Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2014, 6(4):898-904

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Analysis on influencing factors during coal desulfurization with microwave

Xu Ning, Tao Xiuxiang* and Sheng Yuhang

Key Laboratory of Coal Processing and Efficient Utilization of Ministry of Education, School of Chemical Engineering and Technology, China University of Mining and Technology, Xuzhou, Jiangsu, China

---

ABSTRACT

In the paper, with the high-sulfur bituminous coal from Chongqing Songzao(S_t 1.62, S_p 0.94, S_s 0.11, S_o 0.57) as the research object, a desulfurization test was conducted with microwave combined with NaOH solution to study the effects of various factors on the results of coal desulfurization and the proximate analysis index. The test results show that increasing the microwave power and the irradiation time can reduce the content of the total sulphur in clean coal and improve the desulphurization rate, but excessive increase is useless; the additive amount of the NaOH solution also has an optimum value. The content of total sulfur in the desulfurated clean coal falls to around 0.80%, the content of organic sulfur is around 0.40%, and the content of the pyritic sulphur falls to around 0.18% under the best conditions (microwave power 1000W, irradiation time 5 min, solid-to-liquid ratio 1:4, concentration of NaOH solution 300 g/L). The ash content and volatile content of the desulfurated clean coal also change while desulfurization.

Keywords: coal desulfurization; microwave; NaOH solution; influencing factor

---

INTRODUCTION

Microwave, as an energy field, heats substance fastly, uniformly and selectively. It has been used widely in fields including organic synthesis[1-3], mineral leaching[4], wastewater treatment[5], oil sand and petroleum upgrading[6]. With people's increasing emphasis on environmental issues, the application of microwave technology in clean coal technology has attracted attention of the related experts[7-8].

With the high-sulfur bituminous coal from Chongqing Songzao as the research object, desulfurization tests were carried out by microwave combined with NaOH solution to study the effects of such factors as microwave power, irradiation time, solid-to-liquid ratio, and concentration of NaOH solution on the results of coal desulfurization as well as the proximate analysis index. And the principles of coal microwave desulfurization were also discussed.

EXPERIMENTAL SECTION

Coal sample

The high-sulfur bituminous coal sample from Chongqing Songzao (flotation clean coal). In the following text, the coal samples before desulfurization were called raw coal, and the coal samples after desulfurization were called clean coal.

The results of the proximate analysis and elemental analysis on the coal sample are shown in Table 1 and Table 2.

Table 1 Proximate analysis of coal sample

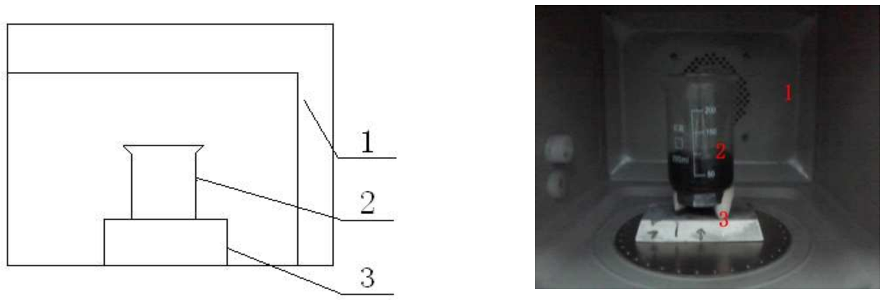
Item	M_{ad},%	A_d,%	V_{daf},%	FC_{daf},%
Content	1.48	11.20	9.51	90.49

Table 2 Determination of total sulfur and sulfur forms in coal sample

Item	$S_{t,d}$,%	$S_{s,d}$,%	$S_{p,d}$,%	$S_{o,d}$,%
Content	1.62	0.11	0.94	0.57

Experimental methods

The microwave reaction equipment Model No.MAS-II is manufactured by Sineo Microwave Chemistry Technology (Shanghai) Co., LTD. The microwave frequency is 2.45 GHz, as shown in Figure 1.



(a) Schematic diagram **(b) Real diagram**

Figure 1 Microwave oven used for experiments

1- Microwave oven; 2- Quartz beaker; 3- Ceramic blocks

The test flow chart is shown in Figure 2.

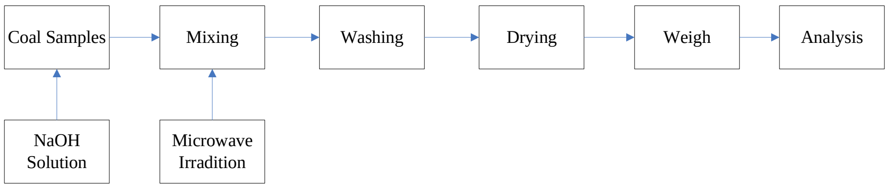


Figure 2 The flow chart of coal desulfurization with microwave combined with NaOH solution

RESULTS AND DISCUSSION

Discussion on the Principles of Coal Microwave Desulfurization

The dielectric loss value of pyrite in coal is much larger than that of coal substance, which enables the pyrite to be heated selectively[9]. The Fe-S bonds in pyrite molecules can be induced to break down by the high temperature of microwave radiation and then combine with the surrounding activated H, O and CO in coal[10-12]. The reactions are as below,

$$FeS_2 + (H - coal) \rightarrow Fe_{1-x}S + H_2S \uparrow \quad 0 < x \leqslant 0.125$$
$$Fe_{1-x}S + (H - coal) \rightarrow FeS + H_2S \uparrow$$
$$FeS_2 + (O - coal) \rightarrow Fe_{1-x}S + SO_2 \uparrow$$
$$Fe_{1-x}S + (O - coal) \rightarrow FeS + SO_2 \uparrow$$
$$FeS_2 + (CO - coal) \rightarrow Fe_{1-x}S + COS \uparrow$$
$$Fe_{1-x}S + (CO - coal) \rightarrow FeS + COS \uparrow$$

Thus, pyrite changes into pyrrhotine($Fe_{1-x}S$) and troilite(FeS), and further converts to sulfate under oxidation environment.

At the same time, such pyrolytic reactions happened to the organic sulfur in coal[13-14],

$$(organic\ sulfur - coal) + (H - coal) \rightarrow coal + H_2S \uparrow$$
$$(organic\ sulfur - coal) + (O - coal) \rightarrow coal + SO_2 \uparrow$$
$$(organic\ sulfur - coal) + (CO - coal) \rightarrow coal + COS \uparrow$$

In order to increase the temperature and accelerate the reactions, agents with large dielectric loss(such caustic alkali) are usually used. The addition of NaOH can increase the dielectric loss and thus increasing the temperature of the system, and can even react with sulfur-containing components. The reactions are as follows[15-16],

$2FeS_2+6NaOH \rightarrow NaFeO_2+4Na_2S+2H_2O$
$O_2R\text{- }SH+2NaOH \rightarrow R+Na_2S+H_2O$
$R\text{- }S\text{- }R'+2NaOH \rightarrow R'OH+ROH+Na_2S$

The solube sulfide generated will further convert to sulfate under oxidation environment. And an excessive extension of reaction time may enable the soluble sulfide generated to further react and produce insoluble sulfide thus reducing the desulphurization efficiency[17]. Moreover, NaOH can also react with minerals in coal and generate solube sodium salts thereby reducing the ash content of desulfurization coal.

Effect of microwave power on the result of desulfurization
The selected range of microwave power is 600-1000 W at an interval of 100 W. Other conditions are: irradiation time 5 min, solid-to-liquid ratio 1:4, concentration of NaOH solution 300 g/L. The results are as shown in Figure 3 and Table 3.

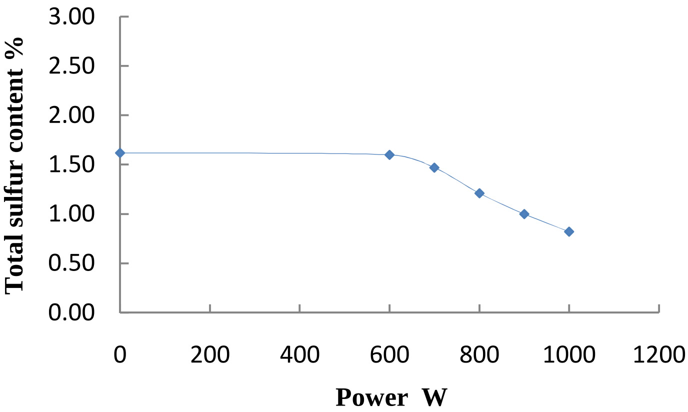


Figure 3 Effect of microwave power on total sulfur content of desulfurized coal

Table 3 Effect of microwave power on various forms of sulphur

Power, W	Content of sulfur,%				Clean coal yield, %	Desulfurization rate, %
	$S_{t,d}$	$S_{s,d}$	$S_{p,d}$	$S_{o,d}$		
Raw coal	1.62	0.11	0.94	0.57	-	-
600	1.60	0.07	0.88	0.65	87.97	13.12
700	1.47	0.08	0.71	0.68	91.17	17.27
800	1.21	0.05	0.59	0.57	89.06	33.48
900	1.00	0.10	0.43	0.47	88.42	45.42
1000	0.82	0.21	0.21	0.40	88.82	55.04

From Figure 3, the content of sulphur in the clean coal decreases gradually with the increase of the microwave output power. The content of sulphur in clean coal is only 0.82%, and the desulfurization rate is 55.04% under the condition of 1000 W, indicating a satisfactory desulfurization result.

Based on changes in various forms of sulphur in clean coal after desulfurization (Table 3), it is discovered that the content of pyritic sulfur and organic sulphur in clean coal decreased and the content of pyritic sulfur could be decreased to as low as 0.21%; the sulfate sulfur in clean coal exhibited a first decrease and then increase rather than a constant increase. And the sulfate sulphur content reached up to 0.21% at 1000 W, indicating the increase of power could promote conversion of pyritic sulfur and organic sulphur in coal into sulfate sulfur.

Table 4 The change of proximate analysis indexes of coal with microwave power

Power, W	M_{ad}, %	A_d, %	V_{daf}, %
Raw coal	1.48	11.20	9.50
600	0.87	8.62	9.15
700	0.83	7.54	8.99
800	1.01	7.53	8.93
900	0.86	7.30	9.07
1000	1.25	8.22	9.35

Table 4 shows the result of proximate analysis of clean coal after desulfurization under different power conditions. The ash content of the clean coal was decreasing with the increase of the power ranging between 600W and 900W. When the microwave power increased to 1000 W, the ash content in clean coal increased somewhat but it was still below the ash content of raw coal. Compared with the raw coal, the volatile content in the desulfurized clean coal decreased and reached the lowest at 800W. Moreover, the volatile content in the clean coal increased somewhat after the microwave power exceeded 800W, indicating that the microwave power imposed a slight effect on the macromolecular structure of coal.

Effect of irradiation time on the desulfurization result

The effect of irradiation time on the desulfurization result was studied at a microwave power of 1000 W, and other conditions were: solid-to-liquid ratio 1:4, concentration of NaOH solution 300 g/L. The irradiation times chosen were 3 min, 3.5 min, 4 min, 4.5 min and 5 min respectively. The test result is as shown in Figure 4, Table 5 and Table 6.

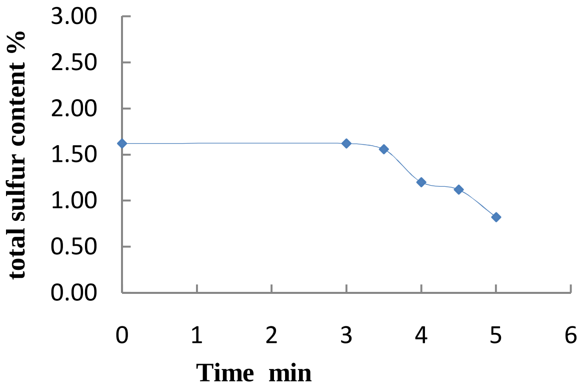


Figure 4 Effect of irradiation time on total sulfur content of desulfurized coal

From Figure 4, with the increase of the irradiation time, the content of sulphur in clean coal decreased subsequently and reached the lowest, 0.82%, at 5 min. Therefore, the increase of the irradiation time facilitates the desulfurization reaction.

Table 5 Effect of irradiation time on various forms of sulphur

Time, min	Content of sulfur,%				Clean coal yield, %	Desulfurization rate, %
	$S_{t,d}$	$S_{s,d}$	$S_{p,d}$	$S_{o,d}$		
Raw coal	1.62	0.11	0.94	0.57	-	-
3	1.62	0.04	0.98	0.60	92.50	7.50
3.5	1.56	0.07	0.93	0.56	88.44	14.84
4	1.20	0.05	0.58	0.57	89.85	33.44
4.5	1.12	0.16	0.39	0.57	90.00	37.78
5	0.82	0.24	0.19	0.41	87.78	55.57

Based on the analysis on various forms of sulphur in the clean coal (Table 5), it is discovered that the content of the pyritic sulphur and the content of organic sulphur decrease with the increase of the irradiation time and the sulfate sulphur will first decrease and then increase. And the rules showed by the sulfate sulphur, pyritic sulphur, and organic sulphur in desulphurized clean coal after increasing the irradiation time are similar to those after increasing the microwave power. It indicates that increasing the microwave energy inputted to the reaction system can reduce pyritic sulphur and organic sulphur in coal, promote their conversion into sulfate sulphur, and improve the reaction between pyritic sulphur and NaOH and then strengthen the desulfurization effect.

Table 6 The change of proximate analysis indexes of coal with irradiation time

Time, min	M_{ad}, %	A_d, %	V_{daf},%
Raw coal	1.48	11.20	9.50
3	0.80	9.15	8.89
3.5	0.53	7.90	9.12
4	0.84	7.24	8.97
4.5	0.53	7.86	9.30
5	1.47	8.54	9.55

From Table 6, compared with the raw coal, the ash content of the clean coal decreased somewhat and reached as low as 7.24% (4 min) while the volatile components reached the lowest. And the volatile content of the desulphurized clean coal increased compared to that of the raw coal under the condition of optimum desulfurization time (5 min). It was indicated that Increasing the input of the microwave energy can reduce the ash content and also has an slight effect on the macromolecular structure of coal.

Effect of the solid-to-liquid ratio on the desulfurization result

The effect of solid-to-liquid ratio on the desulfurization result was studied under the conditions of microwave power 1000 W, irradiation time 5 min, and alkali liquor 300g/L. The sulphur content in the clean coal and content of various forms of sulphur are as shown in Figure 5 and Table 7.

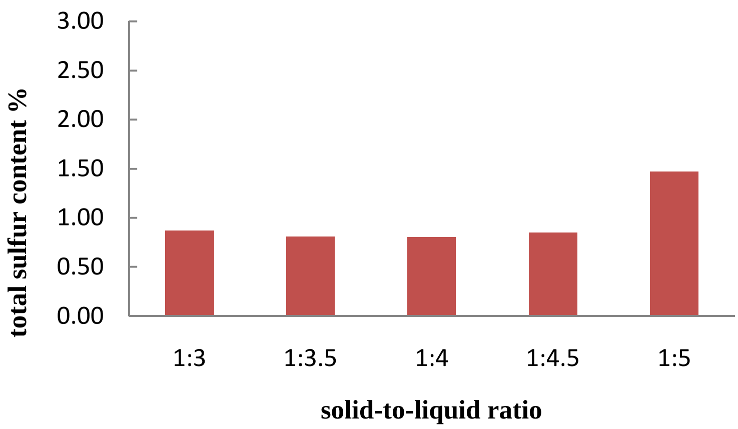


Figure 5 Effect of solid-to-liquid ratio on total sulfur content of desulfurized coal

Table 7 Effect of solid-to-liquid ratio on various forms of sulphur

solid-to-liquid ratio	Content of sulfur, %				Clean coal yield, %	Desulfurization rate, %
	$S_{t,d}$	$S_{s,d}$	$S_{p,d}$	$S_{o,d}$		
Raw coal	1.62	0.11	0.94	0.57	-	-
1:3	0.87	0.19	0.29	0.39	90.54	51.38
1:3.5	0.81	0.18	0.26	0.37	89.80	55.10
1:4	0.80	0.23	0.19	0.38	88.60	55.70
1:4.5	0.95	0.10	0.45	0.40	87.98	48.41
1:5	1.47	0.07	0.86	0.54	89.74	18.57

From Figure 5, there was a relatively complex trend in the effect of solid-to-liquid ratio on the sulphur content in the clean coal. The sulphur content in the clean coal was 0.87% when the solid-to-liquid ratio was 1:3. When the solid-to-liquid ratio reached 1:4 the sulphur content in the clean coal was 0.80% exhibiting a small decreasing amplitude. The desulfurization trend would become poor when the solid-to-liquid ratio was increased subsequently, and the sulphur content in the clean coal was 1.47% when the solid-to-liquid ratio was 1:5.

An analysis was conducted for various forms of sulphur in the desulphurized clean coal under different solid-to-liquid ratios to explain the test result. As shown in Table 7, under the optimum solid-to-liquid ratio for desulfurization(1:4), the content of sulfate sulphur, pyritic sulphur, and organic sulphur in the desulfurized clean coal were 0.23%, 0.19% and 0.38% respectively. When the solid-to-liquid ratio was less than 1:4, the content of pyritic sulphur and organic sulphur in the clean coal would further decrease with the increase of ratio indicating that the addition of alkali liquor could promote their conversion and decomposition; when the ratio was more than 1:4, the energy used for conversion and decomposition of pyritic sulphur and organic sulphur would decrease and the desulfurization would be unsatisfactory due to the fact that excessive amount of alkali liquor had to absorb partial microwave energy but the microwave energy inputted was limited.

From Table 8, based on the result of a proximate analysis of the desulphurized clean coal, under the chosen test conditions, there was an slight effect of ash reduction for the coal. The ash content reached the lowest when the solid-to-liquid ratio was 1:4.5. The volatile components in the clean coal increased somewhat when the solid-to-liquid ratio was less than 1:5, but decreased when 1:5.

Table 8 The change of proximate analysis indexes of coal with solid-to-liquid ratio

solid-to-liquid ratio	M_{ad}, %	A_d, %	V_{daf}, %
Raw coal	1.48	11.20	9.50
1:3	1.59	9.51	9.79
1:3.5	0.79	8.44	9.57
1:4	0.87	8.47	9.45
1:4.5	0.54	7.64	9.51
1:5	1.00	8.34	8.90

Effect of concentration of NaOH solution on the desulfurization result

The concentration of NaOH solution was another important factor influencing desulfurization when added as an extracting agent. Under the conditions that were progressively optimized, the effect of alkali liquor concentration on the desulfurization result was investigated. The test result is as shown in Figure 6, Table 9 and Table 10.

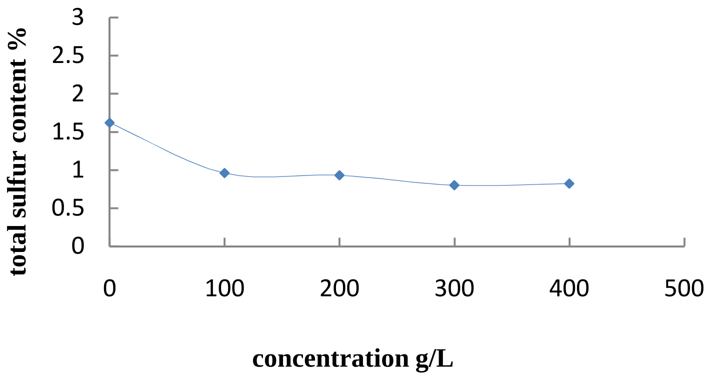


Figure 6 Effect of the concentration of NaOH solution on total sulfur content of desulfurized coal

From Figure 6, the addition of NaOH solution can improve the desulfurization result. But when it was more than 300 g/L, the sulphur content in the clean coal basically remained unchanged. Any further increase of the alkali liquor concentration would cause "waste" of NaOH solution. Thus, the best alkali liquor concentration should be 300 g/L.

Table 9 Effect of the concentration of NaOH solution on various forms of sulphur

Concentration, g/L	Content of sulphur, %				Clean coal yield, %	Desulfurization rate, %
	$S_{t,d}$	$S_{s,d}$	$S_{p,d}$	$S_{o,d}$		
Raw coal	1.62	0.11	0.94	0.57	-	-
100	0.96	0.14	0.39	0.43	85.36	49.42
200	0.93	0.11	0.34	0.48	90.14	48.25
300	0.80	0.21	0.18	0.41	89.64	54.63
400	0.82	0.19	0.24	0.39	89.27	54.81

Table 9 presents the content of various forms of sulphur in the desulphurized clean coal under different alkali liquor concentrations. The content of the sulfate sulphur in the clean coal was the highest and the content of pyritic sulfur and the content of the organic sulphur were the lowest when the alkali liquor concentration was 300 g/L.

Table 10 The change of proximate analysis indexes of coal with the concentration of alkali liquor

Concentration, g/L	M_{ad}, %	A_d, %	V_{daf}, %
Raw coal	1.48	11.20	9.50
100	1.12	13.06	10.21
200	1.19	8.91	9.36
300	1.62	8.51	9.64
400	1.72	8.01	9.04

Table 10 presents the result of the proximate analysis of the desulphurized clean coal. It can be seen that all the ash contents in the clean coal decreased somewhat except the concentration of 100 g/L. The ash content after desulfurization also changed but the differences were not significant.

CONCLUSION

The paper studies the effects of the microwave power, irradiation time, solid-to-liquid ratio, and the alkali liquor on the coal desulfurization result and proximate analysis index and obtains the following conclusions:

With the irradiation time extending, the total sulphur in clean coal decreased, and the increase of microwave power helps removal of sulphur in coal. But the excessive increase of irradiation time and power shall be inadvisable in consideration of coal properties. There is an optimum value for the amount of NaOH added, and an excessively higher solid-to-liquid ratio will reduce the desulphurization result. And the coal desulphurization rate will increase when the alkali liquor concentration is increased within a certain range but the desulphurization result tends to be stable when it exceeds 300 g/L , however, an excessive amount of alkali liquor contributes to reduction of ash in coal.

The content of total sulfur in the desulfurated clean coal falls to around 0.80%, the content of organic sulfur in the clean coal is around 0.40%, and the content of the pyritic sulphur falls to around 0.18% under the best conditions (microwave power 1000W, irradiation time 5 min, solid-to-liquid ratio 1:4, alkali liquor concentration 300 g/L). The ash content and volatile components of the the desulfurated clean coal also change while desulfurization. The ash content of the desulphurized clean coal exhibits an overall decreasing trend but the decreasing amplitude is not significant, which indicates that the method of microwave combined with NaOH solution also plays a role in ash reduction as well as in desulfurization. The changes in volatile components are also not significant, which indicates that the molecular structure of the coal also changes slightly during sulphur removal.

Acknowledgements
The authors would like to thank the National Natural Science Foundation of China (Grant No. 51274199) and the Specialized Research Fund for the Doctoral Program of Higher Education (Grant No. 20130095110008) for their support in this research.

REFERENCES

[1] Sagar A D, Chamle S N, Yadav M V. *Journal of Chemical & Pharmaceutical Research*, **2013**, 5(7):156-160.
[2] Aravind K, Ganesh A, Ashok D. *Journal of Chemical & Pharmaceutical Research*, **2013**, 5(6):34-39.
[3] Ashraf F, Khajuria R, Khan K Z. *Journal of Chemical & Pharmaceutical Research*, **2013**, 5(8):33-36.
[4] Al-Harahsheh M, Kingman S W. *Hydrometallurgy*, **2004**, 73(3): 189-203.
[5] Remya N, Lin J G. *Chemical Engineering Journal*, **2011**, 166(3): 797-813.
[6] Mutyala S, Fairbridge C, Pare J R, *et al*. *Fuel Processing Technology*, **2010**, 91(2): 127-135.
[7] Royaei M M, Jorjani E, Chelgani S C. *International Journal of Coal Preparation and Utilization*, **2012**, 32(3): 143-155.
[8] Xia W C, Yang J G, Liang C. *Powder Technology*, **2013**, 233: 186-189.
[9] Han L C, Li E, Guo G F, *et al*. *Progress In Electromagnetics Research Letters*, **2013**,37:177-87.
[10] Uslu T, Atalay Ü, Arol A I. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **2003**, 225(1): 161-167.
[11] Waters K E, Rowson N A, Greenwood R W, *et al*. *Separation and purification technology*, **2007**, 56(1): 9-17.
[12] Weng S, Wang J. *Fuel processing technology*, **1992**, 31(3): 233-240.
[13] Zhao H, Li Y, Qu Y, *et al*. Experimental study on microwave desulfurization of coal[C]//Materials for Renewable Energy & Environment (ICMREE), **2011** *International Conference on. IEEE*, **2011**, 2: 1706-1710.
[14] Jorjani E, Rezai B, Vossoughi M, *et al*. *Fuel*, **2004**, 83(7): 943-949.
[15] Mohamed W. Desulfurization of south African coal using low power microwave energy. Ph.D. diss., University of the Witwatersrand Johannesburg, **2008**.
[16] Zhou M, Yang X, and Song L Q. *Journal of HeNan Polytechnic University*, **2013**,32:760-763.
[17] Zhao J L., Zhang Y Y, Chen Q Y. *J. Microwaves*,**2002**,18:80-84.