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Pyrolysis of wood to biochar: Increasing yield while maintaining microporosity

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HIGHLIGHTS

- Reactor geometry was beneficial for the study of volatile species deposition.
- Volatile species migrate along the bed length affecting biochar yield.
- Volatile species and bio-oil carbonization produces microporous structures.
- Similar R134a uptake by biochar after deposition of volatile species and bio-oil.
- Recycling of bio-oil is an effective way to increase biochar yield.

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ABSTRACT

The objective of this study was to determine if biochar yield could be increased by the deposition of volatile pyrolysis species within the bed during production, without negatively influencing the microporosity and adsorption properties. Aspen (*Populus tremuloides*) wood chips were loaded into three vertically stacked zones within a reactor and heated in nitrogen to temperatures between 420 and 650 °C (i.e., pyrolyzed). The yield did increase from the zone at the reactor inlet to the subsequent zones as volatile species deposited and carbonized, and importantly, the carbonized deposits had a similar microporous structure and organic vapor uptake (1,1,1,2-tetrafluoroethane) to that of the primary biochar. Based on these results, bio-oil from previous runs at 600 °C was recycled to the bed, which further increased the yield while maintaining the desirable adsorption properties of the biochar.

1. Introduction

Pyrolysis of biomass results in the production of a solid material with high carbon content called biochar and this biochar has promise either as a soil amendment that sequesters carbon to address climate change (Sohi et al., 2010) or a chemical adsorbent (Chun et al., 2004). To be an effective adsorbent, biochar needs to have sufficient porosity to create the required surface area for the adsorption of various organic compounds including phenol (Han et al., 2013), catechol (Kasozi et al., 2010), soil herbicides (Graber et al., 2012) or trichloroethylene (Ahmad et al., 2012). The pyrolysis process will be more economically favorable if the biochar yield can be maximized while maintaining the adsorption properties.

During pyrolysis, the carbon component of biomass is converted not only to biochar but also to volatile products (both organic and inorganic), reducing the biochar yield. It is known that the biochar yield can be increased by the recycling of volatile products, which can undergo cracking and polymerization and then condense onto the surface of the biochar during pyrolysis (Boroson et al., 1989; Gilbert et al., 2009). The extent of these reactions and the amount of condensation increases with residence time within the reaction bed, resulting in higher biochar yields. Previous studies have shown higher biochar yields with lower heating rates (Mackay and Roberts, 1982), lower gas flow rates (Katyal et al., 2003) or greater pressure within the reactor during pyrolysis (Mok and Antal, 1983). A second approach to increase biochar yield is co-pyrolysis of biomass and bio-oil (Huang et al., 2012). Bio-oil is a carbon rich material, which is partially converted to char under pyrolysis conditions.

Despite the existing studies on the deposition of volatiles and bio-oil recycling to increase biochar yields, there is scarce literature data on the effect of these processes on the porous properties of the resulting biochar. To address this need, in the present study

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biochar samples with different amounts of deposited volatile species were produced under a variety of conditions. In addition, co-pyrolysis of biomass with bio-oil was carried out to investigate the effect of bio-oil recycling on the porous properties of the biochar. In a recent study (Yamashita and Machida, 2011), the conditions that were conducive to high biochar yields and attributed to higher amounts of deposited volatile species were shown to decrease the porosity of the resulting biochar. However, Yamashita and Machida used N_2 adsorption at −196 °C, which underestimates the porous structure of biochar due to the limited diffusion of N_2 into the micropores of biochar at these conditions (Marsh and Wynne-Jones, 1964). Therefore, in the present study, both N_2 adsorption at −196 °C and CO_2 adsorption at 0 °C as well as gas phase adsorption of 1,1,1,2-tetrafluoroethane were used to characterize the biochar samples.

2. Methods

2.1. Preparation of biochar

The biochar was prepared from aspen (*Populus tremuloides*) wood chips provided by Alberta-Pacific Forest Industries Inc. (Boyle, AB, Canada). The chips were dried and crushed, using a blender, into smaller wood particles (0.3–2.0 mm diameter and lengths of 2–10 mm) hereafter referred to as “biomass”.

Pyrolysis was carried out in a vertical quartz reactor with an inner diameter of 21.5 mm (Fig. 1). The purge gas (99.999% pure nitrogen; Praxair Canada Inc., Mississauga, ON, Canada) was supplied to the top of the reactor. The effluent from the bottom of the reactor was connected to a flask (bio-oil trap) that was submerged in a water bath at ambient temperature and used to collect the bio-oil formed during pyrolysis. After pyrolysis, the amount of bio-oil collected was quantified. The exhaust gases were then cleaned up by passing through two flasks, the first containing 1-methoxy-2-propanol and the second containing water. 1-methoxy-2-propanol was chosen for gas cleaning as it is an effective solvent for volatile organic species formed during pyrolysis (Morf et al., 2002).

To investigate the effects of the deposition of volatile species on the properties of the biochar, the biomass was separated into three zones (A, B and C) within the reactor (40 mL total volume) using two stainless steel screens (mesh size of 0.177 mm). At the bottom of the reactor, the biomass was supported by a quartz frit (pore size of 0.055 mm). For each run, 2.5 g of biomass was loaded into each zone of the reactor. Various space velocities, defined as the ratio of N_2 flow rate to the initial volume of biomass loaded into the reactor, were used: 0.5, 1, 2 and 2.8 min^{-1}.

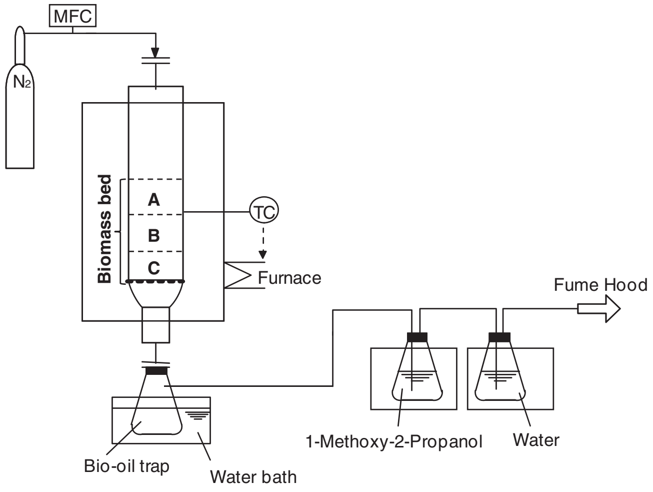

Fig. 1. Pyrolysis setup showing biomass bed separated into three zones (A, B and C) inside the reactor.

After loading, the biomass was purged with N_2 for 15 min to remove residual oxygen from the reactor. Then the temperature of the furnace was increased at a constant rate (4 °C min^{-1}) to 450, 500, 550 or 600 °C and maintained at this temperature for 0.5, 2 or 4 h. In any vertical reactor, temperature gradients can be present and so preliminary tests were done to measure the temperatures within each zone. After loading the reactor with biomass, a thermocouple was inserted into zone A and then the temperature was increased to 450 °C. This temperature was maintained for 20 min and then increased in 50 °C increments to 600 °C. The entire procedure was repeated twice, with fresh biomass, but with the thermocouple in zone B and then zone C. The differences between the temperature of the furnace and the temperatures within the bed in zones A and B did not exceed 3 °C, whereas the temperature from zone C was approximately 30 °C lower. After pyrolysis, the furnace was cooled down under N_2 flow. The biochar prepared in each reactor zone was weighed to calculate the yield and then placed into sealed plastic bags for storage. Each sample was prepared at least three times to verify the reproducibility of the results. The yield of biochar is reported as an average ± standard error.

2.2. Characterization of biochar

Porous properties of the prepared biochar were characterized by N_2 and CO_2 adsorption at −196 and 0 °C, respectively, using a Tristar 3000 instrument (Micromeritics Instrument Corporation, Norcross, GA, USA). Prior to adsorption, the biochar samples were outgassed under vacuum at 300 °C for 3 h. Micropore volumes were calculated from N_2 and CO_2 adsorption isotherms using *t*-plot and Dubinin-Radushkevich methods, respectively. The densities of adsorbed N_2 and CO_2 were taken as 0.808 g mL^{-1} and 1.023 g mL^{-1}, respectively (Cazorla-Amoros et al., 1996). The reported values for micropore volumes are averages ± standard errors from biochar samples prepared in three different runs. Micropore size distribution was calculated from CO_2 adsorption isotherms using the non-local density functional theory method and assuming a slit pore model.

Total pore volume was determined from the N_2 adsorption isotherms at relative pressures of 0.96–0.97, which corresponded to adsorption in pores with widths up to 56–65 nm. For all biochar samples, the total pore volumes were only 0.02–0.03 mL g^{-1} greater than the corresponding micropore volumes determined by N_2 adsorption, suggesting that the majority of pores developed during pyrolysis were microporous (<2 nm) in size. Therefore, only the changes in micropore volumes are discussed in the manuscript.

The amount of fixed carbon in the biochar was characterized by thermogravimetric analysis using a Cahn Thermax 500 apparatus (Thermo Fisher Scientific Inc., Rockford, IL, USA). Triplicate samples were analyzed in the thermogravimetric apparatus. Approximately 10 mg of the biochar was placed into a quartz crucible and heated in flowing N_2 (300 mL min^{-1}) to 105 °C for drying. After drying, the temperature was increased at 10 °C min^{-1} to 900 °C, and then the sample was held at this temperature for 15 min in flowing N_2 to determine the mass of carbon and ash ($m_{carbon} + m_{ash}$). After 15 min, N_2 was switched to air (300 mL min^{-1}; Praxair Canada Inc., Mississauga, ON, Canada) for an additional 15 min to burn carbon and determine the ash content (m_{ash}). The fixed carbon content was calculated from the difference between these masses. The percent of volatile matter in the biochar was calculated as 100 minus the percents of fixed carbon and ash.

The statistical significance of differences between obtained results was determined using a two-tailed t-test with a confidence interval of 95%.

2.3. Adsorption of 1,1,1,2-tetrafluoroethane

The adsorption capacity of the biochar towards volatile organic compounds was measured by the uptake of 1,1,1,2-tetrafluoroethane (R134a) at 101 °C in a lab-built thermogravimetric apparatus. The detailed description of the adsorption apparatus and measurement procedure has been provided in the Supplementary material. Summarizing the analytical method, ~0.3 g of biochar was placed into a wire basket with a thermocouple located just above the sample. The sample was heated up to 300 °C in N_2 for outgassing. The heating supply was then turned off and the N_2 switched to pure R134a (automotive-grade refrigerant, CAS# 811-97-2, China National BlueStar (Group) Co, Ltd.). The biochar was cooled to 101 °C in a flowing stream of R134a and the sample temperature and mass were recorded every 30 s. Duplicate experiments were carried out for randomly selected samples. The adsorption capacity was calculated as the volume of liquid R134a per mass of outgassed biochar, assuming a liquid density of R134a of 0.515 g cm^{-1} (Morrison and Ward, 1991).

3. Results and discussion

3.1. Deposition of volatiles on biochar

The yield of biochar produced as a function of different variables is presented in Fig. 2. In Fig. 2a, the yield is plotted as a function of bed temperature in each of the zones (420–650 °C). The yield of biochar from each reactor zone decreased with increasing temperature, presumably due to an increase in the release of volatile species with temperature. In all experiments, the yield of biochar from zone A was lower than the yields of biochar from zones B and C. At 450 °C, the yields of biochar from zones A and B were 24.6 ± 0.1% and 26.9 ± 0.1%, respectively, while at 650 °C, the yields were 21.3 ± 0.2% and 23.3 ± 0.1%, respectively. Based on these yields, for each gram of biochar produced in zone A, ~1.09 g of biochar was produced in zone B (i.e., an additional 0.09 g was produced in zone B).

To better understand the observed increases in the yield of biochar in zones B and C, several experiments were performed with different reactor loading patterns as described in Table 1. All experiments in Table 1 were performed with a furnace temperature of 600 °C, space velocity of 1 min^{-1}, which corresponds to ~40 mL min^{-1} of N_2 flow, and holding time of 0.5 h. Experiment 1 was the base case with 2.5 g of biomass loaded in the three zones; these results were shown in Fig. 2.

In Experiments 2, 3 and 4 only a single reactor zone (A, B, or C, respectively) was loaded with biomass. The yields of biochar produced in Experiments 2, 3 and 4 were similar (22.1 ± 0.2%, 21.9 ± 0.1% and 22.3 ± 0.1% in Experiments 2, 3 and 4, respectively). The yields of biochar prepared in zone A in Experiments 1 and 2 were similar while the yield of biochar in zone C of Experiment 1 was higher than that of Experiment 4. These results suggested that the higher yields in zones B and C of Experiment 1 were a result of the presence of biomass in the other reactor zones.

This phenomenon was further confirmed by replacement of biomass in either one or two zones by biochar produced in Experiment 2 (Experiments 5, 6 and 7). The amount of biochar loaded into reactor zones was equivalent to the amount produced from 2.5 g of biomass (i.e. ~0.55 g). The changes in the biochar yield before and after reheating (e.g. mass loss due to reactor loading or moisture content) was determined in Experiment 8 by pyrolyzing a similar amount of biochar to that produced in Experiment 2 in the absence of biomass in the reactor. The resulting yield of 96.0 ± 0.2% confirmed that little if any change occurred to the biochar upon reheating. When the biomass in zone A was replaced with biochar (Experiment 5), the yield of biochar produced in zone B was similar to the yield obtained when the reactor contained biomass in only zone B (Experiment 3). When biomass in both zones A and B was replaced with biochar (Experiment 6), the yield of biochar produced in zone C was similar to the yield obtained when the reactor contained biomass in only zone C (Experiment 4). On the other hand, when zones A and B were loaded with biomass and zone C was loaded with biochar, the yield of biochar produced in zone B was similar to that in Experiment 1 in which all zones contained biomass. Thus, only the replacement of biomass in the upstream zone decreased the biochar yield produced in the subsequent zone. These results are consistent with volatile species formed upstream depositing and increasing the yield in the zones downstream.

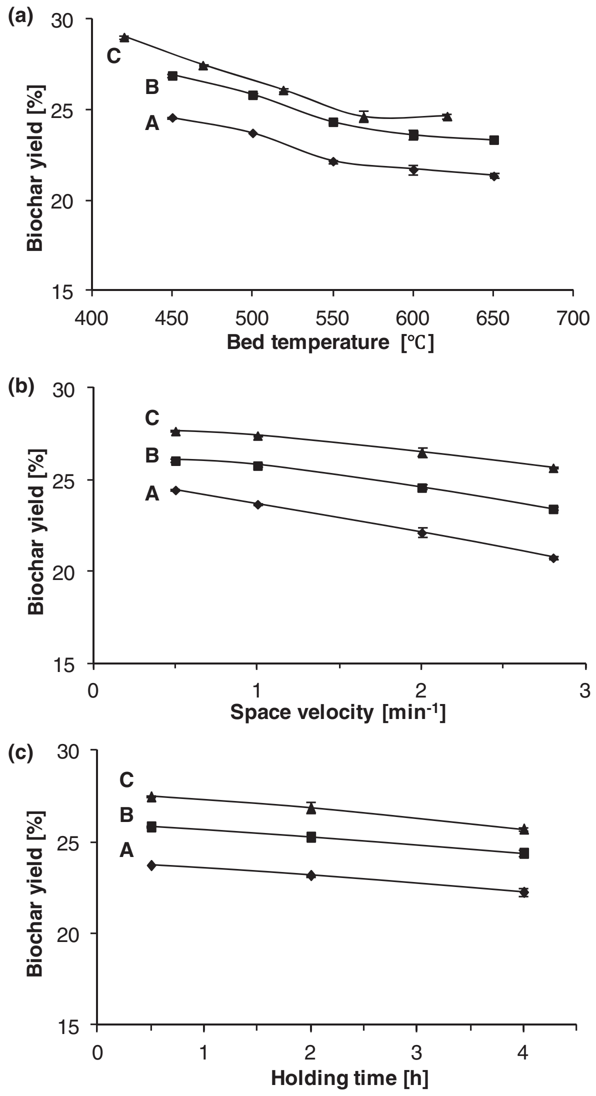

Fig. 2. Biochar yields from reactor zones A, B and C as a function of (a) temperature, with holding time of 0.5 h and space velocity of 1 min^{-1}, (b) space velocity, with holding time of 0.5 h and 500 °C (zones A and B) or 469 °C (zone C), and (c) holding time, with space velocity of 1 min^{-1} and 500 °C (zones A and B) or 469 °C (zone C). The symbols correspond to the mean values of three runs, and the lines are only to guide the eye.

Further evidence for increased yield due to migration and deposition of volatile species on biochar was provided in Experiments 9 and 10. In Experiment 9, zones A and C were loaded with biomass whereas zone B was left empty. As expected, the yield of biochar produced in zone C was higher than that in zone A (24.7 ± 0.2%

Table 1
Influence of reactor loading pattern on biochar yield in zones A, B and C.

Reactor zone	Experiment 1		Experiment 2		Experiment 3		Experiment 4	
	Material loaded	Yield (%)	Material loaded	Yield (%)	Material loaded	Yield (%)	Material loaded	Yield (%)
A	Biomass	21.8 ± 0.2	Biomass	22.1 ± 0.2	Empty	–	Empty	–
B	Biomass	23.7 ± 0.3	Empty	–	Biomass	21.9 ± 0.1	Empty	–
C	Biomass	24.8 ± 0.3	Empty	–	Empty	–	Biomass	22.3 ± 0.1
	Experiment 5		Experiment 6		Experiment 7		Experiment 8	
A	Biochar	96.6 ± 0.2	Biochar	95.6 ± 0.1	Biomass	21.9 ± 0.1	Biochar	96.0 ± 0.2
B	Biomass	21.9 ± 0.1	Biochar	96.8 ± 0.1	Biomass	23.9 ± 0.1	Empty	–
C	Biomass	24.4 ± 0.1	Biomass	22.4 ± 0.1	Biochar	102.2 ± 0.4	Empty	–
	Experiment 9		Experiment 10					
A	Biomass	21.9 ± 0.2	Biomass	21.9 ± 0.1				
B	Empty	–	Silica gel	–[a]				
C	Biomass	24.7 ± 0.2	Biomass	21.7 ± 0.2				

[a] The amount of deposited carbon after pyrolysis was 0.165 ± 0.001 g.

Table 2
Composition of biochar produced at different conditions: fixed carbon, volatile matter and ash (dry basis).

Bed temperature (°C)	Space velocity (min^{-1})	Holding time (h)	Reactor zone	Fixed carbon (%)	Volatile matter (%)	Ash (%)
500	1	0.5	A	79.8 ± 0.3	17.7 ± 0.3	2.5 ± 0.3
500	1	0.5	B	80.5 ± 0.5	17.5 ± 0.4	2.0 ± 0.2
469	1	0.5	C	78.2 ± 0.4	19.7 ± 0.4	2.1 ± 0.3
500	2.8	0.5	A	79.5 ± 0.3	18.0 ± 0.2	2.5 ± 0.1
500	2.8	0.5	B	80.5 ± 0.4	17.8 ± 0.3	1.7 ± 0.5
469	2.8	0.5	C	78.4 ± 0.3	19.9 ± 0.4	1.7 ± 0.2
500	1	4	A	84.4 ± 0.6	13.2 ± 0.8	2.4 ± 0.6
500	1	4	B	85.6 ± 0.8	12.9 ± 0.8	1.5 ± 0.1
469	1	4	C	83.4 ± 0.7	15.1 ± 0.9	1.5 ± 0.4

and 21.9 ± 0.2%, respectively). In Experiment 10, zone B was loaded with silica gel (Davisil, grade 646, mesh 35–60, Sigma–Aldrich), which is able to capture volatile species, and the yield of the biochar produced in zone C was similar to that in zone A (21.7 ± 0.2% and 21.9 ± 0.1%, respectively).

When at least one of the upstream zones was loaded with biomass and no silica gel was used to capture the volatile species, the yield of biochar produced in zone C was higher than the yield in zone B (Experiments 5 and 9). The deposition of volatile species in zone C is likely enhanced by the lower temperature in this zone. In Experiment 7, the biochar yield was greater than 100%, which is consistent with deposition of volatile species.

The fixed carbon, volatile matter and ash contents of the produced biochar are listed in Table 2. The amounts of volatile matter in the biochar from zones A and B were similar (17.7 ± 0.3% and 17.5 ± 0.4%, respectively) for the first set of experiments listed, suggesting that the volatile species deposited in zone B could be carbonized and converted to char during pyrolysis. The content of volatile matter in the biochar from zone C was higher (19.7 ± 0.4%) compared to the biochar from zones A and B, possibly due to the lower temperature such that the original volatile matter was not removed, and/or due to volatile species from the other zones condensing in this lower temperature zone.

Fig. 2b shows the influence of space velocity on the yield of biochar produced in zones A, B and C. At each space velocity, the biochar yields in zones B and C were higher than that in zone A. Similar results were obtained when the holding time was increased from 0.5 to 4 h at a space velocity of 1 min^{-1} (Fig. 2c). The observed decrease in biochar yield from each zone with higher space velocity (Fig. 2b) and holding time (Fig. 2c) was consistent with the reported data for pyrolysis of other carbonaceous materials, including cellulose, oil palm waste and sugar cane bagasse (Mok and Antal, 1983; Lua and Guo, 1998; Katyal et al., 2003). The amounts of fixed carbon and volatile matter in the biochar from the three zones prepared at different conditions are given in Table 2. The degree of carbonization (i.e., the amount of fixed carbon) was relatively insensitive to changes in flow rate, but increased by ~5% with an increase in holding time from 0.5 to 4 h for all three reactor zones, suggesting that prolonged treatment could improve the degree of carbonization for any deposited volatile species.

3.2. Influence of deposited volatile species on biochar adsorption capacity

The biochar adsorption capacity for a gas phase fluorinated organic species, 1,1,1,2-tetrafluoroethane (R134a), was investigated and compared to the micropore volumes determined from the CO_2 and N_2 adsorption isotherms (Fig. 3). In Fig. 3a, the uptakes of R134a of biochar samples produced in each reactor zone are shown as a function of bed temperature (420–650 °C). The adsorption capacities of the biochar from the three zones were similar, which suggests that the deposition of volatiles in zones B and C (Fig. 2) did not detract from the biochar adsorption capacity, at least in terms of the R134a adsorbate. The uptake of R134a increased slightly for the biochar samples prepared at higher temperatures.

Fig. 3b shows the micropore volumes determined by N_2 and CO_2 adsorption for the biochar samples. As with the adsorption of R134a, at all temperatures, the measured micropore volumes of the biochar samples from zones A, B and C were essentially the same (the symbols are overlapping in Fig. 3b). Furthermore, the biochar samples from the three zones prepared at various temperatures had similar micropore size distributions (Fig. 3c, representative distributions are shown in this plot). At all temperatures, the micropore size distributions of biochar from the three zones were similar. Micropore volume and micropore size distribution of an adsorbent are important parameters that influence organic species

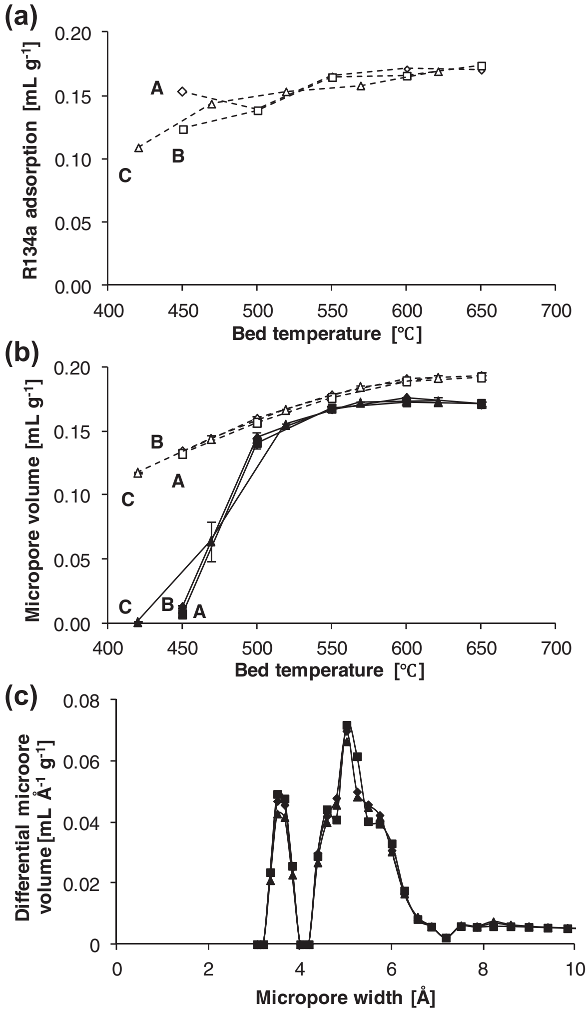

Fig. 3. Influence of temperature (0.5 h and 1 min^{-1}) on characteristics of biochar produced in zones A, B and C: (a) R134a adsorption at 101 °C, (b) micropore volumes determined from N_2 and CO_2 adsorption (solid and dashed lines, respectively) and (c) typical micropore size distributions of biochar produced in reactor zones A (▲) and B (■) at bed temperature 600 °C, and C (♦) at bed temperature 569 °C. The symbols correspond to the mean values of three runs, and the lines are only to guide the eye.

removal from the gas phase. Thus, it is not surprising that the microporosity properties as a function of reactor zone are consistent with the corresponding R134a capacities.

According to Fig. 3b, micropore volume is not a function of the zone in which the biochar was produced, suggesting that the deposited volatile species were probably converted to microporous carbon during pyrolysis. As mentioned in Section 3.1, for each gram of biochar prepared in zone A, the amount of biochar produced in zone B was ~1.09 g (1 g of biochar from biomass pyrolysis in zone B and ~0.09 g due to the deposition of volatile species transferred from zone A). If the deposited volatile species in zone B were inert non-porous compounds and/or blocked the pores, the porosity would decrease in zone B by ~8% (0.09 g × 100%/1.09 g) compared to zone A. According to a two sample t-test with a confidence interval of 95%, this decrease would be statistically significant for biochar produced at all temperatures except 450 °C.

The micropore volumes determined by N_2 adsorption were lower than those determined by CO_2 adsorption (Fig. 3b), as seen previously for biochar samples prepared from other feedstocks (Mackay and Roberts, 1982; Baklanova et al., 2003; Mukherjee et al., 2011). The diffusion of N_2 is relatively slow at the temperature of the measurement (−196 °C) and, thus, fewer micropores are accessed compared to those accessed by CO_2 at 0 °C (Marsh and Wynne-Jones, 1964). The difference between the micropore volumes was significantly greater for the biochar samples produced at the lowest temperature (i.e., furnace temperature of 450 °C).

To provide more insight on the relationship between the R134a uptake and the micropore volumes measured by N_2 and CO_2 adsorption, these quantities were plotted against each other. Fig. 4 shows the data collected for biochar produced in all three reactor zones at temperatures between 420 and 650 °C with a space velocity of 1 min^{-1}. There is a reasonable linear relationship ($R^2 = 0.72$) between the R134a uptake and the micropore volume determined by CO_2 adsorption (Fig. 4a). In contrast, there is not such a clear trend with the micropore volume determined by N_2 adsorption (Fig. 4b). Biochar samples with essentially no micropore volume as measured by N_2 adsorption had R134a uptakes of more than 0.1 mL g^{-1}, suggesting that some pores are accessible to R134a at 101 °C that are not accessible to N_2 at −196 °C. Therefore, micropore volumes determined from CO_2 adsorption are more relevant to higher temperature (101 °C) gas phase adsorption than the micropore volumes calculated from N_2 adsorption.

3.3. Conversion of bio-oil to biochar

The results of the adsorption measurements (Fig. 3) suggest that the deposition of volatile species within the reactor could increase biochar yield without sacrificing adsorption capacity. Thus, the hypothesis that the bio-oil collected at the exit of the furnace could

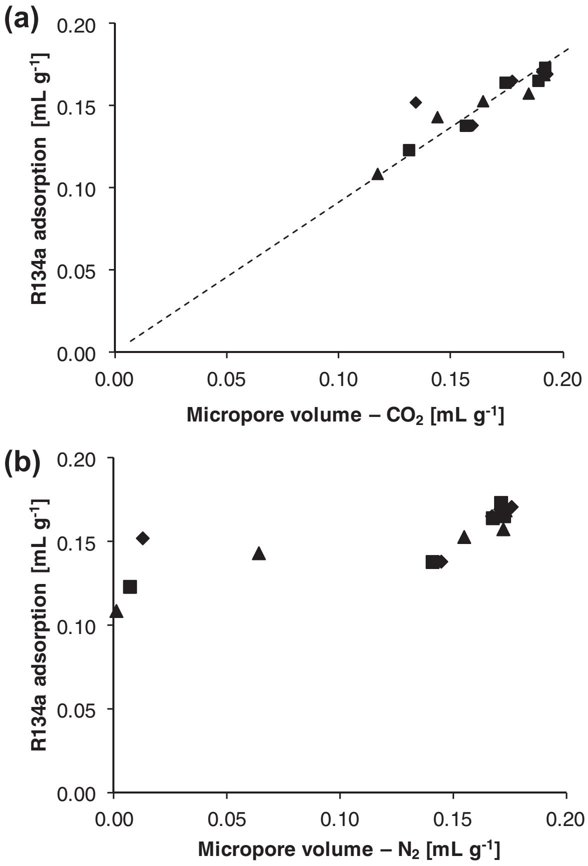

Fig. 4. R134a adsorption at 101 °C as a function of micropore volume determined by (a) CO_2 and (b) N_2 adsorption for biochar produced in reactor zones A(▲), B (■), and C (♦).

be recycled to the bed to further increase the yield while maintaining the desired adsorption properties in the produced biochar was tested. During the pyrolysis of biomass, the formation of bio-oil and a vapor stream significantly decreases the yield of biochar such that only between 43% and 63% (value depends on the feedstock) of the carbon in the original biomass is converted to biochar (Ben and Ragauskas, 2013; Lee et al., 2013). Thus the recycling of the bio-oil would be a feasible approach to increase the efficiency of biochar production.

Accordingly, the bio-oil (a mixture condensed at ambient temperature, ~23 °C) was collected from previous runs at 600 °C, and ~3.27 g was added to the top of the biomass bed (i.e., zone A) using a syringe. The yield of bio-oil produced at this temperature was 51.0 ± 0.5%, which is approximately two times higher than the yield of biochar (Table 1, Experiment 1). After addition of the bio-oil to the bed, the upper half of zone A had a darker color, suggesting that the added bio-oil accumulated mainly in zone A and did not distribute throughout the bed. The biomass impregnated with bio-oil was pyrolyzed at 500 or 600 °C. According to FTIR spectra of the biochar (Supplementary material), no difference in the surface chemistry of the samples prepared at the same temperature without and with bio-oil addition to biomass was observed. Further experiments were performed in which bio-oil was added to biochar rather than biomass, as follows. At first, the biomass was pyrolyzed at 600 °C with a space velocity of 1 min^{-1} and a holding time of 0.5 h. After cooling, the parent biochar produced in each zone was weighed and loaded back into the reactor. The bio-oil was added to the top of zone A and the mixture was pyrolyzed again at the same conditions.

The results of these experiments and those done previously without the addition of bio-oil are shown in Table 3. The masses of biochar produced as an average of three runs ± standard errors are reported in this table. After pyrolysis with the addition of bio-oil, the largest mass gain (0.261 g) was observed in zone A, increasing the biochar yield in this zone by 44%. The mass gain was significantly less in zones B and C – 0.030 g and 0.015 g, respectively. A similar mass gain was achieved by bio-oil addition in zone A (0.263 g) when the pyrolysis temperature was increased to 600 °C. The mass of biochar produced from biomass at 600 °C, however, was lower than at 500 °C (0.545 and 0.593 g, respectively) so that the percent increase in the biochar yield at 600 °C was actually higher (48%).

To verify that the bio-oil was converted to biochar during the pyrolysis, an experiment was done using quartz wool instead of biomass as the substrate for the bio-oil. That is, the reactor zones were loaded with quartz wool and then bio-oil was added to the top of zone A using the procedure described above. Similar to the pyrolysis of biomass impregnated with bio-oil, the largest mass gain (0.153 g) was observed in zone A (Table 3), suggesting that bio-oil could be converted to biochar under these conditions. Similar results were reported in a study of pyrolysis of Japanese cedar chips impregnated with bio-oil, which showed that bio-oil undergoes self-charring at 500 °C (Huang et al., 2012). As the mass increase in zone A was lower with quartz wool than with biomass, there may be some interaction between the bio-oil and biomass but further studies are needed to investigate this phenomenon. The addition of bio-oil to the quartz wool also resulted in biochar production in zones B and C –0.049 and 0.014 g, respectively (Table 3), consistent with the previous results (Fig. 2) showing that volatile species, in this case originating from the bio-oil, deposit on the bed while passing through the reactor.

The characterization results for biochar produced from biomass only and with bio-oil addition are summarized in Table 4. The micropore volumes, determined by CO_2 adsorption, and R134a uptakes were essentially the same at 500 and 600 °C, with and without bio-oil addition. There was a modest decrease in the micropore volume determined by N_2 adsorption for the biochar samples in zone A produced at 500 °C with bio-oil addition (0.101 mL g^{-1} versus 0.145 mL g^{-1}), possibly due to micropore blockage by pyrolyzed bio-oil. There was, however, no significant difference in micropore volumes determined by N_2 adsorption for biochar prepared in zone A with and without bio-oil addition at 600 °C. As there was a mass gain with bio-oil addition, the similar microporosity of biochar produced at 600 °C with and without bio-oil addition, as well as similar R134a uptake, suggest that the additional bio-oil does not change the characteristics of the produced biochar. Thus, an increased yield has been achieved while maintaining the microporous properties and adsorption capacity.

The addition of bio-oil to a parent biochar followed by pyrolysis at 600 °C resulted in a smaller increase in mass compared to the addition of bio-oil to biomass (Table 3). The co-pyrolysis of bio-oil with biochar produced a product with lower micropore volumes determined by N_2 and CO_2 adsorption (Table 5) compared to that prepared from the mixture of bio-oil with biomass at the same conditions (Table 4). This decrease in micropore volumes is similar to the phenomenon observed during chemical vapor deposition of organic vapors on activated carbons and could be attributed to the formation of carbon deposits from bio-oil at the micropore entrances and inside the micropores (Villar-Rodil et al., 2005). For adsorption applications, the addition of bio-oil

Table 3
Amount of biochar produced from biomass only and with bio-oil addition (0.5 h and 1 min^{-1}).

Bed temperature (°C)	Reactor zone	Biomass only (g)		With bio-oil (g)	
		Before pyrolysis	After pyrolysis	Before pyrolysis	After pyrolysis
500	A	2.499 ± 0.001	0.593 ± 0.001	5.767 ± 0.037[a]	0.854 ± 0.010
500	B	2.500 ± 0.001	0.646 ± 0.002	2.500 ± 0.001	0.676 ± 0.004
469	C	2.501 ± 0.001	0.687 ± 0.001	2.500 ± 0.001	0.702 ± 0.002
600	A	2.500 ± 0.001	0.545 ± 0.005	5.772 ± 0.027	0.808 ± 0.006
600	B	2.500 ± 0.001	0.593 ± 0.005	2.500 ± 0.001	0.640 ± 0.003
569	C	2.500 ± 0.001	0.619 ± 0.007	2.500 ± 0.001	0.660 ± 0.004
				Biochar with bio-oil (g)	
600	A			3.810 ± 0.004[b]	0.705 ± 0.007
600	B			0.598 ± 0.002	0.622 ± 0.006
569	C			0.621 ± 0.001	0.638 ± 0.002
				Bio-oil only (g)	
500	A			3.264 ± 0.002[c]	0.153 ± 0.024
500	B			0	0.049 ± 0.012
469	C			0	0.014 ± 0.009

[a] Mixture of biomass (2.500 g) and bio-oil (remainder of mass).
[b] Mixture of biochar (0.545 g) and bio-oil (remainder of mass).
[c] Mass of bio-oil loaded on quartz wool.

Table 4
Micropore volumes and R134a uptakes on biochar produced from biomass only and with bio-oil addition (0.5 h and 1 min^{-1}).

Bed temperature (°C)	Reactor zone	Micropore volume – N_2 (mL g^{-1})		Micropore volume – CO_2 (mL g^{-1})		R134a uptake (mL g^{-1})	
		Biomass only	With bio-oil	Biomass only	With bio-oil	Biomass only	With bio-oil
500	A	0.145 ± 0.004	0.101 ± 0.008	0.159 ± 0.002	0.155 ± 0.002	0.14 ± 0.02	0.12 ± 0.01
500	B	0.141 ± 0.004	0.132 ± 0.005	0.156 ± 0.003	0.155 ± 0.002	0.14[a]	0.13
469	C	0.064 ± 0.016	0.089 ± 0.003	0.144 ± 0.003	0.147 ± 0.001	0.14	0.12
600	A	0.176 ± 0.001	0.177 ± 0.010	0.190 ± 0.001	0.185 ± 0.004	0.17 ± 0.02	0.15 ± 0.01
600	B	0.172 ± 0.001	0.177 ± 0.008	0.189 ± 0.001	0.186 ± 0.003	0.17	0.17
569	C	0.172 ± 0.001	0.182 ± 0.012	0.184 ± 0.001	0.183 ± 0.003	0.16	0.15

[a] Standard errors are not provided as only one measurement was done.

Table 5
Micropore volumes of biochar produced by co-pyrolysis of parent biochar with bio-oil (0.5 h and 1 min^{-1}).

Bed temperature (°C)	Reactor zone	Micropore volume – N_2 (mL g^{-1})	Micropore volume – CO_2 (mL g^{-1})
600	A	0.067 ± 0.004	0.164 ± 0.002
600	B	0.049 ± 0.009	0.158 ± 0.003
569	C	0.095 ± 0.009	0.156 ± 0.002

to biomass, rather than biochar is more beneficial as higher biochar yields can be obtained without a decrease in microporous properties.

4. Conclusion

This study investigated the pyrolysis of aspen wood chips and the conversion of the produced volatile species and bio-oil into biochar. At the same conditions, no effect of the deposited volatiles on microporous structure (N_2 and CO_2 adsorption) was observed. Co-pyrolysis of bio-oil with biomass at 600 °C resulted in biochar with microporosity similar to the biochar produced without bio-oil addition. The benefit of the bio-oil addition to biomass was the increase in biochar yield. Addition of bio-oil to biochar also increased the yield but the microporosity was compromised.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.biortech.2013.11.082.

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