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Cleaner production of flexographic ink by substituting carbon black with biochar

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ABSTRACT

There is growing interest in making printing inks more sustainable, and lowering the overall carbon footprint of the printing industry. A recent surge of research activity has emerged to develop "green" inks with bio-based solvents and binders, but little attention has been given to replacing the pigments that give inks their distinctive color. In this study, flexographic inks were formulated by replacing carbon black with a more sustainable biochar pigment derived from recycled paper, and fast growth cycle wood pulp. Obtained from fossil fuel sources, carbon black imparts high quality black prints, but at a significant environmental cost. Biochar, derived from recycled and renewable resources, has the potential to replace carbon black in many applications. Canceled United States currency stock was pyrolyzed at 1600 °C to produce a black biochar. Eastern White Pine (Pinus strobus) was selected for comparison, and converted to biochar at 550 °C and 1600 °C. Each biochar was functionalized and formulated into a simple ink composition optimized for flexographic printing. Prints exhibiting reflective optical densities exceeding 1.0 with excellent tone reproduction were obtained. Comparable print quality was achieved on both coated and uncoated paper substrates. Although further work would be required to fully optimize a biochar ink to match current print industry standards, a viable pathway for sustainable black ink development with good black density derived from recycled resources has been demonstrated. Our results indicate that it is possible to replace fossil fuel-based carbon black with biomass derived biochar, potentially resulting in cleaner production of flexographic printing inks.

1. Introduction

Printing inks are principally made of colorants, vehicles (binders), additives and carrier substances (solvents). The type of printing process determines the required flow properties of an ink, ranging from low viscosity fluids to dry powders (Kipphan, 2001). Carbon black (CB) is the primary source of black pigment in commercial printing inks, and is manufactured in an energy intensive manner, requiring the incomplete combustion of natural gas . In 2015, the global usage of CB for printing inks was approximately 260,000 t (Diamond, 2016) making its manufacture a meaningful global contributor of greenhouse gas emissions. This paper proposes a more sustainable alternative to CB in printing inks using biochar. The International Biochar Initiative (IBI) defines biochar as "a solid material obtained from thermochemical conversion of biomass in an oxygen-limited environment" (IBI, 2015). Biochar may be considered a more sustainable option because the biomass feedstock is derived from a renewable sun-driven resource, whereas natural gas, though currently abundant and inexpensive by historical standards, is finite and non-renewable. Biochar is currently utilized in many applications, such as soil amendment (Lehmann et al., 2011; Steinbeiss et al., 2009), contaminant sorbent (Ahmad et al., 2014), catalysis (Dehkhoda et al., 2010; Kastner et al., 2012), and fuel cells (Huggins et al., 2014; Yuan et al., 2013). Several recent review articles have described a variety of other industrial uses of biochar (Bartoli et al., 2020; Hersh et al., 2019). Biochar has been incorporated into inks to impart specialized functionality such as screen printed biochar with electrical properties (Quaranta et al., 2016) and 3D printed biochar-polymer composites with improved physical characteristics (Ertane et al., 2018; Idrees et al., 2018). Studies using biochar as a replacement printing ink pigment used in commercial print or packaging applications have not yet been reported to our knowledge. One principal reason may be that biochar often contains elemental and chemical compound contaminants. Without

Abbreviations: CB, Carbon Black; BC, Biochar; USC, Surplus US Currency; PWC, Eastern White Pine Biochar.

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contaminant removal (i.e. demineralization), the final print quality diminishes. CB, produced by natural gas, is highly refined and relatively contaminant free (Donnet, 1982). Raw material cost differentials between the two pigment sources may also be a significant market driver (Sovacool, 2014). Consumer end-use demand for "greener" print options that minimize lifecycle carbon footprint (Vachon and Klassen, 2006; PR Newswire Association LLC, 2018), coupled with uncertainty over how long low-cost natural gas reserves can be sustained at the current rate of depletion (Bentley, 2002), compels a complete re-examination of the entire black pigment manufacturing process which has remained relatively unchanged since the late 19th century.

This paper introduces and examines the viability of demineralized and functionalized biochar derived from plant and wood fibers as a sustainable and reliable substitute for CB in flexographic printing inks. Our efforts have focused on cleaner production because the primary feedstocks for biochar production are often treated as "waste", and their application in ink production will ultimately enhance material, energy and water use efficiency in the broader printing industry. Understanding the ability of these materials to be converted to viable printing pigments could have important future environmental and financial implications for the paper recycling, renewable biomass, ink production and printing industries, to name a few. This work provides a novel contribution toward development of sustainable printing inks by complementing other recent research in the printing sector that has focused primarily on "green" solvents and binders (e.g., Robert, 2015) instead of substituting petrochemical-based pigment material as described below.

2. Materials and methods

2.1. Biochar feedstock sources

Two feedstocks to create biochar (BC) pigment were examined: 1) cancelled surplus U.S. currency (USC) and 2) Eastern White Pine (*Pinus strobus*) softwood (PWC). USC is newly cancelled and shredded surplus $100 U.S. currency notes obtained from the U.S. Federal Reserve Bank of Atlanta, New Orleans branch. The Federal Reserve annually pays commercial composters to dispose of several dozen tons of USC after its physical conversion to a shredded rag paper. PWC biochar was provided by Cornell University (Ithaca, NY). USC composition is 75% cotton (plant fiber) and 25% wood fiber, whereas PWC is derived from 100% wood fiber. USC is representative of a pure scrap paper, and was specifically chosen to establish a future benchmark from which to compare BC pigment produced from 'less pure' recycled paper sources. Likewise, PWC is an appealing large-scale wood fiber source since it is readily abundant, low cost, and relatively free of mineral contaminants (Enders et al., 2012).

2.2. Biochar purification and ink formulation materials

For ink preparation, 85.0% w/w phosphoric acid (H_3PO_4) ACS grade was purchased from Aqua Solutions, Inc., 30% hydrogen peroxide (H_2O_2) AR grade from Macron Fine Chemicals, and 200 proof pure ethanol from Koptec. Polyvinylpyrrolidone (PVP) with an average molecular weight of 40,000 g/mol was procured from Alfa Aesar. Spectra/Por® 3 Dialysis Membrane (Standard RC Tubing, Approximate Molecular Weight Cut Off (MWCO) 3.5 kD, 45 mm flat width) was obtained from Spectrum Labs. White copy paper (92 bright, 20 lb.) was purchased from Staples Inc. and Utopia Two White Paper (14.33 × 24 in 100 lb. Text Gloss C/2 S) from The Paper Mill, which were used as substrates to test print quality.

2.3. Biochar production

USC was pyrolyzed in inert nitrogen gas conditions using a batch CM 1700 Series Rapid Temp Laboratory Furnace (CM Furnace, Bloomfield, NJ) at a 15 °C/min ramp and high heating temperature of 1600 °C for 1 h. At 1600 °C, all lignin, cellulose and hemicellulose are converted to high C content turbostratic crystallites (Lehmann and Joseph, 2009), similar to the well-organized para-crystalline CB structure (Donnet, 1982). Industrial grade nitrogen gas flow was steadily supplied to fix the furnace absolute pressure at 205 kPa. The USC feedstock as received had a moisture content of approximately 8%. The USC feedstock and USC biochar produced are shown in Fig. 1.

PWC was pyrolyzed at 550 °C in oxygen-deprived conditions using a continuous feed slow pyrolysis research kiln (Full Circle Biochar, CA) in the Leland Laboratory at Cornell University. 550 °C was chosen because other studies have shown that further increases in processing temperatures only nominally increase stable C yields in pine wood feedstock (Crombie et al., 2013; Enders et al., 2012). However, to more accurately compare CB, USC and PWC, a separate batch of PWC biochar was further pyrolyzed at 1600 °C in the CM 1700 Furnace. In both cases, the PWC biochar was produced using raw pine wood mechanically processed in a standard commercial wood chipper to ~3–4 cm pieces, and air dried to ~8% moisture content before pyrolysis. PWC produced using the two pyrolysis conditions are shown in Fig. 2.

2.4. Biochar Functionalization

Biochar Demineralization. 5 g of USC biochar were digested in 200 mL of 1 M H_3PO_4 at 90 °C for 24 h. The biochar suspension was then filtered and washed with deionized (DI) water until the supernatant pH was neutralized. The biochar was recovered by freeze drying and elemental composition analysis was performed using a scanning electron microscope (SEM) with energy-dispersive x-ray spectroscopy (EDS; Jeol, JSM- IT100LA, USA).

Biochar Functionalization. The purified USC biochar was then refluxed in 50 mL of 30% H_2O_2 at 60 °C for 24 h. This step was performed to functionalize the biochar with polar surface groups. Excess H_2O_2 was then removed via dialysis, and the remaining suspension transferred into two or three separate sections of Spectra/Por® 3 Dialysis Membrane tubing. The water bath was periodically tested for the presence of H_2O_2 with an iodine strip, and renewed with fresh DI water until a positive iodine test was no longer observed. The functionalized biochar was then recovered by freeze drying and SEM/EDS was performed.

2.5. Biochar milling

USC biochar was ball milled for a total of 50 and 75 min using 1 mm stainless steel balls with an Across International LLC VQ-N High Speed Ball Mill. 10 min milling intervals were used to prevent overheating. SEM images were taken between intervals to determine finished size. Ball milling continued until the observed particles size, visually determined using SEM analysis, appeared constant. For PWC biochar, the ball milling particle reduction step was modified slightly based on work reported by Peterson et al. (2012). This process consisted of milling with a 1:1:40 (biochar:ethanol:stainless steel ball) ratio by weight in 10 min intervals. During milling for all pigment types, pigment size reduction was observed in between intervals via SEM imaging. Once the pigments were no longer reduced in apparent size, the biochar was removed, collected by vacuum filtration and rinsed with DI water.

2.6. Ink formulation

To formulate biochar ink, 30 wt % PVP (average molecular weight of 40,000 g/mol) in DI water served as the ink vehicle. To produce 5 g of ink, 1–2 g of biochar were added to the solution to achieve a matching final printed black color density to a commercial standard ink used in this study (Performa 4CPC K, GAT Technologies). The biochar weight was used to determine the pigment loading fraction. Biochar was incorporated into the PVP vehicle using a Thinky ARM-310 planetary centrifugal mixer set for 10 min at 2000 RPM.

(a) (b)

Fig. 1. (a) USC feedstock as received and (b) SEM image of USC biochar pyrolyzed at 1600 °C (USC 1600).

(a) (b)

Fig. 2. PWC (Pinus strobus) biochar pyrolyzed at (a) 550 °C (PWC 550) and (b) 1600 °C (PWC 1600).

2.7. *Flexographic printing*

A standard Harper QD™ Proofing System was used to create all test prints made. For USC biochar ink, white copy paper was used as the substrate. The printer was set up with a 6.01 cm^3/m^2 anilox, 4.1 kg springs, and printed at a speed of 3.4 m/min. For PWC biochar ink, Utopia Two White Paper was used as the substrate. The printer was set up with a 7.44 cm^3/m^2 anilox, 6.8 kg springs, and run at a speed of 4.3 m/min. Substrate and printing parameter criteria were selected to obtain the highest visual print quality.

2.8. *Characterization*

Average pigment size determination and elemental analysis were performed using SEM/EDS (Leach, 2012). Average particle size was evaluated using a line intercept approach in ImageJ. A 10 line segment sample average was evaluated per image. The optical visual and color densities (Visual, C, M, Y and K) of the prints were measured using a spectrodensitometer (X-rite 500 Series). The optical visual and color densities and tone reproduction of the biochar ink were compared to a control flexographic ink, Performa 4CPC K (GAT Technologies). Ink viscosity was measured using a Brookfield viscometer, and ink shear information was obtained by recording the ink viscosity as a function of spindle rotation rate from 30 to 100 RPM (#2 Spindle). Three measurements per shear rate setting were obtained and staggered, to minimize viscosity memory effects with shear rate. Since the flexographic print proofer was set to a print speed of about 4 m/min, this setting translated to an anilox rotation rate of about 60 RPM. Single viscosity number reported was the Brookfield value obtained at a shear rate of 60 RPM. Tone reproduction was evaluated by a dot gain analysis method using optical microscopy on a Hirox KH-3000 microscope. Pigment dispersion was evaluated using a NIPIRI grind gauge according to the ASTM D1316 standard.

3. Results and discussion

3.1. *Biochar Functionalization*

Table 1 shows the EDS analysis of USC biochar at different treatment stages. The H_3PO_4 treatment effectively removed most of the mineral contaminants except for titanium dioxide (TiO_2) and silicon dioxide (SiO_2). Converting and recycling paper feedstocks into biochar pigments was a special challenge due to the ubiquitous presence of TiO_2, generously added to brighten white paper. In this case, TiO_2 was considered a contaminant, and completely counterproductive to producing a black pigment. Silicon oxides are mineral clay remnants added to improve ink hold-out in paper. As with TiO_2, a significant amount of coated clays (e.g., Kaolin) found in recycled boxboard pulp will be a challenge to eliminate completely. The H_2O_2 treatment increased the oxygen mole percent from 15 to 21%, suggesting increased biochar surface oxidation. Surface oxidation increases the hydrophilicity of the biochar particles which, in turn, promotes improved dispersion stability in aqueous ink

Table 1
Biochar EDS analysis after chemical treatment (mole percent).

USC biochar Treatment Stages	C	O	Na	Si	Cl	K	Ca	Ti
Untreated	**80.07**	**13.05**	**0.90**	**0.39**	**0.24**	**0.55**	**1.35**	**2.48**
H_3PO_4	**80.69**	**15.23**	-	-	-	-	-	**4.08**
H_2O_2	**73.54**	**20.67**	-	**0.20**	-	-	-	**5.60**

solutions. SEM/EDS analysis interrogates a small sample area, and there can be some sample variation. Future work may include mineral analysis using methods that interrogate a larger portion of the bulk pigment material, such as energy dispersive x-ray fluorescence or atomic absorption spectroscopy.

3.2. Biochar characterization

After 75 min of dry steel ball milling, SEM images of USC biochar revealed average particle sizes of 0.34 (0.08) μm (Fig. 3). Particle size has a significant impact on the fundamental print quality properties of a printed film (Leach, 2012). The average particle size falls within the 0.1–2 μm range used in commercial printing inks (Kipphan, 2001). Although SEM provides only local information regarding pigment size, large pigment grains were found to be less than 2 μm, and therefore within the acceptable range for commercial inks. The TiO_2 contaminant, which typically ranges from 0.25 to 0.4 μm (Hubbe, 2011), may have interfered with the milling reduction efficiency due to its greater density and hardness compared with that of BC.

With PWC biochar, the wet ball milling process appeared to yield a smaller average particle size as determined by SEM (Fig. 4). PWC processed at 550 °C (PWC 550) that was wet ball milled for a total of 50 min yielded an average particle size of 0.24 (0.06) μm. PWC processed at 1600 °C (PWC 1600) for a total of 70 min yielded particles of 0.27 (0.06) μm. Our results suggest, with our laboratory-based wet milling methods, there was a limit to the reduction in pigment size with increased milling time. Since particle sizes of less than 2 μm are considered most ideal for flexographic printing, and CB for inks is typically less than 0.1 μm, this procedure needs to be further investigated and refined in future work.

3.3. Flexographic ink formulation

A flexographic ink standard, Performa 4CPC K, has a measured viscosity of 168 cP. A 30% (w/w) PVP solution was found to have a viscosity of 120 (1.4) cP. The PVP solution viscosity was made a little lower than Performa 4CPC K to compensate for the dry weight of biochar

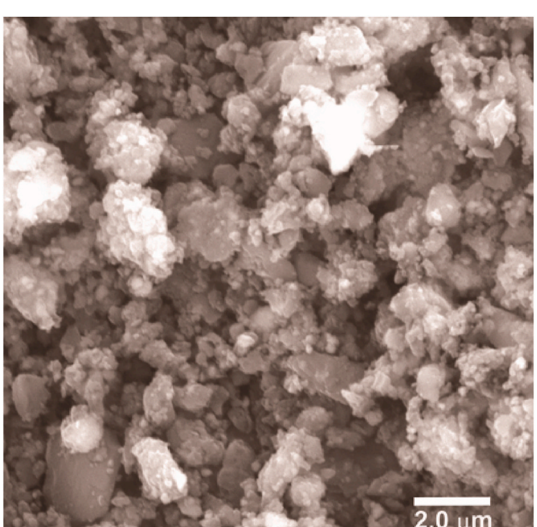


Fig. 3. SEM image of USC biochar ball milled for 75 min.

pigment added during ink formulation. A homogenous biochar ink was achieved when the PVP solution, and the ball milled biochar pigments were mixed with a planetary centrifugal mixer (Fig. 5). Pigment dispersion, using a NIPIRI grind gauge, indicated that the biochar ink possessed pigment particles less than 1 μm, consistent with our SEM analysis.

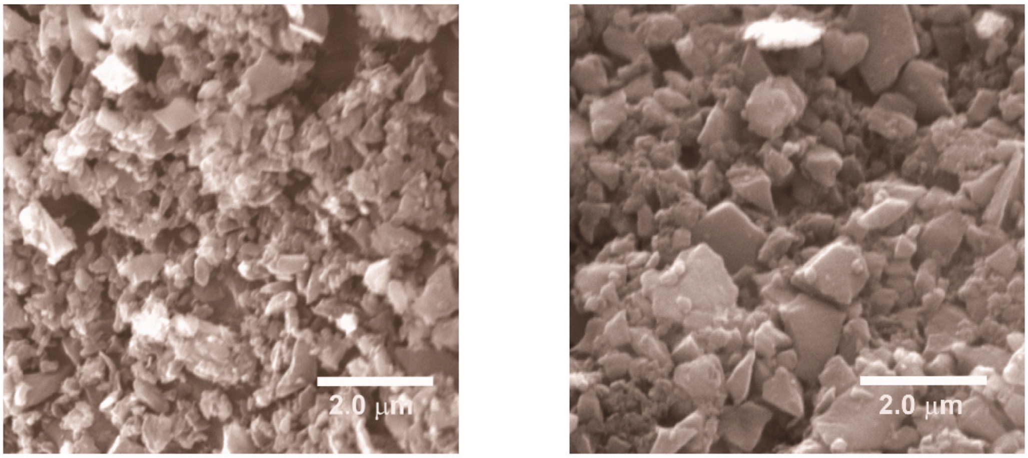
3.4. Flexographic printing using biochar ink

There were significant visual and optical differences between the USC biochar print and the Performa 4CPC K print under the same print conditions. PWC biochar prints showed promising results when compared with the Performa 4CPC K print. Sections 3.4.1 and 3.4.2 illustrate in detail the results of flexographic printing using USC biochar ink and PWC biochar ink, respectively.

3.4.1. USC biochar ink

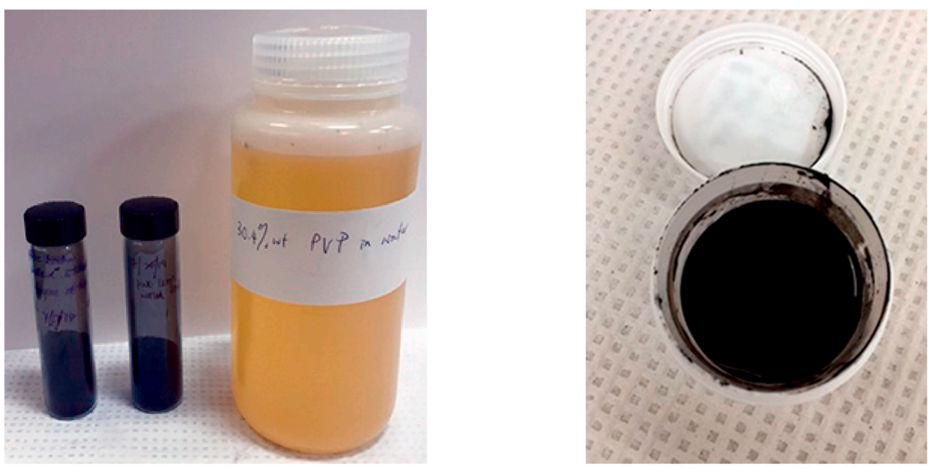
As prepared, the USC flexographic ink contained 18% USC biochar to obtain a black print. Commercial flexographic inks typically contain between 8 and 12% pigment loading (Laden, 1996). When printed using the same uncoated white paper substrate and print settings, flexographic print of USC biochar yielded a visual density of only 0.67, whereas the model flexographic ink Performa 4CPC K yielded a visual density of 1.12 (see Fig. 6 and Table 2). Since we did not have information regarding the pigment loading in the commercially available Performa ink, we prepared a CB ink in a PVP vehicle, and found the visual optical density to closely match the Performa standard when the CB pigment loading was 12% (Sid Richardson SR201 CB, data not shown). The CB ink pigment loading was roughly half the USC amount, and consistent with the CB pigment loading generally used in commercial flexographic inks. There are several potential reasons for the different observed print densities between the USC and Performa commercial inks. USC pigment contains mineral impurities not present in CB or PWC (e.g. TiO_2) which lightens the black pigment covering power. CB and biochar may also have different material densities due to process-dependent changes in biochar porosity or skeletal structure. For example, Lange et al. (2018) reported that biochars derived from resinous softwoods (including pine) have bulk density in the range of 140–420 kg/m^3, whereas carbon black bulk density is typically in the range of 1700–1900 kg/m^3 (Wypych, 2006). More work will need to be performed to improve the covering power of the USC pigment by developing process strategies to remove impurities, and determine accurate material density values. Finally, knowledge of the USC and CB pigment distribution would be required to evaluate the optical effects that pigment distribution imparts on print density. Optimized black density comparable to current commercial inks, however, may not be a necessary goal in all circumstances, as it would necessitate more complex chemical treatments and thus potential adverse environmental costs. In other words, if a sustainable ink from USC could be easily produced to achieve ‘good enough’ black density for common applications such as packaging box marking, the need to out-perform current commercial standards may be moot.

In terms of tone reproduction, however, the dot structure produced between the USC and Performa inks match quite well with some noticeable differences (Fig. 6A and B inset). Using ImageJ to measure the printed dot area on each print (average of 100 dot areas per image) at the 30% screen value, there is a 25% reduction in the average dot area when printing with the USC ink (Fig. 6B, inset). If the USC ink printed with a dot area equal to the Performa standard, the anticipated increase



(a) (b)

Fig. 4. SEM image of (a) PWC 550 ball milled for 50 min; (b) PWC 1600 ball milled for 70 min.



(a) (b)

Fig. 5. (a) Ball milled biochar and 30% (w/w) PVP solution before mixing. (b) Homogenous biochar ink achieved by using a planetary centrifugal mixer.

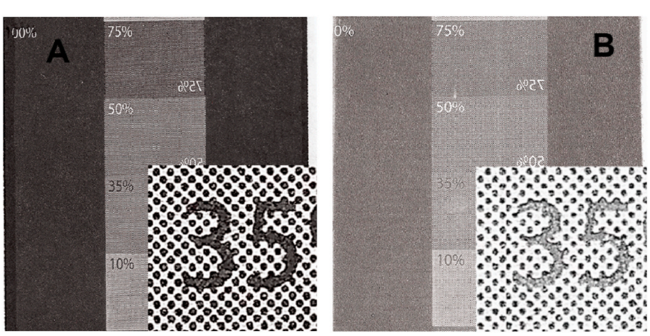


Fig. 6. Flexographic prints of (A) Performa 4CPC K and (B) USC biochar (18.8 wt %), printed with 6.01 cm^3/m^2 anilox, light spring, and 3.4 m/min speed.

in visual density would be from 0.67 to about 0.8. There appears to be less visual density within the printed USC dot, on average; so, it is possible the difference between the USC ink and Performa could be matched with more attention placed to ink transfer efficiency during printing. Clearly, determining the ink or printing parameter optimization would be the subject of future work.

Table 2
Print color densitometry comparison (USC).

	Ink	Performa 4CPC K	USC Biochar
Color density	**Visual**	1.12	0.67
	Cyan	1.10	0.64
	Magenta	1.13	0.69
	Yellow	1.14	0.71

3.4.2. PWC biochar ink

Fig. 7 shows a visual comparison of the commercial Performa 4CPC K, 27% solid loading of PWC 550 and 40% solid loading of PWC 1600 that was thermally processed in conditions comparable to USC. All ink samples were printed using the same conditions. With each PWC ink, the biochar pigment loading was steadily increased until the commercial print density was matched, or until a stable flexographic ink formulation could no longer be obtained. Optical density measurements in Table 3 show that both 27% PWC 550 and 40% PWC 1600 inks could be formulated with a visually distinct black density.

Using ImageJ to determine the average dot area in the 30% line screen image under magnification, dot gain observed between the PWC samples relative to the Performa standard, does not account for the

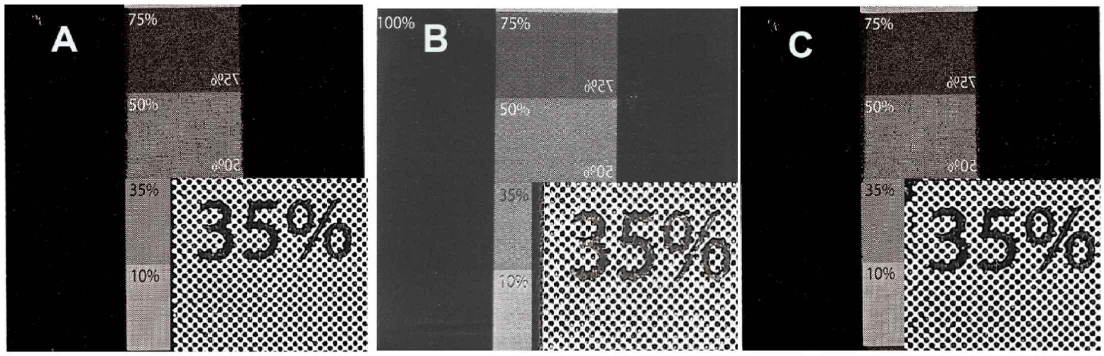


Fig. 7. Flexographic prints of (A) Performa 4CPC K, (B) 27% PWC 550, and (C) 40% PWC 1600, printed with 7.44 cm^3/m^2 anilox, medium-heavy spring, and 4.3 m/min speed.

Table 3
Print color densitometry comparison (PWC).

	Ink	Performa 4CPC K	27% PWC 550	40% PWC 1600
Color density	**Visual**	**2.08**	**1.30**	**1.21**
	Cyan	2.09	**1.28**	**1.20**
	Magenta	2.06	**1.31**	**1.21**
	Yellow	1.99	**1.31**	**1.21**

nearly two-fold difference in visual density. The average dot area reduction for PWC 550 and PWC 1600 ink was 30 and 15%, respectively. A closer dot structure analysis of the PWC prints indicate significant presence of what is known in flexography and gravure printing as a "doughnut" (Keif and Goglio, 2005; Janjomsuke, 2015). The name describes missing ink density in the printed dot center. Missing density, in many of the printed dots, could explain the visual density differences. As observed with the USC prints, doughnut defects may result when there is more ink cohesion, as opposed to ink-substrate adhesion, resulting in more ink remaining on the plate; or, ink being removed during the transfer process. Ink surface tension was not adjusted in this proof-of-concept work. The measured surface tensions for the biochar inks in this study were roughly 20 mN/m higher than the Performa ink. More ink cohesion would result from a higher surface tension, and could explain the transfer issues observed. Printing ink optimization would be more appropriate when a commercially relevant vehicle system is identified, or the printing press is capable of simulating commercial printing conditions. Since the Harper proofing platform used in this study did not have roll-to-roll capabilities, where line speed and plate pressures could be dynamically adjusted, optimizing ink transfer phenomena would be the subject of future work.

Even though the PWC print opacities did not match that obtained with the Performa 4CPC K ink, the print density and resolution were clearly sufficient to convey information. The print results have several potential positive outcomes. First, sustainability is enhanced by the reduced use of fossil fuel feedstocks and fixed C is sequestered in the printed product by a generous use of pigment. It is also important to note that different printing applications may have different standards for print quality and "blackness". Whereas a printed document must meet stringent requirements related to resolution and clarity for readability, the standard for flexographic printing of a box for product packaging could be much less demanding. In the latter case, biochar ink printing that is slightly "brown" or of somewhat lower resolution would still satisfy its functional requirements, while offering the potential for substantially lower environmental impact.

One distinctive characteristic that separated 27% PWC 550 from 40% PWC 1600 was the cyan density relative to the magenta and yellow densities (see Table 3). In 27% PWC 550, the cyan density was 0.03 lower than the magenta and yellow density, while in 40% PWC 1600, the cyan density was 0.01 lower than the magenta and yellow density. Consequently, 27% PWC 550 had a warmer tone, while 40% PWC 1600 exhibited a cooler tone. Generally, black inks that are cooler in tone are often favored. To compare tone reproduction of the PWC inks versus the commercial Performa ink, a dot gain comparison was made (Fig. 8). A linear relationship between the measured dot area as a function of the nominal dot area for all three inks show that biochar ink was capable of replicating tonality over a wide range print density. Both the 27% PWC 550 and 40% PWC 1600 closely matched Performa 4CPC K. As noted, the dot areas obtained when printing with PWC inks are slightly smaller than with the commercial standard ink. Tone reproduction with smaller dot areas may be leveraged to provide print information that requires high resolution, such as QR or bar codes. It is important to note, however, that the PVP polymer vehicle used in this study would not be a vehicle found in typical flexographic printing or packaging inks. Yet, the possibility of formulating an ink where raw material resources are less available, has been realized.

3.5. Discussion of biochar pigment economics

From an economic standpoint, the development of a functional flexographic (flexo) biochar pigment ink is intriguing as the overall global market for inks in general is projected to reach 23 billion USD by 2023 (PS Market Research, 2017) and "… the increasing prominence of flexography printing inks and growing shift towards environment-friendly printing inks" (PR Newswire Association LLC, 2018). It stands to reason that a biochar ink that can be produced for as much or less than the CB standard becomes the superior choice in terms

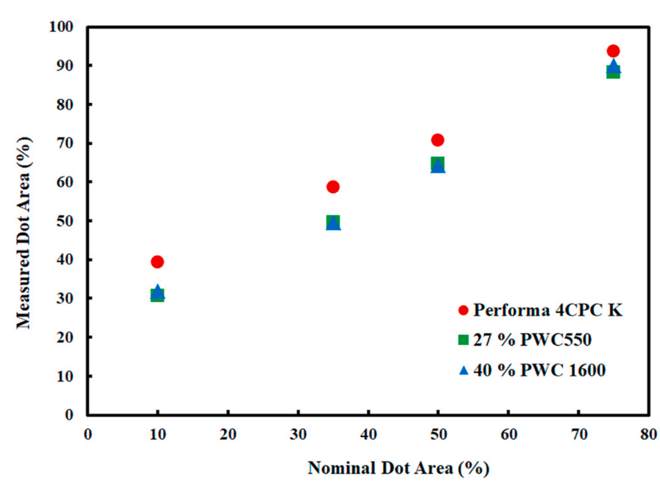


Fig. 8. Measured percent dot area against nominal percent dot area of flexographic prints using Performa 4CPC K, 27% PWC 550, and 40% PWC 1600.

of cost and sustainability for the simple conveyance of black and white text information in many flexo applications. According to the International Carbon Black Association (ICBA), CB is one of the top 50 industrial chemicals produced worldwide with 8.1×10^6 t manufactured annually. Approximately 9% (0.73×10^6 t) are utilized as black pigments with the remainder in tire rubber and other applications (ICBA, 2017). According to industry consultants, CB's "… market volume will increase to more than 15 million tonnes by 2022." and "… the global carbon black market will surpass a value of $25 billion by 2020, growing with a CAGR of over 4% during the 2015–2020 period." (CMR Institute, 2016). Based on discussions with industry contacts familiar with carbon black production, it is reasonable to estimate the average factory gate price (i.e. undelivered) cost of CB to range between $4.09 and $5.51 kg^{-1} (average $4.80 kg^{-1}).

To illustrate the potential cost differentials between CB and BC in common applications, it is helpful to examine the potential use of BC in ink jet printers. Although it is understood that flexographic and ink jet inks are quite different, we base the following analysis on the latter because commercial cost and composition data are more readily available. Given that a typical black inkjet ink is comprised of 4–8% per volume pigment, an ink jet cartridge would contain between 0.08 and 0.16 g or $0.00038 and $0.00077 worth of CB (Average: 6%, 0.12 g, $0.000575 respectively). According to industry research performed by the International Biochar Initiative, the average cost of biochar in the U. S is $3.63 kg^{-1} (IBI, 2017). The same ink cartridge filled with a functional equivalent of 0.54 g of 27% PWC 550 at this $3.63 kg^{-1} price would cost $0.00196, equivalent to $0.00139 more per cartridge, or ~240% over CB. Even though the average cost of BC per kg is ~34% less than that of CB, 4.5 times more mass of BC would be required, leading to the ~240% cost disadvantage. Though this cost differential would seem impossible to overcome, it is worth noting that the actual CB pigment cost in a black ink cartridge is a mere fraction of the average retail cost of the cartridge itself. Considering that the average black ink cartridge (HP 60) can print ~200 pages (Krystofik et al., 2014) and currently costs less than $25, it seems plausible that the average consumer would not hesitate to pay an extra 1/10th of 1 cent for a "green" alternative, assuming it meets their functional needs. Even if significant additional processing is required to formulate an ink suitable for ink jet printing (especially related to particle size reduction) the cost premium for a retail ink cartridge would still not be significantly impacted. In short, the limiting factor for the widespread adoption of BC ink appears not to be the cost of pigment, but rather its functionality.

4. Conclusions

There is significant current interest in developing more sustainable printing inks and lowering the overall carbon footprint of the printing industry, with a particular focus on "green" solvents and vehicles. However, to our knowledge, there are no published studies of biochar as a replacement for carbon black based pigments in flexographic printing inks. Our results indicate that there is a viable technical pathway to replace or augment a carbon intensive pigment, carbon black, with a more sustainable biochar substitute derived from recycled or naturally abundant feedstocks in commercial black printing inks. While these results point to a promising development pathway, a broader set of experiments need to be performed on each feedstock to overcome and optimize the main limiting factors identified to the commercialization of biochar as a replacement to carbon black. The major challenge in BC implementation is the presence of mineral contaminants that would vary in relation and proportion to the feedstock source. Intensive chemical treatment and purification may put biochar out of reach as an economically, or even environmentally, beneficial option over carbon black. We are currently evaluating waste pulp treatment and purification strategies before and after pyrolysis of the starting biomass material. Biochar surface modifications are also being investigated to improve ink dispersion stability in demanding printing systems such as ink jet. In summary, our results suggest that biochar black inks as developed in this study may have many uses and value-added applications today. Combining biochar-based pigments with "greener" solvents and vehicles offers even greater potential to achieve cleaner production of future printing inks.

Credit authorship contribution statement

Yang Goh: Methodology, Investigation, Writing – original draft. **Samantha Lauro:** Methodology, Investigation, Writing – original draft. **Steven T. Barber:** Investigation, Writing – original draft. **Scott A. Williams:** Conceptualization, Methodology, Writing – review & editing, Supervision. **Thomas A. Trabold:** Conceptualization, Writing – review & editing, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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