# Quantitative Analysis and Performance Evaluation of Lignosulfonate as a Comprehensive Experimental for Environmental Education

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**Abstract:** The effective content of lignin in industrial lignin determines the properties of lignin products, which is of great significance to understand the performance of lignin products. In this experiment, industrial lignin was used as raw material to prepare green drilling fluid treatment agent lignin by chromatography column, and the effect of lignin as drilling fluid additive before and after separation was evaluated. In addition, the experiment include organic chemistry knowledge, oilfield chemistry and experimental teaching, which is beneficial to improving the comprehensive experimental skills of undergraduate students and facilitating the development of green environmental protection concept and guiding the cleaner production of oil field in the future.

## 1. Introduction

Lignin is an aggregates that are complex and difficult to hydrolyze. The three major natural polymer compounds that make up the plant skeleton are composed of the lignin, cellulose and hemicellulose, their weight is about 20% of the weight of the plant. In addition, the world can produce a large number of lignin that are cheap, no-toxic and pollution-free, so it are excellent raw materials of green chemistry[1,2]. The massive paper pulping waste fluid will be produced in paper-making industry and the lignin that is extracted from paper pulping waste fluid is called as the industrial lignin[3,4]. Thus, lignin extracted from industrial lignin not only has low cost and renewable degradation, but also has many kind of active functional group, so it has attracted much attention. For example, the main chemical components of lignin are lignosulfonate (Figure 1) and alkali lignin with some surface active groups, such as hydrophilic groups of carboxyl and phenolic hydroxyl groups and hydrophobic groups of propyl and benzene rings. Thus, the lignin has become potential raw material of the green chemistry in oilfield chemicals, surfactants, environmental protection corrosion inhibitors and bitumen modification agents[5-9]. Zhang[10] modified the lignosulfonate with formaldehyde, and it is found that the modified hydroxymethylated lignin sulfonate had a viscosity-raising effect on the base slurry at room temperature and the effect of viscosity reduction and filtration loss after high-temperature aging. Aminated lignin can effectively improve the looseness of oil field sludge and increase the water absorption of oil field sludge[11]. Chen[12] prepared a series of lignin sulfonate Mannich base drilling fluid treating agents using lignin sulfonate, formaldehyde and primar/secondary amine, the results show that these compounds can increase viscosity, reduce filtration and resist high temperature in water-based drilling fluid. At present, industrial lignin still contains impurities such as semi-cellulose, inorganic salt and oligosaccharide of deep color, which may have a large influence on the performance of industrial lignin-derived products. In addition, if lignin is used in the fields of cosmetics and detergents, the quality of industrial lignin must be made higher. Therefore, in this paper, industrial lignin was separated and purified by chromatography column to obtain high concentration lignin, and then industrial lignin and purified lignin were added into water-based drilling fluid to evaluate the performance of drilling fluid, finally, the differences and reasons of lignin in drilling fluid before and after purification were analyzed.

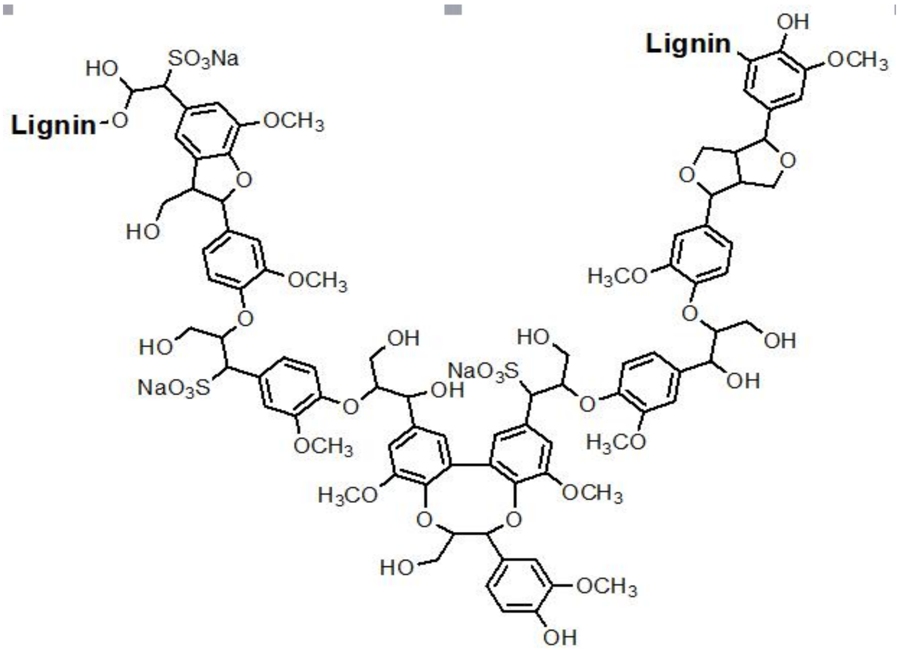

Figure 1 Molecular structure of lignosulfonate

## 2. Design of the Experiment

### 2.1. Purpose

(1) Master the chemical structure and related properties of lignin.

(2) Separation and purification of Industrial lignin by similarity dissolution principle.

(3) Master the function of drilling fluid and the use of common instruments (six-speed rotary viscometer, funnel viscometer, filter, etc.).

(4) The reasons for the change of main performance parameters of drilling fluid are analyzed by means of experimental data and literature review.

### 2.2. Principle

Drilling fluid is the "blood" of drilling. The drilling fluid should have the functions of suspending and carrying cuttings, cooling and lubricating drilling tools, stabilizing wellbore and balancing formation pressure, transferring hydrodynamic force, etc. The lignin-based drilling fluid additive is often used as a diluent for drilling working fluid due to its multi-hydroxyl property, which is mainly used for reducing the viscosity of the drilling fluid, preventing the occurrence of the condition of the card drill and the mud bag, and improving the drilling time. In addition, the mechanism of the filter loss of the lignin is due to the adsorption of the multi-component hydroxyl in the lignin and the hydrophobic nature of the multi-element benzene ring in the well, so that the clay is adsorbed on the well wall and the pore diameter of the well wall is blocked, so that the loss of the fluid loss of the drilling fluid is reduced. The separation principle of column chromatography is to separate the components according to the difference of the adsorption force of the substance on silica gel. Generally, the more polar substances are easily adsorbed by silica gel, and the less polar substances are not easily adsorbed by silica gel. When the solvent is used for elution, the components with weaker adsorption force move out of the column first, and the components with stronger adsorption force move out of the column first. As shown in Figure 2.

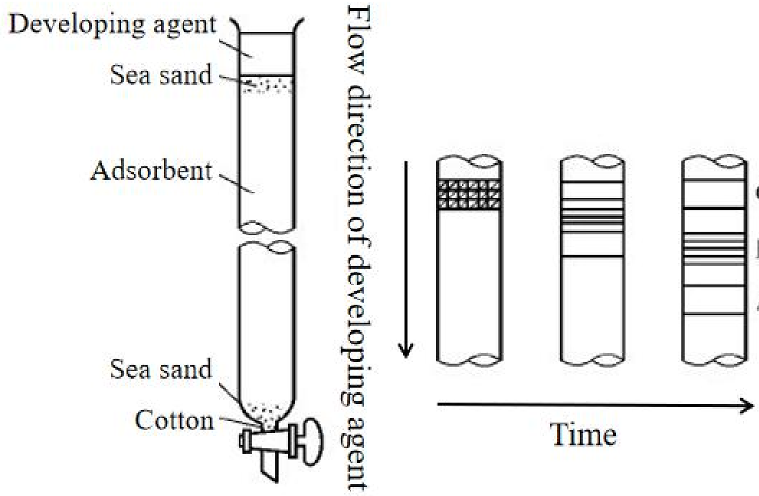


Figure 2 Mechanism of c column chromatography

**2.3. Materials and Instruments**

The industrial lignin were purchased from the market. Modified starch and PAM and CMC were supplied in domestic market. Bentonite was obtained from Changqing Chemical Engineering Group Co., Ltd., China.

**2.4. Purification of Lignin**

According to the mass ratio of 10:1, industrial lignin and silica gel (200 mesh, industrial grade) were weighed and packed in a chromatography column. 2g of industrial lignin was weighed and dissolved in 20 times of water to make an industrial lignin solution. The industrial lignin solution was uniformly poured on the top of the silica gel in the filled chromatography column. After the industrial lignin solution completely penetrated into the silica gel, a layer of silica gel was placed on top of the silica gel, and deionized water was added to elute the solution. The elution solution was received according to the color distribution until the brown part completely disappeared on the silica gel column, and the brown eluent was received in the second container. The light colored part before the brown eluent was received in the first container, and then sent to the silica gel column. Adding 0.05 mol/L hydrochloric acid, wash until the silica gel in the column becomes white, and receive the acid eluent in the third container. The $FeCl_3$ solution was added to the second container, and the color of the solution was significantly changed, so it was purified lignin. The solution received in the second container is evaporated to dryness and set aside.

**2.5. Preparation and Evaluation of Lignin Treated Water-based Drilling Fluid.**

**2.5.1. Preparation of Base Pulp**

Adding 3500 mL of clear water into the slurry mixing barrel, then adding 0.2% of sodium carbonate and 4.0% of clay, stirring for 2h, and standing for 24h for backup (Preparation shall be made in advance before the test).

**2.5.2. Effect of the Lignin on the Performance of Drilling Fluid-based Slurry**

Three cups of 350mL drilling fluid slurry were taken, 1.0% lignin before and after purification was added to the two parts, and the other cup of the base pulp was blank.

**2.5.3. Compatibility Evaluation**

1.0% the lignin before and after purification were added to 1% CMC, 1% Modified starch and 1% PAM treated pulp, respectively. The treated pulp was aged at room temperature for 6h after high speed stirring for 30min. The rheological properties, the non-volatile and the lubricating properties of the drilling fluid can be evaluated after the high-speed and uniform stirring.

### 2.5.4. Performance Evaluation of Drilling Fluid

The montmorillonite was dispersed in Sodium carbonate aqueous solution or tap water with a dosage of 4% (m/m), after stirring for 30min, it was handled for 16 hours at 298K, then the rheological performances and filter loss of drilling fluids were evaluated using a viscometer (ZNN-D6S, Haitongda, Co., Ltd., Qingdao), like AV(Apparent viscosity), PV(Plastic viscosity), YP (Yield point), FL(API Filtration) and tg (Friction coefficient). Depending on the National Standard GB/T 16783.1-2006 "Field testing of oil and gas industry drilling fluids-part 1: water-based drilling fluids", the performance of water-based drilling fluids was evaluated. The main evaluation properties include: apparent viscosity (AV), plastic viscosity (PV), dynamic shear force (YP), dynamic plastic ratio (YP/PV), filtration loss (FL), filter cake friction (tg) etc. [13].

### 2.5.5. Inhibitive Ability Evaluation

100mL 4% fresh water base pulp, 100mL4%KCl solution and 100mL 1.0% lignin treated pulp were prepared respectively First, the secondary sodium bentonite was dried in an oven at 105℃ for 4h. Secondly, 8.05g of the secondary sodium bentonite which had been dried was weighed and pressed by a tablet press at 10MPa for 5min to form a sample sheet. The sample was taken out and the sample thickness $h_2$ was measured. Finally, the sample expansion amount $h_1$ was measured within 2h by NP-01 normal temperature atmospheric pressure expansion tester and the sample was blanked with distilled water.

## 3. Data Processing

(1) The rheological parameters are calculated according to the following formula.

$$YP = 0.5(\Phi_{300} - PV) \quad (1)$$

$$AV = \frac{1}{2}\Phi_{600} \quad (2)$$

$$YP/PV = 0.5(2\Phi_{300} - \Phi_{600})/(\Phi_{600} - \Phi_{300}) \quad (3)$$

$$PV = \Phi_{600} - \Phi_{300} \quad (4)$$

(2) According to the linear expansion rate formula, the linear expansion rate of clay in different solutions is calculated, and the relationship curve between linear expansion rate and soaking time of clay is drawn. The formula is as follows: $R(\%) = h_1/h_2 \times 100\%$.

## 4. Questions and Exercises

(1) What are the main components of lignin?
(2) What changes in the chemical composition of lignin before and after purification?
(3) How can the lignin interact with the clay in the drilling fluid? What does the macro play?

## 5. Conclusion

In this experiment, the industrial lignin was purified, and then the drilling fluid performance of lignin before and after purification was evaluated. In the experiment process, the water-based drilling fluid drilling fluid test method is adopted in the drilling field.[14] Through the training of this experiment, on the one hand, the students can master the principle of separation and purification, on the other hand, the students can master the field test method of drilling fluid performance and the use of the instrument, so that they can better connect with the drilling operation site in the future. It is of great significance to use industrial lignin as raw material to make students understand the structure and properties of lignin and to combine theory with practice in order to expand students undefined thinking. In addition, industrial lignin is extracted from pulping waste liquor, which is beneficial to the practice of green development in China.

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