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РАЗРАБОТКА ХИМИЧЕСКИХ ДОБАВОК ДЛЯ ИСПОЛЬЗОВАНИЯ В БУРОВЫХ РАСТВОРАХ НА БИОДИЗЕЛЬНОЙ ОСНОВЕ

DEVELOPMENT OF CHEMICAL ADDITIVES FOR USE IN BIODIESEL – BASED DRILLING FLUIDS

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Аннотация. Буровой раствор на основе биодизеля (BBDF) демонстрирует большой потенциал в качестве базового масла для буровых растворов, заменяющих обычные буровые растворы на масляной основе. Это связано с их превосходным соответствием экологическим требованиям и большим потенциалом для обеспечения высокой производительности бурения. Представлены и обсуждены некоторые репрезентативные данные, относящиеся к разработке биодизеля. В статье также освещается важность выбора модифицированных органофильных глин в качестве подходящих добавок для обеспечения подходящих реологических и фильтрационных свойств бурового раствора на основе биодизеля.

Ключевые слова: биодизель, Буровой раствор, Добавка, Эквивалентная плотность циркуляции, Бензо дизель.

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Annotation. Biodiesel-based drilling fluid (BBDF) exhibits great potential to serve as the base oil of drilling fluids substituting for conventional oil-based drilling fluids. This is due to their excellent environmental compliance and great potential to provide high drilling performance. Some representative data related to the development of biodiesel are presented and discussed. The article also elucidates the importance of selecting modified organophilic clays as suitable additives to provide proper rheological and filtration properties in biodiesel-based drilling fluid.

Keywords: biodiesel, Drilling fluid, Additives, Equivalent Circulation Density (ECD), Petro diesel.

Biodiesel-based drilling fluid (BBDF) has drawn considerable attention because of it is environmentally friendly, it has high-performance and it is a low-cost drilling fluid. The advantageous properties of biodiesel – such as a high flash point (for fire safety), sufficient viscosity (to carry cuttings to the surface during drilling), low eco-toxicity, excellent biodegradability, and good lubricity – make it suitable as a base oil for drilling fluid. Biodiesel also is relatively inexpensive in many situations. Many investigations and trials are being conducted on BBDF, suggesting some more promising results. Preliminary experience has shown that an additive used in traditional oil-based drilling fluids (OBDFs) may be unable to perform well in a BBDF system. Consequently, new additives are being developed for BBDF in order to obtain the optimal operational and environmental properties.

Some basic properties of biodiesel are listed in Table 1. The properties of commercial petro diesel and white oil (a kind of paraffin oil often employed as the base oil of drilling fluids) are also presented for the purpose of comparison. The selected biodiesel has a density (0.87 g/cm^3) which is comparable to petro diesel (0.86 g/cm^3). This implies that the density of formulated BBDF can be modified accordingly. Flash point of the biodiesel (168 °C) is significantly higher than those of petro diesel (78 °C) and white oil (120 °C) this implies a better fire safety of the biodiesel. There are no aromatics in the biodiesel as compared to the commonly existing aromatics in petro diesel, signifying a lower toxicity of biodiesel as compared to petro diesel. The absence of aromatics in biodiesel is also a symbol of non-fluorescence, which is beneficial in well logging operations [1].

Table 1 – Basic properties of biodiesel as compared to petrodiesel and white oil

Properties	Biodiesel	Petrodiesel	White oil
Appearance	Light yellow viscous liquid	Light yellow viscous liquid	Transparent viscous liquid
Density (g/cm^3)	0.8	0.86	0.82
Kinematic viscosity (mm^2/S)	4.4	3.5	4.0
Flash point (closed cup, ^{o}C)	168	78	120
Pour point (^{o}C)	4	4	–5
Cold filter plugging point (^{o}C)	–3	3	4
Sediment (W %)	None	None	None
Water content (W %)	None	None	None
Sulphur (W %)	None	< 0.1	< 0.1
Aromatic materials (W %)	None	< 40.0	< 0.3
Copper strip corrosion (3hr ranking)	1a	1a	1a
Acid value (mgKOH/g)	0.12	0.005	–
Free glycerin (W %)	0.01	–	–
Total glycerin (W %)	0.02	–	–
Oxidation stability (oil stability index @ 100 ^{o}C)	> 6	–	–

Sulfide may result in corrosion of equipment, so the absence of sulfur in the biodiesel ensures a high copper-strip corrosion rank, reflecting the nonexistence of extra corrosion damage when using biodiesel. Generally, high acid value of biodiesel implies high free fatty acid (FFA) content, high viscosity and poor oxidation stability [2]. On the other hand, glycerin, including glycerol, mono-, di- and triacylglycerol, has negative effects on the kinematic viscosity and low-temperature liquidity of biodiesel [3]. Consequently, acid value and glycerin content are two noteworthy indices. The chosen biodiesel has an acceptable acid value and a glycerin content according to ASTM D6751 specification (free glycerin ≤ 0.02 wt. %; total glycerin ≤ 0.24 wt. %). The oxidation stability index (> 6 h) of biodiesel suggests a competent oxidation stability ensuring a half-year shelf life. The pour point (PP) and the cold filter plugging point (CFPP) of the biodiesel are both near to those of petro diesel and white oil. Hence, the three kinds of oils have similar low-temperature operability. These data reveal that biodiesel has great potential to provide high drilling performance. The kinematic viscosity of biodiesel at 40 °C is higher than petro diesel and white oil. Normally, this causes undesirably excessive equivalent circulation density (ECD), break circulation pressure (BCP) and gel strength of BBDF. In deepwater drilling environment, the harm of highly viscous fluid is particularly remarkable due to a series of resultant problems such as the limitation of rate of penetration (ROP), high surge pressure, long downtime and large circulation loss. Besides, the high viscosity of drilling fluid needs to be controlled by using coarser shaker screens to prevent the fluid losses over the shaker. This practice leads to a build-up of the drilled solids in the mud, which requires a higher dilution rate to mitigate, increasing the drilling fluid cost. The biodiesel used here also exhibits non-toxicity and excellent biodegradability. Another important property is the degree of dispersion of base oil in water, which is directly related to the actual dissipation process after BBDF disposed to the water body. Octanol/water partition coefficient (Po/w) is an indicator depicting the ratio of an organic fluid dissolving or dispersing in octanol versus water. A low Po/w signifies the good dispersibility of oil. Biodiesel exhibits excellent dispersibility, which is much better than those of white oil and diesel, and slightly greater than those of soybean oil, rapeseed oil and palm oil [3, 4].

The use of organophilic clays as additives to provide proper rheological and filtration properties in nonaqueous drilling fluids has long been a topic of study. Currently, most of these clays are based on the modification of bentonite with quaternary ammonium salts. As new NADF systems emerge, novel clay-modification technologies are needed to obtain more-effective organophilic clays for specific drilling fluids. In particular, organorectorites designed for use in biodiesel-based drilling fluid are introduce by some researchers – these are clay mineral formed by dioctahedral mica layer and dioctahedral smectite layer – often modified by non-ionic surfactants. Rectorite Like bentonite has excellent colloid properties (i.e., swelling and gelation in water), which implies that it has the potential to be organophilized. The bonding between rectorite crystal layers is weak, and numerous exchangeable cations exist on the rectorite surface. This, coupled with a large specific surface area, facilitates surfactant intercalation into rectorite. This enable them to have better performance in biodiesel-based drilling fluid as compared to traditional organophilic bentonites. Commercial rectorite are also generally cheaper than its bentonite counterpart by about 20 %. A comparison of the basic properties of organorectorites to commercial organobentonites is presented in table 2 [5, 6, 7].

Traditionally, most organophilic clays for drilling fluids are based on the intercalating reaction between bentonite and quaternary ammonium salts, which are classified as cationic surfactants. However, these types of organobentonites still have some disadvantages, such as ecotoxicity and high resistance to degradation when discarded in the environment. Inexpensive organorectorites are used to replace the commonly used bentonite as the raw clay to produce organophilic clay through a modification reaction with nonionic surfactants [2, 5].

Table 2 – Basic properties of organorectorites as compared to commercial organobentonites

Property	Organorectorites	Organobentonites
Appearance	Grey powder	White powder
ρ (g/cm^3)	1.78	1.69
D_{001} (nm)	1.619	1.200
Particle size (μm)	< 75 (200 mesh)	< 75 (200 mesh)
Grain size (nm)	31.5	25.8
Organic mineral content (g/gclay)	17.2	11.9

The selection of additives in BBDF is based on test results for the specific base oil. If the composition of biodiesel changes, some adjustment in the combination of additives may be needed. To determine the effects of the organorectorites on the rheological parameters and suspendability of BBDF and establish their superiority over commercial organobentonites, crucial properties, including swelling index, viscosity, yield point, gel strength, and suspendability, must be evaluated:

Swelling index test (SI)

This performed in order to evaluate the swelling ability of organophilic clays in the base fluid. The ASTM (American Society of Testing Materials) standard specification procedure for the SI test is defined for water-swell clay minerals while replacing water by non-water based fluids including biodiesel, petrodiesel, white oil and their invert emulsions. The emulsions, subsumed into 70:30 of oil-water ratio by volume are hot rolled at 100°C for 16hrs before the beginning the test. 1–2 g of the organophilic clay is then gradually added to 100mL of oil or emulsion by 0.1g increments after which the mixture is allowed to stand still for 16hrs. After that, the liquid is poured out carefully and the volume of the swelled organoclay is recorded (V_{sw}, mL). The swelling index is then calculated by the following equation:

$$SI = \frac{Vsw}{Mc},$$

where Mc = weight of the clay, (g).

Following the above procedure, the swelling indices of various organic liquids can be determined and the Organorectorites (OR) that swells better both in biodiesel and biodiesel emulsion is regarded as the most suitable for BBDF and diesel-based drilling fluids.

Emulsion rheology test

As observed by several researchers both the OR and OB enhance the apparent viscosity (AV) and the yield point (YP) of biodiesel emulsions with intense agitation. Therefore, the emulsion test is performed in order to evaluate the viscosity growth rates of biodiesel emulsions with different organoclays under high speed agitation. The variations of apparent viscosity (AV) and the yield point (YP) of biodiesel emulsions with string time are recorded. The times required to reach the accretion of different OR clays are determined. The additives with better timing indicates their better ability to disperse and swell in biodiesel emulsions, hence suggesting a higher efficiency in BBDF.

Electrical stability test

The effects of OR on the electrical stability (ES) of biodiesel emulsion with various oil-water ratios are evaluated, because the addition of organoclays is considered to influence the stability of invert emulsion and consequently the corresponding BBDF. The OR with a better SI signifies a better emulsion stability. A Turbiscan near-infrared spectroscopy stability tester is of late being employed in the determination of the Turbiscan stability indices (TSIs) of different biodiesel emulsions containing organoclays. The tester, which is based on multiple-light-scattering technique, is regarded as a better option to the traditional ES test. It provides a reliable approach in investigating the stability of emulsions [8].

Conclusively, the ability of additives such as modified rectorites to enhance the ES, improve the apparent viscosity (AV) and yield point (YP) of biodiesel drilling fluids suggests a higher efficiency of adjusting their rheology. When combined with rheological modifiers, they can provide a formulated BBDF with a higher suspendability and stable properties. This make them a better substitute for conventional organobentonites.

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