Melting Characteristics of Coal Ash and Properties of Fly Ash to Understand the Slag Formation in the Shell Gasifier

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ABSTRACT: The flow temperature (FT) of the coal ash from the Liuqiao no. 2 mine in North Anhui Province (C00) is too high (∼1520 °C) to fit the Shell gasifier due to its relatively high content of SiO2 and Al2O3. To solve this problem, a series of coals were blended with C00 with different ratios, and the relations between FT and the ash composition were investigated. The coal ash was analyzed by X-ray diffraction, Fourier transform infrared (FTIR) spectroscopy, and scanning electron microscopy−EDX to elucidate the mechanism of the improved ash fusion performance and the slag formation in the waste heat boiler of the gasifier. It is shown that FT is relevant to the coal ash compositions as well as the structures formed at high temperatures. The existence of alkaline oxides (CaO, MgO, and Fe2O3) decreases the coal ash FT to a low level. The FT can decrease to <1350 °C to cater to the Shell gasifier by blending C00 and C03 with a mass ratio of 4:6 owing to the plentiful alkaline oxides in C03. The FTIR results indicate that the high flow temperature of C00 is attributed to the formation of mullite at high temperatures. The coal blending with various ratios changes the compositions of CaO, MgO, and Fe2O3, which can form some low-melting-point eutectic compounds with SiO2 and Al2O3 under high temperatures, inhibit the formation of mullite, and thus decrease the ash FT. The coal ash FT was found to have a good linear relation with the ash compositions, which can serve as a reference to the coal blending. According to the model parameters, it is shown that Mg has the most significant promoting effect on the decrease in FT of the coal ash. The caking tendency of fly ash increases with the rising Ca content and an excessive Ca-based fluxing agent used in the coal blending will lead to the aggregation of the Ca-rich clasts around the fly ash particle, resulting in the plugging of the waste heat boiler in the gasifier. Therefore, the Mg-based fluxing agent is more promising to improve the ash fusion performance and reduce the caking tendency of the coal fly ash.

1. INTRODUCTION

China has abundant coal reserves; nevertheless, the severe air pollution and global warming caused by the direct combustion in recent years need further coal upgrading. One efficient approach is through gasification to convert coal into gas with various heat values. Since the 1970s, the developed countries have accelerated the pace of new coal gasification technologies toward the middle−high pressure (8.5 MPa), high temperatures (1500−1600 °C), diversified feedstocks, and liquidus slagging. The Shell Corp. has been developing the coal gasification technology since the 1950s, and its present industrialized technology adopts a waste heat boiler process, that is, the milled coal, oxygen, and steam are converted into carbon oxides in the gasifier under ∼1500 °C; then, the heat is recycled by a waste heat boiler. The formed high-temperature slag at the bottom of the gasifier is chilled into millimeter-sized particles that can be used as a construction or roadbed material.

To ensure smooth slagging, the Shell gasifier requires that an operating temperature should be 100−150 °C higher than the coal ash FT which greatly depends on the ash composition. The coal ash is formed from the inorganic components in the coal during the combustion or gasification, and it is a key factor for the safe and proper coal application. Therefore, the coal ash fusion characteristic should be carefully studied and an appropriate slagging way should be determined before the coal gasification to ensure the smooth operation of the gasifier. The coal ash is mainly composed of acidic (SiO2, Al2O3, TiO2, etc.) and alkaline compositions (Fe2O3, CaO, MgO, K2O, Na2O, etc.). Previous studies show that the ash fusion temperatures are related to the coal ash compositions. Generally, the ash fusion temperatures increase with the content of acid oxides (SiO2, Al2O3, TiO2, etc.) but decrease with the alkaline compositions. Si/Al ratio is also a key
factor affecting the fluidity of the coal at high temperatures since SiO2 and Al2O3 are the main components of the coal ash. Al2O3 has ionic crystal structures and has a high melting point, while quartz is mainly in the amorphous form; thus, the ash fusion temperature generally decreases with the increasing Si/Al ratio. Liu et al. studied the relations between the coal ash compositions and ash fusion temperatures by using synthetic ashes composed of SiO2, Al2O3, CaO, Fe2O3, and K2O, finding that the increasing Si/A ratio and Fe2O3 content were favorable to the ash fusion, and K2O showed no significant effect on the ash fusion temperature, while a minimum value of the ash fusion temperature for the CaO effect was observed. Chakravarty et al. obtained similar conclusions that the presence of quartz contributed to the high ash fusion temperature, while the presence of Fe2O3 decreased the ash fusion temperatures when they studied the ash fusion behavior of Indian coals. Nevertheless, Song et al. obtained different conclusions when using the coal mixtures in China with various additives, and their results showed that the effects of CaO, Fe2O3, and MgO displayed minimum values, while the ash fusion temperatures always increased with the increasing Si/Al ratios owing to the formation of the high-melting-point mullite and corundum. This indicates that the effect of ash composition on its fusion behavior is rather complicated since the various components always interact with each other, forming some refractory minerals (quartz, mullite, rutile, and kaolinite) and low-melting eutectics. To improve the viscosity—temperature characteristics of the coal ash, blending is a promising method by which the high-melting-point mullite and quartz are transformed into the low-melting-point eutectics. Many researchers have established various models to find an empirical or statistical correlation between the ash fusion temperatures and ash composition. Sasi et al. devised the prediction model using two approaches, namely, a thermodynamic approach using the ChemApp subroutine and a purely data-driven approach using artificial neural networks, obtaining a conclusion that a combination of these two approaches provided an efficient and reliable way toward the industrial application.

Sinopec Anqing Company brought in the Shell gasification technology to perform coal gasification in 2006 using the coal blending from the Liuqiao no. 2 mine in North Anhui Province as a feedstock, while the gasifier was interrupted frequently by the plugging of the slag because of the high FT of the coal ash, indicating that the industrialization of the Shell coal gasification technology was still under development. In this study, to solve this problem, the effect of various coal blends with the feedstock coal on the coal ash fusion temperature was investigated. The coal ash samples were treated at various temperatures under a weak reducing atmosphere, and the coal ash fusion behavior was studied by Fourier transform infrared (FTIR) spectroscopy. The relation between the ash composition and FT was established by a linear model, and an empirical or statistical correlation each other and form high-melting-ash coal; thus, the Shell gasifier cannot directly process C00 since its designed temperature is only 1350 °C. The samples with a high content of SiO2 and Al2O3 (C00, C01, and C02) show relatively high FT, while C03, C04, and C05 with less SiO2 and Al2O3 show a much lower FT, indicating that the plentiful SiO2 and Al2O3 are unfavorable to the coal ash fluidity, which has been confirmed by many researchers. Besides the effect of SiO2 and Al2O3, the more CaO, Fe2O3, and MgO in C03, C04, and C05 are considered as the other important reasons for their lower fusion temperature since the alkaline oxides are observed to greatly influence the coal ash melting characteristics. Although C01 contains more CaO (7.12 wt %) and Fe2O3 (8.32 wt %) than C02 (5.66 wt % CaO and 5.76 wt % Fe2O3), the FT of C01 is much higher (1465 °C) than that of C02 (1345 °C), which is probably explained by the higher content of MgO in C02 because increasing the content of MgO is more effective to enhance the coal ash fluidity. C03 shows the lowest FT (1200 °C) owing to its much more MgO, CaO, and Fe2O3 and certainly the less SiO2 + Al2O3. On the contrary, the C00 sample consists of more SiO2 + Al2O3 and less alkaline oxides, leading to the highest flow temperature (1520 °C) among these samples, which severely impedes its direct gasification on the Shell gasifier. Although the contents of Na2O, TiO2, and SO2 are low, they may also transform into some eutectics such as feldspar and anhydrite that affect the ash fusion temperatures of the coal ash.

X-ray diffraction (XRD) patterns of C00, C03, and C05 treated at 815 °C are shown in Figure 1. All the samples are mainly composed of quartz (SiO2), lime (CaO), anhydrite (CaSO4), hematite (Fe2O3), magnesium oxide (MgO), grossite (CaAl2O4), sandine (KAlSiO4), and muscovite (KAl3(SiAlO10) (OH)2]. Most of the elements exist in multiple crystal phases, for example, calcium is mainly in the form of lime, anhydrite, and grossite. This suggests that the various elements in the coal ash affect each other and form some new solid phases, which greatly influences the ash fusion temperature. In comparison with C00 and C05, C03 shows stronger diffraction peaks corresponding to lime and hematite, while much weaker peaks associated with Al and Si contained

| Table 1. Properties and Element Analysis of the Raw Coal (C00) |
|---------------------------------|
| proximate analysis (wt %)      | ultimate analysis (wt %) |
| moisture, ad                   | C, ad                     | 73.07 |
| ash, ad                        | H, ad                     | 3.14  |
| volatile matter, daf           | S, ad                     | 0.46  |
| fixed carbon, daf              | N, ad                     | 1.07  |
| calorific value (Qc), ad (MJ/kg) | 27.58                    |

ad: air-dry basis; daf: dry ash-free basis.

can be conveniently guided the industrial coal blending. The properties and element analysis of the feed coal (C00) for the Shell gasifier in Sinopec Anqing Company are listed in Table 1. C00 coal is mainly composed of C and H, accounting for 73.07 and 3.14 wt %, respectively, and traces of S (0.46 wt %) and N (1.07 wt %) with a heat value of 27.58 MJ/kg. By calcining the coal at 815 °C, 22.24 wt % coal ash (air-dry basis) was obtained.

The chemical compositions of various coal ashes are listed in Table 2. SiO2 and Al2O3 are the main components of the coal ash, and other oxides such as CaO, Fe2O3, MgO, Na2O, and TiO2 are also detected. The ash fusion temperatures of C00 are extremely high (1520 °C), indicating that C00 pertains to high-fusion-ash coal; thus, the Shell gasifier cannot directly process C00 since its designed temperature is only 1350 °C. The samples with a high content of SiO2 and Al2O3 (C00, C01, and C02) show relatively high FT, while C03, C04, and C05 with less SiO2 and Al2O3 show a much lower FT, indicating that the plentiful SiO2 and Al2O3 are unfavorable to the coal ash fluidity, which has been confirmed by many researchers. Besides the effect of SiO2 and Al2O3, the more CaO, Fe2O3, and MgO in C03, C04, and C05 are considered as the other important reasons for their lower fusion temperature since the alkaline oxides are observed to greatly influence the coal ash melting characteristics. Although C01 contains more CaO (7.12 wt %) and Fe2O3 (8.32 wt %) than C02 (5.66 wt % CaO and 5.76 wt % Fe2O3), the FT of C01 is much higher (1465 °C) than that of C02 (1345 °C), which is probably explained by the higher content of MgO in C02 because increasing the content of MgO is more effective to enhance the coal ash fluidity. C03 shows the lowest FT (1200 °C) owing to its much more MgO, CaO, and Fe2O3 and certainly the less SiO2 + Al2O3. On the contrary, the C00 sample consists of more SiO2 + Al2O3 and less alkaline oxides, leading to the highest flow temperature (1520 °C) among these samples, which severely impedes its direct gasification on the Shell gasifier. Although the contents of Na2O, TiO2, and SO2 are low, they may also transform into some eutectics such as feldspar and anhydrite that affect the ash fusion temperatures of the coal ash.

2. RESULTS AND DISCUSSION

2.1. Physical and Chemical Properties. The properties and element analysis of the feed coal (C00) for the Shell gasifier in Sinopec Anqing Company are listed in Table 1. C00 coal is mainly composed of C and H, accounting for 73.07 and 3.14 wt %, respectively, and traces of S (0.46 wt %) and N (1.07 wt %) with a heat value of 27.58 MJ/kg. By calcining the coal at 815 °C, 22.24 wt % coal ash (air-dry basis) was obtained.

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2.2. Effect of Coal Blending on the Melting Characteristics. The ash fusion behavior can be divided into three stages: sintering, primary fusion, and the free liquid stage. The endpoints of the sintering and primary fusion stages agree well with the deformation temperature and flow temperature, respectively.\(^2\) As shown in Figure 2a, the deformation temperature decreases with the addition of C01 to C00, while both the softening temperature and flow temperature have no significant changes. The flow temperature is still above 1495 °C, although the ratio of C01 to C00 is 10:0, indicating that the coal blending of C01 and C00 cannot cater to the designed ash fusion temperature requirements (1350 °C) of the Shell gasifier, which is explained by the similar compositions of C00 and C01. For the coal blending of C02 and C00, as shown in Figure 2b, the ash fusion temperatures decrease with the addition of C02 to C00 observably. As shown in Table 2, C00 and C02 have similar SiO\(_2\) and Al\(_2\)O\(_3\) compositions, but the alkaline oxides (CaO, Fe\(_2\)O\(_3\), and MgO) in C02 are slightly higher than C00. Considering that the content of CaO and Fe\(_2\)O\(_3\) in C02 is less than that in C01, it is concluded that more MgO in C02 makes a great contribution to the decrease in the ash fusion temperature of the C00 and C02 coal blending. However, the flow temperature is still above 1350 °C even with a high ratio of C02 to C00 up to 9:1, indicating that the blending of C02 and C00 cannot be directly used as the feedstock for the Shell gasifier. The ash fusion temperatures for the coal blending of C00 and C03 with various ratios are presented in Figure 2c. It is shown that the blending of C00 and C03 significantly improves the ash fusion performance, with drastic drops of deformation temperature, softening temperature, and flow temperature. The flow temperature drops to approximately 1350 °C when the composition of C03 reaches 60%, which can meet the designed ash fusion temperature of the Shell gasifier. This is attributed to the less SiO\(_2\) and Al\(_2\)O\(_3\) and more CaO and Fe\(_2\)O\(_3\) particularly the more MgO in C03, as shown in Table 2. Therefore, it is an efficient approach to solve the plugging problem of the Shell gasifier in Sinopec Anqing Company by blending C03 and C00 with a ratio above 6:4. The residual errors of the ash fusion temperatures are presented in Figure 2d. The residual errors are centered at about 13 °C, which is much smaller than the ash fusion temperatures, suggesting that the measured temperatures are reliable.

As discussed above, the flow temperature of the coal ash greatly depends on its compositions. A model that can predict the flow temperature according to the composition is needed to help conveniently determine the ratio of various coal blends. However, the effect of the ash composition on the flow temperature is rather complicated, and hence, a precise mechanism model is rather difficult. In this study, a simple empirical model was employed to predict the ash flow temperature derived from various coal blends. The flow temperatures are correlated with the ash compositions by using eq 1

\[
FT = a + b \times W(SiO_2) + c \times W(Al_2O_3) + d \times W(CaO) + e \times W(Fe_2O_3) + f \times W(MgO)
\]

where \(W(SiO_2)\), \(W(Al_2O_3)\), \(W(CaO)\), \(W(Fe_2O_3)\), and \(W(MgO)\) are the mass fractions of SO\(_2\), Al\(_2\)O\(_3\), CaO, Fe\(_2\)O\(_3\), and MgO, respectively. \(a, b, c, d, e,\) and \(f\) are the model parameters.

The ash compositions and flow temperatures of the coal blends with various ratios are listed in Table 3. To improve the reliability of the model, all the data in Tables 2 and 3 are used to estimate the parameters in eq 1. The model parameters are estimated by using a linear least-squares method with a 95% confidence interval, and the fitted parameters are listed in Table 4. The linearly dependent coefficient \((R^2)\) is 0.9591, indicating that the flow temperature and the coal ash composition have a good linear relation. The predicted values with error bars are shown in Figure 3a. It is shown that the predicted flow temperature and the real value are evenly distributed on both sides of the line, suggesting the good linear relations between the flow temperature and ash compositions. According to the statistical analysis (Figure 3b), most of the residual errors are distributed between \(-20\) and \(20\ °C\), which are much smaller than the predicted values, indicating that the model is reliable and its precision is enough to meet the practical usage.

![Figure 1. XRD patterns of C00, C03, and C05 ashed at 815 °C.](https://doi.org/10.1021/acsomega.1c01949)
However, it is rather difficult to find the exact law of how these compositions affect the ash fusion temperatures due to the complicated interactions among the various oxides. The empirical model is not based on any melting mechanisms; thus, the coefficients in the predictive equation have no specific physical significance. Nevertheless, the absolute value of the coefficient can reflect the contribution of each oxide to the fusion temperature. MgO has the largest absolute value of the coefficient (1253 °C), indicating that the addition of MgO can efficiently decrease the flow temperature of the coal ash, which is well conformed with the results that the presence of MgO significantly decreases the flow temperature.

2.3. Mechanisms of the Improved Ash Fusion Performance by Coal Blending. The FTIR spectra of the coal ash derived from various coal blends are presented in Figure 4. The absorption peaks centered at 3452 cm$^{-1}$ are owing to the stretching vibration of O–H, suggesting the presence of the physically absorbed water during the sample preparation procedure. The peaks at 1620 cm$^{-1}$ are attributed to the bending vibration of the chemisorbed water. The disappearance of these two peaks at high temperatures indicates the removal of water. For the FTIR spectra of C00, peaks at 1430, 877, and 742 cm$^{-1}$ are associated with carbonate. Considering the composition of the coal ash, it can be speculated that these absorption peaks mainly originate from calcite (CaCO$_3$) as well as a small amount of siderite (FeCO$_3$) and dolomite [CaMg(CO$_3$)$_2$]. The disappearance of

![Figure 2](https://example.com/image2.png)

**Figure 2.** Ash fusion temperatures for the coal blending of C00 with (a) C01, (b) C02, and (c) C03. (d): statistical analysis of residual errors of ash fusion temperatures.

| sample | SiO$_2$/wt % | Al$_2$O$_3$/wt % | CaO/wt % | Fe$_2$O$_3$/wt % | MgO/wt % | FT, °C |
|--------|--------------|-----------------|----------|-----------------|---------|-------|
| 6C04 + 4C00 | 37.02         | 25.33           | 9.17     | 12.52           | 1.26    | 1380  |
| 7C04 + 3C00 | 35.73         | 23.50           | 9.79     | 13.78           | 1.33    | 1304  |
| 8C04 + 2C00 | 34.43         | 21.68           | 10.40    | 15.04           | 1.39    | 1275  |
| 9C04 + 1C00 | 33.14         | 19.85           | 11.02    | 16.30           | 1.46    | 1269  |
| 4C05 + 6C00 | 39.16         | 32.90           | 6.98     | 11.22           | 0.93    | 1482  |
| 6C05 + 4C00 | 36.34         | 31.20           | 7.72     | 14.34           | 0.98    | 1450  |
| 8C05 + 2C00 | 33.52         | 29.50           | 8.47     | 17.47           | 1.02    | 1360  |

$^a$FT: flow temperature.

| $a$/°C | $b$/°C | $c$/°C | $d$/°C | $e$/°C | $f$/°C | $R^2$ |
|--------|--------|--------|--------|--------|--------|-------|
| −12.091| 406    | −126   | −96    | 324    | −1253  | 0.959 |

Table 3. Ash Compositions and Flow Temperatures Derived from Various Coal Blends$^a$

Table 4. Regressed Model Parameters and Linearly Dependent Coefficient $R^2$
these absorption peaks above 1000 °C indicates that calcite is completely decomposed into calcium oxide (CaCO3 → CaO + CO2, ∆G = −16.17 kJ/mol, 1000 °C). The formed calcium oxide further reacts with SO3 derived from the decomposition of sulfur-containing compounds, forming a small amount of anhydrite (CaO + SO3 → CaSO4, ∆G = −176.07 kJ/mol, 1000 °C), leading to the appearance of the weak absorption peaks at 676, 610, and 597 cm−1 corresponding to anhydrite. These weak absorption peaks disappeared above 815 °C, indicating the decomposition of anhydrite at high temperatures under the weakly reducing atmosphere (CaSO4 + H2 = CaO + SO2 + H2O, ∆G = −21.97 kJ/mol, 1000 °C). The existence of calcite in the coal ash can decrease the ash fusion temperature by suppressing the formation of mullite (3Al2O3·2SiO2).27,28 The absorption peaks at 1082, 798, and 482 cm−1 correspond to the characteristic peaks of silica, which become weak along with the increasing temperature, indicating that the crystal silica is transformed. Peaks at 1100 and 565 cm−1 pertain to the kaolinite family (Al4[Si4O10](OH)8). CO0 contains much more kaolinite and less calcite, which leads to the formation of a large amount of mullite under high-treated temperature. Therefore, the characteristic absorption peaks of mullite at 1123–1027, 773–726, and 563 cm−1 are conspicuous above 1200 °C due to the crystal transformation of SiO2 and Al2O3 (3Al2O3 + 2SiO2 → 3Al2O3·2SiO2, ∆G = −24.06 kJ/mol, 1200 °C). The formation of mullite is the main reason for the high fusion temperature of the coal ash because it is rather difficult to be decomposed even at high temperatures.25,29 The adequate mullite and quartz in the slag can cause a rapid increase in viscosity due to the solid-phase separation from the molten slag. Therefore, the formation of refractory mullite in the coal ash is unfavorable to the liquidus slagging of the gasifier.

The FTIR spectra of the ash derived from the coal blending of C00 and C01 with a ratio of 5:5 are shown in Figure 4c. The peaks at 563 cm−1 correspond to hematite and its intensity recedes along with the increasing temperature, but the peak shape has no change, indicating that Fe2O3 is transformed into other forms. Fe2O3 can be reduced into FeO under the weakly reducing atmosphere (Fe2O3 + H2 = 2FeO + H2O, ∆G = −47.44 kJ/mol, 1000 °C) and then reacts with other aluminosilicates to form the low-temperature eutectic compounds such as Fe2SiO4 at 563 and 942–870 cm−1 (2FeO + SiO2 → Fe2SiO4, ∆G = −1.69 kJ/mol, 1000 °C) and MgAl2O4 at 500 and 655 cm−1 (FeO + Al2O3 → FeAl2O4, ∆G = −13.54 kJ/mol, 1000 °C). Therefore, the existence of hematite acts as a fluxing agent making the fusion temperature of the coal ash for C00 and C02 blending (5:5) drop to a low level. Although both CaO and FeO have a significant inhibitory effect on the formation of the high-melting-point mullite, CaO has a higher conversion effect on SiO2, Al2O3, and mullite than FeO.33 The peaks at 890 and 610 cm−1 corresponding to Mg2SiO4 appear when the treated temperature is above 1000 °C, indicating that Mg and Si are transformed into the low-temperature Mg2SiO4 under high temperatures (2MgO + SiO2 → Mg2SiO4, ∆G = −58.25 kJ/mol, 1000 °C). According to the literature, Mg2SiO4 is also transformed into other low-temperature eutectic compounds such as CaMgSiO4 (CaO + MgO + SiO2 → CaMgSiO4, ∆G = −105.11 kJ/mol, 1000 °C), MgAl2O4 (3MgO + Al2O3 + 3SiO2 → Mg3Al2O6·3SiO2, ∆G = −72.89 kJ/mol, 1000 °C), and MgAl2Si2O6 (2MgO + 2Al2O3 + 3SiO2 → MgAl2Si2O6, ∆G = −92.80 kJ/mol, 1000 °C), decreasing the ash fusion temperature significantly.25,34 The peak at 798 cm−1 is...
attributed to quartz and its shape changes with the increasing temperature, indicating that the crystal structure of quartz is transformed into the low-temperature Fe$_2$SiO$_4$, Mg$_2$SiO$_4$, CaMgSiO$_4$, etc.,$^{35}$ which leads to a drop in the ash fusion temperature for the coal blending of C00 and C02. It is reported that the formation of low-melting-point eutectics enriched with Ca, Al, Fe, and S during the combustion can decrease the fusion temperatures of the coal ash.$^{13}$ However, the refractory quartz can inhibit the formation of low-melting-point eutectics, which consequently increases the ash fusion temperatures.$^{36}$

The FTIR spectra of the coal ash for the blending of C00 and C03 (5:5) are presented in Figure 4d. C03 contains much more Fe$_2$O$_3$ and MgO than C00. Peaks at 463 cm$^{-1}$ corresponding to Fe$_2$O$_3$ become weaker along with the heated temperature and peaks at 565 cm$^{-1}$ corresponding to Fe$_2$SiO$_4$ become stronger, indicating that the crystal structure of hematite is transformed into the low-temperature Fe$_2$SiO$_4$. Peaks at 610 and 890 cm$^{-1}$ become stronger along with the increasing temperature, indicating that MgO is transformed into the low-temperature Mg$_2$SiO$_4$. Both the peak at 798 cm$^{-1}$ corresponding to quartz and the peak at 677 cm$^{-1}$ corresponding to Al$_2$O$_3$ change in the shape with the treated temperature, indicating that the crystal structures of quartz and Al$_2$O$_3$ are transformed into the low-temperature eutectic compounds. When the content of C03 increases to 80 wt %, that is, C00/C03 = 2:8, as shown in Figure 4e, the peak at 565 cm$^{-1}$ corresponding to Fe$_2$SiO$_4$ and the peak at 890 cm$^{-1}$ corresponding to Mg$_2$SiO$_4$ become stronger because of the more Fe$_2$O$_3$ and MgO in C03, indicating that the formation of

![Figure 4. FTIR spectra of the coal ashes treated at various temperatures: (a) C00, (b) C00/C01 = 5:5, (c) C00/C02 = 5:5, (d) C00/C03 = 5:5, (e) C00/C03 = 2:8, and (f) C00/C03 = 8:2. Heat treatment atmosphere: H$_2$/N$_2$ = 1:1 (vol/vol).](https://doi.org/10.1021/acsomega.1c01949)
high-melting-point mullite is significantly inhibited under high temperatures by transforming SiO$_2$ into the low-melting-point eutectics. On the other hand, the more calcite in C03 also hinders the formation of mullite by forming the SiO$_2$−Al$_2$O$_3$−CaO low-melting-point eutectics. Therefore, the coal blending of C00 and C03 showed a significant decrease in the ash fusion temperatures, which could well fit the requirements of the Shell gasifier. However, when the content of C03 decreases to 20 wt %, as shown in Figure 4f, peaks at 1123−1027 cm$^{-1}$ corresponding to mullite become stronger, resulting in a high flow temperature (1468 °C).

It is concluded that the ash fusion temperature of various coal blends depends on the compositions of coal ash and the transformation of the mineral substances during the high-temperature-treated process. The formation of the high-melting-point mullite is the main reason for the high fusion temperatures. Ca, Mg, and Fe in the coal ash decrease the fusion temperatures by forming the low-melting-point eutectics.

2.4. Effects of fly Ash on the Slag Formation. The cooler of the Shell coal gasifier process is a waste heat boiler, which is designed for non-viscous fly ash. However, because of the high fusion temperature, C00 is usually blended with 7−10% calcium-based flux, which leads to the formation of a large amount of fly ash. The fly ash is accumulated, deposited, and blocked in the waste heat boiler, affecting the safe and stable operation of the gasifier. In the real operating process, we found that the fly ash of C00 was easily deposited in the waste heat boiler, while C06 did not have a severe blocking problem. Therefore, the fly ash properties of these two samples were compared in this study to better understand the slag formation process in the waste heat boiler.

The morphology of the fly ash is characterized by scanning electron microscopy (SEM), as shown in Figure 5. Both types of fly ash are ball-shaped with a broad diameter distribution. As shown in Figure 5c, the particle size distribution of C06 was broader and the average diameter is larger than that of C00, which increases the fluidity of the fly ash. This indicates that the formation of large-sized fly ash alleviates the slag formation in the waste heat boiler because of its low adhesiveness. Therefore, no severe deposition and blocking problem of the fly ash in the waste heat boiler was observed when using C06 as the feedstock. The particle size depends on the contents of elements in the fly ash. As shown in Table 5, the contents of Al$_2$O$_3$ and SiO$_2$ are similar in these two types of fly ash, while the caked fly ash of C00 contains more CaO and less Fe$_2$O$_3$ than the non-caked C06, suggesting that the caking property of the fly ash is probably related to the contents of CaO and Fe$_2$O$_3$. To further investigate the caking reason for C00, EDX area scanning of various particles was performed and similar

Table 5. Element Compositions of the Fly Ash$^a$

| sample | SiO$_2$/wt % | Al$_2$O$_3$/wt % | CaO/wt % | Fe$_2$O$_3$/wt % | SO$_3$/wt % | K$_2$O/wt % |
|--------|-------------|-----------------|---------|-----------------|-------------|-------------|
| FA00   | 48.89       | 21.77           | 16.13   | 3.18            | 1.01        | 2.48        |
| FA06   | 48.10       | 22.51           | 11.56   | 7.97            | 4.22        | 1.43        |

$^a$FA00: fly ash derived from C00; FA06: fly ash derived from C06.

Figure 5. SEM image of fly ash derived from (a) C00 and (b) C06, (c) size distribution of the fly ash, and (d) micromorphology of the fly ash derived from C00.
element distributions were obtained. As shown in Figure 5d, there are three sections on the surface of a representative fly ash particle: the light section (S1), dark section (S2), and clastic section (S3). The element compositions of these three regions are listed in Table 6. The main body of the fly ash particle is composed of Al and Si. No adhesion of the small particle is observed in the light section (S1) of the large particle. The content of Mg in the adhesive cluster (S3) is much less than that in the main body (S1) of the ash particle, indicating that Mg is not the origin for the high caking tendency of FA00. On the other hand, the content of Ca in the attached clastic particle (S3) is higher than that in the S1 and S2 sections. CaO has a high caking tendency below 1200 °C and can attach many clastic particles to the surface of the large particle. When CaCO3 is largely used as a flux, it will be decomposed into CaO under high temperatures and more fly ash particles will adhere together, leading to a severe ash deposition in the waste heat boiler. The caked fly ash from C00 is attributed to the high content of Ca in the coal ash, forming some Ca-containing clast around the ash particle, leading to the plugging of the waste heat boiler. Therefore, the Mg-based fluxing agent is more suitable because it does not cause a plugging problem and is more effective for the decrease in FT.

3. CONCLUSIONS
In this study, the effect of coal blending on the ash fusion temperature was investigated and the slag formation mechanism in the waste heat boiler of the Shell gasifier was illustrated. It is shown that the existence of CaO, MgO, and Fe2O3 decreases the ash fusion temperature. C00 contains more SiO2 and Al2O3 but less CaO, MgO, and Fe2O3, which forms the high-melting-point mullite at the high temperatures, resulting in its high ash flow temperature. However, CaO, Fe2O3, and MgO in the coal ash can decrease the ash fusion temperature by forming low-melting-point eutectics. The slag formation in the waste heated boiler of the Shell gasifier is illustrated. It is shown that the existence of CaO, MgO, and Fe2O3 decreases the ash fusion temperature of the coal ash.

Table 6. EDX Element Composition in Different Regions of the Fly Ash Particle from C00

| element | S1 wt % | S2 wt % | S3 wt % |
|---------|---------|---------|---------|
| O       | 14.30   | 11.92   | 7.50    |
| Na      | 1.24    | 0.62    | 0.00    |
| Mg      | 1.86    | 0.43    | 0.43    |
| Al      | 19.88   | 22.22   | 20.48   |
| Si      | 39.08   | 40.69   | 41.32   |
| S       | 0.55    | 1.05    | 1.00    |
| K       | 3.11    | 5.40    | 6.36    |
| Ca      | 14.40   | 11.96   | 17.74   |
| Fe      | 5.57    | 5.71    | 5.19    |

4. EXPERIMENTAL SECTION

4.1. Materials. Coal blends from the Liuqiao no. 2 mine in North Anhui Province, coal from the Pingdingshan no. 2 mine in the Henan province, coal blends from the Yima mine in the Henan province, coal blends from the Beisu mine in Shandong Province, clean coal blends from the Sanhejian mine in Jiangsu Province, coal blends from the Sanhejian mine in Jiangsu Province, and high-sulfur coal in Yunnan Province (donated as C00, C01, C02, C03, C04, C05, and C06, respectively) are used as the raw materials.

4.2. Coal Ash Sample Preparation. The raw coal samples were blended thoroughly with various ratios before they were calcined in the muffle furnace (KSMF-2000, Kaiyuan Instruments Corp.) at 815 °C. Then, the obtained high-temperature samples were cooled down using tap water, followed by 36 h of drying at 105 °C in the vacuum drier. Finally, the prepared coal ash samples were stored in the airproof containers.

4.3. Sample High-Temperature Treatment. The coal ash samples were loaded into an alumina ceramic tube to conduct the high-temperature treatment from 815 to 1400 °C with a heating rate of 5 °C/min. The gaseous products in Shell gasification are complex and usually consist of CO, H2, CO2, CH4, and O2, which is a weak reducing atmosphere. The reducing capacity of CO is slightly different from that of H2; however, after dilution with N2, both the H2/N2 and CO/N2 mixtures show a weak reducing atmosphere, which can well reflect the real reducing atmosphere in the gasifier. Therefore, in the present study, a gaseous mixture composed of hydrogen and nitrogen (VH2/VN2 = 1:1) was used as the carrier gas. After the high-temperature treatment, the samples were then rapidly cooled down to room temperature using tap water, dried at 105 °C for 36 h in the vacuum drier, and stored in the airproof containers.

4.4. Sample Analysis. The melting characteristics, that is, deformation temperature (DT), softening temperature (ST), and flow temperature (FT), of the coal ash were measured by a standard method (GB/T219-1996) on an intelligent ash melting point measuring device (SE-AF III, Kaiyuan Instruments Corp.) under a weakly reducing atmosphere.

XRD analysis was performed with an XRD instrument (2550VB/PC, Rigaku Corp.) with Cu-Kα radiation (36 kV, 40 mA) to determine the crystal phase in the coal samples. FTIR studies were conducted on a Vector33 instrument (Bruker Corp.) by adding 16 scans for the coal ash samples at a resolution of 4 cm−1. The coal ash samples were mixed with potassium bromide in a proportion of 1/250 and then pressed into a self-supporting wafer under 12 MPa for 3 min.

SEM was conducted with an SM-6360LV microscope (JEOL Corp.) at an accelerating voltage of 30 kV to determine the morphology of the fly ash. The SEM instrument is equipped with an EDX system (FALCON, EDAX Corp.) to perform elemental analysis of the fly ash.

The particle size distribution of the fly ash was measured in a laser particle size analyzer (MS-2000, Malvern Corp.) with high-performance He–Ne laser (λ = 632.8 nm).
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