Release of Sulfur and Nitrogen during Co-pyrolysis of Coal and Biomass under Inert Atmosphere

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ABSTRACT: Coal combustion is a major energy provider but also a serious pollutant emitter worldwide. Biomass has attracted increasing research attention due to its carbon neutral and other advantages during co-pyrolysis of coal. Therefore, pyrolysis of corn straw, lignite coal, and their mixed fuel was investigated using a horizontal tube furnace at a temperature range of 300−900 °C in this study by concentrating on emissions of nitrogen- and sulfur-bearing gases. Emissions of HCN, NH3, COS, and SO2 were monitored, and char yield was calculated during pyrolysis. Results showed that char yield decreases with increasing temperature due to the decomposition of heterocyclic aromatic hydrocarbon. Sulfur (42.45 wt %, 900 °C) and nitrogen (73.23 wt %, 600 °C) were released from the mixed fuel during pyrolysis. The synergistic effect between corn straw and coal was evaluated and their experimental and calculated values were compared. The synergistic effect on emissions was remarkable at a temperature range of 600−800 °C due to high biomass content and desynchronization of volatile matter emissions between the coal and biomass. Volatiles in the biomass, which are released before coal, stimulated the volatilization of coal. Several conventional gases, such as CH4 and C2H6, were also analyzed to investigate emission patterns at different temperatures.

1. INTRODUCTION

Coal is a traditional fuel that has been used in thermal power plants to generate electricity for decades, and coal combustion is considered a major generator of particulate matter and producer of carbon dioxide. The total CO2 emissions in China have increased by 340% since 1990 at 9191 tons in 2017, and at least 80% of CO2 emissions are caused by coal combustion, which accounts for 59% of the country’s energy utilization.1−3 Over 600 million tons of coal, which accounted for 1260 million tons of CO2 emissions in 2018, are consumed to generate electricity despite a decline of five consecutive years in the United States.4−6 Economic activities in Europe, except for the United Kingdom, released 4 billion tons of CO2 equivalents in 2019.7 EU has pledged to decrease its CO2 emissions by 80−95% before 2050.8 Biomass is commonly accepted as a type of carbon-neutral fuel because it can store carbon while growing through photosynthesis.9 For this reason, many countries have concentrated on biomass utilization. Only 4% of energy consumption in China was made up of biomass in 2018.10 However, in accordance with the 2016 Paris Agreement, China committed to converting 20% of its energy supply into nonfossil fuel energy by 2030.11 Renewable energy in the United States constitutes 11% of its primary energy consumption, in which 5% accounted for biomass in 2018.6 Biomass in Europe accounted for approximately 9% of primary renewable energy production in 2019.11 Compared with coal, biomass is a clean and renewable energy source because of its carbon-neutral property and relatively lower sulfur and nitrogen contents. Therefore, biomass is considered an alternative resource to fossil fuels for combustion and becomes a central point in the field of energy utilization.

Co-firing of coal and biomass reduces economic cost because existing power plant equipment can be used directly or after applying minor adjustments.12 The high content of alkaline earth metals and volatile matter as well as low content of sulfur and nitrogen in the co-combustion of coal and biomass can reduce pollutant gas emissions.13−16 Molcan et al.17 demonstrated the reduction in SO2 emissions by co-firing coal with biomass at different blend ratios ranging from 0 to 20% compared with coal combustion alone. The remaining alkaline earth ash from the co-combustion may contain SO2, which can also lead to reduced SO2 emissions.18−20 Dan et al.22 demonstrated from a more macro perspective that emissions, including but not limited to SO2, are projected to be in a low range of 15−82% during the combustion of mixed fuel (20% forest biomass and 80% coal).

Nitrogen compounds are mostly released in the form of NO, NO2, NH3, HCN, and traces of N2O. Given that biomass has...
different nitrogen contents, co-firing of coal and biomass reduces nitrogen gas emissions and clearly increases the biomass fraction while reducing NO\textsubscript{x} compared with coal combustion alone.\textsuperscript{13,23–29} Dong et al.\textsuperscript{30} modeled the co-firing process of biomass and coal in a 600 MW tangential pulverized coal boiler from another point of view; their results revealed that NO\textsubscript{x} emissions demonstrate a 50–70\% reduction when exhausted gas is injected into the bottom layer of the boiler.

Despite its many advantages, the co-combustion of biomass and lignite has the following limitations. High moisture content and low energy density of raw biomass deteriorates burning properties and suppresses combustion efficiency while reducing grindability due to its high fiber content.\textsuperscript{31–33} The high content of volatile matter but lack of fixed carbon in low-quality lignite coals characterize it as a type of fuel with low calorific value.\textsuperscript{34} Such characteristics of biomass and lignite coal deteriorate burning conditions and stability of fire.\textsuperscript{35} Therefore, technology upgrades of biomass and low-quality lignite coal, such as gasification, pyrolysis, and co-firing with various fuels, are necessary.\textsuperscript{36,37}

Co-pyrolysis of coal and biomass has attracted considerable research attention due to its ability to improve the quality of biomass remarkably while offsetting the release of pollutants into the environment.\textsuperscript{31} Co-gasification of biomass and coal typically conducted at high temperatures (500–900 °C) can promote efficient energy utilization.\textsuperscript{38} The removal of the majority of moisture and some pollutants from both biomass (200–300 °C) and coal (200–300 °C) via torrefaction (pyrolysis carried out at low temperatures) can achieve stable, clean, and high-energy-density mixed fuel.\textsuperscript{39–44} Torrefaction in a pure nitrogen atmosphere (low or the absence of oxygen concentration) remarkably reduces hydrophilicity and minimizes biodegradability. The promotion of fixed carbon content and hydrophobia capacity in torrefaction can improve the combustion profile and prolong storage time.\textsuperscript{13,14} Singh et al.\textsuperscript{39} determined that the complete destruction of hemicellulose content in both red maple and yellow poplar during torrefaction at 300 °C in nitrogen atmosphere improved the grindability; this finding is consistent with the results of previous studies.\textsuperscript{36,34} Mild pyrolysis releases many pollutant elements, such as chlorine, nitrogen, and sulfur, to the gas phase.\textsuperscript{45} Synergy between the coal and biomass benefited from catalytic effects of minerals in biomass during co-pyrolysis.\textsuperscript{46} From another aspect, volatiles in biomass mainly released at low temperatures while volatiles in coal released at high temperatures can also enhance the synergy effect.\textsuperscript{47} Furthermore, co-pyrolysis of coal and biomass enhances desulfurization of coal due to the hydrogen donor property of biomass, which allows the easy release of sulfur in the form of H\textsubscript{2}S.\textsuperscript{35,49} Cordero et al.\textsuperscript{50} co-pyrolyzed high-sulfur coal and four biomass residues and Blesa et al.\textsuperscript{51} co-processed coal and biomass to observe the enhanced desulfurization in the pyrolysis gas. Meanwhile, sulfur is fixed in the form of CaS and CaSO\textsubscript{4} instead of being released into the atmosphere during combustion due to the presence of alkali and alkali earth metals during co-pyrolysis.\textsuperscript{12,52} Regarding the nitrogen content, Yuan et al.\textsuperscript{53} determined that co-processing of biomass and coal can transform char-N to volatile N, which alleviates NO\textsubscript{x} emissions during combustion.

According to the literature review, limited studies focus on the release of sulfur and nitrogen during the co-pyrolysis of lignite and biomass. Therefore, this work concentrated on gas emissions during the co-pyrolysis of corn stalk and coal in a temperature range of 300–900 °C, in a pure nitrogen atmosphere, and with a residence time of 3–8 min to determine the releasing pattern of sulfur and nitrogen compounds. At higher temperatures, more aromatic rings tend to break into light hydrocarbon and emit more pollutant gases, such as NH\textsubscript{3}, HCN, and SO\textsubscript{2}. In the meantime, the catalysis effect of alkaline earth metals can be observed more clearly. Based on the status of co-firing coal with biomass, this report aimed to improve the release of sulfur and nitrogen compounds from the fuel for high economic and environmental efficiency of power plant utilization. Desulfurization and denitrification can efficiently avoid corrosion of flue gases in power plants and collectively address byproducts. As much as 44.82\% of the nitrogen in coal was released at 900 °C, while 76.39\% of sulfur in corn straw was emitted at 600 °C. Volatile matters emitted during co-pyrolysis including H\textsubscript{2}, CH\textsubscript{4}, and CO could be synthesized to liquefied natural gas (LNG). These volatile matters can be combusted directly to provide the heat needed for the co-pyrolysis process to make the whole process self-sufficient. NO\textsubscript{x}, HCN, NH\textsubscript{3}, and SO\textsubscript{2} are monitored via Fourier transform infrared (FTIR) spectrometry during co-pyrolysis in a laboratory-scale horizontal tube furnace.

2. RESULTS AND DISCUSSION

2.1. Char Yield. Char produced during pyrolysis forms a porous material due to the escape of volatile matters.\textsuperscript{46} Based on our previous work and other literature, metal elements, such as calcium and iron, could enrich the pore structure during pyrolysis.\textsuperscript{56} Therefore, char could be used as pollutant absorber under a specific atmosphere.

Error bars shown in Figure 1 represent one standard deviation of data points in each case. Inaccuracy in the data is due to nonhuman factors, such as constrain of apparatus accuracy, during the experiment. Char yield, \(\phi\), is calculated as follows

\[
\phi = \left( 1 - \frac{M_{\text{before pyrolysis}} - M_{\text{after pyrolysis}}}{M_{\text{before pyrolysis}}} \right) \times 100\%
\]

The char yield of samples decreases with increasing temperature due to thermal decomposition of hemicellulose and such substances in biomass and polycyclic aromatic hydrocarbons (PAHs) in coal. Notably, coal has a higher char yield compared with biomass and mixed fuel at the same temperature because of its high content of fixed carbon, which cannot decompose in the nitrogen atmosphere.

Unlike biomass, PAHs, the main component of coal, is powerfully bonded and resistant to decomposition.\textsuperscript{57} Biomass
likely breaks into light gas products at mild temperatures due to the difference in structure. The char yield of biomass demonstrated minimal changes with increasing temperature because its major components, such as hemicellulose, cellulose, and lignin, completely decomposed at temperatures lower than 700 °C.\textsuperscript{58}

Figure 2 shows that 95.57 wt % of coal remains at a temperature of 300 °C, while 65.48 wt % of coal and only 27.06 wt % of biomass survive at a temperature of 900 °C. The apparent difference between coal and biomass indicated that coal has higher fixed carbon content, while biomass has higher volatile content; this result is consistent with the findings of previous studies.\textsuperscript{46,59}

As shown in Figure 1, the pyrolysis profile of the mixed fuel is distinct compared with those of coal and biomass and more like a compromise of coal and biomass. Hence, the synergy effect of biomass and coal during co-pyrolysis is explored by calculating the char yield, \( \phi' \), as follows

\[
\phi' = \left( \frac{M_{\text{coal}} \times \phi_{\text{coal}} - M_{\text{biomass}} \times \phi_{\text{biomass}}}{M_{\text{coal}} \times M_{\text{biomass}}} \right) \times 100\% \tag{2}
\]

Figure 2. Calculated and experimental char yield of the mixed fuel after pyrolysis.

Compared with experimental values, calculated values are relatively higher at 400, 500, 700, 800, and 900 °C, as depicted in Figure 2. The synergistic effect is negligible due to the limited interface between biomass and coal. However, Kastanaki\textsuperscript{60} highlighted the notable synergistic effect between gas and solid phases. The high content of hydrogen in biomass likely plays the synergistic role of a hydrogen donor during co-pyrolysis. Hydrogen free radicals intend to interact with aromatics in coal and break into gaseous products.

The high content of ash alkali earth metals (AAEMs) in biomass plays a vital role in the catalytic effect.\textsuperscript{47,48,61} The easy absorption of polar gaseous products in the solid phase by alkaline earth metals increases the char yield after pyrolysis. The synergistic effect can be evaluated precisely when we focus not only on the yield but also on the composition and quantity of pyrolysis products.

2.2. Evolution of Sulfur-Bearing Gas. As shown in Table 3, the higher content of oxygen and hydrogen in biomass compared with that of coal may account for the increasing trend of sulfur-bearing gas release. Figure 3 illustrates the percentage of sulfur converted to COS and SO\(_2\) in the gas phase. The maximum conversion rate was observed in the corn straw sample at 600 °C and reached as high as 76.39 wt %. Free radicals generated during the biomass pyrolysis are responsible for the high conversion rate of sulfur. The low conversion rate of coal and mixed fuel is due to H\(_2\)S emissions,\textsuperscript{62} which are not depicted in Figure 3. Even the minimum transformation rate of sulfur in the mixed fuel to sulfur-bearing gas reached 12.73 wt % at a temperature of 300 °C. Mixed fuel obtained a higher conversion rate than coal at low temperatures (300–400 °C) due to the high volatile content in biomass. Volatile matter released at the beginning of pyrolysis promoted the breakdown of PAHs in coal.\textsuperscript{47,51} However, minimal sulfur was released in the form of COS and SO\(_2\) with temperature increasing due to the depletion of volatiles and absorption of AAEMs. Coal released the minimum amount of sulfur in the form of COS and SO\(_2\) at low temperatures (300–600 °C) because the sulfur content in coal mainly has a thiophene structure, which is difficult to be decomposed.\textsuperscript{63}

2.2.1. COS. Iron pyrite is the main form of inorganic sulfur that exists in coal. The decomposition of iron pyrite into FeS and S under inert atmosphere can be expressed as follows\textsuperscript{58,64}

\[
\text{FeS}_2 \rightarrow \text{FeS}_{2-x} \rightarrow \text{FeS} + \frac{1}{n} \times S_n, \text{ where } 0 < x \leq 1 \tag{3}
\]

Fixed carbon reacts with the oxygen-containing group in the sample and generates CO. Apart from the reaction above, iron pyrite and FeS also react with CO and generate COS.\textsuperscript{63}

\[
\text{FeS}_2 + \text{CO} \rightarrow \text{FeS} + \text{COS} \tag{4}
\]

\[
\text{S} + \text{CO} \rightarrow \text{COS} \tag{5}
\]

As much as 47.88 wt % of sulfur in corn straw can be emitted as COS at a temperature of 600 °C. COS emissions are promoted at low temperatures due to the participation of biomass, according to Figure 4. However, the synergistic effect reacts negatively at high temperatures due to the high content of alkaline earth metals and depletion of volatiles.

The previous study showed that the rate of decomposition of iron pyrite increases with increasing temperature and reaches the maximum point in a temperature range of 550–600 °C.\textsuperscript{52} According to Formula 4, the emissions of COS increased with higher concentrations of iron pyrite. This finding is consistent with the results shown in Figure 4. Iron pyrite was completely converted into FeS at 700 °C. Notably, COS production decreases when the concentration of iron pyrite decreases. Minimal CO is produced via oxidative reaction of fixed carbon at high temperatures but consumed to generate CO\(_2\) due to the high reactivity of the oxygen-bearing groups.\textsuperscript{65}

Figure 3. Percentage of S released in the form of COS and SO\(_2\).
Additional aromatic rings broken at high temperatures caused the reaction between hydrogen free radicals and S and subsequently produced H₂S. On the basis of this reaction, the tendency of COS emissions reasonably declined. The absorption of alkaline earth metals is also very important in the reduction of COS release.

The addition of biomass has an inhibitory effect on the formation of COS compared with the pyrolysis of coal in a temperature range of 500−900 °C, as depicted in Figure 5. Further, 0.71 mg/g of COS emissions was reduced due to the synergistic effect at 500 °C. The high content of alkaline earth metals in biomass played a vital role in capturing sulfur-bearing gas, including COS, and suppressing COS emissions in a certain temperature range that decreased after 500 °C, as shown in Figure 5.

2.2.2. SO₂.

Inorganic sulfur in coal exists in the form of sulfates and sulfoxides, such as CaSO₄ and FeSO₄, which react with iron pyrite to produce SO₂. SO₂ was also formed in the pyrolysis of sulfones, but organic sulfones barely exist or absent in coal.

\[
\text{CaSO}_4 + \text{FeS}_2 + \text{H}_2\text{O} \rightarrow \text{CaO} + \text{FeS} + 2\text{SO}_2 + \text{H}_2
\]  

(7)

The increase in the reactivity of the oxygen-bearing groups with increasing temperature accounted for the increasing tendency of SO₂ emissions. Sample emissions peaked in a temperature range of 400−600 °C. SO₂ emissions of corn straw are stable even with a slight decrease due to the balance of oxidative and absorption reactions. Figure 6 shows that high temperatures have an inhibitory effect on the release of SO₂ caused by the high content of alkaline earth metals in biomass. SO₂ is absorbed by alkaline earth metals to generate sulfides and sulfates in the solid phase. From another aspect, SO₂ can also react with broken aromatic rings to form thiophene structures with a stable character. H₂S emissions is another factor that contributes to the decline of SO₂ emissions.

The participation of biomass in the pyrolysis of coal stimulated SO₂ formation at a temperature range of 300−600 °C and subsequently became a negative factor at temperatures beyond 700 °C. The comparison of experimental and calculated values of SO₂ emissions is illustrated in Figure 7. The synergistic effect completely suppressed SO₂ emissions. The presence of alkaline earth metals in biomass was an important factor to consider in the suppression of SO₂ emissions because of their ability to capture SO₂. Moreover, the reaction between hydrogen free radicals and sulfur-bearing compounds produced a considerable amount of H₂S, which reduced the emissions of SO₂.

2.2.3. Sulfur Balance during Pyrolysis.

The transformation rate of sulfur into COS and SO₂, sulfur retention in char, and sulfur balance during co-pyrolysis are indicated in Table 1. Sulfur retained in the solid product reached the minimum point in a temperature range of 600−700 °C. However, the rate of sulfur unaccounted for in the experiment increases with temperature increasing due to H₂S emissions. The declining trend may also be due to the defect of the rubber tube that absorbs some of the sulfur-bearing gases during the experiment. Tar, which includes some sulfur-bearing matter, was generated during co-pyrolysis but excluded in this study.

2.3. Evolution of Nitrogen-Bearing Gas.

Nitrogen-bearing gases is mainly emitted as HCN, NH₃, and NO during pyrolysis. The high content of oxygen and hydrogen in biomass stimulated emissions of nitrogen-bearing gases from coal. As shown in Figures 8, coal demonstrated the maximum emissions

Figure 4. Percentage of S released in the form of COS.

Figure 5. Release of COS.

Figure 6. Percentage of S released in the form of SO₂.

Figure 7. Synergistic effect on the release of SO₂.
of nitrogen-bearing gas due to its high content of inorganic nitrogen-bearing matters and likely emit in the gas phase. Nitrogen mainly exists in corn straw as an organic component resistant to decomposition. Pyridine nitrogen, pyrrole, quaternary nitrogen, and nitric oxide are the major forms of nitrogen in corn straw. Aromatic heterocyclic compounds, such as pyridine nucleotide and nucleic acid, are the major forms of nitrogen in coal. Therefore, corn straw released the minimum amount of nitrogen-bearing gasses. The addition of corn straw facilitated the adsorption of HCN and reduced HCN emissions due to its high content of alkaline earth metals.

2.3.1. HCN. HCN emissions increase with increasing temperature, as shown in Figure 9. Coal, mixed fuel, and corn straw reached the highest emission rate at 11.29, 6.38, and 6.03 wt %, respectively, at 900 °C. Bassilakis and Schäfer revealed the following transition mechanism from HCN to NH₃ that likely causes HCN to react with hydrogen free radicals in the pores of coal and generates NH₃:

\[
\text{HCN} + \text{H}_2\text{O} \leftrightarrow \text{NH}_3 + \text{CO} \quad (8)
\]

Pyridine nitrogen connected with heterocyclic compounds through one single bond and one double bond can lead to the release of the −CN group and immediate transfer to HCN. Nitrogen-bearing heterocycles break down and HCN is formed rapidly in large amounts with increasing temperature. Pyrrole is easily converted to NH₃ due to two single bonds that connect nitrogen in the heterocycle.

As depicted in Figure 10, the significant difference between calculated and experimental values indicates that a synergistic effect exists between biomass and coal during co-pyrolysis. The synergistic effect increases with temperature increasing, and up to 3.14 mg/g of HCN is reduced during co-pyrolysis at 900 °C.

2.3.2. NH₃. NH₃ emissions in the experiment are relatively low compared with the findings of previous studies, but the trend of emissions is consistent with the findings of Wu. The emission rate of NH₃ increased first and then decreased with increasing temperature in the temperature range of 600−900 °C and peaked at 2.44 wt % at 700 °C. Notably, coal released more N in the form of NH₃ compared with corn straw and mixed fuel because N in protein has difficulty in producing NH₃. Additional NH₃ is generated through the reaction between large molecules containing N and hydrogen free radicals at high temperatures. The increased emissions of NH₃ at high temperatures are due to the active decomposition of volatiles, which produce NH₃. The slight decline in NH₃ emissions in coal and corn straw is due to the synergistic reaction between olefin and NH₃ that generates nitrile.

Mixed fuel demonstrates lower NH₃ emissions than coal in a temperature range of 300−700 °C, as shown in Figure 11. Co-pyrolysis of biomass and coal can efficiently suppress NH₃ emissions. NH₃ (0.13 mg/g) was reduced at high temperatures, such as 700 °C, due to the synergistic effect of biomass and coal during co-pyrolysis. The synergistic effect is insignificant, and only 0.003 mg/g of NH₃ declined at 900 °C (Figure 12).

2.3.3. Nitrogen Balance during Co-pyrolysis. The conversion rates of nitrogen to various forms, such as NO, HCN, NH₃, and those retained in solid products, are summarized in Table 2. The results indicate the resistance of nitrogen to be released in the form of gas even at high temperatures (nitrogen retained in solid can reach as high as 57.55 wt % at 900 °C) because nitrogen mainly exists in the form of organic matter, which is difficult to be decomposed.

Table 1. Conversion of S during Co-pyrolysis of Biomass and Coal

| temperature (°C) | released as SO₂ (%) | released as COS (%) | remaining in solid products (%) | unaccounted for (%) |
|------------------|--------------------|--------------------|-------------------------------|--------------------|
| 300              | 14.96              | 24.86              | 49.04                         | 11.14              |
| 400              | 19.39              | 18.84              | 31.12                         | 30.65              |
| 500              | 21.37              | 18.32              | 41.39                         | 18.92              |
| 600              | 17.94              | 18.24              | 26.77                         | 37.05              |
| 700              | 9.10               | 14.14              | 28.74                         | 48.02              |
| 800              | 5.16               | 9.26               | 33.39                         | 52.19              |
| 900              | 5.71               | 7.02               | 34.90                         | 52.37              |

Figure 8. Percentage of N released in the form of HCN and NH₃.

Figure 9. Percentage of N released in the form of HCN.

Figure 10. Synergistic effect on HCN emissions.
2.4. Emissions of Conventional Gas. Apart from nitrogen- and sulfur-bearing gases released during pyrolysis, some conventional gases, such as alkane and olefin, are also emitted. CH₄, C₂H₆, and CO are monitored during pyrolysis, and the results are illustrated in Figures 13–15.

CH₄ and C₂H₆ emissions are shown in Figures 13 and 14, respectively. CH₄ emissions in all the samples clearly increase with increasing temperature due to the decomposition of long-chain hydrocarbons and some aromatic compounds. However, C₂H₆ emissions demonstrated a sudden decline at 700 °C due to the secondary decomposition of C₂H₆. A slight decline in CH₄ emissions from coal samples was observed at 800 °C.

CO emissions are minimal at low temperatures (300–600 °C) during mild pyrolysis. The pyrolysis products of carboxyl and carboxylic acid anhydride are primarily carbon dioxide. CO₂ reacts with fixed carbon in a reductive atmosphere and produces CO, which induces high CO emissions at high temperatures. From another aspect, high temperatures allow for the easy decomposition of oxygen-containing compounds, such as quinonyl, carboxyl, and pyrones. As shown in Figure 15, corn straw demonstrates higher CO emissions due to its higher content of oxygen compared with coal.

3. CONCLUSIONS

Emissions of COS, SO₂, HCN, NH₃, CO, CH₄, and C₂H₆ from the pyrolysis of corn straw, coal, and their mixed fuel were investigated in this study. Notably, many pollutant elements, such as sulfur and nitrogen, are released in different forms. As a general conclusion, the pyrolysis of coal and corn straw can enhance the combustion profile of the remaining char and decrease emissions of pollutant gases. Co-pyrolysis of coal and corn straw can suppress emissions of certain gases. The results of pyrolysis experiments under inert atmosphere in a furnace temperature range of 300–900 °C revealed the following:
4. EXPERIMENTAL SECTION

4.1. Raw Materials. Lignite coal was obtained from Xinjiang Zhunger Basin and ground to a size of 75–125 μm, which was characterized in the previous study. Pulverized corn straw produced by cryogenic grinding was obtained from the Harbin Institute of Technology, China, and then sieved to achieve a particle size of 125–250 μm. The mixed fuel composed of coal and corn straw was blended in a weight ratio of 1:1. All samples were dried in an oven at 105 °C and then stored for 24 h to remove outer moisture before testing.

The proximate and ultimate analysis result listed in Table 3 revealed that corn straw had high volatilization and hydrogen content.

The proximate analysis was carried out according to the GB/T 212-2008 Chinese standard in an electric oven (SE-DHG, Changsha Kaiyuan Instruments Ltd., China) and a muffle furnace (SE-MF6000, Changsha Kaiyuan Instruments Ltd., China). The ultimate analysis of carbon, hydrogen, nitrogen, and sulfur was performed using an elemental analyzer (Thermo Flash2000, Elementar Ltd.) according to GB/T 30733-2014 and GB/T 214-2007 standards.

4.2. Experimental Apparatus and Procedure. Pyrolysis was carried out in the laboratory-scale tube furnace under nitrogen atmosphere. A combustion boat charged with fuel particles was placed in the middle of the furnace tube and heated at 300, 400, 500, 600, 700, 800, and 900 °C and then maintained for 10 min.

Both biomass and coal were heated in the electric-motivated, quartz horizontal tube furnace (Figure 16), which can be adjusted using an AI-518P temperature controller (Yudian). Fuel particles were placed in the middle of the heating area of the alumina combustion boat. A mixture of 300 mg of biomass and 300 mg of coal was placed in the combustion boat. The quartz tube has a length of 1.5 m and an inner diameter of 4 cm, including a heating zone of 1 m. The temperature of the furnace wall was monitored using a type-S thermocouple. A water-cooled cooler was placed at the terminal of the tube to reduce the temperature of samples and avoid the burning of char upon contact with air. High-purity nitrogen gas was introduced to the hot zone using a ball valve and then measured with a gas rotameter (TSMMS). The pressure of the gas cylinder outlet was fixed at 0.2 MPa, and the gas flux was maintained at 2 lpm (liter per minute).

Table 3. Results of Proximate and Ultimate Analyses

| samples      | proximate analysis (wt %) | ultimate analysis (wt %) |
|--------------|----------------------------|--------------------------|
|              | M  | V<sub>d</sub> | A<sub>d</sub> | FC<sub>d</sub> | C  | H  | S  | N  | O* |
| lignite coal | 3.01 | 34.90     | 3.31          | 58.78        | 73.30 | 4.10 | 0.32 | 0.74 | 21.54 |
| corn straw   | 7.40 | 80.92     | 2.52          | 9.16         | 42.55 | 6.61 | 0.531 | 3.63 | 38.88 |

*(M: Moisture, V: volatile matter, A: ash, FC: fixed carbon, ad: air-dried, and *by difference).*

Figure 16. Schematic of the pyrolysis setup for measuring emissions.
The effluent gas of pyrolysis was analyzed using an FTIR spectrometer (Gasmet DX4000, Finland). A sampling pump was utilized before FTIR in the upper vacuum to prevent leakage of the sample gas, and heat tapes were used to increase the temperature of the sample gas to 180 °C to maintain flowability. FTIR data was recorded by a computer using GASMET software.

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**Author Contributions**

The manuscript was written through the contributions of all authors. All authors have given approval to the final version of the manuscript. L.L.: experiments, data analysis, and writing original draft; G.L.: investigation, data analysis, and supervision; Z.Z.: data analysis and supervision; Y.L.: experiments, writing, and reviewing and editing; H.X.: experiments and writing original draft preparation; J.C.: writing, reviewing, and editing; and X.R.: supervision.

**Notes**

The authors declare no competing financial interest.

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