A Review on Nanoparticle Addition in Base Fluid for Improvement of Biodegradable Ester-Based Drilling Fluid Properties

Yee Ho Chai\textsuperscript{a}, Suzana Yusup\textsuperscript{*a}, Vui Soon Chok\textsuperscript{b}

\textsuperscript{a}Biomass Processing Lab, Center of Biomass and Biofuels Research, MOR Green Technology, Chemical Engineering Department, Universiti Teknologi PETRONAS, Perak, Malaysia
\textsuperscript{b}Platinum Nanochem Sdn. Bhd. LOT 15-19 & PT 1409, Senawang Industrial Estate, Batu 4 Jalan Tampin, 70450, Seremban, Negeri Sembilan Darul Khusus, Malaysia
drsuzana_yusuf@petronas.com.my

Nanotechnology is increasingly capturing the attention of material researchers as this technology pushes the limits and boundaries of the pure material itself. Nanofluids usually contain enhanced physical properties such as thermal conductivity and electrical conductivity. The incorporation of such technology can be shifted to the oil and gas industry, especially areas relating to drilling fluid. However, most drilling muds have detrimental effects such as environmental pollution, low degradation of drilling mud and strenuous post-treatment. Thus, the need for the production of a biodegradable drilling fluid is emphasized. However, current limitations imposed on the said drilling fluid restrict its usage on conventional drilling operations. This paper aims to review the effects of addition of powder nanoparticles into base fluid to achieve required criterions of industrial drilling fluid. Generally, the addition of nanoparticles into base fluids will result in better thermophysical properties such as thermal conductivity and convective heat transfer coefficients. The enhancement of thermophysical properties in drilling operations are highly desirable as heat generated from the friction between of drilling bit and the wellbore can be circulated at a higher rate. The addition of nanoparticles also results in changes in electrical conductivity and viscosity of the base fluid. These parameters have been investigated by various researchers and a positive enhancing trend is observed. However, stability of nanofluids has been a wide concern as various researchers struggled to maintain the stability of nanoparticle suspension.

1. Introduction

The formulation of drilling muds are complex as it is made up of multicomponents such as drilling base fluid, lubricant, emulsifiers, bentonites and other external additives. Generally, performance of drilling muds varies at different wellbore conditions. Drilling mud can be classified into three broad categories: mainly water-based mud (WBM), oil-based mud (OBM) and synthetic-based mud (SBM). Generally, WBM is commonly employed in wellbore of shallow depths while OBM is applied deeper drilling operations. Since late 1990s, the United States Environmental Protection Agency (EPA) had outlined new guidelines in controlling offshore discharges, inclusive of drilling mud discharges (Neff et al., 2000). Environmental concerns have been the driving force in the current researches of drilling fluids to formulate an environmental friendly yet performance-savvy drilling mud. The formulation of SBM aims to reduce the toxicity of drilling mud discharged by integration of vegetable ester as synthetic oil. However, the increasing demand of drilling operations in deepwater conditions for higher recovery of oil has been a major challenge due to high temperature and high pressure (HPHT) environment and denature of additives at high temperature. Various researchers have been constantly researching on possible methods to further improve the physical properties of drilling mud. One of the outcomes consists of incorporation of nanotechnology into the oil and gas industry sector.

Please cite this article as: Chai Y.H., Yusup S., Chok V.S., 2015, A review on nanoparticle addition in base fluid for improvement of biodegradable ester-based drilling fluid properties, Chemical Engineering Transactions, 45, 1447-1452
DOI:10.3303/CET1545242
Nanoparticles are particles with sizes 1–100 nm with distinct properties due to its small size and immense surface area (Gusatti et al., 2009). Base fluids which have been blended with nanoparticles are termed as nanofluids. Nanofluids are usually prepared via two methods: mainly one-step method and two-step methods. The preparation of large quantity of nanofluids usually favors two-step methods where dry powder nanoparticles are synthesized and subsequently dispersed in base fluid to obtain nanofluid suspension. Nanotechnology has been increasingly popular in improving the quality of products including heat transfer applications, energy storage, etc but it can be shifted towards the oil and gas industry for the improvement of its applications. The paper aims to compare and incorporate improve the physical properties of drilling fluid such as electrical conductivity, thermal conductivity and rheology where feasible.

2. Experimental Investigations

2.1 Electrical Conductivity

Drilling fluid are formulations of emulsions where water and oil are present. The dispersion of water in oil-based mud or oil in water-based mud is crucial to determine the degree of a good emulsion. Praveen et al. (2014) mentioned that a good emulsion based drilling fluid is useful in low pressure reservoirs and subterranean wells. Electrical image loggings are used in identifying the directions of rock fractures present during drilling operations through varying properties of borehole walls. Fractures are identified through conductivity contrasts between fractures and borehole walls (Davatzes and Hickman, 2005).

Mahboobeh et al. (2014) had dispersed graphene oxide (GO) nanoparticles with average crystallite sizes of 20 nm into distilled water. In their studies, they claimed that they had gained an impressive enhancement of 25,678% in electrical conductivity of distilled water nanofluid compared to its counterpart with loading dispersion of 0.0006 mass fractions of GO nanoparticles. They stated that the presence of electrical double layer (EDL) contributed heavily to the electrical conductivity through electrophoretic mobility. White et al. (2011) reported that 7% nanoparticle volume fractions gives 100-fold in electrical conductivity increment over propylene-glycol based ZnO nanofluid but levelled off at excessive high volume concentrations due to counter-ion condensation in nanofluid. Both Zawrah et al. (2015) and Kole and Dey (2013) correlated their findings on effective electrical conductivity of nanofluids vary with volume fraction of nanoparticles. Both concluded electrical conductivity is dependent on the loadings of particles, ions concentrations and nanofluid dependency on EDL. The findings are summarised in Table 1.

2.2 Thermal Conductivity

In heat transfer applications, the thermal conductivity is an essential parameter in the selection of the coolant fluid. Fluids with high thermal conductivity are able to conduct and dissipate heat generated at a higher rate as compared to fluids with poor thermal conductivity. The same concept is applicable in the oil and gas industry, selectively in drilling operations. Drilling fluids with better heat transfer performance are desirable as drilling operations generates excessive heat due to friction between drilling bit and the rock surface. Overheating of equipment has been a common complication for drilling operators. Therefore, it is required to establish and formulate drilling mud that is capable of delivering better heat transfer performance.

<table>
<thead>
<tr>
<th>References</th>
<th>Nanoparticle(s)</th>
<th>Concentration</th>
<th>Base Fluid(s)</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mahboobeh et al. (2014)</td>
<td>Graphene oxide 0.06% mass fraction</td>
<td>Distilled water</td>
<td>25,678% EC enhancement</td>
<td></td>
</tr>
<tr>
<td>White et al. (2011)</td>
<td>Zinc Oxide (ZnO) 7% volume fractions</td>
<td>Propylene-Glycol</td>
<td>Level off at high nanoparticle concentrations</td>
<td></td>
</tr>
<tr>
<td>Zawrah et al. (2015)</td>
<td>Al₂O₃ 0.2 vol%</td>
<td>Water</td>
<td>EC is dependent on EDL, volume fraction and ionic concentrations</td>
<td></td>
</tr>
<tr>
<td>Kole and Dey (2013)</td>
<td>Functionalized graphene 0 – 0.395 vol%</td>
<td>Deionized water</td>
<td>EC is dependent on particle loadings, charges, sizes and electrolytes present</td>
<td></td>
</tr>
</tbody>
</table>

* EC denotes electrical conductivity

A research carried out by Mahboobeh et al. (2014) utilized graphene oxide, with average size of 20 nm, being dispersed into polar base ethylene glycol. The thermal conductivity of base fluid was 0.249 W m⁻¹ K⁻¹ at room temperature. At 1% GO nanoparticle mass loadings, it was observed that there was 4% increment in thermal conductivity with a maximum yield of 30% thermal conductivity enhancement is obtained with mass loadings of 7% before levelling off. Similarly, Ma et al. (2013) used
functionalized graphene nanosheets to produce silicone oil based nanofluids investigated the thermal conductivity enhancement in nanofluids at different low nanoparticle concentration. At lower nanoparticle loadings of 0.01 % weight fraction, they were able obtain 1.55 % thermal conductivity increment at 293 K. However, at a higher temperature, there are able to obtain 8.48 % increment at 333 K. Nevertheless, higher mass fraction of nanoparticles increases the thermal conductivity effectiveness at a given temperature due to presence of higher nanoparticle concentrations suspended in nanofluid.

In another separate study, Duan (2012) chose aluminium oxide (Al₂O₃) with an average crystallite size of 25 nm with concentrations ranging from 1 % to 5 % was dispersed into 100 mL of de-ionized water. Cetyltrimethylammonium bromide (CTAB) surfactant was added at 0.01 % to 0.02 % volume percentage to stabilise the suspension of the nanofluid. At low levels of concentration, thermal conductivity of nanofluids can be predicted with mathematical models. Thermal conductivity models including Maxwell model, Hamilton & Crosse model, and Bruggeman are used in Duan’s study. All three models assumed spherical nanoparticles as basis for its predictions are compared with their experimental results. The models underpredicted the thermal conductivity effectiveness of the nanofluid although both results yielded increasing thermal conductivity effectiveness. Duan (2012) attributed this to factors such as different particle preparation, source and addition of surfactants as well as differences in preparation of nanofluid.

Another experiment carried out by Murshed et al. (2005) dispersed titanium oxide (TiO₂) nanoparticles of rod-shapes with 10 nm by 40 nm (diameter by length) and average spherical diameter of 15 nm in deionized water with the presence of CATB. Similar to Ma et. al (2013), Bruggeman model is used in predicting the thermal conductivity effectiveness of the nanofluid. Wasp model was preferred in this study though it claimed that it yielded similar results to Maxwell and Hamilton & Crosse model for spherical nanoparticles. Besides that, addition of 5 % volume fraction of spherical nanoparticles yielded nearly 30 % thermal conductivity enhancement. Comparison between experimental results and models proved that the models had underpredicted the thermal conductivity effectiveness of nanofluid. The surface capping decreased the contact angle of nanoparticles against the base fluid to give its highly dispersive properties. 0.5 % mass fraction yields approximately 17.5 % of thermal conductivity enhancement at 323 K. Similarly, Warrier and Teja (2011) used silver nanoparticles with ranging from 20 nm to 80 nm averagely. They found out that thermal conductivity enhancement are affected by nanoparticle size with 80 nm yielding the highest increment. The findings are summarised in Table 2 above.

However, high concentrations of nanoparticles will undoubtedly yield higher thermal conductivity enhancements but this induces greater agglomerations due to strong attraction forces between particles. Consequently, this leads to poorer thermal conductivity enhancements as agglomerates settle down.

Table 2: Summary of experimental studies on thermal conductivity of nanofluids

<table>
<thead>
<tr>
<th>References</th>
<th>Nanoparticle(s)</th>
<th>Size (nm)</th>
<th>Base Fluid (s)</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mahboobeh et al. (2014)</td>
<td>Graphene oxide</td>
<td>20</td>
<td>Distilled water, Ethylene glycol</td>
<td>30 % TC enhancement at 7% mass fraction before level off</td>
</tr>
<tr>
<td>Ma et al. (2013)</td>
<td>Functionalized graphene nanosheet</td>
<td>70 µm, 1.1-2.3 nm thickness 25</td>
<td>Silicone oil</td>
<td>5.74 % TC increment with 0.07 wt% at room temperature</td>
</tr>
<tr>
<td>Duan, Fei (2012)</td>
<td>Al₂O₃</td>
<td>10 (dia.) x 40 (length),</td>
<td>De-ionized water</td>
<td>20 % TC increment with 0.05 volume fraction nanoparticle</td>
</tr>
<tr>
<td>Murshed et al. (2004)</td>
<td>TiO₂</td>
<td>15 (spherical)</td>
<td>Ethylene glycol, distilled water</td>
<td>33 % and 30 % TC increment with 5% volume fraction of TiO₂ rod-shape and spherical.</td>
</tr>
<tr>
<td>Kole and Dey (2013)</td>
<td>Functionalized hydrogen graphene (f-HEG)</td>
<td></td>
<td>Ethylene glycol</td>
<td>15 % TC enhancement with 0.395 vol% f-HEG nanoparticle</td>
</tr>
<tr>
<td>Warrier and Teja (2011)</td>
<td>Silver</td>
<td>20,30,50, 80</td>
<td>Ethylene glycol</td>
<td>Increasing nanofluid TC enhancement with increasing nanoparticle size</td>
</tr>
<tr>
<td>Wang et al. (2012)</td>
<td>Graphene</td>
<td>-</td>
<td>[HMIM]BF₄ (ionic liquid)</td>
<td>15.5 % TC increment with 0.06% mass fraction graphene nanoparticles</td>
</tr>
<tr>
<td>Li et al. (2010)</td>
<td>MWCNT</td>
<td>5</td>
<td>Kerosene, n-hexane, chloroform</td>
<td>Surface capped gives better dispersity and higher TC enhancement at higher temperature</td>
</tr>
</tbody>
</table>

* TC denotes thermal conductivity
2.3 Rheology
The rheology of the drilling mud is an important aspect to be considered during any drilling operations. At low shear rate, it is desirable for the mud to be of high viscosity to be able to suspend the solids present in the fluid (Shah et al., 2010). Maghrabi et al. (2011) stated that the mud possessing high viscosity at inures in additional pumping power consumption and drilling costs for rapid drilling operations. Apart from that, they stated that high viscosity of drilling mud during drilling operations will incur in the increment of fluid pressure losses in the circulating system, hence yielding lower drilling performance in return.

Agarwal et al. (2013) carried out a study to investigate the effects of hydrophobic nanoparticle in invert emulsion muds (IEM) with the presence of organically modified nanoclay acting as stabilisers under various conditions. The addition of Aerosil R104 (hydrophobic nanoparticles) yielded higher viscosity as compared to the additions of stabilisers alone in IEM. However, the combination of both nanoparticles and stabilisers gives a slightly lower viscosity value compared to the addition of nanoparticles alone. The addition of nanoparticles provides an increment over 100-fold in ratio at low shear rate. At higher shear rate, all muds approached towards base fluid’s viscosity.

Sedaghatzadeh et al. (2012) had used carbon nanotubes (CNT) to disperse in water-based drilling fluids at different fractions. They claimed that addition of CNT to the water-based mud increases the shear stress at higher concentrations. Similarly, Ruan and Jacobi (2012) dispersed carbon nanotubes (CNT) in ethylene glycol at increasing shear rate. Its viscosity approaches base fluid viscosity at higher shear rate. However, Wang et al (2012) had carried out similar with experiment with multi-walled carbon nanotubes (MWCNT) and graphene as nanoparticle additives dispersed into ionic liquid. Measurement of viscosity of pure ionic liquid and nano-ionic liquid was compared with respect to temperature. It is noted that at constant temperature and shear rate, viscosity of pure ionic liquid was considerably higher compared to ionic liquid dispersed with nanoparticle additives. Wang et al. (2012) attributed this to the lubricity properties of graphene and MWCNT nanoparticles.

The topics of discussion on the effects of viscosity from the addition of nanoparticles are still widely debatable. Ruan and Jacobi (2012) cited some reports yields inconsistent results with higher, lower and constant changes to the viscosity of nanofluid with respect to its base fluid. An in-depth analysis on the interaction between nanoparticle molecules and liquid molecules should be further studied to understand the influence of nanoparticles addition towards viscosity changes made in nanofluid.

2.4 Stability of nanoparticle additives
The stability of nanofluid suspensions have been one of the greatest concerns and problems to researchers. Most stabilisers fluids have a stable suspension ranging from few hours to few weeks with the help of surfactants or stabilisers to suspend for a longer period. From an industrial point of view, nanofluid suspension must be able to suspend itself when stored before being transported to drilling sites.

Surfactants consist of a hydrophobic tail and a hydrophilic head. They are broken down into four main categories: nonionic surfactants without charge groups, nonionic surfactants with negatively charged head groups, cationic surfactants with positively charged head groups and amphoteric surfactants with zwitterionic head groups (Wei and Xi, 2012). Surfactant particles adsorbed itself upon nanoparticle surface to form a layer surrounding the nanoparticle (Lisunova et al., 2006). This mechanism induces steric hindrance to repel surfactant-coated nanoparticles from each other due to similar charges of the coated layer thus weakening the Van der Waals force between nanoparticles. Surfactants are normally added in minute quantity to improve the stability of nanofluid suspension. Li et al. (2007) reported that to achieve stabilizing effect of nanofluid, the concentration of surfactants proportional to the weight of nanoparticles can be taken as a rule. The presence of surfactants prevents aggregation of nanoparticles, thus promoting excellent dispersity of nanoparticles suspended within nanofluid. A research carried out by Tao et al. (2014) compared the stability of aluminium oxide (Al₂O₃) nanoparticles in deionized water with and without the use of sodium dodecyl benzen sulfonate (SDBS) surfactant. The stability of Al₂O₃ nanoparticles was evaluated after two (2) hours of storage with SEM images as shown in Figure 1. However, they claimed that excessive concentration of surfactant degrades nanofluid’s ability to suspend the nanoparticles. Similarly, Li et al. (2007) carried out a study in evaluating the dispersion behaviour of copper nano-suspensions in water solvents with nonionic (TX-10), cationic (CATB) and anionic (SDBS) surfactants. Non-ionic surfactants were found to provide steric hindrance due to its affinity for water. Hydrophobic groups found in TX-10 attract particles to form coagulation and supersaturation state. Excessive CATB surfactant addition increases the ionic strength and compresses EDL which causes lower dispersion stability of copper nanoparticles. Similarly, SDBS surfactant containing sodium ions at high surfactant concentration adsorbed on copper powder surface reduces the net charge to perform a weaker dispersion system instead. However, all surfactants were able to achieve excellent dispersion stability at each respective optimum surfactant concentrations.
Figure 1: SEM images of aggregates with and without SDBS addition (Source: Mao et al., 2014)

Yang et al. (2013) evaluated the stability of the nanofluid through amount of sonication energy required to achieve similar stability against nanofluid without surfactant. Their results concluded minimum energy is required to achieve stable suspension in carbon nanotube nanofluid containing SDBS. Generally, minute concentrations of surfactants are able to provide stability to nanofluid suspension. However, surfactants induce foaming at high temperature rendering it inapplicable for HPHT applications such as drilling operations. The thermal limitations of surfactants should be improved further for more extensive uses in HPHT applications. The findings are summarised in Table 3 as follows.

<table>
<thead>
<tr>
<th>References</th>
<th>Nanoparticle(s)</th>
<th>Surfactant Type(s)</th>
<th>Base Fluid(s)</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mao et al. (2014)</td>
<td>Al₂O₃</td>
<td>SDBS</td>
<td>Deionized water</td>
<td>Stable suspension with low presence of aggregates</td>
</tr>
<tr>
<td>Li et al. (2007)</td>
<td>Copper</td>
<td>TX-10</td>
<td>Water</td>
<td>Particles form coagulations at supersaturation state</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CATB</td>
<td></td>
<td>Excess concentration compresses EDL to lower dispersion stability</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SDBS</td>
<td></td>
<td>High sodium ions concentration performs weaker dispersion</td>
</tr>
<tr>
<td>Yang et al.</td>
<td>Carbon</td>
<td>SDBS</td>
<td>-</td>
<td>Minimum sonication energy to achieve stable performance</td>
</tr>
<tr>
<td>(2013)</td>
<td>nanotube</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3. Conclusion

The advancement and integration of nanotechnology plays a vital role in improving ester-based drilling fluid. The physical properties enhancements displayed by other studies shows significant potential in developing ester-based drilling fluid that can be or exceed current drilling fluid’s potential. However, stability of nanofluid suspension is a major obstacle which must be overcome. Undoubtedly, higher nanoparticle concentrations provide greater properties enhancements but subsequently decline due to agglomerations of nanoparticles. Further experimental investigations are required to investigate and break through the stability barrier in order to excel and improve the properties of ester-based drilling.

References


Davatzes N.C., Hickman S., 2005, Comparison of Acoustic and Electrical Image Logs From The Coso Geothermal Field, CA, Proceedings of Thirtieth Workshop on Geothermal Reservoir Engineering, SGP-TR-176, Stanford University, Stanford, California


