Research paper

Upgrading of bio-oil distillation bottoms into biorenewable calcined coke

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Abstract

Depleting fossil fuel sources necessitate renewable substitutes for petroleum-based co-products. Fast pyrolysis of biomass generates a hydrocarbon liquid ("bio-oil") amenable to distillation and/or hydro-treatment into hydrocarbon blendstocks. Biorefineries must add value through parallel generation of co-products. We demonstrated a straightforward conversion of bio-oil distillate bottoms into calcined coke. The solid residue was subjected to calcination at 1200 °C for 1 h under N2 atmosphere. The dry calcined product contained 96–99% carbon, was free from sulfur (<0.05% mass fraction), and contained a mass fraction of 0.2–1.1% ash. XRD confirmed steady increases in crystallite size with both devolatilization and calcination. FTIR spectroscopy indicated a loss of functional groups after calcination, except two broad peaks representing C–C and C–O. Temperature programmed oxidation (TPO) of the bottoms before and after calcination illustrates an increasing structural order via the increasing temperature(s) necessary to oxidize the samples. SEM images reveal bubbly morphologies similar to the industrially-favored sponge coke. The electrical resistivity of calcined coke samples measured to be < 1.6 mΩ·m, which closely falls in line with specifications for carbon anodes. Due to the aforementioned qualities and biomass origin, biorenewable calcined coke is an improved alternative to petroleum coke and can find application in carbon anodes, steel carburization, and graphite synthesis.

1. Introduction

Since the worldwide consumption of liquid transportation fuels is outpacing the finite supply of fossil fuels [1,2], applications for petroleum replacements have focused squarely on fuels. Although finished motor fuels comprise the bulk of petrochemical refinery outputs [3], the world economy relies heavily on many everyday products that emanate from petroleum. Altogether, non-fuels co-products comprise 15–20% of all petroleum products [3].

Furthermore, many petrochemical refineries rely on non-fuels applications for the large majority of their product sales. Therefore, a strategy for renewable fuels must be coupled with a strategy to bring economic value via petrochemical co-product replacements. As an example, production of biodiesel was found to be economically viable due to the feasibility of producing glycerol in parallel [4,5].

One of the most crucial yet least discussed coproducts of value is petroleum coke (termed "petcoke"). Typically, the residuals remaining after vacuum distillation of crude oil (>600 °C) enter a delayed coker unit, which thermally cracks the residual into petcoke and lighter fuel components [6]. Petcoke can be used as-is to substitute for coal in fuel applications or, if the metals and sulfur contents are low enough, can be calcined into coke products suitable for use in aluminum smelting anodes. The latter application alone can absorb more than 70% of the petcoke market [7,8]. Other high-volume markets for calcined coke utilize the remaining 30% for production of graphite, steel, and titanium dioxide [8,9]. Globally, 50 M tonne yr−1 of aluminum are produced from approximately 25 M tonne yr−1 of carbon, and low-quality coke can cost smelters more than $100 tonne−1 of product in consumption costs [10,11]. Petcoke demand continues to rise annually, for which the U.S. provides more than half the global supply [12], and the market has gone wanting for sources that are renewable due to several...
sustainability factors [13]. Demand for high-quality calcined coke is
hampered by the continually declining quality of pet coke [14–16],
via high sulfur and metals content (Ni, V). Calculines currently must
desulfurize coke to meet demand for both anodes and steel, which
intensively increases processing costs.

One cannot easily produce coke as a side product from cellulosic
ethanol or lipid-based biodiesel processes. Incidentally, thermo-
chemical methods of biofuels production (e.g. gasification, pyroly-
sis) are well-suited for isolating biochar solid residue in parallel to
the liquid crude oil that is produced (“bio-oil”). However, the high
metals content of biochar render it unsuitable for refined coke and
much more amenable for soil remediation [17]. Distillation of bio-
oil produces solid residues that could serve as a petcoke precursor.
Traditional bio-oil distillation had been largely ignored due to
significant yield losses from thermal instabilities. Recently, we
demonstrated the high-yield distillation [18] of tail-gas reactive
pyrolysis (TGRP) bio-oil under normal atmospheric distillation
conditions. The TGRP process [19] does not utilize any catalyst nor
external hydrogen, yet produces bio-oils with <10% oxygen mass
fraction (vs. 34–40% in traditional bio-oil), which gives rise to
thermally stable bio-oils for distillation. Solid residues remaining
post-distillation amount to >15% mass fraction of the starting bio-
oil, which amounts to a significant profit if it was possible to
be processed into petroleum coke. Herein we discuss bio-oil distillate
bottoms as a potential source for renewable calcined coke in
various applications.

2. Experimental

2.1. Biomass preparation

Switchgrass (Panicum virgatum, carthage cultivar, abbr. “SwG”)
feedstock was grown on and provided by the McDonnell Farm (East
Greenville, PA, USA). Switchgrass was planted in 2007 and har-
vested every April after the first three years (sample harvested in
2013). Post-harvest, switchgrass is cut with a haybine, baled
(3’×3’×7′) and hauled in a barn for storage. The entire switchgrass
plant was used. Eucalyptus biomass (Eucalyptus benthamii, abbr.
“Eucal”) was grown at and provided by Embrapa Forestry (Candoi,
Parana, Brazil). The eucalyptus plants were harvested in July 2012
after six years of growth, then subsequently debarked and stored in
plastic containers at room temperature. Guayule bagasse biomass
(Parthemium argentatum, abbr. “Guay”) was grown at and provided
by Yulex Corporation (Chandler, AZ, USA). Post-harvest, the entirety
of the guayule plant was ground and underwent a proprietary
processing step to remove the rubber resins that are part of the
plant, leaving behind the bagasse used for pyrolysis.

2.2. Fast pyrolysis of biomass

Prior to fast-pyrolysis experiments, all feedstocks were ground
dried. Fast-pyrolysis of feedstock was carried out in the ERRC
fluidized bed fast pyrolysis system, as described previously [19,20].
Briefly, 2 kg h⁻¹ of feedstock is fed through a fluidized sand bed
reactor under 500 °C N₂. The resulting vapors then pass through a
cyclone which separates out char particulates. Liquid phases are
then condensed from the vapor by 4 condensers in series. Oil was
then condensed from the vapor by 4 condensers in series. Oil was
 condensed and collected. After removing the vacuum and turning
off the heating mantle, the round-bottom flask was allowed to cool.
The hard glassy bottoms residue was chipped, scraped, and
collected from the flask and crushed into a granular powder with a
mortar and pestle.

2.4. Devolatilization and calcination of distillate bottoms

For devolatilization, 1–5 g of each distillate bottoms sample was
placed in a high-temperature crucible, with the crucible placed in
a static muffle furnace. The oven with crucibles was purged of air
with nitrogen before placing lids on crucibles. With continuous
nitrogen flow, the oven temperature was gradually raised to 950 °C
over a period of approximately 1 h, then held at that temperature
for 6 min before the crucibles were removed and cooled. Devol-
atilized products were crushed into a powder for further analysis.
For calcination, the same procedure was followed for either
devolatilized bottoms or distillate bottoms, except that the tem-
perature was gradually raised to 1200 °C over a period of 3 h (see
Fig. 1). The crucibles were then held at 1200 °C for 1 h, then the
temperature was gradually lowered to 400 °C before removing the
crucibles from the oven, in order to prevent crucible fracture.
Crucible lids were removed after complete cool-down to room
 temperature. For one-step calcination, distillate bottoms under-
went devolatilization and calcination in series without any inter-
mediate cooling step.

2.5. Characterization

Powder X-ray Diffraction (XRD) was performed on bottoms
samples (as-is, devolatilized, calcined) using a Rigaku MiniFlex II
bench-top system. XRD patterns were compared to reference
spectra using PXDI, (Rigaku Corporation) software. The radiation
source was Cu Kα radiation (λ = 1.5406 Å) at an operating condition
of 30 kV and 15 mA. All spectra were taken at a scan rate of
0.5° min⁻¹ and sampling width of 0.02°. To calculate the crystallite
sizes Lc and La, we used the equations (1) based on the empirical
Scherrer equation [21,22], where 2θ at (002) and (100) are used for
Lc and La, respectively.

\[
L_c = \frac{0.89\lambda}{\Delta \cos \theta_{(002)}} \quad L_a = \frac{1.84\lambda}{\Delta \cos \theta_{(100)}}
\]

\( \Delta \) represents the full width at half-maximum (FWHM).
Elemental analysis (CHN) by combustion, as well as sulfur analysis
by titration, was carried out by Robertson Microlit Laboratories
(Ledgewood, NJ). Oxygen content was determined by difference.
FTIR spectra of solid samples were obtained using a Nicolet Nexus
670 FTIR spectrometer (Madison, WI, USA) with a Smart Orbit
diamond attenuated total reflection (ATR) accessory. Scanning
electron microscopy images were taken using a Quanta 200 FEG
Environmental Scanning Electron Microscope. Higher heating
values of combustion were determined for distillate bottoms
samples using a Leco AC600 bomb calorimeter. Ash content
was determined by heating the sample in a crucible to 750–850 °C.

Bio-oil samples were distilled using either a fractionating col-
umn or a short-path distilling head, as described in recent work
[18] . Briefly, 20, 50, or 100 g of bio-oil was heated in a round-
bottom flask connected to a distillation apparatus. Vapors were
condensed and collected until the bottoms temperature reached
350 °C. Then, vacuum was applied, and more vapors were
condensed and collected. After removing the vacuum and turning
off the heating mantle, the round-bottom flask was allowed to cool.
The hard glassy bottoms residue was chipped, scraped, and
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mortar and pestle.
The mass remaining was weighed to be the ash content. Electrical conductivity measurements were performed using a CE Compass 305D variable DC power supply and a Cen-Tech P37772 multimeter. Calcined samples were cut from a solid sample to various dimensions (see Supplemental Table S1), and a colloidal silver paint was applied to each end of the part. Cut samples were measured for electrical resistance across the length of the sample using a multimeter. Resistivity values were calculated based upon measurements of fixed, longitudinally-shaped samples.

Surface area measurements and temperature programmed oxidations were performed on a Quantachrome ASiQ with an attached Pfeiffer Vacuum PrismaPlus mass spectrometer (Quantachrome Instruments, Boynton Beach, FL, USA). Prior to surface area measurements, samples were outgassed for 12 h at 200 °C. Surface areas were then determined using the BET method over the pressure range of 0.025 < P/P₀ < 0.3. In a typical TPO analysis, about 12 mg of sample were placed in a sample tube sandwiched between packings of quartz wool and dried and degassed at 120 °C under vacuum for 20 min. Gas flow was then started using a mixture of 5% volume fraction O₂ in helium (ILMO gas, Jacksonville, IL) set at a flow rate of 40 cm³ min⁻¹, and the cell purged for 20 min prior to the start of the measurement. Under this gas flow and at this starting temperature, the sample was heated at 10 K min⁻¹ to 1050 °C. The mass spectrometer outputs representing the following m/z were recorded: 18 (H₂O), 28 (CO), 32 (O₂), and 44 (CO₂). X-ray fluorescence (XRF) was performed within a focused ion beam SEM (FEI Strata DB235), using an integrated x-ray fluorescence analyzer with separate x-ray source for trace elemental analysis.

3. Results and discussion

3.1. Coke preparation steps

Although all coke samples originated from bio-oils of varying feedstock origins, we aimed to design a process for upgrading distillate bottoms, such that all products converge towards similar compositions, regardless of feedstock origins. The main reason is to remove feedstock dependence from an eventual biorefinery, which would enhance technology transfer from location to location. Calcined coke consists of >96% mass fraction graphitized carbon domains, so all calcined bottoms products should theoretically be identical. After performing atmospheric and vacuum distillations, a semi-liquid distillate with a jet black residue remained in the flask. Under vacuum, the residue resembles a molten viscous tar. When raised to atmospheric pressure and cooled quickly, the tar solidified into a glassy black solid. Chipping and grinding the solid is the only practical way of utilizing it for post-processing. For industrial purposes, a continuous distillation process would handle the vacuum distillate bottoms under raised temperature, in a manner very analogous to that of a traditional petroleum refinery.

Industrially, calcined coke is manufactured by feeding the coke emanating from the petroleum residue or delayed coker (termed “green coke”) into a rotary kiln. Typical properties can be found in Table 1 [6]. The kiln gradually heats the green coke under inert atmosphere through multiple temperature zones, each of which serves a different purpose, beginning from volatiles evolution to structural adjustments through crystallite growth. For our laboratory batch experiments, we divided the heat treatment steps into multiple stages in order to segregate the phases of coke transformation. As seen in Fig. 1, the first step consisted of removing any volatiles, such that only fixed carbon remained behind. Since fixed carbon consists of very high molecular weight polyaromatic hydrocarbons (PAHs), the devolatilization step serves the purpose of increasing the carbon percentage. A second calcination step was applied to the devolatilized bottoms, which served the purposes of 1) eliminating any heteroatoms, 2) rearranging free carbon chains into polyaromatic domains resembling graphite, and 3) increasing the size of the polyaromatic carbon sheets. We also investigated a one-step calcination process, wherein the calcination occurs immediately after the devolatilization without removing the devolatilized sample from the furnace. The devolatilization step melds the coke into one solid piece, so it is anticipated that the one-step calcination will have a fundamentally different effect on the coke quality and/or structure. This one-step investigation is necessary since it mimics temperature grading through a rotary kiln, and traditional petroleum coke contains only 10–15 % volatiles.
3.2. Elemental analysis

Table 2 presents the elemental and proximate analyses of the distillate bottoms at different processing stages. Comparisons can be made with typical values for petroleum coke (Table 1). Distillate bottoms exhibit differences with respect to feedstock [23]. For example, guayule contains higher concentrations of nitrogen. Overall, the bottoms products exhibit properties which make them useful as-is. Via bomb calorimetry, the bottoms possess higher heating values between 32.6 and 36.4 MJ kg$^{-1}$, a significantly higher range than that of traditional petroleum coke or coal (29.8 and 25.2 MJ kg$^{-1}$, respectively [24]), likely due to the presence of heavy hydrocarbon volatiles [23]. Combined with the tail-gas from the TGRP process (HHV = 12.4 MJ kg$^{-1}$) [19], distillate bottoms can still serve as fuel for the endothermic pyrolysis reaction to reduce heat demand for a pyrolysis biorefinery.

The low ash content and absence of sulfur enable distillate bottoms to be used for both fuel and higher quality coals, if the bottoms calcination step is optimized with respect to material properties. Devolatilization of the distillate bottoms produced a lustrous black solid. Losses due to volatiles comprised at least 38% to upwards of 60% of the distillate bottoms. While these mass fractions are considered relatively high for direct use of distillate bottoms in specific applications, a partial devolatilization step is conceivable, which would remove a portion of the volatiles without further heating. Devolatilization removed nearly all of the residual hydrogen, oxygen was reduced to less than half the original content, and nitrogen remained unchanged. It was only during high-temperature calcination that the nitrogen content fell significantly. Most importantly, the carbon mass fractions increased for both devolatilization and calcination steps. The renewable calcined bottoms could be reduced further, these calcined bottoms products resulted from only 1 h of calcination at 1200 °C, whereas smaller levels of heteroatoms can come about from higher temperatures and longer times. Nevertheless, the results also illustrate the efficiency of calcining distillate bottoms. Elemental analysis (EA) results from the one-step procedure produced similar results, with no indication of improved carbon percentages. Yields of devolatilized bottoms ranged from 50 to 65%, depending on the starting volatiles content. Calculation of devolatilized bottoms consistently resulted in an 85–87% yield across all bottoms samples, which indicates the uniformity of the process into a defined product.

Metallic impurities can alter the application and/or final end-use properties for calcined coke. For aluminum smelting anodes, the electrolysis introduces the metal impurities into the aluminum product and affects the reduction efficiency [25]. Hence, aluminum smelters require low ash and/or metals content. We employed x-ray fluorescence to elucidate the amount and types of metal impurities that make up the ash. Rather than directly scanning the coke samples, increased resolution and accuracy were obtained by scanning the ash and using the results to recalculate concentrations for the coke samples. Table 3 displays the XRF trace metal analysis for detected metals, in comparison with general values for petroleum coke. In general, most metal concentrations fall close to or within limits typically found for petroleum coke, with the exception of silicon. Since steel is an alloy of iron, excess iron levels in calcined coke should only benefit the end composite. Greater incidences of problematic concentrations became more frequent as
the calcined ash content increased. Specifically, calcined coke from pyrolysis liquids made from *Eucalyptus benthamii* contained relatively low concentrations of only a few metals, whereas calcined coke from guayule bagasse had high concentrations of Si, K, Fe, and Cu. Vanadium and nickel are two specific metals which are heavily undesired in the petrochemical and anode industries [26], due to catalyst poisoning and air reactivity, respectively. Their levels in calcined bottoms remained mostly absent or at very low concentrations.

3.3. FTIR spectroscopy

Due to the very heavy and conductive nature of the calcined coke molecules, techniques for characterization are limited. Calcined coke is insoluble in every common solvent. We used FTIR to assess the presence of functional groups and chemical bonds in fresh distillate bottoms, as well as the predominant chemical bonds present in the structured calcined bottoms. While calcined and/or graphitized cokes have been characterized by the complementary Raman spectroscopy method [27,28], a recent study [29] revealed useful information with FTIR as well. Fig. 2 shows FTIR spectra for switchgrass distillate bottoms (as-is, calcined) and eucalyptus distillate bottoms (calcined). From the switchgrass distillate bottoms spectrum, oxygenated species exist as alcohol groups (3336 cm\(^{-1}\)), carbonyls (1684 cm\(^{-1}\)), and C–O linkages (1300–1000 cm\(^{-1}\)). Other functional groups include the C–H stretch (2962 cm\(^{-1}\)) and aromatic C–C (1595 and 1438 cm\(^{-1}\)). In contrast, the calcined samples studied always show only two peaks: a singular aromatic C–C peak (1568 cm\(^{-1}\)) and a C–O stretch (1092–1200 cm\(^{-1}\)). Although all samples contain aromatic C–C bonds, the number of C–C peaks reduces to a single broad band in calcined samples, which reflects two phenomena: 1) homogenization of chemical composition and structure, and 2) increased restriction of bond vibrations due to structural order. While the oxygen content is relatively small in calcined samples, the C–O peak at 1092 and/or 1200 usually appears with strong intensity, compared with peaks of other functional groups. Hence, the C–C and C–O peaks appear to be of similar peak intensity. In addition, the two FTIR bands correspond well with the Raman shift values reported in literature for calcined petroleum cokes [27].

3.4. Temperature programmed oxidation

Temperature programmed oxidation is a method for observing oxidation trends and products, as they relate to the structural and compositional properties. Oxidation temperatures of carbonaceous solids are directly proportional to their degree of structural order [28,30,31]. We used TPO to evaluate oxidation resistance of coke samples by observing the oxidation products produced. Each sample was reacted under 5% oxygen in helium, in order to observe evolution of water and carbon oxides. Fig. 3 displays the TPO profiles for bottoms from two different bio-oils throughout the calcination process. For all bottoms samples, TPO profiles revealed a gradual reduction in the amount of water produced, until the calcined samples produced no water, indicative of the high purity of carbon in calcined coke. Temperatures for peak oxygen consumption and ignition temperature (i.e. onset of oxygen consumption) increased for both devolatilization and calcination steps, indicating the role each step contributes towards structural improvement of distillate bottoms. While peak temperatures may exhibit slight variations due to differences in sample size, the ignition temperature is not affected, and the ignition temperatures confirm the trends found with the peak oxygen consumption temperatures.

Generally speaking, combustion of carbon into CO indicates a degree of resistance against the complete oxidation into CO\(_2\) (and hence so does the CO/CO\(_2\) ratio). As-is, the distillate bottoms exhibit significantly greater levels of CO production relative to CO\(_2\), as compared with typical fast-pyrolysis biochar [32]. Compared with distillate bottoms, biochar carbon morphology is amorphous, as indicated by its low temperature of oxidation [31]. The volatiles

![Fig. 2. FTIR spectra of distillate bottoms is, before and after calcination.](image-url)
content of distillate bottoms plays a role in their higher heating values by facilitating the combustion of the higher molecular weight carbon. This is evidenced by the significant increase in TPO combustion temperature in going from “as-is” to devolatilized bottoms. Although the decrease in elemental oxygen content is much greater for the devolatilization step, the drop in CO/CO\textsubscript{2} ratio is much greater for the calcination step. This disparity indicates that the drop in CO/CO\textsubscript{2} ratio is likely due to the structural reordering rather than due to a loss in reactive oxygen. Another clear indication of the structural homogenization of calcined coke is the similarity of the CO and CO\textsubscript{2} curves. In the bottoms, the CO and CO\textsubscript{2} profiles appear to evolve independently whereas the two gases evolve in parallel in the devolatilized and calcined samples.

With regards to one-step calcination, Fig. 4 displays the TPO of guayule distillate bottoms through the calcination process, in comparison with a two-step calcination. While it appears that the devolatilization step significantly improves the structural ordering via the higher peak temperature, the subsequent calcination step reduces the peak combustion temperature to 810°C while simultaneously segregating the coke into three specific domains. On the other hand, the one-step procedure improves the morphological uniformity by increasing the peak temperature and reducing it to a single curve, with the exception of the small peak at 530°C.

3.5. Crystallinity

High temperature calcination improves structural order by increasing the sizes of nanocrystalline graphitic domains. In this regard, XRD is another critical method for assessing any crystalline structures and/or hierarchical order. We used XRD to examine distillate bottoms at each stage of the calcination process, Fig. 5 displays XRD spectra from switchgrass-derived distillate bottoms, taken at each step of the calcination process. Graphitic domains arrange according to a hexagonal structure [33], so this structure was taken as the basis for interpretation. The (002) peak at 20 = 22–26° indicates interlayer scattering across sheets within a graphite crystallite, whereas the (100) peak at 42–44°C emanates from intralayer scattering across the sheet [34]. As the heat treatment of bottoms progresses, the (002) peak gradually decreases in full width at half maximum (FWHM), indicating a gradual increase in crystallite size. Similarly, the (100) peak appears after devolatilization, then becomes more defined into two separate peaks upon calcination (43 and 52°). A similar trend can be seen for the peak at 78°.

Table 4 shows the calculated values for all samples. The devolatilization step increased the crystallite size, which simply resulted from the absence of scattering from amorphous volatiles. However, further increases in crystallite size occurred for calcination of devolatilized samples, indicating that the calcination process effectively increased the structural order present within the sample. Most of the calcined samples approached >12 Å, which still requires further structural ordering towards anode specifications [35] for calcined petroleum coke. In particular, switchgrass-based samples showed the greatest increases of crystallite dimensions. One interesting correlation exists between the TPO and XRD results, in that an increase or decrease in the peak oxygen consumption temperature resulted in a similar change for crystallite width L\textsubscript{d} (see Supplemental Fig. S1). For example, guayule bagasse distillate bottoms crystallites exhibited the greatest sizes when devolatilized, whereas the calcined version exhibited smaller sizes overall. Similarly, the TPO temperature of combustion for devolatilized guayule bottoms greatly increased to temperatures near 1000°C, whereas the two-step calcined version only reached 810–875°C. One-
step calcination of guayule bottoms produced both a higher temperature stability and a larger crystallite size, thus falling in line with the aforementioned trend. It is crucial to note that the conditions used in these experiments (1200 °C, 1 h) represent relatively mild conditions for coke calcination, yet improved the properties of the coke product. Even better crystallite properties are expected to arise from longer calcination times and/or greater temperatures. This is because the crystallite dimensions each follow tightly linear trends with respect to processing temperature [8,36].

**Table 4**

<table>
<thead>
<tr>
<th>Length (Å)</th>
<th>As-is</th>
<th>Devolatilized</th>
<th>Calcined</th>
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<td></td>
<td>SwG</td>
<td>SwG-R</td>
<td>Eucal</td>
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<tr>
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<td>3.98</td>
<td>3.73</td>
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</tr>
<tr>
<td>Ll</td>
<td>15.7</td>
<td>21.3</td>
<td>21.9</td>
</tr>
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</table>
3.6. Morphology by SEM

Variations in coke morphology play critical roles in their end-use properties. Sponge coke, a coke that is macroporous with a sponge-like appearance, is predominantly preferred in the petcoke industry. Aluminum smelting anodes rely on the sponge coke porosity for diffusion and adhesion of additives like pitch and binders into the coke [8], before the anode is fully baked into a finished product. In contrast, shot coke consists of hard pellets (2–4 mm), which is undesired for many applications. We assessed the morphology of coke samples via images taken by SEM (Fig. 6). The largest magnification image shows that the fragments are irregularly shaped and sized to much less than the 1 mm scale bar. Higher magnification images revealed predominant sections of coke with bubble-like appearances, in addition to a porous structure reflective of sponge coke morphologies. While BET surface area measured to be relatively low for devolatilized samples ($10\,\text{to}\,20\,\text{m}^2\,\text{g}^{-1}$), wider variations occurred for some calcined samples ($150\,\text{to}\,300\,\text{m}^2\,\text{g}^{-1}$). Excessively high porosity and/or mesoporosity diminishes the required density for calcined coke, so optimization of both the temperature heat-up rate and post-calcination grinding steps will be necessary [8,37].

3.7. Electrical Conductivity

Ultimately, an assessment of end-use applications for calcined distillate bottoms requires measurement of end-use properties. To this end, electrical conductivity measurements were performed on switchgrass-based samples calcined in one-step. These samples effectively kept the calcined coke constricted to a solid porous phase that is amenable to cutting and shaping. Long rectangular samples were cut out in order to ensure accurate resistivity calculations, and a colloidal silver paint on opposing faces ensured even distribution of current flow across the sample width. When applied to samples of various dimensions and aspect ratios, an apparent resistivity value of $1.6 \,\text{m}^2\,\text{m} \pm 0.34$ was obtained, which closely meets the requirements for calcined coke properties [6]. The bulk resistivity of the material is suspected to be lower than reported due to the porous nature of the materials tested.

4. Conclusions

We demonstrated the synthesis and end-use properties of calcined coke obtained from bio-oil distillate bottoms. From the various bio-oils that were distilled, we converted the bottoms into products nearly identical in composition and structure. These calcined cokes are superior to calcined petroleum coke by virtue of their low sulfur (trace amounts) and metals content (0.2–1.1% mass fraction). Characterization by FTIR indicated an initial presence of oxygenated functional groups that disappeared upon calcination, leaving only a dominant aromatic carbon peak with a minor C–O peak. TPO studies confirm the progressive stabilization and structural ordering that the calcination process introduces into the distillate bottoms. A one-step calcination process is preferred, wherein the devolatilized samples are immediately calcined in situ. Significant crystallite growth occurred for both devolatilization and calcination steps, verified by XRD, though further optimization will be necessary. SEM images reveal a highly porous structure within sub-mm particles that renders the coke useful for mixtures with carbon anode binders. The electrical conductivity of biorenewable coke enables its application as a valuable substitute for calcined petroleum coke, especially in light of the trace sulfur content.

Acknowledgments

We would like to acknowledge Craig Einfeldt for providing support work for the fast pyrolysis experiments. Also, we acknowledge Joseph Uknalis for the SEM images, Craig Johnson for x-ray fluorescence measurements (Drexel University), and Ed Wickham and Phoebe Qi for use of the FTIR spectrometer. We also...
thank John R. Regalbuto and Qiuli Liu (U. of South Carolina) for performing XRD measurements. USDA-NIFA-BRDI grant 2012-10008-20271 is hereby acknowledged.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.biombioe.2015.07.028.

References