Assessment of the Redox Characteristics of Iron Ore by Introducing Biomass Ash in the Chemical Looping Combustion Process: Biomass Ash Type, Constituent, and Operating Parameters

Lin Mu, Zhaoyi Huo,* Fuxing Chu, Zhen Wang, Yan Shang, Hongchao Yin, and Tingting Xu

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ABSTRACT: Chemical looping combustion (CLC) is a potential CO₂ capture and sequestration (CCS) technology that can easily separate CO₂ and H₂O without energy loss and greatly improve the efficiency of carbon capture. Due to the inherent defects of natural iron ore, such as low reactivity and poor oxygen carrying capacity, four kinds of biomass ashes (rape stalk ash, rice stalk ash, platane wood ash, and U. lactuca ash) that have different constituents of K, Na, Ca, and Si were applied to modify the redox performance of natural iron ore. The effects of biomass ash type, constituent, reaction temperature, H₂O vapor flow rate, and redox cycle on the CLC process were assessed experimentally in a batch fluidized bed reactor system. Oxygen carrier physicochemical characteristics were determined by several analytical techniques. The results showed that rape stalk ash, platane wood ash, and U. lactuca ash with a high K content and high K/Si ratio significantly improved the reactivity and cycle stability of iron ore, even after 10 redox cycles, while rice straw ash with a low K/Si ratio showed an inhibitory effect due to the formation of bridge eutectics, which enhanced agglomeration. In a range from 800 to 950 °C, higher temperatures led to a much better ability to promote the CLC process than lower temperatures. A higher flow rate of H₂O had little effect on the further promotion of the CLC process due to hydrogen inhibition. It is believed that the application of BA-modified iron ore oxygen carriers is an effective strategy to improve the CLC process.

1. INTRODUCTION

Coal is not only the main fossil fuel in China but also the main source of greenhouse gas CO₂ emissions. China has submitted a document to the secretariat of the United Nations Framework Convention on Climate Change in which it guarantees that CO₂ emissions will peak in approximately 2030 and the peak will be met as soon as possible, with CO₂ emissions per unit of gross domestic product (GDP) falling by 60 to 65 percent compared with 2005.¹ Thus, the development of innovative and efficient CO₂ emission reduction technology is of great significance. Among the many technologies related to CO₂ emission reduction, CO₂ capture and sequestration (CCS) technology is suggested to be one of the most promising technologies for development and application.² CCS refers to the technology that separates and traps CO₂ generated in the process of energy utilization for storage and utilization to prevent CO₂ from being discharged into the atmosphere and achieve the purpose of reducing CO₂ emissions. Among them, chemical looping combustion (CLC) technology has received extensive attention and become a research focus due to its inherent separation characteristic of greenhouse CO₂ and low energy penalties around the world. A typical CLC system, as shown in Figure 1, usually consists of two reactors (one is the air reactor,
abbreviated AR, and the other is the fuel reactor, abbreviated FR) and one kind of oxygen carrier (OC, expressed as MeO).

In the FR, the high-valence OC (MeO) is reduced to the low-valence OC (MeO−1) and accompanied by the release of lattice oxygen. Then, lattice oxygen is consumed by reacting with solid, liquid, or gaseous fuel, producing CO2 and H2O. The main reactions in the FR are endothermic reactions. In the AR, the low-valence OC (MeO−1) reacts with air to supplement the consumed lattice oxygen and further transforms to high-valence OC (MeO) in the redox cycle again by the oxidation reaction. The flue gas generated from the exit of the AR is mainly spent air (N2 and trace O2). The main reactions in the AR are exothermic reactions; therefore, heat is transferred by the OC from the AR to the FR, realizing the cascade utilization of energy. As a promising CCS technology, pure CO2 collected from the exit of the FR is further stored through the evaluated CO2 condensation and storage strategy. Moreover, since the fuel does not make contact with air and the reaction temperature is not high, the formation of fuel-type CO2 and H2O. Therefore, when natural iron ore is used as a potential oxygen carrier, an effective modification pathway that can promote the redox ability and reliability of Fe-based oxygen carriers is needed. As the typical oxide minerals of iron and titanium, ilmenite was also used as the oxygen carrier in chemical looping combustion. Bao et al. modified ilmenite (50.54% TiO2, 42.32% Fe2O3, 2.32% SiO2, 1.98% MnO, 1.45% Al2O3 in weight, and some other minor phases) by loading K2CO3, KNO3, Na2CO3, and Ca(NO3)2, which can promote the redox ability and reliability of Fe-based oxygen carriers. Nevertheless, natural iron ore has some inherent defects, such as low reactivity and poor oxygen carrying capacity. In addition, only during the reduction process of Fe2O3 to FeO can the fuel be fully burned, and the resulting product is H2O and CO2. Therefore, when natural iron ore is used as a potential oxygen carrier, an effective modification pathway that can promote the redox ability and reliability of Fe-based oxygen carriers is needed.

The oxygen carrier achieves the transportation of oxygen and heat in the CLC process. The key issues related to appropriate oxygen carriers include chemical reaction performance, mechanical strength, economic and environmental friendliness, continuous circulation ability, and low attrition rate. The common types of oxygen carriers include natural iron ore, artificial oxygen carriers, and waste residue oxygen carriers. According to the types of oxygen carriers, they can be divided into metal oxygen carriers (such as NiO, CuO, FeO, MnO2, and their blends) and nonmetal oxygen carriers (such as CaSO4). The performance of different types of oxygen carriers is quite different. Among the various types of metal oxygen carriers, Ni-based OCs have a higher redox reactivity than other OCs. However, the toxicity of Ni-based OCs can cause environment-related problems; therefore, the feasibility and reliability of the usage of Ni-based OCs are relatively low. Moreover, there were still other unavoidable problems, such as the thermodynamic limitation for conversion of H2 and CO11 and the generation of harmful Ni5S8 when fossil fuels were used. For Cu-based OCs, due to their low melting temperatures, Cu-based materials are prone to agglomeration or sintering, which limits the application of Cu-based OCs at high operating temperatures. Therefore, Fe-based metal oxides are suggested as potentially reliable oxygen carriers with great commercial application and environmental safety prospects. All iron compounds involved have relatively high melting temperatures during both the oxidation and reduction stages.

In addition, thermodynamic analysis and experimental studies have also indicated that when high-valence Fe2O3 is reduced to low-valence FeO, the fuel can be effectively converted to CO2 and H2O. Furthermore, it cannot be denied that the synthetic oxygen carriers have higher reactivity and stability than natural iron ore oxygen carriers, but they are expensive and not suitable for large-scale use, so the natural iron ore oxygen carriers with abundant reserves and low price have the broad prospects and are becoming a focus of research all over the world. Zhang et al. investigated the effect of calcination conditions of iron ore during the CLC process and suggested that the calcination temperature has the greatest effect on the physical and chemical parameters of fresh iron ore and the heating rate of 15 °C min−1 is the best preparation condition. Jiang et al. used natural iron ore as the oxygen carrier in the SS (sewage sludge)-CLC process and showed that the main characteristic parameters, such as the carbon conversion efficiency, carbon-containing gas conversion efficiency, and carbon capture efficiency, improved with increasing reaction temperature. Wang et al. studied separated gasification CLC with char as the fuel and iron ore as the oxygen carriers and showed that there was a great mismatch between the slow gasification of coal char in the gasification reactor and the rapid redox reaction of oxygen carriers and gasification products in the reduction reactor. Yan et al. modified hematite with K2CO3 and CuO and applied it in chemical looping combustion experiments. The results show that both CuO and K2CO3 increase the OC activity and the promoting effect of CuO is more obvious than that of K2CO3. The synthesized oxygen carriers of Fe2O3 and CaO were used as in a CLC process by Ismail et al. The results indicated that CaO-decorated oxygen carriers had better stability performance than undecorated Fe2O3 due to the formation of calcium ferrites, which could fully participate in the redox cycles.
The contents of AAEMs are significantly different in different types of biomass and affected by the biological origin, growth environment, growth cycle, human intervention, and other factors. In addition, some undesirable elements in biological ash will have adverse effects on the redox reactivity and feasibility of decorated Fe-based oxygen carriers. The synergistic effects of AAEMs with other elements should also be taken into consideration. However, few studies have evaluated different contents of AAEMs to determine their ability to improve the effect of iron ore oxygen carriers.

In this work, bituminous coal and natural iron ores were used as the experimental samples for the CLC process in a self-designed batch fluidized bed reactor. Because of the relatively low transformation rate of $\text{Fe}_3\text{O}_4 \rightarrow \text{FeO} \rightarrow \text{Fe}$ and the potential strengthening effect of adding AAEMs, the focus of this work is the influence of original and modified iron ores with different contents of AAEMs, especially K, Na, and Ca, as well as acid species Si. The reaction temperature, $\text{H}_2\text{O}$ content, and redox cycle number were selected as the key operating issues to assess the influence of oxygen carrier performance in the CLC process. In addition, energy-dispersive X-ray spectrometry (EDX), scanning electron microscopy (SEM), BET surface area, and X-ray diffraction (XRD) techniques were applied to determine the oxygen carrier performance characteristics. The main results and conclusions provide a useful guide to develop the conversion efficiency of chemical looping technology.

2. RESULTS AND DISCUSSION

2.1. BA Type Effect on the CLC Process. The modification effects of BA types with different contents of Na, K, and Ca on the reduction characteristics of different oxygen carriers were investigated experimentally to evaluate the most practicable oxygen carrier. In each experimental run, one unmodified oxygen carrier (UOC) and four BA-modified oxygen carriers (RAM−20%, RIm−20%, PWM−20%, and ULm−20%) were selected. The reduction temperature was set to 950 °C, with a reducing gas stream of the mixture of water vapor and nitrogen, as introduced in Section 4.3. Figure 2 illustrates the CO, CO$_2$, CH$_4$, and H$_2$ concentrations at the outlet of the experimental system during each CLC process when different OCs were used. The gaseous product concentrations when four BA-modified oxygen carriers were used had variation trends similar to those when the UOC oxygen carrier was applied. It was obvious that the CH$_4$ and H$_2$ concentrations showed significant growth at the initial stage of each experimental run due to the fast pyrolysis and devolatilization processes of coal particles. Afterward, syngas products were generated by the char gasification process. The produced syngas further reacted with the oxygen carriers, and a large amount of CO$_2$ was generated. Nevertheless, there were some differences worth noting. The CO$_2$ peak value for RAM−20% was the highest compared with other runs followed by ULm−20%, PWM−20%, and RIm−20%. The CO$_2$ peak value of the RIm−20% run is lower than that of the UOC run. The reduction reaction lasted a much longer time for UOC and RIm−20% runs than other runs. Furthermore, the H$_2$ to CO ratio was higher when using RAM−20%, ULm−20%, and PWM−20% as the OCs. Gu et al. also modified iron ore with two kinds of low acid ash and one kind of high acid ash. The results showed that introducing low acid ash promoted the CLC process and high acid ash showed an inhibitory effect in the CLC process.
Figure 3 shows the carbon conversion and carbon conversion rate vs experiment time at 950 °C for the UOC, RAm−20%, RIm−20%, PWm−20%, and ULm−20% runs. Carbon conversion profiles showed roughly similar trends for the five kinds of OCs. Compared with the UOC run, it took less time for RAm−20%, PWm−20%, and ULm−20% to reach a certain carbon conversion rate. Nevertheless, the time for the RIm−20% run to reach a certain conversion rate was slightly longer than that of the UOC run. The times of carbon conversion to reach 95% were 16.6, 24.8, 21.4, 19.1, and 24.0 min for the RAm−20%, RIm−20%, PWm−20%, ULm−20%, and UOC runs, respectively. It was obvious that from the carbon conversion rate curves in Figure 4b, the carbon conversion rate was in the order of RAm−20% > ULm−20% > PWm−20% > UOC > RIm−20%.

The mechanisms by which BAs promote the CLC process involve two main pathways: chemical-based mechanisms and constructive-based mechanisms. Initially, during the coal gasification process, AAEM ions (K+, Na+, and Ca2+) originating from BA served as a catalyst and accelerated the generation of syngas products. Afterward, during the reduction process, the strength of the Fe–O bond was weakened significantly by AAEM ions; thus, the activation energy of the reduction reactions decreased, leading to an increase in the reaction rate of Fe-based oxygen carriers in the reducing process. Moreover, K, Na, and Ca were also conducive to maintaining the porous characteristics of the iron ore oxygen carrier so that the coal sample particles could react with the oxygen carriers more effectively. For the BA-modified oxygen carriers investigated in this study, it can be concluded from Figure 16 that the ratios of (K + Na + Ca) to Fe of RAm−20%, ULm−20%, and PWm−20% were 15.804, 24.315, and 21.324, respectively, which were higher than that
of RIm−20%, which was only 12.708. Furthermore, the ratio of K to Fe of RAm−20% was the highest among the four BA-modified oxygen carriers. The BA-modified oxygen carriers with high ratios of Ca/Si (ULm−20%) and Na/Si (PWm−20%) did not show a more significant promotion than RAm−20%. Therefore, it is supposed that the loaded K content has a more significant effect on the modification performance on the oxygen carrier than Na and Ca. Research investigated by Bao et al.27 also indicated that K had the most significant effect on promoting the reactivity efficiency of oxygen carriers among the different types of AAEMs.

However, RIm−20% has an inhibitory effect on the CLC process compared with other oxygen carriers. It cannot be denied that the loaded K content in RIm−20% is the lowest; therefore, the effect of K promoting the reaction is not obvious. Furthermore, due to the high content of Si in RIA (45.41 wt %), the loaded Si content and the ratio of Si to Fe are relatively high. It can also be evaluated by the ratio of K to Si. The K/Si of RIm−20% was only 0.089, while the K/Si of RAm−20%, PWm−20%, and ULm−20% was 1.244, 0.392, and 1.090, respectively. Excess Si loading in the oxygen carrier favored the formation of low-melting eutectics or amorphous minerals coated on the surfaces of oxygen carriers or implanted into the pores of oxygen carriers, consequently significantly changing the porosity characteristics and microstructures of oxygen carriers by the sintering phenomenon and reducing the performance of the oxygen carrier, which led to the combustible gases being prevented from entering the inside of the oxygen carrier for a deeper reaction.50 Yilmaz and Leon56 also suggested that bridge conglutination, which caused agglomeration and enhanced adhesion, was formed between the oxygen carrier and the ash constituent present of K and Si. Therefore, the inhibitory effect of Si loaded on the oxygen carrier should be taken into consideration when BA with a high Si content is applied as the modification agent for the oxygen carrier.

2.2. Temperature Effect on the CLC Process. Figure 4 shows the exhaust concentrations at the system outlet during the experiment run, and the reaction temperatures were set at four typical levels from 800 to 950 °C with an interval of 50 °C. According to the previous section, RAm−20% showed the best reactivity on the CLC process; therefore, fresh RAm−20% was used as the oxygen carrier in the following sections. In the rapid coal pyrolysis process, a small amount of reducing gas (mainly H2 and CO) that was not oxidized escaped the reactor system. Then, a significant peak of CO2 was observed, which was mainly attributed to the gasification of generated coal char by steam. Then, the oxygen carriers further oxidize gasification products. The reaction temperature had an important role in the gas evolution behavior, as illustrated in Figure 4. As the reaction temperature increased, the peak value of CO2 became higher. Moreover, the redox reaction lasted a much longer time at a lower temperature than at a higher temperature.

The comparison of carbon conversion and carbon conversion rate vs experiment time at different reaction temperatures is depicted in Figure 5. As the reaction temperatures increased, the carbon conversion rose with time and the duration over which carbon conversion reached stability was shortened.59 The carbon conversion did not change remarkably when the chamber temperature rose from 800 to 850 °C. When the chamber temperature further rose from 850 to 900 °C, the carbon conversion changed significantly. From the carbon conversion rate curves shown in Figure 5b, the carbon conversion rate increased as the reaction temperature increased. Two peaks illustrating the carbon conversion rate curves were observed at 800, 850, and 900 °C. The first peak was ascribed to the rapid release of large amounts of carbon-containing gas from the fast pyrolysis of coal, while the gasification reaction at the initial stage was slow. The second peak was the main gasification reaction of char and H2O. Within this stage, the gasification reaction of C and H2O expands and the carbon conversion rate increases to the second peak.

According to the experimental results, within the range of 800–950 °C, a higher temperature exhibited a much better promotion of the CLC process than a lower temperature due to the three typical endothermic reactions 2, 4, and 7 listed in Section 2.3. The above three reactions were enhanced by the higher reaction temperature, and the carbon conversion and carbon conversion rate were also improved accordingly. Yan et al.51 also suggested that the reaction activity of oxygen carriers was enhanced at high reaction temperatures by applying natural iron ore as the oxygen carrier in CLC experiments. It should be noted that the potential sintering problem that occurred at excessive reaction temperatures had a deactivating effect on the oxygen carrier due to thermoplastic deformation effects.44

Figure 6 shows the gas content change curve during the oxidation reaction at different reaction temperatures. No CO and CO2 were generated during the entire oxidation process, indicating that the coal fully reacted during the reduction process. There was also no O2 detected early in the reaction process, indicating that the O2 in the reactor system had already reacted with the oxygen carrier within this time, and
the O₂ that passed in was completely consumed by the oxygen carriers.42 Furthermore, the time to start detecting oxygen at four evaluated temperatures is 3.8, 4.4, 5.7, and 6.3 min. The times for the oxygen carrier to be fully oxidized were 8.1, 9.5, 11.3, and 13.3 min, which indicated that more lattice oxygen originating from the Fe-based oxygen carrier was consumed at high temperatures.27

2.3. H₂O Flow Rate Effect on the CLC Process. The introduction of the gasification agent H₂O can greatly facilitate coal conversion efficiency during the CLC process.40,43 Therefore, the influences of H₂O content on carbon conversion, carbon conversion rate, and carbon capture capacity during the CLC process using fresh RAm–20% as the oxygen carrier at 950 °C were further studied in this section, and three different steam flow rates were selected. As shown in Figure 7, when the steam increased from a small flow rate of 0.25 g·min⁻¹ (0.058 L·min⁻¹), which is approximately 5.5 vol % of the total flow rate, to a medium flow rate of 0.5 g·min⁻¹ (0.116 L·min⁻¹), which is approximately 10.4 vol % of the total flow rate, it took less time to reach a certain carbon conversion, the H₂O flow rate further increased, and the carbon conversion did not change significantly. The carbon conversion rate, which was a function of carbon conversion, evidently accelerated as the H₂O content rose from 0.058 to 0.116 L·min⁻¹, while no obvious effect on the carbon conversion rate was observed when the steam flow rate further increased to a high flow rate of 1.0 g·min⁻¹ (0.233 L·min⁻¹), which is approximately 18.2 vol % of the total flow rate.

Figure 8 shows that the carbon capture capacity increased from 87% at a 0.058 L·min⁻¹ H₂O vapor flow rate to 95% at a 0.116 L·min⁻¹. H₂O vapor flow rate but there was no further increase at a higher H₂O vapor flow rate, which meant that a higher H₂O vapor flow rate was not a wise choice. A higher H₂O vapor flow rate meant that a larger thermal input was needed for the steam generation process and more heat was lost for CO₂ purification in the final condensation stage, as pointed out by Tian et al.42 Furthermore, DT bituminous coal was a typical highly volatile coal; thus, it was easily gasified. Therefore, it was supported that the reactivity of coal particles cannot be improved significantly when the H₂O vapor flow rate increased from 0.116 to 0.233 L·min⁻¹. In addition, Azimi et al.40 concluded that a higher steam fraction in the reactor resulted in a higher hydrogen fraction, further causing a decrease in the rate of conversion due to hydrogen inhibition, and the continuous improvement effect in the CLC process was not obvious. Therefore, 0.5 g·min⁻¹ (0.116 L·min⁻¹) of H₂O in fluidizing gas might be appropriate under the present studied experimental conditions.

2.4. Redox Cycle Effect on the CLC Process. Ten cyclic redox tests were conducted for UOC, RAm–20%, RIm–20%, PWm–20%, and ULm–20% with DT bituminous coal to investigate the cyclic redox performance and stability of the BA-modified oxygen carrier in the CLC process. Figure 9 shows the carbon capture capacity within 10 redox cycles. For all the experimental runs, the reaction temperature was still set at 950 °C, the fluidization agents were N₂ (1 L·min⁻¹) and H₂O (0.116 L·min⁻¹) as introduced above, and the oxygen to fuel ratio was 2.0. As seen from Figure 9, as the number of cycles increased, the carbon capture capacity gradually decreased. It was concluded that a large amount of heat would be released during the multioxidation processes, thereby leading to the loss of AAEMs at high temperatures and gradual sintering of the oxygen carrier. It was also obvious that a relatively stable and high carbon capture capacity can be
attained after 10 cycles when RAm−20%, ULm−20%, and PWm−20% are used as the oxygen carriers. The carbon capture capacity for RAm−20% was maintained at nearly 95.34 to 93.02%. However, as the number of cycles increased, the carbon capture capacity of the UOC and RIm−20% runs decreased significantly. Especially for RIm−20%, the carbon capture capacity decreased from 84.48 to 76.20%, which meant that the reactivity and stability of RAm−20%, PWm−20%, and ULm−20% were more reliable during the 10 redox cycles than those of UOC and RIm−20%.

2.5. Oxygen Carrier Performance Characteristics. The typical oxygen carrier samples investigated were characterized to assess the evolution characteristic differences of morphological structures and chemical compositions between fresh and reacted oxygen carrier samples. The morphological changes of oxygen carrier samples were obtained by SEM microscopic morphology observation. Enlarged SEM patterns of the fresh oxygen carrier particles are shown in Figure 10. The SEM micrographs after 10 redox cycles of testing are illustrated in Figure 11. It was obvious that the microstructures of the fresh UOC, RAm−20%, and ULm−20% samples were characteristic of coarse, irregular, and porous particles, which mainly consisted of crystallized aggregates and cracks, as shown in Figure 10a,b,e. Furthermore, some sintering phenomena were observed from the UOC, RAm−20%, and ULm−20% samples after 10 cycles of testing, and several aggregates with larger sizes were formed. For fresh PWm−20% and RIm−20% samples, slightly sintered microstructures have already occurred on the surfaces of PWm−20% and RIm−20% oxygen carrier particles, as shown in Figure 10c,d. More serious sintered microstructures with large agglomerates for PWm−20% and RIm−20% samples after 10 redox cycles were identified, as shown in Figure 11c,d. The densified and almost nonporous morphology had a prohibitive role in the transportation of reactant gases inside the pores and clearances of oxygen carrier particles, thus deteriorating the reactive activation of oxygen carriers.

In addition, EDX analysis was also carried out to evaluate the distribution of K, Na, and Ca of reacted modified oxygen carrier RAm−20% after 10 cycles of testing, as shown in Figure 12. The main AAEMs still have a favorable distribution on the surface of iron ores, and the main elemental compositions in the mapping area have no significant change. This finding indicates that the reactivity and stability of oxygen carrier RAm−20% are more reliable among the evaluated oxygen carrier samples.

An automatic surface analyzer (Quadrasorb evo TM−KR/MP, Quantachrome Quadrasorb SI Instrument) was used to determine the BET surface areas of the fresh and reacted
oxygen carrier particles. The results are depicted in Figure 13. The RAm−20% (~6.33 m²·g⁻¹), ULm−20% (~5.95 m²·g⁻¹), and PWm−20% (~4.81 m²·g⁻¹) oxygen carriers had larger surface areas than the UOC (~4.74 m²·g⁻¹) and RIm−20% (~4.26 m²·g⁻¹) oxygen carriers, which contributed to the effective contact between oxygen carriers and flammable gases, further promoting the CLC process. The BET surface areas of the oxygen carriers obviously decreased after 10 redox cycles, but the degree of decrease of RAm−20% (by ~7.27%), ULm−20% (by ~5.71%), and RIm−20% (by ~14.34%) was lower than that of UOC (by ~48.10%) and RIm−20% (by ~73.00%). Furthermore, the PWm−20% sample after 10 redox cycles of testing showed a slightly higher BET surface area than the UOC sample after 10 redox cycles of testing, thereby showing better reactivity. Thus, the BET surface areas indicated that RAm−20%, ULm−20%, and PWm−20% had better cycle stability, which was consistent with previous research conclusions.

X-ray diffraction (XRD) patterns of UOC and BA-modified oxygen carrier samples before and after 10 continuous redox cycles are shown in Figure 14. According to the XRD results, the dominant mineral phases of the five types of fresh OCs were similar. The main oxide phase was Fe₂O₃ for the fresh oxygen carrier samples, while the oxygen carriers after 10 redox cycles showed a slightly higher BET surface area than the UOC sample after 10 redox cycles of testing, thereby showing better reactivity. Therefore, the BET surface areas indicated that RAm−20%, ULm−20%, and PWm−20% had better cycle stability.
detected in the reduced oxygen carrier samples was Fe₃O₄. However, the Fe₃O₄ content in UOC and RIM⁻20% was relatively low, indicating a relatively low reaction activity and insufficient reaction ability during the reduction stage. Iron was not only a variable element but also an amphoteric element; therefore, the coordination state of iron was determined by the basicity of the system and the types and contents of components in the system. Potassium iron oxides K₆[Fe₂O₅] and K₃[FeO₄], whose melting temperatures were higher than 900 °C, were detected in the fresh RAM⁻20%, ULm⁻20%, and PWm⁻20% oxygen carrier samples. Research carried out by Yan et al. suggested that K₆[Fe₂O₅] had a stable spinel structure, which acted as a "skeleton" and played a catalytic role in improving the stability and reliability of the reaction. Therefore, BA-modified oxygen carriers generally have better reactivity with a high ratio of K to Si. Furthermore, relatively weak signals of natrosilite (Na₂Si₂O₅) whose melting temperature was approximately 874 °C were detected in the fresh PWm⁻20% and RAM⁻20% oxygen carrier samples. Na₂Si₂O₅ was mainly generated by the interaction of sodium metal with silica-rich particles in the calcination process of oxygen carriers due to the high content of Si and Na in the ash samples PWA and RIA and the main contributor to the formation of sintered microstructures of glassy eutectics on the surfaces of oxygen carriers. Furthermore, no calcic compounds were detected according to the XRD pattern for the PWm⁻20% oxygen carrier sample, which implied that most calcic compounds transferred to the amorphous phase, which cannot be detected by XRD.

3. CONCLUSIONS

The redox performance of the unmodified and BA-modified iron ore oxygen carriers was studied experimentally in a batch fluidized bed—CLC system. The effects of biomass ash types and main operation parameters, including temperature, H₂O flow rate, and redox cycle number, on the gaseous product concentrations, carbon conversion, carbon conversion rate, and carbon capture capacity, were studied. In addition, oxygen carrier performance characteristics were determined by SEM, BET, and XRD techniques. The main conclusions were as follows.

(1) The contents of K, Na, and Ca had different effects on improving the performance of Fe-based oxygen carriers. Biomass ashes with high contents of K, Na, and Ca were also conducive to weakening the Fe—O bond and maintaining the porous characteristics of the iron ore oxygen carrier. Furthermore, the BA-modified oxygen carriers RAM⁻20%, ULm⁻20%, and PWm⁻20% with (K + Na + Ca) Fe and low Si content promoted the reduction reactivity and stability in the CLC process.

(2) RIM⁻20% with a high content of Si and a low ratio of K/Si showed the inhibiting effect on reactivity and reliability due to the formation of low-melting "bridge" eutectics, which coated on the surfaces of oxygen carriers or implanted into the pores of oxygen carriers.

(3) Within the range of 800—950 °C, a higher temperature exhibited a much better promotion effect on the CLC process than a lower temperature, which was mainly due to endothermic reactions. It was proven that a higher H₂O flow rate could promote the CLC process. However, increasing the H₂O content from a low flow rate to a high flow rate did not further improve the CLC process by evaluating the carbon conversion, carbon conversion rate, and carbon capture capacity. Therefore, a medium H₂O vapor flow rate of 0.116 L·min⁻¹ may be suitable for the CLC of highly volatile coal samples.

(4) In brief, RAA, ULA, and PWA with a high content of K and a low content of Si enhance iron ore stability and reliability. The application of BA-modified iron ore oxygen carriers is an effective strategy to improve the CLC process. Moreover, the application of waste and industry byproducts rich in AAEMs as well as the synergistic reaction mechanism of loaded inorganic elements on the oxygen carriers with other operating parameters should be studied in depth in future work.
4. EXPERIMENTAL SECTION

4.1. Properties of Fuel Samples. The coal sample in this study was Datong (DT) bituminous coal originating from Shanxi Province, China. A vacuum drying oven was used to determine the apparent water absorbed by the coal at 105 °C for 10 h. The coal samples in the particle size range of 0.3–0.45 mm were sieved and selected for the following experimental study. Table 1 lists the fuel properties of the bituminous coal sample.

| Table 1. Fuel Properties: Proximate Analysis, Ultimate Analysis, and High Calorific Value |
|-----------------------------------|
| analysis                        | DT                           |
| proximate analysis (wt %, air dried basis) |                        |
| ash                             | 7.43                         |
| volatiles                       | 33.01                        |
| moisture                        | 7.23                         |
| fixed carbon                    | 52.33                        |
| ultimate analysis (wt %, dry ash-free basis) |                        |
| C                               | 71.00                        |
| H                               | 3.92                         |
| N                               | 1.05                         |
| S                               | 0.63                         |
| O, by different                 | 8.74                         |
| high calorific value (MJ·kg⁻¹)  | 27.50                        |

4.2. Preparation and Characterization of Oxygen Carrier Particles. In the present study, the oxygen carrier applied was natural iron ore from the Jinan steel plant, Shandong Province, China. Natural iron ore was sieved by a mechanical screen classifier, and the appropriate particle samples with apparent diameters of 0.30–0.45 mm were selected as the unmodified Fe-based oxygen carrier (UOC). The UOC was further calcined at 950 °C for 4 h in a muffle furnace (AAF 12/18, maximum temperature of 1200 °C, Carbolite Gero Ltd.) to improve the mechanical strength.47

Four kinds of biomass were adopted as the raw materials to prepare the biomass ashes (BAs). Rape stalks (RAs) and rice stalks (RIs) are typical agricultural residues from Jiangxi Province, China, platane wood (PW) is woody biomass from Liaoning Province, China, and U. lactuca (UL) is a typical aquatic biomass in the northern seas of China. AAEMs in BAs easily volatilize and are lost under high-temperature conditions (above 650 °C) during ashing processes. Therefore, the ending temperature of the ashing program was set below 600 °C according to the Chinese standard GB/T 30725–2014. Biomass samples with sizes less than 0.1 mm were selected for BA preparation and heated in a muffle furnace at a low heating rate of 5 °C·min⁻¹ with an ending temperature of 600 °C. Then, the temperature of the muffle furnace was kept at 600 °C for 2 h to guarantee that the residue masses were constant. The chemical compositions of BAs were shown in Table 2. The prepared BAs were abbreviated as RAA (rape stalk ash), RIA (rice stalk ash), PWA (platane wood ash), and ULA (U. lactuca ash).

The oxygen carriers modified by BAs were prepared by the dry calcination method with a BA loading ratio of 20% in mass fraction (the mass ratio of BA and iron ore particles was 0.2:1). The dry calcination method has been proven to be easy to operate, and K and Na can be volatilized and loaded effectively on iron ore particles by calcination.31 Taking the preparation process of rape stalk ash-modified iron ore as an example, the screened RAA and iron ore particles were mechanically mixed and stirred evenly with a loading mass ratio of 20% in a stirring dish. Then, the mixed sample was calcined for 3 h at 950 °C, as suggested by Yilmaz and Leion.36 The calcination process was processed in a limited furnace to ensure mutual interactions between the AAEMs evaporated from BA samples and iron ore. Finally, calcined particle samples with a size range of 0.30–0.45 mm were sieved and selected as the oxygen carriers and denoted as RAm–20%. The residue BAs with diameters lower than 0.30 mm were removed. The mass increase of BA-modified oxygen carriers was no more than 2%, and the differences in Fe₂O₃ contents between the unmodified and BA-modified oxygen carriers were minor and negligible.

The preparation methods of oxygen carriers modified by RIA, PWA, and ULA were the same as above and denoted as RIm–20%, PWm–20%, and ULm–20%. The chemical compositions of unmodified and BA-modified oxygen carriers are shown in Table 3. Furthermore, the EDX analysis was carried out to assess the distribution characteristics of the main AAEMs (K, Na, and Ca) on the surface of iron ores (RAm–20%) decorated by rape stalk ash, as shown in Figure 15. The AAEMs in the RAA were uniformly scattered on the surfaces of iron ore particles after the calcination process. The release of K, Na, and Ca was mainly based on their different valence states in the compounds. K and Na disconnected only one chemical bond from the gaseous phases, such as alkali metal sulfates, chlorides, and hydroxides, which can be evaporated at relatively low volatilization temperatures.38 Then, K and Na gaseous vapors transferred to the surfaces of iron ore particles or immersed into the pores of iron ore particles due to the concentration differences during the co-calcination process of BAs and iron ore particle mixtures under high-temperature conditions. Since K and Na had a lower valence than Ca, the volatilization of Ca from the BAs needed to disconnect two chemical bonds from the calcic compounds simultaneously within a very short time.49 Therefore, it was believed that the modification effect generated by Ca was mainly caused by the direct interaction between the primary oxide Fe₂O₃ in the iron ore and Ca-containing minerals in the BAs. Furthermore, the EDX analysis also demonstrated the reliability of the dry calcination method. The elemental mole ratios K/Fe, Na/Fe, Ca/Fe, and Si/Fe used to evaluate the loading effects of K, Na, and Ca are shown in Figure 16. Generally, a higher ratio corresponds to a better loading effect. Figure 16 shows that the K/Fe ratio of RAm–20% was ~1.134 due to the high content of K in RAA, which was the highest among the BA-modified oxygen carriers, while RAm–

Table 2. Chemical Compositions of Biomass Ashes Used as Modifiers

| chemical composition (wt %) | RAA | RIA | PWA | ULA |
|----------------------------|-----|-----|-----|-----|
| Fe₂O₃                      | 3.13| 1.47| 2.23| 2.69|
| K₂O                        | 32.16| 6.20| 16.19| 25.54|
| Na₂O                       | 3.21| 15.51| 13.20| 26.12|
| CaO                        | 9.62| 8.66| 25.97| 2.41|
| SiO₂                       | 9.12| 45.41| 23.56| 6.58|
| Al₂O₃                      | 7.12| 4.85| 5.01| 9.38|
| MgO                        | 9.85| 2.58| 5.12| 5.95|
| P₂O₅                       | 12.13| 7.64| 3.81| 11.77|
| SO₃                        | 12.15| 6.71| 3.53| 8.96|
| others                     | 1.51| 0.96| 1.37| 0.60|
20% had a low Na/Fe ratio of only ∼1.75. Regarding RIm−20%, due to the high content of Si in RIA, the Si/Fe ratio is relatively high (∼23.56). For the Ca loading effect, PWm−20% has a high ratio of Ca/Fe (∼8.176), while the Ca/Fe ratio of ULm−20% is the lowest (∼0.78).

### 4.3. Experimental Setup and Main Reactions

A comprehensive fluidized bed reactor system that was applied to the CLC experiments is graphically represented in Figure 17. The experimental system consisted of a gas and steam delivery subsystem, a combustion reaction subsystem, and a flue gas purification and analysis subsystem. A cylindrical stainless steel tube ($d_{in} = 32$ mm, $l = 900$ mm) was used as the main reaction chamber, and a distribution plate with a porous microstructure was located 400 mm from the bottom of the cylindrical tube. The electric resistance wires were embedded into the furnace wall to heat the main reaction chamber. Two K-type thermocouples were enclosed in the reactor and used to monitor and control the reaction temperature.

During the experimental runs, distilled water was applied to generate steam, which was adopted as the gasification agent. A constant flow pump (TBP5010S, flow accuracy ≤1%, flow precision ≤1%, Shanghai Tauto Biotech Co., Ltd.) was used to control the flow rate of distilled water, and a self-designed steam generator was used to preheat the distilled water to 200 °C. N2 was used as the carrier gas to transport the steam into the combustion reaction system. The outlet flow was calculated by the mass balance. Nitrogen (purity = 99.999 vol %, Dalian Junfeng Gas Chemicals Co., Ltd.) and oxygen (purity >99.995 vol %, Dalian Junfeng Gas Chemicals Co., Ltd.) were controlled and monitored by compression release valves and mass flow controllers (CS200, ±1.0% S.P., Beijing Sevenstar Flow Co., Ltd.).

In each experimental run, approximately 40 g of oxygen carrier particles was weighed and placed in the porous distribution plate through the feedstock hopper on the top of the reactor immediately when the chamber temperature rose to the initial set condition (approximately 850 °C). Then, the oxidizing gas stream (mixture of 0.1 L·min⁻¹ O₂ and 0.9 L·min⁻¹ N₂) was imported into the reaction system as the fluidizing gas until the oxygen carrier was oxidized completely. Then, the reaction system and pipelines were swept by N₂ for approximately 15 min until there was no O₂ residue in the experimental system. The reactor system was further heated until the furnace temperature reached the reduction reaction temperature, and then the reducing gas stream (mixture of 0.116 L·min⁻¹ H₂O and 1 L·min⁻¹ N₂) was applied as the gasification agent for the reduction reaction. When the set temperature was reached according to the experimental scheme, coal particle samples (approximately 0.5 g) were quickly put into the chamber furnace through the feedstock hopper. The reaction process lasted for approximately 40 min. Moreover, the gas produced was cooled and filtered first. Then, the purified gas was set to a multicomponent infrared gas analyzer (Gasboard−3100, Hubei Cubic−Ruiyi Instrument Co., Ltd., China) to detect the content of carbonous gas (CO₂, CO, and CH₄), O₂, and H₂, with an accuracy ≤2% full scale.

The redox reactions that occurred during the CLC process were mainly as follows:21,33

### Table 3. Chemical Compositions of Unmodified and BA-Modified Iron Ore Oxygen Carriers

| chemical composition (wt %) | UOC   | RAm−20% | RIm−20% | PWm−20% | ULm−20% |
|-----------------------------|-------|---------|---------|---------|---------|
| Fe₂O₃                       | 89.27 | 78.5    | 75.12   | 75.75   | 76.13   |
| K₂O                        | 5.16  | 0.94    | 2.70    | 4.26    |
| Na₂O                       | 0.54  | 2.29    | 2.10    | 4.15    |
| CaO                        | 0.09  | 1.61    | 1.44    | 4.36    | 0.42    |
| SiO₂                       | 4.81  | 5.23    | 13.18   | 8.64    | 4.89    |
| Al₂O₃                       | 4.63  | 2.01    | 2.63    | 2.89    | 3.39    |
| MgO                        | 0.16  | 1.95    | 0.46    | 0.97    | 1.21    |
| P₂O₅                       | 0.39  | 3.12    | 1.83    | 1.12    | 2.93    |
| SO₃                        | 0.07  | 1.03    | 1.32    | 0.59    | 1.89    |
| others                     | 0.58  | 0.86    | 0.79    | 0.88    | 0.73    |
coal → CO + H₂ + CH₄

C + H₂O → CO + H₂

CO + H₂O → CO₂ + H₂

CH₄ + 2H₂O → 3H₂ + CO

CO + 3Fe₃O₄ → CO + 3O₂ + CO₂

H₂ + 3Fe₃O₄ → 3Fe₃O₄ + H₂O

CH₄ + 12Fe₂O₃ → 12FeO₄ + 2H₂O + CO₂

CO + Fe₃O₄ → CO₂ + 3FeO

H₂ + Fe₃O₄ → 3FeO + H₂O

CH₄ + 4FeO₄ → 12FeO + 2H₂O + CO₂

CO + FeO → Fe + CO₂

H₂ + FeO → Fe + H₂O

CH₄ + 4FeO → 4Fe + CO₂ + 2H₂O

4.4. Data Evaluation. The redox performance of unmodified and BA-modified iron ore oxygen carriers was evaluated, and several main evaluation criteria were defined. During the stage of complete oxidation of oxygen carriers, no carbonaceous gas was detected; therefore, it was believed that during the oxygen carrier reduction stage, no carbon deposition phenomenon occurred on the inside and surfaces of oxygen carrier particles.

(1) The carbon conversion \( X_{\text{conv}} (%) \) at time \( t_i \) (min) is determined by

\[
X_{\text{conv}} = \frac{\int_0^{t_i} (n_{CO_2} + n_{CO} + n_{CH_4}) dt}{\int_0^{t_{\text{total}}} (n_{CO_2} + n_{CO} + n_{CH_4}) dt}
\]

where \( n_{CO_2}, n_{CO}, \) and \( n_{CH_4} \) are the gas phase concentrations in the volume fraction and \( t_{\text{total}} \) is the total experimental duration, min.

(2) The carbon conversion rate \( R_{cc} (\text{‰ min}^{-1}) \) at time \( t_i \) is determined as follows:

\[
R_{cc} = \frac{dX_{\text{conv}}}{dt}
\]

(3) The volume fraction of carbonaceous gases \( F_i (%) \) is determined as follows:

\[
F_i = \frac{\int_0^{t_i} n_i dt}{\int_0^{t_{\text{total}}} (n_{CO_2} + n_{CO} + n_{CH_4}) dt}
\]

where \( i \) means CO₂, CO, and CH₄, respectively, and \( F_{CO} \) is defined as the carbon capture capacity for each experimental run.
Corresponding Author
Zhaoyi Huo — School of Material and Metallurgy, University of Science and Technology Liaoning, Anshan City, Liaoning 114051, P. R. China; orcid.org/0000-0001-7325-6481; Email: hyz10710010@163.com

Authors
Lin Mu — School of Energy and Power Engineering, Dalian University of Technology, Dalian City, Liaoning 116024, P. R. China; orcid.org/0000-0002-1020-8716
Fuxing Chu — School of Energy and Power Engineering, Dalian University of Technology, Dalian City, Liaoning 116024, P. R. China
Zhen Wang — School of Energy and Power Engineering, Dalian University of Technology, Dalian City, Liaoning 116024, P. R. China
Yan Shang — School of Energy and Power Engineering, Dalian University of Technology, Dalian City, Liaoning 116024, P. R. China
Hongchao Yin — School of Energy and Power Engineering, Dalian University of Technology, Dalian City, Liaoning 116024, P. R. China
Tingting Xu — School of Material and Metallurgy, University of Science and Technology Liaoning, Anshan City, Liaoning 114051, P. R. China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.1c03113

Notes
The authors declare no competing financial interest.

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