CCEMC Project # E120048

Developing an Adsorbing Biocarbon to Achieve Greenhouse Gas Benefits in the Remediation of Produced Water from Oil Sands Operations

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Holdback: $7,745.24

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[1] Veksha A., McLaughlin H., Layzell D.B., Hill J.M., 2014. Pyrolysis of wood to biochar: Increasing yield while maintaining microporosity. Bioresour. Technol. 153, 173-179.

4. Executive Summary

Previous studies have shown that residual biomass in Alberta could be converted to an activated carbon and used to remove toxic and corrosive organic compounds from oil sands produced waters. This would not only help in oil sands processing, but reduce greenhouse gas (GHG) emissions and create a long-term store for atmospheric carbon.

The work reported here was focused on developing a new technology for converting aspen wood from northern Alberta into an adsorbing biochar with enhanced yield, improved adsorption capacity and lower cost than existing technologies. Experts in biochar production and activation were consulted in the experimental design (Dr. Hugh McLaughlin, AC FOX, USA, Dr. Glenn Weagle, Champion Technologies, Calgary).

To carry out the work, a postdoctoral fellow (Dr. Andrei Veksha) built and used a novel, three chamber pyrolysis unit that allowed studies to be done on how temperature, gas composition and the volatile fraction generated during pyrolysis affected the yield and surface area properties of the biochar that was produced.

To create biochar with a high yield and good adsorption capacity, two approaches were explored. The first consisted of the removal of volatile pyrolysis products from reactor by varying conditions (e.g. temperature, gas flow rate and holding time) to reduce their deposition on biochar. Biochar samples with different amount of deposited volatiles were prepared by this method. Their microporous properties were characterized by N_2 and CO_2 adsorption and organic vapor uptake by 1,1,1,2-tetrafluoroethane adsorption. It was shown that at pyrolysis temperatures between 420 °C and 650 °C, the deposited volatiles were carbonized and converted to material with a similar microporous structure and organic vapor uptake to that of the primary biochar. Based on these results it was concluded that the yield of biochar can be increased without a decrease in adsorption capacity by creating the conditions that facilitate deposition of the volatiles.

In the second approach, liquid pyrolysis products (bio-oil) formed in the previous runs were added to biomass prior to pyrolysis to increase the amount of deposited volatiles. The obtained results clearly demonstrated that it was possible to increase the yield of biochar by recycling bio-oil to biomass while maintaining the desirable adsorption properties.

The results of the research were published in a peer-reviewed journal and disseminated among research community and industry representatives by several conference talks and poster presentations.

5. Introduction and Project Overview

The recovery of bitumen from oil sands uses large volumes of water, regardless of whether recovery is via mining or in situ (Steam Assisted Gravity Drainage or SAGD) operations. Once used, this water is contaminated with high concentrations of organic compounds. In mining operations, some of the water is released to tailings ponds where microbial activity can convert the organics into CH_4, a potent greenhouse gas (GHG). In SAGD operations, most of the water is reused but the organics contribute to the formation of deposits (aka slagging) in the boiler, reducing energy efficiency and forcing periodic shutdown for cleaning. This increases energy use and GHG emissions per barrel of oil produced.

Activated carbons produced from coal or biomass are well known adsorbents that can remove organics from water. Biomass-based adsorbing carbons (i.e. biochars) have an advantage over adsorbing carbons from coal or petcoke in that the biochars typically have fewer contaminating salts / heavy metals and the carbon in the biochar can provide a long term sink for atmospheric carbon.

However, to maximize this carbon sink it is important to reduce the energetic cost and increase the yield associated with making an adsorbing biochar[2]. This is the focus of the CCEMC funded work reported here.

Work to date, generated with funding from industry and the federal government (NSERC – CRD), has shown that 1.2 Mt activated C biochar (ACB)/year would be needed to remove 75%-90% of the organics in produced water from oil sands operations (Table 1, Item F) at a net cost of \$0.11 to \$2.20 per barrel of oil produced.[3]

Table 1. Estimation of the potential activated biochar (ACB) and biomass demands for treating water associated with SAGD and Mining oil sands operations in Alberta (from Kimetu et al. 2014[3])

Item #*	**Units**	**SAGD**		**Mining**		**Total**	
A. Oil production[a]	*boe/day*	750,000		850,000		1,600,000	
B. Produced water[b]	*bw/boe*	2.7		2.5		-	
C. Water needing treatment[c]	*Mm^3/year*	118		123		241	
D. Organic C to be removed[d]	*g-C/m^3*	641		49.5		-	
		Batch	Flow-through	Batch	Flow-through	Batch	Flow-through
E. Adsorption Capacity[e]	*g-C/kgACB*	71.6	90	53.5	141	-	-
F. ACB demand[f]	*Mt ACB/yr*	1.05	0.84	0.11	0.04	1.17	0.88
G. Biomass demand[g]	*Mt biomass/yr*	5.26	4.19	0.57	0.22	5.83	4.40

Footnotes for each item number:

[a] From Canadian Association of Petroleum Producers, 2011[4]

[b] From Alberta Energy, 2013[5]

[c] Calculated as (Item A X Item B) X 159 L/bw X 365 d/yr ÷ 10^9

[d] Assumes 75% of 855 mg-C/L for SAGD water and 90% of 55 mg C/L for tailings water

[e] Experimental data from Fig. 1 and 2

[f] Assumes single use of ACB and calculated as (Item C X Item D)÷(Item E*1000)

[g] Assumes biomass conversion to ACB is 20% by dry weight[6]

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[2] See http://online.liebertpub.com/doi/abs/10.1089/ees.2006.0134, http://pubs.acs.org/doi/pdf/10.1021/es902266r

[3] Kimetu JM, JH Hill, M Husein, J Bergerson & DB Layzell 2014. Adding value to biochar through remediation of produced water from oil sands. (In review)

[4] Canadian Association of Petroleum Producers - CAPP. Water use in Canada's oil sands. Canadian Association of Petroleum Producers, July **2011**. http://www.capp.ca/getdoc.aspx?DocId=193756 (Downloaded: Jan 23, 2013).

[5] Alberta Energy**.** Facts and statistics. **2013** http://www.energy.alberta.ca/oilsands/791.asp, (Downloaded: Feb. 22, 2013).

[6] Klass DL, Ed**.** *Biomass for Renewable Energy, Fuels and Chemicals.* Academic Press. San Diego, CA, USA; **1998.**

The work carried out here explored a number of novel approaches to the production of an adsorbing biocarbon for water treatment. One approach was based on a presentation given by Dr. Hugh McLaughlin (Groton, MA) at an international Biochar conference in 2010[7]. The proposed approach will focus on taking advantage of the three dimensional structure of the xylem tissue in wood (Fig. 1) to provide the surface area needed for optimal adsorption. Key features of this new approach include:

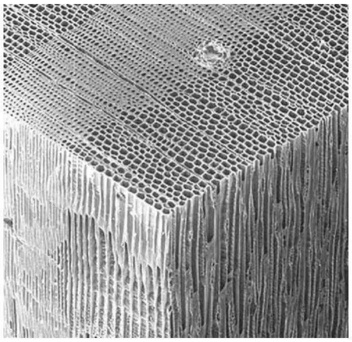

Fig. 1. Spruce xylem.

- ✓ A one step, rather than two step process in converting biomass into an adsorbing biocarbon, thereby reducing overall energy input and achieving higher yields of adsorbing biocarbon as a percentage of the feedstock carbon;
- ✓ Slow pyrolysis of larger pieces of biomass (not sawdust) to ensure maintenance of the 3D structure of wood. (The adsorbing carbon would be reduced to a smaller particle size after production to ensure optimal water contact.);
- ✓ Careful and precise control over the temperature and timing of pyrolysis conditions, with a focus on the optimal temperature/time for creation of an adsorbing biocarbon;
- ✓ Rapid removal of the volatile molecules arising from the pyrolysis in a N_2 gas stream in order to prevent them from re-condensing on the adsorbing surface of the biomass, thereby destroying its adsorbing properties;
- ✓ Subsequent combustion of the volatile molecules within the system to maintain the pyrolysis conditions and reduce the need for exogenous energy input;
- ✓ Possible chemical treatment of the biocarbon surface to improve its capacity to adsorb the organic fraction in water from oil sands operations.

We also tested the hypothesis that adding to biomass, bio-oil from a previous pyrolysis run would increase the biomass carbon recovery of biomass carbon without undermining the surface area properties important for adsorption.

The concepts behind these technologies have not been fully developed. One of the authors of a conference paper on the topic – Dr. Hugh McLaughlin (Groton, MA) – has expressed an interest in working with researchers at the University of Calgary to explore the use of this technology for oil sands operations using biomass feedstocks that are currently available or that could be readily grown in northern Alberta and regions in adjacent provinces.

A post-doctoral fellow (Dr. Andrei Veksha) was hired and carry out most of the laboratory work described here over the period 1 July 2012 to 30 Sept 2013. In addition, we engaged an expert consultant – Dr. Hugh McLaughlin - who made himself available for tele-video or in person visits to the university during the project.

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[7] McLaughlin, H and Shields, FE. 2010. Schenkel and Shexue Revisited – implication on char production and biochar properties. Presentation at Biochar2010 Conference, Ames, Iowa. June 2010.

6. Project Goals

The schedule of activities described in Table 2 was part of the original project and followed in the project execution. The work was carried out by a Post-doctoral fellow, Dr. Andrei Veksha under the supervision of Drs. Josephine Hill and David Layzell. In addition, expert advice was obtained from Drs. Hugh McLaughlin and Joseph Kimetu.

Table 2. Schedule of Project Activities and estimated expenses in the original proposal.

				$ Canadian
Mile-stone	**Activity**	**Start Date**	**End Date**	**CCEMC Funds**
1	PDF training, Workshop with industry experts, Initial tests with AC-biochar prod’n	July 1, 2012	Mar 31, 2013	$22,319.00
2	Produce a variety (4-10) biochar samples, characterize, and test for adsorption capacity	Apr 1, 2013	Jun 30, 2013	$16,944.38
3	Further test with best sample(s) from phase 2 and optimize system; write paper(s)	Jul 1, 2013	Sept 30, 2013	$18,236.62
Total				**$57,500.00**

7. Project Final Outcomes

7.1. Experimental procedures

7.1.1. Pyrolysis setup.

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) hereinafter referred to as "biomass".

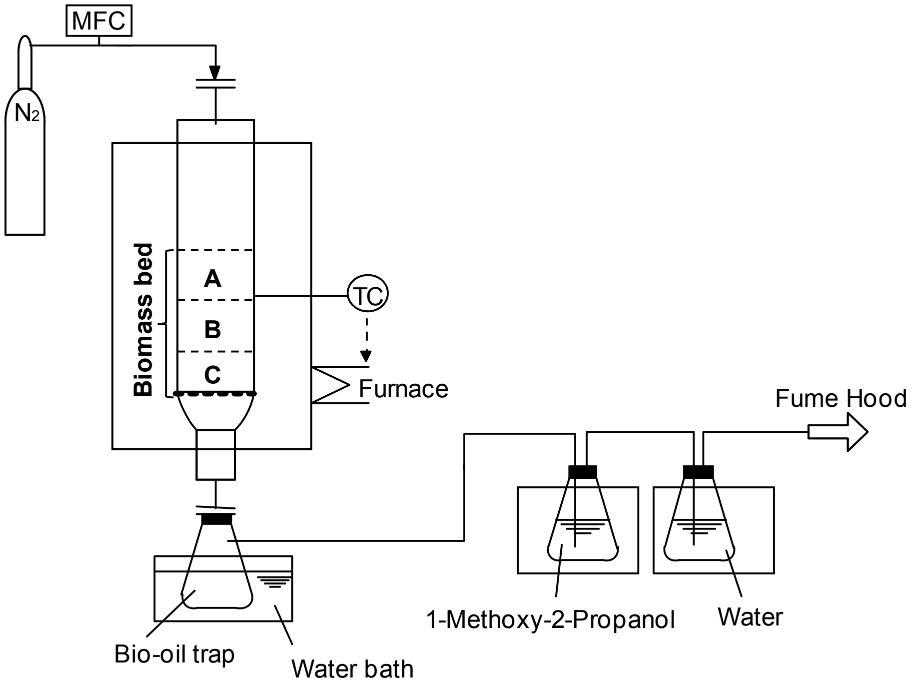

Fig. 2. Pyrolysis setup (from A.Veksha et al., 2014[1]).

Pyrolysis was carried out in a vertical quartz reactor with an inner diameter of 21.5 mm (Fig. 2). 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 collected bio-oil 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.

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 min-1, 1 min-1, 2 min-1 and 2.8 min-1.

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 °C, 500 °C, 550 °C or 600 °C and maintained at this temperature for 0.5 h, 2 h 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.

7.1.2. Characterization of biochar.

Porous properties of the prepared biochar were characterized by N_2 and CO_2 adsorption at -196 °C 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 N2 and CO2 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. 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). Duplicate 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 N2 to determine the mass of carbon and ash (mcarbon + mash). After 15 min, N2 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 (mash). The fixed carbon content was calculated from the difference between these masses. The percent of fixed carbon is reported on a dry, ash-free basis. The percent of volatile matter in the biochar was calculated as 100 minus the percent of fixed carbon.

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

7.1.3. 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-made thermo-gravimetric 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 N2 for outgassing. The heating supply was then turned off and the N2 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}.

7.2. Results of experiments

7.2.1. Effect of the removal of pyrolysis volatiles from reactor on adsorption properties of biochar

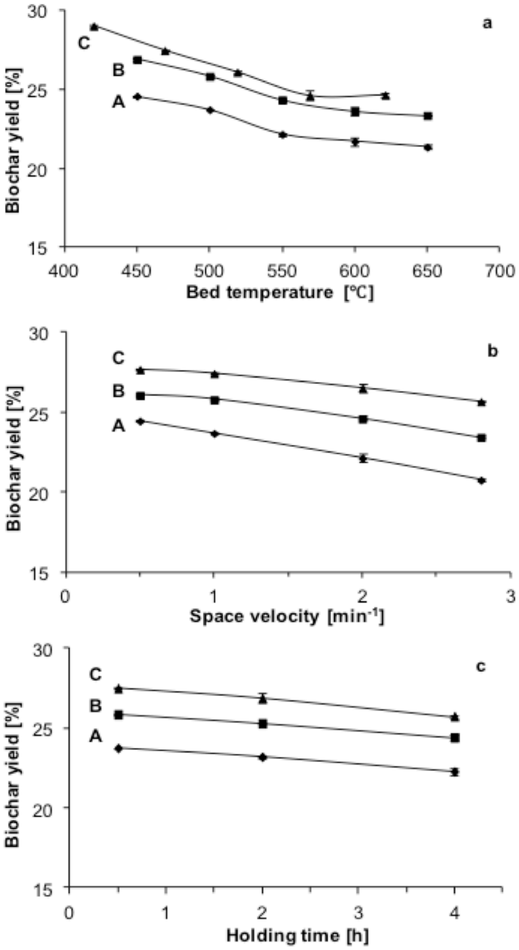

Fig. 3. Biochar yields from reactor zones A, B and C as a function of a) temperature, with holding time of 0.5 h and space velocity of 1 min^{-1}, b) space velocity, with holding time of 0.5 h and 500 °C (zones A and B) or 469 °C (zone C), and c) holding time, with space velocity of 1 min^{-1} and 500 °C (zones A and B) or 469 °C (zone C) (from A. Veksha et al., 2014[1]).

The yield of biochar produced as a function of different variables is presented in Fig. 3. In Fig. 3a, 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. From the yields of biochar in zones A and B can be easily calculated using a proportion that for each gram of biochar produced in zone A, ~ 0.09 g of biochar was additionally produced in zone B.

The compositions – fixed carbon and volatile matter – of the produced biochar are listed in Table 3 for zones A and B (500 °C, 0.5 h) and zone C (469 °C, 0.5 h) at a space velocity of 1 min-1 calculated from thermo-gravimetric analysis. 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), suggesting that the volatiles 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 (19.8 ± 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 volatile species from the other zones condensing in this lower temperature zone.

Fig. 3b 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 holding time was increased from 0.5 h to 4 h at a space velocity of 1 min-1 (Fig. 3c). The amounts of fixed carbon and volatile matter in the biochar from the three zones prepared at different conditions are given in Table 3. 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 h to 4 h for all three reactor zones, suggesting that prolonged treatment could improve the degree of carbonization for any deposited volatile species.

Table 3. Composition of biochar produced at different conditions: fixed carbon, volatile matter and ash (dry basis) (from A. Veksha et al., 2014[1]).

Bed temperature (°C)	Space velocity (min^{-1})	Holding time (h)	Reactor zone	Fixed carbon (%)	Volatile matter (%)	Ash (%)
500	1	0.5	A	79.8	17.7	2.5
500	1	0.5	B	80.5	17.5	2.0
469	1	0.5	C	78.2	19.8	2.1
500	2.8	0.5	A	79.5	18.0	2.5
500	2.8	0.5	B	80.5	17.7	1.7
469	2.8	0.5	C	78.4	19.8	1.7
500	1	4	A	84.4	13.1	2.4
500	1	4	B	85.6	13.0	1.5
469	1	4	C	83.4	15.1	1.5

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 CO2 and N2 adsorption isotherms (Fig. 4). In Fig. 4a, 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. 3) 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. 4b shows the micropore volumes determined by N2 and CO2 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. 4b). Furthermore, the biochar samples from the three zones prepared at various temperatures had similar micropore size distributions (Fig. 4c, 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 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. 4b, 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 shown 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.

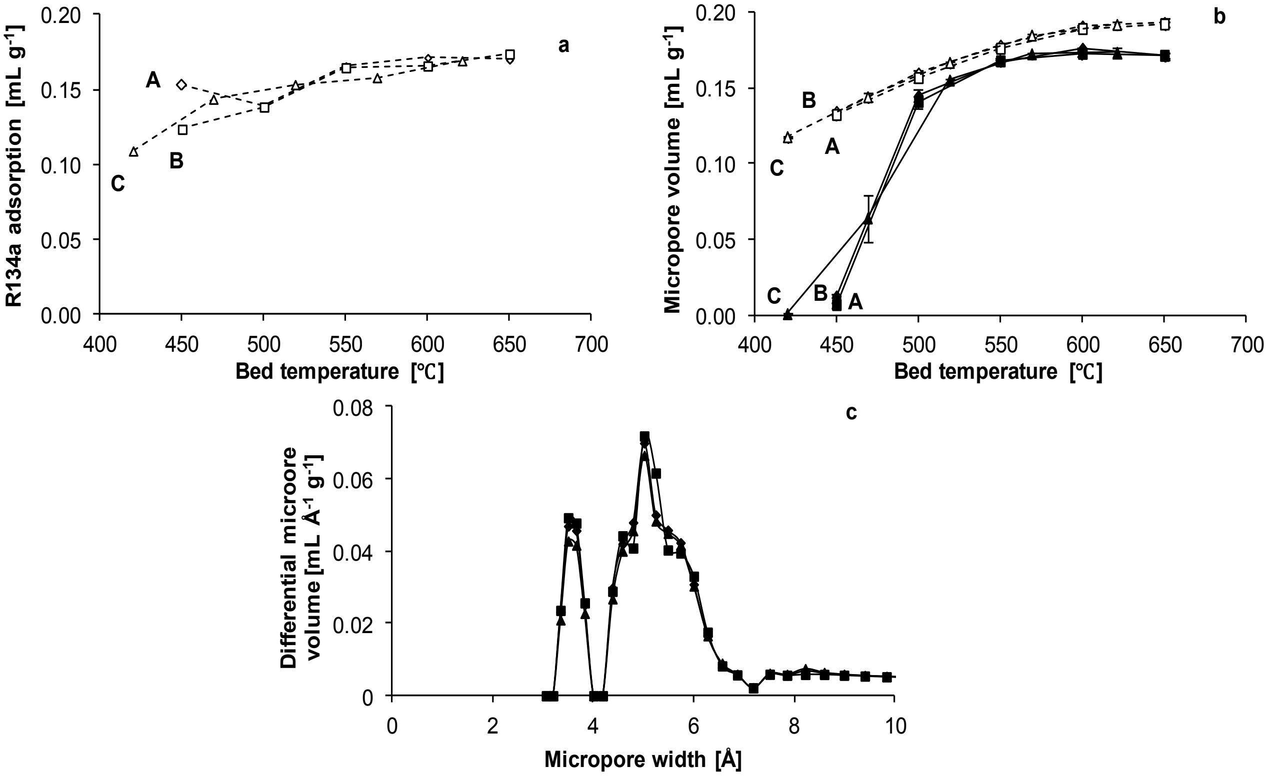

Fig. 4. Influence of temperature (0.5 h and 1 min^{-1}) on characteristics of biochar produced in zones A, B and C: a) R134a adsorption at 101 °C, b) micropore volumes determined from N_2 and CO_2 adsorption (solid and dashed lines, respectively) and c) typical micropore size distributions of biochar produced in reactor zones A(▲) and B (■) at bed temperature 600 °C, and C (♦) at bed temperature 569 °C (from A. Veksha et al., 2014[1]).

7.2.2. Effect of bio-oil addition on biochar yield and adsorption properties

The results of the adsorption measurements (Fig. 4) 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 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 non-condensed vapor stream significantly decreases the yield of biocahr. Depending on feedstock amount of biomass carbon converted to biochar ranged between 43-63 %[8,9]. The rest of carbon containing in biomass is converted to liquid and gas products. The recycling of these products would be a feasible approach to increase the efficiency of biochar production.

The bio-oil (a mixture condensed at ambient temperature, ~ 23 °C) was collected from previous runs at 600 °C, and added to the top of the biomass bed (~ 3.3 g, 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. 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 °C or 600 °C.

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[8] Ben, H., Ragauskas, A.J., 2013. Comparison for the compositions of fast and slow pyrolysis oils by NMR characterization. Bioresour. Technol. 147, 577-584.

[9] Lee, Y., Park, J., Ryu, C., Gang, K.S., Yang, W., Park, Y.K., Jinho, J., Hyun, S., 2013. Comparison of biochar properties from biomass residues produced by slow pyrolysis at 500 °C. Bioresour. Technol. 148, 196-201.

Additionally, the influence of co-pyrolysis of bio-oil and biochar on the yield and porous properties of the resulting carbon was investigated 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 the bio-oil are shown in Table 4. 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. Increasing pyrolysis temperature to 600 °C barely changed the mass gain due to bio-oil addition in zone A (0.263 g). As the mass of biochar produced from biomass was lower at 600 °C than at 500 °C (0.545 g and 0.593 g, respectively) the increase in the biochar yield at 600 °C was higher compared to 500 °C (48 %).

Table 4. Amount of biochar produced from biomass only and with bio-oil addition (0.5 h and 1 min^{-1}) (from A.Veksha et al., 2014[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	0.593	5.767[a]	0.854
500	B	2.500	0.646	2.500	0.676
469	C	2.501	0.687	2.500	0.702
600	A	2.500	0.545	5.772	0.808
600	B	2.500	0.593	2.500	0.640
569	C	2.500	0.619	2.500	0.660
Bed temperature (°C)	Reactor zone			Biochar with bio-oil (g)	
				Before pyrolysis	After pyrolysis
500	A			3.810	0.705
500	B			0.598	0.622
469	C			0.621	0.638
Bed temperature (°C)	Reactor zone			Bio-oil only (g)	
				Before pyrolysis	After pyrolysis
500	A			3.264[c]	0.153
500	B			0	0.049
469	C			0	0.014

[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.

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 4), 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 °C10. 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 characterization results for biochar produced from biomass only and with bio-oil addition are summarized in Table 5. The micropore volumes, determined by CO2 adsorption, and R134a uptakes were essentially the same at 500 °C and 600 °C, with and without bio-oil addition. There was a modest decrease in the micropore volume determined by N2 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 pyrolized bio-oil. There was, however, no significant difference in micropore volumes determined by N2 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.

Table 5. Micropore volumes and R134a uptakes on biochar produced from biomass only and with bio-oil addition (0.5 h and 1 min^{-1}) (from A. Veksha et al., 2014[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	0.101	0.159	0.155	0.14	0.12
500	B	0.141	0.132	0.156	0.155	0.14[a]	0.13
469	C	0.064	0.089	0.144	0.147	0.14	0.12
600	A	0.176	0.177	0.190	0.189	0.17	0.15
600	B	0.172	0.177	0.189	0.184	0.17	0.17
569	C	0.172	0.182	0.184	0.181	0.16	0.15

Table 6. Micropore volumes of biochar produced by co-pyrolysis of parent biochar with bio-oil (0.5 h and 1 min^{-1}) (from A. Veksha et al., 2014[1]).

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

The addition of bio-oil to a parent biochar followed by pyrolysis at 600 °C resulted in a smaller increase in the mass of the produced carbon compared to addition of bio-oil to biomass (Table 6). The co-pyrolysis of bio-oil with biochar produced the carbon with lower micropore volumes determined by N2 and CO2 adsorption (Table 6) compared to the sample prepared from the mixture of bio-oil with biomass at the same conditions (Table 5). The results of bio-oil recycling for pyrolysis suggested that depending on whether bio-oil was added to biomass or to biochar the

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[10] Huang, Y., Kudo, S., Norinaga, K., Amaike, M., Hayashi, J., 2012. Selective production of light oil by biomass pyrolysis with feedstock-mediated recycling of heavy oil. Energy Fuels 26, 256-264.

carbons with different microporous structures were generated at same conditions. For adsorption applications, the addition of bio-oil to biomass for co-pyrolysis seems more beneficial than to biochar as higher biochar yields can be obtained without decrease in microporous properties.

7.2.3. Conclusions

The pyrolysis of aspen wood chips and the conversion of the produced volatile species and bio-oil into biochar was investigated. Under 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 the biochar with microporosity similar to the primary biochar produced without bio-oil addition. The benefit of the bio-oil addition to biomass was the increase in the biochar yield.

8. Scientific Achievements

The results of the research funded by CCEMC were published in a peer-reviewed journal. To disseminate the results among the scientific community and industry, several talks were given on the ongoing research. Poster presentation of the research results by summer student Waheed Zaman at SU Undergraduate Research Symposium (University of Calgary) received “Sustainable Energy Development Master’s Degree Program Award”.

8.1. Peer-reviewed publication:

1. Veksha A., McLaughlin H., Layzell D.B., Hill J.M., 2014. Pyrolysis of Wood to Biochar: Increasing Yield while Maintaining Microporosity. Bioresour. Technol. 153, 173-179.

8.2. Presentations (Oral):

1. Layzell, DB. J Bergerson, M Hussein, J Kimetu & P Lachkov. Removal of organics in steam assisted gravity drainage (SAGD) produced water. Presentation to Oil Sands Leadership Initiative (industry consortia) July 3, 2012.
2. Layzell D.B., Hill J.M., Veksha A. Using Biochar to Remove Organics from Produced Water in Oil & Gas Operations. Champion Technologies, Calgary, Alberta, Canada, March 15, 2013. (as part of the visit to Champion Technologies)
3. Hill J.M. Using Biochar to Remove Organics from Produced Water in Oil & Gas Operations, Alberta Innovates Technology Futures, Vegreville, Alberta, Canada, May 23, 2013. (as part of the opening of the Biochar Centre).
4. Layzell D.B., Hill J.M., Veksha A. Using Biochar to Remove Organics from Produced Water in Oil & Gas Operations. Presentation to industry, academic and NGO group at organizational meeting. June 19, 2013
5. Layzell, DB. An energy systems perspective on the emerging bioeconomy. Agricultural biotechnology International Conference (Food, Water and Energy in a Hungry World) Calgary AB. Sept 15-16, 2013.
6. Layzell, DB. Biological Solutions to Climate Change: An energy systems perspective. CCEMC Biological Solutions Conference. Calgary AB. Oct 9-10, 2013
7. Layzell D.B., Hill J.M., Veksha A. Using Biochar to Remove Organics from Produced Water in Oil & Gas Operations. Biochar Technical Meeting, Olds College, AB Dec 5, 2013

8.3. Presentations (Poster):

1. Veksha A., Hill J.M., McLaughlin H., Layzell D. Preparation of adsorbing biocarbon for remediation of produced water with a carbon benefit. Biological Solutions Forum, Calgary, Alberta, Canada, October 9-10, 2013.

2. Zaman W., Veksha A., Hill J.M. Preparation of Activated Carbon for Treatment of SAGD Water. SU Research Symposium, University of Calgary, Calgary, Alberta, Canada, November 28, 2013.

9. Greenhouse Gas Impacts

Table 7 provides a summary from a paper in review that has estimated the possible GHG benefits to the use of the biochar technology in the treatment of water from oil sands operations in Alberta. In total, there is the potential to mitigate up to 3 million tonnes of CO2e/yr.

If this technology were transferred to use in the mitigation of fracking water from oil and gas operations, then GHG benefits could be larger.

There is also a potential of exporting the technologies for use in other jurisdictions and markets around the world.

Table 7. Summary of the calculations from a previous study[3] of the maximum Greenhouse Gas (GHG) benefit that could be realized with the deployment of the adsorbing biochar technology on water from the 2012 production of Alberta's oil sands (production as shown in Table. 1).

Greenhouse Gas (GHG) Benefit in kt CO2e/yr	**SAGD**		**Mining**		**Total**	
	Conservative	**Optimistic**	**Conservative**	**Optimistic**	**Conservative**	**Optimistic**
From landfilling spent ACB to sequester carbon	2203	2763	239	300	2442	3062
From avoiding CH4 emissions from mine tailings	-		65.6		65.6	
Total GHG emission benefit	2203	2763	304	365	2508	3128

10. Overall Conclusions

The conclusions from this study included:

1. Residual biomass from Alberta forest production can be pyrolyzed to produce an adsorbing biocarbon (biochar) that has the potential to clean oil sands produced water while reducing GHG emissions and creating a significant sink for atmospheric carbon.
2. The deposition on biochar of the volatile fraction did not reduce the adsorption properties of the biochar as hypothesized, but it did reduce the yield.
3. Adding biooil generated from a previous pyrolysis run, to the biomass before pyrolysis, increased the yield of the biochar without having an adverse affect on the surface-active properties of the biochar produced.
4. While the results to date are promising, further work is needed to develop a rapid, cost-effective process to create an adsorbing biocarbon from locally grown biomass.

11. Next Steps

Work is continuing in the laboratory to improve the development of an adsorbing biochar using Alberta's biomass resources.

Once achieved, it will be important to re-engage industry partners with an interest in removing organics from produced waters.

Policy makers will also need to be informed about the potential of this technology to remove organics from water and reduce GHG's as there may be benefits for the introduction of regulations in this area.

Another option is to use biochar created through this process as a material that will support the growth of microbes that could be involved in the bio-degradation of organics and / or the oxidation of methane (a potent GHG) generated by produced waters from oil and gas operations.

12. Communications plan

Our biochar work has already been broadly communicated in industry magazines and in the press:

- phys.org/pdf289491085.pdf
- http://www.laboratoryfocus.ca/research-shows-promise-for-reducing-greenhouse-gases/
- http://www.workingforest.com/biomass-could-help-clean-contaminated-water-oilsands-industry/
- http://www.canadianmanufacturing.com/design-engineering/news/wood-waste-straw-to-clean-oilsands-tailing-ponds-design-eng-105782
- www.biochar.ac.uk/download.php?id=122
- http://www.thecaen.ca/main-streams/wood-and-straw-could-clean-water-and-cut-oilsands-ghgs-say-researchers/
- environment.umn.edu/gsb/presentations/GSB_Layzell.pdf
- http://navigator.oilsandsreview.com/blog/research-shows-promise-inter-industry-synergy-reduce-oilsands-impacts/
- europepmc.org/abstract/MED/24365739
- http://laboratoryfocus.uberflip.com/i/141644
- http://beaconnews.ca/calgary/2013/06/biiomass-could-help-clean-contaminated-water-from-oilsands-industry/

We have also run a Workshop and a lab tour with Champion Technologies (Calgary, Canada), and we regularly talk with individual companies who are interested in the technology.

As we continue to improve the technology associated with the production of the activated carbon, we will continue to engage companies involved in relevant sectors such as:

- ☐ biomass production,
- ☐ processing,
- ☐ oil and gas recovery and processing,
- ☐ Water treatment
- ☐ Environmental mitigation
- ☐ Petroleum service sector
- ☐ Etc

13. Final Financial Report

A record of all project expenditures pertaining to the CCEMC funding is provided in Table 8.

Table 8. Detailed Financial report.

Total of all
Expenses: **57500.00**

Description	**Actual ($)**
POSTDOCTORAL SALARIES	**44097.91**
POSTDOCTORAL SALARIES - Benefits	**1784.15**
MATERIALS and SUPPLIES	**5070.28**
TRAVEL	**1372.66**
CONSULTANCY	**5175.00**

14. Appendix - Copy of Publication Arising from Work

See Attached Publication