

生物炭主要类型、理化性质及其研究展望

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摘要:【目的】生物炭作为工农业生产副产品低碳利用的有效手段, 其改善土壤及提高作物品质的有益功效已被逐步认识, 但对其研究报道分散且差异较大。对已有研究进行梳理总结, 可为生物炭生产施用以及形成有效的产业链提供科学依据。【主要进展】1) 生物炭全碳含量在30%~90%之间, 平均64%。生物炭碳含量由大到小来源依次是木质、秸秆、壳类、粪污和污泥。秸秆类生物炭碳含量大多为40%~80%, 木质类生物炭在60%~85%。生物炭灰分含量在0~40%之间变动, 平均15.52%。灰分含量由大到小依次是污泥、粪污、秸秆、壳类和木质。秸秆生物炭灰分含量主要在20%~35%之间, 较少为15%; 木质炭灰分主要在0~10%范围内。生物炭碳含量和灰分含量相关系数为-0.77。裂解温度与生物炭碳灰组分呈正相关, 相关系数分别为0.17和0.28。施入生物炭可以改善土壤状况, 生物炭灰分通常对养分贫瘠土壤及沙质土壤的一些养分补充作用较明显。2) 生物炭比表面积绝大多数在0~520 m²/g之间, 平均124.83 m²/g, 壳类、秸秆、木质、粪污和污泥生物炭比表面积逐渐降低。秸秆炭比表面积集中在0~200 m²/g以内, 木质炭比表面积集中在0~100 m²/g以内。制备温度与比表面积的相关系数为0.48。生物炭的孔隙结构能降低土壤容重、降低土壤密度, 能较好地去除溶液和钝化土壤中的重金属。3) 生物炭pH值范围在5~12, 平均为9.15。秸秆、污泥、粪污、木质、壳类生物炭pH值中值逐渐降低。秸秆生物炭pH值多集中在8~11范围内, 木质生物炭pH相对一致。生物炭的CEC从0到500 cmol/kg都有分布, 平均为71.91 cmol/kg。秸秆类生物炭CEC值大多集中在0~100 cmol/kg范围内, 木质生物炭则在5~10与15~25 cmol/kg范围内均有一定数量的分布。裂解温度与pH值和CEC的相关系数为0.58和0.30。生物炭施入土壤后可消耗土壤质子, 提高酸性土壤pH值, 提高酸性土壤一些养分的有效性; 其巨大的表面积还可提高对阳离子的吸附, 提高土壤保肥能力。4) 生物炭的裂解温度大都集中在200~800℃之间, 偶有达到1000℃的裂解温度。【建议和展望】目前, 全世界范围内对生物炭的生产和使用还处于就近和来源方便的初级阶段, 影响着生物炭功能和效益的最大化。应从以下几个方面加强研究和应用试验: 首先, 系统研究生物炭制造参数对理化性状的影响, 研究不同原料生物炭的作用机理差异及其针对性, 建立生物炭理化性质参数数据库; 其次, 加强应用研究, 根据土壤理化性状和改良目标选择适宜的生物炭类型, 根据对作物经济性状的要求, 研究选择适宜的生物炭类型, 实现生物炭功效的最大利用。加强不同原料的选配和组合研究, 改良生物炭产品的目标性状, 形成系列化产品。

关键词:生物炭; 理化性质; 参数

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The main types of biochar and their properties and expectative researches

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Abstract:【Objectives】Biochar production and application, as an effective low carbon use of by-products of industrial and agricultural production, have been widely recognized by researchers for their effects in soil improvement and crop production. However, the reports on the effects of biochar are discrepant greatly as the different feedstock and parameters in the production process of biochar. Summarizing previous researches will

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provide academic base for the effective use and production of biochar. **【 Major advances 】** 1) The range of the carbon contents in biochar is 30%–90% with an average of 63.84%, and the carbon contents from different raw materials are in order: wood > straw > shell > manure > sludge. The carbon contents of straw biochar are mainly in 40%–80%, and those of wood biochar are mainly in 60%–85%. The range of biochar ash is 0–40% with an average of 15.52%, and the contents are in order: sludge > manure > straw > shell > wood. The ash contents of straw biochar are generally in 20%–35%, and those of wood biochar are mainly in 0–10%. The correlation coefficient between the carbon contents and the ash contents is -0.77, the correlation coefficients between the pyrolysis temperature and the carbon contents and the ash contents are 0.17 and 0.28 respectively. Adding biochar could improve soil properties. Biochar ash content usually plays a significant role on nutrient supplement of poor and sandy soil. 2) The range of specific surface area is 0–520 m²/g with an average of 124.83 m²/g, and the contents are in order: shell > straw > wood > manure > sludge. The specific surface area of straw biochar is generally in 0–200 m²/g and that of wood biochar is generally in 0–100 m²/g. The correlation coefficient between the pyrolysis temperature and the specific surface area is 0.48. The pore structure of biochar could reduce soil bulk density, soil density, and remove heavy metals in solution and soils. 3) The pH of biochar is in range of 5–12 with an average of 9.15, and in order: straw > sludge > manure > wood > shell. pH of straw biochar is generally in 8–11 and pH of wood biochar has an uniform distribution. The range of CEC is 0–500 cmol/kg with an average of 71.91 cmol/kg. CEC of straw biochar is generally in 0–100 cmol/kg and CEC of wood biochar is generally in 5–10 and 15–25 cmol/kg. The correlation coefficients between the pyrolysis temperature and pH and CEC are respectively 0.58 and 0.30. The biochar could reduce soil proton, improve pH and nutrient availability of acidic soil; biochar also gets the ability of ion exchange adsorption, improves the cation and anion exchange capacity, increase ability to protect fertilizer. 4) All the biochar were prepared at the pyrolysis temperature of 200 °C–800 °C, occasionally at 1000 °C. **【 Suggestions and expectations 】** The production and application of biochar are still in the initial stage in the world. Some researches should be considered in the future. Firstly, the differences in beneficial effects of biochar related manufacture parameters and raw materials should be systematically studied and a database should be setup accordingly; the suitable type of biochar should be made clear according to the expected target and the soil properties, to achieve the highest profit of biochar. More work is also needed for the selection and combination of biochar from different material sources, so to produce multiple functional products to meet the requirement of practical use.

Key words: biochar; property; parameter

生物炭 (Biochar) 是利用生物残体在缺氧的情况下, 经高温慢热解(通常 < 700 °C) 产生的一类难溶的、稳定的、高度芳香化的、富含碳素的固态物^[1]。生物炭多为颗粒细、质地较轻的黑色蓬松状固态物质, 主要组成元素为碳、氢、氧、氮等, 含碳量多在 70% 以上。生物炭可溶性极低, 具有高度羧酸酯化和芳香化结构^[2-3], 其原料来源广泛, 农业废弃物如鸡粪、猪粪、木屑、秸秆以及工业有机废弃物、城市污泥等都可作为其原料^[4]。生物炭原材料尺寸的大小会影响到生物炭产率, 主要表现为尺寸增大生物炭产量随之增加。

生物炭自从被发现之日起, 就以其改良土壤、提高作物产量等众多优点引起科学家的关注。黄超

等^[5]利用盆栽试验, 在肥力较差土壤上施用含碳量为 63.4% 的小麦秸秆生物炭, 施用生物炭量为 10、50 和 200 g/kg 的黑麦草产量分别比对照增加了 7%、27% 和 53%; 句芒芒等^[6]施用碳质量分数为 47.17% 的花生壳生物炭进行盆栽试验, 番茄产量高达 92746 kg/hm²; Luo 等采用田间试验研究发现, 施入碳含量为 67.69% 的稻秆生物炭可以增加玉米干物质量^[7]。生物炭灰分含有一定量的矿质养分, 污泥、畜禽粪便生物炭比木质、秸秆和壳类生物炭含量更高, 可以补充养分贫瘠土壤及沙质土壤的一些养分供应。陈心想等^[8]研究发现, 施用木质生物炭显著提高了新积土有效磷、钾含量。生物炭灰分量与生物炭 pH 值关系密切, 碱性灰分物质高的生物炭 pH 值较高。高

海英等^[9]发现,竹炭灰分含量、矿质养分元素种类和含量均高于木炭,所以pH值也高于木炭。

生物炭的理化参数主要包括:全碳含量、灰分含量、挥发成分含量、表面元素组成及表面官能团种类和含量、表面负电荷含量等;结构表征主要包括:表面形态和孔隙结构(如比表面积、孔容积和孔径分布等)。由于原材料、技术工艺及热解条件等差异,生物炭在结构、挥发成分含量、灰分含量、孔容、比表面积等理化性质上表现出非常广泛的多样性,进而使其拥有不同的环境效应^[10]。目前,国内学者就生物炭的特性^[11-12]、环境行为和效应^[13-14]、土壤性状和产量^[15-16]、碳截留与温室气体减排^[17-18]及其对全球生物地球化学循环影响等领域^[19-20]已开展了大量研究,但仍然没有针对性地开展生物炭理化参数的总结及归纳工作,本文主要针对生物炭的一些重要和常见参数进行归类总结与研究,试图对这些性状的参数范围有更清晰的认识。

Lehmann 和 Joseph 在其专著《Biochar for Environmental Management》中,将碳组分、灰分、比表面积、pH值、CEC(Cation exchange capacity)、有机碳、孔隙度等几大性状作为生物炭分类的指标和依据^[21]。本文参考此专著,选择碳组分、灰组分、比表面积、pH值、阳离子交换量CEC几大性状为分析探讨的对象,另外将裂解温度也考虑在内,试图从他人的研究中总结出一些规律,对已有研究进行梳理,对今后的生物炭研究及其生产实践进行指导。

1 全碳组分和灰组分

1.1 不同原料对全碳组分和灰组分的影响

生物炭的主要组成一般包括全碳、挥发物、矿物和水分^[22]。生物炭的全碳组分组成是异质的,包含易降解的脂肪碳组分和稳定的芳香碳组分^[23-24]。原料和制备条件的多样性导致其各组分含量的差异^[25]。生物炭各组分的相对比例决定了生物炭的物理化学行为和功用,从而决定了其用途的适宜性以及在环境中的迁移和转化^[26-27]。

生物炭的组成元素主要为碳、氢、氧等,而且以高度富含碳(约70%~80%)为主要标志,灰分也是生物炭的重要组成部分。Balwant等^[28]的研究表明,生物炭的全碳含量在16.5%~83.6%范围内,灰分含量在3.2%~76.2%范围内;Spokas^[24]研究表明,木质和秸秆生物炭的全碳含量在38.3%~53.0%范围内,而煤和其他化石燃料生物炭的碳含量高达98.4%。

生物炭自身的高含碳量可引起生物炭施用到土壤中后C/N显著增高,生物炭中灰分含有更多的盐基离子,可以增大土壤的pH值。通过文献总结,对研究中生物炭的碳组分和灰组分数据进行归纳整理,见表1。

如表1所示,不同原料的生物炭其全碳组分和灰组分不同,原材料的种类会影响生物炭的碳组分和灰分。对119份生物炭全碳含量进行分析,其范围大多在30~90%之间,平均63.84%,其中秸秆样本数为41个、壳类14个、木质42个、粪污9个、污泥2个,其他类11个。以碳含量中值进行比较,碳含量由大到小分别是木质、秸秆、壳类、粪污和污泥(图1)。由于原材料性质、裂解工艺、设备、温度和裂解时长以及其他多种复杂不可控客观条件的影响,同一种原料的碳和灰分含量也不同,需要根据生物炭原料性质、生产各环节参数具体分析。

对不同原料生物炭碳组分进行频度分析[图2]。结果表明,秸秆生物炭全碳含量在40%~80%范围内分布较多;木质生物炭在60%~85%范围内分布较广。

选取总共82个生物炭数据(包括秸秆生物炭20个、壳类5个、木质42个、粪污10个、污泥1个及其他类4个)进行灰分含量分析,大多数生物炭灰分含量在0~40%之间变动,平均值为15.52%,只有污泥生物炭灰分含量达到80%以上。5类生物炭灰分含量由大到小分别是污泥、粪污、秸秆、壳类和木质(图3)。

选取秸秆和木质生物炭进行灰分频度分析[图4]。结果显示,秸秆生物炭灰分含量多在20%至35%,少量低于15%;木质碳灰分在0~10%范围内分布较多,与木质生物炭含碳量高有关。

1.2 不同裂解温度对全碳组分和灰组分的影响

生物炭的含碳量随炭化温度的不同而发生改变,生物炭性质也受到制备温度、加热速率、通气条件等条件的影响,以温度影响较大。随制备温度的升高,生物炭产量下降,但其碳含量、灰分含量、比表面积以及孔隙度却随着温度的升高而升高。

裂解温度与生物炭碳、灰分含量呈显著正相关,相关系数分别为0.17和0.28。随着裂解温度的升高,生物炭碳含量和灰分含量都增大。生物炭碳含量和灰分含量呈极显著负相关,相关系数为-0.77。因为热裂解温度增高,易热解含碳化合物残留降低,生物炭中难分解碳物质比例相应增高,固定碳含量增大,继而碳含量增多。热裂解温度升高,有机物损失增大,灰分在生物炭中含量相应增大,由

表 1 生物炭全碳组分和灰组分分析表
Table 1 Carbon and ash contents of biochar

种类 Type	原料类型 Feedstock	温度 Temperature	碳含量 (%) C content	灰组分 Ash content (%)
秸秆 Straw	玉米秸秆 Corn straw ^[1, 7, 14, 24, 29-33]	250~700	51.8~78.1	5.4~37.3
	小麦秸秆 Wheat straw ^[5, 7, 34-39]	300~600	60.12~74.46	—
	稻秆炭 Rice straw ^[7, 40-44]	250~600	38.39~71.86	23.13~30.1
	秸秆 Straw ^[45-47]	350~500	57.2~65.7	28.6~33.2
	水稻糠 Rice bran ^[48]	—	51.06	27.6
	再力花等 Hardy canna etc ^[49]	600	69.33~82.15	—
	玉米芯 Corn cob ^[50]	350~400	63.9~71.4	2.9~3.8
	作物秸秆 Straw ^[51]	240~360	65.0	—
	芦苇 Reed ^[49, 52]	550	69.33~96.10	—
	棉秆 Cotton ^[7, 53]	575	68.33~78.01	—
壳类 Shell	花生壳 Peanut shell ^[6, 37, 50, 54-56]	300~600	45.2~68.19	3.2~28.6
	榛子壳 Hazelnut shell ^[57]	370~620	78.3~92	2.3~2.5
木质 Wood	木质 Wood ^[8-9, 33, 48-50, 57-63]	250~620	52.7~92.1	0.011~15.4
	竹炭 Bamboo charcoal ^[9, 40, 48, 64]	—, 350	62.61~86.9	19.71
粪污 manure	鸡粪 Fowl dung ^[59, 65]	400~750	38.56~50.03	33.87~53.88
	猪粪 Pig manure ^[33, 66]	250~700	25.2~44.30	29.5~66.8
	家畜粪便 Livestock manure ^[7]	500	65.43	—
	牛粪 Cow dung ^[45]	350	—	68.6
	污泥 Sludge ^[67-68]	—, 500	8.15~8.16	84, —
其他 Others	其他类 Others ^[31, 34, 49-50, 55, 69-72]	300~600	31.7~82.15	7.54~20.8

注 (Note) : “—”表示没有数据 NO data.

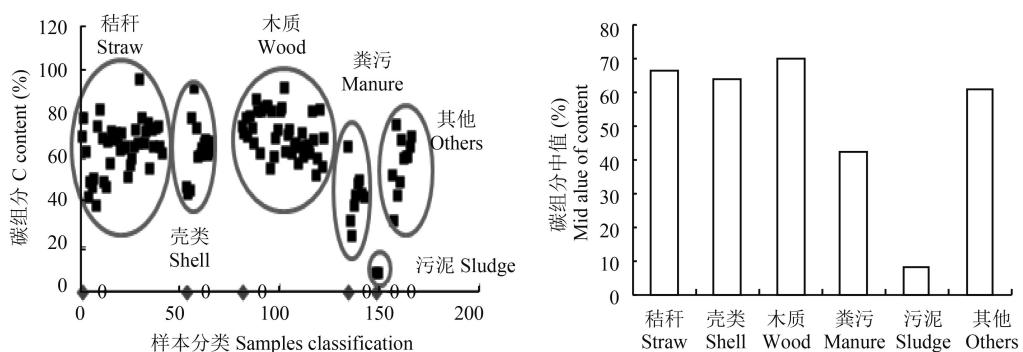


图 1 不同原料生物炭碳含量分布与中值 ($n = 119$)
Fig. 1 Carbon contents and mid values of biochar from different sources

于灰分是碱性物质, 生物炭 pH 因生物质热解温度增高而提高。生物炭碳含量高意味着被氧化为无机灰分的部分减少, 反之亦然。

1.3 碳组分和灰分含量对土壤的影响

施用生物炭可以增加土壤碳素含量, 提高土壤

碳氮比, 改善土壤养分供应状况。黄超等^[5]在肥力较差土壤上施用含碳量为 63.4% 的小麦秸秆生物炭, 施用生物质炭量为 10、50 和 200 g/kg 的盆栽黑麦草产量分别比对照增加了 7%、27% 和 53%; 句芒芒等^[6]施用碳质量分数为 47.17% 的花生壳生物炭, 盆

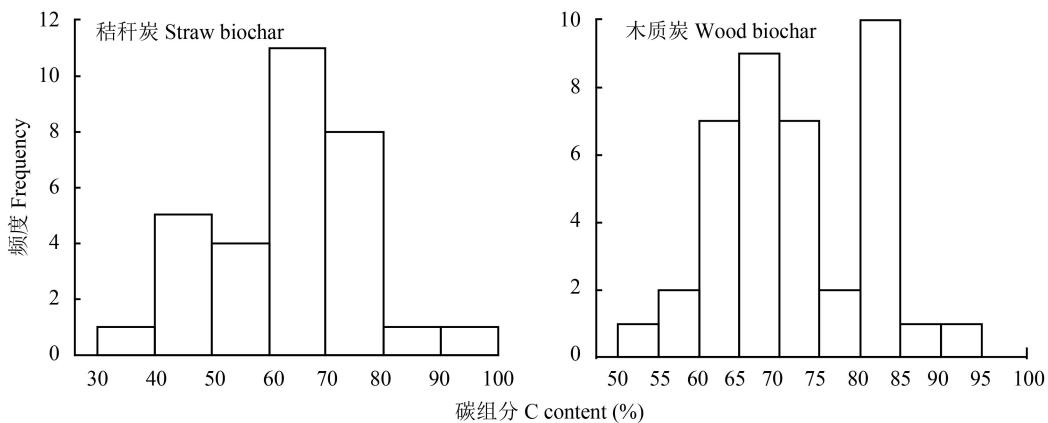


图 2 稻秆和木质生物炭碳组分分布频度

Fig. 2 Frequency of the C contents in straw and wood biochar

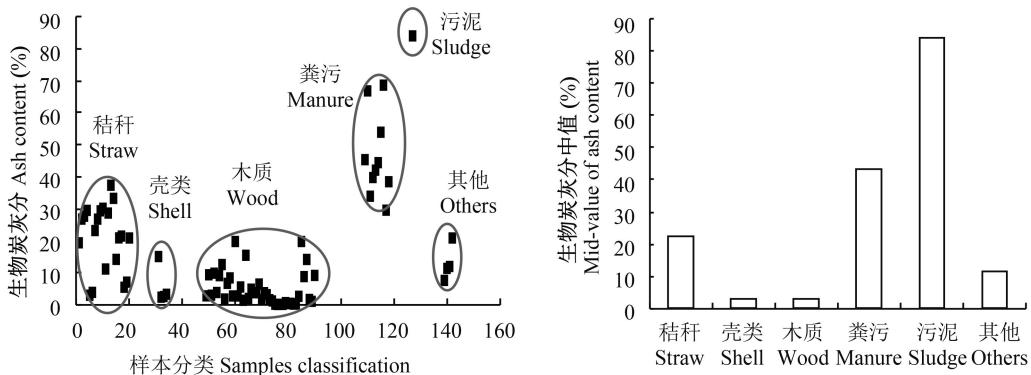
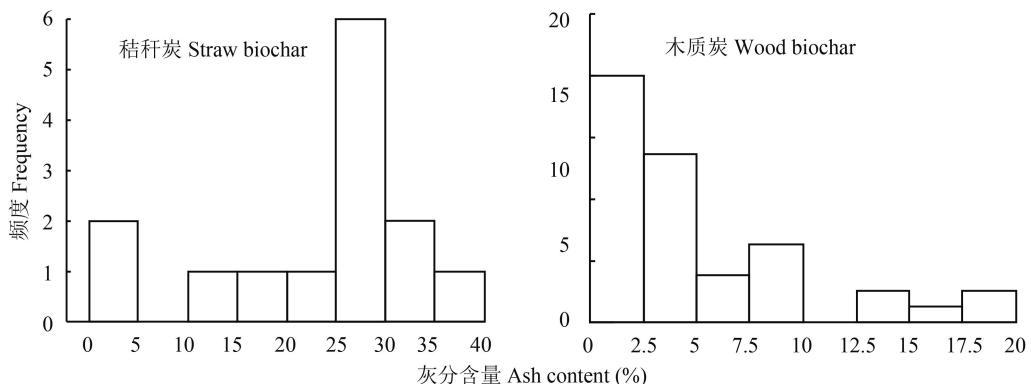
图 3 不同来源生物炭灰分含量分布与中值 ($n = 82$)Fig. 3 Ash contents and mid values of biochar from different sources ($n = 82$)

图 4 稻秆和木质生物炭灰分频度

Fig. 4 Frequency of the ash contents in straw and wood biochar

栽番茄产量高达 $92746 \text{ kg}/\text{hm}^2$; Luo 等研究施入碳含量为 67.69% 的稻秆生物炭发现, 可以增加玉米干物质量^[7]。

生物炭灰分含有一定量的矿质养分, 污泥、畜禽粪便生物炭比木质、秸秆和壳类生物炭含量更高, 可以补充养分贫瘠土壤及沙质土壤的一些养分

供应。生物炭灰分量与生物炭 pH 值关系密切, 碱性灰分物质高的生物炭 pH 值较高。高海英等^[9]发现, 竹炭灰分含量明显高于木炭, 矿质养分元素种类和含量也均高于木炭, 所以竹炭 pH 值高于木炭。陈心想等^[8]研究发现, 施用木质生物炭显著提高了新积土有效磷、钾含量。

2 比表面积

2.1 不同原材料对比表面积的影响

热解过程中, 生物质原料的结构基本印记在了生物炭中, 对生物炭的物理化学性质具有决定性影响^[73-75]。生物质热解过程中, 质量损失(大部分以挥发有机物的形式)及不相称的收缩或体积减少的发生, 导致矿物及碳骨架形成, 并且保留了原料的基本孔隙和结构特征^[76]。生物炭的孔一般按直径大小分为大孔($ID > 50 \text{ nm}$)、中孔($2 \text{ nm} < ID < 50 \text{ nm}$)和微孔($ID < 2 \text{ nm}$)^[75]。生物炭中保留的植物生物质原料的蜂窝状结构构成了其主要的大孔。微孔主要由热解过程中碳的损失及碳架的断裂收缩形成。虽然大孔可能会作为微孔的前体, 但是微孔贡献了生物炭的大部分比表面积, 微孔的含量与比表面积呈正相关^[77]。

生物炭的多孔性和低密度性, 可改善土壤通气状况, 降低厌氧程度。生物炭的大比表面等特性, 可以使其具有强的吸附和固定重金属能力^[78]、成为土壤微生物栖息的良好环境^[79]、提高土壤对氮素及其他

养分元素吸持容量等^[80]。对不同材料的生物炭比表面积进行分析, 得到表2。

不同材料, 不同裂解方式对生物炭的比表面积影响很大, 有的只有 $0.7\sim 15 \text{ m}^2/\text{g}$ ^[75], 有的可高达几百个 m^2/g ^[97], 本研究中生物炭比表面积参数范围与其研究类似, 生物炭比表面积的变化范围绝大多数在0到 $520 \text{ m}^2/\text{g}$ 之间, 平均为 $124.83 \text{ m}^2/\text{g}$; 另外, 几类生物炭中, 壳类生物炭比表面积中值比其他几类都大, 其他依次为粪污、秸秆、木质和污泥, 如图5。其中, 秸秆生物炭样品36个、壳类11个、木质17个、粪污10个、污泥10个、其他类9个, 总共93个样品。

生物炭本来就具有多孔隙的性质, 数量庞大的微孔隙导致生物炭巨大的表面积。因为裂解温度、原材料种类等因素的变化, 致使生物炭的微孔隙数量变化, 以至于生物炭比表面积的巨大差距。

对部分种类生物炭的比表面积数据进行频度分析(图6)。结果显示, 秸秆炭比表面积集中在 $0\sim 200 \text{ m}^2/\text{g}$ 以内, 木质炭比表面积集中在 $0\sim 100 \text{ m}^2/\text{g}$ 以内。

表2 生物炭比表面积
Table 2 Specific surface area of biochar

种类 Type	原料类型 Feedstock	裂解温度(°C) Pyrolysis temperature	比表面积(m^2/g) Specific surface area
秸秆 Straw	玉米秸秆 Corn straw ^[1, 29-30, 33, 81-83]	350~825	7.72~449.7
	稻秆 Rice straw ^[40, 43, 74, 82-85]	300~700	7.74~123.60
	稻壳 Rice shell ^[42, 83, 86]	—, 500	3.58~504.3
	小麦秸秆 Wheat straw ^[36, 37, 87-89]	300~600	8.73~1279
	棉秆 Cotton straw ^[53, 78]	550~600	64.32
	秸秆 Straw ^[46]	500	33.2
	米糠等 Rice bran ^[82]	700	73.4~255.65
	玉米芯 Corn cob ^[50]	350~400	0.1
	甘蔗叶 Sugarcane top ^[90]	500	197.48
壳类 Shell	花生壳 peanut shell ^[37, 50, 54-55, 74]	300~600	1~353.2
木质 Wood	竹炭 Bamboo charcoal ^[40, 91]	—, 1000	189.6~517.28
	雷竹落叶 Bamboo leaves ^[92]	300~550	8.87~87.09
	木质 Hard wood ^[33, 50, 61, 82, 86, 93]	250~700	0.28~391.12
粪污 Faeces	猪粪 Pig manure ^[33, 66, 94]	250~700	5.721~166.9
	鸡粪 Fowl dung ^[65]	500~750	48.79~246.17
	蚕沙 Silkworm excrement ^[90]	500	9.80
污泥 Sludge	污泥 Sludge ^[67-68, 95-96]	300~700	14.28~297.5
其他 Others	其他 Others ^[50, 70-71]	350~500	0.28~68.7

注 (Note) : “—”表示没有数据 NO data.

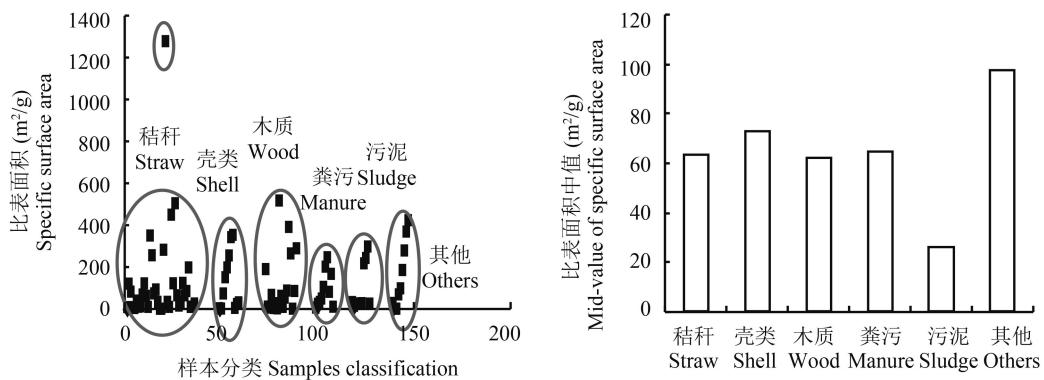
图 5 生物炭比表面积范围示意图 ($n = 93$)

Fig. 5 Specific surface area of biochar

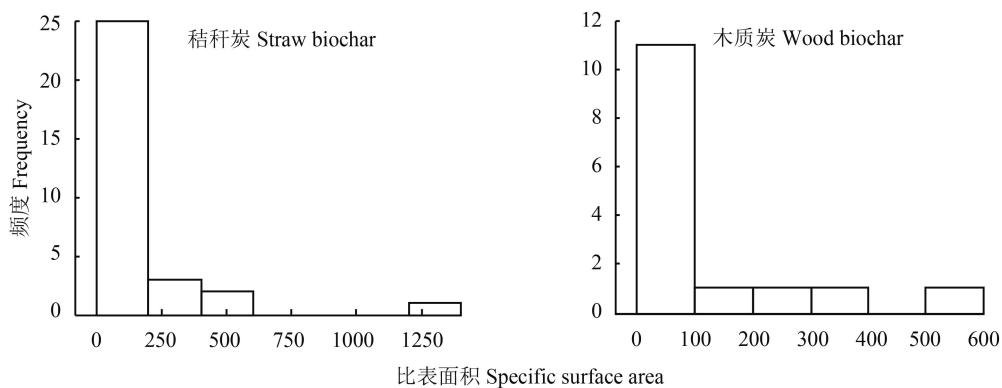


图 6 生物炭比表面积范围频度分析

Fig. 6 Frequency of specific surface area

2.2 裂解温度对生物炭比表面积的影响

研究表明制备温度对生物炭的吸附有很大的影响, 因为随着制备温度的升高生物炭的比表面积增大, 碳含量增加而氧含量降低, O/C 降低, 生物炭的亲水性和极性降低, 对水分子的亲和力降低, 对疏水性污染物的吸附增强。因此表现为比表面积越大吸附作用越强。

本研究将裂解温度与生物炭比表面积的相关性进行了分析, 发现它们呈显著正相关, 相关系数为 0.48, 即裂解温度的升高可以增加生物炭孔隙度和比表面积, 这与之前的研究结论一致。这是因为温度升高, 孔结构及复杂性降低, 导致比表面积增大。

2.3 比表面积对土壤的影响

生物炭具有高的吸附能力。生物炭的孔隙结构能降低土壤容重、降低土壤密度, 生物炭具有较大的比表面积和较高表面能, 有结合重金属离子的强烈倾向, 因此能够较好地去除溶液和钝化土壤中的重金属。李力等^[1]的镉去除实验中 BC350 和 BC700 两种玉米生物炭的比表面积分别为 $7.72 \text{ m}^2/\text{g}$ 和 $120 \text{ m}^2/\text{g}$ 。

m^2/g , 结果显示 BC700 对 Cd (II) 的吸附容量大于 BC350, 解吸率远小于 BC350, 吸附效果更好; 刘玉学等^[40]研究比表面积为 $81.8 \text{ m}^2/\text{g}$ 、总孔容积为 $0.080 \text{ cm}^3/\text{g}$ 的稻秆炭和比表面积 $189.6 \text{ m}^2/\text{g}$ 、总孔容积为 $0.175 \text{ cm}^3/\text{g}$ 的竹炭对小青菜及其土壤的影响, 结果显示生物炭的施入能显著降低土壤容重。

3 pH 和 CEC

3.1 不同原材料对 pH 值和 CEC 的影响

生物炭的 pH 一般呈碱性, Balwant 等研究发现, 生物炭 pH 介于 $6.93\sim10.26$ 范围之间^[28], 也有研究报道可以制备 pH 介于 $4\sim12$ 之间的生物炭^[98]。生物炭中无机矿物是造成生物炭 pH 偏碱的主要原因^[98-99], 生物炭的表面含氧官能团(如羧基和羟基)也可能对生物炭的 pH 有一定的贡献。阳离子交换量(CEC)是反映生物炭表面负电荷的参数, 也决定其在土壤中保留铵、钙和钾等阳离子的能力^[26], 生物炭 CEC 与其表面含氧官能团含量正相关^[100]。现有报道中生物炭的 CEC 差异很大, 介于 71 mmol/kg ^[101] 和 34 cmol/kg ^[100-102]。

之间, Balwant 等认为生物炭的 CEC 介于 71.0~451.5 mmol/kg 范围之间^[28]。

本研究中生物炭 pH 值及 CEC 信息如表 3。对表中生物炭 pH 值信息进行分析得到图 7。由图 7 可以看出, 整体上看无论是什么材料的生物炭、裂解温度为多少, 生物炭 pH 值范围在 5~12 的范围, 平均为 9.15。收集到的 pH 值数据共有 86 个, 其中秸

秆 41 个、壳类 7 个、木质 25 个、粪污 4 个、污泥 3 个, 其他类 6 个, 颗粒、污泥、粪污、木质、壳类生物炭 pH 值中值依次递减。

分析颗粒和木质类生物炭的 pH 值分布频数, 得到图 8。结果表明颗粒生物炭 pH 值多集中在 8~11 范围内; 木质生物炭的 pH 分布范围比较广且比较均匀, 在 5~11 范围内均有一定数量的分布。

表 3 生物炭裂解温度、pH 值与 CEC
Table 3 Pyrolysis temperature, pH and CEC of biochar

种类 Type	原料类型 feedstock	温度 T (°C)	pH	CEC (cmol/kg)
秸秆 Straw	玉米秸秆 Corn straw ^[1, 30-31, 83, 103]	350~825	6.75~10.73	—
	小麦秸秆 Wheat straw ^[5, 34-36, 38, 88-89, 104-107]	350~550	7.85~10.5	9.74~21.7
	稻秆 Corn straw ^[13, 44, 74, 83, 85, 108-111]	4500~700	7.78~11.30	44.7~316.88
	水稻糠 Rice bran ^[48]	—	9.45	—
	秸秆 Straw ^[45-46]	350~500	8.72~10.5	95.5, —
	棉秆 Cotton stalk ^[53, 112]	450~575	10.24~10.48	12.65, —
	大豆秸秆等 Soybean straw etc ^[98, 108, 113]	—, 400	9.1, —	229.49~483.35
	油菜秸秆炭等 Rape straw etc ^[31, 108, 113]	—	8.5~10.7	—, 483.35
	再力花等 Hardy canna etc ^[49]	500	10.2~10.39	21.07~31.23
	甘蔗渣 Bagasse ^[114]	550	8.4	3.5
	甘蔗叶 Sugarcane top ^[90]	500	9.44	27.85
壳类 Shell	花生壳 Peanut shell ^[6, 56, 74, 108, 115-116]	350~450	7.94~9.12	—
木质 Wood	竹炭 Bamboo charcoal ^[40, 64, 109-110]	350~600	9.8~10.05	15.3~17.20
	木质 Wood ^[8, 48-49, 58]	300~900	5.26~10.77	6.63~23.47
粪污 Manure	猪粪 Pig manure ^[66]	350~700	8.3~9.5	—
	牛粪 Cow dung ^[45]	350	9.13	—
	蚕沙 Silkworm excrement ^[90]	500	10.40	71.59
污泥 Sludge	污泥 Sludge ^[67, 96, 117]	—	9.43~9.54	2.36~39.88
其他 Others	其他 Others ^[69, 71, 114, 118-122]	450~550	8.81~10.09	0.8~41

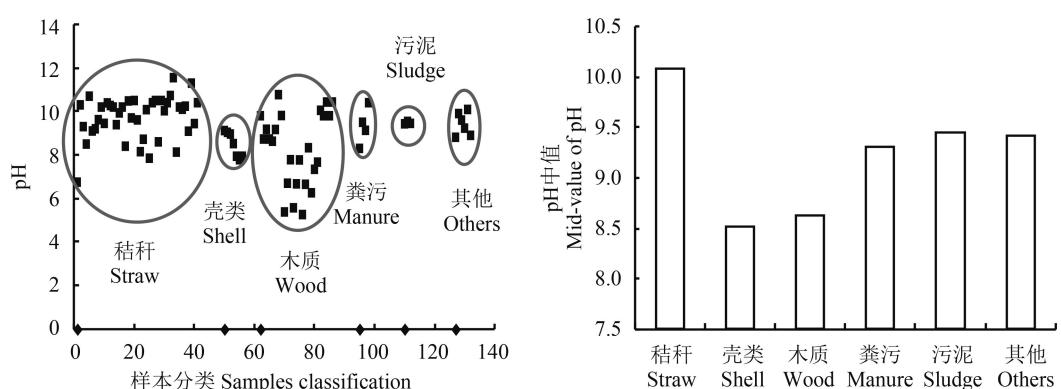


图 7 生物炭 pH 值范围分析 (n = 86)
Fig. 7 pH of biochar from different material

对生物炭的 CEC 进行分析得到图 9, 分析表明生物炭的 CEC 变化范围范围比较大, 从 0 到 500 cmol/kg 都有分布, 平均为 71.91 cmol/kg。分析数据中秸秆炭 17 个、壳类 1 个、木质 7 个、粪污 1 个、污泥 2 个, 其他类 5 个, 总共 33 个。CEC 的变化范围比较大, 这与生物炭原材料和裂解温度等因素有关。

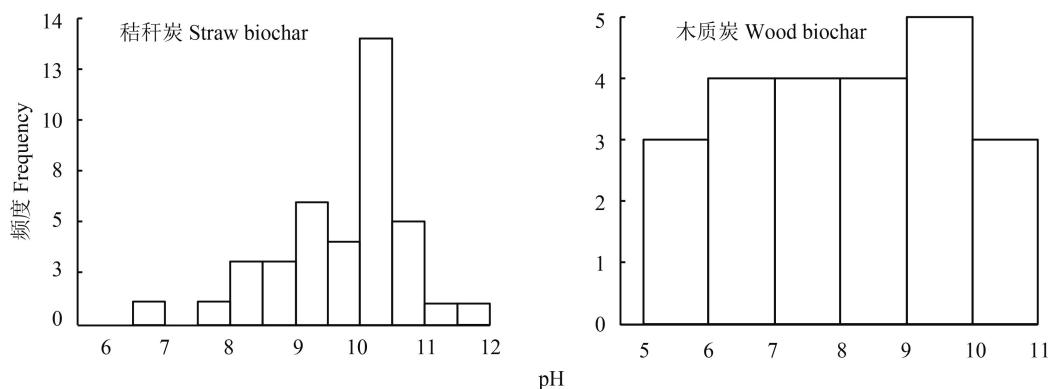


图 8 生物炭 pH 值频度分析
Fig. 8 pH frequency of biochar

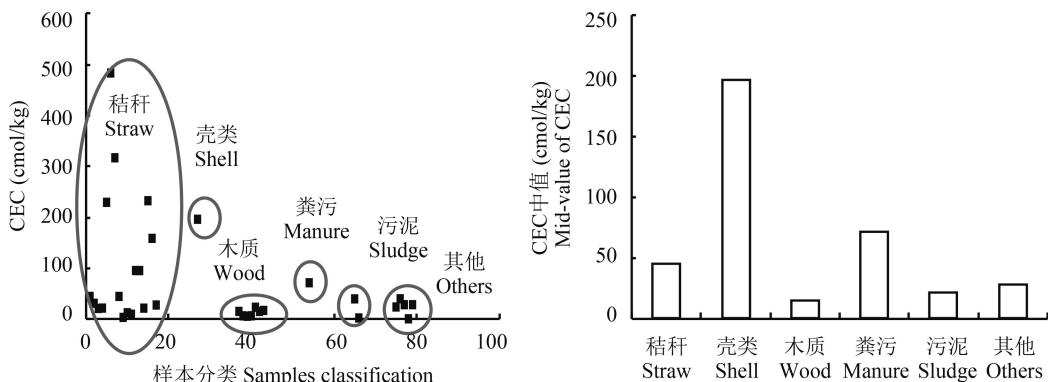


图 9 生物炭 CEC 范围分析 ($n=33$)
Fig. 9 CEC of biochar from different materials

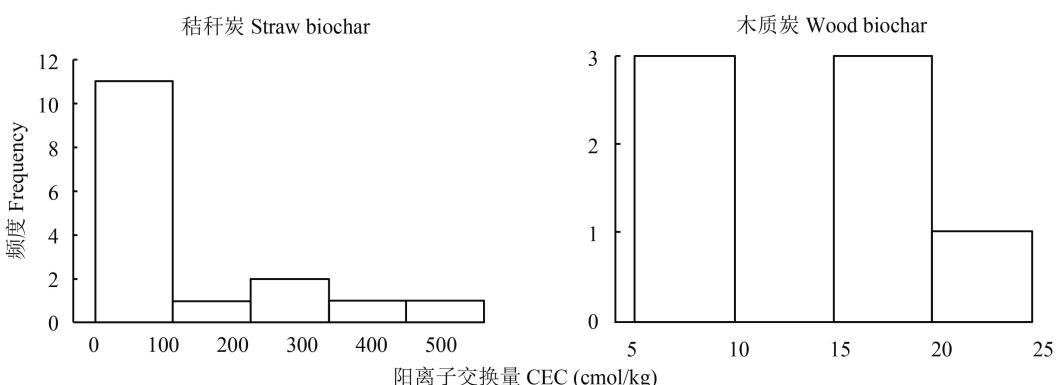


图 10 生物炭 CEC 频度分析
Fig. 10 CEC frequency of biochar

分析秸秆和木质类生物炭的 CEC 分布频数(图 10), 结果表明秸秆生物炭 CEC 值大多集中在 0~100 cmol/kg 范围内; 木质生物炭的 CEC 分布范围在 5~10 与 15~25 cmol/kg 范围内均有一定数量的分布。

3.2 不同裂解温度对 pH 值和 CEC 的影响

高温热裂解的生物炭比低温热裂解的生物炭中

具有更少的酸性挥发物及更多的灰分, 因而 pH 更高。CEC 与生物炭 O/C 比相关, 热解温度较低时纤维素分解不完全, 含氧官能团如羟基、羧基和羰基被保留, 生物炭具有更高的 O/C 比和较大的 CEC。

本研究表明, 裂解温度与 pH 值和 CEC 的相关系数为 0.58 和 0.30。即随着裂解温度的升高, 生物炭的 pH 值增加, 这是因为裂解温度增加了生物炭的灰分含量; 裂解温度与生物炭 CEC 呈正相关, 这可能是由于过高的裂解温度增加了生物炭的灰分, 进而增大了生物炭的 CEC。另外, 对 pH 值和 CEC 的相关性进行了分析, 结果显示 pH 值和 CEC 呈显著正相关, 相关系数为 0.26。生物炭呈碱性, 能够明显提高土壤 pH, 改变土壤质地, 增大盐基交换量, 从而引起土壤 CEC 增加, 影响植物对营养元素的吸收效果^[79, 123]。

3.3 pH 值和 CEC 对土壤的影响

生物炭大多呈碱性, 或者具有较大石灰当量值, 可以作为石灰替代物, 生物炭含大量的有机官能团 (-COO-、-COOH、-O-、-OH 等), 能够吸收土壤中的 H⁺, 而其灰分含有的钙、镁、钾、钠等盐基离子可以交换土壤中吸附的氢离子及交换性铝离子, 降低土壤中其含量^[124]。因此, 可改良酸性土壤一些养分的有效性。黄超等^[5]运用 pH 值为 9.2 的小麦秸秆生物炭研究其对红壤的影响, 结果表明红壤施用生物质炭不仅大大提高了土壤碳库, 还可降低土壤酸度, 增加土壤 pH 值; 何飞飞等^[74]研究 pH 值分别为 9.62 和 8.96、BET 比表面积分别为 7.74 m²/g 和 2.45 m²/g 的水稻秸秆炭和花生壳炭对红壤菜田土理化性质的影响, 结果显示蕹菜收获后, 土壤 pH 值、CEC 值和持水量 (WHC) 随生物炭用量增加而升高。

生物炭具有离子吸附交换能力及一定吸附容量, 其可改善土壤的阳离子或阴离子交换量, 从而可提高土壤的保肥能力。生物炭对土壤阳离子交换量 CEC 或保肥能力的改善取决于生物炭的 CEC, pH 及生物炭在土壤中氧化。生物炭比表面积大, 可以增强土壤对阳离子的吸附能力, 增加耕层土壤 CEC。生物炭对低 CEC 和 pH 的酸性土壤中的 CEC 改良特别有效, 其中土壤 CEC 的改良与生物炭的原料的碱度、有机氮的矿化和铵根的硝化作用有关^[125]。生物炭的 pH 升高, 其对重金属离子的吸附和固定加强, 说明了生物炭对重金属的吸附与生物炭的表面官能团和 pH 值有关^[124, 126]。

4 问题与展望

在查阅的 100 多篇文献中, 分别得到碳组分、灰分、比表面积、pH 值和 CEC 几种参数数据 119、82、93、86、33 个, 反映出目前生物炭理化特性研究者对这几大参数重视程度不一, 这与裂解材料的来源、实验成本、实验复杂性以及研究方向有直接关系。另外, 在裂解温度方面, Balwant 等的研究认为生物炭裂解温度在 100℃ 至 900℃ 范围内^[28]; 本研究表明, 生物炭的裂解温度大都集中在 200℃ 至 800℃ 之间, 偶有达到 1000℃ 的裂解温度。

生物炭的研究是最近几年才出现在人们视野中的新兴研究领域, 虽然国内外专家学者已经做了大量关于生物炭原材料、性状、对土壤效应以及作用机理等多方面的研究, 但是全世界范围内对生物炭的生产和使用还处于就近和来源方便的初级阶段, 影响着生物炭功能和效益的最大化。从生物炭的裂解原料、裂解工艺、裂解设备, 及生物炭对土壤、作物、重金属、有机污染物及碳循环等的作用效果, 再到生物炭作用机理的整个产业链的研究(甚至各个环节相互影响的研究), 都还只是比较分散、零散的研究堆积, 并没有形成系统的、全面的生物炭研究体系, 对生物炭的生产、应用还没有成熟理论的指导, 尤其是生物炭理化性状参数的研究。生物炭的理化性质直接反映其原材料、生产水平和后端应用等。比如目前还没有非常详实和确定的论据来证明生物炭的何种性状对土壤或者作物的何种效应作用最大, 对于生物炭的理化参数最优范围仍然没有确定值, 比如生物炭灰分能增加土壤 pH 值, 究竟何种类型生物炭含有多少灰分能在多大程度上增加 pH 值? 玉米秸秆生物炭比表面积为多少时可以吸附 Cd 的量为多少等等。另外, 不同生物炭的应用还处于探索阶段, 功效不能有效发挥。并且应用研究大多针对单一类型生物炭, 缺乏不同原料生物炭的选配和组合研究。综上所述, 未来应从以下几个方面加强研究和应用试验。首先, 系统研究生物炭制造参数对理化性状的影响, 研究不同原料生物炭的作用机理差异及其针对性, 建立生物炭理化性质参数数据库, 生物炭理化性质参数数据库的建立十分必要, 这对于生物炭详细参数的研究和相关标准的制定具有指导意义, 需要广大专家学者一同努力; 其次, 加强应用研究, 根据土壤理化性状和改良目标选择适宜的生物炭类型, 根据对作物经济性状的要求, 研究选择适宜的生物炭类型, 实现生物炭功效的最大利用。再次, 加强不同原料的选配和组合研究, 改良生物炭产品的目标性状, 形成系列化产品。

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