



Article

Lauric Acid Treatments to Oxidized and Control Biochars and Their Effects on Rubber Composite Tensile Properties

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Abstract: Biochar is a renewable source of carbon that can partially replace carbon black as filler in rubber composites. Since the carbon content of biochar is less pure than carbon black, improvements and modifications must be made to biochar to make it a viable co-filler. In this work, two methods to change the surface chemistry of biochar were employed: (1) gas treatment at 300 °C with either air or carbon dioxide, and (2) coating with lauric acid. Both methods are amenable to the current rubber processing industry. After biochar was treated with these methods, it was used as co-filler in rubber composite samples. Gas treatment with either air or carbon dioxide was found to increase stiffness in the final composites. Although lauric acid coating of biochar by itself did not have a significant effect on tensile properties, biochar that was first treated with carbon dioxide and then coated with lauric acid showed a 19% increase in tensile strength and a 48% increase in toughness. Gas treatment and lauric acid coating of biochar provide relatively simple processing techniques to improve the stiffness and tensile strength of biochar as rubber composite filler.

Keywords: biochar; surface treatment; lauric acid; rubber composite



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1. Introduction

Carbon black (CB) has been the dominant filler in the tire industry for over a century [1]. However, there are important reasons why sustainable alternatives should be pursued. CB is a petroleum product, and dependence on foreign fossil fuel sources is challenging since oil prices can be very unstable due to global conflicts and other political reasons [2]. Shrinking CB's footprint in the global marketplace also improves air quality with less pollution [3].

Biochar has been a popular candidate as a sustainable source of carbon from biomass [4]. Most biochar research has been carried out with intended applications being carbon sequestration [5], catalysts [6–8], energy storage [9–11], filtration media [12,13], and sorptive media [14–16], the latter two taking advantage of the (frequently) porous nature of most biochars, although porosity does depend on many factors such as feedstock and processing conditions [17]. However, when using biochar as rubber composite filler, porosity is not as important as other characteristics such as carbon content and particle size. Current literature for using biochar as rubber composite filler is limited but slowly growing. Greenough has reviewed the relevance of biochar as rubber composite filler [18]. Current examples include Xue et al. [19] using rice husk, with its high silica content, as feedstock to make biochar that was ball-milled and used as reinforcing filler. Other sustainable feedstocks studied for biochar use as rubber composite filler include waste lignin [20] and leaf biomass [21].

Suliman and coauthors have studied biochar surface chemistry extensively; both in how feedstock and pyrolysis temperature affect it [22] as well as how oxidation by air has a role in modifying it [23]. Suliman found that for poplar wood as a biochar feedstock, greater quantities of carbonyl and other carboxyl groups were formed on biochar

surfaces produced at lower temperatures of 300–400 °C as opposed to higher temperatures ranging up to 600 °C. The formation of these oxygenated functional groups would increase negative charges on the biochar. Carbon dioxide was chosen for comparison with air as a biochar gas treatment. Yi and co-workers studied the influence of CO₂ on cellulose biochar properties and found that it enhanced carbon content and increased the C:O ratio [24], and others [25,26] have also observed that gaseous CO₂ can react favorably to increase the carbon content in biochar production.

For biochar used as rubber composite filler, modifying the surface chemistry to make the biochar more hydrophobic will improve dispersion in the rubber matrix. Traditionally this has been done using stearic acid [27] (pp. 170–171). Since most biochars have highly charged surfaces [28], adding surfactants creates a ‘coated’ biochar that will then have an outer surface with many aliphatic long-chain hydrophobic tail groups and thus make the biochar particles themselves more hydrophobic. Navarathna et al. employed this method by saturating biochar with lauric acid (LA) to make it more hydrophobic [29]. Navarathna proposed that the polar carboxylic acid groups in LA are attracted to the oxygenated functional groups on the surface of the biochar, which results in the hydrocarbon chains creating a more hydrophobic outer surface layer on the biochar particles. We hypothesize that this same mechanism will work in dry milling LA with biochar as carried out in this manuscript.

In this work, our goal was to study these two surface chemistry modification methods as a two-step process for biochar, with the first step being gas treatment of the biochar. Using a technique similar to that of Suliman [23], separate samples of poplar biochar were treated with either air or carbon dioxide. In the secondary step, each of these three biochar samples (untreated biochar control, air-treated, or CO₂-treated) were then coated with lauric acid using a method similar to that of Navarathna [29], but altered to a dry-milling method more amenable (and scalable) to the rubber compounding industry. Our hypothesis was that LA-coated biochar, being more hydrophobic than uncoated biochar, would have better dispersion in the rubber matrix during compounding and result in more strongly reinforced rubber composites that would show higher tensile strength and/or stiffness than uncoated biochar samples. We were also interested to observe any differences in the gas treatments combined with LA coating, and to determine if the gas treatments acted as favorable or unfavorable pre-treatments for LA coating in terms of final tensile properties of the composites.

2. Materials and Methods

2.1. Materials Used

Biochar samples made from *Populus tremuloides* (commonly known as poplar) were provided by Green Carbon Nanostructures Corporation (Hartland, WI, USA). Three poplar biochar samples were provided: (1) an unadulterated biochar control, designated “BC control”; (2) a biochar sample that was air-oxidized at 300 °C for 30 min designated “BC air”, and (3) a biochar sample treated with carbon dioxide at 300 °C for 30 min designated “BC CO₂”. An N-339 CB (Vulcan M) was supplied by the Cabot Corporation (Alpharetta, GA, USA). Styrene-butadiene rubber (SBR) provided by Michelin (Greenville, SC, USA) was used as the rubber matrix for composite samples. Lauric acid (98%) was provided by Aldrich Chemical Company (Milwaukee, WI, USA). Precipitated stearic acid-coated calcium carbonate (SA-CC) nanopowder was bought from US Research Nanomaterials, Inc. (Houston, TX, USA) and used as a dry-milling aid.

2.2. Chemical and Physical Material Properties

Elemental analysis was done using a PerkinElmer 2400 CHNS/O series II analyzer (Waltham, MA, USA) using cysteine as a standard. Each measurement used approximately 2 mg of biochar and was done in triplicate. Ash content of the biochar samples was determined using a TA Instruments Q2950 thermogravimetric analyzer (New Castle, DE, USA) by heating to 1000 °C at a heating rate of 10 °C per minute in an air atmosphere.

Ash content was determined to be the weight percentage remaining, and oxygen (O) was determined by difference from the original dried sample and the sum of C, H, N, and ash. Densities of the biochar samples were measured in triplicate using a Micromeritics Accupyc II 1340 helium pycnometer (Norcross, GA, USA) using the 10 cm³ sample cup. Infrared spectra were obtained using a Frontier attenuated total reflectance (ATR) Fourier-Transform Infrared Spectrometer (FTIR) (Perkin Elmer, Waltham, MA, USA) fitted with a diamond crystal. The background scan was conducted under ambient atmosphere. Powdered samples were placed directly on the crystal. For each sample, 64 scans were conducted from 650–4000 cm^{−1} at a spectral resolution of 4 cm^{−1}. The baseline correction function of the Spectrum software was utilized for all samples.

2.3. Lauric Acid Coating of Biochar

The biochar surface was modified by taking 24 g biochar, adding 2.4 g SA-CC and 2.4 g lauric acid, and dry milling this mixture with an SFM-1 (model QM-3SP2) planetary ball mill (MTI Corporation, Richmond, CA, USA). The optimum quantity of lauric acid to use was a matter of investigation and is described in Section 3.2. The milling media used was yttrium-stabilized zirconia spheres (3 mm diameter) supplied by the Inframat Corporation (Manchester, CT, USA). A 50:1 weight ratio of milling media:biochar was used with 500 mL capacity stainless steel jars and lids. Ball milling was done at 500 rpm for 30 min, the samples decelerated to zero rpm and rested for 6 min, then were increased to 500 rpm for 30 min in the opposite direction.

2.4. Creation and Tensile Testing of Rubber Composite Samples

Table 1 below contains the recipe for the rubber composite masterbatch used to make rubber composite samples. Amounts listed are in parts per hundred (phr). Each sample was differentiated according to which biochar filler was used; see the following list with their shorthand notation in parentheses: (1) biochar control (BC control); (2) air-oxidized biochar (BC air); (3) carbon dioxide treated biochar (BC CO₂); (4) biochar control coated with lauric acid (BC control LA); (5) air-oxidized biochar coated with lauric acid (BC air LA); (6) carbon dioxide treated biochar coated with lauric acid (BC CO₂ LA).

Table 1. Rubber composite formulation (phr).

SBR	CB	Filler	MBTBM	SA	ZnO	Sulfur	CBTS
100	30	12.86	0.80	2.00	3.00	2.00	1.00

SBR: styrene butadiene rubber; CB: carbon black; MBTBM: 2,2'-methylenebis(6-tert-butyl-4-methylphenol); SA: stearic acid; ZnO: zinc oxide; CBTS: N-cyclohexyl-2-benzothiazolesulfenamide.

Tensile properties were measured on an Instron 55R1123C5420 (Instron, Inc., Norwood, MA, USA) and data was processed using Bluehill Universal Software version 4.32. For each rubber composite sample at least 4 replicates were run.

3. Results

3.1. Biochar Characterization

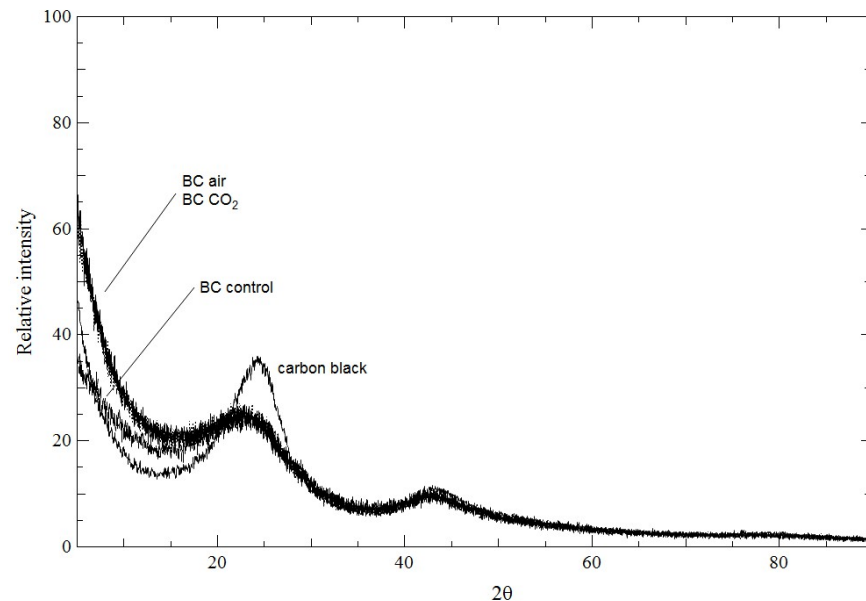
Physical characteristics of the biochar samples can be seen in Table 2 below. Carbon content in these samples is very high, although not approaching the >99% purity of CB. Density of these biochars is also nearly identical to the density of CB used (1.7–1.9 g/cm³).

Relative purity of these biochars are also shown in the X-ray diffraction spectra seen in Figure 1. Graphitic d-spacing peaks that are typical in CB and other high-carbon containing materials at 24 and 43° 2θ [30] are most prominent in the CB trace, but can also be seen for the biochar samples. No other sharp peaks are seen, meaning there are no appreciable crystalline impurities present in any of the biochar samples.

Table 2. Material properties of carbon black and biochar samples.

Sample	C (%)	H (%)	N (%)	O (%) ^a	Ash (%)	Density (g/cm ³)
CB ^b	>99	<1	<1	<1	<1	1.7–1.9
BC control	87.22 ± 0.50	1.81 ± 0.18	0.12 ± 0.04	6.52	4.33	1.68
BC air	86.42 ± 0.38	1.63 ± 0.20	0.13 ± 0.02	7.93	3.89	1.69
BC CO ₂	88.67 ± 0.32	1.49 ± 0.03	0.15 ± 0.03	5.96	3.73	1.69

^a oxygen calculated by difference; ^b data supplied by the manufacturer.

**Figure 1.** X-ray diffraction spectra of CB, biochar control, and gas-treated biochar samples. Graphitic d-spacing peaks at 24° and 43° 2θ are typical of high carbon content materials such as CB and are seen in all four samples.

3.2. Determination of Lauric Acid Coating Concentration

To determine the appropriate amount of LA to use to coat biochar particles, several different concentrations (5, 10, and 20% relative to biochar weight) of LA were milled with a control biochar. The 5, 10, and 20% LA-coated control biochar samples were then molded into rubber composite samples and their tensile properties were measured. Results can be seen in Table 3.

Table 3. Tensile properties of biochar as a function of LA concentration.

LA Concentration (%)	Tensile Strength (MPa)	Elongation (%)	Toughness (MPa)
0	19.8 ± 0.4	526 ± 14	49.1 ± 2.7
5	19.2 ± 0.5	527 ± 5	46.3 ± 1.8
10	20.5 ± 1.1	552 ± 20	53.2 ± 3.7
20	19.3 ± 0.8	513 ± 10	45.6 ± 0.9

Tensile results over the LA range tested for these rubber composites were similar, but since the 10% LA-coated composite had a slightly higher tensile strength and increased toughness, this concentration was selected to coat all the biochar samples.

Confirmation of LA coating on biochar samples can be seen by the presence of the characteristic LA C-H stretching vibrations at 2915 and 2847 cm^{−1} [31] in Figure 2. These biochars were then used to create rubber composite samples for tensile testing.

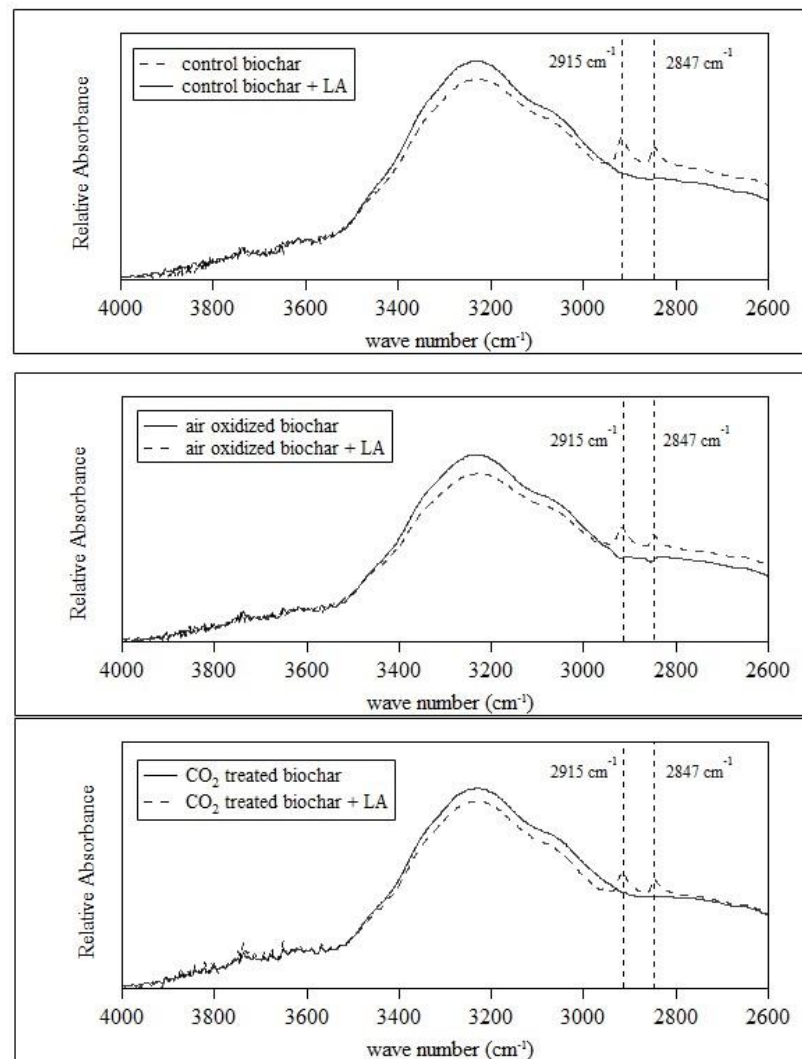


Figure 2. FTIR spectra for LA-coated vs. uncoated biochar samples showing the presence of LA by the peaks at 2847 and 2915 cm^{-1} .

3.3. Tensile Property Results

Tensile results for both uncoated and 10% LA-coated biochar samples are shown in Table 4. The effect of gas treatments to the biochar with air and CO_2 can be seen in the first three rows of Table 4. Tensile strength remains similar with all three samples, however both gas treatments reduce elongation relative to the control.

Table 4. Tensile properties of uncoated and 10% LA-coated biochar samples.

Sample	<i>n</i>	Tensile Strength (MPa)	Elongation (%)	Toughness (MPa)
BC control	8	20.1 ± 2.1	501 ± 42	43.1 ± 8.5
BC air	5	21.2 ± 1.0	488 ± 17	44.8 ± 4.0
BC CO_2	4	18.6 ± 1.1	447 ± 20	34.9 ± 3.9
BC control LA	5	20.7 ± 0.9	532 ± 18	47.9 ± 3.7
BC air LA	4	20.8 ± 1.3	504 ± 25	45.4 ± 5.7
BC CO_2 LA	5	22.1 ± 0.6	536 ± 12	51.6 ± 2.7

n = number of replicate runs.

By examining the stress–strain curves for these three samples (Figure 3), the higher stiffness of the gas-treated samples is evident in the steeper slopes compared to that of the control. It should be noted that in all stress–strain plots presented in this work, the

representative curve that was closest to the average tensile strength and elongation for each sample was selected and shown for clarity.

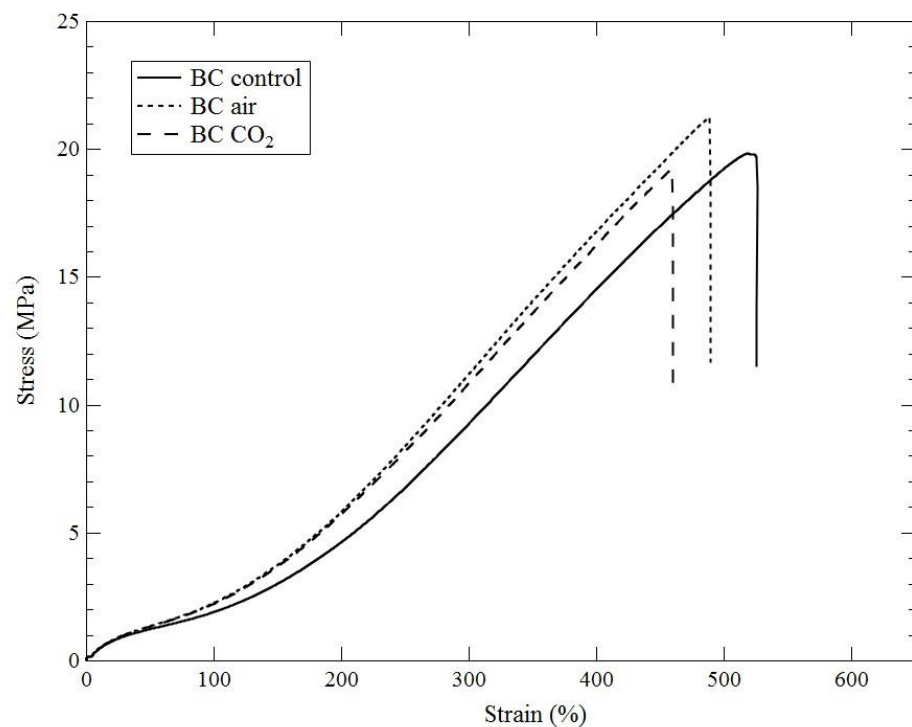


Figure 3. Stress vs. strain curve for the three uncoated biochar samples, illustrating the effect of air and CO₂ treatment during biochar processing.

To show the effect of LA coating, Figure 4 shows each of the stress–strain curves for the BC control, BC air, and BC CO₂ samples with and without LA coating. For the control biochar, LA coating showed no appreciable change in the tensile strength or elongation as the stress–strain curves were nearly identical. For the air-treated biochar sample, tensile strength remained unchanged and there was a slight increase in stiffness relative to the uncoated sample. The effect of LA coating on the CO₂ treated biochar sample showed that stiffness was essentially unchanged, but the tensile strength increased nearly 20%.

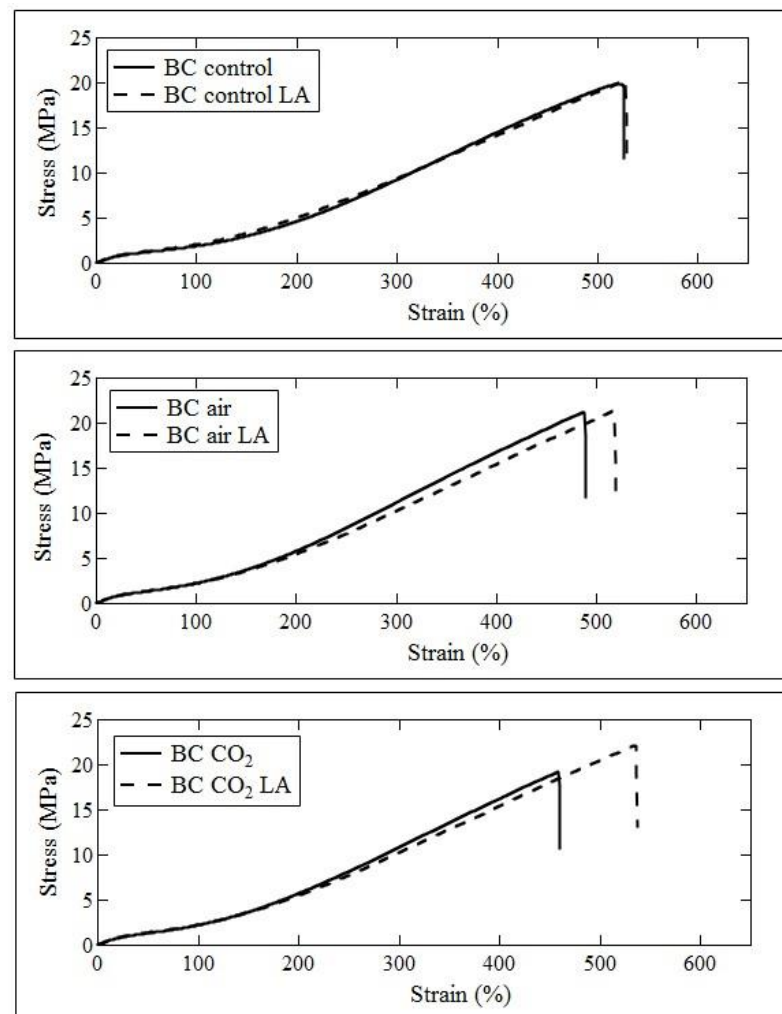


Figure 4. Stress–strain curves of LA-coated vs. uncoated rubber composite samples for the control (top), air-treated (middle), and CO₂-treated (bottom) biochar samples. For each plot the single representative curve closest to the average tensile strength and elongation was chosen for clarity.

4. Conclusions

For this work we wanted to observe two separate surface chemistry modifications to biochar; a gas treatment step followed by the addition of LA. Both treatments are amenable to the rubber processing industry as they only involve gas treatment to the biochar at controlled temperature and dry-milling, two processes that are both easily scalable. Gas treatment of the biochars with air and CO₂ at 300 °C did not appreciably affect the tensile strength of the resulting filled rubber composites, but did increase their stiffness relative to the untreated biochar control.

Biochar control coated with LA appeared to have no effect on the tensile properties of the resulting filled rubber composite. For the air-treated biochar sample, coating with LA did not appreciably change the tensile strength, but did slightly increase the elongation of the composite, making it slightly softer. The most notable difference in tensile properties occurred when the CO₂-treated biochar was then LA-coated; composites made from this biochar sample increased their tensile strength by 19%, and their toughness by 48%. This suggests that the CO₂ gas treatment helps condition the biochar so that LA coating is more effective. CO₂ treatment of biochar increased its carbon content and reduced its oxygen content, reducing the number of charged, oxygen-containing functional groups on the biochar and making it more hydrophobic. Further investigation to understand the relative

roles of CO₂ treatment in conjunction with LA coating is needed to help optimize and improve biochar reinforcement of rubber composites.

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Conflicts of Interest: The authors declare no conflict of interest.

References

- Carbon Black in Tires. Available online: <https://www.orioncarbons.com/tire> (accessed on 30 September 2022).
- Lee, C.-C.; Olasehinde-Williams, G.; Akadiri, S.S. Are geopolitical threats powerful enough to predict global oil price volatility? *Environ. Sci. Pollut. Res.* **2021**, *28*, 28720–28731. [CrossRef] [PubMed]
- Ragothaman, A.; Anderson, W.A. Air Quality Impacts of Petroleum Refining and Petrochemical Industries. *Environments* **2017**, *4*, 66. [CrossRef]
- Liu, W.-J.; Jiang, H.; Yu, H.-Q. Development of Biochar-Based Functional Materials: Toward a Sustainable Platform Carbon Material. *Chem. Rev* **2015**, *115*, 12251–12285. [CrossRef] [PubMed]
- Gross, A.; Bromm, T.; Glaser, B. Soil Organic Carbon Sequestration after Biochar Application: A Global Meta-Analysis. *Agronomy* **2021**, *11*, 2474. [CrossRef]
- Cheng, F.; Li, X. Preparation and Application of Biochar-Based Catalysts for Biofuel Production. *Catalysts* **2018**, *8*, 346. [CrossRef]
- Wang, R.-Z.; Huang, D.-L.; Liu, Y.-G.; Zhang, C.; Lai, C.; Wang, X.; Zeng, G.-M.; Gong, X.-M.; Duan, A.; Zhang, Q.; et al. Recent advances in biochar-based catalysts: Properties, applications and mechanisms for pollution remediation. *Chem. Eng. J.* **2019**, *371*, 380–403. [CrossRef]
- Do Minh, T.; Song, J.; Deb, A.; Cha, L.; Srivastava, V.; Sillanpää, M. Biochar based catalysts for the abatement of emerging pollutants: A review. *Chem. Eng. J.* **2020**, *394*, 124856. [CrossRef]
- Liu, W.-J.; Jiang, H.; Yu, H.-Q. Emerging applications of biochar-based materials for energy storage and conversion. *Energy Environ. Sci.* **2019**, *12*, 1751–1779. [CrossRef]
- Senthil, C.; Lee, C.W. Biomass-derived biochar materials as sustainable energy sources for electrochemical energy storage devices. *Renew. Sustain. Energy Rev.* **2021**, *137*, 110464. [CrossRef]
- Ehsani, A.; Parsimehr, H. Electrochemical energy storage electrodes from fruit biochar. *Adv. Colloid Interface Sci.* **2020**, *284*, 102263. [CrossRef] [PubMed]
- Xiang, W.; Zhang, X.; Chen, J.; Zou, W.; He, F.; Hu, X.; Tsang, D.C.W.; Ok, Y.S.; Gao, B. Biochar technology in wastewater treatment: A critical review. *Chemosphere* **2020**, *252*, 126539. [CrossRef] [PubMed]
- Palansooriya, K.N.; Yang, Y.; Tsang, Y.F.; Sarkar, B.; Hou, D.; Cao, X.; Meers, E.; Rinklebe, J.; Kim, K.-H.; Ok, Y.S. Occurrence of contaminants in drinking water sources and the potential of biochar for water quality improvement: A review. *Crit. Rev. Env. Sci. Technol.* **2020**, *50*, 549–611. [CrossRef]
- Gwenzi, W.; Chaukura, N.; Wenga, T.; Mtisi, M. Biochars as media for air pollution control systems: Contaminant removal, applications and future research directions. *Sci. Total Environ.* **2021**, *753*, 142249. [CrossRef] [PubMed]
- Peiris, C.; Nawalage, S.; Wewalwela, J.J.; Gunatilake, S.R.; Vithanage, M. Biochar based sorptive remediation of steroidal estrogen contaminated aqueous systems: A critical review. *Environ. Res.* **2020**, *191*, 110183. [CrossRef] [PubMed]
- Ghosh, D.; Maiti, S.K. Can biochar reclaim coal mine spoil? *J. Environ. Manag.* **2020**, *272*, 111097. [CrossRef] [PubMed]
- Weber, K.; Quicker, P. Properties of biochar. *Fuel* **2018**, *217*, 240–261. [CrossRef]
- Greenough, S.; Dumont, M.-J.; Prasher, S. The physicochemical properties of biochar and its applicability as a filler in rubber composites: A review. *Mater. Today Commun.* **2021**, *29*, 102912. [CrossRef]
- Xue, B.; Wang, X.; Sui, J.; Xu, D.; Zhu, Y.; Liu, X. A facile ball milling method to produce sustainable pyrolytic rice husk bio-filler for reinforcement of rubber mechanical property. *Ind. Crop. Prod.* **2019**, *141*, 111791. [CrossRef]
- Jiang, C.; Bo, J.; Xiao, X.; Zhang, S.; Wang, Z.; Yan, G.; Wu, Y.; Wong, C.; He, H. Converting waste lignin into nano-biochar as a renewable substitute of carbon black for reinforcing styrene-butadiene rubber. *Waste Manag.* **2020**, *102*, 732–742. [CrossRef]
- Lay, M.; Rusli, A.; Abdullah, M.K.; Abdul Hamid, Z.A.; Shuib, R.K. Converting dead leaf biomass into activated carbon as a potential replacement for carbon black filler in rubber composites. *Compos. Part B Eng.* **2020**, *201*, 108366. [CrossRef]
- Suliman, W.; Harsh, J.B.; Abu-Lail, N.I.; Fortuna, A.-M.; Dallmeyer, I.; Garcia-Perez, M. Influence of feedstock source and pyrolysis temperature on biochar bulk and surface properties. *Biomass Bioenerg.* **2016**, *84*, 37–48. [CrossRef]

23. Suliman, W.; Harsh, J.B.; Abu-Lail, N.I.; Fortuna, A.-M.; Dallmeyer, I.; Garcia-Perez, M. Modification of biochar surface by air oxidation: Role of pyrolysis temperature. *Biomass Bioenerg.* **2016**, *85*, 1–11. [[CrossRef](#)]
24. Yi, Z.; Li, C.; Li, Q.; Zhang, L.; Zhang, S.; Wang, S.; Qin, L.; Hu, X. Influence of CO₂ atmosphere on property of biochar from pyrolysis of cellulose. *J. Environ. Chem. Eng.* **2022**, *10*, 107339. [[CrossRef](#)]
25. Shen, Y.; Ma, D.; Ge, X. CO₂-looping in biomass pyrolysis or gasification. *Sustain. Energy Fuels* **2017**, *1*, 1700–1729. [[CrossRef](#)]
26. Jung, S.-H.; Kim, J.-S. Production of biochars by intermediate pyrolysis and activated carbons from oak by three activation methods using CO₂. *J. Anal. Appl. Pyrol.* **2014**, *107*, 116–122. [[CrossRef](#)]
27. Rothon, R.N. *Rapra Technology Limited. Particulate-Filled Polymer Composites*, 2nd ed.; Rapra Technology: Shrewsbury, UK, 2003; 544p.
28. Mukherjee, A.; Zimmerman, A.R.; Harris, W. Surface chemistry variations among a series of laboratory-produced biochars. *Geoderma* **2011**, *163*, 247–255. [[CrossRef](#)]
29. Navarathna, C.M.; Bompuwala Dewage, N.; Keeton, C.; Pennisson, J.; Henderson, R.; Lashley, B.; Zhang, X.; Hassan, E.B.; Perez, F.; Mohan, D.; et al. Biochar Adsorbents with Enhanced Hydrophobicity for Oil Spill Removal. *ACS Appl. Mater. Interfaces* **2020**, *12*, 9248–9260. [[CrossRef](#)] [[PubMed](#)]
30. Darmstadt, H.; Roy, C.; Kaliaguine, S.; Xu, G.; Auger, M.; Tuel, A.; Ramaswamy, V. Solid state ¹³C-NMR spectroscopy and XRD studies of commercial and pyrolytic carbon blacks. *Carbon* **2000**, *38*, 1279–1287. [[CrossRef](#)]
31. Kong, W.; Fu, X.; Yuan, Y.; Liu, Z.; Lei, J. Preparation and thermal properties of crosslinked polyurethane/lauric acid composites as novel form stable phase change materials with a low degree of supercooling. *RSC Adv.* **2017**, *7*, 29554–29562. [[CrossRef](#)]