International Conference on Applied Energy 2019
Aug 12-15, 2019, Västerås, Sweden
Paper ID: 895

CONVERSION OF MAIZE STRAW TO BLAST FURNACE INJECTED FUEL BY HYDROTHERMAL CARBONIZATION

Haipeng Teng[1], Guangwei Wang[1*], Jianliang Zhang[1], Nan Zhang[1], Chuan Wang[2]

1 School of Metallurgical and Ecological Engineering, University of Science and Technology Beijing, Beijing 100083, China

2 Swerim AB, SE-971 25 Luleå, Sweden

(*Corresponding Author: guangwei_wang@ustb.edu.cn)

ABSTRACT

In this work, the maize straw based hydrochars were produced under various conditions by the hydrothermal carbonization (HTC) process. The properties of prepared hydrochar were analyzed experimentally in order to evaluate the feasibility for the blast furnace injection. It was found out that the carbonization temperature of 280 °C with a holding time of 60 minutes was the optimal operating condition to produce the hydrochar. The evaluation results show that the produced hydrochar has the required fuel properties and combustion performance.

Keywords: Hydrothermal carbonization, Biomass, Maize straw, Hydrochar, Blast furnace injection

1. INTRODUCTION

In China, most steel is produced from the coal-based BF-BOF production route, which makes the steel industry one largest CO_2 emission sector. Meanwhile, as one of largest agriculture countries, China has a wide range of biomass resources and generates huge amount of agriculture residues each year. It is of great interest to use agriculture residues as alternative fuels in BFs to replace coal, thereby, fossil CO_2 emission can be reduced significantly as biomass is one type of carbon neutral energy carrier. However, biomass residues have to be upgraded to remove the volatile content, increase fixed carbon content and calorific value, in addition, some harmful components (e.g. alkali, S, P, etc.) also need to be further reduced to an acceptable level for the usage in BF.

In this study, the maize straw (MS) was chosen as one type of agriculture resides, and it was upgraded by the hydrothermal carbonization (HTC) process to produce one type of biochar, named hydrochar. HTC technology is a thermochemical process that transforms organic matter into products with high carbon content. Its principle is to utilize the special physicochemical properties of water under supercritical or subcritical conditions to obtain products with high carbon content and high heat value through a series of complex chemical transformations. Compared with conventional approach such as direct combustion or pyrolysis, HTC has the advantages of mild reaction conditions, low process energy consumption and good removal effect of impurity.

In this study, the chemical composition and combustion characteristics of the produced MS based hydrochars were analyzed experimentally in order to investigate the feasibility for BF injection to replace the pulverized coal.

2. MATERIALS AND METHODS

2.1 Raw materials

The maize straw (MS) was taken from Henan Province, China. First, the samples were crushed into small particles of less than 2 cm by a scissor. After that, they were dried in an oven at 105°C for 12h. The proximate analysis of the MS showed the percentage of volatile matter (78.37%), ash content (5.46%) and fixed carbon (16.17%). The ultimate analysis indicated the content of C, H, N and S in MS, which were 45.30%, 5.85%, 0.78%, 0.21%, respectively. The content of O (42.40wt%) was obtained by difference. The main components in the ash are SiO_2 (38.5%), K_2O (24.8%), CaO (12.7%), MgO (7.6%), P_2O_5 (5.3%). In addition, it also contains some other compounds, for instance, SO_3 (3.7wt%), Al_2O_3 (2.1%), Fe_2O_3 (1.9%), Na_2O (1.2%), etc.

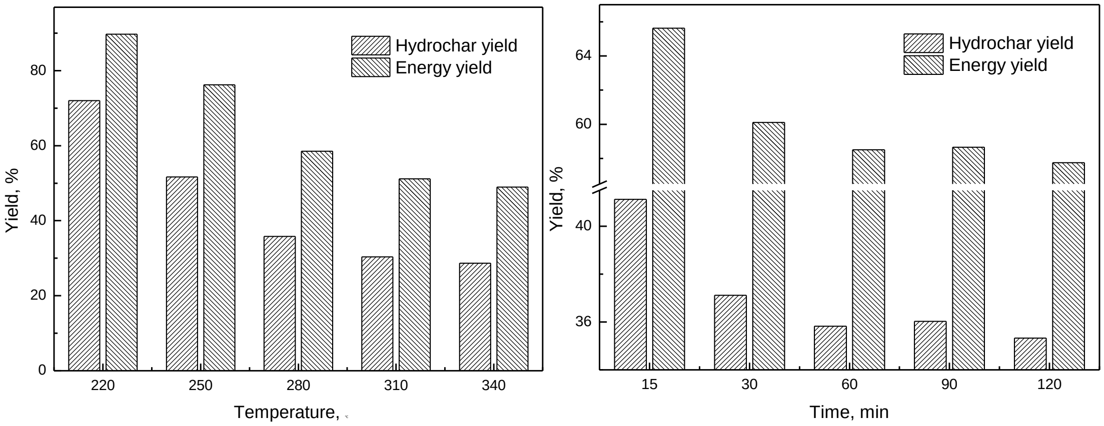

Fig 1 Hydrochar and energy yield at different carbonization temperature and time

2.2 *Hydrothermal carbonization process*

The HTC tests were performed in a 250 ml stainless steel hydrothermal reactor. The HTC temperature and holding time were controlled by a PID controller. To analyze the effect of the HTC temperature on the MS, 220 °C, 250 °C, 280 °C, 310 °C and 340 °C (pressure was not controlled) were adopted with the holding time of 60 min. In order to investigate the effect of the holding time, 15 min, 30 min, 60 min, 90 min and 120 min were selected under the same reaction temperature of 280°C. In each test, about 20 g of MS feedstock was dispersed in 60 ml deionized water, then transferred into the stainless steel reactor. The initial pressure of all tests was at atmospheric pressure under nitrogen protection environment. The reaction system was continuously stirred at 200 rpm during the HTC process. After the reaction process, the HTC reactor was automatically cooled to room temperature. The hydrochar was washed with deionized water and then dried at 105°C for 24h. After that, the dry hydrochar samples were crushed and screened to the size below 74 μm, then them in the sealed bag ready for tests. Different hydrochars were denoted as HTC-X-Y, where X represents the HTC temperature (°C) and Y is the holding time (min).

3. RESULTS AND DISSCUSSION

3.1 Hydrochar and energy yields

HTC temperature and time are the main factors affecting the performance of hydrochar. Results of the solid and biomass energy yield prepared under the condition of different temperatures and holding time were shown in Fig.1. It can be seen that with the increase of HTC temperature and time, the hydrochar and energy yield were continuously reduced, and its decreasing extent was gradually decreasing as well. When the HTC temperature exceeded 280 °C or the holding time longer than 60 min, the hydrochar and energy yield remained basically unchanged. The HTC-280-60 sample had a hydrochar yield of 35.8% with an energy yield of 58.5%. Additionally, the energy yield value was higher than that of hydrochar yield. This phenomenon indicated that the hydrochar obtained has higher energy density than the original biomass. Furthermore, the HTC process can destroy the structure of cellulose, hemicellulose and lignin in MS samples. Direct observation of the treated sample showed that the hydrochar generated became powder under the action of rotor stirring, indicating that hydrochar's pulverability could be improved significantly during the HTC process.

3.2 Fuel properties of hydrochar

The components of MS changed considerably by the HTC treatment. Proximate and ultimate analysis of samples under different HTC conditions were shown in Table 1. It can be seen that the volatiles of MS samples is decreased and meanwhile the fixed carbon content is increased. The other important observation was that with the precipitation of volatiles, the ash content decreased to some extent as well, which cannot be seen from the biomass pyrolysis process. The main reason was that the high content of water-soluble potassium, sodium and phosphorus in MS samples were largely dissolved into the water solution during the HTC process, resulting in the decrease of ash content in hydrochar. While in the biomass pyrolysis process, alkali metals cannot be removed along with the progress of pyrolysis, and most alkali are remained in the biochar. Alkali metals are harmful for the BF operation, and it is considered as one major limiting factor when evaluating biochar for BF injection. From the above analysis, we could conclude that the HTC technology can be one of the most feasible technical routes to upgrade biomass for the BF applications. Besides the alkali content, Table 1 also shows a decreased ash content and volatile content in the HTC-280-60 sample, meantime, the fixed carbon content is increased almost 3 times compared to the raw maize straw. The results of ultimate analysis showed that the O content in hydrochar decreased significantly, and the C content increased. The content of H and N changed slightly, while the content of S, which is harmful to blast furnace, decreased obviously.

In order to clearly analyze the change rule of the element, the H/C and O/C atomic ratios were calculated to evaluate the changes in coalification degree after the HTC treatment, which can be seen in Table 1. The Van Krevelen digram was also used to assess the coalification effect of HTC treatment [1]. It was shown that the position of H/C and O/C value shift from the upper right to the lower left with the increase of HTC temperature. The lower the respective ratios, the greater the energy potential of the products [2]. For comparison, the H/C vs. O/C atomic ratios of four typical coals, i.e., anthracite, bituminous, lignite and peat, were also plotted in Fig.2. By the comparative analysis, it can be found that the value of HTC-220-60 fell in the peat region, the value of HTC-250-60 fell in the lignite region, and all other samples fell in the bituminite region. It shows that MS can improve the rank of hydrochar by decarboxylation and dehydration under HTC conditions. The experimental results also imply that the effect of holding time on rank of hydrochar was less than the carbonization temperature.

HHVs of different hydrochars were greatly improved by the HTC treatment. HHV was calculated by using the following equation [3].

$$\begin{aligned} HHV = 0.394\cdot C + 1.1783\cdot H + 0.1005\cdot S \\ - 0.1034\cdot O - 0.0015\cdot N - 0.0211\cdot A \end{aligned} \quad (1)$$

where, C, H, S, O, N and A represent the mass percentage of carbon, hydrogen, oxygen, nitrogen, sulfur and ash content on dry basis. As shown in Table 1, the HHV value of the MS sample was only 18.22 MJ/kg, and the HHV of the HTC-280-60 was increased to 29.87 MJ/kg with an increase of 11.65 MJ/kg. However, it was found that the increasing tendency of calorific value became flat when further increasing the HTC temperature. For example, the calorific value of the HTC-340-60 sample obtains a calorific value of 31.24 MJ/kg, which is only 2.37 MJ/kg higher than that of HTC-280-60 sample. Moreover, by comparing the effect of holding time on HHV, it can be concluded that the effect of extended holding time on sample calorific value was small. By taking HTC-280-60 as one sample, the calorific value increased only 0.71 MJ/kg with an increase of the holding time from 15 min to 120 min, under the condition of 280 ℃. The bituminous coal is commonly used in blast furnace injection, by comparison it was found that the calorific value of HTC-280-60 was higher than that of bituminite (25-28MJ/kg). The main reason was that the soluble substance in ash was removed in the HTC process, and the ash content in the hydrochar sample was only about 2%, much lower than the bituminous coal.

Sample	Proximate analysis(wt,%)			Ultimate analysis(wt,%)					H/C	O/C	HHV(MJ/kg）
	FC_d^a	A_d	V_d	C_d	H_d	O_d^a	N_d	S_d			
MS	16.17	5.46	78.37	45.30	5.85	42.40	0.78	0.21	1.55	0.70	18.22
HTC-220-60	21.53	3.59	74.88	56.50	5.59	33.24	0.93	0.15	1.19	0.44	22.80
HTC-250-60	38.35	1.33	60.32	66.80	5.36	25.31	1.08	0.12	0.96	0.28	26.99
HTC-280-60	47.28	2.07	50.65	72.98	5.36	18.09	1.36	0.14	0.88	0.19	29.87
HTC-310-60	53.63	1.58	44.79	75.75	5.16	16.07	1.29	0.15	0.82	0.16	30.82
HTC-340-60	59.07	1.85	39.08	77.44	4.85	14.16	1.55	0.15	0.75	0.14	31.24
HTC-280-15	46.24	2.13	51.63	71.36	5.37	19.37	1.59	0.18	0.90	0.20	29.19
HTC-280-30	46.35	1.68	51.97	72.46	5.38	19.16	1.16	0.16	0.89	0.20	29.62
HTC-280-90	48.68	1.62	49.77	73.15	5.25	18.44	1.40	0.14	0.86	0.19	29.77
HTC-280-120	51.34	1.58	47.08	73.50	5.23	18.23	1.31	0.15	0.85	0.19	29.90

[a] Calculated by difference. FC, fixed carbon; A, ash; V, volatile matter; d, dry basis.

Table 1 Proximate, ultimate and HHV analyses of hydrochars

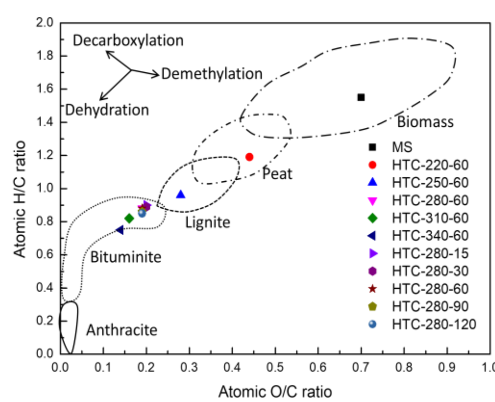

Fig 2 Van Krevelen diagram for LEA and hydrochar samples

3.3 Combustion behavior of MS and hydrochars

The combustion profiles of different samples were analyzed by the thermogravimetric analysis (TGA) and the results were shown in Fig.3. As shown in the figure, the combustion process of MS samples was relatively complex, in which the combustion conversion curve was obviously divided into two stages. Accordingly, the combustion rate curve also had two obvious weightlessness peaks, which corresponded to the combustion of volatiles and fixed carbon respectively. Moreover, the combustion curve of the sample after HTC process moved towards the high temperature zone. The combustion process of the HTC-220-60 and HTC-250-60 samples was similar to that of the MS sample and also divided into two distinct stages. Whereas, in the first stage, the conversion rate and the combustion rate peak were significantly reduced. For the second stage, the conversion rate peak was enhanced and both peaks moved towards the high temperature zone. The main reason is that HTC is actually a process of decarboxylation and dehydration, that is, the removal of volatile matter in hydrochar. Therefore, the observed peak of the volatiles in the corresponding combustion curve is lowered. When HTC temperature was higher than 280 ℃, two stages of combustion process were very difficult to distinguish clearly. There was only one apparent weightlessness peak that can be observed in the combustion rate curve. The temperature range corresponding to the combustion curve was consistent with that of bituminous coal. When the HTC temperature continued to rise, the two curves moved slightly towards the high temperature zone but with a small change range. This phenomenon further illustrated that the optimal temperature for the preparation of hydrochar from MS by HTC was 280 °C. The effect of excessive temperature on reducing the volatile content and increasing the calorific value of hydrochar was not obvious. From the energy saving point of view, it is more appropriate to operate HTC process under the condition of temperature of 280 °C with a holding time of 60 min.

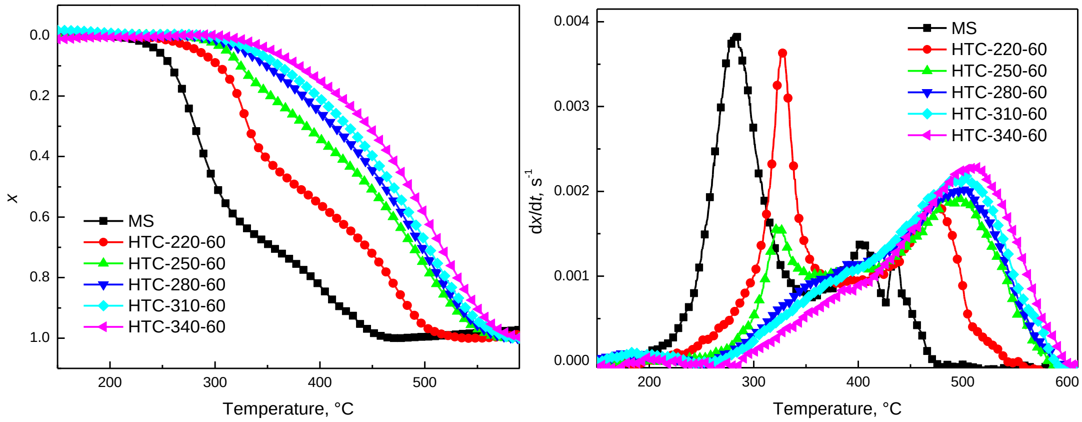

Fig.3 The combustion curves of hydrochar with different carbonization temperature

4. CONCLUSIONS

HTC technology was used to convert the maize straw to an alternative solid fuel, hydrochar, with high energy efficiency. The volatile matter and ash content of hydrochar were reduced, and the fixed carbon content and calorific value were increased correspondingly. The hydrochar's combustion performance was similar to that of bituminous coal used in blast furnace. The analysis results showed the potential to convert the maize straw via HTC process into a low ash, high calorific value solid fuel for the blast furnace injection. The optimal conditions for the HTC process were the carbonization temperature at 280 ℃ and the holding time of 60 minutes.

ACKNOWLEDGEMENT

This work was supported by the NSFC (No. 51804026), CAST (2017QNRC001), VINNOVA (dnr:2017-01327) and SK funding of Swerim AB (pnr:70.101155.10).

REFERENCE

[1] Lee JK, Lee KY, Sohn DH, Kim YM, Park KY. Hydrothermal carbonization of lipid extracted algae for hydrochar production and feasibility of using hydrochar as a solid fuel. Energy 2018;153:913-20.

[2] McKendry P. Energy production from biomass (part 2): conversion technologies. Bioresource Technol 2002;83:47-54.

[3] Channiwala SA, Parikh PP. A unified correlation for estimating HHV of solid liquid and gaseous fuels. Fuel 2002,81:1051-63.

