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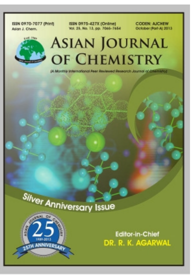

Effects of Potassium Additive on Transformation of Sulphur in Coal During Pyrolysis

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Three coals of different rank with rich organic sulphur were chosen as the experimental samples. Effects of addition of KCl into coal on sulphur transfer and release were studied in the fixed bed pyrolysis-gas chromatographic analysis apparatus. The results show that KCl in coals obviously affects the releasing temperature of sulphur and its ratio in gas and char. The role of KCl in coal mainly presents to promote the release of sulphur in Shuiyu coal to gas and slightly inhibits the formation of sulphur-containing gases in Zunyi coal. For Ximeng coal, it is more obvious to promote the formation of COS than H_2S. The sulphur contents in chars from pyrolysis of three coals at 1000 ºC are 39.8, 67.39 and 62.08 %, while they change respectively to 29.24, 64.04 and 53.95 % for coals containing KCl, showing that the sulphur-containing groups in the coal with high organic sulphur are more easily transformed to other forms by KCl additive.

Key Words: Coal, Pyrolysis, High organic sulphur, KCl.

INTRODUCTION

During the processing and utilization of coal, the sulphur content in coal is one of the most important indexes to evaluate the quality of coal. In China, coal is taken as the key primary energy. Although the high quality coal with less than 1 % sulphur content is mainly used in the commercial coal, the serious environmental contamination has been brought about and the harmonious development among economy, society and environment has been restricted. With the rapid development of social economy, the supply situation of high quality coal with low sulphur and ash contents is not optimistic. Meanwhile, the reserve of coals with high sulphur content of more than 1 % is relatively abundant, accounting for about a quarter of the coal resources in China and the exploitation and utilization of them will relieve the pressure of energy shortage. Sulphur in coal mainly exists in two kinds of types, inorganic sulphur and organic sulphur. Inorganic sulphur consists of sulphide, sulfate and a small amount of element sulphur, thereinto, pyrite is the main existing form, which can be easily removed with traditional physical and chemical methods to reach the general requirements. Comparing with inorganic sulphur in coal, the existing form of organic sulphur is more complicated. The organic sulphur, including a series of sulphur containing organic functional groups, is part of macromolecular organic structure in coal. It is required for removal of organic sulphur from coal to damage the structure of coal, which may change the forms of sulphur in it. Therefore, characterizing the existing forms of sulphur in coal, regulating and controlling the transformation and emission of sulphur during coal pyrolysis have become a hot topic in clean coal technology research[1-3].

Organic sulphur in coal mainly contains thiol, hydroxylate, thioether, thiophene heterocyclic sulfide, sulfide quinone, disulphide, thioxanthene, *etc*.[4]. In organic sulphur, the proportion of thiophenic sulphur increases with the increasing of coal rank. The thiophenic sulphur is very stable, so it is hardly separated out under mild pyrolysis condition[5, 6]. With the improvement of modern analytical methods, more and more attention is focused on environment protection by people, it should be possible to obtain much more details for existing form of sulphur in coal and to explore the increasing knowledge on chemical reaction and transformation of sulphur during thermal processing. Due to the complexity of coal structure and characteristics, the diversity of sulphur containing functional groups and side chain structures in different types coals will lead to the great difference on the transformation of sulphur in gaseous phase, liquid phase and solid phase during pyrolysis of coal. Also, the conditions of coal pyrolysis has strong effect on sulphur transformation. The effects of inorganic matters added and contained in coal on its pyrolysis performance[7,8] show that the majority of metals and their oxides have actions to a varying degree and then influence the distribution and form changing of sulphur in gaseous phase, tar and char during the pyrolysis. It's worth noting that alkali

TABLE-1
PROXIMATE AND ULTIMATE ANALYSES OF COAL SAMPLES USED IN THE EXPERIMENTS

Sample	Proximate analysis (wt/%)			Ultimate analysis (wt/%) (daf)				
	M_{ad}	A_d	V_{daf}	C	H	O*	N	S
Ximeng	28.07	10.52	45.46	66.11	2.28	27.48	1.26	2.87
Shuiyu	0.44	10.91	20.86	84.70	3.93	7.77	1.33	2.27
Zunyi	0.87	22.00	10.79	84.28	3.22	4.31	0.92	7.27

Note: ad, air-dried basis; d, dry basis; daf, dry and ash-free basis; *Determined by difference.

metal potassium has obviously different affection from other metals in the process of coal pyrolysis, because potassium can transfer, diffuse and form liquid membrane on the surface of coal and then potassium contacts with carbon easily. No matter which loading method of potassium is used, good catalytic effect can be obtained[9,10]. Based on the above discussion, three different ranks of coals with high sulphur content are chosen and the samples added 2 % mass fraction KCl into them through mechanical mixing method were prepared in this experiment. The transfer and release of sulphur during pyrolysis of raw coals and samples with KCl additive were investigated in the fixed bed pyrolysis apparatus using temperature programming method. Based on the results of sulphur content in char characterized by sulphur analyzer and in pyrolysis gases measured by gas chromatography, the effects of KCl for sulphur transformation during pyrolysis of different ranks of coal were analyzed in order to provide the theoretical basis for rationally and effectively utilization coals with high sulphur content.

EXPERIMENTAL

Preparation of coal sample: Ximeng (XM), Shuiyu (SY) and Zunyi (ZY) coals from Chinese mines were used in this study. They were crushed and sieved to obtain the experimental samples with the particle sizes between 0.125-0.149 mm. The proximate, ultimate and sulphur forms analyses of coal are shown in Tables 1 and 2. Data present that all the sulphur content of three varieties of coals is all more than 2 % and the content of organic sulphur is more than 78 %. Analyses of ash components in the coal samples are shown in Table-3. It can be seen that the ash content of Zunyi coal is obviously higher than that of the other two coals, in which the silicon, aluminum and iron content are dominant.

TABLE-2
ANALYSIS DATA OF SULPHUR
FORMS IN THE COAL SAMPLES

Sample	Sulphur forms in coal (wt%) (daf)			Sulphur forms in totalS (wt%)		
	S_s	S_o	S_p	S_s	S_o	S_p
XM	0.17	2.70	0.00	5.92	94.08	0.00
SY	0.03	1.83	0.41	1.32	80.62	18.06
ZY	0.12	5.71	1.44	1.65	78.54	19.81

Note: St, total sulphur, Ss, sulfate sulphur, Sp, pyretic sulphur, So, organic sulphur.

Three coals are weighed for 5 g and mixed mechanically with KCl with 2 % potassium mass fraction, then the coal samples containing KCl additive were obtained and saved in brown bottle away from sunshine, labeled with XMK, SYK and ZYK.

Procedure: In this study, fixed bed pyrolysis-gas chromatographic analysis apparatus were used to perform the pyrolysis experiment of sample. A quartz glass tube with inside diameter of 20 mm was used as reactor, in which a quartz sintered plate was placed in the constant temperature stage. H_2S and COS were quantitatively analyzed by GC-950 with FPD made by Shanghai Haixin Instrument Ltd.

0.5 g sample was weighed firstly and then, put on the sintered plate in the reaction tube, blowing by argon pyrolysis carrier gas with the flow rate of 600 mL/min. Above all, reactor should be cleaned by pyrolysis ambience. After the air is entirely replaced, the reactor was heated to reach the final temperature with the heating rate of 10 ºC/min using temperature controlling instrument and then kept for 20 min. Sulphur-containing gas, H_2S and COS, produced in the process of pyrolysis were sampled by gas injection needle in an interval of 5 min and then, quantitatively analyzed by GC-950-FPD.

At a certain time, the release quantity (C_i) of H_2S and COS can be detected by chromatograph, and the proportion of products in total outlet gas can be calculated by the equation below:

$$C_i = S_{d,i}\, C_{s,i}/S_{s,i} \tag{1}$$

where $S_{d,i}$ is the peak area of pyrolysis gas; $C_{s,i}$ is the concentration of corresponding standard gas; $S_{s,i}$ is the peak area of corresponding gas in standard sample. Standard gas was provided by Beijing ZG Special Gases Science & Technology Co., Ltd.

Data processing: At a certain experimental final temperature, the release ratio (Y_i) of sulphur containing gas, H_2S and COS, can be calculated by the eqns. 2 and 3, on the basis of sulphur in coal sample.

$$Y_i = \sum \frac{(C_{1,i} + C_{2,i}) \times V \times t \times 273.15 \times M_S}{2 \times 22.4 \times (273.15 + T) \times 1000 \times W} \tag{2}$$

$$W = m_0 \times (1 - m) \times (1 - M_{ad}) \times (1 - A_d) \times P_S \tag{3}$$

where $C_{1,i}$, $C_{2,i}$ is the instantaneous release amount of H_2S or COS in sampling interval, respectively; V is the gas flow rate after pyrolysis, in this experiment, the carrier gas flow rate is 600 mL/min, which is far more than that of gas produced in the process of pyrolysis, so V is approximately equal to 600 mL/min here; t is sampling interval, which is set for 5 min in this experiment; M_s is the mole fraction of atomic sulphur in sulphur containing gas; T is room temperature during the experiment, ºC; W is the weight of element sulfur in coal sample without KCl additive on dry ash-free basis, m_0 is the weight of coal sample, g; m is the weight of KCl additive loaden on 1 g coal sample, g; M_{ad} is the moisture of coal sample; A_d is the ash content of coal sample; P_s is the percentage of element sulphur in coal sample on dry ash-free basis.

TABLE-3
ANALYSIS DATA OF ASH COMPOSITIONS IN THE COAL SAMPLES

Sample	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	SO_3	K_2O	Na_2O	P_2O_5
XM	3.18	1.53	1.01	0.12	1.91	0.51	1.95	0.05	0.09	0.06
SY	3.83	4.13	0.36	0.14	1.71	0.21	0.31	0.04	0.03	0.03
ZY	9.11	7.87	2.07	1.15	0.54	0.51	0.29	0.13	0.09	0.08

RESULTS AND DISCUSSION

Release of H_2S and COS during raw coal pyrolysis: Release amounts of H_2S and COS during coal pyrolysis at different temperature are shown in Fig. 1. H_2S and COS were produced during the pyrolysis of all the three varieties of coals and H_2S is dominant. With the increasing of temperature, the release amounts of both H_2S and COS firstly reached the maximum and then decreased. But the release amount and the maximum release temperature of sulphur containing gas of three coal samples were diverse, which should be related to the difference of sulphur content and existing forms in coal. Combined with the data in Table-1, it can be considered that the maximum release temperature of H_2S and COS increases with the increasing of coal rank. The organic sulphur occupies the major position in the sulphur forms of three coals, which presents that the thermal stability of organic sulphur existing in coal has corresponding relationship with coal rank. The lower coal rank is, the easier the migration of sulphur in coal to gaseous phase products is.

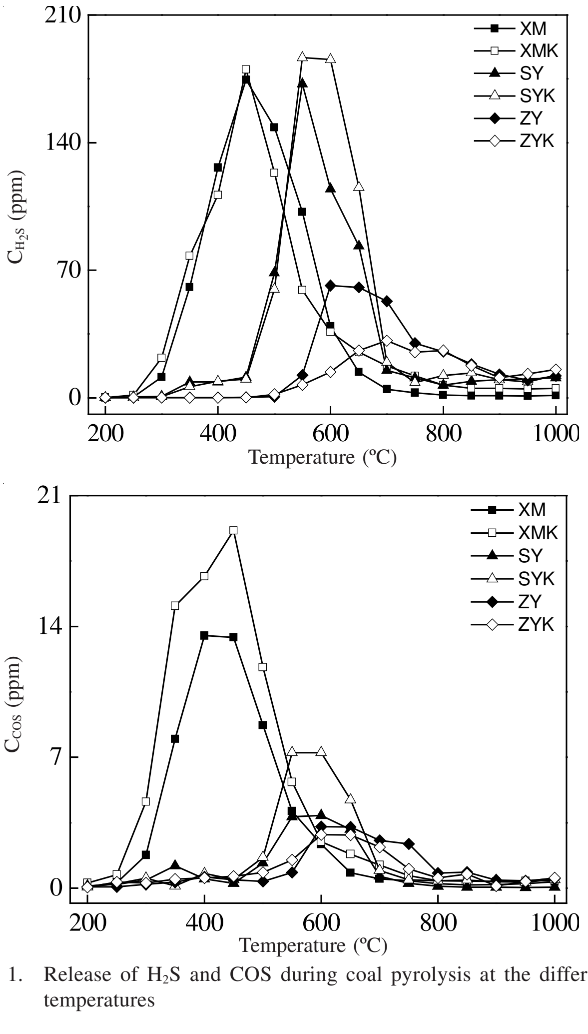

Fig. 1. Release of H_2S and COS during coal pyrolysis at the different temperatures

During the pyrolysis of Ximeng raw coal, the release of H_2S reaches the maximum at *ca.* 450 °C and endes at 800 °C. In Ximeng coal, the content of organic sulphur is above 94 % and no pyrite exists. For sulphur in low rank coal of Ximeng, the forms of thioether and aliphatic sulfide with low thermal stability are major, while thiophene structure with high thermal stability takes a minor place[11]. Sulphur-containing gas starts to be formed during the thermal decomposition of coal at 250 °C, the main release stage in the range of 250-700 °C. The rank of Shuiyu coal is relatively higher, the initial release temperature of H_2S in pyrolysis process rises to 300 °C, but the obvious release occurs until 450 °C. The peak temperature is 550 °C and the release tends to be stable at 800 °C with few release of H_2S yet. Aliphatic sulfide decomposes to form sulphur containing gas at 500 °C, while thiophene compounds decompose at 600 °C or much higher temperature[12]. Shuiyu coal belongs to medium rank coal, it can be inferred that the existing form of organic sulphur in it contains aliphatic structure with low thermal stability and thiophene sulphur structure with high thermal stability. Further more, H_2S can be also produced by the decomposition of pyrite ($FeS_2 \rightarrow FeS + \cdot S$, $\cdot S + 2\cdot H \rightarrow H_2S$) in coal at *ca.* 600 °C. The content of pyrite in total sulphur of Shuiyu coal is *ca.* 18 %, so it should be also the main source of hydrogen sulfide. Zunyi coal is a kind of high rank coal and the volatile matter content in Zunyi coal is only 10.79 %. Thiophene structure with high thermal stability is the main form of organic sulphur existing in Zunyi coal, so the release amount of sulphur-containing gas will be less than that of other two coal and its release temperature range will also move to higher temperature. H_2S starts to be released at 500 °C, then obviously appears at the temperature range of 600-700 °C. The sulphur content of Zunyi coal is as high as 7.27 %, in which pyrite accounts for 19.81 %, so it can be considered that the H_2S in gaseous products is mainly from the decomposition of pyrite and the participation of organic sulphur groups with high thermal stability in high rank coal is not significant.

For the formation of COS, the maximum release amount and temperature range is diverse among three raw coals. The main release temperature area of COS from Ximeng coal pyrolysis, similar to H_2S, is also relatively low. The release amount at temperature range of 300-600 °C is dominant and it is much more than that of other two coals. The release amount of COS during Shuiyu coal pyrolysis is approximate to that of Zunyi coal, but the maximum release temperature range of 500-700 °C is lower than that of Zunyi coal (550-800 °C), which is obviously different from the order of H_2S release. The formation course of COS should be different from that of H_2S in the pyrolysis process of coal. COS can be formed by the reaction of sulphur-containing groups from the decomposition of pyretic sulphur ($FeS_2 \rightarrow FeS + \cdot S$) or the cracking of organic sulphur and the oxygen-containing groups formed during coal pyrolysis, but the formation of H_2S is dominated by hydrogen-containing groups. As is shown in Table-1, the oxygen content in Ximeng, Shuiyu and Zunyi coals (27.48, 7.77 and 4.41 %, respectively) is obviously different, but the difference of hydrogen content in them is not very significant, which is related to the forming tendency of COS and H_2S.

Effects of KCl additive in coal on the release of H_2S and COS: Results in Fig 1. show that KCl additive in coal presents significant effects. The change tendencies of H_2S release during pyrolysis of coal with KCl are different for three kinds of coals. For Ximeng coal with KCl additive, the release amount of H_2S from 450-600 ºC is slightly lower than that of Ximeng raw coal, but H_2S is initially formed at 250 ºC and the maximum releasing temperature is 450 ºC, which is similar to Ximeng raw coal. These results demonstrate that the addition of KCl does not apparently affect the transformation of H_2S in the process of Ximeng coal pyrolysis. At the temperature range of below 550 ºC, the release of H_2S during pyrolysis of Shuiyu coal loaded by KCl is similar to that of Shuiyu raw coal, but the release amount of H_2S is obviously increased in the temperature range of 550-700 ºC, indicating that at higher temperature range the release of sulphur-containing groups in Shuiyu coal can be promoted to form H_2S by adding KCl. The release of H_2S in Zunyi loaded by KCl additive, similar to Zunyi raw coal, is inapparent at the temperature of below 500 ºC, but it apparently reduces when pyrolysis temperature is risen to at above 500 ºC, showing the inhibitory action of KCl for releasing of H_2S in the process of Zunyi coal pyrolysis at high temperature. The potassium in coal can catalyze the reaction between carbon in char and carbon dioxide in volatiles[13], increase significantly the pyrolysis reactivity of coal and then damage the organic structure of coal, which will result in much more decomposition of organic sulphur in coal and benefit the release of sulphur-containing gases. On the other hand, H_2S in gases can react with KCl added in coal and is retained in char in the form of potassium sulfide. From above experimental results, it can be seen that the contribution of these two effects of KCl additive is closely related the types of coal during pyrolysis.

After adding KCl, the COS release amount from Ximeng and Shuiyu coal pyrolysis is obviously larger than that of raw coal, which demonstrates that the potassium additive makes the decomposition of organic sulphur functional groups in low and medium rank coals and the formation of COS easier. But the catalysis of KCl in the process of high rank Zunyi coal pyrolysis is not significant, it presents a small effect for the formation of COS.

The accumulated yields of H_2S and COS during coal pyrolysis at 1000 ºC are shown in Fig. 2. It can be seen that the addition of KCl promotes obviously the transformation of sulphur in Ximeng and Shuiyu coals. To the contrary, the addition of KCl slightly reduces the conversion of sulphur in Zunyi coal. According to the accumulated yields data of H_2S and COS, the effect of additional KCl for release of H_2S and COS in different rank coal during pyrolysis is distinct. For Ximeng coal, the additional KCl has more obvious promoting effect on the release of COS than H_2S. As medium rank Shuiyu coal, the addition of KCl promotes obviously the formation of H_2S and COS at the same time. In high rank Zunyi coal, the KCl inhibits the release of H_2S and COS simultaneously.

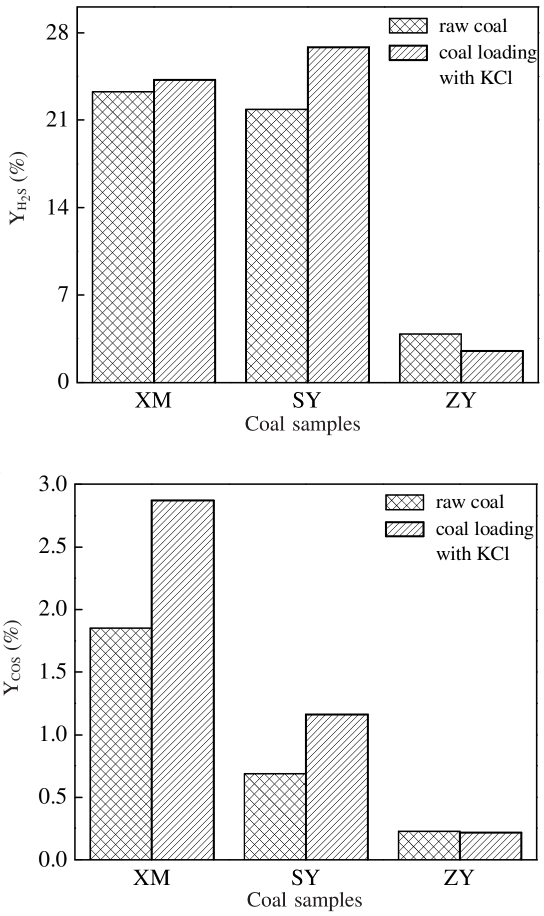

Fig. 2. Yields of H_2S and COS during coal pyrolysis

The distribution of sulphur-containing compounds in gases and char during coal pyrolysis is shown in Fig. 3. During coal pyrolysis, the distribution of sulphur in pyrolysis gas, char and tar is related to the coal characters and pyrolysis operating conditions. Under the same operating conditions, the sulphur contents of Ximeng, Shuiyu and Zunyi coal chars obtained after pyrolysis are 39.8, 67.39 and 62.08 %, respectively. The sulphur contents in the chars of after pyrolysis of three coal samples loaded with KCl are 29.24, 64.04 and 53.95 %, respectively, which indicates that KCl has obvious effect on the transformation of sulfide during coal pyrolysis and this effect is related to the characters of coal. The existing form of

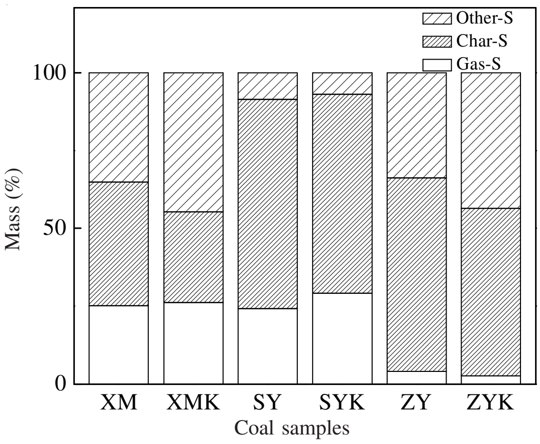

Fig. 3. Distribution of sulphur-containing compounds during coal pyrolysis

sulfide in three coal samples is mainly organic sulphur with different content. KCl added in all the three varieties of coals reduce the sulphur content in char after pyrolysis, showing that KCl can promote the conversion of sulphur-containing groups in coal through thermal decomposition. After contrastive analysis, it is easy to find the accumulative release rate of sulphur containing gas in coal decreases with the increasing of coal rank, which should be dominated by the molecular structure of organic sulphur in low rank coal tending to transform to a more stable structure in high rank coal. The forms of sulphur in char obtained from coal pyrolysis is different from that of raw coal. The relative unstable organic sulphur forms have been decomposed and released and those sulphur detained in char mainly exists in the forms of non-volatile inorganic sulphide, thiophene sulphur and other stable organic sulphur formed during pyrolysis. Non-volatile inorganic sulphide mainly comes from the thermal decomposition of pyrite and the reactions between alkaline minerals and H_2S.

Conclusion

The release characteristics of sulphur-containing gases during coal pyrolysis is different for different rank of coal sample and those loaded by KCl. The addition of potassium only changes the release amounts of sulphur-containing gases in pyrolysis at different temperature, without changing its tendency along the variation of temperature. Among them, the KCl added more obviously affects the release of COS in the process of low rank Ximeng coal pyrolysis than H_2S, simultaneously promotes the release of H_2S and COS in medium rank Shuiyu coal and slightly inhibits the formation of sulphur-containing gases in high rank Zunyi coal. The addition of KCl also shows different effects on the sulphur content in char after coal pyrolysis. The sulphur contents of Ximeng, Shuiyu, Zunyi coal chars obtained at 1000 ºC with and without potassium additive are 39.8, 67.39, 62.08, 29.24, 64.04 and 53.95 %, respectively, which show that the KCl added promotes the transformation of sulphur forms in three coal with high organic sulphur.

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