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Enhancing biochar yield by co-pyrolysis of bio-oil with biomass: Impacts of potassium hydroxide addition and air pretreatment prior to co-pyrolysis

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HIGHLIGHTS

- Air pretreatment and KOH addition prior to co-pyrolysis increased biochar yield.
- An increased yield was maintained in six consecutive co-pyrolysis runs.
- Air pretreatment produced biochar with higher porosity and lower ash content.
- KOH catalyzed oxidation of mixture during air pretreatment reducing yield.

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ABSTRACT

The influence of KOH addition and air pretreatment on co-pyrolysis (600 °C) of a mixture of bio-oil and biomass (aspen wood) was investigated with the goal of increasing biochar yield. The bio-oil was produced as a byproduct of the pyrolysis of biomass and recycled in subsequent runs. Co-pyrolysis of the biomass with the recycled bio-oil resulted in a 16% mass increase in produced biochar. The yields were further increased by either air pretreatment or KOH addition prior to co-pyrolysis. Air pretreatment at 220 °C for 3 h resulted in the highest mass increase (32%) compared to the base case of pyrolysis of biomass only. No synergistic benefit was observed by combining KOH addition with air pretreatment. In fact, KOH catalyzed reactions that increased the bed temperature resulting in carbon loss via formation of CO and CO_2.

1. Introduction

Biochar produced from biomass can be used as a renewable fuel, adsorbent, precursor of activated carbon, or soil amendment (Antal and Gronli, 2003; Lehmann et al., 2006). Furthermore, due to its stability against biological decomposition, the biochar is considered as a carbon sink for anthropogenic CO_2 emissions (Lehmann et al., 2006). Only 43–63% of the carbon contained in biomass is typically converted to biochar during pyrolysis (Lee et al., 2013). The remaining carbon is released as volatile species that upon cooling either form condensable liquids (often called “bio-oil”) or non-condensable vapors (i.e., gases). Both products have high calorific values and can be used as fuel (Bridgwater and Peacocke, 2000).

The use of bio-oil, however, is complicated by its acidity, toxicity, high water and oxygen contents, and propensity to form a solid residue upon reheating (Oasmaa and Czernik, 1999). On the other hand, the low volatility of bio-oil makes it a good precursor for biochar production. In a recent study, bio-oil was successfully recycled to increase the biochar yield with no deterioration of the microporous structure and organic vapor uptake (1,1,1,2-tetrafluoroethane) of the produced biochar compared to the primary biochar from biomass (Veksha et al., 2014). Previously, Huang et al. (2012) demonstrated that the proposed recycling approach is also advantageous in simultaneous refining of bio-oil.

The conversion efficiency during pyrolysis of bio-oil with biomass to produce biochar can potentially be further increased. For example, DeGroot and Shafizadeh (1984) have reported that addition of potassium compounds increases biochar formation during biomass pyrolysis by catalyzed decomposition of primary liquid products into solid carbon and gases. An increase in solid carbon yield after air pretreatment at temperatures between

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approximately 200 °C and 300 °C was reported for pyrolyzed coal- and petroleum-derived pitches and polymers (White and Sheaffer, 1989; Fernandez et al., 1995; Worasuwannarak et al., 2003). This phenomenon is most likely attributed to an increase in the aromaticity and molecular cross-linking due to oxidation (Barr and Lewis, 1978; Zeng et al., 1993).

Although both potassium addition and air pretreatment are well-known techniques, they have not been applied to the co-pyrolysis of bio-oil with biomass. As such, the influences of potassium hydroxide addition (0.24% or 0.48%, note all percentages in this manuscript refer to mass percent) and air pretreatment (180 °C–240 °C for 3 h) prior to co-pyrolysis at 600 °C on biochar yield and the porous properties of the produced biochar were investigated in this study. The porous properties of the biochar were determined by nitrogen and carbon dioxide adsorption. According to the literature cited above, the mechanisms by which biochar yield is increased by potassium hydroxide addition and air pretreatment are likely different and, thus, these methods were combined in this study to see if a synergistic effect would result. A series of pyrolysis experiments were done to demonstrate the feasibility of a production process with recycled bio-oil.

2. Methods

2.1. Preparation of bio-oil

Bio-oil was prepared by the pyrolysis of aspen wood particles (*Populus tremuloides*), which will be referred to as biomass throughout this paper. Pyrolysis was carried out in a vertical down-flow packed bed reactor set-up described in detail elsewhere (Veksha et al., 2014). Briefly, the reactor consisted of a quartz tube surrounded by a furnace. The bottom of the reactor (outlet) was connected to a trap for any bio-oil produced. This trap was submerged in a water bath at ambient temperature. A thermocouple controlling the furnace temperature was inserted in the middle of the furnace between the quartz reactor and the heating element of the furnace. The distance between the thermocouple tip and the reactor wall was 5 mm. Approximately 7.5 g of biomass (particle diameter 0.3–2.0 mm and particle length 0.3–5.0 mm) was packed in the reactor to form a bed with a volume of ~35 mL. The biomass was heated at 4 °C min^{-1} under nitrogen flow (space velocity 1 min^{-1}) to 600 °C and pyrolyzed with this gas flow for 0.5 h. After pyrolysis, the reactor was cooled to 70 °C in N_2 and the masses of produced bio-oil and biochar were quantified.

2.2. Co-pyrolysis of bio-oil with biomass

To study the effect of potassium hydroxide addition, 85% pure KOH (Lot 10144950, Alfa Aesar, USA) was used for the experiments. The mixtures of bio-oil with biomass containing either 0.24% or 0.48% by weight of KOH were prepared. The small amounts of KOH were used to limit ash content in the final product to approximately 5%, which is considered a maximum for typical good-quality char (Antal and Gronli, 2003). Either 0.034 g or 0.068 g of potassium hydroxide was weighed in a 10 mL vial and then dissolved in 0.1 g of deionized water followed by addition of 4.0 g of bio-oil. The contents of the vial were transferred into a beaker with 7.5 g of biomass and mixed. Considering a mass loss of 5% during transfer, the actual mass of bio-oil added to the biomass was 3.8 g. The prepared mixture of bio-oil with biomass containing KOH was loaded into the reactor and pyrolyzed at the conditions used for the preparation of bio-oil (Section 2.1).

For experiments with air pretreatment, 3.8 g of bio-oil and 7.5 g of biomass were mixed in a beaker and then loaded into the reactor. The reactor was heated at 4 °C min^{-1} in air (space velocity 1 min^{-1}) to 180 °C, 200 °C, 220 °C or 240 °C and held for 3 h. After the air pretreatment, samples were purged with N_2 (space velocity 1 min^{-1}) for 0.5 h and pyrolyzed at the conditions used for preparation of bio-oil (Section 2.1).

Additionally, pyrolysis of bio-oil without biomass was carried out after air pretreatment (220 °C for 3 h) and KOH addition (0.48%). Expanded perlite (Schultz, United Industries Corp., Canada) was used as a support due to its low bulk density, spherical particle shape, low surface area (BET surface area 2 $\text{m}^2\ \text{g}^{-1}$) and thermal stability at pyrolysis conditions. Approximately 3.8 g of bio-oil either without KOH or containing 0.48% KOH was mixed with 4.8 g of expanded perlite (particle diameter 0.6–2.0 mm) and then the mixture was packed into the reactor (bed volume ~35 mL) and pyrolyzed as described above.

The prepared biochar samples were weighed and placed into sealed plastic bags for storage. Each sample was prepared three times and the different batches were stored and characterized separately.

2.3. Characterization of biochar

Ash contents of bio-oil and biochar were determined by combusting the samples in a muffle furnace (Vulcan 3-130 Furnace, Dentsply Ceramco, USA) at 650 °C until constant residue mass (approximately 4 h). Biochar samples were characterized by N_2 and CO_2 adsorption isotherms measured at −196 °C and 0 °C, respectively (Tristar 3000, Micromeritics Instrument Co., USA). Surface areas were calculated from N_2 adsorption isotherms using the BET method. Total pore volumes were determined by N_2 adsorption at relative pressures of 0.96–0.97. Micropore volumes were calculated from N_2 and CO_2 adsorption isotherms using the *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). Unless otherwise stated, all reported values in the manuscript are averages ± standard errors from biochar samples prepared in three different batches. The statistical significance of differences between obtained results was determined using a two-tailed *t*-test with a confidence interval of 95%.

An infrared gas analyzer (Uras 26, ABB AO2020, ABB Automation GmbH, Germany) connected to a thermogravimetric analysis unit (Cahn Thermax 500 apparatus, Thermo Fisher Scientific Inc., USA) was used to characterize the release of CO and CO_2 from the mixture of bio-oil with biomass during the air pretreatment. Approximately 10 mg of a sample was heated in the thermogravimetric apparatus at 4 °C min^{-1} and held for 3 h in air (280 $\text{mL}_{\text{STP}}\ \text{min}^{-1}$) at various pretreatment temperatures. The gas exiting the thermogravimetric apparatus was diluted to 1140 $\text{mL}_{\text{STP}}\ \text{min}^{-1}$ with N_2 prior to the measurement of CO and CO_2 concentrations in the gas analyzer. These experiments were duplicated and similar results were obtained (the difference in gas concentrations between duplicates was less than 10%). The results from one of two runs are shown in the figures.

3. Results and discussion

3.1. Co-pyrolysis of bio-oil with biomass

Table 1 contains the yields and elemental analysis of the pyrolysis products produced from biomass only. The values indicate that less than half the carbon contained in the biomass feed was retained in the produced biochar. That is, 1 g of biomass contains 0.49 g C which is converted to 0.21 g biochar (23.7 g biochar per 100 g biomass × 0.89 g carbon per g biochar), 0.20 g bio-oil (50.6 g bio-oil per 100 g biomass × 0.387 g carbon per g bio-oil)

Table 1
Yield and elemental analysis of biomass and pyrolysis products (600 °C, holding time 0.5 h and space velocity 1 min^{-1}).

Material	Yield (%)	Ash (%)[a]	C (%)[a]	H (%)[a]	N (%)[a]
Biomass	–	0.6 ± 0.1	48.6	6.0	0.6
Biochar	23.7 ± 0.2	2.0 ± 0.2	89.0	2.4	0.7
Bio-oil	50.6 ± 0.4	<0.1	38.7	8.8	0.5
Gas	25.7[b]	–	30.7[c]	3.8[c]	1.1[c]

[a] Ash and elemental compositions are given as mass percent on a dry basis for biomass and biochar, and as produced for bio-oil; elemental analysis was performed once.

[b] Calculated as Gas yield = 100% − Biochar yield − Bio-oil yield.

[c] Calculated as Element% in gas = [1 × (Element% in biomass) – 0.237 × (Element% in biochar) – 0.506 × (Element% in bio-oil)]/0.257.

and, by difference, 0.08 g gas. These data are consistent with the results reported by Lee et al. (2013) who showed that typically 43–63% of carbon in biomass is converted to biochar during pyrolysis and the remaining carbon is contained in liquid and gaseous products.

The addition of the produced bio-oil to fresh biomass recycled this liquid product. The increase in biochar yield by the recycling process is shown in Table 2. The results are presented as the mass of produced biochar (ash-free basis) and biochar mass change (in percent) compared to the mass of biochar produced by pyrolysis of biomass only (i.e., 1.744 g in Part 1 of Table 2). The same treatment conditions were used for the first set of results (i.e., Part 1, Base cases in Table 2). The recycling of bio-oil increased the biochar mass by 16.2% compared to that prepared from biomass. Based on the masses of biochar produced separately from biomass (1.744 g) and bio-oil (0.257 g), this mass increase was attributed to the conversion of bio-oil to biochar. The increase in biochar mass with the addition of bio-oil could be attributed to the presence of non-volatile components in the fresh bio-oil or the formation of these components during storage and reheating (Oasmaa and Czernik, 1999; Mohan et al., 2006). In particular, non-volatile oligomeric compounds with molecular weights of several thousand g/mol were detected in bio-oil (Mohan et al., 2006).

The increase in the amount of biochar due to bio-oil recycling (16.2%, Part 1 of Table 2) is less than that reported by Huang et al. (2013) for the recycling of bio-oil from pine and cherry wood sawdust at 600 °C – increase of 23–43% compared to pyrolysis of the feedstock without bio-oil. As the amount of biochar formed is dependent on the pyrolysis conditions, pyrolysis set-up, and variations in bio-oil (Branca et al., 2005), it is difficult to compare absolute values between different studies.

3.2. Influence of KOH on yield

The results of the co-pyrolysis of mixtures of bio-oil and biomass containing either 0.24% or 0.48% of KOH are given in Part 2 of Table 2 (Addition of KOH). The biochar mass increased by 22.3% and 25.2%, respectively, compared to 16.2% without KOH, suggesting that KOH facilitated biochar formation. Note, the mass gains are reported on an ash-free basis so any remaining potassium in the biochar would not influence the mass gain.

To investigate whether biomass and/or bio-oil were impacted by the addition of KOH, several experiments were performed as follows. In the first experiment, a mixture of 7.5 g of biomass and 3.8 g of deionized water was pyrolyzed in the presence of 0.48% KOH (Part 2 of Table 2) and the results compared to the base case without KOH (Part 1 of Table 2). In the second experiment, 3.8 g of bio-oil was pyrolyzed in the presence of 0.48% KOH (Part 2 of Table 2) and the results were compared to the case without KOH (Part 1 of Table 2). In these experiments, biochar mass produced from both biomass and bio-oil increased in the presence of KOH. Therefore, it is likely that during co-pyrolysis of the mixtures, the potassium hydroxide catalyzed the conversion of both biomass and bio-oil to biochar. Previously, DeGroot and Shafizadeh (1984) ascribed the effect of potassium compounds during biomass pyrolysis to the catalytic conversion of primary pyrolysis products from biomass into biochar and gases. However, the catalytic effect of KOH on conversion of bio-oil to biochar was not reported.

3.3. Influence of air pretreatment on yield

Air pretreatment for 3 h at various temperatures increased the biochar mass gain as shown in Part 3 of Table 2. The biochar mass gain increased by 20.2%, 23.9%, 31.7% and 25.7% for pretreatment

Table 2
Influence of air pretreatment and KOH addition on biochar mass gain (ash-free basis) produced by co-pyrolysis of bio-oil with biomass (600 °C, holding time 0.5 h and space velocity 1 min^{-1}).

Feedstock	KOH (%)	Pretreatment			Biochar produced (g)	Biochar mass change (%)
		Furnace temperature (°C)	Atmosphere	Time (h)		
1. Base cases						
Biomass	0		None		1.744 ± 0.012	0
Biomass + bio-oil	0		None		2.026 ± 0.011	16.2 ± 1.1
Biomass + H_2O[a]	0		None		1.667 ± 0.008	−4.4 ± 0.8
Bio-oil	0		None		0.257 ± 0.003	N.A.[b]
2. Addition of KOH						
Biomass + bio-oil	0.24		None		2.133 ± 0.012	22.3 ± 1.1
Biomass + bio-oil	0.48		None		2.183 ± 0.017	25.2 ± 1.4
Biomass + H_2O[a]	0.48		None		1.867 ± 0.016	7.1 ± 1.3
Bio-oil	0.48		None		0.309 ± 0.003	N.A.
3. Air pretreatment						
Biomass + bio-oil	0	180	Air	3	2.097 ± 0.031	20.2 ± 2.0
Biomass + bio-oil	0	200	Air	3	2.160 ± 0.027	23.9 ± 1.8
Biomass + bio-oil	0	220	Air	3	2.300 ± 0.012	31.7 ± 1.6
Biomass + bio-oil	0	240	Air	3	2.192 ± 0.025	25.7 ± 1.5
Biomass + bio-oil	0	220	Nitrogen	3	2.015 ± 0.018	15.5 ± 1.4
Biomass	0	220	Air	3	1.834 ± 0.018	5.2 ± 1.4
Bio-oil	0	220	Air	3	0.376 ± 0.014	N.A.
4. Air pretreatment with KOH addition						
Biomass + bio-oil	0.48	220	Air	0	2.271 ± 0.010	30.2 ± 1.1
Biomass + bio-oil	0.48	220	Air	3	2.181 ± 0.023	25.1 ± 1.7

[a] Mass of water added to biomass was equivalent to the mass of bio-oil used for co-pyrolysis in other experiments (i.e., 3.8 g).

[b] Not applicable.

temperatures of 180 °C, 200 °C, 220 °C, and 240 °C, respectively. As the highest increase in yield was obtained at 220 °C, the impact of pretreatment time was investigated at this temperature as well (Supplementary material). Increasing the pretreatment time up to 3 h was beneficial but beyond this time, the mass gain was constant, probably due to the reaction of all active species in the biomass and bio-oil mixture with air within 3 h of pretreatment.

To eliminate the possibility that the yield increase during air pretreatment was a purely thermal effect, the 3 h pretreatment was performed in N_2, instead of air at 220 °C (Part 3 of Table 2). In this case, the mass of biochar increased by only 15.5%, which is essentially the same as the mass gain with no pretreatment (i.e., 16.2%). Thus, the presence of oxygen during the pretreatment was required to promote biochar formation during pyrolysis. The biochar mass increased compared to base cases in Part 1 of Table 2 when both biomass and bio-oil were separately pre-treated in air for 3 h at 220 °C and then pyrolyzed (Part 3 of Table 2). Therefore, it is likely that the presence of oxygen had a significant impact on the conversion of both components of the mixture to biochar during the co-pyrolysis.

There are no published reports addressing the mechanisms of interaction between air and bio-oil at the studied temperatures, to the best of our knowledge. Extensive studies on the oxidation of coal- and petroleum-derived pitches, however, suggest that two possible reaction pathways could result in higher biochar yields under the conditions used in the present study. The first mechanism involves the attack of aromatic rings by oxygen followed by polymerization of the oxidized rings (Barr and Lewis, 1978). This process most likely occurs through the formation of aryloxy peroxide radicals as intermediates (Lewis and Singer, 1981; Zeng et al., 1993) and does not introduce new oxygen groups into the structure (Barr and Lewis, 1978; Alcaniz-Monge et al., 1997). The second mechanism involves the attack of alkyl groups accompanied by the introduction of oxygen (Otani, 1967). The attack occurs preferentially at the α-carbon in an alkylated aromatic molecule (Otani, 1965) and leads to intermolecular linking (Zeng et al., 1993). These mechanisms could explain the interactions between bio-oil and air at the studied temperatures, as bio-oil contains organic compounds with both aromatic rings and alkyl groups (Branca et al., 2005; Ingram et al., 2008).

In the absence of bio-oil, the mass gain (5.2%) produced by pretreating biomass with air may be a result of intermolecular linking due to oxidation of wood components. A similar increase in the yields of biochar was reported by Chaiwat et al. (2009) for Japanese cedar wood heated to 240 °C–340 °C in air and then pyrolyzed in N_2. In the cited paper, oxidation of the biomass by air was confirmed using Fourier transform infrared spectroscopy to analyze the surface species.

3.4. Influence of air pretreatment in the presence of KOH

As both the KOH addition and air pretreatment increased the amount of produced biochar during co-pyrolysis of bio-oil with biomass (Part 2 and Part 3 of Table 2), the effect of combining these methods on biochar production was investigated. A mixture of bio-oil and biomass containing 0.48% KOH was pre-treated in air and then co-pyrolyzed. In the first set of these experiments, the gas flow was switched from air to N_2 immediately after the furnace temperature reached 220 °C (pretreatment time is 0 h). Under these conditions, the mass of biochar increased by 30.2% (Part 4 of Table 2), which is not higher than the increase achieved with only air pretreatment for 3 h (i.e., 31.7%). A longer air pretreatment in the presence of KOH actually had a detrimental effect on the biochar mass gain (25.1%).

A possible reason for the detrimental effect of KOH is that KOH catalyzed the decomposition of the bio-oil and biomass mixture during exposure to air, resulting in a temperature increase in the bed. To further investigate this hypothesis, the temperature inside the reactor bed was measured with a thermocouple inserted in the middle of the bed at the same height as the thermocouple controlling the furnace temperature. In a N_2 atmosphere with a temperature set point of 220 °C, the temperature inside the bed was 221 °C whether or not the mixture of biomass and bio-oil contained 0.48% KOH. In an air atmosphere, however, the maximum bed temperatures were 245 °C and 312 °C in the absence and presence of KOH, respectively. These temperature maxima were reached after 1–1.5 h of air pretreatment (depending on the sample). In N_2 at the set point temperature, neither endo- nor exothermic effects were observed, while in air, exothermic reactions occurred that released heat and significantly increased the bed temperature. The addition of KOH catalyzed these exothermic reactions, further increasing the heat released.

To provide more evidence of the influence of KOH on the air pretreatment of the mixture, the experiments were carried out in a thermogravimetric apparatus equipped with a CO and CO_2 analyzer. The catalytic effect of 0.48% KOH addition on the reaction between air and the mixture of bio-oil with biomass was confirmed by the concentrations of CO and CO_2 gases evolved during the heating (Fig. 1a and b). At each temperature, larger amounts of CO and CO_2 were evolved from the mixture containing KOH. Regardless of the presence or absence of KOH, the release of CO and CO_2 was intensified with increasing temperature. These gases are mainly formed due to the oxidation of organic compounds by air, as suggested by lower concentrations of CO and CO_2 during heating of the mixture in N_2.

Fig. 1c and d shows the amounts of CO and CO_2 released during isothermal pretreatment of the mixture at 245 °C and 312 °C, respectively (the maximum temperatures observed in the packed-bed reactor during air pretreatment). In air, the amounts of evolved CO and CO_2 were larger at 312 °C, especially in the presence of KOH. Regardless of the presence or absence of KOH, evolution of the gases at 312 °C was more intense in the beginning of the pretreatment and decreased thereafter, probably due to the decrease in the amount of organic compounds in the mixture and/or due to the formation of stable oxygen-carbon complexes on the remaining compounds. At this temperature, CO and CO_2 resulted from exposure to air, as in N_2, the concentrations of these gases were lower (Fig. 1c and d).

The concentrations of CO and CO_2 evolved during air pretreatment in the thermogravimetric apparatus (Fig. 1) were used to calculate the carbon loss of the mixture containing 0.48% KOH at 245 °C and 312 °C. The carbon loss during heating and holding in air for 3 h at 245 °C was ~0.1 mg, while the carbon loss at 312 °C increased by over an order of magnitude to ~1.8 mg. These results suggest that simply due to the higher temperature during air pretreatment, the mixture loses more carbon, which could result in a lower biochar mass after pyrolysis. More specifically, according to Table 1, the initial content of carbon in the mixture with 7.5 g of biomass and 3.8 g of bio-oil was 45%. As for the thermogravimetric analysis, 10 mg of sample was used and so the total mass of carbon loaded to the apparatus was 4.5 mg. Therefore, during the air pretreatment of the mixture at 245 °C and 312 °C, ~2% (i.e., 0.1 mg out of 4.5 mg) and ~40% (i.e., 1.8 mg out of 4.5 mg) of the initial carbon was lost, respectively. Similar calculations were carried out for the N_2 pretreatment of the mixture at 312 °C and the loss of carbon was only 7% (0.3 mg out of 4.5 mg).

3.5. Porous properties of produced biochar

Table 3 contains the surface areas and pore volumes of several biochar samples produced in this study. After pyrolysis of the biomass or co-pyrolysis of biomass with bio-oil, the values of surface

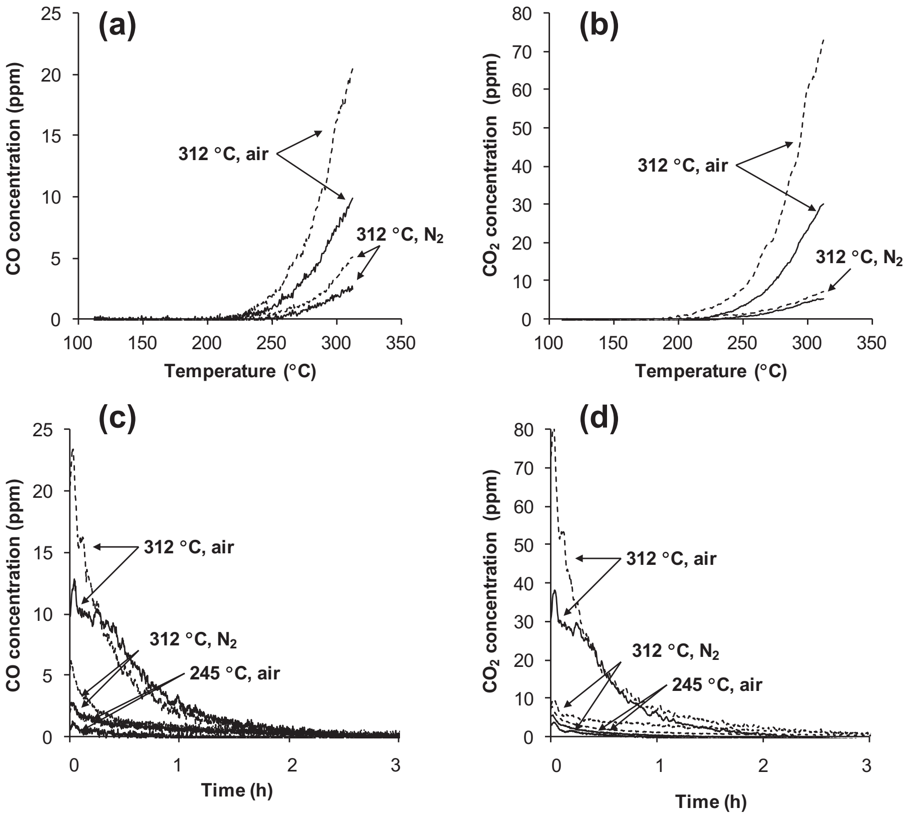

Fig. 1. Typical profiles of CO and CO_2 evolution from the mixture of bio-oil with biomass in the absence (solid lines) and presence of 0.48% KOH (dashed lines) during thermogravimetric experiments: (a) and (b) during heating in either air or N_2; (c) and (d) during isothermal pretreatment at 245 °C and 312 °C either in air or N_2.

area and total pore volume were ~440 $m^2\,g^{-1}$ and ~0.195 $mL\,g^{-1}$, respectively, with most of the porosity from micropores (Base cases, Table 3). The data suggest that recycling of the bio-oil to biomass for co-pyrolysis at the studied conditions does not deteriorate the porous properties of the biochar, as reported previously (Veksha et al., 2014).

The addition of KOH to the mixture of biomass and bio-oil produced biochar with lower surface area and total pore volume (140 $m^2\,g^{-1}$ and 0.064 $mL\,g^{-1}$) as measured by N_2 adsorption (Addition of KOH, Table 3). Based on previous experience (Veksha et al., 2008), this phenomena is likely due to the inorganic compounds (here, potassium compounds) blocking pores. After washing, the ash content in the biochar decreased from 5.5% ± 0.2% to 2.4% ± 0.4%, and the surface area and pore volume increased significantly to 387 $m^2\,g^{-1}$ and 0.170 $mL\,g^{-1}$, but not to the values of the base cases, probably due to incomplete removal of potassium compounds from the pores of the biochar. The presence of potassium compounds in biochar had less influence on the micropore volume determined by CO_2 adsorption than by N_2 adsorption (Table 3). A possible explanation is that due to the higher adsorption temperature (0 °C) CO_2 was able to penetrate into the micropores partially blocked by potassium compounds.

In contrast to the KOH addition, the air pretreatment produced biochar with surface areas and pore volumes that were not

Table 3
Surface areas and pore volumes of selected biochar samples produced by co-pyrolysis of bio-oil with biomass (600 °C, holding time 0.5 h and space velocity 1 min^{-1}).

Feedstock	KOH (%)	Pretreatment			Surface Area (N_2) ($m^2\,g^{-1}$)	Total pore volume (N_2) ($mL\,g^{-1}$)	Micropore volume (N_2) ($mL\,g^{-1}$)	Micropore volume (CO_2) ($mL\,g^{-1}$)
		Temperature (°C)	Atmosphere	Time (h)				
1. Base cases								
Biomass	0		None		439 ± 8	0.194 ± 0.004	0.168 ± 0.003	0.183 ± 0.001
Biomass + bio-oil	0		None		442 ± 12	0.196 ± 0.005	0.170 ± 0.005	0.186 ± 0.001
2. Addition of KOH								
Biomass + bio-oil	0.48		None		140 ± 19	0.064 ± 0.009	0.055 ± 0.008	0.151 ± 0.007
Biomass + bio-oil (washed)	0.48		None		387 ± 7	0.170 ± 0.002	0.151 ± 0.002	0.172 ± 0.001
3. Air pretreatment								
Biomass + bio-oil	0	220	Air	3	479 ± 15	0.206 ± 0.006	0.185 ± 0.006	0.194 ± 0.003
Biomass + bio-oil (washed)	0	220	Air	3	452 ± 14	0.189 ± 0.005	0.176 ± 0.005	0.182 ± 0.003
4. Air pretreatment with KOH addition								
Biomass + bio-oil	0.48	220	Air	3	214 ± 34	0.095 ± 0.013	0.083 ± 0.013	0.171 ± 0.003

statistically different from the properties obtained in the base cases (air pretreatment, Table 3). Therefore, if higher porosity is preferable in the product (e.g., the biochar is produced for adsorption) then air pretreatment prior to co-pyrolysis of bio-oil with biomass can be more beneficial than KOH addition. Washing the sample produced by the air pretreatment did not change the porous properties or ash content (1.4% ± 0.2% and 1.7% ± 0.3% before and after washing, respectively) significantly. The combination of KOH addition and air pretreatment resulted in biochar with a surface area and total pore volume between those of the individual treatments, i.e., 214 $m^2\ g^{-1}$ and 0.095 $mL\ g^{-1}$, respectively (Air pretreatment with KOH addition, Table 3).

3.6. Repeated recycling of bio-oil to biomass for co-pyrolysis

The results presented in Table 2 suggested that either addition of KOH or air pretreatment could be used to increase the yield of biochar produced by co-pyrolysis of biomass with bio-oil. Thus, experiments were carried out to investigate whether a pseudo-continuous process could be developed in which the bio-oil generated by co-pyrolysis could be repeatedly recycled to a new batch of biomass for biochar production. A schematic of the experimental procedure is shown in Fig. 2.

In these experiments, biomass and bio-oil were mixed and co-pyrolyzed to produce a new batch of bio-oil, which was then mixed with a fresh batch of biomass and the process repeated. The co-pyrolysis process was essentially the same as that described in Section 2.2, except, prior to the co-pyrolysis, the mixture of bio-oil with biomass was heated to 150 °C for 1 h to separate liquids with a boiling point of 150 °C or lower, here referred to as "distillate", such as water and organic compounds, from the fraction with higher boiling points (recycled bio-oil). Some bio-oil components have boiling temperatures as high as ~390 °C (Branca et al., 2005). This additional step was added to reduce the accumulation of the distillate components in the system.

Fig. 3 illustrates material balances for co-pyrolysis of recycled bio-oil with biomass after air pretreatment (220 °C, 3 h) and KOH addition (0.48%). Each co-pyrolysis run produced approximately 2 g of distillate. However, the mass of produced bio-oil and bio-oil added to biomass still increased with the number of runs (Fig. 3a and b), probably due to accumulation of bio-oil components with boiling points above the distillation temperature (150 °C). Nevertheless, within the six consecutive runs, the mass of biochar produced by co-pyrolysis of bio-oil with biomass remained similar both after air pretreatment and after KOH addition as suggested by Fig. 3a and b, respectively. The biochar mass produced by the co-pyrolysis was essentially the same as in Table 2 for co-pyrolysis of fresh bio-oil with biomass. After six times of repeated bio-oil recycling to a new batch of biomass, the ash contents of the biochar produced by air pretreatment and KOH addition were 1.8% ± 0.1% and 5.4% ± 0.3%, respectively. These values are similar to the ash contents in the biochar produced by the co-pyrolysis of fresh bio-oil with biomass (see Section 3.5 for the ash contents). The results in Fig. 3 suggest that the generated bio-oil can be processed repeatedly to increase the biochar production.

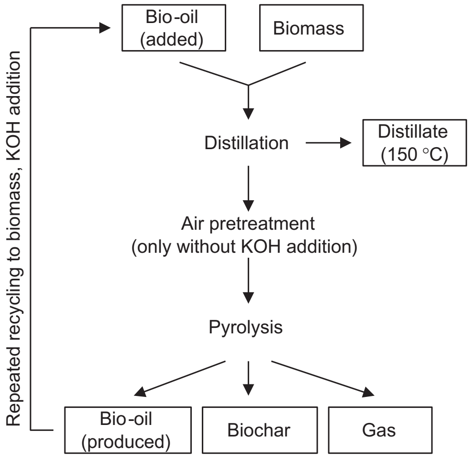

Fig. 2. Production of biochar by repeated recycling of generated bio-oil to biomass.

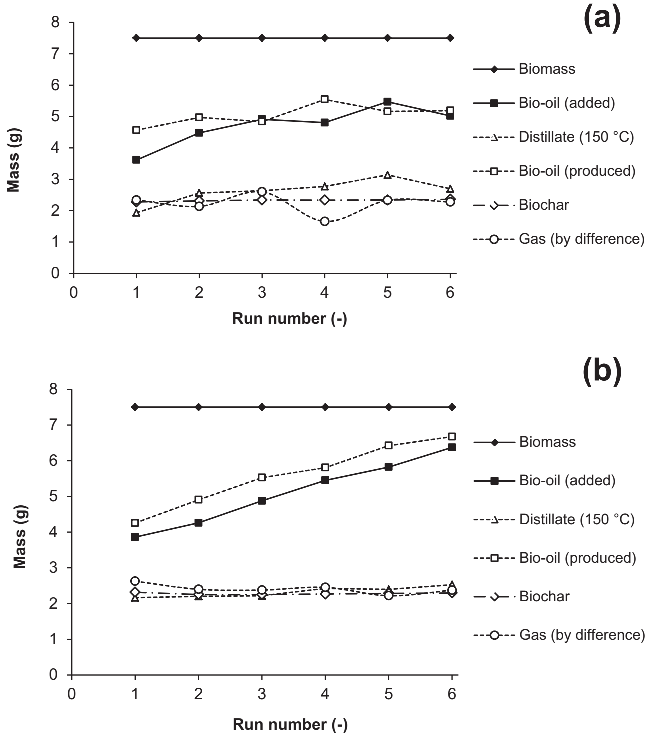

Fig. 3. Mass of feed and products produced by repeated recycling of bio-oil to biomass for the co-pyrolysis: (a) after air pretreatment at 220 °C for 3 h and (b) after 0.48% KOH addition. The lines are shown only to guide the eye. Standard errors are not shown for clarity.

4. Conclusions

Both air pretreatment and KOH addition methods increased the mass of biochar produced from a mixture of bio-oil with biomass (aspen wood). An increased biochar yield was maintained in six consecutive co-pyrolysis runs, indicating that both methods can be effectively used for bio-oil recycling. The biochar produced with the air pretreatment, however, had a higher porosity and lower ash content than that produced by KOH addition. Combining the methods resulted in reduced yields from KOH catalyzing oxidation reactions and increasing the bed temperature.

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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.2014.08.040.

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