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The application of Zinc catalyst in the coal thermal solvent extraction

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The application of Zinc catalyst in the coal thermal solvent extraction

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Abstract. Lewis-acid Zinc metal salt as catalyst, catalytic performance of thermal extraction was studied on Sima lean coal. The effects of different Zinc catalysts on the extraction rate of Sima lean coal were investigated in the conditions of extraction temperature 380℃, the solvent coal ratio was 6:1, and the residence time was 30min.The results showed that $ZnSO_4$ can improve the thermal extraction rate of high rank coal to 46.1%, and the optimal quantity of catalyst was 5%. Recovered $ZnSO_4$ can be recycled, and had good catalytic performance.

1. Introduction

The thermal solvent extraction of coal is the process of extraction super clean coal with organic solvent at high temperature. Research group of Yong-qi Hu found that organic molecules of coal can dissolve in the solvent, and the solid super clean coal was obtained by the solvent processing [1-2]. Shanxi Sima lean coal is a kind of slightly-caking coal, it can be observed that the coal sample is not coked during coking test; Glial layer determination of the mix coal（20% super clean coal with 80% Sima lean coal) showed that the sample has good coking value and was in a state of complete fusion [3]. This result makes it possible to concentrate more weak caking coal and non-caking coal in coking production [4].

At present, the research focus at home and abroad is limited to different organic solvents and technological conditions. For example, Rahman et al. [5] found that the use of polar solvents can achieve higher extraction rates than the use of non-polar solvents. Takanohashi et al. [6] investigated the effects of different types of acids on metal ions and ash content in coal. It was found that acid pretreatment of coal samples could improve the thermal extraction rate of solvents. Takanohashi et al. [7-8] studied the effects of extraction temperature and time on the extraction rate, and found that the extraction rate increased significantly with the increase of extraction temperature. However, these studies are mainly aimed at low rank coal.

High rank coal is coal with a deeper degree of coalification [9-11].As the degree of coal metamorphism increases, the degree of aromatization of coal increases and the coal structure is more ordered [9]. Therefore, the conventional thermal extraction reaction is difficult to destroy the covalent bond and hydrogen bond in the high-order coal macromolecular skeleton, resulting in a low thermal extraction rate. Meager lean coal is typical high rank coal with deeper degree of coalification. Because of the weak caking property, the meager lean coal is classified as inferior coking coal [12]. In the coking process, the mix of super clean coal with meager lean coal showed excellent coking performance [13-14]. So how to develop the utilization of meager lean coal is our concern.

During research we found that the catalyst can increase the rate of high rank coal extraction. Because there is no relevant research in China, it is of great significance to find efficient and cheap catalysts. This paper will study the application of catalyst in high rank coal.

2. Experiment

2.1. Coal sample

Sima lean coal, Wuhai lean coal and Sanjizhuang lean coal were used in this study. According to the national standard GB474 - 1996 for sample preparation, the coal samples were crushed, divided and dried at 100°C vacuum conditions for 150 min. They were stored in a desiccator, low temperature and avoiding light. Coal proximate and ultimate analysis data is shown in Table 1.

Table 1. Proximate and ultimate analysis of samples%.

Sample	Proximate analysis / %[a]			Ultimate analysis / %[a], daf				
	Mad	Aad	Vad	C	H	O[b]	N	S
WH	1.47	10.88	27.19	74.95	4.01	5.41	1.32	1.96
SJ	3.24	9.38	14.44	92.29	4.09	1.57	0.96	1.09
SM	0.91	9.05	13.06	90.78	4.21	3.00	1.60	0.41

[a] Percent of weight
[b] By difference

2.2. Experimental method

The experiments were carried out in a thermal extraction device which was designed by us [2]. A certain size of coal sample was added in an autoclave after full mixing with the industry washing oil. The coal was extracted at a certain temperature in N_2 atmosphere for 30min. After a period of constant temperature, rely on the pressure between upper and lower autoclave to heat filtration. The residue was on the upper reactor, the lower is the extraction; the super clean coal in extraction was extracted by the anhydrous ethanol and the wash oil also was recycled. The residue was detected by method B in the determination of ash according to GB212-1991 "industrial analysis method of coal", and the ash content of super clean coal is 0.02%. Based on literature’s calculation method of thermal extraction rate [14], the data given in the paper for the extraction rate are all under the dry ash-free basis.

3. Results and discussion

3.1. Coal's influence on extraction rate

The influence of $ZnCl_2$ on thermal extraction was investigated under the conditions of extraction temperature 380 °C, the mass ratio of solvent to coal was 6:1, the mass of $ZnCl_2$ was 15% of coal quality, and the residence time was 30min. As is can be seen in Figure 1, the extraction rates of different kinds of lean coal have been increased greatly after adding catalyst. Among them, catalysts have the largest contribution to Wuhai lean coal, its extraction rate was increased 15.6%. Because different lean coals have different molecular structure, even in the same extraction, the extraction rate can be difference.

The chemical structure of modern coal shows that with the increasing of metamorphic grade, the number and the size of condensed aromatic in coal are also increase. Under the thermal extraction conditions, $ZnCl_2$ was in molten state, and its strong Lewis acidity have high catalytic cracking activity, that can break the condensed aromatic structure without destroying the structure of monocyclic product, resulting in more weaker binding aliphatic chain and ether bond be broken in the thermal extraction process, and the extraction rate is obviously improved.

As can be seen in Table 1, among three kinds of lean coal, Wuhai lean coal have higher oxygen content, in the process of thermal extraction, oxygen-containing functional groups such as carboxyl, hydroxyl, carbonyl, methoxyl, ether group and other small molecule organic matter can be break easily from the aromatic and become free radical fragments then extracted by organic solvent. Moreover, the volatiles of Wuhai lean coal are relatively high, leading to more free radical fragments dissolved in the extraction solvent.

3.2. *Effect of Catalyst on Extraction Rate*

The effects of different Zinc catalysts on the extraction rate of Sima lean coal were investigated in the conditions of extraction temperature 380 °C, the mass ratio of solvent to coal was 6:1, the residence time was 30min. The results are shown in Figure 2. It can be seen that the extraction rate of coal without catalyst is 19.3%, and the extraction rate improved obviously when catalyst added. The extraction rate is 46.1%, after using $ZnSO_4$ as catalyst.

The influence of $ZnSO_4$ which used as catalyst on extraction rate was investigated, and the result is shown in Figure 3. It can be seen that with the increase of catalyst mass, the extraction rate increase firstly and then decrease. When catalyst used too small, a considerable part of organic molecules in coal molecules are not break, While used too much, the catalytic effect is exacerbated, fragments were broke into smaller molecules and turn to pyrolysis gas leading to the reduced of extraction rate. The extraction rate came to the highest when catalyst mass was 5%.

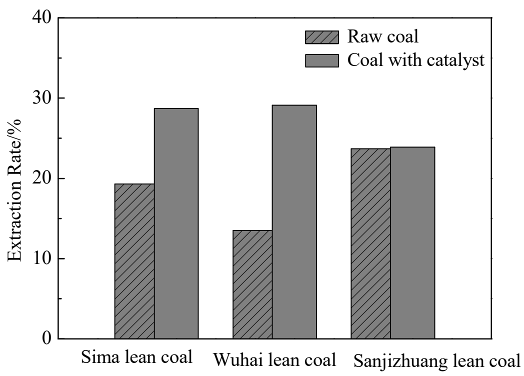

Figure 1. Coal's influence on extraction rate.

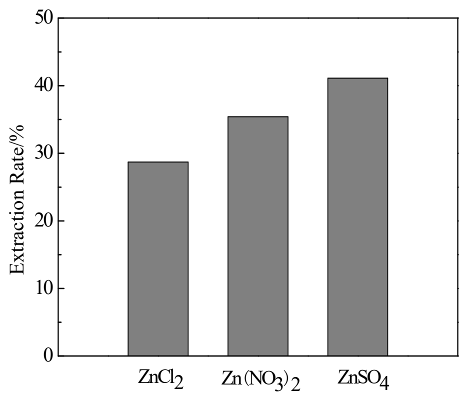

Figure 2. Effect of Catalyst on Extraction.

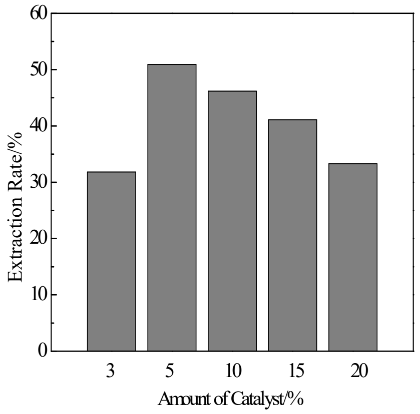

Figure 3. Effect of catalyst dosage on extraction rate.

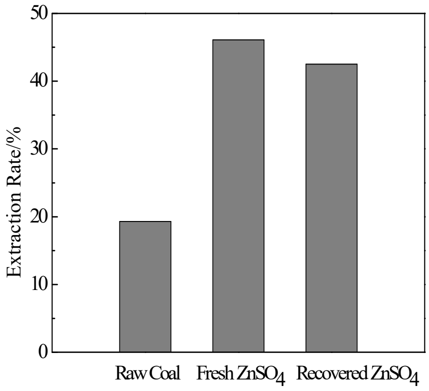

Figure 4. Recovery catalyst catalytic effect.

3.3. Catalyst recovery and recycling use
The residue and extract were washed with distilled water to obtain the combined liquid, and the catalyst in combined liquid was extracted with anhydrous ethanol. The recovered catalyst, still used into the thermal extraction experiment, the result is shown in Figure 4. It can be seen that the extraction rate is 42.5% with the recovered catalyst, which is slightly lower than the fresh catalyst extraction rate 46.1%, that maybe caused by slightly loss of the catalyst during the recovery process. X-ray diffraction was carried out to determine the recovery of catalyst active component, and the result is shown in Figure 5. It can be seen the active ingredient in recovery catalyst is still $ZnSO_4$.

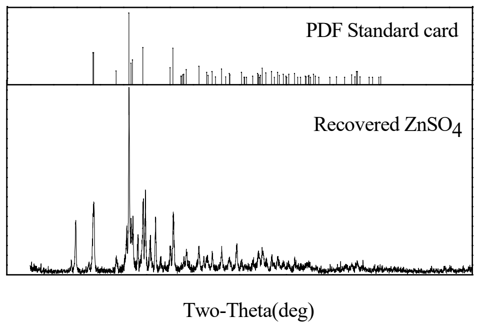

Figure 5. Comparison of recovered $ZnSO_4$ and $ZnSO_4$ standard card.

4. Conclusions

1. Using typical Lewis-acid metal salt $ZnCl_2$ as catalyst, thermal solvent extraction of three kinds of high rank coal was investigated, the extraction rate were all improved.

2. Using Zinc metal salts as catalyst, thermal extraction of Sima lean coal was investigated. $ZnSO_4$ have the best catalytic effect, the extraction rate come to 46.1% with the optimal quantity of catalyst 5%.

3. Recovered $ZnSO_4$ also have good catalytic performance compared with fresh $ZnSO_4$, XRD analysis showed that the active ingredient in recovery catalyst is still $ZnSO_4$.

References

[1] Cui Y M, Zhao F Y, Zhang Z X, et al 2014 Research progress on preparation of ultralow-ash coal by solvent thermal extraction *J. Modern Chemical Industry* **34(4)** 34
[2] Cui Y M, Hu Y Q, Xu Y Q, et al 2014 Study on Super Clean Coal Preparation Technique with 1 /3 Coking Coal from Xiaokang Village by Heat Extraction *J. Coal Science and Technology* **42(1)** 121
[3] Cui, Y. M., Xu, Y. Q., Hu, Y. Q. et al. 2013 Preparation and characterization of super pure coal. *J. Advanced Materials Research* **2657 (798)** 49
[4] Luda R, Quan R 2008 Low-quality coal coking using thermal solvent extraction. *J. Fuel&Chemical Processes* 39 (6) 54
[5] Rahman M, Samanta A, Gupta R 2013 Production and characterization of ash-free coal from low-rank Canadian coal by solvent extraction. *J. Fuel Processing Technology* **115** 88-98
[6] Zhang L, Takanohashi T, Saito I, et al. 2008 Coordination structures of organically bound paramagnetic metals in coal and their transformation upon solvent extraction *J. Fuel* **87(11)** 2628-2640
[7] Li C Q, Takanohashi T, Yoshida T, et al. 2004 Elucidation of mechanisms involved in acid pretreatment and thermal extraction during ashless coal production. *J. Energy＆Fuels* **18(1)** 97-101
[8] Shi Z J, Zhang S Z, Xing L Y et al. 2009 Thermal extraction performance of low rank coal in coal liquefaction derived oil. *J. Coal Conversion* **32(1)** 34-39
[9] Zhang S, Zhang X D 2016 Chemical composition and Structure change of high rank coal under different solvent extraction. *J. Coal Conversion* **39 (3)** 1
[10] Liu S Q, Sang Sh X, Wang G et al. 2017 FIB-SEM and X-ray CT characterization of interconnected pores in high-rank coal formed from regional metamorphism *J. Journal of Petroleum Science and Engineering* **148** 21
[11] Shan C G, Zhang T S, Guo J J et al. 2015 Characterization of the micropore systems in high-rank coal reservoirs of the southern Sichuan Basin, China *J. Royal Society* **99 (11)** 2099
[12] Zhang X H, Chen P, Xu G M et al. 2016 Analysis of blending technology on the weakly caking coal with low volatile *J. Wisco Technology* **54 (5)** 13
[13] Ren X Y, Zhang D L, Wang K et al. 2016 Study on Vitrinite Properties of Different Rank Coking Coals *J. Anhui University of Technology* **33 (1)** 38
[14] Seiji N, Merrick M, Koichi F et al. 2010 The mechanism of coking pressure generation: Effect of high volatile matter coking coal, semi-anthracite and coke breeze on coking pressure and plastic coal layer permeability *J. Fuel* **89** 1549