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第19回　木質炭化学会

研究発表会　講演要旨集

2021年9月16日(木)・17日(金)
立命館大学　大阪いばらきキャンパス
オンライン

主催：木質炭化学会
共催：日本バイオ炭普及会
　　　立命館大学サステイナビリティ学研究センター
後援：林野庁

Valorization of miscanthus biomass for the production of effective adsorbent materials through hydrothermal carbonization

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Introduction

Hydrothermal carbonization (HTC) of biomass takes place in a closed reactor at temperatures between 180 - 260° C and self-sustained pressure using the influence of subcritical water as a reaction medium. In most cases, treatment duration is within the range of 1-24 h. The outcomes of the process are, a solid material with a higher carbon content, called hydrochar and the residual HTC wastewater. Due to their surface structure and tunable properties, hydrochars have been applied as solid fuels, soil conditioners and adsorbents[1)].

Miscanthus giganteus, a perennial purpose-grown crop, has been primarily used as an energy source. However, with low bulk density and moisture and significant transportation costs, thermochemical pretreatment of this feedstock has been suggested as the best way to overcome these issues and to increase its use-value. Besides, miscanthus is characterized by a very low ash content and this attribute is advantageous for HTC[2)].

The scope of this work was to offer new insights into the application of miscanthus hydrochars as adsorbent materials. The main objectives were the following: a) valorization of *Miscanthus giganteus* for the production of an added-value material (adsorbent) at different HTC temperatures and a short residence time b) application of the 'as produced' hydrochars in the adsorption of Cu^{2+} and NH_4^+ c) investigation of the influence of the production temperature and correlation of the process severity to the properties and adsorption behaviour of the samples.

Experimental method

Miscanthus giganteus biomass was air-dried and homogenized to a fraction below 1 mm. NH_4^+ and Cu^{2+} test solutions were prepared by dillution of the respective stock solutions (1000 ppm), which were prepared by dissolution of NH_4Cl (Sigma Aldrich) and $CuSO_4 \cdot 5H_2O$ (Sigma Aldrich) salts, respectively. Aqeuous solutions of $NaClO_4$ (Sigma Aldrich) were used as background eletrolyte for the investigation of the effect of ionic strength.

The HTC of the biomass was performed in a high-pressure laboratory autoclave (250 ml capacity, Carl Roth, Model II), at temperatures of 180, 200, 220, 240, and 260° C) at a rate of 4° C min^{-1} and treated for 60 min. After treatment the autoclave was allowed to cool to room temperature and the solids (hydrochar) were recovered by vacuum filtration. All experiments were performed in triplicate. The produced miscanthus hydrochars were repeatedly washed with ultrapure water and dried at 105° C for 12 h followed by storage at 4℃ waiting further analyses. No activation or other modifications were performed. The miscanthus hydrochars were coded as MIS-180, MIS-200, MIS-220, MIS-240 and MIS-260 and these names will be used thereof.

Mass yields (%) of hydrochars were calculated based on weight measurements of miscanthus before and after HTC. Hydrochars were characterized by elemental analysis (C, H, N content), ash content analysis, Fourier-transform infrared spectroscopy and X-ray photoelectron spectroscopy. The oxygenated surface groups were determined by the Boehm titration.

The cation adsorption was investigated at pH 5.5 and pH 5.0 for the Cu^{2+} and NH_4^+, respectively, under ambient conditions. The initial cation concentration was varied between 5 and 200 mg L^{-1}, the contact time to reach equilibrium was set at 24 h and the determination of Cu^{2+} and NH_4^+ in the solutions was carried out potentiometrically by means of the corresponding ion selective electrodes. The kinetic experiments were carried out under similar conditions using the MIS-180 hydrochar at cation concentrations equal to 100 mg L^{-1}.

Results and discussion

The C, H, O, N and ash content of the MIS samples were within the typical range of hydrochars prepared from this biomass[3)]. The fixed carbon and total carbon content increased with temperature, whereas the yields followed the opposite trend. This was due to the increasing lignin content which remained essentially undegraded in the range of 180 - 260℃ and became part of the gradually decreasing mass of hydrochars.

Table 1. Properties of miscanthus biomass and the produced hydrochar samples. No sulfur was detected in any of the samples

Sample	Ash (%)	Fixed Carbon (%)	C_{av} (%)	H_{av} (%)	O_{av} (%)	N_{av} (%)	Mass yield (%)	Volatile matter (%)	H/C	O/C
Miscanthus	2.67	6.25	44.10	5.77	47.17	0.30		84.02	1.57	0.8
MIS-180	1.50	10.83	47.92	6.10	44.27	0.22	73.00	82.30	1.52	0.69
MIS-200	1.07	16.82	49.13	5.98	43.61	0.22	54.00	80.44	1.46	0.66
MIS-220	0.88	22.90	51.63	5.91	41.42	0.17	51.00	74.36	1.37	0.6
MIS-240	1.49	27.51	65.35	5.34	28.95	0.37	49.18	68.89	0.98	0.33
MIS-260	1.41	37.65	68.99	5.07	25.56	0.39	35.04	59.25	0.88	0.27

Figure 1 shows the Van Krevelen diagram for the original miscanthus and the respective hydrochars. Both H/C and O/C ratios decrease almost linearly with temperature, whereas the slope of the linear fit establishes dehydration as the dominant pathway during the process. The excellent linear agreement between the H/C and O/C values is due to the uniform HTC conditions throughout all experiments and the low initial ash content of miscanthus. Both ratios decrease as oxygen and hydrogen are removed as CO, CO_2, H_2O and other O- and H-containing volatiles, resulting in carbon-richer hydrochars.

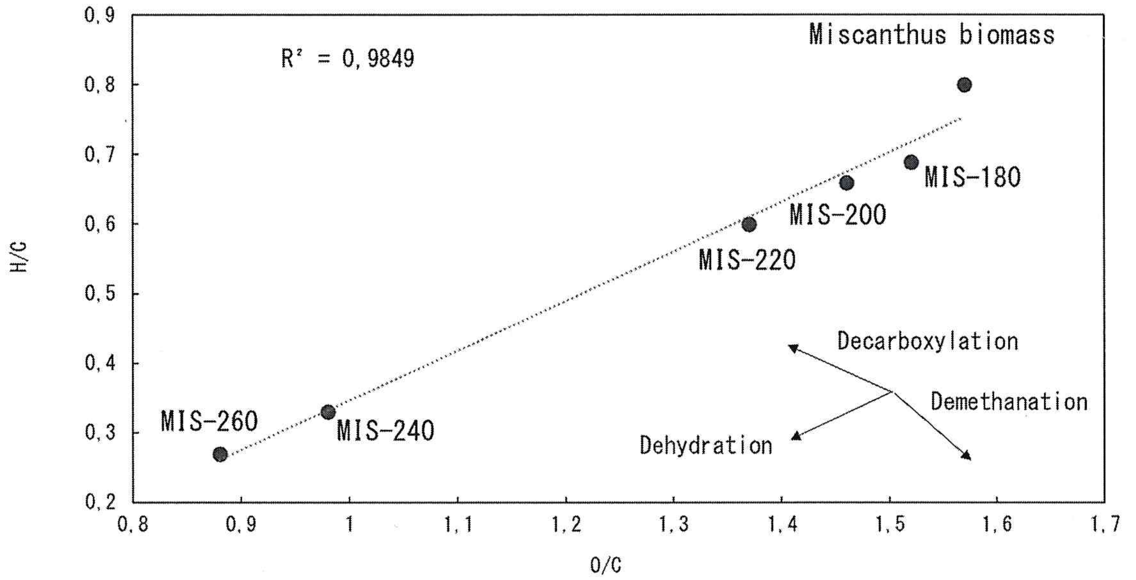

Figure 1. Van Krevelen diagram of the miscanthus and the hydrochar samples used in this study

Table 2 shows a gradual decline of the adsorption capacity for the NH_4^+ cations as we proceed from MIS 180 to MIS 260. On the other hand, in the case of the Cu^{2+} cation adsorption there is dramatic decrease when the higher temperature hydrochars were used (MIS 200 - 260). This observation is most probably associated with the decomposition of oxygen-containing moieties which form stable inner-sphere complexes with Cu^{2+}cations. Generally, as O/C decreases with increasing temperature, the adsorption mechanism shifts from mainly ion exchange based to physisorption (van der Waals, London dipole), resulting in sorption capacity reduction due to the weaker nature of physisorption.

Table 2. q_{max} and R values by applying the *Langmuir* isotherm model to the experimental data obtained for the adsorption of NH_4^+ and Cu^{2+} cations on the MIS samples

Sample	NH_4^+		Cu^{2+}	
	q_{max} (mg g^{-1})	R^2	q_{max} (mg g^{-1})	R^2
MIS-180	71	0.998	301	0.985
MIS-200	50	0.987	14.3	0.927
MIS-220	27	0.998	59.1	0.993
MIS-240	23	0.985	23.0	0.968
MIS-260	39	0.993	33.9	0.981

References

1) Sharma, H.B., Sarmah, A.K., Dubey, B., 2020. Hydrothermal carbonization of renewable waste biomass for solid biofuel production: A discussion on process mechanism, the influence of process parameters, environmental performance and fuel properties of hydrochar. Renew. Sustain. Energy Rev. 123, 109761.

2) Mihajlović, M., Petrović, J., Maletić, S., Isakovski, M.K., Stojanović, M., Lopičić, Z., Trifunović, S., 2018. Hydrothermal carbonization of *Miscanthus × giganteus*: Structural and fuel properties of hydrochars and organic profile with the ecotoxicological assessment of the liquid phase. Energy Convers. Manag. 159, 254-263.

3) Zhang, Y., Zahid, I., Danial, A., Minaret, J., Cao, Y., Dutta, A., 2021. Hydrothermal carbonization of miscanthus: Processing, properties, and synergistic co-combustion with lignite. Energy 225, 120200.

第 19 回 木質炭化学会研究発表会

【研究発表会プログラム】（発表 12 分、質疑応答 2 分、交代 1 分）〇は登壇者

2021 年 9 月 16 日（木）

セッション１ 13:30 ～ 14:30

座長：梶本 武志（和歌山工技セ）

1-1.「酸性化バイオ炭によるカドミウム汚染土壌のファイトレメディエーション」
（創価大）〇戸張 寛子，佐藤 伸二郎

1-2.「窒素ドープ酸化チタン担持スギ炭化物の光触媒性能－速度論による解析－」
（福島大）〇渡辺 夏希，浅田 隆志

1-3.「卵殻カルシウム担持もみ殻炭の水中リン吸着性能と評価
－速度論と吸着機構解析－」 （福島大）〇荒 実咲，浅田 隆志，
（新潟薬大）大野 正貴，小瀬 知洋，川田 邦明

1-4.「異なる金属処理したコーヒー粕由来の機能性バイオ炭による栄養塩吸脱着性能」
（創価大）〇小平 友大，佐藤 伸二郎

セッション２ 14:40 ～ 15:55

座長：畑 俊充（京都大）

2-1.「光音響赤外分光法で視た鉄含浸木粉の熱分解：熱分解と炭素結晶化の相関」
（東京大）山岍 崇之，（秋田県立大）澁谷 栄，鈴木 暎，〇山内 繁

2-2.「木質ペレット由来ガス化発電副産物の性状」
（道総研林産試）〇本間 千晶，西宮 耕栄，（京都大）畑 俊充

2-3.「籾殻の炭・灰化時に揮発するケイ素」
（中京大）〇林 寛大，佐伯 省吾，野浪 亨

2-4.「Valorization of miscanthus biomass for the production of effective adsorbent materialsthrough hydrothermal carbonization」
（Hellenic Mediterranean Univ）〇Dimitrios Kalderis, Ioannis Anastopoulos,
（kyushu Institute of Technology）Toshiki Tsubota,
（University of Cyprus）Efthalia Georgiou, Ioannis Pashalidis,
（Institute for Technology of Nuclear and Other Mineral Raw Materials）
Marija Mihajlović, Jelena Petrović,
（Carl von Ossietzky University of Oldenburg）Carsten Dosche

2-5.「エアロゾルフロー法によるリグニンナノ粒子を前駆体とする
真球状カーボンナノ粒子の合成」
（明星大）〇吾郷 万里子，櫻庭 悠真，五十嵐 勉，
鈴木 真由，川島 希世子，上本 道久，
（Aalto University）Luiz Greca,（Aalto University・UBC）Orlando J.Rojas

セッション３ 16:05 ～ 17:20

座長：沖森 泰行（日本バイオ炭普及会副会長）

3-1.「もみ殻を原料としたバイオ炭の製炭および施用に伴う温室効果ガス排出量」
（立命館大）〇金井 真也，土井 美奈子，柴田 晃，中野 勝行

3-2.「連続炭化装置で製造したもみ殻炭の農地施用による炭素貯留のＪクレジット申請」

（明星大）〇吉澤 秀治

3-3.「ホテイアオイ原料バイオ炭の炭団化における添加結着材と有機物の最適化」
（創価大）〇村上 海斗，佐藤 伸二郎

3-4.「備長炭窯内の温度測定と評価　－第２報－」
（弓削商船高専）〇森 耕太郎

3-5「紀州備長炭の、窯の素材による炭化の差異」
（紀伊の森）〇土谷 惠司

2021 年 9 月 17 日（金）

セッション４　9:00 ～ 10:00

座長：凌 祥之（九州大）

4-1. 「バイオマスの混焼が籾殻シリカ灰の結晶化に及ぼす影響」
（東京大）〇大平 怜也，斎藤 幸恵，黒河内 葉子

4-2. 「炭化温度と竹炭の肥料成分の変動」
（京都先端大）〇藤井 康代，岡本 真由美，水口 梨沙

4-3. 「木質ペレット由来ガス化残渣の賦活による活性炭の製造」
（京都大）〇畑 俊充，（道総研林産試）本間 千晶，西宮 耕栄

4-4. 「鉄含浸水熱炭化物を前駆体としたグラファイト状炭素の作製」
（東北大）〇中安 祐太，後藤 泰斗，伊藤 隆，渡邉 賢

セッション５　10:10 ～ 11:10

座長：佐野 修司（摂南大）

5-1. 「水熱処理により成分分離可溶化されたコーヒー抽出残渣ヘミセルロースを原料とする水熱炭化物の製造」
（産総研）〇井上 誠一，遠藤 貴士，（佐賀大）熊谷 聡

5-2. 「水産業由来竹廃材を炭焼きにより資源化する試み―松島湾の牡蠣養殖を例に―」
（宮城教育大）〇西城 潔，（阿部式炭焼研究所）阿部 壽夫

5-3.「牡蠣イカダの炭化特性について―松島湾の牡蠣養殖を例に―」
（阿部式炭焼研究所）〇阿部 壽夫，（宮城教育大）西城 潔

5-4.「岩崎式炭焼き窯を使用した廃貝殻の消石灰化方法について」
（岩崎式炭焼き窯普及会）〇岩﨑 眞理，（東京大）空閑 重則，木村 聡

セッション６　11:20 ～ 12:20

座長：柴田 晃（立命館大）

6-1.「有機肥料原料のバイオ炭ペレット肥料の施用効果」
（創価大）姫野 正俊，〇佐藤 伸二郎

6-2.「ゴルフ芝（高麗芝）へのバイオ炭施用効果」
（摂南大）〇佐野 修司，（立命館大）深尾 陽一朗，柴田 晃

6-3.「籾殻炭の施用が温室効果ガスの発生に与える影響」
（愛媛大）〇溝手 桃花，（北海道大）当真 要，（愛媛大）上野 秀人

6-4.「もみ殻炭の農地施用による野菜生育促進と炭素貯留―福島県川俣町での事例―」
（明星大）〇吉澤 秀治（（一社）次世代産業創出構想）菅野 文吉，宮地 勝志