A new 3D conceptual structure modeling of biochars by molecular mechanic and molecular dynamic simulation

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Received: 25 July 2015 / Accepted: 16 November 2015 / Published online: 26 November 2015
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Abstract

Purpose The combination of analytical chemistry and simulation methods provides more complete information about biochars.

Materials and methods The biochars prepared by pyrolysis of the crop straw at 300 and 500 °C were investigated by elemental analysis, pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS) and solid-state ¹³C nuclear magnetic resonance (NMR) spectrometry to build the 2D structural models of biochars. The most stable and balanced 3D conformations were gained by optimizing in the optimized potential for liquid simulation (OPLS) force field of molecular mechanic and molecular dynamic simulation of HyperChem® software.

Results and discussion There were few O-containing and N-containing compounds in biochars. According to the results of Py-GC-MS, 41 and 28 pyrolysis products were identified for the building of the conceptual models of 300 and 500 °C biochars. Solid-state ¹³C NMR data also demonstrated that there were very high values of unsaturated C in biochars. The agreement between elemental concentration and chemical

functional groups of two simulated models and experimental biochars was successfully achieved. Quantitative structure activity relationship (QSAR) properties were calculated and indicated the correlation of molecular structures with properties such as surface area, volume, polarizability, refractivity, and hydration energy.

Conclusions The conceptual structural models of corn straw biochars produced at 300 and 500 °C were C₇₈H₆₈N₂O₂₅ and C₅₉H₂₉NO₁₀, respectively. The simulation results showed that the 3D structure of the 300 °C biochar with −4 charges and the nonprotonated 3D structure of the 500 °C biochar were the most stable. Deprotonation reaction is an endothermic process.

Keywords ¹³C nuclear magnetic resonance · 3D structure · Biochar · Conceptual model · Elemental concentration · Pyrolysis-gas chromatography-mass spectrometry · Molecular simulation · Optimized potential for liquid simulation force field

1 Introduction

Powerful simulation software for modern quantum chemistry has become a powerful tool for developing model structures of organomineral and macromolecular complexes. Biochar is one of the research hotspots, and in essence, it is a kind of activated carbon. It refers to the carbon-rich residues which come from the incomplete thermal decomposition of biomass (Chen et al. 2008), and its main functional groups are aromatic and heterocyclic carbons. It shows strong potentials in soil remediation (Glaser et al. 2002), carbon sequestration (Day et al. 2004; Elad et al. 2010), crop yield improvement (Asai et al. 2009), soil immobilization (Chen and Chen 2009), etc.

Responsible editor: Yu Luo

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Fig. 1 Total ion chromatogram of pyrolysis products of 300 °C biochar

Schulten (1995) modeled the mineral matrix SiO_4 tetraeders with an elemental composition of $\text{H}_{36}\text{O}_{172}\text{Si}_{77}$ by geometry optimization. This is a meaningful model for the inorganic matrix in natural soils. Schulten (1996) also did a pioneering study of building the 3D structure of humic acid (HA). He used molecular mechanic calculations to develop a 3D structure of HA in the molecular mechanic (MM+) force field. From the results, we can easily investigate the energy differences in the structural configurations. Zhao et al. (2013) combined molecular mechanic and molecular dynamic methods to obtain a balanced 3D structural conformation of alluvial soil HA. Using this method, it was helpful to determine the stability of the 3D structure of HA. The topic is of particular practical interest because molecular simulation methods could provide information about biochars which cannot be obtained with experiments. Molecular simulations were carried out to determine the 3D structures and explore the relationship between biochars' structures and properties, and a reasonable theory to explain the experimental results was produced. To our knowledge, until now, there has been no report about the 3D structures of biochars. In our study, we used elemental analysis and spectroscopic

techniques to analyze the molecular structures of biochars and build the 2D models. The experimental elemental concentrations and chemical functional groups were compared with the simulated ones to confirm the availability of 2D models. This is the first time that molecular simulation methods are used to optimize and simulate the 3D structures of biochars at the molecular level in order to better understand their structures and properties in an interdisciplinary field. At the same time, quantum chemistry offers an economic tool to illustrate the formation of biochar through various physical, chemical, and biological processes.

2 Materials and methods

2.1 Preparation of biochar

Crop straw-derived biochars were obtained by pyrolysis in a furnace at a heating rate of 10 °C/min up to 300 and 500 °C and held for 2 h. The ash contents were measured after calcination at 750 °C for 4 h in a furnace.

Fig. 2 Total ion chromatogram of pyrolysis products of 500 °C biochar

Table 1 Pyrolysis products of the measured 300 °C biochar

Number	Retention time	Pyrolysis product	Molecular formula	Molecular structure
1	4.111	Carbon dioxide	CO ₂
2	4.204	Ammonia	NH ₃	NH ₃
3	4.375	Cyclopentene	C ₅ H ₈
4	4.873	Acetone	C ₃ H ₆ O
5	4.973	1,3-Cyclopentadiene	C ₅ H ₆
6	5.728	3-Methylfuran	C ₈ H ₁₀
7	6.000	Glacial acetic acid	C ₂ H ₄ O ₂	CH ₃ COOH
8	7.253	Benzene	C ₆ H ₆
9	11.767	Toluene	C ₇ H ₈
10	16.825	Ethylbenzene	C ₈ H ₁₀
11	17.202	1,4-Xylene	C ₈ H ₁₀
12	18.667	1,2-Xylene	C ₈ H ₁₀
13	19.211	Phenylethylene	C ₈ H ₈
14	21.789	2-Cyclopenten-1-on e,2-methyl-	C ₆ H ₈ O ₂

Table 1 (continued)

15	23.022	1,3,5-Trimethylbenzene	C ₉ H ₁₂
16	24.361	Phenol	C ₆ H ₆ O
17	24.779	Benzofuran	C ₈ H ₆ O
18	25.077	2,5-Dimethylfuran	C ₇ H ₁₀ O
19	25.780	Benzonitrile	C ₇ H ₅ N
20	26.483	Indene	C ₉ H ₈
21	27.092	m-Cresol	C ₇ H ₈ O
22	27.192	2-Cyclopenten-1-one, 2,3-dimethyl-	C ₇ H ₁₀ O
23	27.934	p-Cresol	C ₇ H ₈ O
24	28.683	4-Methoxyphenol	C ₇ H ₈ O ₂
25	28.803	2-Methylbenzofuran	C ₉ H ₁₀ O
26	30.009	1H-Indene, 1-methyl-	C ₁₀ H ₁₀
27	30.281	2,4-Dimethylphenol	C ₈ H ₁₀ O

Table 1 (continued)

28	30.957	4-Ethylphenol	$C_8H_{10}O$
29	31.819	2-Methoxy-4-methylphenol	$C_8H_{10}O_2$
30	32.090	Naphthalene	$C_{10}H_8$
31	33.197	2,3-Dihydrobenzofuran	C_8H_8O
32	34.192	4-Ethyl-2-methoxyphenol	$C_9H_{12}O_2$
33	35.259	1-Methylnaphthalene	$C_{11}H_{10}$
34	35.816	Ethanone,1-(4-hydroxy-2-methylphenyl)-	$C_9H_{10}O_2$
35	35.948	2-Methylnaphthalene	$C_{11}H_{10}$
36	36.333	1-Indanone	C_9H_8O
37	40.529	Acenaphthylene	$C_{12}H_8$
38	42.550	2-Naphthol	$C_{10}H_8O$

Table 1 (continued)

39	48.549	Phthalic acid, butyl hexyl ester	$C_{13}H_{16}O_4$
40	49.106	9-Methylidenefluorene	$C_{14}H_{10}$
41	64.789	Diisooctyl phthalate	$C_{24}H_{38}O_4$

2.2 Elemental analysis

The contents of C, H, and N in biochars were determined using a Vario EL III elemental analyzer (Elementar, Germany). The O content was calculated by subtracting the sum of C, N, H, and ash contents.

2.3 Pyrolysis-gas chromatography-mass spectrometry analysis

Biochars were pyrolyzed in a model JHP-5 Curie point pyrolyzer (Japan Analytical Industry Co., Ltd., Japan). Samples (0.3 mg each) were pyrolyzed for 20 s at the temperature of 920 °C before injecting into a gas chromatograph (Agilent 6890) with a 60-m capillary column (SGE BPX35), coated with 0.25 µm film thickness. The initial temperature for the gas chromatographic temperature program was 50 °C, and the heating time of 10 min was applied to increase the temperature from 50 to 250 °C. The final temperature is 300 °C, with a heating rate of 10 °C/min. The electron ionization mode with 70 eV electron energy, 1 s scan speed, and 35–600 m/z mass range was set for mass spectrometric detection.

2.4 Nuclear magnetic resonance analysis

Spectra of biochars were obtained on a Bruker DSX 2300 (Bruker, Switzerland) spectrometer equipped with a 4-mm

probe at a frequency of 5 kHz and a spectrometer frequency of 100.37 MHz for ^{13}C spinning at 5 kHz. The line broadening was 80.00 Hz. Acquisition conditions were as follows: a contact time of 3000 s, a recycle time of 2 s, and a scan number of more than 22,880. The spectra were acquired using the cross-polar sideband suppression.

2.5 Building the 2D molecular structures of biochars

The molecular structures of biochars were determined from the results of the elemental concentration, pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS), and chemical functional groups. The 2D structures of biochars were constructed using ChemDraw V10.0. The measured and modeled results were compared to confirm their accuracy. A personal computer consisted of the Core™ processor with 2-GB random access memory and 300-GB hard disk was used.

2.6 Simulation and optimization of 3D structures

Three-dimensional models of the representative biochars were built in two steps by HyperChem® (Hypercube, USA) as described in Zhao et al. (2013). First, geometrical optimization by single-point calculation was applied using the Polak-Ribiere algorithm to get the optimized configuration and the gradient was set at <0.04184 kJ/mol/nm in the optimized potential for liquid simulation (OPLS) force field. Second, molecular dynamic simulations were applied based on the

Table 2 Pyrolysis products of the measured 500 °C biochar

Number	Retention time	Pyrolysis product	Molecular formula	Molecular structure
1	4.168	Carbon dioxide	CO ₂
2	5.053	Acetone	C ₃ H ₆ O
3	5.342	Acetonitrile	C ₂ H ₃ N
4	7.670	Benzene	C ₆ H ₆
5	12.514	Toluene	C ₇ H ₈
6	17.954	1,4-Xylene	C ₈ H ₁₀
7	19.924	Phenylethylene	C ₈ H ₈
8	24.658	Phenol	C ₆ H ₆ O
9	25.434	Benzofuran	C ₈ H ₆ O
10	26.397	Benzonitrile	C ₇ H ₅ N
11	27.160	Benzene, 1-propyn-1-yl-	C ₉ H ₈

Table 2 (continued)

12	28.328	1-Dodecene	$C_{12}H_{24}$
13	32.754	Naphthalene	$C_{10}H_8$
14	35.333	Isoquinoline	C_9H_7N
15	35.936	1-Methylnaphthalene	$C_{11}H_{10}$
16	36.629	2-Methylnaphthalene	$C_{11}H_{10}$
17	38.496	Biphenyl	$C_{12}H_{10}$
18	42.691	Dibenzofuran	$C_{12}H_8O$
19	43.949	2-Naphthonitrile	$C_{11}H_7N$
20	44.494	Fluorene	$C_{13}H_{10}$

Table 2 (continued)

21	45.373	Naphthalene,1,2,3-trimethyl-4-(1 <i>E</i>)-1-propenyl-	$C_{16}H_{18}$
22	49.120	9-Fluorenone	$C_{13}H_8O$
23	49.819	Anthracene	$C_{14}H_{10}$
24	50.031	Phenanthrene	$C_{14}H_{10}$
25	54.111	Naphthalene, phenyl-	$C_{16}H_{12}$
26	57.915	Fluoranthene	$C_{16}H_{10}$
27	60.616	Pyrene	$C_{16}H_{10}$
28	65.780	Diisooctyl phthalate	$C_{24}H_{38}O_4$

Fig. 3 Measured and simulated ^{13}C -NMR spectra of biochars

optimized configuration using the simulated annealing method. The temperature was increased from 298 to 700 K in a 1-fs step during 2 ps. After simulating at 700 K for 2 ps, the temperature was decreased to 298 K by 1-K step and simulated for 2 ps. These two steps were recycled to obtain a stable, balanced conformation with the lowest energy.

3 Results and discussion

3.1 The structural characteristics and 2D structural models of biochars

The N contents of 1.72 and 1.14 % of 300 and 500 °C biochars, respectively, reflect the low presence of N-containing compounds of biochars. Lehmann et al. (2003) also noted that plant biochars were low in N. The low contents of O and O/C ratios of 0.20 and 0.06 for the two biochars indicated that the carbohydrate and carboxylic acid contents of biochars were low (Rosa et al. 2011). The low H/C ratios of 0.95

and 0.54 demonstrated the high aromatization of biochars (Purevsuren et al. 2003). The contents of C and H of these two biochars were similar. With the increase of the pyrolysis temperature, the contents of H and O decreased.

Figures 1 and 2 show that the 41 and 28 pyrolysis products which mainly came from aromatic hydrocarbon were identified from the characteristics of pyrolysis fragments and the mass spectroscopy database NIST 05. As shown in Tables 1 and 2, the biochars contained benzene, heterocycle, carboxyl group, phenolic hydroxyl group, aliphatics, amino, and so on. Biochars produced at 300 and 500 °C only contained two and four N-containing compounds, respectively. It indicated that biochars contain little protein materials. The pyrolysis compounds from 300 and 500 °C biochars were similar, containing carbon dioxide, acetone, benzene, toluene, 1,4-xylene, benzonitrile, phenylethylene, phenol, benzofuran, naphthalene, 1-methylnaphthalene, 2-methylnaphthalene, and diisooctyl phthalate. The 300 °C biochar contained indene aromatic hydrocarbon, acenaphthene, and fluorene, while the 500 °C

Fig. 4 The conceptual structures of 300 °C (a) and 500 °C (b) biochars

biochar had fluorine, anthracene, phenanthrene, and pyrene, all of these materials existed in coal tar (Mao 2007). High temperature caused condensation of aromatic rings, so the structures of aromatic materials in the 500 °C biochar were more complex than those in the 300 °C biochar. At the same time, high temperature led to a loss of partial structures, which were mainly O-containing compounds, such as acetic acid, phenols, and ketones. These fundamental structures were used to build for the complex and variable 2D structures of biochars. There were many possible combinations for the 2D structures, and we chose the models whose elemental composition and chemical functional groups were consistent with measured biochars.

3.2 ^{13}C nuclear magnetic resonance spectra of biochar

Figure 3 reports the ^{13}C nuclear magnetic resonance (NMR) spectra of the experimental biochars. The spectra of the 300 °C biochar that exhibited a signal at 23 ppm may be attributed to a short-chain polymethylene structure. The peak around 31 ppm was most likely due to aliphatic C, including long-chain fatty acids, surface waxes, lipids, resins, protein-like structures, or polymethylene in lipids (Chen and Chiu 2003; Tinoco et al. 2004). The ring C of carbohydrates occurred at 74 ppm (González-Vila et al. 1983). The peak signal at 173 ppm was carboxyl C (Carvalho et al. 2009). The spectra of the 500 °C biochar showed a broad signal spanning from 90

Table 3 Measured and modeled elemental concentrations of biochars

Sample	Elemental concentration (%)				Molecular structural formula
	C	H	N	O	
300 °C biochar	57.85	4.56	1.72	25.08	$\text{C}_{78}\text{H}_{74}\text{N}_2\text{O}_{26}$
Simulated 300 °C biochar model	56.97	3.85	1.73	26.61	$\text{C}_{77}\text{H}_{62}\text{N}_2\text{O}_{27}$
500 °C biochar	58.61	2.66	1.14	14.56	$\text{C}_{60}\text{H}_{32}\text{NO}_{11}$
Simulated 500 °C biochar model	56.84	2.94	1.10	13.22	$\text{C}_{60}\text{H}_{37}\text{NO}_{13}$

Table 4 The peak areas of different chemical functional groups in the ^{13}C -NMR spectra

Samples	Alkyl C δ 0–50	O-alkyl C δ 50–110	Aryl C δ 110–165	Carboxyl C δ 165–190	Carbonyl C δ 190–200
300 °C biochar	25.67	18.58	45.80	8.06	1.88
Simulated 300 °C biochar model	25.73	19.15	43.43	9.14	2.55
500 °C biochar	9.49	15.36	70.01	5.00	0.14
Simulated 500 °C biochar model	8.23	16.40	70.38	4.79	0.20

to 170 ppm, the predominant component of the 500 °C biochar which was centered at 128 ppm. The 110–165-ppm region was attributed to aromatic carbon and that between 165 and 190 ppm to carboxyl group. For crop straw biochar, the amounts of aromatic carbons were 45.80 and 70.01 %, respectively. Table 4 lists the chemical functional groups and the percentage area of each functional group region (Baldock and Skjemstad 2000).

3.3 The 2D molecular structure of biochar

The general empirical formula for conceptual model of biochar was set as $\text{C}_x\text{H}_y\text{N}_z\text{O}_k$. The normalizing coefficient was calculated according to the elemental percent concentration ($\text{C}\% + \text{H}\% + \text{N}\% + \text{O}\% = 100\%$) of experimental biochars (Yarkova and Gyul'maliev 2012), so elemental compositions of $\text{C}_{78}\text{H}_{74}\text{N}_2\text{O}_{37}$ and $\text{C}_{60}\text{H}_{32}\text{NO}_{29}$ were obtained for 300 and 500 °C biochars. However, the ash contents of 300 and 500 °C crop straw biochars were 10.79 and 23.27 %, so it was necessary to correct for the ash contents in calculating their elemental compositions: the final compositions were $\text{C}_{78}\text{H}_{74}\text{N}_2\text{O}_{26}$ and $\text{C}_{60}\text{H}_{32}\text{NO}_{11}$ respectively. The conceptual structures of biochars obtained from our pyrolysis structures yielded many combinations, and we chose the most representative models, which are shown in Fig. 4 for molecular simulation to get the most stable conformation. There were obvious differences for the conceptual structures of 300 and 500 °C crop straw biochars, the former contained a diisooctyl phthalate contaminant. This pyrolysis product had alkyl chain which was

consistent with the higher aliphaticity of 300 °C crop straw biochars.

3.4 Verification of the conceptual models

Table 3 shows that the elemental concentrations of the measured samples are in close agreement with the simulated models. To test our models, the proportion of different chemical functional groups of the measured and simulated biochar models was calculated from solid-state ^{13}C NMR spectra and is shown in Table 4. We also can see that the chemical functional groups of experimental means and simulated biochar models were similar. This suggested that the conceptual models fitted the measured data, and they can better represent the structural characteristics of the biochars, so they are more adaptable to be used as the molecule structures of biochars.

3.5 Molecular modeling of biochar

Biochars contained small contents of carboxyl and hydroxy groups, which make them neutral to alkaline. The 500 °C biochar has a stronger alkaline character, due to a higher pH of 9.11, so it is difficult to donate protons. According to the 2D molecular structures of biochars which were determined on the basis of analytical and spectroscopic studies, the computation of biochar models was carried out by geometric optimization using the molecular mechanic method in the OPLS force field of HyperChem® and molecular dynamic simulation. Nonprotonated and protonated biochar models with -2

Table 5 Energy distribution of the molecular modeling of biochars in OPLS force field

	300 °C biochar			500 °C biochar		
	COOH/OH	COO ⁻² /OH	COO ⁻³ /O ⁻¹	COOH/OH	COO ⁻² /OH	COO ⁻³ /O ⁻¹
E-bond (kJ/mol)	9.78	10.27	7.99	4.68	4.77	4.83
E-angle (kJ/mol)	179.62	173.94	158.44	226.03	224.24	221.93
E-dihedral (kJ/mol)	285.86	265.04	256.53	103.13	96.41	94.58
E-vdw (kJ/mol)	-206.01	-182.26	-207.94	-61.79	-50.90	-47.72
E-electrostatic (kJ/mol)	0	0	0	0	0	0
E-total (kJ/mol)	269.24	266.99	215.02	272.05	274.52	273.62
Gradient (kJ/mol/nm)	0.041422	0.041505	0.040961	0.040878	0.041422	0.039957

Fig. 5 Original 3D structure (a), nonprotonated 3D structure (b), and protonated 3D structure with -2 charges (c) of the 300 °C straw biochar. The oxygen atoms are shown in *red*, hydrogen atoms in *grayish white*, carbon atoms in *green*, and nitrogen atoms in *blue*

Fig. 6 Original 3D structure (a), nonprotonated 3D structure (b) and protonated 3D structure with -2 charges (c) of the 500 °C straw biochar. The oxygen atoms are shown in *red*, hydrogen atoms in *grayish white*, carbon atoms in *green*, and nitrogen atoms in *blue*

Table 6 Calculated properties for biochar models in vacuum using the SE method PM3

	300 °C biochar			500 °C biochar		
	COOH/OH	COO ⁻² /OH	COO ⁻³ /O ⁻¹	COOH/OH	COO ⁻² /OH	COO ⁻³ /O ⁻¹
Charge	0	2	4	0	2	4
Heat of formation (kJ/mol)	-2577.29	-1847.41	-1177.55	-524.53	350.42	1051.11
Gradient (kJ/mol/nm)	114.03	118.84	151.37	146.76	153.82	194.95

charges (H^+ of the two carboxyl groups dissociated) and a protonated biochar model with -4 charges (H^+ of three carboxyl and one hydroxyl groups dissociated) were computed. The total energy and energy species are shown in Table 5, and the 3D structures of simulated biochar models are proposed in Figs. 5 and 6. The bond energy demands a relatively little energy, and the angle and dihedral energies require the higher energy requirements. The high contribution of van der Waals energy leads to a general contraction and higher stability of biochar (Schulten and Leinweber 2000; Lan et al. 2013). The 3D conformations of biochars have net structures with clear stereo voids. The spaces of the voids can bind protein, biological molecules, metal ions, and environmental pollutants, which give biochars good adsorption capacity and fertilizer properties. For the modeled 300 °C biochar, the connection between long-chain alkyl and aromatic ring made it more porous and flexible (Li 2009). The aromaticity of the 500 °C biochar is higher, so the flexibility of the 3D structure decreased. From Fig. 5, we can see that the intramolecular hydrogen bond appeared after optimization and it is the geometry optimization which caused the formation of the intramolecular hydrogen bond. There is no intramolecular hydrogen bond in the 3D structures of the 500 °C biochar (Fig. 6). By increasing the number of the dissociated protons, the total energies decreased for the 300 °C biochar, so the 3D structure with -4 charges of it is the most stable. However, for the 500 °C biochar, the 3D structure of nonprotonated is the most stable.

A parameterized model number 3 (PM3) semi-empirical quantum chemistry method was used to calculate the heat of formation (Zhao et al. 2013). According to Table 6, we can know that the process of deprotonation is an endothermic process. With the going on of the deprotonation, the needed energies increase. The research about deprotonation can simulate the effects of alkaline solution on the surface of biochars.

3.6 Quantitative structure activity relationship properties

A wide variety of quantitative structure activity relationship (QSAR) properties of 3D structures of biochars can be calculated using the HyperChem® software. These results are helpful to understand the structure-property relationships of biochars in natural and ecological systems. From Table 7, we can see that the 300 °C biochar had the larger polarizability, refractivity, hydration energy, volume, and surface area. The 300 °C biochar will have a higher adsorption capacity due to its higher surface areas. Log P is the hydrophobic parameter, and the higher value of it for the 500 °C biochar suggested the greater hydrophobicity, which had an agreement with the result of ^{13}C NMR. Xu et al. (2004) also suggested that the structure with a high Log P value will have a small total energy.

4 Conclusions

In this paper, we proposed two 3D molecular models for two corn straw biochars in order to gain a better understanding of their structures. The biochars had low contents of carbohydrate, carboxylic acid, and N-containing groups. Small H/C and more aryl C indicated that the biochars were aromatic. Py-GC-MS gave pyrolysis products mainly produced from aromatic hydrocarbon. The agreement of the measured and simulated elemental composition and chemical functional groups demonstrated that the 2D structures were representative. The conceptual molecular formula of 300 and 500 °C biochars was $C_{78}H_{68}N_2O_{25}$ and $C_{59}H_{29}NO_{10}$, respectively. Molecular mechanic and molecular dynamic calculations were performed for simulated models in order to obtain the most stable conformation. The 3D conformations of biochars had net structures with clear void spaces. The 300 °C biochar model with -4 charges is the most stable structure with the smallest total

Table 7 QSAR properties of modeled biochars

Sample	Mass	Polarizability (nm ³)	Refractivity (nm ³)	Log P	Hydration energy (kJ/mol)	Volume (nm ³)	Surface area (grid, nm ²)	Surface area (approx, nm ²)
300 °C biochar	1433.40	139.51	377.45	-6.47	2059.49	2912.96	1249.83	2492.70
500 °C biochar	949.93	99.61	281.38	-5.43	574.59	2042.44	993.80	1663.67

energy of 215.02 kJ/mol. The optimized 3D structure of the simulated 500 °C biochar model which did not have negative charge was the most stable. The van der Waals energy played an important role in the stability of 3D structures. QSAR properties showed that the modeled 300 °C biochar had the larger polarizability, refractivity, Log*P*, hydration energy, volume, and smaller surface areas. Computational chemistry provided a relatively innovative, powerful method to investigate physical and chemical properties of biochars at the molecular level. Our 3D model is able, for the first time, to successfully demonstrate the structural characteristic of crop straw biochars obtained at different temperatures.

Acknowledgments This research was supported by the National Natural Science Foundation of China (41271331).

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