Pyrolysis of Switchgrass (Panicum virgatum L.) at Low Temperatures within N2 and CO2 Environments: Product Yield Study

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Pyrolysis of Switchgrass (*Panicum virgatum* L.) at Low Temperatures within N_2 and CO_2 Environments: Product Yield Study

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Ⓢ *Supporting Information*

ABSTRACT: Bioproducts and biofuels production from pyrolysis might benefit from recycling CO_2 within the process instead of using conventional inert gases such as N_2. In this study switchgrass (*Panicum virgatum* L.) was pyrolyzed within CO_2 and N_2 environments at 300, 400, and 500 °C for 2.5 min in a labscale fixed-bed reactor of 25 g/batch capacity. Chars, liquids, and noncondensable gases were monitored and characterized and yields were compared. A significantly lower liquid yield was observed at 300 °C−CO_2 in comparison to a 300 °C−N_2 environment, which was reflected with the char volatile content being higher under 300 °C−CO_2 and within the elemental composition of the solid and liquid products. Carbon dioxide also showed an effect at 500 °C, where liquid and gas yields significantly reduced and increased, respectively. At 400 °C−CO_2, CO concentrations were lower and CO_2 was higher compared to the levels at 400 °C−N_2, while at 500 °C−CO_2, CO concentrations were higher, CO_2 was lower, and CH_4 was lower compared to levels at 500 °C−N_2. At 500 °C, a significant ash content reduction with respect to original biomass was observed only in the CO_2 environment, suggesting that CO_2 may effect inorganic content and subsequently the feedstock conversions since some feedstock inorganic elements are known to play a catalyst role along these reactions. Additional tests were conducted by following regular 500 °C tests with a char air quench. This resulted in a char specific surface increase of about 20 times; CO_2 and N_2 initial environments confounded.

KEYWORDS: *Pyrolysis, Torrefaction, Carbon dioxide, Yields, Physicochemical properties*
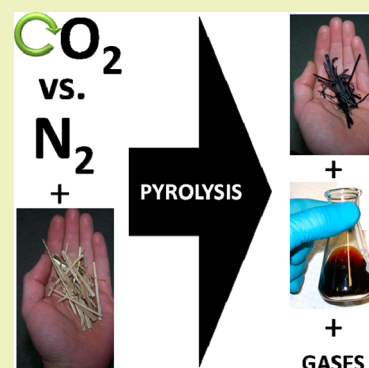
■ INTRODUCTION

Plant biomass represents an important source for sustainable energy as well as a neat feedstock for bioproducts and green chemistry development. Biomass use also represents the potential to reduce CO_2 emissions in comparison to petroleum-based products since the balance between CO_2 emissions during combustion or biodegradation of biobased product and CO_2 capture during photosynthesis for biomass growth is theoretically neutral. On the other hand, in order to reach this neutral CO_2 balance, biomass value addition overall chain must be well implemented. Cultivation (for agro-energy crops), harvesting, and transportation may themselves represent a major cost, energy needs, and CO_2 emissions sources. Cherubini and Jungmeier[1] did a life cycle analysis (LCA) on a biorefinery from switchgrass for bioethanol, bioenergy, and biochemicals and showed that in comparison to petroleum products, biorefinery products reduced the greenhouse gas (GHG) emissions by 79% and the nonrenewable energy by 80%. Along their study, they pointed out that their results were mostly affected by switchgrass production, especially due to the pelletizing, the drying, the transport of biomass, and the manufacturing of N-based fertilizers. Since torrefied biomass (char) may benefit the energy balance and GHG emissions reduction during transportation, pelletization, and grinding[2,3] and biochar pyrolysis (char for soil amendment) has the potential for increasing plant yield, doing N-

retention through adsorption (then potentially reducing N-based fertilizer needs) while sequestering carbon from its soil incorporation,[4,5] the use of these two chars at the beginning of the chain represents great potential in terms of energy use efficiency and GHG reductions. In addition to these benefits, a rising hope is whether it would be possible to recycle residual CO_2 within the torrefaction or pyrolysis process instead of using N_2 or another inert (O_2 free) atmospheres. Some drying systems as well as oxy-fuel combustion technology already make use of residual CO_2 from flue gases and reduce their energy needs by benefitting from the sensible heat content of gases.[6,7] Recycling CO_2 from residual gases into the pyrolysis process is something that might be economically beneficial.[8] However, it is expected that modifying the inert environment (N_2 or Ar) to CO_2 may have an effect on product composition as previous observations have shown.[8−10]

Use of CO_2 along gasification was already studied in order to enhance char conversion in CO (a targeted syngas constituent) or to enhance char surface area along activated char production; however, the use of CO_2 within torrefaction and pyrolysis conditions (especially from 300 to 500 °C) has been sparsely reported.[9,11,12] Recently it was reported that pyrolysis studies in

a CO_2 atmosphere were lacking.[12] To the best knowledge of the authors, literature covering pyrolysis in a CO_2 environment at lower temperatures (300−500 °C) is really sparse.

Among the few studies known to be available about the subject, very few of them used lignocellulosic biomass at low severity temperatures. Zhang et al.[10] compared CO_2 and N_2 pyrolysis environments within a fluidized bed reactor at 550 °C using corncob. They observed a slight decrease in condensable gases with slightly higher water content and lesser bio-oil fraction. Char decreased in the presence of CO_2 while noncondensable gases increased. Coking was observed in the presence of CO_2 in comparison to N_2 on their silica sand bed material. The same authors observed a decreased production in methoxy-containing compounds and an increase in monofunctional phenols in the condensable products in presence of CO_2. As for Jindarom et al.,[13] who studied sewage sludge pyrolysis in a CO_2 environment, Zhang et al.[10] also observed an increase in acetic acid production in presence of CO_2, which may be attributed to carboxylation reactions. Butterman and Castaldi[14] conducted tests with woody and herbaceous biomass in CO_2 environment compared to steam mixed with N_2. Within the 110−450 °C range, their analyses with thermogravimetric apparatus (TGA) showed that these two particular gaseous environments (CO_2 vs N_2 + steam) lead to fairly similar results. Jindarom et al.,[11] who conducted tests with sewage sludges in CO_2 vs N_2 environments observed higher specific surface for 550 °C (20 vs 15 m^2/g, in CO_2 vs N_2, respectively). In a complementary study, Jindarom et al.[8] continued the investigation using TGA, differential thermal gravimetry (DTG), and a batch-type thermal process. DTG curves presenting two steps along decomposition reactions, the kinetics under the two atmospheres were similar for their feedstock; however they noticed that, in the presence of CO_2, the first pyrolysis reactions were accelerated and the secondary reactions were shifted to lower temperature. Their results with DTG showed, in the presence of CO_2, a significant increase in the mass loss rate between 275 and 325 °C, and TGA results showed weight loss difference starting at 300 °C; both with respect to an N_2 environment.

In this study, switchgrass (*Panicum virgatum* L.) was pyrolyzed within two respective gas environments (CO_2 and N_2) using a fixed bed batch type reactor that was operated at three temperatures (300, 400, and 500 °C) for a 2.5 min residence time. Two additional tests were also performed at 500 °C (CO_2 and N_2 environments, respectively) with a special air quench following the above process at 500 °C for 2.5 min in order to compare the actual work with a preliminary study presented in the work of Pilon and Lavoie.[15]

■ MATERIALS AND METHODS

Feedstock. Switchgrass, Cave-in-Rock species (*Panicum virgatum* L.) was the feedstock utilized for the experiments. Further details about switchgrass origin utilized and composition are presented in the work of Pilon and Lavoie.[16]

Experimental Setup Operation and Description. Before each test, switchgrass was cut into <10 cm pieces, about 25 g of feedstock was utilized per test. Feedstock was not ground in order to convert it without the energy intensive pretreatment of biomass feedstock size reduction that could be economically beneficial to avoid prior to the industrial process. Feedstock humidity levels were evaluated prior to each test; levels that typically ranged from 4 to 9%.

Thermochemical conversions were conducted into a lab-scale fixed bed reactor. The reactor is composed of a thin stainless steel tube with wall thickness of 1 mm, inner diameter of 83.5 mm, and length of 370

mm. The reactor's surface is surrounded by electrical band heaters, which provides an equally distributed heat flux. Tests were conducted at 300, 400, and 500 °C for two distinct gas environment types (CO_2 and N_2). Heating rate, which was independent of the targeted temperature, was set to 55 °C/min by controlling the inline gas preheater as well as the reactor's band heaters. This heating rate level corresponded to moderate pyrolysis rate. Gas inflow used for experiments is either CO_2 or N_2, and the flow rate was set to 0.5 L/s (STP: 101.3 kPa and 25 °C). Gas is first preheated at reactor's average temperature using inline gas heater and then enters the vertically positioned reactor from its bottom (Figure S1 in the Supporting Information (SI)). Band heaters are surrounded by insulated shell covers in order to minimize thermal losses. The latter are removed once the desired reacting time is reached (allowing a faster temperature drop). A pressure gauge is installed near the gas outlet (SI Figure S1). Reactor operating absolute pressure corresponded to about 115 kPa, which is slightly higher than atmospheric pressure resulting from friction along gases outlet system. Gases produced must pass through a heated line maintained at around 250 °C before passing through a series of four empty glass condensing tubes (38 mm o.d. by 23 cm long; C1−C4) immersed into ice baths (water and ice), all connected by stainless steel tubing and followed by a filter (tube filled with cotton wool pieces) (Figure S1). Part of noncondensable gases pass throughout a molecular sieve (Aldrich 3A; 1.6 mm pellets) before being collected in 25 L Tedlar gas sampling bags (Supelco). Gas sampling was done throughout the experiment at constant flow rate starting from a reference reactor temperature of 100 °C. Temperature was monitored using K-type thermocouples, after gas inlet (T-0), inside the reactor (T-1−T-4), at the reactor's surface, at its outlet (T-5), and before the condensing train (T-6) (Figure S1). Real time temperature monitoring is done on the overall system using National Instrument Data Acquisition System NI cDAQ-9172 equipped with Labview software. Every tested condition was conducted in triplicates. Statistical analyses of result averages comparison was expressed with the P value. The P value corresponds to the smallest level of significance that lead to the rejection of the null hypothesis (where averages compared are equal).

For two additional tests, specific treatments were given. For both additional tests (one in a 500 °C−N_2 environment and the other at 500 °C−CO_2), they were first conducted normally, except that after completing the normal tests period with 2.5 min residence time, air was entered instead of N_2 or CO_2 (from 400 °C), at the same flow rate (0.5 L/s), for 2 min. After air treatment, the reactor was left cooling as for the previous tests. These two tests were carried in order to compare with results obtained within a previous analysis, which were in contact with ambient air after the pyrolysis reaction.[15] Since these tests were conducted especially for BET measurements, only char yields and BET analyses were conducted.

Feedstock and Char Characterization. Analytical methods for proximate analysis, organic elemental analysis, and BET surface area as well as cellulose, hemicellulose, and lignin content, in the feedstock and to a lower extent on char, were all reported in the work of Pilon and Lavoie.[16] For further analyses, elemental analysis was transferred on an original biomass basis using, for each replicate, its respective pyrolysis fraction yield. Each sample from the triplicated conditions was analyzed following the above methods.

Condensable Product Preparation and Analyses. Condensable products were first analyzed by gravimetry using the content collected within the condensing tubes, the connecting tubings, and the filter cotton wool. After each experiment, each condenser and their lines were thoroughly washed and rinsed with water followed by acetone, and the cotton wool in the filter was replaced. Only the condensable products from condensing tubes (not from the cotton wool) were collected for further analyses. Their content collection was completed using acetone after which the solution was filtered through glass frits to remove any suspension particles. Before analyses, acetone was removed from condensable product samples by a rotary evaporator at a temperature of 65 °C and a vacuum pressure of 15 mmHg (50 kPa).

Condensable products organic elemental composition were analyzed using the same methods as for char and feedstock described in a previous section. Water content in bio-oil was analyzed using Mettler Toledo DL31 Karl Fischer Titrator and anhydrous ethanol reagent.

Gas Analyses. Noncondensable gas analyses were conducted with a gas chromatograph (GC; Varian CP3800) using a thermal conductivity detector (TCD) for CO_2, N_2, and CO and a flame ionization detector (FID) for CH_4, C_2H_4, and C_2H_6. For GC-TCD analyses, columns used are Hayesep T (CP81072), followed by Hayesep Q (CP81073), and Molecular Sieve 13X (CP81071), using He as a carrier gas. The FID is installed in series with the TCD. Gas analyses were conducted in duplicates. For gas results analyses, CO_2 from vector gas was considered as inert; therefore, the inflow volume was removed within the calculations. Hydrogen could not be analyzed due to its low abundance, overall interfering with the injection valve peak.

RESULTS AND DISCUSSION

Reactor Operation. A reactor was operated in order to reach an average of the set point temperature within its core. Results for the oil condensing train as well as bio-oil collection efficiency are presented in Figure S2 in the SI. Interestingly, about a third of liquid obtained was in cotton wool following the condensing train. These results are similar to those of Boateng et al.[17] who collected their pyrolysis condensable products using a condensing train of four tubes followed by an electrostatic precipitator (ESP) and obtained an additional 42.7% of liquids within the ESP. In their case, it appeared that most of the water present in the oil was condensed within the four condensers and higher molecular compounds resulting from lignin decomposition were collected with the ESP.[17] Since only the liquid from the condensing tubes was considered for further analysis, it is then possible that higher molecular weight compounds were not in the sample.

Product Yield Comparison. Among the products yields (Figure 1), a first most significant result observed is the bio-oil
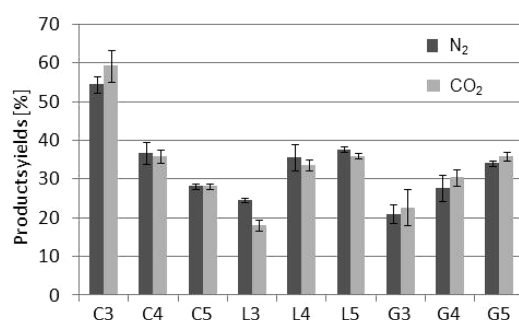

Figure 1. Pyrolysis products yields. Error bars correspond to standard deviation, for $n = 3$. Legend: {(C, L, or G), (3, 4, or 5), (N or C)} standing for {(char, liquid, or noncondensable gases), (300, 400, or 500 °C), and (N_2 or CO_2)} respectively; applicable to Figures 2a to 3b as well.

yield at 300 °C, which is significantly lower ($P < 0.002$) in the presence of CO_2 (18.0 vs 24.6% in CO_2 vs N_2, respectively). From Figure 1, it is also possible to observe a tendency for 300 °C chars to reach higher yields in the presence of CO_2 than with N_2 (59.2 vs 54.4%, respectively); therefore, less products possibly converted into liquid products. No major noncondensable gas yield variation with respect to the gas environment was observed (Figure 1).

These primary observations may provide an overview of the reactions that were affected during pyrolysis at 300 °C using CO_2 as vector gas. Liquid condensable products are the result of depolymerization and fragmentation reactions of the original feedstock polymers (holocelluloses and lignin) leading to products that may tend to recombine and be condensed as liquids.[14,18] Therefore, a first explanation is that CO_2 could affect the decomposition reactions or the volatile products recombination. Analyses on the 300 °C chars showed that char volatile content is higher in the presence of CO_2 than in the presence of N_2 (61.0 vs 57.1% corresponding to 0.35 ± 0.05 vs 0.29 ± 0.01 g/g biom$_{wb}$, respectively; $P = 0.1$) (Table 1). These results are consistent with char elemental composition where carbon, hydrogen and oxygen contents were higher in presence of CO_2 with regards to N_2 (Figure 2a and b). In the case of liquid products at 300 °C, C, H, and O are all statistically significantly in lower quantity within a CO_2 atmosphere ($P <$ 0.1, 0.002, and 0.02, respectively) (Figure 3a and b). Since the conversion of char material is not as complete in CO_2 as in an N_2 environment (for 300 °C), it would then be consistent with the assumption that CO_2 environments affect reactions such as decomposition. During torrefaction (up to 300 °C), important reactions taking place are the dehydration and decarboxylation.[19] On the other hand, because the gas yield (noncondensable) is slightly higher in the presence of CO_2 (Figure 1) that means the simple compounds of low molecular weight that may result from these decomposition reactions are not much affected; otherwise positively. In addition, there is no difference among gas composition at 300 °C (CO_2 vs N_2) and the specific CO_2 gas composition content is quite high (85–87%; Table 1), which is consistent with decarboxylation known to occur at 300 °C.[19] As a result, that could mean that it is either the cleavage of the original feedstock polymer into heavier molecular weight fragments or the recombination of small molecular weight fragments into heavier compounds that could be impaired by a CO_2 environment. This behavior appears to be enhanced especially at 300 °C since bio-oil yield difference with respect to gas environments reduces with increasing operating temperature (Figure 1). Further characterization of organic chemical composition of char and bio-oil produced at that temperature would contribute in clarifying these assumptions.

The feedstock polymer constituents that are known to decompose around 300 °C are mostly related to hemicellulose and lignin.[20−22] In addition, cellulose which is usually known to decompose from about 325 °C was shown to be more vulnerable to temperature in the presence of minerals.[23] Since xylans are abundant polymers within hemicelluloses and they especially tend to decompose at torrefaction temperatures,[24] it could be interesting to verify with TGA whether CO_2 has an effect especially with these polymers. In addition, Prins et al.[19] observed that deciduous trees and straw containing more xylans and minerals produced more acetic acid; moreover acetic acid was reported to be enhanced during CO_2 pyrolysis[10,13] as a result, this would all be consistent. As reported in Amonette and Joseph,[25] lignocellulose degradations in the vicinity of 300 °C are believed to be free-radical processes initiated by the thermal action of inorganic impurities present in the feedstock as well as the thermal effect on structural O. As a result, CO_2 could perhaps affect the inorganic impurities, which would subsequentially affect the condensable product formation and content. Some observations on the effect of CO_2 on the

Table 1. Switchgrass Pyrolysis Products Characterization[a]

conditions		solids					liquids		gases					
T	gas	yields	ash	volatiles	FC	SA	yields	water	yields	CO_2	CO	CH_4	C_2H_4	C_2H_6
[°C]	env	[%][b]	[%][b]	[%][b]	[%][b]	m^2/g	[%]	[%][b]	[%]	[%]	[%]	[%]	[%]	[%]
RSW		na	3.7 ± 0.2	81.0 ± 0.2	15.3 ± 0.2	<1	na	na	na	na	na	na	na	na
300	N_2	54.4	7.3 ± 1.0	57.1 ± 0.6	35.6 ± 1.2	1.3	24.6	26.6 ± 5.3	21.0	84.8	14.8	0.3	0.06	0.04
300	CO_2	59.2	6.3 ± 0.5	61.0 ± 3.9	32.8 ± 3.5	1.4	18.0	23.5 ± 12.9	22.7	86.8	12.8	0.3	0.05	0.05
400	N_2	36.7	10.8 ± 0.7	35.8 ± 2.8	53.5 ± 3.4	1.1	35.6	25.5 ± 5.3	27.7	64.1	34.6	0.9	0.26	0.24
400	CO_2	35.9	11.5 ± 0.3	36.5 ± 2.1	52.0 ± 1.9	1.1	33.7	27.6 ± 3.6	30.4	74.5	24.5	0.7	0.12	0.12
500	N_2	28.2	13.5 ± 0.6	28.3 ± 1.9	58.3 ± 1.7	9.3	37.7	39.0 ± 2.2	34.1	58.7	35.4	4.1	0.97	0.86
500	CO_2	28.1	11.5 ± 0.7	24.8 ± 3.4	63.7 ± 3.1	9.2	36.0	36.7 ± 2.6	35.9	52.9	42.8	2.2	0.78	1.39

[a]Legend: (RSW) raw switchgrass, (T) temperatures, (env) environments, (FC) fixed carbon, (SA) surface areas, (na) not applicable, (±) std. dev. (for n = 3). [b]Dry basis.
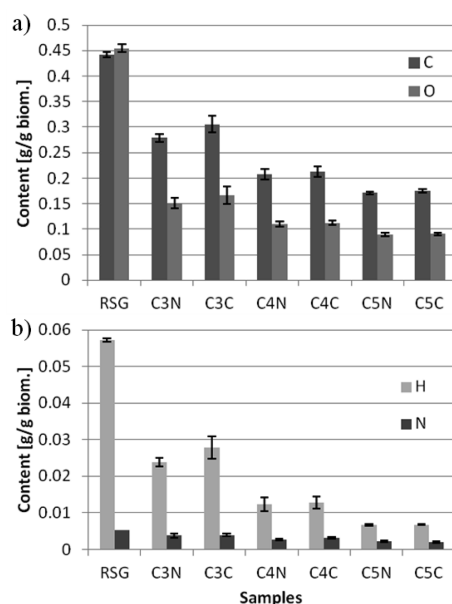

Figure 2. Char elemental organic content expressed on original feedstock basis (wet basis): (a) carbon and oxygen content; (b) hydrogen and nitrogen content. Error bars correspond to standard deviation, for n = 3. Legend: (RSG) raw switchgrass.
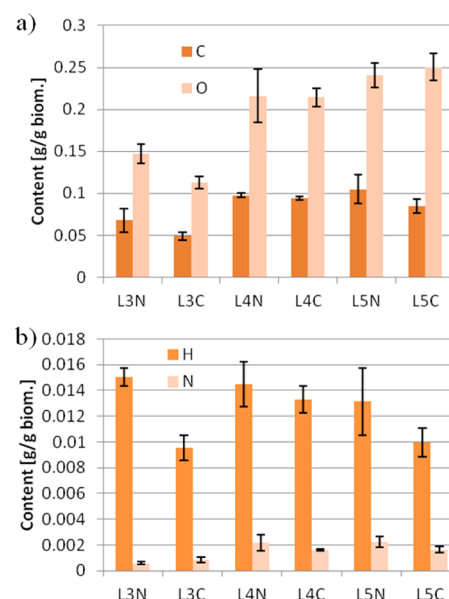

Figure 3. Liquid elemental organic content expressed on original feedstock basis (wet basis): (a) carbon and oxygen content; (b) hydrogen and nitrogen content. Error bars correspond to standard deviation, for n = 3.

inorganic content were made at 500 °C conditions and are presented in the following sections.

At temperatures of 300 °C, very few studies are reported with respect to a CO_2 gas environment. Jindarom et al.[8] had observed a difference at 300 °C with respect to gas environment through DTG analysis; however, their results presented an enhanced mass loss rate in a CO_2 environment, which appears contradictory to the results of this research. However this contradictory result could be due to the fact that their feedstock was sewage sludge, which is fairly different than switchgrass in terms of mineral content, moisture content, and hemicellulose content and composition, to note only these three differences in feedstock characteristics.[26,27]

Increasing temperature from 300 to 400 °C behaved as expected on initial biomass conversion. It lead to lower char yields and favored an increase in liquids as well as non-condensable gases (Figure 1). Gas composition, with respect to temperature only, shows a decrease in CO_2 concentrations at 400 °C in comparison to 300 °C while the CO content increased (both in N_2 and CO_2 environments) (Table 1). This can result from oxygen content (trapped in biomass) reacting with carbon; however, being in limited amounts within

biomass, the incomplete combustion reaction no. 3 (Table 2) may be enhanced instead of complete carbon oxidation (C + $O_2 \rightarrow CO_2$). As O radicals are formed, carboxyl and carbonyl groups are cleaved to yield CO_2 and CO.[25] Another explanation comes from Butterman and Castaldi[14] who suggest that OH

Table 2. Reactions Possibly Occurring at Pyrolysis Conditions

no.	reactions	ΔH (300 °C) kJ/mol	ΔH (500 °C) kJ/mol	T ($\Delta G < 0$)[a] °C
1	$2CO \rightarrow C + CO_2$	−174	−172	<700
2	$CO + H_2 \rightarrow C + H_2O$	−134	−135	<672
3	$C + 1/2O_2 \rightarrow CO$	−110	−111	b
4	$2CO + 2H_2 \rightarrow CH_4 + CO_2$	−256	−259	<640
5	$CO + 3H_2 \rightarrow CH_4 + H_2O$	−217	−222	<612
6	$C + 2H_2 \rightarrow CH_4$	−83	−87	<532
7	$CO + OH \rightarrow CO_2 + H$	−103	−101	b

[a]Obtained from FactSage software (P = 1 atm). [b]For values from 0 to 1200 °C.

which usually reacts with CO to form CO_2 (reaction 7; Table 2) would not be produced from lignin at 400 °C (needing higher temperature levels for its decomposition) and would then increase CO concentrations.

Still at 400 °C, but comparing N_2 and CO_2 atmospheres, no statistically significant difference was noted on the conversion of the original feedstock in each fraction; either for char, liquid, or gas yield (Figure 1). The fraction where a difference (with respect to gas atmosphere) may be noted is the non-condensable gas compositions. Gas composition in CO_2 environment led to higher CO_2 concentrations while CO, C_2H_4, and C_2H_6 all decreased compared to a N_2 pyrolysis atmosphere (Table 1). In order to explain these gas composition differences, it is first possible to observe that oxygen elemental content, with respect to char and liquid fractions, is not significantly affected by gas environment (Figures 2a and 3a). As a result, a lower CO concentration in a CO_2 environment could be enhanced by the Boudouard reaction or reversed steam-reforming reaction (reactions 1 and 2; Table 2). Zhang et al.[10] observed that under CO_2 atmosphere (at 550 °C), coking occurred on their silica sand bed which was not observed under N_2. Since this reaction (Boudouard, reaction 1; Table 2) is thermodynamically favored at lower temperatures, a CO_2 environment could affect indirectly the reaction thus enhancing carbon deposition and increasing carbon dioxide formation. As for the C_2H_4 and C_2H_6 concentrations obtained in CO_2 environments versus N_2 (0.12 and 0.12 vs 0.26 and 0.24% for C_2H_4 and C_2H_6 respectively; Table 1), this might be consistent with the previous observations at 300 °C where CO_2 could have affected some decomposition reactions. The reaction that could have been impaired in this case is demethylation leading to subsequent formation of these compounds through combination of radicals. Demethylation is known to decompose biomass constituents from 350 to 450 °C and especially phenol methoxy groups from lignin.[14,18] This could be consistent with the previous assumption where CO_2 would have induced a reduction of the depolymerization process of lignin which usually leads to high molecular weight compounds during pyrolysis and where CH_3 radicals could be exposed following depolymerization. A lower depolymerization of lignin would have reduced the amount of methyl groups being exposed thus lowering ethylene and ethane formation.

At 500 °C, feedstock conversion was further enhanced in comparison to 400 °C conditions; char yields passing from about 36 to 28% (400 vs 500 °C respectively, N_2 and CO_2 environments confounded; Table 1). Glancing at the 500 °C experiments, with respect to gas environment, it appeared that char yield was not affected, but condensable gas yields were significantly lower under a CO_2 environment ($p < 0.05$) and noncondensable gases were higher ($p < 0.1$). Condensable gas yield results, showing a diminution in the presence of CO_2 vs N_2, are consistent with the results obtained by Zhang et al.[10] with corncob. As for gas composition, the CO_2 environment appears as having enhanced the formation of CO. Therefore, a reversed Boudouard reaction (reaction 1 inversed; Table 2) might have taken place, enhancing the formation of CO instead of bio-oil. Despite the fact that thermodynamics usually do not enhance the reversed Boudouard reaction below 700 °C (C + $CO_2 \rightarrow$ 2 CO; reversed reaction no. 1, Table 2), but mostly the forward reaction, previous observations showed that in the presence of Ni from stainless steel material or from feedstock inorganic content, reversed Boudouard reaction may be catalyzed thus allowing the reaction at lower temperatures.[28] Despite the fact that char yield did not vary with respect to the gas environment, 500 °C $-CO_2$ char's volatile content was reduced and fixed carbon ended up being almost significantly higher (Table 1). As a result, this could mean that the occurrence of CO_2 enhances the formation of gases from the volatile part of the feedstock, but not from the most stable carbon structure, a behavior that would be consistent with the use of CO_2 for activated char through the removal of tar within its pores. In fact, in a CO_2 atmosphere compared to N_2, bio-oil was shown to have a lower elemental carbon content while char carbon content remained essentially stable (Figures 3a and 2a, respectively). Carbon dioxide content was also lower in the CO_2 environment than in N_2, which would be consistent with the possible enhancement of a reversed Boudouard reaction. On the basis of a mechanism reported in Butterman and Castaldi,[14] another explanation for the higher CO concentration (at 500 °C under CO_2) could be due to a decrease in OH radical branching off from lignin and cellulose which usually tends to combine with CO (reaction no. 7; Table 2) producing CO_2 and new H radicals. Since it was hypothesized from our observations along this study that a CO_2 environment could affect production of heavier compounds through depolymerization, the "OH branching off" could then have been reduced, consequently avoiding CO reduction through reaction 7 (Table 2).

It can be observed from the 500 °C reaction that the formation of CH_4 was enhanced compared to 300 and 400 °C (Table 1). CH_4 may be formed from hydrogenation—methanation reactions (reaction nos. 4, 5, and 6; Table 2) as well as from H and CH_3 radicals formed above 250 °C and combining into CH_4.[14] This is consistent with the fact that hydrogen content was reduced in chars when comparing the reactions performed at 300 and 400 °C, respectively (Figure 2b). Results showing higher CH_4 yield around 500 °C as well as a lower CH_4 yield in the presence of CO_2 than in N_2 (500 °C) are consistent with the ones from Butterman and Castaldi.[14] It is also consistent with the explanation given at 400 °C concerning demethylation reactions which could have decreased due to lower depolymerization of biomass constituents such as lignin (at these temperatures) under a CO_2 environment. Another explanation for the lower CH_4 content under CO_2 environment at 500 °C would be the enhancement of CO_2 reforming of CH_4 reaction which could occur to some extent at 500 °C.[29] This latter reaction could also have contributed in CO enhancement observed under CO_2 atmosphere (Table 1).

Hydrogen content in bio-oils appeared lower in the presence of CO_2 than with N_2 (Figure 3b). Despite the fact H_2 was not analyzed in gases, gas composition did not show higher content in hydrogen-containing compounds (Table 1). Hydrogen is known to appear essentially starting at 600 °C.[14] It can also be observed that water content in bio-oils was significantly higher at 500 °C than most conditions at 300 and 400 °C. This may result from the 500 °C temperature range enhancing combustion reaction of H_2 with O_2 (from biomass).

Still at 500 °C, the char ash content was significantly lower under a CO_2 environment (11.5 ± 0.7 vs 13.5 ± 0.6%, $P < 0.02$, corresponding to 31.2 ± 2.6 vs 36.4 ± 2.6 mg/g biomass$_{db}$, $P < 0.06$; CO_2 vs N_2 respectively; Table 1). Such ash content difference was not observed from the previous temperatures and conditions along this study. Since an effect from CO_2 was noted all along the conditions, further investigation of mineral

interaction with respect to CO_2 atmosphere and pyrolysis reactions mechanisms would be of great interest along further studies. As reported in the work of Fryda et al.,[30] the fate of minerals (e.g.: lowering ash melting temperature and vaporization) may be affected by reacting conditions. Therefore, since CO_2 was observed to have an effect on ash content at 500 °C, the variations noted with respect to gas environment (in CO_2) could then be the result of the interaction of the CO_2 and the minerals present in biomass. Frequently it was observed and reported that inherent biomass inorganic content had an effect on pyrolysis mechanisms and often a catalytic effect during biomass pyrolysis.[8,14,18,19] Overall, that could mean that CO_2 simply inhibits catalytic action of some biomass inorganic content. Further analyses of char inorganic content such as XRD might be used to verify reaction of CO_2 with inorganics and corroborate the assumption. Noteworthy that during pyrolysis experiments, CO_2 seemed to affect the stainless steel material exposed to the reaction by modifying the color (some multiple-color reflects) as well as having a different smell under CO_2 compared to N_2 when opening the reactor. This may be in agreement with CO_2 affecting some inorganic components. As a result, it could be of great interest to investigate especially the effect of Fe, Ni, or other stainless steel constituents on CO_2 biomass pyrolysis.

Specific Surface Area Development. It can be observed that the surface area slightly increased at 500 °C (Table 1). It first passed from <1 m^2/g for original feedstock, to about 1 m^2/g for 300 and 400 °C chars and 9 m^2/g for 500 °C chars (for both gaseous environments; Table 1). Results for surface area with respect to temperature are consistent with other studies on switchgrass pyrolysis, such as that of Boateng et al.[17] who obtained 7.8 m^2/g with a fluidized bed pyrolysis reactor (at 480 °C). Nonetheless, Brewer et al.[31] and Pilon and Lavoie[16] observed 50.2 and 66.6 m^2/g, respectively, for similar reacting conditions (at 500 °C). With respect to the gas environment, especially for higher temperatures, higher surface area could have been expected due to possible reversed Boudouard reaction (possibly catalyzed by feedstock minerals) enhancing conversion of carbon and emptying pores. Butterman and Castaldi[14] had observed higher pore formation behavior in presence of CO_2, although chars were tested following higher temperature treatments (860 °C), which is known to enhance surface area.[32] Since lower volatile content was obtained at 500 °C−CO_2 (Table 1), it could have been expected that pores cleaning was enhanced and affected the specific surface as well, which did not occur.

As reported in a preliminary study on the subject,[15] in the presence of CO_2, higher specific surface had been observed in the presence of CO_2 (189 vs 82 m^2/g in CO_2 and N_2 environments, respectively; Table 3). The possible reasons leading to this important difference may be related to the two reactors designs and operating conditions which imply: the superficial velocity of gas environment is lower in this study (0.24 vs 0.54 m/s; for 500 °C, at 1 atm), the amount of material varies mostly (25 vs 1 g), and there was a contact with air after the test within the preliminary study.[15] In order to verify whether the gas environment (N_2 or CO_2) followed by air contact had an effect on char porosity, two additional tests were conducted specifically for 500 °C conditions at which high surface area were observed.[15] The results obtained in both cases lead to chars with similar surface area 183 and 198 m^2/g for N_2 + air and CO_2 + air environments, respectively (Table 3). In both cases, the maximum temperature reached was 650 °C (Figure S3 in the SI). As a result, the CO_2 environment used during the heating period and the 500 °C treatment, previous to the oxygen quenching treatment, did not show an impact on surface area compared to N_2. It is noteworthy that char yield for these two additional treatments gave 15.8 and 15.1% char yield for N_2−air and CO_2−air, respectively (Table 3). Despite the fact that CO_2−air in comparison to N_2−air did not show any specific difference, the air insertion after pyrolysis treatment appears to significantly increase surface area. This simple technique of air insertion within reactor (at low temperature char production) may have important implications, especially in char value additions where high surface area is desired; such as biochar−soil amendment applications. On the other hand, the technique would gain at being optimized since char yield decreased drastically in the actual conditions (decreased from about 28−15% in both gaseous environments; Table 3). In addition, clarifications whether it is the oxidation, the temperature, or a correlation between both factors which had this effect on specific surface enhancement should be further investigated.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Information as noted in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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Table 3. Char Surface Area after Specific Treatments

	char yields	surface areas	
conditions	[%][b]	m^2/g	ref
500 °C−N_2	28.2	9	this study
500 °C−CO_2	28.1	9	this study
500 °C−N_2[a]	15.8	183	this study
500 °C−CO_2[a]	15.1	198	this study
500 °C−N_2[a]	15.9	82	15
500 °C−CO_2[a]	13.6	189	15

[a]Chars made in contact with air after the O_2-free test. [b]Dry basis.

Clément, switchgrass producer (Qc, Canada), for providing the feedstock used in this research.

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