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Biochar elemental composition and factors influencing nutrient retention

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Introduction

Pyrolysis temperature and type may be varied to optimize the desired biochar product. In general, increasing pyrolysis temperature tends to decrease biochar yield but increase biochar total C, K and Mg content, pH (ash content) and surface area, and decrease cation exchange capacity (CEC). Slow pyrolysis, in general, tends to produce biochars with greater N, S, available P, Ca, Mg, surface area and CEC as compared to fast pyrolysis.

In addition to altering temperature and time, the importance of feedstock source needs to be recognized when utilizing biochar in situations such as a soil conditioner (Sohi et al, 2009). Over the last 10 years biochar research has expanded exponentially and so have the feedstocks utilized. Biochars have been created from, amongst others, corn, wheat, barley and rice straw, switchgrass, peanut, pecan and hazelnut shells, sugarcane bagasse, coconut coir, food waste, hardwood and softwood species, poultry and turkey litter, swine, dairy and cattle manure and biosolids. Quality of feedstock source influences end-product characteristics; in general, most plant-based biochars contain elevated C content and lesser quantities of necessary plant nutrients as compared to manure-based biochars as plants uptake only a small fraction of elements from soil.

Feedstock variety for biochar creation (at least for research purposes) has increased exponentially over the last decade, warranting an updated look into biochar-specific properties. Thus, this chapter focuses attention on a number of biochars and the effects pyrolysis temperatures and types have on inherent biochar nutrients (total and available), pH and potential liming value, cation exchange capacity and nutrient sorption and entrapment. Finally, a brief section describing the creation of tailor-made biochars (from a mixed feedstock source) for improving biochar nutrient content is presented.

Total nutrients

Although initial feedstock nutrient concentrations cannot be used to quantitatively predict total or bioavailable biochar nutrient content, feedstock type used during pyrolysis has a strong influence on biochar characteristics (e.g., see Gaskin et al, 2008; Cantrell et al, 2012; Kloss et al, 2012; Spokas et al, 2012a). For example, Gaskin et al (2008) showed that the amount of total N conserved from feedstock to biochar ranged from 27.4 per cent to 89.6 per cent in poultry litter and pine chip biochars, respectively. Furthermore, the authors showed that the range of total P, K, Ca and Mg conserved varied from 60 per cent to 100 per cent, with bioavailability ranging from about 10 per cent to upwards of 80 per cent depending on feedstock source (Gaskin et al, 2008).

Table 7.1 illustrates the importance of feedstock source for the determination of nutrients present in biochar. Most plant-based biochars contain elevated C contents with lesser quantities of other essential nutrients as compared to biochars created from manures. The results in Table 7.1 are consistent with those of others (e.g. Cantrell and Martin, 2012). Within the plant-based biochars, lower C contents are often due to higher concentrations of other minerals present in the feedstock (e.g., silica mineral species; Brewer et al, 2012). However, plant based biochars often have relatively lower nutrient contents (Cantrell et al, 2012) as compared to their manure-based biochar counterparts. This is especially true for total N content as the initial N content of plant-based feedstocks is typically lower than that of manures; greater N concentrations in manure-based biochars can be attributable to the high protein content in the feedstock (Tsai et al, 2012). Concomitantly, this tends to place plant-based biochars at a disadvantage in terms of acting as a direct source of nutrients (Cantrell et al, 2012). Manure-based biochars, on the other hand, may be more suitable for supplying nutrients following land application (Chapter 8).

Biochar average total nutrient content sorted by pyrolysis temperature, type and the interaction, over a range of biochar feedstocks, is shown in Table 7.2. In general, increasing pyrolysis temperature increases the total nutrient concentration present. Increasing pyrolysis temperatures typically leads to a loss of easily decomposable substances, volatile compounds and elements (e.g., O, H, N, S) and thus concentrates other nutrients present in biochar, including C, Ca, Mg and K (Kim et al, 2012; Kinney et al, 2012). In fact, increases in nutrient concentrations, such as C, with increasing pyrolysis temperature are often associated with H and O loss from biochar (Antal and Grønli, 2003). Furthermore, during pyrolysis a series of cleavage and polymerization reactions occur that result in the creation of thermally stable fixed C structures (Spokas et al, 2012a), which are directly related to increased biochar C content. In support of these facts, Bolan et al (2012) performed a sequential C fractionation technique, noting that the majority of biochar C remained in a non-labile form (i.e., not available for microbial degradation). However, C availability is temperature dependent with higher pyrolysis temperatures related to larger non-labile C fractions (Nelissen et al, 2012).

In addition, greater temperatures could cause a concentration effect due to loss of other elements by volatilization. For example, it appears that total N content reached a maximum between 300 to 399°C and decreased at greater temperatures (Table 7.2). Cantrell et al (2012) observed a similar response in manure

Table 7.1 *Average biochar total nutrient concentrations based on various feedstock sources (dry weight basis)*

Source[†]	*C* (%)	*N* (%)	*P* ($g\ kg^{-1}$)	*K* ($g\ kg^{-1}$)	*S* ($g\ kg^{-1}$)	*Ca* ($g\ kg^{-1}$)	*Mg* ($g\ kg^{-1}$)	*Fe* ($g\ kg^{-1}$)	*Cu*
Corn	58.8	1.06	2.35	19.0	0.37	8.64	7.10	7.30	115
Wheat/barley	60.8	1.41	---[‡]	1.26	---	12.6	9.88	1.94	---
Rice straw/husk	43.6	1.40	1.20	0.70	3.90	---	---	---	---
Sorghum	56.4	0.74	2.34	4.14	---	---	---	---	---
Soybean stover	75.4	1.59	---	---	0.40	---	---	---	---
Peanut shell	75.3	1.83	2.05	11.0	0.90	3.30	1.48	---	---
Pecan shell	75.9	0.26	---	116	0.20	6.00	0.59	0.04	34.0
Hazelnut shell	77.5	0.52	0.32	4.73	---	3.13	0.61	---‡	---
Switchgrass	73.9	0.98	1.70	8.25	---	3.10	---	0.10	8.28
Bagasse	78.6	0.87	0.67	2.23	---	7.33	1.77	0.43	---
Coconut coir	73.8	0.88	---	---	---	---	---	---	---
Food waste	44.4	3.28	6.64	19.2	---	51.8	4.93	---	---
Other (grass, leaves, orange peel, other green wastes)	64.9	1.16	1.62	14.4	1.30	5.92	3.31	1.35	66.2
Hardwoods	74.4	0.72	1.14	9.47	15.6	10.1	9.53	1.80	4.76
Softwoods	74.6	0.79	0.74	16.9	0.23	20.7	18.0	9.64	1.38
Papermill waste	19.9	0.09	0.85	3.31	---	281	2.73	---	---
Poultry manure/litter	35.3	2.15	33.1	60.2	9.26	103	12.2	2.91	513
Turkey manure/litter	31.8	2.02	31.4	48.0	4.80	48.2	10.4	3.22	648
Swine manure	44.9	2.79	60.8	23.4	8.25	48.0	29.0	6.17	472
Dairy manure	58.1	2.37	8.59	17.2	2.70	26.9	11.8	5.87	107
Cattle manure	48.5	1.90	9.17	40.6	4.25	28.8	9.93	2.86	114
Biosolids/sewage sludge	23.8	1.12	42.4	---	---	---	---	---	222

[†] Data obtained from cited 2012 published data (~80 articles; see note at end of chapter before the references) [‡] --- = Below detection or not determined.

Table 7.2 *Average biochar total nutrient concentrations based on pyrolysis temperature, pyrolysis type and pyrolysis temperature by type (dry weight basis)*

	C (%)	*N* (%)	*P* ($g\ kg^{-1}$)	*K* ($g\ kg^{-1}$)	*S* ($g\ kg^{-1}$)	*Ca* ($g\ kg^{-1}$)	*Mg* ($g\ kg^{-1}$)	*Fe* ($g\ kg^{-1}$)	*Cu*
Pyrolysis temperature†									
<300°C	53.6	1.25	11.4	4.90	7.05	1.10	---	0.05	5.16
300–399°C	57.1	1.99	13.7	21.1	14.0	39.1	7.07	2.49	330
400–499°C	62.1	1.29	13.0	17.7	0.17	52.4	5.05	2.79	124
500–599°C	63.2	1.15	11.8	14.9	2.00	49.9	6.93	2.19	105
600–699°C	62.4	0.94	11.4	14.9	0.60	55.6	6.73	1.25	115
700–799°C	63.7	1.50	42.9	54.0	6.57	46.8	18.8	4.32	545
>800°C	63.2	0.84	25.4	77.2	92.0	78.4	72.6	7.93	330
Pyrolysis type†									
Fast	56.2	0.74	14.8	53.2	0.33	60.5	60.6	5.75	8.52
Slow	60.2	1.44	15.4	20.8	8.97	47.8	8.65	2.67	294
Pyrolysis temp. × type†									
Fast, 300–499°C	61.0	0.92	31.5	51.2	0.23	58.0	1.79	---	---
Fast, 500–699°C	51.1	0.72	0.30	3.40	0.37	3.70	1.50	1.40	17.0
Fast, 700–900°C	59.1	0.34	3.39	105.5	---‡	92.8	120	7.93	---
Slow, <300°C	53.6	1.25	11.4	4.90	7.05	1.10	---	0.05	5.16
Slow, 300–499°C	60.0	1.71	11.9	17.0	13.0	43.4	6.25	2.11	289
Slow, 500–699°C	62.8	1.17	12.5	15.6	2.30	54.4	7.19	1.90	124
Slow, 700–900°C	64.2	1.53	43.7	53.2	6.57	49.5	20.0	4.32	509

† Data obtained from cited 2012 published data (~80 articles; see note at end of chapter before the references) ‡ --- = Below detection or not determined.

biochars, attributing their findings to the potential presence of recalcitrant heterocyclic N-containing compounds. These compounds likely volatilized at greater pyrolysis temperatures. Koutcheiko et al (2007) found a similar response, potentially due to loss of N containing aliphatic amino chains that are released upon greater heating. Loss in total P content with increasing pyrolysis temperatures has also been observed. Knicker (2007) showed that P containing compounds can volatilize near 760°C, which explains the decrease in total P content when feedstocks are pyrolysed at temperatures greater than 800°C.

The influence of pyrolysis temperature on biochar's total nutrient content differs depending on the length of the pyrolysis reaction period (Table 7.2). More specifically, increasing temperature during slow pyrolysis tends to concentrate and thus increase total nutrient content (e.g., see Gaskin et al, 2008) as compared to fast pyrolysis. However, it has been shown that, as compared to slow pyrolysis, fast pyrolysis may result in an incomplete conversion of C to more recalcitrant forms (Bruun et al, 2012a). Thus, it is possible that the total C present in fast pyrolysis biochars is more readily mineralizable.

Available nutrients

In the most general sense, available nutrients are that portion of an element or compound that can be assimilated by growing plants (for a more detailed explanation regarding the concept of element bioavailability, we refer the reader to: Barber, 1995). In soils, various extractants (e.g. water, 1M KCl, 0.5M K_2SO_4, NH_4OAc at pH 7, Morgan, Mehlich-III, Mehlich-I, Bray, Olsen, DTPA, etc.) have been used to correlate soil extractable nutrients with plant uptake. This approach has been loosely used to distinguish elements that may be available from biochar.

Biochars obviously contain a plethora of inorganic elements, but the supply of available nutrients can be quite variable (e.g., Lentz and Ippolito, 2012; Liu et al, 2012). An examination of research performed in 2012, where both available and total nutrient analysis was reported, supports this contention (Figure 7.1). No relationship exists between available and total P ($r^2 = 0.05$) across the range of biochars reported. In contrast, between 55 and 65 per cent of the K, Mg and Ca available from biochars can be related to total concentration. It is immediately obvious that total elemental concentration cannot accurately predict available nutrient content in biochars, as other factors such as pyrolysis conditions affect retained and lost nutrients.

Average available nutrients present in biochars produced from various feedstocks are presented in Table 7.3. Although the total N content of biochars ranged from 0.09 to 3.3 per cent (Table 7.1), the literature has reported that the amount of available N as nitrate (NO_3) is negligible. In fact, the percentage available N as compared to total in all cases is < 0.01 per cent. Low extractable N concentrations (as NO_3, NH_4, NO_2) in biochars have been frequently observed (Belyaeva and Haynes, 2012) and can be attributable to gaseous N loss during pyrolysis (Amonette and Joseph, 2009). At pyrolysis temperatures < 760°C (Knicker, 2007), P availability is likely controlled by the coordinated cations present (Al, Fe, Ca, Mg) and is dependent on feedstock (T. Wang et al, 2012). In the case of most biochars, P will likely be associated with Ca and Mg due to biochar's elevated pH, with some of these compounds in the readily available form. Comparison between Table 7.1 and Table 7.3 shows that available P ranges from 0.4 to 34 per cent of total P in biochar. Potassium also typically concentrates in biochar and tends to be highly available. For example, Cantrell et al (2012) showed that total K (in combination with Na) concentration was an important predictor of biochar electrical conductivity, or the amount of salt present. This indicates that the form of K in biochar is water-soluble. Potassium availability ranged from 3.5 to 100 per cent of the total K present (comparison between Table 7.1 and 7.3).

Initial feedstock selection, however, strongly influences the final product and data in Table 7.3 suggest that utilizing manure-based feedstocks produces biochars with increased available nutrients. A comparison between poultry litter, peanut hulls and pine chips by Gaskin et al (2008) showed a similar trend. T. Wang et al (2012) compared nutrient availability between dairy manure- and biosolids-derived biochars. The authors showed that available P increased with dairy manure biochar due to P being associated with more readily soluble Ca and Mg compounds present. In contrast, elevated concentrations of N and P in wastewater sludge-derived biochar, as well as other micro and macro nutrients, has also been the primary reason for agricultural utilization of wastewater sludge biochar (Hossain et al, 2011). Compared to the widely used lignocellulosic or manure-based biochar feedstocks, algae-based biochar tends to be comparatively lower in C, but often high in N, P and other nutrients (Bird et al, 2011; Torri et al, 2011). Thus, it is imprudent to assume that all biochars are capable of supplying initial plant-available nutrients to a crop as diverse biochars will likely have dissimilar effects (Graber et al, 2012).

Table 7.4 illustrates how increasing temperature, pyrolysis type or their interaction influence nutrient availability in biochar. In general, increasing pyrolysis temperature produced mixed results in terms of biochar available nutrient status. Increasing pyrolysis temperature has been shown to cause a decrease in available nutrients (Uchimiya et al, 2012a). For example, P availability may be inversely related to pyrolysis temperature (Table 7.4; see for example, Zheng et al, 2013). However, other research (Chan et al, 2007, 2008; Gaskin et al, 2008; Qayyum et al, 2012) showed that both feedstock material and pyrolysis temperature had an influence on available nutrients in biochar, with nutrient content generally increasing with increasing temperature (Gaskin et al, 2008). One should also consider the use of slow as compared to fast pyrolysis when desiring increased available nutrients in biochar; Table 7.4 clearly shows that available P, K, Ca and Mg concentrations are greater in slow as compared to fast pyrolysis.

The potential is present for all biochars to act as a soil conditioner (to increase soil organic C and organic matter content, or to improve soil physical properties such as water holding capacity; Chapter 19); yet, not all biochars will supply relevant amounts of plant nutrients (Figure 7.2). For example, softwood biochars contain (on average) 200mg kg^{-1} of available P. Considering a medium soil P test value for irrigated corn in South Carolina (USA) would suggest that 67kg of P_2O_5 ha^{-1} would be necessary for optimal crop yield. Given the P concentration in softwood biochar, approximately 145Mg ha^{-1} would be required to supply the P needs of the crop. In comparison, turkey litter biochar, which contains seven times as much available P, would need to be applied at about 20Mg ha^{-1}. This value may still be considered unreasonable for production agricultural systems. For comparison sake, let us compare hazelnut and papermill waste biochars in terms of supplying available K. Average available K concentrations for hazelnut and papermill waste biochars are 890 and 20,800mg kg^{-1}, respectively. Once again considering a medium soil K test value for irrigated corn in South Carolina would suggest that 67kg of K_2O ha^{-1} would be required by the crop. Given the K

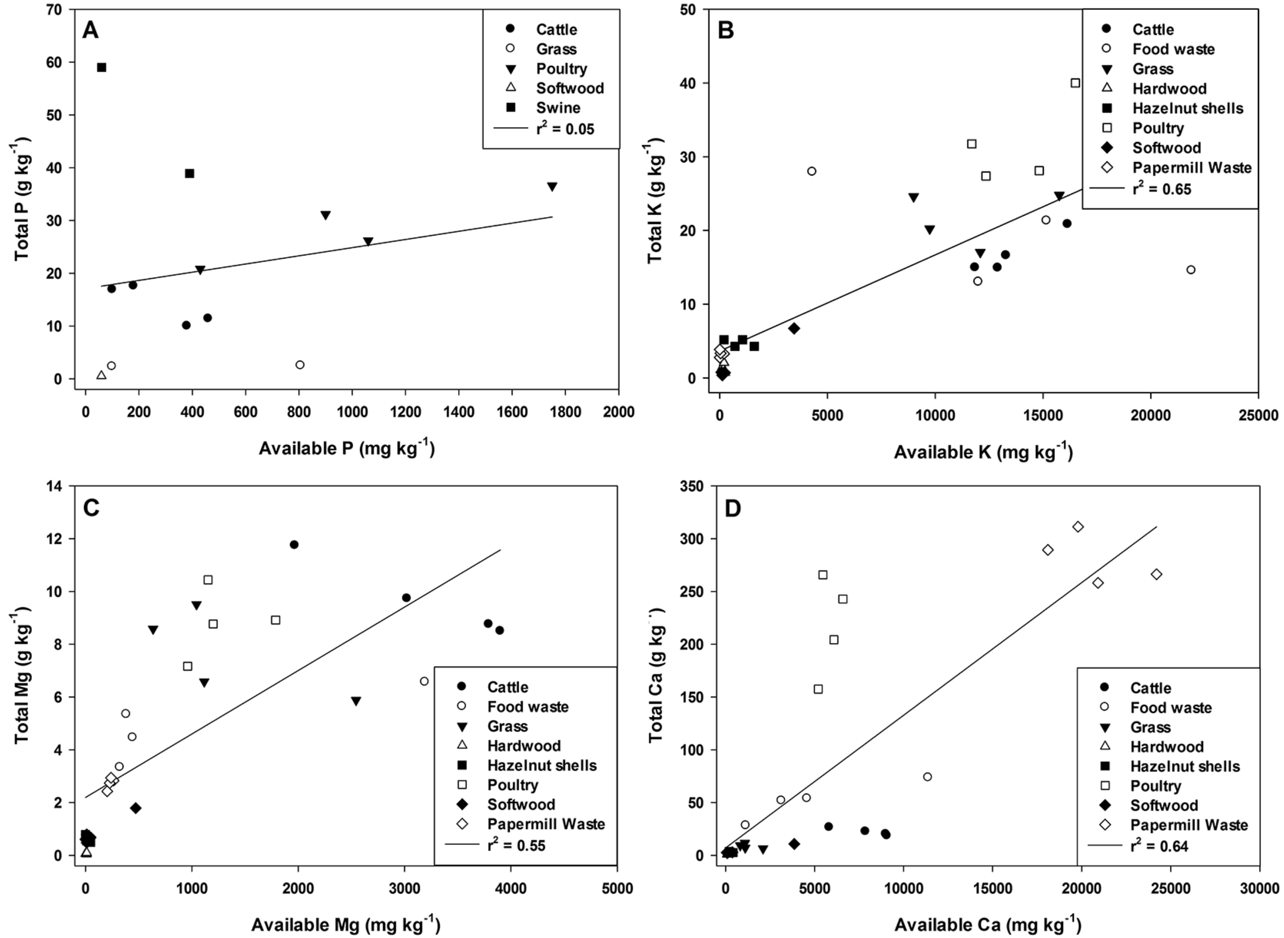

Figure 7.1 *Available (based on water, NH_4OAc at pH 7, Morgan and Mehlich-III extractions) versus total A) phosphorus, B) potassium, C) magnesium and D) calcium from various types of biochars. Data obtained from cited 2012 published data (available versus total P data from: Cantrell et al, 2012; Jia et al, 2012; and Robertson et al, 2012; available versus total K, Ca and Mg data from: Mekuria et al, 2012; Rajkovich et al, 2012; and Robertson et al, 2012)*

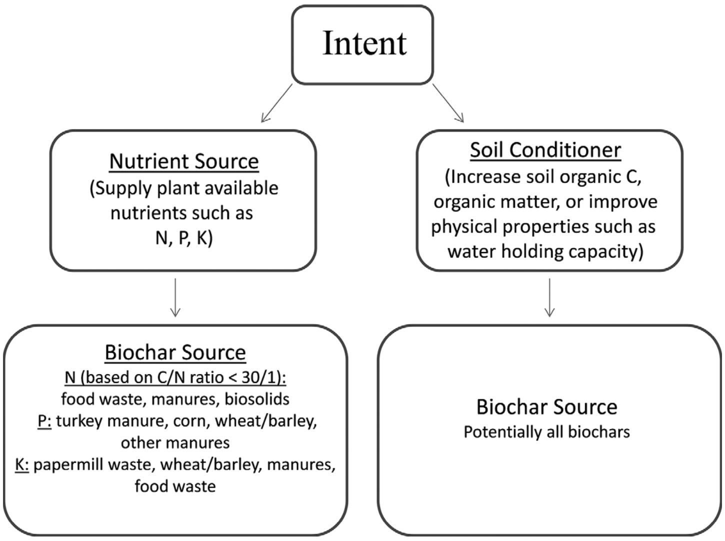

Figure 7.2 *Intended use of biochar as a nutrient source or a soil conditioner*

Table 7.3 *Average biochar available nutrient concentrations† based on various feedstock sources (dry weight basis)*

Source‡	*NO_3 (mg kg^{-1})*	*P (mg kg^{-1})*	*K (mg kg^{-1})*	*Ca (mg kg^{-1})*	*Mg (mg kg^{-1})*
Corn	0.85	806	11600	1280	1340
Wheat/barley	1.05	596	14000	379	112
Rice straw/husk	---¶	---	---	840	552
Sorghum	---	99.5	---	---	---
Soybean stover	---	---	---	---	---
Peanut shell	---	---	---	---	---
Pecan shell	---	---	---	---	---
Hazelnut shell	---	---	889	270	28.0
Switchgrass	---	---	---	---	---
Bagasse	---	76.0	---	---	---
Coconut coir	---	---	---	---	---
Food waste	---	---	13300	5060	1090
Other (grass, leaves, orange peel, other green wastes)	0.92	307	8370	680	574
Hardwoods	0.12	25.1	1620	652	116
Softwoods	---	200	1020	684	103
Papermill waste	---	---	117	20800	234

Poultry manure/litter	---	448	13800	5830	1280
Turkey manure/litter	---	1400	---	---	---
Swine manure	---	225	---	---	---
Dairy manure	---	240	13500	7940	3170
Cattle manure	---	320	---	---	---
Biosolids/sewage sludge	---	---	---	---	---

† Available NO_3 data based on water, 1M KCl and 0.5M K_2SO_4 extractions. Available P, K, Ca and Mg data based on water, NH_4OAc at pH 7, Morgan and Mehlich-III extractions.
‡ Data obtained from cited 2012 published data (~80 articles; see note at end of chapter before the references).
¶ --- = Below detection or not determined.

Table 7.4 *Average biochar available nutrient concentrations† based on pyrolysis temperature, pyrolysis type and pyrolysis temperature by type (dry weight basis)*

	NO_3 (mg kg^{-1})	P (mg kg^{-1})	K (mg kg^{-1})	Ca (mg kg^{-1})	Mg (mg kg^{-1})
Pyrolysis temperature‡					
<300°C	---¶	---	---	---	---
300–399°C	1.10	544	7580	4880	1240
400–499°C	0.36	196	5570	2850	425
500–599°C	0.37	219	7470	3640	694
600–699°C	0.10	51.3	5450	5020	915
700–799°C	---	511	---	---	---
>800°C	---	76.0	---	---	---
Pyrolysis type‡					
Fast	1.05	51.4	4740	3100	374
Slow	0.34	314	6420	3660	713
Pyrolysis temp. × type‡					
Fast, 300–499°C	1.05	35.4	4740	3100	374
Fast, 500–699°C	---	---	---	---	---
Fast, 700–900°C	---	---	---	---	---
Slow, <300°C	---	---	---	---	---
Slow, 300–499°C	0.38	303	6260	3480	679
Slow, 500–699°C	0.30	183	6620	4260	792
Slow, 700–900°C	---	449	---	---	---

† Available NO_3 data based on water, 1M KCl and 0.5M K_2SO_4 extractions. Available P, K, Ca and Mg data based on water, NH_4OAc at pH 7, Morgan and Mehlich-III extractions.
‡ Data obtained from cited 2012 published data (~80 articles; see note at end of chapter before the references).
¶ --- = Below detection or not determined.

concentration in both materials, it would require 41.4 and 1.8Mg ha^{-1} of hazelnut or papermill waste biochar to meet the crop K demands. It becomes readily apparent that not all biochars are created equal in terms of supplying plant available nutrients.

pH and liming value

Pyrolysis temperature is known to have an impact on biochar pH. Specifically, increasing pyrolysis temperature removes acidic functional groups and the ash content increases, causing biochar to be more basic (Novak et al, 2009; Li et al, 2002; Ahmad et al, 2012;

Table 7.5 *Average biochar pH, calcium carbonate equivalent (CCE), surface area and cation exchange capacity (CEC) based on various feedstock sources*

Source†	pH	CCE (%)	Surface Area (m^2 g^{-1})	CEC ($mmol_c$ kg^{-1})
Corn	9.27	---	107.2	607
Wheat/barley	8.80	---	26.65	103
Rice straw/husk	9.17	---	42.15	212
Sorghum	---‡	---	---‡	---
Soybean stover	9.30	---	4.375	---
Peanut shell	8.52	---	115.1	---
Pecan shell	6.97	---	111.5	---
Hazelnut shell	7.86	---	467.5	83.8
Switchgrass	9.28	---	52.96	---
Bagasse	7.59	---	113.6	115
Coconut coir	---	---	114.8	---
Food waste	9.09	---	0.803	81.0
Other (grass, leaves, orange peel, other green wastes)	8.72	---	119.8	290
Hardwoods	7.94	---	171.3	138
Softwoods	7.48	---	194.2	145
Papermill waste	9.13	---	10.08	52.0
Poultry manure/litter	9.80	18.4	50.35	538
Turkey manure/litter	8.95	---	24.70	---
Swine manure	9.37	---	26.89	---
Dairy manure	9.45	---	33.38	342
Cattle manure	8.99	13.4	73.27	---
Biosolids/sewage sludge	6.90	12.9	102.1	23.6

† Data obtained from cited 2012 published data (~80 articles; see note at end of chapter before the references) ‡ --- = Below detection or not determined.

Table 7.6 *Average biochar pH, calcium carbonate equivalent (CCE), surface area and cation exchange capacity (CEC) based on pyrolysis temperature, pyrolysis type and pyrolysis temperature by type*

Source†	*pH*	*CCE (%)*	*Surface Area ($m^2\ g^{-1}$)*	*CEC ($mmol_c\ kg^{-1}$)*
Pyrolysis temperature†				
<300°C	5.01	7.95	1.686	327
300–399°C	7.60	13.7	65.36	371
400–499°C	8.10	17.2	83.98	191
500–599°C	8.71	15.6	111.8	283
600–699°C	9.00	---‡	217.0	126
700–799°C	9.83	21.0	176.2	39.0
>800°C	10.8	---	213.8	44.0
Pyrolysis type†				
Fast	8.38	---	69.38	28.8
Slow	8.50	14.9	124.4	250
Pyrolysis temp. × type†				
Fast, 300–499°C	8.33	---	44.74	28.8
Fast, 500–699°C	7.70	---	40.99	ND
Fast, 700–900°C	10.1	---	178.2	ND
Slow, <300°C	5.01	7.95	1.686	327
Slow, 300–499°C	7.81	14.9	81.32	268
Slow, 500–699°C	9.09	15.6	180.5	218
Slow, 700–900°C	10.1	21.0	189.8	41.5

† Data obtained from cited 2012 published data (~80 articles; see note at end of chapter before the references) ‡ --- = Below detection or not determined.

Cantrell et al, 2012). Enders et al (2012) showed that as pyrolysis temperature increased from 300 to 600°C, pH increased in cow manure, annual biomass and woody biomass-based biochars. Furthermore, at greater pyrolysis temperatures nutrients in mineral form, or salts (such as KOH, NaOH, $MgCO_3$, $CaCO_3$, organic metal salts) separate from the solid organic matrix, resulting in elevated pH values (Cao and Harris, 2010; Knicker, 2007). In plant-based biochars, pH is lower as compared to manure-based biochars (Table 7.5). This is further supported by data presented by Enders et al (2012) and conforms to individual study progressions found by Rajkovich et al (2012).

Because of its basic pH, biochar has been used to ameliorate acidic soil conditions (Yuan and Xu, 2011; Uchimiya et al, 2012b), thus it could serve as a liming agent (Kloss et al, 2012). The liming effect may be quantified by biochar's calcium carbonate equivalency (CCE, the value biochar has related to an equivalent quantity of $CaCO_3$). Although data is largely lacking for individual biochars based on feedstock (Table 7.5), increasing pyrolysis temperature increases the CCE of biochar (Table 7.6). This effect has been illustrated by several studies (Hass et al, 2012; T. Wang et al, 2012). In addition, steam activation during pyrolysis can increase biochar pH as well as calcium carbonate equivalent (CCE) as compared to non-activated biochars (Hass et al, 2012).

Nutrient retention

Biochar can retain nutrients via several mechanisms including electrostatic adsorption and the retention of dissolved nutrients in water (i.e., entrapment; Lehmann et al, 2003). More specifically, the ability of some biochars to retain nutrients is attributed to its large surface area and quantity of functional groups and to great porosity. Surface area and porosity in biochars can vary greatly depending on feedstock and pyrolysis conditions (Verheijen et al, 2010). Jeong et al (2012) showed that hardwood biochar (comprised mostly of sweetgum and oak chips) had a greater specific surface area as compared to softwood biochar (comprised mostly of southern yellow and loblolly pine chips) at 242 versus 159m^2 g^{-1}, respectively. However, when averaged across all hardwood and softwood biochar data published in 2012, little difference between the two exist (Table 7.5). In fact, it is difficult to draw any conclusions with respect to biochar surface area based on feedstock alone. Thus, it is difficult to draw any conclusions of nutrient retention based on feedstock either.

However, specific surface area tends to increase with pyrolysis temperature (Table 7.6) as illustrated by numerous studies (Ahmad et al, 2012; Lu et al, 2012; Cantrell et al, 2012; Chen et al, 2012; Hass et al, 2012; Shen et al, 2012) and may lead to greater nutrient retention. The increase in specific surface area with pyrolysis temperature is most often associated with both physical and chemical changes in the biochar. For example, Ahmad et al (2012) utilized scanning electron microscopy to study soybean stover and peanut shell biochar structural changes following pyrolysis. Cell pore diameter was reduced, internal pores appeared and a subsequent increase in surface area occurred. Furthermore, it is possible that at lower pyrolysis temperatures tars block micropores; thus, yielding a lower surface area biochar compared to higher temperature biochars where these same tars are volatilized leading to an increase in surface area (Munoz et al, 2003; Kloss et al, 2012). Chen et al (2008) showed that increasing pyrolysis temperatures removed H and O containing functional groups, greatly increasing biochar surface areas. Chen et al (2012) explained that increasing pyrolysis temperature decomposed cellulose and lignin, also leading to an increase in surface area. In addition, steam, NaOH, or H_3PO_4 activation of biochar has been shown to remove low-volatile tar constituents (in the case of steam activation) or create holes in the skeletal C structure (in the case of NaOH or H_3PO_4 activation) with a concomitant increase in specific surface area (e.g., Borchard et al, 2012b). The aforementioned processes where pore size is reduced and surface area is increased may lead to an increase in nutrient retention.

Comparing fast versus slow pyrolysis biochars in terms of surface area, one may assume that fast pyrolysis biochars would contain a greater surface area and thus exhibit greater nutrient retention, as these biochars require a smaller initial feedstock particle size as compared to slow pyrolysis. However, it is not apparent that smaller initial particle size influences specific surface area and in fact it appears quite the opposite holds true (Table 7.6).

Others have both speculated and shown that fast pyrolysis biochars have low surface areas (<8.0m^2 g^{-1}; Boateng, 2007; Hilber et al, 2012) as compared to slow pyrolysis biochars. This likely is due to incomplete physico-chemical transformation during fast pyrolysis. In addition, during fast pyrolysis gases contained within the biochar can escape at different rates (dependent on a combination of temperature, temperature ramp speed and residence time) and disrupt the C skeletal complex, thus decreasing surface area and likely the amount of nutrients that can be retained by the biochar (Chapter 5).

Cation Exchange Capacity (CEC)

Biochar CEC is developed when the product is exposed to oxygen and water, creating oxygenated surface functional groups (Briggs et al, 2012; Chan and Xu, 2009; Chapter 9). Similar to soils, biochar CEC represents its ability to electrostatically sorb or attract cations. Although biochars are organically based and therefore should carry pH dependent charge much like soil organic matter, increasing pyrolysis temperature tends to cause a decrease in CEC; this phenomenon was observed by both Lin et al (2012) and Rajkovich et al (2012). This is due to the removal of organic functional groups (i.e., more volatile matter) at greater pyrolysis temperatures (Gaskin et al, 2008; Cantrell and Martin, 2012; Kloss et al, 2012). Indeed, increasing pyrolysis temperatures increase lignin and cellulose decomposition in feedstock materials (Novak et al, 2009) leading to a loss of functional groups. Thus, the potential exists for lower initial nutrient retention with biochars created at higher versus lower pyrolysis temperatures (Ippolito et al, 2012a). However, nutrient retention may also be a function of short- and long-term oxidation once biochar is introduced into the environment (Quilliam et al, 2012; Chapter 10).

Specific nutrient sorption research has been performed with Cu, NH_3 and NH_4. Borchard et al (2012a) suggested that oxygen-containing functional groups present in biochar are responsible for overall sorption. In their work, Cu was found to interact chemically with biochar and physical interaction (i.e., entrapment) was negligible. A similar response was observed for hexavalent Cr reduction by coconut coir biochar (Shen et al, 2012). Ippolito et al (2012b) showed that, in part, Cu was bound to biochar via organic ligand functional groups, yet some carbonate/oxide precipitation did occur. Uchimiya et al (2012b) showed removal of leachable aliphatic and N-containing heteroaromatic functional groups with elevated pyrolysis temperatures, which positively correlated with Cu retention in manure-based biochars. Biochar sorption of nitrogenous compounds has also been suggested (Dempster et al, 2012a; Kammann et al, 2012; Sarkhot et al, 2012). Ding et al (2010) and Hina et al (2010) noted that NH_4 sorption onto biochar occurred primarily through ion exchange, coulombic forces, chemisorptions-ammonia fixation or associations with S-functional groups. Taghizadeh-Toosi et al (2012) showed that biochars with lower pH values sorbed greater NH_4 (due to transformation of NH_3 into NH_4) than higher pH biochars, suggesting chemical rather than physical attraction. Nelissen et al (2012) suggested that NH_4 sorption onto biochar was due to its elevated CEC. As CEC is directly related to surface functional groups, changes in functional group chemistries are likely the main reason for differences in N sorption (Spokas et al, 2012a).

Nutrient entrapment

Research regarding physical nutrient entrapment by biochar has been primarily limited to NO_3 studies, most likely because biochar typically has very little anion exchange capacity (Laird et al, 2008). Cheng et al (2012) and Jones et al (2012) found that wheat straw or hardwood biochar had negligible effect on retaining NO_3. In contrast, Case et al (2012) suggested that NO_3 may be held by biochar via physical means. Further, Prendergast-Miller et al (2011) proposed that mass solution flow into biochar particles could potentially hold NO_3. The authors showed that NO_3 was the dominant form of N extracted (using 1M KCl) from biochar and was likely held within biochar pore solution, physically trapped within the biochar particle itself. Kameyama et al (2012) showed that NO_3 sorption by sugar cane bagasse biochar increased dramatically when pyrolysis temperature exceeded 700°C, with sorption uncorrelated to micropore volume. This suggested that physical entrapment did not play a role, as well as that high pyrolysis temperatures formed base-functional groups capable of sorbing NO_3. A similar response was observed by Yao et al (2012) and by Cheng et al (2008) with newly made biochar. However, pyrolysis temperatures greater than 700°C are atypical; thus, the potential anion exchange response shown by Kameyama et al (2012) and Yao et al (2012) would likely not be observed in most biochars outlined in this chapter. This conclusion is further supported by the findings of Hollister et al (2013) who found little to no sorption of NO_3 (or PO_4) with either freshly created biochars or following several hydration events.

Designing relevant biochars

The variability in biochars' elemental composition, as outlined in this chapter, corroborates the notion that not all biochars are created equal (Atkinson et al, 2010; Novak and Busscher, 2012, Harvey et al, 2012). The inherent variability of biochars when used as a soil amendment suggests that the production of biochars can be designed for specific situations (as cited by Ippolito et al, 2012a; Novak et al, 2014). For example, Novak and Busscher (2012) presented an outline for how biochar chemical and physical characteristics can be tailored for use to resolve specific limitations in sandy soils. Biochars produced from animal manures, which have inherently high concentrations of plant nutrients, can be blended with feedstocks containing lower quantities of nutrients (Table 7.7). In this regard, the high P and Ca contents in biochars pyrolysed from swine solids could be reduced by blending with switchgrass biochar. An elemental compositional analysis of the blended biochars using these two different feedstocks exemplifies the dramatic reductions in P and Ca contents. Other manure feedstocks (i.e., poultry litter) that contain high P contents can also be blended with a nutrient poor feedstock (e.g., pine chips) to obtain designer biochars that are more nutrient-balanced (Novak et al, 2014). In turn, this biochar blended from poultry litter + pine chips can be used on soils without dramatically increasing plant available P. A similar approach was suggested by Tsai et al (2012) with woody-based biochars (containing mostly C) to create an optimal biochar end-product that positively influences nutrient availability. In addition, biochars could

Table 7.7 *The total (EPA Method 3050a) P and Ca concentration in pure feedstocks and in biochars made at specific blending ratios (unpublished data)*

Feedstocks	*Blending ratio (w w^{-1})*†	*P (mg kg^{-1})*	*Ca (mg kg^{-1})*
Switchgrass (SG)	100:0	384	2130
Swine solids (SS)	100:0	27,026	23,214
SG:SS	80:20	14,831	13,538
SG:SS	90:10	8254	5535

† Blending ratio determined to balance a corn crop P uptake requirement (Novak et al, 2013).

be blended with non-pyrolysed feedstocks to achieve a desired end-product. Overall, tailor-made biochars could potentially fill the need of supplying nutrients as well as improving soil physical properties as outlined in Figure 7.2.

Accepting that not all biochars are the same will require a paradigm shift in their creation and specific uses as soil amendments. As outlined by Novak et al (2014) the tailor-made or designer biochar concept is still in its infancy and will require further evaluation of biochar performance from various feedstocks and in other agricultural soils containing diverse fertility or physical characteristics.

Conclusions

Based on evidence provided in this chapter, it is obvious that pyrolysis temperature and type can have dramatic effects on both total and available nutrients in biochar. Increasing temperature during slow pyrolysis appears to concentrate total nutrient content in biochars as compared to fast pyrolysis. As compared to slow pyrolysis, fast pyrolysis may result in an incomplete conversion of C to more recalcitrant forms leading to a more readily mineralizable biochar. The relation between pyrolysis temperature or type and available nutrients in biochar is less clear. In most instances correlations do not exist; however, one may draw conclusions between increasing pyrolysis temperatures, increasing concentrations of K, Mg and Ca in the final product and the availability of these elements (~55–65 per cent available).

In addition, initial feedstock selection strongly influences the final product. Data provided in this chapter suggest that utilizing manure-based feedstocks produce biochars with increased available nutrients as compared to plant-based feedstocks. Thus, in addition to pyrolysis temperature and type, proper feedstock selection is crucial when considering the intended end-use for biochar (see Chapter 8 for more details).

Notes to Tables

Data in Tables 7.1, 7.3 and 7.5

Corn data averaged from: Brewer et al, 2012; Enders and Lehmann, 2012; Feng et al, 2012; Freddo et al, 2012; Hale et al, 2012; Jia et al, 2012; Kammann et al, 2012; Kinney et al, 2012; Nelissen et al, 2012; and Rajkovich et al, 2012.

Wheat/barley data averaged from: Bruun et al, 2012a, b; Bruun and El-Zehery, 2012; Cheng et al, 2012; Kloss et al, 2012; Solaiman et al, 2012; Sun et al, 2012; Yoo and Kang, 2012; and Zhang et al, 2012a, b.

Rice straw/husk data averaged from: Lu et al, 2012; Mekuria et al, 2012; T. Wang et al, 2012; and R. Zheng et al, 2012.

Sorghum data obtained from: Schnell et al, 2012.

Soybean stover data obtained from: Ahmad et al, 2012.

Peanut shell data averaged from: Ahmad et al, 2012; Kammann et al, 2012; Karlen and Kerr, 2012; Novak et al, 2012; and Yao et al, 2012.

Pecan shell data averaged from: Ippolito et al, 2012b and Novak et al, 2012.

Hazelnut shell data obtained from: Rajkovich et al, 2012.

Switchgrass data averaged from: Hale et al, 2012; Ippolito et al, 2012a; and Novak et al, 2012.

Bagasse data averaged from: Kameyama et al, 2012; and Yao et al, 2012.

Coconut coir (i.e. husk fiber) data obtained from: Shen et al, 2012.

Food waste data averaged from: Hale et al, 2012 and Rajkovich et al, 2012.

Other waste data averaged from: Bolan et al, 2012; Choppala et al, 2012; Galvez et al, 2012; Hale et al, 2012; Hilber et al, 2012; Kinney et al, 2012; and Oh et al, 2012.

Hardwood data averaged from: Ballantine et al, 2012; Borchard et al, 2012a; Case et al, 2012; Dempster et al, 2012a, b; Enders and Lehmann, 2012; Freddo et al, 2012; Graber et al, 2012; Hale et al, 2012; Jeong et al, 2012; Jones et al, 2012; Kammann et al, 2012; Kinney et al, 2012; Kloss et al, 2012; Lentz and Ippolito, 2012; Lin et al, 2012; Novak et al, 2012; Pereira et al, 2012; Rajkovich et al, 2012; Sarkhot et al, 2012; Solaiman et al, 2012; Xu et al, 2012a; Yao et al, 2012; and J. Zheng et al, 2012.

Softwood data averaged from: Chen et al, 2012; Freddo et al, 2012; Hale et al, 2012; Hilber et al, 2012; Jeong et al, 2012; Karlen and Kerr, 2012; Kim et al, 2012; Kloss et al, 2012; Rajkovich et al, 2012; Robertson et al, 2012; Spokas et al, 2012b; and Taghizadeh-Toosi et al, 2012.

Papermill waste data averaged from: Hale et al, 2012 and Rajkovich et al, 2012.

Poultry manure/litter data averaged from: Belyaeva and Haynes, 2012; Cantrell et al, 2012; Choppala et al, 2012; Enders and Lehmann, 2012; Hass et al, 2012; Novak et al, 2012; Rajkovich et al, 2012; Revell, Maguire and Agblevor, 2012a, b; Sun et al, 2012; and Uchimiya et al., 2012a.

Turkey manure/litter data averaged from: Cantrell et al, 2012 and Karlen and Kerr, 2012.

Swine manure data averaged from: Cantrell and Martin, 2012; Cantrell et al, 2012; Tsai et al, 2012; and Yoo and Kang, 2012.

Dairy manure data averaged from: Cantrell et al, 2012; Hale et al, 2012; Rajkovich et al, 2012; and Streubel et al., 2012.

Cattle manure data averaged from: Cantrell et al, 2012; Schouten et al, 2012; and T. Wang et al, 2012.

Biosolids/sewage sludge data averaged from: Mendez et al, 2012; Oh et al, 2012; and T. Wang et al, 2012.

Data in Tables 7.2, 7.4 and 7.6

Data for Pyrolysis Temperature averaged from:

<300°C: Chen et al, 2012; Lu et al, 2012; Hale et al, 2012; Ippolito et al, 2012a.; Novak et al, 2012; Shen et al, 2012; and T. Wang et al, 2012.

300–399°C: Ahmad et al, 2012; Cantrell and Martin, 2012; Chen et al, 2012; Choppala et al, 2012; Enders and Lehmann, 2012; Feng et al, 2012; Freddo et al, 2012; Graber et al, 2012; Hale et al, 2012; Kim et al, 2012; Kinney et al, 2012; Lin et al, 2012; Lu et al, 2012; Nelissen et al, 2012; Novak et al, 2012; Rajkovich et al, 2012; Sarkhot et al, 2012; Shen et al, 2012; Taghizadeh-Toosi et al, 2012; Uchimiya et al, 2012a; T. Wang et al, 2012; Yao et al, 2012; and Yoo and Kang, 2012.

400–499°C: Ballantine et al, 2012; Belyaeva and Haynes, 2012; Borchard et al, 2012a, b; Briggs et al, 2012; Bruun and El-Zehery, 2012; Case et al, 2012; Cheng et al, 2012; Dempster et al, 2012b; Hale et al, 2012, Jia et al, 2012; Jones et al, 2012; Kameyama et al, 2012; Karlen and Kerr, 2012; Kim et al, 2012; Kinney et al, 2012; Kloss et al, 2012; Lin et al, 2012; Novak et al, 2012; Oh et al, 2012; Pereira et al, 2012; Rajkovich et al, 2012; Revell, Maguire and Agblevor, 2012a, b; Spokas et al, 2012b; Sun et al, 2012; Tsai et al, 2012; Robertson et al, 2012; J. Wang et al, 2012; T. Wang et al, 2012; Yao et al, 2012; and Zhang et al, 2012a, b.

500–599°C: Brewer et al, 2012; Bruun et al, 2012a, b; Busch et al, 2012; Chen et al, 2012; Choppala et al, 2012; Feng et al, 2012; Freddo et al, 2012; Galvez et al, 2012; Hale et al, 2012; Ippolito et al, 2012a; Kameyama et al, 2012; Kammann et al, 2012; Karlen and Kerr, 2012; Kim et al, 2012; Kinney et al, 2012; Kloss et al, 2012; Lentz and Ippolito, 2012; Lin et al, 2012; Lu et al, 2012; Mendez et al, 2012; Nelissen et al, 2012; Novak et al, 2012; Qayyum et al, 2012; Rajkovich et al, 2012; Shen et al, 2012; Schouten et al, 2012; Schnell et al, 2012; Spokas et al, 2012b; Struebel et al, 2012; Taghizadeh-Toosi et al, 2012; Tsai et al, 2012; Uchimiya et al, 2012a; T. Wang et al, 2012; J. Zheng et al, 2012; and R. Zheng et al, 2012.

600–699°C: Brewer et al, 2012; Carlsson et al, 2012; Dempster et al, 2012a; Enders and Lehmann, 2012; Freddo et al, 2012; Hale et al, 2012; Hilber et al, 2012; Kameyama et al, 2012; Kinney et al, 2012; Lin et al, 2012; Major et al, 2012; Oh et al, 2012; Rajkovich et al, 2012; Shen et al, 2012; Solaiman et al, 2012; Tsai et al, 2012; Uchimiya et al, 2012a; Xu et al, 2012a; and Yao et al, 2012.

700–799°C: Ahmad et al, 2012; Cantrell and Martin, 2012; Cantrell et al, 2012; Chen et al, 2012; Hale et al, 2012; Hilber et al, 2012; Ippolito et al, 2012b; Kameyama et al, 2012; Kammann et al, 2012; Kinney et al, 2012; Novak et al, 2012; Oh et al, 2012; Tsai et al, 2012; and Yoo and Kang, 2012.

>800°C: Graber et al, 2012; Hale et al, 2012; Jeong et al, 2012; Kameyama et al, 2012; Karlen and Kerr, 2012; Tsai et al, 2012; and Uchimiya et al, 2012a.

Data for Pyrolysis Type averaged from:

Fast: Ballantine et al, 2012; Borchard et al, 2012a; Brewer et al, 2012; Bruun et al, 2012a, b; Cheng et al, 2012; Dempster et al, 2012b; Freddo et al, 2012; Hale et al, 2012; Jeong et al, 2012; Kim et al, 2012; Lentz and Ippolito, 2012; Novak et al, 2012; Revel, Maguire and Agblevor, 2012a, b; Robertson et al, 2012; Schnell et al, 2012; Schouten et al, 2012; and J. Zheng et al, 2012.

Slow: Ahmad et al, 2012; Borchard et al, 2012a; Briggs et al, 2012; Bruun et al, 2012a, b; Bruun and El-Zehery, 2012; Busch et al, 2012; Cantrell and Martin, 2012; Cantrell et al, 2012; Case et al, 2012; Chen et al, 2012; Choppala et al, 2012; Dempster et al, 2012a, b; Enders and Lehmann, 2012; Feng et al, 2012; Freddo et al, 2012; Galvez et al, 2012; Graber et al, 2012; Hale et al, 2012; Hass et al, 2012, Ippolito et al, 2012a, b; Jones et al, 2012; Kameyama et al, 2012; Kinney et al, 2012; Kloss et al, 2012, Lin et al, 2012; Lu et al, 2012; Major et al, 2012; Mekuria et al, 2012; Mendez et al, 2012; Nelissen et al, 2012; Novak et al, 2012; Oh et al, 2012, Pereira et al, 2012; Qayyum et al, 2012; Rajkovich et al, 2012; Sarkhot et al, 2012; Shen et al, 2012; Struebel et al, 2012; Sun et al, 2012; Taghizadeh-Toosi et al, 2012; Tsai et al, 2012; Uchimiya et al, 2012a; T. Wang et al, 2012; Yao et al, 2012; Yoo and Kang, 2012; a, b., 2012; and R. Zheng et al, 2012.

Data for Pyrolysis Temperature X Type averaged from:

Fast:

300–499°C: Ballantine et al, 2012; Borchard et al, 2012a; Cheng et al, 2012; Dempster et al, 2012a; Hale et al, 2012; Kim et al, 2012; Revell, Maguire and Agblevor, 2012a, b; and Robertson et al, 2012.

500–699°C: Brewer et al, 2012; Bruun et al, 2012a, b; Kim et al, 2012; Lentz and Ippolito, 2012; Novak et al, 2012; Schouten et al, 2012; and J. Zheng et al, 2012.

700–900°C: Hale et al, 2012 and Jeong et al, 2012.

Slow:

<300°C: Chen et al, 2012; Lu et al, 2012; Hale et al, 2012; Ippolito et al, 2012a; Novak et al, 2012; Shen et al, 2012; and T. Wang et al, 2012.

300–499°C: Ahmad et al, 2012; Borchard et al, 2012b; Briggs et al, 2012; Bruun and El-Zehery, 2012; Cantrell and Martin, 2012; Cantrell et al, 2012; Case et al, 2012; Chen et al, 2012; Choppala et al, 2012; Dempster et al., 2012b; Enders and Lehmann, 2012; Feng et al, 2012; Freddo et al, 2012; Graber et al, 2012; Hale et al, 2012; Hass et al, 2012; Jones et al, 2012; Kameyama et al, 2012; Kinney et al, 2012; Kloss et al, 2012; Lin et al, 2012; Lu et al, 2012; Nelissen et al, 2012; Novak et al, 2012; Oh et al, 2012; Pereira et al, 2012; Rajkovich et al, 2012; Sarkhot et al, 2012; Shen et al, 2012; Sun et al, 2012; Taghizadeh-Toosi et al, 2012; Tsai et al, 2012; T. Wang et al, 2012; Yao et al, 2012; Yoo and Kang, 2012; and Zhang et al, 2012a, b.

500–699°C: Bruun et al, 2012a, b; Busch et al, 2012; Choppala et al, 2012; Dempster et al, 2012a; Enders and Lehmann, 2012; Feng et al, 2012; Freddo et al, 2012; Hale et al, 2012; Ippolito et al, 2012a; Kameyama et al, 2012; Kinney et al, 2012; Kloss et al, 2012; Lin et al, 2012; Lu et al, 2012; Major et al, 2012; Mendez et al, 2012; Nelissen et al, 2012; Novak et al, 2012; Oh et al, 2012; Qayyum et al, 2012; Rajkovich et al, 2012; Shen et al, 2012; Taghizadeh-Toosi et al, 2012; Tsai et al, 2012; Uchimiya et al, 2012a; T. Wang et al, 2012; Yao et al, 2012; and R. Zheng et al, 2012.

700–900°C: Ahmad et al, 2012; Cantrell and Martin, 2012; Cantrell et al, 2012; Chen et al, 2012; Hale et al, 2012; Hass et al, 2012; Ippolito et al, 2012b; Kameyama et al, 2012; Kinney et al, 2012; Novak et al, 2012; Oh et al, 2012; Tsai et al, 2012; Yoo and Kang, 2012; and Uchimiya et al, 2012a.

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