

List of Figures, Tables and Boxes

Figures

1.1	Structure of graphite as proven for the first time by J. D. Bernal in 1924	2
1.2	Advertisement for biochar to be used as a soil amendment in turf greens	4
1.3	Motivation for applying biochar technology	5
1.4	The global carbon cycle of net primary productivity and release to the atmosphere from soil in comparison to total amounts of carbon in soil, plant and atmosphere, and anthropogenic carbon emissions	8
2.1	Ideal biochar structure development with highest treatment temperature (HTT)	18
2.2	Relationship between biochar surface area and micropore volume	23
2.3	Biochar surface area plotted against highest treatment temperature (HTT)	24
2.4	Scanning electron microscope (SEM) image showing macroporosity of a wood-derived biochar produced by 'slow' pyrolysis	25
2.5	SEM image showing macroporosity in biochar produced from poultry manure using slow pyrolysis	26
2.6	Influence of biomass pre-treatment and HTT on the particle-size distribution of different biochars	27
2.7	Helium-based solid densities of biochars with HTT	28
2.8	Bulk density of wood biochar, plotted against that of its feedstock	28
3.1	Biochar yields for wood feedstock under different pyrolysis conditions	34
3.2	Selected small-angle X-ray scattering (SAXS) profiles from normal wood	37
3.3	Transmission electron microscopy (TEM) images of modern biochar samples	37
3.4	Schematics demonstrating the concepts of the quasi-percolation model of Kercher and Nagle (2003)	38
3.5	Scanning electron microscopy (SEM) micrographs of different mineral phases in chicken manure biochar and their energy-dispersive X-ray spectroscopy (EDS) spectra	41
3.6	Distribution of non-C elements on the surface of wood biochar determined by microprobe analysis	42
3.7	SEM micrographs and associated EDS spectra for mineral phases in maize-cob biochar prepared by flash pyrolysis	43
3.8	SEM micrographs and associated EDS spectra for mineral phases in white oak biochar prepared by fast pyrolysis	44
3.9	SEM micrographs and associated EDS spectra for mineral phases in poplar wood biochar from a combustion facility	45
3.10	Heteroatoms and functional groups commonly found in activated carbons	47

xii BIOCHAR FOR ENVIRONMENTAL MANAGEMENT

3.11	Macroscopic representation of the features of C surface chemistry thought to be sufficient for understanding aqueous-phase sorption phenomena; microscopic representation of the functional groups thought to be sufficient for understanding aqueous-phase adsorption phenomena	49
4.1	Van Krevelen diagram of H/C and O/C ratios of biochars made under different temperature regimes between low-temperature biochars and those produced by high-temperature pyrolysis, as well as naturally occurring black C	55
4.2	Changes in elements with increasing temperature during the charring process of wood, as well as data from fast pyrolysis products and biochar	59
4.3	Changes in functional group chemistry obtained by nuclear magnetic resonance (NMR) spectroscopy with increasing temperature	60
4.4	Cross-polarization (CP) NMR spectra from biochar derived from wood (<i>Eucalyptus camaldulensis</i>) and pea straw (<i>Pisum sativum</i>) materials (biochar produced in the laboratory at 450°C in a muffle furnace for 1 hour) and vegetation fire residues from a natural fire	60
4.5	Changes in the proportions of O-alkyl, aryl and alkyl C from grass biochars produced at different temperatures	62
4.6	Comparison of the proportion of total signal intensity from CP ¹³ C-NMR of biochars produced at unknown temperatures with those from known temperatures	62
5.1	Dry matter production of radish as a function of biochar application rate, either with or without N fertilizer application	73
5.2	Changes in total N, P and K concentrations in biochars produced from sewage sludge at different temperatures	76
5.3	Changes in K contents of rice straw biochar as a function of temperature during pyrolysis	77
5.4	Available P (bicarbonate extractable) as a percentage of total P of biochar as compared to biosolid and dried biosolid pellet	78
6.1	The porous structure of biochar invites microbial colonization	86
6.2	Arbuscular mycorrhiza fungal hyphae growing into biochar pores from a germinating spore	87
6.3	Time course of dissolved organic carbon (DOC) adsorption in slurries of soil with 30t biochar ha ⁻¹ added compared to unamended soil	91
6.4	Soil respiration rate decreases as the rate of biochar applied increases	92
6.5	Potential simultaneous adsorption of microbes, soil organic matter, extracellular enzymes and inorganic nutrients to biochar surfaces	94
6.6	Taxonomic cluster analysis of 16S rRNA gene sequences from Amazonian Dark Earths (ADE) and adjacent pristine forest soil based on oligonucleotide fingerprinting	96
6.7	Bacteria, fungi and fine roots readily colonize biochar surfaces	97
7.1	Classification of biochars as high, medium and low C-containing as a function of temperature for different feedstocks	117
7.2	Possible framework for classifying biochars	122
8.1	Large pit kiln	129
8.2	Mound kiln	129
8.3	Operation of a mound kiln showing the heavy smoke emitted during the carbonization process	129
8.4	Brick kiln	130

8.5	Transportable metal kiln, Tropical Products Institute (TPI)	130
8.6	The Missouri-type charcoal kiln	131
8.7	The continuous multiple hearth kiln for charcoal production	131
8.8	Chemical structure of cellulose	133
8.9	Structural formula for a common hemicellulose found in softwoods	134
8.10	Monomers from which lignin is assembled	134
8.11	Thermogravimetric analysis of the pyrolysis of cellulose, hemicellulose (xylan) and lignin at constant heating rate ($10^{\circ}\text{C min}^{-1}$) with N_2 (99.9995 per cent) sweep gas at 120mL min^{-1}	135
8.12	Reaction pathways for cellulose decomposition	136
8.13	Chemical equilibrium products of cellulose pyrolysis: (a) effect of pressure at 400°C ; (b) effects of temperature at 1MPa	136
8.14	Carbon conversion for gasification of cellulose as a function of equivalence ratio (fraction of stoichiometric O requirement for theoretical complete combustion) calculated with STANJAN chemical equilibrium software	137
8.15	Effect of pressure and purge gas flow rate on carbonization of cellulose	138
8.16	Effect of pressure and purge gas flow rate on heat of pyrolysis for cellulose	139
8.17	Screw pyrolyser with heat carrier	141
8.18	Fluidized-bed fast pyrolysis reactor	141
8.19	Different kinds of gasifiers suitable for co-production of producer gas and biochar	142
8.20	Wood-gas stove	143
9.1	Components of biochar systems	149
9.2	Energy use in transportation of wood chips (<i>Salix</i>) as a percentage of energy delivered by the biomass	152
9.3	Pyrolysis unit and adjacent poultry house, Wardensville, West Virginia	157
9.4	Estimated annual production of the main biomass resources appropriate for biochar and bioenergy production of a 2.7ha farm in western Kenya	159
9.5	Production of biochar using simple earthen mound kilns	160
9.6	Highly diverse cropping system (maize, yam) with secondary forest in Ghana managed with rotational slash-and-char for 20 years	163
9.7	Batch kiln for production of biochar without energy capture	164
9.8	Case study from Sumatra, Indonesia	165
10.1	A basic model of a complex biochar particle in the soil, containing two main distinguished structures of biochar: crystalline graphene-like sheets surrounded by randomly ordered amorphous aromatic structures and pores of various sizes	173
10.2	Van Krevelen plot of the elemental composition change of five types of biochar with incubation and over time	175
10.3	Scanning electron micrographs of biochar particles (a) in the clay fraction and (b) in the density fraction $<2.0\text{g cm}^{-3}$	176
11.1	Mineralization of organic C in glucose, cellulose and <i>Pinus resinosa</i> sapwood heated to equilibrium at increasing temperatures	187
11.2	Schematic representation of the factors that may influence stability or decay and transport of biochar, and their proposed importance over time	189
11.3	Scanning electron micrographs of biochar samples produced from <i>Fagus crenata</i> Blume sawdust with and without ozone treatment for two hours	190

xiv BIOCHAR FOR ENVIRONMENTAL MANAGEMENT

11.4	Schematic of the structure of crystalline graphite, turbostratic C, turbostratic crystallites (or non-graphitizing C) and fullerene-type structures	192
11.5	Particulate and finely divided biochar embedded within micrometre-size aggregates from a biochar-rich Anthrosol of the central Amazon region	193
11.6	Long-term dynamics of Si, Al and Fe on biochar surfaces originating from forest clearing in western Kenya	194
11.7	Mineralogy and relative proportion of aromatic C forms as an indicator of biochar in coarse, medium and fine clay fractions of a Typic Endoaquoll from Iowa, US	195
11.8	Double-exponential model fitted to hypothetical data of biochar decay	199
11.9	Conceptual model of C remaining from biomass using a double-exponential decay model with a mean residence time of 10 years for the labile C pool and 1000 years for the stable C pool, but different proportions of labile C	200
12.1	Spreading biochar into planting holes for banana near Manaus, Brazil	217
12.2	Rotary hoeing to mix biochar uniformly in field plots in Bolivia	218
12.3	Side dressing compost into rows of trees in an organic orchard within Okura Plantations, Kerikeri, New Zealand	218
12.4	Deep banding of biochar into soil before planting a crop, Western Australia	220
12.5	Trenching method to incorporate biochar and correct wilting of a pine tree; addition of biochar to holes around mature orchard trees near Wollongbar, New South Wales, Australia	221
13.1	Municipal waste biochar decreased emission of N ₂ O in an incubation study	229
13.2	N ₂ O generated from a Ferrosol amended with biochar in laboratory mesocosms	230
13.3	Scanning electron microscopy (SEM) of aged (six months in a Ferrosol) poultry litter biochar with regions of energy dispersive spectroscopy (EDS) analysis (UNSW Electron Microscope Unit)	242
13.4	Proposed oxidation of aromatic C by N ₂ O	242
13.5	Proposed structure of biochar that could interact with N ₂ O	243
13.6	Summary schematic for reduced emissions of N ₂ O from soil	244
14.1	The pH, electrical conductivity (EC), cation exchange capacity (CEC) and density of biochar produced from Douglas-fir or ponderosa pine wood or bark at 350°C or 800°C	253
14.2	The soluble PO ₄ ³⁻ , NH ₄ ⁺ and NO ₃ ⁻ concentration in biochar produced from Douglas-fir or ponderosa pine wood or bark at 350°C or 800°C	253
14.3	Hypothetical change in N availability with time since the last fire, where biochar induces a fast turnover of N for years after a fire event	258
14.4	Soluble P leached from columns filled with calcareous soil (pH = 8) amended with catechin alone or with biochar; or acid and Al-rich soil (pH = 6) amended with 8-hydroxy quinoline alone or with biochar	263
15.1	Surface area of activated and non-activated biochar produced at varying temperatures	275
15.2	Particle-size distribution of naturally occurring chars in fertilized intensive crop soil, Germany; in burned savannah soil, Zimbabwe; in a Russian steppe Mollisol; and hardwood biochar produced traditionally in mounds for soil application, hand ground to pass through a 0.9mm sieve	276

15.3	Compilation of results obtained by Dünisch et al (2007) for wood feedstocks and biochar–ash mixtures obtained after pyrolysis	277
15.4	Adsorption isotherms for biochar from the tree <i>Robinia pseudoacacia</i> L., with and without manure	278
15.5	Leaching reduction data compiled from the literature	280
15.6	Reduction in leaching for nutrient-impregnated biochar particles of different sizes	281
15.7	Recovery of ¹⁵ N-labelled fertilizer applied to an Oxisol in the Brazilian Amazon during two growing seasons	282
15.8	Schematic representation of proposed biochar effects on nutrient leaching	284
16.1	Comparison of sorption properties of biochar (ash containing char), plant residues and soil for the pesticide diuron	290
16.2	¹³ C cross-polarization (CP) nuclear magnetic resonance (NMR) spectra of ¹³ C-benzene sorbed to four different biochars exposed to 100mg L ⁻¹ of ¹³ C-benzene	295
16.3	¹³ C CP-NMR spectra of mixtures of biochar L-450 and biochar L-850 exposed to 100mg L ⁻¹ of ¹³ C-benzene	295
17.1	Secondary electron image of biochar produced from poultry litter (450°C for 20 minutes using slow pyrolysis without activation) after 12 months in soil	302
17.2	Comparison of analytical methods used to determine black C contents of biochar and soils	305
17.3	Structures of selected benzene polycarboxylic acids used in the determination of black C: hemimellitic acid, mellophanic acid, benzene pentacarboxylic acid, mellitic acid and levoglucosan	306
17.4	Characterization of a reference set of industrial biochars by thermogravimetry and differential scanning calorimetry (TG-DSC)	310
17.5	Determination of biochar in soil samples, measured using infrared spectroscopy	312
20.1	Framework for socio-economic assessment of biochar projects	360
21.1	Payback period as a function of the price of C (in CO ₂ equivalents)	385
21.2	Proposed protocol for developing sustainable land use with bioenergy recovery	386
22.1	Excess CO ₂ over the pre-industrial level for the last 50 years and (assuming emissions fall to zero by 2035 and remain zero thereafter) for the next 50 years	395
22.2	Comparison of zero emission systems and negative emissions systems in mitigating the level of CO ₂ in the atmosphere	396

Tables

2.1	Surface areas and volumes of different sizes of biochar pores	25
3.1	Ash content and elemental composition of representative feedstocks and an oak wood biochar	39
3.2	Summary of functional groups of S and N in a chicken-manure biochar	46
4.1	The data illustrate the chemical changes that occur during the charring process and the influence of charring temperature	56
5.1	Nutrient contents, pH and carbonate contents of biochars	69
5.2	Typical N, P and K contents of common organic fertilizers	70
5.3	Crop yield responses as related to relevant biochar properties	72

5.4	Effect of temperature and holding time on C and N composition and pH (measured in aqueous slurries) of sewage sludge biochar	76
6.1	Pore diameters in wood and bamboo biochar compared to the ranges in the diameter of various soil microorganisms	87
7.1	Common classification of carbonized organic materials	109
7.2	Characterization of charcoal for fuel or as a reductant	111
7.3	Classification of biosolids according to NSW EPA (1997)	111
8.1	Air emissions per kilogram biomass from different kinds of charcoal kilns	132
8.2	Charcoal yields (dry weight basis) for different kinds of batch kilns	132
8.3	Typical product yields (dry basis) for different modes of pyrolysis	132
8.4	Typical content of several examples of biomass (dry basis)	133
8.5	Influence of heating rate on pyrolysis of cellulose in a thermogravimetric analyser with nitrogen as sweep gas (flow rate unspecified)	135
9.1	Availability, moisture and transportation requirements for different resource base options for biochar production	150
9.2	Categories of biochar systems	153
12.1	List of published field experiments regarding the application of biochar to soil for growing agricultural crops	209
12.2	Summary of methods of incorporating biochar within soil, their characteristics and current need for information	222
13.1	Source, pyrolysis conditions and biochar characteristics	230
13.2	Nitrate and ammonium concentration in soils following incubation with various biochars for 47 days	231
14.1	Effect of biochar (natural biochar, lab-generated biochar or activated carbon) on nitrogen mineralization and nitrification from studies performed in different forest ecosystems	256
15.1	Proposed biochar characteristics affecting nutrient leaching, related mechanisms and degree of certainty associated with each process	283
17.1	Summary of key methods for determining black C in environmental samples and their relevance to biochar determination	304
18.1	Assumptions for the calculation of avoided emissions from feedstock management and pyrolysis	327
18.2	Net emissions associated with the use of a range of feedstocks for slow pyrolysis expressed either relative to mass of feedstock used or mass of biochar produced	329
18.3	Assumptions used in calculation of emissions reduction from the application of biochar to crops	331
18.4	Net emissions ($t\ CO_2e\ ha^{-1}\ yr^{-1}$) for biochar applied to agricultural crops at a rate of $5t\ biochar\ ha^{-1}$ once	332
18.5	Total avoided emissions ($t\ CO_2e$) over a ten-year period, per tonne of biochar applied, at an application rate of $5t\ biochar\ ha^{-1}$ once, assuming a constant influence of biochar	332
19.1	Fast pyrolysis of maize stover: Summary of modelling assumptions relative to fast pyrolysis at $10t\ hr^{-1}$ (dry feedstock basis)	346
19.2	Summary of primary process inputs and outputs	347
19.3	Total capital investment cost estimates for the three plant modules in US\$ million (2007 basis)	347

19.4	Annual costs of raw pyrolysis liquids production in US\$1000 yr ⁻¹ and variation with delivered feedstock cost	348
19.5	Costs of electricity production in US\$1000 yr ⁻¹ and their variation with delivered feedstock cost	349
19.6	Returns and costs as well as biochar yields for fast and slow pyrolysis as value items are applied	350
19.7	Estimated GHG offsets for fast and slow pyrolysis	353
19.8	Economic assumption and results summary with economic results reported per tonne of feedstock	354
20.1	Classes of data to determine vulnerability context	362
20.2	Summary of all impact indicators for the biochar technologies considered	363
20.3	Vulnerability context (assumptions for model scenario)	366
20.4	Summary of the assumptions of community assets	367
20.5	Cost-benefit analysis of the project	369
20.6	Summary of community perception of non-quantifiable costs and benefits of improved stoves, biochar application and improved charcoal kilns	370

Boxes

7.1	Process parameters affecting yields and composition of the pyrolysis products the most	113
9.1	Case study 1: Large-scale bioenergy and biochar	155
9.2	Case study 2: Farm-scale bioenergy and biochar	156
9.3	Case study 3: Household-scale bioenergy and biochar in developing countries	158
9.4	Case study 4: Biochar and shifting cultivation	159
9.5	Case study 5: Traditional biochar-based management of tropical soil in subsistence agriculture	161
9.6	Case study 6: Biochar production from dedicated plantations for sustainable agriculture	164
9.7	Case study 7: Biochar as a waste or bio-product management tool	165
11.1	Terminology for quantification of decay	185
12.1	Safe handling of biochar in Australia	216
18.1	Concepts of relevance for emissions trading with biochar	320