Study on the effect of molten ash on the combustion process for biomass

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Abstract. In this study, the high temperature visual test system (HTVTS) and high temperature thermogravimetric test system (HTTTS) were set up to observe the formation process of ash, thereby analyzing the mechanism of biomass melt combustion. Then, the effect of the molten ash on the combustion process was investigated. Results show that during the combustion, once the local temperature of the biomass particle is higher than the ash melting temperature, the generated ash could be melted and contracted into a spherical shape by the surface tension. The molten ash located in the interior of the biomass particle adhere to the char surface, thereby preventing the contact between char and oxygen. The molten ash located on the surface of biomass particle could drop down from the surface of biomass particle. When the conversion rate is higher than 45%, the effect of molten ash on the reaction rate becomes more obvious.

1. Introduction
One of the biggest challenges facing in 21st century is overcoming the shortage of fossil fuels and controlling greenhouse gas emissions [1]. This challenge has prompted industry and academia to study the feasibility of using renewable fuels[2-3]. In general alternative energy sources, biomass has the advantages of renewability, cleanliness and abundant sources, and it has become a potential energy source to replace fossil fuels [4-5,6]. Combustion is the most mature and widely used technology in biomass utilization. Many scholars have studied the combustion characteristics of biomass particles from different perspectives [7-9]. However, these studies are mainly focus on the temperature range below 1000 °C, corresponding to the operating temperature range of fluidized bed and fixed bed. In the recent retrofit of a suspended-fired boiler, biomass was first granulated and then pulverized into millimeter-sized particles [10]. Abbas et al. [11] found that when milled biomass is less than 1 mm, energy demand is significantly increased. This indicates that it is important to study the combustion characteristics of biomass particles larger than 1 mm in the higher temperature range.

Biomass combustion can be divided into a pyrolysis stage and a char conversion stage, in which the char conversion stage is considered as a rate limiting process [13]. During the char conversion stage, ash is formed on the surface of the char. Due to the large amount of alkali metals and alkaline earth metals (AAEMs), these ash can be melted and fused, thereby changing the particle structure[14-16]. It is not difficult to imagine that as the particle size of biomass particles increases, the char conversion stage is mainly controlled by the gas diffusion. Therefore, the effect of ash fusion on char conversion stage is more pronounced. However, similar studies are rarely mentioned in the combustion of biomass pellets.
In this study, the high temperature visual test system (HTVTS) and high temperature thermogravimetric test system (HTTTS) were set up to observe the formation process of ash, thereby analyzing the mechanism of biomass melt combustion. Then, the effect of the molten ash on the combustion process was investigated, which could provide the experimental references for the numerical modeling of biomass particles.

2. Experimental part
The biomass (corn stalk) used in this work comes from Heilongjiang province, China. Its fuel characteristics are shown in Table 1. Before the experiment, the biomass particles are polished into the regular samples. High-temperature combustion experiments are carried out on the self-designed high temperature visual test system (HTVTS) (figure 1(a)) and high temperature thermogravimetric test system (HTTTS) (figure 1(b)). The furnace temperature is increased to the setting temperature at the rate of 20℃/min firstly. Then starts the air intake device. The flow rate is controlled to 5 L/min. For HTVTS, when the morphology of the sample is no longer changed, the experiment is stopped. After that, the thermocouple is buried in the particle center and quickly placed into the furnace of HTTTS. When the temperature and mass are no longer changed, the experiment is finished.

| Sample       | Proximate analysis | AFT test     |
|--------------|--------------------|--------------|
|              | M_ad%/ | V_ad%/ | A_ad%/ | FC_ad%/ | Q_net,ar/kJ/kg | IDT/℃ | ST/℃ | HT/℃ | FT/℃ |
| Corn stalk   | 7.24   | 71.69  | 12.2   | 14.5    | 17.5            | 1045  | 1101 | 1152 | 1185 |

M: Moisture. V: Volatile. A: Ash. FC: Fixed carbon. a ad: Air drying base. b daf: Dry ash free base

3. Results and discussion
Figure 2(a) shows the morphology changes of biomass particle during combustion at different ambient temperatures. It can be found that the biomass combustion process could be divided into the three stages: the combustion stage of volatiles, the co-combustion stage of volatiles and char, as well as the combustion stage of char. When the ambient temperature are 920℃ and 1053℃, biomass particle could maintain the initial cylindrical structure during the combustion. Once the temperature increases to 1192℃ and 1345℃, the particle shape of biomass changes significantly. Firstly, the smaller spherical particles are formed on the surface of biomass particle. Then, the neighboring spherical particles are coalesced into the large spherical particle. Under the action of gravity, the large spherical particles drop down from the surface of biomass particle. Figure 2(b) shows the changes of the section area during the combustion. It can be seen that the particle size of biomass decreases with the progress of the reaction. Moreover, the decreasing tendency increases with the ambient temperature. It is important to note that there is a critical point at 1192℃ and 1345℃. After the critical point, the particle size decreases rapidly. Combined with figure 2(a), the critical point corresponds to the time...
range of large spherical particles appearing on the particle surface. This means that the obvious change of particle size at 1192°C and 1345°C could be attributed to the merging and peeling of adjacent spherical particles.

![Figure 2](image_url)

Figure 2. Combustion process: (a) direct observation; (b) evolution of particle size.

Figure 3 shows the results of SEM-DES analysis. When the ambient temperature is 920°C, the biomass particle exhibits an irregular loose structure. Meanwhile, the clusters of spherical particles could be observed. The loose structure of the particle contains a large amount of Si, C and O elements, and a small amount of Al, Mg, Fe, K, Ca. While, the spherical particle cluster contains Si, O, Al, Mg, Fe, K and a small amount of C elements. Studies have shown that Si, Al and Fe elements are stable and retained elements in the molten ash. During the combustion, due to the exothermic heat of combustion, the local temperature of the biomass particle is higher than the ash melting temperature. At this time, the generated ash is melted and further contracted into a spherical shape by the surface tension. When the carbon is present, the spherical particles exist in the form of clusters of particles. As the decrease of the carbon, the spherical particles exist in form of the individuals. When the temperature rises to 1053 °C, the structure of the biomass particle becomes smoother. The reason may be caused by the melting and plastic transformation of the cell structure. When the ambient temperature is increased to 1192°C and 1345°C, the biomass particle is almost completely covered by the independent spherical particles. Meanwhile, the C element is not detected in the spherical particles, which means that the ash melting and peeling could not cause char loss.
Figure 3. SEM image: (a) 920°C; (b) 1053°C; (c) 1192°C; (d) 1345°C; (e) 1192°C molten sphere; (f) 1345°C molten sphere.

Figure 4. Center temperature and mass of biomass particle as a function of time.

Fig. 4 shows the change of the center temperature and mass for biomass particle during the combustion. When the biomass particle is exposed to a high-temperature environment, the external heat transfers to the biomass particle by the radiation and convection. Therefore, the temperature of the particle rises rapidly because of the large initial temperature difference between the particle and the environment. In addition, the volatiles in the particle sharply release and react, which leads to the particle temperature is higher than the ambient temperature. As the reaction proceeds, the biomass reaction gradually changes from the volatiles combustion to char combustion, thereby reducing the rate of heat release. At the same time, the heat dissipation of the particle and the ash fusion also suppress the increase of the particle temperature. When the heat released by the combustion is less than the heat dissipation of the particles and the heat absorption of ash melting, the particle temperature decreases and finally is consistent with the ambient temperature. The initial temperature difference between the environment and the biomass particle increases with the ambient temperature, so that the weight loss curve and the temperature curve move to the upper left. However, the increase of the particle temperature results in the increase of the heat transfer between the particle and the environment. Therefore, the heating rate of the second stage decreases with the increase of the ambient temperatures.
Fig. 5 shows the reaction rate of biomass particle as a function of conversion. It can be found that the reaction rate of the biomass increases firstly and then decreases with the conversion rate. When the conversion rate is lower than 45%, rising ambient temperature could increase the reaction rate, which is because that the release of volatiles is mainly controlled by the heat transfer. When the conversion rate is higher than 45%, with the increase of the ambient temperature from 920°C to 1053°C, the reaction rate increases. However, the reaction rate at 1192°C is nearly same as that at 1053°C, which means that the reaction stage is in the diffusion control area. Compared to the reaction rate at 1192°C, when the temperature rises to 1345°C, the reaction rate of the particle is further raised. The reason can be explained by that rising temperature speeds up the ash melting. The molten ash falls off the particle surface of the biomass, which decreases the diffusion resistance of the oxygen.

4. Conclusions

- During the combustion, once the local temperature of the biomass particle is higher than the ash melting temperature. The generated ash could be melted and contracted into a spherical shape by the surface tension. When the carbon is present, the spherical particles exists in the form of clusters of particles. As the decrease of the carbon, the spherical particles exist in form of the individuals.
- The molten ash located in the interior of the biomass particle adhere to the char surface, thereby preventing the contact between char and oxygen. The molten ash located on the surface of biomass particle could drop down from the surface of biomass particle.
- When the conversion rate is higher than 45%, the effect of molten ash on the reaction rate becomes more obvious.

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References
[1] Dhamodaran G, Esakkimuthu GS, Pochareddy YK, Sivasubramanian H. Investigation of n-butanol as fuel in a four-cylinder MPFI SI engine. Energy, 2017, 125: 726-735.
[2] Haseli Y, Oijen JAV, Goey LPHD. A detailed one-dimensional model of combustion of a woody biomass particle. Bioresource Technology, 2011, 102(20): 9772-9782.
[3] Singh A, Pant D, Korres NE, Nizami AS, Prasad S, Murphy JD. Key issues in life cycle assessment of ethanol production from lignocellulosic biomass: challenges and perspectives. Bioresource Technology, 2010, 101(13): 5003-5012.
[4] Shan F, Lin Q, Zhou K, Wu Y, Fu W, Zhang P, Song L, Shao C, Yi B. An experimental study of ignition and combustion of single biomass pellets in air and oxy-fuel. Fuel, 2017, 188: 277-284.
[5] Liang F, Wang R, Jiang C, Yang X, Zhang T, Hu W, Mi B, Liu Z. Investigating co-combustion characteristics of bamboo and wood. Bioresource Technology, 2017, 243: 556-565.

[6] Werther J, Saenger M, Hartge E U, et al. Combustion of agricultural residues. Progress in Energy Combustion Science, 2000, 26(1):1-27.

[7] Shan F, Lin Q, Zhou K, et al., 2017. An experimental study of ignition and combustion of single biomass pellets in air and oxy-fuel[J]. Fuel, 2017, 188:277-284.

[8] Kuo, J. T., Hsi, C. L., 2005. Pyrolysis and ignition of single wooden spheres heated in high-temperature streams of air. Combustion and Flame, 142 (4), 401-412.

[9] Roy, M. M., Dutta, A., Corscadden, K., 2013. An experimental study of combustion and emissions of biomass pellets in a prototype pellet furnace. Applied Energy, 108, 298-307.

[10] Momenikouchaksaraei M. Fundamental Study of Single Biomass Particle Combustion. 2013.

[11] Abbas T, Costen P G, Lockwood F C. Solid fuel utilization: From coal to biomass. Symposium on Combustion, 1996, 26(2):3041-3058.

[12] Momeni M, Yin C, K? R S K , et al. Experimental Study on Effects of Particle Shape and Operating Conditions on Combustion Characteristics of Single Biomass Particles[J]. Energy & Fuels, 2013, 27(1):507-514.

[13] Kim YT, Seo DK, Hwang J. Study of the Effect of Coal Type and Particle Size on Char-CO2 Gasification via Gas Analysis. Energy & Fuels, 2011, 25(11):5044-5054.

[14] Damoe A J, Jensen P A, Frandsen F J, et al. Fly Ash Formation during Suspension-Firing of Biomass. Effects of Residence Time and Fuel-Type. Energy Fuels, 2017, 31(1): 555-570.

[15] Liu M, Shen Z, Liang Q, et al. Morphological evolution of single char particle with low ash fusion temperature during the whole gasification process. Energy & Fuels, 2018, 32, 1550-1557.

[16] Lin S, Hirato M, Horio M. The characteristics of coal char gasification at around ash melting temperature Energy & Fuels, 1994, 8, 598-606.