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Investigation of grafted sulfonated alkali lignin polymer as dispersant in coal-water slurry

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ABSTRACT

A novel grafted sulfonated alkali lignin polymers (GSAL) with hydrophilic side chain and different molecular weights prepared were used as dispersants for coal-water slurry (CWS). The viscosity reduction for CWS had been attributed primarily to the diminution of coal particles (adsorbed GSAL) interaction of steric electrostatic repulsion and dramatic wettability. The adsorption amount of GSAL-3 can reach to 1.58 mg/g, and the isotherm of GSAL on coal surface belongs to the Langmuir model, the electrostatic self-assembly result indicated the dominant driving force of GSAL absorbed on coal surface was the π–π interaction. GSAL was superior in reducing the viscosities of CWS.

Introduction

Coal-water slurry (CWS) consists of about 60-70% coal, 30% water and 1% chemical additives. As one of the ideal alternatives to fuel oil, the high concentrated CWS should possess an excellent fluidity and stability like fuel oil. However, CWS belongs to a thermodynamic and unstable dispersed system, so it can easily form aggregate structures which enclosing lots of water and result in increasing the viscosity and decreasing the fluidity of CWS. Since the dispersant can absorb on coal particles and change the surface properties of coal to improve the stability and rheological properties of CWS, the dispersant is a key factor for preparing CWS.

At present, the main type of dispersants for CWS includes naphthalene sulphonate formaldehyde condensate [1] (NSF), polystyrene sulfonate, humic acids [2], lignosulfonate [3], sulfonated acetone–formaldehyde condensate [4] (SAF), polycarboxylic acid [5], etc. Recent researches showed that the molecular structures of dispersants such as molecular weight, the functional group such as sulfonic group have great influences on the viscosity and stability of CWS. Sirkeci et al. [6] found that anionic type of dispersant with different hydrophilic groups can increase the electronegativity of the coal surface and be beneficial for reducing the viscosity of CWS. Moreover, the sulfonic group in the dispersants molecules can form chemical bonds between coal particles and dispersants, thus can improve the stability and rheological properties of CWS. For NDF (methylene naphthalene sulfonate–styrene sulfonate–maleate copolymer), the higher molecular weight would be better in reducing the viscosity of CWS [3]. Sodium lignosulfonate is a by-product from sulfite pulping and has been used as dispersant in CWS, when its molecular weight is ranging from 10,000–30,000, it has both a higher adsorbed amount and zeta potential on the coal surface and performs well in reducing the viscosity of CWS [7] and the molecular weight of sodium lignosulfonate obviously affect the viscosity and rheological properties of CWS [8,9].

Lignin exists in plants' cell walls and is the second abundant organic polymer containing benzene ring in the plant kingdom. In pulp and papermaking process, an enormous amount of industrial lignin exists in pulping waste liquor some in pretreatment bath of biomass ethanol product process [10], which is considered as a kind of by-product. Alkali lignin is the main component of alkaline pulping black liquor which accounts for about 90% pulping waste liquor. Generally, a 1 ton by-product of alkali lignin is produced when producing 1 ton of pulp during the pulping process [11]. Due to the advantages it being a rich source and is cheap, the application of alkali lignin as chemicals materials can effectively

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alleviate the shortages of oil resources and environmental pollution problems. In the last few years, alkali lignin has been modified to apply in areas. Shujun Li [12] synthesized phenol-formaldehyde resin using lignin. Hongming Lou [13] explored modified lignin as lignocellulosic substrate to reduce non-productive adsorption of cellulase and enhancing enzymatic hydrolysis of lignocelluloses. Karthikeyan [14] examined lignin for metal sorption as a function of solution chemistry and reaction time. Lots of alkali lignin has been modified by chemical methods used for dispersant, such as cement water-reducing agent [15], pesticide dispersant [16], CWS dispersant [17].

However, alkali lignin has insolubility in water at neutral or acid conditions, due the lack of an effective amount of hydrophilic groups, and which limits its application as CWS dispersant. Sulfonation modification is the simplest way to improve its water-solubility and physicochemical properties, and the increase in the molecular weight of alkali lignin can improve its adsorption and dispersion properties by polycondensation reaction. However, during the drastic isolation procedures of lignin and pulping processes employed for delignification, its various linkages may be broken or polymerized, the chemical reaction activity of alkali lignin decreases so that the sulfonation and polycondensation reaction of alkali lignin was always carried out under the high pressure and high temperature [18]. Moreover, the sulfonation and polycondensation of alkali lignin are both more likely to react on the ortho position of the phenolic hydroxyl group in lignin, and the competition of sulfonation and polycondensation makes it quite difficult to synthetize the lignin-based dispersant having both high sulfonation degree and high molecular weight [17]. The molecular weight and the sulfonation degree of sulfonated alkali lignin are quite low, and its weight average molecular weight M_w is usually lower than 10,000 Da and the sulfonation degree is below 2.0 mmol/g. How to increase the content of sulfonic groups and molecular weight simultaneously would be the key factors for preparing high-performance lignin-based CWS dispersants.

The objective of the present study was to prepare grafted sulfonated alkali lignin polymer (GSAL) with higher sulfonic groups and molecular weight and investigate the influence of the molecular weight on its properties and its adsorption mechanism.

The alkali lignin was obtained from the bamboo-pulp paper-making black liquor. GSAL was developed by sulfomethylation, etherification and polycondensation modification. A series of GSAL samples with different molecular weights were obtained by adjusting the reaction process parameters. The structure of GSAL-3 was characterized by FT-IR, ^{1}H NMR and gel-permeation chromatography. The influence of molecular weights of GSAL on the properties of CWS was investigated by determining the rheological performances. The adsorption characteristics and action mechanism of GSAL on coal particle were further discussed by the investigations of surface tension, the electrostatic self-assembly, zeta potential and contact angle.

Materials and methods

Alkali lignin, dispersant and coal

Alkali lignin (AL) was isolated from bamboo-pulp papermaking black liquor, which was kindly supplied by a paper mill (Hunan province, China); it was composed of approximately 70% lignin, about 10% reductive substances, and low molecular weight organic compounds, inorganic salts and other impurities.

Lignin based dispersant, grafted sulfonated alkali lignin (GSAL), used in this study was synthesized from alkali lignin using sulfomethylation, etherification and polycondensation modification.

The naphthalene sulfonate formaldehyde condensate (FDN, commonly used as a dispersant of CWS and supplied by Zhanjiang additive company in Guangdong province, China) was used for comparison.

Coal sample obtained for this study was a kind of brown coal named Shenhua coal (Shanxi province, China). On the basis of the pretreatment of coal reported by Qiu et al. [19], the pretreatment of the coal is as follows: firstly, the coal was crushed in a jaw crusher to obtain coal particle below 10 mm, then the coal particles were dried under vacuum at 105 °C for 24 h. The crushed dry coal was comminuted in the ball mill (dry grinding) for 40 min or 3 h. Then, the obtained coal powder was screened through a 70-mesh (0.212 mm) or 100-mesh (0.150 mm) screener, respectively. The two powders with different particle size distribution were mixed according to 1:1 when preparing CWS.

The elemental and proximate analyses of the coal are given in Table 1. The BET surface area of coal powder is 12.30 m^2/g (N_2 adsorption, Micromeritics ASAP2010, USA) and the average particle size is about 16.74 μm (Malvern Mastersizer 2000). As can be observed from Table 1 Shenmue coal powder has high inherent moisture and O/C. It was considered to be a kind of low rank coal, which is difficult to prepare CWS with a good dispersion performance.

Synthesis of GSAL

GSAL used in this study was synthesized using alkali lignin as main material. The sulfonation of ligninis carried out by a conventional process, which involves the sulfonation of alkali lignin with sulfomethylation with a mixture of sulfite. The process consists of three steps: sulfomethylation, etherification and grafting and poly reaction.

The first step is sulfomethylation. Alkali lignin was dissolved in distilled water in the flask. After stirring, 5% (w/w) NaOH solution was used to adjust the pH to 10.0 hydrochloric acid and sodium hydroxide, and the concentration was 30 wt%, and then the mixture was heated to 60 °C, formaldehyde aqueous solution (37 wt%) and sodium bisulfite were fed into the reactor by means of a dropping funnel for sulfomethylation reaction for 1 h (Scheme 1). In the second step, formaldehyde and acetone were added to gain dihydroxy acetone for etherification reaction for 1 h, holding the temperature at 65 °C and pH is 10.0 (Scheme 2). Finally, hydroxyl sulfonic acid sodium was grafted. Sodium bisulfite reacting with dihydroxy acetone at 65 °C and pH is 10.0 to gain the intermediates hydroxyl sulfonic acid sodium (Scheme 3). Subsequently, the intermediates and the formaldehyde aqueous solution of 37% concentration were added, the temperature was raised to 90 °C and the reaction continued for 3 h. The GSAL was obtained after cooling, according to the above procedure (Scheme 4). GSAL-1–GSAL-6 with different molecular weight were synthesized by controlling the mass concentration of solution in the condensation reaction.

Structure characterization of dispersants

Infrared and ^{1}H-NMR spectrum analyses

Infrared (FTIR) spectrum were obtained on a potassium bromide pellet (1.5/300 mg) using a NicoLet 380 FT-IR spectrometer (Thermo

Table 1
Proximate and ultimate analyses of coal samples on air dried basis.

Proximate analysis (wt%)				Ultimate analysis (wt%)			
Inherent moisture	Ash	Volatile matter	Total sulfur	C	H	O	N
7.16	8.14	34.77	0.50	81.97	4.64	11.96	0.91