

Characterization and Thermal Conversion of Charcoal Derived from Fluidized-Bed Fast Pyrolysis Oil Production of Switchgrass[†]

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The charcoal coproduct associated with pyrolysis oil (bio-oil) production can add economic value to the process operation if it can be successfully employed as an activated biochar for soil amendment applications or can be used as a combustion fuel to power the pyrolysis process or as a gasifier feedstock. Although proposed, none of these have been extensively studied. In this submission, the surfaces and interfaces of the charcoal produced from making pyrolysis oil from switchgrass in a fluidized bed were characterized to establish its usefulness as an adsorbent material. Its reactivity in air and in CO₂ were also determined to establish its potential as combustion fuel or gasification feedstock. It was found that the surface areas were low, typically 7.7 and 7.9 m²/g, 2 orders of magnitude of the areas encountered in activated charcoal. Compounding this was high surface crystallinity of the structure as measured by X-ray diffraction, thereby suggesting poor characteristics as a sorption agent without further activation. However, this does not preclude its use for other soil applications including carbon storage and as a nutrient delivery substrate. Upon further pyrolysis in helium, the charcoal yielded equal amounts of CO and CO₂, exhibiting reaction kinetics similar to that of coal pyrolysis. Furthermore, reactivity in CO₂ and in air atmosphere resulted in activation energies of 8 411 and 11 487 J/mol, respectively. It appears that the charcoal could be better used as combustion fuel or gasification feedstock than as an activated charcoal applied for metal sorption for the fact that the latter application will require higher surface and interfacial areas than measured.

Introduction

Fast pyrolysis of biomass can yield as much as 60–70 wt % bio-oil. Accompanying the oil production is ~20–40 wt % charcoal. The economic viability of the production of bio-oil as a fuel intermediate has been tied to the economic value of the charcoal coproduct, and many potential uses of the charcoal have been proposed.^{1,2} The most recent development and, perhaps, most interesting is the proposed charcoal vision, whereby a biorefinery system could produce vehicular fuel intermediates by pyrolyzing biomass, burying some of the charcoal produced to reduce our carbon footprint and using some of it to fire up the endothermic pyrolysis reaction.³ Although there is much discussion about the use of the charcoal for soil amendment, the role that the alkali metals play in nutrient balance and plant growth is not well-resolved. However, application of charcoal for the sorption of on-farm chemicals has been demonstrated. For example, Pils and Laird used charcoal to treat tetracycline (TC) and chlortetracycline (CTC) that are applied extensively for growth promotion and therapeutic purposes in livestock production with success.³ The potential use of the charcoal as combustion fuel to fire up the pyrolysis system has been discussed or theoretically established. Boateng et al.⁴ showed that theoretically 15–20% charcoal with an energy content in the 20 000–25 000 kJ/kg range can fulfill all the energy requirements for the production of 60–70 wt % bio-oil in a fast pyrolysis system. Furthermore, techno-economic analysis performed for a 550 standard dry ton per day crude pyrolysis oil plant⁵ showed an economic advantage when the

Table 1. Fluidized-Bed Fast Pyrolysis Conditions under Which Charcoal Samples Were Produced⁴

biomass type	switchgrass (cave-in-rock variety)
fluidized-bed material	silica sand
particle size of bed material	–20 + 25 U.S. mesh
fluidizing gas	N ₂
gas flow rate	4.81 kg·h ⁻¹
minimum fluidizing velocity	0.23 m·s ⁻¹
superficial velocity	0.65 m·s ⁻¹
reactor temperature at run	480 °C
biomass feed rate	2.22 kg·h ⁻¹
biomass/N ₂ ratio	0.46
feed mean particle size	<0.5 mm
bed pressure	4.0 kPa

charcoal was used in a combustor to provide energy for the drying of the feedstock and for the pyrolysis. Perhaps the most practical application of the charcoal is the proposed distributed biorefinery system; with this system, bio-oil is produced as an energy-dense fuel intermediate, combining it with the charcoal to form char–oil slurry, which can be used as a feedstock to produce syngas and further synthesis of the syngas to Fischer–Tropsch liquids.⁶ Economic studies have shown that hauling the char–oil slurry instead of bulky herbaceous energy crops would reduce transportation costs, one of the major cost factors in a biorefinery system.⁶ The potential use of the charcoal derived from fast pyrolysis oil production as a feedstock for pyrolysis, gasification, or combustion is not widely studied. In this paper, we report the results of an analysis of charcoal accompanying bio-oil production that was reported earlier in *Ind. Eng. Chem. Res.* In that work, Boateng et al.⁴ reported the production of bio-oil from switchgrass of the cave-in-rock cultivar in a bench-scale fluidized-bed reactor. The operating conditions of the fast pyrolysis reactor are given in Table 1. The switchgrass used was ground in a Wiley mill and sifted through –2 mm mesh before use. Biomass-to-N₂ ratio was 0.46 with a superficial bed velocity of 0.65 m s⁻¹. Pyrolysis yield

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[†] Mention of trade names or commercial products in this publication is solely for the purpose of providing specific information and does not imply recommendation or endorsement by the U.S. Department of Agriculture.

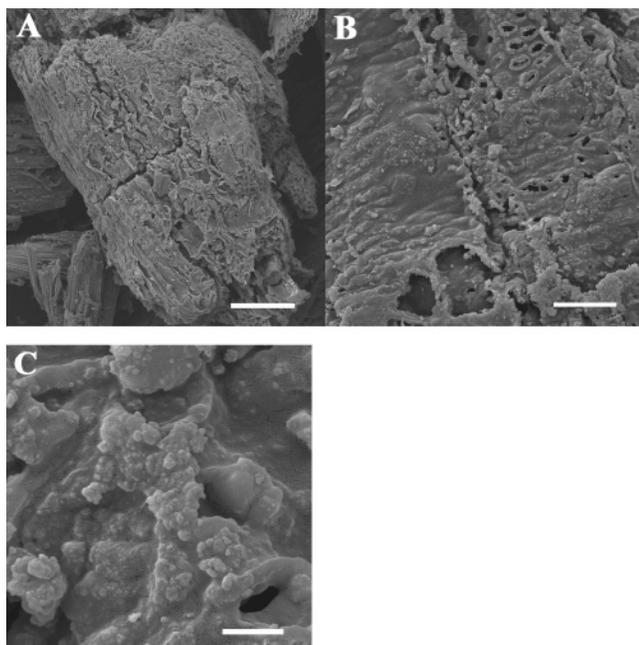


Figure 1. SEM photomicrographs of charcoal coproduct from run 1 of fluidized-bed pyrolysis of switchgrass: (A) bar = 100 μm , (B) bar = 5 μm , and (C) bar = 0.5 μm .

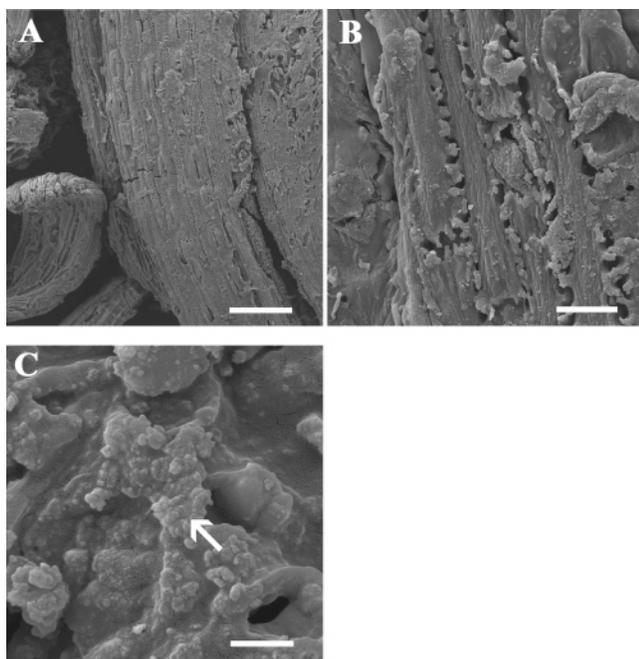


Figure 2. SEM photomicrographs of charcoal coproduct from run 2 of fluidized-bed pyrolysis of switchgrass: (A) bar = 100 μm , (B) bar = 5 μm , and (C) bar = 0.5 μm . The arrow in C depicts vesicle formation.

comprised 61% bio-oil, 11% noncondensable gas (NCG), and 15% charcoal. The objective was to establish the charcoal's characteristics as an absorbent material and also its use as a potential combustion fuel and as a gasification feedstock. To do so, the produced charcoal was pyrolyzed in an analytical pyroprobe coupled with a gas chromatograph (PY-GC) at temperatures ranging between 500 and 1100 $^{\circ}\text{C}$. The evolved gas was analyzed for gas composition and yield. Further pyrolysis experiments were carried out in CO_2 and in air atmosphere to establish the charcoal reactivity to gasification and combustion, respectively.

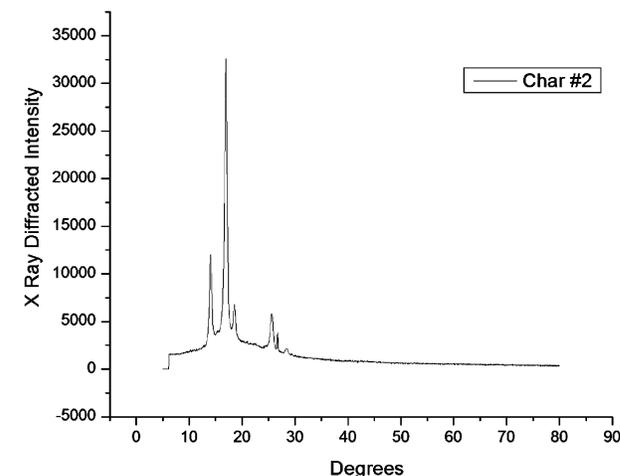
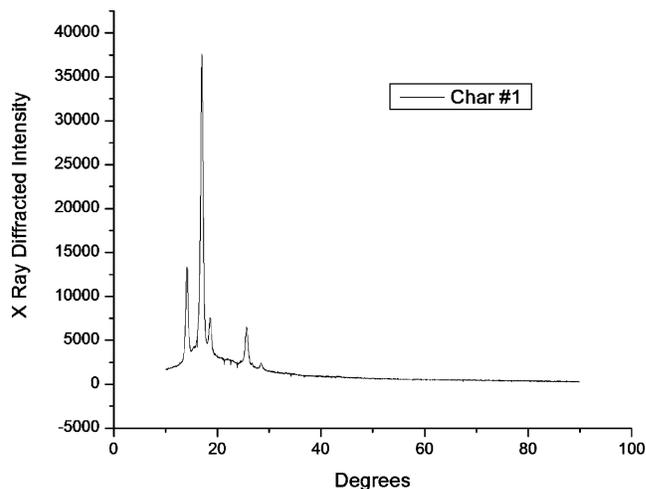


Figure 3. X-ray diffraction of charcoal samples from two fluidized-bed fast pyrolysis runs.

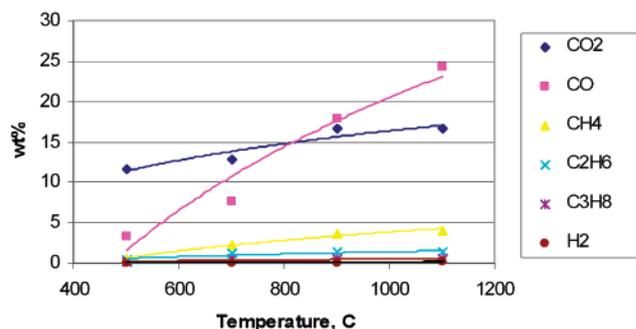
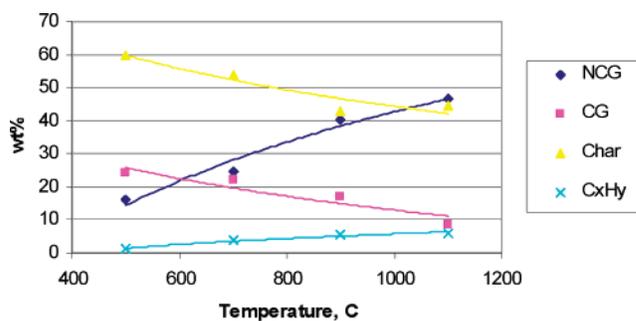


Figure 4. Pyrolysis of the charcoal samples derived from bio-oil production.

Materials and Methods

The charcoal samples from the bio-oil production were pyrolyzed using a Chemical Data System (CDS) analytical

Table 2. Analysis of Switchgrass Charcoal Remaining after Pyrolysis Experiment Compared with Some PA Coals

	as received	dry basis	DAF basis ^a	Schuykill, PA ¹⁰	Indiana, PA ¹⁰
proximate analysis (wt %)				raw coal (dry basis)	raw coal (dry basis)
moisture	3.78				
ash	25.85	26.87		59.1	31.7
volatile matter	28.37	29.48	40.31	8.3	22.3
fixed C	42.00	43.65	59.69	32.6	46.0
ultimate analysis (wt %)					
H	3.99	3.71	5.07	1.2	3.5
C	60.71	63.09	86.27	33.5	57.1
N	0.75	0.78	1.07	0.6	1.7
O	8.70	5.55	7.59	5.1	4.0
S				0.5	1.9
heating value (kJ kg ⁻¹)	19 368.60	20 129.20	27 525.20	11 432.50	23 801.90

^a DAF = dry ash free.**Table 3. Typical Particle Size Analysis of Switchgrass Charcoal Samples from Fluidized-Bed Bio-oil Production**

run #1 typical size analysis					run #2 typical size analysis				
sieve size		sample weight			sieve size		sample weight		
[micron]	[U.S. mesh #]	before (g)	after (g)	% pass cum.	[micron]	[U.S. mesh #]	before (g)	after (g)	% pass cum.
20					20				
32	450	10.11	9.49	6.13	32	450	10.4	9.93	4.52
63	230	9.49	9.3	2.00	90	170	9.93	7.78	25.19
90	170	9.3	7.34	27.40	125	120	7.78	6.07	41.63
125	120	7.34	5.5	45.60	150	100	6.07	4.28	58.85
150	100	5.5	3.84	62.02	180	80	4.28	2.84	72.69
180	80	3.84	2.23	77.94	212	70	2.84	2.05	80.29
212	70	2.23	1.53	84.87	225	>70	2.05	0	100.00
225	>70	1.53	0	100.00					
average particle size									
					microns		st dev		
run #1					149.54		4.78		
run #2					155.01		1.05		

(Oxford, PA) flash pyrolyzer (Pyroprobe). The experimental procedure is reported elsewhere⁷ but further elaborated herein. The setup comprised the pyroprobe, which consisted of a 1 cm quartz tube heated by a platinum filament of 2–3 mm diameter that is capable of maintaining up to 1200 °C temperature at a heating rate of 20 °C ms⁻¹. Although the nominal heating rate is about 20 °C ms⁻¹, the sample heating rate can be much slower, typically 0.3 °C ms⁻¹, and because of the associated thermal mass, the true sample temperature during pyrolysis can typically be a few degrees below the set-point temperature. For the pyrolysis experiments, a charcoal sample weighing ~1 mg was charged into the pyrolyzer (PY) (~1–1.5 mm deep in the probe's quartz tube holder), packed with quartz wool, and purged with helium gas. The evolved gas was directed toward a gas chromatograph (GC) (SRI, CA) interfaced with the pyroprobe (PY) for analysis of gaseous compounds formed during flash pyrolysis. Separation of the NCG fractions of the pyrolysis products (syngas), except H₂, was carried out with a Shincarbon ST 80/100, 2 m × 2.0 mm packed column (Restek, Bellefonte, PA). The GC was programmed to maintain 45 °C for 3 min after injection, followed by a 10 °C/min ramp to 250 °C, then held at 250 °C for 10 min for a total time of 34.4 min. H₂ detection was accomplished by a 4-filament Wheatstone bridge thermal conductivity detector (TCD) (SRI Instruments, CA). The yields of the major noncondensable gas (NCG) produced by primary and secondary pyrolysis reactions were quantified by calibration with a standard gas mixture consisting of H₂, CO, CO₂, CH₄, C₂H₄, C₂H₆, C₃H₈, and C₄H₁₀ in helium (custom-mixed by Scott Specialty Gases, Plumsteadville, PA).

Methods for the quantification of the NCG, char, and condensable aerosol gases (CGs) are described by Boateng et al.⁷ Pyrolysis was carried out in triplicates for the two charcoal samples produced at two fluidized-bed pyrolysis oil production runs (run #1 and run #2) of similar condition as shown in Table 1 at 500, 700, 900, and 1100 °C all at a retention time of 20 s, the time when devolatilization is observed to be complete.⁸

Experiments involving reactivity of the charcoal were conducted in a batch pyrolysis reaction chamber coupled with the CDS pyroprobe temperature controller. The reaction chamber previously described by Boateng and co-workers⁶ was constructed of a 38 mm (1.5 in) stainless steel jacket with 12.7 mm (0.5 in) purge gas inlet and outlet nipples into which the heating coil of the pyroprobe was mounted. The arrangement allowed batch charcoal samples of ~5 mg to be charged into a quartz tube. Combustion reaction, C + O₂ = CO₂, and the Boudouard reaction, C + CO₂ = 2CO, a key gasification reaction step, were carried out at the same temperatures, i.e., 500, 700, 900, and 1100 °C in air and CO₂ atmosphere, respectively, with the samples held at each temperature for 2, 5, 15, 20, and 25 s.

The surface areas and the crystalline structures of the charcoal samples were analyzed using the Brunauer–Emmett–Teller (BET)⁷ and X-ray diffraction (XRD) methods, respectively. The BET N₂ adsorption isotherms of the chars at 77 K were obtained with a gas sorption analyzer, Autosorb-1-MP-LP (Quantachrome), at relative pressure p/p_0 ranging between 10⁻⁶ and 1.⁹

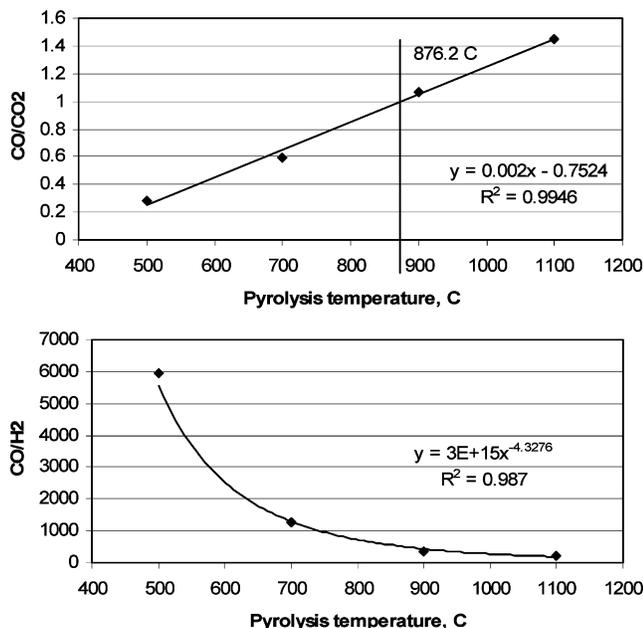


Figure 5. CO/CO₂ and CO/H₂ ratios of produced gas from charcoal at pyrolysis temperature.

Results and Discussion

Proximate and ultimate analyses of a composite charcoal from the two sets of fluidized-bed reactor runs for switchgrass bio-oil production are presented in Table 2. Since the switchgrass feedstock was dried during bio-oil production, the reported water content of the charcoal, ~4%, appears to be reabsorbed fast pyrolysis reaction water, a major component of the bio-oil (20–30%). The high ash content, ~27% dry basis, might present a concern because it could lead to large amounts of alkali metals that could be deployed to the ground should the charcoal be buried or used for soil enrichment. However, the reported 30% volatile matter with 43% fixed carbon and a heating value of 20 MJ/kg make the charcoal comparable with some Pennsylvania coals¹⁰ that are fired in industrial furnaces (Table 2).

The average particle sizes determined by a duplicate analysis of charcoal samples from runs #1 and #2 (Table 3) were 149.54 (± 4.78) μm and 155.01 (± 1.05) μm , respectively. The photomicrographs (Figures 1 and 2) show the structure of the switchgrass charcoal residues from run #1 and run #2, respectively, during the fast pyrolysis oil production in the fluidized-bed reactor.⁴ Increased magnification reveals signs of vesicle formation probably due to either bio-oil or tar coating. Given that the reactor temperature at which the charcoal was produced was 480 °C, these vesicles are unlikely to be the outcome of plastic deformation caused by melting. Such glassy coating will impair the surface and interfacial sorption activity because of the closing of the interfacial pores within the char matrix. BET results indicate that the surface areas of the charcoal accompanying the bio-oil were only 7.7 and 7.9 m²/g for the respective two charcoal samples compared with the original biomass, which was 1.2 m²/g, that is, an increase of only about 6-fold. Total pore volume was 0.042 cm³/g for pores smaller than 5878 Å diameter for the run #1 samples and 0.026 cm³/g for pores smaller than 3274 Å diameter for the run #2 samples, both at $p/p_0 = 0.99$. The average pore diameters for the samples from the two runs were about 216 and 130 Å, respectively, indicating insufficient pore evolution or pore growth. With these low surface areas and pore volumes, it was important to check the crystallinity of the structure to see if a phase change occurred at the fluidized-bed conditions at which the charcoal was

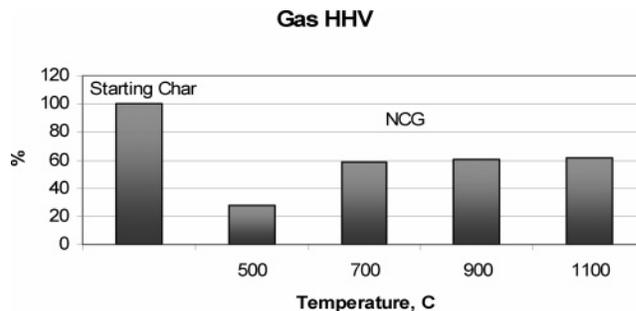


Figure 6. Heat content of noncondensable gas (NCG) yielded during pyrolysis of the charcoal as percent of charcoal HHV.

produced. The XRD scans (Figure 3) show a peak at 15–18°, indicating a high crystallinity index consistent with a change from amorphous phase to crystalline charcoal structure associated with excessive temperature conditions (>1200 °C),¹¹ although the operating reactor temperature was not higher than 500 °C. With the surface characterization results, it is fair to say that the charcoal resulting as a coproduct of the fast pyrolysis oil production, at least from switchgrass, may not possess adequate characteristics for use as activated charcoal “as produced” without further activation. For such applications, surface areas in the 400–1000 m²/g are typical with larger interfacial pore distribution.⁹ This notwithstanding, it is hopeful that the charcoal can still be returned to the soil for a potential use for carbon sequestration.¹² Although charcoals may be applied to the soil for several other applications that may not require larger surface areas, e.g., nutrient delivery and carbon sequestration, it is presumed that soil amendment applications such as sorption of metals would be more effective if the surface areas and the pores are larger than that measured for the bio-oil charcoal produced herein. Sorption efficiencies or the effectiveness of soil contaminants remediation applications similar to the TC and CTC studied by Pils and Laird,³ and other mineral matters on clays and humic substances, are based on the phenomenon of adsorption and require larger char surfaces and interfacial surface areas in addition to activity and metal affinity. The foregoing arguments suggest that charcoal produced alongside fast pyrolysis bio-oil production may be better utilized as a combustion fuel or as a feedstock for gasification rather than as an activated charcoal. The results of further pyrolysis of the charcoal in inert (helium), oxidative (air), and reducing (CO₂) atmospheres are presented herein.

As the ultimate analysis (Table 2) indicates, the charcoal remaining after the fluidized-bed pyrolysis has high ash and high carbon contents and low oxygen content. Further pyrolysis of this product should be similar to coals of similar composition (Table 3), except that, with the charcoal, low tar content product, an important combustion attribute, would be expected. The major fractions of the pyrolysis of the charcoal in the CDS pyroprobe are presented in Figure 4. At 500 °C pyrolysis temperature, the same temperature at which the charcoal was produced in the fluidized-bed reactor, very low gas yield was obtained. The gas yielded at 500 °C when the organic compounds are already devolatilized could come from the dehydration and/or pyrolysis of any recondensed tar or bio-oil. Between 500 and 1150 °C pyrolysis temperature, gas evolution of up to 30% with charcoal mass reduction of ~20% was observed. There was little condensable gas (CG), the aerosols that condense to form bio-oil. It can be reasoned that the marginal yields of CG must be due to that fact that all the tar might have been volatilized during the fluidized-bed bio-oil production. Like coal, the composition of the NCG (Figure 4) comprises mainly CO and CO₂. By extrapolation (Figure 5),

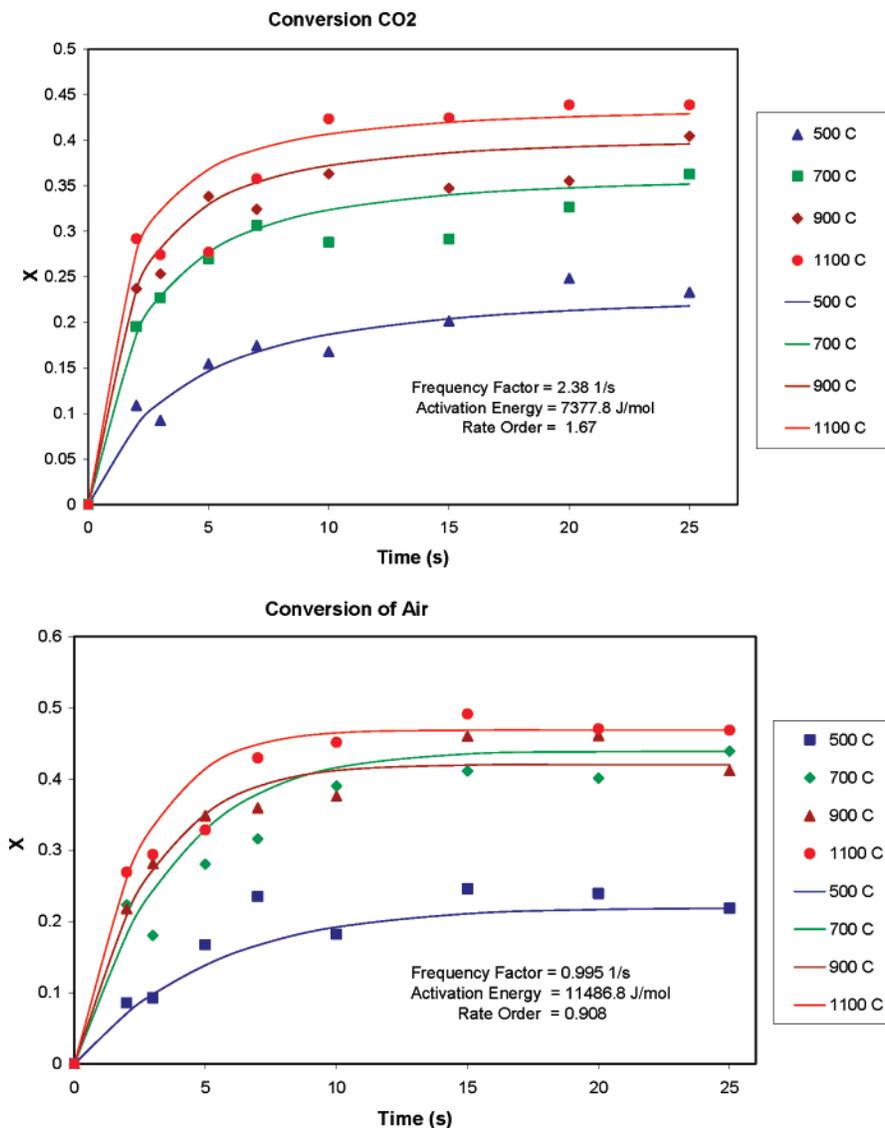


Figure 7. Conversion [$X = (m - m_f)/(m_o - m_f)$] of charcoal samples in a batch system in CO₂ (gasification) and air (combustion) atmospheres. The points are experimental data, and the lines are model $X = A \exp(E/RT)^n$, where A is the frequency factor, E is the activation energy, and n is the reaction order.

the temperature at which equal fractions ($\text{CO}/\text{CO}_2 = 1$) were obtained was ~ 876 °C. Beyond this threshold temperature, $\text{CO}/\text{CO}_2 > 1$ and the heating value of the produced gas improved (Figure 6). However, the high heating value (HHV) peaked at ~ 876 °C, indicating the possibility of CO enrichment via the Boudouard reaction between CO₂ and any residual carbon. Unlike the CO/CO₂ ratio, the CO/H₂ ratio was high at the lower end of the charcoal pyrolysis temperature, reducing exponentially to lower ratios at higher temperatures. This is due to the fact that the H₂ content of the charcoal (Figure 2) is < 4 wt % dry basis and, aside from the low content, the pathway to its cleavage is highly temperature-dependent, making the gas mixture a very dilute H₂ concentration at the pyrolysis conditions studied. The heating value of the gas at this point was $\sim 61\%$ of that of the parent charcoal, indicating that combustion of the char would be more beneficial in terms of direct energy usage. It is worth noting that combustion and gasification of charcoal begin with flaming pyrolysis, which will produce volatile gas that possesses 61% of the available energy at the onset of oxidation (combustion) or reduction (gasification) reactions, respectively.

Combustion and gasification of the charcoal are some of the potential uses given that the surface area is low and the

crystallinity is high. The degrees of the reactions were evaluated by the charcoal conversion defined as $X = (m - m_f)/(m_o - m_f)$, where m , m_o , and m_f are, respectively, the current, initial, and final mass remaining taken as the measured ash content.¹³ The conversion curves (Figure 7) follow the Arrhenius-type reaction kinetics with rates increasing with time and temperature. The extent of the conversion of the reactions in these two atmospheres was about the same with $\sim 50\%$ reacted at the highest temperature, i.e., 1100 °C. However, the kinetic parameters of the conversions were slightly different. The activation energy, E , the frequency factor, A_o , and the reaction order, n , were estimated using the MATLAB parameter-estimation program. The activation energy for the CO₂ reaction was 8 411 J/mol, while that for the reaction in air atmosphere was 11 487 J/mol based on the fits shown in Figure 6 ($R^2 = 0.84\text{--}0.91$). Reactivity of the charcoal, defined as $R_n = -(dm/dt)/(m - m_f)$,¹⁴ was directly proportional to the temperature and inversely proportional to the exposure time. They were similar in the CO₂ and air atmospheres (Figure 8).

Given that the ash was $\sim 30\%$ dry basis, the extent to which carbon is consumed in the air and CO₂ atmospheres was high despite mass transfer limitations in the packed quartz tube used in the batch system. As a result, it would appear that the charcoal

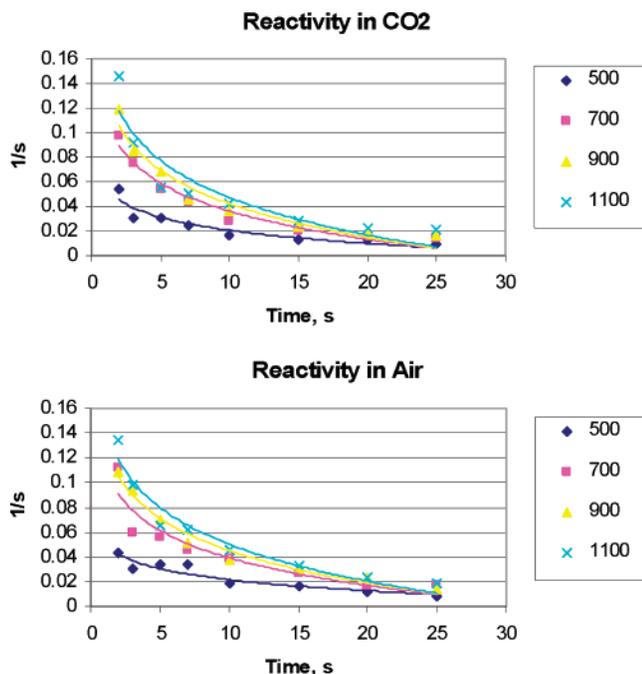


Figure 8. Reactivity curves established from conversion of charcoal samples in CO₂ atmosphere and air atmospheres. The temperatures shown in the legend are in °C.

from bio-oil production with switchgrass might be better used as a gasification feedstock or as a combustion fuel. It would seem that, given its high heating value and small particle size (~150 μm), combustion could be easily carried out with little or no further pulverization to provide the necessary heat for the endothermic reaction of the biomass pyrolysis. However, the high ash content might present a slagging challenge whereby low-melting-point alkali metals might foul heat transfer equipment during combustion. In that regard, using the charcoal as a gasification feedstock might be a better disposal proposition.

Conclusions

The char coproduct accompanying pyrolysis of switchgrass was analyzed for its surface area, and the crystallinity of the structure was characterized to explore possible applications including whether it could be used as an active substrate for adsorption and subsequent soil amendment use. The switchgrass charcoal was also further pyrolyzed in helium to determine yields of condensable, noncondensable, and residual char at temperatures ranging between 500 and 1100 °C. The charcoal was subjected to gasification and combustion in a batch reactor to determine its reactivity in CO₂ and air atmospheres. The surface areas were low and the crystallinity was high, suggesting that the char may not be readily suitable for use as an activated charcoal. However, further pyrolysis in helium yielded syngas similar to that of coal. Between 25 and 50% of the charcoal

was converted between 500 and 1100 °C temperatures in a batch reactor in CO₂ and air atmospheres. The charcoal coproduct of pyrolysis oil production could be a good combustion fuel to power the pyrolysis of the biomass and also a good feedstock for the production of syngas. More research is needed to quantify all potential uses.

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