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Effect of Ionic Liquids on the Pyrolysis of Coal

Chuanbo Cui[a, b],

[a] School of Safety Engineering,China University of Mining&Technology, Xuzhou, Jiangsu 221116, China
[b] State Key Laboratory of Coal Resources and Safe Mining,Xuzhou221116,China
e-mail:cbcui1999@163.com

Shuguang Jiang[a, b], Liwen Kou[a, b], Lanyun Wang[c], Weiqing Zhang[b], Zhengyan Wu[a, b], Kai Wang[a, b], Hao Shao[a, b]

[a] School of Safety Engineering,China University of Mining&Technology, Xuzhou, Jiangsu 221116, China
[b] State Key Laboratory of Coal Resources and Safe Mining,Xuzhou221116, China
[c] State Key Laboratory Cultivation Base for Gas Geology and Gas Control,Henan Polytechnic University, Jiaozuo 454003, China

ABSTRACT

Three kinds of ionic liquids (ILs), [Amim]Cl, [Emim]AC, and [HOEmim]BF_4, were chosen to study the effect of ILs on the coal pyrolysis. The structure characteristics of the raw coal and ILs-treated coals are analyzed by the Fourier transform infrared spectroscopy (FTIR). In the pyrolysis process, the TG-DTG-DSC curves of raw coal and ILs-treated coal were detected by the thermal gravity combined with infrared spectrum instrument. And then the effect of ILs on the pyrolysis of coal was further studied.Finally, the effect of ILs on the pyrolysis of coal was inhibited or enhanced, and the enhancement effect is in the order of [Amim]Cl pretreated coal> [Emim]AC pretreated coal> raw coal> [HOEmim]BF_4 pretreated coal.

KEYWORDS: Coal; Ionic liquids; Pyrolysis of coal; Thermo gravimetric; Solvent swelling

INTRODUCTION

Coal is the most abundant fossil fuel in the world. It is also one of the most important energy sources in China. It plays a decisive role in the national economic construction and people's daily life. However, direct combustion of coal has resulted in a large number of soot and SO_2 gases and other pollutants discharged into the environment, causing acid rain, greenhouse effect and a series of environmental pollution problems [1-5]. Therefore, how to develop and utilize coal resources reasonably, efficiently and cleanly is the key point of coal workers' research in the future, and is also one of the main ways to develop clean energy in China [6-11].

Through the way of coal pyrolysis to produce clean or modifying the fuel can reduce environmental pollution caused by coal burning, and can make full use of the compounds contained in coal with high economic value, which has environmental protection, energy conservation and rational utilization of coal resources in the broad sense [12-14].

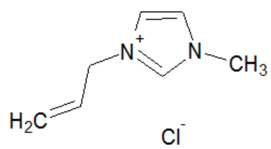
ILs with special physico-chemical characteristics such as low melting point, negligible volatility, nonflammability, and good solubility have been widely used as environment-friendly solvents [15]. As novel green solvents, ILs exhibit excellent performance in dissolution materials such as cellulose [16,17], glucose [17], carbon nanotubes [18], and coal [19-20].Zhu et al.[21] through the study of 18 different metamorphic degree of coal pyrolysis found that with the reduction of coal metamorphism, the pyrolysis conversion rate increased.Yun et al.[22] studied the pyrolysis of coal by differential scanning calorimeter (DSC) and swelling technique, and found two more obvious changes in the pyrolysis of coal.One of the obvious changes is caused by the non covalent bond binding force at the range of 250~300 ℃, and the other is due to the rupture of the covalent bond above 340 ℃. Forrester et al. [23-24] thought that swelling of coal processing can break weak bonds such as hydrogen bonds and small molecules, reduce coal association free energy, so as to increase the volume of coal sample, change and rearrange coal structures. Rinco and Cruz.[25] firstly studied the swelling pretreatment of different coal samples with hydrogen donor solvent, and found that the performance of the coal liquefaction can be improved after the treatment of the hydrogen donor solvent. Miura et al.[26] used hydrogen bond solvent to swell the coal, found that the solvent can significantly improve the pyrolysis performance of coal, and can effectively improve the pyrolysis volatile and tar yield. By studying the swelling pretreatment of the [Bmim]BF4 pretreated coal, Cao.[27] and Geng.[28] obtained the swelling law of [Bmim]BF4 pretreated coal, and got the optimum reaction temperature and time.

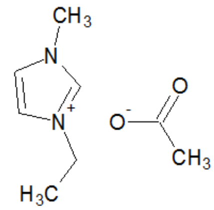
Although the above studies show that coal swelling treatment can affect the structure of coal, and then affect the pyrolysis performance of coal, but there is little research on the effect of ILs on coal pyrolysis. In this article, the ILs, [Amim]Cl, [HOEmim]BF4, and [Emim]AC, were selected to investigate their effects on the pyrolysis of coal comparing with that of raw coal sample during a temperature range (25-900℃). The coal structures were characterized by Fourier transform infrared spectroscopy (FTIR), and the thermo gravimetric (TG), the differential thermo gravimetric (DTG) and the differential scanning calorimetry (DSC) of coal samples were analyzed by the thermal gravity combined with infrared spectrum instrument.

EXPERIMENTAL STUDIES

Experimental coal samples and reagents

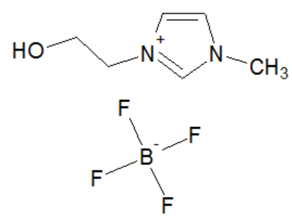
Fresh coal sample were obtained from a newly exposed surface in an underground coal seam and then were transported to the laboratory hermetically sealed. The underground coal seam is 15# coal seam of Wenzhuang Coal Mine in China, which is prone to spontaneous combustion. The volatile matter, ash, moisture, sulfur amount, and combustion heat are 15.93%, 17.62%, 0.97%, 2.49% and 26.58MJ/kg, respectively. The ILs were purchased from Lanzhou Green Chem ILs, LICP. CAS., China. Figure 1 shows the chemical structures and abbreviations of these ILs.





1- allyl -3- methyl imidazole chloride 1- ethyl -3- methyl imidazole acetate

([Amim]Cl) ([Emim]AC)



1- hydroxyethyl -3- methyl imidazole tetrafluoroborate

([HOEmim]BF_4)

Figure 1: Chemical structures, chemical names, and abbreviations of ILs.

Experimental procedures

1. The interior part of the coal was ground and sieved to a particle size smaller than 0.075 mm and then dried under vacuum for 48 hours at room temperature.The dried coal sample was put into four shares.

2. Three shares were mixed well with three kinds of isometric ILs respectively for 48 hours under ambient conditions. Then the mixtures were washed by distilled water and filtrated until the filtrate was colorless and showed a neutral pH. The residues were dried under vacuum at room temperature. These dried residues are ILs-treated coal samples, named [Amim]Cl pretreated coal, [Emim]AC pretreated coal, and [HOEmim]BF_4 pretreated coal respectively. The fourth share of untreated coal is raw coal.

3. The FTIR spectra of raw coal and three ILs-treated coals were recorded in the range 400~4 000 cm^{-1} and accumulated for 32 scans at a resolution of 4 cm^{-1} on a TENSOR-37 spectrometer (German).

4. The thermo gravimetric loss of raw coal and three ILs-treated coals in the pyrolysis process was detected by the thermal gravity combined with infrared spectrum instrument (Figure 2). Before the experiment, the experimental system was evacuated firstly, and then the flow rate of nitrogen was 45 mL/min, and the temperature of the sample was raised from 25℃ to 900℃ at the heating rate of 15 ℃/min

Figure 2: Thermal gravity combined with infrared spectrum instrument

RESULTS AND DISCUSSION

Effect of ILs on the dissolution of coal

K-M FTIR spectrum of raw coal and ILs-treated coals

The infrared spectra of organic compounds can reflect the characteristics of their chemical structure, and the different functional groups can be reflected by different characteristic absorption peaks. Figure 3 - Figure 6 are infrared spectrums after the conversion of Kubelka-Munk function.

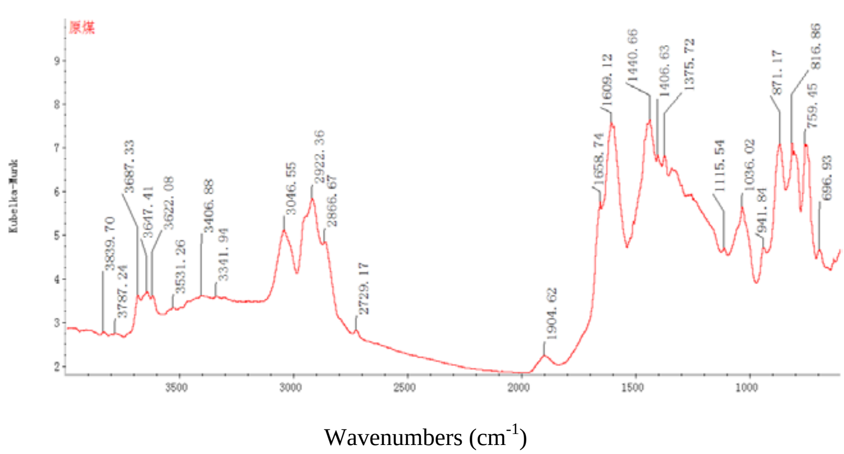
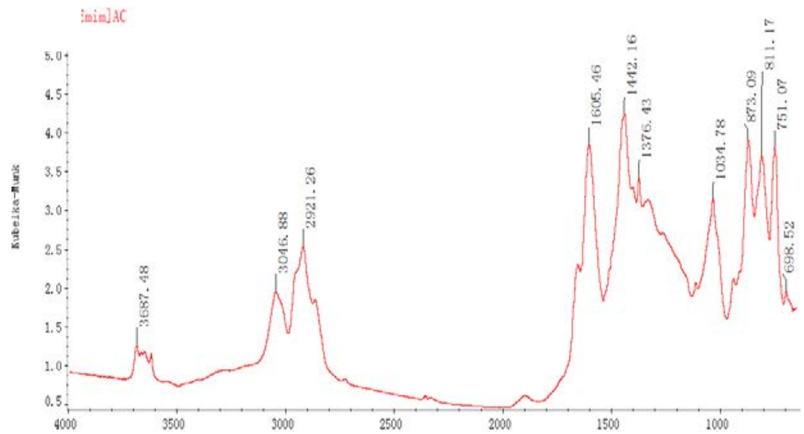
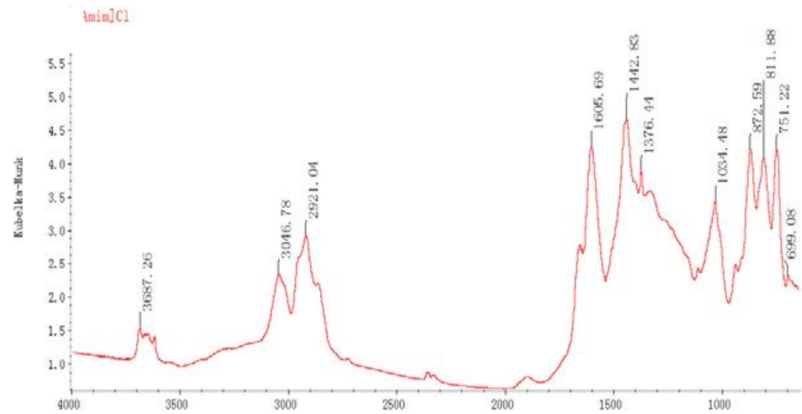


Figure 3: FTIR spectrum of the raw coal



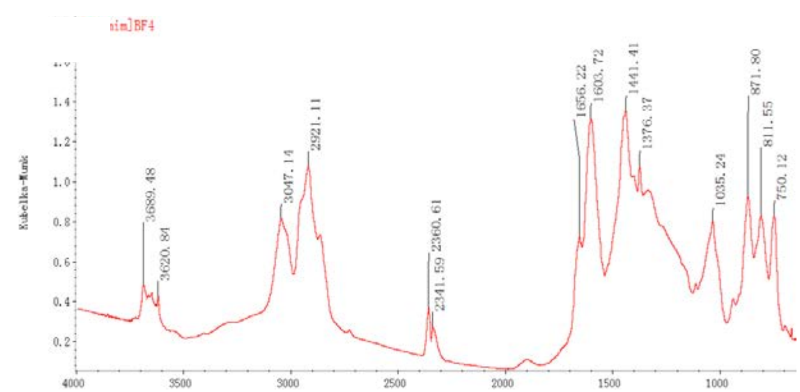
Wavenumbers (cm^{-1})

Figure 4: FTIR spectrum of the [Emim]AC pretreated coal



Wavenumbers (cm^{-1})

Figure 5: FTIR spectrum of the [Amim]Cl pretreated coal



Wavenumbers (cm^{-1})

Figure 6: FTIR spectrum of the [HOEmim]BF_4 pretreated coal

Combining the spectrum and the characteristic peak area ratio of all the coal samples shown in Figure 3-Figure 6, analyze the difference of characteristic functional groups' types and quantity between tne raw coal and ILs-retreated coals.The following results are obtained:

1) Compared with the raw coal, the characteristic functional groups' types of ILs-treated coals are essentially unchanged.

2) The main differences between the functional groups in raw coal and ILs-treated coals are as follows:

(1) Hydroxyl: In the raw coal, the hydroxyl (-OH) absorption peak of alcohol and phenol was appeared in the vicinity of 3655, 3629 cm^{-1}. The characteristic peaks of hydroxyl (-OH) groups formated by hydrogen bonds and the π bond appear at 3531 cm^{-1}. And, there are many hydroxyls (-OH) that occur as associated hydrogen bonds in the vicinity of 3406, 3341 cm^{-1}. However, there was no hydrogen bond hydroxyl absorption peak in the ILs-treated coals, except for the free hydroxyl (-OH) absorption peak. The proportion of free hydroxyl (-OH) in the ILs-treated coals is all slightly increased, and the content of free hydroxyl (-OH) in [HOEmim]BF_4 pretreated coal and [Emim]AC pretreated coal is even more than that of raw coal.

(2) Carboxyl: The weak absorption peak of carboxyl (-COOH) group in raw coal is at 2700 cm^{-1}, while the absorption peak of carboxyl (-COOH) group in ILs-treated coal is generally shifted to 2340 cm^{-1}. Compared with the raw coal, the characteristic peak area proportion of carboxyl (-COOH) of all ILs-treated coal at 1705 cm^{-1} was increased in different degree. Among them, the absorption peak area proportion of [HOEmim]BF_4 pretreated coal at 2360 cm^{-1} was the largest.

(3) Aliphatic branched chain: In the [Emim]AC pretreated coal, telescopic vibration absorption peak of fatty hydrocarbon methyl ($-CH_3$) and methylene ($-CH_2$) is significantly reduced in the vicinity of 2922 cm^{-1}.

(4) Substituted benzene: Compared with the raw coal, the proportion of substituted benzene in all ILs-treated coals have decreased. The absorption peak area proportion of substituted benzene in [Amim]Cl pretreated coal is relatively smallest.

Analysis on dissolution mechanism of IL and coal

IL, as a new type of solvent with strong polarity, can greatly reduce the phenomenon of solvation and lyolysis, and it is a good reaction solvent. It is generally believed that there is a close relationship between the polarity and the saturation of ILs group and the solubility of ILs. Therefore, from its structure, [HOEmim]BF_4 has better solubility than [Amim]Cl with double bond and [Emim]AC with alkyl chain, because of its hydroxyl (-OH) group on the side chain.

The dissolution mechanism of ILs and coal can be explained by the EDA theory and the model of action. IL cation and anion act as a electronic donor and acceptor, form a complex to weaken the hydrogen bond in coal, and then break the weak bond between the small molecule and the structural unit in coal. With permeating of ILs, the volume of coal expands, the structure changes and recombines, and the strong π-π bond is formed ultimately. The physical and chemical interaction between small molecule and coal structure in coal is weakened, which makes the free energy of coal structure decreased.

The [Emim]AC, whose side chains are all alkyls, is taken as an example. Combining Figureure 6, the dissolution mechanism and process of ILs and coal are analyzed. As shown in Figureure 6, the free $[Emim]^+$ and $[AC]^-$ in the IL react with the O atom and H atom of hydroxyl group in coal respectively. The strong negative electricity of $[AC]^-$ weakens the intramolecular and intermolecular hydrogen bonding in coal.Due to the strong negative $[AC]^-$, the hydrogen bond between the coal and the hydrogen bond is weakened, and the strong polar group of the cation is promoted. And the imidazolium cation with strong polar groups promotes the destruction of hydrogen bonds in coal. When the hydroxyl (-OH) charge in coal is separated to the proper amount, the coal molecular chain is broken, which causes the coal to be dissolved.

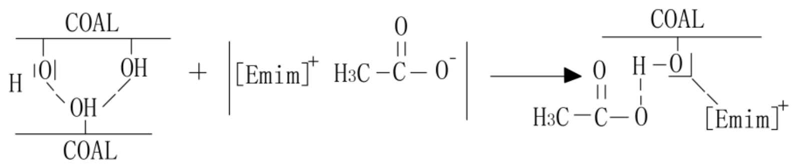


Figure 6: Interaction mechanism of coal and [Emim]AC

The dissolution effect of some ILs with unsaturated double bond and hydroxyl (-OH) functional groups at the side chain is better than [Emim]AC whose side chain are all alkyls. This indicates that the hydroxyl (-OH) functional groups and the unsaturated properties of ILs can influence the hydrogen bond in coal structure to a great extent. It is easier to react with the O atom of the hydroxyl (-OH) group in the coal structure, and it is easier to promote the destruction of the hydrogen bond. However, [Amim]Cl and $[HOEmim]BF_4$ only destroy the non chemical bonds in the molecular structure of coal.

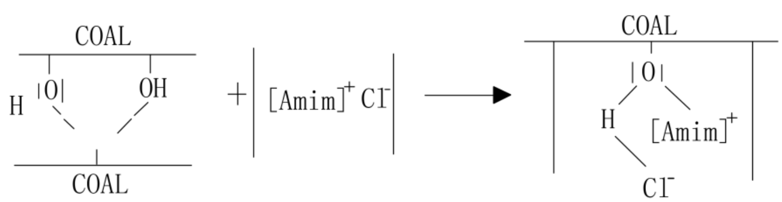


Figure 7: Interaction mechanism of coal and [Amim]Cl

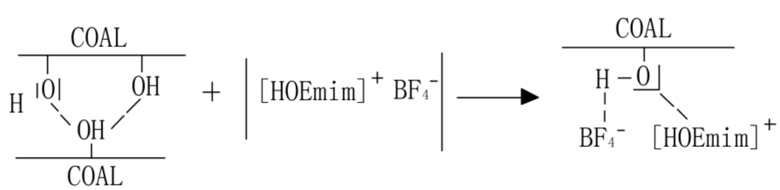


Figure 8: Interaction mechanism of coal and $[HOEmim]BF_4$

By means of infrared spectrum and EDA theory, it can be seen that the characteristics of the functional groups in the ILs-treated coal and raw coal are almost unchanged, but the quantity is different: 1)Because of [Emim]AC and $[HOEmim]BF_4$ with a strongly electronegative atom, it is easy to form hydrogen bonds with the hydroxyl group and destruct the associative hydrogen bond in coal. So that the free hydroxyl content in coal is increased compared with that of raw coal; 2)$[HOEmim]BF_4$ and [Amim]Cl are types of iminazole ILs. Because of the carbonyl group in their structures, the carbonyl species in coal are reduced; 3)The three ILs, [Amim]Cl, [Emim]AC and [HOEmim]BF_4, all make the proportion of carboxyl in coal increased; 4)Compared with the [Amim]Cl and [HOEmim]BF_4, [Emim]AC dissolved most of aliphatic straight chain hydrocarbon in the coal, such as methyl, methylene; 5)[Amim]Cl, [HOEmim]BF_4 and [Emim]AC have destroyed the aromatic structure in raw coal, in which the [Emim]AC has strong ability to dissolve the aromatic ring (C=C) structure of the coal; 6)[Amim]Cl, [HOEmim]BF_4 and [Emim]AC have a strong solution to the substitution of benzene in coal, and the [Amim]Cl has the most destructive power to the substitution of benzene.

Effect of ILs on pyrolysis of coal

TG-DTG-DSC Experimetal results of the raw coal and ILs-treated coals

Under the condition of nitrogen gas, the pyrolysis characteristic parameters of raw coal and ILs-treated coals were tested, and the TG-DTG-DSC curves of each coal sample at 25~900℃ were obtained, as shown in Figure 9~ Figure 12.

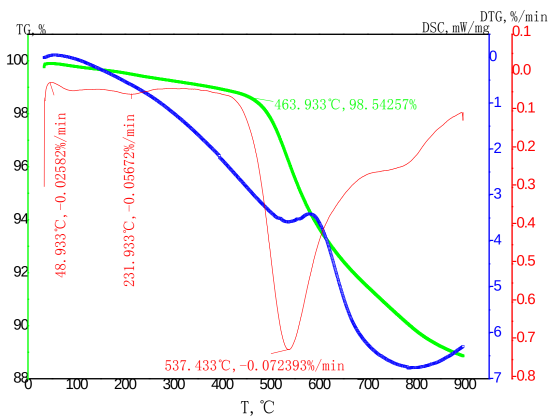


Figure 9: TG-DTG-DSC curves and inflection points of the raw coal

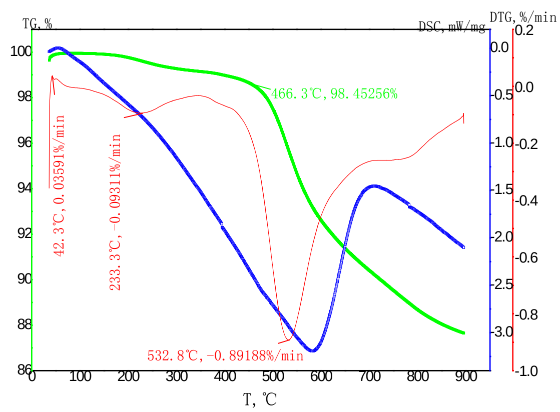


Figure 10: TG-DTG-DSC curves and inflection points of the [Amim]Cl pretreated coal

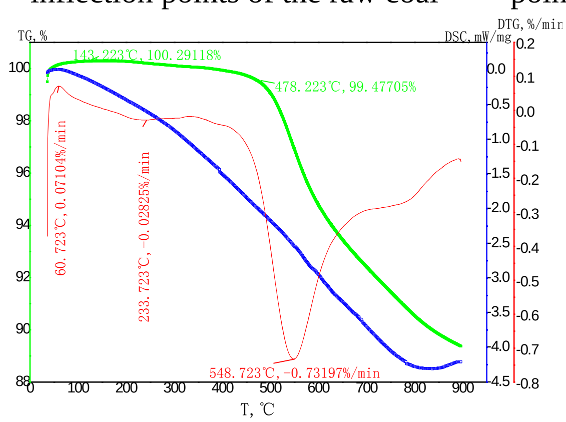


Figure 11: TG-DTG-DSC curves and inflection points of the [HOEmim]BF_4 pretreated coal

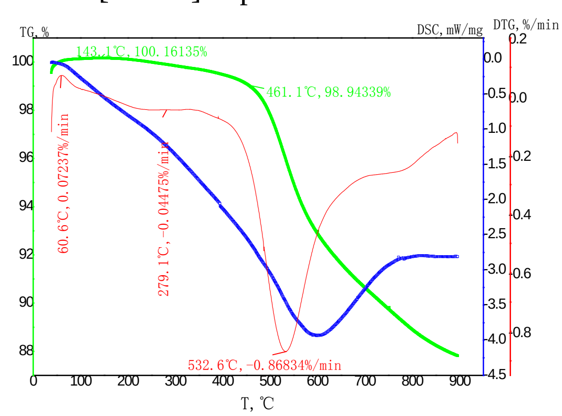


Figure 12: TG-DTG-DSC curves and inflection points of the [Emim]AC pretreated coal

Thermo gravimetric loss characteristics of coal

Under the control of the temperature, pyrolysis weight loss method is a kind of thermal analysis method to measure the relationship between the temperature and the time function of the sample.

The thermo gravimetric (TG) curve and differential thermo gravimetric (DTG) curve of the raw coal and three kinds of ILs-treated coals were shown in Figure 10 and Figure 11 respectively. Among them, the TG curve is the change of the coal sample mass with temperature under certain heating rate, the DTG curve is the first derivative of the time of the TG curve, which indicates the severity of the weight loss of the coal sample at a certain time.

1) TG curve analysis of coal pyrolysis.

As can be seen from Figure 10, the TG curves of raw coal showed a decreasing trend before the pyrolysis temperature was 300℃. The TG curves of the ILs-treated coals are higher than that of the raw coal, and the oder of TG curves from top to bottom is roughly [HOEmim]BF_4 pretreated coal > [Emim]AC pretreated coal > [Amim]Cl pretreated coal > raw coal. The mass loss of the ILs-treated coals is smaller than that of the raw coal.

The weight loss curve of each coal sample is slowly declining, and the raw coal and ILs- treated coals stay in the process of softening and melting in the range of 300~450℃. Compared with the raw coal, the weight loss of [Amim]Cl pretreated coal and [Emim]AC pretreated coal is more obvious. Between 500~600℃, the thermal weight loss of coal is the most obvious, which is in the active thermal decomposition reaction stage.

After the 700 ℃, the weight loss curve of all coal samples continues to decline, but the trend changes to ease, this stage is mainly the two decomposition of semi coke. In this stage, the weight loss of [Amim]Cl pretreated coal and [Emim]AC pretreated coal is larger than that of raw coal and [HOEmim]BF_4 pretreated coal. In addition, as can be seen from Figure.10, compared to the other three kinds of coal samples, the thermal weight loss rate of [HOEmim]BF_4 pretreated coal has been low all the time.

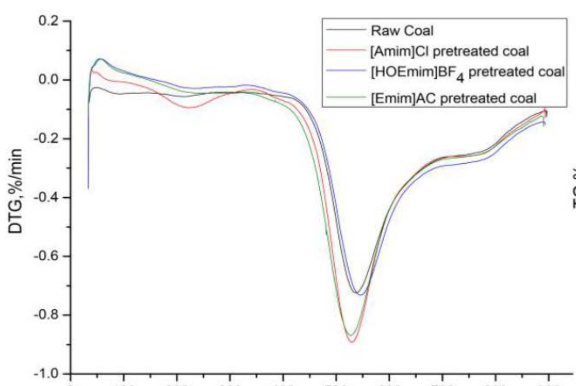


Figure 10: TG curves of the raw coal and three ILs pretreated coals

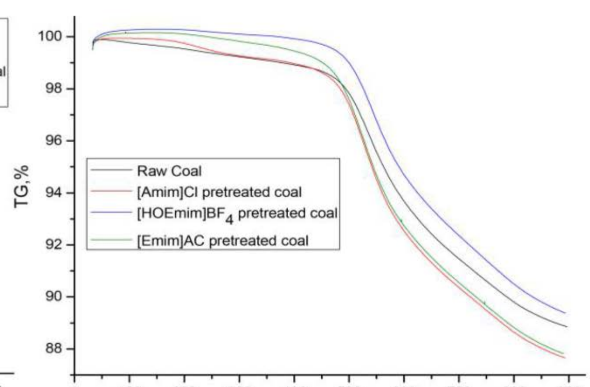


Figure 11: DTG curves of the raw coal and three ILs pretreated coals

2) DTG curve analysis of coal pyrolysis.

DTG curves indicate the intensity of weightlessness during a certain time in the process of coal pyrolysis. Three severe weight loss peaks in the pyrolysis process can be seen from the DTG curves of raw coal and ILs-treated coals, which are shown in Figure 11.

(1) During the range of 200~300 ℃, the heat loss rate of the four samples is relatively slow, and there is a peak of the weight loss rate. The weight loss rate of [Amim]Cl pretreated coal is the largest, and the weight loss rate of [HOEmim]BF_4 pretreated coal is the lowest.

(2) At the range of 500~600 ℃, the pyrolysis of coal is in the most active stage, and the heat loss rate of the four samples is the fastest. Among four coal samples, the weight loss rate of [Amim]Cl pretreated coal and [Emim]AC pretreated coal is relatively fast.

(3) At about 800 ℃, a small peak appears on the DTG curve, and the heat loss rate of [HOEmim]BF_4 pretreated coal is relatively fast.

Combined with TG-DTG curve indicated that, the pyrolysis of coal basically divided into three stages, namely degassing stage of drying, lively heat decomposition stage and thermal polycondensation stage. In addition, ILs have a certain effect on the pyrolysis reaction of coal, and the swelling effect of [Amim]Cl and [Emim]AC is better than others. They can break the weak side chain and the active group of the coal structure as well as part of the free state of small molecules, so that the coal structure is loose, the porosity and the specific surface area increase. Compared with that of the raw coal, they make the oxygen containing functional groups, branched chain and bridge bonds in the coal structure have more free space, and make them can be more fully involved in the pyrolysis reaction. From the experimental analysis, it can be found that the swelling effect of [Amim]Cl on coal is the best, and the second is the [Emim]AC. The [HOEmim]BF_4 has better effect on the dissolution of coal, which makes the part of the active structure in coal dissolve in it. And it makes the active structive of [HOEmim]BF_4 pretreated coal less than that of raw coal, which reduces the number of active structure in the pyrolysis reaction, so that the pyrolysis reactivity of coal decreases.In conclusion, the ILs have inhibition or enhancement effect on coal pyrolysis.

Analysis of heat release rate of raw coal and ionic liquid treating coal

Under the control of the program temperature conditions, differential scanning calorimetry (DSC) is a kind of thermal analysis method to measure the relationship between the power difference and the tempreature, which reflects the change of the enthalpy of the sample. DSC can not only measure the phase transition temperature point, but also can be used to study the change of coal heat quantity. Compared with differential thermal analysis (DTA), the influence factor is small, and the resolution of thermal effect is high. By using DSC to measure the heat in the coal pyrolysis process, we can understand the heating carbonization mechanism and the heat release rate of each coal sample.

The DSC curves of each coal sample are shown in Figure 12. As can be seen from Figure 12, in the drying process of the coal pyrolysis, ILs have different effects on the heat release rate of coal.

1) Before 200 ℃, the heat rate of raw coal is relatively slow, which is because the coal to remove the physical adsorption of water and some of the primary gas. And in this process, the raw coal will absorb the external heat, which leads to a reduction in the measured heat.

2) Different ILs have different effects on the heat release rate of coal. During the drying and degassing stage, the heat release rate of [HOEmim]BF_4 pretreated coal is lower than that of raw coal, and the heat release rate of [Emim]AC pretreated coal and [Amim]Cl pretreated coal is higher than that of raw coal.

3) During the drying and degassing phase, the heat release rate of [HOEmim]BF_4 pretreated coal is minimum, which shows that the reaction rate of [HOEmim]BF_4 pretreated coal is smaller than that of [Emim]AC pretreated coal and [Amim]Cl pretreated coal in this process. The heat release trend is similar to that of raw coal, indicating that there is a lot of inherent moisture and association structure in [HOEmim]BF_4 pretreated coal.

4) At the range of 0~270℃, the heat release rate of ILs with good swelling effect is higher than the rate of heat release rate of raw coal. It is possible that the cross link of the ILs-treated coal is destroyed, the coal porosity increases, and the cross link have more relative free space to participate in the pyrolysis reaction, which leads to the fast heat release rate of the ILs treatment coal.

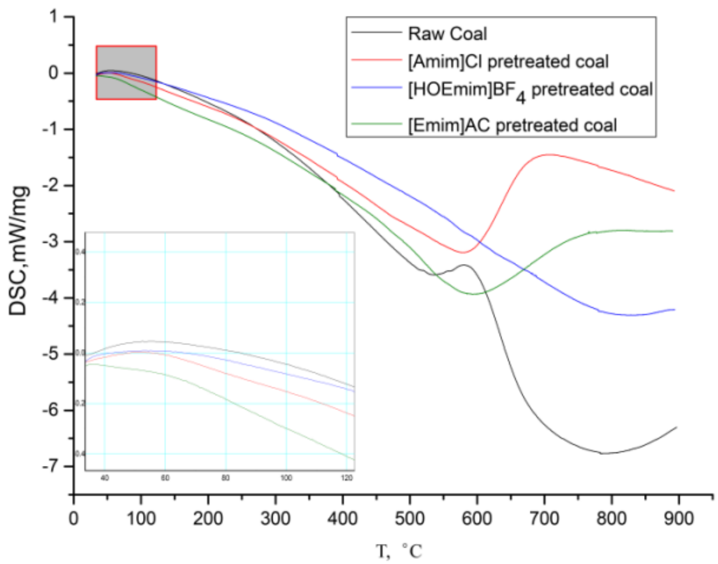


Figure 12: DSC curves of the raw coal and three ILs pretreated coals

CONCLUSIONS

The effects of ILs on the pyrolysis characteristics and reactivity of coal were studied in this paper. The pyrolysis characteristics of raw coal and ILs-treated coal were studied, and the dissolution mechanism of ILs and coal were revealed, and the main conclusions were drawn:

1) Use FTIR spectra to analyze the structure characteristics of coal and ILs-treated coal, and further use the current EDA theory to analyze the interaction mechanism between coal and ILs.

2) In this paper, the heat and weight of raw coal and ILs-treated coal were analyzed, the heat release rate of the four kinds of coal samples were studied, and the influence of the ILs on the pyrolysis of coal was further investigated.

(1) The thermal weight loss of each coal sample is roughly [Amim]Cl pretreated coal > [Emim]AC pretreated coal > raw coal > [HOEmim]BF_4 pretreated coal.It indicates that the thermal decomposition of coal can be inhibited or enhanced by ILs.

(2) The swelling effect of [Amim]Cl and [Emim]AC on coal is better. They can not only make the coal structure loose and porosity increase, but also make the chemical bond, the side chain, the branched chain and the bridge key to fully participate in the pyrolysis reaction. So the pyrolysis reaction is relatively strong.

(3) [HOEmim]BF_4 has a good solubility effect on coal and it can dissolve some weak active structure in the coal, which makes the coal structure involved in the pyrolysis reaction less than the raw coal, so the pyrolysis reaction is weak.

(4) During the drying and degassing stage, the heat release rate of [HOEmim]BF_4 is lower than that of raw coal, and the heat release rate of [Emim]AC and [Amim]Cl is higher than that of raw coal.

(5) Anion and cation of ILs act as the electron donor and acceptor, and they forms complex with coal, which weakened the hydrogen bond in coal, and broke the weak bond between the small molecule and the structural unit in coal. With permeating of ILs, the volume of coal structure expands, the coal structure changes and rearranges, and forms the strong π-π bond. And the physical chemical reaction force between the small molecular phase and coal structure is weaken, so that the free energy of the coal structure can be reduced.

ACKNOWLEDGEMENTS

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