SO$_2$ Absorption by Multiple Biomass Ash Types

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1. INTRODUCTION

The ecological environment is suffering from enormous stress due to the extensive use of fossil fuels. Direct combustion power generation is an important form of large-scale utilization of biomass energy. Although biomass is a clean fuel, some of it contains a small amount of sulfur and releases SO$_2$ in combustion. The monitoring of biomass power plants showed that the concentration of SO$_2$ in flue gas exceeded 100 mg/m$^3$ at the highest. It is difficult for biomass power plants to meet the standards of ultralow pollutant emission in key areas where SO$_2$ emission is required to be less than 35 mg/m$^3$. Therefore, desulfurization equipment is necessary to control SO$_2$ emission in biomass power plants.

With the rapid development of biomass power plants, the amount of ash produced by biomass power plants is increasing, reaching tens of thousands of tons per year. Research on the resource utilization of biomass ash is concentrated in the fields of architecture, chemical engineering, agriculture, and the environment according to different properties of various ashes. There are some studies on the utilization of ash, such as a cement or concrete product replacement material and an adsorbent for the removal of heavy metals from aqueous solution. Untreated ash tends to have alkaline properties, is reactive, and will produce a high pH in water; this provides a liming quality that can be utilized in the treatment of acidic soils. Alkaline biomass ash is able to absorb harmful substances. Substituting biomass for fossil fuels or cofiring biomass with coal has the capability to reduce both NO$_x$ and SO$_x$ levels from existing coal-fired power plants. One reason is that most biomass contains almost no sulfur compared to coal and thus its combustion produces no SO$_2$. The other one is that the high alkali-earth-metal content of biomass can capture gas-phase SO$_2$ heterogeneously in the ash. In addition, it was reported to use biomass ash to fix CO$_2$ through the bicarbonation reactions between CO$_2$ and carbonates in ash. Rice husk ash sorbent developed by the sol–gel method was reported to be used to remove acid violet dye from synthetic wastewater.

Some researchers have studied the removal of SO$_2$ by hydrated biomass ash. Zainudin et al. prepared the sorbents from the hydration of oil palm ash for desulfurization. The results indicated that the K ions in the ash probably reacted with other species such as SiO$_2$, Al$_2$O$_3$, and Ca ions to produce reactive species. Lau et al. studied the effect of various sorbent preparation parameters on simultaneous removal of SO$_2$ and NO by rice husk ash sorbent doped with copper. They optimized the operating conditions with 100 °C temperature, 2000 ppm SO$_2$, and 500 ppm NO and obtained the largest absorption capacity values of 53.4 mg of SO$_2$/g and 6.9 mg of NO/g. Dahlan et al. conducted a series of studies on the use of hydrated biomass ash to absorb SO$_2$. The as the severity of environmental pollution continues to increase and ultralow emission standards are proposed, biomass power plants must implement additional processes to control SO$_2$ emission. Biomass ash can be utilized as a sorbent for flue gas desulfurization because of its strong alkalinity. In this study, the characteristics of SO$_2$ absorption in simulated flue gas using four types of typical biomass ashes were studied in fixed bed experiments. The results showed that the addition of water, the increase in water vapor, and the lower temperature were beneficial for SO$_2$ absorption. The main components of wheat straw ash are KCl and SiO$_2$, cotton stalk ash is rich in K$_2$O and calcium compounds, poplar bark ash has a considerable content of calcium compounds, and corncob ash contains large amounts of KCl and K$_2$O. Alkali substances, such as oxides or carbonates of potassium and calcium, play a crucial role in SO$_2$ absorption. The SO$_2$ removal effect of corncob ash was the best owing to the abundance of potassium oxides. Meanwhile, wheat straw ash performed worst in SO$_2$ removal due to the small amount of K$_2$O and Ca. The desulfurization products were mainly potassium and calcium sulfate.

ABSTRACT: As the severity of environmental pollution continues to increase and ultralow emission standards are proposed, biomass power plants must implement additional processes to control SO$_2$ emission. Biomass ash can be utilized as a sorbent for flue gas desulfurization because of its strong alkalinity. In this study, the characteristics of SO$_2$ absorption in simulated flue gas using four types of typical biomass ashes were studied in fixed bed experiments. The results showed that the addition of water, the increase in water vapor, and the lower temperature were beneficial for SO$_2$ absorption. The main components of wheat straw ash are KCl and SiO$_2$, cotton stalk ash is rich in K$_2$O and calcium compounds, poplar bark ash has a considerable content of calcium compounds, and corncob ash contains large amounts of KCl and K$_2$O. Alkali substances, such as oxides or carbonates of potassium and calcium, play a crucial role in SO$_2$ absorption. The SO$_2$ removal effect of corncob ash was the best owing to the abundance of potassium oxides. Meanwhile, wheat straw ash performed worst in SO$_2$ removal due to the small amount of K$_2$O and Ca. The desulfurization products were mainly potassium and calcium sulfate.
specific reactive species formed in the hydration of rice husk ash and CaO were believed to be the key factor responsible for high desulfurization activity in the sorbent. They carried out the fixed bed experiments and studied the effect of feed concentration of SO₂ and NO, relative humidity, operating temperature, and space velocity on the absorption capacity of rice husk ash/CaO/CeO₂ sorbent. Nevertheless, the reaction between SO₂ and sorbents is very complicated because of the complex mineral composition of biomass ash. There are other rare studies on the direct use of biomass ash for desulfurization because of its strong alkalinity, while studies using biomass char or activated carbon prepared from complex mineral composition of biomass ash. There are other studies using biomass char or activated carbon prepared from biomass to remove SO₂.²⁰,²¹ Biomass ash can be utilized for desulfurization experiments involving SO₂ absorption from flue gas by biomass ash was conducted in a fixed bed reactor, which has a simple structure and is easy to operate. As shown in Figure 1, the experimental system is mainly composed of five parts: gas distribution, humidification, fixed bed reaction, temperature control, and measurement systems.

In the present work, the effects of water content in ash, vapor concentration in flue gas, and flue gas temperature on the SO₂ absorption of biomass ash sorbents were studied. Dry biomass ash (0.8 g) or wet sorbent mixed with 0.042 (5%), 0.089 (10%), or 0.2 g (20%) of water was placed on a glass filter in the middle of a heated tubular reactor. Simulated flue gas containing SO₂ (190 ppm), O₂ (6%), water vapor (0, 4, 8%), and balance N₂ flowed through the sorbent at a rate of 0.0167 dm³/s. The water vapor was generated by a humidification system in which N₂ was bubbled through two gas wash bottles immersed in a water bath and emitted water vapor. The vapor quality could be controlled by adjusting the temperature of the water bath and the flow rate of N₂. The reaction temperature was maintained at 75, 85, and 95 °C, which was in the temperature window of semidry desulfurization. The flue gas was analyzed using a MADUR Photon II flue gas analyzer to measure the concentration of SO₂ before and after the absorption experiment, which was recorded every 2 s over 60 min. Knowing the gas flow rate and concentration, the SO₂ absorptivity and the absorption capacity were calculated based on the mass balance between the inlet and outlet gas.

The equations are shown in eqs 1 and 2 respectively.

\[ \eta = \frac{C_{\text{in}} - C_{\text{out}}}{C_{\text{in}}} \times 100\% \]  

(1)

\[ q = 2.86 \times 10^{-3} \int_0^t \frac{(C_{\text{in}} - C_{\text{out}})Q}{m} \, dt \]  

(2)

where η and q (mgSO₂/gash) represent the SO₂ absorptivity and absorption capacity, respectively, C_{\text{in}} and C_{\text{out}} (ppm) are the SO₂ concentrations of inlet and outlet gas, respectively, Q (dm³/min) is the volume rate of total flow, m (g) is the mass of biomass ash, and t (min) is the absorption time.

### 2.2. SO₂ Absorption Experiment

The SO₂ absorption ability of the sorbent can be expressed by the SO₂ absorption capacity, which is defined as the weight of SO₂ absorbed from the flue gas per gram of the sorbent.²² The experiment involving SO₂ absorption from flue gas by biomass ash was conducted in a fixed bed reactor, which has a simple structure and is easy to operate. As shown in Figure 1, the experimental system is mainly composed of five parts: gas distribution, humidification, fixed bed reaction, temperature control, and measurement systems.

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#### 2.2.1. Sorbent Preparation

In this work, four species of typical biomass ashes in northern China, wheat straw, cotton stalk, poplar bark, and corncob, were collected and burned at 550 °C for 2 h in a muffle furnace. The ash was then ground and sieved to have less than 212 μm particle size for the SO₂ absorption experiment.

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#### 2.2.3. Characterization of Sorbents

The qualitative elemental content of ash was determined using a PW4400 XRF spectrometer. Powder XRD analysis was performed using a Dmax 2500 XRD diffractometer with a scanning angle range of 2θ = 10–80°. A SUPRA 55 SEM equipped with an INCA Exact EDS was employed to observe the micromorphology of ash powders that were sprayed with gold using a Desk V HP sputter coater. XRD patterns can identify the mineral phases present in the different ash types, and EDS can indicate the

### Table 1. Chemical Composition of Ash from XRF Analysis (%)

| biomass ash | K₂O | KCl | SiO₂ | CaO | MgO | SO₂ | P₂O₅ | Fe₂O₃ | Al₂O₃ | others | total |
|-------------|-----|-----|------|-----|-----|-----|------|-------|-------|--------|------|
| WSA         | 11.34 | 33.07 | 33.29 | 6.84 | 1.99 | 6.44 | 2.46 | 0.724 | 3.84 | 100     |
| CSA         | 27.89 | 8.04 | 8.66 | 33.41 | 7.96 | 3.28 | 6.86 | 2.30 | 1.60 | 100    |
| PBA         | 8.71 | 13.32 | 62.66 | 5.15 | 2.26 | 4.18 | 4.18 | 2.56 | 1.16 | 100    |
| CCA         | 38.16 | 28.47 | 14.79 | 4.12 | 1.62 | 4.26 | 4.73 | 0.53 | 3.34 | 100    |

https://dx.doi.org/10.1021/acsomega.0b04364
ACS Omega 2021, 6, 1872–1882
content or distribution of elements of a point or microregion in the SEM image.

3. RESULTS AND DISCUSSION

3.1. Mineral Composition of Biomass Ash. In ash, chlorine takes the form of KCl, and the remaining potassium and all other elements can be expressed in the form of simple oxides. Table 1 presents the results of XRF analysis, which indicates that the main inorganic substances in biomass ash are chlorides and oxides of Si, K, Ca, Mg, and other elements, accounting for more than 90% of the total weight. Commonly, herbs consist of larger amounts of silicon and potassium, whereas woody plants contain more calcium. Among the four kinds of biomass ashes, WSA contains the most silicon and sulfur. WSA and CCA contain a lot of potassium, some of which is present in KCl, accounting for approximately 30% of the weight. CCA contains the most K2O of 38.16%. However, PBA is abundant in calcium and lacks potassium and chlorine; it contains up to 62.66% CaO and almost no KCl. CSA has a considerable content of potassium and calcium and contains the least silicon and most magnesium.

The alkalinity of biomass ash results from oxides of alkali metals (K and Na) and alkaline-earth metals (Ca and Mg). Although alkaline elements may exist in the form of complex compounds, they still have the potential to absorb acid pollutants.

Figure 2 shows the XRD patterns, which reveal that the main mineral phases of PBA are SiO2 and CaCO3; CaO, K2Si2O5, and MgCO3 were detected as well. Peaks in WSA and CCA patterns primarily refer to KCl and SiO2, and K2SO4 and K2O were detected, respectively. In addition to KCl, SiO2, K2O, and MgO, CSA contains the complex compounds CaSi2O5, (Ca, Mg)CO3, Ca2P2O7, and K2Ca(CO3)2.

Figure 3 illustrates the micrographs of the biomass ash sorbent. Biomass ash consists of irregular particles with different sizes and shapes, including flakes, blocks, strips, etc. Moreover, there are always attachments on the particle surface.
WSA retains the original fiber skeleton, which is caused by incomplete combustion. Mineral fissure joints appear on PBA particles because of the high calcium content. There is little adhesion between CSA particles, whereas several attachments occur on CCA particles and result in agglomeration owing to the abundance of potassium that contributes to low melting point and makes it easy to bond small particles together. The complex and diverse particle morphologies reflect the complexity of the existing forms of inorganic elements in the ash.

Table 2. Elemental Content of Points (a–l) in Figure 4 from EDS (%)

| EDS point | C  | O  | Na | Mg | Al | Si | P  | S  | Cl | K  | Ca | Mn | Fe | total |
|-----------|----|----|----|----|----|----|----|----|----|----|----|----|----|-------|
| WSA       |    |    |    |    |    |    |    |    |    |    |    |    |    |       |
| a         | 4.80 | 27.43 | 0.68 | 1.47 | 21.53 | 0.48 | 13.77 | 26.86 | 2.98 | 100.00 |
| b         | 6.12 | 35.57 | 0.98 | 2.95 | 12.62 | 0.22 | 0.53 | 14.92 | 22.26 | 3.26 | 0.57 | 100.00 |
| c         | 2.18 | 39.45 | 1.93 | 1.09 | 38.61 | 1.67 | 13.84 | 1.23 | 100.00 |
| CSA       |    |    |    |    |    |    |    |    |    |    |    |    |    |       |
| d         | 0.84 | 47.48 | 4.65 | 0.92 | 0.13 | 1.99 | 1.03 | 25.56 | 17.40 | 100.00 |
| e         | 0.5 | 38.19 | 2.79 | 13.39 | 4.99 | 1.31 | 2.68 | 27.13 | 9.02 | 100.00 |
| f         | 0.86 | 24.75 | 0.71 | 11.82 | 2.47 | 24.86 | 28.54 | 5.99 | 100.00 |
| PBA       |    |    |    |    |    |    |    |    |    |    |    |    |    |       |
| g         | 0.69 | 28.4 | 0.96 | 0.44 | 69.51 | 100.00 |
| h         | 6.98 | 0.19 | 0.72 | 92.11 | 100.00 |
| i         | 0.87 | 46.47 | 0.97 | 5.66 | 1.03 | 1.30 | 3.98 | 30.3 | 0.52 | 100.00 |
| CCA       |    |    |    |    |    |    |    |    |    |    |    |    |    |       |
| j         | 0.56 | 7.18 | 0.29 | 2 | 2.35 | 9.7 | 28.48 | 46.67 | 2.77 | 100.00 |
| k         | 5.59 | 8.95 | 1.31 | 2.4 | 3.87 | 1.89 | 26.94 | 49.05 | 100.00 |
| l         | 8.51 | 0.26 | 0.49 | 0.27 | 8.9 | 0.78 | 27.08 | 53.71 | 100.00 |

Figure 4 and Table 2 show the results of the EDS test at typical point locations (a–l) in the ash micrographs, which demonstrate the weight percentage of elemental content. In WSA, K, Si, Cl, and O are the main elements of the rod-like particle "a" and flocculent particle "b". Therefore, they can be SiO₂ particles attached to KCl and K₂O. The spherical particle "c" mainly consists of SiO₂ and K₂O and a small amount of Cl. In addition, elemental C is detected in all three particles, which may be unburned carbon or carbonate. Regarding CSA, the main elements of point "d" are K, Ca, and O, which form K₂O.
and CaO. For "e", K, Ca, Mg, O, and P may exist in forms of K$_2$O, MgO, CaO, and Ca$_2$P$_2$O$_7$. The composition of "f" is supposed to be KCl and MgO attributed to equal moles of K and Cl. Points "g−i" of PBA are almost all Ca and CaO owing to the extremely high content of Ca and O. In CCA, high contents of K and Cl are found in all three particles "j−l", which exist in forms of KCl and K$_2$O.

The results of the above analyses are consistent with each other. It can be recognized that alkaline substances such as K$_2$O, CaO, MgO, and CaCO$_3$ in biomass ash are capable of absorbing SO$_2$ in flue gas. Considering the character of composition, biomass ash was proposed to absorb SO$_2$ as a novel sorbent, and the following experiments were performed to verify its feasibility.

3.2. Effect of Water Content of Biomass Ash on SO$_2$ Absorption. The absorption of SO$_2$ is a typical gas, liquid, and solid three-phase reaction accompanied by the drying of the sorbent. As shown in Figure 5, SO$_2$ is completely absorbed by the ash in the initial period of the experiment. Then, the absorptivity decreases rapidly, finally declines slowly, and tends to be stable over 60 min. The absorptivity curves vary among the four types of biomass ashes. In the case of no water, CCA has the longest total absorption time of approximately 10 min followed by CSA. According to the previous analysis in Section 3.1, a large amount of K$_2$O exists in CSA and CCA, which is a strong hygroscopic substance capable of absorbing the water vapor in flue gas and generating a water film on the surface of the ash sorbent. Therefore, it is beneficial for the dissolution of alkaline substances and improves SO$_2$ absorption.

In general, the total absorption time is prolonged and the decrease rate slows down with the addition of water. The ash sorbents become wet with a water film on the particle surface when mixed with water. SO$_2$ is absorbed by the three-phase reaction, which corresponds to the constant drying period in the process of semidry flue gas desulfurization and hence promotes the reaction rate. The water in biomass ash continuously evaporates and turns into the falling rate drying period with flue gas flows, causing the SO$_2$ absorption rate to decrease. Thus, the constant drying time and total absorption time are prolonged as water content increases. Figure 6 shows the SO$_2$ absorption capacity in 60 min corresponding to the experimental conditions in Figure 5. In the absence of water, the SO$_2$ absorption capacity of the four kinds of biomass ashes in 60 min was 12.5–24 mg per gram of ash, while it increased by 6.6–8.2 mg with 10% water mixed, which proves that the addition of water in biomass ash increases the absorption capacity of SO$_2$.

If excess water was added, the ash might bond seriously or even become a suspension solution, which will reduce the contact area with the flue gas and cause SO$_2$ to break through earlier. As a consequence, the maximum water content of CCA was 10% rather than 20%, which became slurry, and semidry desulfurization was no longer possible. Similarly, in the following experiments at different vapor concentrations in Section 3.3 and different temperatures in Section 3.4, the water content of CCA was 10% and those of the others were 20%.  

![Figure 5. Changes of SO$_2$ absorptivity by biomass ash sorbents with different water contents. (Total flow: 0.0167 dm$^3$/s; SO$_2$: 190 ppm; O$_2$: 6%; vapor concentration: 8%; temperature: 85 °C; and ash mass: 0.8 g.)](https://dx.doi.org/10.1021/acsomega.0c04364)

![Figure 6. SO$_2$ absorption capacity over 60 min.](https://dx.doi.org/10.1021/acsomega.0c04364)
3.3. Effect of Vapor Concentration in Flue Gas on SO₂ Absorption.

To study the influence of vapor concentration on the desulfurization by biomass ash, single-factor experiments were conducted with varying concentrations of water vapor and the results are shown in Figure 7. In the case of no vapor in the flue gas, the SO₂ absorptivity of biomass ash degraded rapidly from 100% to less than 20%. The SO₂ absorptivity of WSA decreased below 10% in 10 min and became stable over 20 min, exhibiting the worst performance. The reduction rate of SO₂ absorptivity slowed down as the result of the addition of 8% water vapor in the simulated flue gas. The absorptivity of CSA and CCA was maintained at over 47% at 60 min. Increased SO₂ absorption with increasing vapor concentration has been reported throughout the literature. It can be explained by the fact that the higher content of water vapor led to a longer drying time for the ash sorbents, which indicates that the liquid film on the sorbent surface lasts longer. Consequently, the total absorption time of SO₂ increased and the rate of absorption decrease slowed down. As relative humidity determines a balanced state of condensation and evaporation, the liquid film on the particle surface of solid sorbents will not disappear if the relative humidity increases to a certain extent. Similarly, Figure 8 shows the absorption capacity of SO₂ over 60 min. It was found that water vapor significantly improved SO₂ absorption capacity. Compared with no vapor in flue gas, the SO₂ absorption capacity of WSA in 60 min quadrupled from 5.4 mg per gram to 21.5 mg in the condition of 8% vapor concentration, and that of CCA increased by 71% from 18.3 to 31.3 mg.

3.4. Effect of Flue Gas Temperature on SO₂ Absorption. Temperature is an essential factor for SO₂ absorption. Figure 9 shows the SO₂ absorptivity of the four types of biomass ashes at different temperatures. The total absorption time of CCA increased from 5 to 10 min when the temperature decreased from 95 to 75 °C, and the decline in absorptivity was slower at lower temperatures. After 80 min, the SO₂ absorptivity of CCA was less than 30% at 95 °C while it exceeded 50% at 75 °C. The relative humidity of the flue gas increased as reaction temperature decreased when the vapor concentration remained constant. As a result, the evaporation of moisture in the ash slowed down, and the ionic reaction in the liquid film on the particle surface lasted longer; thus, the total absorption time of SO₂ increased. When the liquid film evaporated completely, the water tended to transfer to the ash surface with increasing relative humidity at lower temperatures; thus, the decline in absorptivity also slowed down. Furthermore, the dissolution and hydrolysis of SO₂ and neutralization are exothermic reactions. Therefore, SO₂ absorptivity and absorption capacity (Figure 10) increased as temperature decreased, which promoted the reaction. The effect of temperature is inconsistent in the literature. Some reports are consistent with this study, and it is believed that high temperature would reduce water accumulating and gas dissolving on the sorbent surface. However, opposite results were reported that SO₂ absorption was enhanced as operating temperatures increased. This is because an increase in operating temperature could enhance the chemical reaction rate and the ionic diffusion rate. In addition, Lau et al. investigated simultaneous removal of SO₂ and NO using copper-modified rice husk ash. It was found that there was no clear trend of the temperature effect but there was an
optimum operating temperature of 100 °C. They believed that the effect of temperature is very complex since reactions between the heterogeneous mixtures of flue gas and sorbent are very complex. In this study, the negative effect of higher temperature on SO₂ absorption overshadowed the positive effect.

3.5. SO₂ Absorption by Different Biomass Ash Sorbents. The results of SO₂ absorption under the same conditions for the four types of biomass ashes are shown in Figure 11. The findings illustrate that SO₂ absorption characteristics vary in different biomass ashes. The SO₂ absorption capacity of CCA was the largest followed by CSA, and the desulfurization effect of WSA was the worst. K and Ca play a vital role in SO₂ removal by biomass ash. According to the results of mineral composition analysis in Section 3.1, K₂O is the most abundant in CCA, the second is CSA, and CSA is rich in calcium compounds as well, which accounts for the improved desulfurization performance of CCA and CSA. Although PBA contains a small amount of K₂O, other alkaline substances such as CaCO₃, CaO, and MgO can react with SO₂. As shown in Table 1 and Figure 2, although the content of K₂O in WSA is slightly higher than that in PBA, more K₂O in WSA exists in the form of K₂SO₄ due to the higher content of sulfur. As a result, WSA contains a
relatively small amount of K2O and Ca, and its desulfurization effect is the worst.

In this study, the SO2 absorption capacity in different conditions was between 5.4 and 33.4 mg of SO2/g over 60 min. Lau et al.22 prepared the sorbent from rice husk ash impregnated with copper for simultaneous removal of SO2 and NO. They found that the range of absorption capacity was $11.10^{-13.50}$ mg of SO2/g under the optimum preparation condition. Furthermore, they optimized the operating conditions and obtained the largest absorption capacity of 53.4 mg of SO2/g.23 Dahlan et al.24 studied the activity of rice husk ash/CaO-based sorbent supported with various metal oxides for the removal of SO2 and NO. The simulated flue gas with a flow rate of 150 mL/min was composed of 2000 ppm SO2, 500 ppm NO, 10% O2, 3.1% H2O, and balance N2. The reaction temperature was set to 87 °C. The results showed that the SO2 and NO absorption capacity values were in the range of $7.074^{-28.296}$ and $0.138^{-2.761}$ mg/g, respectively, which was similar to our work. Krammer et al.46 studied the sorbents prepared from Ca(OH)2/CaCO3/CaSO4 and found that SO2 sorption capacity was in the range of $85.2^{-250.6}$ mmol of SO2/g, which was much larger than our work. This is explained by the high content of Ca(OH)2 and CaCO3 in their sorbents. Furthermore, the particle size of their sorbents is much smaller.

| spent ash | K2O (%) | KCl (%) | SiO2 (%) | CaO (%) | MgO (%) | SO3 (%) | P2O5 (%) | Fe2O3 (%) | others (%) | total (%) |
|-----------|---------|---------|----------|---------|---------|---------|---------|-----------|------------|-----------|
| WSA       | 17.21   | 28.33   | 29.29    | 7.29    | 1.97    | 10.53   | 1.12    | 0.778     | 3.48       | 100       |
| CSA       | 30.89   | 7.53    | 6.07     | 30.55   | 6.7     | 11.99   | 2.05    | 2.66      | 1.56       | 100       |
| PBA       | 9.07    | 20.90   | 10.83    | 5.67    | 0.42    | 10.43   | 1.81    | 0.501     | 2.61       | 100       |
| CCA       | 46.82   | 2.09    | 10.42    | 5.67    | 0.42    | 10.43   | 1.81    | 0.501     | 2.61       | 100       |

Table 3. Chemical Composition of Spent Ash from XRF Analysis (%)

Table 4. Elemental Content of Points (a−h) in Figure 12 from EDS (%)

| EDS point | C (%) | O (%) | Na (%) | Mg (%) | Al (%) | Si (%) | P (%) | S (%) | Cl (%) | K (%) | Ca (%) | Ti (%) | Fe (%) | total (%) |
|-----------|-------|-------|--------|--------|--------|--------|-------|-------|--------|-------|--------|-------|--------|-----------|
| a         | 34.01 | 0.96  | 1.68   | 35.79  | 0.91   | 3.00   | 1.89  | 13.34  | 8.43   |       | 100.00 |       |       |           |
| b         | 43.73 | 0.70  | 2.78   | 2.13   | 22.00  | 1.01   | 3.77  | 1.62   | 10.78  | 9.67  | 0.53   | 1.29  | 100.00 |           |
| c         | 43.90 | 2.39  | 0.79   | 3.14   | 4.52   | 0.34   | 7.49  | 0.74   | 21.47  | 14.29 | 0.93   |       | 100.00 |           |
| d         | 32.89 | 0.41  | 0.45   | 3.52   | 14.66  | 0.53   | 35.88 | 11.66  |       |       |       |       | 100.00 |           |
| e         | 26.40 | 0.40  | 2.78   | 4.13   | 7.42   | 11.49  | 33.87 | 11.71  | 1.80   | 100.00 |       |       |           |
| f         | 26.46 | 1.99  | 1.04   | 2.56   | 2.45   | 10.45  | 54.85 |       | 100.00 |       |       |       |       |           |
| g         | 14.97 | 3.09  | 2.78   | 4.44   | 13.22  | 5.50   | 56.00 |       | 100.00 |       |       |       |       |           |
| h         | 28.49 | 0.45  | 1.13   | 12.17  | 4.82   | 52.94  |       |       | 100.00 |       |       |       |       |           |

Figure 12. SEM images of four kinds of spent ash sorbents and point locations (a−h) for the EDS test.
Nevertheless, the comparison of sorption capacity shows that the four types of biomass ashes have potential to be used as sorbents for flue gas desulfurization.

3.6. Product Characteristics. After the absorption experiment, the characteristics of the spent ash were analyzed to investigate the absorption mechanism. As shown in Table 3, the content of SO$_3$ in spent ash sorbents increased by 4−8% compared with the original ash (Table 1), indicating the creation of sulfates.

Micrographs of spent biomass ash sorbents in Figure 12 illustrate that the surface of the spent ash is covered by irregular and uneven shapes of the desulfurization products. Burrs appear on the surface of the WSA particles. CSA particles are attached to smooth and irregularly shaped products. PBA and CCA particles are covered with many coarse attachments. Table 4 shows the elemental content at points (a–h) in Figure 12, analyzed by EDS. Note that there is a considerable amount of sulfur detected on the attachments.

The elemental distribution of the PBA particle in Figure 12 was further analyzed and is shown in Figure 13. The elements Ca, O, Al, Si, S, Na, and Mg were widely distributed in the microzone. Note that sulfur was concentrated the most in the

Figure 13. Elemental distribution of the spent PBA particle from the EDS test.

Figure 14. XRD patterns of spent ash sorbents. (XRD patterns of original ash (Figure 2) are shown here again for comparison.)
area marked with a red circle, where potassium was the most abundant. Meanwhile, large amounts of sulfur were associated with large amounts of calcium in the two areas in orange circles. In other words, potassium and calcium are active substances in SO2 absorption.

As shown in Figure 14, the biomass ash sorbents after SO2 absorption were detected by XRD and compared with that before the experiments. In the XRD pattern of spent CSA, the peaks of K2O disappeared and the peaks of K2SO4 and CaSO4 occurred, indicating that K2O reacted completely to form K2SO4 and part of the calcium compounds reacted to form calcium sulfate. Other unreacted phases from the original ash adsorbent were still detected. Similarly, in the XRD pattern of spent PBA, the absence of CaO and K2Si2O5 and the creation of sulfate compound K2Ca(SO4)2 showed that K and Ca were participating in the SO2 absorption. In both patterns of original and spent CCA, three phases of KCl, SiO2, and K2O were detected. The reaction product was detected as K2SO4 in spent CCA. This indicated that K 2O in CCA did not react completely during SO2 absorption. As for WSA, there was little change between the XRD patterns of original and spent WSA. The same three phases of KCl, SiO2, and K2SO4 were detected in original and spent WSA.

Zainudin et al.21 reported that during hydration, the K and other components in oil palm ash were able to inter-reacted within each other to form a microline, which was able to absorb SO2. The desulfurization products were K2S2O3·H2O and KAl(SO4)2·12H2O. Lau et al.22 reported that silicate compounds formed in the hydration of rice husk ash with CaO and NaOH were the active species that could reduce SO2. The desulfurization products were Na3Cu(SO4)2·2H2O, Ca2(SO4)2·12(SO3)0.33Sr and CaSO4·2H2O. However, alkaline substances, such as oxides or carbonates of potassium and calcium in biomass ash without the hydration process, were also found to have the desulfurization ability to a certain degree.

4. CONCLUSIONS

Four kinds of biomass ashes were investigated for SO2 absorption in simulated flue gas by fixed bed experiments. The effects of water content in ash, vapor concentration in flue gas, and flue gas temperature on desulfurization characteristics were studied. The results showed that the total absorption time was prolonged when water was added to the ash, and the rate of decrease slowed down, which obviously promoted the absorption of SO2. Similarly, the SO2 absorption increased when the vapor concentration in the simulated flue gas increased. A lower reaction temperature is beneficial for SO2 absorption. It is found that the main components of WSA are KCl and SiO2. CSA is rich in K2O and calcium compounds, PBA has a considerable content of calcium compounds, and CCA contains large amounts of KCl and K2O. Alkaline substances, such as oxides or carbonates of potassium and calcium were found to involve in SO2 absorption. Among the four types of biomass ashes, CSA performed best in SO2 removal owing to the abundance of potassium oxides followed by CSA, and WSA was the worst due to the small amount of K2O and Ca. The surface of the spent ash was covered by irregular and uneven shapes of the desulfurization products, which were mainly potassium and calcium sulfates.
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