

Release Behavior of Arsenic During Pyrolysis of Two Chinese Coal Gangues

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Release behaviors of arsenic (As) during pyrolysis of two Chinese coal gangues were studied in this report. The pyrolysis experiments were carried out in a temperature programmed tube furnace under N₂ atmosphere with different temperature (200-1200 °C), residence time (0-50 min), heating rate (10-50 °C min⁻¹) and N₂ gas flow rate (100-500 cm³ min⁻¹). The experiment results, under different pyrolysis conditions, indicate that the release ratio of As increases with increasing temperature, as well as residence time during pyrolysis of coal gangues. Besides that, higher heating rate during pyrolysis of coal gangues can stimulate the As release from coal gangue to some extent. The release ratio of As increases to a maximum and then decreases when the N₂ gas flow rate is increased. The results imply that different modes of occurrence of As exist in two coal gangues. The As release has positive relation with the volatile matter release. As is more easily released than coal gangue matrix during coal gangue pyrolysis.

Keywords: coal gangue, arsenic, release behavior, pyrolysis, modes of occurrence

Introduction

Coal gangue is an industrial solid waste from coal mining or coal washing, occupying a large amount of land and leading to serious environmental pollution in China.¹⁻³ In recent years, the utilization of coal gangue has attracted wide interest and coal gangue blended with coal has been widely utilized as a raw material in some power plants in China to effectively utilize the calorific value in coal gangue.⁴⁻⁶ However, the arsenic (As) in coal gangue has become a new discharge source of As pollution because it can be released into atmosphere during the coal gangue combustion.

As is a kind of hazardous element because of its potential carcinogenic characters.⁷⁻¹⁰ It is generally accepted that one of the main sources of As pollution is from the emission from coal utilization, which can cause environmental and human health problems.¹¹⁻¹³ Meanwhile, As has negative effect on the activation of selective catalytic reduction (SCR) catalysts and it can affect the NO_x removal efficiency in power plant.¹⁴ Coal gangue combustion is something like coal combustion and it also causes environmental problems of As pollution. Consequently, it is important to develop effective As control technologies during coal

gangue combustion. And thus, it is crucial to understand the As release behavior during the pyrolysis of coal gangue, because pyrolysis is a heat treatment process that occurs in most of the fuel utilization.

In recent years, extensive researches about the release behavior of As during coal pyrolysis have been done.¹⁵⁻¹⁹ It has been found that the increasing pyrolysis temperature and residence time lead to an increasing release of As. It is reported that the release behavior of As during coal pyrolysis mainly depends on its modes of occurrence in coals and different modes of occurrence of As in coals undergoes complex reactions during coal pyrolysis. Meanwhile, the release behavior of As during pyrolysis of arsenic-bearing gypsum sludge and arsenic-bearing copper slag have been reported, which showed obvious arsenic removal effect.^{20,21} Overall, the information about As release behavior during coal pyrolysis or other solid wastes is useful for the development of As control technology. However, the report considering the release behavior of As during coal gangue pyrolysis is few, which hinders the development of As control technology during coal gangue utilization.

Coal gangue is associated with coal in coal mine and thus coal gangue is similar to coal. For example, they both contain organic material and inorganic material. However, coal gangue contains higher content of mineral

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and lower content of organic material than coal. In addition, higher content of trace elements such as As exist in coal gangue compared to coal. Therefore, the information about the release behavior of As during coal pyrolysis may not be applicable to the coal gangue.

The aim of this study is to obtain a clear understanding on the release behavior of As during coal gangue pyrolysis. The different pyrolysis conditions were used to investigate the effect of the pyrolysis temperature, residence time, heating rate and gas flow rate on As release behavior during pyrolysis of coal gangues, which could provide meaningful information for As emission control during coal gangues utilization. In this paper, two coal gangues used in power plant were studied in detail with a fixed-bed reactor.

Experimental

Coal gangue samples

Two Chinese coal gangues, 1 and 2, collected from Taiyuan power plant and Taiyuan Coal washery in Shanxi province were used in this study. In order to prevent contamination as well as minimize oxidation, the samples were placed in plastic storage bags. Before use, the two coal gangue samples were crushed and sieved into a size range of 0.16-0.27 mm, then dried. Table 1 shows the proximate and ultimate analyses and the concentration of As in the two coal gangues. The proximate analysis of the coal gangue provides moisture (M), volatile matter (V) and ash contents (A). Ultimate analysis of the coal gangue provides weight percentage of carbon, hydrogen, nitrogen, sulfur and oxygen (by subtraction) elements.

Pyrolysis procedures

The pyrolysis experiments were carried out in a quartz boat within a fixed bed tube reactor of 20 mm inner diameter under a N₂ atmosphere flow. Approximately 1.0 g coal gangue sample charged into a quartz boat in the reactor was used for each experiment. Before pyrolysis of coal gangue, 10 min purge time for the reactor was used to assure the N₂ atmosphere purity. The reactor with quartz boat was

purged with N₂ flow and heated from room temperature to a predetermined final temperature (200, 400, 600, 800, 1000 or 1200 °C) at a heating rate of 10, 20, or 50 °C min⁻¹ with a desired residence time (0, 5, 10, 20, 30, 40 or 50 min) and a N₂ gas flow rate (100, 300, 500, 700 or 900 cm³ min⁻¹). At the predetermined final temperature and residence time, the sample boat was moved to a cold end of the reactor quickly and then cooled down to room temperature in a N₂ flow. Finally, the weight of the pyrolysis residue (PR) of coal gangues in the quartz boat was determined and the As content in PR was analyzed.

To clearly show the result, the term of release ratio (RR) of As is used, which can quantify the amount of As released during coal gangue pyrolysis. It is abbreviated as RR and defined as follow:

$$RR(\%) = \frac{\text{As content in coal gangue} - \text{As content in PR} \times \text{PR yield}}{\text{As content in coal gangue}} \times 100 \quad (1)$$

Volatile yield (VY) is used to evaluate the quantity of volatile matters released during the coal gangue pyrolysis, which is abbreviated as VY and defined as:

$$VY(\%) = 100 - \frac{\text{Char mass}}{\text{Coal mass}} \times 100 \quad (2)$$

Determination of arsenic in coal gangues and pyrolysis residue samples

Firstly, the 0.1 g powdery coal gangue or PR sample was precisely weighed and placed in Teflon digestion vessel. Then, the sample in the Teflon digestion vessel was acid-digested with 10 mL oxidizing mixture (HNO₃:HCl, 3:1, volume ratio) in a microwave oven (130 °C, 10 min; 150 °C, 5 min; 180 °C, 5 min; 200 °C, 25 min). After cooling, the recovered samples were diluted with double-distilled deionized water. At last, the As in the volumetric flask was reduced with the solution of potassium borohydride (KBH₄) and then measured by an atomic fluorescence spectrometer. The limit of detection of AFS (atomic fluorescence spectrometry) for As in solution is 0.01 ng mL⁻¹ and the analysis uncertainty of obtained As content was less than 3%.

Table 1. Proximate and ultimate analyses of the coal gangues

Coal gangues sample	As in coal gangues / (ng g ⁻¹)	Proximate analysis, ad ^a / wt.%			Ultimate analysis, daf ^b / wt.%				
		V ^c	A ^d	M ^e	C	H	N	S	O ^f
1	9.00	14.87	70.33	0.87	56.70	5.80	0.80	13.06	23.64
2	11.19	10.79	77.81	0.76	48.20	6.49	0.93	15.77	28.61

^aad: air dried basis; ^bdaf: dry ash-free basis; ^cV: volatile matter; ^dA: ash; ^eM: moisture; ^fweight percentage of oxygen obtained by difference.

Results and Discussion

Release behavior of As during pyrolysis of coal gangues at different temperature

Figure 1a shows the RR of As at different pyrolysis temperature (heating rate of $20\text{ }^{\circ}\text{C min}^{-1}$, N_2 flow rate of $300\text{ cm}^3\text{ min}^{-1}$ and 0 min residence time). Figure 1b shows the corresponding VY at the same pyrolysis conditions. It can be clearly seen that, with the increasing of pyrolysis temperature, the RR of As for both coal gangues increases linearly, which indicates that temperature is one of the key factors for As release during pyrolysis of coal gangues, and this result is in agreement with the report about coal.¹⁵

The VY for both coal gangues also increases with the increasing pyrolysis temperature. However, the VY does not show a linearly increase with temperature. For example, coal gangue 1 shows a sharp increase at $600\text{--}800\text{ }^{\circ}\text{C}$ while coal gangue 2 shows a sharp increase at $400\text{--}600\text{ }^{\circ}\text{C}$, indicating different volatile characters for two coal gangues.

Figures 1a and 1b show that As and the volatiles in the coal gangues present different release behavior, but they also show that a higher VY corresponds to a higher As RR. Meanwhile, the RR of As is always much higher than its corresponding VY, implying that As in coal gangue is more easily released than coal gangue matrix.⁴

Although there are many similarities in As release behaviors for the two coal gangues, the RR of As for coal gangue 1 are always higher than that for coal gangue 2 at the temperature range studied, which may suggest that coal gangue 1 contains more relatively unstable thermally As in comparison to coal gangue 2. Similar to the RR of As, the VY for coal gangue 1 is also always higher than that for coal gangue 2, which is consistent with the proximate analysis of two coal gangues in Table 1. It indicates that the As release has some relations with the volatile character of coal gangue and the more volatile matter release, the

more As releases, which is consistent with the previous study about coal.¹⁷⁻¹⁹

It is important to note that the amount of As from coal gangue 1 (26.21%) is significantly higher than that from coal gangue 2 (8.83%) at temperature of $200\text{ }^{\circ}\text{C}$, even though coal gangue 2 contains more As ($11.19\text{ }\mu\text{g g}^{-1}$) than coal gangue 1 does ($9.0\text{ }\mu\text{g g}^{-1}$). This difference may be attributed to the different modes of occurrence of As in two coal gangues and suggests that coal gangue 1 contains more easily released As (such as organic-bound arsenic) than coal gangue 2.²²⁻²⁵ At temperature range of $200\text{--}800\text{ }^{\circ}\text{C}$, the RR of As for coal gangue 1 increases by approximately 10% while for coal gangue 2 increases by approximately 20%, which suggests that coal gangue 2 contains more relatively easily released As (such as sulfide-bound arsenic) than coal gangue 1.²²⁻²⁵ In the temperature range of $800\text{--}1200\text{ }^{\circ}\text{C}$, the RR of As for both coal gangues increases with a similar increasing rate and it reaches 48.87% for coal gangue 1 and 42.85% for coal gangue 2 at $1200\text{ }^{\circ}\text{C}$, suggesting 51.13 and 57.15% of unreleased As for coal gangue 1 and 2, respectively. It implies that coal gangue 2 contains more thermal stable As (such as silicate-bound arsenic) than coal gangue 1 does.²²⁻²⁵

In summary, the release behavior of As for two coal gangues indicates a different distribution of modes of occurrence of As existing in two coal gangues and the As release has positive relation with the volatile character of coal gangue.

Release behavior of As during pyrolysis of coal gangues at different heating rate

The pyrolysis experiments were conducted under a N_2 flow rate of $300\text{ cm}^3\text{ min}^{-1}$ at heating rate of 10, 20 or $50\text{ }^{\circ}\text{C min}^{-1}$ with 0 min residence time. The temperature of $800\text{ }^{\circ}\text{C}$ was chosen as a typical temperature to show the effect of heating rate on the As release during pyrolysis

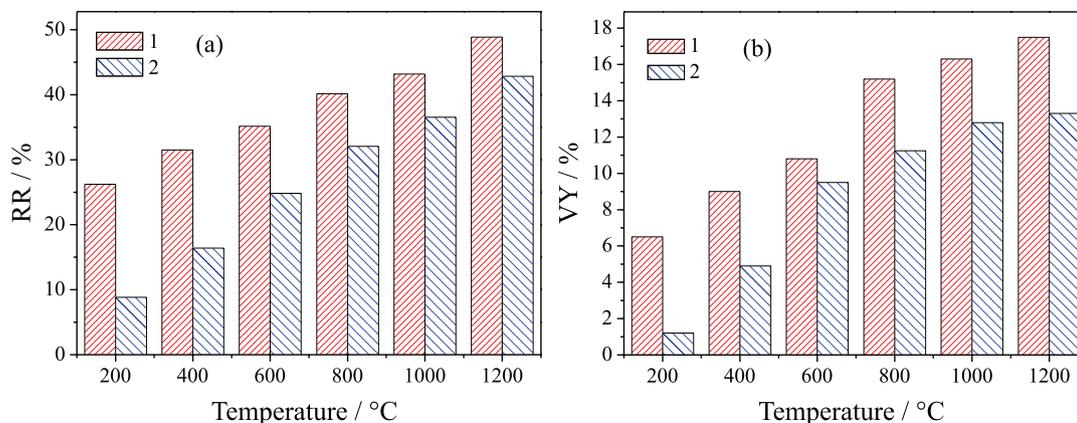


Figure 1. Release behavior of As during pyrolysis of coal gangues 1 and 2, at different temperature.

of two coal gangues. Figure 2 presents the RR of As and the corresponding VY at 800 °C for both coal gangues at different heating rate.

It is interesting to note that the RR of As at 800 °C for both coal gangues increases when the heating rate is increased from 10 to 50 °C min⁻¹. Meanwhile, the VY shows a similar tendency with the corresponding RR of As, suggesting that a higher heating rate can promote the As release as well as the volatile matter release, which further indicates a positive relation between As release and volatile matter release during coal gangue pyrolysis. It is likely that the coal gangue pyrolysis is an endothermic reaction and higher heating rate could stimulate the pyrolysis of coal gangue, and thus the As, as well as volatile matter, is released more easily from the coal gangue.²⁶ Also, it should be noted that the value of VY is always less than that of As RR, which is consistent with the result at sub-section "Release behavior of As during pyrolysis of coal gangues at different temperature", further verifying that As in coal gangue is released more easily than coal gangue matrix.

When the heating rate was changed from 10 to 20 °C min⁻¹, the RR of As obviously increased from 32.18 to 40.16% for coal gangue 1 and from 29.56 to 32.06% for coal gangue 2, respectively. Clearly, the RR increase for coal gangue 1 is higher than that for coal gangue 2, possibly attributing to the difference of two coal gangues character. However, the RR of As only increased by 2% for coal gangue 1 while it increased by 7% for coal gangue 2 when the heating rate was increased from 20 to 50 °C min⁻¹. In summary, the RR of As for two coal gangues both increased by approximately 10% from 10 to 50 °C min⁻¹. Meanwhile, the VY has a similar tendency with RR of As, showing a sharp increase from 10 to 20 °C min⁻¹ and then a slightly increase from 20 to 50 °C min⁻¹ for coal gangue 1 while a slightly increase from 10 to 20 °C min⁻¹ and then a sharp increase from 20 to 50 °C min⁻¹ for coal gangue 2. Finally, the VY increased by approximately 4% for coal gangue 1

and 3% for coal gangue 2, respectively, which was lower than the increase amount of As RR. It suggests that the promotion effect of heating rate on RR of As is higher than that on VY, which agree with the fact that As in coal gangue is more easily release out than coal gangue matrix.

Release behavior of As during pyrolysis of coal gangues at different residence time

The pyrolysis experiments were conducted at different residence time (0, 5, 10, 20, 30, 40 or 50 min) under a N₂ flow rate of 300 cm³ min⁻¹ at heating rate of 20 °C min⁻¹. The temperature of 800 °C is an example to show the effect of residence time on the As release and the result is shown in Figure 3.

From Figure 3, it can be seen that the RR of As for two coal gangues increases obviously from 0 to 5 min residence time and then gradually increases after 5 min residence time. Finally, with the increasing of residence time, the RR reaches to the maximum and nearly keeps constant at 40-50 min residence time. It suggests that As release is only influenced significantly by a shorter residence time and the long residence time has limited effect on As release. Also, the corresponding VY has a positive correlation with the RR of As for both coal gangues.

It is important to note that both the increasing amount of As RR and VY for coal gangue 1 (1% of As RR, 1.5% of VY) are less than that for coal gangue 2 (1.5% of As RR, 2% of VY) when the residence time is prolonged from 0 to 5 min, which possibly attributes to the different type of coal gangue as well as the different modes of occurrence of As existing in two coal gangues. Actually, the RR of As increasing with the residence time may correspond to some reactions regarding the decomposition of inorganic As material in coal gangues.^{27,28} When the decomposition of inorganic As material stops, the As release also stops, leading to a constant RR of As. It seems that the amount of

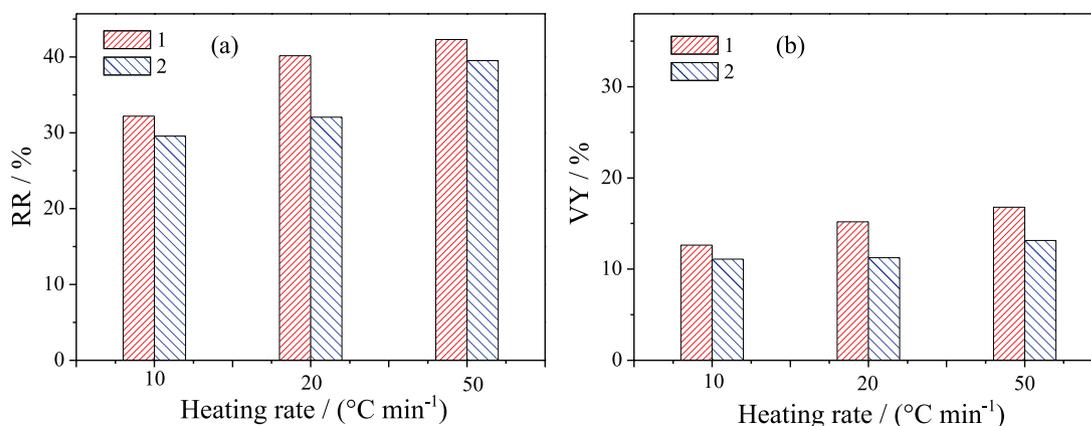


Figure 2. Release behavior of As during pyrolysis of coal gangues at different heating rate.

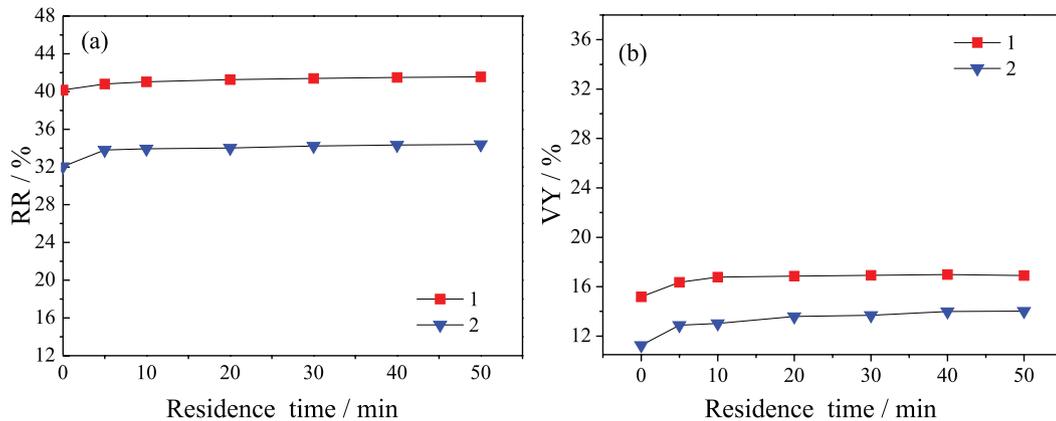


Figure 3. Release behavior of As during pyrolysis of coal gangues at different residence time.

inorganic As material for coal gangue 2 is higher than that for coal gangue 1 since coal gangue 2 contains higher ash content than coal gangue 1 (listed in Table 1). However, the further verification is needed in the future.

Overall, although the RR of As for both coal gangues increases with the increased residence time, the increasing amount of RR is less than 2%, suggesting a limited promoting effect of residence time on As release.

Release behavior of As during pyrolysis of coal gangues at different N_2 gas flow rate

The pyrolysis experiments were conducted under different N_2 gas flow rate (100, 300, 500, 700 or $900 \text{ cm}^3 \text{ min}^{-1}$) at heating rate of $20 \text{ }^\circ\text{C min}^{-1}$ with 0 min residence time. The result at $800 \text{ }^\circ\text{C}$ is shown in Figure 4.

Figure 4 shows that the RR of As increases firstly and then decreases with the increased N_2 gas flow rate for the two coal gangues. At the gas flow rate of $100 \text{ cm}^3 \text{ min}^{-1}$, the RR of As is 38.65 and 30.18% for coal gangues 1 and 2, respectively. As the N_2 gas flow rate increases, the RR of As increases. For coal gangue 1, the RR of As reaches to the maximum of 47.29% (increase by 8.64%) under the gas

flow of $500 \text{ cm}^3 \text{ min}^{-1}$, while for coal gangue 2, the RR of As reaches to the maximum of 36.85% (increase by 6.67%) under the gas flow of $700 \text{ cm}^3 \text{ min}^{-1}$. When the gas flow rate is increased to $900 \text{ cm}^3 \text{ min}^{-1}$, the RR of As is decreased by 13.49 and 3.05% for coal gangues 1 and 2, respectively. Clearly, the RR of As is influenced by the gas flow rate, which agrees with previous report.²⁹ However, the effect of gas flow rate on As release is different with different coal gangues, possibly due to the different character of coal gangues.

Conclusions

In this study, two coal gangues were selected to study the As release behavior under different pyrolysis conditions of temperature, heating rate, residence time and N_2 gas flow rate. The results are as follows.

Temperature is one of the key factors in As release during pyrolysis of coal gangues and the RR of As increases with the increasing of pyrolysis temperature. Higher heating rate could stimulate the As release and VY for two coal gangues. The RR of As for two coal gangues gradually increases with the extension of residence time and reaches

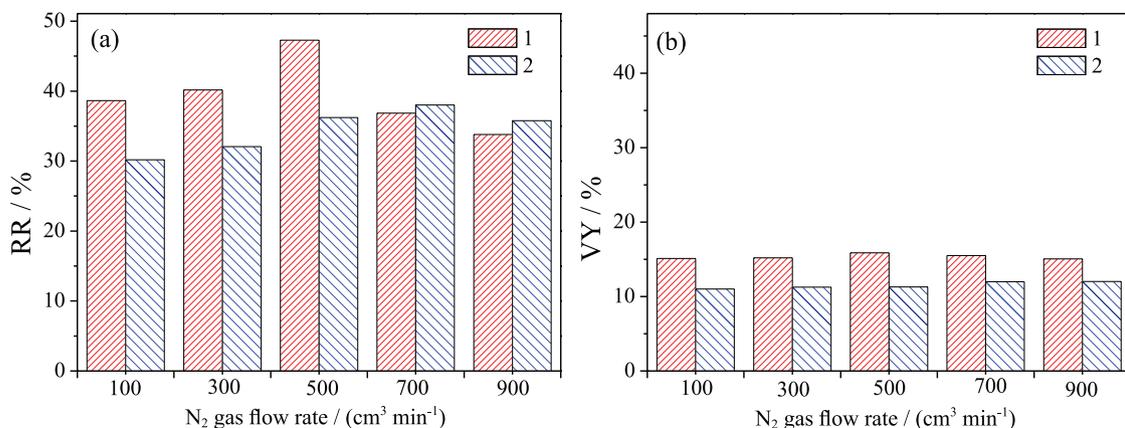


Figure 4. Release behavior of As during pyrolysis of coal gangues at different N_2 gas flow rate.

a constant value, suggesting a limited promoting effect of residence time on the As release. The RR of As increases to a maximum and then decreases with the increased N₂ gas flow rate. The release behavior of As for two coal gangues indicates that different modes of occurrence of As exist in two coal gangues. As in coal gangue releases more easily than coal gangue matrix during pyrolysis.

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References

1. Querol, X.; Izquierdo, M.; Monfort, E.; Alvarez, E.; Font, O.; Moreno, T.; Alastuey, A.; Zhuang, X.; Lu, W.; Wang, Y.; *Int. J. Coal Geol.* **2008**, *75*, 93.
2. Zhou, B. B.; Shao, M. A.; Wen, M. X.; Wang, Q. J.; Robert, H.; *Clean: Soil, Air, Water* **2010**, *38*, 1031.
3. Bell, F. G.; Stacey, T. R.; Genske, D. D.; *Environ. Geol.* **2000**, *40*, 135.
4. Meng, F. R.; Yu, J. L.; Tahmasebi, A.; Yanna, H.; *Energy Fuels* **2013**, *27*, 2923.
5. Chugh, Y. P.; Patwardhan, A.; *Resour., Conserv. Recycl.* **2004**, *40*, 225.
6. Zhou, C. C.; Liu, G. J.; Yan, Z. C.; Fang, T.; Wang, R. W.; *Fuel* **2012**, *97*, 644.
7. Swaine, D. J.; *Fuel Process. Technol.* **2000**, *65*, 21.
8. Guo, X.; Zheng, C. G.; Xu, M. H.; *Energy Fuels* **2004**, *18*, 1822.
9. Lashkenari, M. S.; Davodi, B.; Eisazadeh, H.; *Korean J. Chem. Eng.* **2011**, *28*, 1352.
10. Ghosh, M. K.; Poinern, G. E. J.; Issa, T. B.; Singh, P.; *Korean J. Chem. Eng.* **2012**, *29*, 95.
11. Lu, X. H.; Zeng, H. C.; Yan, R.; Chen, G. N.; *Environ. Chem.* **1997**, *16*, 306.
12. Feng, X. B.; Ni, J. Y.; Hong, Y. T.; Zhu, J. M.; Zhou, B.; Wang, Y.; *Environ. Chem.* **1998**, *17*, 148.
13. Zhao, Y. C.; Zhang, J. Y.; Huang, W. C.; Wang, Z. H.; Li, Y.; Song, D. Y.; Zhao, F. H.; Zheng, C. G.; *Energy Convers. Manage.* **2008**, *49*, 615.
14. Shah, P.; Strezov, V.; Stevanov, C.; Nelson, F.; *Energy Fuels* **2007**, *21*, 506.
15. Zajusz-Zubek, E.; Konieczynski, J.; *Fuel* **2003**, *82*, 1281.
16. Wang, J.; Atul, S.; Akira, T.; *Energy Fuels* **2003**, *17*, 954.
17. Guo, R. X.; Yang, J. L.; Liu, D. Y.; Liu, Z. Y.; *Fuel Process. Technol.* **2002**, *77-78*, 137.
18. Liu, R. Q.; Yang, J. L.; Yao, Y.; Liu, Z. Y.; *Energy Fuels* **2009**, *23*, 2013.
19. Wei, X. F.; Zhang, G. P.; Li, L.; Xian, M.; Cai, Y. B.; *China Environ. Sci.* **2011**, *31*, 2005.
20. Li, X.; Zhu, X.; Qi, X.; Li, K.; Wei, Y.; Wang, H.; Hu, J.; Hui, X.; Zhang, X.; *J. Anal. Appl. Pyrolysis* **2018**, *130*, 19.
21. Wan, X.; Qi, Y.; Gao, J.; Wu, B.; *Nonferrous Met. Eng.* **2017**, *04*, 40.
22. Zhou, C. C.; Liu, G. J.; Wu, D.; Fang, T.; Wang, R. W.; Fan, X.; *Chemosphere* **2014**, *95*, 193.
23. Zhou, C. C.; Liu, G. J.; Fang, T.; Lam, S. K. P.; *Bioresour. Technol.* **2015**, *175*, 454.
24. Querol, X.; Fernandez-Turiel, J. L.; Lopez-Soler, A.; *Fuel* **1995**, *74*, 331.
25. Vassilev, S. V.; Braekman-Danheux, C.; *Fuel Process. Technol.* **1999**, *59*, 135.
26. Wang, M. M.; Zhang, J. S.; Zhang, S. Y.; *J. China Coal Soc.* **2008**, *33*, 76.
27. Liu, G. J.; Yang, P. Y.; Peng, Z. C.; Wang, G. L.; Cao, Z. H.; *Geo. Chem.* **2002**, *31*, 85.
28. Lu, H. L.; Chen, H. K.; Li, W.; Li, B. Q.; *Fuel* **2004**, *83*, 645.
29. Han, J.; Wang, G. H.; Xu, M. H.; Yao, H.; *J. Huazhong Univ. Sci. Technol., Med. Sci.* **2009**, *37*, 85113.

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