Phospholipids Polysaccharide and Its Application as Inhibitive Drilling Fluid Additive

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Abstract. For the improvement of solubility and the performance of the sample that derived plant polysaccharide(SJ) in drilling fluid based on water, which was improved by phosphoric esterification with phospholipids reagent. The conditions of the reaction were discussed by orthogonal ways in four factors and three levels, and the optimization of handling approaches were found out: With pH=12 at the temperature of 80 ℃, the mass ratio between phospholipids agent and SJ is 0.1g/1g. The viscosity about the system added by sulfonated SJ (SJP) was extremely increased and below 120 ℃, rheological properties had a slight change. The inhibitive ability of SJP is assessed by the mud ball immersing tests and clay-swelling experiments, that is apparently better than SJ and even 4wt% KCl in free water.

1. Introduction
Drilling fluids based on water are more easily acceptable than in which drilling fluids based on oil may be limited like cost, logistical or environmental constraints. For components added in drilling fluid, the agent modeled rheology is critically significant for a appropriate rheological property that performs particular functions like weighting agents used to suspend, additive used to clean hole and suspending cutting and transporting them up the link to the surface and so on[1-3]. The additive in water-based drilling fluids is asked to offer an obviously effective shear-shinning rheology with enough suspension power [4]. The viscosity distribution wished by the oil field production can been given from many kinds of polysaccharides as eco-friendly drilling fluid additive [5,6].

SJ named by plant polysaccharide derives from sample, which is the resin getted by Prunus persica L. Batsch. Basically, SJ with great molecular weight is composed of aldohexose and aldopentose, which is joined by L-arabinose (42.8%), D-galactose (35.7%), D-xylose (14.3%) and D-sedoheptulose (7.2%). The drilling fluid additives is friendly to nature, which can promote viscosity property [7], shear-shinning stability, bio-degrading ability and good cooperation ability. However, the disadvantages of SJ are the low solubility. Somebody once attempted to promote its solubility in drilling fluid based on water by chemical modifications. The worth we searched is that show the phosphoric esterification to SJ, whose performance as a additive in drilling fluid.

2. Experimental
2.1. Synthesis
SJ was mixed with NaOH solution and mixed at a fixed temperature when a gel that is homogeneous was gotten. A fixed dose of phospholipids agent (prepared by our lab) was then joined. The product was handled by a fixed thermo for some times, and the pH was adjusted with sodium hydroxide (10wt%). At the ending of
the progress, gel whose thermo is as same as the room was adjusted to pH=7~9 with dilute hydrochloric acid. The modified product (SJP) get from the residue that was distilled dried and crushed under reduced pressure. The synthetic principle, in Scheme 1, is given. The conditions of that reaction that were selected by orthogonal orthogonal ways in four factors and three levels and the properties of phosphoric esterification of SJ, in drilling fluid, were discussed.

Scheme 1 Phosphoric esterification of SJ

2.2. Results and discussion

On the basis of preparation we once did, such factors, which are the thermo expressed by temperature (A), the pH (B), the reaction days (C) and the mass percentages of phospholipids agent to SJ (D) is major impact for the modification. For finding the best appropriate conditions about synthesis, as shown in Table 1, four factors and three levels were listed to match. The standard L$_9$ (3$^4$) table shown in Table 2 was referred to designed orthogonal experiments. The conditions are assessed by the increasing ratio based on apparent viscosity in the fluids handled with sample which was modified.

| Factor | Temperature (℃) (A) | pH (B) | Reaction time (h) (C) | The mass ratio of sodium phosphate to SJ (D) |
|--------|-------------------|------|----------------|----------------------------------|
| Level 1 | 40                | 8    | 6              | 0.1                              |
| Level 2 | 60                | 10   | 8              | 0.3                              |
| Level 3 | 80                | 12   | 10             | 0.6                              |

Orthogonal experiments were used to make sure the optimized reaction conditions, and analyzing the range can get the links between four conditions. As shown in Table 2, the temperature mainly influences the phosphoric esterification. The second is mass rate of esterifying agent to SJ, next pH and the last reaction period. The best proper conditions were shown bellow: the mass percentage of 0.1g.phospholipids agent to 1g.SJ is 10% when the pH is equal to 12 at such thermo like 80℃.

| No. | Factor | AV | Increases % |
|-----|--------|----|-------------|
| 1#  | A 1 B 1 C 1 D 1 |  7.00 | 48.9        |
| 2#  | A 1 B 2 C 2 D 2 |  6.90 | 46.8        |
| 3#  | A 1 B 3 C 3 D 3 |  8.05 | 71.3        |
| 4#  | A 2 B 1 C 2 D 3 |  6.45 | 37.2        |
| 5#  | A 2 B 2 C 3 D 1 |  6.55 | 39.4        |
| 6#  | A 2 B 3 C 1 D 2 |  7.55 | 60.6        |
| 7#  | A 3 B 1 C 3 D 2 |  5.85 | 24.5        |
| 8#  | A 3 B 2 C 1 D 3 |  7.05 | 50.0        |
| 9#  | A 3 B 3 C 2 D 1 |  7.05 | 50.0        |
| K1  | 167.01 110.61 159.51 138.30  | |
| K2  | 137.19 136.20 134.01 131.91  | |
| K3  | 124.50 181.89 135.21 158.49  | |
| R   | 42.51  71.28  25.50  26.58    | |
The rheological performances and filter loss of drilling fluids handled with esterified SJ (SJP) need to be assessed. Comparing SJP with a mass percentage of 0.3% with SJ, which increased the apparent viscosity obviously by 60.6%, and decreased the filter volume by 30.6%.

With the optimized reaction conditions, the SJ was modified, and the product suspending in water was shown in Fig. 1. It can be found that before modification, SJ is hard to resolve or suspend in water, most of which precipitates at the bottom of the bottle. After modification, SJP is well dispersed or resolved in water, which makes a uniform liquid. Based on this test, it can be concluded that sulfonation of SJ can enhance the water solubility, which may be useful for the performance in water-based drilling fluid.

![Fig. 1 The suspension of SJ(left) and SJP(right)](image)

SJP was added in drilling fluids, which were heated and rolled for two-third days at some thermo between 25°C and 180°C. Results, in Fig. 2, both the apparent viscosity and plastic viscosity decreased when the temperature increased from 25°C to 90°C can be gotten; but the variety of apparent viscosity has a similar trend with that of plastic viscosity when the thermo floated up at 90°C~180°C. While the filter-water gotten from drilling fluids increased gradually from the temperature 25°C increasing to 120°C but increased dramatically from the temperature 120°C increasing to 180°C. Compared to SJ, the temperature resistance of SJP decreased slightly. The fact may owe to the larger dose of SJP and more stable cross linking effect with clay as the increasing temperature.

With the successive increasing temperature, the rheological property and filtration loss got worse remarkably, to a large extent, which because the enhancement of the repulsive force between the anions and the hydrogen bond more easily damaged.[10]
Under normal and atmospheric pressure, the clay expansion test was used to evaluate the inhibition performance. The linear expansion rate shown in Figure 3, the universal core made from bentonite is immersed in distilled water, 4wt% KCl solution, 10wt% solution of Na₂SiO₃, 0.3wt% SJ in free water, 0.3wt% solution of SJ, 0.3wt% solution of SJP and 0.5wt% SJP for 3h one by one. It was shown that the clay swelling rate was 75.14%, 56.71%, 72.83%, 65.95%, 58.58%, 43.88% and 38.82%, respectively. Obviously, the swelling rate of SJ solution enhanced with its concentration increasing. Moreover, the swelling rate of both 0.3wt% solution of SJ and 0.5% wt.SJ were more effective than that of Na₂SiO₃ solution but lower than that of 4wt% KCl solution. While, the swelling rate of both 0.3wt% solution of SJP and 0.5wt% SJP were significantly improved and also enhanced with their concentration increasing.

This particle size distribution of montmorillonite in water, SJ suspension and SJP suspension is tested to realize the interaction between SJ/SJP and montmorillonite. It can be seen from Fig. 4 that the SJ can inhibit montmorillonite hydration so that the particle size is much larger than that of the blank test. When SJP was added before montmorillonite hydration, the particle size of montmorillonite is slightly reduce diminish, and the particle size is much larger than that of SJ, which can be attribute to the high absorption of SJS on montmorillonite by the abundant hydroxyl groups.
For the anti-swelling ability of SJS as additive, it was discussed by a more intuitive style the mud ball immersing tests. The balls were mixed free water and bentonite, which were handled by water, 4wt% KCl in free water, the same style as 0.5%wt SJ and 0.5%wt SJP, one by one. The appearance of the balls mixed and experienced for 2 days were taken pictures as shown in Fig. 5. The obviously cracked ball mixed was soaked in free water, but slight which is in SJ in free water, but hardly by 4wt% KCl solution. In SJS solution, the mud ball immersed swelled a little and the face of it was so sleek without splits.

Their special structure may result in the inhibitive property of SJP. A hydrated case on the bentonite appearance was formed by a large number of hydroxyl groups absorbed in the bentonite appearance by the bond like water, which obstructs the water extruded in the bentonite and stop bentonite from further hydrated expansion. The hydrophilic phosphate radical of the modified products can weaken the hydrogen bonding interaction in the molecular chain, improved the water solubility of SJS. Furthermore, a diffusion double layer is formed to stabilize the bentonite particles in the drilling fluid [3-5].

3. Conclusion
For the capability each other, phosphoric esterification was applied to modify a plant polysaccharide derivative (SJ). As discussed, the follows were the optimal conditions: the mass scale of phospholipids agent to SJ is 0.1/1, at the same time, adjusting pH to 12 with the thermo like 80°C. The viscosity of drilling fluid treated with SJP was obviously decreased and at 120°C, such influenced factors of rheological properties have a slight relationship with the temperature. Clay-expansion experiment proves that SJP can apparently inhibit the bentonite expansion in the drilling fluids based on free water.
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