Are Ionic Liquids Suitable for Suppressing Coal Spontaneous Combustion?

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ABSTRACT: Due to the reported fact that the active functional groups in coal can be dissolved and destroyed by ionic liquids, it is expected that the spontaneous combustion of coal can be affected from a thermodynamic perspective. However, ionic liquids with different thermal stabilities have distinct influences on coal combustion. Here, the thermal stability of long-flame coal in the presence of five pure ionic liquids ([Bmim][BF₄], [Bmim][Ac], [Bmim][NO₃], [Hoemim][BF₄], and [Pmim][BF₄]) was analyzed by thermogravimetric analysis, and the flammability of the raw coal, pure ionic liquids, and coal–IL mixtures (mass ratio of 1:1) were tested using a cone calorimeter according to the indexes of the time to ignition (TTI), mass loss rate (MLR), heat release rate (HRR), total heat release rate (THR), specific extinction area (SEA), and CO production. It is shown that the TTIs of mixtures containing coal–[Bmim][BF₄], coal–[Hoemim][BF₄], and coal–[Pmim][BF₄] are relatively long, and the MLR, HRR, THR, and SEA values are relatively low, indicating that these fluorine-containing ionic liquids have a better flame-retardant effect than the other two fluorine-free ones, which may be ascribed to their similar role to halogen inhibitors. In addition, the endothermic process of [Bmim][BF₄], [Hoemim][BF₄], and [Pmim][BF₄] can reduce the temperature of the coal surface and delay the ignition time of coal. In contrast, the TTI of coal–[Bmim][NO₃] and coal–[Bmim][Ac] mixtures is much shorter than that of coal alone, and the MLR, HRR, and THR values are larger. This may be caused by the poor thermal stability of the two non-fluorine ionic liquids that began to decompose and release heat prior to coal, providing a large amount of heat for the low-temperature oxidation of coal and thus accelerating coal oxidation and combustion. Although the F-containing ionic liquids show the ability to inhibit spontaneous combustion of coal to some extent, their organic cations are potentially combustible and release large amounts of heat, smoke, and CO under high temperatures.

1. INTRODUCTION

As an important fossil fuel, coal releases massive amounts of energy by spontaneous combustion.¹,² The spontaneous combustion of coal releases not only a large amount of toxic and harmful gases such as CO, H₂S, and SO₂ but also heat and open flames that may cause gas explosions. The methyl-, methylene-, and oxygen-containing functional groups (e.g., the hydroxyl, carboxyl, and ether groups) play a major role in the oxidation process of coal.³ The physical and chemical reactions between these active structures and oxygen will generate a large amount of heat, which may provide energy for the spontaneous combustion of coal.

Commonly used coal combustion inhibitors⁴⁻⁸ include halogen salts (CaCl₂, MgCl₂, and NaCl aqueous solution), ammonium salts (ammonium bicarbonate, ammonium dihydrogen phosphate, etc.), gel inhibitors (e.g., silicone gel), and so on. Metal ions in halogen salts can complex with C=O in coal, and halogen atoms can replace H atoms on methyl and methylene groups, which can break off and prevent free radical reactions.⁹

Ammonium salts undergo an endothermic process during pyrolysis, which can absorb the heat generated from the spontaneous combustion of coal. However, they can only prolong the coal ignition time but cannot prevent coal burning. Gel inhibitors can cover the coal surface to prevent coal from coming into contact with oxygen. However, a large amount of ammonia gas is released during the gel formation process, which endangers the health of staff. In addition, the gel is prone to cracking after water loss, resulting in the weakening of its blocking performance.

Ionic liquids (ILs) are environmental-friendly green solvents that have attracted much attention in recent years. Compared with traditional solvents, ILs have very low vapor pressure,
good thermal stability, and excellent dissolving ability and are expected to be good combustion inhibitors.10–16 Painter et al. conducted experimental studies on [Bmim][Cl], [Bmim][I], [Bmim][PF6], [Bmim][CF3SO3], and [Bmim][BF4] dissolved coal and believed that ILs can destroy the intermolecular forces in coal, thus dissolving and dispersing coal.17,18 Wang et al.13,19 analyzed the influence of [Aemim][BF4] and [Hoemim][BF4], with oxygen-containing functional groups in the cations, on the functional groups of coal and confirmed that ILs can dissolve the oxygen-containing functional groups on the coal surface and thus inhibit the spontaneous combustion of coal. In addition, this research group subsequently applied [HOOCCH2amin][HSO4] to efficiently extract sulfur structures, which are also important inducing factors for the spontaneous combustion of coal.20 ILs with fluorinated anions were stated to be better inhibitors than those with [NO3]− and [I]− anions,14–16 with the ability to lower the decomposition temperature, reducing the heat release rate of coal while increasing CO production.21 In addition, some choline amino acid ionic liquids were reported to be able to lower the decomposition temperature, fracture the coal particles, and reduce aliphatic carbon, carbonyl, and sulfur functional groups.19

However, not all kinds of ILs can inhibit combustion due to their different functional structures and properties. ILs with poor thermal stability may generate large amounts of heat early, providing a heat source to support further coal combustion. To obtain deep insight into the effect of IL thermal stability on coal combustion, ILs with fluorine and nonfluorine anion ILs are selected, and thermogravimetric and differential scanning calorimetry (TG-DSC) and the conical calorimeter are used to analyze the thermal stability and flammability of ILs, as well as the combustion characteristics of coal–IL mixtures. To explore whether the thermal stability of ionic liquids has an impact on the suppression of coal spontaneous combustion and whether ionic liquids can be applied to mining goaf sites, several experiments have been designed to reveal the feasibility of using ionic liquids as combustion-suppressing materials for coal in goaf. By mixing ionic liquids with coal, some flammability indexes, i.e., TTI, MLR, HRR, THR, SEA, and CO production, will be measured to analyze the influence of ionic liquid on the spontaneous combustion of coal.

2. RESULTS AND DISCUSSION

2.1. Results

2.1.1. Thermal Stability Based on TG-DSC

Figure 1a,b demonstrates the TG and DTG curves of coal and ionic liquids, respectively. The thermal decomposition temperature is defined as the intersection point of the tangent line at the horizontal position in front of the TG step and the tangent line at the inflection point of curve. It can be used as the reference temperature point for the initial weight change of materials, which is often used to characterize the thermal stability of materials.22 It is observed that the thermal decomposition temperatures of coal and ILs follows an order of [Pmim][BF4] > [Bmim][BF4] > [Hoemim][BF4] > Coal > [Bmim][NO3] > [Bmim][Ac] from Figure 1a. The decomposition temperature of [Pmim][BF4], i.e., 433.0 °C, is the highest and those of [Bmim][Ac] and [Bmim][NO3] are much lower at 228.5 and 296.6 °C, respectively. The thermal stability order of ionic liquids is consistent with the results reported by Cao et al.23 They investigated the thermal stability of 66 ILs composed of 19 kinds of cations and 20 kinds of anions using the thermogravimetric analysis (TGA) method. The result shows that the thermal stability of ionic liquids composed of different types of anions follows the order of [PF6]− > [Tf2N]− > [BF4]− > [TFO]− > [TS]− > [HSO4]− > [ClO4]− > [NO3]− > [I]− > [Br]− > [Cl]− > [Ac]− (for [Bmim]+ cation), and all of the imidazolium ILs containing [BF4]−, [PF6]−, and [Tf2N]− anions have stronger stability.23 Besides, the thermal stability of ionic liquids depends on not only the anions24 but also the cations. Longer chain lengths, on one hand, lead to greater van der Waals force and reduce the intramolecular electrostatic interaction, resulting in low thermal stability. On the other hand, longer alkyl chain length may create substantial stable carbon cations and carbon-free radicals and thus are prone to decomposition.25–28 This explains the larger T onset of [Pmim][BF4] than that of [Bmim][BF4]. Moreover, the hydroxyl-substituted alkyl chain can reduce the thermal stability of the ionic liquids due to its higher chemical activity.23 This is the reason why [Hoemim]−[BF4] has lower thermal stability compared to those of [Pmim][BF4] and [Bmim][BF4]. Generally, the decomposition temperature of the three fluorinated ionic liquids is higher than that of the raw coal of 334 °C. Two fluorine-free ILs ([Bmim][NO3] and [Bmim][Ac]) have weaker thermal
stability than coal, implying their ability to be combusted before coal.

Besides, from Figure 1b, it can be seen that the temperature at the DTG peak follows the order of coal > [Pmim][BF_4] > [Bmim][BF_4] > [Hoemim][BF_4] > [Bmim][NO_3] > [Bmim][Ac], and the DTG peak value follows the order [Bmim][NO_3] > [Pmim][BF_4] > [Bmim][Ac] > [Bmim][BF_4] > [Hoemim][BF_4] > coal, respectively. Clearly, three F-containing ionic liquids reached their DTG peaks much later than F-free ones, and their decomposing rates are relatively lower except that of [Pmim][BF_4]. However, all ionic liquids generally can reach their largest decomposition rate much earlier than coal, and furthermore each ionic liquid decomposes much faster than raw coal. A combination of the two aspects shows that covering ionic liquids on coal for suppressing the spontaneous combustion of coal may not be feasible especially when the coal temperature is high.

Figure 2 illustrates the heat release rates of the raw coal and pure ionic liquids, showing that the heat release rate of coal is much faster than that of the ILs and approaches the DSC peak at approximately 515 °C. By contrast, the ILs, especially [Bmim][Ac] and [Bmim][NO_3], reach the maximum heat release rates much earlier than the raw coal at 247.2 and 318.5 °C, respectively. This implies that during the oxidation stage of coal, [Bmim][Ac] and [Bmim][NO_3] are thermally decomposed and the produced heat of [Bmim][Ac] and [Bmim][NO_3] could act as the accelerating energy for coal oxidation and thus promote the oxidation process of coal. In contrast, [Bmim][BF_4], [Hoemim][BF_4], and [Pmim][BF_4] show higher decomposition temperatures and stronger thermal stability. In addition, there are significantly endothermic peaks during the oxidation process of pure [Bmim][BF_4], [Hoemim][BF_4], and [Pmim][BF_4] ionic liquids. The negative heat release of these three ILs can reduce the surface temperature of coal and postpone the time of reaching coal ignition if a larger amount of ionic liquids were applied.

2.1.2.1. Flammability Based on Cone Calorimeter.

2.1.2.2. Flammability of Coal−IL Mixtures. To show the combustion behaviors after directly applying ionic liquids on coal, an additional 3 g of ionic liquid was used to mix with 3 g of coal. The flammability of five coal−IL mixtures (3 g coal + 3 g IL) was measured by the cone calorimeter. The ignition time and extinguishing time of the raw coal, ionic liquids, and coal−IL mixtures are shown in Figure 5; generally, ionic liquids undergo longer ignition times than coal, and coal−IL mixtures show slightly increased ignition times.

Figure 6 shows the mass variation in the raw coal and the coal−IL mixtures with time during combustion. It can be seen that the coal−[Bmim][Ac] and coal−[Bmim][NO_3] mixtures...
lost mass much faster than the other mixtures, and the residual mass of the coal-[Bmim][Ac] mixtures is the lowest, indicating the worst performance of [Bmim][Ac] in retarding coal combustion.

Figure 7 shows the exothermic rates of coal combustion and that of its mixtures with ionic liquids. Due to the poor thermal stability of [Bmim][Ac] and [Bmim][NO₃], the two mixed samples reach the maximum heat release rate obviously earlier than the other mixed samples, which may be due to the rapid decomposition and much greater heat release of pure [Bmim][Ac] and [Bmim][NO₃], as mentioned above in the section of TG-DSC analysis. The heat released by coal oxidation can also accelerate the combustion of ILs, creating a “mutual thermal improvement” between the coal and ILs, promoting complete oxidation and combustion.

Figure 8 illustrates the total heat released from the raw coal and coal–IL mixtures during combustion. It is shown that the total heat released from the coal–IL mixtures is larger than that from the raw coal combustion due to the addition of the ionic liquids into the raw coal. In addition, the combustion time of coal-[Bmim][BF₄], coal-[Hoemim][BF₄], and coal-[Pmim][BF₄] mixtures is shorter than those of other coal–IL samples due to the poor thermal stability of [Bmim][BF₄] and [Bmim][NO₃], which is consistent with the above results of TG-DSC measurements. This, therefore, confirms again that the two F-free ionic liquids are not applicable as inhibitors. Another important issue that should be noted is that although the burnout times of coal-[Bmim][BF₄], coal-[Hoemim][BF₄], and coal-[Pmim][BF₄] mixtures are slightly prolonged, the abundant heat released from the combustion of ionic liquids cannot be ignored in terms of the considerations of using ionic liquids as combustion suppressors.

In Figures 9 and 10, the average specific extinction area (ASEA) and CO production of raw coal, pure ILs, and coal–IL mixtures in the cone calorimetry experiment are demonstrated.
It is seen that the ASEA of raw coal is the largest, reaching 3818.749 m²·kg⁻¹, indicating the strongest smoke-producing ability of the raw coal. The ASEA of the five pure ILs is smaller than that of raw coal, where that of [Bmim][BF₄] is the largest among the five ILs, reaching 3330.755 m²·kg⁻¹, indicating that its smoke production capacity is the largest compared with other ILs. [Bmim][Ac] shows the smallest ASEA of 1330.866 m²·kg⁻¹, indicating its weakest smoke production capacity. In addition, the ASEA of all coal–IL mixtures is generally much lower than that of the raw coal. Moreover, as Figure 10 demonstrates, the CO amounts produced from the coal–IL mixtures are also much less than that from the raw coal.

### 2.2. Discussion.

The thermal stability of ionic liquids is a fundamental property that should be considered when considering their application for coal spontaneous combustion suppression.

[Bmim][Ac] and [Bmim][NO₃] have been confirmed to be thermally unstable and produce large amounts of heat, which is expected to become an energy resource for accelerating coal oxidation. The flammability analysis confirmed this deduction, showing that both the coal-[Bmim][Ac] and coal-[Bmim]-[NO₃] mixtures combusted much faster than the other mixed samples and reached the maximum heat release rate much earlier than the other mixed samples. Comparably, during the flammability measurements, the mixtures containing [BF₄]⁻ ionic liquids show longer ignition times and much lower heat-releasing rates than the other mixtures. The three F-containing ionic liquids not only have better thermal stability but can also vaporize in an endothermic process, absorbing the heat of the coal surface with the potential to inhibit the early-stage oxidation of coal. Another important reason is that these F-containing ILs may play a similar role as that of traditional halogenated inhibitors; F atoms have extreme electronegativity and can reduce the active free radicals on the coal surface, thus delaying the reaction between coal and oxygen. The free radical reduction mechanism is illustrated as eqs 1 and 2.

\[
R – O – O + 2F^- + H_2O \rightarrow ROF + OH^- + HF
\]  \hspace{1cm} (1)

\[
R – O – O + HF \rightarrow ROF + OH.
\]  \hspace{1cm} (2)

The reason why the coal–IL mixtures were ignited quickly is due to the release of some small molecular hydrocarbons, including flammable CH₄ and C₂H₂/C₂H₄/C₂H₆ from the coal at high temperatures. Therefore, the coverage of ionic liquids on the coal surface has little effect on preventing the release of these flammable alkanes and alkenes, and furthermore, ionic liquids are essentially organic structures that can also thermally decompose. Compared to coal, ionic liquids produce much less smoke and CO during combustion. The coal is usually composed of aromatic clusters, bridges, and aliphatic hydrocarbon branches and a carbonized layer will be formed after the aromatic groups are heated. The carbonized layer can act as an insulator preventing oxygen from contacting the coal surface, resulting in a longer oxidation and decomposition time and more smoke and CO production.
composed of inorganic anions and organic cations, the intramolecular interactions of which are mainly van der Waals forces. The high temperature can easily destroy the van der Waals force and thus the ILs are much easier to break. Furthermore, these ionic liquids usually have no polycyclic aromatic hydrocarbons, so there are much fewer carbonized layers during the heating process, which explains why ionic liquids produce a relatively small amount of smoke and CO.

According to the above-mentioned analysis, ILs covering the coal surface can be oxidized and decomposed, accumulating the amount of heat required for coal combustion. After the ILs are burned out, the spaces originally filled with ILs can be occupied by oxygen, so full combustion with reduced CO production is more likely to occur for the coal−IL mixtures than for raw coal.

In general, during the low-temperature stage, most ionic liquids may act as a cover, preventing the contact of oxygen with the coal surface, as the reference states. However, when the temperatures increase, some ionic liquids, e.g., [Bmim]−[Ac] and [Bmim][NO3], may oxidize and decompose before coal combustion and provide thermal energy for coal oxidation and decomposition. Once the flame appears, the ionic liquids may combust together with coal and produce heat. Although coal−IL mixtures release less smoke and CO during combustion, large amounts of heat are released, which could accelerate the oxidation and combustion of coal in an extensive area. Therefore, the application of ILs as combustion inhibitors would be counterproductive, and their thermal stability must be taken into consideration.

### 3. CONCLUSIONS

In light of the current research on inhibiting spontaneous combustion of coal using ILs, this paper investigates the thermal stability of ionic liquids by TG-DSC and reveals the flammability of ILs and coal−IL mixtures using a cone calorimeter.

The three kinds of ILs with the [BF4]− anion were confirmed to have high thermal stability ([Bmim][BF4], [Pmim][BF4] and [Hoemim][BF4]), while the two F-free ILs ([Bmim][NO3] and [Bmim][Ac]) had poor thermal stability. [Bmim][BF4], [Pmim][BF4], and [Hoemim][BF4] all exhibited vaporization via an endothermic process, which is possibly favorable for reducing the heating of the coal surface and extends the time to reach the coal ignition temperature. Similar to halogenated inhibitors, F atoms in these ionic liquids can interrupt the free radical reaction during coal combustion, leading to a lower MLR, HRR, and THR compared to those of [Bmim][NO3] and [Bmim][Ac].

Although ILs can reduce the production of smoke and CO from coal combustion, which reduces the risk of poisoning and asphyxia, they also release large amounts of heat and are able to enhance the heat transfer and accelerate coal oxidation and combustion. Ionic liquids usually have organic cations, which may decompose at high temperatures and produce toxic smoke, which can threaten the health of humans. Therefore, the application of ILs as combustion inhibitors would be counterproductive, and their inferior thermal stability and superior flammability could become the stumbling block for application as coal combustion suppressors.

### 4. EXPERIMENTAL SECTION

#### 4.1. Experimental Materials

Raw coal was taken from the long flame coal of the Chenjiashan Coal Mine in Shanxi Province. The industrial analysis and elemental analysis results of the raw coal are shown in Table 1. The ILs, i.e., [Bmim][BF4], [Bmim][Ac], [Bmim][NO3], [Pmim][BF4], and [Hoemim][BF4], were purchased from Lanzhou Institute of Chemical Physics, with a sample purity of 99%. Table 2 shows the schematic structure and physical properties of ILs. The density, melting point, and viscosity are reported in the references, while others are provided by the Lanzhou Institute of Chemical Physics.

| Ionic liquid | Structure diagram | molecular formula | density/ (g cm⁻³) | melting point °C | viscosity/ cp |
|--------------|------------------|------------------|------------------|-----------------|--------------|
| [Bmim][BF4]  | ![Structure](image) | C₇H₁₅N₂BF₄      | 1.21             | -82⁰C           | 133⁰C        |
| [Bmim][Ac]   | ![Structure](image) | C₉H₁₅N₂O₂        | 1.05             | -20             | 732.5⁰C      |
| [Bmim][NO3]  | ![Structure](image) | C₅H₁₃N₂O₃        | 1.16             | -40→36          | 156.3⁰C      |
| [Pmim][BF4]  | ![Structure](image) | C₅H₁₃BF₂N₂       | 1.24             | -17⁰C           | 103.⁰C       |
| [Hoemim][BF4]| ![Structure](image) | C₆H₁₃BF₄N₂O      | 1.33             | -111            | 90⁰C        |
system under an air atmosphere. The atmospheric N₂ and O₂ was performed using a NETZSCH STA 449 C thermal analysis Al₂O₃ crucible and heated from 30 to 800 °C. Approximately 10 mg of the coal sample was placed in an sample, and starting the experiment. To improve the accuracy of the calibration of the gas analyzer, weighing the experimental divided into four steps, i.e., the calibration of the gas analyzer, the calibration of the optical path, weighing the experimental and the ignition needle was moved to the materials (Figure 11).

4.2. Coal Sample Preparation. The coal was crushed and ground into particles with diameters of 0.075–0.18 mm and then dried at 30 °C in a vacuum oven for 72 h. Each coal–IL mixed sample (mass ratio of 1:1) was stirred for 15 min under a N₂ atmosphere.

4.3. Experiments. Simultaneous thermogravimetric and differential scanning calorimetry (TG-DSC) of the samples was performed using a NETZSCH STA 449 C thermal analysis system under an air atmosphere. The atmospheric N₂ and O₂ gas flow rates were 20 and 10 mL·min⁻¹, respectively. Approximately 10 mg of the coal sample was placed in an Al₂O₃ crucible and heated from 30 to 800 °C with a heating rate of 10 K·min⁻¹.

The conical calorimeter is widely recognized as the best means to measure the fire response and combustion characteristics of materials, especially the fire performance, flame retardancy, and fire prediction. The experiments were conducted by the conical calorimeter produced by Fehrman Safety Technology Co., Ltd., according to the ISO 5660 measuring standard. The combustion sample box (100 mm × 100 mm × 30 mm) was wrapped with a single layer of aluminum foil paper with a thickness of 0.025–0.04 mm. The radiant heat flux was set to 50 kW·m⁻². The experiment is divided into four steps, i.e., the calibration of the gas analyzer, the calibration of the optical path, weighing the experimental sample, and starting the experiment. To improve the accuracy of the experiments, the baseline was determined for 1 min before the experiment. Then, the shielding cover was opened, and the ignition needle was moved to the materials (Figure 11).

Time to ignition (TTI), mass loss rate (MLR), heat release rate (HRR), total heat release (THR), specific extinction area (SEA), and CO output values were determined from the measurements according to the method described in the literature. TTI can reflect the difficulty of ignition of the experimental sample being ignited. Under the same conditions, the shorter the ignition time, the more easily the sample burns out.

MLR refers to the changing rate of the mass of the experimental sample overtime during the combustion process, which can reflect the pyrolysis rate and combustion degree of the material. The value of MLR is to calculate the mass loss rate of each time interval by five-point numerical differentiation, −dm/dt. The equation used is as follows: For the first scan (i = 0)

\[
-\frac{dm}{dt}_{i=0} = \frac{25m_0 - 48m_1 + 36m_2 - 16m_3 + 3m_4}{12\Delta t}
\]  

For the first scan (i = 1)

\[
-\frac{dm}{dt}_{i=1} = \frac{3m_0 + 10m_1 - 18m_2 + 6m_3 - m_4}{12\Delta t}
\]

For any scan (1 < i < n – 1, n is the total number of scans)

\[
-\frac{dm}{dt}_{i} = \frac{-m_{i-2} + 8m_{i-1} - 8m_{i+1} + m_{i+2}}{12\Delta t}
\]

When i = n – 1

\[
-\frac{dm}{dt}_{i=n-1} = -\frac{3m_n - 10m_{n-1} + 18m_{n-2} - 6m_{n-3} + m_{n-4}}{12\Delta t}
\]

When i = n

\[
-\frac{dm}{dt}_{i=n} = -\frac{25m_n + 48m_{n-1} - 36m_{n-2} + 16m_{n-3} - 3m_{n-4}}{12\Delta t}
\]

where Δt is the sample time interval, s, 0, 1, n – 1, and n are the first, second, n – 1, and nth acquisition points, respectively.

Heat release rate (HRR) is an important parameter to describe fire intensity. The cone calorimeter is designed to measure the combustion heat release rate of the experimental samples according to the oxygen consumption principle. The relationship between the change of O₂ volume fraction and heat release rate q is shown in the following eq 8

\[
q = \frac{\Delta h_c}{T_0} C \sqrt{\frac{\Delta P}{T_c}} \left[ \frac{X_{O_2}^0 - X_{O_2}(t)}{1.105 - 1.5X_{O_2}(t)} \right]
\]
In the equation, $\Delta h_{f}/r_0 \text{ (CH}_4\text{)} = 12.54 \times 103$, $\Delta h_{f}/T_e = 13.1 \times 103 \text{ kJkg}^{-1}$, $X^0_{O_2}$ is the oxygen analyzer reading, mole fraction $O_2$, $\Delta P$ is the orifice meter pressure differential, $P_a$, $T_e$ is the absolute temperature of gas at the orifice meter, $K$, and $C$ is the methane calibration constant.

The total heat release (THR) refers to the sum of the amount of heat released from an obvious flame to complete flame extinction when the shield is opened and the shield is ignited by an electric spark under the illumination of 50 kWm$^{-2}$ heat radiation illumination, which can more directly reflect the combustion performance of experimental materials. First, according to the heat release rate (HRR), the heat release rate per unit area is calculated as follows

$$q = \frac{q}{A}$$

In the formula, $A$ is the nominal specimen exposed surface area, $A = 100 \text{ mm} \times 100 \text{ mm} = 0.01 \text{ m}^2$, and then the total heat release $Q$ is calculated by the cumulative summation method, as shown in formula 10

$$Q = \sum_i q_i \Delta t$$

The specific extinction area (SEA) can reflect the amount of smoke produced by the combustion of a unit mass sample at a certain time during the combustion process, which can be used to measure the decomposition ability of the sample to produce smoke. Combined with the amount of CO gas released, it can be used to evaluate the degree of harm of coal combustion to the environment and the human body.

The calculation process of extinction coefficient $k$ is shown in formula 11

$$k = \left(\frac{1}{L}\right) \ln \frac{I_0}{I}$$

The average extinction area is shown in formula 12

$$\sigma_{(avg)} = \frac{\sum_i V_i k_i \Delta t_i}{m_i - m_f}$$

In this formula, $L$ is the extinction beam path length, $m_i$; $I_0$ is the beam intensity with no smoke; $I$ is the actual beam intensity; and $V$ is the volumetric exhaust flow rate, measured at the location of the laser photometer, m$^3$s$^{-1}$.

HRR and THR can reflect the combustion intensity. SEA is used to evaluate the ability of decomposition and smoke production. Combined with the amount of released CO, the degree of harm of coal combustion to the environment and human body could be evaluated.

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**Notes**

The authors declare no competing financial interest.

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