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Influence of Impurity Ions on Rice Husk Combustion

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Abstract

Rice husk (RH) contains various impurity ions such as K^+, Al^{3+}, Fe^{3+}, Mn^{n+} (n = 2 – 4), and P-containing acid ions. In the present work, some of their oxides, formed in RH combustion, were found to exert a strong influence on the middle- and late stages of RH combustion, and consequently, strongly affected the structure and properties of the final ash. Very recently, we proved for the first time that the existence of the transition metallic ions in rice husk can lead to a decrease of about 70°C in the terminal combustion temperature (T_{tc}) of RH. This catalytic behavior was demonstrated by a Mn re-loading and catalytic combustion experiment. By leaching out most of the impurity ions from RH with HCl and subsequently re-loading some Mn^{2+} ions into the HCl-washed RH host for co-combustion, the T_{tc} of RH was also decreased. T_{tc} can be decreased by more than 100°C. This is of high benefit not only for the industrial combustion of RH, but also for the high value-added applications of the final MnO_x-supported ash (x = 1 – 2). This ash can, for example, be directly used as a complete combustion catalyst of other organics.

Key words: Rice husk, Transition metallic ions, Catalytic combustion, Catalyst.

Introduction

Rice husk (RH) is one of the main agricultural disposals in the rice-producing countries. According to the newest statistical data of the Food and Agriculture Organization (FAO, 2009), the annual paddy production of the 20 largest rice-producing countries amounts to 616 million tons (in 2007). It is well-known that about 20 ~ 25 wt% of a paddy is rice husk (RH), so in these countries about 123 ~ 132 million tons of RH were produced in 2007. How to properly dispose of such a huge amount of regenerable agricultural by-product RH has become a big issue for a long time.

RH has a high C content, giving RH a heating value of ~16.3 MJ kg^{-1} (Armesto, *et al.* 2002), so it is a good fuel candidate. The C content exists in RH mainly as (hemi-) cellulose and lignin. RH has also a high Si content, existing in RH as hydrated silica. In addition, RH also contains K, Al, P, Fe, Mn, Cl, and so on. Due to its porous structure, RH can adsorb a large amount of moisture. The chemical compositions of RH vary from sample to sample, related to the type of paddy, crop year, climatic variation, geographical conditions, and even the fertilizers used in paddy growth.(4)

Combustion is the conventional technique for RH to exploit the calorific value and to obtain silica for commercial use, but such cations as K^+, Al^{3+}, P^{5+}, Fe^{3+}, and Mn^{n+} can remain in rice husk ash (RHA) as oxides, decreasing the purity of RHA and further limiting its use. Moreover, in the direct combustion process of RH, the obtained RHA consists of many black particles, which are very difficult to be fully burned off. The high impurity K content is generally recognized to be the cause (Krishnarao, *et al.* 2001) for this phenomenon. To remove such impurity ions and to obtain high-quality RHA with a predominant composition of silica, treatments such as acid washing RH before combustion were widely employed by many researchers (Chakraverty, *et al.* 1985 and 1988), Rahman, *et al.* 1997 and Umeda, *et al.* 2008). These researches have also examined the similarities and differences in the combustion process of the non-treated and acid-treated RHs by using thermal analysis techniques. However, little attention has been paid to the influence of the

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impurity ions on RH combustion behavior and process. Herein, therefore, we present a work focusing on this influence and demonstrate that impurity ions, especially the transition metallic ions, play a catalyst role in RH combustion. Based on this discovery, we propose a new catalytic route to decrease the complete combustion temperature of RH.

Materials and Experimental Procedures

Three kinds of RHs, designated as *r*-RH, *h*-RH, and *w*-RH, respectively, were employed for combustion in this work. *r*-RH is the raw RH as received. *h*-RH is husk which was just washed with tap water and then dried. *w*-RH is husk that was first washed with tap water followed by drying, then further treated with HCl acid, repeatedly filtered and washed with deionized water, and finally dried. *r*-RH, *h*-RH, and *w*-RH were combusted under the same conditions: 600 °C for 10 – 120 min as well as for 600 min for *r*-RH. Their corresponding ashes are designated as *r*-RHA, *h*-RHA, and *w*-RHA, respectively. Some of *w*-RH was immersed into a $Mn(AC)_2$ solution and then filtered and dried. The Mn-loaded RH is named *m*-RH. *r*-, *w*-, and *m*-RH were used for thermal analyses, respectively.

The solid products were weighed immediately after processes like drying or combustion. X-ray fluorescence (XRF) spectroscopy was used to determine the chemical compositions of *r*-RHA, *h*-RHA, and *w*-RHA. TG-DTA was conducted on a Rigaku Thermo plus 2 TG 8120 analyzer by heating at a rate of either 10 or 5 K min^{-1} in air and using Al_2O_3 as reference.

Results and Discussion

Figure 1 shows the mass change of *r*-RHA, *h*-RHA, and *w*-RHA with the burning time. It is obvious that all RHs experienced a quick mass loss during burning, and after ~30 min burning, the relative mass of the solid products became steady, about 0.15 ± 0.005. An average mass difference in the three RHAs was also found, but it was too little. Moreover, the mass ratio of RHA to RH is also dependent on the amount of adsorbed gases, e.g. moisture, within RH before combustion. Therefore, only judging from the mass ratio, it can not necessarily be concluded that the pretreatments influence on the combustion of RHs at the same temperature, or the mass of the final solid products.

Figure 2 shows the macro-morphologies of *r*-RHA, *h*-RHA, and *w*-RHA. Obviously, the ashes of each RH became progressively white with increasing burning time; about 30 min later, the color changed slightly. For *r*-RH, even though it was burned for 600 min, the ash still looked grayblack, almost the same as the one burned for 30 min. However, *r*-RHA, *h*-RHA, and *w*-RHA obtained under the same conditions show negligible resemblance in terms of color. *h*-RHA is much whiter than *r*-RHA, and *w*-RHA is the whitest. This means pretreatment by tap water washing only is enough to burn RH into white ash with few C residues. Some metallic ions may have still remained in *h*-RH, which gave *h*-RHA a beige color. By a further HCl washing, the residual metallic ions were mostly leached out, so the obtained ashes became snow-white, like *w*-RHA. Therefore, judged from the macro-morphology, the leached-out ions by both tap water and HCl produced a strong influence on the RH combustion.

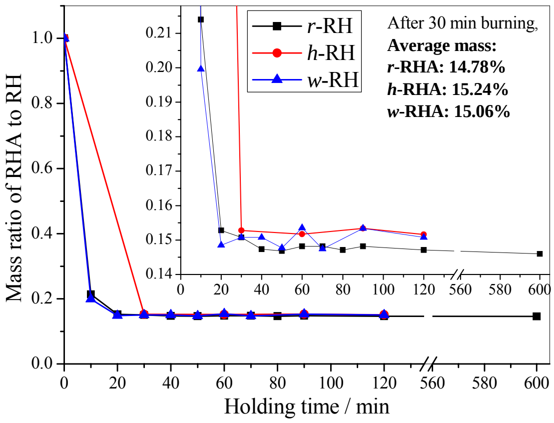

Figure 1. Mass change of *r*-, *h*-, and *w*- RHA with burning time.

Figure 2. Macro-morphologies of *r*-, *h*-, and *w*- RHA

Table 1 lists the main components and the mass ratio of the impurity components to SiO_2 in the ashes *r*-RHA, *h*-RHA, and *w*-RHA obtained by

60 min burning. Evidently, the predominant component of RHA is silica, about 92.66 wt% in *r*-RHA, 93.64 wt% in *h*-RHA, and 93.60 wt% in *w*-RHA. LOI is the loss on ignition, about 3.53, 4.66 and 5.87 wt% in *r*-, *h*-, and *w*- RHA, respectively. LOI is mainly due to the emission of the absorbed gases in the ashes. For *r*- and *h*-RHA, it is also due to the burn-off of some carbon residues. Excluding the influence of the adsorbed gases, the purity of SiO_2 in *w*-RHA can reach 99.1 wt%, high enough for many applications. The rest is impurity, of which the main components are K_2O, P_2O_5, Fe_2O_3, and CaO. Taking into account that the amount of SiO_2 of RH does not vary with the pretreatments, it seems more reasonable to consider the impurity-to-SiO_2 ratio change with the pretreatments. From Table 1, it is clear that K_2O, P_2O_5, Fe_2O_3, and CaO were about 0.61, 0.37, 0.06, and 0.60 mass% of SiO_2, respectively, in the raw husk. After washing with tap water, they changed to about 0.27, 0.14, 0.04, and 1.1%. The increase of CaO must be due to the Ca^{2+} in the tap water, which contaminated the husk. Except for Ca^{2+}, other impurity ions were partially washed out. K content was removed by about 50%. In particular, P content was removed by much more than half by the tap water washing. In some sense, apart from K, the P content must be also responsible for black C residues in *r*-RHA, because the melting points of its oxides are below 600°C. After further washing with HCl, the ratios became 0.05, 0.17, 0, and 0%, respectively. That means the metallic ions were almost completely leached out by HCl. Comparing the water washing and the HCl washing, HCl did not exert much influence on the P content. This may be due to the fact that P^{5+} exists in RH in the form of negative phosphonic ions or groups, which can not be exchanged with H^+ in HCl like the metallic cations. Owing to the limitation of the measurement, about 0.36, 0.26, and 0.32% of the ash mass were not specified for *r*-RHA, *h*-RHA, and *w*-RHA, respectively. According to the previous results published by other researchers (Krishnarao, *et al.* 2001, Shinohara, *et al.* 2004 and Umeda, et al. 2008), the unspecified part should include such transition metallic ions as Mn^{n+} and Zn^{2+}. Some raw RHs Shinohara and Kohyama (2004) and Umeda and Kondoh (2008) were received from the same producing region as ours, and their RHs were found to also contain Mn ions. Therefore, the beige color of *h*-RHA must be due mainly to the existence of such transition metallic ions as Fe^{3+} and Mn^{4+}. However, it may also be partially due to a few highly-dispersed C residues.

Table 1. Chemical composition and impurity-to-SiO_2 ratio of RHA.

Composition or ratio	*r*-RHA (%)	*h*-RHA (%)	*w*-RHA (%)
LOI	**3.53**	**4.66**	**5.87**
SiO_2	**92.66**	**93.64**	**93.60**
K_2O/SiO_2	**0.61**	**0.27**	**0.05**
P_2O_5/SiO_2	**0.37**	**0.14**	**0.17**
Fe_2O_3/SiO_2	**0.06**	**0.04**	**0**
CaO/SiO_2	**0.60**	**1.10**	**0**
Na_2O/SiO_2	**< 0.01**	**< 0.01**	**< 0.01**
MgO/SiO_2	**< 0.01**	**< 0.01**	**< 0.01**
TiO_2/SiO_2	**< 0.01**	**< 0.01**	**< 0.01**
Others	**~0.36**	**~0.26**	**~0.32**

Figure 3 shows the DTA curves of *r*-RH and *w*-RH versus time by heating at different rates. The endothermic troughs at ~70°C were attributed to the evaporation of the adsorbed moisture. The broad exothermic processes in 220 – 550°C correspond to the combustion of RH, and were attributed to the oxidation of organic components. The monitored *T* in this range was higher than the theoretical heating value in all cases because of corruption from the strong exotherm. Hereafter, the mentioned *T* values, if between 220 – 550°C, are referred to theoretical values. For *r*-RH (Figure 3(a)), at least 2 strong exothermic peaks occurred during the combustion. The first (T_{p1}) occurred at ~300°C, and the last (T_{p2}) at ~420°C. Both varied modestly with the heating process, but the terminal combustion *T* (T_{tc}) depends on the heating rate. The one for 10 K min^{-1} is ~500°C, thus higher than the other two for 5 K min^{-1} which, however, are close, ~470°C. This higher-*T*-for-faster-heating phenomenon generally occurs in DTA analysis of slow-heat-transfer samples. For *w*-RH (Figure 3(b)), T_{p1} is almost the same as the T_{p1} of *r*-RH, implying that the ions, leached out by pretreatments, should not exert influence on the early combustion process. However, T_{p2} became 480°C for 10 K min^{-1} and 460°C for 5 K min^{-1}, respectively. Both are higher than those of *r*-RH (~420°C). Especially, T_{tc} of *w*-RH reached ~570°C for 10 K min^{-1} and ~540°C for 5 K min^{-1}. Thus temperatures recorded were by 70°C higher than those of *r*-RH, respectively. This means that, at the same heating rate of 10 K min^{-1}, the *r*-RH combustion can be completed at ~500°C, but the *w*-RH combustion needs ~570°C to be completed. Therefore, compared with the *w*-RH combustion, the *r*-RH combustion must be a catalytic process. The catalyst ions or precursors must have been leached out from *w*-RH by the pretreatments.

According to the chemical compositions of RHA in Table l, K_2O and CaO are well-known for not catalyzing combustion or oxidation reactions of organics, and in general P_2O_5 is not a combustion or oxidation catalyst either. In spite of this, oxides of transition metals such as Mn, Cu, Mo, Fe, V, Co, Ni, and Zn are widely used as catalysts in the complete oxidation of many organic compounds.$^{(6, 9)}$ Thus, transition metallic oxides as Fe_2O_3 and MnO_x for instance should be the catalysts in the *r*-RH combustion. Taking into account the higher catalytic activity of MnO_x compared with Fe_2O_3 (Kim, 2002), Mn^{2+} ions were chosen in this work for the demonstration experiment on the catalytic combustion.

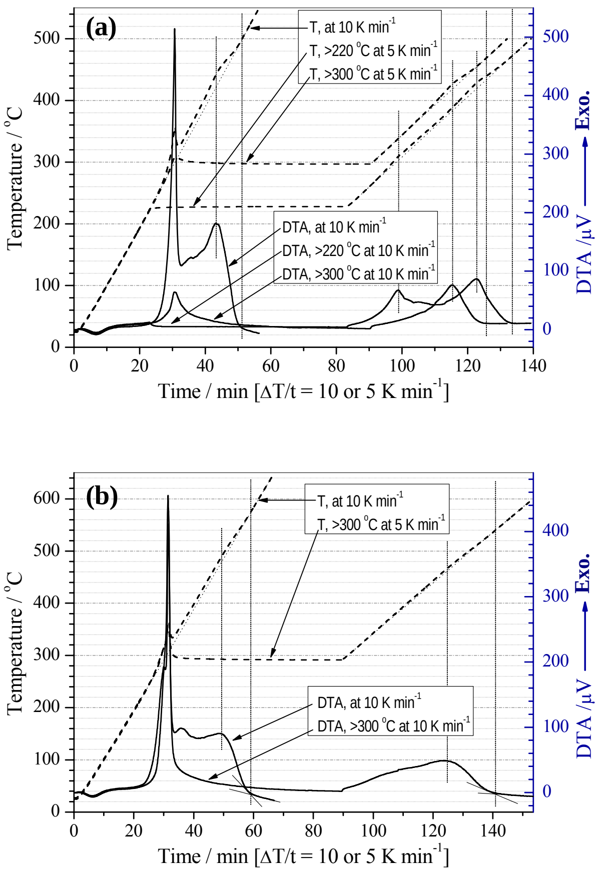

Figure 3. DTA curves of *r*-RH (a) and *w*-RH (b) at various heating rates.

Figure 4 shows the DTA results of an *m*-RH sample at a heating rate of 10 K min^{-1}. For this Mn-loaded *w*-RH sample, obviously, T_{p1} is still near 300°C, very close to the temperatures of *r*-RH and *w*-RH, but T_{p2} and T_{tc} were decreased to ~375°C and ~470°C, respectively. Both are by ~100°C lower than those of the non-loaded *w*-RH, respectively, and also lower than those of the raw RH, respectively. Compared with *w*-RH combustion, *m*-RH combustion is undoubtedly a catalytic process, and the catalyst must be the oxidation derivatives of $Mn(AC)_2$, like MnO_x. Before combustion of *m*-RH, MnO_x has not been contained, so the early combustion stage is not a catalytic process, which could be confirmed by the similar T_{p1} to that of *w*-RH. By the same token, it can be extrapolated that before combustion *r*-RH should contain few or no oxides of such transition metals as Fe and Mn. Oxides like Fe_2O_3 and MnO_x must be formed in the early combustion stages and then catalyze the subsequent stages, resulting in a greatly decreased T_{p2} and T_{tc} compared with those of the ion-leached-out *w*-RH. Therefore, these transition metallic ions play a catalyst role in the RH combustion, favoring the combustion oxidation. According to this discovery, it is not difficult to explain why the ashes of the raw husks, when burned at below 500°C, always look whiter than those of the acid-washed husks.

A larger T_{tc} decrease, over 100°C, is probable by a higher Mn uptake within *w*-RH. This catalytic combustion route is of particular interest for industrial burning of RH to exploit its calorific value. It is also of practical interest in preparing high value-added ash products. Taking into account that the influence of pretreatments on the mass loss is not remarkable, as discussed above, the mass loss with the temperature would not be further discussed, and thus the TG curves were not shown in this work. A more detailed study of this catalytic combustion route will be published soon.

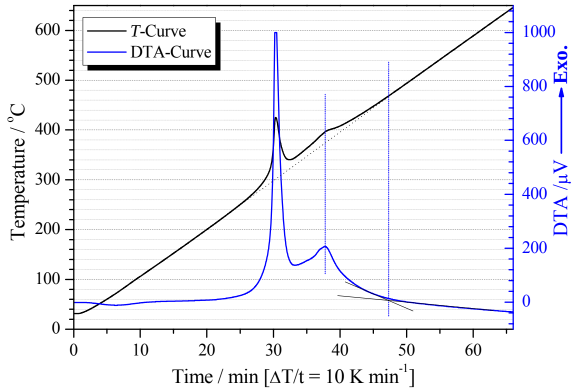

Figure 4. DTA curves of an *m*-RH sample at 10 K min^{-1}.

Conclusions

In summary, we conducted a study of the influence of impurity ions on RH combustion. Apart from K content, P content also influences the burning off of the C residues; transition metallic ions such as Fe^{3+} and Mn^{3+}, for example, not only change the color of the solid combustion products, but also catalyze the RH combustion. Based on this discovery, we also proposed a catalytic route via the impregnation of catalyst ions within RH. This route possesses advantages in decreasing the complete combustion temperature by over 100°C and preparing high value-added ashes for catalysis and adsorption applications, which, indeed, can be of practical interest for rice-growing countries.

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