube furnace was maintained at a fixed temperature. Chars were produced at 300 and 500 °C +/- 10°C. Chars produced for specific conditions were mixed together before analysis. For moderated heating rate only, a mass balance on products was performed. Bio-oil was collected using condensers and non-condensable gases were determined by difference.

2.4 Feedstock characterization

2.4.1 Proximate analysis and calorific value
Char as well as original feedstock were both characterized for ash content and volatile content following ASTM E1755-01 and ASTM E 872 methods. Fixed carbon was determined by difference from the ash and volatile content. Higher heating value (HHV) was determined using an oxygen bomb calorimeter; Model 1341 from Parr company.

2.4.2 Organic elemental analysis
For CHON organic elemental content analysis, finely powdered feedstock was analyzed using a Leco TruSpec Micro CHNS equipped with the TruSpec Micro Oxygen Add-On Module for oxygen analysis.

2.4.3 BET analyses
Biomass samples were first sieved and the range between 40-60 mesh was used for BET analyses. Surface area characterization was performed using Micromeretic physical adsorption apparatus, ASAP 2020, using nitrogen

adsorption based on BET theory. Degas conditions were done under vacuum from an initial heating rate of 10 °C/min up to a temperature of 110 °C kept for a minimum of 16 hours.

2.4.4 Organic components, extractions and GC-MS analysis

Char Organic components extraction was done using Soxhlet. These tests were conducted on high heating rate chars only. Prior to Soxhlet extractions, char was grinded to a fine powder. For each extraction, one gram of char was placed in Whatman cellulose cartridges of (25 mm ID X 90 mm) and extracted with 150 ml of dichloromethane. The solution was concentrated using roto-evaporator. Biooils obtained from slow heating rate conditions were also analyzed. These latter collected into condensers were diluted into acetone before being injected into GC-MS. The gas chromatogram utilized is a HP 5890 Series II equipped with HP 5971A Mass Selective Detector and HP 7673 Controller.

3   Results and discussion

3.1 Heating rate effect

At 300 °C, change in heating rate does not seem to have a major effect on physical properties despite the fact the char yield varied slightly as well as higher heating value (HHV), tab.1. Char yield would have been expected to decrease with increased heating rate, as well as volatile content since generally increasing heating rate results in higher liquid yields and lower char yields, as for 500 °C. Perhaps that at lower temperature, this principle does not hold and the longer temperature progression temperature period had a more pronounced effect on char yield. Char yield being lower at 300 °C is at least consistent with the higher fixed carbon content that may have resulted from longer residence time, releasing more volatiles at temperatures lower than 300 °C. This latter would also explain the increase in heating value content. Higher heating value obtained for 500 °C in this research is really close to what was previously reported in literature using a bench scale fluidized bed reactor design (21.5 vs. 18.6 MJ/kg) (Boateng *et al.* [21]). At 500 °C, decreasing heating rate seems to have a pronounced effect on surface area passing from 52 to 82 m^2/g. Effect on biooil content was not observed since biomass carrier preheating step for higher heating rates resulted in some volatiles losses. It has to be kept in mind that oxygen introduction resulting from carrier preheating may have major effect on the results.

3.2 Gas environment effect

At 300 °C, gas environment does not seem to have a major effect on physical properties. All parameters studied did not vary, which is consistent to theory mentioning that CO_2 is inert at lower temperature (Jindarom *et al.* [16], tab. 1). On the other hand, despite the fact it would require further analyses, presence of compounds such as syringol, methoxyeugenol and palmitic acid was noted in

300 °C CO_2 oils which was not at 300 °C N_2. A further investigation on oil is however required in order to prove that observation.

At 500 °C though, gas environment seems to have a more pronounced effect. First of all, decrease in char yield and carbon content in presence of CO_2 shows that Boudouard reversed reaction could have taken place, resulting in higher carbon conversion and gas yield. Since 500 °C is a relatively low temperature for Boudouard reaction to take place, it seems that at least an element acted as a catalyst. It this case, two factors may be the catalyst source: the first could be Ni element present in stainless steel of the reactor, the thermocouple and the biomass carrier. As reported by Osaki and Mori [22], in presence of Ni, the reversed Boudouard reaction along gasification operates at same rate at 500 °C than without catalyst at 800 °C. The second factor could come from the high ash content into switchgrass that could act as catalyst for Boudouard reversed reaction.   Butterman and Castaldi [15] observed that activation energy for pyrolysis and gasification in CO_2 atmosphere was lowered in presence of herbaceous feedstock in comparison to wood. This difference was attributed mostly to higher ash content in herbaceous feedstock than for wood.

Specific surface is also another parameter which was influenced by carbon dioxide. At 300 °C there was no change noticed, however at 500 °C, specific surface passed from 82 to 189 m^2/g, tab.1, which is consistent to results from Jindarom *et al.* [16] who observed a drastic change in specific surface from 550°C.

3.3 Temperature effect

Temperature treatments add a pronounced effect on surface area. Increasing temperature from 300 to 500 °C increased surface area from less than 1m^2/g for all 300 °C char production studied, to more than 50 m^2/g at high heating rate and to more than 80 m^2/g at low heating rate, tab. 1. Despite the fact the high increase in surface area at 500 °C might be beneficial on a soil amendment application, the decrease in char yield passing from about 68% to 14% must be considered among the economics of the process depending on the application. Char yield from 66 to 70% at 300 °C could result mostly from hemicellulose decomposition as reported by Prins *et al.* [8]. This latter assumption would be consistent with switchgrass hemicelluloses content which was estimated at 36.3%, tab. 2. In each case, char yield decreased with increasing temperature with respect to specific factors studied. This mass balance is consistent with observations made by other authors showing that cellulose decomposition occurs at temperature from 305 to 375 °C and lignin at temperature from 250 to 500 °C (Prins *et al.* [8]). Switchgrass cellulose content represents 33.7% of biomass composition, (tab. 2), lignin being more reluctant to decomposition, this latter would then potentially balance the remaining losses. Boateng et al. [21] worked on the same species using a bench-scale fluidized bed fast pyrolysis reactor. They run their tests at a temperature of 500 °C and the char produced corresponded to 12.9% of the original biomass, which is close to the actual values obtained (Boateng *et al.* [21]).

It has to be noted that char was removed from the reactor once the residence time was completed. As a result, for higher temperature, 500 °C, the biomass and biomass carrier remain at temperature high enough for char reacting with the ambient oxygen, resulting in char glowing red. This definitely may have an effect on char yields by reducing it as well as an effect on its characteristics.

3.4 DCM extractions and analyses

Char organic content using Soxhlet extractions with dichloromethane were used to investigate if PAHs would be present within the char studied. This study was completed only for the high heating rate and within the studied conditions, only naphthalene was qualitatively noticed at 500 °C temperature. In literature, operating temperature increase was already reported to increase PAH formation (McGrath *et al.* [23] and Nakajima *et al.* [24]). Since extractions requires substantial amount of char in order to be extracted, further investigation of such parameter will be carried using a reactor with higher feedstock capacity.

4   Conclusion

Preliminary investigations of char formation from switchgrass show results similar to those reported so far. Lowering the heating rate would enhance the specific char surface area especially at 500 °C. It would also result in slightly higher char yield, which may be beneficial in a production point of view. Carbon dioxide showed to have a great impact on specific surface at 500 °C, leading to a specific surface of 189 m^2/g, which more than doubled the N_2 results. For a biochar-soil amendment application, where optimized yields are desired as well as high specific surface, residual CO_2 might then represent a strong potential since the yield compared to 500 °C N_2 was reported as similar. Leaching of ashes prior to pyrolysis or using a reactor free of Ni could be recommended in further experiments in order to target whether an element or another was responsible for the enhancement of CO_2 effect. Despite the fact CO_2 seems to be inert at 300 °C based on physical characteristics of chars, preliminary results for biooil content analysis revealed some differences which must be further investigated. Further investigation about chemical composition of char obtained under 500 °C would also be interesting since appearance of PAHs occurred at higher heating rates with N_2, however in presence of CO_2, the content could potentially be reduced since char tar content could react with CO_2 and enhance CO formation. It was also reported that final reacting conditions at open atmosphere resulted in decrease of char yield. Despite the fact this obvious reaction with oxygen could easily be reduced by waiting for char to cool down, the effect of such post treatment on char properties should also be analyzed further with respect to char value additions and the practical applications of the technology.

Table 1: Torrefaction and pyrolysis products analyses.

Production conditions				Mass balance			Char analyses								
Feedstock	Heating rate	T° [°C]	Gas Env.	Char [%]	Oil [%]	Gas [%]	C [%]	H [%]	O [%]	N [%]	Ash [%]	Volatiles [%]	FC [%]	HHV MJ/kg	S.A. m²/g
Raw sg.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	44.5	5.8	45.7	<1	3.7	81	15.3	19.5	--
Char	FAST	300	N_2	70.9	--	--	51.3	5.5	38.8	<1	6.7	72.8	20.5	20.3	<1
Char	FAST	500	N_2	12.4	--	--	63.9	2.6	15	<1	26.6	20.8	52.6	19.6	52
Char	SLOW	300	N_2	66.9	9	24.1	53.3	5.5	38.9	<1	4.7	70.9	24.4	23.5	<1
Char	SLOW	300	CO_2	66.6	10.6	22.8	54.9	5.5	38.4	<1	5.4	68.9	25.7	23.1	<1
Char	SLOW	500	N_2	15.9	10.6	73.6	65.4	2.6	17.4	1	15.1	19.7	65.2	23.5	82
Char	SLOW	500	CO_2	13.6	6.9	79.5	61.8	2.1	18.6	1	14.7	21.5	63.8	25.1	189

n.b.: Percentages are expressed on a dry basis.
Legend: sg.: Switchgrass T°: Temperature FC: Fixed carbon
n.a.: Not applicable Env.: Environment S.A.: Surface area

Table 2: Original composition of *Panicum virgatum* straw.

Identification	Standard Test	Mass Units (±*S.D*)*
Ash	ASTM E1755-01	3.7 (±0.2)
α-cellulose	ASTM D1103-60	33.7 (±0.7)
Hemicellulose	By difference	36.3 (±1)
Lignin	ASTM D1106-56	17.3 (±0.6)
Total		**100**

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

Acknowledgements

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