

Article

# Comparisons of Acid and Water Solubilities of Rice Straw Ash Together with Its Major Ash-Forming Elements at Different Ashing Temperatures: An Experimental Study

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**Abstract:** Recycling utilization of straw ash as a fertilizer in farmland is expected to play an important role in the sustainable development of both agriculture and biomass energy. However, the ashing temperature and the aqueous solution characteristics may affect the recycling properties of the nutrients contained in the ash. The solubilities of both the ash and its elements can represent the above recycling properties. This paper presents a systematic experimental investigation on the acid solubilities of both rice straw ash and its major elements produced from combustion at 400–800 °C, and these findings are compared with the corresponding water solubilities obtained from the authors' previous work. Meanwhile, the correlations of two solubilities with the ashing temperature were given based on the experimental data. Results show that the acid solubility of rice straw ash decreases linearly by approximately 76% as the ashing temperature increases from 400 to 800 °C, while it is significantly higher than the corresponding water solubility at different temperatures. The acid solubilities of K, P, Ca, Mg, and Na are higher than their water solubilities, whereas two solubilities of S and Cl have almost no dependence on the temperature and the acidity of solution. This study also reveals a strong negative linear relationship between the solubility of K and the temperature. The solubilities of other elements (P, S, Na, Ca, Mg, and Cl) with the temperature have quadratic curve or cubic curve relationships. Furthermore, it is recommended that the ashing temperature should be lower than 600 °C to avoid the loss of some nutrients in the straw ash.

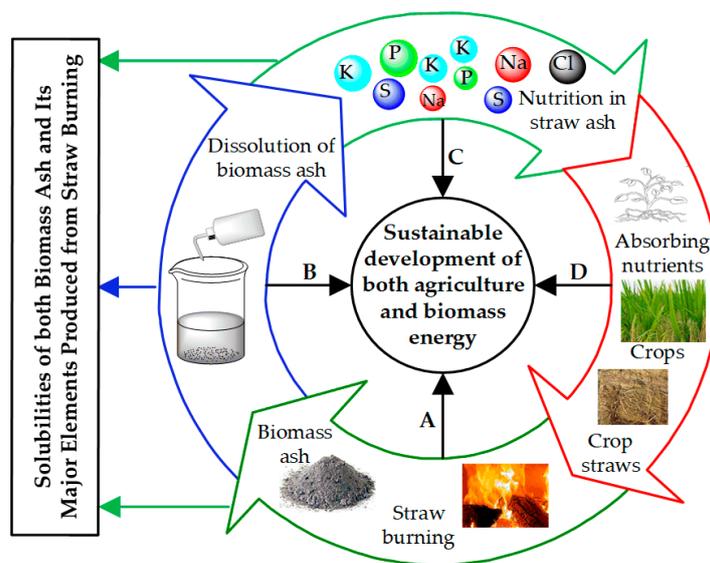
**Keywords:** rice straw ash; ash-forming elements; solubility; sustainable development of both agriculture and biomass energy; recycling property; ashing temperature

## 1. Introduction

Applications of biomass ash have been attracting a lot of attention recently in various fields, such as farmland fertilizer [1–3], construction material [4,5], adsorbent material [6,7], production material of ceramics, and raw material of metal recovery [7,8]. In all these applications, the soil application as a green, cyclic, and sustainable way has a huge potential and better prospect [9,10]. According to the statistics, approximately 85–95% of nutrients taken up from soil by plants during growth—including potassium (K), phosphorus (P), calcium (Ca), and magnesium (Mg)—are contained in biomass ash [11]. The recirculation of these nutrients to farmland soil is important in agricultural

sustainable development [12,13]. Furthermore, using biomass ash as an alternative to chemical fertilizer [14,15] would not only balance the fertility of agricultural soil, but also reduce the amount of both the ash disposal and the chemical fertilizer of consumption, and thus alleviate loss of soil nutrients and environment pollution [16] and reduce the investment cost of agricultural production process. Comparing to direct straw returning, ash recirculation could prevent plants from being infected by pathogens and pests contained in the straw [17], and thus reduce the utilization of chemical pesticide. Therefore, the recycling of biomass ash as fertilizer to farmland soil plays a great role in the sustainable development of both agriculture and biomass energy.

In farmland soil, most of the nutrients are accessible to plants only in their free ionic form. One of the fundamental questions in the soil application of straw ash is transforming biomass ash to accessible (soluble or bioavailable) nutrients [18]. Therefore, the solubilities of biomass ash together with its major ash-forming elements are vital properties for the recirculation of nutrients, as shown in Figure 1. These solubilities are greatly determined by the pH values or acidity of solution and soil [11]. It is common knowledge that soil acidification is a serious global problem [19]. The main reasons for the soil acidification can be explained as follows: (1) the osmosis effect of the natural or artificial acidic rain resulting from dissolving of  $\text{CO}_2$ ,  $\text{SO}_2$ , and  $\text{NO}_x$  in air [20] and (2) the extensive application of chemical nitrogen fertilizers [7]. This seriously limits the sustainable development of eco-agriculture in the new era. According to the reference [19], 40–50% of the potentially arable lands were acidic in the world. In China, the area of acid land (about 200 million ha) accounted for 23% of total land area [19]. Biomass ash contains various alkali metal compounds, which can improve acidic soil. As a result, the acid-soluble characteristics of both biomass ash and its ash-forming elements can partially represent the recycling property of the nutrients in the ash.



**Figure 1.** Schematic diagram of recycling application of biomass ash as a fertilizer in farmland.

The solubilities of both biomass ash and its ash-forming elements have been extensively reported in the published literatures. The total dissolved mass content of wood ash increased by 500% as the pH value of aqueous solution decreased from 13 to 5 [21]. In the bottom ash of municipal solid waste incineration, the solubilities of aluminum (Al), calcium (Ca), magnesium (Mg), sulfur (S), sodium (Na), and iron (Fe) in nitric acid solution (pH = 4, 6) increased significantly with the increase of the leaching time [22]. At the same time, the elements solubilities differ significantly with each other. Most of Ca and Fe, 30% of K, 32% of Na, 48% of Al, 25% of S, and 48% of P in the solid residue of cane bagasse gasification were acid-soluble [23]. Moreover, in wood combustion ash, 81% of Ca, 57% of Mg, 34% of K, and 20% of P were soluble in the ammonium acetate aqueous solution of pH = 4.2 [24]. In addition, based on their water solubilities, these elements were classified into the following three categories:

(1) easily soluble nutrients (K, boron (B), Na, chlorine (Cl), and S); (2) slightly soluble nutrients (Ca, Mg, silicon (Si), Fe, and Al); and (3) highly insoluble nutrients (P) [22,25].

Rice is the third-largest agricultural product in the world. In China, rice accounts for about 40% of the total agricultural products according to the statistical data of Food and Agriculture Organization of the United States, meaning that a large amount of biomass ashes are produced from the burning of rice straw every year. Biomass ash properties are significantly affected by the combustion temperature or ashing temperature [26–32]. Effects of the temperature on the water solubilities of rice residue ashes or ash-forming elements have been investigated by some scholars. As reported by the references [17,33], after rice straw was pretreated at 300–1000 °C for 2 h, the water-soluble Si, P, and K in the treated residues firstly increased and gradually decreased with increasing the heating temperature. According to our previous study [22], the water solubilities of both rice straw ash and rice husk ash decreased obviously with the increase of ashing temperature from 400 °C to 800 °C. The water solubilities of K and Na contained in rice straw ash decreased with increasing the temperature, while those of S and Cl did not depend on the ashing temperature. In addition, Si, Ca, Mg, and P contained in rice residue ashes prepared at different temperatures were almost insoluble in water [22].

As an important follow-up work of our previous study, this paper will present an investigation on the solubilities of rice straw ash together with major ash-forming elements in 20% acetic acid aqueous solution of pH = 2.11. Meanwhile, through the least square method, the functional relationship between the solubilities of rice straw ash together with its major elements and the ashing temperature will be established, aiming at providing a reference for the sustainable development of biomass energy and the developing of low-temperature biomass combustion equipment. In addition, based on the practical background of agricultural residues ashes in soil application, this study will attempt to clarify the effects of the ashing temperature on the recycling properties of the nutrients contained in rice straw ash in different solutions.

In the rest of this paper, we will firstly introduce the material and methods used in this study. Then, the characteristics of rice straw ash, and the acid solubilities of the ash together with its major ash-forming elements will be given and compared with the corresponding water solubilities obtained from the authors' previous work [22]. Finally, some main conclusions will be summarized and the future studies related to the utilization of biomass ash also will be proposed.

## 2. Materials and Methods

### 2.1. Experimental Material

The rice straw raw material used in this study was collected from farmland of rural area of Gaoqing County, Zibo City, Shandong Province, China. Then it was pulverized to the rice straw powder sample with the particle size <1 mm using a blade pulverizer (DXF-20C) in Key Laboratory of Low-grade Energy and Waste Heat Utilization, Shandong University of Technology. The properties of the prepared rice straw powder are listed in Table 1. To facilitate the pulverized process, the rice straw material was dried in a constant-temperature drying oven at 105 °C for 12 h. This also causes the moisture of the rice straw powder to be less than 4% as shown in Table 1. It should be noted that in order to compare with the water solubility, the straw material used in this paper is the same as that in the authors' previous research.

**Table 1.** Properties of experimental rice straw material.

Experimental Material	Proximate Analysis (%)				Ultimate Analysis (%)		
	Moisture	Volatiles	Ash	Fixed Carbon	C	H	O
Rice straw	3.6	68.9	13.2	14.3	42.4	6.9	48.8

## 2.2. Experimental Scheme

### 2.2.1. Selection of Ashing Temperature

According to the published references [34,35], the temperatures of the reactors in various biomass thermo-chemical conversion technologies are generally controlled within the range of 250–1200 °C. The results of our pre-experimental study showed that (1) when the temperature was below 400 °C, the colors of rice straw combustion residues were obviously black, indicating that the rice straw may not be completely combusted; and (2) when the temperature was above 800 °C, almost all of the rice straw ash was sintered and adhered to the crucible bottom. The main components of sintered ash are silicate or aluminosilicate and it is difficult to be taken out from the crucible for further analysis and utilization [36,37]. In addition, most of the other components contained in straw are volatilized in the form of gas phase during the straw ashing at high temperature [38]. Therefore, we consider the temperature range of 400–800 °C with the interval of 50 °C in this study.

In addition, the scanning electron microscopy (SEM) experiments of the rice straw ashes at 400 °C and 800 °C are employed to confirm whether the sintering phenomenon of rice straw ash happens.

### 2.2.2. Selection of Residence Time

Residence times of biomass fuels in various thermo-chemical conversion devices are different according to the literature. For example, the residence time varies from a few seconds to a few minutes in a fluidized bed [39], and from several minutes to a few hours in a grate-fired furnace [35]. During the proximate analysis of solid biomass fuel in a muffle furnace, the fuel usually can be kept for several hours [40].

According to the pre-experimental data in our previous work, when the residence time was more than 4 h, the changes of the water solubilities of rice straw ashes were not significant at different ashing temperatures. Thus, in the presented work, the residence time is selected for 4 h.

## 2.3. Experimental Method

### 2.3.1. Ash Sample Preparation Process

The rice straw ash sample was prepared in a muffle furnace at different ashing temperatures (400–800 °C). The ash preparation process is similar to that in our previous study [22], which can be summarized in the following five steps:

- Step 1: Approximately 5 g samples of the prepared rice straw powder sample were put into a crucible (90 × 60 × 15 mm).
- Step 2: The crucible being put the rice straw powder sample was heated in the muffle furnace from the room temperature to the experimental temperature with the heating rate of 10 °C per minute.
- Step 3: After staying 4 h at the experimental temperature, the muffle furnace was closed and cooled naturally to below 200 °C.
- Step 4: The residual ash in the crucible was taken out to place in a desiccator with silica gel.
- Step 5: After being further cooled to the room temperature, the rice straw ash was sealed in a sample bag for analysis.

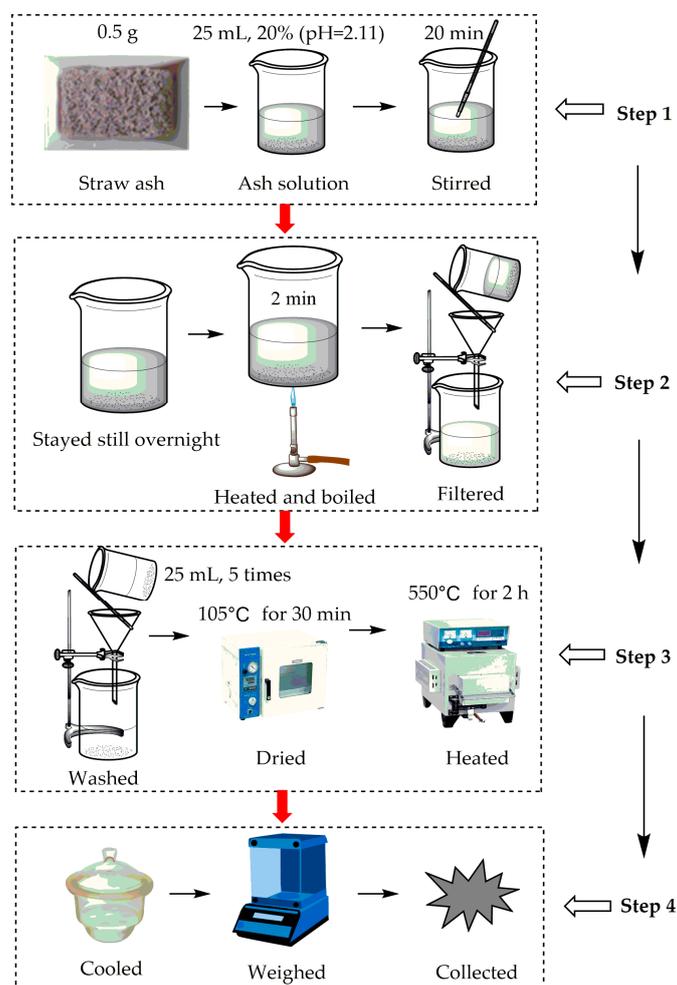
### 2.3.2. Ash Dissolution Process

The sample preparation process of the acid solubilities measurements of rice straw ash and its elements is shown in Figure 2. From Figure 2, as we can see that the dissolving process of the rice straw ash sample is mainly divided into four steps:

- Step 1: Approximately 0.5 g samples of the original rice straw ash were accurately weighed into the beaker. 25 mL of 20% acetic acid aqueous solution of pH = 2.11 was added to the sample and stirred in the beaker of 50 mL for 20 min.

- Step 2: After being stored overnight, the mixture consisting of ash and acetic acid aqueous solution was boiled for 2 min, and then filtered using a quantitative filter paper with pore size of 30–50 microns.
- Step 3: The acid-insoluble rice straw ash was washed using deionized water (25 mL each time) five times. Subsequently, the acid-insoluble rice straw ash wrapped in the filter paper was dried in the constant-temperature drying oven at 105 °C for 30 min and then it was burned at 550 °C for 2 h (according to the Chinese standard GB/T 8307-2002).
- Step 4: The acid-insoluble rice straw ash was weighted and kept in another sample bag for the measurement of element contents.

It should be noted that the dissolution experiments of the rice straw ashes at different ash-forming temperatures were repeated three times.



**Figure 2.** The dissolving process of rice straw ashes at different ashing temperatures.

### 2.3.3. Element Content Measurement in Ashes

A semi-quantitative X-ray fluorescence spectrometer (XRF) is widely used to analyze inorganic non-metallic materials. The XRF can measure various kinds of elements contents in the sample of biomass ash at one time [22,26,36,41]. Thus, to obtain the solubilities of various main nutrient elements in the rice straw ash, these elements contents in the original rice straw ash and the acid-insoluble rice straw ash were measured using the semi-quantitative ZSX-100e XRF analyzer.

In our pre-test, tests were carried out in triplicate to determine the accuracy of XRF for measurement of elements in straw ash [42]. The results showed that the standard deviations for

all elements were less than 1%, illustrating that the results of each test are reliable. As a result, in the presented work, the XRF measurement of elements contents in the original ash and the acid-insoluble ash is only carried out once at different ashing temperatures.

#### 2.4. Experimental Data Processing

According to the mass conservation of rice straw ash and its ash-forming elements before and after dissolution, the acid solubilities of rice straw ash together with its elements can be obtained using the above measurement data. It should be noted that the rice straw ashes from different ashing temperatures are taken as the research object in this paper. Thus, the volatilization of the elements is not taken into account during combustion when calculating the solubilities of ash and its major elements.

The acid solubility of the ash is the ratio of the mass of acid-soluble rice straw ash to the mass of original rice straw ash. It was calculated as

$$AS_A = (1 - m_r/m_o) \times 100\% \quad (1)$$

where  $AS_A$  is the acid solubility of rice straw ash;  $m_o$  and  $m_r$  are the mass of original rice straw ash and acid-insoluble rice straw ash, respectively. It should be noted that the acid solubilities of the ashes at different temperatures were the average values of experiments repeated in triplicate.

The acid solubility of element  $i$  in rice straw ash is the ratio of the acid-soluble mass of  $i$  to the total mass of  $i$  in the original rice straw ash. It was calculated using Equation (2).

$$AS_{A,i} = [1 - (m_r \times Y_{r,i})/(m_o \times Y_{o,i})] \times 100\% \quad (2)$$

where  $AS_{A,i}$  is the acid solubility of element  $i$  in rice straw ash;  $Y_{r,i}$  and  $Y_{o,i}$  are the mass fractions of element  $i$  in the acid-insoluble rice straw ash and the original rice straw ash, respectively.

In addition, in order to further clarify the relationships between the solubilities of rice straw ash together with its elements and the ashing temperature, the correlation functions between both of them are given based on experimental data using least squares method.

Of note, in the authors' previous work [22], the dissolution process of rice straw ash in water, the methods of calculation of the water solubility of both rice straw ash and its elements have been given in detail. Therefore, in order to avoid the identical content, they were not given again in the materials and methods section in the presented work.

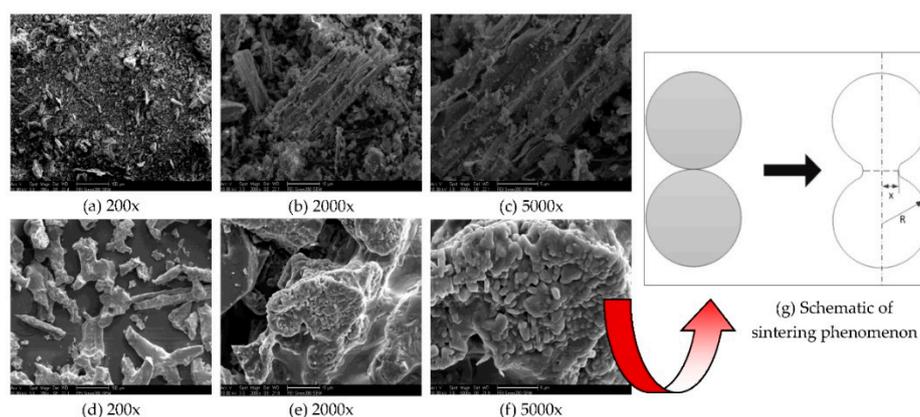
### 3. Results and Discussion

#### 3.1. Ash Characteristics

##### 3.1.1. SEM Analysis

The SEM images of the rice straw ashes prepared at 400 °C and 800 °C are shown in Figure 3a–f. As can be seen, the particles size of the rice straw ash prepared at 800 °C are larger and more compact than that prepared at 400 °C, suggesting that ash sintering has occurred after the rice straw is kept at 800 °C for 4 h. The ash sintering is referred to the bonding or welding of adjacent particles under the influence of the excess surface tension as shown Figure 3g [43,44]. According to some previous works, it is also a phenomenon of the combination of particles caused by the synthetic effect of partial melting, viscous flow, and gas–solid chemical reactions [22,45]. Obviously, the rice straw ash with high sintering tendency is expected to have greater ash particle sizes.

In addition, the high alkali metals contents in rice straw ash can also accelerate the straw ash sintering [44], and the surface of sintered ash particle is smoother in comparison to unsintered ash. This resulted from the molten ash forming a coating and blocking up the holes on the surface of the ash particles [17]. As a result, some inorganic nutrients may be trapped inside rice straw ash particle at high combustion temperatures.



**Figure 3.** SEM images of rice straw ash at 400 °C (a–c) and 800 °C (d–f) and schematic of sintering phenomenon (g).

### 3.1.2. Ash-Forming Elements

The XRF measurement results show that there are O, Si, K, Na, Cl, Ca, Mg, S, P, Fe, Al, Mn, Ni, As, Br, Sr, Pb, Rb, and Ba in both original rice straw ash and two insoluble rice straw ashes (the acid-insoluble ash and the water-insoluble ash [22]) at different ashing temperatures. Mass fractions of major ash-forming elements (more than 0.2%) in these ashes, including O, Si, K, Na, Ca, Mg, Cl, P and S, are listed in Table 2.

**Table 2.** Mass fractions of major ash-forming elements in original and insoluble rice straw ashes at different ashing temperatures.

Mass Fractions of Major Ash-Forming Elements in Original Rice Straw Ashes (>0.2%)									
T (°C)	O	Si	K	Na	Ca	Mg	Cl	P	S
400	41.20	22.50	10.80	6.33	4.63	2.60	6.15	1.29	2.64
450	40.50	23.00	11.30	6.15	4.50	2.69	6.11	1.32	2.63
500	42.30	22.70	10.90	5.74	4.26	2.70	5.96	1.26	2.44
550	41.50	23.00	10.90	5.91	4.51	2.76	5.55	1.33	2.22
600	42.30	24.30	10.20	5.20	4.00	2.10	4.90	1.03	1.94
650	40.80	23.80	11.30	5.04	4.95	1.90	4.90	1.09	1.72
700	39.10	21.70	11.80	5.82	5.64	2.44	6.36	1.53	2.74
750	44.30	26.00	9.07	6.04	5.35	2.26	0.55	1.14	2.89
800	44.30	25.10	8.98	6.05	6.33	2.22	0.25	1.24	3.04
Mass Fractions of Major Ash-Forming Elements in Water-Insoluble Rice Straw Ashes (>0.2%)									
T (°C)	O	Si	K	Na	Ca	Mg	Cl	P	S
400	46.90	32.90	2.53	1.31	7.28	3.85	0.34	1.67	0.45
450	51.50	29.80	3.19	1.97	5.62	3.39	0.47	1.43	0.53
500	41.70	34.40	5.08	3.50	6.27	3.68	0.71	1.77	0.54
550	42.50	31.80	6.03	3.97	6.12	3.51	1.17	1.69	0.64
600	46.30	29.50	6.52	3.82	5.45	3.02	1.08	1.64	0.48
650	46.70	29.00	7.06	3.85	4.98	3.15	1.31	1.45	0.46
700	44.10	30.60	7.33	4.16	5.55	2.93	0.98	1.43	0.42
750	44.00	31.30	7.43	4.14	5.32	2.90	0.76	1.40	0.41
800	42.30	31.30	8.18	4.39	6.14	2.80	0.34	1.63	0.34
Mass Fractions of Major Ash-Forming Elements in Acid-Insoluble Rice Straw Ashes (>0.2%)									
T (°C)	O	Si	K	Na	Ca	Mg	Cl	P	S
400	49.80	45.10	0.86	0.41	0.37	0.30	0.15	0.20	0.16
450	46.10	41.40	3.07	2.93	1.78	1.01	0.62	0.26	0.29
500	44.60	39.00	4.91	2.62	2.98	1.43	0.87	0.41	0.40
550	46.20	34.20	5.68	3.39	3.65	1.95	0.98	0.81	0.46
600	44.10	35.50	6.62	3.53	3.64	2.33	1.01	0.38	0.47
650	47.50	32.20	6.95	3.40	3.57	2.41	0.97	0.47	0.43
700	44.30	32.50	7.72	4.17	4.36	2.66	0.89	0.52	0.38
750	48.60	31.50	6.70	2.97	4.04	2.81	0.45	0.37	0.41
800	43.00	33.60	8.19	3.68	4.83	2.96	0.25	0.49	0.37

From Table 2, it can be seen that the mass fractions of major ash-forming elements in the original rice straw ash at different ashing temperatures vary basically in the following decreasing order of quantity: O > Si > K > Na > Cl > Ca > Mg > S > P. Also, the elements contents in both the acid-insoluble ashes and water-insoluble ashes vary in the following decreasing order of quantity: O > Si > K > Ca > Na > Mg > Cl > P > S and O > Si > K > Ca > Na > Mg > P > Cl > S, respectively. It should be noted that the contents of the individual elements (such as Na, Ca, Mg, Cl, and P) in the original and insoluble rice straw ashes at different temperatures do not strictly follow the order mentioned above. The reason is that the contents of these elements present different changing trends with the increase of the ashing temperature.

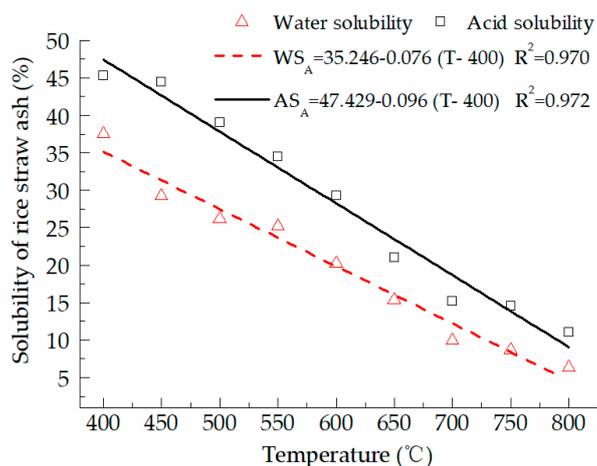
As shown in Table 2, the major ingredients of both original ashes and insoluble ashes are O and Si (the sum of mass fractions of them >60%) at different ashing temperatures. The contents of K, Na, Ca, Mg, Cl, P, and S in the water-insoluble ashes are basically higher than these in the acid-insoluble ashes, indicating that some compounds consisting of these elements are only soluble in acid solution but not insoluble in deionized water [11].

The XRF measurement data of two insoluble ashes in Table 2 also show that the mass fractions of K increase with increasing the ashing temperature. This is due to the following two reasons [7]: (1) the high temperature makes soluble salts transform into different insoluble silicate compounds, and some key reactions can see the reference [46]; and (2) the sintered materials or insoluble components on the surface of rice straw ash particles prevent internal substances from dissolving in the deionized water.

### 3.2. Comparisons of Acid and Water Solubilities of Rice Straw Ashes

Two solubilities of rice straw ashes, created at different ashing temperatures, in the acetic acid solution and the deionized water are shown in Figure 4. It can be seen that they are significantly lower than the water solubility (61%) of fly ash from straw combustion [47]. This can be attributed to the release of many soluble substances. It can be also found from the Figure 4 that the acid solubilities (45.3–11.1%) of the ashes in the acetic acid solution are approximately 5–15% higher than the corresponding water solubilities (37.5–6.3%) of those in the deionized water in the temperature range of 400–800 °C. However, their values are low and more than 50% of rice straw ash is insoluble in the acetic acid solution and the deionized water. According to the literature [21], for the same biomass ash sample, the total dissolved mass content increased by 500% with the increased acidity of aqueous solutions (the pH value decreased from 13 to 5). This means that most of the ash-forming elements are acid-soluble, Zevenhoven-Onderwater et al. [48] also confirmed this result. For example, some compounds (e.g., CaCO<sub>3</sub>, MgCO<sub>3</sub>) are acid-soluble but water-insoluble. In our experiments, we found that there is gas escaping from the solution while the acetic acid solution is added into the water-insoluble ash. The possible reactions of this phenomenon are R1.

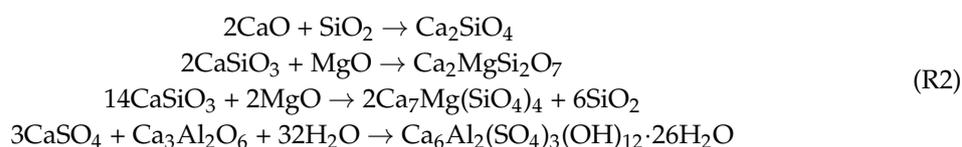




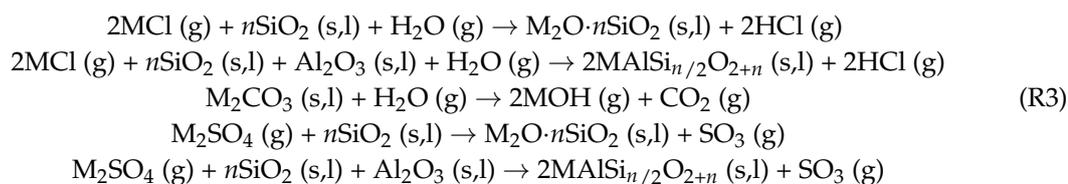
**Figure 4.** Solubilities of rice straw ash in acetic acid and water at different ashing temperatures.  $WS_A$  is the water solubility of the ash;  $AS_A$  is the acid solubility of the ash;  $T$  is temperature;  $R^2$  is determination coefficient.

Additionally, the Figure 4 also shows that as the ashing temperature increases from 400 °C to 800 °C, two solubilities of rice straw ash decrease by about 70–80%. To further clarify the relationship between the ash solubility and the ashing temperature, the functional dependencies and determination coefficients between the solubilities of rice straw ash and the ashing temperature are given in Figure 4. It is found that a close negative linear relationship exists between the solubility (including acid solubility and water solubility) of rice straw ash and the ashing temperature. This suggests that a low temperature combustion is more beneficial to the resource utilization of straw ash as a fertilizer.

One of the main reasons for the decline is the severe sintering of straw ash at high temperature [49,50]. The ash sintering leads to the transformation of Ca and Mg in the ashes from oxides or sulphates to acid-insoluble Ca-silicate, Ca-Mg-silicate [7], and the melted insoluble inorganic components covering the soluble nutrients [22]. Some important reactions are seen in R2 [7,51].



Besides ash sintering, the decreasing of both solubilities are also attributed to the release [7,38] or the transformation [52] of partially soluble compounds (e.g.,  $\text{HCl}(\text{g})$ ,  $\text{SO}_3(\text{g})$ ,  $\text{MCl}(\text{g})$  and  $\text{MOH}(\text{g})$ , where  $M$  represents  $K$  and  $Na$ , similarly hereinafter). According to the reference [2], approximately 80–98% of  $Cl$  is released between 700 °C and 800 °C, and 40% of the total  $K$  is released at 800 °C. For  $S$ , 25–35% is released to the gas phase at 500 °C, and up to 40–50% when the combustion temperature increases from 500 °C to 800 °C. The potential reactions are listed below as R3 [7].



### 3.3. Comparisons of Acid and Water Solubilities of Major Elements

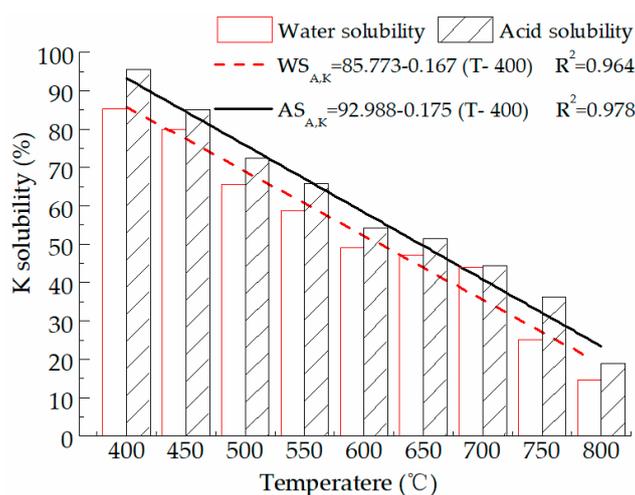
It is well known that crop straw ash contains some essential nutrients and beneficial elements (e.g.,  $Na$ ,  $Si$ ), which can contribute to plant growth. The essential nutrients can be classified into three types: (1) macronutrients ( $K$ ,  $P$ ); (2) medium nutrients ( $Ca$ ,  $Mg$ ,  $S$ ); and (3) micronutrients ( $Cl$ ). In this

section, the acid and water solubilities of K, P, Ca, Mg, S, Cl, and Na are analyzed. Of note, according to our experimental data, Si is almost insoluble in both the acetic acid solution and the deionized water, so it will not be discussed in this section.

### 3.3.1. Solubility of Macronutrients

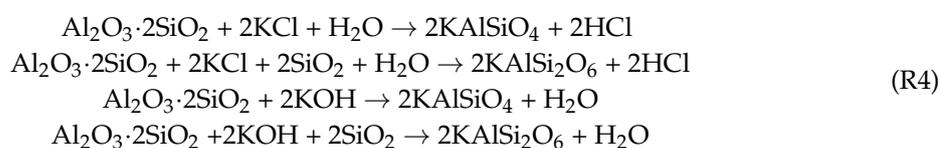
K and P are indispensable as essential nutrients for the growth of organisms in the ecosystem. In general, K in biomass ash is mainly in the form of KCl,  $K_2SO_4$  and  $K_2CO_3$  [53] as well as potassium silicate, aluminosilicate, and sulphate ( $K_2Ca(SO_4)_2$ ,  $K_3Na(SO_4)_2$ ) [54]. P is mainly in the form of phosphates.

The acid and water solubilities of macronutrients K in rice straw ashes prepared at different ashing temperatures are shown in Figure 5. As shown in Figure 5, the acid solubility of K is about 6% higher than its water solubility in the temperature range from 400 °C to 800 °C. This can be explained as follows: (1) some sintered compounds in the ashes, such as the mixture of potassium-rich silicate and phosphate melts [55,56], are only acid-soluble; (2) the transport channels of some internal K may be occluded by some of acid-soluble salts in the surface of ash particles formed during the rice straw powder combustion [17]. Moreover, Liu et al. [57] indicated that 93% of K in rice straw is mainly enriched by acid-soluble salts, and 73% of K is water-soluble in rice straw. This trend is similar to the results of K solubilities contained in rice straw ash in this paper.



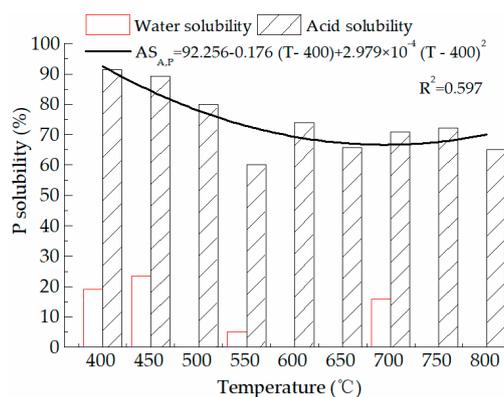
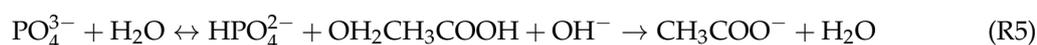
**Figure 5.** Acid and water solubilities of K in rice straw ashes at different ashing temperatures.  $WS_{A,i}$  is the water solubility of element  $i$  in the ash;  $AS_{A,i}$  is the acid solubility of  $i$  in the ash.

From the figure, we can also see there is a strong negative linear relationship between the solubility of K and the ashing temperature. As the temperature increases from 400 °C to 800 °C, the acid and water solubility of K decrease linearly by approximately 80% (from 95.6% to 18.9%) and 83% (from 85.4% to 14.7%), respectively. Vassilev et al. [11] also reported similar trends in K solubility. Of note, when the ashing temperature is lower than 600 °C, both solubilities are more than 50%, indicating that a lower combustion temperature is beneficial to the recycling application of K contained in ash in farmland. The main reason of this decrease with temperature, as pointed out in previous works, is the transformation of K from K-sulphate, K-chloride, and K-hydroxide to K-aluminosilicates via the reactions R3 and R4 [7,37,50,53,58].



Furthermore, as reported in [17,59], K solubility is determined by the dissolution of Si, and this dissolution rate increases with increasing the pH value of solution. However, according to the experimental data in both the present study and our previous study [22], Si in rice straw ash is almost insoluble in the acetic acid solution and the deionized water, but K is easily soluble. It suggests that K solubility does not depend on Si solubility. This significant difference of Si solubility in the references and our studies is due to the differences of both the experimental conditions and the characteristics of extraction solutions. Therefore, the correlations between the solubilities of other elements and Si solubility are not considered and analyzed in this paper.

The acid and water solubilities of macronutrients P in rice straw ashes prepared at different ashing temperatures are shown in Figure 6. As we can see, when the ashing temperature is less than 600 °C, the acid solubility of P decreases slowly with the increase of the temperature. When the temperature is higher than 600 °C, the effect of the ashing temperature on the acid solubility of P is not significant. In addition, Figure 6 indicates that in the whole experimental temperature range (400–800 °C), the acid solubility of P contained in rice straw ashes is tremendously higher than its water solubility. More than 60% of P is acid-soluble at different temperatures, while its water solubility is less than 25%. This indicates that most of phosphates (e.g., 72–80% of  $\text{Ca}_3(\text{PO}_4)_2$ , 8–10% of  $\text{Na}_6(\text{PO}_4)_2$ ) [11,60] are dissolved in the acetic acid solution through the neutralization reaction of acetic acid and hydroxide ion ( $\text{OH}^-$ ) produced from the hydrolysis of phosphate radical ( $\text{PO}_4^{3-}$ ) (R5).



**Figure 6.** Acid and water solubilities of P in rice straw ashes at different ashing temperatures.

As Figure 6 shows, the determination coefficient ( $R^2$ ) of the correlation of the acid solubility with the ashing temperature is equal to 0.597, which is obviously less than 1.0. Thus, there is not a significant quadratic curve relationship between the acid solubility of P and the temperature.

### 3.3.2. Solubility of Medium and Micronutrients

The acid and water solubilities of medium nutrients Ca, Mg, and S contained in rice straw ashes at different ashing temperatures are presented in Figures 7–9, respectively. As shown in Figures 7 and 8, the acid solubilities of both Ca and Mg are significantly higher than their water solubilities. Both Ca and Mg are almost water-insoluble because most of them are in the form of carbonates in the whole experimental temperature range (400–800 °C) [53]. These carbonates are insoluble in water but soluble in acetic acid solution as shown in reaction R1. Especially, when the temperature is less than 600 °C, more than 50% of both Ca and Mg contained in rice straw ash is acid-soluble.

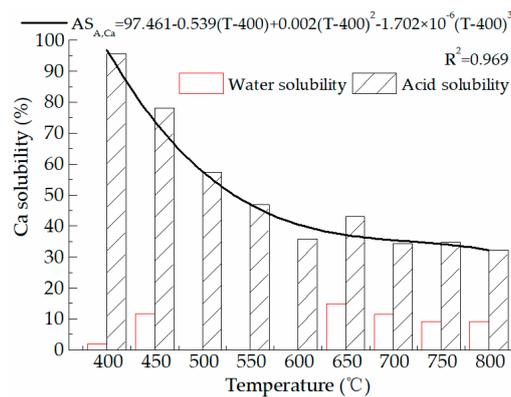


Figure 7. Acid and water solubilities of medium nutrient Ca at different ashing temperatures.

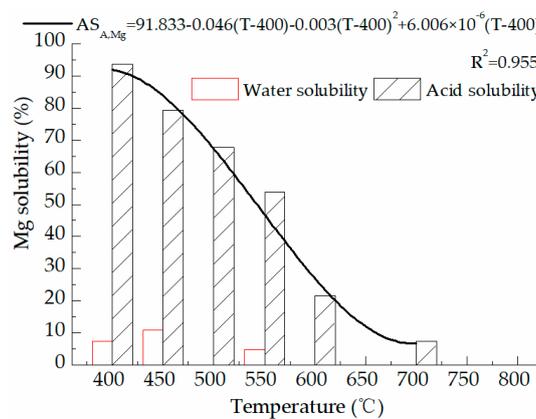


Figure 8. Acid and water solubilities of medium nutrient Mg at different ashing temperatures.

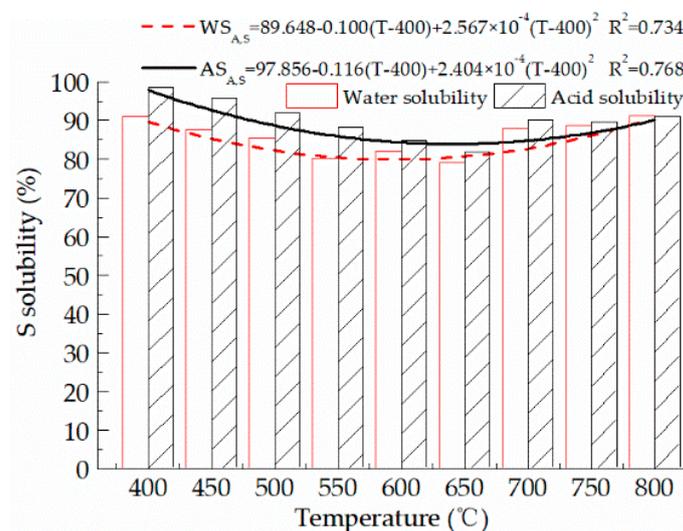


Figure 9. Acid and water solubilities of medium nutrient S at different ashing temperatures.

It is clearly shown in Figures 7 and 8 that a strong cubic curve relationship exists between the acid solubility of Ca/Mg and the ashing temperature. When the temperature increases from 400 °C to 600 °C, the acid solubilities of Ca and Mg decrease significantly from 95.68% to 35.73% (decrease by about 63%) and from 93.69% to 21.64% (decrease by about 77%), respectively. This change trend is similar to that of P. The partial reason of this decrease, as pointed out in previous works [7], may be that alkaline-earth metals transform into molten silicates (via the equation R4) which coat the surface of straw ash particles to prevent the dissolution of nutrients at high temperature. In addition, the change

of the acid solubility of Ca is small as the temperature increases from 600 °C to 800 °C, indicating that the calcium compounds in the ashes may approach phase equilibrium at the temperatures above 600 °C.

For medium nutrient S, it is mainly concentrated in straw ash in the form of the sulphates of K, Na, etc. [11]. It is well known that most of sulphates are soluble in both the acetic acid solution and the deionized water. As shown in Figure 9, the acid solubility of S contained in the rice straw ashes is slightly higher than the corresponding water solubility at 400–750 °C. The acid and water solubilities of S are more than 75% at different temperatures. With the increase of the ashing temperature, the changes of both solubilities are firstly decreased and then slightly increased. Consequently, the effect of the ashing temperature on the solubility of S contained in rice straw ash is slight in different solutions.

Micronutrient Cl is an important component of rice straw ash. It can form a variety of chlorides with Ca, Na, K, Zn, etc. [11] and they are the main forms of Cl in rice straw ashes at different ashing temperatures. Like the sulphates, the chlorides are also soluble in the acetic acid solution and the deionized water.

Figure 10 describes the acid and water solubilities of micronutrient Cl contained in rice straw ashes prepared at different ashing temperatures. As we can see, both the acid and water solubilities of Cl are higher than 75% in the ashing temperature range of 400–700 °C. In this temperature range, two solubilities of Cl are slightly decreased with the increase of the temperature. However, when the temperature is higher than 700 °C, two solubilities of Cl contained in the rice straw ashes decrease rapidly. The reason for that is that most of Cl in the ashes are released, as shown in Table 2.

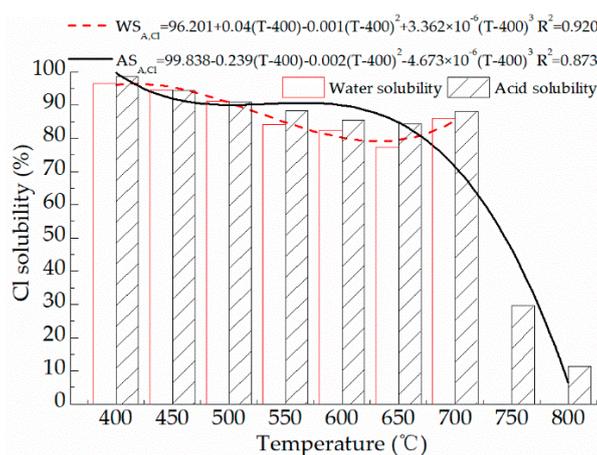
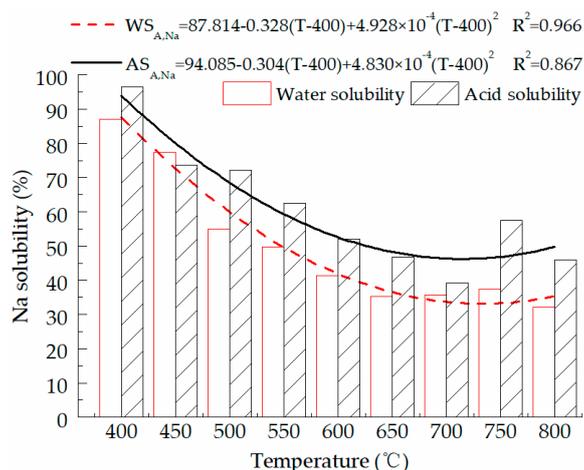


Figure 10. Acid and water solubilities of micronutrient Cl at different ashing temperatures.

### 3.3.3. Solubility of Beneficial Element

The acid and water solubilities of beneficial element Na contained in rice straw ashes prepared at different ashing temperatures are shown in Figure 11. It can be seen that the acid solubilities of Na contained in the ashes are about 4–7% higher than the corresponding water solubilities at different temperatures.



**Figure 11.** Acid and water solubility of beneficial element Na at different ashing temperatures.

Figure 11 also shows that there is a close quadratic curve relationship between the solubility of Na and the temperature. The acid and water solubility of Na decrease gradually from about 96% to 39% and from about 87% to 32% with increasing the temperature, respectively. The reasons for these decreases are similar to those of K.

From the comparison results of two solubilities of different nutrient elements mentioned above, it is not difficult to find that the acid solubilities of the major ash-forming elements are always higher than the water solubilities of those. When the ashing temperature is less than 600 °C, their solubilities are basically higher than 50%. Especially, most of P, Ca, and Mg are acid-soluble but water-insoluble. This conclusion is also confirmed by some previous work [23,24]. Hence, to better realize the closed cycle of nutrients in rice straw, the following two principles should be followed: (1) the ashing temperature should not be higher than 600 °C, (2) the rice straw ash should be applied to acidic soil.

#### 4. Conclusions

The acid solubilities of rice straw ash together with its major ash-forming elements in the ashing temperature range of 400–800 °C have been experimentally studied and compared with the corresponding water solubilities of them in this paper. The main results are as follows:

- The acid solubility of rice straw ash is approximately 5–15% higher than the water solubility of that in the experimental temperature range. Two solubilities of the ash decrease linearly with the increase of the ashing temperature, and the acid solubility of the ash decreases by about 76% when the temperature increases from 400 °C to 800 °C.
- The acid and water solubility of K decreases linearly by approximately 80% and 83% as the ashing temperature increases, respectively. The acid solubility of K is about 6% higher than its water solubility. P, S, and Na solubilities with the temperature have quadratic curve relationships. The solubilities of Ca, Mg, and Cl have significant cubic curve correlations with the temperature.
- P, Ca, and Mg are soluble in the acetic acid solution but almost insoluble in the deionized water. The solubilities of K, P, Ca, Mg, and Na vary obviously with increasing the temperature, and the acid solubilities of them are higher than the corresponding water solubilities. Whereas two solubilities of S and Cl are slightly affected by the ashing temperature.
- When the ashing temperature of rice straw is lower than 600 °C, the rice straw ash will have a more accessible (soluble or bioavailable) nutrient content. Otherwise, most nutrients contained in the ash will be sintered or released with the flue gas.

It can be concluded that the recycling property of the nutrients in rice straw ash is significantly affected by the combustion temperature and the acidity of solution. A lower combustion temperature and a lower pH value can lead to a better recycling property of the nutrients in straw ash. In other

words, the application of straw ash produced from low-temperature in acid soil will have a better prospect. This can not only contribute to the sustainable application of biomass energy, but also reduce the amount of utilization of chemical fertilizer, the area of acid soil and the cost of agricultural production, thus achieving the sustainable development of modern agriculture. Therefore, low temperature combustion technology for biomass should be considered and developed, and some fundamental studies on recycling of straw ash as a fertilizer to agricultural land should be also strengthened in the future.

## 5. Patents

According to the above conclusion that the low temperature combustion technology of biomass can be beneficial to the recycling utilization of biomass ash as a fertilizer in farmland, a patent for invention of a method and device for low-temperature solid phase, high-temperature gas phase combustion of biomass briquette fuel has been applied by the authors, and it has been authorized by the State Intellectual Property Office of the P.R.C (Patent no. CN 201710174853.0).

**Author Contributions:** Conception of the idea, Y.Z., G.Z., and F.H.; Methodology of the study, Y.Z. and G.Z.; Material collection and treatment, Y.Z.; Data curation, Y.Z.; Result analysis, Y.Z. and F.H.; Writing—original draft preparation, Y.Z.; Writing—review and editing, Y.Z., M.W., M.T., Z.G., G.Z., and F.H.; Funding acquisition, G.Z. and F.H.; Contributed equally, G.Z. and F.H.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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