Fuel 222 (2018) 407–415

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full Length Article

Investigation of potassium transformation characteristics and the influence of additives during biochar briquette combustion

Qian Wang[a,b,*], Kuihua Han[a,*], Jianhui Qi[a,c], Jigang Zhang[d], Haopeng Li[a], Chunmei Lu[a]

[a] School of Energy and Power Engineering, Shandong University, Jinan, China
[b] Department of Thermal Engineering, Shandong Jianzhu University, Jinan, China
[c] School of Mechanical and Mining Engineering, The University of Queensland, Brisbane, Australia
[d] Jinan YuXuan Environmental Technology Co., Ltd, Jinan, China

ARTICLE INFO

Keywords:
Biomass
Char
Briquettes
Potassium
Additive

ABSTRACT

Low energy density and ash fusion problem were problems that limit biomass widespread utilization. To avoid these, maize straw (MS) was blended with two additive –$NH_4H_2PO_4$ (ADP) and $Ca(H_2PO_4)_2$ (CPM)-respectively, and the production chain of mixing additive-briquetting-pyrolysis was put forward to produce MS char briquettes (MSC, MSC-ADP and MSC-CPM). Ash fusion characteristics of MS char briquettes after combustion was investigated by XRF, XRD, SEM-EDS and simulation. Results show that the softening temperature increased with the enhanced ratio of P_2O_5/K_2O until 0.2, and CaO/K_2O until 0.9. The higher amount of CaO and P_2O_5, the lower amount of K_2O, the better ash fusion characteristics. The P_2O_5 had larger influence on softening temperature. The surfaces of MSC ashes formed at 1000 °C were fusion and smooth in micro observation, while surfaces of MSC-ADP and MSC-CPM ashes were coarse and the particles were much looser. Both SEM-EDS and XRD results illustrated that phosphorus in additives combined with potassium to produce high melting temperature potassium phosphates rather than low melting temperature potassium silicates. The potassium fixation ability of ADP was better than that of CPM. The calcium silicates and calcium phosphates produced by CPM could improve ash characteristics.

1. Introduction

With the growth of environmental problems such as global warming derived from fossil fuels and the prospective depletion of them, biomass is regarded as an alternative renewable energy resource [1,2]. However, the drawbacks of storage and transportation such as low densities, low calorific value, high volatile contents of raw biomass will restrict its development [3]. Besides, it is found that the variations among biomass composition were greater than coal, which will limit its widespread use [4]. Among biomass upgrading technologies, densification and pyrolysis are two available and simple pretreatment methods [5]. The pyrolysis promotes the homogeneity of various kinds of biomass [6], and the physical and energy properties of biochar briquettes are enhanced by pyrolysis of maize straw briquettes [7]. Biochar briquettes even have the potential for replacing the natural gas and oil in power generation, so developing the industry of biochar briquettes are profitable for agricultural country to export upgrade fuels to other countries [8].

However, the inorganic minerals in biomass can be responsible for enhanced corrosion, agglomeration, slagging, fouling, bed defluidization during biomass heating [9]. These ash related problems induced by inorganic minerals cannot be relieved by pretreatments such as densification and pyrolysis [10]. It is widely accepted that most of serious slagging and fouling problems during biomass combustion result from the low ash melting temperatures [33]. In comparison with coal, natural biomass is normally enriched in potassium [34], and higher concentration of potassium usually contributes to decreased ash fusion temperatures [35]. During thermal conversion, the potassium exist in the form of potassium silicate, chloride, sulfate and aluminosilicate. The formed alkali metal silicates will melt partially or totally when the temperature is high [36]. K, Cl, and S are partly or wholly released from biomass fuels to the gas phase [37]. So the coarse fly ash such as KCl and K_2SO_4 may condense on tube surface during the cooling process of gaseous potassium [11,12]. The emission of aerosols is also closely

Abbreviations: MS, maize straw; MSC, maize straw char; ADP, ammonium dihydrogen phosphate, $NH_4H_2PO_4$; CPM, calcium phosphate monobasic, $Ca(H_2PO_4)_2$; FC, fixed carbon; V, volatile matters; A, ashes; ST, softening temperature; T_p, pyrolysis temperature

* Corresponding authors at: School of Energy and Power Engineering, Shandong University, Jinan, China; Department of Thermal Engineering, Shandong Jianzhu University, Jinan, China (Q. Wang); School of Energy and Power Engineering, Shandong University, Jinan, China (K. Han).
E-mail addresses: sherrywang1010@163.com (Q. Wang), hankh@163.com (K. Han).

https://doi.org/10.1016/j.fuel.2018.02.156
Received 13 November 2017; Received in revised form 26 January 2018; Accepted 24 February 2018
Available online 23 March 2018
0016-2361/

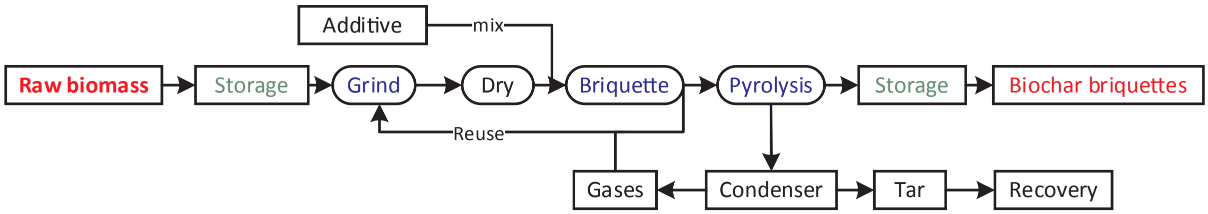

Fig. 1. Flow diagram of an improved mixing additive-briquetting-pyrolysis process.

Table 1
Proximate, ultimate and ash composition analysis of MS char briquettes/(wt%, on dry basis).

Sample	Proximate analysis[a]			Ultimate analysis				
	FC	A	V	C	O[b]	H	N	S
Raw MS	15.59	9.36	75.04	42.33	41.16	5.78	1.06	0.31
MSC-250	26.57	10.46	65.18	44.69	38.36	4.75	1.45	0.27
MSC-350	38.21	16.69	44.99	50.29	26.1	3.63	1.45	0.28
MSC-450	49.57	21.89	29.98	54.18	19.33	3.13	1.28	0.27
MSC-550	54.42	25.82	10.80	57.75	12.37	2.53	1.28	0.25
MSC-650	59.13	26.10	15.46	58.00	12.74	1.82	1.11	0.23

Samples	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl	K_2O	CaO	TiO_2	Cr_2O_3	MnO	Fe_2O_3	Others
250-MSC	0.99	0.75	20.50	2.46	2.86	4.42	44.30	17.60	0.28	0.25	0.24	4.93	0.42
350-MSC	0.87	0.76	21.20	2.50	2.41	4.34	43.40	17.90	0.26	0.31	0.17	5.15	0.73
450-MSC	0.82	0.70	21.80	2.31	2.49	4.34	42.70	18.50	0.25	0.31	0.25	5.21	0.32
550-MSC	0.88	0.71	22.40	2.35	2.99	4.30	42.10	17.70	0.26	0.31	0.24	5.33	0.43
650-MSC	0.85	0.76	23.40	2.43	2.25	4.08	40.30	18.50	0.34	0.27	0.25	5.33	1.23

[a] FC = fixed carbon. V = volatile matters. A = ashes.
[b] O was calculated by difference.

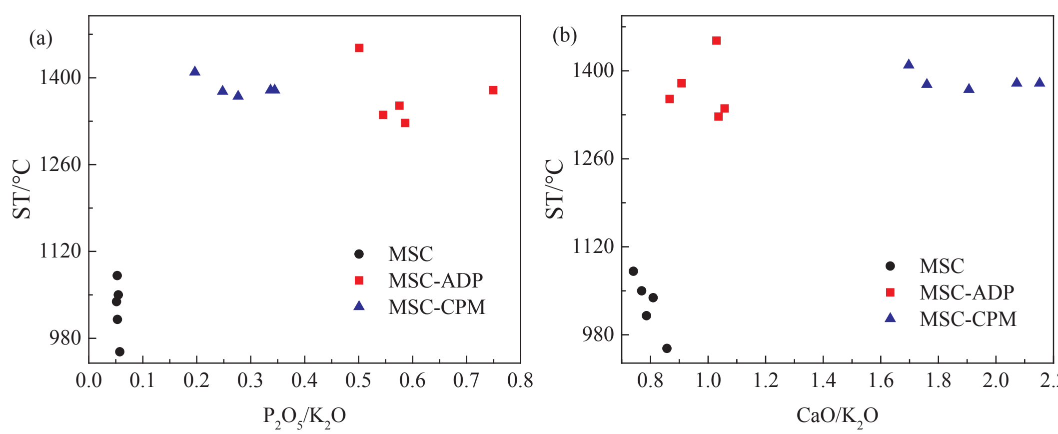

Fig. 2. The relationship between ash content and softening temperature (ST). (a) P_2O_5/K_2O; (b) CaO/K_2O.

linked with gaseous potassium [13,14]. Except raw biomass, the ash fusion tendencies of biochar briquettes are also in the range of seriousness, and the ash fusion temperature of biochar briquettes were lower than 1081 °C [15].

Among the methods to control these ash related problems, mixing mineral additive is an effective way to operate. Phosphorus can dominate over silicon for alkali fixation. Some phosphates in biomass present relatively high decomposition and melting temperatures during heating [16]. Compared with low melting point potassium silicates, the high melting point calcium potassium phosphate could inhibit fusion phenomenon [17]. In addition, the fixation of alkali in ashes could prevent emission of gaseous potassium [18], which is benefit for particulate emission. Fusco pointed out that ash behaviour of co-firing a high phosphorus fuel with a high calcium fuel should be further assessed by experimental work [19]. By increasing phosphorus content in the fuel, a reduction of volatilized deposit and fine particle forming matter containing KCl as the main component was observed [20]. The potassium fixed ratio increasing rate of additives was 35.90%–64.89% at 1100 °C, and the ash fusion temperature of biomass briquettes was increased by 55–277 °C [21,22]. Thus, phosphorus based additives are benefit for solving ash related problems in biomass combustion. In addition, biochar briquettes and its ashes are benefit for soil improvement if external phosphorus element is adsorbed [23]. Although the effectiveness of phosphorus based additives in preventing melting and fusion in raw biomass combustion is reported, detailed melting or fusion mechanism of biochar and the influence of additives on it is still unclear.

Based on the above, an improved production process is put forward, as shown in Fig. 1, which is mixing additive-briquetting-pyrolysis process. Typically, the production process of densified biochar is pyrolysis first and then densification. However, the worse compaction characteristics caused by fiber destruction and moisture loss lead to the difficulty in densification of biochar fibers [24]. The advantages of process in Fig. 1 are utilizing the pyrolysis tar to strength the physical